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Analytical Chemistry Laboratory Department

ANALYTICAL CHEMISTRY
LABORATORY (ACL)
PROCEDURE COMPENDIUM

Volume 5: Radiochemistry Analyses

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A. G. King
Department Manager

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**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-MA-599-Vol.5-1

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A.

Document Number: See Attachment Revision Number: _____

Document Title: See Attachment

Document's Original Author: See Attachment

Effective Date
of ICN: 12 / 23 / 92

Change Requested by:
AG King

B. Action: Place the attached procedures in PNL-MA-599 manual, Volume 5. Place this ICN and attachment with the Table of Contents.

C. Effect of Change: Incorporates the procedures from the PNL-MA-597 manual into PNL-MA-599.

D. Reason for Change/Description of Change:

Incorporates the procedures from PNL-MA-597 manual into PNL-MA-599 manual by changing the procedure numbers. This eliminates the need for maintaining two sets of technical procedures. Procedural references in these procedures have been updated. See attachment for the procedures to be incorporated into PNL-MA-599 manual, Volume 5.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert TL Ehlert Date: 12/23/92

Approval Authority: AG King AG King Date: 12/23/92

Other Approvals: _____ Date: 1 / 1

: _____ Date: 1 / 1

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New Doc#	Rev.	Author	Document Title	Old Doc#
PNL-ALO-400	3	WY Matsumoto	Sample Preparation: Dissolution of LWR fuel samples	HTA-4-24
PNL-ALO-401	2	GE Meadows	Burnup analysis: Neodymium- 148 method	HTA-4-25
PNL-ALO-402	2	GE Meadows	Sample preparation: LWR Fuel solution	HTA-4-26
PNL-ALO-403	2	GE Meadows	Measurement of Neptunium- 237 in dissolved fuel solutions	HTA-4-27
PNL-ALO-404	3	FE Holt	Solutions sample preparation and handling for I-129 measurement by activation analysis	HTA-4-32
PNL-ALO-405	3	FE Holt	Solutions analysis: measurement of gamma-ray emitting isotopes by the sample/standard comparator method	HTA-4-33
PNL-ALO-406	2	GE Meadows	Separation of Uranium from brine solutions by ion exchange	HTA-4-36
PNL-ALO-407	0	AC Leaf	Separation of chlorine-36 by ion exchange, distillation and measurement by beta counting	GRLT-1
PNL-ALO-408	0	AC Leaf	Low background alpha and beta counting using the LB-1000	GRLT-3
PNL-ALO-409	4	AC Leaf	Solutions analysis: Preparation of alpha Spectrometry sources by Electrodeposition	HTA-4-7
PNL-ALO-411	3	AC Leaf	Separation of selenium-75 by precipitation prior to measurement by gamma counting	HTA-4-19
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PNL-ALO-414	0	AC Leaf	Separation of Americium-241 and Curium-244 by cation and anion exchange separation from BWIP hydrothermal test solutions prior to measurement by alpha counting	HTA-4-38
PNL-ALO-416	1	AC Leaf	Separation of Iodine-129 by solvent extraction and distillation from brine solutions prior to measurement by gamma (x-ray) counting	HTA-4-42
PNL-ALO-429	0	MR Weiler	Laboratory preparation of samples for counting	6-40.1
PNL-ALO-434	0	MR Weiler	Beta and alpha proportional counting: particle filter analysis	6-40.2
PNL-ALO-440	7	TC Maiti/ AE Kozelisky	Selenium-79 by ion exchange and distillation separation prior to measurement by liquid scintillation counting	HTA-4-18 & 7-40.15
PNL-ALO-446	0	MR Weiler	4 x 5 NaI well crystal detector and intrinsic germanium detector gamma spectrometry: charcoal cartridge and particle filter analysis	6-40.3
PNL-ALO-447	0	MR Weiler	Data processing, analytical report production, and records management	6-40.4
PNL-ALO-448	0	FE Holt	Detector/Dewar acceptance tests	7-30.6
PNL-ALO-449	0	FE Holt	Zero and gain checks and control charts-- track detector	7-30.9
PNL-ALO-451	4	AC Leaf	Solutions analysis: Gamma spectrometry	HTA-4-9
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PNL-ALO-453	3	AC Leaf	Separation of Tin-126 by anion exchange prior to measurement by gamma counting	HTA-4-21
PNL-ALO-454	2	AC Leaf	Separation of Iodine-129 by cation exchange and distillation prior to measurement by gamma (x-ray) counting	7-40.17 & HTA-4-41
PNL-ALO-455	0	WY Matsumoto	Isotopic composition of plutonium and uranium by mass spectrometry	2-30.6
PNL-ALO-456	2	AC Leaf	Separation of Iodine-129 by solvent extraction and distillation from chloride solutions prior to measurement by gamma (x-ray) counting	7-40.26 & HTA-4-42
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PNL-ALO-459	1	FE Holt	Radiometric analysis of FFTF sodium samples	7-40.14
PNL-ALO-479	0	DL Baldwin	Tritium in irradiated cladding materials	7-40.34
PNL-ALO-480	0	NL Wynhoff	Determination of ⁹⁹ Tc	7-40.39
PNL-ALO-481	0	WY Matsumoto	Gamma-Ray spectral analysis of irradiated iron or nickel containing alloys (including zircaloy-2) by high resolution gamma spectrometry for use in characterizing neutron fluence and spectra	7-40.40
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PNL-ALO-486	1	RS Strebin	Total strontium- Rapid analysis for urine	7-40.56

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PNL-ALO-488	0	JH Kaye	Liquid scintillation counting procedure for measurement of tritium in urine by method of standard additions	7-40.64
PNL-ALO-489	0	AE Kozelisky/ TC Maiti	Solutions analysis: Americium and Curium isotopes by cation and anion exchange	7-40.65 & HTA-4-35
PNL-ALO-490	0	DL Baldwin	Liquid scintillation counting procedure for packard model 4430 in 325 building	7-40.66
PNL-ALO-491	0	DL Baldwin	Analysis for tritium in gas	7-40.74
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Volume 5: Radiochemistry Analyses**

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PNL-ALO-409	4	0	SOLUTIONS ANALYSIS: PREPARATION OF ALPHA SPECTROMETRY SOURCES BY ELECTRODEPOSITION	07/01/87
PNL-ALO-411	3	0	SEPARATION OF SELENIUM-75 BY PRECIPITATION PRIOR TO MEASUREMENT BY GAMMA COUNTING	07/01/87
PNL-ALO-412	0	0	MEASUREMENT OF CARBON-14 IN METALS	11/12/92
PNL-ALO-413	2	0	SOLUTIONS ANALYSIS: AMERICIUM AND CURIUM ISOTOPES BY CATION AND ANION EXCHANGE SEPARATION FROM PBB-1 AND PBB-3 BRINE TEST SOLUTIONS	07/01/87
PNL-ALO-414	0	0	SEPARATION OF AMERICIUM-241 AND CURIUM-244 BY CATION AND ANION EXCHANGE SEPARATION FROM BWIP HYDROTHERMAL TEST SOLUTIONS PRIOR TO MEASUREMENT BY ALPHA COUNTING	07/01/87
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PNL-ALO-453	3	0	SEPARATION OF TIN-126 BY ANION EXCHANGE PRIOR TO MEASUREMENT BY GAMMA COUNTING	07/03/87

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PNL-ALO-470	0	2	PROCEDURE FOR MAINTAINING CONTROL OF GERMANIUM SPECTROMETERS USED FOR GAMMA-RAY SPECTROSCOPY	05/07/92
PNL-ALO-471	0	1	DETERMINATION OF LOW CONCENTRATION OF ^{106}Ru IN GROUND WATER BY DIRECT COUNTING ON DUAL LARGE SODIUM IODIDE DETECTORS WITH COINCIDENCE/ANTICOINCIDENCE MULTIDIMENSIONAL ANALYSIS	05/07/92
PNL-ALO-472	0	0	DETERMINATION OF ^{93}MnB AND ^{94}Nb	08/15/91
PNL-ALO-473	0	0	NICKEL SEPARATION FROM RADIOACTIVE SOLUTIONS	04/24/92
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PNL-ALO-479	0	0	TRITIUM IN IRRADIATED CLADDING MATERIALS	07/31/89
PNL-ALO-480	0	0	DETERMINATION OF ^{99}Tc	12/05/89
PNL-ALO-481	0	0	GAMMA-RAY SPECTRAL ANALYSIS OF IRRADIATED IRON OR NICKEL CONTAINING ALLOYS (INCLUDING ZIRCALOY-2) BY HIGH RESOLUTION GAMMA SPECTROMETRY FOR USE IN CHARACTERIZING NEUTRON FLUENCE AND SPECTRA	08/08/88
PNL-ALO-483	1	0	PLUTONIUM-RAPID PROCEDURE FOR URINE	07/17/92

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PNL-ALO-486	1	0	TOTAL STRONTIUM-RAPID ANALYSIS FOR URINE	07/17/92
PNL-ALO-487	0	0	TRITIUM IN URINE BY THE METHOD OF STANDARD ADDITION-RAPID AND NORMAL PROCEDURES	10/12/90
PNL-ALO-488	0	0	LIQUID SCINTILLATION COUNTING PROCEDURE FOR MEASUREMENT OF TRITIUM IN URINE BY METHOD OF STANDARD ADDITIONS	10/12/90
PNL-ALO-489	0	0	SOLUTIONS ANALYSIS: AMERICIUM AND CURIUM ISOTOPES BY CATION AND ANION EXCHANGE SEPARATION	11/20/90
PNL-ALO-490	0	0	LIQUID SCINTILLATION COUNTING PROCEDURE FOR PACKARD MODEL 4430 IN 325 BUILDING	12/04/90
PNL-ALO-491	0	0	ANALYSIS FOR TRITIUM IN GAS	10/03/91
PNL-ALO-492	0	0	TRITIUM/HELIUM MEASUREMENT IN LITHIUM CERAMICS BY HIGH TEMPERATURE VACUUM EXTRACTION/INDUCTION HEATING	10/03/91
PNL-ALO-495	0	0	NICKELS SEPARATION FROM RADIOACTIVE SOLUTIONS USING CHROMATOGRAPHY	02/05/93
PNL-MA-496	0	0	PRECIPITATION PLATING OF ACTINIDES FOR HIGH-RESOLUTION ALPHA SPECTROMETRY	01/14/93
PNL-ALO-497	0	0	DETERMINATION OF SR-90 IN Y-90	12/15/92
PNL-MA-499	0	0	SEPARATION OF ACTINIDES BY EXTRACTION	02/01/93

PNL TEST PROCEDURE

TITLE: HTA-4-13, SEPARATION OF AMERICIUM-241 AND CURIUM-244 BY ANION EXCHANGE PRIOR TO MEASUREMENT BY ALPHA COUNTING

1.0 APPLICABILITY

This procedure is for the separation of americium and curium from plutonium in hydrothermal test solutions so that ^{241}Am and ^{244}Cm can be determined without interference from ^{238}Pu . Following the separation, the ^{241}Am and ^{244}Cm are measured by alpha counting methods HTA-4-5 and HTA-4-6.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Hydroxylamine hydrochloride, 5 M -- Dissolve 34.8 (± 0.1) g of reagent in 100 (± 1) mL of deionized water; mix thoroughly.
- Nitric Acid, reagent-grade, concentrated.
- AG-1,[®] X-4, 100 to 200 mesh resin.
- Nitric acid, 1 M -- Dilute 63 (± 1) mL of concentrated reagent-grade acid to 1000 (± 1) mL with deionized water; mix thoroughly.
- Nitric acid, 8 M -- Dilute 500 (± 5) mL of reagent-grade acid to 1000 (± 10) mL with deionized water; mix thoroughly.
- Vials, 15-mL, glass, screw-cap.
- Vials, 2-dram, glass, screw-cap.
- Heating block, aluminum, to hold vials in heating mantle.

[®]AG-1 is a registered trademark of Bio-Rad Laboratories, Richmond, California.

Concurrence NA	Date	Approved [Signature]	Date 7/2/87
Prepared by AC Lee	Date 7/1/87	QAD Concurrence B.O. BARNES	Date 6/30/87
Procedure No. HTA-4-13	Revision No. 6	Effective Date JUL 01 1987	Page of 1 3

PNL TEST PROCEDURE

- Droppers, 7.5-mL, plastic.
- Disks, 7/8-in., stainless steel.
- Stir bar, magnetic, glass-covered.
- Ammonium hydroxide, concentrated, reagent-grade.

4.0 PROCEDURE

Plutonium is loaded onto an anion exchange resin while americium and curium pass through the resin. The ^{241}Am and ^{244}Cm are then measured by alpha counting and alpha spectrometry.

- Step 1) Add to a 15-mL screw-cap vial 500 (± 10) μL of test solutions. Record the sample volumes on the analytical report for ^{241}Am .
- Step 2) Add 200 (± 10) μL of 5 M hydroxylamine hydrochloride.
- Step 3) Heat at 80° to 90°C for 45 (± 5) minutes.
- Step 4) Allow to cool to room temperature.
- Step 5) Add 1000 (± 10) μL of 8 M nitric acid. Add the acid slowly and swirl frequently to avoid excessive reaction of the solutions.
- Step 6) Let stand 10 (± 1) minutes, swirling frequently.
- Step 7) Heat 5 minutes at 80° to 90°C to complete the reaction.
- Step 8) Prepare a 500 (± 50) μL column of AG-1, X-4, 100 to 200 mesh resin. Remove the bulb from a 7.5-mL plastic dropper. Place a small cotton ball into the tip of the dropper and tamp lightly. Measure a volume of 500 μL above the cotton ball and mark. Fill the dropper to the mark with a slurry of AG-1, X-4, 100 to 200 mesh resin. Wash the resin with 2 (± 0.2) mL of 8 M nitric acid.
- Step 9) Transfer the solutions in the vial to the anion-exchange resin column, using a plastic dropper. Collect the column effluent in a 2-dram, screw-cap vial.
- Step 10) Wash the sample vial with four 1000 (± 10) μL portions of 8 M nitric acid.
- Step 11) Add each portion of 8 M nitric to the column, allowing each portion to drain through the column before adding the next. Collect all column effluent in the 2-dram screw-cap vial from Step 9. Discard the 15 mL vial, dropper and column in the radioactive dry waste.

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- Step 12) Evaporate the solution in the vial to dryness.
- Step 13) Add 500 (± 10) μL of 1 M nitric acid to the dried residue in the vial.
- Step 14) Cap the vial and roll the vial for about 1 minute to dissolve residue on all inner surfaces of the vial. Centrifuge for about 2 minutes to bring solution to bottom of vial.
- Step 15) Evaporate a measured portion of the solution on a 7/8-in. stainless steel alpha disk. Add deionized water dropwise to the disk to cover the dried residue then add one drop of concentrated ammonium hydroxide. Evaporate to dryness.
- Step 16) Heat the disk to a dull red heat by directing a flame to the bottom of the disk or heat on a hot plate on high heat until organic residue has been removed.
- Step 17) Measure the ^{241}Am and ^{244}Cm activity on the disk, using Alpha Spectrometry (HTA-4-5) and Alpha Counting (HTA-4-6) procedures.
- Step 18) Record volumes, counting data, and calculations on the cognizant scientist's copy of the analytical report.

4.1 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TEST PROCEDURE

TITLE: 2-30.6; ISOTOPIC COMPOSITION OF PLUTONIUM AND URANIUM BY MASS SPECTROMETRY

1.0 APPLICABILITY

The isotopic abundances of plutonium and uranium are determined by thermal ionization mass spectrometry. Purified portions of these elements are prepared using ion exchange chromatography. The separation of americium and uranium from plutonium is complete enough to permit the unbiased measurement of ^{241}Pu and ^{238}Pu . Ions are produced from a carbonized, single rhenium filament. An ion current measuring technique is used in the analysis.

- (a) Material Plutonium and uranium bearing materials.
- (b) Range Between 0.05 and 0.2 μg of plutonium or uranium are required per measurement. Mass ratios from 1 to 0.0001 (and their reciprocals) can be measured.
- (c) Reliability Relative standard deviations of 0.03 and 0.3 percent have been obtained for the ^{239}Pu and ^{241}Pu isotopes respectively, for the abundances of these isotopes present in NBS SRM 946 Pu Isotopic Standard.
- (d) Interferences With the separation procedure included in this method, interferences are not expected.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Analyst

4.0 PROCEDURE

4.1 DISCUSSION

When atoms or molecules are evaporated from a surface heated to a sufficiently high temperature, thermal ionization occurs in which a fraction of the atoms or molecules are ionized. The ionization efficiency, which is the ratio of ions produced to the remaining atoms or molecules, depends upon the ionization potential of the atoms or molecules and upon

Concurrence <i>KAB</i> <i>O. P. Amacker, Jr.</i> Date <i>6/17/88</i>		Approved <i>J. J. McCown</i> Date <i>6/16/88</i>	
Prepared by <i>W. Y. Matsumoto</i> Date <i>6/15/88</i>		QAD Concurrence <i>L. J. Ethridge</i> Date <i>6/16/88</i>	
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the work function and temperature of the surface.(c) The ionization efficiency increases with increased temperature and work function and it favors atoms or molecules with low ionization potentials.

One commonly used method for enhancing the ionization efficiency is the multiple-filament technique first proposed by Inghram and Chupka.(b) The advantage of the multiple filament is that the temperatures of the ionizing filament and the sample filament can be independently controlled to optimize the ionization and evaporation rates. Unfortunately, uranium atoms are preferentially ionized over plutonium atoms and trace amounts of uranium in plutonium will interfere in the determination of ^{238}Pu . Further, if the ionizing filament contains traces of natural thorium, the thorium will interfere with the ^{232}U determination.

A method to overcome the disadvantage of the multiple filament with respect to uranium and plutonium analyses is the single-filament technique in which a carbonized rhenium filament is used. The carbonization can be done in an auxiliary vacuum system before loading sample onto the filament as is done at PNL. To decrease fractionation and increase reproducibility a solution of chloroplatinic acid and sucrose is loaded over the sample. The filament is then heated to produce a platinum overplate.

The advantage of the single-filament method is that the ionization of plutonium atoms is enhanced over uranium atoms. This permits the determination of ^{238}Pu in plutonium that has been separated from uranium with simple ion exchange or solvent extraction procedures. In addition, the carbonized filament significantly reduces americium interference in the plutonium analysis and it permits the determination of ^{232}U without interference from the trace amount of natural thorium that are usually present in the filament material.

Although the carbonized single-filament technique improves the analysis of plutonium and uranium, these elements, if together, must be separated from each other before analysis. Also, americium should be separated from plutonium within a few weeks of a plutonium analysis. The separation procedure, which uses a single anion exchange column, provides adequate separation of these elements. During the sample preparation work leading to the mass spectrometric measurement, care must always be taken to avoid contamination of the sample with extraneous uranium or plutonium.

The specific separation procedure used depends upon the elements being analyzed. If only the isotopic composition of plutonium is required, the plutonium in solution is reduced to the three valence state with ferrous ammonium sulfate and it is then oxidized to the four state with nitric acid. As the solution is passed through an anion exchange resin, the plutonium as a nitrate complex is retained, while uranium and americium pass through the resin. If the isotopic composition of both plutonium and uranium is required, both are loaded onto an anion exchange resin as

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chloride complexes while americium passes through the resin. The uranium is eluted from the resin with 8M nitric acid and the plutonium is eluted subsequently with 0.1M nitric acid.

In calibrating the mass spectrometer, attention must be given to bias and linearity. A bias factor is determined using NBS plutonium and uranium isotopic standards and the factor is checked each day that the instrument is used by analyzing an NBS standard. If the calibration check indicates that a significant change in calibration occurred or if maintenance problems develop, the bias factor is redetermined.

4.2 APPARATUS

- (a) Heating Block. Aluminum, for 7-ml vials. A heating mantle is normally used with the heating block.
- (b) Ion Exchange Column. Plastic 6-mm diam, 6-cm long with a 2-ml reservoir. Snip off the top of a plastic dropper⁽¹⁾ to form the reservoir and place a cotton plug in the tip. Use a column only once and then discard it.
- (c) Mass Spectrometers. The two following instruments are used.
 - 1. C.E.C. (DuPont Instruments, Inc.), Model 21-703A, Thermal Ionization Mass Spectrometer.
 - 2. Nuclide Corp., Model 12-90-3S, Thermal Ionization Mass Spectrometer.
- (d) Mass Spectrometer Accessories. The following items are used in the analysis:
 - 1. Forming jig, used to form filaments into the configuration required and to hold the filaments in place for welding.
 - 2. Spot welder, used to weld the filament ribbons to the support posts. Welds must be made carefully to ensure good electrical contact, which is necessary for beam stability.
 - 3. Sample loading unit, used to evaporate a sample solution on a filament by passing an electrical current through the filament.
 - 4. Bakeout chamber, used to clean and degas filaments under a vacuum of at least 10^{-6} Torr at about 2000°C.

(1) Plastic dropper, Catalog No. 6219, Nalge Co., Rochester, NY.

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- (e) Plastic Pipet. A 10- μ l pipet with disposable plastic tip.(1) Use a pipet only once and then discard it.
- (f) Transfer Pipets. Pyrex, 2-ml capacity. Prepare before use as indicated for vials, item (g).
- (g) Vials. 7-ml. Prepare the vials before use as follows: heat in 0.1M ammonium hydroxide to near boiling; cool and rinse with distilled water. Heat in 0.1M HNO₃ to near boiling; allow to stand overnight. Rinse with distilled water and then with triple distilled water. Drain dry and store in a sealed plastic bag. Important: all vials used in this method must be treated prior to use to avoid contamination from extraneous uranium. Use a vial only once and then discard it.

4.3 REAGENTS

- (a) Acetone or methanol.
- (b) Anion Exchange Resin. Bio-Rad, AG-1, x-4, 200-400 mesh. Rinse in a polyethylene bottle by shaking with triple distilled water and decanting the fines. Repeat the rinse two or three times. Repeat again with 0.1M HCl and store the resin in 0.1M HCl.
- (c) Benzene or trans-2-butene.
- (d) Ferrous Ammonium Sulfate. Add 40 mg of ferrous ammonium sulfate and one drop of 18M H₂SO₄ to triple distilled water. Dilute to 100-ml volume and mix. Prepare fresh each day used.
- (e) Hydrochloric Acid. 1M and 10M. Prepare from HCl gas and triple distilled water or from ultrapure hydrochloric acid reagent such as J. T. Baker Company's ULTREX grade.
- (f) Nitric Acid. 0.1M, 2M, 3M, and 8M. Prepare from redistilled 15.6M nitric acid and triple distilled water or from ultrapure nitric acid reagent such as J. T. Baker Company's ULTREX grade.
- (g) Rhenium Ribbon. Nominally 0.076-cm wide by 0.0025-cm thick.
- (h) Chloroplatinic acid 0.05 g/ml in 0.02M sucrose solution.

4.4 STANDARDS

For both calibration and control, NBS plutonium and uranium isotopic standards are used as appropriate.

(1) A Kimble 10- μ l automatic pipet (#56300) with disposable polypropylene tips (#56305) can be used.

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4.5 SAFETY

- (a) Plutonium bearing materials are radioactive and toxic. Precautions are required to avoid the contamination of the laboratory and personnel.
- (b) Observe the general laboratory safety rules.

4.6 QUALITY CONTROL

4.6.1 Calibration

Periodic attention must be given to bias and linearity. These factors were determined when the mass spectrometer was first used and they are checked whenever a control result is obtained that significantly deviates from the accepted value.

4.6.2 Control

An NBS standard is analyzed at least once in each 8-hr shift in which isotopic analyses are made. If the control result deviates significantly from the accepted value, the calibration factors are rechecked (see Volume 1, Section 7.0).

4.7 ANALYSIS

4.7.1 Sample Preparation: Mixed Oxide

This procedure is used to prepare mixed oxide samples for both uranium and plutonium mass spectrometric measurements.

- (a) Dissolve the sample according to Method 30.1.

Care must be taken to avoid contamination from extraneous uranium and plutonium during dissolution and subsequent separation of uranium and plutonium.

- (b) Add an appropriate amount of sample solution to a 7-ml vial containing 500 μL of 2M HNO_3 .

At least 40 μg of uranium and 30 μg of plutonium should be taken for this preparation procedure.

- (c) Add 100 μL of the ferrous ammonium sulfate solution and heat for 10 min at about 90°C in the heating block.

The plutonium is reduced to the three valence state.

- (d) Remove the vial from the heating block and add 300 μL of concentrated ultrapure nitric acid.

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- (e) Heat again for 5 min at about 90°C and then cool to room temperature.

The plutonium is oxidized to the four valence state.

- (f) Add 1 ml of 10M HCl and swirl the vial to mix.
- (g) Prepare a 300- μ l column of anion exchange resin.
- (h) Wash the resin column first with 1 ml of 1M HCl and then with 1 ml of 10M HCl.
- (i) Transfer the sample solution from the vial to the resin column; discard the effluent.

All vials, ion-exchange columns, and transfer pipettes are used only once and then they are discarded.

The effluent contains americium. The uranium and plutonium are absorbed on the resin as the chloride complexes of U(VI) and Pu(IV).

- (j) Wash the resin column with six 1-ml portions of 10M HCl; discard the effluents.

Do not add the next portion until the previous portion has drained completely from the column.

- (k) Wash the resin column next with 600 μ l of 8M HNO₃, discard the effluent.
- (l) Elute the uranium with four 300- μ l portions of 8M HNO₃, collecting the effluents in a 7-ml vial.
- (m) Swirl the vial to mix and transfer a portion of solution containing about 40 μ g of uranium to a second vial.
- (n) Take the solution in the second vial to dryness and dissolve the residue in 1 ml of 0.1M HNO₃; heat slightly to ensure complete dissolution.

This solution contains about 40 μ g U/ml and it is saved for the uranium mass spectrometric measurement.

- (o) Wash the resin column with three 1-ml portions of 3M HNO₃; discard the effluents.
- (p) Wash the resin column with 300 μ g of 0.1M HNO₃; discard the effluent.

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- (q) Elute the plutonium with three 300- μ l portions of 0.1M HNO₃, collecting the effluents in a 7-ml vial.
- (r) Swirl the vial to mix and dilute a portion with 0.1M HNO₃, give about 10 μ g Pu/ml in the dilution.

This dilution is saved for the plutonium mass spectrometric measurement.

4.7.2 Sample Preparation: Plutonium Oxide and Mixed Oxide

This procedure is used to prepare plutonium oxide and mixed oxide for only plutonium mass spectrometric measurements.

- (a) Repeat steps (a) through (c) of Subsection 10.1.

At least 30 μ g of plutonium should be taken for this preparation procedure.

- (b) Remove the vial from the heating block and add 1 ml of 8M HNO₃.
- (c) Heat again for 5 min at about 90°C and then cool to room temperature.

The plutonium is oxidized to the four valence state.

- (d) Prepare a 300- μ l column of anion exchange resin.
- (e) Wash the resin column first with 1 ml of 8M HNO₃.
- (f) Transfer the sample solution from the vial to the resin column; discard the effluent.

All vials, ion-exchange columns, and transfer pipettes are used only once and they are discarded.

The effluent contains americium and it contains uranium when samples are mixed oxide. The plutonium is absorbed on the resin as the nitrate complex of Pu(IV).

- (g) Wash the resin column with six 1-ml portions of 8M HNO₃; discard the effluents.

Do not add the next portion until the previous portion has drained completely from the column.

- (h) Wash the resin column next with three 1-ml portions of 3M HNO₃; discard the effluents.

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(i) Wash the resin column with 300 μL of 0.1M HNO_3 ; discard the effluent.

(j) Repeat steps (q) and (r) of Subsection 10.1.

4.7.3 Sample Preparation: Uranium Oxide

This procedure is used to prepare uranium oxide for uranium mass spectrometric measurements.

(a) Dissolve the sample according to Method 30.1.

Care must be taken to avoid contamination from extraneous uranium

(b) Transfer a portion of sample solution containing about 40 μg of uranium to a vial.

All vials and transfer pipettes are used only once and then they are discarded.

(c) Take the solution in the vial to dryness and dissolve the residue in 1 ml of 0.1M HNO_3 ; heat slightly to ensure complete dissolution.

This solution contains about 40 μg U/ml and it is saved for the uranium mass spectrometric measurement.

4.7.4 Filament Preparation and Loading

(a) Prepare a single-filament assembly for rhenium ribbon using an appropriate forming jig.

Filament assemblies are made according to a procedure that is appropriate for the mass spectrometer used.

(b) Rinse the assembly twice with acetone or methanol.

(c) Dry the assembly under a heat lamp.

(d) Place the assembly into the bakeout chamber.

(e) Evacuate the chamber to at least 10^{-6} Torr and heat the filament to 2000°C for at least 10 min.

(f) Decrease the temperature of the filament in the bakeout chamber from 2000°C to 1600°C .

(g) Pass benzene vapor into the bakeout chamber until the pressure is about 5×10^{-4} Torr.

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- (h) Allow the carbonization reaction to continue for 90 min or until the filament is carbonized to the point of becoming quite brittle.

Temperature, pressure, and time used in steps (f), (g) and (h) depend upon the specific bakeout chamber and the thickness of the rhenium ribbon used to make the filament. Specific conditions required to carbonize the rhenium to the point of becoming quite brittle must be determined by experiment.

- (i) Cool the filament and bring the chamber to atmospheric pressure.

- (j) Remove the filament assembly.

If the assembly is not used immediately, store in a desiccator until used. Care must be taken to avoid breaking the brittle filament.

- (k) Mount the filament assembly in the sample loading unit.

- (l) Load about 10 μL of a solution containing uranium or plutonium onto the filament with a disposable pipet and evaporate to dryness by passing about 1 A of current through the filament.

The disposable pipet is used only once and then it is discarded.

The amount of uranium or plutonium loaded onto the filament will depend upon the particular mass spectrometer used.

- (m) Add 5 μL of the 0.05 g/ml chloroplatinic acid in 0.02M sucrose solution and evaporate to dryness. Then heat until a matt gray platinum overplate is produced. Usually 1.2 to 1.5 amps will suffice.

The filament assembly is ready for insertion into the mass spectrometer.

4.7.5 Mass Spectrometric Measurement

- (a) Insert the filament assembly into the mass spectrometer.
- (b) Slowly increase the filament temperature until a stable ion beam of the major isotope is obtained.

The intensity of the beam must be such that the minor isotopes are measurable.

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- (c) Scan the spectrum repeatedly in both directions over the mass range desired until at least nine spectra have been recorded.

4.8 CALCULATION

Calculate the weight percent of each isotope measured. The calculation procedure is governed by the type of instrumentation used. With the computerized system, results are calculated automatically and printed out as atom percents, weight percents, and isotopic ratios along with the standard deviation and other statistical information. Unless otherwise instructed, report isotopic results to the nearest 0.01% (weight or atom percent) for those results $\geq 1\%$ and to the nearest 0.001% for results $< 1\%$.

5.0 BIBLIOGRAPHY

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- (b) M. G. Inghram and W. A. Chupka, "Surface Ionization Source Using Multiple Filaments," Rev. Sci. Instr., 24, 518 (1953).
- (c) C. A. McDowell, Editor, Mass Spectrometry, McGraw-Hill Book Co., NY, p. 81 (1963).
- (d) J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps, and C. F. Metz, Methods for Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials, LA-4622, pp. 9, 15, 23 and 33, March (1971).

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PNL TEST PROCEDURE

TITLE: HTA-4-17, SOLUTIONS ANALYSIS: CARBON-14 BY DISTILLATION SEPARATION PRIOR TO MEASUREMENT BY LIQUID SCINTILLATION COUNTING

1.0 APPLICABILITY

This procedure applies to the preparation of aqueous samples for the determination of ^{14}C using Procedure HTA-4-4.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Liquid scintillation cocktail, Altex Ready-Solv® CP.
- Sodium hydroxide, 0.3 M -- Prepare by dissolving 12 (± 0.1) g of reagent-grade NaOH in 1000 mL of deionized water.
- Sulfuric acid, 1 M -- Prepared by diluting 55 (± 5) mL of concentrated reagent-grade sulfuric acid to 1000 (± 1) mL with deionized water.
- Sodium carbonate, 0.1 M -- Prepare by dissolving 1.06 (± 0.01) g of anhydrous reagent-grade Na_2CO_3 in 100 (± 1) mL of deionized water.
- Sulfuric acid, 4 M, potassium peroxydisulfate, saturated -- Prepare by diluting 222 (± 5) mL of concentrated reagent-grade sulfuric acid to 1000 (± 10) mL with deionized water and adding reagent-grade potassium peroxydisulfate crystals until excess crystals will not dissolve.
- Silver nitrate, 2 M -- Prepare by dissolving 34 (± 0.1) g of reagent-grade AgNO_3 in 100 (± 1) mL of deionized water.

®Altex Ready-Solv is a registered trademark of Beckman Instruments, Fullerton, California.

Concurrence NA	Date	Approved <i>[Signature]</i>	Date 7/2/87
Prepared by AC Leaf	Date 7/1/87	QAD Concurrence B. O. BARNES	Date 6/30/87
Procedure No. HTA-4-17	Revision No. 4	Effective Date JUL 01 1987	Page of 1 4

PNL TEST PROCEDURE

- Anhydrone,[®] anhydrous magnesium perchlorate, reagent-grade.
- Ascarite II,[®] 8 to 20 mesh.
- Carbon distillation apparatus.
- Vials, liquid scintillation, glass, Packard, 6001018.
- Vials, 35-mL, glass, screw-cap.
- Heating mantle, 100-mL, round bottom.
- Variac, 7.5-ampere, 0- to 140-volts output.
- Thermometer.

4.0 PROCEDURES

4.1 Sample Distillation

Carbon-14 is separated from other radioactive species by distillation of carbon dioxide from an acidic oxidizing solution. The carrier gas (air) is passed through Ascarite II to remove the carbon dioxide. The distilled carbon-14 dioxide is trapped in a liquid scintillation cocktail made basic with sodium hydroxide.

Step 1) To the CO₂ trap add 18 (± 0.1) mL Altex Ready-Solv CP liquid scintillation cocktail plus 2 (± 0.02) mL of 0.3 M sodium hydroxide; swirl to mix.

Step 2) To the water trap add Anhydrone to a depth of ~10 cm. Use a cotton plug to hold the Anhydrone in place.

Step 3) To the gas scrubber add 70 (± 5) mL of 1 M sulfuric acid.

Step 4) Place the heating mantle in position to heat the still.

Step 5) Connect the entire system and regulate the air flow to 40 (± 2) cc/min, as indicated by the flow meter. Be sure the system is sealed using stopcock grease at all joints. Secure ball and socket connections with suitable clamps.

[®]Anhydrone is a registered trademark of J. T. Baker Chemical Co., Phillipsburg, New Jersey.

[®]Ascarite II is a registered trademark of Authur H. Thomas Co., Philadelphia, Pennsylvania.

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- Step 6) Remove the still inlet and add in the following order:
- 500 (± 5) μL of hydrothermal test solution (unacidified)
 - 500 (± 5) μL of sodium carbonate
 - 100 (± 10) μL of silver nitrate
 - 15 (± 1) mL of 4 M sulfuric acid saturated with potassium peroxydisulfate.
- Step 7) Connect the inlet to the still. Adjust the air flow to between 30 and 50 cc/min.
- Step 8) Turn on condenser water; monitor flow through flow meters.
- Step 9) Turn on variac and set dial to 80. Temperature should rise to $\sim 104^\circ\text{C}$. Continue the distillation for 1 (± 0.2) hour after reaching maximum temperature.
- Step 10) Turn off the variac and allow the system to cool for 2 to 3 minutes.
- Step 11) Remove the heating mantle.
- Step 12) Disconnect the CO_2 trap from the Anhydrone trap.
- Step 13) Disconnect the CO_2 trap from the vacuum line.
- Step 14) Transfer the caustic scintillation cocktail from the CO_2 trap to a 35-mL screw-cap vial; mix the solution while transferring.
- Step 15) Pipet 15 (± 0.2) mL of the scintillation cocktail into a Packard liquid scintillation vial. Label the vial cap with "C-14 Sample ID."
- Step 16) Measure the ^{14}C activity using Procedure HTA-4-4, "Solutions Analysis: Liquid Scintillation." Record counting data in laboratory notebook.
- Step 17) Record volumes and calculation on the analytical report for ^{14}C .
- Step 18) Clean the CO_2 trap using a vacuum radioactive liquid waste jug. Rinse the trap three times with hot tap water and vacuum into the radioactive waste jug. Rinse the trap with tap distilled water and discard down the sink drain. Dry the trap with methanol.

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Step 19) Rinse the still by flushing with water. Vacuum the water from the still through the still entrance using the vacuum waste jug. Continue the vacuum to dry the still.

4.2 Calibration Standards Preparation

Step 1) To a 35 mL screw cap vial add 18 (± 0.1) mL Altex Ready-Solv® CP liquid scintillation cocktail plus 2 (± 0.02) mL of 0.3 M sodium hydroxide.

Step 2) To the vial from Step 1) add a measured amount (≤ 100 μ L) of ^{14}C Standard Solution containing a known amount of ^{14}C ($\sim 3 \times 10^4$ d/m). Standard must be NBS or NBS traceable. Carbon-14 supplier records, all volumes and calculations shall be recorded in the laboratory notebook.

Step 3) Cap the vial from Step 2) and shake vigorously until a clear solution is obtained upon standing.

Step 4) Pipet 15 (± 0.2) mL of the solution from Step 3) into a Packard liquid scintillation vial.

Step 5) Cap the vial and label the vial on the cap as "C-14 Std."

Step 6) Count the standard with samples and background solutions as described in Procedure HTA-4-4.

4.3 Background Solution Preparation

Step 1) Repeat Steps 1), 3), 4), 5) (label as " ^{14}C blank") of Section 4.2.

Step 2) Count the blank (background) solution with the sample and standards as described in Procedure HTA-4-4.

4.4 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TEST PROCEDURE

TITLE: 7-40.42, Rev. 0; DETERMINATION OF CARBON-14 IN RADIOACTIVE LIQUIDS, SOILS, AND SLUDGES

1.0 APPLICABILITY

This Test Procedure covers the determination of Total Carbon-14 (organic plus inorganic) in a variety of sample types, including liquids, soils, sludges and solids, as would particularly be expected from radioactive waste storage tanks. This broad range of sample types requires a broad flexibility in the method of oxidation/extraction. The radiation involved may range from mildly radioactive liquids, which may be handled in a fume hood, to intense, gamma-active sludges, requiring shielded cell operation. This single Test Procedure, therefore, covers two different oxidation/extraction methods, the method of furnace combustion and the method of wet persulfate oxidation. The choice of oxidation/extraction method will be determined by sample type and the decision made by the Cognizant Scientist. The primary method of choice will be the furnace combustion method. The two oxidation/extraction methods each cause total oxidation of all carbon species present, including organic species as well as inorganic carbonates.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

The two methods involve different oxidation/extraction techniques only. Both use the measurement method of liquid scintillation counting for measuring the carbon-14. Discussion of the two methods follow:

The furnace method A, is oxidation/extraction by total dry combustion in oxygen in a furnace. A Coulometrics Inc. Carbon Analyzer Furnace is used and standard procedure as described in procedure 7-40.37 ("Determination of Carbon in Solids") applies for operating the furnace.

Concurrence M. C. Burt	Date 2/26/90	Approved W. C. Weimer	Date 2/27/90
Prepared by D. L. Baldwin	Date 2/26/90	QAD Concurrence G. R. Gerke	Date 2/26/90
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PNL TEST PROCEDURE

The weighed solid, sludge or liquid sample is inserted into the furnace tube, combusted in a flowing oxygen stream, and the gas routed out of the cell for trapping. Alternatively, a liquid sample may be syringe injected into the furnace tube.

Method B uses the oxidation/extraction method of hot acidic persulfate oxidation. Excess potassium persulfate oxidant, added to heated sulfuric acid solution with silver catalyst, causes oxidation of all carbon species. All carbon, including ^{14}C , is oxidized to CO_2 , and swept away by the carrier gas. Method B uses a Coulometrics Carbon Analyzer Acidification unit, modified for this procedure, with the operation described in procedure 7-40.36 ("Analysis of Solid Samples for Carbonate By Use of Coulometrics Model 5011 Coulometer").

After the oxidation/extraction from each of these methods, the $^{14}\text{CO}_2$ is trapped in a NaOH trap solution and measured by liquid scintillation counting.

Typically, Method A (furnace method) should be the method of choice for all solid, soil, sludge or liquid samples. Method B (automated persulfate method) will be the secondary method used for some solids and liquid samples.

4.2 APPARATUS AND REAGENTS

4.2.1 Method A: Furnace Method

- 4.2.1.1 Coulometrics Carbon Furnace, plus standard operating reagents. (see Procedure 7-40.37 "Determination of Carbon in Solids".)
- 4.2.1.2 Sodium hydroxide trap solution, 0.6 M--prepare by dissolving 24 (± 0.1) g of reagent-grade NaOH in 1000 (± 1) ml of deionized water.
- 4.2.1.3 Liquid Scintillation cocktail, Beckman Ready-Gel.
- 4.2.1.4 Glass sparge trap for containing 15 ml trap solution.

4.2.2 Method B: Automated Persulfate Method

- 4.2.2.1 Coulometrics, Model 5030 Acidification Apparatus
- 4.2.2.2 Sulfuric acid, 4 M--prepare by diluting 220 (± 5) mL of concentrated, reagent-grade sulfuric acid to 1000 (± 1) mL with deionized, Type II water.
- 4.2.2.3 Sulfuric acid, 1 M--prepare by diluting 55 (± 5) mL of concentrated, reagent-grade sulfuric acid to 1000 (± 1) ml with deionized, Type II water.

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- 4.2.2.4 Potassium persulfate, (potassium peroxydisulfate), crystals, reagent-grade.
- 4.2.2.5 Sodium hydroxide trap solution, 0.6 M--prepare by dissolving 24 (± 0.1) g of reagent-grade NaOH in 1000 (± 1) ml of deionized water.
- 4.2.2.6 Silver nitrate, 2 M--prepare by dissolving 34 (± 0.1) g of reagent-grade AgNO₃ in 100 (± 1) ml of deionized water.
- 4.2.2.7 Ascarite for the absorption of CO₂ from air.
- 4.2.2.8 Trap Glassware for containing 15 ml trap solution.
- 4.2.2.9 Liquid Scintillation cocktail, Beckman Ready-Gel.

4.3 ANALYSIS

4.3.1 Method A: Furnace Combustion Method

The oxidation/extraction method is exactly as described in Procedure 7-40.37 ("Determination of Carbon in Solids"). The operation of the furnace, column prep and reagent prep is identical. References to the coulometer operation can be ignored, since this procedure uses the measurement method of liquid scintillation counting, not coulometry. At the location where the gas line normally enters the coulometer, the gas line is disconnected and attached to the carbon-14 trapping glassware. Various carbon-14 NIST referenceable-standards are available for use, primarily an organic dodecane standard and an inorganic sodium carbonate standard.

The Analyst will be responsible for all operations of equipment and reagents, obtaining results, recording all data in LRB and performing calculations. The Cognizant Scientist will be responsible for checking work and calculations, reporting data to customer, and decisions concerning sample problems.

4.3.1.1 Follow normal operating procedure for operation of the furnace (see procedure 7-40.37, "Determination of Carbon in Solids"). Disconnect gas line after the water trap, Ascarite and MnO₂, leading to Coulometer, and connect to trap glassware, within the fume hood.

4.3.1.2 Weigh solid or sludge sample or standard in boat to ± 0.0001 g, and record weight in LRB. Insert into quartz ladle and insert ladle into furnace tube cool end

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as per normal procedure 7-40.37. Operate furnace at 900-1000°C for total carbon-14. Record actual temperature in LRB. (If NIST standard is used, result is used to calculate F, Gas Collection Recovery Factor, as $[F = \text{C-14 measured} / \text{C-14 expected}]$. Record in LRB).

- 4.3.1.3 Alternatively, for liquid sample or standard, pipet 100 ± 1 ul, or volume as specified by Cognizant Scientist, into boat loaded full with calcium carbonate, CaCO_3 . The carbonate both absorbs the liquid sample and provides carbon carrier. Record volume in LRB. Insert into quartz ladle and insert ladle into furnace tube cool end as per normal procedure 7-40.37. Operate furnace at 900-1000°C for total carbon-14. Record actual temperature in LRB. (If NIST standard is used, result is used to calculate F, Gas Collection Recovery Factor, as $[F = \text{C-14 measured} / \text{C-14 expected}]$. Record in LRB).
- 4.3.1.4 Add 15.0 ± 1 ml 0.6 M NaOH trap solution into trap. Insert clean fritted sparge tube for connection to incoming gas line.
- 4.3.1.5 Begin furnace operation for carbon analysis by inserting sample ladle into furnace hot zone. Collect carbon-14 for 20 ± 1 minutes. Record time in LRB. Analysis complete.
- 4.3.1.6 Note condition of furnace combustion tube, barium chromate, and silver and record any unusual observations in LRB.
- 4.3.1.7 Transfer trap solution to labeled archive vial. Pipet 2.00 ± 0.1 ml trap solution into 18 ± 1 ml scintillation cocktail in labeled counting vial, mix and count in liquid scintillation counter. The Dilution Factor, DF, used in the calculations is equal to $(15.0 \text{ ml} / 2.0 \text{ ml})$, or 7.5.

4.3.2 Method B: Automated Persulfate Method

4.3.2.1 Preparation

- 4.3.2.1.1 Set up Coulometric Acidification unit for normal operation as per Procedure 7-40.36 ("Analysis of Solid Samples for Carbonate By Use of Coulometrics Model 5011 Coulometer"). Connect gas line to carbon-14 trap glassware.

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4.3.2.1.2 Prepare all reagents for operation, i.e., solid persulfate, silver nitrate in pipettor container, sulfuric acid in pipettor container, trap mixture, etc.

4.3.2.1.3 Begin heatup of heater well, set dial to 6.

4.3.2.2 Analysis

4.3.2.2.1 Blanks, standards, and samples all require identical operation of the apparatus.

4.3.2.2.2 Weigh standard or solid/sludge sample to ± 0.001 g into platinum or ceramic boat, and record weight in LRB. Insert into dissolution flask. Alternatively, pipet 1.00 ± 0.01 ml of liquid sample into dissolution flask. Record volume in LRB. Add 1.0 ± 0.1 g solid persulfate to flask. Close system and begin gas flow at 100 ± 10 cc/min through flask and through trap sparger. (If NIST standard is used, result is used to calculate F, Gas Collection Recovery Factor, as $[F = C-14 \text{ measured} / C-14 \text{ expected}]$. Record in LRB).

4.3.2.2.3 Add 15.0 ± 0.1 ml 0.6 M NaOH trap solution into trap. Insert clean fritted sparge tube for connection to incoming gas line.

4.3.2.2.4 Inject $10 \text{ ml} \pm 0.1$ sulfuric acid into flask. Inject $100 \pm 1 \mu\text{l}$ silver nitrate into flask. Lower flask assembly into heater well.

4.3.2.2.5 Allow 20 ± 1 minutes for oxidation/extraction to complete and all CO_2 swept out and through sparge trap. Record time in LRB. Analysis complete.

4.3.2.2.6 Transfer trap solution to labeled archive vial. Pipet 2.00 ± 0.01 ml trap solution into 18 ± 0.1 ml scintillation cocktail in labeled counting vial, mix and count in liquid scintillation counter. The Dilution Factor, DF, used in the calculations is equal to $(15.0 \text{ ml} / 2.0 \text{ ml})$, or 7.5.

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4.4 CALCULATIONS

All calculations for the two methods are performed identically, as follows:

Calculate C-14 in this manner, and record in LRB:

$$\begin{array}{l} \text{C-14 (Ci/g)} = \frac{(A - B) \times D \times DF}{(C - B) \times W \times E \times F} \\ \text{or Ci/ml} \end{array}$$

Where:

- A = sample ct/min
- B = blank ct/min
- C = standard ct/min
- D = standard dis/min
- DF = dilution factor (generally 7.5)
(determined by pipetting required)
- W = weight of sample (g) (or volume in ml for liquids)
- E = 2.22 E12 dis/min per Ci
- F = gas collection recovery factor (determined by injection and recovery of C-14 standard, traceable to NIST. Either inorganic or organic C-14 standard may be used.)

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PNL TEST PROCEDURE

TITLE: HTA-4-4, SOLUTIONS ANALYSIS: LIQUID SCINTILLATION

1.0 APPLICABILITY

This procedure provides instructions for the measurement of alpha or beta activity in solution by the liquid scintillation method. This procedure applies to the analysis of samples by the liquid scintillation method prepared using Procedures HTA-4-18 and HTA-4-17.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Liquid scintillation counting system, Nuclear Chicago Mark I.

3.1 Calibration Standards

Calibration standards of the isotope being counted are prepared in a matrix as nearly identical as possible to that of the sample. See Procedure HTA-4-17, Section 4.2. Standards are NBS or NBS-traceable whenever possible. When no standards are available for an isotope such as ^{79}Se an alternate standard isotope of similar maximum and average beta energy may be used. See Procedure HTA-4-18, Section 4.0, Step 23.

3.2 Background Solutions

Background solutions are prepared in a matrix as nearly identical to that of the sample as possible. Such solutions will then give a measure of all sources of background counts when counted before and after the samples and standards. See Procedure HTA-4-17, Section 4.3 and Procedure HTA-4-18, Section 4.2.

Concurrence <i>NA</i>	Date	Approved <i>[Signature]</i>	Date <i>7/2/87</i>
Prepared by <i>A. Cleaf</i>	Date <i>7/1/87</i>	QAD Concurrence <i>B.O. BARNES</i>	Date <i>6/30/87</i>
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4.0 PROCEDURE

Prior to operation, the operator must be adequately trained in Section III, Controls and Readout of the Mark I Liquid Scintillation Counter Manual.

Step 1) Place the standards, background solutions and samples in the automatic sample changer system. The testing order is standard, background solution, samples, standard and background solution. (Note on the data printout the position number for each vial.)

Step 2) Set the counting time to 40 minutes. (All solutions will be counted 40 minutes.)

Step 3) Set the channel width and attenuator to give the maximum efficiency for the isotope being counted. The isotopes counted are ^{129}I , ^{79}Se , and ^{14}C . These isotopes all have essentially the same beta energy, and all are counted with the following settings:

Attenuator Course Setting: D
 Attenuator Fine Setting: 5.0
 Window Lower Level: 0.5
 Window Upper Level: 9.9

Step 4) Set the system to PROGRAM and AUTO RECYCLE. (Solutions will count and change automatically until the system is halted.)

Step 5) Calculate the disintegrations per count (dis/ct) in the standard using the following equation. Counting rates are automatically calculated by the counting system. Use the average of all standard and background counting rates. The average of each standard counting rate must be within 5% of the average of all standard counting rates. If not, two new standards must be prepared.

$$\text{dis/ct} = \frac{A}{S - B}$$

where: A = disintegrations per minute of standard in vial (overall uncertainties of standards used are: ^{129}I = 1% and ^{14}C = 2%, as supplied by Amersham)

S = standard counting rate (ct/min)

B = background counting rate (ct/min).

Step 6) Calculate the disintegration rate in the sample using the following equation. Counting rates are automatically calculated by the counting system. Use the average of all counting rates measured for each individual solution and the average of all background counting rates.

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$$\text{dis/min/mL} = (A - B) \times C \times D$$

where: A = counting rate of sample (ct/min)
 B = background counting rate (ct/min)
 C = dis/ct factor from Step 5
 D = volume factor to convert dis/min/mL of sample

$$D = \frac{1}{V E}$$

where: V = volume of sample taken for separation (mL)
 E = fraction of sample taken that is counted

EXAMPLE: If 0.5 mL of sample is separated and diluted to 20 mL of scintillation cocktail and 15 mL is actually counted, then V = 0.5 mL and E = 15/20.

The estimate of precision is based on the equation:

$$\sigma = \pm \frac{\sqrt{A + B}}{40} \times \frac{1}{V E} \times C$$

where: σ = relative standard deviation ($\pm$ dis/min/mL)
 A = average counts in sample (ct/40 min)
 B = average counts in background (ct/40 min)
 V = volume of sample taken for separation (mL)
 E = fraction of sample taken that is counted
 C = dis/ct factor from Step 5.

Step 7) Retain liquid scintillation data and dis/ct calculations in numbered laboratory notebook. Record dis/min/mL results on the analytical report form.

4.1 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-400, (Replaces HTA-4-24), SAMPLE PREPARATION: DISSOLUTION OF LWR FUEL SAMPLES

1.0 APPLICABILITY

This procedure applies to the dissolution of LWR (PWR or BWR) uranium oxide fuel samples for subsequent radiochemical analysis. The fuel exposure may range from non-irradiated fuel samples to high burnup spent fuel exceeding 50 GWD/MTM. The size of the sample for dissolution should normally be less than 10 g. It is essential that the cognizant scientist be knowledgeable and experienced in all aspects involved in the analysis of highly irradiated nuclear fuel for the parameters of interest, and capable of making adjustments needed to accommodate special samples or requirements without comprising the integrity of this basic procedure.

This procedure is also applicable to uranium metal fuel, uranium nitride fuel and uranium-plutonium mixed oxide fuels clad in stainless steel or zirconium alloys and irradiated in thermal (light water or graphite moderated) or fast (sodium cooled) reactor environments.

This procedure is not applicable to dissolution of samples requiring analysis for iodine isotopes or any element likely to form volatile compounds with the reagents used for dissolution.

2.0 DEFINITIONS

- 2.1 LWR- Light Water (moderated) Reactor.
- 2.2 PWR, BWR- Pressurized Water Reactor, Boiling Water Reactor.
- 2.3 GWD/MTM- GigaWatt days/Metric Ton of Metal fuel equivalent.
- 2.4 Metric Ton- Equals 1000 kg.
- 2.5 Reagent-grade- As used here, chemicals meeting or exceeding the standards for reagent chemicals in, "Reagent Chemicals, American Chemical Society Specifications, "Am. Chemical Soc., Washington, DC.

Author	Date	Project Mgr.	Date	QAD Representative	Date
WY Matsumoto	06/23/88	N/A		LJ Ethridge	06/24/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	06/24/88	All original signatures on file	
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2.6 Cognizant Scientist- As used in this procedure, the professional or managerial person who is responsible for the process and results.

3.0 RESPONSIBLE STAFF

- Cognizant Scientist(s)
- Qualified Technician-Analyst(s)

4.0 PROCEDURE

4.1 Equipment and Materials

- Nitric acid, ~12 M -- Prepared by diluting 746 (± 20) mL of concentrated Ultrex[®] or equivalent nitric acid with 235 (± 5) mL H₂O sub-boiling quartz distilled water.
- Nitric acid, ~2 M -- Prepared by diluting concentrated Ultrex[®] or equivalent nitric acid with sub-boiling quartz distilled water, dilute 1 volume of nitric acid with 7 volumes of water keeping the ratio to within $\pm 2\%$.
- Hydrochloric acid, ~12 M -- concentrated Ultrex[®] or equivalent hydrochloric acid.
- Hydrofluoric acid, reagent-grade, 48%.
- Ammonium hydroxide, ~0.1 M -- Prepared by diluting 7 (± 1) mL of concentrated reagent-grade 14.8 M NH₄OH in 990 (± 20) mL of deionized water.
- Nitric acid, ~0.1 M -- Prepared by diluting 6 (± 1) mL of concentrated reagent-grade 15.7 M HNO₃ in 990 (± 20) mL of deionized water.
- Cesium carrier solution, ~10 Cs⁺ mg/mL -- Prepared by dissolving 1.5 ± 0.05 grams reagent grade cesium nitrate in 100 mL of 2 M HNO₃.
- Sub-boiling quartz distilled water.

[®] Ultrex is a registered trademark of J. T. Baker Chemical Co., Phillipsburg, New Jersey.

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- Deionized water.
- Vials, 2-dram, borosilicate glass with Polyseal[®] screw caps.
- Hot plate with continuously variable heat control.
- Vials, 20-mL, borosilicate glass with Polyseal[®] screw caps.
- Flasks, volumetric, 50-mL to 500-mL, depending on sample size.
- Beakers or Erlenmeyer flasks 125-mL to 500-mL.
- Wash bottles, polyethylene, 500-mL.
- Vials, "peanut," plastic.
- Stirring bars, magnetic, glass or teflon encapsulated, and of a size to obtain good stirring efficiency in the volumetric flasks used.
- Watch glasses sized to fit the dissolution beakers or Erlenmeyer flasks used.
- Forceps, 10-inch long, stainless steel.
- Plastic bag, 6-in. x 9-in. (for forcep storage).
- Cartons, drug (4 oz.)
- Pipet tips.
- Dental roll handle for each watch glass.
- Lead brick sample holders with holes drilled to accommodate the 2-dram screw cap vials and provide a minimum 5/8 inch of lead shielding for transporting to the radiochemistry laboratory.

4.2 Description and Stepwise Operation

Dissolve the main bulk of the fuel sample by heating in 12 M HNO_3 until there is no visible fuel attached to the cladding.

[®] Polyseal is a registered trademark of All-Pak, Inc.

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If necessary remove part of the clear supernatant solution to the volumetric flask and treat the sample by heating with additional portions of 12 M HNO_3 . Remove the cladding from the solution using clean stainless steel forceps, rinse the cladding and forceps into the dissolution vessel (dissolver) with 2 M HNO_3 from a wash bottle. Rinse the cladding with distilled water, discarding the rinse solution, and allow the cladding to air dry before weighing to the nearest 0.1 mg. HF is added to the dissolution flask to catalyze the dissolution of plutonium oxides, as a general rule the higher burnup (exposure) fuels are more difficult to dissolve and may require several repeated treatments of heating with 12 M HNO_3 and 0.01 to 0.05 M HF to get the sample into solution. With very high burnup fuel samples, it may be necessary to transfer the clear supernatant solution to another vessel and treat the difficulty soluble dark residu with a mixture of 3:1, 12 M HCl and 12 M HNO_3 repeated several times. In these cases the use of erlenmeyer flasks for dissolution vessels is advantageous due to increased refluxing action. Before combining this solution with the main bulk of the fuel in the 12 M HNO_3 solution it should be combined and evaporated with enough excess HNO_3 to insure destruction of almost all of the chloride in solution. The dissolved sample is evaporated to about 20% of its planned final volume with excess nitric acid then quantitatively transfereed to the volumetric flask with 2 M HNO_3 and equilibrated to the ambient conditions before final dilution to volume, mixing and aliquoting for sample analysis and "archive" sample storage.

- Step 1) Place the 2-dram vials, 20-mL vials, watch glasses, appropriately sized beakers or Erlenmeyer flasks and volumetric flask in a large beaker. Cover with 0.1 M NH_4OH and heat on a hot plate at low heat for ~8 hours.
- Step 2) Drain the liquid added in Step 1 and rinse the contents with deionized water.
- Step 3) Cover the components listed in Step 1 with 0.1 M HNO_3 and heat a hot plate at low heat for ~8 hours.
- Step 4) Drain and rinse the components with deionized water.
- Step 5) Then rinse the components with sub-boiling quartz distilled water.
- Step 6) Air-dry the components in a laminar flow hood.

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NOTE: In normal practice the components listed in Step 1) through Step 6) are preleached in batches and stored in clean polyethylene bags after drying. It is important to keep the equipment and chemicals that contact or become part of the sample as clean as possible.

Step 7) Prepare the following and transfer into the hot cell.

- Beakers, flasks, and "peanut" vials labeled with sample ID
- Wash bottle filled with 12 M HNO_3
- Wash bottle filled with 2 M HNO_3
- Sample beakers or Erlenmeyer flasks containing ~100 ml of 12 M HNO_3 and enough Cs carrier to give a Cs concentration of ~1 ppm in the final dilution volume.
- Watch glasses with dental roll handle attached.

Step 8) Visually examine each fuel specimen and record any unusual characteristics such as; loose separated fuel chunks, paint markings or excessive corrosion product deposits on the cladding surface, lack of cladding, etc., in the appropriate Laboratory Record Book(LRB).

Step 9) If paint markings or excessive deposits are observed on the cladding, these should be removed chemically or mechanically before proceeding. Toluene, xylene, acetone, amyl acetate and methanol can be used singly or in combination to remove paint marks using a swabbing technique. Heavy deposits can be scraped off with a sharp edged tool or file. Dilute HNO_3 or HCl used with swabs can remove light deposits and can be used to complete the job on heavy deposits.

Care should be taken to prevent the contact of the cleaning reagents with the interior fuel sample. The last steps in cleaning should be: swabbing with distilled water to remove any acid remaining on the surface, then swabbing with methanol to remove the water and promote rapid drying of the sample.

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- Step 10) Place each fuel specimen in its prelabeled "peanut" vial and weigh on an analytical balance. Record the weight to the nearest 0.1 mg and the sample ID in the burnup logbook.
- Step 11) Carefully transfer the sample into its dissolution vessel (here-after called the "dissolver") containing about 100 mL of 12 M HNO_3 .
- Step 12) Weigh the empty "peanut" vial and record the vial's (tare) weight to the nearest 0.1 mg in the burnup logbook.
- Step 13) Place watch glasses on dissolvers and heat on the hot plate at low heat.
- Step 14) When the brown fumes (oxide of nitrogen) have ceased, remove the dissolvers from the hot plate and cool.
- Step 15) Remove and discard the watch glasses. Pick up the fuel cladding in each dissolver with clean forceps and rinse the cladding and the forcep into the dissolver with 2 M HNO_3 . Examine the inside surface of the cladding for undissolved fuel and treat with a fresh batch of 12 M HNO_3 if necessary.
- Step 16) Rinse the cladding with deionized water and air-dry thoroughly.
- Step 17) Weigh the cladding to the nearest 0.1 mg and enter weight in the burnup logbook. Calculate the net fuel weight by subtracting the cladding weight and vial tare weight from the original gross weight obtained in Step 10. Record the net fuel weight in the logbook.
- Step 18) Add ~2 drops concentrated HF per 100-mL volume in the dissolver.
- Step 19) Return the dissolvers to the hot plate and continue heating, adding 12 M HNO_3 and HF, until the residue is dissolved or treatment with $\text{HCl} - \text{HNO}_3$ mixture is deemed necessary by the cognizant scientist. After dissolution, continue heating until the volume of the solution in the beaker has been reduced to about 20% of the final solution volume, add excess HNO_3 if needed to destroy chloride in the solution.

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- Step 20) Remove the dissolvers from the hot plate and cool.
- Step 21) Pour the contents of the dissolver into the volumetric flask selected for the final solution volume. This should be determined by the cognizant scientist based on the original sample size and other considerations such as the difficulty of dissolution. Rinse the dissolver several times with 2 M HNO_3 , adding the rinses to the volumetric flask. Swirl the volumetric flask after each addition. Add 2 M HNO_3 until the volume is just below the neck of the flask. Allow the contents of the flask to equilibrate with the hot cell temperature.
- Step 22) Adjust the volume in the flask to the calibration mark with the 2 M HNO_3 .
- Step 23) Add the stirring bar and stir thoroughly. A 15-minute stirring time is adequate if a good vortex is observed on the upper surface of the liquid in the neck of the volumetric flask.
- Step 24) Prepare the following and transfer into the hot cell.
- Step 24.1) Cardboard drug cartons -- Tape the lids on the cartons; then cut each drug carton in half transversely. Label the halves with the sample ID.
- Step 24.2) 2-dram vials -- Label with sample ID. Pack the 2-dram vials in the drug cartons (2 vials per 1/2 carton) by separating the vials with folded facial tissue.
- Step 24.3) 20-mL sample storage vials -- Label with sample ID.
- Step 24.4) Pipet tips -- Place in a plastic vial.
- Step 25) Pour several mL of the solution in the volumetric flask into a waste beaker. Fill the 20-mL storage vial to the shoulder with solution from the volumetric flask.

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- Step 26) Pipet an aliquot (volume to be specified by cognizant scientist or designate) from the 20-mL storage vial into a 2-dram sample vial. Record the sample volume in the burnup logbook. If the aliquot removed is 2-mL or more, add solution from the volumetric flask to bring the volume in the vial up to the shoulder.
- Step 27) Carefully cap the 20-mL storage vial using a Polyseal* or equivalent cap and place it in the storage rack.
- Step 28) Call Radiation Protection and transfer the sample out of the hot cell.
- Step 29) Prepare Sample Follower Cards or equivalent documentation and transfer these and the samples to the laboratory designated by the cognizant scientist.
- Step 30) Pour the remainder of the sample solution from the volumetric flask into a beaker and evaporate to dryness.
- Step 31) Dispose of the beaker in hot cell solid waste, after recording the fissile weight and the waste can ID used.
- Step 32) Dispose of the cladding in hot cell solid waste.
- Step 33) Rinse the glassware and dispose of the rinse solution down the hot cell drain. Break up the used glassware and dispose of the broken glass in hot cell solid waste.

4.3 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033. ~~Laboratory Record Books maintained and controlled to conform with the requirements of PAP 1704 provide a mechanism for control of most records.~~

4.4 Procedure Qualification

This procedure is based on well-understood chemical properties and is considered qualified by the Independent Technical Review process.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-401, (Replaces HTA-4-25), BURNUP ANALYSIS: NEODYMIUM-148 METHOD

1.0 APPLICABILITY

This procedure describes the technique for determination of stable fission product ^{148}Nd in irradiated uranium and plutonium as a measure of fuel burnup. Uranium (U) and plutonium are also determined by isotopic dilution mass spectrometry after chemical separation on the same sample aliquot.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Hydrochloric acid (HCl), concentrated, 12 M, Ultrex[®] or equivalent.
- Nitric acid (HNO_3), concentrated, 15.7 M, Ultrex or equivalent.
- Hydrofluoric acid (HF), concentrated, 28 M, analytical reagent-grade.
- Perchloric acid (HClO_4), concentrated, 70%, analytical reagent-grade.
- Sulfuric acid (H_2SO_4), concentrated, 18 M, Ultrex or equivalent.

[®]Ultrex is a registered trademark of Baker Chemical Co., Phillipsburg, New Jersey.

Author	Date	Project Mgr.	Date	QAD Representative	Date
GE Meadows	07/01/87	N/A		BO Barnes	06/30/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	07/02/87	All original signatures on file	
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- Fuming nitric acid, analytical reagent-grade.
- HCl, 10 M and 1 M -- Prepared by diluting concentrated Ultrex or equivalent HCl with sub-boiling quartz distilled water.
- HNO₃ acid, 2 M, 3M, 8M, 10M, 1:500, 1:100, 1:1 -- Prepared by diluting concentrated Ultrex or equivalent HNO₃ with sub-boiling quartz distilled water.
- Ferrous ammonium sulfate solution, 0.001 M -- Add 40 mg of reagent-grade ferrous ammonium sulfate [Fe(NH₄)₂(SO₄)₂ · 6H₂O and 1 drop concentrated H₂SO₄ to 5 (±1) mL of sub-boiling quartz distilled water. Dilute to 100 (±2) mL with sub-boiling quartz distilled water and mix.
NOTE: This solution has a short shelf life. It should be prepared fresh daily.
- Calibration standard (¹⁴⁸Nd, ²³⁹Pu, and ²³⁸U) -- The standard solution is prepared per ANSI/ASTM Standard E321-79, Section 5.3, using NBS uranium and plutonium standards and reagent-grade (>99.9% pure) Nd₂O₃. The standard solution can be stored in sealed glass ampoules for future use and is used to standardize the spike solution.
- Spike solution (blended ¹⁵⁰Nd, ²³³U, and ²⁴²Pu) -- The spike solution prepared and standardized per ANSI/ASTM Standard E 321-79, Section 5.4, and sealed in glass ampoules. An ampoule is opened for each burnup analysis, and the volume required to perform the analysis is removed with a pipet.
- Methanol, absolute, analytical reagent-grade
- Eluent, methanolic HNO₃ -- Pipet 10 (±1) mL of HNO₃ (1:500) into a 100-mL volumetric flask and dilute to the mark with absolute methanol. Protect this reagent against preferential evaporation of methanol by keeping it in a polyethylene wash bottle. Prepare fresh weekly.
- Loading solution, methanolic HNO₃ -- Pipet 1 (±0.02) mL of HNO₃ (1:1) into a 10-mL volumetric flask and dilute to the mark with absolute methanol.
- Wash solution, methanolic HNO₃ -- Pipet 10 (±0.1) mL of HNO₃ (1:100) into a 100-mL volumetric flask and dilute to the mark with absolute methanol.

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PNL TECHNICAL PROCEDURE

- Dowex[®] 1 resin -- Convert Dowex 1-X2 or 1-X4 (200 to 400 mesh) chloride form resin or equivalent to nitrate form by washing the resin in a suitable column with HNO₃ (1:1) until a drop of effluent falling into AgNO₃ solution remains clear. Rinse the resin with water and dry overnight in a vacuum dessicator. Store the resin in an airtight container. Since the characteristics of the resin vary from lot to lot, when lots and/or supplies are changed, the elution characteristics for Nd should be determined using the technique described in ANSI/ASTM Standard E 321-79, Section 5.13.
- Ion Exchange Column (Type A) -- Prepare by drawing out of the end of a pretreated glass tube. Pretreat one or several 15-cm long X4-mm ID Pyrex[®] glass tube(s). Use a glass wool or cotton plug in the drawn-down section of the column to support the resin.
- Ion Exchange Column (Type B) -- Pretreat commercial disposable polyethylene dropper(s), 6-mm ID and 11mm long with a 2-mL reservoir. Cut off the top reservoir end of the pretreated dropper and use the bottom 11 cm for the column. Use a glass wool plug to support the resin.
- Ion Exchange Column (Type C) -- Fabricate the resin column from a 15-cm long x 4-mm ID Pyrex tube and the reservoir section from a 7-cm long x 17-mm ID Pyrex tube.
- Vials, 2-dram, borosilicate glass
- Vials, 15-mL
- Pipets, assorted sizes
- Counting disk, stainless steel, mirror finish, 7/8-in diam x 0.01-in. thick

® Dowex is a registered trademark of Bio-Rad Laboratories, Richmond, California.

® Pyrex is registered trademark of Pittsburgh Corning, Pittsburgh, Pennsylvania.

* Pretreat Pyrex glass tube(s) per PNL-ALO-400, Section 4, Steps 1 thru 6.

**Pretreat polyethylene dropper(s) by rinsing with deionized water and air drying.

Store unused droppers in unused polyethylene bag.

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PNL TECHNICAL PROCEDURE

- Heat lamp
- Heating block
- Hot plate
- Flasks, volumetric, 10-mL
- Flasks, volumetric, 100-mL

4.0 PROCEDURE

Fission product neodymium (Nd) is chemically separated from irradiated fuel and determined by isotopic dilution mass spectrometry. Enriched ^{150}Nd is used as the Nd isotope diluent, and mass 142 is used to determine natural Nd contamination. Uranium (U) and plutonium (Pu) are also determined by sample aliquot. The method uses a calibrated triple spike of ^{150}Nd , ^{233}U , and ^{242}Pu per ANSI/ASTM Standard Test Method E321- 79.

- Step 1) Add an appropriate amount of spike solution to a sample aliquot from the 2-dram vial (from PNL-ALO-400, Step 23). The amounts of spike and sample solutions are per ANSI/ASTM Standard E321-79. This sample plus another aliquot of the sample without a spike are processed by the following steps.
- Step 2) Add 100 (± 2) μL of 70% HClO_4 .
- Step 3) Heat the solution on the hot plate to about 210°C until dense white fumes are observed.
- Step 4) Add 500 (± 10) μL of 2 M HNO_3 .
- Step 5) Add 100 (± 2) μL of ferrous ammonium sulfate solution. Mix well and let stand for about 5 minutes.
- Step 6) Add 200 (± 4) μL of fuming nitric acid and evaporate to near dryness.
- Step 7) Dissolve the residue in 1 (± 0.02) mL of 10 M HCl .
- Step 8) Add 50 (± 1) μL of fuming HNO_3 and heat until fumes stop.
- Step 9) Prepare a 300- μL anion-exchange column, Type B. Wash the column with 2 (± 0.04) mL of 1 M HCl . Wash the column with 2 (± 0.04) mL 10 M HCl . Discard wash solutions.

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PNL TECHNICAL PROCEDURE

- Step 10) Place a 2-dram vial under the column.
- Step 11) Transfer the sample solution onto the column. Rinse the vial with two 1 (± 0.02) mL portions of 10 M HCl and use the rinse solution to wash the column.
- Step 12) Remove the 2-dram vial containing the Nd and heat to near dryness. Reserve the 2-dram vial for further purification, starting with Step 24.
- Step 13) Place a 15-mL vial under the column. Then wash with six 1 (± 0.02) mL portions of 10 M HNO₃. Discard wash solutions.
- Step 14) Place a 2-dram vial under the column. Elute the U with four 300 (± 6) μ L portions of 8 M HNO₃.
- Step 15) Heat to near dryness.
- Step 16) Add 1 (± 0.02) mL of 2 M HNO₃. Estimate μ g U/mL from sample weight, U composition, and dilutions.
- Step 17) Remove an aliquot of solution and place it in a 2-dram vial. Add water and 1:100 HNO₃ so that the final solution concentration will be ~ 40 μ g U/mL in a 0.1 M HNO₃. Reserve the solution for U mass spectrometry.
- Step 18) Place a 2-dram vial under the column. Wash the column with three 1 (± 0.02) mL portions of 3 M HNO₃. Wash the column with 300 (± 6) μ L of 0.1 M HNO₃. Discard wash solutions.
- Step 19) Elute Pu with three 300 (± 6) μ L portions of 0.1 M HNO₃. Remove solution from under the column and swirl to mix thoroughly.
- Step 20) Pipet a 10 (± 0.2) μ L aliquot of the solution from Step 19 onto a 7/8-in. diameter counting disk and dry.
- Step 21) Count on a proportional alpha counter per PNL-ALO-421.
- Step 22) Calculate Pu concentration in the vial, using results from Step 21.
- Step 23) Adjust solution concentration to about 19 μ g Pu/mL using 0.1 M HNO₃.

NOTE : Reserve the solution for Pu mass spectrometry.

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PNL TECHNICAL PROCEDURE

4.1 Neodymium Purification

Step 24) Add 150 (± 3) mL of 1:1 HNO_3 and evaporate to near dryness.

Step 25) Dissolve the residue in 500 (± 10) μL of loading solution.

NOTE: In Steps 26 through 38, adjust volumes per results in ANSI/ASTM Standards E321-79, Section 5.13.1.

Step 26) Prepare a 2-cm-long anion-exchange column, Type A. Place a vial under the column. Wash column with 1 (± 0.02) mL of loading solution.

Step 27) Transfer the Nd solution onto the column. Wash down the walls of the column with a few drops of loading solution.

Step 28) Elute the Nd using 10 (± 0.2) mL of eluent solution. Discard the first ~ 2.5 mL of eluent. Collect in a 2-dram vial the next ~ 7.5 mL of eluent containing the Nd.

Step 29) Evaporate the solution to dryness under a heat lamp.

Step 30) Redissolve the residue in 500 (± 10) μL of loading solution.

Step 31) Prepare a 6-cm-long ion-exchange column with a reservoir.

Step 32) Place a 35-mL vial under the column. Wash with 1 (± 0.02) mL of loading solution.

Step 33) Transfer the sample solution onto the columns. Rinse the sample vial with several drops of loading solution and rinse down the walls of the column with loading solution.

Step 34) Wash the column with 26 (± 0.5) mL of wash solution. Discard the wash solution.

Step 35) Elute the Nd from the column with 8 (± 0.2) mL of eluent. Collect the Nd in a 2-dram vial.

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PNL TECHNICAL PROCEDURE

- Step 36) Evaporate the solution to dryness under a heat lamp.
- Step 37) Add 50 (± 1) μL of 2 M HNO_3 and dissolve the residue by warming the vial.
- Step 38) Add 200 (± 4) μL of sub-boiling quartz distilled water and swirl to mix. The solution concentration should be $\sim 1 \mu\text{g Nd/mL}$.
NOTE: Reserve the solution for Nd mass spectrometry.
- Step 39) Fill out a Mass Spectrometer Analysis Request Form and submit samples for mass spectrometry.

4.2 Mass Spectrometric Measurement

The isotopic abundance of Nd, Pu, and U are determined by thermal ionization mass spectrometry. The mass spectrometer linearity and bias factor are checked each day that the instrument is used by analyzing NBS Pu and U standards and Research Chemicals Nd_2O_3 (99.999% pure). Preparation of rhenium filaments, loading samples on the filaments, and operation of the mass spectrometer for isotopic measurements are detailed in the Analytical Chemistry Laboratory Manual, PNL-ALO-428. The results are calculated automatically by a computer, and the printout tabulates atom percents, weight percents, and isotope ratios along with standard deviation.

4.3 Burnup Calculations

Calculations are performed using the data obtained from mass spectrometry and a computer program for burnup analyses using the ^{148}Nd Isotopic Dilution Mass Spectrometry method. The results are printed out on the data sheet that includes U percent, Pu percent, Nd isotopic ratios, and burnup. Assumptions and nuclear parameter values used to perform the calculation are provided with each result. All sample information is kept on file in the 325 building.

4.4 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033. Laboratory notebooks provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-402, (Replaces HTA-4-26), SAMPLE PREPARATION: LWR FUEL SOLUTION

1.0 APPLICABILITY

This procedure applies to the preparation of test solutions of LWR fuel for subsequent analysis.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

3.1 Reagents for Section 4.1 (Determining ^{137}Cs , ^{99}Tc , ^{90}Sr , and ^{241}Am).

- Nitric acid, 2 M -- Prepared by diluting 127 (± 2) mL of concentrated nitric acid with 872 (± 20) mL of deionized water.

3.2 Reagents of Section 4.2 (Determining ^{79}Se).

- Selenium carrier, 10 mg/mL -- Prepare by dissolving 1.0 (± 0.1) g of grey selenium metal in ~5 mL of hot reagent-grade nitric acid and diluting to 100 (± 2) mL with 0.5 M HNO_3 .
- Nitric acid, 0.5 M -- Prepare by diluting 32 (± 2) mL of reagent-grade concentrated nitric acid to 1000 (± 20) mL with deionized water.

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N/A		JJ McCown	07/02/87	All original signatures on file	
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PNL TECHNICAL PROCEDURE

- Ion-exchange resin, AG-50W,[®] X-8, 100 to 200 mesh, H⁺ form.
- Ion-exchange resin, AG-1[®], X-4, 100 to 200 mesh, Cl⁻ form.
- Nitric acid, 0.5 M + bromine saturated -- Prepare by adding ~100 μ L of reagent-grade bromine to ~15 mL of 0.5 M nitric acid; swirl to mix.
- Nitric acid, 69% to 71%, reagent-grade.
- Deionized water.

3.3 Reagents for Section 4.3 (Determining ¹²⁶Sn).

- Hydrochloric acid, 2 M -- Dilute 167 ($\pm$ 2) mL of concentrated reagent-grade hydrochloric acid to 1000 ($\pm$ 20) mL with deionized water; mix.
- Hydrochloric acid, 1 M -- Dilute 83 ($\pm$ 2) mL of concentrated reagent-grade hydrochloric acid to 1000 ($\pm$ 20) mL with deionized water; mix.
- Hydrochloric acid, 2 M with bromine, 1 M with bromine -- Add ~100 μ L of bromine to ~15 mL of appropriate acid in a 35-mL screw-cap vial; cap and shake vigorously.
NOTE: Excess bromine must be present.
- Ion-exchange resins, AG-50W, X-8, 100 to 200 mesh, H⁺ form, and AG-1, X-4, 100 to 200 mesh, Cl⁻ form.
- Hydrochloric acid, concentrated, 37%, reagent-grade.
- Deionized water.
- Bromine, reagent-grade.

3.4 Materials for Section 4.1 (Determining ¹³⁷Cs, ⁹⁹Tc, ⁹⁰Sr, and ²⁴¹Am).

- Flask, volumetric, 10-mL.
- Pipets, 100- μ L and 2-mL.
- Stirring bars, 5/8-in.

®AG-50W and AG-1 are registered trademarks of Bio-Rad Laboratories, Richmond, California.

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PNL TECHNICAL PROCEDURE

- Vial, 15-mL.
- Vial, 2-dram.

3.5 Materials for Section 4.2 (Determining ^{79}Se).

- Vial, 2-dram.
- Vial, 35-mL, screw-cap.
- Pipets, 100- μL , 2000- μL , 500- μL , and 1-mL.
- Droppers, 7.5-mL, plastic.
- Cotton.

3.6 Materials for Section 4.4 (Determining ^{126}Sn)

- Vial, 2-dram.
- Vial, 17-mL.
- Droppers, 7.5-mL, plastic.
- Cotton.
- Pipets, 1000- μL .

4.0 PROCEDURE

4.1 Preparation of Solution (Determining ^{137}Cs , ^{99}Tc , ^{90}Sr , and ^{241}Am)

Aliquots, dilutions, or ion exchange separations are used to prepare test solutions for analysis. The preparations are performed in the Shielded Analytical Laboratory (SAL), and the prepared solutions are then taken for analysis to one or more of the Chemistry and Analysis laboratories.

Step 1) Add ~5 mL of 2 M HNO_3 to a 10-mL volumetric flask.

Step 2) Pipet 100 (± 2) μL sample solution (see PNL-ALO-400, Step 22) into the 10-mL volumetric flask. Swirl contents of the flask to mix.

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PNL TECHNICAL PROCEDURE

- Step 3) Add 2 M nitric acid to the volumetric flask up to the 10-mL calibration mark.
- Step 4) Add a stirring bar and stir for a minimum of 15 minutes.
- Step 5) Label a 2-dram vial with the sample ID and transfer it into the hot cell.
- Step 6) Transfer the contents of the 10-mL volumetric flask to a 15-mL vial.
- Step 7) Pipet 2 (± 0.04) mL (or a volume specified by the cognizant scientist) into the 2-dram vial.
- Step 8) On a Sample Follower Card, record all pertinent sample information, sample ID, volume, sample status, and radiation survey summary.
- Step 9) Transfer sample to Room 309 of the 325 Building or to the laboratory designated by the cognizant scientist.
- Step 10) Aliquots are removed from the 2-dram vial to determine the following isotopes, using the procedures designated.

<u>Isotopes</u>	<u>Procedure</u>	<u>Section</u>	<u>Step</u>
¹³⁷ Cs	PNL-ALO-451	4	1
⁹⁰ Sr	PNL-ALO-433	4	1
⁹⁹ Tc	PNL-ALO-432	4	1
²⁴¹ Am	PNL-ALO-424	4	1

4.2 Preparation of Solution (Determining ⁷⁹Se)

- Step 1) In the hot cell, add to a 2-dram vial 100(± 2) μ L of fuel solution (see PNL-ALO-400, Step 22, or use a volume specified by the cognizant scientist), 2000 (± 20) μ L of selenium carrier, and 500 (± 10) μ L of 0.5 M HNO₃ saturated with bromine; mix thoroughly.
- Step 2) Prepare an ion-exchange column containing 500 (± 50) μ L of AG-50W, X-8, 100 to 200 mesh, H⁺ form resin and 500 (± 50) μ L of AG-1, X-4, 100 to 200 mesh, Cl⁻ form resin.

Step 2.1) Cut off the bulb of a plastic dropper.

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PNL TECHNICAL PROCEDURE

Step 2.2) Insert a small cotton ball into the tip of the dropper and tamp lightly.

Step 2.3) Measure and mark two ~5- μ L increments above the cotton.

Step 2.4) Fill the dropper to the first 500- μ L mark with AG-1, X-4, 100 to 200 mesh, Cl^- form resin.

Step 2.5) Fill the dropper to the second 500- μ L mark with AG-50W, X-8, 100 to 200 mesh, H^+ form resin.

Step 3) Transfer the solution prepared in Step 1 to the ion-exchange column. Collect the column effluent in a 35-mL screw-cap vial.

Step 4) Wash the 2-dram vial from Step 1 with four 1-mL portions of 0.5 M nitric acid plus bromine. Transfer each portion to the ion-exchange column and allow each portion to drain completely before adding the next. Collect all column effluent in the 35-mL screw-cap vial used in Step 3.

Step 5) On a Sample Follower Card, record all pertinent sample information, including sample ID, volume, sample status, and radiation survey summary.

Step 6) Transfer the 35-mL screw-cap vial and the sampler follower card to Room 309 of the 325 Building or to the laboratory designated by the cognizant scientist.

Step 7) Continue selenium analysis from PNL-ALO-476, Section 4.0, Step 5.

4.3 Preparation of Solution (Determining ^{126}Sn)

Step 1) In the hot cell add an aliquot of the fuel solution (see PNL-ALO-400, Step 22 or use a volume specified by the cognizant scientist) to a 2-dram vial.

Step 2) Add to the 2-dram vial 1000 (± 20) μ L of 2 M hydrochloric acid saturated with bromine; swirl to mix.

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PNL TECHNICAL PROCEDURE

- Step 3) Prepare a 1000 (± 100) μL column of AG-50W, X-8, 100 to 200 mesh, H^+ form, ion-exchange resin. Remove the bulb from a 7.5-mL plastic dropper. Insert a small ball of cotton and tamp lightly into the tip of the dropper. Measure and mark a 1000 (± 100) μL volume above the cotton plug. Fill the dropper to the 1000- μL mark with a slurry of the resin. Wash the resin column with 2 or 3 mL of deionized water.
- Step 4) Transfer the hydrochloric acid bromine solution to the column of AG-50W ion-exchange resin. Collect the column effluent in a 15-mL screw-cap vial.
- Step 5) Wash the 2-dram vial with three 1000(± 20) μL portions of 1 M hydrochloric acid saturated with bromine. Transfer each wash portion to the column of ion-exchange resin. Allow each portion to drain completely before adding the next. Collect all column effluent in the 15-mL screw-cap vial used in Step 4. Discard the ion-exchange column.
- Step 6) On Sample Follower Card, record all pertinent sample information, including sample ID, volume, sample dilution, sample status, and radiation survey summary.
- Step 7) Transfer the 15-mL screw-cap vial and the Sample Follower Card to Room 309 or to the laboratory designated by the cognizant scientist.
- Step 8) Continue tin analysis from PNL-ALO-453, Section 4.0, Step 6.

4.4 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033. Laboratory notebooks provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-403, (Replaces HTA-4-27), MEASUREMENT OF NEPTUNIUM-237
IN DISSOLVED FUEL SOLUTIONS

1.0 APPLICABILITY

This procedure applies to the determination of ^{237}Np in dissolver LWR fuel solution.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Nitric acid, 6 M -- Prepared by diluting 380 (± 20) mL of concentrated Ultrex[®] or equivalent nitric acid with 620 (± 20) mL of deionized water.
- Hydrochloric acid, 0.5 M -- Prepared by diluting 42 (± 2) mL of concentrated Ultrex or equivalent hydrochloric acid with 960 (± 20) mL of deionized water.
- Ferrous sulfamate, 2.2 M, prepared by dissolving pure iron i sulfamic acid, while covering the solution with a blanket of inert gas (nitrogen).
- Hydrazine, 5.5 M -- Prepared by dissolving 17.6 (± 0.1) g of reagent-grade hydrazine in 100 (± 2) mL of deionized water.

[®]Ultrex is a registered trademark of J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Author	Date	Project Mgr.	Date	QAD Representative	Date
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N/A		JJ McCown	07/02/87	All original signatures on file	
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PNL TECHNICAL PROCEDURE

- Hydrochloric acid, 1 M -- Prepared by diluting 83 (± 2) mL of concentrated Ultrex or equivalent hydrochloric acid with 917 (± 20) mL of deionized water.
- Xylene, reagent-grade.
- Tri-iso-octyl-amine (TiOA) solution-- Prepared by mixing 10 (± 1) mL of TiOA with 90 (± 2) mL of xylene.
- Hydroxylamine-hydrochloride, 5 M -- Prepared by dissolving 34.7 (± 0.1) g of reagent-grade crystals in 100 (± 2) mL of deionized water.
- Thenoyltrifluoroacetone (TTA), 0.5 M, in xylene-- Prepared by dissolving 11.1 (± 0.1) g of TTA in 100 (± 2) mL of xylene.
- Neptunium-239 tracer solution -- Prepared by extracting the ^{239}Np (a product of ^{243}Am decay) from a 99% pure ^{243}Am source into TTA and stripping it with an 8 M nitric acid solution.
- Vials, 35-mL.
- Vials, 20-mL.
- Vials, 2-dram.
- Stirring bars, 5/8-in.
- Disks, alpha-counting.
- Cold spot heater.
- Burner, gas.
- Heat lamp.

4.0 PROCEDURE

Neptunium-237 in a dissolver solution is separated from other radioactive species by extraction into a mixture of tri-iso-octyl-amine (TiOA) in xylene, stripped from the TiOA phase with HCl and re-extraction into a mixture of thenoyltri-fluoroacetone (TTA) in xylene for additional separation. Neptunium-237 is measured by alpha counting. A ^{239}Np tracer is added to the sample and gamma-counted to determine a recovery factor.

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PNL TECHNICAL PROCEDURE

- Step 1) Label 4 vials as follows:
- 35-mL vial with sample ID (Vial 1)
 - 20-mL vial with sample ID (Vial 2)
 - 35-mL vial with sample ID plus tracer (Vial 3)
 - 20-mL vial with sample ID plus tracer (Vial 4).
- Step 2) Add 7.5 mL of 6 M HNO_3 and a stirring bar to Vials 1 and 3.
- Step 3) To vial 3, add a volume of ^{239}Np tracer as specified by the cognizant scientist.
- Step 4) Prepare two direct amounts of the ^{239}Np tracer by pipetting 0.5 of the tracer volume in Step 3 on each alpha-counting disk.
- Step 5) Immediately before putting the vials into the Shielded Analytical Laboratory (SAL), add 15 drops of 2.2 M ferrous sulfamate and 5 drops of 5.5 M hydrazine to Vials 1 and 3.
- Step 6) Transfer the vials into the SAL.
- Step 7) Add a volume ($\pm 2\%$) of sample specified by cognizant scientist (using dissolver solution from PNL-ALO-400, Step 22) to Vials 1 and 3 with an Eppendorf-type pipet.
- Step 8) Stir for 3 minutes (at room temperature).
- Step 9) Let sample stand for 15 minutes for complete reduction of the Np to the $+4$ valence state.
- Step 10) Add 5 (± 0.1) mL of 10% tri-iso-octyl-amine (TiOA) in xylene to Vials 1 and 3.
- Step 11) Stir vigorously for at least 3 minutes.
- Step 12) Allow the phases to separate. Transfer the upper (TiOA) phases to the clean 20-mL vials. Transfer the upper phase from Vial 1 to Vial 2 and the upper phase from vial 3 to vial 4). Avoid transfer of any aqueous phase. Do not contaminate the outside of the vials.
- Step 13) Add 2.5 (± 0.05) mL of 10% TiOA in xylene to Vials 1 and 3.

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PNL TECHNICAL PROCEDURE

- Step 14) Stir vigorously for 3 minutes.
- Step 15) Allow the phases to separate and transfer the upper (TiOA) phases to their respective 20-mL vials. Avoid transfer of any aqueous phase. Do not contaminate the outside of the vials.
- Step 16) Enter sample information on Sample Follower Cards.
- Step 17) Cap Vials 2 and 4 and remove from the SAL. Transfer samples and Sample Follower Cards to Room 317.
- Step 18) Discard the aqueous phase and Vials 1 and 3.

4.1 Radiochemistry Laboratory Steps

- Step 19) Add to Vials 2 and 4 (20-mL vials transferred from SAL):
- 7.5 mL of 6 M HNO_3
 - 15 drops of ferrous sulfamate solution
 - A stirring bar
- Step 20) Stir vigorously for 2 minutes.
- Step 21) Allow the phases to separate.
- Step 22) Label two new vials:
- 35-mL vial with sample ID (Vial 5)
 - 35-mL vial with sample ID plus tracer (Vial 6).
- Step 23) To Vials 5 and 6, add 8 (± 0.2) mL of xylene and 13 (± 0.2) mL of 1 M HCl .
- Step 24) Transfer upper (TiOA) phases from the 20-mL Vials 2 and 4 to their corresponding 35-mL Vials 5 and 6. Discard Vials 2 and 4.
- Step 25) Stir vigorously for about 4 minutes.
- Step 26) Allow the phases to separate.
- Step 27) Remove the upper (TiOA) phase from each vial. Discard the TiOA in a waste container.
- Step 28) Add 2 (± 0.04) mL of xylene to each vial.

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PNL TECHNICAL PROCEDURE

- Step 29) Stir for 1 minute.
- Step 30) Allow phases to separate.
- Step 31) Remove the upper (xylene) phases; discard the xylene in a waste container.
- Step 32) Evaporate the aqueous phases to near dryness.
- Step 33) Label two 2-dram vials and transfer the samples from the 35-mL vials with 1 M HCl. Warm the 2-dram vials under a heat lamp to keep the total volume in each vial to less than 3 mL.
- Step 34) Add 5 drops of 5 M hydroxylamine-hydrochloride to each vial.
- Step 35) Add 3 drops of 2.2 M ferrous sulfamate to each vial.
- Step 36) Stir well.
- Step 37) Heat to 65° to 75°C for 3 minutes.
- Step 38) Cool.
- Step 39) Add 1.5 (± 0.03) mL of 0.5 M thenoyltrifluoroacetone (TTA) in xylene.
- Step 40) Stir vigorously for 3 minutes.
- Step 41) Allow the phases to separate.
- Step 42) Label two 2-dram vials.
- Step 43) Transfer the TTA phases to the 2-dram vials.
- Step 44) Repeat Steps 39 and 40.
- Step 45) Transfer the TTA phases from Step 44 to the two 2-dram vials. Discard the aqueous phases in a waste container.
- Step 46) Add 3 (± 0.05) mL of 0.5 M HCl to each vial.

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PNL TECHNICAL PROCEDURE

- Step 47) Add 3 drops of hydroxylamine-hydrochloride to each vial.
- Step 48) Stir vigorously for 3 minutes.
- Step 49) Allow the phases to separate.
- Step 50) Label two 2-dram vials with sample ID and transfer the TTA phases to the vials.
- Step 51) Evaporate under a heat lamp to a convenient volume for mounting on an alpha-counting disk.
- Step 52) Mount the TTA on an alpha-counting disk using a cold spot heater and xylene to rinse the vials.
- Step 53) Flame the dried deposit gently.
- Step 54) Gamma-count the sample discs and the two direct-mount discs (prepared in Step 4) to determine the chemical recovery factor for the Np. The gamma counting is performed in accordance with PNL-ALO-451 and in the same geometry. Therefore, the ratio of the counts establishes the recovery factor. Correct all ^{239}Np gamma count data for radioactive decay to the same reference time. (See calculations for details.)

4.2 Calculations

- Step 55) Calculate Np recovery factor as follows:

$$L = J - \frac{G}{H} \times I$$

$$R = \frac{L}{2K}$$

where: $J = ^{239}\text{Np} \text{ } \gamma \text{ ct/min from sample + spike}$
 $G = ^{239}\text{Np} \text{ } \gamma \text{ ct/min from unspiked sample}$

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H = ^{237}Np α ct/min from unspiked sample,
determined by combined alpha counting
and alpha spectrometry
I = ^{237}Np α ct/min from sample + spike,
determined by combined alpha counting
and alpha spectrometry
L = ^{239}Np γ ct/min from spike recovered
K = ^{239}Np γ ct/min from direct mounts of
the ^{239}Np tracer (from Step 4)
R = Recovery (decimal fraction).

- Step 56) Count and record the alpha (A) disintegrations per minute as per PNL-ALO-421.
- Step 57) Count the discs by alpha spectrometry (see PNL-ALO-422) and obtain an alpha energy spectrum on each to determine an non- ^{237}Np contribution to the alpha counts.
- Step 58) Calculate the alpha fraction (AF) activity from ^{237}Np using PNL-ALO-422, Step 13.
- Step 59) Calculate the grams of ^{237}Np per gram of fuel as follows:

$$\frac{{}^{237}\text{Np (g)}}{\text{fuel (g)}} = \frac{(A)(AF)}{(1.565 \times 10^9) * (R)(W)}$$

where:

A = alpha dis/min (from Step 56)
AF = alpha fraction of ^{237}Np in total alpha activity (from Step 58)
R = recovery factor (from Step 55)
W = fuel (g) represented by aliquot (from Step 7).
* = 1.565×10^9 is ^{237}Np specific activity (dis/min per g).

4.3 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033. Laboratory notebooks provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-404, (Replaces HTA-4-32), SOLUTIONS SAMPLE PREPARATION AND HANDLING FOR I-129 MEASUREMENT BY ACTIVATION ANALYSIS

1.0 APPLICABILITY

This procedure applies to sample preparation and handling for the determination of iodine-129 in solution using activation analysis.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Company format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

- RPT- radiation protection technologist.
- RWP- radiation work procedure.

3.0 EQUIPMENT AND MATERIALS

- ^{129}I Standard, ~ 1.0 nCi of ^{129}I per mL solution -- traceable to an NBS or equivalent solution.
- "Rabbit," 3.75-in. long x 1.3-in. OD, polyethylene.
- Vials, 2/5-dram, polyethylene, snap-cap.
- Vials, 0.3-mL, polyethylene, snap-cap.
- Vials, 2-dram, polyethylene, cut down to 2 in.
- Counting vials: 15-mL, screw-cap, or snap-cap, glass or polyethylene.
- Metal can, slip-on lid.

Author	Date	Project Mgr.	Date	QAD Representative	Date
FE Holt	07/01/87	N/A		BO Barnes	06/30/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	07/02/87	All original signatures on file	
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PNL TECHNICAL PROCEDURE

- Gloves, lint and talcum-free.
- Soldering iron, flat or special tip.
- Tweezers, 8-in. long.
- Micropipets, replaceable plastic tip, Eppendorf-type.

4.0 PROCEDURE

4.1 Introduction

Iodine-129 is converted to 12.36 hr. I-130 by an (n, γ) reaction. That nuclide emits several gamma rays suitable for measurement. The most prominent of those are: 536 KeV @ 99%, 669 keV 96%, and 740 KeV @ 82%. This procedure is concerned with pre- and post-irradiation handling. Samples and standards are counted after irradiation, using gamma ray spectrometry. The iodine-129 content of a sample is obtained from the ratio of the sample and the standard counting data using Procedure PNL-ALO-405, Solutions Analysis: Measurement of Gamma-Ray Emitting Isotopes by the Sample/Standard Comparator Method. Since there are no chemical separations performed, the detection limit is between 1 and 10 d/m-mL of solution.

4.2 Sample Preparation

Prepare samples and standard solutions at least one day ahead of time and deliver them to the reactor for irradiation. These samples are usually returned to the laboratory on the day of irradiation. Samples should be counted on the day received. Standards may be counted the following day. Sample preparation shall be performed in a clean hood, and all items therein shall be handled with lint- and talcum-free gloves.

- Step 1) Mark and set 2/5-dram vials and their corresponding 0.3-mL vials in appropriate holders so that they can be easily matched.
- Step 2) Prepare a set of two or more aliquots of the sample and two or three standard solutions for irradiation in their marked containers.
- Step 3) Pipette appropriate amounts of sample into their matching 0.3-mL snap-cap vials.

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- Step 4) Remove protrusions from each snap-cap with a sharp tool, and place each 0.3-mL vial into its matching 2/5-dram vial. Close vial cap tightly.
- Step 5) Pipet appropriate amounts of ^{129}I standard solution into their 0.3-mL snap-cap vials. Close vial caps tightly.
- Step 6) Remove protrusions from each snap cap with a sharp tool and place each 0.3-mL vial into its matching 2/5-dram vial. Close all vial caps tightly.
- Step 7) With flat-tipped or specially prepared soldering iron, seal each vial's cap onto its body if required by Reactor Operations or the cognizant scientist.
- Step 8) Mark a "rabbit" with an appropriate ID (such as BW-1 or BW-2) so that its contents can be identified upon its return from the reactor and load the 2/5-dram vials into it. Place some packing material atop the vials (e.g., polyethylene washers or caps) to restrict vial movement. Close the "rabbit" with its screw cap.
- Step 9) Complete a "Shuttle Facility Irradiation Request" form (UNI-M-96, Rev 1) and specify a 1-hour or more specimen irradiation with return delivery on the same morning that the irradiation ends.
NOTE : Irradiation should normally occur on Monday, Tuesday, or Wednesday so that two days are available for counting, if needed.
- Step 10) Record the volumes and sample/standard IDs on the analytical report for each sample. Record data in the laboratory notebook.

4.3 Sample Counting and Analysis

- Step 1) Upon receipt of the sample from the reactor, request that an RPT monitor the shuttle cask unloading and the empty cask for return, if the applicable RWP limits are exceeded.
- Step 2) Remove the "rabbit" from the shuttle cask and place in the lead brick provided.
- Step 3) Remove and discard the cap from the "rabbit," using the rod provided (squared at one end).

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- Step 4) Remove and discard the packing material.
- Step 5) Mark counting vials with appropriate sample ID and/or standard designation. Place a cut-down polyethylene vial inside each counting vial.
- Step 6) Remove one of the 2/5-dram marked vials using tweezers and place it inside its corresponding counting vial.
NOTE: Do NOT touch the outside of the vial. Close vial tightly.
- Step 7) Repeat Step 6 for each of the remaining 2/5-dram vials.
- Step 8) Check each counting vial for external contamination and for dose rate.
- Step 9) Measure the iodine-130 activity using Procedure PNL-ALO-405, "Solutions Analysis: Measurement of Gamma-Ray Emitting Isotopes by the Sample/Standard Comparator Method."

4.4 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033. Laboratory notebooks provide a mechanism for control of most records. As a minimum, the information in the laboratory notebook shall contain the sample and standard, identification and volume.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-405, (Replaces HTA-4-33), SOLUTIONS ANALYSIS: MEASUREMENT OF GAMMA-RAY EMITTING ISOTOPES BY THE SAMPLE/STANDARD COMPARATOR METHOD

1.0 APPLICABILITY

This procedure applies to the determination of concentrations of gamma-emitting species in hydrothermal autoclave water leachate solutions by comparison of gamma ray intensities from a sample and a standard.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Company format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Gamma-ray spectrometer, Tracor Northern TN-4000, Nuclear Data ND-50/50, or other comparable system with its associated Ge(Li) detector.
- Associated computer-based peak search and calculation routines for normalizing data (helpful but not necessary).

3.1 Calibration Standards

During the data reduction process for a desired gamma ray peak, the relative disintegration rates of both standards and samples are calculated. In this method, these calculations serve to normalize the sample and standard counting data to equivalent units. The standard shall be obtained from the NBS or other certified organizations. A record of the standard and modifications shall be documented in the appropriate laboratory notebook.

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PNL TECHNICAL PROCEDURE

4.0 PROCEDURE

4.1 Introduction

The abundance of each isotope measured is accomplished by comparing the counts observed in one or more full-energy photopeaks characteristic of that isotope with the number of counts observed in those same peaks from a standard. A comparison of the counts in the sample to those in the standard and the known concentration and disintegration rate of the standard (dis/s per mL) yields the activity of the isotope in the sample. The counts observed in one or more photopeaks are converted to disintegrations at a common date and time using the detector efficiency for each energy, the gamma ray abundance, and the decay factor for that isotope.

4.2 Daily Control Standards

The control standard used to check the suitability of a gamma-ray counting system is a mixture of isotopes, often ^{241}Am , ^{137}Cs , and ^{60}Co . Those or similar standards cover an energy range from 59 to 1332 keV. The standard is dried and encapsulated to maintain a constant and reproducible geometry. Limits are determined by counting the standard 20 or more times and by calculating the average and the statistical counting limits. Daily counts should fall within defined limits before samples are counted. However, in this method, some counts outside those limits are acceptable because the sample and standard counts yield equivalent outputs. The cognizant scientist will determine whether or not the counts can be used for the current analysis.

Step 1) Adjust Gain and Zero as required with the daily control standard using the daily control and energy calibration guide.

Step 2) Count the daily standard for the specified time and record the counts or counting rates on the control charts provided for that system. The plotted data should be within the limits shown before samples are counted. If they are not, repeat the control count.
NOTE: The cognizant scientist or team leader shall determine whether or not to count samples with this method or abort the analysis until the equipment is repaired.

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4.3 Sample Preparation and Counting

- Step 1) Samples and standards must have almost identical geometrics. See for example Sample Counting and Analysis in PNL-ALO-404.
- Step 2) Put the analyzer in the ACQUIRE mode. Place a sample on one of the counting positions and observe the deadtime meter. Adjust the sample position to obtain a deadtime of <20%.
- Step 3) Check one or more of the least and most active samples within a set to determine suitable counting positions. Usually all samples and at least one or more of the standards must be counted within one day. One or more standards may be counted the following day, depending on their activities.
- Step 4) Count each sample for the time specified by the team leader or cognizant scientist.
- Step 5) Record counting data, calculations and other pertinent information in the laboratory notebook.

4.4 Calculations

- 1) Determine the relative concentrations of the isotope(s) of interest from the counting rate of each gamma ray used for the measurement:

$$A_{i\gamma} = (C_{i\gamma})(\gamma/c)(d/\gamma)e^{\lambda t}/V$$

where:

$A_{i\gamma}$ = relative concentration of isotope i from its gamma ray energy γ

$C_{i\gamma}$ = counting rate of gamma ray energy γ from isotope i

γ/c = gamma ray efficiency of counting system (γ/count)

d/γ = number of disintegrations per gamma ray

λ = decay constant of isotope i per s^{-1} or min^{-1}

t = time (in s or min) between counting time and sampling time

v = sample volume

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- 2) Calculate the absolute concentration of the isotope in the sample using the A_{iy} values just determined:

$$(N_{iy})_{sa} = \frac{(A_{iy})_{sa} (N_{iy})_{std}(F)}{(A_{iy})_{std}}$$

where: $(N_{iy})_{sa}$ = absolute concentration of the isotope in the sample
 $(N_{iy})_{std}$ = absolute concentration of the isotope in the standard
 $F = 60$ = conversion factor to obtain units required, e.g., to convert d/s per mL to d/min per mL

- 3) Calculate the standard deviation around the results from:

$$Q = \frac{X}{Y} = \frac{(N_{iy})_{sa} \times F}{(N_{iy})_{std}}$$

$$\sigma_Q = Q \sqrt{\frac{\sigma_X^2}{X^2} + \frac{\sigma_Y^2}{Y^2}}$$

4.5 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033. Laboratory notebooks provide a mechanism for control of most records. As a minimum, the laboratory notebook shall contain the sample and standard identification, a reference to the counting data, the individual results, and calculations used to arrive at the reported results.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-406, (Replaces HTA-4-36), SEPARATION OF URANIUM FROM BRINE SOLUTIONS BY ION EXCHANGE

1.0 APPLICABILITY

This procedure describes the technique for the separation of uranium from brine solutions.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Company format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Vials, 2-dram, borosilicate glass (leached per Procedure PNL-ALO-400, Step 1) through Step 6).
- Vials, 20-mL, borosilicate glass (leached per Procedure PNL-ALO-400, Step 1) through Step 6).
- Vials, 35-mL.
- Polyethylene droppers, 7.5-mL.
- Medical cotton.
- Heat lamp.
- Ring stand with column holders.
- Rod, glass ~25 cm long x 3 mm in diameter.
- Pipettes and assorted pipette tips.

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PNL TECHNICAL PROCEDURE

- Hydrochloric acid, 10 M - Prepared by diluting 833 (± 20) mL of concentrated hydrochloric acid with 167 (± 2) mL of subboiling quartz-distilled water. Check the hydrochloric acid for uranium in accordance with Procedure PNL-ALO-445, since any uranium in the acid is collected on the ion-exchange column and will be eluted along with the uranium in the sample. Uranium can be removed from the hydrochloric acid by ion exchange. The column effluent is used for the 10 M hydrochloric acid reagent to process the samples.
- Hydrochloric acid, 4 M - Prepared by diluting 40 (± 2) mL of 10 M hydrochloric acid with 60 (± 2) mL of subboiling quartz-distilled water.
- Nitric acid, concentrated, Ultrex[®] or equivalent.
- Nitric acid, 8 M - Prepared by diluting 50 (± 2) mL of concentrated nitric acid (Ultrex or equivalent) with 50 (± 2) mL subboiling quartz-distilled water.
- Nitric acid, 0.2 M - Prepared by diluting 2.5 (± 0.05) mL of 8 M nitric acid with 98 (± 2) mL of subboiling quartz-distilled water.
- Hydrochloric acid, 0.1 M - Prepared by diluting 1.00 (± 0.010) mL of 10 M hydrochloric acid with 99 (± 2.0) mL of subboiling quartz-distilled water.
- Ion-exchange resin, AG-1[®], X-4, 200 to 400 mesh, Cl⁻ form.

3.1 Calibration Standard

A standard solution containing uranium is added to a sample for each set of samples (ion exchanged) to determine a percent recovery. Standards are NBS or NBS-traceable whenever possible.

4.0 PROCEDURE

The presence of relatively large amounts of brine in samples can interfere with the determination of uranium by the laser-excited fluorescence method (PNL-ALO-445). This procedure separates the uranium on an ion exchange column while the brine solution is eluted with a 10 M

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[®]AG-1 is a registered trademark of Bio-Rad Laboratories, Richmond, California.

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PNL TECHNICAL PROCEDURE

HCl wash solution. After the 10 M wash, the uranium is eluted from the column with 0.2 M HNO₃. The uranium is then determined by the laser-excited fluorescence method (PNL-ALO-445). A 92% recovery was achieved when brine samples were spiked with a known quantity of uranium.

- Step 1) With each set of separations, process a reagent blank and a sample spiked with an amount of uranium specified by the cognizant scientist, and record the results in a laboratory notebook.
- Step 2) Cut off the rounded tip of a 7.5-mL polyethylene dropper, leaving the rest of the bulb to act as a reservoir.
- Step 3) Add a small amount of medical cotton to the column and, using a glass rod, form a plug of cotton at the tip of the dropper to support the resin.
- Step 4) Calibrate the dropper for 400 μ L, using subboiling quartz-distilled water.
- Step 5) Load resin in the column to the 400- μ L mark, using subboiling quartz-distilled water.
- Step 6) Label the 2-dram vials or other leached vials (appropriate volume) with the sample identification.
- Step 7) Pipette a 100 ($\pm$ 2) μ L (or a volume specified by the cognizant scientist) into the vials. Record the sample volume on the analytical report form.
- Step 8) Add a volume of 10 M hydrochloric acid and a volume of subboiling quartz distilled water to the vials. Volume of acid and water shall be specified by the cognizant scientist. Record volumes on the analytical report form.
- Step 9) Add 100 ($\pm$ 2) μ L of concentrated nitric acid (Ultrex or equivalent) to each vial.
- Step 10) Place the vials under a heat lamp and warm until the color of the solution is yellow.
- Step 11) Remove the vials and allow the contents to cool.
- Step 12) Place the ion exchange column in the holder with a 35-mL vial under each column.
- Step 13) Prewash each column with 4.0 ($\pm$ 0.04) mL of 0.2 M nitric acid.

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PNL TECHNICAL PROCEDURE

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-407, (Replaces GRLT-1), SEPARATION OF CHLORINE-36 BY ION EXCHANGE, DISTILLATION AND MEASUREMENT BY BETA COUNTING

1.0 APPLICABILITY

This procedure applies to the separation and measurement of chlorine-36 in deionized water-graphite leach solutions or other similar solutions.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Beaker, glass, 400 mL, 100 mL or other sizes as may be required.
- Stir bar, glass covered, one inch or other suitable size.
- Chloride carrier, 10.0 mg Cl^- /mL -- Prepare by dissolving 1.649 (± 0.001) g of sodium chloride in a 100 (± 0.08) mL volumetric flask with deionized water. Mix thoroughly. Record the weight of sodium chloride and volume in the laboratory record book (LRB) and record the mg/mL chloride, date and initials on the chloride container. Record the balance used in the LRB.
- Nitric acid, concentrated, reagent grade or better.
- Nitric acid, 8 M -- Prepare by diluting 506 (± 1) mL of concentrated nitric acid to 1000 (± 1) mL. Mix thoroughly.

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PNL TECHNICAL PROCEDURE

- Ion exchange resin, AG-50W, X-8, 100-200 mesh, H⁺ form.
- Ion exchange resin column, as specified by the COGNIZANT SCIENTIST.
- Silver nitrate, 0.1 M -- Prepare by dissolving 1.70 (± 0.01) g of silver nitrate in 100 (± 1) mL of deionized water; mix thoroughly.
- Filter, 24 mm, Whatman 934-AH glass microfiber or equivalent.
- Filter holder, Swinnex, 25 mm.
- Vial, glass, 35 mL.
- Ammonium hydroxide, concentrated, reagent grade or better.
- Carbonate carrier, 10 mg CO₃⁼/mL -- Prepare by dissolving 1.77 (± 0.01) g of sodium carbonate in 100 (± 1) mL of deionized water; mix thoroughly.
- Barium nitrate, 0.1 M -- Prepare by dissolving 2.6 (± 0.1) g of reagent grade barium nitrate in 100 (± 1) mL of deionized water; mix thoroughly.
- Syringe, 10 mL, plastic, Luer-Lok.[®]
- Dropper, plastic.
- Distillation flask -- use ⁷⁹Se still; see PNL-ALO-440, Figure PNL-ALO-440.1. Selenium still.
- Nitrogen gas -- Reduce pressure to ~2 psi using a nitrogen gas pressure-reducing valve. A purity of 99.5% nitrogen is acceptable.
- Sulfuric acid, concentrated, reagent grade or better.
- Heating mantle, 50 mL, round bottom.
- Variac, 1.5 ampere output, 0-140 volts.
- Thermometer, to read at least 360°C.

[®]Luer-Lok is a registered trademark of Becton, Dickenson & Co.; Rutherford, New Jersey

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PN: TECHNICAL PROCEDURE

- Mercurous nitrate, 0.1 M -- Prepare by dissolving 2.8 (± 0.1) g of mercurous nitrate monohydrate in 100 (± 1) mL of deionized water plus 3 (± 0.01) mL of concentrated nitric acid. After dissolution is complete add about 1 mL of clean mercury metal to the solution and stir vigorously for at least 2 hours. When making additional mercurous nitrate use the same bottle and leave the mercury metal in the vial. The mercury metal reduces any mercuric ion to mercurous ion.
- Filter, 47 mm Gelman A/E glass.
- Filter holder, millipore, to hold 47 mm filter.
- Methanol, reagent grade.
- Planchet, 2-inch diameter, aluminum.
- LB-1000, low background beta counter.

4.2 Chloride Separation

Chloride-36 is separated from other radioactive species by passing the acidified solution through a cation exchange resin column. The chlorine-36 passes through the column while most cations are retained. The chlorine-36 is further purified by silver chloride precipitation followed by a barium carbonate precipitation from concentrated ammonium hydroxide. The chloride is finally distilled as hydrochloric acid and is precipitated as mercurous chloride for counting.

The ANALYST shall perform the following steps unless otherwise specified.

- Step 1) To a 400 mL, or other suitable size, beaker or vial the ANALYST shall add a stir bar and a volume ($\pm 1\%$) of test solution specified by the COGNIZANT SCIENTIST. Record the volume taken on the Analytical Report Form.
- Step 2) While stirring add 1.0 (± 0.01) mL of chloride carrier and a volume ($\pm 1\%$) of concentrated nitric acid specified by the COGNIZANT SCIENTIST to make the solution 0.2 (± 0.02) M in acid.
- Step 3) Prepare a cation exchange column containing a volume ($\pm 1\%$) of resin and assembled as specified by the COGNIZANT SCIENTIST.

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PNL TECHNICAL PROCEDURE

Note: The volume of resin must be at least 1/25 the volume of sample taken in Step 1.

- Step 4) Transfer the solution from the beaker or vial in Step 2 to the ion exchange column. Collect the column effluent in a clean beaker or vial of the same size.
- Step 5) After all of the solution has passed through the resin column rinse the beaker from Step 2 with about one column volume of deionized water and transfer the rinse to the ion exchange column. Collect the effluent in the same effluent beaker or vial as Step 4. Discard the empty beaker and ion exchange resin column in the dry radioactive waste.
- Step 6) To the beaker or vial containing the effluent add a stir bar.
- Step 7) While stirring add 4 (± 0.04) mL of 0.1 M silver nitrate. Stir for 15 (± 2) minutes to coagulate the precipitate.
- Step 8) Collect the precipitate by filtering on a 24 mm Whatman 934-AH glass microfiber filter using a Swinnex 25 mm filter holder. Discard the solution (filtrate) in the liquid radioactive waste.
- Step 9) Transfer the filter plus silver chloride precipitate to a 35 mL glass vial.
- Step 10) To the vial add 2 (± 0.1) mL of concentrated ammonium hydroxide. Add a stir bar and stir until the silver chloride dissolves then add 5 (± 0.1) mL of deionized water.
- Step 11) To the vial add 1 (± 0.1) mL of carbonate carrier.
- Step 12) While stirring add 2 (± 0.1) of 0.1 M barium nitrate. Stir for 1-2 minutes.
- Step 13) Assemble a 25 mm Swinnex filter holder with a 24 mm glass filter and attach a 10 mL Luer Lok syringe with the plunger removed.

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PNL TECHNICAL PROCEDURE

- Step 14) Position the filter holder on a 35 mL vial in such a manner that will allow the filtrate to flow into the vial.
- Step 15) Using a plastic dropper transfer the barium carbonate slurry from Step 12 into the syringe.
- Step 16) Rinse the vial twice with 2 (± 0.1) mL of water and transfer to the syringe.
- Step 17) After transferring all of the slurry and rinse to the syringe use the plunger to push any remaining solution in the syringe through the filter. Discard the filter assembly and syringe in the radioactive waste.
- Step 18) To the filtrate in the 35 mL vial add a stir bar.
- Step 19) While stirring add 5 (± 0.1) mL of 8 M nitric acid. Silver chloride should form. If not add 1 (± 0.1) mL portions of 8 M nitric acid until the precipitate forms. Add 100 (± 1) μ L of 0.1 M silver nitrate and stir for at least 5 minutes to coagulate the precipitate.
- Step 20) Filter the silver chloride slurry using a 24 mm glass filter placed on a Swinnex 25 mm filter holder base. Transfer the silver chloride to the filter using a plastic dropper.
- Step 21) Wash the vial twice with 2 to 3 mL of deionized water and transfer to the filter. Discard the filtrate (solution) to the liquid radioactive waste.
- Step 22) Transfer the filter plus silver chloride to a 35 mL vial.
- Step 23) To the 35 mL vial add 2 (± 0.1) mL of concentrated ammonium hydroxide and a stir bar. Stir until the silver chloride dissolves.
- Step 24) Using a plastic dropper transfer the solution to a selenium distillation flask (still).
- Step 25) Wash the vial twice with 2 (± 0.1) mL of deionized water and transfer to the still. Leave the filter in the vial and discard in the radioactive waste.

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- Step 26) Place the top in the still and bubble nitrogen through the still (10-20 bubbles/second) for at least 10 minutes to remove excess ammonia.
- Step 27) Carefully add 1000 (± 100) μL of concentrated sulfuric acid to the still. Replace the still top and bubble nitrogen for 5-10 seconds to mix the solution.
- Step 28) Repeat Step 27 until 6 (± 0.6) mL of concentrated sulfuric acid has been added to the still.
- Step 29) Place the still in the heating mantle and place the still outlet beneath the surface of 10 (± 0.1) mL of deionized water in a 35 mL vial in an ice bath.
- Note: Keep the ice bath full of ice. If the water level in the ice bath becomes too high remove some using a vacuum slurp line.
- Step 30) Adjust the nitrogen flow to about five bubbles per second.
- Step 31) Set the variac to 110 and turn on.
- Step 32) Insert a 360°C or a 400°C thermometer into the still thermometer hole and monitor the temperature.
- Step 33) When the temperature reaches 300°C distill for 5 (± 1) additional minutes. Total distillation time is about 45 to 60 minutes.
- Step 34) Turn off the variac and nitrogen. Remove the distillate vial from the still outlet and the ice bath.
- Step 35) Clean the still by pulling the flask contents into a vacuum liquid waste jug through the still inlet. Rinse with deionized water by pulling through the still outlet in the still and through the still inlet into the vacuum radioactive liquid waste jug.
- Step 36) To the vial containing the distillate add a stir bar.

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- Step 37) While stirring add 2 (± 0.01) mL of concentrated nitric acid and 4 (± 0.01) mL of 0.1 M mercurous nitrate. Stir for 5 (± 1) minutes.
- Step 38) Dry a 47 mm glass filter at 100°-120°C for at least 20 minutes.
- Step 39) Cool the filter for 5 to 10 minutes and weigh to 0.00001 g or better. Record the weight on the Analytical Report Form.
- Step 40) Assemble the millipore filter holder with the tared glass filter (Step 39).
- Step 41) Using a magnet remove the stir bar from the vial from Step 37.
- Step 42) Swirl the mercurous chloride precipitate and filter with vacuum through the 47 mm glass filter.

Note: Pour the solution and precipitate rapidly into the filter holder top to provide good mixing and a relatively smooth and equal distribution of the mercurous chloride on the filter.

- Step 43) Rinse the vial twice with 10 (± 1) mL of deionized water and add to the filter.
- Step 44) Rinse the vial with 10 (± 1) mL of methanol and add to the filter. Wash down the inside of the filter holder top with methanol.
- Step 45) Disassemble the filter holder and place the filter in a 2-inch planchet which is fixed with tape to a cardboard beta dish holder. Label the holder with the sample ID and chlorine-36.
- Step 46) Dry the planchet plus filter at 110° to 120° for 20 (± 2) minutes.
- Step 47) Cool for 10 (± 1) minutes and weigh the filter plus precipitate to 0.00001 g or better. Record the weight on the Analytical Report Form and the identification of the balance used. Use the same balance used for Step 39.

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Step 48) Place the filter back in the planchet and count the chlorine-36 activity using the LB-1000 Low Background Alpha and Beta Counter. Record counts, time counted and other pertinent data on the Analytical Report Form.

4.3 Calibrations

4.3.1 Calibration of LB-1000 Counter for Chlorine-36

The LB-1000 is calibrated using NBS SRM-4943 chlorine-36. An equal volume of chlorine-36 was added to vials containing 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 mg of chloride carrier. After thorough mixing the chloride was precipitated with mercurous nitrate and filtered on tared 47 mm glass filters. Each filter was dried, weighed and counted on the LB-1000.

Disintegrations/counts (d/c) were calculated for each weight of mercurous chloride using the known disintegrations/minute (d/m) of chlorine-36 added corrected for recovery and the counts/minute (c/m) obtained on the LB-1000.

From a graphic plot of the d/c versus weight of mercurous chloride a table of sample weight and d/c values was generated. See Table 1, Section 4.4.3, Standard-Disintegrations/Count (d/c).

All data for calibrations may be found in Laboratory Record Book (LRB) BNW 52346, pages 13 through 22.

4.3.2 Daily Performance Check of LB-1000

Daily control checks are made using an alpha source prepared from a plutonium-239 NBS certified solution T-1350.

The beta control source is prepared from a SrY-90 solution T-1204, ICN Lot #705.

NBS Traceability is not essential for these sources since they are used only as daily control sources and are not primary standards. Primary calibration of chlorine-36 is described in Section 4.3.1.

4.4 Calculations

4.4.1 Counts/Minute from Sample

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$$A \pm \alpha = \left(\frac{B}{D} - \frac{C}{E} \right) \pm \sqrt{\frac{B}{D^2} + \frac{C}{E^2}}$$

Where $A \pm \alpha = c/m \pm 1$ sigma in the sample

B = total counts obtained from sample count

C = total counts obtained from background count

D = time in minutes taken for sample count

E = time in minutes taken for the background count.

4.4.2 Yield Calculation

$$Y = \frac{A-B}{C}$$

where Y = yield (or recovery) expressed as a decimal fraction

A = weight (mg) of filter plus mercurous chloride from
Section 4.2, Step 47

B = weight (mg) of filter only from Section 4.2, Step 39

C = 66.586 mg which is the weight of mercurous chloride
calculated from 10.0 mg of chloride carrier.

4.4.3 Standard - Disintegration/Count (d/c)

$$W = A-B$$

where: W = weight (mg) of mercurous chloride on filter

A = weight (mg) of filter plus mercurous chloride from
Section 4.2, Step 47

B = weight (mg) of filter only from Section 4.2,
Step 39.

From Table 1, determine the d/c factor closest to the weight (w)
for use in the following sample d/m/mL calculation.

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TABLE 1. Disintegration/Count Versus Weight of Mercurous Chloride

<u>wt. mg</u>	<u>d/c</u>	<u>wt. mg</u>	<u>d/c</u>	<u>wt. mg</u>	<u>d/c</u>
20	2.231	38	2.295	56	2.366
22	2.239	40	2.304	58	2.375
24	2.245	42	2.311	60	2.383
26	2.251	44	2.320	62	2.390
28	2.260	46	2.327	64	2.399
30	2.265	48	2.335	66	2.406
32	2.274	50	2.343	68	2.415
34	2.280	52	2.351	70	2.424
36	2.289	54	2.359		

4.4.4 Sample - Disintegration/Minute/Milliliter (d/m/mL)

$$B \pm \beta = \frac{(A \pm \alpha) \times C}{D \times E}$$

where: $B \pm \beta$ = the sample chlorine-36 d/m/mL ± 1 sigma

$A \pm \alpha$ = the sample c/m $\pm$ sigma calculated in Section 4.4.1

C = the d/c factor obtained in Section 4.4.3

D = the volume of sample (in mL) added in Section 4.2, Step 1

E = the yield (recovery) factor calculated in Section 4.4.2.

4.5 Records

Records will be maintained and controlled so as to conform with requirements if MCS-033. LRBs and Analytical Report Forms provide a mechanism for control of most records.

4.6 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally it is considered qualified because it has received an independent technical review.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-408, (Replaces GRLT-3), LOW BACKGROUND ALPHA AND BETA COUNTING USING THE LB-1000

1.0 APPLICABILITY

This procedure provides instructions for simultaneously measuring the activity of alpha-emitting and beta emitting radionuclides in a low background environment.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

4.0 PROCEDURES

4.1 Equipment and Materials

- Tennelec Model LB-1000 Low Background Alpha/Beta Counter
- P-10 gas (90% argon, 10% methane), commercial grade, Union Carbide Corp.
- Dish, 2-in diameter x 1/8-in deep, flat bottomed, cupped aluminum.

4.2 Calibration Standards

The LB-1000 is initially calibrated by the COGNIZANT SCIENTIST using a series of replicate essentially zero-mass sources prepared by evaporating accurately measured aliquots of NBS ²³⁹Pu and ⁹⁰SrY Standard Reference Materials spread across a 47 mm diameter bottom

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AC Leaf	11/2/87	N/A		LE Thompson	11/04/87
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N/A		JJ McCown	11/05/87	All original signatures on file	
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area of 2-in diameter aluminum dishes. At zero-mass counting efficiency is essentially constant for all alpha energies, but decreases as a function of decreasing beta energy. All beta and non zero-mass alpha counting operations require special calibrations be performed using sources simulating the nuclide and chemical composition of the test sample sources. Calibration sources are used only to recalibrate the LB-1000 after instrument repair; to avoid loss of integrity through daily handling, calibration sources are not used to routinely verify counter control.

4.3 Daily Control Standards

Control Standards are sources of high-purity ^{239}Pu and ^{90}SrY used by the ANALYST on a daily basis to insure the LB-1000 is operating within control limits. Each control source is counted ten times when the LB-1000 is initially calibrated for general alpha/beta counting and limits that must be met on a daily basis are defined by statistical analysis of the counting data obtained. Control sources prepared by evaporating radionuclide solution aliquots in 2-in aluminum dishes are rugged enough to retain their integrity with daily handling unless the active deposit is abraded through negligence.

The following daily control standard count procedure shall be used:

- Step 1) Carefully pull out the sample transport slide until the stop is encountered. A slight initial resistance due to the position locking mechanism will be felt.
- Step 2) Remove the round plastic sample holder from the sample well of the slide. Remove any sample dish currently in the holder, raising it by inserting a finger through the hole in the bottom of the sample holder and grasping the outside of the dish walls.

Insert the ^{239}Pu control source dish into the sample holder and return the holder to the slide sample well. Orientation is not important; the sample holder is automatically repositioned correctly with respect to the counter detector when moved into counting position. Push the slide in until the resistance of the position locking mechanism is felt, then gently push the slide all the way in.

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- Step 3) Counter operation is controlled from the TIMER module. Adjust the time preset to 10 minutes.
- Step 4) Clear existing data from the alpha and beta module registers by pressing RESET on the TIMER module. If the count toggle is in the STOP position, initiate counting by switching the toggle to COUNT. If the toggle is already in COUNT position counting automatically begins when RESET is pressed. Record the time counting was begun in the control log alpha control section in the TIME column of a line labeled with the current date.
- Step 5) When the preset time interval has elapsed counting will automatically stop. Record the accumulated counts in the alpha and beta channels in the alpha control section of the control log in corresponding columns on the line labeled with the current date.
- Step 6) Calculate the alpha channel count rate, expressed in counts per minute background corrected, and enter the result in the corresponding column. Plot the value on the alpha channel control chart at the current date. If the count does not fall within the limits defined on the control chart, perform a recount. If the initial count or recount is within limits the alpha channel is considered to be operating in control. If both counts are outside limits sample counting must not be performed until control is returned by repair of the instrument.
- Step 7) Repeat steps 3, 4, 5, and 6, using the SrY beta control source, recording and plotting the results of the measurement in the beta control section of the control log.

4.4 Daily Background Count

The ANALYST shall complete the following steps:

- Step 1) When not in use, the LB-1000 is left in indeterminate count mode with a clean 2-in dish in counting position. These background counts will vary in length from approximately 900 minutes during the work week to 3900 minutes over a weekend. When the timer indicates an integral number of minutes have elapsed, switch the count toggle of the timer module to the STOP position.

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- Step 2) Label lines in both the alpha and beta sections of the control log with the current date and record the elapsed time of the background count and the observed counts accumulated in the alpha and beta channels in the background columns of their respective sections.
- Step 3) Calculate the alpha and beta backgrounds by dividing the respective accumulated counts by the counting interval and record the results in the corresponding background columns.

4.5 Sample Counting

The ANALYST shall complete the following steps:

- Step 1) Survey the source prepared for sample counting using both alpha and beta survey instruments to insure that alpha and beta activity are both less than 1000 counts per minute.

Sources exceeding this limit will produce LB-1000 count rates that include significant live time error and may also contaminate the low background counting environment.

- Step 2) Carefully pull out the sample transport slide until the stop is encountered. A slight initial resistance due to the position locking mechanism will be felt.

- Step 3) Remove the round plastic sample holder from the sample well of the slide. Remove any sample dish currently in the holder, raising it by inserting a finger through the hole in the bottom of the sample holder and grasping the outside walls of the dish.

Insert the sample dish into the sample holder and return the holder to the slide sample well. Orientation is not important; the sample holder is automatically positioned correctly with respect to the counter detector when pushed into counting position.

- Step 4) Counter operation is controlled from the TIMER module. Adjust the time preset to the desired counting interval.

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- Step 5) Clear existing data from the alpha and beta module registers by pressing RESET on the TIMER module. If the count toggle is in the STOP position, initiate counting by switching the toggle to COUNT. If the toggle is already in COUNT position counting automatically begins when RESET is pressed.
- Step 6) Record "LB-1000", the date and time the count was begun, the length of the count in minutes, and (as appropriate to the specific sample) the alpha and beta channel accumulated counts and measured background in corresponding parts of the Sample Report Card.

4.6 Sample Calculations

The COGNIZANT SCIENTIST OR ANALYST shall complete the sample calculations using the following equations:

The uncertainty 1 sigma of either an alpha or beta count is calculated from the corresponding channel sample and background counts:

$$u = \sqrt{\left(\frac{\sqrt{C}}{t_c}\right)^2 + \left(\frac{\sqrt{B}}{t_b}\right)^2}$$

- where
- u = uncertainty in the observed sample count per minute, background corrected
 - c = total sample count (Section 4.5)
 - t_c = sample count duration (minutes)
 - b = total background count (Section 4.4)
 - t_b = background count duration (minutes)

Sample alpha and beta activity are calculated from the corresponding channel sample counts and uncertainties:

$$A \pm a = (B \pm u) \times C \times D$$

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where

- A = activity in disintegrations per minute per milliliter
- a = uncertainty in the calculated activity
- B = calculated count rate, background corrected, expressed in counts per minute
- u = uncertainty in the calculated count rate
- C = dilution factor or volume factor to correct the sample aliquot counted to 1 milliliter
- D = disintegration to count ratio for the specific nuclide and sample composition

4.7 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

4.8 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally it is considered qualified because it has received an independent technical review.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-409, (Replaces HTA-4-7), SOLUTIONS ANALYSIS: PREPARATION OF ALPHA SPECTROMETRY SOURCES BY ELECTRODEPOSITION

1.0 APPLICABILITY

This procedure provides instructions for the preparation of thin, uniform sources for the analysis of alpha-emitting isotopes by alpha spectrometry. This procedure can be used to prepare liquid leachate samples into sources for alpha spectrometry.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Dimethyl sulfoxide (DMSO), Fisher.
- Scandium carrier, 1.00 g of scandium per liter -- Dissolve 153 (± 15) mg of Sc_2O_3 in hot 6 M hydrochloric acid. Evaporate to dryness and dissolve the residue in 0.5 M hydrochloric acid. Dilute to 100 (± 1) mL with 0.5 M hydrochloric acid and mix.
- Nitric acid, 0.1 M -- Dilute 6.3 (± 0.3) mL of concentrated nitric acid to 1000 (± 1) mL with deionized water and mix.
- Power supply, direct current; Kepco Model BHK 2000-0.1, 0 to 2000 V, 0 to 100 mA.
- Electrodeposition cell.
- Discs, 7/8-in. diameter, stainless steel.

Author	Date	Project Mgr.	Date	QAD Representative	Date
AC Leaf	07/01/87	N/A		BO Barnes	06/30/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	07/02/87	All original signatures on file	
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4.0 PROCEDURE

- Step 1) Place stainless steel disc in base of electrodeposition cell, and assemble the cell.
- Step 2) Connect d-c power leads to cell [(-) to base side and (+) to anode].
- Step 3) Pipet 5 (± 0.05) mL of DMSO into cell, and add 20 (± 2) mL of scandium carrier solution.
- Step 4) Add sample to be electrodeposited. Final acid concentration in the cell must be less than 0.02 M. Sample volume should be less than 500 mL.
- Step 5) Add water or 0.1 M of nitric acid to give a final aqueous concentration of ~10% and an acid concentration of 0.01 to 0.02 M; mix solution.
- Step 6) Place anode just beneath solution surface.
- Step 7) Turn on a-c power (if not on), and turn on d-c power to cell. Adjust d-c amperage to 50 mA. Adjust d-c voltage so that the power supply is current-limited to give a constant current of 50 mA. Electrodeposit for 15 minutes.
- Step 8) Turn off d-c power to cell, and remove cell from holder.
- Step 9) Remove solution from cell using a vacuum waste container, and wash the cell twice with methyl alcohol.
- Step 10) Remove disc from cell, and dry disc under a heat lamp, until the DMSO or methyl alcohol residue has evaporated.
- Step 11) Perform alpha analysis using Alpha Counting (PNL-ALO-421) and Alpha Spectrometry (PNL-ALO-422) analysis procedures.

4.1 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-411, (Replaces HTA-4-19), SEPARATION OF SELENIUM-75 BY PRECIPITATION PRIOR TO MEASUREMENT BY GAMMA COUNTING

1.0 APPLICABILITY

This procedure is for the separation of selenium from test solutions for subsequent determination of ^{75}Se by gamma spectrometry using PNL-ALO-451.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Selenium carrier, 10 mg/mL -- Weigh 1.0 (± 0.1) g of gray selenium metal in a 200-mL beaker. Dissolve by heating in ~5 mL of concentrated reagent-grade nitric acid. Dilute to 100 (± 1) mL with 0.5 M nitric acid.
- Nitric acid, 0.5 M -- Prepare by diluting 32 (± 1) mL of reagent-grade concentrated nitric acid to 1000 (± 1) mL with deionized water.
- Bromine water -- Prepare by adding ~500 μL of bromine to ~100 mL of deionized water in a 4-oz glass bottle. Cap and shake. Excess bromine should be observable in the bottom of the bottle. If not, add more bromine.
- Hydroxylamine hydrochloride, 25% -- Prepare by dissolving 25 (± 1) g of the reagent-grade material in deionized water. Dilute to 100 (± 1) mL, and mix.

Author	Date	Project Mgr.	Date	QAD Representative	Date
AC Leaf	07/01/87	N/A		BO Barnes	06/30/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	07/02/87	All original signatures on file	
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- Methanol, reagent-grade.
- Nitric acid, concentrated, reagent-grade.
- Deionized water.
- Vial, 35-mL, glass, screw-cap.
- Centrifuge, with shields, to hold 35-mL vials.
- Bottle, 4-oz, glass.
- Transfer pipets, 5-mL, glass.
- Stir bar, 5/8-in.

4.0 PROCEDURE

Selenium-75, a gamma-emitting isotope used in some tracer-level glass waste forms, is frequently masked by ^{137}Cs during gamma spectral analysis. Selenium-75 is separated by adding a nonradioactive selenium carrier and precipitating selenium metal by using hydroxylamine. Cesium remains in solution. The selenium is dissolved in nitric acid and measured by gamma spectrometry.

Step 1) Add to a 35-mL screw-cap vial:

- Up to 1 mL of acidified test solution, recording the volume used in Step 14
- 2 (± 0.1) mL of selenium carrier
- Bromine water, to give a total volume of 10 (± 0.1) mL; swirl to mix.

Step 2) Measure ^{137}Cs activity, using Procedure PNL-ALO-451, "Solutions Analysis: Gamma Spectrometry." (^{137}Cs and ^{75}Se are determined on the same sample.)

Step 3) Add 10 (± 0.5) mL of hydroxylamine; swirl to mix.

Step 4) Heat under a heat lamp until the black selenium metal has precipitated.

Step 5) Centrifuge for about 5 minutes.

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- Step 6) Remove and discard the solution, using a 5-mL glass transfer pipet.
NOTE: Do NOT remove any precipitate.
- Step 7) Wash down the sides of the vial with ~5 mL of methanol. Swirl to wash precipitate.
- Step 8) Centrifuge for about 5 minutes.
- Step 9) Remove and discard the methanol wash, using a 5-mL glass transfer pipet. NOTE: Do NOT remove any precipitate.
- Step 10) Add 500 (± 50) μ L of concentrated reagent-grade nitric acid.
- Step 11) Heat under a heat lamp until the selenium is completely dissolved.
- Step 12) Add 10 (± 0.1) mL of 0.5 M nitric acid and a 5/8-in. stir bar; stir to mix.
- Step 13) Measure the ^{75}Se activity using Procedure PNL-AL0-451, "Solutions Analysis: Gamma Spectrometry."
- Step 14) Record the volume used and the results on the analytical report. Retain the gamma analysis data.

4.1 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-412, REV. 0; MEASUREMENT OF CARBON-14 IN METALS

1.0 APPLICABILITY

This procedure applies to the analysis of total carbon-14 in irradiated metals, such as Zircaloy cladding and stainless steel components. The method involves total combustion in oxygen in a LECO induction furnace within shielded hot cells, collection of the carbon-14 in NaOH collection bubblers and measurement by liquid scintillation counting. In the absence of suitable NIST-traceable carbon-14 in metal standards, the method can be calibrated for percent recovery by measurement of stainless steel carbon standards using a Total Carbon Coulometrics carbon determinator.

2.0 DEFINITIONS

LSC - Liquid Scintillation Counter.
TC - Total Carbon Analysis

3.0 RESPONSIBLE STAFF

Cognizant Scientist - a chemist or other scientist familiar with this procedure and having an in-depth knowledge of the chemistry.

Analyst - an individual who is qualified in the use of this procedure, and for whom this has been documented in the analyst's qualification training records.

4.0 PROCEDURE

Carbon-14 is determined by a total combustion method, using an in-cell induction furnace to fuse the metal sample in pure oxygen with a copper flux. The gas stream exiting from the combustion tube is passed through a catalytic heater for conversion of any CO to CO₂, as well as H₂ to H₂O. All forms of carbon are oxidized and converted to CO₂ in this procedure. The gas is routed out of the shielded cell through a drying column for removal of any H₂O. The gas is then sparged through a pair of dilute-NaOH bubblers for collection of ¹⁴CO₂. Measurement of the bubbler solution is

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Technical Reviewer <i>LR Greenwood</i> LR Greenwood	Date <i>11/12/92</i>	Line Mgr. <i>A. K. Fudge</i> AG King	Date <i>11/14/92</i>	Other	Date
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by liquid scintillation counting. Since there are no existing suitable carbon-14 in metal standards, the method can be calibrated for percent recovery of carbon by measurement of NIST-traceable stainless steel carbon standards using a Coulometrics carbon analyzer. Recovery of carbon-14 should be equal to recovery of natural carbon.

4.1 Equipment and Materials for Calibration Procedure by Carbon Standard

- 4.1.1 Apparatus and materials as described in procedure PNL-ALO-380 in PNL-MA-599, "Determination of Carbon in Solids using the Coulometrics Carbon Dioxide Coulometer".
- 4.1.2 ss/carbon standards. Stainless steel (ss) rings or granules, in range of 300-2000 ppm C, NIST-traceable. Keep clean.

4.2 Equipment and Materials for Carbon-14 Analysis

- 4.2.1 Sodium hydroxide bubbler solution, 0.6 M -- Prepared by dissolving 24 ± 0.5 g of reagent-grade NaOH in 1000 ± 20 ml of deionized water.
- 4.2.2 Scintillation cocktail, Packard Ultima Gold®, or suitable equivalent.
- 4.2.3 Induction furnace for carbon analysis, manufacturer by Leco Corporation, St. Joseph, MI, or equivalent.
- 4.2.4 Copper flux, manufactured by Leco Corporation, or equivalent. Keep clean.
- 4.2.5 Combustion crucibles and lids, alumina, for carbon analysis, from Leco Corp, or equivalent. Keep clean.
- 4.2.6 Glass collection bubblers, pair, for carbon-14 collection, labeled "1st Bubbler" and "2nd Bubbler". Bubbler dimensions are 1.0" OD top two inches, 0.7" OD bottom six inches, total length 8 inches.
- 4.2.7 Ultra high purity oxygen (99.999%) in 200 cu.ft. cylinder.

4.3 Percent Recovery Determination by Total Carbon (TC) Measurement

- 4.3.1 Use the TC Coulometer measurement procedure as described in

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procedure PNL-ALO-380 in PNL-MA-599.

- 4.3.2 Set valving on inlet manifold valves for Cell 5 Carbon Analyzer Induction Furnace and outlet 3-way valve for TC measurement by Coulometer.
- 4.3.3 Perform pressure test leak check by closing final valve on outlet line and checking for a flow drop to zero on flowmeter readout. If test fails, continue determining location of leak or contact Cognizant Scientist.
- 4.3.4 Start up the carbon analyzer Induction Furnace according to manufacturer's operating manual. Turn on power for warmup by switching right-hand FILAMENT VOLTAGE switch to ON, turning on green lamp. The GRID TAP switch should be set to HIGH. Only during the analysis of large samples ($>>1$ g) may this tap setting have to be set back to MED or even LOW. With sample loaded, switch on left-hand HIGH VOLTAGE switch, turning on red lamp, to turn on induction heat. Both Plate and Grid ammeters should be near full scale. If full scale is exceeded, the breaker may trip. If so, immediately decrease GRID TAP setting, reset breaker, and continue with analysis. Normal analysis time is 90 sec. At end of burn, switch off HIGH VOLTAGE.
- 4.3.5 Perform normal furnace operation with blanks and ss/carbon standards as described in steps 4.4.7 to 4.4.10.
- 4.3.6 Run several TC blanks until blank level is low and stable. The TC blank acceptance criteria are 1) two consecutive blanks each at <300 ug C and 2) the two ranging no greater than 30 ug C. If above this limit, repeat blank and inform Cognizant Scientist. Normal collection time of carbon is 15 minutes. Record all Coulometer output in LRB or data sheet.
- 4.3.7 Run at least two ss/carbon ring standards to determine TC Percent Recovery (used in calculation 4.6.1). TC Percent Recovery acceptance criteria are 1) two consecutive ss/carbon ring standards each measuring within 85% - 102% recovery and 2) the two ranging no greater than 6% recovery. If standard value is outside these limits, repeat standard and inform Cognizant Scientist. Record data in LRB or data sheet. Any deviation in the time required for recovery should also be noted, i.e., recovery should be completed within 15 minutes. After completion of this part, the TC calibration step is completed and carbon-14 analysis procedure may be started.

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4.4 Carbon-14 Analysis Procedure

- 4.4.1 Doublecheck valving on inlet manifold valves for Cell 5 Carbon Analyzer Induction Furnace and set outlet 3-way valve for C-14 measurement by collection bubblers.
- 4.4.2 Start or restart the carbon analyzer Induction Furnace, see 4.3.4.
- 4.4.3 Set oxygen flow to 180 (± 20) std cm³/min on the rotometer.
- 4.4.4 System blanks, ss/carbon standards (see 4.3.7), and samples are treated similarly, using the identical procedure for combustion crucibles, lids and copper flux, and system operation. Run at least two system blanks at the beginning of a batch and at least one at the end of a batch. Discard the first blank value and average the remaining blanks for the calculation. No need to run any ss/carbon standard at end of batch.
- 4.4.5 Weigh sample to an accuracy of ± 0.001 g. Depending upon carbon-14 levels and sample availability, typical sample sizes range from 100 mg to 1.0 g. Record sample ID and weight in LRB or data sheet.
- 4.4.6 Place 15 (± 0.5) ml of fresh NaOH bubbler solution into each collection bubbler. Install bubblers in bubbler manifold.
- 4.4.7 Load two scoops (vendor-supplied glass scoop - about 0.3 cc) of copper flux into the crucible.
- 4.4.8 If C-14 sample is being run, place sample in crucible plus one ss/carbon ring standard for natural carbon carrier. If C-14 liquid standard is being run, inject C-14 liquid standard plus one ss/carbon ring standard for carbon carrier. If total carbon standard is being run, load ss/carbon ring standard only. If C-14 blank is being run, load ss/carbon ring in crucible. If carbon blank is being run, do not load any ss/carbon ring in crucible. Add crucible lid onto crucible.
- 4.4.9 Carefully place loaded crucible with lid onto furnace pedestal and close and lock into place, actuating safety switch.
- 4.4.10 Restart gas flow if turned off. Doublecheck that valving is proper for C-14 collection (or for carbon operation if TC is being done). Check that flow is correct through the pair of collection bubblers (or through the Coulometrics detector

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cell if TC is being done). When all is ready, turn on high voltage power to furnace and burn at least 90 (-0/+30 sec) seconds or until reaction is complete. Record burn time in LRB or data sheet.

- 4.4.11 Collect gas in pair of collection bubblers for 15 ± 2 minutes.
- 4.4.12 After gas collection is complete, stop gas flow. Remove each collection bubbler and allow dip tube to drain into bubbler until dripping appears to cease (usually about 20 sec). Rinse each dip tube with water from a squirt bottle and discard rinsings.
- 4.4.13 Transfer each bubbler solution, respectively, to a 20-ml poly-lid glass vial, labeled "Sample ID/Archive-1st Bubbler" and "Sample ID/Archive-2nd Bubbler". Tighten lid tightly.
- 4.4.14 Rinse glass bubblers with distilled water. Glassware may require soap solution cleaning, if glass does not drain evenly. Refill with fresh NaOH bubbler solution (see 4.4.6) in preparation for next analysis.
- 4.4.15 Lower furnace pedestal and remove crucible. Examine melt for normal appearance, i.e., smooth, homogeneously-gray melt, wetting crucible walls, with no unmelted pieces of sample protruding from melt. Record unusual observations in LRB or data sheet. Dispose of crucible and lid.

4.5 Carbon-14 Counting Procedure

- 4.5.1 All samples, blanks and standards are archived at the time of analysis. The entire group of samples, blanks and standards, even accumulated over multiple days, may be batched for counting preparation and liquid scintillation counting as described in the following sections 4.5.2 to 4.5.5.
- 4.5.2 Label four counting vials for duplicate counts on each of the two bubbler solutions.
- 4.5.3 Add 12 (± 0.3) ml of Ultima Gold scintillation cocktail to each vial.
- 4.5.4 Remove a 2.0 (± 0.02) ml aliquot from an archive vial and add aliquot to the properly labeled counting vial. Mix the contents of the vial thoroughly for at least 10 sec.
- 4.5.5 Measure the ^{14}C activity, within a 48 hr period, in the Packard 2550 liquid scintillation counter, or equivalent,

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using procedure PNL-ALO-474, "Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry".

4.6 Calculations for TC Percent Recovery Determination

4.6.1 Calculate Percent Recovery of TC in the ss/carbon standard.

$$\text{TC Recovery Fraction} = \frac{\text{ug(std)} - \text{ug(blank)}}{\text{known C in Std (ug)}}$$

4.7 Calculation for Carbon-14 Measurement

4.7.1 Calculate ^{14}C in the sample.

$$\text{uCi } ^{14}\text{C/g} = \frac{\frac{A-B}{C-B} \times D \times G}{W \times E \times F}$$

where:

A = Sample cpm
B = Blank cpm
C = Standard cpm
D = Standard dpm
G = Dilution factor, typically (15ml/2ml)
W = Weight of sample (g)
F = TC Recovery Fraction
E = 2.2×10^6 dpm per uCi

4.8 Possible Sources of Uncertainties and Errors

Several possible sources of uncertainty or error (bias) have been identified. In cases of potential system bias, the error has been corrected for with the TC Recovery Fraction determination and accounted for in the result.

Possible sources of system error are as follows: extraction efficiency, incomplete melting, incomplete oxidation, wall adsorption of CO_2 , and bubbler collection efficiency, though this procedure should minimize the probability of such errors. The TC Recovery Fraction value or the presence of CO_2 carrier should account for or correct these sources of error.

Possible random uncertainties are: uncertainty in carbon standard,

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carbon-14 standard, volume uncertainties, TC background levels, C-14 background levels, and in the Percent Recovery Factor. The major concern, particularly for low carbon-14 levels in samples, is the uncertainty in the C-14 background, which may be a sizable percentage of the level in the sample. This must be determined from replicate blank determinations. Uncertainty in the TC Recovery Fraction must also be determined through replicate standard recoveries. The other uncertainties are known or can be estimated.

5.0 RECORDS

All sample identification, specific conditions and specific parameters for each sample shall be recorded into LRB or data sheet. Counting results are entered into spreadsheet for final calculation.

Records shall include: the LRB pages or data sheet containing sample weights, volumes, run information, pipet calibrations, etc.; the LSC printout of count data; the spreadsheet printout of final calculations; and the report containing a summary of results, summary of secondary data and QA information, and a narrative providing explanation of analysis results, discussion of deviations, discussion of outliers, etc.

6.0 SPECIFIC QUALIFICATION

This procedure is a controlled process, self-qualifying due to its dependence on analytical standards, and therefore is considered qualified through the ITR of the procedure, as per PAP-70-901.

7.0 REFERENCES

- 7.1 Goodspeed, H.T., Holt, B.D., Marsh, J.H., Stoessel, J.E., "Remote Analysis of Radioactive Alloys for Carbon, Oxygen, Nitrogen, and Hydrogen", Analytical Chemistry, Vol. 40, No. 4, April 1968, 682-685.
- 7.2 Instrument Manual, System 150, Coulometrics Inc., Golden, CO.
- 7.3 E. W. D. Huffman, "Performance of a New Automatic Carbon Dioxide Coulometer, Microchemical Journal, 22, 567-573 (1977).
- 7.4 Total and Organic Carbon by Coulometric Detection, ASTM D-4129-82.

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CARBON-14 ANALYSIS DATA SHEET

Procedure: 7-40.42 _____
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Date Analyzed _____
Project No. _____

Sample Information:

Instrument No. _____
Balance No. _____

[illegible]

Pipet Calibrations:

Analyst's Signature date

Reviewer's Signature _____ date _____

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-413, (Replaces HTA-4-35), SOLUTIONS ANALYSIS: AMERICIUM AND CURIUM ISOTOPES BY CATION AND ANION EXCHANGE SEPARATION FROM PBB-1 AND PBB-3 BRINE TEST SOLUTIONS

1.0 APPLICABILITY

This procedure applies to the preparation of brine samples for the determination of americium and curium isotopes.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Company format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Nitric acid, 1 M - Dilute 63 (± 1) mL of concentrated reagent-grade acid to 1000 (± 1) mL with deionized water; mix thoroughly.
- Nitric acid, 1.85 M - Dilute 117 (± 1) mL of concentrated reagent-grade acid to 1000 (± 1) mL with deionized water, mix thoroughly.
- Nitric acid, 8 M - Dilute 506 (± 1) mL of concentrated reagent-grade acid to 1000 (± 1) mL with deionized water, mix thoroughly.
- Ammonium hydroxide, concentrated.
- AG-50[®], X-8, 200 to 400 mesh, H⁺ form resin.
- AG-1[®], X-4, 100 to 200 mesh, Cl⁻ form resin.

®AG-1 and AG-50 are registered trademarks of Bio-Rad Laboratories, Richmond, California.

Author	Date	Project Mgr.	Date	QAD Representative	Date
AC Leaf	07/01/87	N/A		BO Barnes	06/30/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	07/02/87	All original signatures on file	
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- Pipet, serological, disposable, Kimble 72120, 10mL x 1/10 mL, to be used as ion exchange columns.
- Vials, 2-dram, 15-mL, 35-mL, glass.
- Droppers, 7.5-mL, plastic.
- Heat lamp, infrared.
- Disk, 7/8-in., stainless steel.
- Hot plate.

4.0 PROCEDURE

The americium and curium isotopes are separated by loading onto a cation exchange resin column and washing the brine as well as ^{137}Cs and ^{90}Sr from the column with 1.85 M nitric acid. The americium and curium are eluted from the column with 8 M nitric acid, and plutonium is removed by loading onto an anion exchange column while the americium plus curium pass through. The americium and curium isotopes are then measured and resolved by alpha counting and alpha spectrometry.

Recoveries are estimated at $94 \pm 2\%$. Data from ^{241}Am plus brine recovery tests are located in notebook HEDL-N-3472, pp. 52-53. Normally the sample calculation does not include any bias correction.

- Step 1) Add to a 2-dram vial 500 (± 5) μL of brine test solution. Record the sample volume on the analytical report.
- Step 2) Add 5.0 (± 0.1) mL of 1.85 M nitric acid to the brine sample in the 2-dram vial.
- Step 3) Prepare a 3 (± 0.1) mL column of AG-50, X-8, 200 to 400 mesh, H^+ form resin. Remove the top of the 10-mL serological pipet down to Mark 0. Fill the tip of the pipet with cotton to Mark 9. Fill the pipet with AG-50, X-8, 200 to 400 mesh, H^+ form resin to Mark 6. Adjust the top of the resin bed at Mark 6 to compensate for any deviation of the bottom of the resin bed at Mark 9. Total resin bed volume must be 3 (± 0.1) mL.
- Step 4) Using a plastic dropper, mix the solution in the 2-dram vial (see Step 2) and transfer the solution to the 3-mL column (see Step 3). Disturb the resin bed as little as possible by running the solution slowly down the side of the glass column. Collect the effluent as waste in a 35-mL vial.

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- Step 5) Wash the 2-dram vial with six 5 (± 0.05) mL portions of 1.85 M nitric acid transfer the solution to the column. Allow each portion to drain completely from the column before adding the next. Disturb the resin bed as little as possible. The effluent is collected as waste and contains the salts from the brine as well as ^{137}Cs and ^{90}Sr activities. The americium and curium isotopes remain on the column.
- Step 6) Elute the americium and curium isotopes with two 5 (± 0.05) mL portions of 8 M nitric acid. Collect the effluent in a 15-mL vial.
- Step 7) Heat the 15-mL vial containing the americium and curium for 15 (± 2) minutes at 80 (± 10) $^{\circ}\text{C}$. Allow to cool for at least 10 minutes.
- Step 8) Prepare a 500 (± 50) μL column of AG-1, X-4, 100 to 200 mesh, Cl^- form resin. Remove the top of the bulb from a 7.5-mL plastic dropper. Place a small cotton ball into the tip of the dropper and tamp lightly. Measure a volume of 500 μL above the cotton and mark. Fill the dropper to the mark with a slurry of AG-1, X-4, 100 to 200 mesh resin. Wash the resin with 2 mL of 8 M nitric acid just prior to use.
- Step 9) Using a plastic dropper, transfer the americium plus curium solution (see Step 7) to the resin column (see Step 8). Collect the effluent containing the americium and curium in a 35-mL vial. The plutonium is retained on the resin.
- Step 10) Wash the 15-mL vial with four 1-mL portions of 8 M nitric acid and transfer the solution to the column. Collect the effluent in the 35-mL vial containing the americium and curium (see Step 9).
- Step 11) Evaporate the americium and curium solution to dryness (normally overnight under a heat lamp).
- Step 12) Add 500 (± 5) μL of 1 M nitric acid to the dry residue in the americium and curium vial. Cap tightly, record the volume used on the analytical report form.
- Step 13) Swirl to dissolve the residue. Rotate the vial several times to make sure that all residue from all of the glass surface is dissolved in the acid.
- Step 14) Centrifuge for at least 1 minute to bring the solution to the bottom of the vial.

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- Step 15) Add a small stir bar and stir for 1 (± 0.1) minute.
- Step 16) Plate up to 100 (± 1) μL of the solution onto a 7/8-in. stainless steel disc. Record the volume on the analytical report form.
- Step 17) Evaporate the solution to dryness under a heat lamp.
- Step 18) Add a few drops of deionized water to the disc to cover the dried residue. Then add 1 drop of concentrated ammonium hydroxide.
- Step 19) Evaporate to dryness under the heat lamp.
- Step 20) Place the disc on a hot plate on high heat for up to 30 minutes until the organic residue is burned off the disc.
- Step 21) Count the americium and/or curium isotopes using Alpha Counting (Procedure PNL-ALO-421) and Alpha Spectrometry (Procedure PNL-ALO-422).

4.1 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-414, (Replaces HTA-4-38), SEPARATION OF AMERICIUM-241 AND CURIUM-244 BY CATION AND ANION EXCHANGE SEPARATION FROM BWIP HYDROTHERMAL TEST SOLUTIONS PRIOR TO MEASUREMENT BY ALPHA COUNTING

1.0 APPLICABILITY

This procedure is for the separation of americium and curium so that ^{241}Am and ^{244}Cm can be determined without interference from ^{238}Pu . Groundwater salts and beta activities from ^{137}Cs and ^{90}Sr are also removed. This improves the resolution of the ^{241}Am and ^{244}Cm in the alpha spectrum used to separate ^{241}Am from ^{244}Cm . Following the separation, the ^{241}Am and ^{244}Cm are measured by alpha counting methods PNL-ALO-422 and PNL-ALO-421.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Company format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Nitric acid, 1 M - Dilute 63 (± 1) mL of concentrated reagent-grade acid to 1000(± 1) mL with deionized water; mix thoroughly.
- Nitric acid, 1.85 M - Dilute 117 (± 1) mL of concentrated reagent-grade acid to 1000(± 1) mL with deionized water; mix thoroughly.
- Nitric acid, 8 M - Dilute 506 (± 1) mL of concentrated reagent grade acid to 1000 (± 1) mL with deionized water; mix thoroughly.
- AG-50[®], X-8, 200 to 400 mesh, H^+ form resin.
- AG-1[®], X-4, 100 to 200 mesh, Cl^- form resin.

®AG-1 and AG-50 are registered trademarks of Bio-Rad Laboratories, Richmond, California.

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AC Leaf	07/01/87	N/A		BO Barnes	06/30/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	07/02/87	All original signatures on file	
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- Vials, 15-mL, glass, screw-cap.
- Vials, 2-dram, glass, screw-cap.
- Heating block, aluminum, to hold vials in heating mantle.
- Droppers, 7.5-mL, plastic.
- Disks, 7/8-in., stainless steel.
- Stir bar, magnetic, glass-covered.

4.0 PROCEDURE

Americium and curium are loaded onto a cation exchange resin where they are held while sodium, calcium, and magnesium salts, as well as ^{137}Cs and ^{90}Sr activities, are eluted with 1.85 M nitric acid. The americium and curium are eluted with 8 M nitric acid and are passed through an anion exchange resin (where plutonium loads) and is separated from the americium and curium (which do not load). The americium and curium are then measured by alpha counting and alpha spectrometry.

- Step 1) Prepare a 1.0 (± 0.05) mL column of AG-50, X-8, 200 to 400 mesh H^+ form resin. Remove the top of the bulb from a 7.5-mL plastic dropper. Place a small cotton ball into the tip and tamp lightly. Measure a volume of 1.0 (± 0.05) mL above the cotton ball and mark. Fill the dropper to the mark with AG-50, X-8, 200 to 400 mesh H^+ form resin. Wash the column with (± 0.05) mL of 8 M nitric acid followed by 2 (± 0.02) mL of deionized water. Collect the wash in a 15 mL vial and discard in the liquid radioactive waste.
- Step 2) Load 500 (± 5) μL of hydrothermal test solution onto the resin. Disturb the resin bed as little as possible while loading. Collect the load effluent in a 35-mL vial as waste. Record the volume taken on an analytical report.
- Step 3) Wash the column with four 3 (± 0.1) mL portions of 1.85 M nitric acid. Allow each portion to drain completely before adding the next. Disturb the resin bed as little as possible. Collect the effluent in the 35-mL vial from Step 2. Discard as waste.
- Step 4) Elute the americium and curium with 10 (± 0.1) mL of 8 M nitric acid. Collect the effluent containing the americium and curium in a 15-mL vial.

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- Step 5) Heat the vial of americium plus curium for 15 (± 2) minutes at 80 (± 10) $^{\circ}\text{C}$.
- Step 6) Allow to cool for at least 10 minutes.
- Step 7) Prepare a 500 (± 50) μL column of AG-1, X-4, 100 to 200 mesh, Cl^- form resin. Wash the resin with 2 mL of 8 M nitric acid just prior to use. Remove the bulb top from a 7.5-mL plastic dropper. Place a small cotton ball in the tip and tamp lightly. Measure a volume of 500 (± 50) μL above the cotton ball and mark. Fill the dropper to the mark with a slurry of AG-1, X-4, 100 to 200 mesh, Cl^- form resin.
- Step 8) Transfer the americium-curium solution to the anion resin column using a plastic dropper. Collect the effluent containing the americium and curium in a 35-mL screw-cap vial.
- Step 9) Wash the 15-mL vial with four 1-mL portions of 8 M nitric acid and transfer the solution to the column. Collect the solution in the effluent vial containing americium and curium (see Step 8).
- Step 10) Evaporate the americium-curium solution to dryness (usually overnight under a heat lamp).
- Step 11) Add 500 (± 5) μL of 1 M nitric acid to the dried residue and cap tightly. Record the volume on the analytical report.
- Step 12) Swirl to dissolve the residue. Rotate the vial until the residue on all surfaces of the glass vial has been dissolved.
- Step 13) Centrifuge for about 1 minute to move the nitric acid solution to the bottom of the vial.
- Step 14) Add a small stir bar and stir 1 (± 0.1) minute to mix the solution.
- Step 15) Evaporate a measured volume ($\pm 1\%$) of the solution on a 7/8-in. stainless steel disk. Record the volume on the analytical report.
- Step 16) Add a few drops of deionized water to the disk to cover the dried residue.
- Step 17) To the water on the disk add 1 drop of concentrated ammonium hydroxide and evaporate to dryness.

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- Step 18) Heat the disk on a HIGH setting on a hot plate up to 30 minutes to burn off the organic residue.
- Step 19) Measure the ^{241}Am and the ^{244}Cm on the disk using Alpha Spectrometry (Procedure PNL-ALO-422) and Alpha Counting (Procedure PNL-ALO-421).

4.1 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-416, (Replaces HTA-4-42), SEPARATION OF IODINE-129 BY SOLVENT EXTRACTION AND DISTILLATION FROM BRINE SOLUTIONS PRIOR TO MEASUREMENT BY GAMMA (X-RAY) COUNTING

1.0 APPLICABILITY

This procedure describes the separation of iodine from brine solutions or similar test solutions and the subsequent x-ray counting of iodine-129 using a GeLi well gamma spectrometer.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Iodine carrier, 10.0 mg/mL iodine -- Prepare by dissolving 1.181 (± 0.001) g of reagent-grade sodium iodide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Potassium permanganate, 0.2 M -- Prepare by dissolving 3.16 (± 0.01) g of reagent-grade potassium permanganate in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sulfuric acid, 10% -- Prepare by diluting 10 (± 0.1) mL of concentrated reagent-grade sulfuric acid to 100 (± 0.1) mL with deionized water. Mix thoroughly.
- Sodium sulfite, 1 M -- Prepare by dissolving 12.6 (± 0.1) g of reagent-grade sodium sulfite in 100 (± 0.1) mL of deionized water. Mix thoroughly.

Author	Date	Project Mgr.	Date	QAD Representative	Date
AC Leaf	10/13/87	N/A		LE Thompson	10/14/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	10/13/87	All original signatures on file	
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- Carbon tetrachloride, reagent grade.
- Sodium hydroxide, 1 M -- Prepare by dissolving 4.0 (± 0.1) g of reagent-grade sodium hydroxide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sodium nitrite, 1 M -- Prepare by dissolving 6.9 (± 0.1) g of reagent-grade sodium nitrite in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Silver nitrate, 0.1 M -- Prepare by dissolving 1.70 (± 0.01) g of reagent-grade silver nitrate in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sodium cyanide, 1 M -- Prepare by dissolving 4.9 (± 0.1) g of reagent-grade sodium cyanide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Stir bars, 5/8 in., 1/8 in., glass covered.
- Vials, 35 mL, glass.
- Vials, 2 dram, plastic, 14 mm ID with snap cap.
- Heating block, for heating 35 mL glass vials.
- Stirrer, magnetic.
- Droppers, plastic.
- Still, see selenium still, Figure PNL-ALO-440.1, Procedure PNL-ALO-440.
- Heating mantle, round bottom for 50 mL round bottom flask.
- Variac, 0 to 140 volts, 1.5 ampere output.
- Lab-jack, suitable size to hold 35 mL glass vial.
- Nitrogen gas -- Reduce pressure to ~ 2 psi using a nitrogen gas pressure reducing valve. A purity of 99.5% nitrogen is acceptable.
- Filters, 13 mm -- Prepare by cutting filter sections from Whatman 934AH glass microfiber filters of a larger size using #9 cork borer. Place the filter on a hard flat surface and press down with the #9 cork borer. Each filter

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must be dried at 110° to 120°C for at least 30 minutes, cooled and weighed just prior to use to obtain the tare weight in Step 45, Section 4.2, Iodine Separation. Carry the filters on a numbered beaker cover and cover with a larger beaker cover to avoid loss of filters due to air currents. Record the tare weight on the Analytical Data Sheet.

- Filter holder, Swinnex, 13 mm or equivalent.
- Vacuum jug with hole in stopper to accommodate the base of the 13 mm Swinnex filter holder.
- Beaker covers, 3 in. and 4 in. or other suitable sizes.

4.2 Iodine Separation

Iodine-129 is separated from brine solutions containing other radioactive species by extracting the iodine (I_2) into carbon tetrachloride, washing and stripping into an aqueous phase as the iodide (I^-). The iodide solution is transferred to a still and is distilled as iodine (I_2). The iodide (I^-) is precipitated as silver iodide (AgI) and is filtered and weighed to measure recovery. The AgI and filter are transferred to a plastic vial and the AgI is dissolved in sodium cyanide prior to counting in the GeLi well gamma spectrometer.

The ANALYST shall perform the following steps unless otherwise specified.

- Step 1) To a 35 mL vial add a 5/8 in. stir bar, up to 1.0 mL ($\pm 1\%$) volume of brine solution, as specified by the COGNIZANT SCIENTIST, 2.0 (± 0.02) mL of deionized water, 1.0 (± 0.01) mL of iodide carrier, 1.0 (± 0.01) mL of potassium permanganate and 2.0 (± 0.02) mL of 10% sulfuric acid. Record the volume of brine solution taken on the Analytical Report Form.
- Step 2) Stir the solution in the vial about 30 seconds.
- Step 3) Heat the solution in a heating block at 80° to 95°C for 10 (± 1) minutes.
- Step 4) Remove the solution from the heating block and cool at least 5 minutes.
- Step 5) Add 1 (± 0.01) mL of sodium sulfite and swirl to mix. Solution should become colorless but may have some precipitated salts.

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- Step 6) Heat the solution in the heating mantle for 5 (± 1) minutes at 80° to 95° C.
- Step 7) Remove from the heating mantle and cool at least 5 minutes.
- Step 8) Add 5 (± 0.5) mL of carbon tetrachloride.
- Step 9) Add 2 (± 0.02) mL of sodium nitrite and cap the vial tightly.
- Step 10) Shake the vial for about 1 minute. Then stir for 5 (± 1) minutes. Iodine color will form in the carbon tetrachloride phase (bottom).
- Step 11) Centrifuge for 1 to 2 minutes to separate phases.
- Step 12) Remove the cap and, using a transfer pipet, transfer the carbon tetrachloride phase to a clean vial #2.
- Step 13) To the aqueous phase remaining in the first vial, add 5 (± 0.5) mL of carbon tetrachloride.
- Step 14) Cap the vial tightly and shake for about 1 minute, then stir for 5 (± 1) minutes.
- Step 15) Centrifuge for 1 to 2 minutes to separate phases.
- Step 16) Remove the cap and transfer the carbon tetrachloride phase to the vial #2 using the transfer pipet used in the first transfer. Add a 5/8 in. stir bar to the vial #2 containing the carbon tetrachloride.
- Step 17) Discard the first vial to the liquid radioactive waste and the transfer pipet to the radioactive dry waste.
- Step 18) Fill the vial containing the carbon tetrachloride to the neck with deionized water.
- Step 19) Cap tightly and stir for 5 (± 1) minutes).
- Step 20) Centrifuge for 1 or 2 minutes to separate phases.
- Step 21) Remove the cap and slurp the aqueous phase (top) into the vacuum radioactive liquid waste container. Do not disturb the carbon tetrachloride phase (bottom).
- Step 22) Repeat Steps 18, 19, 20 and 21 one time.

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- Step 23) To the washed carbon tetrachloride phase, add 10 (± 0.1) mL of deionized water, 2 (± 0.02) mL of 10% sulfuric acid and 1 (± 0.01) mL of 1 M sodium sulfite.
- Step 24) Cap tightly and shake until colorless, then stir for at least 5 minutes.
- Step 25) Centrifuge for 1 to 2 minutes to separate phases.
- Step 26) Transfer the aqueous phase (top) to the iodine still using a transfer pipet. Avoid the carbon tetrachloride phase (bottom).
- Step 27) Add 5 (± 0.1) mL of deionized water to the vial containing the carbon tetrachloride.
- Step 28) Cap the vial tightly and shake for 20 to 30 seconds.
- Step 29) Centrifuge for 1 to 2 minutes to separate the phases.
- Step 30) Transfer the aqueous phase (top) to the iodine still, using a transfer pipet. Avoid the carbon tetrachloride phases. Cap the vial containing the residual carbon tetrachloride and dispose of in the radioactive waste container. Discard the transfer pipet in the dry radioactive waste.
- Step 31) To a 35 mL glass vial add 2 (± 0.02) mL of 1 M sodium hydroxide and 2 (± 0.02) mL of 1 M sodium sulfite. Place the still outlet beneath the solution in the vial and support the vial with a Lab-Jack.
- Step 32) Add 2 (± 0.02) mL of 1 M sodium nitrite to the still through the still inlet and connect the nitrogen gas inlet cover. Adjust the nitrogen flow to about 5 to 6 bubbles per second.
- Step 33) Set the Variac to 110 and turn on.
- Step 34) Distill until the iodine color is gone; usually about 5 to 10 minutes. The completion of the distillation is very sudden.
- Step 35) Immediately turn off the Variac and remove the 35 mL vial from the still outlet. Place a beaker under the still outlet to catch any residual distillation which is discarded as liquid radioactive waste.

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- Step 36) To the vial containing the distillate, add 2 (± 0.02) mL of 10% sulfuric acid and a 5/8 in. stir bar. Stir for a few seconds to mix.
- Step 37) Heat the distillate vial for 10 (± 1) minutes at 80° to 95°C in the heating mantle.
- Step 38) Cool at least 10 minutes.
- Step 39) While stirring the solution in the distillate vial, add 20 (± 1) mL of deionized water; then add 1 (± 0.01) mL of M silver nitrate dropwise to precipitate silver iodide. Stir for 10 to 20 seconds. Remove from the stirrer.
- Step 40) Heat the distillate vial containing the silver iodide precipitate for 10 (± 1) minutes at 80° to 95°C in the heating block.
- Step 41) Cool for at least 10 minutes.
- Step 42) Centrifuge for 2 to 3 minutes.
- Step 43) Using a transfer pipet transfer the solution to the liquid radioactive waste. Do not disturb the precipitate.
- Step 44) Add 2 to 3 mL of deionized water to the precipitate and slurry.
- Step 45) Place a 13 mm dried and tared glass filter on the base of a 13 mm Swinnex filter holder. While vacuum is applied, place the base of the Swinnex holder with filter on top into the hole of a stopper in the top of the vacuum flask. See instructions in 4.1, Equipment and Materials, for Preparation of 13 mm glass filters.
- Step 46) Using a plastic dropper, transfer the precipitate slurry onto the center of the filter.
- Step 47) Wash the vial with 3 to 4 mL portions of deionized water and transfer as much of the precipitate as possible to the filter.
- Step 48) Wash the vial with 3 to 4 mL of methanol and transfer as much of the residual precipitate to the filter as possible.

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- Step 49) Remove the filter holder from the stopper in the vacuum flask.
- Step 50) Remove the filter from the filter holder and place the filter on a suitable carrier, such as a beaker cover, and dry in an oven at 110° to 120°C for 30 (±2) minutes. Cover with a larger beaker cover when transporting filters to avoid loss of filters due to air currents.
- Step 51) Remove the filter plus precipitate from the oven and allow to cool at least 10 minutes.
- Step 52) Weigh the filter plus precipitate on a balance that weighs up to 10 μ g (0.00001 g) or better. Record the weight on the Analytical Report Form and the identification of the balance used. Use the same balance used for Step 45.
- Step 53) Calculate the weight of the silver iodide on the filter using the tare weight (Step 45) and the gross weight (Step 52). Record the precipitate weight on the Analytical Report Form.
- Step 54) Transfer the filter plus silver iodide to a plastic 2 dram vial (14 mm ID). Be sure no precipitate is lost during the transfer.
- Step 55) Add a 1/8 in. glass covered stir bar and 2 (+0.02) mL of 1 M sodium cyanide to the plastic vial containing the filter and silver iodide.
- Step 56) Close the top of the plastic vial and stir until the silver iodide dissolves.
- Step 57) Clean the still using a vacuum waste jug and slurp the solution from the still through the still top. Flush the still with water by drawing water into the still through the still outlet and through the still inlet to the vacuum waste jug.
- Step 58) Count the dissolved silver iodide in the plastic vials in the GeLi well gamma spectrometer using procedure PNL-ALO-451.
- Step 59) Calculate the I-129 concentration in the sample using Section 4.4, Calculations. Record sample counting

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data and calculations on the Analytical Report Form. Retain raw counting data in the BWIP files. Record all standard information and records in the BWIP files or LRB.

4.3 Preparation of I-129 Standards

Complete Step 1 through Step 58 of Section 4.2, Iodine Separation, using an NBS or equivalent I-129 standard instead of a sample. The amount of I-129 standard used shall be specified by the COGNIZANT SCIENTIST. Standard identification, volumes taken and other pertinent data shall be recorded on the Analytical Report Form and in the LRB. At least four standards should be prepared and the average used as the standard value. The standards are to be done once and the d/c factor calculated in Section 4.4 shall be used permanently as long as the daily calibration of the ND-66 GeLi well is in control. See PNL-ALO-451, Section 4.1.

4.4 Calculations

4.4.1 Counts in Spectrum from Standard or Sample Count

Gamma spectrometer energy calibration equals 1 keV/channel

$$A \pm \alpha = \frac{B - \left[\left(\frac{C}{2}\right) \times 9\right] \pm \sqrt{B + \left[\left(\frac{C}{2}\right) \times 9\right]}}{D}$$

where: $A \pm \alpha$ = the net counts/minute ± 1 sigma in a sample count

B = sum of all counts in channels 27 through 35 inclusive

C = sum of channels 26 and 36

D = minutes counted.

4.4.2 Yield Calculation

$$Y = \frac{A-B}{C}$$

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where:

- Y = yield as a decimal fraction
- A = weight of silver iodide plus filter in grams from Section 4.2, Step 52
- B = weight of filter only in grams from Section 4.2, Step 45; see instructions in Section 4.1, Equipment and Materials
- C = 0.01850 g which is the weight of silver iodide calculated from 1 (± 0.01) mL of 10.0 mg/mL iodide carrier.

4.4.3 Standard- Disintegration/Count Factor (d/c)

$$A = \frac{B \times C}{D}$$

where:

- A = disintegration/count (d/c) factor to be used in subsequent calculations
- B = disintegrations/minute of I-129 standard used in Section 4.3, Preparation of I-129 Standards.
- C = yield of standards calculated in Section 4.4.2.
- D = net counts/minute for standard as calculated in Section 4.4.1, Counts in Spectrum.

4.4.4 Sample - Disintegration/Minute/Milliliter (d/m/mL)

$$B \pm \beta = \frac{(A \pm \alpha) \times C}{D \times E}$$

where

- $B \pm \beta$ = the I-129 d/m/mL ± 1 sigma
- $A \pm \alpha$ = the sample counts/minute ± 1 sigma calculated in Section 4.4.1, Counts in Spectrum
- C = d/c factor calculated in Section 4.4.3, Standard (d/c)

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D = volume of sample (in mL) added in
Section 4.2, Step 1, Iodine Separation

E = Yield for sample calculated in Section
4.4.2, Yield Calculation

4.5 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. LRBs and Analytical Report Forms provide a mechanism for control of most records.

4.6 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally, it is considered qualified because it has received an independent technical review.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-420, SOLUTIONS ANALYSIS: PREPARATION OF ALPHA SOURCES BY DIRECT EVAPORATION

APPLICABILITY

This procedure is for the preparation of alpha-counting sources by direct evaporation of test solution on a stainless steel disc. This procedure can be used to prepare samples for alpha counting using Procedures PNL-ALO-421 and PNL-ALO-422.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

1.1 Tolerance:

All measurements in this procedure unless otherwise stated are +/- 10%.

1.2 Performance Verification

To assure the performance of the method and check for possible contamination of the sample, a spike and a blank shall be analyzed with each batch of samples. These requirements may be waived or others stipulated by the client in the ARFS, SOW, TI or other instructions. A batch shall not exceed 20 samples.

Author <i>CO Harvey</i> CO Harvey	Date <i>2/27/92</i>	Project Mgr. <i>TE Jones</i> TE Jones	Date <i>2/27/92</i>	QAD Representative <i>GK Gerke</i> GK Gerke	Date <i>2/27/92</i>
Technical Reviewer <i>LR Greenwood</i> LR Greenwood	Date <i>2/27/92</i>	Line Mgr. <i>AG King</i> AG King	Date <i>2/27/92</i>	Other	Date
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Spikes and blanks run through a separation method along with the sample batch satisfy this requirement.

A spike yield of $\pm 20\%$ of the known value is acceptable if the following conditions are met: The count rate of the spike is ten times the background count rate of the counter on which it is counted and the counts attributable to the spike are at least 30% of the total counts.

A spike is, preferably, a sample but may be matrix solution or reagent blank to which a known amount of analyte or tracer has been added. The material to be spiked and the quantity of nuclide to be added shall be selected by the cognizant scientist based on the concentration and make up of the samples.

A blank is a volume of deionized water or matrix solution approximately equal to the sample volume.

2.0 Equipment and Materials

- Deionized Water
- Ammonium Hydroxide, Reagent-Grade, Concentrated
- Disc, 7/8-in. Diameter, Stainless Steel
- Heat Lamp
- Droppers, Plastic
- Propane Torch or Hot Plate

3.0 Procedural Steps

- 3.1 Based on expected alpha activity, pipet a suitable aliquot of sample onto a stainless steel disc. The volume should be no more than 100 μL to avoid flow of solution off the edge of the disc while drying. Record the volume on the Analytical Data Sheet.
- 3.2 Evaporate the solution to dryness under a heat lamp.
- 3.3 Add deionized water to the disc dropwise until the dried residue is completely covered. NOTE: DO NOT touch the disc with the dropper tip.
- 3.4 Heat for a few seconds to dissolve the residue.
- 3.5 Add one drop of ammonium hydroxide to the water on the disc. NOTE: DO NOT touch the water with the dropper tip.
- 3.6 Evaporate the solution to dryness under the heat lamp.

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- 3.7 Heat the disc to a dull red by directing a flame to the underside of the disc or heat on a hot plate on high heat for about 30 minutes.
- 3.8 Using a PAM, check the activity of the mount. If greater than 3000 CPM, mount a smaller aliquot.
- 3.9 Check mount with GM, if reading is greater than 5000 c/m, affix radiation sticker to the alpha disc holder.
- 3.10 Submit the mount to the counting room for counting.
- 3.11 The alpha activity on the disc is measured using the Alpha Counting Procedure (PNL-ALO-421) and, if requested, the Alpha Spectrometry Procedure (PNL-ALO-422).

4.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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A.

Document Number: PNL-ALO-421 Revision Number: 0

Document Title: SOLUTIONS ANALYSIS: ALPHA COUNTING

Document's Original Author: CO HARVEY

Effective Date
of ICN: 04 / 10 / 92

Change Requested by: TE JONES

B.

Action:

Replace pages 1 and 2 with new pages 1 and 2.

C.

Effect of Change:

Minor editorial changes and minor technical corrections.

D.

Reason for Change/Description of Change:

Client requirement.

See redline/strikout in APPLICABILITY Section and Sections 3.1.1 and 3.2.1.

E.

Approval Signatures:
(Please sign and date)

Process

Quality Department: TL Ehlert

Approval Authority: ⁷⁵ AG King

Other Approvals: CO Harvey

Type of Change: (Check one):

 X Minor Major

Date: 4/10/92

Date: 7/10/92

Date: 4/10/82

Date: / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-421, SOLUTIONS ANALYSIS: ALPHA COUNTING

APPLICABILITY

This procedure provides instructions for measuring the activity of alpha-emitting radionuclides in ~~test~~ sample solutions.

DEFINITIONS/ACRONYMS

cpm: Counts per minute
dpm: Disintegrations per minute

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

Alpha Counter must be:

- calibrated (see Section 4)
- in control (see Section 5)
- have correct background (see Section 6)

2.0 Equipment and Materials

- Proportional Alpha Counter (PAC)
- Ludlum ZnS Scintillation Alpha Counter (SAC)
- Methane Gas, Commercial-Grade, Union Carbide Corporation
- Disc, 7/8-in. Diameter, Stainless Steel

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Greenwood		AG King		SIGNATURES ON FILE	
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3.0 Sample Counting

3.1 Using PACs:

- 3.1.1 Survey prepared sample counting source using an alpha survey instrument to insure that the alpha activity on the disk is not excessive (<20,000 d cpm).
- 3.1.2 Open counting chamber and insert sample source.
- 3.1.3 Close chamber and allow the gas to purge 10 to 15 seconds.
- 3.1.4 Preset desired counting time. (This may vary from 10 to 1000 minutes depending on activity level and counting statistics required.)
- 3.1.5 Press STOP, RESET, and START buttons. (Count will stop automatically at the preset time.)
- 3.1.6 Record the data counted, PAC efficiency, minutes counted, and total counts; calculate the counts per minute less the background count (Refer to 6.1.3) in the Alpha Counting Data portion of the Analytical Data Sheet.

3.2 Using SACs:

- 3.2.1 Survey prepared sample counting source using an alpha survey instrument to ensure that the alpha activity on the disc is not excessive (<50 d cpm). (SACs are low-level counters, hence the lower maximum activity level.)
- 3.2.2 Open chamber and insert sample disc.
- 3.2.3 Close and lock chamber.
- 3.2.4 Preset desired counting time (normally 100 minutes).
- 3.2.5 Press COUNT button. (Count register will clear and count will stop at preset time.)
- 3.2.6 Record the date counted, SAC efficiency, minutes counted, and total counts; calculate the counts per minute less the background counts (Refer to 6.2) as outlined in the Alpha Counting Data portion of the Analytical Data Sheet.

4.0 Calibration Standards

The PAC and the SAC are initially calibrated using replicate counting sources prepared from an NIST-calibrated, high-purity, plutonium-239

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solution (Radioactivity Standard T-1350). The replicate sources are counted a minimum of 4 separate times each on two successive days. If the ($\frac{\text{Chi squared}}{N}$) test indicates the data meets random counting

statistical requirements, the average of the two sets of source measurements is used for the calibration. The efficiency is calculated by dividing the Net CPM (Counts - Background) by the dpm of the standard. The measured efficiency and limit of error are recorded in the Daily Control and Calibration LRB and posted on each counter. Recalibration is required whenever major changes are made to the system. In order to maintain their integrity calibration sources are used only for PAC and SAC calibration or recalibration after counter modification or repair.

5.0 Daily Control Standards

Control standards are electroplated counting sources of high-purity ^{239}Pu that are used on a daily basis to insure control of the PACs and SACs. Each source is counted ten times when the instrument is calibrated and using the CONCHT program (Counting Instrument Control Chart Generation and Extension Program) located on the Micro-Vax computer, limits that must be met on a daily basis, are determined. Using the data from this program, control charts are prepared on which the daily performance is plotted. The chart may show a number of limits. Normally Control Limits are set at 2 sigma or the 95% confidence interval.

Electroplated sources are more rugged and will retain their integrity even with daily handling.

The following daily control standard count procedure shall be used.

5.1 For PACs:

- 5.1.1 Open counting chamber and insert control counting source provided for the specific PAC.
- 5.1.2 Close chamber and allow gas to purge for 10 to 15 seconds.
- 5.1.3 Preset time to 10 minutes.
- 5.1.4 Press STOP, RESET, and START buttons. (Count will stop automatically at the end of 10 minutes.)
- 5.1.5 Record total counts in the PAC's LRB on daily control data sheet and plot counts per minute on daily control chart.
- 5.1.6 If the measured cpm value falls out of limit, immediately recount the control source. If the recount, also falls out

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of limits, the system shall be removed from use until the problem has been corrected.

5.2 For SACs:

- 5.2.1 Open counting chamber and insert control counting source provided for the specific SAC.
- 5.2.2 Close and lock the chamber.
- 5.2.3 Preset time for 10 minutes.
- 5.2.4 Press COUNT button. This will clear the count register and start the count. The count will stop at 10 minutes.
- 5.2.5 Record total counts in the SAC's LRB and plot counts per minute on daily control chart.
- 5.2.6 If the measured cpm value falls out of limit, immediately recount the control source. If the recount, also falls out of limits, the system shall be removed from use until the problem has been corrected.

6.0 Daily Background Count

6.1 For PACs:

- 6.1.1 Using a clean background disk with preset time at 10 min., repeat 3.1.2 through 3.1.5.
- 6.1.2 Record counts per minute in the PAC's LRB.
- 6.1.3 Repeat 3.1.2 through 3.1.5 with the preset timer set at 100 minutes. (This count is normally started at the end of the day shift and is recorded the following morning.)

6.2 For SACs:

- 6.2.1 Using a clean background disc and with a present time of 900 minutes. Repeat 3.2.2 through 3.2.5.

- 6.2.2 Record counts per minute in the SAC's LRB.

NOTE: The PAC 100-minute and SAC 900-minute background counts are used in the sample calculations in 3.1.6 and 3.2.6 for the appropriate counter.

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7.0 Sample Calculations

Complete the sample calculations using the following equations. For the estimate of uncertainty (1σ) on the PAC or SAC gross alpha counts (B):

$$\beta = \sqrt{\frac{c}{tc^2} + \frac{b}{tb^2}}$$

where:

- β = uncertainty in gross alpha counts (B) per minute less background
- c = total sample counts (Section 3.0)
- tc = counting time of sample (minutes)
- b = total background counts (Section 6.0)
- tb = counting time of background (minutes)

$$A \pm \alpha = \frac{(B \pm \beta) \times C \times (F \pm f)}{D}$$

where:

- A = disintegrations per minute per milliliter (dis/min/mL) for a particular isotope having an alpha fraction of (F)
- B = counts per minute (Section 3.0)
- C = dilution factor or volume factor to correct to 1 milliliter
- D = PAC or SAC counting efficiency as posted on the PAC or SAC
- F = alpha fraction for a particular isotope (from Alpha Spectrometry procedure, PNL-ALO-422)
- α = uncertainty of A (dis/min/mL)
- β = uncertainty of B
- f = uncertainty of alpha fraction (from Alpha Spectrometry procedure, PNL-ALO-422)

PNL TECHNICAL PROCEDURE

NOTE: If alpha spectrometry was not performed on the sample
(F+f) = 1

$$\alpha = \sqrt{\frac{\beta^2}{B} + \frac{f^2}{F}} \times A$$

where:

- α = uncertainty in the dis/min/mL of a particular isotope "A" calculated above
- β = uncertainty in "B" calculated above
- f = uncertainty in alpha fraction (F) for a particular isotope (from Alpha Spectrometry procedure, PNL-ALO-422, Section 1.0, Step 13)
- B = counts per minute (Section 3, Step 6 for PAC or SAC)
- F = alpha fraction for a particular isotope (from Alpha Spectrometry procedure, PNL-ALO-422, Section 4.3)
- A = dis/min/mL for a particular isotope calculated above.

8.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-422, SOLUTIONS ANALYSIS: ALPHA SPECTROMETRY

APPLICABILITY

This procedure provides instructions for measuring the relative abundance of each alpha-emitting radionuclide in a sample. Alpha spectrometry is performed to: 1) ensure isotopic purity of a separated element or 2) measure the abundance of each isomer in a separated source, or 3) each isotope in an unseparated source. The relative abundance of each alpha active isotope present is determined by measuring the number of alpha events recorded for each alpha energy associated with a given isotope and comparing that number to the total number of events recorded for all isotopes.

This procedure applies to the analysis of samples by alpha spectrometry as prepared in procedures such as PNL-ALO-420 and PNL-ALO-423, in which the alpha activity is measured by mounting the sample or separated aliquot of the sample on a 7/8-in. stainless steel disc.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

1.1 Tolerances

All measurements in this procedure unless otherwise stated are +/- 10%.

Author <i>CO Harvey</i> CO Harvey	Date <i>2/27/92</i>	Project Mgr. <i>2 E Jones</i> TE Jones	Date <i>2/27/92</i>	QAD Representative <i>GK Gerke</i> GK Gerke	Date <i>2/27/92</i>
Technical Reviewer <i>LR Greenwood</i> LR Greenwood	Date <i>2/27/92</i>	Line Mgr. <i>AG King</i> AG King	Date <i>2/27/92</i>	Other	Date
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1.2 Control Standards

Control standards are electroplated sources of a mixture of ^{237}Np , ^{239}Pu and ^{241}Am . Absolute values of each isotope are not required (as in a calibration standard) since only relative count rates are required to obtain ratios and the detector efficiency is the same for all alpha particles.

A tracer may be used to determine yield.

As a calibration check, a control standard shall be counted once for each detector to ensure that the detector is functioning and that the peak channels for each isotope are identified. Subsequent use of the control standards is limited to unusual situations when a "peak" in an unknown sample is not readily identifiable. Frequent use of the control standards tends to result in high-level backgrounds and makes the detectors unsuitable for low-level counting.

If isotopes other than ^{237}Np , ^{239}Pu , and ^{241}Am are observed in the spectrometry of an unknown sample, the energies may be obtained by preparing a linear graph of the channel number versus the energy for the standard isotopes. The alpha energy of the unknown sample may then be obtained from the channel-vs-energy graph.

2.0 Equipment and Materials

- Alpha spectrometer.

3.0 Counting

Samples, control standards and backgrounds are counted in a similar manner.

- 3.1 If the power to the analyzer is off, turn it on and wait 1 hr for instrument to warm up and stabilize.
- 3.2 To terminate counting, press either the ACQUIRE or STOP ACQUIRE switch.
- 3.3 On the selected detector module(s) do the following:
 - 3.3.1 Turn the voltage OFF.
 - 3.3.2 Turn Pump/Vent valve to VENT.
 - 3.3.3 Remove chamber cover and place control standard, sample or clean background disc in counting chamber.

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PNL TECHNICAL PROCEDURE

- 3.3.4 Replace chamber cover.
- 3.3.5 Turn Pump/Vent valve to PUMP. Allow it to pump for about 15 seconds before proceeding to the next Step.
- 3.3.6 Turn Detector voltage ON. Allow system to stabilize for about 1 minute before proceeding.
- 3.4 Set Live Time Scan on the analyzer to 0 seconds for control standard counting, sample counting, or background counting. (A 0-second setting will acquire counts until the system is halted by pressing the STOP ACQUIRE switch.)
- 3.5 Select the sector(s) of the analyzer in which data from the detector(s) just loaded is stored then press ERASE DATA and set analyzer selector switch to 1/1 and press START ACQUIRE. To stop data acquisition, press the ACQUIRE or STOP ACQUIRE switch.
- 3.6 Print out spectra or desired regions. Time counted is automatically printed with spectral data.
- 3.7 Record Detector Number, ALO Number and Sample ID on print out.
- 4.0 Calculations
- 4.1 Calculate the fraction of alpha activity for each isotope (F) and the % uncertainty around (f) as follows:

$$F = \frac{A-E-B}{\Sigma (A-E-B)}$$

$$f = \frac{\sqrt{A+E+B}}{A-E-B}$$

where:

A = Sum of selected channels in the peak of interest. Under normal circumstances where the peak resolution is ~5 channels FWHM, 16 channels for ²³⁷Np and 8 channels for other isotopes, routinely analyzed. Decay mode of isotopes not routinely analyzed, must be reviewed to determine energy spread and subsequent peak channel width.

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E = Sum of three channels in valley above the peak of interest.

B = Background which is A - E of the peak of interest from an empty chamber count.

$\Sigma(A - E - B)$ = Sum of edge and background corrected counts for all peaks observed.

Note: Background count shall be normalized to the counting time of the samples from which it is subtracted.

4.2 Record the alpha fraction (F) and uncertainty (f) on the Analytical Data Sheet and attach the data printout spectrum from 3.6.

NOTE: Use $F \pm f$ in the calculations for a particular isotope. (See Alpha Counting procedure, PNL-ALO-421, Section 7.0.)

5.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and Analytical Data Sheets provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-423, SEPARATION OF PLUTONIUM BY SOLVENT EXTRACTION PRIOR TO MEASUREMENT BY ALPHA COUNTING

APPLICABILITY

This procedure can be used to separate plutonium from other alpha emitting radionuclides in liquid samples. The Pu is then measured by alpha counting using PNL-ALO-421 and PNL-ALO-422.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

1.1 Tolerances

All measurements in this procedure unless otherwise stated are +/- 10%.

1.2 Performance Verification

To assure the performance of the method and check for possible contamination of the sample, a spike and a blank shall be analyzed with each batch of samples. These requirements may be waived or others stipulated by the client in the ARFS, SOW, TI or other instructions. A batch shall not exceed 20 samples.

A spike yield of $\pm 20\%$ of the known value is acceptable if the following conditions are met: The count rate of the spike is ten times the background count rate of the counter on which it is counted and the counts attributable to the spike are at least 30% of the total counts.

Author <i>CO Harvey</i> CO Harvey	Date 2/27/92	Project Mgr. <i>TE Jones</i> TE Jones	Date 2/27/92	QAD Representative <i>GK Gerke</i> GK Gerke	Date 2/27/92
Technical Reviewer <i>LR Greenwood</i> LR Greenwood	Date 2/27/92	Line Mgr. <i>AG King</i> AG King	Date 2/27/92	Other	Date
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PNL TECHNICAL PROCEDURE

A spike is, preferably, a sample but may be matrix solution or reagent blank to which a known amount of analyte or tracer has been added. The material to be spiked and the quantity of nuclide to be added shall be selected by the cognizant scientist based on the concentration and make up of the samples.

A blank is a volume of deionized water or matrix solution approximately equal to the sample volume.

2.0 Equipment and Materials

- Aluminum nitrate, 1 M nitric acid - Dissolve 37.5 (± 0.1) g of aluminum nitrate in 100 (± 1) mL of 1 M nitric acid; mix thoroughly.
- Hydroxylamine hydrochloride, 5 M -- Dissolve 34.8 (± 0.1) g of hydroxylamine hydrochloride in 100 (± 1) mL of deionized water; mix thoroughly.
- Sodium nitrite, 2 M (prepared fresh weekly) -- Dissolve 13.8 (± 0.1) g of sodium nitrite in 100 (1) mL of deionized water; mix thoroughly.
- Thenoyltrifluoroacetone (TTA), 0.5 M in xylene -- Dissolve 111 (± 1) g of TTA in 1000 (± 10) mL of xylene; mix thoroughly.
- Xylene, reagent-grade (FLAMMABLE).
- Nitric acid, 2 M -- Dilute 126 (± 1) mL of concentrated reagent-grade nitric acid to 1000 (± 10) mL with deionized water; mix thoroughly.
- Hydrochloric acid, 1 M -- Dilute 83 (± 1) mL of concentrated reagent-grade hydrochloric acid to 1000 (± 10) mL with deionized water; mix thoroughly.
- Centrifuge, clinical.
- Cold spot heater.
- Counting discs, 7/8-in. diameter, stainless steel.
- Disc holder, cardboard.
- Heating block, aluminum, 1/2 inch deep holes.
- Vials, 2-dram.
- Vortex mixer.
- Hot plate.

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PNL TECHNICAL PROCEDURE

3.0 Separation

The plutonium is separated from other radioactive species by extraction of the Pu^{+4} ion into thenoyltrifluoroacetone in xylene. The plutonium activity is measured by alpha counting and alpha spectrometry.

- 3.1 Based on expected Pu concentration, add a suitable aliquot of the sample to a 2-dram vial. Record the volume on the Analytical Data Sheet.
- 3.2 Add to the vial 50 (± 5) μL of 1 M aluminum nitrate and 100 (± 10) μL of 5 M hydroxylamine hydrochloride; swirl to mix.
- 3.3 Evaporate the solution in the vial to dryness using a heat lamp. Do not overbake sample as it may not redissolve.
- 3.4 Remove from the heat and allow to cool for at least 10 minutes.
- 3.5 Add 1 (± 0.01) mL of 2 M nitric acid.
- 3.6 Heat for 20 minutes at 90 (± 5) $^{\circ}\text{C}$ in the 1/2-in. deep heat block.
- 3.7 Remove from the heat block and cool for at least 10 minutes.
- 3.8 Add 1 mL of 2 M sodium nitrite dropwise; swirl frequently while adding.
- 3.9 Allow the reaction to subside for 5 minutes; swirl frequently.
- 3.10 Heat for 15 minutes at 90 (± 5) $^{\circ}\text{C}$ in the 1/2-in. deep heating block.
- 3.11 Remove from the heating block and allow to cool for at least 10 minutes.
- 3.12 Add 2 (± 0.02) mL of 0.5 M TTA in xylene. Record the volume on the Analytical Data Sheet.
- 3.13 Cap the vial tightly and mix by vortexing 3 minutes.
- 3.14 Centrifuge for ~1 minute to separate the phases.
- 3.15 Transfer most of the TTA phase (top) to a clean 2-dram vial.
- 3.16 To the vial containing the TTA phase add:
 - 1 mL of 1 M hydrochloric acid
 - 100 μL of 2 M sodium nitrite.

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PNL TECHNICAL PROCEDURE

- 3.17 Cap the vial and vortex for 3 minutes.
- 3.18 Centrifuge for about 1 minute to separate the phases.
- 3.19 Mount up to 1 mL of the TTA phase on a stainless steel counting disc using the cold spot heater. Record the volume mounted on the Analytical Data Sheet.
- 3.20 Rinse the pipet with xylene and add the rinse to the disc.
- 3.21 Heat the disc on the hot plate on high heat to burn off the organic residue.
- 3.22 Count the plutonium using the Alpha Counting (PNL-ALO-421) and, if required, Alpha Spectrometry (PNL-ALO-422) analysis procedures. Record as specified in the referenced procedures.

4.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-425 SEPARATION OF NEPTUNIUM BY CATION EXCHANGE AND SOLVENT EXTRACTION PRIOR TO MEASUREMENT BY ALPHA COUNTING

APPLICABILITY

This procedure can be used for separating ^{237}Np from other alpha emitting radio nuclides in aqueous samples. Following the separation, the ^{237}Np is measured by alpha counting methods PNL-ALO-421 and PNL-ALO-422.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

1.1 Tolerances

All measurements in this procedure unless otherwise stated are +/- 10%.

1.2 Performance Verification

To assure the performance of the method and check for possible contamination of the sample, a spike and a blank shall be analyzed with each batch of samples. These requirements may be waived or others stipulated by the client in the ARFS, SOW, TI or other instructions. A batch shall not exceed 20 samples.

A spike yield of $\pm 20\%$ of the known value is acceptable if the following conditions are met: The count rate of the spike is ten times the background count rate of the counter on which it is counted and the counts attributable to the spike are at least 30% of the total counts.

Author <i>CO Harvey</i> CO Harvey	Date <i>2/27/92</i>	Project Mgr. <i>TE Jones</i> TE Jones	Date <i>2/27/92</i>	QAD Representative <i>GK Gerke</i> GK Gerke	Date <i>2/27/92</i>
Technical Reviewer <i>LR Greenwood</i> LR Greenwood	Date <i>2/27/92</i>	Line Mgr. <i>AG King</i> AG King	Date <i>2/27/92</i>	Other	Date
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PNL TECHNICAL PROCEDURE

A spike is, preferably, a sample but may be matrix solution or reagent blank to which a known amount of analyte or tracer has been added. The material to be spiked and the quantity of nuclide to be added shall be selected by the cognizant scientist based on the concentration and make up of the samples.

A blank is a volume of deionized water or matrix solution approximately equal to the sample volume.

2.0 Equipment and Materials

- Cation exchange resin, Dowex-50[®] (or AG-50W[®]), X-8 or equivalent, 200 to 400 mesh, H⁺ form -- Prepare resin by mixing in a volume of deionized water about 5 times the volume of the resin. Allow resin to settle until only suspended fines remain. Decant the water to remove the fines. Repeat the mixing, settling, and decanting two or three times.
- Nitric Acid, 2 M -- Dilute 126 (±2) mL of reagent-grade concentrated nitric acid to 1000 (±1) mL with deionized water; mix thoroughly.
- Nitric Acid, 1 M -- Dilute 63 (±1) mL of reagent-grade concentrated nitric acid to 1000 (±1) mL with deionized water; mix thoroughly.
- Ceric sulfate, 0.1 M -- Dissolve 5.28 g of ceric sulfate [H₄Ce(SO₄)₄] in 100 (±1) mL of 1 M nitric acid. Stir vigorously until dissolved. Allow any undissolved residue to settle before using solution. Filtration is unnecessary.
- Sodium nitrite, 2 M -- Dissolve 13.8 g of sodium nitrite in 100 mL of deionized water; mix thoroughly.
- Hydrochloric acid, 0.5 M -- Dilute 42 (±1) mL of reagent-grade concentrated hydrochloric acid to 1000 (±1) mL of deionized water; mix thoroughly.
- Hydroxylamine hydrochloride, 5 M -- Dissolve 34.8 g of hydroxylamine hydrochloride in 100 mL of deionized water; mix thoroughly.
- Ferrous ammonium sulfate, 0.1 M -- Dissolve .39 (±0.01) g of ferrous ammonium sulfate in 10 mL of deionized water plus 0.1 (±0.01) mL of 1 M hydrochloric acid; mix thoroughly. NOTE: Prepare just prior to use.

[®]Dowex-50 and AG-50W are registered trademarks of Bio-Rad Laboratories, Richmond, California

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PNL TECHNICAL PROCEDURE

- Xylene, reagent-grade, (FLAMMABLE).
- Thenoyltrifluoroacetone (TTA), 0.5 M in xylene -- Dissolve 111 g of TTA salt in 1000 mL of reagent-grade xylene; mix thoroughly.
- Centrifuge, clinical.
- Cold spot heater.
- Counting discs, 7/8-in. diameter, stainless steel.
- Disc holder, cardboard.
- Heating block, aluminum.
- Vials, 2-dram, glass.
- Vortex mixer.
- Hot plate.
- Dropper, 7-mL, plastic.
- Cotton.

3.0 Separation

The neptunium is separated from other radioactive species by a process that absorbs most of the other species on a cation exchange resin, followed by solvent extraction of NP^{+4} into thenoyltrifluoroacetone in xylene. The neptunium activity is measured by alpha counting and when necessary, alpha spectrometry.

- 3.1 To a two dram vial add up to 2 mL of sample. Record volume on Analytical Data Sheet. NOTE: If the acid concentration of the sample is known to be .5 M or less, add an equal volume of 2 M. HNO_3 and proceed to Step 3.4.
- 3.2 Take sample to incipient dryness under heat lamp. (Do Not Bake).
- 3.3 Redissolve the sample in a volume of 1 M. HNO_3 equal to the original sample volume or a minimum of 1 mL.
- 3.4 Add 100 μL of 0.1 M ceric sulfate; swirl to mix.
- 3.5 Heat for 5 minutes at 65° in heating block.

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- 3.6 Remove from heating block, and allow to cool for 5 minutes or longer.
- 3.7 Add 200 μ L of 2 M sodium nitrite; swirl to mix.
- 3.8 Heat for 15 minutes at 90°C ($\pm 5^\circ$ C) in heating block.
- 3.9 Remove from heat, and allow to cool for 10 minutes or longer.
- 3.10 Prepare a 2 mL column of Dowex-50, X-8, 200 to 400 mesh, H⁺ form resin as follows:
- Cut off the top of a 7-mL plastic dropper.
 - Fill the tip with a small ball of cotton to support the resin.
 - Measure a 2 mL volume above the cotton plug.
 - Mark the column at the 2-mL volume.
 - Add a slurry of resin to the column until the settled bed of resin is to the mark.
- 3.11 Transfer the solution from 3.9 onto the prepared resin column. Collect the column effluent in a 2-dram vial.
- 3.12 Rinse the vial from 3.9 with five 1 mL portions of 1 M nitric acid and add the solution to the column. Allow each portion to drain through the column before adding the next. Collect all column effluent in the 2-dram vial from 3.11. Discard the column.
- 3.13 Evaporate the column effluent to dryness under a heat lamp. (Do Not Bake).
- 3.14 To the residue in the vial, add 1 mL of 0.5 M hydrochloric acid plus 200 μ L of 5 M hydroxylamine hydrochloride; swirl to mix.
- 3.15 Heat for 20 minutes at 90°C ($\pm 5^\circ$ C) in heating block.
- 3.16 Remove from heating block.
- 3.17 Add 100 μ L of 0.1 M ferrous ammonium sulfate; swirl to mix.
NOTE: Ferrous ammonium sulfate must be prepared just prior to use.
- 3.18 Heat for 10 minutes at 90°C ($\pm 5^\circ$ C) in heating block.
- 3.19 Remove from heating block and cool for 10 minutes or longer.

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PNL TECHNICAL PROCEDURE

- 3.20 Add 1 (± 0.01) mL of 0.5 M TTA in xylene. Record the exact volume on the Analytical Data Sheet. Cap the vial tightly.
- 3.21 Mix for at least 3 minutes, using a vortex mixer.
- 3.22 Centrifuge for 1 minute to separate phases.
- 3.23 Plate up to 500 μ L of the TTA-xylene phase on a 7/8-in. stainless steel disc, using the cold-spot heater. Record the volume on the Analytical Data Sheet.
- 3.24 Heat the disc to dull red with burner or on a hot plate at high heat for 30 minutes to burn off organic residue.
- 3.25 Count the neptunium using the Alpha Counting procedure (PNL-ALO-421) and Alpha Spectrometry procedure (PNL-ALO-422) as necessary to assure complete separation of the MC.

4.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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(ICN)

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A.

Document Number: PNL-ALO-426 Revision Number: 0

Document Title: Sequential Separation of
Americium/Curium, Plutonium, Neptunium, and Uranium
by Combined Anion and Cation Exchange

Document's Original Author: AE Kozelisky

Effective Date
of ICN: 5/7/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 8 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

X Minor Major

Process

Quality Department: TL Ehler TL Ehler

Date: 5/7/92

Approval Authority: AG King AG King

Date: 5/7/92

Other Approvals: _____

Date: 1/1

:

Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-426, SEQUENTIAL SEPARATION OF AMERICIUM/CURIUM, PLUTONIUM, NEPTUNIUM, AND URANIUM BY COMBINED ANION AND CATION EXCHANGE

APPLICABILITY

This procedure applies to samples which are fused in potassium hydroxide or sodium peroxide and dissolved in hydrochloric acid. It is also applicable to other aqueous samples in a hydrochloric acid matrix which may or may not contain salts.

DEFINITIONS

None.

RESPONSIBLE STAFF

Cognizant Scientist
Analyst - See 5.0

QUALITY CONTROL REQUIREMENTS

For all (PNL) Impact Level I and II projects, a spiked sample (sample spiked with standard, also known as spiked matrix), and a methods blank (simulated sample matrix solution) will be processed with every separation group (number of samples analyst processes together), not to exceed 20 samples, or as directed in a Request for Analytical Services (RFAS) or Test Instructions (TI).

Project specific quality control, if different from above will be specified in a TI or RFAS.

Standard laboratory practices in accordance with PNL-MA-597 Volume 1.

PROCEDURES

1.0 Equipment and Materials

NOTE: All chemicals used must be of reagent grade. Ultrex, or equivalent, if Mass Spectrometry is requested.

Author	Date	Project Mgr.	Date	QAD Representative	Date
AE Kozelisky		TE Jones		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
JL Ryan		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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PNL TECHNICAL PROCEDURE

The volumes in this procedure do not require a tolerance, unless specified, due to their non-critical nature. Manufacturer's specifications meet this procedure.

- Ammonium iodide, 2M -- Dissolve 7.25g ammonium iodide (NH_4I) in 25mL deionized water; mix thoroughly. Store in an amber colored bottle. Prepare fresh every six months.
- 30% Hydrogen Peroxide (H_2O_2). Keep refrigerated.
- Hydrochloric acid, 9M -- Dilute 188mL (± 1)mL of concentrated acid to 250mL with deionized water; mix thoroughly.
- Nitric acid, (HNO_3), concentrated, 15.7M Ultrex® or equivalent.
- Nitric acid, 0.2M -- Dilute 12.7 (± 0.5)mL of concentrated acid to 1000 (± 1)mL with deionized water; mix thoroughly.
- Nitric acid, 1M -- Dilute 63 (± 1)mL of concentrated acid (HNO_3) to 1000 (± 1)mL with deionized water; mix thoroughly.
- Nitric acid, 1.85M -- Dilute 117 (± 1)mL of concentrated acid to 1000 (± 1)mL with deionized water; mix thoroughly.
- Nitric acid, 2M -- Dilute 126 (± 1)mL of concentrated acid to 1000 (± 1)mL with deionized water; mix thoroughly.
- Nitric acid, 8M -- Dilute 506 (± 1)mL of concentrated acid to 1000 (± 1)mL with deionized water; mix thoroughly.
- 9M HCl -0.05M NH_4I Solution -- 10 mL solution is prepared by mixing 7.5mL of concentrated hydrochloric acid, 250 μL of 2M ammonium iodide and 2.25mL deionized water; mix thoroughly. Prepare prior to use, fresh daily.
- 9M HCl -0.05M HNO_3 Solution -- Add 2.5mL of 2M HNO_3 to 75mL of concentrated HCl . Dilute to 100mL with deionized water; mix thoroughly. Prepare fresh every 2 months.

CAUTION: Hydrofluoric acid must not contact skin! Wear proper safety apparel (e.g. rubber gloves and eye goggles) and use extreme caution.

- 4M HCl -0.1M HF Solution -- Add 400 μL of concentrated hydrofluoric acid to 33mL of concentrated HCl . Dilute to 100mL with deionized water; mix thoroughly in polyethylene flask. Store in a polyethylene bottle.
- 0.5M HCl -1M HF Solution -- Add 3.5mL of concentrated hydrofluoric acid to 4.2mL of concentrated HCl and dilute to 100mL with deionized

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PNL TECHNICAL PROCEDURE

water; mix thoroughly in polyethylene flask. Store in a polyethylene bottle.

- Anion exchange resin, AG-1[®], X-4, 100 to 200 mesh, Cl⁻ form. Prepare by mixing in a volume of deionized water about 5 times the volume of the resin. Allow resin to settle until only suspended fines remain. Decant the water to remove the fines. Repeat the mixing, settling, and decanting two or three times. Store resin in deionized water.
- Anion column -- Prepare a 1-mL anion column of AG-1[®], X-4, 100 to 200 mesh, Cl⁻ form resin. Remove the top of the bulb from a 7.5-mL plastic dropper. Place a small cotton ball into the tip of the dropper and tamp lightly. Measure a volume of 1mL above the cotton and mark. Fill the dropper to the mark with the resin.
- Cation exchange resin, AG-50W[®], X-8, 200 to 400 mesh, H⁺ form. Prepare by mixing in a volume of deionized water about 5 times the volume of the resin. Allow resin to settle until only suspended fines remain. Decant the water to remove the fines. Repeat the mixing, settling, and decanting two or three times. Store resin in deionized water.
- Cation column -- Prepare a 1-mL cation column of AG-50[®], X-8, 200 to 400 mesh, H⁺ form resin. Remove the top of the bulb from a 7.5-mL plastic dropper. Place a small cotton ball into the tip and tamp lightly. Measure a volume of 1mL above the cotton ball and mark. Fill the dropper to the mark with the resin.
- Vials, 2-dram, 15-mL, 35-mL, glass. Leached per HTA-4-25, Section 4, Steps 1 through 6, if Mass Spectrometry is requested.
- Vials, 15-mL, polyethylene. Leached if Mass Spectrometry is requested.
- Flasks, 10-mL or 5-mL. Leached if Mass Spectrometry is requested.
- Centrifuge tube, transparent, polycarbonate, heat resistant, Nalgene or equivalent. Leached if Mass Spectrometry is requested.
- Centrifuge with tube racks and canisters.
- Droppers, 7.5-mL, plastic.
- Stir bar, small glass.
- Heat lamp, infrared.
- Disc, 7/8-in., stainless steel.

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PNL TECHNICAL PROCEDURE

- Heating block.
- Hot plate.

2.0 Performance Check of the Weighing Balance and Volume Determination

Recorded volumes shall be determined on a calibrated balance. The volume dispensed shall be determined the day the pipet is used as follows:

Dispense an aliquot and record the weight, then tare the balance. Repeat four more times. Record the temperature. Average the weights and multiply by the volume factor (Ref. 1) for the recorded temperature. Calculate and record in the LRB the percent variance of the dispensed aliquots ($\sigma\bar{x} * 100$). This variance shall be equal to or less than the manufacture's specifications. Record the pipet number, volume dispensed, the weights, temperature, volume factor, and calculation in the LRB. The calculation yields the volume dispensed and is recorded on the Analytical Report form. The LRB and page number is also recorded on the Analytical Report form.

The balance is performance checked prior to any volume determination on a daily-as-used basis, per PAP-70-1201.

3.0 Separation

The isotopes are separated by loading onto an anion exchange resin column. The americium and curium pass through the anion column and are further separated by loading onto a cation exchange resin column and washing salts as well as Cs^{137} and Sr^{90} from the column with 1.85M nitric acid. The americium and curium are eluted from the cation column with 8M nitric acid. Plutonium is eluted from the anion column with 9M HCl-0.05M NH_4I Solution. Neptunium is eluted from the anion column with 4M HCl-0.1M HF. Uranium is eluted from the same anion column with 0.5M HCl-1M HF. Plutonium, neptunium, americium/curium isotopes are measured and resolved by alpha counting and alpha spectrometry. Uranium is measured by Laser Fluorimetry.

Spiked recoveries for Pu^{239} , Np^{237} , Am^{241} and U^{238} in 2-mL of simulated fused matrix solution (potassium hydroxide in hydrochloric acid) were found to be 99 ± 2 , 101 ± 2 , 100 ± 3 , and 95 ± 3 percents respectively. Procedure development works and the results of the experiments have been documented in BNW 52911, pages 21-50.

- 1) To a 15-mL vial the ANALYST shall add up to 2mL of sample. Record the sample volume on the analytical report.
- 2) Evaporate the sample to near dryness under a heat lamp. Cool for 10 minutes.
- 3) Dissolve residue in 2mL of 9M HCl-0.05M HNO_3 Solution.

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- 4) Heat for 10 minutes in a 80°C heating block. Cool for 10 minutes.
- 5) Activate the anion column by washing with 3mL of 9M HCl. Collect the wash as waste in a 35-mL vial.
- 6) Using a plastic dropper, carefully transfer the solution, 0.5mL at a time, to the anion column by slowly running the solution down the side of the column. **DO NOT DISTURB** the resin bed. Collect the eluate (containing Am/Cm, Cs¹³⁷ and Sr⁹⁰, Th, and salts) in a 35-mL vial. (Note: Thorium will load onto the cation column in a later part of the procedure at 1.85M HNO₃ but will not elute with 8M HNO₃.)
- 7) Wash the 15-mL vial from Step 4 with five 1-mL portions of 9M HCl and transfer the solution slowly onto the anion column. Allow each portion to drain completely before adding the next. Do not disturb the resin bed. Collect the eluate in the 35-mL vial from Step 6 and retain for the americium/curium purification beginning at Step 11a.
- 8) Elute plutonium with 8mL of 9M HCl-0.05M NH₄I Solution, one mL at a time. Collect the eluate in a 35-mL vial.
 - 8a) Add 1.3mL of concentrated ULTREX HNO₃ and 600μL of 30% H₂O₂ to the 35-mL vial from Step 8 and swirl to mix. Save eluate for Step 12.
- 9) Elute neptunium with 4mL of 4M HCl-0.1M HF Solution, one mL at a time. Collect the eluate in a heat resistant tube. Save eluate for Step 12.
- 10) Elute uranium with 3mL of 0.5M HCl-1M HF Solution, one mL at a time. Collect eluate in a heat resistant tube.
 - 10a) Evaporate the uranium solution to dryness under a heat lamp.
 - 10b) Dissolve the residue in 1mL of 1M HNO₃.
 - 10c) With a transfer pipet, transfer solution to a 10-mL volumetric flask.
 - 10d) Rinse the tube with three 1mL portions of 1M HNO₃, transferring each portion to the volumetric flask.
 - 10e) Dilute to 10mL with 1M HNO₃.

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- 10f) Add a stir bar and mix. Transfer to a 15-mL polyethylene vial for storage. Measure uranium content by Laser Fluorimetry.

Uranium Solution Mass Spectrometry Preparation

- 10g) To a leached 2-dram vial, add a quantity yielding approximately $1\mu\text{g/mL}$ uranium.
- 10h) Evaporate to dryness under a heat lamp.
- 10i) Dissolve residue in an appropriate volume of 0.2M HNO_3 to yield approximately $1\text{ng}/\mu\text{L}$. Determine isotopic composition per PNL-ALO-455.

11) Americium/curium purification:

- 11a) Evaporate the solution to dryness under a heat lamp. Cool for 10 minutes.
- 11b) Dissolve the residue in 5mL of 1.85M HNO_3 .
- 11c) Activate the cation column by washing with 5mL of 1.85M HNO_3 . Collect the wash as waste in a 35-mL vial from Step 5.
- 11d) Transfer the solution to the cation column slowly, one mL at a time. Do not disturb the resin bed. Collect the effluent as waste.
- 11e) Wash the 35-mL vial with four 3-mL portions of 1.85M HNO_3 , and transfer each portion to the column. Collect the effluent as waste.
- 11f) Elute the americium/curium slowly with ten 1-mL portions of 8M HNO_3 . Collect the eluate in a 35-mL vial. Go to Step 12.

12) Preparation of Alpha Plates

- 12a) Evaporate Am, Pu and Np fractions to dryness under a heat lamp. Cool for 10 minutes.
- 12b) Add known amount of 1M HNO_3 , preferably $500\mu\text{L}$ to $1000\mu\text{L}$. Record the volume on the analytical report.
- 12c) Swirl to dissolve the residue on all surfaces. If residue is found undissolved after this step, repeat Steps 12a, 12b, 12c.

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- 12d) Centrifuge for about one minute. The purpose of this step is to coalesce droplets on the sides of the containers and draw them to the bottom in order to thoroughly mix the sample.

Caution: Use extreme care when transferring (capless) centrifuge tubes to the centrifuge. Always maintain radiological control. Prepare canister with the appropriate sized tube rack. Transfer canister to the hood. Insert the tubes into the tube rack. Secure the canister's lid, then transfer the canister to the centrifuge. After centrifugation, transfer the canister to the hood and remove the tubes.

- 12e) Add a small stir bar and stir one minute.

- 12f) Evaporate a measured volume of the solution, preferably 50 μ L to 200 μ L on a 7/8-in stainless steel disk. Record the volume on the analytical report. **Note:** Np solution has a tendency to spread out off the plate, therefore, try to plate smallest volume possible e.g. 50 μ L aliquot.

- 12g) Place the disc on a hot plate and heat on high until the organic residue is burned off.

- 13) Determine the alpha activities by Alpha Counting and Alpha Spectrometry procedures.

14) Plutonium Solution Mass Spectrometry Preparation

- 14a) To a leached 2-dram vial, add a quantity yielding approximately 1 μ g/mL plutonium.

- 14b) Evaporate to dryness under a heat lamp.

- 14c) Dissolve residue in an appropriate volume of 0.2M HNO₃ to yield approximately 1ng/ μ L. Determine isotopic composition per PNL-ALO-455.

4.0 Records

Records will be maintained and controlled so as to conform with requirements of PNL MA-70, PAP-70-1701. Laboratory Record Books (LRB's) shall be used in accordance with ~~ACT NOW 89-1~~ established records management practices.

LRB's and analytical report cards provide a mechanism for control of most records.

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5.0 Analyst Qualification

The analyst shall be trained on this procedure before being qualified to perform the analysis on samples. The COGNIZANT SCIENTIST, or their designee, shall train the analyst. The procedure shall be performed on at least three standards. Recovery shall be $95 \pm 5\%$. Qualification shall be determined by the COGNIZANT SCIENTIST or their designee.

6.0 References

- 1) Relative Density and Volume of Water, page 2198, Handbook of Chemistry and Physics, 44th Edition, Chemical Rubber Publishing Co.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-427, SEPARATION OF ALPHA-EMITTING RADIONUCLIDES FROM SOLUTIONS CONTAINING DISSOLVED SALTS PRIOR TO ALPHA COUNTING

APPLICABILITY

This procedure is applicable to the analysis of alpha activity in liquid samples which contain a high content of dissolved salts, such as those resulting from fusion of single- and double-shell waste tank core material. For plutonium, americium and neptunium the recovery is better than 97 percent, and the method is also applicable to thorium and uranium. It is not applicable to the alkaline earth radium which does not co-precipitate with ferric hydroxide.

DEFINITIONS

None

RESPONSIBLE STAFF

Trained Analyst
Cognizant Scientist

PROCEDURE

1.0 Equipment and Materials

- Hydrochloric Acid, 8M - Dilute 677 (± 1)mL concentrated reagent-grade acid to 1000 (± 1)mL with deionized water; mix thoroughly.
- Nitric Acid, 8M - Dilute 506 (± 1)mL of concentrated reagent-grade acid to 1000 (± 1)mL with deionized water; mix thoroughly.
- Nitric Acid, 1M - Dilute 63 (± 1)mL concentrated reagent-grade acid to 1000 (± 1) mL with deionized water; mix thoroughly.
- Ammonium hydroxide, concentrated - reagent grade.

Author <i>Japas Chandra Mani</i>	Date <i>8/31/90</i>	Project Mgr. <i>2 E G...</i>	Date <i>9/5/90</i>	QAD Representative <i>GK Gerte</i>	Date <i>9/6/90</i>
Technical Reviewer <i>Ban M. Dillipuri</i>	Date <i>9-4-90</i>	Line Mgr. <i>Patte C. M...</i>	Date <i>9/7/90</i>	Other	Date
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- Ferric Iron Carrier Solution (10 mg/ml) - Dissolve 4.84 ($\pm$ 0.01)g Fe $\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ in deionized water, add 500 μ l of concentrated HCl and dilute to 100 ($\pm$ 1) mL with deionized water; mix thoroughly.
- 2-Heptanone - reagent grade
- Glass vial with screw cap, 35-mL
- Plastic transfer pipets - 5 ml or 7.5 ml (VWR Cat. No. 14670-001 or 103 or comparable)
- 15 mL printed polypropylene centrifuge tubes with caps - Manufacturer, (VWR Cat. No. 21008-088 or comparable)
- Heat lamp, infrared
- Counting Disc, 7/8-inch, stainless steel
- Vortex
- Hot plate
- Centrifuge for 15 ml tubes listed above.

2.0 Quality Control

For all QA level I and II projects, a process blank, duplicate sample and a standard spike will be processed with every set of samples or with every 20 samples, whichever is less unless otherwise directed in a Request for Analytical Services (RFAS) or Test Instructions (TI).

The QC samples will be made up of the same acid or water that the sample matrix is in (i.e. HCl, HNO_3 , or water) and of the same volume of sample taken in Step 3.1 below. Each QC sample will be treated identically with each sample in the batch.

Project specific quality control, if different from above, will be specified in a TI or RFAS.

3.0 Method

Alpha emitting radionuclides are quantitatively co-precipitated with ferric hydroxide. The precipitate is dissolved in 8M HCl and the ferric iron is removed by solvent extraction into 2-Heptanone. The aqueous phase containing the actinides is now virtually free of alkali and alkaline earth metals. Nitric acid (8M) is added to the aqueous phase,

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which is then dried under a heat lamp. Any traces of organic residue are destroyed by oxidation with nitric and hydrochloric acids. The dried residue is dissolved in 1M nitric acid and evaporated onto a stainless steel disk. The alpha activity is then measured by an alpha counting procedure.

- 3.1 Add to a 15-ml centrifuge tube (label as CFT-1) a known volume of sample solution as determined by the cognizant scientist. Record the sample volume.
- 3.2 Add 1 mL of deionized water.
- 3.3 Add 1.2 mL (10 mg/mL) of ferric iron carrier.
- 3.4 Add concentrated ammonium hydroxide until distinctly basic (check with pH paper). Actinides co-precipitate along with ferric hydroxide. Cap the centrifuge tube.
- 3.5 Vortex for one minute.
- 3.6 Let sit overnight. This is essential in order to obtain good recovery.
- 3.7 Centrifuge for five minutes.
- 3.8 Uncap the centrifuge tube (CFT-1) and decant the ammonium hydroxide supernate into a second 15-mL centrifuge tube (labeled as CFT-2) containing 200 μ L of ferric iron carrier (10 mg/mL).
- 3.9 Cap the second centrifuge tube (CFT-2). Vortex for one minute and let sit for five minutes.
- 3.10 Add 1 mL of 8M HCl to the first centrifuge tube (CFT-1). Cap and let sit for five minutes.
- 3.11 Centrifuge second centrifuge tube (CFT-2) for five minutes. Uncap and decant the ammonium hydroxide supernate into a radioactive liquid waste container.
- 3.12 Add 500 μ L of 8M HCl to the second centrifuge tube (CFT-2). Cap and let sit for five minutes.
- 3.13 Vortex the first centrifuge tube (CFT-1) until the ferric hydroxide precipitate is dissolved.

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- 3.14 Dissolve the ferric hydroxide precipitate in the second centrifuge tube (CFT-2) by gentle shaking.
- 3.15 Transfer the contents of the second centrifuge tube (CFT-2) to the first (CFT-1) quantitatively with the aid of a transfer pipet.
- 3.16 Wash down the sides of the second centrifuge tube (CFT-2) with 500 μ L of 8M HCl and transfer the contents to the first centrifuge tube (CFT-1).
- 3.17 Mark the level of aqueous phase with a marking pen on the first centrifuge tube (CFT-1). This marking is useful later in the procedure.
- 3.18 Wash down the sides of the second centrifuge tube (CFT-2) with 5 mL of 2-Heptanone. Transfer the contents of the second centrifuge tube (CFT-2) to the first (CFT-1). Cap the first centrifuge tube (CFT-1). Discard the second centrifuge tube (CFT-2) to the dry radioactive waste.
- 3.19 Vortex the first centrifuge tube (CFT-1) for three minutes; allow time for complete phase separation.
- 3.20 Uncap the first centrifuge tube (CFT-1) and remove most of the organic phase with a transfer pipet. Discard the organic phase to the liquid radioactive waste container.

NOTE: DO NOT REMOVE AQUEOUS PHASE.

- 3.21 Pipet another 5 mL of 2-Heptanone into the first centrifuge tube (CFT-1), cap and vortex for three minutes; allow time for complete phase separation.
- 3.22 Repeat Step 3.20.
- 3.23 Pipet last 4 mL of 2-Heptanone, cap and vortex for three minutes; allow time for complete phase separation.
- 3.24 Repeat Step 3.20.
- 3.25 Quantitatively transfer the aqueous phase to a 35 mL glass vial with the help of a transfer pipet.
- 3.26 Wash down the sides of the centrifuge tube (CFT-1) with four 1 mL portions of 8M HNO₃ and transfer the contents to the 35 mL glass vial.

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- 3.27 Evaporate the solution to dryness under a heat lamp.
- 3.28 Add 1 mL of 8M HNO_3 to the dry residue. Cap, swirl to dissolve the residue. Rotate the vial several times to dissolve all the residue from the glass surfaces.
- 3.29 Centrifuge for at least one minute to bring the solution to the bottom of the vial.
- 3.30 Evaporate the solution to dryness under a heat lamp.
- 3.31 Add 500 μL of 1M nitric acid to the dry residue. Cap the vial and record the volume. Rotate the vial several times to dissolve all the residues from the glass surfaces.
- 3.32 Centrifuge for at least one minute to bring the solution to the bottom of the vial.
- 3.33 Uncap the vial, add a small stirring bar and stir for one minute.
- 3.34 Place an aliquot of the solution onto a 7/8-inch stainless steel disc. Record the volume.
- 3.35 Evaporate the solution on disc to dryness under a heat lamp.
- 3.36 Add a few drops of deionized water to cover the dried residue.
- 3.37 Evaporate the solution on disc to dryness under a heat lamp.
- 3.38 Place the disc on a hot plate on a high heat setting for thirty minutes or until the organic residues are burned off the disc.
- 3.39 Count the alpha activity using an Alpha Counting procedure.

4.0 Records

Records will be maintained and controlled so as to conform with requirements of PNL-MA-70. Laboratory Record Books (LRB) and analytical report cards provide a mechanism for control of most records.

5.0 References

Kuznetsov, V. I., 1947. J. Gen. Chem (U.S.S.R.) 17, 175.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-429, (Replaces 6-40.1), LABORATORY PREPARATION OF SAMPLES FOR COUNTING

1.0 APPLICABILITY

Samples are submitted to Chemistry and Analysis by Westinghouse Hanford Company's OHP and Pacific Northwest Laboratory's Radiation Protection. Particle filters are mounted routinely on dishes for counting and occasionally are dissolved for special analysis. Charcoal cartridges are disassembled and the charcoal is transferred to jars for analysis.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

Two types of samplers, micropore filters and charcoal cartridges, are used to trap particulate and gaseous radionuclides, respectively, from building exhaust streams.

Samples are submitted to Chemistry and Analysis by Westinghouse Hanford Company's OHP and PNL's Radiation Protection. These groups remove each micropore filter from its particulate sampler holder and place it in an envelope; the entire gaseous sampler (charcoal cartridge) is submitted after removing it from the sampling leg. Each sample is labeled for location and sampling interval. OHP submits a Weekly Stack Filter Change data sheet with 300 area building samples and a FFTF Effluent Monitor Filter Change data sheet with 400 area samples, summarizing all essential sampling data. PNL's Radiation Protection does not issue a sample data sheet; for sample documentation purposes, Chemistry and Analysis completes a 300 Area Weekly Stack Filter Change report, filling in

Author	Date	Project Mgr.	Date	QAD Representative	Date
MR Weiler	9/19/88	N/A		LJ Ethridge	9/19/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	9/19/88	All original signatures on file	
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the sampling dates indicated on the respective samples and the established sampler flow rates. It is the responsibility of Radiation Protection to notify the laboratory of any departure of sampler flow rates from these established values. All samples are surveyed by OHP and Radiation Protection prior to submission to the laboratory; any exhibiting significant activity are clearly labeled.

The micropore filters are mounted on aluminum dishes for routine counting. The standard 47-mm diameter filter easily fits into a two-inch (50.8-mm) diameter dish. Occasionally, when a slightly larger size filter is submitted, there is a visible perimeter that was masked by the filter holder during sampling that may be trimmed to permit mounting. Grossly oversized filters must be cut into several pieces and mounted for counting on two or more dishes that are counted separately and the results summed. Should the amount of activity on any filter be substantial, that filter is placed into a glass vial for special analytical treatment since highly active filters can easily contaminate counting instruments.

In this and other special cases requiring a more detailed analysis, the particle filter is dissolved in acid, the solution adjusted to a known volume, and an aliquot evaporated to dryness on a dish for alpha and beta counting. Subsequent additional analyses may be performed on the filter dissolution.

Charcoal cartridges are disassembled and the charcoal and the retaining filter papers are transferred into wide-mouth jars for analysis. Experience with 327 building I-131 release tests indicates that iodine is absorbed on the surface layer of charcoal on the inlet side of a cartridge. A very small fraction is absorbed by the retaining filter on the inlet side; no detachable activity has been found on a cartridge screen or plastic shell. Because of the surface layer adsorption, mixing of the charcoal bed is important to maintain sample counting geometry.

4.2 APPARATUS

- (a) Dish. Aluminum, 2-in. (50.8-mm) diameter, 0.118-in. (3-mm) deep, flat bottom. Nuclear Equipment Chemical Corp., Farmingdale, NY.
- (b) Dish Holder Card. Cardboard, 3 3/16-in. (81.0-mm) by 2 1/2-in. (63.5-mm), with a 1 1/2-in. (38.1-mm) diameter hole.
- (c) Holder Rack.
- (d) Jar. Wide-mouth, 8-oz (236-ml), styrene, with molded plastic screw cap.

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(e) Vial. Glass, 15-ml.

4.3 REAGENTS

(a) Nitric Acid. 8M.

(b) Plastic Coating. Vinyl plastic material in aerosol spray can.

(c) Rubber Cement.

4.4 STANDARDS

4.5 SAFETY

(a) Observe the general laboratory safety rules.

(b) Follow the requirements of applicable RWP's.

4.6 QUALITY CONTROL

4.7 ANALYSIS

4.8 CALCULATION

4.9 PREPARATION

4.9.1 Receipt of Samples

OHP and Radiation Protection deliver the samples to the laboratory, usually on Tuesdays, for preparation and analysis on the following Thursday. OHP must provide completed sample data sheets with each set of samples submitted.

- (a) For the OHP submitted samples, check the ON and OFF dates and times for each sample given on the Data Sheet with any corresponding dates and times indicated on the individual samples; compare the ON times to the OFF times of the preceding samples.

If there is a disagreement between dates or times, check with OHP to resolve serious discrepancies before proceeding with the preparation. Small discrepancies in sampling hour are usually accommodated by noting differences in a comment on the analytical report.

For the Radiation Protection submitted samples, complete a 300 Area Weekly Stack Filter Change report. Enter the established sampler flow rates and the ON and OFF dates indicated on the samples; enter 1200 hours unless an

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hour is specified. Adopt as ON time hour any OFF time hour specified for the preceding sample.

- (b) Verify no sample exhibits more than 6000 c/m beta-gamma or 2000 d/m alpha activity. Any filter exceeding these limits requires special treatment (refer to subsection 9.3).

4.9.2 Preparation of Particle Filters (normal activity)

Samples that are less than or equal to 6000 c/m beta-gamma and 2000 d/m alpha are prepared using this subsection. Samples exceeding these limits are prepared using Subsection 9.3.

- (a) Verify that the sample activity determined and recorded by OHP or Radiation Protection is less than 6000 c/m beta-gamma and 2000 d/m alpha. If no activity data is provided, proceed as follows:

1. Survey the envelope containing the filter for beta-gamma activity.

If the activity found is 6000 c/m or greater, proceed to Subsection 9.3 without removing the filter from the envelope. Notify the appropriate engineering group of the high activity.

2. Carefully remove the filter from the envelope and survey the filter for alpha activity.

If the activity found is 2000 d/m or greater, place the filter back into its envelope and proceed to Subsection 9.3. Notify the appropriate engineering group.

- (b) Coat the bottom of a 2-in. dish with rubber cement.
- (c) Carefully place the filter face up in the dish, avoiding wrinkles or trapped air bubbles.

Because the filter matrix will completely absorb alpha activity and may significantly attenuate beta activity, it is important that the filter face upon which the activity accumulates be mounted upward in the dish so that it will face the detector during counting. Filters are usually labeled by writing on the sampling face but it is best to identify the deposition face by independent means. Usually there is sufficient sample

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stream borne dust to produce a clearly defined deposition area. It is often possible to identify the direction of flow through the filter by the direction the filter is embossed by the backup supporting screen in the sampling apparatus. As a last resort, the filter should be dish mounted by applying rubber cement only at the perimeter and both faces counted. The highest counting data set is adopted.

If the filter is slightly large and exhibits a clearly defined deposition area, it may be trimmed with scissors to fit into the dish. If the filter is grossly larger than 50 mm in diameter, carefully cut it into several pieces and mount the pieces in 2 or more dishes.

- (d) Push down and, if necessary, recement any curled edges.
- (e) Place a strip of masking tape across the hole of a cardboard dish holder.
- (f) Copy the sample identification and other sample information onto the face of the holder that exposes the adhesive on the tape covering the hole.
- (g) Place the dish over the hole of the holder so that the bottom of the dish adheres to the adhesive on the tape.
- (h) Place the holder in a holder rack with other mounted samples for submission to the counting room.

4.9.3 Preparation of Particle Filters (high activity)

Samples that exceed 6000 c/m beta-gamma and/or 2000 d/m alpha are prepared using this subsection.

- (a) Carefully remove the filter from its envelope using forceps.
- (b) Roll the filter carefully into a cylinder and place it into a 15-ml glass vial.
- (c) Place the cap on the vial and label the vial with the sample identification and other sample information.
- (d) Send the vial to the counting room for a gamma spectrometric analysis.
- (e) If total alpha and total beta analysis are still required, proceed as in Section 9.5.

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4.9.4 Preparation of Charcoal (commercial cartridges)

- (a) Survey the charcoal cartridge for beta-gamma activity.

If the activity is greater than 6000 c/m, notify the appropriate engineering group. Be sure to label the sample jar going to the counting room accordingly at Step (b).

- (b) If possible, peel the information label from the cartridge shell and place it on an 8 oz styrene jar; otherwise, copy the information onto a jar using a marking pen.
- (c) Carefully open the cartridge and transfer the charcoal and the thin filter membranes behind each screen into the 8 oz styrene jar.

Three types of commercial cartridges are currently in use, each requiring a slightly different charcoal transfer technique. Operations should be performed on a clean paper towel to facilitate recovery of spilled charcoal granules.

Plastic Shell, wire screens held in place by shell flange: HI-Q products Division of AF&W Industries, La Jolla, California

1. Place the cartridges on a flat surface, either side up. Grasp the screen near an edge with sharp-tipped forceps and remove the screen by pulling upward and toward the cartridge center. Try not to damage the filter membrane under the screen.
2. Position the cartridge horizontally over the 8 oz. styrene jar, the remaining screen up. Similarly remove the second screen.
3. Position the cartridge vertically in the jar with the shell extending one-half inch above the rim. Push one blade of a pair of sharp pointed scissors entirely through the cartridge at the edge of the flange. Cut straight across the flange.
4. Rotate the cartridge 180 degrees and similarly cut through the flange at a point opposite the first cut.

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5. Allow the cartridge shell to separate and the contents to fall into the jar. Use forceps to separate the two thin filter membranes from the shell. Discard the plastic shell parts and the wire screens.

Plastic Shell, plastic screens integrally molded: Hi-Q Environmental Products #TC-12, La Jolla, California

1. Place the cartridge on a flat surface, either side up. Using a pair of sharp pointed scissors, snip through each screen element where it joins the shell flange. Remove and discard the screen.
2. Cut the thin filter membrane loose along the edge of the shell flange. Transfer the membrane into the 8 oz. styrene jar.
3. Lower the cartridge into the jar, invert the cartridge, and shake out the charcoal.
4. Detach the remaining thin filter membrane by scraping along the inside edge of the shell on the opposite cartridge face with sharp-tipped forceps. Transfer the membrane to the jar. Discard the plastic shell with its remaining screen attached.

Metal Shell, wire screen held in place by shell flange:

1. Place the cartridge on a flat surface with the arrow on the side pointing DOWN. When positioned this way, the loose thin filter membrane is facing down and is removed last, reducing charcoal granule spill.
2. Force a heavy pair of forceps through the screen near the edge of the flange just enough to pry up a screen edge. Grasp the screen by hand, pull it from the shell, and discard.
3. Invert the cartridge and similarly remove the remaining screen.
4. Position the cartridge vertically in the 8 oz. styrene jar with the shell below the rim. With forceps, dislodge the thin filter membrane from the face where the last screen was removed (this membrane is loose) and allow the charcoal to fall into the jar.

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5. Scribe the remaining thin filter membrane loose by running sharp-tipped forceps along the metal flange and transfer it to the jar. Discard the metal shell.
- (d) Place the cap on the jar and mix the charcoal by inverting the jar several times. Level the contents of the jar. Be sure no voids are created in the charcoal mass by the filter membrane positions.
- (e) Send the jar to the counting room.

4.9.5 Dissolution of Particle Filter

This subsection is used to dissolve the particle filter should a high activity sample be received or should special analyses be required. Since volatile radionuclides may be lost during dissolution, a gamma spectrometric analysis should be performed before beginning Step (a) (refer to Subsection 9.3).

- (a) Place the filter face up in a beaker large enough to contain the filter flat.

The beaker should be no larger than necessary.

- (b) Add 8M HNO_3 until the filter is completely covered.
- (c) Heat the beaker on a hotplate (without boiling the solution) at least 15 minutes and until either the filter dissolves completely or disintegrates into a pulp slurry.

Additional acid should be added during the heating to maintain the volume.

- (d) Let the solution cool and any pulp residue settle. Transfer the solution to a 25-ml volumetric flask.

The volume of solution should be no more than 20 ml.

- (e) Rinse the beaker and any residue with small amounts of water, adding the rinses to the flask; adjust to volume with water and mix the solution thoroughly.
- (f) The following steps are used to mount and aliquot of the solution for alpha and beta counting:

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PNL TECHNICAL PROCEDURE

1. Use the Stainless Steel model of the 2-inch dish for this analysis. The aluminum dishes are attacked by the acid used in this procedure.
2. Plate an appropriate aliquot of the filter solution on the dish spreading the aliquot as evenly as possible over the bottom of the dish, strippling if the aliquot is small, and leaving enough perimeter that sample does not reach the dish edge and walls. Select the aliquot so that the dish exhibits no more than 1000 c/m beta gamma and 2000 d/m alpha when surveyed.
3. Dry the plate under a heat lamp.
4. Prepare the dish for the counting room by following Steps (e) through (h) of Subsection 9.2. Be sure to record the volume of the filter dissolution (25 ml) and the size of the plated aliquot on the cardboard dish holder.

5.0 BIBLIOGRAPHY

None

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-430, SOLUTIONS ANALYSIS: PREPARATION OF BETA SOURCES BY DIRECT EVAPORATION

APPLICABILITY

This procedure is for preparation of beta-counting sources by direct evaporation of test solution on a stainless steel dish prior to measurement of beta counts by PNL-ALO-431.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

1.1 Tolerances

All measurements in this procedure unless otherwise stated are +/- 10%.

1.2 Performance Verification

To assure the performance of the method and check for possible contamination of the sample, a spike and a blank shall be analyzed with each batch of samples. These requirements may be waived or others stipulated by the client in the ARFS, SOW, TI or other instructions. A batch shall not exceed 20 samples.

Spikes and blanks run through a separation method along with a sample batch satisfy this requirement.

Author <i>CO Harvey</i> CO Harvey	Date <i>2/27/92</i>	Project Mgr. <i>TE Jones</i> TE Jones	Date <i>2/27/92</i>	QAD Representative <i>GK Gerke</i> GK Gerke	Date <i>2/27/92</i>
Technical Reviewer <i>LR Greenwood</i> LR Greenwood	Date <i>2/27/92</i>	Line Mgr. <i>AG King</i> AG King	Date <i>2/27/92</i>	Other	Date
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PNL TECHNICAL PROCEDURE

A spike yield of $\pm 20\%$ of the known value is acceptable if the following conditions are met: The count rate of the spike is ten times the background count rate of the counter on which it is counted and the counts attributable to the spike are at least 30% of the total counts.

A spike is, preferably, a sample but may be matrix solution or reagent blank to which a known amount of analyte or tracer has been added. The material to be spiked and the quantity of nuclide to be added shall be selected by the cognizant scientist based on the concentration and make up of the samples.

A blank is a volume of deionized water or matrix solution approximately equal to the sample volume.

2.0 Equipment and Materials

- Dish, 1-1/8-in. diameter, stainless steel
- Heat lamp

3.0 Procedural Steps

- 3.1 Based on expected concentration, pipet a suitable aliquot volume of sample into a stainless steel dish. Volume should be $<1000\mu\text{L}$ to avoid overflow of the solution from the dish. Record the volume on the Analytical Data Sheet.
- 3.2 Evaporate the solution to dryness under a heat lamp.
- 3.3 Using a G.M., measure the activity on the dish, if greater than 3,000 CPM, mount a smaller aliquot.
- 3.4 Submit the mount to the counting room for counting.
- 3.5 The beta activity is measured using Procedure PNL-ALO-431, "Solutions Analysis: Beta Counting."

4.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and Analytical Data Sheet provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-431, SOLUTIONS ANALYSIS: BETA COUNTING

APPLICABILITY

This procedure applies to the analysis of solutions by beta counting a source which has been prepared by the complete evaporation of an aliquot of the solution in a small dish.

The number of beta particles emitted from a prepared counting source is measured using a gas flow beta proportional counter (BPC). Normally a separation will be required if the isotope to be measured is in a solution containing other radioactive species. Beta counting is usually restricted to those isotopes that do not emit gamma photons and cannot be measured by gamma spectrometry.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

Beta Proportional Counter shall be:

- calibrated (see Section 4.0)
- in control (see Section 5.0)
- have correct background (see Section 6.0)

Standards used for calibration shall be NIST traceable.

Author <i>CO Harvey</i> 2/27/92 CO Harvey	Date 2/27/92	Project Mgr. <i>TE Jones</i> 2/27/92 TE Jones	Date 2/27/92	QAD Representative <i>GK Gerke</i> 2/27/92 GK Gerke	Date 2/27/92
Technical Reviewer <i>LR Greenwood</i> 2/27/92 LR Greenwood	Date 2/27/92	Line Mgr. <i>AG King</i> 2/27/92 AG King	Date 2/27/92	Other	Date
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PNL TECHNICAL PROCEDURE

2.0 Equipment and Materials

- Proportional beta counter.
- Methane gas, commercial-grade.
- Dish, 7/8-in. diameter, stainless steel.

3.0 Sample Count

- 3.1 Survey the prepared sample counting source using a beta survey instrument to ensure that beta activity is not excessive (<3000 counts per minute on GM). If the 3000 c/m is exceeded, adjust as required using sample preparation procedure.
- 3.2 Open shield door and place sample source on Shelf 1; close shield door.
- 3.3 Preset desired counting time. (This typically varies from 10 to 100 minutes depending on activity levels.)
- 3.4 Press STOP, RESET and START buttons. (Count will stop automatically at the end of preset counting time.)
- 3.5 Record the data counted, BPC efficiency for isotope counted, minutes counted and total counts; calculate counts per minute less the background count (Section 6) as outlined in the beta counting data portion of the Analytical Data Sheet.

4.0 Calibration Standards

Calibration standards of the isotope being counted shall be prepared on stainless steel beta-counting dishes. Standards shall be NIST-traceable. Replicate standard sources shall be counted, and the efficiency calculated by dividing the disintegration per minute of standard on the dish by the average net counts per minute measured. The counting data and efficiency shall be recorded in the beta LRB.

5.0 Daily Control Standards

Control standards are sources of ⁹⁰Sr-Y (high beta energy) and ⁹⁹Tc (low beta energy) that are used on a daily basis to ensure control of the Proportional Beta Counters. Each source is counted at least 10 times when the instrument is calibrated and using the CONCHT program (Counting Instrument Control Chart Generation and Extension Program) located on the Micro-Vax computer, limits that must be met on a daily basis, shall be determined. Using the data from this program, control charts shall be prepared on which the daily performance is plotted. The chart may

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PNL TECHNICAL PROCEDURE

show a number of limits. Normally, Control Limits are set at 2sigma or 2% of $\bar{x}$.

The following daily control standard count procedure shall be used.

- 5.1 Open shield door and place ^{90}Sr -Y control source on Shelf 1.
- 5.2 Close shield door and preset counting time for 10 minutes.
- 5.3 Press STOP, RESET and START buttons. (Count will stop automatically at the end of 10 minutes).
- 5.4 Record total counts in Beta LRB; plot counts per minute less background (6.2) on daily control chart. Counts per minute shall fall within limits defined on control chart. Data Sheets and Control Charts are located in the beta LRB.
- 5.5 Repeat 5.1 through 5.4 using ^{99}Tc daily control standard.

6.0 Daily Background Count

- 6.1 Using a clean background dish, repeat Steps 1 through 3 of Section 5.0 above.
- 6.2 Record counts per minute on daily control data sheet in the beta LRB.
- 6.3 Repeat 6.1, except now preset the time to 100 minutes. (This count is normally started at the end of the day shift and recorded the following morning in the beta LRB.)

7.0 Sample Calculations

Complete sample calculation using the equation:

$$A = B \times C \times D$$

where: A = disintegrations per minute per milliliter of sample
B = counts per minute as calculated in 3.5
C = dilution factor or volume factor to correct to 1 mL
D = BPC disintegrations/count as posted on counter for the specific isotope.

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PNL TECHNICAL PROCEDURE

8.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory Record Books and Analytical Data Sheets provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-432, SEPARATION OF TECHNETIUM BY CATION EXCHANGE AND SOLUTION EXTRACTION PRIOR TO MEASUREMENT BY BETA COUNTING

APPLICABILITY

This procedure can be used for separating technetium from other beta counting radionuclides in aqueous samples.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

1.1 Tolerances

All measurements in this procedure unless otherwise stated are +/- 10%.

1.2 Performance Verification

To assure the performance of the method and check for possible contamination of the sample, a spike and a blank shall be analyzed with each batch of samples. These requirements may be waived or others stipulated by the client in the ARFS, SOW, TI or other instructions. A batch shall not exceed 20 samples.

A spike yield of $\pm 20\%$ of the known value is acceptable if the following conditions are met: The count rate of the spike is ten times the background count rate of the counter on which it is counted and the counts attributable to the spike are at least 30% of the total counts.

Author <i>CO Harvey</i> CO Harvey	Date <i>2/27/92</i>	Project Mgr. <i>TE Jones</i> TE Jones	Date <i>2/27/92</i>	QAD Representative <i>GK Gerke</i> GK Gerke	Date <i>2/27/92</i>
Technical Reviewer <i>LR Greenwood</i> LR Greenwood	Date <i>2/27/92</i>	Line Mgr. <i>AG King</i> AG King	Date <i>2/27/92</i>	Other	Date
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PNL TECHNICAL PROCEDURE

A spike is, preferably, a sample but may be matrix solution or reagent blank to which a known amount of analyte or tracer has been added. The material to be spiked and the quantity of nuclide to be added shall be selected by the cognizant scientist based on the concentration and make up of the samples.

A blank is a volume of deionized water or matrix solution approximately equal to the sample volume.

The effectiveness of this procedure in separating Tc from other beta emitters can be determined by beta absorption measurements.

2.0 Equipment and Materials

- Sodium dichromate, 0.1 M -- Dissolve 2.98 (± 0.01) g of sodium dichromate in 100 (± 1) mL of deionized water; mix thoroughly.
- AG-50W, X-8, 100 to 200 mesh, or equivalent, H^+ form, cation exchange resin.
- Tartaric acid, 1 M -- Dissolve 15.0 (± 0.1) g of tartaric acid in 100 (± 1) mL of deionized water; mix thoroughly.
- Tetraphenylarsonium chloride, 0.01 M -- Dissolve 0.455 (± 0.001) g of tetraphenylarsonium chloride in 100 (± 1) mL of deionized water; mix thoroughly.
- Sodium hydroxide, 10 M -- Carefully dissolve 400 (± 4) g of sodium hydroxide pellets in about 800 mL of deionized water. Dilute to 1000 (± 1) mL and mix thoroughly.
- Methylisobutyl ketone (hexone) (FLAMMABLE).
- Vials, 2-dram and 35-mL, glass, with polyseal-screw cap.
- Ion-exchange columns made from 2-mL plastic droppers with the bulb removed.
- Beta-counting dishes.
- Pancake probe, P-11.
- Heat lamp.

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PNL TECHNICAL PROCEDURE

3.0 Separation

Technetium is separated from other radioactive species by a process that absorbs most of the other species onto a cation exchange resin. The technetium is extracted from the effluent into hexone as tetraphenylarsonium pertechnetate. The technetium activity is then measured by beta counting using Procedure PNL-ALO-431.

3.1 Prepare a 500 (± 50) μL column of AG-50W, X-8, 100 to 200 mesh, H^+ form, cation-exchange resin as follows:

- Cut off the top of a 7-ml plastic dropper.
- Fill the tip with a small ball of cotton to support the resin.
- Measure and mark the dropper at 0.50 ml above the cotton plug.
- Add a slurry of resin to the dropper until the settled bed of resin is to the mark.

3.2 Based on expected Tc concentration, pipet up to a 5-ml aliquot of the sample solution into a 2-dram vial. Record the volume on the Analytical Data Sheet to the nearest 0.01 mL.

3.3 Add to the solution 100 (± 10) μL of 0.1 M sodium dichromate; swirl to mix.

3.4 Load the solution onto the ion-exchange column. Collect all ion-exchange column effluent in a 35-ml screw-cap vial. NOTE: DO NOT disturb the resin bed.

3.5 Wash the 2-dram sample vial with four 1 (± 0.01) mL portions of deionized water, and transfer each portion to the ion-exchange column. Use the washes to wash down the inside of the plastic dropper containing the resin. Collect effluent in the vial from Step 3.4.

3.6 Discard the ion-exchange column in the dry radioactive waste.

3.7 To the effluent solution in the 35-ml screw-cap vial, add 100 (± 10) μL of 0.1 M sodium dichromate, 100 (± 10) μL of 1 M tartaric acid, 200 (± 10) μL of 0.01 M tetraphenylarsonium chloride, and 1.0 (± 0.01) mL of 10 M sodium hydroxide; swirl to mix.

3.8 Add 5.0 (± 0.1) mL of hexone; cap the vial tightly and record the volume of Hexone added on the Analytical Data Sheet.

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PNL TECHNICAL PROCEDURE

- 3.9 Mix the solution on the vortex mixer for 3 minutes.
- 3.10 Centrifuge for 1 to 2 minutes to separate phases.
- 3.11 To a two dram vial add 1 mL H₂O, 0.5 mL of 10 M sodium hydroxide, 100 μ L of 1 M tartaric acid and 100 μ L of 0.1 M sodium dichromate.
- 3.12 Transfer most of the hexone phase (top layer) to the 2-dram vial. Cap the vial tightly.
- 3.13 Mix the solution on the vortex mixer for 3 minutes.
- 3.14 Centrifuge for about 1 minute to separate phases.
- 3.15 Repeat Steps 3.11, 3.12, and 3.13.
- 3.16 Pipet the desired amount of the hexone phase onto a stainless steel beta-counting dish. Record the volume on the Analytical Data Sheet.
- 3.17 Dry under a heat lamp. Check for acceptable activity using a P-11 pancake probe. The reading should be as high as possible but not exceed 2000 counts/min with the probe directly on the mount. If not acceptable, repeat 3.16 with a larger or smaller volume of hexone as appropriate.
- NOTE: Care must be taken that the organic does not creep over the edge of the dish. If more than 1 ml is to be plated, it shall be done in increments.
- Note: Adding an additional aliquot to a dish after it has been checked for activity is acceptable.
- 3.18 Measure the technetium activity using the Beta Counting (PNL-ALO-431) procedure. Record counting data volumes and calculations on the Analytical Data Sheet.

4.0 Calculations

Tc-99 Concentration

$$T = \frac{(A)(B)(H)}{(C)P}$$

where T = Tc-99 d/m/mL

A = Net Count CPM observed

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PNL TECHNICAL PROCEDURE

B = Counter efficiency for Tc-99 disintegrations/count

C = Volume of sample analyzed (mL)

H = Volume of Hexone added in 3.8

P = Volume of Hexone plated 3.16

5.0 Records

Records shall be maintained and controlled so as to conform with the requirements of PAP-1701. Laboratory notebooks and Analytical Data Sheets provide a mechanism for control of most records.

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INTERIM CHANGE NOTICE
ICN

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<p>A. Document Number: <u>PNL-ALO-433</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Separation of Sr-90 by Cation Exchange</u> <u>Prior to Measurement by Beta Counting</u></p> <p>Document's Original Author: <u>CO Harvey</u></p>	<p>Effective Date of ICN: <u>02/11/93</u></p> <hr/> <p>Change Requested by: <u>CO Harvey</u></p>
<p>B. Action:</p> <p style="text-align: center;">Replace pages 1 - 4 with the attached pages 1 - 4.</p>	
<p>C. Effect of Change:</p> <p style="text-align: center;">N/A</p>	
<p>D. Reason for Change/Description of Change:</p> <p>Reason: Removed redundant variance stipulations.</p> <p>Description: See strikeout on pages 1 through 4.</p>	
<p>E. Approval Signatures: (Please Sign and Date)</p> <p>QP Concurrence: <u>TL Ehlert</u> <u>TL Ehlert</u> Date: <u>2/11/93</u></p> <p>Approval Authority: <u>AG King</u> <u>AG King for AGK</u> Date: <u>3/2/93</u></p> <p>Other Approvals: <u>CO Harvey</u> <u>CO Harvey</u> Date: <u>2/16/93</u></p> <p style="margin-left: 100px;">: <u>LR Greenwood</u> <u>LR Greenwood</u> Date: <u>3/5/93</u></p>	<p>Type of Change (Check (✓) one) (✓) Minor Change () Major Change</p>

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-433, SEPARATION OF STRONTIUM-90 BY CATION EXCHANGE PRIOR TO MEASUREMENT BY BETA COUNTING

APPLICABILITY

This procedure is used for separating ^{90}Sr from other beta emitting radionuclides in aqueous samples, and determining its concentration by measuring the ingrowth of the Y-90 daughter.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

1.1 Tolerances

All measurements in this procedure unless otherwise stated are +/- 10%.

1.2 Performance Verification

To assure the performance of the method and check for possible contamination of the sample, a spike and a blank shall be analyzed with each batch of samples. These requirements may be waived or others stipulated by the client in the ARFS, SOW, TI or other instructions. A batch shall not exceed 20 samples. A spike is, preferably, a sample but may be matrix solution or reagent blank to which a known amount of analyte or tracer has been added. The material to be spiked and the quantity of nuclide to be added shall be selected by the cognizant scientist based on the concentration and make up of the samples.

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CO Harvey		TE Jones		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LR Greenwood		AG King		ALL ORIGINAL SIGNATURES ON FILE.	
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PNL TECHNICAL PROCEDURE

A spike yield of $\pm 20\%$ of the known value is acceptable if the following conditions are met: The count rate of the spike is ten times the background count rate of the counter on which it is counted and the counts attributable to the spike are at least 30% of the total counts.

A blank is a volume of deionized water or matrix solution approximately equal to the sample volume.

2.0 Equipment and Materials

- Hydrofluoric acid, 0.2 M -- Dilute 7 (~~± 0.1~~) mL of concentrated hydrofluoric acid to 1000 (± 1) mL with deionized water; mix thoroughly. Store in a 1-L plastic bottle.
- Nitric acid, 8 M -- Dilute 506 (~~± 5~~) mL of concentrated reagent-grade nitric acid to 1000 (± 1) mL with deionized water; mix thoroughly.
- AG-50W,[®] X-8, 200 to 400 mesh or equivalent, NH_4 form, ion-exchange resin.
- 2-Methylactic acid, 0.7 M pH 4.60 -- Dissolve 72.9 (± 0.1) g of reagent in about 900 mL of deionized water. Adjust the pH to 4.60 (± 0.1) by adding concentrated ammonium hydroxide dropwise while stirring. Monitor the pH using a digital pH meter that has been calibrated with pH 4.0 and 7.0 buffers. Transfer to a 1000-mL volumetric flask, and dilute to volume with deionized water; mix thoroughly.
- 2-Methylactic acid, 1.0 M pH 5.00 -- Dissolve 104 (~~± 0.2~~) g of reagent in about 800 mL of deionized water. Adjust the pH to 5.00 (± 0.1) and dilute as described above.
- Ion-exchange column (made from 4-mm glass tubing with a 5-mL reservoir).
- Flasks, 10-mL, volumetric.
- Vials, 2-dram, 15 mL.
- Dishes, 1 1/8-in. diameter, stainless steel.
- Dropper, plastic.

[®]AG-50W is a registered trademark of Bio-Rad Laboratories, Richmond, California.

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PNL TECHNICAL PROCEDURE

3.0 Separation

The ^{90}Sr is separated from other radioactive species by selective elution from a cation exchange resin using 2-methylsuccinic acid. Following separation, the growth of ^{90}Y is measured by beta counting. The ^{90}Sr is then calculated, based on the growth of the ^{90}Y daughter over a measured period of time.

- 3.1 Prepare a 300 (~~± 20~~) μL column of AG-50W, X-8, 200 to 400 mesh, NH_4^+ form, ion exchange resin, as follows:

3.1.1 Fill the tip of a glass column with a small ball of cotton to support the resin.

Measure and mark the column 0.30 mL above the cotton plug.

Add a slurry of resin to the column until the settled bed of resin is to the mark.

- 3.2 Based on expected Sr concentration, accurately add up to 4 mL ~~± 0.1~~ mL of sample solution to the column. Record the volume used on the Analytical Data Sheet. Collect the column effluent in a screw cap vial.
- 3.3 Wash the resin column with 500 (~~± 10~~) μL of deionized water. Collect effluent in vial from Step 3.2.
- 3.4 Wash the resin column with three 1 (~~± 0.01~~) mL portions of 0.2 M hydrofluoric acid. Collect effluent in vial from Step 3.2.
- 3.5 Wash the resin column with four 1 (~~± 0.01~~) mL portions of 0.7 M methylsuccinic acid. Collect effluent in vial from Step 2. Cap the vial and discard in the radioactive liquid waste.
- 3.6 Elute strontium with 3.5 (~~± 0.1~~) mL of 1.0 M methylsuccinic acid; collect the effluent in a 2-dram vial containing 400 (~~± 10~~) μL of 8 M nitric acid.
- 3.7 Mix the solution in the 2-dram vial, and transfer the solution to a fresh 300- μL column of AG-50W, X-8, 200 to 400 mesh, NH_4^+ form, ion-exchange resin using a plastic dropper. Collect the effluent in a 15 mL vial as waste.
- 3.8 Wash the 2-dram vial with three 1 (~~± 0.01~~) mL portions of deionized water, and transfer the washes to the resin column. Collect the effluent in the vial from Step 3.7. Discard the 2 dram vial and dropper in the dry radioactive waste.

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PNL TECHNICAL PROCEDURE

- 3.9 Wash the resin column with three 1 ~~(±0.01)~~ mL portions of 0.7 M methylactic acid. Record date and time (T_0) that the last drop leaves the column on the Analytical Data Sheet. Collect the effluent in the vial from 3.7. Cap the waste vial and discard in the radioactive liquid waste.
- 3.10 Elute the strontium with 3.5 ~~(±0.05)~~ mL of 1.0 M methylactic acid. Collect in a 10-mL volumetric flask.
- 3.11 Dilute the solution in the volumetric flask to 10 mL using deionized water. Add a stirring bar and stir thoroughly. Transfer the solution from the 10 mL volumetric flask to a 15 mL vial for easier pipetting.
- 3.12 Accurately pipet the volume required onto a stainless steel beta-counting dish. Record volume on the Analytical Data Sheet.
- 3.13 Dry under a lamp until completely dry.
- 3.14 Using a GM, check the activity on the dish, if too high (>1000 CPM) plate smaller aliquot. If there is very little count, more sample can be added to the dish. Record volume on Analytical Data Sheet.
- 3.15 Immediately count the activity on the dish for 10 minutes using the Beta Counting (PNL-ALO-431) procedure. Record the date and time (T_1) that the count is started on the analytical report.
- 3.16 After 3 to 4 days, recount the beta dish for 10 minutes. Record time (T_2) and the date that the count is started on the Analytical Data Sheet.

4.0 Calculations

- 4.1 Calculate the ^{90}Y counts at equilibrium using the equation:

$$Y = \frac{A - B}{C - D}$$

where: $Y = ^{90}\text{Y}$ equilibrium count rate (ct/min)

$A = (\text{ct/min-bkg})$ at T_2

$B = (\text{ct/min-bkg})$ at T_1

$$C = e^{-\frac{\ln 2 \times (\Delta T_1)}{64}}$$

$\Delta T_1 =$ time elapsed from T_0 to T_1 hours

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PNL TECHNICAL PROCEDURE

$$D = e^{-\frac{\ln 2 \times (\Delta T_2)}{64}}$$

ΔT_2 = time elapsed from T_0 to T_2 hours

- 4.2 Calculate the ^{90}Sr disintegrations per minute per milliliter (dis/min/mL) using the following equation.

$$S = Y \times D \times V$$

$$\text{where: } V = \frac{1}{V_A} \times 10 \times \frac{1}{V_B}$$

$S = ^{90}\text{Sr}$ (dis/min/mL)

$Y = ^{90}\text{Y}$ equilibrium count rate from Step 4.1 (ct/min)

D = disintegrations per count factor for ^{90}Y

V = column correction factor to correct activity to 1 mL

V_A = volume of sample from Step 3.2 (mL)

V_B = volume of sample pipetted into counting dish in Step 3.12 (mL)

10 = volume from Step 3.11 (mL)

- 4.3 Record the calculation results on the Analytical Data Sheet.

5.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical Data Sheets provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-434, (Replaces 6-40.2), BETA AND ALPHA PROPORTIONAL COUNTING:
PARTICLE FILTER ANALYSIS

1.0 APPLICABILITY

Beta and alpha particles are detected by the ionization of a gas flowing in a detector positioned above the sample. An applied potential gradient between the anode and the cathode of the detector causes the ions to be collected, thereby creating current pulses in the detector system. The current pulses are converted to voltage pulses, amplified, and fed to a discriminator which excludes small pulses arising from electronic noise, differentiates alpha and beta pulses on the basis of pulse amplitude, and generates constant amplitude pulses that drive scalers, recording the pulses as counts. Observed count rates are converted to absolute disintegration rates through calibration of the system using sources of accurately known activity.

- (a) Material The particle filters used in the Stack Monitoring Program (refer to Method PNL-ALO-429).
- (b) Range The counting rate for most SMP samples is small. Rarely, if ever, does the alpha exceed 100 c/m or the beta exceed 1000 c/m.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

Author	Date	Project Mgr.	Date	QAD Representative	Date
MR Weiler	9/19/88	N/A		LJ Ethridge	9/19/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
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4.0 PROCEDURE

4.1 DISCUSSION

The Tennelec LB-1000 low background alpha beta proportional counter is used to measure alpha and beta disintegration rates associated with particle filters. Detection and measurement of activity is based upon the ionization of a 90% argon, 10% methane gas mixture as it flows through the counting system detector.

A particle filter, mounted on a 5-cm diameter dish (method PNL-ALO-429), is placed on the sample slide of the counter and pushed into a position directly below a thin-windowed detector. Ions generated within the detector chamber by interaction of alpha and beta particles from the sample with the detector gas are collected at a wire anode within the chamber by a high voltage gradient maintained between the anode and the wall of the detector. The collected ions from a single sample particle emission event constitute a current pulse that is next converted into a voltage pulse and amplified. Voltage pulses are passed to a discriminator which excludes very small pulses arising from electronic noise, differentiates alpha and beta pulses on the basis of pulse amplitude, and generates separate alpha and beta channels consisting of constant amplitude pulses. A second detector chamber surrounds the top of the sample detector. Voltage pulses from this "guard" detector originate from penetrating external radiation such as cosmic rays and constitute an external background of the counting system. The output pulses from the guard detector and the beta channel of the sample detector are processed by an anticoincidence circuit which does not pass a pulse in the beta channel if there is a time correspondent pulse from the guard detector, thereby essentially eliminating external background. Finally, the alpha and beta channels drive respective scalers that record the individual pulses as "counts." A sample is counted for an accurately measured time by means of a "timer" module and the respective accumulated alpha and beta counts are recorded.

Differentiation of alpha and beta pulses on the basis of pulse amplitude is possible because the high specific ionization of an alpha particle produces considerably more ion pairs in the counter gas than a beta particle. Unfortunately, alpha particle energies are readily degraded by the filter mass itself, the air column an alpha particle must traverse enroute to the detector, the detector window, and scattering effects, resulting in a low energy pulse continuum that extends through the beta pulse height region. Detector operating voltage is a compromise between optimum alpha

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channel alpha plateau position, optimum beta channel beta plateau position, and position of the threshold of the alpha channel with respect to the beta plateau. As a result of less than ideal alpha-beta differentiation, the LB-1000 exhibits approximately 0.00089 of the observed beta channel count as crosstalk in the alpha channel for beta emitters above 0.5 MeV in energy; for near zero mass alpha sources approximately 0.076 of the observed alpha channel count is present as crosstalk in the beta channel, with crosstalk increasing with source mass. Thus, near detection limit amounts of beta activity cannot be confirmed in the presence of more than 10 counts per minute alpha activity and trace alpha activity cannot be verified in high beta counting samples. Alternative counting methods are the solution to both problems: beta proportional counting with a thin absorber in the former case and alpha scintillation counting in the later.

Recorded counts are not equal to the number of radionuclide disintegrations occurring in a sample because at least half of the emissions are emitted or scattered in a direction away from the detector chamber or absorbed. The ratio between observed count and true disintegration rate is referred to as the "counting efficiency" and can be determined by counting sources of accurately known activity. Counter alpha efficiency is essentially constant over the 3 MeV to 8 MeV alpha energy range typical of almost all alpha emitting radionuclides. Counter beta efficiency is very nearly constant above 0.5 MeV but decreases rapidly at lower energies, making it necessary to calibrate the counter for each beta-emitting radionuclide. When a mixture of beta emitting radionuclides is involved, a counting efficiency can be estimated by considering the radioisotopic composition of the mixture and their individual counting efficiencies. The STACK Program specifies that all gross beta measurements shall be calculated as strontium-yttrium-90 and all gross alpha measurements as plutonium-239, both environmental worst cases.

Identification of radionuclide species and individual assay is subsequently required for all samples exceeding prescribed limits (refer to Method PNL-ALO-429); the responsible engineering group may request further analysis of any sample exhibiting statistically positive activity.

In the event the LB-100 counting system is malfunctioning or otherwise unavailable, the gas-flow proportional beta counters are available for backup use. The detectors of these instruments operate on an identical principle, but the systems provide neither pulse height differentiation nor anticoincidence background

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reduction. It is necessary to perform beta counts with a thin absorber to exclude alpha activity and to perform the alpha counts at an operating voltage reduced to below the beta threshold. The detection limits employing the gas flow beta proportional counters are, therefore, significantly higher than those of the LB-1000 low background counting system and each sample must be counted twice.

4.2 APPARATUS

Low Background Proportional Counter, LB-1000, Tennelec, with the following components:

- (a) Preamplifier, TC-175 (Tennelec).
- (b) Guard Detector Signal Processor, TC-264.
- (c) Amplifier/Discriminator, TC-265.
- (d) High Voltage Power Supply, TC-945.
- (e) Sample chamber. The sample slide is designed to hold various sizes of discs and dishes through use of appropriate plastic holder inserts. The detector windows are gold-plated Mylar thin enough to permit all alpha particles and all but very low energy beta particles to enter the detectors while excluding air. The detectors are housed in a lead brick shield.
- (f) Scalers, TC-546P, two are used.
- (g) Timer/Scaler, TC-547P

Normal settings for controls on these instrument components are given in Table 1.

4.3 REAGENTS

P10 gas (90% argon and 10% methane), commercial grade. Matheson Gas Data Book, The Matheson Company, Inc., East Rutherford, New Jersey, 4th Ed., 1966.

4.4 STANDARDS

- (a) Calibration Standards. The counter must be calibrated for each beta emitting isotope. The counting efficiency for alpha activity between 4 MeV and 8 MeV is essentially constant. A known amount of an isotope that produces 10 to 20 thousand c/m is plated on an appropriate metal dish so that the active area corresponds to that of a filter sample.

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In the absence of identifiable activity in a sample, beta and alpha results are arbitrarily calculated and reported as SrY-90 and Pu-239, respectively, therefore, these two nuclides are essential calibration standards. To avoid affecting counting characteristics, calibration standards are not given a protective coating; calibration standards must be carefully handled, safely stored, and used only when recalibration is necessary.

- (b) **Control Sources.** Control sources are sources of radioactive material chosen on the basis of long half-life, the energy of the radiation, and physical-chemical stability. The source need not necessarily simulate sample configuration. The count rate for a control source is established at the same time the instrument is calibrated; the control source is thereafter counted regularly and the observed count verified as falling within statistical error limits of the decay corrected original value. If this condition is met, the instrument is considered to be in control and previous calibrations are assumed to remain valid. If a control count falls out of limits, it is repeated; if still outside limits the instrument must not be used to count samples until either repair brings control counts back within limits or new calibrations and controls are established. Alpha counting efficiency is essentially constant as a function of alpha energy, therefore one alpha control suffices; since beta counting efficiency varies considerably as a function of beta energy, control at both high and low beta energy is required. The control sources for the LB-1000 are three metal dishes: the alpha control contains 3.33×10^4 d/m Pu-239; the high energy beta control contains 3.54×10^4 d/m of SrY-90; the low energy beta control contains 1.40×10^4 d/m of Tc-99. These are "reduced area" sources where the active area is smaller in diameter than a particle filter so that sensitivity to lateral source position is reduced. The control sources are given a protective coating to maintain the integrity of the active deposit and to reduce the possibility of contaminating the counter.
- (c) **Plateau Sources.** These are two metal dishes, one containing 4×10^4 d/m Pu-239 and the other 2.6×10^4 d/m Pm-147. These sources serve for the measurement of alpha and beta plateaus in the determination of optimum operating voltage.

4.5 SAFETY

- (a) Observe the general laboratory safety rules and the counting room Radiation Work Procedure.

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- (b) P10 is a flammable gas. Cylinders containing the gas must be grounded. Portable gas cylinder permits must be renewed on expiration.

4.6 QUALITY CONTROL

Exclusive of errors relating to individual samples themselves, quality of a radiochemical measurement is primarily a function of the accuracy of counting system calibration and the degree to which counting system performance can be maintained at the level existing at the time of calibration.

4.6.1 Calibration

In alpha and beta counting, calibration involves measurement of the ratio of the absolute disintegration rate of atoms producing beta or alpha radiation to observed count rate on a system scaler, the d/c ratio, for a specific radionuclide. These measurements are performed when the counter is first set up to determine a specific radionuclide; recalibration is required whenever a problem develops that requires change in system operating parameter such as detector operating voltage or a discriminator adjustment. The stack program requires that the systems on which filter samples are counted be calibrated for SrY-90 and Pu-239 beta and alpha activity, respectively. All alpha and beta calibration data are entered in the calibration section of the LB-1000 Calibration and Control Log.

Calibrations are performed as follows:

- (a) Verify the counter is set to the proper operating voltage (refer to Subsection 4.9.4 and Table 1) and that the gas flow is 0.125 SCFH.
- (b) Determine the background count for the alpha and beta channels using the procedure of Subsection 4.9.2.
- (c) Count the calibration standard for a sufficient length of time to accumulate at least 10000 counts in the channel for the type of radiation emitted by the source, but not less than five minutes, using the procedure of Subsection 4.9.3. Record the date, time and total accumulated count.
- (d) Repeat Step (c) nine more times and then repeat Step

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(b). If the second background count is statistically identical to the first, proceed with Step (e). If not, correct the problem and repeat Step (b), (c), and (d).

(e) Calculate the count rate for each ten minute count:

$$c/m = \frac{c}{T} - b$$

where c = the observed total count
 T = the length of each count in minutes
 b = the background count in counts per minute.

In the calculation, use the average of the background counts from Steps (b) and (d) for the quantity b . Refer to step (h) for discussion of applications of decay corrections to the individual count measurements at this step.

(f) Calculate the $(\text{Chi})^2/n$ or χ^2/n of the data:

$$\frac{\chi^2}{n} = \left[\frac{\sum x^2 - \bar{x} \sum x}{\bar{x}} \right] \frac{1}{n}$$

where x = an observed count rate expressed in counts/minute

$\bar{x}$ = the arithmetic mean of the values obtained for x .
 $\bar{x} = \sum x/n$.

n = the number of counts performed, 10.

T = the length of each count in minutes

Should χ^2/n not fall between 0.2088 and 2.167, the 99% confidence limits for ten counts, data distribution is not consistent with a random disintegration process and the cause must be investigated, corrected, and the calibration repeated.

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- (g) Calculate the relative standard deviation of the data.

$$\sigma = \sqrt{\frac{\sum x^2 - \bar{x} \sum x}{n - 1}}$$

where σ = the relative standard deviation in counts per minute and other quantities are the same as in (f) above

Relative standard deviations greater than 1% of the average count, $\bar{x}$, are atypical of the LB-1000 system and should be investigated.

- (h) Calculate the disintegration to count ratio for the nuclide represented by the calibration source:

$$d/c = \frac{[D]}{\bar{x}} \left[\epsilon^{-\frac{(0.693147)(DI)}{T1/2}} \right]$$

where d/c = the disintegration to count rate for the nuclide

D = the absolute disintegration rate of the calibration source in disintegrations per minute.

$\bar{x}$ = the arithmetic mean of the observed counter rates calculated in (f) above.

0.693147 = the ϵ base (natural) logarithm of 2.

DI = the decay interval between the reference date stated for the calibration source disintegration rate and the time a count was made. Here the activity of the calibration source at the reference date is decay corrected to the date the calibration counting was performed.

$T1/2$ = the half life of the calibration source nuclide, expressed in the same time units as the decay interval.

The sign of the exponential factor assumes the reference date precedes the counting date.

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Usually the half life of the calibration source is large compared to the time required to perform the ten replicate counts; a decay interval calculated using the midpoint between the beginning of the first count and the end of the last ordinarily introduces negligible error. If the half life is small, the decay correction must be applied to the observed count rates individually at step (e), in which case the sign of the exponential function is positive; that is, the observed count rates are decay corrected to the calibration source reference date.

4.6.2 Control

Establishing Control. Control is a process by which a counting system is verified to be currently operating at the performance level existing when that system was calibrated. Control sources containing radionuclides which emit radiation of types and energies that effectively test the response of all system components are measured when the counter is calibrated. The ability of the system to reproduce these initial measurements is the criteria by which operation is routinely evaluated. Controls must be re-established whenever system problems develop that require system recalibration. A given control source may be replaced, or an additional control introduced, provided the existing controls indicate the system is operating within limits at the time the measurements establishing the new control source are performed. All control data are entered in the control section of the LB-1000 Calibration and Control Log. A plutonium-239 control source is used to monitor the LB-1000 system alpha channel performance; strontium-yttrium-90 and technetium-99 control sources monitor beta channel performance at high and low beta energy respectively.

Control source reference values are established using the following procedure. It is assumed that counting system parameters have been established, backgrounds measured, and any calibration or recalibration counting just completed.

- (a) Count the control source for a sufficient length of time to accumulate at least 10,000 counts in the channel for the type of radiation emitted by the source, but not less than five minutes, using the procedure of Subsection 4.9.3. Record the date, time, and the total accumulated count. This date and time is the reference date for the control data set.

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- (b) Repeat step (a) nine additional times.
- (c) Calculate the background corrected count rate for each count:

$$c/m = \frac{c}{T} - b$$

where c = the observed total count

T = the length of the count in minutes

b = the background count for the corresponding channel in counts per minute.

- (d) Calculate the $(\text{Chi})^2/n$ or X^2/n of the data:

$$\frac{X^2}{n} = \left[\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n} \right] \frac{1}{n}$$

where x = the observed count rate expressed in counts/minute

$\bar{x}$ = the arithmetic mean of the values obtained for x .

$$\bar{x} = \sum x/n.$$

n = the number of counts performed, 10.

T = the length of each count in minutes

Should X^2/n not fall between 0.2088 and 2.167, the 99% confidence level limits for ten counts, data distribution is not consistent with a random disintegration process. X^2/n values below this range indicate a tight clustering of data that will produce unreasonably narrow control limits; if such counting precision persists it may prove necessary to repeat the control measurements performing each of the ten counts on a different day, or re-evaluate the control limits at a later date using the routine control count data after a large number have accumulated. In either case, decay corrections must be applied to adjust each

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measurement to a common reference date. Data sets with a X^2/n value above the range should be inspected for outliers using standard statistical methods and either additional measurements performed to bring the set within limits or the counting system repaired and a new data set acquired, as indicated by the results of the distribution analysis.

The CONCHT program, a control chart generation and extension program resident on the 1123+ computer system, should be used to perform all necessary calculations and complete the controls generation process. Decay correction capability for the individual data is incorporated in the program. Instructions for using the CONCHT program are included in the MISCELLANEOUS PROGRAMS RSX-11M SYSTEM BASED documentation manual. The remaining steps of this procedure serve primarily to document the necessary operations.

- (e) Calculate the relative standard deviation of the data.

$$\sigma = \sqrt{\frac{\sum x^2 - \bar{x} \sum x}{n - 1}}$$

where σ = the relative standard deviation in counts per minute and other quantities are the same as in (d) above.

Relative standard deviations greater than 1% of the average count, $\bar{x}$, are atypical of the LB-1000 system and should be investigated.

- (f) Calculate control limits corresponding to the desired statistical confidence level, usually the 95%.

$$\text{statistical confidence level limits} = \bar{x} \pm \zeta a$$

where ζ = a factor from a statistical table of cumulative distribution at $n - 1$ degrees of freedom for the desired confidence level, and other quantities are the same as in (e) above for ten counts. (10 - 1 = 9 degrees of freedom).

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$\zeta = 2.262$ at the 95%, 3.250 at the 99%, and 4.781 at the 99.9% confidence level limits.

Calculate control limits corresponding to $\pm 1\%$, $\pm 2\%$, and $\pm 3\%$ of the average count, $\bar{x}$.

$$\begin{aligned}\pm 1\% \bar{x} \text{ limits} &= \bar{x} \pm 0.01 \bar{x} \\ \pm 2\% \bar{x} \text{ limits} &= \bar{x} \pm 0.02 \bar{x} \\ \pm 3\% \bar{x} \text{ limits} &= \bar{x} \pm 0.03 \bar{x}\end{aligned}$$

- (g) Calculate the corresponding detection limits on December 31 of the current calendar year for $\bar{x}$ and each of the control limits calculated at (f) by decay correction.

$$\text{decay corrected value} = [V] \left[e^{-\frac{(0.693147)(DI)}{T_{1/2}}} \right]$$

where V = the value measured on the reference date of the control data set

0.693147 = the natural logarithm of 2

DI = the decay interval between the reference date of the control data set and December 31 of the current year

$T_{1/2}$ = the half life of the control source nuclide expressed in the same time units as the decay interval.

This equation is used thereafter to extend the control data set limits for use on control charts for subsequent years so long as the data remains valid.

- (h) Prepare a control chart using 1 year by days x 180 divisions graph paper (K+E 47-2730).
1. Label the blocks of daily numbered lines of the horizontal scale January through December.
 2. Calculate a scale increment for the vertical scale that will accommodate the range in count rate that the control limit set requires.

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$$\text{scale increment (counts/division)} = (L_H - L_L)/180$$

where L_H = the highest of the limits of the control data set, usually the +3% of $\bar{x}$ value of the reference data set, expressed in counts per minute.

L_L = the lowest of the limits, usually the -3% of $\bar{x}$ value of the decay corrected data set.

180 = the number of vertical divisions available.

3. Adopt a vertical scale increment that is minimally larger than that calculated in (2) so that some space is available for plotting near outliers and each increment is equal to the product of 1, 2, 2.5, or 5 and a power of 10; that is, each vertical division corresponds to 1, 10, 100, 1000, ... 2, 20, 200, 2000, ... 2.5, 25, 250, 2500, ... or 5, 50, 500, 5000 ... counts per minute. Label the vertical scale accordingly.
4. Plot the count rates corresponding to the control limits of (f) on the reference date at the horizontal co-ordinate for that reference date. Similarly plot the decay corrected limits of (g) on the December 31 horizontal coordinate. Rule lines between the corresponding limits of the reference date and December 31, differentiating them by color if desired. Label each line with the identity of that limit (x, $\pm 1\%$, 95% confidence level, etc.).

Radioactive decay is an exponential process. Drawing a straight line between calculated control values provides a practical approximation of the true control limits between these values. The slope of a true decay-based limit would be greater initially and lesser at the end than the straight line function; the two coincide at the extremes of the control range.

Label the chart with the instrument or system to which it applies (LB-100), the control source to

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which it applies (Pu-239, SrY-90, or Tc-99), and the year represented. The control chart is now ready for use in evaluating routine control counts (refer to section Control Maintenance).

So long as the current control set data remains valid, control charts may be prepared for subsequent years by using step (g) to decay correct the data to additional December 31s and preparing new charts (step h). This capability is incorporated into the CONCHT computer program.

Control Maintenance. SrY-90, Tc-99, and Pu-239 control standards are counted at least once during each day on which the counter is used. Normally this is done at the beginning of the day shift, immediately after satisfactory background counts are obtained. All alpha and beta control measurements are recorded in the control section of the LB-1000 Calibration and Control Log.

Control source counting is performed using the following procedure:

- (a) Make a background count using the procedure of Subsection 4.9.2.
- (b) Count each control standard using the procedure of Subsection 4.9.3. Calculate the observed count rate. The Pu-239 alpha control and the SrY-90 beta control are counted 10 minutes; the Tc-99 beta control is counted 20 minutes.

$$c/m = \frac{C}{T} - b$$

where C = the observed total count

T = the counting time in minutes

b = the background in counts per minutes determined at (a) above.

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- (c) Record the alpha and beta control count data in their respective columns in the control section of the LB-1000 Calibration and Control Log as follows:

alpha: date and time of count, gross alpha count, and gross beta channel count (alpha crosstalk to the beta channel).

beta: Date and time of count, gross beta count, and for the SrY-90 control source, the gross alpha channel count (beta crosstalk to the alpha channel).

Gross beta channel count for an alpha control (alpha crosstalk to the beta channel) and gross alpha channel count for a beta control (beta crosstalk to the alpha channel) are recorded for historical purposes; they are useful when instrument malfunctions develop.

- (d) Plot the background corrected count rates obtained on their respective control charts in the control section of the LB-1000 Calibration and Control Log and determine control status. Limits for the 95% confidence level, $\pm 1\% \bar{x}$, $\pm 2\% \bar{x}$, and $\pm 3\% \bar{x}$ are indicated on the control charts. If all the control measurements are within their respective $\pm 3\% \bar{x}$ control limits, the instrument is ready for use.

Should one or more control measurements fall outside of $\pm 3\% \bar{x}$ control limits, repeat those control counts. If the recount(s) fall within limits the instrument is considered to be operating in control and can be used for sample counting. If any recount again falls out of limits, the instrument must not be used until the problem is investigated and corrected.

4.7 ANALYSIS

4.8 CALCULATION

4.9 OPERATION

4.9.1 Gas Flow

Gas flow through the LB-1000 detectors must be maintained at 0.125 SCFH as indicated by the flow meter on the

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instrument face plate. Gas cylinders should be changed when the cylinder pressure falls to 500 psi; experience has shown the control tends to drift outside established limits as this last gas fraction in a cylinder is used. When a cylinder is changed, or the gas supply is interrupted for other reasons, purge the detector at least 30 minutes at full scale flow rate on the flowmeter. Failure to purge at a flow rate higher than operating flow rate may result in a low bias in the low energy beta control, followed by a slow drift requiring as long as two weeks to return to former control level.

4.9.2 Background Count

Background is usually measured as a count of approximately 900 minutes duration begun at the end of the day shift and terminated at the beginning of the next. The background values obtained are recorded in the control section of the LB-1000 Calibration and Control Log and are used with all subsequent counts until a new background is run.

- (a) Check the operational controls on the counter and adjust settings if necessary to conform to Table 1.

Table 1 gives the normal operational settings. Do not use different settings unless otherwise instructed.

- (b) Pull the sample slide out.
- (c) Place a blank (background) dish in the plastic sampler holder.

This dish must be clean; handle it only with a pair of forceps.

- (d) Place the sample holder into the sample slide and push the slide slowly into the instrument until a slight resistance is felt; then carefully push the slide all the way in.

At the point of resistance, the handle on the slide will be about 5.7 cm (2 1/4 inch) from the face of the instrument.

- (e) Clear the scalers by switching the count toggle switch of the timer/scaler to STOP and pushing the RESET button.

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- (f) Set the preset time on the timer/scaler to OFF. This is an indeterminate count mode that allows counting to continue until manually halted (refer to Subsection 4.9.3 Step (c) for a description of the preset time function).
- (g) Switch the count toggle to COUNT to begin counting.
- (h) When the count is to be terminated, switch the timer/scaler count toggle switch to STOP.
- (i) Record the current date in the Date column of the first blank line in the control section of the LB-1000 Calibration and Control Log, then record the length of the background count and the total counts accumulated in both the alpha and the beta scalers together with the count duration indicated on the timer/scaler in the alpha and beta background column's, respectively. The timer/scaler overflows to 0 after 9999.9 minutes, about 6.9 days.

Calculate the alpha and beta channel backgrounds:

$$c/m = \frac{C}{T}$$

where C = the observed total count accumulated in a given scaler

T = the count duration in minutes.

The backgrounds should not be greater than 0.3 c/m for the alpha channel or 3.0 c/m for the beta channel. If either level is exceeded, investigate the correct problem. A common source of high background is contamination on the sample holder and blank dish.

Record the calculated background count rates next to the respective gross background count date in the alpha and beta background columns of the LB-1000 Calibration and Control Log.

- (j) Pull out the sample slide and remove the sampler holder and blank dish. If no more counting is to be performed immediately, leave the blank dish in

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be performed immediately, leave the blank dish in the counter with the instrument running in the indeterminate count mode.

4.9.3 Sample Count

Counting data is recorded on a preprinted two page stack program particle filter counting data sheet. Filter samples currently active in the STACK program are printed in numerical order by building designation. Separate lines for alpha and beta channel count data are provided for each sample. Designation of the LB-1000 counter, a 1650V operating voltage, P-10 gas, and a ten minute counting interval are also preprinted. Table 2 indicates the data and other information that is to be entered on the form. The form is reproduced by copying machine so that it can be readily revised to reflect changes in program sampling schedules.

- (a) Place the sample dish in the counter, following Steps (b) through (d) of Subsection 4.9.2.

Handle each dish with a pair of forceps.

- (b) Clear the scalers by switching the count toggle switch of the timer/scaler to "STOP" and pushing the RESET button.
- (c) Set the preset time on the timer/scaler to the desired counting interval, usually 10 minutes. Counting will stop automatically when the preset time has elapsed.

Operation of the TC-547P timer/scaler module as a TIMER is controlled by two toggle switches and two multi-position knobs on the front panel.

1. The scaler/timer toggle switch determines whether the TC-546P functions as a timer or simply as a scaler for accumulating counts. The toggle always remains in the TIMER position.
2. The .01 min/.1 sec toggle switch determines whether the two multi-position preset selection knobs function in units of 0.01 minute or 0.1 second. Since the .01 minute position provides a range of counting times from .01 minute (0.6 second) to 9000 minutes,

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the toggle conveniently remains in the .01 MINUTE position.

3. The upper multi-position preset selection knob with positions labeled OFF and "1" through "9" sets the one significant digit of the count duration. The OFF position is an indeterminate count mode which disables the preset function and allows manual operation of the TC-547P via the count/stop toggle.
4. The lower multi-position preset selection knob with positions labeled " 10^0 " through " 10^5 " sets the multiplier of the .01 minute/.1 second toggle setting that is applied. Since $10^0 = 1$, with the toggle in the .01 minute position, the settings of this knob establishes counts in the .01 minute through 9000 minutes range.

To obtain a 10.0 minute preset count, the upper and lower preset selection knobs would be set to "1" and " 10^3 " respectively since $1 \times 10^3 \times .01 = 10$. Note that only the first significant digit of a count duration is selectable. Counting intervals between these values can be obtained by changing to 0.1 SECOND MODE and adjusting the preset selection knobs to the nearest approximation expressed in seconds.

- (d) Switch the count toggle to COUNT to begin counting. Record the date and time the count was begun on the sample counting data sheet on the corresponding sample line. After the first count of a series, subsequent counts can be started by simply pressing "RESET;" it is not necessary to use the COUNT/STOP toggle function.
- (e) After counting stops, record the total counts accumulated on both the alpha and beta scalers (and the count duration if it is different then the 10.0 minutes preprinted on the data sheet) on the sample counting data sheet on their respective lines under the corresponding sample. Copy the alpha and beta channel background from the corresponding date lines of the LB-1000 Calibration and Control Log to the background column of their respective lines of the counting data sheet.

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- (f) Remove the plastic sampler holder and sample dish. When no more counting is to be performed, install a blank dish in the counter and start the instrument counting in the indeterminate count mode (refer to step (c) above).

4.9.4 Determination of Beta and Alpha Response and Optimum Operating Voltage

Alpha and beta plateau measurements are performed whenever a counter is set up, when problems develop in the operation of the counter, when system parameters are changed, or after repair work. All alpha and beta plateau data are entered in their respective sections of the LB-1000 Calibration and Control Log. Proceed as follows:

- (a) Place the Pm-147 beta plateau source in the counter (refer to Steps (b) through (d) of Subsection 4.9.2).
- (b) Set the high voltage power supply to 900 V.
- (c) Set the preset time on the timer/scaler to 5 minutes.
- (d) Clear the scalers by switching the count toggle switch on the timer/scaler to STOP and pushing the RESET button.
- (e) Switch the count toggle switch to COUNT to begin counting.

Counting is automatic and will stop after the preset time has elapsed.

- (f) Record the voltage setting and the total counts accumulated in both the alpha and beta scalers.
- (g) Increase the voltage of the power supply by 50 V. Press RESET to repeat the count.
- (h) Repeat Step (g) until both the beta and the alpha channel counts are approximately double the count observed at the beta channel "plateau" and are increasing rapidly (approximately 2200 V).

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- (i) Plot each beta-channel total count (y-axis) versus voltage (x-axis) in blue on a 11 x 15 inch sheet of 10 x 10 to 1/2 inch scale linear graph paper. Similarly plot each alpha-channel total count in red on this chart.

Mark the voltage point on the alpha-channel curve where more than two counts first appear in the alpha channel. Label that point "threshold of beta crosstalk into alpha channel."

- (j) Repeat Steps (c) through (h) with the Pu-239 alpha plateau source, beginning with a high voltage power supply setting of 100 V.
- (k) On another sheet of graph paper, plot each alpha-channel total count (y-axis) versus voltage (x-axis) on linear graph paper in red. Similarly plot the total beta-channel counts obtained from the Pu-239 standard on this chart in blue.
- (l) From the curve obtained at Step (i), determine the voltage corresponding to a point 50 volts above the beginning of the plateau of the beta channel. The point should lie approximately 100 volts above the "knee" at the lower end of the plateau.
- (m) From the curves obtained at Step (k), determine the voltage corresponding to the minimum count in the plot of beta channel data under the plateau in the alpha channel.

This voltage corresponds to the position on the alpha plateau where alpha crosstalk into the beta channel is a minimum.

- (n) Select the lower of the two voltages found in Steps (l) and (m) as the operating voltage.

Ideally both points are the same. The voltage selected must fall somewhere on the alpha channel plateau for the alpha source and on the beta channel plateau for the beta source. It should also lie below the "threshold of beta crosstalk into alpha channel" determined at Step (i). If not, determine if a problem exists.

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PNL TECHNICAL PROCEDURE

5.0 BIBLIOGRAPHY

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- (b) Instruction Manual, LB-1000 Low Background Counting System, Tenelec Corp., Oak Ridge, Tennessee.
- (c) W. J. Price, Nuclear Radiation Detection, McGraw-Hill, New York, (1958).
- (d) J. Sharpe and D. Taylor. Nuclear Particles and Radiation Detectors, Part II. Counters and Counting System, Proc. Inst. Elec. Engrs. 98 (II), 209-30 (1951).
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TABLE 1. Normal Operational Settings for LB-1000 Counter System Components

<u>TC-264</u>		<u>TC-546P</u>	
Gain (front panel)	<u>32</u>	Scaler Toggle	<u>Count</u>
Polarity (internal) ^(a)	<u>Positive</u>	Gate Toggle	<u>Coincidence</u>
Gain Range (internal) ^(a)	<u>X1</u>	Threshold	<u>0.5 V d.c.</u>
Discriminator ^(a)	<u>CCW</u>		
Delay ^(a)	<u>CCW</u>		
Pulse Width ^(a)	<u>50μ sec</u>		
<u>TC-265</u>		<u>TC-547P</u>	
Gain (front panel)	<u>16</u>	Mode Toggle	<u>Master</u>
Polarity (internal) ^(a)	<u>Positive</u>	Gate Toggle	<u>Either Position</u>
Gain Range (internal) ^(a)	<u>X1</u>	Function Toggle	<u>Timer</u>
ULD Hi/Lo (internal) ^(a)	<u>Hi</u>	Time Base Toggle	<u>0.01 min.</u>
Delay (internal) ^(a)	<u>10μ sec</u>	(for timer to function in minutes)	
$\alpha + \beta$ Discriminator ^(a)	<u>CCW</u>		
<u>TC-945</u>			
Output Voltage	<u>1650 V</u> for P10 gas		
Gas Flow Meter	<u>0.125</u> (halfway between 0.10 and the next higher red line marker)		

(a) This adjustment is made by instrument personnel and must not be changed by an operator.

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TABLE 2. Information Required on Counting Data Sheets

The following information is recorded for each particle filter on a two page preprinted counting data sheet on which samples current to the program are listed in numerical order by building or FFTF sample code.

- On date
- Off date
- Instrument used, mode of operation, and operating voltage
- Length of count, usually 10 minutes
- Data and time of count.
- Total sample count, alpha and beta channels
- Background in c/m, alpha and beta channels

With the exception of the date and time of a count and the total sample count in both alpha and beta channels, the above information need be entered only once on the counting data sheets unless there is a change from that entry.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-439, REV. 0, DETERMINATION OF ^{63}Ni AND ^{59}Ni

APPLICABILITY

This procedure is used to separate Ni from beta and gamma emitting radionuclides in water and aqueous leachate or dissolved samples. The separation is accomplished by precipitation separations. The Ni is then electroplated. Yield (or recovery) is determined from the 2.5 hour ^{65}Ni tracer by gamma spectroscopy. ^{59}Ni decays by electron capture and is determined by measuring the Co X-rays of its daughter with a low energy photon (LEP) detector. ^{63}Ni is determined by beta counting.

DEFINITIONS

squirt - typical volume delivered from transfer pipet in step 3.12
 ppt - precipitate
 sat. - saturated
 conc - concentrated
 keV - kilo electron volt
 MeV - mega electron volt
 dpm - disintegrations per minute
 DMG - dimethylglyoxime
 NMF - neutron multiplier facility
 SSA - self absorption factor
 std - standard

RESPONSIBLE STAFF

Cognizant Scientist
 Analyst

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during analysis shall be specified. A tolerance limit can be stated with a measurement value given in a method. If a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

Author N. L. Wynhoff	Date 7-11-91	Project Mgr. B. M. Gillespie	Date 7-15-91	QAD Representative G. K. Gerke	Date 7-2/91
Technical Reviewer C. W. Thomas	Date 6-20-91	Line Mgr. J. M. Latkovich	Date 7-5-91	Other	Date
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- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Reagents

All chemicals used are reagent grade unless otherwise specified. The water used is deionized or distilled water.

- 2.1 Ni tracer, 10 mg/ml - Dissolve 24.77 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water. Dilute with water to 500 ml in a Class A volumetric flask.
- 2.2 Sr carrier (holdback carrier), 10 mg/ml - Dissolve 18.1 g SrCl_2 in water. Dilute to 1 liter with water. (Note: another strontium salt may be used or another concentration as long as the required mg of Sr^{+2} are added.)
- 2.3 Cs carrier (holdback carrier), 10 mg/ml - Dissolve 12.7 g CsCl in water. Dilute to 1 liter with water. (Note: another cesium salt may be used or another concentration as long as the required mg of Cs^{+1} are added.)
- 2.4 Fe carrier, 10 mg/ml - Dissolve 18.1 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in water. Dilute to 250 ml with water. (Note: another ferric salt may be used or another concentration as long as the required mg of Fe^{+3} are added.)
- 2.5 6 M NaOH - Dissolve 24 g of NaOH in 80 ml of water, allow to cool. Dilute to 100 ml with water. (Note: Other concentrations may be used for better control of neutralization.)
- 2.6 6 M HCl - 50 ml conc HCl and 50 ml water
- 2.7 5% NH_4Cl - Dissolve 5 g NH_4Cl in 80 ml water. Dilute to 100 ml with water.
- 2.8 conc NH_4OH
- 2.9 conc HCl

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2.10 Dimethylglyoxime (DMG), sat. - Add sufficient DMG (2 - 3 g) to 50 ml ethanol with mixing to form a saturated solution. Let stand overnight (Note: Solution is saturated when solid DMG is still present).

2.11 conc HNO_3

2.12 conc H_2SO_4

2.13 Thymol Blue indicator, 0.04% - Dissolve 0.1 g in 18 ml of 0.012 M NaOH (1:500 dilution of 6 M NaOH with water) with stirring and heat if necessary. Dilute to 250 ml with water. (Note: Commercially prepared indicator may be used with proper dilution.)

2.14 50% NH_4OH - A fresh solution of 50 ml water and 50 ml conc NH_4OH shall be made within a week of use. Label container with the preparation date. (Note: Other concentrations lower than 50% may be used for better control of neutralization.)

2.15 Ethanol

3.0 Supplies

3.1 Small polyethylene snap-cap irradiation vials (1.3 ml maximum capacity)

3.2 Large polyethylene snap-cap irradiation vials (7 ml maximum capacity)

3.3 Soldering iron

3.4 Neutron multiplier facility (NMF)

3.5 Stainless steel electroplating disc, 7/8 in. (22 mm) diameter

3.6 Heat lamp

3.7 Mylar sheet, nominal thickness 5/10,000 in.

3.8 50 ml conical centrifuge tube, glass or plastic

3.9 pH paper, fine range with range centered near pH 7

3.10 pH paper, gross range, pH 2 to 10

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3.11 Centrifuge for tubes from Sec. 3.8 and 3.14

3.12 Plastic disposable transfer pipet that delivers 2 - 3 ml per squirt

3.13 50 ml glass beakers (or larger)

3.14 50 ml plastic conical centrifuge tubes with screw caps

3.15 Hot plate

3.16 Engraver

3.17 Electroplating apparatus: consists of power supply, electrical leads, plating cell, and platinum strip electrodes

4.0 Chemical Procedure

Except where responsibility is specifically assigned to a cognizant scientist, the analyst may perform all work.

All pertinent data (e.g., aliquot volumes), observations, and calculations shall be recorded in a project record in a manner traceable to the sample.

When an added volume is a feature of the general calculation, the automatic pipette must have had an acceptable performance check before use on the day the volume is pipetted. To performance check a pipette, pipet and weigh at least three aliquots of D.I. water equal to the volume being used, into a tared container. Weigh and determine the net weight of water. Calculate the average, standard deviation and % standard deviation. The weights must agree to within $\pm 3\%$ of the measured volume or a different pipette shall be checked and used. Correct the weight measured and the standard deviation for temperature effects on the actual delivered volume using the formulas:

$$\text{avg. weight (g)} \times \text{volume factor (ml/g)} = \text{volume (ml)}$$

$$\text{std deviation (g)} \times \text{volume factor (ml/g)} = \text{std deviation (ml)}$$

The value of the volume factor is dependent on the ambient temperature and is found the Relative Density and Volume of Water table (Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, and Exhibit

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1). The data and this calculation shall be recorded in the Pipet Calibration Logbook.

- 4.1 Transfer at least 1.2 ml of 10 mg/ml Ni tracer to a 1.3 ml polyethylene snap-cap vial. Heat seal it closed with a soldering iron.

Note: Several vials of tracer are usually prepared at one time to assure a readily available supply for future use.

- 4.2 Put one small vial full of Ni tracer and one empty small vial (as a spacer), into a 7 ml polyethylene vial and heat seal shut.

- 4.3 The day before Ni analysis is run, deliver one prepared tracer vial to the NMF for overnight irradiation.

- 4.4 Reserve two high resolution Ge gamma detectors and verify that they have current background counts and are in control per procedure No. PNL-ALO-470.

- 4.5 Pipet 200 μ l irradiated Ni tracer onto a clean stainless electroplating disk that has been labelled with "Ni tracer" and the date. Dry under a heat lamp. This is the tracer std. Wrap in Mylar, seal with tape and count on each of the high resolution Ge gamma detectors to be used to count the samples.

Note: Record the exact volume (and std deviation) of Ni tracer pipetted.

Note: Complete step 4.5 immediately to complete counting as soon as possible. This early count gives the best counting statistics for this yield standard and prevents scheduling delays in counting the samples.

- 4.6 Transfer the sample aliquot (specified by a cognizant scientist) to a 50 ml conical centrifuge tube. Dilute to 5 - 15 ml with water.

Note: Record the exact volume (and std deviation) of the sample aliquot.

- 4.7 Add 5 mg Sr carrier, 5 mg Cs carrier, and 1 mg Fe carrier.

- 4.8 Add 200 μ l irradiated Ni tracer.

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Note: Record exact volume (and std deviation) of Ni tracer pipetted.

4.9 With mixing, adjust pH to 7 (not basic) with 6 M NaOH solution (and, if necessary, 6 M HCl), checking pH with a fine range pH paper whose range is centered near pH 7. Centrifuge and discard solution.

Note: Other concentrations of NaOH and HCl may be used for better control of neutralization.

4.10 Dissolve ppt with a few drops 6 M HCl.

4.11 To acid solution add 2 squirts of 5% NH_4Cl . Make solution basic with conc NH_4OH (about 3 or 4 squirts), until rust-colored $\text{Fe}(\text{OH})_x$ ppt is present or gross range pH paper indicates $\text{pH} \geq 8$. Allow to sit for 10-20 minutes.

4.12 Centrifuge; decant and save solution in 50 ml glass beaker (or larger).

4.13 Make solution acid with conc HCl, visually checking with gross range pH paper ($\text{pH} \leq 2$).

4.14 Add 4 squirts DMG solution. Make basic with conc NH_4OH , visually checking with gross range pH paper ($\text{pH} \geq 8$). Allow to sit until red ppt forms (about 1 hour).

4.15 Transfer to a 50 ml plastic, conical centrifuge tube with water. Cap and centrifuge 5 to 10 minutes. Discard solution.

4.16 Dissolve red ppt with a minimum of conc HNO_3 and quantitatively transfer to a 50 ml beaker.

4.17 Take this solution to dryness on a hot plate (setting of 3) 3 times with conc HNO_3 . (This destroys the DMG.)

4.18 Dissolve in 500 μl conc H_2SO_4 . Cautiously add 3 ml H_2O .

4.19 Remove from hot plate and cool to near room temperature.

4.20 Add 2 - 6 drops of 0.04% thymol blue indicator.

4.21 Add 50% NH_4OH solution (and conc H_2SO_4 , if needed) until color just changes to green.

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Note: NH_4OH reagent shall be made within a week of use. 50% NH_4OH and conc H_2SO_4 usually work well. Lower concentrations may be used for better control of neutralization.

4.22 Remove disk cover from a 7/8" polished metal plating disk which has the sample i.d. engraved on the back. Wash with ethanol and wipe with a tissue paper to remove adhesive. Let dry.

4.23 Mount sample disk in electroplating cell.

4.24 With water, quantitatively transfer sample to cell and fill cell to near top.

4.25 Insert electrodes and electroplate at 1 amp for 1 hour.

4.26 Wash electrodes with water while removing them and turn power off. Remove sample solution from cell and discard.

4.27 Remove electroplated disk from cell and wash disk with water, then with ethanol. Let dry.

4.28 Wrap disk in Mylar and seal with tape.

5.0 Gamma Counting Procedure

5.1 Count as soon as possible (definitely before the end of the day) on the high resolution Ge gamma detectors used in step 4.5 to count the tracer std. This sample count is for ^{65}Ni yield. The peaks are at 1482 and 1116 keV.

5.2 Let ^{65}Ni ($t_{1/2} = 2.5$ hr) decay at least 24 hours after counting for ^{65}Ni yield before doing step 5.3.

5.3 If ^{59}Ni analysis is requested, count on an LEP diode. ^{59}Ni decays by electron capture and has a Co x-ray at 6.9 keV.

5.4 After gamma counting is complete, store sample disks in cardboard holders labelled with matching sample identifications.

5.5 Beta counting for ^{63}Ni is described in Sec. 6.3.

6.0 Calculation and Beta Counting Procedure

6.1 ^{65}Ni Tracer Yield

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The 1482 keV and the 1116 keV peaks or the 1482 keV peak alone may be used from the high resolution Ge gamma counts to calculate the ^{65}Ni yield. This is used to correct the ^{63}Ni and ^{59}Ni results for processing losses.

For each sample or tracer std count, the net cpm (i.e., background-corrected cpm) of ^{65}Ni is calculated and decay-corrected to time zero. (Time zero is chosen to be an arbitrary time before the first tracer std is counted.)

The net cpm of the ^{65}Ni tracer is converted to yield (fractional) by the following equation:

$$^{65}\text{Ni Yield} = \frac{(\text{sample net cpm}) (A)}{(\text{tracer std net cpm})} \quad (1)$$

where: net cpm for both sample and tracer std are decay-corrected to time zero and are from gamma counts on the same detector

A = a factor to account for any differences between the aliquot of tracer added to the sample and that evaporated as the tracer std.

6.2 ^{59}Ni Calculation

The 6.9 keV Co x-ray peak (from the electron capture decay of ^{59}Ni) counted on the LEP diode is used to calculate ^{59}Ni in the sample using the following equation:

$$^{59}\text{Ni} = \frac{(\text{net cpm})(d/c)(B)}{(\text{Ni-65 yield})} \quad (2)$$

where: net cpm = gross cpm - background cpm

d/c = disintegration per count, an efficiency factor for ^{59}Ni for this electroplated disk geometry for the detector used

B = a factor or factors to account for sample volumes, dilutions, aliquots, weights and any

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other factors needed to produce the appropriate reporting units. These factors shall be documented as part of the project record.

6.3 ^{63}Ni Calculation

The 67 keV (maximum energy) ^{63}Ni beta particle counted on a beta proportional counter may be used to calculate ^{63}Ni in the sample using the following procedure. The sample is counted through at least one aluminum absorber as well as without an absorber. A cognizant scientist will decide whether a "single absorber" count will be taken or whether a series of absorber counts will be required. This determination is based on the gamma count in Sec. 5.1 (see Note below) and on the final review of the beta counting data. Beta counting data shall be recorded on a Beta Counting Sheet (Exhibit 2).

Note: The gamma count of the ^{65}Ni tracer on the electroplated sample for yield determination (Sec 5.1) also informs us of the degree of contamination from gamma-emitting radionuclides such as ^{60}Co and ^{125}Sb . This measurement allows the cognizant scientist to determine how extensive the beta absorber counting must be to measure ^{63}Ni and/or whether the sample must be reanalyzed. The most common interfering activity in activated metal samples is ^{60}Co carried through the separation procedure. Such a single interference can usually be separated by beta absorption corrections. However, if several interfering nuclides have carried through the procedure, further radiochemical separation may be necessary. This will also be determined by the cognizant scientist.

Note: Beta-gamma anticoincidence and liquid scintillation counting are alternative measurement techniques.

6.3.1 Single Absorber Count

- a) Count the sample twice on the same beta counter: once with no absorber (i.e., 0 mg/cm²) and once with a 4 - 10 mg/cm² aluminum absorber between the sample disk and the detector (for ^{60}Co). Record the shelf number and the exact absorber thickness with the counts observed.
- b) Establish the ^{60}Co factor (for each exact absorber thickness) by counting a ^{60}Co electroplated standard with

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the same absorber used for the sample and with no absorber. Record the shelf number and the exact absorber thickness with the counts observed. (The activity need not be known accurately but should be sufficient to obtain enough counts to achieve a reasonable uncertainty, usually $\geq 10,000$ counts.)

Calculate the fraction of ^{60}Co through the absorber:

$$^{60}\text{Co} \text{ frac} = \frac{\text{net cpm through absorber}}{\text{net cpm, no absorber}} \quad (3)$$

- c) Calculate the interference-corrected net cpm (corr net cpm) of ^{63}Ni :

$$\text{corr net cpm} = (\text{no-abs cpm}) - \frac{\text{net cpm thru absorber}}{\text{Co-60 frac}} \quad (4)$$

where: (no-abs cpm) = net cpm without an absorber.

Note: For other interferences, other thicknesses of single absorbers (depending on the energy of the interfering activity and the energy of the ^{63}Ni beta) or a series of absorbers may be specified by a cognizant scientist.

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6.3.2 ^{63}Ni is calculated using the following equation:

$$^{63}\text{Ni} = \frac{(\text{corr net cpm})(d/c)(B)}{(\text{Ni-65 yield})(\text{SSA})} \quad (5)$$

where: d/c = disintegration per count, an efficiency factor for ^{63}Ni for this electroplated disk geometry for the detector used

B = a factor or factors to account for sample volumes, dilutions, aliquots, weights and any other factors needed to produce the appropriate reporting units. These factors shall be documented as part of the project record.

SSA = the self absorption factor to correct for count rate losses due to absorption and scatter of the beta particles within the nickel electroplated on the disk and thus not measured by the detector. This factor is calculated according to Sec. 6.3.3 and documented in the project record.

6.3.3 Calculation of the Self Absorption Factor (SSA)

a) The self absorption factor (SSA) may be calculated from the following equation or taken from a graph of SSA vs weight of electroplated Ni:

$$\text{SSA} = \frac{A}{A_0} = \frac{(1 - e^{-\mu x})}{\mu x} \quad (6)$$

where: A = the activity reaching the detector
 A_0 = the total activity of the electroplated ^{63}Ni
 μ = mass absorption coefficient in cm^2/mg (Eqn. 7)
 x = density thickness of electroplated deposit in mg/cm^2 (Eqn. 8)

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- b) The mass absorption coefficient, μ , in cm^2/mg , may be determined directly from an absorption curve using a ^{63}Ni standard or may be estimated from an empirical equation, such as the following:

$$\mu = 0.01367 (E_{\text{max}})^{-1.633} \quad (7)$$

where: E_{max} = the maximum beta energy (MeV) of the nuclide being analyzed.

- c) Density thickness, x : The amount of Ni carrier (i.e., Ni, not Ni salt) added to the sample is known. The total fraction of Ni carried through the procedure has been determined above as the ^{65}Ni yield. Therefore, the mass of Ni electroplated on the disk (see Note below) and contributing to the SSA expressed in units of density thickness (mg/cm^2) can be calculated using the following equation:

$$x = \frac{(\text{mg Ni carrier added}) (\text{^{65}Ni yield})}{(\text{area of electroplate on disk})} \quad (8)$$

Note: Normally the mass of nickel present in the sample aliquot is insignificant for determination of SSA when compared to the amount of carrier added. However, for certain metal samples (e.g., Inconel containing about 50% Ni), the mass of nickel in the sample aliquot analyzed will have to be estimated or determined and possibly included with the carrier mass in the above equation.

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RELATIVE DENSITY AND VOLUME OF WATER

The mass of one cubic centimeter of water at 4° C is taken as unity.

The values given are numerically equal to the absolute density in grams per milliliter.

(Smithsonian Tables, compiled from Various Authors.)

Temp. ° C.	Density.	Volume.	Temp. ° C.	Density.	Volume.
-10	0.99815	1.00186	+35	0.99406	1.00598
-9	843	157	36	371	633
-8	809	131	37	336	669
-7	892	108	38	299	706
-6	912	988	39	262	743
-5	0.99930	1.00070	40	0.99224	1.00782
-4	915	055	41	186	821
-3	958	012	42	147	861
-2	970	031	43	107	901
-1	979	021	44	066	943
+0	0.99987	1.00013	45	0.99025	1.00986
1	993	007	46	0.98982	1.01028
2	997	003	47	940	072
3	999	001	48	896	116
4	1.00000	1.00000	49	852	162
5	0.99999	1.00001	50	0.98807	1.01207
6	997	003	51	762	254
7	993	007	52	715	301
8	988	012	53	669	349
9	981	019	54	621	398
10	0.99973	1.00027	55	0.98573	1.01448
11	963	037	60	324	706
12	952	048	65	059	979
13	910	060	70	0.97781	1.02270
14	927	073	75	489	576
15	0.99913	1.00087	80	0.97183	1.02899
16	897	103	85	0.96865	1.03237
17	890	120	90	534	590
18	862	138	95	192	959
19	843	157	100	0.95838	1.04343
20	0.99823	1.00177	110	0.9510	1.0515
21	802	198	120	0.9434	1.0601
22	780	221	130	0.9352	1.0693
23	756	244	140	0.9264	1.0794
24	732	268	150	0.9173	1.0902
25	0.99707	1.00293	160	0.9075	1.1019
26	681	320	170	0.8973	1.1145
27	654	347	180	0.8866	1.1279
28	626	375	190	0.8750	1.1429
29	597	405	200	0.8628	1.1590
30	0.99567	1.00433	210	0.850	1.177
31	537	466	220	0.837	1.195
32	505	497	230	0.823	1.215
33	473	530	240	0.809	1.236
34	440	563	250	0.794	1.259

BETA COUNTING DATA

REQUESTED BY		DATE ANALYZED	SAMPLE TYPE	CHARGE CODE
REMARKS				
SAMPLE DESIGNATION	DATE - TIME SAMPLED	CARRIER (M L)	PROCESS	WT. - VOL. ANALYZED
ANALYST	WT. RESIDUE	SET NUMBER	SHELF	DATE - TIME COUNTED
COUNTS	MINUTES	BKG. C/M	BKG. CORR. C/M	TECHNICIAN
CALCULATIONS		RESULTS		
$\frac{(C/M) (VOLUME FACTOR)}{(C/M) (2.22 \times 10^6) (1.51) (85) (55.5) (4.47) (1710)}$		UNITS OF μC		

No 1673

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-440, (Replaces HTA-4-18 & 7-40.15), SELENIUM-79 BY ION EXCHANGE AND DISTILLATION SEPARATION PRIOR TO MEASUREMENT BY LIQUID SCINTILLATION COUNTING

1.0 APPLICABILITY

This procedure applies to the preparation of aqueous samples for the determination of Se^{79} measured using liquid scintillation counting (Procedure PNL-ALO-490).

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

4.0 PROCEDURES

4.1 Equipment and Materials

- Selenium carrier, 10 mg/mL -- Prepare by dissolving about 1.0 g (weighed to 0.1%) of gray selenium metal in a 100 (± 0.08) mL volumetric flask using 5 to 6 mL of hot concentrated reagent- grade nitric acid. When dissolution is complete, remove from the heat and dilute the selenium solution to slightly less than the volumetric mark with 0.5 M nitric acid. Allow the solution to cool to ambient temperature and dilute to the volume mark with 0.5 M nitric acid. Stopper the volumetric flask and mix the solution by inverting the flask, while holding the stopper in place, at least 20 times, and swirling the solution each time. Record the weight of selenium metal used and the volume in the Laboratory Record book and record the mg/mL of selenium on the container used for storing the selenium carrier.

Author	Date	Project Mgr.	Date	QAD Representative	Date
TC Maiti/AE Kozelisky	8/13/90	N/A		GK Gerke	9/4/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
BM Gillespie	8/14/90	JH Kaye	10/11/90	All original signatures on file	
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PNL TECHNICAL PROCEDURE

- Nitric acid, 0.5 M -- Prepare by diluting 32 (± 1) mL of Ultrex concentrated nitric acid to 1000 (± 1) mL with deionized water.
- Carbon-14 Standard -- Must be NBS or NBS traceable if possible. For preparation see section 4.4.
- Ion exchange resin, AG-50W,[®] X-8, 100 to 200 mesh, H⁺ form.
- Ion exchange resin, AG-1,[®] X-4, 100 to 200 mesh, Cl⁻ form.
- Nitric acid saturated with bromine -- Prepare by adding ≈ 100 μ L of reagent-grade bromine (Br₂) to 15 mL of 0.5 M nitric acid; swirl to mix.
- Bromine water -- Prepare by adding ≈ 100 μ L of reagent-grade bromine to 15 mL of deionized water; swirl to mix.
- Hydrobromic acid, 47% to 49%, reagent-grade.
- Nitrogen gas -- Reduce pressure to ≈ 2 psi, using a nitrogen gas pressure-reducing valve.
- Liquid scintillation cocktail, Altex, CP, or equivalent.
- Hydroxylamine hydrochloride, 25 wt% -- Prepare by dissolving 25 (± 1) g of the reagent-grade material in deionized water, dilute to 100 (± 1) mL, and mix. Make fresh every two weeks.
- Sodium hydroxide, 0.3 M -- Prepare by dissolving 12 (± 0.1) g of reagent-grade NaOH in 1000 (± 1) mL of deionized water.
- Ethanol, reagent-grade.
- Ultrex Nitric acid, 69% to 71%.
- Beaker, 400-mL, Pyrex[®].
- Deionized water.

[®]AG-50W and AG-1 are registered trademarks of Bio-Rad Laboratories, Richmond, California.

[®]Pyrex is registered trademark of Pittsburgh Corning, Pittsburgh, Pennsylvania.

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PNL TECHNICAL PROCEDURE

- Ice.
- Vial, 2-dram, glass, screw-cap.
- Vial, 35-mL, glass, screw-cap.
- Vial, liquid scintillation, Packard 6001018.
- Heating Block 100°C ($\pm 5^\circ\text{C}$).
- Selenium still (see Figure 1).
- Variac, 1.5-ampere output, 0 to 140 volts.
- Heating mantle, 50-mL, round bottom.
- Dropper, 7.5-mL, plastic.
- Transfer pipets, 5-mL, glass.
- Thermometer.
- Filters. 13mm -- Prepare by cutting filter sections from Whatman 934AH glass microfiber filters of a larger size using a #9 cork borer. Place the filter on a hard, flat surface and press down with the cutting edge of #9 cork borer. Each filter must be dried at 110°C to 120°C for at least 30 minutes, cooled in a desiccator and weighed to 0.00001 g or better just prior to use to obtain the tare weight in Step 23, Section 4.2, Selenium Separation.
- Filter holder, Swinnex, 13 mm or equivalent.
- Vacuum jug with hole in stopper to accommodate the base of the 13 mm Swinnex fiber holder base.
- Petri dishes, 3 inch and 4 inch or other suitable carriers for filters.

4.2 Selenium Separation

Selenium-75 is separated from other radioactive species by passing the prepared solution through a cation plus anion exchange resin column. The selenium in the column effluent is distilled from hydrobromic acid and precipitated as metal by reducing it with hydroxylamine hydrochloride. The metal is dissolved in nitric acid, and the Se^{75} is measured using liquid scintillation counting.

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PNL TECHNICAL PROCEDURE

At least two blanks shall be analyzed with every sample set. See section 4.3.

The ANALYST shall perform the following steps unless otherwise specified. For fused samples begin at Step 1, for non-fused samples, begin at Step 1a.

- Step 1) For fused samples the ANALYST shall add to a 35-mL screw-cap vial a volume ($\pm 1\%$), up to 20 mL, of the dissolved fused sample test solution specified by the COGNIZANT SCIENTIST. Record the sample volume on the analytical report form. Add 2000 (± 20) μL of selenium carrier, and 20 (± 1) μL of bromine; add a stir bar and mix thoroughly; allow to stand 10 (± 1) minutes.
- To the vial add 10 (± 0.1) mL of 25% hydroxylamine hydrochloride and mix.
 - Place the vial in the heating block and heat until the black selenium metal precipitates, this takes about 45 minutes; then cool.
 - Centrifuge for 5 minutes.
 - Carefully remove the supernate using a transfer pipet. Wash down the sides with ≈ 10 mL of ethanol and swirl the precipitate.
 - Centrifuge for five minutes. Remove the ethanol wash using a transfer pipet.
 - Slightly warm the vial in the heating block to vaporize residual ethanol.
 - To the selenium metal slowly add 500 (± 5) μL of Ultrex concentrated nitric acid.
 - Place vial in the heating block and heat until the selenium metal dissolves.
 - Add 5 mL of bromine water to the vial. Proceed to Step 2.

- Step 1a) For non-fused samples, the ANALYST shall add to a 2-dram vial a volume ($\pm 1\%$) of test solution specified by

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PNL TECHNICAL PROCEDURE

the COGNIZANT SCIENTIST. Record the sample volume on the analytical report form. Add 2000 (± 20) μL of selenium carrier, and 500 (± 5) μL of 0.5 M nitric acid saturated with bromine; swirl to mix thoroughly.

Proceed to Step 2.

- Step 2) Prepare an ion exchange column containing 1000 (± 100) μL of AG-50W, X-8, 100 to 200 mesh, H^+ form resin and 1000 (± 100) μL of AG-1, X-4, 100 to 200 mesh, Cl^- form resin.
- Cut off the top of the bulb of a 7.5-mL plastic dropper.
 - Insert a small cotton ball into the tip of the dropper and tap lightly.
 - Measure and mark two 1000 (± 100) μL increments above the cotton.
 - Fill the dropper to the first 1000 μL mark with AG-1, X-4, 100 to 200 mesh, Cl^- form resin.
 - Fill the dropper to the second 1000 μL mark with AG-50W, X-8, 100 to 200 mesh, H^+ form resin.
 - Wash the resin column with 5 mL of deionized water.
- Step 3) Transfer the solution from Step 1 or Step 1a to the ion exchange column. Collect the column effluent in a 35-mL screw-cap vial.
- Step 4) Wash the 2-dram or 35-mL vial from Step 1 or Step 1a with four 1 mL portions of 0.5 M nitric acid plus bromine. Transfer each portion to the ion exchange column and allow each portion to drain completely before adding the next. Collect all column effluent in the 35-mL screw-cap vial from Step 3.
- Step 5) Transfer all the solution from the 35-mL screw-cap vial to a selenium still, using a plastic dropper.
- Step 6) Rinse the 35-mL vial with two 5 (± 0.1) mL portions of hydrobromic acid and transfer to the still.

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- Step 7) Adjust the heating mantle such that the still's bottom is in the mantle.
- Step 8) Place a 35-mL vial containing 5 (± 0.1) mL of 25% hydroxylamine hydrochloride in a 400-mL beaker and add ice to fill the beaker.
Note: Do NOT add ice to vial. Position the vial so that the tip of the still's exit is below the liquid level of the hydroxylamine hydrochloride in the vial.
- Step 9) Connect the still's inlet and adjust the nitrogen flow to about 5 bubbles per second.
- Step 10) Turn on the variac and set to 110 V. The temperature should rise to $\approx 120^{\circ}\text{C}$. Continue distillation for about 35 minutes. The solution in the still should be pale yellow when distillation is complete.
- Step 11) Turn off the variac and allow to cool for 2 to 3 minutes. Then remove the still from the heating mantle. Remove the vial containing the distillate and turn off the nitrogen flow.
- Step 12) To the distillate in the 35-mL vial add 5 (± 0.1) mL of 25% hydroxylamine hydrochloride.
- Step 13) Place the 35-mL vial in the heating block and heat until the black selenium metal has settled to the bottom of the vial (normally about one hour); allow to cool for 10 minutes. To clean the still at this time, see steps 38 and 39.
- Step 14) Centrifuge the 35-mL vial containing the selenium metal for 5 minutes.
- Step 15) Using a transfer pipet, remove the solution and discard. **NOTE:** Do NOT remove the black precipitate.
- Step 16) Wash down the sides of the vial with ≈ 10 mL of ethanol, and swirl the precipitate.
- Step 17) Centrifuge for 5 minutes. Remove the ethanol wash using a transfer pipet.
- Step 18) Warm the vial in a heating block to vaporize the residual ethanol.

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- Step 19) Slowly add 500 (± 50) μL of Ultrex nitric acid (69% to 71%) to the vial and heat until the selenium dissolves.
- Step 20) Add 10 (± 1) mL of deionized water to the vial and swirl to mix.
- Step 21) Add 10 (± 0.2) mL of 25% hydroxylamine hydrochloride to the vial and swirl to mix.
- Step 22) Repeat Steps 13, 14, 15, and 16.
- Step 23) Place a 13 mm dried and tared glass filter on the base of a 13 mm Swinnex filter holder. While vacuum is applied, place the base of the Swinnex holder, with the filter on top, into the hole of the stopper in the top of the vacuum flask. See instructions in 4.1, Equipment and Materials, for preparation of 13 mm glass filters. Record the tare weight on the analytical report form or in the LRB.
- Step 24) Using a glass transfer pipet, mount the black selenium metal onto the center of the filter.
- Step 25) Wash the vial with 3 to 4 mL of ethanol and transfer the residual selenium metal to the filter.
- Step 26) Remove the filter holder from the stopper in the vacuum flask.
- Step 27) Remove the filter from the filter holder and place the filter plus the selenium metal on a petri dish, or other suitable carrier, and dry in an oven at 110°C to 120°C for 30 (± 2) minutes. Cover the carrier when transporting filters to avoid loss of selenium metal from the filters due to air currents.
- Step 28) Remove the filter plus selenium metal from the oven and allow to cool in a desiccator for at least 10 minutes.
- Step 29) Weigh the filter plus selenium metal on a balance that weighs to 10 μg (0.00001 g) or better. Record the weight on the analytical report form or in the LRB.
- Step 30) Transfer the filter plus selenium metal to a liquid scintillation counting vial. Be sure no metal is lost during the transfer.

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- Step 31) Add 150 (~2) μL of concentrated nitric acid to the liquid scintillation vial to dissolve the selenium metal. Allow the selenium metal to dissolve completely before going to Step 32.
- Step 32) Add 1.0 (~0.1) mL of 0.3 M NaOH.
- Step 33) Add 14 mL of a ~~Altex-CP~~ liquid scintillation cocktail, ~~or equivalent~~, for which the quench characteristics for Se are known, such as Altex, Ultima Gold, Optiflour, etc., to the selenium solution.
- Step 34) Place the cap on the liquid scintillation vial and tighten. Label the cap with the sample I.D. and Se^{79} .
- Step 35) Mix the solution in the vial thoroughly until a clear solution is obtained.
- Step 36) Measure the Se^{79} activity using Procedure PNL-ALO-490. Since no Se^{79} standard is available for calibrations, a C^{14} standard is used. Carbon-14 and Se^{79} have similar maximum and average beta energies which makes the C^{14} standards acceptable for the measurement of Se^{79} . See Radioactive Decay Data Tables (DOE/T/C-11026). See Section 4.4, Standard Preparation.
- Step 37) Calculate yield, standard d/c, quench factor and sample d/m/mL using Section 4.5 calculations. Record volumes and calculations on the analytical report. Record liquid scintillation data in the LRB.
- Step 38) Discard the waste in the still by pulling into a vacuum radioactive waste jug through the still top.
- Step 39) Continue pulling a vacuum through the top of the still and flush the still by allowing water to be pulled up the exit arm of the still. The water in the beaker used for cooling may be used. Clean still with a series of flushes as above, with 25% hydroxylamine hydrochloride, deionized water, 8 M nitric acid, and finally with deionized water.

4.3 Blank (Background) Solution Preparation

- Step 1) Prepare Se^{79} blank (background) solutions using 500 (~5) μL of deionized water as the test solution through Section 4.2, Selenium Separation, Step 1) through Step 36).

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- Step 2) Label the vial cap as "Se79 Blank." Count the "Se79 Blank" with the samples and standards as described in Procedure PNL-ALO-415.

4.4 Standard Preparation

This solution must be made fresh during sample preparation.

- Step 1) In a liquid scintillation counting vial, mix 14 mL Altex CP liquid scintillation cocktail, 1 mL 0.3 M NaOH, and 100 μ L C14 standard solution. The C-14 standard activity should be about 3×10^5 dpm/mL.

- Step 2) Label the vial cap as "Se79 Standard." Count this with the samples and backgrounds using PNL-ALO-415.

4.5 Calculations

4.5.1 Yield Calculations

$$Y = \frac{A-B}{2C} \quad \text{where,}$$

Y = Yield as a decimal fraction

A = Weight of selenium metal plus filter as milligrams from Section 4.2, Step 29

B = Weight of filter only as milligrams from Section 4.2, Step 23

C = Selenium concentration in carrier as milligrams/milliliter. See Selenium Carrier, Section 4.1

4.5.2 Standard Disintegration/Count Factor (d/c)

$$A = \frac{B}{C-D} \quad \text{where,}$$

A = Disintegrations/count (d/c) factor used in subsequent sample calculations

B = Disintegrations/minute of C^{14} used in the standard in Section 4.4

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- C = Counts/minute in standard from liquid scintillation counting data
- D = Counts/minute in Se^{79} blank prepared in Section 4.3

4.5.3 Quench Factor

See BNW52626 for quenching factor to be used.

4.5.4 Sample Disintegrations/Minute/Milliliter (d/m/mL)

If a non-fused sample is being analyzed the calculation is:

$$S = \frac{(A-B)(C)}{(D)(E)(F)} \quad \text{where,}$$

- S = The sample Se^{79} d/m/mL
- A = The Se^{79} counts/minute obtained from the liquid scintillation counting data
- B = The Se^{79} "blank" counts/minute obtained from the liquid scintillation counting data
- C = The d/c factor calculated in Section 4.5.2
- D = Volume of sample (in milliliters) added in Section 4.2 Step 1a
- E = Yield factor calculated for sample in Section 4.5.1
- F = Quench Factor obtained in table in Section 4.5.3

4.5.5 Sample Disintegration/Minute/Gram (d/m/g)

If a fused sample is being analyzed the calculation becomes:

$$S = \frac{(A-B)(C)(G)}{(D)(E)(F)(H)} \quad \text{where,}$$

- S = The sample Se^{79} d/m/g

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PNL TECHNICAL PROCEDURE

- A = The Se^{79} counts/minute obtained from liquid scintillation counting data
- B = The Se^{79} "blank" counts/minute obtained from the liquid scintillation counting data
- C = The d/c factor calculated in Section 4.5.2
- D = Volume of sample (in milliliters) added in Section 4.2 Step 1
- E = Yield factor calculated for sample in Section 4.5.1
- F = Quench Factor obtained in table in Section 4.5.3
- G = Volume the fused sample was dissolved into
- H = The weight of the sample that was fused in grams

4.5.6 Records

Records will be maintained and controlled so as to conform with requirements of PNL MA-70, PAP-70-1701. Laboratory Record Books (LRB's) shall be used in accordance with ~~ACT~~ ~~NOW 89-1~~ established records management practices.

LRB's and analytical report cards provide a mechanism for control of most records.

4.5.7 Procedure Qualification

This procedure is considered self-qualifying since recoveries are measured using a standard selenium carrier and samples are compared to a radiochemical standard. In addition, this procedure is considered qualified through an Independent Technical Review.

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Figure 1. Selenium Still

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**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-441.2 R0

Page 1 of 1

A.

Document Number: PNL-ALO-441 Revision Number: 0

Document Title: Radionuclide Separation and Analysis
Procedure for Tritium

Document's Original Author: BM Gillespie

Effective Date
of ICN: 09 / 29 / 92

Change Requested by:
NL Wynhoff

B. Action:

Replace pages 3 through 9 and Exhibit 1 with pages 3 through 9 and new Exhibit 1.

C. Effect of Change:

Correctly accounts for water content of soil leachates and decreases water/tritium loss during soil leaching.

D. Reason for Change/Description of Change:

Hot leach causes water evaporation and previous measurements and calculations did not properly correct for water content of leachates.

See strikeout/redline in Sections 4.3, 6.3 and 6.4. Also new Exhibit 1.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert

Date: 9/28/92

Approval Authority: AG King

Date: 9/29/92

Other Approvals: BM Gillespie

Date: 9/29/92

: NL Wynhoff

Date: 9/28/92

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-441.1 R0
Page 1 of 1

A.

Document Number: PNL-ALO-441 Revision Number: 0

Document Title: Radionuclide Separation and Analysis
Procedure for Tritium

Document's Original Author: BM Gillespie

Effective Date
of ICN: 5/12/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 10 with pages 1 through 9 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert TL Ehlert Date: 5/7/92

Approval Authority: AG King A. V. King Date: 5/7/92

Other Approvals: NL Wynhoff NL Wynhoff Date: 5/12/92

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-441, RADIONUCLIDE SEPARATION AND ANALYSIS PROCEDURE FOR TRITIUM

APPLICABILITY

This procedure describes methods used to determine the concentration of ^3H in sample matrices. Primarily, the procedure is designed for dissolved species, although solid sample analysis can be performed as well. This procedure describes initial radionuclide separation and radionuclide purification methods. This procedure was developed by Pacific Northwest Laboratory's radioanalytical scientists, and is based on over 10 years experience in analyzing a variety of samples for tritium by liquid scintillation counting.

DEFINITIONS/ACRONYMS

dpm - Disintegration per minute (number of atoms of a radioactive sample which decay in a one minute interval)

cpm - Counts per minute (counting rate measured with a radiation detection instrument)

d/c - Disintegrations per count (i.e., efficiency factor)

LRB - Laboratory Record Book

LSC - Liquid Scintillation Cocktail

RESPONSIBLE STAFF

Cognizant Scientist
Analyst/Technician

PROCEDURES

Prerequisites: Personnel trained in this procedure may perform the work.
Personnel training records are kept in the Section office.

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method; or 2) if a tolerance limit is

Author	Date	Project Mgr.	Date	QAD Representative	Date
BM Gillespie		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
J. Wynoff		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Reagents

- 2.1 Low-tritium background water - water that contains less than required detection limits of tritium as demonstrated by the methods blank.
- 2.2 6 M HCl - 50 mL low-tritium water (2.1) and 50 mLs conc. HCl
- 2.3 Sodium Carbonate, Na_2CO_3 - Reagent grade
- 2.4 Hold Back Carrier - 10 g cupric sulfide, 10 g sodium carbonate, 10 g strontium nitrate, 10 g potassium iodide and 40 g silver nitrate, mixed thoroughly until it appears homogeneous (i.e., even distribution of color and particle size).
- 2.5 Packard Opti Fluor LSC. (Or equivalent)

3.0 Equipment

- 3.1 Distillation Apparatus: For aqueous distillation: 125 mL or 250 mL short neck, flat bottom boiling flask, connecting side arm adapter, condenser and heating mantle or hot plate.
- 3.2 Polyethylene or glass liquid scintillation vials - 25 mL
- 3.3 Coincidence-type liquid scintillation spectrometer. (See appropriate liquid scintillation counting procedure for LSC system to be used such as Procedure PNL-ALO-443.)
- 3.4 Stirrer/Hot plate
- 3.5 Filter paper - Whatman 934-AH glass microfiber, or membrane filter, 1.5 mm effective retention or better (or comparable).
- 3.6 Glass vials - 25 mL
- 3.7 Volumetric flasks, various sizes

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3.8 Balance capable of accurately weighing to the nearest 0.01 g

3.9 Graduated cylinders - 20 mL, 50 mL or 100 mL (or other size to meet volume requirements)

4.0 Sample Preparation

The procedure is written for 125 mL flat bottom boiling flasks but may be scaled up appropriately to 250 mL or larger flat bottom boiling flasks as necessary for environmental samples or leachate volumes.

The aliquot sizes specified are for low level test well samples. For other samples, the cognizant scientist may specify smaller aliquots due to the radioactivity levels and waste minimization issues. In the analysis of radioactive samples, the distillate receiving vessel is different. The receiving vessel is attached such that it is not easily removed from the distillation condenser and the first 5-10 mL distilled aliquot is not discarded.

All data for sample preparation shall be recorded on a Tritium Analysis Log Sheet (Exhibit 1). This attached Data Sheet is an example of the Tritium Analysis Log Sheet which may be expanded to include more samples per batch or modified to delete the solid samples section if only liquid samples are analyzed.

4.1 Quality Control (QC)

All QC data shall be maintained as hard copy and available for easy reference or inspection (QC samples are recorded on a Tritium Analysis Log Sheet [Exhibit 1] and on the data forms associated with the appropriate liquid scintillation counting procedure).

Two QC options (A and B) are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. The analyst will recognize the need to use option B when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a SOW, and these will be conveyed to the analyst through a TI.

- A. Employ a minimum of one methods blank per sample batch (20 samples or less) to determine if contamination is occurring. Run duplicate analysis upon client request. Except when client requires Impact Level III analysis, a spiked sample or standard (NIST traceable) shall be analyzed per batch to ensure that the correct procedure is followed and that all equipment is operating properly.
- B. For all SOWs written by a client to meet CERCLA requirements that request analysis, employ a minimum of one methods blank

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per sample batch/set (20 samples or less) to determine if contamination is occurring. Run one duplicate sample for every 20 samples or for each set, whichever is smaller. A duplicate sample is a sample brought through the whole sample-preparation and analytical process. A spike sample or standard (NIST traceable) shall be employed for every 20 samples analyzed or per every set of samples, whichever is smaller. A matrix spike duplicate and/or laboratory control sample may be analyzed with a set/batch of samples if so directed by a TI.

A flow diagram of samples and QC requirements is attached (Exhibit 2).

4.2 Liquid Samples

- 4.2.1 Put an aliquot of solution into a 125 mL flat bottom boiling flask. Use a 50 mL aliquot of solution if possible. Proceed to step 4.4 for blank and standard make-up and on to step 5.0 for distillation and counting. The cognizant scientist may specify a second distillation by repeating steps 5.1 - 5.3 again.

4.3 Soil/Sediment/Sludge/Solid Samples

- 4.3.1 Weigh a 1-50 g aliquot of sample, as received, into an appropriate size beaker. Record weight on the Tritium Analysis Log Sheet (Exhibit 1).
- 4.3.2 Add enough 6 M HCl to cover the sample aliquot plus about 3-5 mL in excess. Add a stirring bar and watch glass cover.
- 4.3.3 ~~Heat on a stirring hot plate at 50-70°C (hot plate setting of 4-5) for at least 10 - 15 min. Do not apply heat let the sample go dry. Add additional 6 M HCl as necessary.~~
- 4.3.4 ~~Cool and~~ Filter through a Whatman 934-AH glass microfiber filter (or comparable).
- 4.3.5 Return filtered solids aliquot and filter paper to the leaching beaker. Repeat steps 4.3.2 through 4.3.4 on the same filtered solids aliquot; combine filtered leachates.
- 4.3.6 Return filtered solids aliquot and filter papers to the leaching beaker. Repeat steps 4.3.2 through 4.3.4 using low-tritium water in place of HCl.

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- 4.3.7 Combine filtered water leachate with the other 2 combined filtered acid leachates. Bring this leach solution to a known volume with low-tritium water using an appropriate size graduated cylinder. Record volume on the Tritium Analysis Log Sheet (Exhibit 1).
- 4.3.8 ~~Put up to 80 mL (if possible) of the combined acid leachates and water leachate from step 4.3.7~~ Using a graduated cylinder, measure a known volume (up to 80 mL) of the leach solution into a 125 mL distillation flask. Record the volume on the Tritium Analysis Log sheet (Exhibit 1).
- 4.3.9 Add a spatula tip (~0.5 g) of holdback carrier. Make basic with Na_2CO_3 (pH > 7 with gross range pH paper). Final volume should be about 80 mL. Cool to room temperature.
- 4.3.10 Weigh and record total weight of flask and contents on the Tritium Analysis Log Sheet (Exhibit 1).
- 4.3.11 Connect the side arm adapter and condenser to the outlet of the flask, and insert a beaker under the outlet of the condenser. Heat the sample to boiling to distill. Distill 5-10 mL into the beaker and discard the distillate. This cleans the condenser.
- 4.3.12 Place a clean beaker under the condenser to collect the next 50 mL (if possible) of distillate. Preparation of this distillate will continue in step 4.3.14.
- 4.3.13 Continue distillation until the flask is dry. Cool to room temperature. Weigh flask and record the weight on the Tritium Analysis Log sheet (Exhibit 1).
- 4.3.14 Transfer distillate from step 4.3.12 to another 125 mL flat bottom distillation flask. Proceed to step 4.4.2 for preparation of blanks, standards and spikes and then on to step 5.0 for the second distillation.
- 4.3.15 To prepare a QC matrix spike or standard recovery correction factor, if requested by an SOW, ARF or TI, use the filtered solid from step 4.3.4 and spike with a known amount of tritium standard as directed by the cognizant scientist. The spike should be similar in concentration to the concentration anticipated in the samples being analyzed or at a minimum a detectable amount (3 to 5 times background). Record the spike aliquot on the Tritium Analysis Log Sheet (Exhibit 1). Follow procedure in steps 4.3.2 through 4.3.14. The filtered solid is used as it provides a tritium free sample to spike.

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4.4 Blanks/Raw Water Standard/Distilled Water Standard

- 4.4.1 If liquid samples are being analyzed and if requested by a SOW, ARF or TI, prepare raw water standard distillate by placing 50 mL low tritium water in a 125 mL distillation flask. Prepare in duplicate. Add (NIST traceable) tritium standard spikes to each as determined by the cognizant scientist (activity added to achieve about 1000 dpm/mL). Record spike aliquots on the Tritium Analysis Log Sheet (Exhibit 1). Distill raw water standards as per section 5.0.
- 4.4.2 To prepare blanks and distilled water standards, place 60 mL of low tritium water in a 125 mL distillation flask. Add a spatula tip (~0.5 g) of holdback carrier.
- 4.4.3 Connect the side arm adapter and condenser to the outlet of the flask, and insert a beaker under the outlet of the condenser. Heat the sample to boiling to distill. Distill 5 to 10 mL of solution into a flask and discard distillate. This cleans the condenser.
- 4.4.4 Place a clean beaker under the outlet of the condenser. Collect 20-35 mL of distillate for use in the following steps.
- Note: A large volume (e.g., 1 liter) of low tritium water may be distilled and used for several sets of sample analyses. Therefore, step 4.4.2 may not be necessary.
- 4.4.5 Prepare methods blank (background) solutions from 4 mL aliquot of low tritium background water distillate from step 4.4.4 thoroughly mixed with 19 mL of scintillator solution in liquid scintillation counting vials. Prepare in duplicate. Record volume on Tritium Analysis Log Sheet (Exhibit 1).
- 4.4.6 Prepare two distilled water standards by adding spike to each of two liquid scintillation counting vials containing 19 mL of scintillation solution. Each vial shall be spiked with a different activity as specified by the cognizant scientist. The spike activities are normally ~50,000 dpm and ~100,000 dpm or less, respectively, but may be increased if higher tritium activity is expected in the samples. Record spike aliquots on the Tritium Analysis Log Sheet (Exhibit 1).
- 4.4.7 Add low tritium background water distillate from step 4.4.4 to each standard to make 4 mL total aqueous volume in each vial. Mix each vial thoroughly.

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5.0 Tritium Analysis

- 5.1 To a sample aliquot from the sample preparation (step 4.2.1, 4.3.11 or 4.3.12) add a spatula tip (~0.5 g) of holdback carrier. If solution is not already basic (pH>7) add Na_2CO_3 until basic (check with pH paper).
- 5.2 Connect the side arm adapter and condenser to the outlet of the flask, and insert a beaker under the outlet of the condenser. Heat the sample to boiling to distill. Distill 5 to 10 mL of solution into a flask and discard distillate. This cleanses the condenser.
- 5.3 Place a clean beaker under the outlet of the condenser. Distill until about 10-25 mL of distillate is collected into a 25 mL glass vial.
- 5.4 To prepare sample aliquot for counting, thoroughly mix a 4 mL aliquot of distillate from 5.3 with 19 mL of scintillator solution in a liquid scintillation counting vial. Prepare in duplicate. Record the sample aliquot volume on the Tritium Analysis Log Sheet (Exhibit 1). Save remaining sample distillate pending analysis of sample counting data.

Note: Less than 4 mL of sample may be used as the aliquot size depending on the concentration of tritium anticipated in the samples. Low tritium background water distillate from step 4.4.4 shall be added to each vial to bring to 4 mL total aqueous volume.
- 5.5 Count all samples in the liquid scintillation spectrometer for 100 minutes or 2σ counting statistics, whichever comes first. Refer to the Liquid Scintillation (LSC) Counting Procedure appropriate for the LSC system being used.
- 5.6 Using the background-corrected count rates of the standards, determine the efficiency of the scintillator solution. Use this efficiency to determine the tritium concentrations of the background-corrected sample solutions.
- 5.7 If a sample count rate exceeds 60,000 cpm, the cognizant scientist shall determine a smaller appropriate aliquot size. This sample aliquot shall be prepared and counted according to steps 5.4 and 5.5.

6.0 Calculations

- 6.1 Efficiency factor, E, d/c

$$E = \frac{G}{D - B}$$

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where:

D = distilled Water standard (from 4.4.7) count rate, cpm,
 B = background count rate (from 4.4.5), cpm, and
 G = activity of distilled water standard (dpm)

6.2 Recovery correction factor for raw water standard, F_w

$$F_w = \frac{(L - B) \times E}{M}$$

where:

L = raw water standard distillate (from 4.4.1) count rate, cpm,
 B = background count rate (from 4.4.5), cpm,
 E = counting efficiency, as determined in 6.1, and
 M = activity of raw water standard (before distillation), dpm

6.3 Recovery correction factor for solids/soils/sludges, F_s ,

$$F_s = \frac{(L - B) \times E \times TV \times (WB - WF)}{VL \times V \times M}$$

L = soil matrix spike distillate (from 4.3.12) count rate, cpm,
 B = background count rate (from 4.4.5), cpm,
 E = counting efficiency, as determined in 6.1,
 TV = total volume of leach soln, ml,
 VL = volume of leach soln before pH adjustment and distillation,
 WB = weight of flask and basic solution before distillation,
 WF = weight of dry flask after distillation,
 V = volume of the distilled sample aliquot mixed with LSC in ml
 (example: 4 ml), (from 5.4 or 4.4.7), and
 M = activity of spike in soil matrix (before distillation), dpm

6.4 Activity of Tritium in aqueous sample, A

$$A = \frac{(C - B) \times E \times Q}{V \times F_w}$$

where:

C = sample count rate, cpm,
 B = background count rate, cpm,
 E = counting efficiency, as determined in 6.1,
 V = volume of the distilled sample aliquot mixed with LSC in mL
 (example: 4 mL), (from 5.4 or 4.4.7)
 F_w = recovery factor, as determined in 6.2,
 Q = factor or factors to account for sample dilutions or needed to
 produce the appropriate reporting units. These factors shall
 be documented as part of the project record.

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6.5 Activity of Tritium in soils/solids/sludge sample, A

$$A = \frac{(C - B) \times \cancel{VL} \times E \times TV \times (WB - WF) \times Q}{\cancel{VL} \times V \times F_s \times W}$$

where:

C = sample count rate, cpm,

B = background count rate, cpm,

E = counting efficiency, as determined in 6.1,

TV = total volume of leach soln, mL,

VL = ~~volume of filtered leachate~~, volume of leach soln before pH adjustment and distillation, mL,

WB = weight of flask and basic solution before distillation,

WF = weight of dry flask after distillation,

V = volume of the distilled sample aliquot mixed with LSC in mL (example: 4 mL), (from 5.4 or 4.4.7)

F_s = recovery factor, as determined in 6.3,

W = weight of sample leached, g,

Q = factor or factors to account for sample dilutions or needed to produce the appropriate reporting units. These factors shall be documented as part of the project record.

7.0 Records

Records will be maintained and controlled so as to conform to requirements of Manual PNL-MA-70, Procedure PAP-70-1701. LRBs and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with the established records management practices.

8.0 Specific Qualification

This procedure describes the calibration of instrumentation using radionuclide standards in analysis process control and, as such, is considered self-qualifying as defined in Manual PNL-MA-70, Procedure PAP-70-901.

9.0 References

"Tritium in Drinking Water, Method 906.0", Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, August 1980.

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Pacific Northwest Laboratory

TRITIUM ANALYSIS LOG SHEET

Pipet No. Nominal Vol. Calibrated Vol. + Error Date Pipetted

50 lambda

100 lambda

4 ml

1000 lambda

SOLID SAMPLES: Balance M&TE No. _____

Sample No: _____

Sample No: _____

sample wt. _____

sample wt. _____

total leach vol. _____

total leach vol. _____

leach aliquot vol. _____

leach aliquot vol. _____

basic solution
+ flask wt. _____

basic solution
+ flask wt. _____

flask wt. after
distilled dry _____

flask wt. after
distilled dry _____

counting aliquot
nominal vol. _____

counting aliquot
nominal vol. _____

Backgrounds: Blanks #1 & 2 Nominal Vol: _____

Distilled Water Stds: Spike i.d. _____

Std #1 nominal vol. _____

Std #2 nominal volume _____

Analyst

Date

Reviewer

Date

Exhibit 2

FLOW DIAGRAM FOR TRITIUM ANALYSIS

Water Standards and Blanks

**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-443.2

Page 1 of 1

A.

Document Number: PNL-ALO-443 Revision Number: 0

Document Title: Liquid Scintillation Counting
Procedure for Tritium

Document's Original Author: BM Gillespie

Effective Date
of ICN: 07 / 07 / 1992

Change Requested by:
TE Jones / NL Wynhoff

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.
Replace pages 1 through 5 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

Manual PNL-MA-597, Volume 1, no longer in existence. Section 1.3.1.1 should reference MCS-033.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert

Date: 6/23/92

Approval Authority: ^{for} AG King

Date: 7/7/92

Other Approvals: NL Wynhoff

Date: 6/30/92

:

Date: 1/1

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-443.1
Page 1 of 1

A. Document Number: <u>PNL-ALO-443</u> Revision Number: <u>0</u> Document <u>Liquid Scintillation Counting Procedure</u> Title: <u>for Tritium</u> Document's Original Author: <u>B. M. Gillespie</u>		Effective Date of ICN: <u>4/26/91</u> Change Requested By: <u>NL Wynhoff</u>
B. Action: Replace pages 3 and 4.		
C. Effect of Change: Discontinue counting of a C-14 standard which is irrelevant to tritium counting.		
D. Reason for Change/Description of Change 1. Delete references to a C-14 standard. 2. Delete reference to a C-14 standard and to a raw water standard since soil samples do not include a raw water std. and the recovery factor spike for either waters or soils may be counted in any order with the samples. <u>DESCRIPTION OF CHANGE</u> - Edit Sec. 1.3.1, First sentence to read: "Sealed ³ H and blank standards (Beckman Nos. H277092 and B11080, respectively, or equivalent) shall be...." Edit Sec. 2.1, First sentence to read: "... tower #1, the sealed blank, the sealed ³ H standard, blanks (backgrounds), distilled water standards (for d/c), samples and then a stop tower."		
E. Approval Signatures (Please Sign and Date)	Type of Change: (Check (☒) one) (☐) Minor Change (☒) Major Change	
Process Quality QA Department Concurrence: <u>GT Gerbe, QE</u> Date: <u>3/5/91</u> Approval Authority: <u>[Signature]</u> Date: <u>3/18/91</u> Other Approvals: <u>B. M. Gillespie</u> Date: <u>3/18/91</u> : _____ Date: <u>1/1</u>		

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-443, LIQUID SCINTILLATION COUNTING PROCEDURE FOR TRITIUM

APPLICABILITY

This procedure is applicable to the operation of the Beckman LS 8000 liquid scintillation counting system located in the 329 Building. The procedure was developed by Pacific Northwest Laboratory's scientists and reflects over 10 years of experience in liquid scintillation counting methods.

DEFINITIONS/ACRONYMS

LRB - Laboratory Record Book
LSC - Liquid Scintillation Counting
DR - Deficiency Report

RESPONSIBLE STAFF

Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 LSC SYSTEM DESCRIPTION

The LSC system is designed for counting ^3H , ^{14}C , ^{32}P and other beta-emitters. However, virtually all alpha, beta, x-ray, positron, and gamma emitters, properly prepared, can be counted with good efficiency.

The 329 Building LSC system is a two-channel spectrometer with a 300-sample capacity. The instrument utilizes microprocessor technology and is equipped with Automatic Quench Compensation (AQC), H-Number (quench monitor), Graphic Display, ten factory-installed counting programs (Library Programs) in an unalterable memory, keyboard operations, program editing feature, and an interrupt function. The system is provided with a Teletypewriter for data readout, a Bar Graph Display, and a Random Coincidence Monitor.

The LSC system is intended for use by operators experienced with the methodology of in vitro diagnostic, radioassay, and nuclear chemistry procedures which require nuclear counting of certain reagents with particular energy bands by liquid scintillation techniques.

Author	Date	Project Mgr.	Date	QAD Representative	Date
BM Gillespie		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
NL Wynoff		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
Procedure No.	Revision No.	Effective Date	Page		
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1.1 Components in the LSC System

The LSC system is a Beckman LS-8000, serial number 7804114. The system consists of a 300-sample conveyor sample changer, photomultiplier tubes, circuit boards and operator/program selection towers.

1.2 Counter Quench Correction

The system is equipped with an external standardization method in which a high-energy gamma source (^{137}Cs) can be automatically positioned near the sample vial to produce a continuum of Compton recoil electrons which can excite solvent molecules that will eventually transfer the energy of excitation to solute molecules to produce photons. If quenching is present in the sample, the resulting Compton pulse height distribution is affected in the same manner as the light distribution of the radioactive sample. The true quench level of the sample is expressed as a shift in the Compton edge of the sample relative to an unquenched sample and the difference in the channel settings represents the extent quenching has affected the light output.

The microprocessors in the LS 8000 system analyze the Compton distribution to determine the location of the Compton edge of the sample. This determination is based on measuring the area of the Compton edge in special, discrete counting channels to determine the inflection point of the edge. When compared to the channel setting of the inflection point of an unquenched sample, the H-Number or difference in channel settings is determined.

Samples counted with an H-Number can be subjected to quench correction in order to determine actual sample activity-disintegrations per minute (dpm) - regardless of quenching in the sample. Quenched standards, which contain the same type of isotope as in the sample but whose activity is known, are prepared and counted to determine count rates-counts per minute (cpm). H-Numbers are measured for each standard and a quench curve generated which relates the counting efficiency of each standard to its corresponding H-Number. This becomes part of the permanent record in the software program used for the specific analysis.

1.3 Counter Performance Tests

The geometry of the LSC system is fixed and depends on the smooth operation of the sample changer and the pedestal of which counting vials are lowered in front of the photomultiplier tube. Any malfunction of this portion of the LSC system will be recognized by the control circuits and printed as an appropriate note on the readout tape.

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- 1.3.1 Sealed ^3H and blank standards (Beckman Nos. H277092, and B11080, respectively or equivalent) shall be counted before each set of samples and the count rates compared with previously recorded counts to verify consistent system operation. The count rates of these standards shall be recorded in the Beckman LSC LS8000 notebook. The isotope standard count rates shall be within 3σ of the mean as established previously, after decay correction, and background count rates shall be within 3σ of the previously recorded backgrounds.
- 1.3.1.1 Control charts shall be set up and maintained as per MCS-033, ~~PNL MA 597, Vol 1, Section 7.~~
- 1.3.2 Discontinue counting the sample set if the sealed standards exceed the control limits specified in 1.3.1. After cleaning the vials, recount the sealed standards two times.
- 1.3.3 If both recounts are in control, counting may continue on any remaining samples in the set. If both recounts of each standard are not within the control limits, any data collected is disqualified. The samples shall be recounted after the equipment is repaired or the samples may be prepared again and reanalyzed. A sign shall be posted on the LSC system indicating the instrument is out of control and shall not be used until repaired and recalibrated. A DR is needed if samples have been counted.
- 1.3.4 The record of these count rates also assists the Beckman service representative to analyze specific system operating parameters during preventive maintenance and troubleshooting activities. The LSC system performance is also monitored with each set of samples inserted for analysis. At least two spiked samples and two blanks, matching the specific characteristics of the sample set with respect to scintillator and dissolved sample aliquot, are counted scintillator and dissolved sample aliquot, are counted (corrected for ^3H decay) and compared with previously recorded ^3H count rates.

2.0 SAMPLE COUNTING

- 2.1 When setting up blanks, standards and samples in the conveyor sample changer for counting in the liquid scintillation system, place them in the following order: tower #1, the sealed blank, the sealed ^3H standard, blanks (backgrounds), distilled water standards, (for d/c), samples and then a stop tower. Log positions on the 3000 Tri Carb data sheet (Exhibit 1. It is only used to log in the blanks,

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PNL TECHNICAL PROCEDURE

standards and sample positions in the cassette. The control settings section of the form shall not be filled in for this instrument).

- 2.2 Print out the program logged into the system by pressing the following key on the key pad of the LSC system:

Print Program Summary

If the current operator number is not 1 and the program is not 1 then proceed. If the operator number is 1 and the program is 1 and the sample count time is 100 min. then proceed to step 2.7.

- 2.3 Recall the operator's number using the key pad on the LSC system by pressing the following keys in the following order:

User Number - #1 - Enter - Proceed.

- 2.4 Input the correct program by pressing the following keys in the following order on the key pad:

Library Program - 1 - Enter - Proceed

- 2.5 Input the correct count time for samples by pressing the following keys in the following order on the key pad:

Common Parameters - 1 - Enter - 100 (min) - Enter - Proceed

- 2.6 Print out the program to make sure the parameters are correct by pressing the following key on the key pad:

Print Program Summary

- 2.7 If all is correct on print-out as above, start counting the sample set by pressing the following key on the key pad:

Auto Count

- 2.8 When all counting is complete for the sample batch/set, evaluate the instrument printed data for the sealed blank and standards per section 1.3.

- 2.9 Calculate activities of samples, raw standards, distilled standards and blanks/backgrounds in accordance with instructions from the cognizant scientist or as required by the analyte analysis procedure (e.g. PNL-ALO-441).

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PNL TECHNICAL PROCEDURE

3.0 RECORDS

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~ACT NOW Directive 89-1~~ established records management practices.

4.0 SPECIFIC QUALIFICATIONS

This instrument is calibrated using radiochemical standards and as such is self qualifying as per definitions in PNL-MA-70, PAP-70-901.

5.0 REFERENCES

Beckman LS 8000 Series Liquid Scintillation System Manual

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3000 TRI CARB

[illegible]

INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-445.2, R0
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<p>A. Document Number: <u>PNL-ALO-445</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Solutions Analysis: Uranium By Laser-Excited Fluorescence</u></p> <p>Document's Original Author: <u>CO Harvey</u></p>	<p>Effective Date of ICN: <u>02/11/93</u></p> <hr/> <p>Change Requested by: <u>CO Harvey</u></p>
<p>B. Action:</p> <p style="margin-left: 40px;">Replace pages 1 and 2 with the attached pages 1 and 2.</p>	
<p>C. Effect of Change:</p> <p style="margin-left: 40px;">N/A</p>	
<p>D. Reason for Change/Description of Change:</p> <p style="margin-left: 40px;">Reason: This sentence does not apply to this method. Deleted last sentence of 2nd paragraph in 1.2.</p> <p style="margin-left: 40px;">Description: See redline & strikeout on page 1.</p>	
<p>E. Approval Signatures: (Please Sign and Date)</p> <p>QP Concurrence: <u>TL Ehlert</u> <i>TL Ehlert</i></p> <p>Approval Authority: <u>AG King</u> <i>OK Plurben for AGK</i></p> <p>Other Approvals: <u>CO Harvey</u> <i>CO Harvey</i></p> <p style="margin-left: 40px;">: <u>LR Greenwood</u> <i>LR Greenwood</i></p>	<p>Type of Change (Check (✓) one) (✓) Minor Change () Major Change</p> <p>Date: <u>2/11/93</u></p> <p>Date: <u>3/2/93</u></p> <p>Date: <u>2/16/93</u></p> <p>Date: <u>3/5/93</u></p>

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-445, SOLUTIONS ANALYSIS: URANIUM BY LASER-EXCITED FLUORESCENCE

APPLICABILITY

This procedure applies to the laser-excitation fluorimetry method of determining uranium concentration in sample solutions.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Quality Control

1.1 Tolerances

All measurements in this procedure unless otherwise stated are $\pm 10\%$.

1.2 Performance Verification

To assure the performance of the method and check for possible contamination of the sample, a standard and a blank shall be analyzed with each batch of samples. A standard shall be run at each instrument sensitivity setting used in analyzing the sample batch. These requirements may be waived or others stipulated by the client in the ARFS, SOW, TI or other instructions. A batch shall not exceed 20 samples.

~~A spike yield of $\pm 10\% \pm 20\%$ of the known value is acceptable. If the following conditions are met: The count rate of the spike is ten times the background count rate of the counter on which it is counted and the counts attributable to the spike are at least 30% of the total counts.~~

Author	Date	Project Mgr.	Date	QAD Representative	Date
CO Harvey		TE Jones		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LR Greenwood		AG King		ALL ORIGINAL SIGNATURES ON FILE	
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PNL TECHNICAL PROCEDURE

The standard shall be a uranium solution NIST traceable and independent of the working standard. The blank shall be the cell filled with deionized water.

Working standards shall be prepared from NIST traceable materials.

2.0 Equipment and Materials

- Uranium analyzer, Scintrex UA-3, Scintrex Ltd, Concord, Ontario, Canada.
- Sample cell, UV-quartz, 1 x 2 x 4.5 cm with ~7-mL volume.
- Magnetic stirrer with magnetic stir bar for sample cell (optional).
- Fluorescence enhancement buffer, FLURAN, Scintrex Ltd, Concord, Ontario, Canada.
- NIST Uranium standard, metal or solution.
- Deionized water, greater than 10-megohm resistance, as indicated by the deionizer meter readout.

3.0 Working Standard Preparation

Calibration is performed as part of the determination using the standard addition technique described in Section 4.0. The standard is prepared by dissolving about 10 g (record actual weight to the nearest 0.1 mg) of NIST SRM uranium metal in a minimal volume of 8 M HNO_3 . The solution is diluted to about 500 g (record actual weight to the nearest 0.1 mg) with 1 M H_2SO_4 . About 5.0 g (record actual weight to the nearest 0.1 mg) of this solution is diluted to 100 mL with deionized water, giving a nominal 100 $\mu\text{g/mL}$ uranium. If NIST standard uranium solution is used, prepare a 100 $\mu\text{g/mL}$ standard by exact dilution using 2M HNO_3 . The diluted standards are prepared by accurate 1 to 10, 1 to 100 and 1 to 1000 dilutions of the 100 $\mu\text{g/mL}$ standard with 0.1 M nitric acid, giving solutions that are nominally 10, 1, and 0.1 $\mu\text{g/mL}$ respectively. Store standards in bottles that have been conditioned by having had standards at the same concentration stored in them for several weeks.

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4.0 Method

Trace-level concentrations of uranium in aqueous solutions containing a buffered complexing reagent are determined by measuring the emitted green luminescence upon excitation with a UV-emitting pulsed nitrogen laser. Discrimination against fluorescing organics is provided by using a green filter and a gated detection circuit that measures the long-lived uranium fluorescence after the short-lived organic fluorescence has decayed. Correction for interference by quencher constituents is accomplished by the standard addition method. The fluorescence of the sample is determined and a known amount of uranium is added. The increase in signal due to the standard addition is then related to the sample signal to calculate the sample uranium. The assumption is that the solution matrix quenching effect on the added uranium is the same as on the sample uranium.

5.0 Sample Analysis

- 5.1 Prepare the analyzer. Switch POWER on. Wait until the READY light comes on and switch LASER on. Wait 30 minutes for the laser to stabilize. Set RANGE to LOW. Zero the meter with the ZERO control, allowing 4 seconds for the meter to respond each time between adjustments.
- 5.2 Place the cell in its holder on the cell compartment door.
- 5.3 Pipet 5 mL of deionized water into the sample cell. Add sample into the deionized water. Mix the solution by one of the following; stirring with pipet tip, drawing it in and out of a disposable plastic dropper or with a stir bar and magnetic stirrer.
- 5.4 Close the door and turn on the photomultiplier tube (PMT) with the PMT switch. CAUTION: NEVER open the door with the PMT switch on.
- 5.5 Zero the meter with the BALANCE control. If the meter will not zero, the uranium or the acid concentration of the sample may be too high or the sensitivity setting on the instrument is too high. Dilution or neutralization of the sample or a less sensitive instrument setting will be required. After making the necessary adjustment(s), zero the meter. Record sensitivity setting on the Analytical Data Sheet.
- 5.6 Turn off the PMT, open the door, and pipet 500 μ L of FLURAN into the sample. Mix the solution as in Step 5.3.
- 5.7 Return the cell to its compartment (if removed), close the cell door, and turn on the PMT. Record the meter reading (R1) on the Analytical Data Sheet. If the reading is too low, add more sample to the cell (if the sample matrix does not cause a zero shift). A

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large initial balance adjustment in 5.5 should indicate this problem. Otherwise, the procedure must be repeated, starting at Step 5.2. If the reading is off-scale, switch to HIGH RANGE. If the reading is too high, dilute the sample and repeat the procedure starting at Step 5.2.

- 5.8 Turn off the PMT and open the cell door. Add sufficient standard (of the appropriate concentration) to cause an increase in meter reading approximately equal to the sample reading, or as a minimum an increased reading of at least 0.1 meter units. NOTE: Do these steps rapidly to prevent significant solution temperature changes, as this affects fluorescent intensity. Record the meter reading (R_2), working standard concentration and volume used on the Analytical Data Sheet.

6.0 Calculations

For small volume change with standard addition:

$$U = \frac{R_1 SK}{(R_2 - R_1)V}$$

where: U = uranium concentration ($\mu\text{g/mL}$)
 R_1 = initial meter reading for sample uranium
 R_2 = final meter reading for sample plus standard uranium
S = standard concentration ($\mu\text{g/mL}$)
K = standard volume (mL)
V = sample volume (mL).

7.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and Analytical Data Sheet provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-446, (Replaces 6-40.3), 4 x 5 NaI WELL CRYSTAL DETECTOR AND INTRINSIC GERMANIUM DETECTOR GAMMA SPECTROMETRY: CHARCOAL CARTRIDGE AND PARTICLE FILTER ANALYSIS

1.0 APPLICABILITY

Gamma ray spectrometry provides a rapid method of qualitatively and quantitatively determining the individual components in a mixture of gamma-emitting radionuclides without preliminary chemical separations. It is based upon the principle that if a gamma ray is absorbed in a suitable detector an output voltage pulse is produced that is proportional in amplitude to the energy of the gamma. By processing the detector output through a multi-channel pulse height analyzer, a spectrum of the gamma energies present can be accumulated where the total count accumulated in a given channel is a function of the number of gammas of a given energy range detected and the number of the channel in which a count accumulates is a function of the energy of the gamma that produced it. A variety of gamma detectors are available, ranging from highly efficient sodium iodide detectors with poor ability to discriminate gammas that differ only a few KeV in energy to intrinsic germanium detectors with excellent energy discrimination but lower efficiency.

- (a) Sample Analysis Qualitative and quantitative analysis of gamma emitting nuclides in charcoal cartridges and particle filters used in the Stack Monitoring Program.
- (b) Range Depending upon the detector and counting geometry, activities ranging from ten disintegrations per minute to practically unlimited activity can be analyzed. Actual samples rarely exceed a few hundred disintegrations per minute.

2.0 DEFINITIONS

NONE

Author	Date	Project Mgr.	Date	QAD Representative	Date
MR Weiler	9/19/88	N/A		LJ Ethridge	9/19/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	9/19/88	All original signatures on file	
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3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

Charcoal cartridges are routinely screened for significant detectable gamma activity by gamma spectrometric analysis of their contents. The jar containing the transferred charcoal (refer to Method PNL-ALO-429 Section 4.9.4) is positioned on the face of the 4 x 5 inch NaI detector system and counted ten minutes.

Particle filter samples that are found to contain significant beta activities (Method PNL-ALO-434 Section 4.9.3) may also be analyzed by gamma ray spectrometry to identify the nuclides present; usually the disk-mounted filter prepared for alpha and beta counting (Method PNL-ALO-429 Section 4.9.2) is counted on the intrinsic germanium system. High activity filter samples prepared in vials using Method PNL-ALO-429, Section 4.9.3 are counted in the well of the 4 x 5" NaI system; those prepared by dissolution and plating on 2-inch disks using Method PNL-ALO-429, Section 4.9.5 are counted on the intrinsic germanium system. Filter sample counts vary widely in duration; the general rule is to continue a count until statistically significant peak areas accumulate.

The 4 x 5" NaI System

The 4 x 5" NaI/ND-66 system consists of a Harshaw integral line 4 x 5 inch sodium iodide thallium-activated crystal detector with a 1.56 inch diameter by 2.375 inch well, a Tennelec TC-145 preamplifier, and a Tennelec TC-202 BLR amplifier. Detector output is digitized with a Nuclear Data GEN II 100 MHz analog to digital converter; spectra are accumulated on a Nuclear Data ND-66 pulse height analyzer.

The detector is housed in a 32 inch by 32 inch by 36 inch high 4 inch walled cave with full front door access, constructed from lead brick and lined with copper and cadmium shields. Since resolution of the sodium iodide detector is relatively poor, the system is operated at 10 KeV per channel and a 256 channel spectrum covering a zero to 2.5 meV gamma energy range is collected. This mode of operation is insufficient to adequately resolve the complex gamma spectra of nuclides that potentially

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occur in the sample; the analysis serves primarily as a highly efficient screening process to determine whether any gamma activity is present in amount statistically significant with respect to background. Typical detection limits are approximately 8 disintegrations per minute for the iodine-131 364 KeV gamma and approximately 10 disintegrations per minute for the cobalt-60 1332.5 KeV gamma. Since iodine-131 determinations are required for all cartridge samples, spectral data obtained with the system is used to calculate I-131 detection limit values for samples exhibiting no significant activity with respect to background. In the event the 4 x 5" NaI/ND-66 system is malfunctioning or otherwise unavailable, a 3-inch sodium iodide detector equipped system is available for backup use.

The Intrinsic Germanium System

Should a sample exhibit significant gamma activity, more detailed analysis using the high resolution intrinsic germanium detector system is required. This system is designated as the "Facilities Off-Gas" or "FOG" system. The system consists of a vertically upright Princeton Gamma-Tech 130cc closed end coaxial intrinsic germanium detector mounted on a NPR-30 cryostat, a preamplifier that is integral to the detector assembly, a Princeton Gamma-Tech 315 5KV bias supply, and a Canberra 2010 spectroscopy amplifier. Detector output is digitized with a Tracor Northern TN-1242 100 MHz analog to digital converter and spectra are accumulated on a TN-4000 multi-channel analyzer system. The detector is housed in a 24 inch by 24-inch by 24 inch 4 inch walled cave with top access, constructed from lead brick.

The intrinsic germanium system is operated at 1 KeV per channel and a 2048 channel spectrum covering a 40 KeV to 2050 KeV gamma energy range is accumulated. Should there be evidence of a principal gamma less than 50 KeV in energy, the sample should also be counted on a system intended for low energy gamma and x-ray spectral measurements such as the germanium well detector. Cartridge samples transferred to jars (Method PNL-ALO-429, Section 4.9.4) and 2-inch disk mounted filter samples (Method PNL-ALO-429, Sections 4.9.2 and 4.9.5) are counted with the sample centered on the face of the detector. Sixty minute counts are usually required, but the general rule is to continue a count until statistically significant peak areas accumulate. Typical detection limits are approximately 10 disintegrations per minute for the iodine-131 364 KeV gamma and approximately 5 disintegrations per minute for the cobalt-60 1332.5 KeV gamma.

NOTE: Multi-channel analyzers are complex devices; many operations require several steps and interactions with a

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microprocessor control. Details of operations are beyond the scope of this volume; in describing counting procedures only the desired end result of an operation will be specified. For detailed operating instructions refer to the multi-channel analyzer operating manual for the instrument system.

4.2 APPARATUS

4 x 5 inch NaI/ND-66 gamma spectrometry system, with the following components:

- (a) Harshaw Integral Line 4 x 5: NaI (Te) well crystal and photomultiplier.
- (b) Preamplifier, TC-145 (Tennelec).
- (c) Amplifier, TC-202 BLR (Tennelec).
- (d) High Voltage Power Supply, 412B (John FLuke).
- (e) Analog to Digital Converter, GEN II (Nuclear Data).
- (f) Multi-channel Analyzer, ND-66 (Nuclear Data).
- (g) Printer, Decwriter LA120-AA (Digital Equipment Corp.).

Intrinsic germanium/TN-4000 gamma spectrometry system, with the following components:

- (a) Coaxial Intrinsic Germanium Detector assembly: detector IGC36 (Princeton Gamma Tech); preamplifier RG-11A (Princeton Gamma-Tech); cryostat, NPR-30 (Princeton Gamma-Tech).
- (b) 5 KV Bias Supply, 315 (Princeton Gamma-Tech).
- (c) Spectroscopy Amplifier, 2010 (Canberra).
- (d) Analog to Digital converter, TN-1242 (Tracor Northern).
- (e) Multi-channel Analyzer, TN-4000 (Tracor Northern).
- (f) Printer, Decwriter LA120-AA (Digital Equipment Corp.).

Materials: Plastic bags, 6 inches by 9 inches.

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4.3 REAGENTS

4.4 STANDARDS

- (a) Calibration Standards. The efficiency of gamma detectors varies greatly as a function of gamma energy. Since charcoal cartridges are preceded by particulate filters in the sampling process, volatile fission products such as the noble gases, iodine-131, ruthenium-103, ruthenium-106, antimony-125, and tellurium-125m, activation products such as bromine-82 and mercury-203, and daughters of noble gases such as lead-212, bismuth-212, polonium-212, thallium-208, lead-214, bismuth-214, and polonium-214, are the most likely nuclides to occur in these samples. Each of these nuclides emits a unique spectrum of gamma energies. Gamma ray spectrometers could be directly calibrated using simulated charcoal sources of each of these nuclides, but it is best to establish efficiency equations for the detector response at each counting configuration as a function of gamma energy across the entire zero to 2000 KeV energy range. Using 51 milliliters charcoal in a 8 ounce styrene jar as the standard counting configuration, the 4 x 5 NaI/ND-66 system was directly calibrated for ruthenium-106 and iodine-131. The calibration of the intrinsic germanium/TN-4000 system consists of efficiency equations developed from measurements at nine energies in the 40 KeV to 250 KeV range and fourteen energies in the 120 KeV to 1274 KeV range using National Bureau of Standards Standard Reference Material 4276-107 (antimony-125 + europium-154 + europium-155), and individual standards of cobalt-57, cobalt-60, cesium-127, barium-133, and americium-241.
- (b) Control Sources. The function of control sources is discussed in Section PNL-ALO-434 Subsection 4.4. In gamma ray spectrometry two control sources, one of low gamma energy and one of high gamma energy, are used; the same sources are also used to adjust system zero and gain so that the KeV/channel energy response of the system is accurately established. For the 4 x 5" NaI/ND-66 system the low energy control is the cobalt-57 122.06 KeV gamma and the high energy control is the cobalt-60 1332.46 KeV gamma. For the intrinsic germanium/TN-4000 system the low energy control is the europium-152 121.78 KeV gamma and the high energy control is the cobalt-60 1332.46 KeV gamma.

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4.5 SAFETY

Observe the general laboratory safety rules and the counting room Radiation Work Procedure.

4.6 QUALITY CONTROL

4.6.1 Calibration

In gamma ray spectrometry, calibration involves determining the ratio of the absolute number of gamma photons of given energies emitted by a radioactive source in sample counting configuration to the observed accumulated count in the channels of the multi-channel analyzer corresponding to those respective energies. All gamma calibration data is preserved in a Stack Monitoring Program Gamma Calibration File.

Calibrations are performed as follows (refer to the NOTE, Procedure PNL-ALO-446, Section 4.1):

- (a) Verify the detector high voltage (NaI) or bias voltage (intrinsic Ge), is set to the proper value (refer to Table 2).
- (b) Verify gain and zero are properly set (refer to Subsection 4.6.2 Control Maintenance).
- (c) Count each calibration source using the procedure of Subsection 4.9.2. The length of the count should be chosen such that the total peak area(s) for the gamma(s) of interest consist of at least 10000 counts; a count is never less than 5 minutes in length.
- (d) Print out an identification heading for the calibration count. This usually will consist of one line describing the standard and a second describing counting parameters. Print out a channel listing of the spectrum.
- (e) If the NaI/ND-66 is being calibrated, perform a background count using the sample count procedure of Subsection 4.9.2 with a "blank" simulation of the sample matrix in sample position. Print a complete channel listing of the background spectrum.

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(f) Calculate a corrected count rate for each total peak area corresponding to each gamma of interest.

1. NaI/ND-66 system: On the sample spectrum printout mark off a group of channels that constitute the total peak area, sum their contents, and divide by the length of the count in minutes. Perform the same operation for the same group of channels of the background count. Subtract the background count rate from the standard count rate.

$$R_c = \frac{A_s}{T_s} - \frac{A_b}{T_b}$$

Where R_c = the corrected count rate in counts per minute

A_s = the sum of the channels contributing to the peak in the sample spectrum

A_b = the sum of the channels, used to determine A_s , in the background spectra

T_s = the length of the sample count in minutes

T_b = the length of the background count in minutes

2. Intrinsic Ge/TN-4000 system: On the sample spectrum mark off a group of channels that constitute the total peak area; sum their contents. Locate a group of at least two channels next to or slightly above the highest channel of the total peak area group where the channel count is reasonably constant and average the contents of these channels; this is the high energy edge correction. Repeat that the process using a set of channels next to or slightly below the

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lowest channel of the total peak area group to obtain a low energy edge correction. Average these high and low edge correction values and multiply the result by the number of channels included in the total peak area to obtain the total peak correction (refer to Figure PNL-ALO-446.1). Finally, calculate the corrected count rate in counts per minute by subtracting the total peak correction from the total peak area and dividing the result by the length of the count in minutes.

$$R_c = \frac{A_T - \frac{(C_H + C_L)(n)}{2}}{T}$$

Where R_c = the corrected count rate in counts per minute

A_T = the peak area, the sum of the channels constituting the peak total area

C_H = the high energy edge correction, an average of typical high energy edge channel contents

C_L = the low energy edge correction, an average of typical low energy edge channel contents

n = the number of channels constituting the total peak area

T = the length of the count in minutes

- (f) Using the known absolute activity and branching ratio for the nuclide in the calibration source correlated with each gamma, calculate the gamma/count efficiency ratio for the respective gammas of interest.

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$$E_{\gamma} = \frac{(D) (DC) (BR)}{R_c}$$

Where E_{γ} = the efficiency at a specific gamma energy expressed in gammas/ count

D = the disintegration rate of the nuclide correlated with the specific gamma, expressed in disintegrations per minute.

DC = the decay correction from the date of the stated activity for the calibration source to the time the counting was performed.

BR = the branching ratio for the specific gamma in the decay scheme of the correlated nuclide expressed in gammas/disintegration

R_c = the corrected count rate of the specific gamma, expressed in counts per minute, calculated in (e) above.

If a calibration nuclide is one that is likely to occur in a charcoal cartridge sample [refer to Section 7.0 Subsection (a)], also calculate the disintegration/count ratio (d/c):

$$d/c = \frac{(D) (DC)}{R_c}$$

where d/c is the disintegration to count ratio and the remaining terms are the same as defined above.

- (g) Generate the equation for a least square fit of a parabolic curve of the form $X = a + bY + cY^2 + dY^3$ to the efficiency data using the 1123 + computer based EFFIT program (refer to the EFFIT section, Miscellaneous Programs, RSX-11M System Based Program documentation manual). For germanium detectors, a plot of efficiency (gamma/count ratio) versus gamma energy (KeV) is fitted as two regions, the lower usually extending from about 40 KeV to 250 KeV and the upper from 200 KeV to the upper energy limit. Plot the individual data points

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and the efficiency equations together on semilogarithmic graph paper with efficiency as a logarithmic ordinate and energy as a linear abscissa. Significant differences between individual data points and the fitted equations must be resolved.

4.6.2 Control

Control Sources

NaI/ND-66 System:

The control source activity is deposited on the inside surface of the cap of a styrene vial; for ease in handling, the vial is cemented into the end of a styrene test tube with the activity at the lip of the tube. Counting is performed with the control source face at the bottom of the detector well.

Intrinsic Ge/TN-4000:

The control source activity is deposited on 1" stainless steel dishes; a plastic spray coating has been applied to make the sources non-smearable. Counting is performed with the control source dish in position on the dish holder and the holder placed directly over the detector.

Establishing Controls

Control is a process by which a counting system is verified to be currently operating at the performance level existing when that system was calibrated; controls must be re-established whenever system problems develop that require system recalibration. Control sources containing radionuclides which emit gamma energies that effectively test the response all system components are measured when the counter is calibrated. The ability of the system to reproduce these initial measurements is the criteria by which operation is routinely evaluated. High resolution gamma detectors exhibit a response of rapidly increasing efficiency as gamma or X-radiation increases in energy above the noise threshold of the system. An inflection occurs at maximum response, approximately 100 KeV; thereafter efficiency decreases at a

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moderating rate as a function of increasing energy, approaching an almost linear function above 700 KeV. The critical response regions are, therefore, the 100 KeV region and the region above 1000 KeV.

The cobalt-57 122.06 KeV gamma is used to monitor low energy response of the 4 x 5 NaI/NO-66 system. Its chief liability is the relatively short half life, 270.9 days; experience indicates that a pronounced drift toward upper control limits is detectable after two years decay, probably due to half life uncertainty. It is also difficult to construct a control chart with adequately large increments on the vertical count scale to permit easy plotting while covering more than a two month interval on the horizontal time scale.

The europium-152 121.78 KeV gamma is used to monitor low energy response of the intrinsic germanium/TN-4000 system. Its liabilities relate to the effect of the complexity of the gamma spectrum when used with low resolution detectors.

Cobalt-60 is a satisfactory control source for monitoring high energy response of most detectors. The half life is long, the decay scheme simple, and the two gamma components well separated in energy.

Control source reference values are established using the following procedure. It is assumed that counting system parameters such as zero and gain have been established, background measured, and any calibration or recalibration counting just completed.

- (a) Count the control source for a sufficient length of time to accumulate at least 10,000 counts in the peak area corresponding to the control gamma energy. Counts must be at least 5 minutes in length; ADC dead time must not exceed 10%.

Print out at least a portion of the accumulated gamma spectrum including ten channels both above and below the control gamma peak and record the date, time, and length of the count on it.

- (b) Repeat step (a) nine additional times.
- (c) Select a spectral area or band of channels to represent the control gamma. This is a range of channels usually chosen to include the theoretical peak location and adjacent

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channels that equal or exceed approximately half the count obtained in the channel with the highest count; inclusion of the entire peak area makes the control measurement insensitive to small errors in gain and zero set, selection of a single channel is unnecessarily restrictive.

- (d) Calculate the background corrected count rate corresponding to the control gamma for each count.

$$c/m = \frac{A_c}{T_c} - \frac{b}{T_B}$$

where A_c = total area of (sum of the channels designated as) the control gamma in a control source count

T_c = the length of the control count and T_B of the background count in minutes

b = the total area of the control gamma in a background count.

- (e) Calculate and evaluate the $(\chi)^2/n$ for the control data set using the procedure of Method PNL-ALO-434 Section 4.6.2 Establishing Control step (d).

The CONCHT program, a control chart generation and extension program resident on the 1123+ computer system, should be used to perform all necessary calculations and complete the controls generation procedure. Instructions for using the CONCHT program are included in the MISCELLANEOUS PROGRAM RSX-11M SYSTEM BASES documentation manual. The remaining steps of this procedure serve primarily to document the necessary operations.

- (f) When a set of control data that meets the requirements of step (e) has been assembled, calculate the relative standard deviation of the data and the corresponding control limits using the procedures of Method PNL-ALO-434 Section 4.6.2 Establishing Control steps (e) and (f).
- (g) Calculate the corresponding detection limits for the end of the current control chart, usually December 31 of the current year, using the decay correction procedure of Method PNL-ALO-434 Section 4.6.2 Establishing Control step (g). If the control nuclide is cobalt-57, the control chart should include only a two month interval, not a calendar year,

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because the short half life results in sufficient decay to produce a count rate (vertical scale increment that is extremely small and difficult to use when the control chart is prepared using K&E 47-2730 paper. For cobalt-57, calculate corresponding detection limits for the last day of each even numbered month (February, April, ... December).

- (h) Prepare the control chart using the procedure of Method PNL-ALO-434 Section 4.6.2 Establishing Control step (h). If the nuclide is cobalt-57, the control charts may be laid out in sets of three 2-month intervals on two separate sheets of K&E 47-2730 paper.

The control chart is now ready for use in evaluating routine control counts (refer to Section 4.6.2 Control Maintenance). So long as the current control set data remains valid, control charts may be prepared for subsequent years by using step (g) to decay correct the data and preparing new charts (step h). This capability is incorporated into the CONCHT computer program.

Control Maintenance

Control standards are counted at least once during each day on which that counting system is used; normally this is done at the beginning of the day shift. Control counts are entered into the Sample Counting Log for the respective counting system using the format designated for sample count entry. The data resulting from each control count is entered into the respective section for that control source in the Control Log for that counting system.

Control source counting is performed using the following procedure:

- (a) Verify the detector high voltage (NaI system) or bias voltage (intrinsic Ge system) is set of the proper value (refer to Table 2).
- (b) Place the high energy control source (Co^{60}) in counting position. Adjust the fine gain of the amplifier until the 1332.5 KeV peak is positioned in the appropriate channels as follows:

NaI system- peak centered with equal count rates in channels 128 and 138.

Ge system- peak maximum in channel 1332.5 (equal count rates in channels 1332 and 1333).

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- (c) Place the low energy calibration source (NaI system- ^{60}Co ; Ge system- ^{152}Eu) in counting position. Adjust zero on the analog to digital converter until the appropriate peak (NaI system - 122.06 KeV gamma; Ge system - 121.78 KeV gamma) accumulates in the appropriate channels as follows:

NaI system- peak maximum in channel 12.25 (peak maximum in channel 12, channel 13 midway between channels 11 and 12 in amplitude).

Ge system- peak maximum in channel 121.8 (count rate in channel 122 is twice that in channel 121).

- (d) Since zero and gain adjustments are interactive, repeat steps (b) and (c) until both conditions are met.
- (e) Perform 10.0 minute counts for each control source (refer to Section 4.9.2).
- (f) Perform a 10.0 minute background count (refer to Section 4.9.1).
- (g) Calculate the background corrected count rates corresponding to each control count using the range of channels indicated in the Control Log.

$$R_c = \frac{A_s}{T_s} - \frac{A_b}{T_b}$$

where R_c = the corrected count rate in counts per minute.

A_s = the sum of the channels corresponding to the control count designated channel range.

A_b = the sum of the same channels used to determine A_s in the background spectrum.

T_s = the length of the control count in minutes.

T_b = the length of the background count in minutes.

Record the date, time, total count (A_s), corresponding background count rate (A_b/T_b), and the control corrected count rate (R_c) for each control source in their respective section of the Control Log for the counting system.

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- (h) Plot the control corrected count rates (R_c) on the appropriate control chart in their respective sections of the Control Log for the counting system and determine control status. Limits for the 95% confidence level, $\pm 1\% \bar{x}$, $+ 2\% \bar{x}$, and $+ 3\% \bar{x}$ are indicated on the control charts. If both control the measurements for a given instrument are within their respective $\pm 3\% \bar{x}$ control limits, that instrument is ready for use.

Should one or more control measurements fall outside of $\pm 3\% \bar{x}$ control limits, repeat those control counts. If the recounts fall within limits the instrument is considered to be operating in control and can be used for sample counting. If any recount again falls out of limits, the instrument must not be used until the problem is investigated and corrected.

4.7 ANALYSIS

4.8 CALCULATION

4.9 OPERATION

4.9.1 Background Count

Background spectra are used to correct sample count data for activity contributions external to the sample and to calculate detection limits where no significant gamma component is observed. At least one background count is made for each gamma ray spectrometry system on each day it is used. This is usually a 10.0 minute count performed at the beginning of the day shift after system control counts have been run that is a part of the control procedure. Since sample spectra that are obtained with the intrinsic germanium/TN-4000 system, excepting control source counts, are calculated using a leading-trailing edge correction to the individual peak areas rather than subtracting the corresponding peak area of a background count, the principal function of a background count is to identify trace gamma components that are background contributed rather than sample contained. Sixty minute backgrounds are often started at the end of the day shift and interpreted at the beginning of the next day. Fifty-five thousand second background spectral counts are accumulated over a weekend on at least a monthly basis.

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All background counts are recorded in the counting log for the counting system using the format designated for sample count entry.

- (a) Verify operational parameters are correctly set (refer to Table 2).
- (b) Place a "blank" source corresponding in form to the samples to be counted on the system in the sample geometric configuration with respect to the detector that will be used in counting.
- (c) Accumulate a spectrum for an interval at least equal in length to the sample count.
- (d) Printout an identification heading for the background count. This usually will consist of one line describing the sample and a second describing counting parameters. When counting is completed, print out a channel listing of the spectrum on the printer.
- (e) For the NaI/ND-66 system spectrum, calculate an iodine-131 background by summing channels 32 through 44 and dividing the result by the duration of the count in minutes:

$$c/m = \frac{C}{T}$$

where c/m = the background in counts per minute
 C = the sum of channels 32 through 44
 T = the length of the count in minutes.

Detection limit calculations from background spectra are discussed in Method PNL-ALO-447 Section 4.8.2.

4.9.2 Sample Count

All charcoal cartridge samples are counted ten minutes on the NaI/ND-66 as a rapid screening process for significant activity. Should the calculated iodine-131 count rate be less than the detection limit calculated from a background count (refer to Method PNL-ALO-447 Section 4.8.2) or should the result be slightly positive

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and there be no observable "peak" in the iodine channel, and should there be no "peaks" anywhere in the spectrum, counting is complete. Should "peaks" be observable in the NaI/ND-66 system spectra, a 3600 second sample count is performed on the intrinsic germanium/TN-4000 system to produce a spectrum of sufficient resolution to permit identification and calculation of the gamma components of the nuclide mixture present.

All sample counts are recorded in the Sample Counting Log for that system using the format designated in that log. Counting data is recorded on a preprinted CHARCOAL CARTRIDGE GAMMA ANALYSIS data sheet. Cartridge samples currently active in the STACK program are printed in numerical order by building designation. A sampling and counting data line is provided for each sample together with separate sublines for individual nuclides identified in the sample. The form is reproduced by copying machine so that it can be readily revised to reflect changes in program sampling schedules.

- (a) Verify operational controls are correctly set (refer to Table 2) and that the system is operating within control limits (refer to Section 4.6.2 Control Maintenance).
- (b) Place the 8 oz styrene jar containing the charcoal from the cartridge in a 6 inch by 9 inch plastic bag and position it on the detector, centered on the face. The bag serves to prevent possible contamination of the detector.
- (c) Accumulate a spectrum. The count duration for the NaI/ND-66 system is 10.0 minutes; for the Ge/TN-4000 system it is 3600 seconds (1 hour).
- (d) Print out an identification heading for the sample. This usually will consist of one line describing the sample and a second describing counting parameters. When counting is completed print out a spectrum channel listing on the printer. NOTIFY THE APPROPRIATE SAFETY ORGANIZATION IMMEDIATELY SHOULD PEAKS WITH TOTAL PEAK AREAS OF THE ORDER OF 10,000 COUNTS OR MORE IN TEN MINUTES BE OBSERVED.
- (e) Record the sample data on the Charcoal Cartridge Gamma Analysis Summary sheet. One or more lines

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are provided for each sample; each radionuclide identified in a given sample is entered on a separate line. Columns are provided for entry of each cartridge's sampler flow rate, sample on date and time, sample off date and time, count date and time, nuclide count rates in counts per minute, and comment.

4.9.3 NaI/ND-66 System Spectra

Calculate the background corrected count rate for the iodine-131 channel band:

$$c/m = \frac{A_s}{T_s} - \frac{A_b}{T_b}$$

where c/m = the background corrected iodine-131 count rate in counts per minute

A_s = the Iodine-131 total peak area, the sum of channels 32 through 44

A_b = the corresponding sum of channels 32 through 44 of a background count

T_s = the length of the sample count in minutes

T_b = the length of the background in minutes

If the calculated iodine-131 count rate is equal to or less than the detection limit (refer to Method PNL-ALO-447 Section 4.8.2), record the calculated detection limit value, preceded by a "<" symbol, on the Charcoal Cartridge Gamma Analysis Summary sheet on the line for that sample together with sampler flow rate, sample on and off times, and counting date and time. If the calculated count rate is slightly greater than the detection limit and NO "PEAKS" ARE VISIBLE, similarly record a zero on the summary sheet. The STACK computer program recognizes input zeros as a code for a positive result with no evidence of I-131 itself and proceeds to report a "less than" value on the detection limit.

Should the iodine-131 or any other peak be visible in the spectrum, the sample must be subsequently counted on the intrinsic Ge/TN-4000 system.

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4.9.4 Intrinsic Ge/TN-4000 System Spectra

- (a) Using the spectrum display on the system terminal and the channel cursor, mark all observed peaks in the printed sample spectrum and identify the nuclide each is associated with.
- (b) Calculate the leading-trailing edge corrected total peak area of at least one principal peak for each nuclide identified in the sample spectrum. The leading-trailing edge corrected total peak area calculation is discussed in Section 4.6 Subsection 4.6.1. Calculate the total peak count rate in counts per minute by dividing each principal peak corrected total peak area by the length of the count in minutes. Lead-214 and bismuth-214 of the radium-222 decay chain, nuclides whose identification is questionable, and nuclides present in amounts only slightly above their level of occurrence in background are not calculated; such nuclides are reported as present or probably present in the report comment section, but no numerical values are stated.
- (c) Record the principal peak count rates on the Charcoal Cartridge Gamma Analysis Summary sheet on the line(s) for that sample. Format entries on the sheet as follows to make data entry into the STACK computer program less subject to input error or omission:

With a red pencil, draw a line through the date and time of the NaI/ND-66 count and write those for the Ge/TN-4000 count above them. In the data sheet right margin bracket the sample line(s) in red and label as "FOG DATA." Nuclides for which numerical results are not to be reported are entered in the COMMENT column of the summary sheet to serve as a reminder during generation of the printed report. Typical entries are "Pb-214 + Bi-214" and "probable trace Cs-137."

5.0 BIBLIOGRAPHY

- (a) J.B. Birk. The Theory of Practice of Scintillation Counting, MacMillan Co., New York (1964).

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- (b) D.C. Camp. Application and Optimization of the Lithium Drifted Germanium Detector System. VCRL 50156, March (1967).
- (c) C.E. Crouthamel. Applied Gamma Ray Spectrometry; MacMillan Co., New York (1960).
- (d) H. Fiedler and O. Tench. Germanium (Li) Gamma Spectrometry Systems, Canberra Industries, Inc., Middletown, Connecticut (1968).

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TABLE 3: Normal Operational Settings for Gamma Spectrometry Systems

4x5 NaI/ND-66 System:

TC-145

Input Cap pF 100

TC-202 BLR

Coarse Gain 10

Fine Gain set to position Co⁶⁰
1332.5 KeV peak

P/Z set ^(a)

DC set ^(a)

Restorer Out

Shaping Unipolar

Rate High

Polarity Inverted

412A

High Voltage 1077 V
Polarity +

GEN II

Conversion Gain 1024

Group Selector 1024

Lower Level Discriminator 0 20.7

Analog Zero set to position
122.06 KeV peak

Upper Level Discriminator 10 0.0

Zero Suppression (13) all set to 0

ADC Input Mode DC

ADC Baseline Restorer Out

Discriminator Input Signal

Discr. Gate Auto Normal

Discr. Gate Coinc. Anti

ND-66

Set-up Parameter Page

ADC (SP) 1

Groups 2

Chans 256

Digoff 0

Spectrum Data Page

KeV/ch 1.000

Zero 0.000

LA120-AA

REC 1200 H 10 R 1

XMT 1200 J 1 S 0

A 0 K 0 U 1

B 1 L 0 V 6

C 1 M 1 W 1

D 1 N 1 X 1

E 0 O 1 Y 0

F 1 P 1 Z 1

G 1 Q 0

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TABLE 3. (contd)

INTRINSIC GE/TN-4000 SYSTEM:

315
Output 7 00 = 3500 V
Polarity (internal) POSITIVE

TN-1242
Analyze up (ON)
Coinc/Anticoinc Anticoinc
Discriminator LLD 0 10.0
Discriminator ULD 10 0.0

2010
Coarse Gain 30
Fine Gain set to position Co⁶⁰
1332.5 KeV peak

Threshold(a)
Zero Level set to posit. Eu¹⁵²
121.78 KeV peak

Pole Zero^(a)
Shaping ASYM
Restorer LO
Threshold VAR(a)
Polarity Input NEG
Unipolar Output DC Level (a)
Unipolar Output Polarity POS

Group Size 4096
Conversion Gain 4096

TN-4000
Data Mem 1
Select first half

LA120-AA
REC 1200 H 10 R 1
XMT 1200 J 1 S 1
A 0 K 0 U 1
B 1 L 0 V 6
C 1 M 1 W 1
D 1 N 1 X 1
E 0 O 1 Y 0
F 66 P 1 Z 1
G 1 Q 0

(a) This adjustment is made by instrument personnel and must not be changed by the operator.

FIGURE 6-40.3.1. Calculation of Corrected Total Peak Area for a Typical High Resolution Gamma Spectral Peak

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-447, (Replaces 6-40.4), DATA PROCESSING, ANALYTICAL REPORT
PRODUCTION, AND RECORDS MANAGEMENT

1.0 APPLICABILITY

Calculations are automatically performed and printed analytical reports are generated for distribution by manual entry of sample and sample counting data into a 1123+ computer based STACK program.

The computer based data processing program is designed with sufficient flexibility and internally selectable options to permit adaption or expansion to include most conceivable requirements of an exhaust stream monitoring program such as the STACK program.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

Effort required to process counting data and produce an analytical report in a format suitable for distribution to involved parties is both more labor intensive than accumulation of the data and more subject to the introduction of error. A computer based data processing program has been developed to reduce manual operations as much as possible at the present state of laboratory instrumentation. By combining minimal manual data interaction

Author	Date	Project Mgr.	Date	QAD Representative	Date
MR Weiler	9/19/88	N/A		LJ Ethridge	9/19/88
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N/A		WC Weimer	9/19/88	All original signatures on file	
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with active data input monitoring and complete input data proofing, potential for errors other than interpretational has been greatly reduced.

The STACK Computer Program is a DEC 1123+ RSX-11M system based program written in compiled Basic-Plus-2. Counting systems employed in the production of analytical data are identified by responding to program prompts; all applicable systems calibration data, nuclear data, fixed sample parameters, and report distribution lists are automatically called from files internal to the program. All sampling and counting data are input in response to specific program prompts. Particle filter sample alpha and beta count data is entered in exactly the gross count form it is recorded from counting instrument scalers. Current laboratory instrumentation requires charcoal cartridge gamma spectra be manually interpreted and isotopic components calculated to a background corrected count rate basis for entry.

The computer program output consists of two parts for each sample entered. The first is a listing to the terminal screen of all data for the sample that was input to the program; it is intended to serve in proofreading for data input errors. The second is a printed analytical report in a format suitable for direct distribution. The program provides the options to save particle filter total alpha and total beta and cartridge iodine-131 curie per run results to a data summary file for that specific sample. The contents of these files can be printed out in sample data summary form.

Computer system operating instructions, a step-by-step guide to use of the STACK Computer Program, instructions for changing data in internal program files, and complete Basic-Plus-2 listings for all the program modules of the STACK Computer Program are available for reference in the STANDARDS PROGRAM RSK-11M SYSTEM BASED documentation manual.

4.2 APPARATUS

4.3 REAGENTS

4.4 STANDARDS

4.5 SAFETY

4.6 QUALITY CONTROL

4.6.1 Calibration

4.6.2 Control

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4.7 ANALYSIS

4.8 CALCULATION

Excepting the manual interpretation and calculation of gamma spectra on an individual isotopic count rate basis, all sampling data and sample count data is entered into the STACK program in the form in which it is received or produced, all subsequent calculations are automatically performed. For documentation purposes these calculations are presented below. Numerical values for factors relating to counting instrument calibration, radionuclide decay, and fixed sampling parameters can be retrieved from STACK program data files by means of the appropriate utility module.

4.8.1 Fundamental Assumptions

(a) Radioactive Decay Corrections:

Alpha and beta results are reported as of counting time and, therefore, are not decay corrected.

Gamma spectral analysis results are decay corrected to the midpoint of sampling unless definite reasons exist for other actions. Decay corrections to the time sampling was terminated is appropriate where very short-lived daughter activity is not associated with an observable long-lived parent. No decay correction is applied to nuclides with half-lives that are very short compared to the duration of the sampling interval where presence of a long lived precursor is ambiguous.

The computer program automatically generates appropriate footnotes on the printed reports indicating what decay corrections have been applied.

(b) Sampling Efficiency:

Particle filter and charcoal cartridge collection efficiency are assumed to be 1.000.

4.8.2 Detection Limits

Statistical detection limits for alpha, beta, and gamma spectrometric measurements are defined on a count rate

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basis and are equal to two standard deviations of the background count observed:

$$\text{detection limit} = \frac{2\sqrt{B}}{T}$$

where B = the observed accumulated background count
T = the total counting time in minutes.

Should an observed background count be zero, a value of 1 is adopted.

If an observed sample count rate is less than this statistical limit, the calculations are performed using the statistical limit and the result is prefixed with the "<" (less than) symbol.

4.8.3 Calculation of Results

All measurements are calculated as both $\mu\text{Ci/cc}$ (microcuries per cubic centimeter stack stream) and Ci/R (total curies for the sampling interval or run) except those samples, such as a room air samples, that do not relate to an effluent stream and only $\mu\text{Ci/cc}$ values are meaningful.

$$\mu\text{Ci/cc} = \frac{(c/m) (d/c) (0.45045 \times 10^{-6}) (DC)}{(CE) (24317) (F_{sa}) (I) (60)}$$

where c/m = the observed count rate in counts per minute, background corrected.

d/c = the counting instrument disintegration/count ratio obtained by calibration.

0.45045×10^{-6} = the fraction of a microcurie corresponding to 1 disintegration per minute.

DC = the decay correction [refer to Subsection 4.8.1 part (a)].

CE = the sampling device collection efficiency [refer to Subsection 4.8.1 part (b)].

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24317 = the number of cubic centimeters in one cubic foot.

F_{sa} = the SAMPLER flow in cubic feet per minute.

I = the sampling interval expressed in hours.

60 = the number of minutes in 1 hour.

$$Ci/R = \frac{(c/m) (d/c) (0.45045 \times 10^{-12}) (F_{st}) (DC)}{(CE) (F_{sa})}$$

where 0.45045×10^{-12} = the fraction of a curie corresponding to 1 disintegration per minute.

F_{st} = the STACK STREAM flow in cubic feet per minute.

Other variables are as above.

4.9 RECORD MANAGEMENT

Archive copies of Basic-Plus-2 source code files, compiled executable task files, and data files for all STACK program modules, together with SAT based word processor files containing the text of the STACK PROGRAM documentation and instruction manual are preserved by the cognizant scientist on 8 inch floppy discs. This archive is supplemental to the routine backup procedures in 1123+ system management.

The computer-produced input variable listings printed to the terminal screen for the individual samples are proof checked for possible errors in data input; should an error be discovered, no analytical report is generated and all the sample data must be re-entered from the beginning.

The analytical report is photocopied for distribution to individuals on the sample distribution lists. Original copies for the entire sample set of a given weekly sampling interval are filed together with Filter Change Data Sheets and the analytical data in a folder. Sample set folders are retained at Chemistry

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and Analysis in a chronologically ordered file for at least one year, after which they may be transferred to the Hanford Records Holding Center where they are stored permanently according to schedule appendix 1324.2 CRS25, item no. 10E.

Three types of files relating to the Stack Program are maintained permanently by Chemistry and Analysis:

- (a) A correspondence file, containing all written communications and memos of telephone communications from operating groups at Westinghouse Hanford Co. and PNL that relate to the program. This file generally consists of notices of changes in building stack flow rates, changes in locations to be sampled, and changes in report distribution.
- (b) Calibration data files for each instrument used in performing Stack Program analytical measurements. These files generally consist of the standard source preparation instructions, the counting data obtained using the standards, and all data processing work sheets generated in the production of calibration factors that relate to Stack Program counting procedures.
- (c) Copies of Records Transfer forms relating to transfer of Stack Program sample set folders to the Hanford Records Holding Center. The Transfer Records are useful in identifying the box number of a given sample set should it be necessary to recover the file.

Since the laboratory instruments employed in Stack Program sample analysis are in general laboratory use, plateaus and control records are maintained under applicable laboratory procedures apart from the Stack Program.

5.0 BIBLIOGRAPHY

NONE

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TITLE: PNL-ALO-448, (Replaces 7-30.6), DETECTOR/DEWAR ACCEPTANCE TESTS

1.0 APPLICABILITY

This procedure describes the tests to be conducted to determine that a Detector/Dewar meets specifications. The tests consist of checking the Dewar's LN₂ consumption and the detector's resolution, noise level and D.C. voltage at the preamplifier's test point.

2.0 DEFINITIONS

ADC	Analog-to-digital converter
FWHM	Full width at half maximum
FWTM	Full width at tenth maximum
LN ₂	Liquid nitrogen
LRB	Laboratory Record Book
NIM Bin	Nuclear Instrument Module which conforms to report TID-20893 (Rev.), January 1968.

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Detector test stand consisting of lead cave, NIM bin, H.V. power supply, amplifier, ADC, countrate meter, multichannel analyzer (4096 min.) and printer.
- Oscilloscope
- LN₂
- Vendor's data sheet
- Radioactive sources such as Co-57, Co-60, Ba-133, Cs-137

Author	Date	Project Mgr.	Date	QAD Representative	Date
FE Holt	10/7/88	N/A		LJ Ethridge	10/7/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	10/7/88	All original signatures on file	
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- Acceptance Sheet, Figure 2.

4.2 Dewar Check

Set detector/Dewar on test stand and add LN_2 as needed. The system shall be under LN_2 conditions for at least 8 hours before proceeding. Add LN_2 weekly noting the amount of LN_2 required to fill. LN_2 consumption shall not exceed manufacturer's specification. The Dewar shall be checked over a period of at least 2 weeks.

4.3 Resolution Checks

Using appropriate radioactive sources, adjust zero, gain and digital off-set so that there are ~10 channels in the FWHM region. Position the source relative to the detector so that there is <10% dead time at the ADC or <2000 c/min at the countrate meter. Count the source until at least 5000 counts have been collected in the peak region. Plot at least 20 channels of the counting data so that both the leading and trailing edges are at their respective baselines. Calculate the FWHM for low energy (<100 KeV) and both FWHM and FWTM for other energies (>500 KeV). Compare results with manufacturer's data sheet. The values obtained should be within $\pm 10\%$ of the listed numbers.

4.5 Calculations

Step 1) As shown in Figure 1 below, obtain the FWHM in channels.

Figure 1. Measurement of FWHM by Linear Interpolation

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Step 2) Calculate the FWHM in units of eV or KeV by dividing the # channels from 1 by the channel/eV or channels/KeV obtained in 3.

Step 3) Channels/eV: Divide the peak channel number by the peak energy;

$$\frac{\text{peak channel \#}}{\text{peak eV}} \quad \text{or} \quad \frac{\text{peak channel \#}}{\text{peak KeV}}$$

Step 4) The FWTM is calculated in the same way, except that $H = P/10$.

4.6 Records

Record pertinent data on the Acceptance Sheet (Figure 2). Place a filled-out copy of the sheet in a LRB and attach a copy to the Dewar/Detector. Place another copy along with printouts, plots, calculations, and the manufacturer's data sheet in the LRB or in a folder referenced in the LRB.

Records will be maintained and controlled so as to conform with the requirements of MCS-033. ~~Laboratory record books and analytical report forms provide a mechanism for control of most records. Laboratory record book will be used in accordance with PAP 70-1704.~~

4.7 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally it is considered qualified because it has independent technical review.

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PNL TECHNICAL PROCEDURE

Acceptance Sheet

Detector Type _____ Serial Number _____ Manufacturer _____

Manufacturer Specification

Measured

Energy Resolutions: _____ ev@ _____ KeV _____
 _____ ev@ _____ KeV _____
 _____ ev@ _____ KeV _____

FWHM: _____ @ 1.33 MeV _____

FWTM: _____ @ 1.33 MeV _____

DC Voltage @ P.A. Test Point _____ *

*Must be within ± 0.5 v of manufacturer's specification

Noise Levels: Observed by oscilloscope or countrate meter?

☐ | | NONE

LN₂ Consumption _____ L/day _____ L/day

Comments: _____

Tested from _____ to _____ Signature _____

Figure 2. Acceptance Sheet

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INTERIM CHANGE NOTICE
ICN

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<p>A. Document Number: <u>PNL-ALO-449 R0-1</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Zero and Gain checks and Control Charts</u> <u>Track Detector</u></p> <p>Document's Original Author <u>FE Holt</u></p>		<p>Effective Date of ICN: <u>APR 08 1993</u></p> <p>APR 08 1993 <u>XX 4-8-93</u></p> <p>Change Requested by: <u>TL Ehlert</u></p>
<p>B. Action: Replace pages 1 and 2. DO NOT REMOVE FIGURE 1 ON PAGE 3 OF 3.</p>		
<p>C. Effect of Change: Updates procedure so that alternate sources and laboratory record books may be used.</p>		
<p>D. Reason for Change/Description of Change:</p> <ol style="list-style-type: none">1. To allow the use of alternate sources, the description of the source has been deleted from section 4.1, step 1. See strike-out.2. To allow the use of alternate laboratory record books (LRB), the description of the LRB has been deleted from section 4.2, step 6. See redline and strike-out.		
<p>E. Approval Signatures: (Please Sign and Date)</p>	<p>Type of Change (Check (✓) one) (✓) Minor Change () Major Change</p>	
<p>QP Concurrence: <u>TL Ehlert</u> <u>TL Ehlert</u> Date: <u>4/8/93</u></p> <p>Approval Authority: <u>AG King</u> <u>AG King</u> Date: <u>4/8/93</u></p> <p>Other Approvals: <u>LR Greenwood</u> <u>LR Greenwood</u> Date: <u>4/8/93</u></p> <p>: _____ Date: _____</p>		

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-449 (Replaces 7-30.9), ZERO AND GAIN CHECKS AND CONTROL CHARTS--TRACK DETECTOR

1.0 APPLICABILITY

The computer-based (μ VAX) MCA with the Track detector is currently set to operate at 0.75 KeV per channel. This procedure describes how to check that relationship and to obtain and record Control Chart data.

2.0 DEFINITIONS

MCA - Multichannel analyzer

@ - The control character that processes a command (file-spec.Com) file

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Zero and Gain check for 0.75 KeV/channel.

- Step 1) Place the Am/Cs/Co source (~~MS-130-1~~) in the pill vial holder and set in position 6 on the Track Detector.
- Step 2) Start a count and expand the regions around the 59 KeV and 1333 KeV peaks
- Step 3) The 59.5 KeV peak from Am-241 should be in channel 97.3 ± 0.5 channel. See Figure 1.
- Step 4) The 1332.5 KeV peak from Co-60 should be in channel 1776.7 ± 1 channel as shown on Figure 1.

4.2 Control Data Charts

- Step 1) Set the Am/Cs/Co source (PV) in position 6 on the Track Detector.

Author	Date	Project Mgr.	Date	QAD Representative	Date
FE Holt	2/2/89	N/A		LJ Ethridge	2/6/89
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	2/3/89	All original signature on file	
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- Step 2) Set μ VAX terminal screen to ADC2.
- Step 3) Type @Track-Con and <Return> on keyboard.
The system will clear the screen, display the previous control count, clear that and begin a 15 minute count.
- Step 4) Set the printer to print (yellow light ON).
- Step 5) At the end of the count the system will subtract background; print a report; store the spectrum onto DUA0; purge the file T89.CNF.
- Step 6) Record results in ~~in BNW-52327~~ in a LRB and plot. Data points shall fall within the 95% boundaries. Repeat the count if outside the 95% boundaries but within the 99% boundaries. The second count shall fall within the 95% boundaries. Reset zero and gain and recount if the first count is outside the 99% boundaries or the second count is outside the 95% boundaries.

5.0 BIBLIOGRAPHY

Instruction manual: VAX/VMS Spectroscopy Applications Package, User's Manual (07-0196), December, 1987, Nuclear Data Instrumentation, Schaumburg, Il.

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PNL TECHNICAL PROCEDURE

FIGURE 1. Counts vs. Channel Number

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-450, GAMMA ENERGY ANALYSIS - TRACK DETECTOR

APPLICABILITY

This procedure describes the use of the ND9900 with the Track Detector. The ND9900 is a computer-based multichannel analyzer with an acquisition module which can collect data from up to four detectors, simultaneously. The current Track Detector is a 67.6 cc, coaxial Ge(Li) system whose size is 44.3 mm diameter by 48.5 mm long with a drift depth of 17.9 mm. The detectors measured efficiency is 14.8% @1.333 MeV relative to a 3" x 3" NaI(Tl) detector @25 cm. (This procedure will be equally applicable with a comparable or additional Ge(Li) detection system.) Samples can be placed as close as 1/4-inch from the detector or up to 35-1/2 feet away in 29 discrete positions.

DEFINITIONS

- BOC - Beginning of count time
- PARS - One of a number of ND9900 commands, others are SET, MOVE, PEAK, etc.
- ND9900 - A computer-based gamma counting and data reduction system
- NaI(Tl) - Sodium Iodide, thallium activated
- Ge(Li) - Germanium, Lithium drifted
- 9X-XXXX - Chemical Measurements Laboratory sample log-in number. (9X signifies year)

RESPONSIBLE STAFF

- Cognizant Scientist
- ND9900 System Manager
- Analyst

PROCEDURE

1.0 Equipment and Materials

Author: <i>W. E. Hall</i>	Date <i>4/17/90</i>	Project Mgr. <i>2E8</i>	Date <i>4/16/90</i>	QAD Representative <i>F. L. English</i>	Date <i>4-12-90</i>
Technical Reviewer <i>James H. Kays</i>	Date <i>4/17/90</i>	Line Mgr. <i>Walter C. Meunier</i>	Date <i>4/17/90</i>	Other <i>N/A</i>	Date
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PNL TECHNICAL PROCEDURE

2.0 Daily Control Counts

Each day or shift that the Track Detector is to be used, a control count shall be performed using procedure 7-30.9, Zero and Gain Checks and Control Charts - Track Detector.

3.0 Sample Counts

- 3.1 While the ND9900 is in the MCA ON mode, place the prepared sample in the appropriate pill vial (PV) or scintillation counting vial (SCV) holder and set that on one of the detector's counting positions. Counting rates shall normally be less than 4000/sec to avoid having to make dead time corrections to the data.
- 3.2 Count the sample for the time needed to give the required counting statistics as determined by the Cognizant Scientist.
- 3.3 Assign the sample count a log number, TXXXX, in the Laboratory Notebook (LRB) and record the sample identification, BOC, counting time, and length of count.
- 3.4 Use the PARS commands to identify the sample and counting parameters, e.g., PARS ADC2, SET TITLE (include the sample log-in number, "9X-XXXX" in the TITLE), SET sample parameters. To set desired counting time use SET PLIVE. Type EX to exit PARS.
- 3.5 At the end of the count, type MOVE ADC2 TXXXX (TXXXX = log number assigned to the sample count).
- 3.6 Using the appropriate commands from the ND9900 Instruction Manual obtain printed reports of a peak analysis and nuclide identification. The usual set of commands is:
 - a) PEAK/START=30/LIST=TTA1: TXXXX (log number used in Step 3.3)
 - b) ENBACK/CLEAR/BKGND=TRBACK/LIST=TTA1: (optional)
 - c) MOVE/PARTIAL TXXPOINT/EFF/CAL TXXXX (where TXX is the sample position number, e.g. T2POINT up to T29POINT. Other sample geometries are TXXGAS and TXXSCV).

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- d) NID/REP=ACT/LIBRARY=TRPOINT/TOLER=0.8/ABUND=30/LIST=TTA1:
(other library files are RARE-EARTHS, LIBD, COVGAS, DOSLIB,
etc.)

3.7 Write the requested information on an Analytical Report form, noting the M&TE number (WB37560) and the LRB containing the daily control data.

3.8 Initial the Analytical Report form and submit all data to the Cognizant Scientist for review and approval.

4.0 Specific Qualification

This procedure is self qualifying due to dependence on daily control counts.

5.0 Bibliography

Instruction Manual: VAX/VMS Spectroscopy Application Package User's Manual (07-0196), December 1987 (or latest revision). Nuclear Data Instruments, Schaumburg, IL.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-451, (Replaces HTA-4-9), SOLUTIONS ANALYSIS: GAMMA SPECTROMETRY

1.0 APPLICABILITY

This procedure applies to the analysis of aqueous samples by gamma ray spectrometry as prepared in Section 4.3 of this procedure.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Gamma spectrometer, Tracor-Northern TN-4000 with GeLi detector or equivalent.
- Gamma spectrometer, Nuclear Data ND-66 with GeLi well detector or equivalent.
- Nitric acid, 2 M -- Dilute 126 (± 2) mL of concentrated reagent-grade acid to 1000 mL (± 2) mL with deionized water, mix thoroughly.

4.0 PROCEDURE

4.1 Daily Control Standards

The daily control standards for both the TN-4000 and the ND-66 gamma spectrometers are mixtures of ^{241}Am , ^{137}Cs and ^{60}Co . The gamma sources are dried on a circular ($\sim 3/8$ in. diameter) piece of mylar stuck onto a piece of tape and covered with a slightly larger piece of tape to hold the activity in place. The taped

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AC Leaf	07/01/87	N/A		BO Barnes	06/30/87
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N/A		JJ McCown	07/02/87	All original signatures on file	
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mylar piece containing the gamma activity is placed in the cap of a polystyrene vial lid and is held in place using a dental roll in the vial which is placed into the lid. The vial lid is secured on the vial using tape. The mixed gamma source is counted at least 10 times and the average count and statistical limits of each isotope count is calculated. Daily counts must fall within defined limits before samples may be counted. (See Daily Control Charts which are found in the TN-4000 and ND-66 notebooks.)

The following daily control standard count procedures shall be used for either system.

- Step 1) Adjust gain and zero as required with the daily control standard using the appropriate daily control and energy calibration guide.
- Step 2) Count the daily standard for 600 seconds and record counts on the appropriate control chart in the gamma notebook(s). Counts must be within limits before samples may be counted. These Steps 1 and 2 are to be done at the beginning of each shift.

4.2 Calibration Standards

- TN-4000 -- An efficiency curve for each counting position is generated from several NBS gamma standards. The efficiency curve relates gamma counts to actual gamma activity over the energy range of ~40 keV to 2 MeV, and each efficiency curve is stored in the computer memory. This calibration is done only once when the spectrometer is initially placed in service. See TN-4000 Automatic Isotope Analysis Program Description and Operation Procedures. Daily calibration is made using the daily control sources defined in Section 4.1.
- ND-66 -- An efficiency curve for the ND-66 GeLi well system is generated using ^{243}Am , ^{241}Am and ^{57}Co standards. The efficiency curve is limit to ~60 keV to 228 keV, and data reduction and calculations are made manually.

4.3 Sample Count - TN-4000

- Step 1) Sample volumes must be adjusted to a total of 10 ± 0.1 mL with 2 M nitric acid and mixed in a 15-mL screw-cap vial to conform to the geometry used in the initial calibration of the gamma spectrometry system.

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- Step 2) While the TN-4000 is in the ACQUIRE mode, place the prepared sample on one of the counting positions on the GeLi detector; observe the dead time on the dead time meter. (The counting position used must give a dead time of less than 10%.)
- Step 3) Stop the ACQUIRE mode, clear the memory, and restart the ACQUIRE mode. Sample counting times may vary from 10 to 60 minutes depending on the activity level of the sample.
- Step 4) Using the appropriate file(s) in the computer memory, perform the peak search and automatic calculations for the isotopes observed. Record results on analytical report. If an observed isotope is not calculated automatically, manually calculate the abundance of the isotope using the calculation in Section 4.5. Record the calculations on the analytical report.

4.4 Sample Count -ND-66

The ND-66 gamma spectrometer usually will be used only for counting ^{126}Sn as prepared using Procedure PNL-ALO-453.

- Step 1) Place prepared sample (in a 2-dram vial) in GeLi well detector.
NOTE: The 5/8-in. plug must be at the bottom of the well.
- Step 2) With the sample in place, start the ACQUIRE mode and count the sample for a preset 16 hour (overnight) period.
- Step 3) Calculate the activity using the efficiency and gamma abundance given in the calculations in Section 4.5. For ^{126}Sn , the sum of the counts in the 86.9-keV and 87.6-keV peaks will be used.
- Step 4) Retain counting data. Record volumes, calculations, and results on the analytical report.

4.5 Calculations

- TN-4000

$$A = \frac{(B) (C) (D)}{(E) (F)}$$

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Where:

- A = dis/min/mL of observed isotope
- B = net counts in "peak"
- C = volume factor to relate to 1 mL
- D = Efficiency as γ /ct
- E = Minutes counted
- F = γ /dis in decay scheme expressed as a decimal fraction.

• ND-66

$$A = \frac{(B) (C) (D)}{(E) (F)}$$

where:

- A = ^{126}Sn dis/min/mL
- B = sum of net counts in 86.9-keV and 87.6-keV "peak"
- C = volume factor to relate to 1 mL
- D = 1.55 γ /ct
- E = minutes counted
- F = 0.459 γ /dis.

4.6 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-452, (Replaces HTA-4-40), SEPARATION OF CESIUM PRIOR TO MEASUREMENT OF Cs-135 BY MASS SPECTROMETRY AND GAMMA SPECTROMETRY

1.0 APPLICABILITY

This procedure describes a method for separating cesium from spent fuel solutions. Following the cesium separation, cesium-135 is measured by mass spectrometry and gamma spectrometry using Technical Procedure PNL-ALO-451.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Nitric acid, 1.5 M - Dilute 47 ($\pm$ 1) mL of concentrated Ultrex nitric acid to 500 ($\pm$ 1) mL with deionized water. Mix thoroughly.
- AG-50W, X-8, 200-400 mesh, H⁺ form, ion exchange resin.
- Ion exchange column, glass. Column shall have a 6-inch segment of 4 mm ID tubing to hold the resin, a 1-inch, 10 mm ID reservoir at the top, and a 2 mm bore stopcock with a tapered outlet tip at the bottom.
- Vials, 2-dram, glass, leached as described in Procedure PNL-ALO-400, "Sample Preparation: Dissolution of LWR Fuel Samples " Section 4.0 PROCEDURE, Step 1) through Step 6).
- Vials, 15 mL, glass.

4.0 PROCEDURE

The cesium is separated from other elements by chromatographic elution from a cation exchange resin column using 1.5 M nitric acid.

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AC Leaf	07/01/87	N/A		BO Barnes	06/30/87
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PNL TECHNICAL PROCEDURE

- Step 1) Prepare a 1.5 (± 0.1) mL column of AG-50W, X-8, 200-400 mesh, H^+ resin. Place a cotton plug in the bottom of the 4 mm ID glass column and tamp in place to hold the resin. Measure a 1.5 mL volume above the cotton plug and mark. Fill the column to the mark with resin. Wash the column with 3 mL of 1.5 M nitric acid, discarding the acid. The slight shrinking of the column level that will occur should be disregarded.
- Step 2) Load a portion of spent fuel dissolver solution containing approximately 200 nanograms of cesium onto the top of the resin column. The volume to be used will be determined by the cognizant scientist. Record the volume of solution used on the analytical report form.
- Step 3) Wash the sample into the resin column with five 100 (± 1) μ L portions of 1.5 M nitric acid followed by one 500 (± 5) μ L portion of the same acid. Disturb the resin as little as possible. Collect the column effluent in a 15 mL screw cap vial.
- Step 4) Wash the column with four 1 (± 0.01) mL portions of 1.5 M nitric acid. Collect the column effluent in the 15 mL vial from Step 3). Allow each portion to drain completely before adding the next. Discard the collected effluents as waste.
- Step 5) Wash the column with three or four 1 (± 0.01) mL portions of 1.5 M nitric acid. Collect each 1-mL portion in a separate leached 2-dram vial.
- Step 6) Using a P-11 pancake probe equipped GM survey instrument, or equivalent instrument, check each individual 1-mL fraction to determine which fraction contains the maximum activity (Cs-137).
- Step 7) Fill out a Mass Spectrometry Analysis Request Form and submit the maximum activity fraction from Step 6) for mass spectrometry.
- Step 8) Measure the Cs-137 activity in the spent fuel dissolver solution using gamma spectrometry per Procedure PNL-AL0-451, "Solution Analysis: Gamma Spectrometry."
- Step 9) Calculate the Cs-135 activity using the following equation:
- $$\text{Cs-135 disintegrations/minute/gram fuel} = \frac{(A) (B) (C) (G)}{(D) (E) (F)}$$

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PNL TECHNICAL PROCEDURE

where:

- A = Cs-137 disintegrations/minute/ml in the dissolved fuel solution from Step 8)
- B = atom % Cs-135 from Step 7)
- C = half life of Cs-137 (30.17 years)
- D = atom % Cs-137 from Step 7)
- E = half life of Cs-135 (2.3×10^6 years)
- F = grams of fuel dissolved for analysis
- G = final volume (mL) of the dissolved fuel.

4.1 Mass Spectrometric Measurements

The isotopic abundance of Li, K, Rb, and Cs are determined by thermal ionization mass spectrometry. The mass spectrometer bias factors are determined by analyzing National Bureau of Standards reference materials. Each day the instrument is used, an appropriate standard is run. An isotopic Rb standard is used for checking instrument correction factors. Factors for cesium are then calculated, taking into account the difference in mass to charge ratios for rubidium and cesium.

Mass spectrometric data are calculated automatically by computer. The resulting printout tabulates atom percents, weight percents, and isotopic ratios of the mass numbers together with their respective standard deviations.

- Step 1) Prepare rhodium filaments and load sample onto filaments as detailed in Procedure PNL-ALO-428; except cesium samples are mounted by simple evaporation and with no overcoating of platinum.
- Step 2) Record the sample ID in the mass spectrometer logbook. File a copy of the report and the associated instrument calibration data in the mass spectrometer data file.

4.2 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-453, (Replaces HTA-4-21), SEPARATION OF TIN-126 BY ANION EXCHANGE PRIOR TO MEASUREMENT BY GAMMA COUNTING

1.0 APPLICABILITY

This procedure is for the separation of tin in hydrothermal test solutions and the subsequent determination of ^{126}Sn by gamma spectrometry using PNL-ALO-451.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Hydrochloric acid, 2 M -- Dilute 167 (± 2) mL of concentrated reagent-grade hydrochloric acid to 1000 (± 1) mL with deionized water; mix.
- Hydrochloric acid, 1 M -- Dilute 83 (± 1) mL of concentrated reagent-grade hydrochloric acid to 1000 (± 1) mL with deionized water; mix.
- Hydrochloric acid, 2 M with bromine, 1 M with bromine -- Add ~100 μL of bromine to 15 mL of appropriate acid in a 35-mL screw-cap vial; cap and shake vigorously.
NOTE: Excess bromine must be present.
- Ion-exchange resins, AG-50W,[®] X-8, 100 to 200 mesh, H^+ form, and AG-1,[®] X-4, 100 to 200 mesh, Cl^- form.

[®]AG-50W and AG-1 are registered trademarks of Bio-rad Laboratories, Richmond, California.

Author	Date	Project Mgr.	Date	QAD Representative	Date
AC Leaf	07/01/87	N/A		BO Barnes	06/30/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	06/30/87	All original signatures on file	
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PNL TECHNICAL PROCEDURE

- Hydrochloric acid, 6 M -- Dilute 500 (± 5) mL concentrated reagent-grade acid to 1000 (± 1) mL with deionized water; mix.
- Nitric acid, 1 M -- Dilute 63 (± 2) mL of concentrated reagent-grade acid to 1000 (± 1) mL with deionized water; mix.
- Vial, 2-dram, glass, screw-cap.
- Vial, 15-mL, glass, screw-cap.
- Dropper, 7.5-mL, plastic.
- Stir bar, 5/8-in.

4.0 PROCEDURE

The test solution is passed through a cation exchange resin to remove essentially all cations. Tin is loaded onto an anion exchange resin and is washed free of other anions with dilute hydrochloric acid. Tin is eluted with dilute nitric acid and ^{126}Sn is measured using a GeLi well gamma spectrometer.

- Step 1) Add to a 2-dram vial 500 (± 5) μL of acidified test solution.
- Step 2) Add to the vial 1000 (± 10) μL of 2 M hydrochloric acid saturated with bromine; mix the solution by swirling.
- Step 3) Prepare a 1000 (± 00) μL column of AG-50W, X-8, 100 to 200 mesh, H^+ form, ion-exchange resin. Remove the bulb from a 7.5-mL plastic dropper. Insert a small ball of cotton and tamp lightly into the tip of the dropper. Measure and mark a 1000 (± 100) mL volume above the cotton plug. Fill the dropper to the mark with a slurry of the resin. Wash the resin in the column with 2 to 3 mL of deionized water.
- Step 4) Transfer the solution from Step 2 to the column of AG-50W ion-exchange resin. Collect the column effluent in a 15-mL screw-cap vial.
- Step 5) Wash the 2-dram vial with three 1000 (± 10) mL portions of 1 M hydrochloric acid saturated with bromine. Transfer each wash portion to the column of ion-exchange resin. Allow each portion to drain completely before adding the next. Collect all column effluent in the 15-mL screw-cap vial from Step 4. Discard the ion-exchange column.

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- Step 6) To the column effluent collected in Step 5 add 1.25 (± 0.05) mL of 6 M hydrochloric acid and a 5/8-in. stir bar, stir to mix.
- Step 7) Prepare a 1000 (± 50) mL column of AG-1, X-4, 100 to 200 mesh, Cl^- form resin. Remove the bulb from a 7.5-mL plastic dropper. Insert a small cotton ball into the tip of the dropper and tamp lightly. Measure and mark a 1000 (± 50) μL volume above the cotton. Fill the dropper to the mark with a slurry of AG-1, X-4, 100 to 200 mesh, Cl^- form resin. Wash the resin in the column with 2000 (± 200) μL of 2 M hydrochloric acid.
- Step 8) Transfer the solution from Step 6 to the ion-exchange column using a plastic dropper. Collect the column effluent in a 35 mL vial as liquid waste. The tin is retained on the column.
- Step 9) Wash the vial with three 1000 (± 10) μL portions of 2 M hydrochloric acid and transfer each wash portion to the ion-exchange column. The column effluent is waste.
- Step 10) Wash the column with ten 1000 (± 10) μL portions of 2 M hydrochloric acid. Allow each portion to drain completely before adding the next. The column effluent is collected as waste. Cap the 35 mL waste vial and discard in the radioactive liquid waste.
- Step 11) Elute the ^{126}Sn into a 2-dram screw-cap vial with four 1000 (± 10) μL portions of 1 M nitric acid. Allow each portion to drain completely before adding the next. Cap the vial and swirl to mix the solution.
- Step 12) Measure the ^{126}Sn gamma activity using the GeLi well portion of the Gamma Spectrometry procedure PNL-ALO-451.
- Step 13) Record data, calculations and results on the analytical report. Retain gamma analysis data.

4.1 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-454, (Replaces 7-40.17 & HTA-4-41), SEPARATION OF IODINE-129 BY CATION EXCHANGE AND DISTILLATION PRIOR TO MEASUREMENT BY GAMMA (X-RAY) COUNTING

1.0 APPLICABILITY

This procedure describes the separation of iodine from suitable test solutions and the subsequent x-ray counting of iodine-129 using a GeLi well gamma spectrometer.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Staff responsible for implementing this procedure are:

- Cognizant Scientist
- Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Iodine carrier, 10.0 mg/mL iodide -- Prepare by dissolving 1.308 (± 0.001) g of reagent-grade potassium iodide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Potassium permanganate, 0.2 M -- Prepare by dissolving 3.16 (± 0.01) g of reagent-grade potassium permanganate in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sulfuric acid, 10% -- Prepare by diluting 10 (± 0.1) mL of concentrated reagent-grade sulfuric acid to 100 (± 0.1) mL with deionized water. Mix thoroughly.
- Sodium sulfite, 1 M -- Prepare by dissolving 12.6 (± 0.1) g of reagent-grade sodium sulfite in 100 (± 0.1) mL of deionized water. Mix thoroughly.

Author	Date	Project Mgr.	Date	QAD Representative	Date
AC Leaf	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	6/15/88	All original signatures on file	
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- Sodium sulfite, 0.1 M -- Prepare by diluting 10 (± 0.1) mL of 1 M sodium sulfite to 100 (± 0.1) mL with deionized water. Mix thoroughly.
- Ion exchange resin, AG-50, X-8, 100 to 200 mesh, H⁺ form.
- Sodium hydroxide, 1 M -- Prepare by dissolving 4.0 (± 0.1) g of reagent-grade sodium hydroxide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sodium nitrite, 1 M -- Prepare by dissolving 6.9 (± 0.1) g of reagent-grade sodium nitrite in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Silver nitrate, 0.1 M -- Prepare by dissolving 1.70 (± 0.01) g of reagent-grade silver nitrite in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sodium cyanide, 1 M -- Prepare by dissolving 4.9 (± 0.1) g of reagent-grade sodium cyanide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Stir bars, 5/8 in., 1/8 in., glass covered.
- Vials, 35 mL, glass.
- Vials, 2 dram, plastic, 14 mm ID with snap cap.
- Heating block for heating 35 mL glass vials.
- Stirrer, magnetic.
- Droppers, plastic, 7.5 mL.
- Cotton.
- Still, see selenium still, Figure PNL-ALO-440.1
Procedure PNL-ALO-440.
- Heating mantle, round bottom for 50 mL round bottom flask.
- Variac, 0 to 140 volts, 1.5 ampere output.
- Lab-jack, suitable size to hold 35 mL glass vial.
- Nitrogen gas -- Reduce pressure to ~2 psi using a nitrogen gas pressure reducing valve. A purity of 99.5% nitrogen is acceptable.

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- Filters, 13 mm -- Prepare by cutting filter sections from Whatman 934AH glass microfiber filters of a larger size using #9 cork borer. Place the filter on a hard flat surface and press down with the #9 cork borer. Each filter must be dried at 110° to 120°C for at least 30 minutes, cooled and weighed just prior to use to obtain the tare weight in Step 26), Section 4.2, Iodine Separation. Carry the filters on a numbered beaker cover and cover with a larger beaker cover to avoid loss of filters due to air currents. Record the tare weight on the Analytical Report Form.
- Filter holder, Swinnex, 13 mm or equivalent.
- Vacuum jug with hole in stopper to accommodate the base of the 13 mm Swinnex filter holder.
- Beaker covers, 3 in. and 4 in.

4.2 Iodine Separation

Iodine-129 is separated from other radioactive species by passing the iodide (I-) through a cation exchange column. The effluent from the column flows into a still where the iodine (I₂) is distilled into a caustic trap. The iodide (I-) is then precipitated as silver iodide (AgI) and is filtered and weighed to measure recovery. The AgI and filter are transferred to a plastic vial and the AgI is dissolved in NaCN solution prior to counting in the GeLi gamma spectrometer.

The ANALYST shall perform the following steps unless otherwise specified.

- Step 1) To a 35 mL vial add 5/8 in. glass covered stir bar, 1.0 (±0.1) mL of iodide carrier, 1.0 (±0.1) mL of potassium permanganate, 1.0 (±0.1) mL of 10% sulfuric acid and a sample volume (±1%) specified by the COGNIZANT SCIENTIST. Record the volume taken on the Analytical Report Form.
- Step 2) Stir the solution about 30 seconds.
- Step 3) Heat the solution in a heating block at 90° to 95°C for 10 (±1) minutes.
- Step 4) Cool for at least 10 minutes.
- Step 5) To the cooled vial add 1 (±0.01) mL of 1 M sodium sulfite.

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- Step 6) Stir until the solution clears.
- Step 7) Prepare a 2 (± 0.1) mL column of AG-50, X-8, 100-200, H^+ ion exchange resin.
- Remove the top of the bulb from a 7.5 mL plastic dropper.
 - Place a small cotton ball in the tip of the dropper and tamp lightly.
 - Measure a volume of 2 (± 0.1) mL above the cotton plug and mark.
 - Fill the dropper to the mark with a slurry of AG-50, X-8, 100-200 mesh, H^+ form ion exchange resin.
 - Wash the resin with 2 to 3 mL of deionized water.
- Step 8) Remove the nitrogen inlet from the still and place the ion exchange resin column tip in the still inlet at the top of the still. (The still should be in its heating mantle and the mantle connected to the Variac.)
- Step 9) Using a plastic dropper, transfer the solution from Step 6) to the ion exchange column in the top of the still. Allow the effluent from the column to flow into the still.
- Step 10) Wash the vial from Step 9) with 1 (± 0.1) mL of 0.1 M sodium sulfite and transfer the wash to the column in the top of the still.
- Step 11) Repeat Step 10) three more times allowing each wash to pass through the column before adding the next. Discard the column, vial and plastic dropper in the dry radioactive waste.
- Step 12) To a 35 mL glass vial add 2 (± 0.02) mL of 1 M sodium hydroxide and 2 (± 0.02) mL of 1 M sodium sulfite. Place the still outlet beneath the solution in the vial and support the vial with a Lab-jack.

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- Step 13) Add 2 (± 0.02) mL of 1 M sodium nitrite to the still through the still inlet and connect the nitrogen gas inlet cover. Adjust the nitrogen flow to about 5 or 6 bubbles per second.
- Step 14) Set the Variac to 110 and turn on.
- Step 15) Distill until the iodine color is gone; usually about 5 to 10 minutes. The completion of the distillation is very sudden.
- Step 16) Immediately turn off the Variac and remove the 35 mL vial from the still outlet. Place a beaker under the still outlet to catch any residual distillation which is discarded as liquid radioactive waste.
- Step 17) To the vial containing the distillate, add 2 (± 0.02) mL of 10% sulfuric acid and a 5/8 in. stir bar. Stir for a few seconds to mix.
- Step 18) Heat the distillate vial for 10 (± 1) minutes at 90° to 95°C in the heating block.
- Step 19) Cool at least 10 minutes.
- Step 20) While stirring the solution in the distillate vial, add 20 (± 1) mL of deionized water; then add 1 (± 0.01) mL of 0.1 M silver nitrate dropwise to precipitate silver iodide. Stir for 10 to 20 seconds. Remove from the stirrer.
- Step 21) Heat the distillate vial containing the silver iodide precipitate for 10 (± 1) minutes at 90° to 95°C in the heating mantle.
- Step 22) Cool for at least 10 minutes.
- Step 23) Centrifuge for 2 to 3 minutes.
- Step 24) Using a transfer pipet, transfer the solution to the liquid radioactive waste. Do not disturb the precipitate.
- Step 25) Add 2 to 3 mL of deionized water to the precipitate and slurry.
- Step 26) Place a 13 mm dried and tared glass filter on the base of a 13 mm Swinnex filter holder. While vacuum is applied, place the base of the Swinnex holder with

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filter on top into the hole of a stopper in the top of the vacuum flask. See instructions in 4.1, Equipment and Materials, for preparation of 13 mm glass filters.

- Step 27) Using a plastic dropper, transfer the precipitate slurry onto the center of the filter.
- Step 28) Wash the vial with 3 to 4 mL portions of deionized water and transfer as much of the precipitate as possible to the filter.
- Step 29) Wash the vial with 3 to 4 mL of ethanol and transfer as much of the residual precipitate to the filter as possible.
- Step 30) Remove the filter holder from the stopper in the vacuum flask.
- Step 31) Remove the filter from the filter holder and place the filter on a suitable carrier, such as a beaker cover, and dry in an oven at 110°C to 120°C for 30 (±2) minutes. Cover with a larger beaker cover when transporting filters to avoid loss of filters due to air currents.
- Step 32) Remove the filter plus precipitate from the oven and allow to cool at least 10 minutes.
- Step 33) Weigh the filter plus precipitate on a balance that weighs to 10 µg (0.00001 g) or better. Record the weight on the Analytical Report Form and the identification of the balance used. Use the same balance used for Step 26).
- Step 34) Calculate the weight of the silver iodide on the filter using the tare weight (Step 26) and the gross weight (Step 33). Record the precipitate weight on the Analytical Report Form.
- Step 35) Transfer the filter plus silver iodide to a plastic 2 dram vial (14 mm ID). Be sure no precipitate is lost during the transfer.
- Step 36) Add a 1/8 in. glass covered stir bar and 2 (+0.02) mL of 1 M sodium cyanide to the plastic vial containing the filter and silver iodide.
- Step 37) Close the top of the plastic vial and stir until the silver iodide dissolves.

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- Step 38) Clean the still using a vacuum waste jug and slurp the solution from the still through the still top. Flush the still with water by drawing water into the still through the still outlet and through the still inlet to the vacuum waste jug.
- Step 39) Count the dissolved silver iodide in the plastic vials in the GeLi well gamma spectrometer using procedure PNL-ALO-410.
- Step 40) Calculate the I-129 concentration in the sample using Section 4.4, Calculations. Record sample counting data and calculations on the Analytical Report Form. Retain raw counting data in the appropriate files. Record all standard information and records in the appropriate files or LRB.

4.3 Preparation of I-129 Standards

Complete Step 1) through Step 39) of Section 4.2, Iodine Separation, using an NBS or equivalent I-129 standard instead of sample. The amount of I-129 standard used shall be specified by the COGNIZANT SCIENTIST. Standard identification, volume taken, and other pertinent data shall be recorded on the Analytical Report Form and in the LRB. At least four standards should be prepared and the average used as the standard value. The standards are to be done once and the d/c factor calculated in Section 4.4 shall be used permanently as long as the daily calibration of the ND-66 GeLi well is in control. See PNL-ALO-410, Section 4.1.

4.4 Calculations

4.4.1 Counts in Spectrum from Standard or Sample Count

Gamma spectrometer energy vs. channel number is
1 keV/channel

$$A \pm \alpha = \frac{B - \left[\left(\frac{C}{2} \right) \times 9 \right]}{D} \pm \sqrt{\frac{B + \left[\left(\frac{C}{2} \right) \times 9 \right]}{D}}$$

Where $A \pm \alpha$ = the net counts/minute ± 1 sigma in a sample count

B = sum of all counts in channels 27 through 35 inclusive

C = sum of channels 26 and 36

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D = minutes counted.

4.4.2 Yield Calculation

$$Y = \frac{A-B}{C}$$

where Y = yield as a decimal fraction

A = weight of silver iodide plus filter in grams from Section 4.2, Step 33)

B = weight of filter only in grams from Section 4.2, Step 26); see instructions in Section 4.1, Equipment and Materials

C = 0.01850 grams which is the weight of silver iodide calculated from 1 (± 0.01) mL of 10.0 mg/mL iodide carrier.

4.4.3 Standard - disintegration/Count Factor (d/c)

$$A = \frac{B \times C}{D}$$

where A = disintegration/count (d/c) factor to be used in subsequent sample calculations = 2.895, see BNW52626 page 90

B = disintegrations/minute of I-129 standard used in Section 4.3, Preparation of I-129 Standards

C = yield of standards calculated in Section 4.4.2

D = net counts/minute for standard as calculated in Section 4.4.1, Counts in Spectrum.

4.4.4 Corrections for AgI Self-Absorption

The following correction factors are applied to the count rate based on the amount of AgI in the counting vial. See BNW52626 pages 56-64 for details.

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<u>mg AgI</u>	<u>Factor</u>	<u>mg AgI</u>	<u>Factor</u>	<u>mg AgI</u>	<u>Factor</u>
1	.940	15	1.000	29	1.068
2	.944	16	1.005	30	1.073
3	.948	17	1.009	31	1.079
4	.952	18	1.014	32	1.084
5	.956	19	1.019	33	1.089
6	.961	20	1.023	34	1.095
7	.965	21	1.028	35	1.100
8	.969	22	1.033	36	1.106
9	.973	23	1.038	37	1.111
10	.978	24	1.043	38	1.117
11	.982	25	1.048	39	1.123
12	.986	26	1.053	40	1.129
13	.991	27	1.058		
14	.995	28	1.063		

Fifteen mg. is used as unity because most recoveries are about 15 mg. Factor is used in calculations in Section 4.4.5.

4.4.5 Sample - Disintegration/Minute/Milliliter (d/m/mL)

$$B \pm \beta = \frac{(A \pm \alpha) \times C \times F}{D \times E}$$

where $B \pm \beta$ = the sample I-129 d/min/mL $\pm$ counting standard deviation

$A \pm \alpha$ = the sample counts/minute ± 1 sigma calculated in Section 4.4.1, Counts in Spectrum

C = d/c factor calculated in Section 4.4.3 standard (d/c). Factor = 2.895, see BNW 52626 page 90

D = volume of sample (in mL) added in Section 4.2, Step 1), Iodine Separation

E = yield for sample calculated in Section 4.4.2, Yield Calculation

F = self-absorption factor from Section 4.4.4 list.

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4.4.6 Overall Estimated Precision Including the Counting Standard Deviation

The counting standard deviation is converted to a percentage using the following equations:

$$\%Csd = \frac{\alpha}{A} \times 100$$

where %Csd = the counting standard deviation expressed as a percentage

α = the standard deviation of the counts calculated in Section 4.4.1

A = the net counts/minute calculated in Section 4.4.1

then

$$A = \sqrt{B^2 + C^2 + D^2 + E^2 + F^2 + G^2 + H^2 + I^2}$$

where A = the overall estimated % precision of the analysis value calculated in Section 4.4.5

R = the % counting standard deviation calculated above in Section 4.4.6

C = standard deviation of standard I-129 solutions (0.3%)*

D = estimated precision of standard dilution (0.5%)*

E = calibration replicates (1.25%)*

F = sample volume (1%)*

G = carrier preparation (1%)*

H = carrier volumed added (1%)*

I = recovery measurement weight (2%)*

* See BNW 52626 for SOW M 36853 Report - Estimation of Accuracy (Precision and Bias) of Radiochemical Analyses for MCC Characterization of Spent Fuel and Cladding.

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4.5 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033 . ~~Laboratory Record Books shall be used in accordance with PAP-1704.~~ LRBs and Analytical Report Forms provide a mechanism for control of most records.

4.6 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally, it is considered qualified because it has received an independent technical review.

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TITLE: PNL-ALO-455, (Replaces 2-30.6), ISOTOPIC COMPOSITION OF PLUTONIUM AND URANIUM BY MASS SPECTROMETRY

1.0 APPLICABILITY

The isotopic abundances of plutonium and uranium are determined by thermal ionization mass spectrometry. Purified portions of these elements are prepared using ion exchange chromatography. The separation of americium and uranium from plutonium is complete enough to permit the unbiased measurement of ^{241}Pu and ^{238}Pu . Ions are produced from a carbonized, single rhenium filament. An ion current measuring technique is used in the analysis.

- (a) Material Plutonium and uranium bearing materials.
- (b) Range Between 0.05 and 0.2 μg of plutonium or uranium are required per measurement. Mass ratios from 1 to 0.0001 (and their reciprocals) can be measured.
- (c) Reliability Relative standard deviations of 0.03 and 0.3 percent have been obtained for the ^{239}Pu and ^{241}Pu isotopes respectively, for the abundances of these isotopes present in NBS SRM 946 Pu Isotopic Standard.
- (d) Interferences With the separation procedure included in this method, interferences are not expected.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Analyst

Author	Date	Project Mgr.	Date	QAD Representative	Date
WY Matsumoto	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
OP Amacker, Jr.	6/17/88	JJ McCown	6/16/88	All original signatures on file	
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4.0 PROCEDURE

4.1 DISCUSSION

When atoms or molecules are evaporated from a surface heated to a sufficiently high temperature, thermal ionization occurs in which a fraction of the atoms or molecules are ionized. The ionization efficiency, which is the ratio of ions produced to the remaining atoms or molecules, depends upon the ionization potential of the atoms or molecules and upon the work function and temperature of the surface.^(c) The ionization efficiency increases with increased temperature and work function and it favors atoms or molecules with low ionization potentials.

One commonly used method for enhancing the ionization efficiency is the multiple-filament technique first proposed by Inghram and Chupka.^(b) The advantage of the multiple filament is that the temperatures of the ionizing filament and the sample filament can be independently controlled to optimize the ionization and evaporation rates. Unfortunately, uranium atoms are preferentially ionized over plutonium atoms and trace amounts of uranium in plutonium will interfere in the determination of ^{238}Pu . Further, if the ionizing filament contains traces of natural thorium, the thorium will interfere with the ^{232}U determination.

A method to overcome the disadvantage of the multiple filament with respect to uranium and plutonium analyses is the single-filament technique in which a carbonized rhenium filament is used. The carbonization can be done in an auxiliary vacuum system before loading sample onto the filament as is done at PNL. To decrease fractionation and increase reproducibility a solution of chloroplatinic acid and sucrose is loaded over the sample. The filament is then heated to produce a platinum overplate.

The advantage of the single-filament method is that the ionization of plutonium atoms is enhanced over uranium atoms. This permits the determination of ^{238}Pu in plutonium that has been separated from uranium with simple ion exchange or solvent extraction procedures. In addition, the carbonized filament significantly reduces americium interference in the plutonium analysis and it permits the determination of ^{232}U without interference from the trace amount of natural thorium that are usually present in the filament material.

Although the carbonized single-filament technique improves the analysis of plutonium and uranium, these elements, if together, must be separated from each other before analysis. Also, americium should be separated from plutonium within a few weeks of a plutonium analysis. The separation procedure, which uses a

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single anion exchange column, provides adequate separation of these elements. During the sample preparation work leading to the mass spectrometric measurement, care must always be taken to avoid contamination of the sample with extraneous uranium or plutonium.

The specific separation procedure used depends upon the elements being analyzed. If only the isotopic composition of plutonium is required, the plutonium in solution is reduced to the three valence state with ferrous ammonium sulfate and it is then oxidized to the four state with nitric acid. As the solution is passed through an anion exchange resin, the plutonium as a nitrate complex is retained, while uranium and americium pass through the resin. If the isotopic composition of both plutonium and uranium is required, both are loaded onto an anion exchange resin as chloride complexes while americium passes through the resin. The uranium is eluted from the resin with 8M nitric acid and the plutonium is eluted subsequently with 0.1M nitric acid.

In calibrating the mass spectrometer, attention must be given to bias and linearity. A bias factor is determined using NBS plutonium and uranium isotopic standards and the factor is checked each day that the instrument is used by analyzing an NBS standard. If the calibration check indicates that a significant change in calibration occurred or if maintenance problems develop, the bias factor is redetermined.

4.2 APPARATUS

- (a) Heating Block. Aluminum, for 7-ml vials. A heating mantle is normally used with the heating block.
- (b) Ion Exchange Column. Plastic 6-mm diam, 6-cm long with a 2-ml reservoir. Snip off the top of a plastic dropper¹ to form the reservoir and place a cotton plug in the tip. Use a column only once and then discard it.
- (c) Mass Spectrometers. The two following instruments are used.
 - 1. C.E.C. (DuPont Instruments, Inc.), Model 21-703A, Thermal Ionization Mass Spectrometer.
 - 2. Nuclide Corp., Model 12-90-3S, Thermal Ionization Mass Spectrometer.
- (d) Mass Spectrometer Accessories. The following items are used in the analysis:

¹

Plastic dropper, Catalog No. 6219, Nalge Co., Rochester, NY.

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1. Forming jig, used to form filaments into the configuration required and to hold the filaments in place for welding.
 2. Spot welder, used to weld the filament ribbons to the support posts. Welds must be made carefully to ensure good electrical contact, which is necessary for beam stability.
 3. Sample loading unit, used to evaporate a sample solution on a filament by passing an electrical current through the filament.
 4. Bakeout chamber, used to clean and degas filaments under a vacuum of at least 10^{-6} Torr at about 2000°C .
- (e) Plastic Pipet. A $10\text{-}\mu\text{L}$ pipet with disposable plastic tip.¹ Use a pipet only once and then discard it.
- (f) Transfer Pipets. Pyrex, 2-ml capacity. Prepare before use as indicated for vials, item (g).
- (g) Vials. 7-ml. Prepare the vials before use as follows: heat in 0.1M ammonium hydroxide to near boiling; cool and rinse with distilled water. Heat in 0.1M HNO_3 to near boiling; allow to stand overnight. Rinse with distilled water and then with triple distilled water. Drain dry and store in a sealed plastic bag. Important: all vials used in this method must be treated prior to use to avoid contamination from extraneous uranium. Use a vial only once and then discard it.

4.3 REAGENTS

- (a) Acetone or methanol.
- (b) Anion Exchange Resin. Bio-Rad, AG-1, x-4, 200-400 mesh. Rinse in a polyethylene bottle by shaking with triple distilled water and decanting the fines. Repeat the rinse two or three times. Repeat again with 0.1M HCl and store the resin in 0.1M HCl .
- (c) Benzene or trans-2-butene.

¹

A Kimble $10\text{-}\mu\text{l}$ automatic pipet (#56300) with disposable polypropylene tips (#56305) can be used.

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- (d) Ferrous Ammonium Sulfate. Add 40 mg of ferrous ammonium sulfate and one drop of 18M H_2SO_4 to triple distilled water. Dilute to 100-ml volume and mix. Prepare fresh each day used.
- (e) Hydrochloric Acid. 1M and 10M. Prepare from HCl gas and triple distilled water or from ultrapure hydrochloric acid reagent such as J. T. Baker Company's ULTREX grade.
- (f) Nitric Acid. 0.1M, 2M, 3M, and 8M. Prepare from redistilled 15.6M nitric acid and triple distilled water or from ultrapure nitric acid reagent such as J. T. Baker Company's ULTREX grade.
- (g) Rhenium Ribbon. Nominally 0.076-cm wide by 0.0025-cm thick.
- (h) Chloroplatinic acid 0.05 g/ml in 0.02M sucrose solution.

4.4 STANDARDS

For both calibration and control, NBS plutonium and uranium isotopic standards are used as appropriate.

4.5 SAFETY

- (a) Plutonium bearing materials are radioactive and toxic. Precautions are required to avoid the contamination of the laboratory and personnel.
- (b) Observe the general laboratory safety rules.

4.6 QUALITY CONTROL

4.6.1 Calibration

Periodic attention must be given to bias and linearity. These factors were determined when the mass spectrometer was first used and they are checked whenever a control result is obtained that significantly deviates from the accepted value.

4.6.2 Control

An NBS standard is analyzed at least once in each 8-hr shift in which isotopic analyses are made. If the control result deviates significantly from the accepted value, the calibration factors are rechecked (MCS-033).

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4.7 ANALYSIS

4.7.1 Sample Preparation: Mixed Oxide

This procedure is used to prepare mixed oxide samples for both uranium and plutonium mass spectrometric measurements.

- (a) Dissolve the sample according to Method PNL-ALO-222.

Care must be taken to avoid contamination from extraneous uranium and plutonium during dissolution and subsequent separation of uranium and plutonium.

- (b) Add an appropriate amount of sample solution to a 7-ml vial containing 500 μL of 2M HNO_3 .

At least 40 μg of uranium and 30 μg of plutonium should be taken for this preparation procedure.

- (c) Add 100 μL of the ferrous ammonium sulfate solution and heat for 10 min at about 90°C in the heating block.

The plutonium is reduced to the three valence state.

- (d) Remove the vial from the heating block and add 300 μL of concentrated ultrapure nitric acid.

- (e) Heat again for 5 min at about 90°C and then cool to room temperature.

The plutonium is oxidized to the four valence state.

- (f) Add 1 ml of 10M HCl and swirl the vial to mix.

- (g) Prepare a 300- μL column of anion exchange resin.

- (h) Wash the resin column first with 1 ml of 1M HCl and then with 1 ml of 10M HCl .

- (i) Transfer the sample solution from the vial to the resin column; discard the effluent.

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All vials, ion-exchange columns, and transfer pipettes are used only once and then they are discarded.

The effluent contains americium. The uranium and plutonium are absorbed on the resin as the chloride complexes of U(VI) and Pu(IV).

- (j) Wash the resin column with six 1-ml portions of 10M HCl; discard the effluents.

Do not add the next portion until the previous portion has drained completely from the column.

- (k) Wash the resin column next with 600 μ L of 8M HNO₃, discard the effluent.

- (l) Elute the uranium with four 300- μ L portions of 8M HNO₃, collecting the effluents in a 7-ml vial.

- (m) Swirl the vial to mix and transfer a portion of solution containing about 40 μ g of uranium to a second vial.

- (n) Take the solution in the second vial to dryness and dissolve the residue in 1 ml of 0.1M HNO₃; heat slightly to ensure complete dissolution.

This solution contains about 40 μ g U/ml and it is saved for the uranium mass spectrometric measurement.

- (o) Wash the resin column with three 1-ml portions of 3M HNO₃; discard the effluents.

- (p) Wash the resin column with 300 μ L of 0.1M HNO₃; discard the effluent.

- (q) Elute the plutonium with three 300- μ L portions of 0.1M HNO₃, collecting the effluents in a 7-ml vial.

- (r) Swirl the vial to mix and dilute a portion with 0.1M HNO₃, give about 10 μ g Pu/ml in the dilution.

This dilution is saved for the plutonium mass spectrometric measurement.

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4.7.2 Sample Preparation: Plutonium Oxide and Mixed Oxide

This procedure is used to prepare plutonium oxide and mixed oxide for only plutonium mass spectrometric measurements.

- (a) Repeat steps (a) through (c) of Subsection 4.7.1.

At least 30 μg of plutonium should be taken for this preparation procedure.

- (b) Remove the vial from the heating block and add 1 ml of 8M HNO_3 .
- (c) Heat again for 5 min at about 90°C and then cool to room temperature.

The plutonium is oxidized to the four valence state.

- (d) Prepare a 300- μL column of anion exchange resin.
- (e) Wash the resin column first with 1 ml of 8M HNO_3 .
- (f) Transfer the sample solution from the vial to the resin column; discard the effluent.

All vials, ion-exchange columns, and transfer pipettes are used only once and they are discarded.

The effluent contains americium and it contains uranium when samples are mixed oxide. The plutonium is absorbed on the resin as the nitrate complex of Pu(IV).

- (g) Wash the resin column with six 1-ml portions of 8M HNO_3 ; discard the effluents.

Do not add the next portion until the previous portion has drained completely from the column.

- (h) Wash the resin column next with three 1-ml portions of 3M HNO_3 ; discard the effluents.
- (i) Wash the resin column with 300 μL of 0.1M HNO_3 ; discard the effluent.
- (j) Repeat steps (q) and (r) of Subsection 4.7.1.

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4.7.3 Sample Preparation: Uranium Oxide

This procedure is used to prepare uranium oxide for uranium mass spectrometric measurements.

- (a) Dissolve the sample according to Method PNL-ALO-222.

Care must be taken to avoid contamination from extraneous uranium

- (b) Transfer a portion of sample solution containing about 40 μg of uranium to a vial.

All vials and transfer pipettes are used only once and then they are discarded.

- (c) Take the solution in the vial to dryness and dissolve the residue in 1 ml of 0.1M HNO_3 ; heat slightly to ensure complete dissolution.

This solution contains about 40 μg U/ml and it is saved for the uranium mass spectrometric measurement.

4.7.4 Filament Preparation and Loading

- (a) Prepare a single-filament assembly for rhenium ribbon using an appropriate forming jig.

Filament assemblies are made according to a procedure that is appropriate for the mass spectrometer used.

- (b) Rinse the assembly twice with acetone or methanol.

- (c) Dry the assembly under a heat lamp.

- (d) Place the assembly into the bakeout chamber.

- (e) Evacuate the chamber to at least 10^{-6} Torr and heat the filament to 2000°C for at least 10 min.

- (f) Decrease the temperature of the filament in the bakeout chamber from 2000°C to 1600°C.

- (g) Pass benzene vapor into the bakeout chamber until the pressure is about 5×10^{-4} Torr.

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- (h) Allow the carbonization reaction to continue for 90 min or until the filament is carbonized to the point of becoming quite brittle.

Temperature, pressure, and time used in steps (f), (g) and (h) depend upon the specific bakeout chamber and the thickness of the rhenium ribbon used to make the filament. Specific conditions required to carbonize the rhenium to the point of becoming quite brittle must be determined by experiment.

- (i) Cool the filament and bring the chamber to atmospheric pressure.

- (j) Remove the filament assembly.

If the assembly is not used immediately, store in a desiccator until used. Care must be taken to avoid breaking the brittle filament.

- (k) Mount the filament assembly in the sample loading unit.

- (l) Load about 10 μL of a solution containing uranium or plutonium onto the filament with a disposable pipet and evaporate to dryness by passing about 1 A of current through the filament.

The disposable pipet is used only once and then it is discarded.

The amount of uranium or plutonium loaded onto the filament will depend upon the particular mass spectrometer used.

- (m) Add 5 μL of the 0.05 g/ml chloroplatinic acid in 0.02M sucrose solution and evaporate to dryness. Then heat until a matt gray platinum overplate is produced. Usually 1.2 to 1.5 amps will suffice.

The filament assembly is ready for insertion into the mass spectrometer.

4.7.5 Mass Spectrometric Measurement

- (a) Insert the filament assembly into the mass spectrometer.

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- (b) Slowly increase the filament temperature until a stable ion beam of the major isotope is obtained.

The intensity of the beam must be such that the minor isotopes are measurable.

- (c) Scan the spectrum repeatedly in both directions over the mass range desired until at least nine spectra have been recorded.

4.8 CALCULATION

Calculate the weight percent of each isotope measured. The calculation procedure is governed by the type of instrumentation used. With the computerized system, results are calculated automatically and printed out as atom percents, weight percents, and isotopic ratios along with the standard deviation and other statistical information. Unless otherwise instructed, report isotopic results to the nearest 0.01% (weight or atom percent) for those results $\geq 1\%$ and to the nearest 0.001% for results $< 1\%$.

5.0 BIBLIOGRAPHY

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- (b) M. G. Inghram and W. A. Chupka, "Surface Ionization Source Using Multiple Filaments," Rev. Sci. Instr., 24, 518 (1953).
- (c) C. A. McDowell, Editor, Mass Spectrometry, McGraw-Hill Book Co., NY, p. 81 (1963).
- (d) J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps, and C. F. Metz, Methods for Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials, LA-4622, pp. 9, 15, 23 and 33, March (1971).

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-456 (Replaces 7-40.26 & HTA-4-42), SEPARATION OF IODINE-129 BY SOLVENT EXTRACTION AND DISTILLATION FROM CHLORIDE SOLUTIONS PRIOR TO MEASUREMENT BY GAMMA (X-RAY) COUNTING

1.0 APPLICABILITY

This procedure describes the separation of iodine from brine solutions or similar test solutions and the subsequent x-ray counting of iodine-129 using a GeLi well gamma spectrometer.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Iodine carrier, 10.0 mg/mL iodine -- Prepare by dissolving 1.308 (± 0.001) g of reagent-grade potassium iodide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Potassium permanganate, 0.2 M -- Prepare by dissolving 3.16 (± 0.01) g of reagent-grade potassium permanganate in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sulfuric acid, 10% -- Prepare by diluting 10 (± 0.1) mL of concentrated reagent-grade sulfuric acid to 100 (± 0.1) mL with deionized water. Mix thoroughly.
- Sodium sulfite, 1 M -- Prepare by dissolving 12.6 (± 0.1) g of reagent-grade sodium sulfite in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Carbon tetrachloride, reagent grade.

Author	Date	Project Mgr.	Date	QA0 Representative	Date
AC Leaf	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	6/15/88	All original signatures on file	
Procedure No.		Revision No.		Effective Date	
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- Sodium hydroxide, 1 M -- Prepare by dissolving 4.0 (± 0.1) g of reagent-grade sodium hydroxide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sodium nitrite, 1 M -- Prepare by dissolving 6.9 (± 0.1) g of reagent-grade sodium nitrite in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Silver nitrate, 0.1 M -- Prepare by dissolving 1.70 (± 0.01) g of reagent-grade silver nitrate in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Sodium cyanide, 1 M -- Prepare by dissolving 4.9 (± 0.1) g of reagent-grade sodium cyanide in 100 (± 0.1) mL of deionized water. Mix thoroughly.
- Stir bars, 5/8 in., 1/8 in., glass covered.
- Vials, 35 mL, glass.
- Vials, 2 dram, plastic, 14 mm ID with snap cap.
- Heating block for heating 35 mL glass vials.
- Stirrer, magnetic.
- Droppers, plastic, 7.5 mL.
- Still, see selenium still, Figure PNL-ALO-440.1, Procedure PNL-ALO-440.
- Heating mantle, round bottom for 50 mL round bottom flask.
- Variac, 0 to 140 volts, 1.5 ampere output.
- Lab-jack, suitable size to hold 35 mL glass vial.
- Nitrogen gas -- Reduce pressure to ~ 2 psi using a nitrogen gas pressure reducing valve. A purity of 99.5% nitrogen is acceptable.
- Filters, 13 mm -- Prepare by cutting filter sections from Whatman 934AH glass microfiber filters of a larger size using #9 cork borer. Place the filter on a hard flat surface and press down with the #9 cork borer. Each filter must be dried at 110° to 120°C for at least 30 minutes, cooled and weighed just prior to use to obtain the tare weight in Step 45), Section 4.2, Iodine Separation. Carry the filters on a numbered beaker cover and cover with a

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larger beaker cover to avoid loss of filters due to air currents. Record the tare weight on the Analytical Report Form.

- Filter holder, Swinnex, 13 mm or equivalent.
- Vacuum jug with hole in stopper to accommodate the base of the 13 mm Swinnex filter holder.
- Beaker covers, 3 in. and 4 in.

4.2 Iodine Separation

Iodine-129 is separated from brine solutions containing other radioactive species by extracting the (I_2) into carbon tetrachloride, washing and stripping into an aqueous phase as the iodide (I^-). The iodide solution is transferred to a still and is distilled as iodine (I_2). The iodide (I^-) is then precipitated as silver iodide (AgI) and is filtered and weighed to measure recovery. The AgI and filter are transferred to a plastic vial and the AgI is dissolved in sodium cyanide prior to counting in the GeLi well gamma spectrometer.

The ANALYST shall perform the following steps unless otherwise specified.

- Step 1) To a 35 mL vial add 5/8 in. stir bar, up to 1.0 mL ($\pm 1\%$) of sample (brine) solution, or other volume as specified by the COGNIZANT SCIENTIST, 2.0 (± 0.02) mL of deionized water, 1.0 (± 0.01) mL of iodide carrier, 1.0 (± 0.01) mL of potassium permanganate, and 2.0 (± 0.02) mL of 10% sulfuric acid. Record the volume of brine solution taken on the Analytical Report Form.
- Step 2) Stir the solution in the vial about 30 seconds.
- Step 3) Heat the solution in a heating block at 80° to 95°C for 10 (± 1) minutes.
- Step 4) Remove the solution from the heating block and cool at least 5 minutes.
- Step 5) Add 1 (± 0.01) mL of sodium sulfite and swirl to mix. Solution should become colorless but may have some precipitated salts.
- Step 6) Heat the solution in the heating mantle for 5 (± 1) minutes at 80° to 95°C.

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- Step 7) Remove from the heating mantle and cool at least 5 minutes.
- Step 8) Add 5 (± 0.5) mL of carbon tetrachloride.
- Step 9) Add 2 (± 0.02) mL of sodium nitrite and cap the vial tightly.
- Step 10) Shake the vial for about 1 minute. Then stir for 5 (± 1) minutes. Iodine color will form in the carbon tetrachloride phase (bottom).
- Step 11) Centrifuge for 1 or 2 minutes to separate phases.
- Step 12) Remove the cap and, using a transfer pipet, transfer the carbon tetrachloride phase to a clean vial #2.
- Step 13) To the aqueous phase remaining in the first vial, add 5 (± 0.5) mL of carbon tetrachloride.
- Step 14) Cap the vial tightly and shake for about 1 minute, then stir for 5 (± 1) minutes.
- Step 15) Centrifuge for 1 or 2 minutes to separate phases.
- Step 16) Remove the cap and transfer the carbon tetrachloride phase to the vial #2 using the transfer pipet used in the first transfer. Add a 5/8 in. stir bar to the vial #2 containing the carbon tetrachloride.
- Step 17) Discard the first vial to the liquid radioactive waste and the transfer pipet to the radioactive dry waste.
- Step 18) Fill the vial containing the carbon tetrachloride to the neck with deionized water.
- Step 19) Cap tightly and stir for 5 (± 1) minutes.
- Step 20) Centrifuge for 1 to 2 minutes to separate phases.
- Step 21) Remove the cap and slurp the aqueous phase (top) into the vacuum radioactive liquid waste container. Do not disturb the carbon tetrachloride phase (bottom).
- Step 22) Repeat Steps 18), 19), 20) and 21) one time.
- Step 23) To the washed carbon tetrachloride phase, add 10 (± 0.1) mL of deionized water, 2 (± 0.02) mL of 10% sulfuric acid and 1 (± 0.01) mL of 1 M sodium sulfite.

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- Step 24) Cap tightly and shake until colorless, then stir for at least 5 minutes.
- Step 25) Centrifuge for 1 to 2 minutes to separate phases.
- Step 26) Transfer the aqueous phase (top) to the iodine still using a transfer pipet. Avoid the carbon tetrachloride phase (bottom).
- Step 27) Add 5 (± 0.1) mL of deionized water to the vial containing the carbon tetrachloride.
- Step 28) Cap the vial tightly and shake for 20 to 30 seconds.
- Step 29) Centrifuge for 1 to 2 minutes to separate the phases.
- Step 30) Transfer the aqueous phase (top) to the iodine still, using a transfer pipet. Avoid the carbon tetrachloride phases. Cap the vial containing the residual carbon tetrachloride and dispose of in the radioactive waste container. Discard the transfer pipet in the dry radioactive waste.
- Step 31) To a 35 mL glass vial add 2 (± 0.02) mL of 1 M sodium hydroxide and 2 (± 0.02) mL of 1 M sodium sulfite. Place the still outlet beneath the solution in the vial and support the vial with a Lab-jack.
- Step 32) Add 2 (± 0.02) mL of 1 M sodium nitrite to the still through the still inlet and connect the nitrogen gas inlet cover. Adjust the nitrogen flow to about 5 to 6 bubbles per second.
- Step 33) Set the Variac to 110 and turn on.
- Step 34) Distill until the iodine color is gone; usually about 5 to 10 minutes. The completion of the distillation is very sudden.
- Step 35) Immediately turn off the Variac and remove the 35 mL vial from the still outlet. Place a beaker under the still outlet to catch any residual distillation which is discarded as liquid radioactive waste.
- Step 36) To the vial containing the distillate, add 2 (± 0.02) mL of 10% sulfuric acid and a 5/8 in. stir bar. Stir for a few seconds to mix.

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- Step 37) Heat the distillate vial for 10 (± 1) minutes at 80° to 95°C in the heating mantle.
- Step 38) Cool at least 10 minutes.
- Step 39) While stirring the solution in the distillate vial, add 20 (± 1) mL of deionized water; then add 1 (± 0.01) mL of 0.1 M silver nitrate dropwise to precipitate silver iodide. Stir for 10 to 20 seconds. Remove from the stirrer.
- Step 40) Heat the distillate vial containing the silver iodide precipitate for 10 (± 1) minutes at 80° to 95°C in the heating block.
- Step 41) Cool for at least 10 minutes.
- Step 42) Centrifuge for 2 to 3 minutes.
- Step 43) Using a transfer pipet transfer the solution to the liquid radioactive waste. Do not disturb the precipitate.
- Step 44) Add 2 to 3 mL of deionized water to the precipitate and slurry.
- Step 45) Place a 13 mm dried and tared glass filter on the base of a 13 mm Swinnex filter holder. While vacuum is applied, place the base of the Swinnex holder with filter on top into the hole of a stopper in the top of the vacuum flask. See instructions in 4.1, Equipment and Materials, for Preparation of 13 mm glass filters.
- Step 46) Using a plastic dropper, transfer the precipitate slurry onto the center of the filter.
- Step 47) Wash the vial with 3 to 4 mL portions of deionized water and transfer as much of the precipitate as possible to the filter.
- Step 48) Wash the vial with 3 to 4 mL of methanol and transfer as much of the residual precipitate to the filter as possible.
- Step 49) Remove the filter holder from the stopper in the vacuum flask.

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- Step 50) Remove the filter from the filter holder and place the filter on a suitable carrier, such as a beaker cover, and dry in an oven at 110° to 120°C for 30 (±2) minutes. Cover with a larger beaker cover when transporting filters to avoid loss of filters due to air currents.
- Step 51) Remove the filter plus precipitate from the oven and allow to cool at least 10 minutes.
- Step 52) Weigh the filter plus precipitate on a balance that weighs up to 10 µg (0.00001 g) or better. Record the weight on the Analytical Report Form and the identification of the balance used. Use the same balance used for Step 45).
- Step 53) Calculate the weight of the silver iodide on the filter using the tare weight (Step 45) and the gross weight (Step 52). Record the precipitate weight on the Analytical Report Form.
- Step 54) Transfer the filter plus silver iodide to a plastic 2 dram vial (14 mm ID). Be sure no precipitate is lost during the transfer.
- Step 55) Add a 1/8 in. glass covered stir bar and 2 (+0.02) mL of 1 M sodium cyanide to the plastic vial containing the filter and silver iodide.
- Step 56) Close the top of the plastic vial and stir until the silver iodide dissolves.
- Step 57) Clean the still using a vacuum waste jug and slurp the solution from the still through the still top. Flush the still with water by drawing water into the still through the still outlet and through the still inlet to the vacuum waste jug.
- Step 58) Count the dissolved silver iodide in the plastic vials in the GeLi well gamma spectrometer using procedure PNL-ALO-410.
- Step 59) Calculate the I-129 concentration in the sample using Section 4.4, Calculations. Record sample counting data and calculations on the Analytical Report Form. Retain raw counting data in the appropriate files. Record all standard information and records in the appropriate files or LRB.

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4.3 Preparation of I-129 Standards

See Procedure PNL-ALO-454. Use standards prepared in Procedure PNL-ALO-454 and d/c Factor calculated in Procedure PNL-ALO-454.

4.4 Calculations

4.4.1 Counts in Spectrum from Sample Count

Gamma spectrometer energy vs. channel number is
1 keV/channel

$$A \pm \alpha = \frac{B - \left[\left(\frac{C}{2} \right) \times 9 \right]}{D} \pm \sqrt{\frac{B + \left[\left(\frac{C}{2} \right) \times 9 \right]}{D}}$$

Where $A \pm \alpha$ = the net counts/minute ± 1 sigma in a sample count

B = sum of all counts in channels 27 through 35 inclusive

C = sum of channels 26 and 36

D = minutes counted.

4.4.2 Yield Calculation

$$Y = \frac{A-B}{C}$$

where Y = yield as a decimal fraction

A = weight of silver iodide plus filter in grams from Section 4.2, Step 52)

B = weight of filter only in grams from Section 4.2, Step 45); see instructions in Section 4.1, Equipment and Materials

C = 0.01850 g which is the weight of silver iodide calculated from 1 (± 0.01) mL of 10.0 mg/mL iodide carrier.

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4.4.3 Corrections for AgI Self-Absorption

One of the following correction factors is applied to the count rate based on the amount of AgI in the counting vial. See BNW 52626 pages 56-64 for details.

<u>mg AgI</u>	<u>Factor</u>	<u>mg AgI</u>	<u>Factor</u>	<u>mg AgI</u>	<u>Factor</u>
1	.940	15	1.000	29	1.068
2	.944	16	1.005	30	1.073
3	.948	17	1.009	31	1.079
4	.952	18	1.014	32	1.084
5	.956	19	1.019	33	1.089
6	.961	20	1.023	34	1.095
7	.965	21	1.028	35	1.100
8	.969	22	1.033	36	1.106
9	.973	23	1.038	37	1.111
10	.978	24	1.043	38	1.117
11	.982	25	1.048	39	1.123
12	.986	26	1.053	40	1.129
13	.991	27	1.058		
14	.995	28	1.063		

Fifteen mg. is used as unity because most recoveries are about 15 mg. Factor is used in calculations in Section 4.4.4.

4.4.4 Sample - Disintegration/Minute/Milliliter (d/m/mL)

$$B \pm \beta = \frac{(A \pm \alpha) \times C \times F}{D \times E}$$

where $B \pm \beta$ = the sample I-129 d/min/mL $\pm$ counting standard deviation

$A \pm \alpha$ = the sample counts/minute ± 1 sigma calculated in Section 4.4.1, Counts in Spectrum

C = d/c factor = 2.895, see BNW 52626 page 90

D = volume of sample (in mL) added in Section 4.2, Step 1), Iodine Separation

E = yield for sample calculated in Section 4.4.2, Yield Calculation

F = self-absorption factor from Section 4.4.3 list.

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4.4.5 Overall Estimated Precision Including the Counting Standard Deviation

The counting standard deviation is converted to a percentage using the following equations:

$$\%Csd = \frac{\alpha}{A} \times 100$$

where $\%Csd$ = the counting standard deviation expressed as a percentage

α = the standard deviation of the counts calculated in Section 4.4.1

A = the net counts/minute calculated in Section 4.4.1

then

$$A = \sqrt{B^2 + C^2 + D^2 + E^2 + F^2 + G^2 + H^2 + I^2}$$

where A = the overall estimated % precision of the analysis value calculated in Section 4.4.5

B = the % counting standard deviation calculated above in Section 4.4.6

C = standard deviation of standard I-129 solutions (0.3%)*

D = estimated precision of standard dilution (0.5%)*

E = calibration replicates (1.25%)*

F = sample volume (1%)*

G = carrier preparation (1%)*

H = carrier volumed added (1%)*

I = recovery measurement weight (2%)*

* See BNW 52626 for SOW M 36853 Report - Estimation of Accuracy (Precision and Bias) of Radiochemical Analyses for MCC Characterization of Spent Fuel and Cladding.

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4.5 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033. ~~Laboratory Record Books shall be used in accordance with PAP 1704.~~ LRBs and Analytical Report Forms provide a mechanism for control of most records.

4.6 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally, it is considered qualified because it has received an independent technical review.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-457, Technetium-99 Analysis in Irradiated Metals

APPLICABILITY

This procedure is applicable to the determination of ^{99}Tc in highly radioactive stainless steels and inconel reactor parts. The procedure has been tested for up to 0.1 gm of stainless steel and should be applicable for up to 0.25 gm of metal, larger sample sizes would have to be tested to assure that the cation column is large enough and that the TEVA-Spec column washes are adequate.

DEFINITIONS

- LSC - liquid scintillation counter
- gm - grams
- mL - milliliter
- conc - concentrated
- M - molar
- Duplicate - a replicate aliquot of a sample which is brought through the entire sample preparation and analysis process to document the precision of the method.
- Reagent blank - an artificial sample designed to monitor the introduction of contamination into the sample preparation and analysis process; it is treated like a "real sample" as it is carried through the appropriate steps of the process.
- Blank spike - a reagent blank to which a known amount of analyte of interest is added.
- Matrix spike - a replicate sample to which a known amount of analyte of interest is added.

Author <i>Michael H. Hildebrand</i> RS Strebin	Date <i>1-4-93</i>	Project Mgr. <i>Dandra K. Fadoff</i> SK Fadoff	Date <i>1/8/93</i>	PQ Representative <i>TL Ehlert</i> TL Ehlert	Date <i>1/8/93</i>
Technical Reviewer <i>James H. Kaye</i> JH Kaye	Date <i>2/4/93</i>	Line Mgr. <i>A. King</i> AG King	Date <i>2/8/93</i>	Other	Date
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PNL TECHNICAL PROCEDURE

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

PROCEDURE

Prerequisite: Only personnel trained in this procedure may perform the work. Personnel training records are kept in the ACL office.

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method; or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is $\pm 50\%$ in the next digit located beyond the last one stated.

2.0 Reagents

conc HCl - concentrated hydrochloric acid, 12 M

6 M HCl - 50 mL conc hydrochloric acid diluted to 100 mL with water

0.1 M HCl - 1.0 mL conc hydrochloric acid diluted to 120 mL with water

conc HNO₃ - concentrated nitric acid, 16 M

8 M HNO₃ - 50 mL conc nitric acid diluted to 100 mL with water

0.1 M HNO₃ - 1.0 mL concentrated nitric acid diluted to 150 mL with water

conc HF - concentrated hydrofluoric acid, 27 M

H₂O₂ - 30-35% hydrogen peroxide

Dowex 50X4 100-200 mesh or equivalent

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Pre-filter column - Eichrom PF-C sold by Eichrom Industries Inc.,
8205 S. Cass Ave., Suite 107, Darien, IL 60559.

TEVA-Spec column - Eichrom TE-C sold by Eichrom Industries Inc.

Ultima-Gold LSC cocktail - liquid scintillation counting cocktail
sold by Packard Instrument Company or
equivalent.

Insta-Gel LSC Cocktail - liquid scintillation counting cocktail
sold by Packard Instrument Company or
equivalent.

Tracer - ^{95m}Tc , Produced from α -2N reaction on Nb foil.
Alternatively, ^{99m}Tc .

3.0 Equipment

beakers - various sizes

beakers, teflon - various sizes

disposable 5 mL beakers

disposable plastic transfer pipettes

disposable columns, 25 mL

funnels, to fit Eichrom and disposable columns

automatic elution flow system

LSC vials

4.0 Quality Control Instructions

- 4.1 All quality control (QC) data shall be maintained as hard copy and available for easy reference or inspection.
- 4.2 Two QC options are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a SOW, and these may be conveyed to the analyst through a Test Instruction (TI).
- (a) Employ a minimum of one reagent blank and one reagent blank spike per sample batch (20 samples or less). Run duplicate and spike sample analysis upon client request.

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- (b) For all SOWs written by a client to meet CERCLA requirements that request analysis, employ a minimum of one methods blank per sample batch/set (20 samples or less) to determine if contamination is occurring. Run one duplicate sample for every 20 samples or for each set, whichever is smaller. A spike sample or standard (NIST traceable if possible) shall be employed for every 20 samples analyzed or per every set of samples, whichever is smaller. A matrix spike duplicate and/or laboratory control sample may be analyzed with a set/batch of samples if so directed by the client.

- 4.3 Volume Calibration: Critical volume measurements, as indicated in the procedure, shall be made with automatic pipets or equivalent. A performance check of the automatic pipet shall be completed prior to use. This consists of pipetting and weighing at least three aliquots of deionized water, equal to the volume being used, into a container on the balance. The average delivery weight is converted to volume by multiplying the weight by the reciprocal of the density as it applies to the ambient temperature. This calculated delivery volume shall be acceptable for 7 days.

5.0 Separation Procedure

For metal samples go to step 5.1, for previously dissolved samples proceed to step 5.2.

- 5.1 If the sample is stainless steel, dissolve the sample in a minimum of 6 M HCl adding portions of conc HCl as necessary to aid in dissolution. If the sample is inconel add to the sample in a teflon beaker 1 mL of 8 M HNO₃ and one mL of conc HF, repeat as necessary. Warm until the metal dissolves. The dissolution may be carried out remotely in a hot cell due to the radioactivity of the sample. The dissolved sample will be placed in an appropriate tared glass or plastic screw cap vial. Record the weight of the sample and the weight of the sample solution, on the ⁹⁹Tc Analysis Analyst Sheet (see Exhibit 1).
- 5.2 An aliquot of the dissolved sample equivalent to up to 0.25 gm of metal will be taken for analysis. Add an appropriate amount of tracer; the Cognizant Scientist will decide the amount. Record the sample and tracer volumes on the ⁹⁹Tc Analysis Analyst Sheet. Evaporate the dissolved solution to syrup, then add 1-5 mL conc HNO₃ and evaporate to syrup, repeat 3 times to reduce chloride and fluoride concentration.

NOTE: Do not allow the solution to evaporate to dryness to avoid a potential loss of volatile pertechnetate.

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PNL TECHNICAL PROCEDURE

- 5.3 Dissolve the evaporated sample in a minimum of 0.1 M HNO_3 (about 10-25 mL).
- 5.4 Add 0.5 mL of H_2O_2 to the sample (0.5 mL of H_2O_2 for up to 50 mL of sample), cover with a watch glass and heat to near boiling for approximately 1 hour. This assures that technetium is oxidized to the pertechnetate form.
- 5.5 Prepare a cation exchange column. Make up a 25 mL cation exchange column using Dowex 50X4 100-200 mesh hydrogen form or equivalent in a disposable column. Wash the column with 50 mL of water or until color ceases to elute, then wash the column with 30-60 mL of 0.1 M HNO_3 . Discard wash solution.
- 5.6 Add the sample to the column (operate at the natural flow rate of the column). When all the sample is through the column wash the sample beaker with four 2 mL portions of 0.1 M HNO_3 , adding each to the column when the previous addition has passed through, then wash the column with 5 mL of 0.1 M HNO_3 , repeat 5 times. Save all eluents from step 5.6, these contain the Tc fraction.
- 5.7 Remove the top plug from a TEVA-Spec column and replace with a small wad of glass wool. Wash a TEVA-Spec column and a Pre-filter column with 5 mL of water followed by 5 mL of 0.1 M HNO_3 . Set up the columns serially so the pre-filter column will drip into the TEVA-Spec column. Discard wash solutions.
- 5.8 Pass the sample through the serial columns. Wash the sample beaker with three 1 mL portions of 0.1 M HNO_3 , adding the washes to the columns. Wash the pre-filter column with three 1 mL portions of 0.1 M HNO_3 then discard the pre-filter column. Wash the TEVA-Spec column with five 1 mL portions of 0.1 M HNO_3 . Discard the effluent.
- 5.9 Add a funnel to the TEVA-Spec column and set up an automatic elution device. Wash the TEVA-Spec column with 200-300 mL of 0.1 M HNO_3 . The Cognizant Scientist will decide the elution volume required. (To determine if all the unwanted activity is washed off the column the last 50 mL of eluent may be evaporated to dryness in an LSC vial, add 4 mL 0.1 M HCl mix well then add 10 mL of Ultima-Gold cocktail and count on an LSC. If unwanted activity remains continue wash up to 1 liter volume).
- 5.10 Cut the bottom off the TEVA-Spec column and extrude the resin into an LSC vial. Use 4 mL of water to wash all resin into the vial. Add 10 mL of Insta-Gel cocktail to the vial and mix well.
- 5.11 Count on a spectral liquid scintillation counter, procedure PNL-ALO-474.

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PNL TECHNICAL PROCEDURE

6.0 Calculations

The spectra resulting from liquid scintillation counting of Tc samples will be different, depending on whether Tc-99m or Tc-95m is used as an isotopic tracer. If Tc-99m is used, perform the calculations by steps 6.1 - 6.7. If Tc-95m is used, perform the calculations by steps 6.8 - 6.14.

If Tc-99m is used:

- 6.1 Count the sample with a NaI(Tl) or Ge detector. Establish a region-of-interest under the 140.5 keV peak of Tc-99m. Determine the net counting rate, R1, by subtracting the background counting rate from the total count rate.
- 6.2 Count the same amount of Tc-99m as was added to the samples in the same geometry and using the same region-of-interest. Determine the net counting rate, R2, as above.
- 6.3 Decay correct the counting rates of one or both counts to the same time, using a half-life for Tc-99m of 6.04 hours.
- 6.4 The yield (recovery) is given by:

$$Y = \frac{R1 \text{ (decay corrected)}}{R2 \text{ (decay corrected)}}$$

- 6.5 Allow the Tc-99m to decay for at least 5 half-lives (30 hours).
- 6.6 Count the unknown sample by liquid scintillation spectrometry, using procedure PNL-ALO-474. Count a sample containing a known amount of Tc-99 in the same geometry using the same scintillation cocktail. Based on the latter count, establish a region-of-interest under the broad Tc-99 beta peak. This should nominally cover the range of 20-200 keV, but the range will depend on the scintillation cocktail used and the amount of quenching.
- 6.7 If the net counting rate for the unknown sample is R3 and that of the Tc-99 standard is R4, and the activity of the Tc-99 standard is A_{std} , then the amount of Tc-99 originally in the unknown is given by:

$$A = \frac{R3 * A_{std}}{R4 * Y}$$

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PNL TECHNICAL PROCEDURE

If Tc-95m is used:

This method requires that the efficiency of the liquid scintillation detector be determined for two regions of interest for Tc-99 and for Tc-95m. NIST or NIST traceable solutions of Tc-99 should be used. The disintegration rate of the Tc-95m solution needs to be known. This is determined by gamma ray spectrometry using an appropriate gamma counting procedure and a Ge detector calibrated for the geometry utilized.

- 6.8 Using procedure PNL-ALO-474, count the following: 1) spikes containing known amounts of Tc-99 and Tc-95m prepared in the same manner as the samples to be measured; 2) at least one blank; and 3) the samples from step 5.11.
- 6.9 Based on the spectra of Tc-95m and Tc-99, establish low and high regions of interest as follows: The low region shall nominally cover the range 0-20 keV, and shall bracket the Mo x-ray peak from decay of Tc-95m. The high region shall extend from the upper limit of the low region and shall bracket the Tc-99 beta peak region, nominally 20-200 keV. The two regions shall not overlap.
- 6.10 Determine the efficiencies for the low and high regions for the Tc-95m and Tc-99 sources as follows:

$$E_{\text{low, Tc-95m}} = \frac{\text{Net CPM, low region, Tc-95m}}{\text{DPM, Tc-95m}}$$

$$E_{\text{high, Tc-95m}} = \frac{\text{Net CPM, high region, Tc-95m}}{\text{DPM, Tc-95m}}$$

$$E_{\text{low, Tc-99m}} = \frac{\text{Net CPM, low region, Tc-99}}{\text{DPM, Tc-99}}$$

$$E_{\text{high, Tc-99}} = \frac{\text{Net CPM, high region, Tc-99}}{\text{DPM, Tc-99}}$$

- 6.11 Determine the net counting rates for the low and high regions for the unknown sample. The activity of Tc-99 in the unknown sample may then be calculated from:

$$A_{99} = \frac{(\text{CPM high}) * (E_{\text{low Tc-95m}}) - (\text{CPM low}) * (E_{\text{high Tc-95m}})}{(\text{E}_{\text{low Tc-95m}})(\text{E}_{\text{high Tc-99}}) - (\text{E}_{\text{high Tc-95m}})(\text{E}_{\text{low Tc-99}})}$$

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PNL TECHNICAL PROCEDURE

where A99 is the activity of Tc-99 in units of DPM.

- 6.12 Determine the activity of Tc-95m in the unknown sample from the following:

$$A_{95m} = \frac{(\text{CPM low}) * (\text{E high Tc-99}) - (\text{CPM high}) * (\text{E low Tc-99})}{(\text{E low Tc-95m})(\text{E high Tc-99}) - (\text{E high Tc-95m})(\text{E low Tc-99})}$$

where A95m is the activity of Tc-95m in units of DPM.

- 6.13 Determine the yield (recovery) from the following:

$$Y = \frac{A_{95m}}{A \text{ initial}}$$

where A initial is the amount of Tc-95m (in DPM) added to the samples originally.

- 6.14 The amount of Tc-99 in the original sample is given by:

$$A_{99 \text{ initial}} = \frac{A_{99}}{Y}$$

7.0 Specific Qualification

None required.

8.0 References

"Determination of Technetium-99 in Borehole Waters Using an Extraction Chromatographic Resin," T. Sullivan, D. Nelson, E. Thompson, presented at the 37th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry (Ottawa, Canada, 1991).

"Activity Analysis in Liquid Scintillation Counting, A Technical Comparative Summary - Part 1," Stan De Filippis, Radioactivity and Radiochemistry, V1, No.4, 1990, p 31.

9.0 Records

All data and test results shall be maintained as hard copy as required by PNL-MA-70, PAP-70-1701.

10.0 Exhibits

Exhibit 1: Tc-99 Analysis, Analyst Sheet

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-458, (Replaces 7-40.13), FFTF COVER GAS ANALYSIS BY GAMMA RAY SPECTROMETRY

1.0 APPLICABILITY

This procedure applies to the analysis of FFTF cover gas samples to measure the gamma ray emitting radionuclides with the ND9900 counting system.

2.0 DEFINITIONS

FFTF	Fast Flux Test Facility
GTST	Gas tag sample trap
ND9900	A computer-based gamma energy counting, data reduction system.
LRB	Laboratory Record Book
PARS	One of a number of commands used with the ND9900. Others are SET, PEAK, LIST, etc.
TXXXX	A 4 digit counting room log number
9X-XXXX	A 6 digit 325 Building log number

3.0 RESPONSIBLE STAFF

- Cognizant Scientist
- ND9900 System Manager
- Analyst

4.0 PROCEDURE

4.1 Equipment and Material

- Computer-based Gamma Ray Spectrometer, Nuclear Data ND9900 with GE (Li) detector.

Author	Date	Project Mgr.	Date	QAD Representative	Date
FE Holt	5/15/90	N/A		GK Gerke	5/16/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
SW Thompson	5/18/90	WC Weimer	5/18/90	All original signatures on file	
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PNL TECHNICAL PROCEDURE

4.2 Daily Control Standards

Each day or shift that the track detector is to be used a control count shall be performed using procedure number PNL-ALO-449 Zero Checks and Control Charts-Track Detector.

4.3 Calibration Standards

The track detector was calibrated for the cover gas configuration in 1982, checked in 1984 and again in 1988. All pertinent data is in LRB BNW 52601. Tables of efficiency vs. energy are in the LRB and stored in the computer in the TXXGAS.CNF files where XX stands for a position number, e.g. T20GAS.

4.4 Sample Count

Step 1) Samples are received from Mass Spectrometry personnel. Assign the next counting room log number to the sample in LRB BNW 52276 and record the chamber designation, sampling date and time, GTST number, mm of gas pressure in sample chamber and the 325 Building sample log number under Description. Remember all counting room clocks are on Pacific Standard Time (PST), adjust as needed.

Step 2) Count the sample for the time needed to give the required counting statistics as determined by the Cognizant Scientist.

Step 3) Calculate the volume (cc) of gas in the counting chamber from the relation,

$$cc = \frac{\text{mm pressure in chamber}}{760\text{mm}} \times 118 \times 0.916$$

where 118 is the nominal volume of all cover gas counting chambers at standard temperature and pressure, and 0.916 is a temperature correction factor for temperatures between 20 and 30 degrees C.

Step 4) Using the PARS command, PARS ADC2 and SET TITLE and Sample Parameters. The item SQUANT is the cc of gas in the counting chamber calculated above. Under SET TITLE include the 325 Building sample log number, 9X-XXXX. SET PLIVE to the desired counting time.

Step 5) At the end of the count, type MOVE ADC2 TXXXX (the log number assigned to the sample count).

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PNL TECHNICAL PROCEDURE

- Step 4) Using the PARS command, PARS ADC2 and SET TITLE and Sample Parameters. The item SQUANT is the cc of gas in the counting chamber calculated above. Under SET TITLE include the 325 Building sample log number, 9X-XXXX. SET PLIVE to the desired counting time.
- Step 5) At the end of the count, type MOVE ADC2 TXXXX (the log number assigned to the sample count).
- Step 6) Using the appropriate commands from the ND9900's Instruction Manual obtain printed reports of a peak analysis and nuclide identification. The typical set of commands is:
- a) PEAK/START = 30/LIST=TTA1: TXXXX (The log number assigned earlier).
 - b) ENBACK/CLEAR/BKGND = TRBACK/LIST = TTA1: (Optional)
 - c) MOVE/PARTIAL TXXGAS/EFF/CAL TXXXX (the counting log number) (where TXX is the sample position number, e.g. T2GAS or T20GAS).
 - d) NID/REP = ACT/LIBRARY = COVGAS/TOLER = 0.5/ABUND = 50/LIST = TTA1:
 - e) The above commands may be included in a command file. See the ND9900 System Manager for details.
- Step 7) Write the requested information on an Analytical Report form noting the M&TE # (WB37560 and the LRB containing the daily control data (BNW 52327), pages 113 & 118 or other pages).
- Step 8) Initial the Analytical Report form and submit all data to the Cognizant Scientist for review and approval.
- Step 9) Return the sample to the Mass Spectrometry Laboratory for cleanup and possible recount for Background Purposes.

5.0 BIBLIOGRAPHY

Instruction Manual: VAX/VMS Spectroscopy Application Package User's Manual (07-0196), December 1987 (or later revision). Nuclear Data Instruments, Schaumburg, IL.

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PNL-AL0-458	1	5/14/90	3 of 3

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-459, (Replaces 7-40.14), RADIOMETRIC ANALYSIS OF FFTF SODIUM SAMPLES

1.0 APPLICABILITY

This procedure applies to the analysis of sodium samples for their gamma-emitting contents using gamma-ray spectrometric techniques with the ND9900 counting system.

2.0 DEFINITIONS

CR Carriage Return
FFTF Fast Flux Test Facility
Ge(Li) Germanium, Lithium-drifted, diode detector
LRB Laboratory Record Book
MCA Multichannel Analyzer
MCA OF Typical ND9900 command, turns the MCA off. Others are MCA ER, MCA ON, SET ADC2, etc. See Step 5.0
Ta Tantalum
T10 One of 29 counting positions for the Track detector
TXXXX A 4 digit counting room log number
9X-XXXX A 6 digit 325 Building sample log number

3.0 RESPONSIBLE STAFF

. Cognizant Scientist
. ND9900 System Manager
. Analyst

4.0 PROCEDURE

4.1 Summary of Method

The radiometric analysis of sodium by direct gamma-ray counting compares reasonably well with a previously used separation and analysis method. See LRB BNW 52601 for the data that compares two methods. This method was put into place to eliminate the need for additional samples. Accuracies of $\pm 30\%$ for minor and $\pm 10\%$ for major constituents can be expected. At least two counts, several days apart, are required unless the nuclides expected are already known from previous samples. Samples are usually submitted for

Author	Date	Project Mgr.	Date	QAD Representative	Date
FE Holt	5/15/90	N/A		GK Gerke	5/16/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
SW Thompson	5/18/90	WC Weimer	5/18/90	All original signatures on file	
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PNL TECHNICAL PROCEDURE

analysis one or more weeks after sampling to allow Na-24 to decay away.

4.2 Equipment and Materials

- Gamma ray spectrometer, Nuclear Data ND9900 with Ge(Li) detector or equivalent.
- Computer, ND9900 μ VMS with appropriate gamma ray analysis software.

4.3 Range

This method is suitable for a wide range of activities. Samples with low activities (<4000 c/s) are counted in a position that is ~9 inches from the detector (T10). Samples with higher activities are counted up to 20 inches from the detector (T21). Sources in this configuration have efficiencies comparable to "point" sources at T10 and larger. See LRB BNW 52601 for the results of this method's development study.

4.4 Calibrations and Control

See LRB BNW 52327 for calibration and control chart data and Procedure PNL-ALO-458 for taking daily controls.

4.5 Sample Counting

- 4.5.1 The sample is received from the sodium laboratory and contained in a full or 1/2 full Ta cup which has been set inside a Teflon, screw cap vessel and sealed inside a polyethylene envelope. Confirm that the sample description, e.g., C-PRI-XXX, (XXX = an FFTF assigned number, e.g. 123), the date/time sampled, and the sample weight are noted on the container.
- 4.5.2 Assign a counting room log number to the sample and record it in log book LRB BNW 52276. Also record the sample description, date/time sampled, sample weight and 325 Bldg. log number (9X-XXXX).
- 4.5.3 Place the cup on the front of the cover gas sample holder and set in position T10 or larger in achieve <4000 c/s. Use an even-numbered position, e.g., T12, T18, etc. Make sure that the sample portion is facing the detector. The position is the one under the sample holder's center pair of openings.

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- 4.5.4 Type MCA OF ADC2, MCA ER, and MCA ON with a CR after each command at the ND9900 operation terminal.
- 4.5.5 Count the sample for the time needed to yield the required counting statistics as determined by the Cognizant Scientist for the position selected.
- 4.5.6 While the sample is counting use the PARS ADC2 command to SET TITLE, sample parameters and PLIVE. For example:

```

SET TITLE      TXXXX (the counting room log number) C-PRI-
                XXX 9X-XXXX (the 325 Laboratory log
                number)
SET SID        "          "          "          "
SET STYP       FFTF SODIUM
SET SDAT       30-JAN-90 11:00 (Sampling date/time)
SET SQUAN      Grams of sample in cup
SET SUNIT      G
SET SGEOM      TXXPOINT Where XX is position number
SET GEOM       TXX
SET PLIV       12:0:0 (for a 12 hour count)
EX             to exit PARS
    
```

Note: There is more than one way to accomplish the above. Other command sets may be used depending on the operator's experience. See the ND9900 System Manager for details.

- 4.5.7 At the end of the count, type (MOVE ADC2 TXXXX CR.TXXXX=log number assigned to the sample count.
- 4.5.8 Using the appropriate commands from the ND9900 Instruction Manual, obtain printed reports of a peak analysis and nuclide identification. The usual set of commands is:

```

PEAK/START=30/LIST=TTA1:
ENBACK/CLEAR/BKGND=TRBACK/LIST=TTA1:
MOVE/PARTIAL TXXPOINT/EFF/CAL TXXXX where TXXPOINT
is T10POINT, T18POINT, etc.
NID/REP=ACT/LIBRARY=TRPOINT/TOLER=0.8/ABUND=30/LIST=TTA1:
    
```

- 4.5.9 Write the sample information and analytical results on an Analytical Report Form, noting the M&TE number (WB37560) and the LRB containing the daily control data (BNW 52327).
- 4.5.10 Initial the Analytical Report Form and submit all data to the Cognizant Scientist for review and approval.

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PNL TECHNICAL PROCEDURE

- 4.5.11 Return the sample to the Sodium laboratory for further analyses and/or cleanup.

5.0 BIBLIOGRAPHY

Instruction Manual: VAX/VMS Spectroscopy Application Package User's Manual (07-0196), December 1987 (or latest revision). Nuclear Data Instruments, Schaumburg, IL.

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PNL TECHNICAL PROCEDURE

Title: PNL-ALO-460, SOURCE PREPARATION FOR GROSS ALPHA ANALYSIS

APPLICABILITY

This procedure is applicable to the samples received for gross alpha analysis. The methodology in this procedure is consistent with that outlined in procedure 9310 of the SW 846 methods manual.

DEFINITIONS/ACRONYMS

cpm-counts per minute
conc. - concentration

RESPONSIBLE STAFF

Cognizant Scientist
Analyst/Technician

PROCEDURE

Prerequisite = Personnel trained in this procedure may perform the work.
Training records are maintained on file in the Section Office.

1.0 Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

Author <i>N. J. Zupnik</i>	Date 9-21-90	Project Mgr. <i>B. M. Gillespie</i>	Date 9-24-90	QAD Representative <i>GT Coe</i>	Date 9/24/90
Technical Reviewer <i>[Signature]</i>	Date 9-21-90	Line Mgr. <i>[Signature]</i>	Date 9-21-90	Other	Date
Procedure No. PNL-ALO-460	Revision No. 0	Effective Date SEP 26 1990		Page 1	of 4

PNL TECHNICAL PROCEDURE

2.0 Quality Control

Except where responsibility is specifically assigned to a cognizant scientist, the analyst may perform all work. All pertinent data, observations and calculations, e.g., aliquot volumes, shall be recorded in a LRB, on an Alpha Counting Data Form (Exhibit 1), or on an analytical data sheet in a manner traceable to the sample.

All quality control data shall be maintained and available for easy reference or inspection.

Two quality control options (A and B) are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. The analyst will recognize the need to use option B when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a Statement of Work (SOW), and these will be conveyed to the analyst through a TI.

- A. Employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Run duplicate analysis upon client request. Except when Impact Level III is specified, a spike sample or standard (NIST traceable) shall be periodically (1-3 batches) employed to ensure that correct procedure is followed and that all equipment is operating properly.
- B. For all SOWs written by WHC for CERCLA protocol requests for analysis, employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Analyze one duplicate sample for every 20 samples or for each set, whichever is smaller. A duplicate sample is a sample brought through the whole sample-preparation and analytical process. A spike sample or standard (NIST traceable) shall be employed for every 20 samples analyzed or per every set of samples, whichever is smaller. A matrix spike duplicate and/or laboratory control sample may be analyzed with any 20 samples if so directed by a Test Instruction (TI).

3.0 Reagents, Materials, and Apparatus

Nitric acid, 8N - dilute 500 ml reagent grade conc. HNO_3 with deionized or distilled water to 1000 ml.

Heat Lamp

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PNL TECHNICAL PROCEDURE

Hot plate

Stainless steel dish, 1-1/2" diameter, flamed - heat on high setting on a porcelain top hot plate until color changes to dark brown/black (3-5 min). Remove and cool.

4.0 Sample Preparation and Analysis

4.1 Evaporate the sample or sample aliquot to a few ml (1-5 ml) on a hot plate. Do not evaporate to dryness.

4.2 Quantitatively transfer the sample to a flamed 1-1/2" counting dish using 8N HNO₃. Evaporate the solution under a heat lamp to dryness. Transfer dish to hot plate and heat on high for about 2 minutes or until there are no visible fumes (this may be longer than 2 minutes).

4.3 Count the alpha activity (refer to procedure PNL-ALO-461). Record all pertinent data including sample identification, sample volume, and all counting data on an Alpha Counting Data form (Exhibit 1).

4.4 Calculate total alpha activity:

$$A = \frac{\text{cpm} \times \text{d/c}}{B}$$

where:

A = gross alpha activity of the sample

cpm = gross counts per minute alpha less background cpm (from the most recent background count which must have been taken within the last week, see PNL-ALO-461)

d/c = disintegration per count, an efficiency factor (See PNL-ALO-461)

B = factor to account for sample volumes, dilutions, weights, leach solution volumes and any other factors needed to produce the appropriate reporting units. These factors shall be documented as part of the project records on the Alpha Counting Data Form (Exhibit 1) or on an analytical data sheet.

PNL TECHNICAL PROCEDURE

5.0 Reference

SW-846, Method 9310, 3rd Edition.

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Battelle Pacific Northwest Laboratories		ALPHA COUNTING DATA	
REQUESTED BY	DATE ANALYZED	SAMPLE TYPE	CHARGE CODE
REMARKS			
SAMPLE DESIGNATION	COUNTS	RESULTS UNITS OF $\mu\text{C}/$	
DATE - TIME SAMPLED	DATE - TIME COUNTED	CHEMICAL YIELD FACTOR	
PROCESS USED	SET NUMBER	$\mu\text{C PER D/M}$	0.45045 X 10 ⁻⁶
WT. - VOL. ANALYZED	ANALYST	WEIGHT - VOLUME FACTOR	
WT. RESIDUE		GEOMETRY FACTOR	
		TECH.	
		BACKGROUND CORR. C/M	
		BKG. C/M MINUTES	

**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-461.2 R0
Page 1 of 1

A.

Document Number: PNL-ALO-461 Revision Number: 0

Document Title: Alpha Counting Procedure

Document's Original Author: NL Wynoff

Effective Date
of ICN: 5/7/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 6 with 1 through 5 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert TL Ehlert

Date: 5/7/92

Approval Authority: AG King AG King

Date: 5/7/92

Other Approvals: _____

Date: 1/1

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-461, ALPHA COUNTING PROCEDURE

APPLICABILITY

The objective of this procedure is to communicate both specific and general information regarding the analytical operations of an Alpha Counting System. It is specifically applicable to the operation of the 329 Building Alpha Counting Systems. The information shall be complete enough to allow someone trained in the art to be able to reproduce any work performed with this type of a counter. This procedure was developed by PNL analytical radiochemists, and is based on over 10 years of experience in analyzing samples for alpha activity.

DEFINITIONS/ACRONYMS

cpm - counts per minute
dpm - disintegrations per minute (a concentration term)
LRB - Laboratory Record Book
NIST - National Institute of Standards and Technology
bkg - background
std - standard

RESPONSIBLE STAFF

Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
PF Salter		PF Salter		ALL ORIGINAL SIGNATURES ON FILE	
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2.0 Alpha Counting System Description

The alpha counting systems are used to measure concentrations of alpha-emitting radionuclides in samples. Backgrounds on these counters are typically 0.1 - 1.0 cpm.

The alpha counting systems consist of zinc sulfide scintillation counters with photomultipliers, pre-amplifiers, amplifiers, timer and scaler. The sample chambers are shop-made; once the sample is slid under the detector it is elevated and locked in position next to the scintillator. The counter will operate to pre-set time or pre-set count.

3.0 Efficiency Due to Geometry Measurement

The efficiency due to geometry of each instrument shall be measured using the ^{238}Pu + ^{239}Pu standard source after initial instrument set up, and whenever a detector has been repaired. The standard source currently in use contains 1218 ± 30 dpm alpha, traceable to NIST, as referenced in LRB 50335, page 10. The source is electroplated on a stainless steel disk. Using this source, counting efficiency of all shop-made counters in 329 Building has been maintained within $\pm 3\%$ of the efficiency established in 1963. The history of these counters is documented in chronological Alpha Counter Logbooks.

Another NIST-traceable alpha source may be used to maintain the system as long as the efficiency determined with that source is first established in comparison to the historically-used standard source.

- 3.1. To establish the efficiency due to geometry, center the alpha standard source on a 1-1/2" dish and place the dish on the pedestal of the instrument being tested. Slide the pedestal into the counter and elevate and lock it.
- 3.2. Record the date, voltage setting of the power supply and the length of count (example: 10 minutes) in the Alpha Scintillation Counter Controls notebook on a Counter Control Data form (Exhibit 1). Set the counter for a counting interval sufficient to accumulate a minimum of 10,000 counts and start the count. When the count interval is completed, record the number of counts.
- 3.3. Repeat step 3.2 for a total of three counts.
- 3.4. Obtain the most recent background cpm (within the last week, see Section 5.0) and record it. Compute the net cpm for each count as follows:

$$\text{net cpm} = \frac{\text{counts}}{\text{count time}} - \text{bkg cpm}$$

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PNL TECHNICAL PROCEDURE

- 3.5. Determine the average net cpm for the three counts and record it. Determine the geometry as follows:

$$\text{efficiency due to geometry} = \frac{\text{average net cpm}}{\text{dpm in std}}$$

A d/c factor is often used in sample calculations instead of an efficiency factor (c/d). It is defined as:

$$\text{d/c} = \frac{\text{dpm in std}}{\text{net cpm}}$$

- 3.6. Record the efficiency due to geometry. The efficiency due to geometry of the system shall be within $0.416 \pm 3\%$ (i.e., 0.403 - 0.428). If geometry is not within limits, a cognizant scientist shall evaluate the counter and shall perform repairs or adjustments, if necessary, and/or repeat steps in section 3.0. This evaluation shall be documented in the LRB and in a Deficiency Report (DR) per PNL-MA-70, PAP-70-1502.

4.0 Counter Performance Tests and Quality Control

Control of each alpha detector and counting system performance shall be established by measuring NIST-traceable ^{239}Pu control sources. These sources consist of ^{239}Pu solution evaporated on standard 1-1/2" stainless steel dishes.

Control of system performance shall be reestablished according to Section 3.0 and steps 4.1 - 4.5 when a new detector is put in operation, when control source analysis warrants it (see steps 4.4 - 4.6) or when a cognizant scientist determines that the replacement of an electronic component makes it necessary.

When instruments are in nearly continuous use, a periodic check of performance shall be made (at least once a week). If the instrument is not used for an extended period (2-3 weeks or more), these checks may be discontinued until the operations are again started. Control checks shall be made as follows:

- 4.1. Count the assigned control source (^{239}Pu) on each counter for a time sufficient to accumulate a minimum of 10,000 counts (usually 10 minutes). Record the date, high voltage setting, total counts, length of count and the most recently measured background cpm (within the last week, see Section 5.0) in the Alpha Scintillation Counter Controls notebook. In addition, all instrument settings shall be recorded.

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PNL TECHNICAL PROCEDURE

4.2. Calculate the net cpm for each count as follows:

$$\text{net cpm} = \frac{\text{counts}}{\text{count time}} - \text{bkg cpm}$$

- 4.3. After a total of 10 control counts have been recorded, compute the mean and standard deviation and record on the Counter Control Data form.
- 4.4. When each subsequent control count is made, all instrument settings shall be examined and verification made that none of the settings established in step 4.1 have been changed (except for the count time). This verification shall be documented in the Alpha Scintillation Counter Controls notebook with the control count data. If any settings have been changed, this shall also be recorded, and the system shall be posted "Out of Control" until a cognizant scientist evaluates the changes, establishes and documents the effect on any past data, and determines if any instrument repairs or adjustments are required. A DR shall also be prepared per PNL-MA-70, PNL-70-1502.
- 4.5. For control purposes, any subsequent control count shall be within ~~2%~~ 3% of the mean value or within ~~$\pm 2 \pm 3$~~ standard deviations of the mean, whichever is the larger limit.
- 4.6. If a count is not within the control limits, it shall be labelled "out" on the Counter Control Data form and the control source shall be recounted twice and recorded. If either recount is also outside the control limits, a sign shall be posted on the instrument: "Out of Control. Do Not Use" and a DR per PNL-MA-70, PNL-70-1502 shall be prepared. A cognizant scientist shall evaluate the system and determine if instrument adjustments and/or repairs are required and shall reestablish control of the counter. This evaluation and repair shall be documented in the Alpha Scintillation Counter Controls notebook and on the DR. All samples counted on this detector since last acceptable control check shall be reanalyzed or recounted on a detector that is in control unless the cognizant scientist has determined that the problem is clearly with the control count only. An example of this would be an error in the control count calculation.

5.0 Background Measurements

- 5.1. When a counter is in nearly continuous use, a background of the counter shall be taken at least once each week. Determine the background by counting a new, unused, ethanol-rinsed standard 1-1/2" dish. Count for 1000 minutes. Record the date, length of count and total counts in the Alpha Scintillation Counter Controls notebook. Backgrounds are normally recorded on Counter Background forms (Exhibit 2).

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PNL TECHNICAL PROCEDURE

5.2. Calculate the bkg cpm as follows:

$$\text{bkg cpm} = \frac{\text{counts}}{\text{count time}}$$

This bkg cpm is used in calculating control count and sample counting results.

6.0 Counting Samples

Specific sample preparation and count times vary greatly depending on the matrices involved and the analyses desired. Specific step by step radioanalytical preparation procedures have been employed to cover the preparation of samples to be analyzed (e.g. PNL-ALO-460, and/or other procedures designated by the cognizant scientist, TI or ARF.

6.1 Sample Counting Procedure

6.1.1 Place sample on counting dish on the pedestal of the counting instrument. Slide the pedestal into the counter, elevate, and lock it.

6.1.2 Check to make sure voltage setting is the same as that used to establish the current efficiency factor of the detector (Exhibit 1).

6.2 Initiate the count and record the sample identification, the date/time of counting, and the length of count. When the count has completed, record the number of counts and record the most recent background cpm from the background data in the Alpha Scintillation Counter Control notebook. The background shall have been determined within the last week. All data shall be recorded in the sample LRB or on the Alpha Counting Data sheet (Exhibit 3) for the sample.

7.0 Specific Qualification

This procedure describes the calibration of instrumentation using radionuclide standards and, as such, is considered self-qualifying as defined in PNL-MA-70, PAP-70-901.

8.0 Records

All data pertaining to counter performance tests (control source counts), counter background counts, and instrument repairs shall be documented in the "Alpha Scintillation Counter Controls" notebook in Room 16A of 329 Building. Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ACT NOW Directive 89.1 established records management practices.

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COUNTER CONTROL DATA

[illegible]

[illegible]

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-462, SOURCE PREPARATION FOR GROSS BETA ANALYSIS

APPLICABILITY

This procedure is applicable to the samples received for gross beta analysis. The methodology in this procedure is consistent with that outlined in procedure 9310 of the SW 846 methods manual.

DEFINITIONS/ACRONYMS

cpm - counts per minute
conc. - concentrated

RESPONSIBILITIES

Cognizant Scientist
Analyst/Technician

PROCEDURE

Prerequisite: Personnel trained in this procedure may perform the work.
Training Records are kept on file in the Section Office.

1.0 Tolerances for all measurements made during an analysis shall be specified in some manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

Author	Date	Project Mgr.	Date	QAD Representative	Date
<i>N. J. Wynn</i>	9-21-90	<i>B. M. Dillipuri</i>	9-24-90	<i>G. K. Serbe</i>	9/24/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
<i>B. M. Dillipuri</i>	9-24-90	<i>J. J. H. H.</i>	9-24-90		
Procedure No.	Revision No.	Effective Date	Page	of	
PNL-ALO-462	0	SEP 26 1990	1	3	

PNL TECHNICAL PROCEDURE

2.0 Quality Control

Except where responsibility is specifically assigned to a cognizant scientist, the analyst may perform all work. All pertinent data, observations and calculations, e.g., aliquot volumes, shall be recorded on a Beta Counting Data Sheet (Exhibit 1) or on an Analytical Data Sheet.

All quality control data shall be maintained and available for easy reference or inspection.

Two quality control options (A and B) are defined. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. The analyst will recognize the need to use Option B when a Chain-of-Custody (COC) defines a Test Instruction. Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a Statement of Work (SOW), and these will be conveyed to the analyst through a Test Instruction (TI).

- A. A minimum of one blank per sample batch (20 samples or less) shall be employed to determine if contamination is occurring. Run duplicate analysis upon client request. Except when QA Level III is specified, one spike sample or standard (NIST traceable or commercially certified) per batch shall also be analyzed to ensure that correct procedure is followed and that all equipment is operating properly.
- B. For all SOWs written by WHC for CERCLA protocol requests for analysis, a minimum of one blank per sample batch (20 samples or less) shall be analyzed to determine if contamination is occurring. One duplicate sample shall be analyzed for every 20 samples or for each set, whichever is smaller. A duplicate sample is a sample brought through the whole sample-preparation and analytical process. A spike sample or standard (NIST traceable or commercially certified) shall be employed for every 20 samples or per every set of samples, whichever is smaller.

3.0 Reagents and Apparatus

Nitric acid, 8N - dilute 500 ml reagent grade conc. HNO_3 with deionized or distilled water to 1000 ml

Hot plate

Heat Lamp

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PNL TECHNICAL PROCEDURE

Stainless steel dish, 1-inch diameter, flamed - heat on high setting on a porcelain top hot plate until color changes to dark brown/black (3-5 minutes). Remove to cool.

4.0 Sample Preparation and Analysis

- 4.1 Evaporate the sample or sample aliquot to a few ml (1-5) on a hot plate. Do not evaporate to dryness.
- 4.2 Quantitatively transfer the sample to a flamed 1" counting dish using 8N HNO₃. Evaporate the solution under a heat lamp to dryness.
- 4.3 Count the beta activity (refer to procedure PNL-ALO-463). Record all pertinent data including sample identification, sample volume, and all counting data on a Beta Counting Data form (Exhibit 1).
- 4.4 Calculate total beta activity:

$$A = \frac{\text{cpm} \times \text{d/c}}{B}$$

where:

A = net beta activity of the sample

cpm = gross counts per minute beta less background cpm (from the most recent background count which must have been taken within the last week)

d/c = disintegrations per count, an efficiency factor (see PNL-ALO-463)

B = factor to account for sample volumes, dilutions, weights, leach solution volumes and any other factors needed to produce the appropriate reporting units. These factors shall be documented as part of the project records on the Beta Counting Data Sheet (Exhibit 1) or on an Analytical Data Sheet.

5.0 Reference

SW-846, Method 9310, 3rd Edition.

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BETA COUNTING DATA

Battelle
Pacific Northwest Laboratories

[illegible]

No 1000

BD-1700-049 (12-71)

**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-463.1 R0
Page 1 of 1

A.

Document Number: PNL-ALO-463 Revision Number: 0

Document Title: Beta Counting Procedure

Document's Original Author: NL Wynoff

Effective Date
of ICN: 5/11/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 6 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehler TL Ehler

Date: 5/7/92

Approval Authority: AG King AG King

Date: 5/7/92

Other Approvals: BM Gillespie BM Gillespie

Date: 5/11/92

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-463, BETA COUNTING PROCEDURE

APPLICABILITY

This procedure is applicable to the operations of the Beta Counting Systems located in the 329 Building as they are applied to the analyses of samples for beta-emitting radionuclides. The objective of this procedure is to communicate both specific and general information regarding the analytical operations of a beta counting system. The information shall be complete enough to allow someone skilled in the art to be able to reproduce any work performed with this type of a counter. This procedure was developed by PNL analytical radiochemists and is based on over 10 years of experience in analyzing samples for beta activity.

DEFINITIONS/ACRONYMS

cpm - counts per minute
bkg - background
LRB - Laboratory Record Book

RESPONSIBLE STAFF

Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Tolerances for all measurements made during an analysis shall be specified in some manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

(a)

Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however shall be within $\pm 10\%$ of the stated value.

(b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

Author	Date	Project Mgr.	Date	QAD Representative	Date
NL Wynoff		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
BM Gillespie		PF Salter		ALL ORIGINAL SIGNATURES ON FILE	
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PNL TECHNICAL PROCEDURE

Except where responsibility is specifically assigned to a cognizant scientist, the analyst may perform all work. All pertinent data, observations and calculations, e.g., aliquot volumes, shall be recorded in a project record in a manner traceable to the sample (i.e., Beta Counting Data Sheet or an Analytical Data Sheet). All data pertaining to counter performance tests (control source counts), counter background counts, and instrument repairs shall be documented in the "Beta Counter Calibration" notebook.

2.0 Beta Counting Description

Both regular and low-background beta counting systems are located in the 329 Radiochemistry Lab. The background on the low-background systems is typically ≤ 1 cpm while the background on the regular systems is typically 10-20 cpm. Low-background beta counters are used to measure low-level concentrations of beta emitting radionuclides in samples.

The beta counting systems consist of end-window gas-flow proportional counters, pre-amplifiers, amplifiers, timers and scalers. The low background systems have an additional array of gas-flow proportional counters which surround the detector and provide pulses which serve to reduce the registration of counts from cosmic ray and other background sources by means of anticoincidence gate circuitry. The detectors operate with P-10 counting gas (90% argon + 10% methane). The counter windows are aluminized 1/4 mil mylar.

3.0 Geometry Measurement

The efficiency due to geometry of each instrument shall be measured using the $^{90}\text{Sr} + ^{90}\text{Y}$ standard source whenever a detector has been repaired. The standard source currently in use contained 28312 dpm beta $\pm 2\%$ on June 14, 1963, traceable to NIST, as referenced in LRB 53293, page 8. The source is evaporated on a 1-inch stainless steel dish. Using this source, counting efficiency of all shop-made counters in 329 Building has been maintained within $\pm 3\%$ of the efficiency established in 1963. The history of these counters is documented in chronological Beta Counter Logbooks.

Another NIST-traceable beta source may be used to maintain the system as long as the efficiency determined with that source is first established in comparison to the historically-used standard source.

- 3.1. To establish the geometry, place the beta standard source on the 1" dish holder assigned to the instrument being tested. Slide the dish holder into shelf 1 of the counter.
- 3.2 On the low background counters, press the "Noise Rejection Disabled" button. Set the counter for a counting interval sufficient to accumulate a minimum of 10,000 counts and start the count. Record the date, voltage setting of the power supply and the

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PNL TECHNICAL PROCEDURE

count time in minutes in the Beta Counter Calibration notebook on a Counter Control Data form (Exhibit 1). When the count interval is completed, record the number of counts.

3.3 Repeat step 3.2 for a total of five counts.

3.4 Obtain the most recent background cpm (within the last week) and record it. Compute the net cpm for each count as follows:

$$\text{net cpm} = \frac{\text{counts}}{\text{count time}} - \text{bkg cpm}$$

3.5 Determine the average net cpm for the five counts and record it. Determine the geometry as follows:

$$\text{efficiency due to geometry} = \frac{\text{average net cpm}}{\text{dpm in std}}$$

A d/c factor is often used in sample calculations instead of an efficiency factor (c/d). It is defined as:

$$\text{d/c} = \frac{\text{dpm in std}}{\text{net cpm}}$$

3.6 Record the geometry. The geometry of the system shall be within $0.549 \pm 2\%$ (i.e., 0.538 - 0.560). If geometry is not within limits, a cognizant scientist shall evaluate the counter and shall perform repairs or adjustments, if necessary, and/or repeat steps in section 3.0. This evaluation and any actions taken shall be documented.

4.0 Counter Performance Tests and Quality Control

Control of each beta detector and counting system performance shall be established by measuring NIST-traceable control sources. These sources consist of $^{90}\text{Sr} + ^{90}\text{Y}$ solution evaporated on standard 1" stainless steel dishes.

Control of system performance shall be reestablished according to Section 3.0 and steps 4.1 - 4.5 when a new detector is put in operation, when control source analysis warrants it (see steps 4.4 - 4.6) or when a cognizant scientist determines that the replacement of an electronic component makes it necessary.

When instruments are in nearly continuous use, a periodic check of performance shall be made (at least once a week). If the instrument is not used for an extended period (2-3 weeks or more), these checks may be

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discontinued until the operations are again started. Control checks shall be made as follows:

- 4.1 Count the assigned control source (^{90}Sr + ^{90}Y) on each counter for a time sufficient to accumulate a minimum of 10,000 counts (usually 10 minutes). On the low background counters be sure to press the "Noise Rejection Disabled" button. Record the date, high voltage setting, total counts, length of count and the most recently measured background cpm (within the last week) in the Beta Counter Calibration notebook. In addition, all instrument settings shall be recorded.
- 4.2 Calculate the net cpm for each count as follows:
$$\text{net cpm} = \frac{\text{counts}}{\text{count time}} - \text{bkg cpm}$$
- 4.3 After a total of 10 control counts have been recorded, compute the mean and standard deviation and record on the Counter Control Data form.
- 4.4 When each subsequent control count is made, all instrument settings shall be examined and verification made that none of the settings established in step 4.1 have been changed (except for the count time). This verification shall be documented in the Beta Counter Calibration notebook with the control count data. If any settings have been changed, this shall be recorded. The system shall be posted "Out of Control" until a cognizant scientist evaluates the changes, establishes and documents the effect of any past data, and determines if any instrument repairs or adjustments are required.
- 4.5 For control purposes, any subsequent control count shall be within 2% of the mean value or within ± 2 standard deviations of the mean, whichever is the larger limit. Suspect data is rerun.
- 4.6 If a count is not within the control limits, it shall be labelled "out" on the Counter Control Data form and the control source shall be recounted twice and recorded. If either recount is also outside the control limits, a sign shall be posted on the instrument: "Out of Control. Do Not Use" and a DR per PNL-MA-70, PNL-70-1502 shall be prepared. A cognizant scientist shall evaluate the system and determine if instrument adjustments and/or repairs are required and shall reestablish control of the counter. This evaluation and repair shall be documented in the Beta Counter Calibration notebook and on the DR. All samples counted on this detector since last acceptable control check shall be reanalyzed or recounted on detector that is in control unless the cognizant scientist has determined that the problem is clearly with the control count only.

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PNL TECHNICAL PROCEDURE

An example of this would be an error in the control count calculations.

5.0 Background Measurements

5.1 When a counter is in nearly continuous use, a background of the counter shall be taken at least once each week. Determine the background by counting a new, unused, ethanol-rinsed standard 1" dish. Count for 1000 minutes. Record the date, length of count and total counts in the Beta Counter Calibration notebook. Backgrounds are normally recorded on Counter Background forms (Exhibit 2).

5.2 Calculate the bkg cpm as follows:

$$\text{bkg cpm} = \frac{\text{counts}}{\text{count time}}$$

This bkg cpm is used in calculating control count and sample counting results.

5.3 Before using a detector for sample analysis, a Cognizant Scientist compares the current background with sample detection limit requirements and determines if the detector is suitable for the measurement. If the background is too high to achieve the requested detection limit, a different, lower-background detector shall be used, and/or the high-background detector shall be replaced with a new detector.

6.0 Counting Samples

Specific sample preparation and count times vary greatly depending on the matrices involved and the analyses desired. Specific step by step radioanalytical preparation procedures have been employed to cover the samples analyzed.

6.1 Sample Counting Procedures

6.1.1 Place the sample on a counting dish and then place the dish onto the dish holder. Slide the dish holder into the counter.

Check to make sure voltage setting is the same as the current efficiency factor was based on (Exhibit 1).

6.1.2 Initiate the count and record the sample identification, the date/time of counting, and the length of count. When the count has completed, record the number of counts and record the most recent background cpm (within the last week) from the background data in the beta counter control notebook.

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PNL TECHNICAL PROCEDURE

All data shall be recorded in the sample LRB or on the Beta Counting Data Sheet for the sample.

7.0 Specific Qualifications

This procedure utilizes chemical standards for procedure control and as such meets the definition to be self-qualifying as per PNL-MA-70, PAP-70-901.

8.0 Records

All data pertaining to counter performance tests (control source counts), counter background counts, and instrument repairs shall be documented in the "Beta Counter Calibration" notebook in Room 16A of 329 Building.

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ACT NOW Directive 89.1 established records management practices.

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COUNTER CONTROL DATA

[illegible]

AB-1750-557 (3-65)

**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-464.2 RO
Page 1 of 1

A.

Document Number: PNL-ALO-464 Revision Number: 0

Document Title: Procedure for Gamma Counting and Data
Reduction in the Low-Level Counting Room, 329
Building

Document's Original Author: EA Lepe1

Effective Date
of ICN: 5/7/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.
Replace pages 1 through 14 with 1 through 13 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehler

Date: 5/7/92

Approval Authority: AG King

Date: 5/7/92

Other Approvals: _____

Date: 1/1

: _____ Date: 1/1

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-AL0-464.1
Page 1 of 1

A. Document Number: <u>PNL-AL0-464</u> Revision Number: <u>0</u> Document Title: <u>Procedure for Gamma Counting and Data Reduction in the Document's Low-Level Counting Room, 329 Building</u> Original Author: <u>E. A. Lepe1</u>		Effective Date of ICN: <u>4/26/91</u> Change Requested By: <u>E. A. Lepe1</u>
B. Action: Please replace pages 1, 6, 7, 9, 10, and 11 with the attached pages.		
C. Effect of Change: To clarify requirements for use with the Low Energy Photon Detectors located in Rooms 13C and 16A of the 329 building.		
D. Reason for Change/Description of Change Reason for Change: To clarify requirements for use with the Low Energy Photon Detectors located in Rooms 13C and 16A of the 329 building. Description of change: See attached		
E. Approval Signatures (Please Sign and Date)	Type of Change: () Minor Change ☒ Major Change	
Process Quality Dept OSIR Department Concurrence: <u>St George DE</u> Date: <u>4/10/91</u> Approval: <u>[Signature]</u> Date: <u>4/11/91</u> Authority: <u>[Signature]</u> Date: <u>4/12/91</u> Other Approvals: <u>[Signature]</u> Date: <u>4/15/91</u> <u>B M Dillinger</u>		

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-464, PROCEDURE FOR GAMMA COUNTING AND DATA REDUCTION IN THE LOW-LEVEL COUNTING ROOM, 329 BUILDING

SCOPE

This procedure describes the generic methods of Gamma Spectroscopy used to obtain elemental and radionuclide concentrations in test materials (samples). It is applicable to samples that contain radionuclides emitting gamma photons with energies ranging from about 50 to 3000 keV and from about 4 to 250 keV for low energy photon detectors (LEPD).

This procedure is used to ensure that the gamma-ray spectrometry results obtained for various biological, geological, and other samples are accurate and reproducible. Although gamma spectrometry is a relatively straightforward method used to determine gamma-ray emitting radionuclide concentrations, it is crucial that all of the counting system components be operating properly on a day-to-day and year-to-year basis.

This procedure provides an overview of gamma spectroscopy, the spectrometer systems, and the data analysis programs used in the reduction of data. This procedure was developed by PNL Scientists, and reflects over 10 years of experience in gamma-ray spectroscopy of a wide variety of samples.

APPLICABILITY

This procedure is implemented to assure quality and is approved and written to conform with PNL-MA-70.

This procedure is applicable to the Counting Room Manager and trained and qualified personnel within the Analytical Chemistry Laboratory and Nuclear Chemistry Department of PNL.

This procedure is primarily intended to assure that the samples are counted on the gamma spectrometry equipment in the proper manner and that the data reduction is performed appropriately.

Author	Date	Project Mgr.	Date	QAD Representative	Date
EA Lepel		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
KH Abel		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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PNL TECHNICAL PROCEDURE

DEFINITIONS/ACRONYMS

dpm - disintegrations per minute (concentration term)
ng - nanograms (10^{-9} grams)
ug - micrograms (10^{-6} grams)
 $t_{1/2}$ - half life
LRB - Laboratory Record Book
CTL - Control
Count - to acquire data via digitized pulses from radioactive sources in gamma spectrometer systems
Control Source - aliquot of known mixed radioactive source contained in a specific counting geometry
Diode - Detector - Part of the gamma detector system which includes the actual detector crystal in a metal cylindrical housing and its immediate electronics up to the preamplifier
Ge(Li) - Lithium Drifted Germanium Detector.

RESPONSIBLE STAFF

Counting Room Manager
Cognizant Staff Members/Analysts

PROCEDURE

Due to the diverse nature of experimental techniques that employ gamma spectroscopy, it is not feasible to write one all-encompassing procedure in detail to cover all of the possible variables. Rather, a generic procedure follows for a typical gamma spectroscopy system along with the equipment used. A brief discussion of spectrometer stability and reliability will also be included along with its relevance to gamma spectroscopy.

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL.
- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

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2.0 Equipment and Materials

Radioactive Standard Sources such as the Amersham Mixed Radioactive Source which contains the following radionuclides: ^{57}Co , ^{60}Co , ^{85}Sr , ^{88}Y , ^{109}Cd , ^{113}Sn , ^{137}Cs , ^{203}Hg , and ^{241}Am ; and/or other radioactive control sources containing ^{241}Am , ^{137}Cs and ^{60}Co .

Detectors - NaI(Tl), Ge(Li), intrinsic germanium (IG), low-energy photon detector (LEPD), multidimensional detector.

Associated Electronics - high voltage power supply, preamplifier, amplifier, analog-to-digital converter, pulse pile-up rejector/live-time corrector, and multichannel analyzer.

DEC PDP 11/44, DEC uVAX, or a PC computer for data reduction.

3.0 General Information

A wide variety of gamma counters, each with distinct advantages, has been developed. According to common definition, the detectors are called either scintillation or solid-state detectors. The large sodium iodide scintillation detectors can be used to good advantage where it is necessary to count large samples since the counting geometry is not as critical. If the gamma spectrum is simple and of sufficient activity to overcome the system background, then the NaI(Tl) detector can count more samples per time than the solid-state diode detectors for a given accuracy. In general, the NaI(Tl) detector is more sensitive than the solid-state detector. However, the solid-state detector (diode) will have significantly better peak resolution.

3.1 The Building Blocks

A. Detector

The detector for the gamma counter may be NaI(Tl), Ge(Li), an intrinsic semiconductor detector (e.g., pure Ge) or a complex interconnection of the above detectors to enhance background suppression and permit coincidence/noncoincidence modes of operation.

The NaI(Tl) detectors are scintillators which require a photomultiplier closely coupled optically to the detector to change the light pulses occurring in the NaI(Tl) to electrical pulses. The semiconductor detectors generate hole-electron pairs, which induce a current proportional to the incident gamma-ray energy.

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B. Power Supply

Each detector requires a stable high voltage supply. Generally, about 1250 volts on the photomultiplier is used, or 2500-4000 volts on a semiconductor-type detector is used.

C. Preamplifier

The preamplifier is a very stable, linear-pulse amplifier used mainly for conditioning the detector signals and for driving the amplifier transmission line. Most recent preamplifiers are designed with an FET input transistor which operates at very low noise levels and small capacitances. The preamplifier also is designed as a pulse-pass filter, which effectively reduces noise levels passed on to the amplifier. Most preamplifiers have a gain on the order of 1 to 10.

D. Amplifiers

The modern amplifier has two functions: 1) to provide a gain in signal amplitude of about 1000 with very good stability, and 2) to act as a pulse-shaping network. The gain controls (coarse and fine) are two of the most important controls used by the operator, as these controls are used to adjust the standard peaks to the proper channels for energy peak calibration. It is important to remember that because the different electrical system components are interconnected, an adjustment of one component often affects the others. Thus, when an adjustment is made in one section, the total system shall be checked to see that it is working properly.

E. The Analog-To-Digital Converter (ADC)

The purpose of the ADC is to convert the pulse height of the amplifier pulse into a train of pulses (the train length is proportional to pulse height). Once digitized, the pulses are accepted into the analyzer memory. The zero adjust and the upper and lower discriminator controls are on the ADC. Usually, only the zero adjust is changed after the instrument is set up. Usually, this zero adjust is set to allow the first channel to correspond to 0 keV.

The discriminator controls are for eliminating excessive noise counts. Typically, the upper level discriminator should be set just below the maximum energy being converted by the ADC. The lower-level discriminator is set to eliminate low-energy noise signals. Normally, these controls are initially set and require no further adjustment.

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F. Pulse Pile-Up Rejector

The pulse pile-up rejector is a special device connected to the amplifier and ADC. It contains special circuitry that detects incoming pulses that are so close together that the regular circuitry cannot determine that they are separate pulses. If these pulses are allowed to pass through the system, they would be recorded as summed pulses; that is, a large pulse of higher energy than the separate pulses. The pile-up rejector detects changes in the initial slope of the pulse to decide whether or not a pulse is to be accepted. If the pulse is rejected, the pile-up rejector turns off the internal timer and the ADC until sufficient time has elapsed for the sum pulse to decay away. Without the pulse pile-up rejector, the summed pulse would likely be counted as either representing the presence of a nonexistent radioisotope or added to the total counts in the spectrum in a channel area, which may or may not correspond to a real radioisotope. The pulse pile-up rejector is not needed for low count rates.

G. The Analyzer Memory

The peak height of the counted pulse from the ADC is digitized so that it can be stored in the memory as a binary number. This allows a spectrum to be stored in a binary number distribution that is sorted according to precalibrated energy channels. At the end of the counting period, the appropriate channels (2048 or 4096) in the memory will contain the entire integrated spectrum in digitized form. These data may be retrieved in the form of counts per channel or may be transferred to a computer for rapid and complete data analysis.

4.0 Counting Systems

Any of these counting systems may be selected for counting a sample. Selection is based on sample type and size, anticipated level of radioactivity, specific radioisotopes of interest, required detection limits, etc., and the choice is made by the cognizant staff member/analyst.

4.1 Multidimensional Sodium Iodide System

A schematic diagram of a typical detector system with necessary electronics is shown in Figure 1. The electronic components are listed with their manufacturer model numbers. These, equivalent, or superior components are to be used.

A mixed ^{60}Co and ^{137}Cs standard is used for control determinations for each of the four multidimensional counting systems. Each

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standard is housed in a 1" x 6" diameter polyvinyl chloride (PVC) housing and absorbed onto Al_2O_3 powder.

4.2 Low Energy Photon Detectors (LEPD)

The intrinsic Ge detector systems used as Low Energy Photon Detectors (LEPD) and typical associated electronic components are diagrammed in Figure 2. The electronic components are listed with their manufacturer model numbers. These, equivalent, or superior components are to be used.

Natural uranium standards are used for control standards. Each standard is in a pellet geometry enclosed in plastic to prevent detector contamination.

4.3 Conventional Ge(Li) (or Intrinsic Ge) Detector

Diode "L", a typical Ge(Li) detector, is used for measuring the gamma energy spectrum between 50-3000 keV. This diode and its associated electronic components are diagrammed in Figure 3. The electronic component configuration is shown with listed manufacturer model numbers. These components, equivalent, or superior models are to be used with this detector.

A mixed ^{241}Am , ^{60}Co , and ^{137}Cs standard is used for control determination. This standard closely approximates a point source and is mounted on aluminum plates specially designed to fit the machined plexiglass holder used for diode "L".

4.4 Coincidence-Noncoincidence Ge(Li)-NaI(Tl) Detector

The detection capability of these systems is similar to that of a standard Ge(Li) type (i.e., "L"). However, the coincidence-noncoincidence configuration offers better signal-to-noise ratio for single gamma emissions. Diode "I" and its associated electronic components are diagrammed in Figure 4. The electronic component configuration is shown with listed manufacturer model numbers. These components, equivalent, or superior models are to be used with this detector.

The control standard of ^{241}Am , ^{60}Co , and ^{137}Cs is similar to that used with standard Ge(Li) detectors.

5.0 General Gamma Spectrometry Procedure

5.1 Calibration

Gamma-ray spectrometers must be calibrated so that the peak energies appear at identifiable channel numbers. Absolute efficiencies can then be calculated. This is accomplished using

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isotope standards with accurately-known disintegration rates. A typical isotope standard that has been used is a mixed radioisotope Standard Reference Material (SRM) containing ^{57}Co , ^{60}Co , ^{85}Sr , ^{88}Y , ^{109}Cd , ^{113}Sn , ^{137}Cs , and ^{203}Hg . Each radioisotope has known branching ratios for radioactive decay and easily recognizable (interference free) gamma-ray peaks. This SRM is ideally suited for determining the energy calibration and efficiency of the spectrometer. Although it is not necessary that the standard contain as many radioisotopes as indicated above to assure proper operation, it should at least have radionuclides with gamma energies across the spectrum being used for measuring unknown gamma energies. Typically, this covers the energy range of 50 to 3000 keV or about 4 to 250 keV for low energy photon detectors.

5.1.1 Energy Calibration

The gamma-ray spectrometer is calibrated for energy by adjusting the analyzer amplifier gain to achieve the desired resolution. Typically, a gain of 0.5 or 1.0 keV per channel (See Section 3.1.D) is chosen by counting a standard radioisotopic source (control source) containing at least two radioisotopes--one with a high-energy gamma ray, and one with a low-energy gamma ray. After the gain is set by the analyst, the analyzer memory is cleared and the control source is counted per Section 5.2 of this procedure to check the gain setting. This energy calibration is usually performed after initial instrument set-up, after a detector is replaced, or after a detector is found to be out of control as determined by PNL-ALO-470.

5.1.2 Detector System Counting Efficiencies

In addition to energy calibration, the gamma-ray spectrometer absolute counting efficiencies as a function of gamma energy must be determined for each detector and for each counting geometry in use on that detector. These counting-efficiency versus gamma-energy data are determined by counting a "standard" that is made from a nationally-recognized reference material of known radionuclide concentration and that is in the same physical geometry as the "unknown" or samples which are to be counted. The radionuclide reference material must contain known amounts of various radionuclides that emit gamma photons with energies well spaced over the normal range of analysis. The Amersham Mixed Radioactive Source is an example of a good reference material for use in making "standards" to be used in establishing system counting efficiencies.

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The "standard" is counted in accordance with Section 5.2 for the time required to yield specific integrated gamma-ray peaks of $\leq 5\%$ (preferably $\leq 1\%$) relative error from counting statistics. The detector efficiency for a given integrated gamma-ray peak (radionuclide) is calculated by hand and/or by the computer by dividing the net count rate for the peak by the product of the activity of the radionuclide in the "standard" associated with that peak and the gamma-ray abundance of the radionuclide being measured. Efficiencies for radionuclides not specifically determined by counting the "standard" are interpolated by the computer from the efficiency data obtained from that "standard" for the detector and the specified counting geometry. Once the detector system counting efficiencies are established via this "standard," samples can be counted on the same system and quantitative results obtained as long as the samples are in the sample physical geometry and counted in the exact same position relative to the detector as the "standard," and the detector stability is maintained via the control check procedure (PNL-ALO-470). The currently "calibrated" geometries (i.e., sample geometries) for the gamma spectrometer are listed in the "Packaging and Handling Protocol for the Low-Level Counting Rooms 13C, 14C, and 4D, 329 Building," as well as in Procedure PNL-ALO-105, Sample Preparation for Gamma Counting. Counting efficiency data and/or curves are on file for the currently "calibrated" geometries in Room 14C of the 329 Building, and are stored in the counting system computer.

Note: The efficiency for a single specific energy may be determined instead of an efficiency curve as a function of energy when using a LEPS. This efficiency may be determined by a hand-calculated interpolation of data from the "standards" instead of by "computer."

Generally, detector/geometry counting efficiencies are determined at initial system set-up, when a new detector is installed, when new counting geometries are established for a given detector, or when a detector system is determined to be out of control per PNL-ALO-470.

5.1.3 Calibration Control Checks

The calibration of the detector system is monitored and checked by periodic counting of a system "control check source." This control source is a gamma-ray emitting source (of known gamma-ray energies and efficiencies) mounted on a holder which is placed onto the detector in always the exact same position. Spectral data from the counting of the "control check source" are examined for consistency of

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photopeak activities (integrated net peak areas). The counting of the control source checks that 1) the system is functioning properly, and 2) the system remains stable. The procedure for monitoring/checking the germanium spectrometers used in gamma-ray counting is PNL-ALO-470. At a minimum, the calibration control check (PNL-ALO-470) is conducted bi-monthly. More frequent calibration control checks may be conducted as specified by a Statement of Work (SOW), Technical Project Plan (TPP) or Project Quality Assurance Plan (QAPjP), or as determined by the cognizant staff member.

5.2 Sample and Standards Counting

After verifying that the detector system to be used is in control by checking the "Detector Reliability Chart" (See PNL-ALO-470), the basic sample counting/data acquisition procedure is as follows:

5.2.1 Position

Position the sample in front of the detector using the appropriate sample holder for the required geometry.

5.2.2 Analyzer Start-Up

Clear the analyzer memory and store a pre-set live-time value. Start the analyzer counting and record the date and time on a "Counting Sheet," or record directly into memory, if appropriate. A typical counting sheet is shown in Figure 5. Fill in known information on the counting sheet. Initial the sheet with the individual's initials who started the count, and sign the bottom of the sheet. The signature at the bottom is only required once for each Counting Sheet. For non-radioactive and low-level radioactive samples, the sample count time is usually 1000 minutes.

5.2.3 Analyzer Shutdown

If the preset time has not elapsed and sufficient counts have been acquired in the regions of interest to meet precision requirements, stop the multichannel analyzer from acquiring data. The multichannel analyzer stops automatically when the preset time has elapsed. In either case, record the elapsed time if available and initials of the Analyst changing the count on the count sheet. If the Analyst is different than in 5.2.2, the Analyst also signs at the bottom of the sheet. This signature at the bottom is only done once on each Counting Sheet. Ready the analyzer to transmit the spectral data to a computer.

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5.2.4 Data Transfer and Storage

Transfer the spectral data and accompanying sample parameters from the analyzer to the data acquisition computer system, and store the data on a magnetic storage device (hard disk, floppy disk, etc.).

5.2.5 Data Identification

The following parameters shall accompany the spectral data, on a hard copy printout from a printer and in the associated file stored on a magnetic storage device:

- a. Identification (sample description).
- b. Computer file name (if on computer) unique to the particular sample.
- c. Start time of the count.
- d. Time zero, i.e., end of neutron bombardment for INAA and RNAA; or,
Date and time of sample collection for radionuclide direct counting.
- e. Live time of count (actual time the MCA is free to accept pulses). This should be determined by the MCA and transferred within the spectra.
- f. Real time (the actual duration of count in regular clock time).
- g. Sample mass and/or volume.

5.2.6 Data Analysis

Use a gamma-ray data reduction program to analyze the individual spectra and calculate the final concentration values. The calculated values may be verified by hand calculations, if necessary. The programs used are: "CANGAS" and/or "RAYGUN" for Instrumental Neutron Activation Analysis and Radiochemical Neutron Activation Analysis; "SUM" and/or "RAYGUN" for Natural Radionuclide counting; and "MDA" for multidimensional analysis. The data reduction employed for the LEPD systems may include the use of a PC spreadsheet or hand calculations.

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6.0 Gamma Spectroscopy Data Reduction

The gamma-ray data reduction programs are used to generate activity and/or concentration values (d/m/unit, mg/g, %). The following describes a basic method used to calculate the information from results in an activity or concentration value. The same calculation may be performed by hand to verify the information. Pertinent calculations performed determine the net count rate, N , and net count rate uncertainty, σN . The RAYGUN data analysis code is significantly more sophisticated.

The principle of gamma-peak analysis is outlined below.

Net Count Rate (c/m), R : The net count rate for any particular gamma-ray is determined by integrating the channels containing the photopeak and subtracting the background Compton. The net counts, N , divided by the count time (CT) in minutes yields the net count rate (c/m).

This technique can be explained by using a simplified diagram of a gamma photopeak and a Compton continuum (Figure 6)

FIGURE 6: An Idealized Diagram of a Gamma Photopeak on a Compton Continuum

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$$N \pm 1 \sigma_N \text{ error} = T - C \pm \left[\frac{n^2}{4} \left(\frac{t_1}{n_1^2} + \frac{t_2}{n_2^2} \right) + T \right]^{1/2}$$

where

N = net counts
T = total counts in n channels of photopeak

$$= \sum_{i=n_1}^n C (\text{counts})_i$$

t₁ = total counts in n₁ channels of Compton continuum

t₂ = total counts in n₂ channels of Compton continuum

C = total counts in n Compton channels

$$= \frac{n}{2} \left(\frac{t_1}{n_1} + \frac{t_2}{n_2} \right)$$

Finally:

$$R \pm \sigma_R = \frac{N}{CT (\text{min})} \pm \frac{\sigma_R}{CT (\text{min})}$$

In some cases, the system's background (R_{Bkg}) must be corrected for. In this case:

$$N^* \pm \sigma_{N^*} = N - R_{Bkg} (CT) \pm \left[\sigma_N^2 + (\sigma_{Bkg} \times CT)^2 \right]^{1/2}$$

where

R_{Bkg} = System's background count rate (c/m)

N* = System's background corrected net counts

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In all cases, this calculation is performed; generally the system's background count rate is insignificant when counting control standards. The system backgrounds and their uncertainties are obtained from long (≥ 1000 min) background counts.

The count rate (R) is then used in the calculation of activity or concentration as calculated by RAYGUN, SUM, or MDA for "direct counting," and RAYGUN or CANGAS for comparative analysis as used in instrumental neutron activation analysis.

Further information on each program is contained in the User's Guide located in the Low-Level Counting Room in the 329 Building, or from references, Laul, et al. and/or Hensley, et al.

7.0 Specific Qualifications

This procedure utilizes radiochemical standards for control, and as such meets the definition to be self-qualifying as per PNL-MA-70, PAP-70-901.

8.0 Records

Records will be maintained and controlled so as to conform to requirements of PAP-70-1701. Laboratory Record Books (LRBs) and Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~Act Now Directive 89.1~~ established records management practices.

9.0 References

Laul, J. C., C. L. Wilkerson, and V. L. Crow. 1979. "Computer Methodology and It's Application to Geological and Environmental Matrices". Computers in Activation Analysis and Gamma-Ray Spectroscopy, Proceedings of the American Nuclear Society Topical Conference at Mayaguez, Puerto Rico. April 30 - May 4, 1978. CONF-780421: 840-856.

Hensley, W. H., E. A. Lepel, M. E. Yuly, and K. H. Abel. 1988. "Adaptation and Implementation of the RAYGUN Gamma-Ray Analysis Code on the IBM PC." J. Radioanalytical and Nuclear Chemistry, Articles 124(2): 481-499.

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FIGURE 1. Multidimensional System Electronic Block Diagram of a Gamma-Gamma Multidimensional Spectrometer System

FIGURE 2. Low Energy Photon Detector Electronic Block Diagram for Diodes 'D389' and 'D447'

FIGURE 3. Conventional Ge(Li) Detector Electronic Block
Diagram for Diode 'L'.

FIGURE 4. Anticoincidence-Coincidence Electronic Block Diagram for Diode 'I'.

NAME: _____

TIME ZERO= / /

Parameters: _____

Spectra: #channels _____ Gain: _____ KeV/Ch.

FIGURE 5: Typical Counting Sheet Used for Gamma Spectroscopy

INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-465.5

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<p>A. Document Number: <u>PNL-ALO-465.5</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Strontium-90 Analysis</u></p> <p>Document's Original Author <u>NL Wynhoff</u></p>	<p>Effective Date of ICN:</p> <hr/> <p>Change Requested by: <u>RM Nipper</u></p>
<p>B. Action: <u>Replace page 11 with the attached page 11.</u></p>	
<p>C. Effect of Change: <u>This change will give a more accurate records requirements resource.</u></p>	
<p>D. Reason for Change/Description of Change:</p> <p>Reason:</p> <p>1. Deletes inaccurate information.</p> <p>Description:</p> <p>1. Replaced: PNL-MA-70, PAP-70-1701 with Analytical Chemistry Lab (ACL) Quality Assurance Plan, MCS-033.</p> <p>2. Replaced "LRB's will be used in accordance with the ACT Now Directive 89.1" with "LRB's will be used in accordance with established records management practices".</p>	
<p>E. Approval Signatures: (Please Sign and Date)</p>	<p>Type of Change (Check (✓) one) (✓) Minor Change () Major Change</p>
<p>QP Concurrence: <u>TL Ehlert</u> <i>TL Ehlert</i> Date: <u>2/17/93</u></p> <p>Approval Authority: <u>AG King</u> <i>AG King</i> Date: <u>2/20/93</u></p> <p>Other Approvals: <u>NL Wynhoff</u> <i>NL Wynhoff</i> Date: <u>2/19/93</u></p> <p>: _____ Date: _____</p>	

INTERIM CHANGE NOTICE
(ICN)

ICN-PNL-ALO-465.4
Page 1 of 1

A. Document Number: <u>PNL-ALO-465</u> Revision Number: <u>0</u>		Effective Date of ICN: <u>01/27/92</u>
Document Title: <u>Strontium-90 Analysis</u> Document's Original Author: <u>NL Wynhoff</u>		Change Requested By: <u>NL Wynhoff</u>
B. Action Replace pages 9 through 11 with the attached pages.		
C. Effect of Change To make procedure read correctly.		
D. Reason for Change/Description of Change Reason for change: Sections 4.33, 4.34 and 4.35 were inadvertently left out in the last ICN. Description: Insert the attached pages.		
E. Approval Signatures (Please sign and date)		Type of Change: (Check (✓) one) ☒ Minor Change ☐ Major Change
Process Quality Department: GK Gerke <u>[Signature]</u> ^{1/27/92} Date: <u>1/27/92</u> Approval Authority: AG King <u>[Signature]</u> Date: <u>1/24/92</u> Other Approvals: BM Gillespie <u>[Signature]</u> Date: <u>1/27/92</u> : _____ Date: <u> / / </u>		

INTERIM CHANGE NOTICE
(ICN)

ICN-PNL-ALO-465.3

Page 1 of 1

A. Document Number: <u>PNL-ALO-465</u> Revision Number: <u>0</u>		Effective Date of ICN: <u>11/04/91</u>
Document Title: <u>Stontium-90 Analysis</u> Document's Original Author: <u>NL Wynhoff</u>		Change Requested By: <u>SK Fadeff</u>
B. Action Change step 4.41 Replace pages 9-11		
C. Effect of Change Allows for more complete separation of Na_2CO_3 from SrCO_3 . This will provide a more accurate product weight and therefore, more accurate results.		
D. Reason for Change/Description of Change Na_2CO_3 is not always sufficiently washed away from the SrCO_3 product. This procedural change will allow for complete separation. Replace step 4.41 with the following: Repeat step 4.40 except pour off the supernate into a clean beaker. Add a drop of Ca^{2+} solution and visually check for a cloudy precipitate. Discard the supernate solution. Repeat washing step until an insignificant amount of CaCO_3 precipitate forms in the supernte solution (as evidenced by visual examination). At this point, Na_2CO_3 is negligible in solution.		
E. Approval Signatures (Please sign and date)	Type of Change: (Check (✓) one) ☐ Minor Change ☒ Major Change	
Process Quality Department: GK Gerke <u>CK Gerke</u>	Date: <u>11/5/91</u>	
Approval Authority: AG King <u>A. King</u>	Date: <u>11/8/91</u>	
Other Approvals: BM Gillespie <u>B. Gillespie</u>	Date: <u>11/12/91</u>	
:	Date: <u> / / </u>	

INTERIM CHANGE NOTICE
(ICN)

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A. Document Number: <u>PNL-ALO-465</u> Revision Number: <u>0</u>		Effective Date of ICN: <u>9/26/91</u>
Document Title: <u>Strontium - 90 Analysis</u>		Change Requested By: <u>S. K. Fadeff</u>
Document's Original Author: <u>N. L. Wynhoff</u>		
B. Action Replace pages 8 through 11 with the attached pages.		
C. Effect of Change To make procedure read like it did before ICN-PNL-ALO-465.1.		
D. Reason for Change/Description of Change Reason for Change: Sections 4.22 and 4.23 were inadvertently left out in last ICN. Description: Insert sections 4.22 and 4.23 at the top of page 8.		
E. Approval Signatures (Please sign and date)	Type of Change: {Check (✓) one} ☐ Minor Change ☒ Major Change	
Process Quality Department: <u>GK Gerbe, DE</u>	Date: <u>9/30/91</u>	
Approval Authority: <u>A. J. J.</u>	Date: <u>10/6/91</u>	
Other Approvals: <u>B. M. Deffen</u>	Date: <u>10/4/91</u>	
:	Date: <u> / / </u>	

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-465.1
Page 1 of 2

A. Document Number: <u>PNL-ALO-465</u> Revision Number: <u>0</u> Document Title: <u>Strontium - 90 Analysis</u> Document's Original Author: <u>N. L. Wynhoff</u>		Effective Date of ICN: <u>4/8/91</u> Change Requested By: <u>S. K. Fadeff</u>
B. Action: Replace pages ⁹ numbers 6 and 7.		
C. Effect of Change: Allows analyst to address operational needs during the strontium separation that the original procedure version did not allow for.		
D. Reason for Change/Description of Change 1. It is difficult to adjust the pH to exactly 5.0, an acceptable pH range is more appropriate for step 4.14. 2. Plastic centrifuge tubes are less expensive and are perfectly acceptable for use in step 4.16. In some cases, the supernate volume is too large to be handled in one centrifuge tube. 3. Environmental samples can be different enough from each other and thus require a pH range before precipitate will form (section 4.17) upon addition of NH ₄ OH. If pH target is overshot, the analyst needs to back-adjust with acid. 4. Soil samples typically need a larger volume of 6M HCl for complete dissolution of precipitate, Section 4.19. A more successful dissolution can be obtained if oxalic acid is added <u>after</u> the 6M HCl. CONTINUED ON PAGE 2		
E. Approval Signatures (Please Sign and Date)	Type of Change: {Check (✓) one} () Minor Change (x) Major Change	
Process Quality ES&R Department Concurrence: <u>G. K. Gerbe, DE</u> Date: <u>3/15/91</u> Approval Authority: <u>J. M. Farkas</u> Date: <u>3/18/91</u> Other Approvals: <u>B. M. Bellenger</u> Date: <u>3/11/91</u> : _____ Date: <u>1/1</u>		

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(ICN)

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DESCRIPTION OF CHANGES

1. Section 4.14 - Delete "5.0"; insert "4.5 to 5.5".
2. Section 4.16 - In second sentence, add "or plastic" right after the word "glass" and before "centrifuge". Add "(if supernate volume is large, additional centrifuge tubes may be used to collect the supernate.)" to the end of the second sentence.
3. Section 4.17 - After the second sentence, add "If a precipitate does not form after reaching pH 5, continue adding NH_4OH until a precipitate does form (up to pH 7.5).

After the first sentence, add "If the solution volume is large or intensely colored such that the color change of brom cresol green indicator is masked, 5 to 12 more drops of indicator may be added."

At the end of the second sentence, add "and HNO_3 ."

4. Section 4.19, Prior to first sentence, insert "Dissolve sample in 5 mL HCl or the minimum volume needed to obtain complete dissolution."

Delete second and third sentences.

Insert "Stir vigorously and" to the beginning of the last sentence.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-465, STRONTIUM-90 ANALYSIS (OXALATE-NITRIC ACID METHOD)

APPLICABILITY

This procedure is employed to analyze for Sr-90 in water and liquid leachate samples. If the sample volume is large, an initial volume reduction is made by precipitating strontium and other alkaline earth metals as carbonates. The carbonates are then redissolved with nitric acid. Additional purification is accomplished by precipitation as strontium oxalate metathesizing to strontium nitrate. The strontium is finally precipitated as a carbonate, washed to remove the excess carbonate, and dried on a dish. Strontium activity is determined by beta counting. The yield is determined gravimetrically by comparing the amount of stable strontium carrier added with the weight of the strontium carbonate on the dish and by determining the Sr-90 yield from a spiked sample run with each sample batch. This procedure was developed by PNL Radioanalytical Scientists, and is based on over 10 years experience in Sr radioanalytical chemistry.

DEFINITIONS/ACRONYMS

dpm - disintegrations per minute
 cpm - counts per minute
 ppt - precipitate
 sat. - saturated
 conc. - concentrated
 method blank - deionized or distilled water (treated the same as a sample in process).
 LRB - Laboratory Record Book

RESPONSIBLE STAFF

Cognizant Scientist
 Technician/Analyst

(Note: Except where responsibility is specifically assigned to a Cognizant Scientist, the Technician/Analyst may perform all work.)

Author <i>M. W. Luff</i>	Date 9-21-90	Project Mgr. <i>B. M. Sullivan</i>	Date 9-24-90	QAD Representative <i>C. Gerbe</i>	Date 9/24/90
Technical Reviewer <i>C. O. Harvey</i>	Date 9/24/90	Line Mgr. <i>T. J. Salt</i>	Date 9-24-90	Other	Date
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PNL TECHNICAL PROCEDURE

PROCEDURE

1.0 Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the method (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Quality Control

Two quality control options (A and B) are defined. Option A shall be used unless a Statement of Work (SOW) written by the client defines CERCLA requirements. Option B shall then be used. The cognizant scientist will recognize the need to use option B when a Chain-of-custody (COC) defines a Test Instruction. Additional quality control samples may be requested by the client in an Analytical Request Form (ARF) or a Statement of Work (SOW). The cognizant scientist will convey these additional requirements to the analyst through the Test Instruction (TI).

- A. At a minimum a method blank and a Sr-90 spike sample shall be analyzed with every set (8 or less) of samples. This spiked sample is used in calculating the sample yield.

Note: A spike sample for soils/solids/sludges is defined in Section 4.0, QC for Soils/Solids/Sludges.

- B. For all SOWs written by a client for CERCLA requirements that request analysis, employ a minimum of one method blank, one duplicate and a Sr-90 spike sample for each set (set size is 8 or less). This spiked sample is used in calculating the sample yield.

Note: A spike sample for soils/solids/sludges is defined in Section 4.0, QC for Soils/Solids/Sludges.

The beta counting instruments shall be calibrated according to the current beta counting procedure (PNL-ALO-463 or equivalent).

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3.0 Reagents and Materials

Reagents - All reagent chemicals will be reagent grade unless specified.

Deionized or Distilled Water - All water used as a solvent in this procedure will be deionized or distilled.

Sr-Y-90 Spike (Sr-90 and Y-90 in secular equilibrium). Use appropriate concentration as designated by a Cognizant Scientist (See Section 4.0). Documentation of spike origin and traceability is in a LRB under control of a Cognizant Scientist.

Strontium Carrier, 20 mg/ml - Dissolve 48.32 ± 0.01 g strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) in water. Dilute to one liter with water in a Class A volumetric flask.

Nitric Acid, Conc.

Nitric Acid, 8 M - dilute 500 ml conc. HNO_3 with water to 1000 ml.

Nitric Acid, 2 M - dilute 125 ml conc. HNO_3 with water to 1000 ml.

Fuming Nitric Acid, 90%.

Sodium Hydroxide, 12 N - Dissolve 480 g of NaOH in 800 ml of water, allow to cool to less than 30°C , then dilute to one liter with water.

Ammonium Hydroxide - Any concentration from 6 M to concentrated.

Ammonium Hydroxide, 4% - 4 ml conc. NH_4OH diluted to 100 ml with water.

Phenolphthalein, 1% - Dissolve 2.5 g phenolphthalein in 12.5 ml ethanol and dilute to 250 ml with water.

Sodium Carbonate, Sat. - Dissolve anhydrous Na_2CO_3 in one liter of water until saturated.

Brom Cresol Green, 0.04% - Mix 0.1 g brom cresol green with 14.3 ± 0.2 ml 0.01 M NaOH in a mortar and pestle. Transfer to a flask that will hold a volume of 250 ml. Dilute mixture to 250 ml with water.

Iron Carrier, 10 mg/ml - Dissolve 36.23 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in H_2O . Dilute to 500 ml with water. (Note: Another ferric salt may be

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used or another concentration as long as the required mg of Fe^{+3} are added.)

Oxalic Acid, Sat. - Dissolve oxalic acid in one liter of water until saturated.

Hydrochloric Acid, 6 M - Dilute 500 ml conc. HCl with water to 1000 ml.

Ethanol.

Materials and Equipment

Beakers - 150 ml to 4000 ml.

Glass or Plastic Centrifuge Tubes - 50 or 100 ml.

Centrifuge - for above tubes. The centrifuge is operated at the highest, safe speed possible (i.e., such that the glass or plastic centrifuge tubes do not break).

Vortex Stirrer.

Hot Plate/Stirrer.

Heat Lamp.

Stir Bar - 1- to 2-inch, Teflon coated, magnetic.

pH Paper - fine range near 1, and fine range centered near 5.0.

Flamed Stainless Steel Counting Dishes - heat on high on porcelain-top hot plate until color turns dark (2-3 min), then cool.

4.0 Chemical Procedure

QC for Solutions

Unless otherwise specified in project QC requirements (See Section 2.0), take two aliquots of deionized distilled water. Label one "Blank" (method blank) and one "Spike" (spike sample). The volume of these aliquots shall be 25 ml if the sample volumes will be less than 50 ml and 100 ml if the sample volume will be 50 ml or more. Add Sr-Y-90 tracer to "Spike" as directed by the Cognizant Scientist. This is usually 2000-3000 dpm of Sr-Y-90 at secular equilibrium. Analyze the "Blank" and "Spike" along with the sample batch.

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Note: Record in LRB, on Beta Counting Data Sheet or an Analytical Data Sheet the exact volume and calibrated activity of Sr-Y-90 tracer added, since Sr-90 recovery is used in calculating sample yields.

QC for Soils/Solids/Sludges

Unless otherwise specified in project QC requirements (See Section 2.0), take an aliquot of water and label it "Blank" (method blank). The volume of the aliquot shall be 25 ml if the sample volumes will be less than 50 ml and 100 ml if the sample volume will be 50 ml or more. Spike a soil/solid/sludge sample as directed by the Cognizant Scientist before leaching. Label it "Spike" (spike sample). This is usually 2000-3000 dpm of Sr-Y-90 at secular equilibrium. Analyze the "Blank" and "Spike" along with the sample batch.

Note: Record in LRB, on Beta Counting Data Sheet or on an Analytical Data Sheet the exact volume and calibrated activity of Sr-Y-90 tracer added, since Sr-90 recovery is used in calculating sample yields.

- 4.1 If sample volume to be used for Sr analysis, as specified by a Cognizant Scientist, is less than 50 ml, add 2000 ul of standardized 20 mg/ml Sr carrier to sample and proceed to Step 4.11. If sample volume is ≥ 50 ml, proceed to Step 4.2.

Note: Record in the LRB, on Beta Counting Data Sheet, or Analytical Data Sheet the exact volume and standardized concentration of Sr carrier added, since yields are based on carrier recovery.

- 4.2 If sample is not in acid media, add 5 ml conc. HNO_3 to sample. Shake or mix sample and acid until thoroughly mixed.

- 4.3 Transfer an aliquot, as specified by a Cognizant Scientist, of acidified sample to beaker labeled with sample identification. If total sample volume is less than 1 liter, approximately, measure volume of remaining sample. Record volume of aliquot and remaining sample volume, if required, in the LRB, on the Beta Counting Sheet, or Analytical Data Sheet.

- 4.4 Add 2000 ul of standardized 20 mg/ml Sr carrier to beaker.

Note: Record in LRB, on the Beta Counting Data Sheet, or Analytical Data Sheet the exact volume and standardized

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concentration of Sr carrier added, since yields are based on carrier recovery.

- 4.5 Add 3-5 drops phenolphthalein indicator. Add 12 N NaOH drop-wise with stirring until red color persists (pH ~8).
- 4.6 Add sat. sodium carbonate (Na_2CO_3) solution to sample with stirring until precipitate forms. Add an additional 30 ml (± 5) Na_2CO_3 (in excess). Stir vigorously and allow to cool or chill to room temperature or less.

Note: Solution must be basic for (SrCO_3) precipitation. Temperature is also a factor since SrCO_3 is soluble to the extent of 0.01 mg/ml H_2O at 18°C and 0.65 mg/ml at 100°C .

- 4.7 Allow precipitate to settle for at least one hour (preferably overnight or longer) while cold, to achieve a clear supernatant.

Note: Settling must be complete (supernate must be clear) before decanting supernate.

- 4.8 Carefully slurp (withdraw under vacuum) or decant supernate to waste. Quantitatively transfer precipitate to labeled centrifuge tube with minimum (<10 ml) deionized H_2O .
- 4.9 Centrifuge for 5-10 minutes and discard supernate.
- 4.10 Dissolve precipitate with a minimum of 8 M HNO_3 . (It is usually convenient to add it drop-wise with constant stirring using vortex stirrer until all ppt is dissolved.)
- 4.11 Checking pH with a fine range pH paper, continue addition of 8N HNO_3 until pH is less than 1.
- 4.12 Add 6-12 drops brom cresol green indicator.

Note: Indicator is yellow at pH lower than 4.5, green at pH 5, and blue at pH 5.5 and above.

- 4.13 Add 1 ml of 10 mg/ml Fe carrier to acidic sample.
- 4.14 Slowly adjust pH back to 4.5 to 5.5 (green color) with drop-wise addition of ammonium hydroxide (NH_4OH) (any concentration between 6N and conc. may be used). Use vortex stirrer.

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Note: It may be useful to also check pH with a fine range pH paper whose range is centered near pH 5.0.

4.15 Cool to room temperature and allow to sit while precipitate forms. If no precipitate forms, add 5-10 drops of Fe carrier and readjust pH to 5.0.

4.16 Centrifuge for 5-10 minutes. Decant supernate to clean, labeled glass centrifuge tube. Wash precipitate twice thoroughly with 5-10 ml H_2O . Centrifuge after each wash for 5-10 minutes and add supernate to previous supernate in tube. Discard precipitate.

Note: Scavenger step removes insoluble particles, silicates, Fe and other contaminants, leaving a relatively pure solution.

4.17 Add 15 ml sat. oxalic acid to supernate. Stir vigorously, adjusting pH to green point (pH 5.0) with drop-wise addition of NH_4OH . Cool in ice-water bath to below room temperature.

Note: Vigorous stirring is essential: use vortex or mechanical stirrer.

Note: SrC_2O_4 (strontium oxalate) has definite temperature-dependent solubility of 0.05 mg/ml H_2O at 18°C and 50 mg/ml at 100°C.

4.18 Centrifuge 5-10 minutes. Discard supernate.

4.19 Add 5 ml sat. oxalic acid. Stir vigorously until a slurry forms. Dissolve sample in 5 ml 6 M HCl. Dilute with 15 ml (± 5) H_2O .

4.20 Add 8-12 drops of brom cresol green. Increase pH to indicator green point (pH 5.0) with drop-wise addition of conc. NH_4OH , stirring vigorously. Cool to room temperature.

4.21 Centrifuge solution 5-10 minutes. Discard supernate.

4.22 Wash with 20 ml H_2O . Centrifuge and discard supernate.

4.23 Slowly and cautiously add 5 ml of fuming nitric acid and 20 ml of conc. HNO_3 while stirring on vortex stirrer. Stir vigorously for 1 minute. Cool to room temperature.

Note: Wear face shield while handling fuming nitric acid.

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Note: Strontium oxalate metathesizes to strontium nitrate.

4.24 Centrifuge solution 5-10 minutes. Discard supernate.

4.25 Repeat Steps 4.23 and 4.24 one time.

4.26 Dissolve precipitate in 1-3 ml H_2O . Add 5 ml fuming nitric and 20 ml conc. nitric acid, stirring vigorously for 1 minute. Cool to room temperature.

Note: Begin Step 4.30 only when beta counters are in control and when sufficient time is available to complete chemical separation (2 hours or more) and have samples counted within 10 hours of the Sr separation time. It is usually best to allow a full day.

4.27 Check with counting room personnel on availability of beta counters. Reserve counters for overnight background counts and for sample counting.

4.28 Count backgrounds overnight on beta counters. See beta counting procedure, PNL-ALO-463.

4.29 Count control sources and plot on control charts. Confirm that counters are in control per procedure PNL-ALO-463 before continuing with Step 4.30.

4.30 Centrifuge precipitate from Step 4.26 5-10 minutes and discard supernate.

4.31 Wash precipitate once with 15 ml conc. HNO_3 . Centrifuge precipitate 5-10 minutes and discard supernate.

4.32 Dissolve ppt in 10 ml 2N HNO_3 (or more, if necessary). Add 1 ml of 10 mg/ml Fe carrier. Heat in hot water bath to 80°C.

4.33 Adjust to pH 8 with conc. NH_4OH (check with pH paper). Record the time conc. NH_4OH was added as the "Sr separation time" on Beta Counting Data Sheet or Analytical Data Sheet.

4.34 Cool in ice bath. Centrifuge precipitate 5-10 minutes. Decant supernate into a clean centrifuge tube.

4.35 Wash ppt with 4% NH_4OH . Centrifuge precipitate 5-10 minutes. Add supernate to previous supernate in clean tube.

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- 4.33 Adjust to pH 8 with conc. NH_4OH (check with pH paper). Record the time conc. NH_4OH was added as the "Sr separation time" on Beta Counting Data Sheet or Analytical Data Sheet.
- 4.34 Cool in ice bath. Centrifuge precipitate 5-10 minutes. Decant supernate into a clean centrifuge tube.
- 4.35 Wash ppt with 4% NH_4OH . Centrifuge precipitate 5-10 minutes. Add supernate to previous supernate in clean tube.
- 4.36 Repeat Step 4.35. Discard ppt.
- 4.37 Add 1 drop phenolphthalein indicator.
- 4.38 Add 15 ml sat. Na_2CO_3 with vigorous stirring for 1 minute. Cool to room temperature.

Note: Samples must be cool before next step.

- 4.39 Centrifuge precipitate 5-10 minutes. Discard supernate.
- 4.40 Wash with 5-10 ml of H_2O . Centrifuge precipitate and discard supernate.
- 4.41 Repeat Step 4.40, ~~but do not transfer ppt to a new tube, except~~ pour off the supernate into a clean beaker. Add a drop of Ca^{++} solution and visually check for a cloudy precipitate. Discard the supernate solution. Repeat washing step until an insignificant amount of CaCO_3 precipitate forms in the supernate solution (as evidenced by visual examination). At this point, Na_2CO_3 is negligible in solution.

- 4.42 Transfer precipitate on flamed, tared 1" stainless steel dish using H_2O or ethanol. Dry to stable weight under heat lamp.

Note: Be careful to maintain sample identity of sample dishes.

- 4.43 Cool and weigh plated sample. Record net weight and balance identification in LRB, on Beta Counting Data Sheet, or Analytical Data Sheet. Count samples immediately and complete the counting within 10 hours of the Sr separation time.
- 4.44 Take initial 1- to 5-minute count on regular beta counters. If <25 cpm, count samples on low-background counters.
- 4.45 Record all pertinent data, including sample identity, sample volume, Sr separation time, precipitate weight, Analyst, and any other data requested by the Cognizant Scientist. A Beta Counting Sheet is normally used to record this and all counting data.

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5.0 Calculations

$$YS = \frac{\{cpm - cpm (1 - e^{-\lambda y \Delta t})\} \times TSC \times d/c}{WP \times dpm \text{ Sr-90}}$$

Where:

YS = yield of Sr-90 spike.

cpm = Gross counts per minute less background counts per minute, for "Spike".

Net Counts = Gross counts per minute less background counts per minute.

TSC = theoretical SrCO_3 ppt. weight for 100% yield for amount of Sr carrier added to the sample, in mg.

λy = decay constant of Y-90

Δt = interval between the Sr Separation Time and the mid-point of the sample count

d/c = disintegrations per count, an efficiency factor. This factor is provided by a Cognizant Scientist from documented, NIST-traceable calibration measurements. Documentation of origin and traceability is in a LRB under the control of a Cognizant Scientist.

WP = weight of SrCO_3 ppt. on dish, in mg.

dpm Sr-90 = dpm Sr-90 tracer added to "Spike."

$$A = \frac{\{cpm - cpm (1 - e^{-\lambda y \Delta t})\} \times TSC \times d/c}{WP \times YS \times B}$$

Where:

A = Sr-90 activity of the sample (units depend on requested reportable units)

cpm = Gross counts pr minute less background counts per minute, for the sample.

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B = factor or factors to account for sample volumes, dilutions, weights, leach solution volumes and any other factors needed to produce the appropriate reporting units. These factors shall be documented as part of the project record.

These calculations include an approximate correction for the ingrowth of Y-90 from the Sr separation, time to the time the sample is counted. It assumes that the counting efficiencies of Sr-90 and Y-90 are approximately equal. Calculations are not corrected for Sr-89 activity.

5.0 Specific Qualification

NIST-tracable Sr isotopes are used to trace/establish yield for this process. Thus, this procedure is self-qualifying as defined in PNL-MA-70, PAP-70-901.

6.0 Records

Records will be maintained and controlled so as to conform to requirements of the Analytical Chemistry Lab (ACL) Quality Assurance Plan, MCS-033PNL MA 70, PAP 70-1701. Laboratory Records Books (LRB's) and Analytical Data Sheets provide a mechanism for control of most records. LRB's will be used in accordance with established records management practices the ACT New Directive.

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-466.1 R0
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A.

Document Number: PNL-ALO-466 Revision Number: 0

Document Title: Procedure for Plutonium Separation and Initial Americium Separation by Anion Exchange

Document's Original Author: NL Wynoff

Effective Date
of ICN: 5/11/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 10 with 1 through 9 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert *TL Ehlert*

Date: 5/7/92

Approval Authority: AG King *A. G. King*

Date: 5/7/92

Other Approvals: BM Gillespie *B. M. Gillespie*

Date: 5/11/92

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-466, PROCEDURE FOR PLUTONIUM SEPARATION AND INITIAL AMERICIUM SEPARATION BY ANION EXCHANGE

APPLICABILITY

This procedure is used to separate plutonium and americium from other alpha-emitting radionuclides in water and liquid leachate samples by coprecipitation. Plutonium is then separated from americium by anion exchange resin column methodology. The separated Pu is electroplated onto a metal plating disk (PNL-ALO-468) and measured by alpha energy analysis (AEA) (PNL-ALO-469).

This procedure is written for a 5 ml anion exchange resin column but may be scaled up to a 30 ml or other size column as specified by a Cognizant Scientist. All column washes and elutions must be scaled up accordingly. The column size may be scaled up due to large sample sizes that have high concentrations of Pu and Am or other elements that may occupy resin sites. This procedure was developed by PNL Radioanalytical Scientists, and is based on over 10 years of experience in Pu-Am radioanalytical chemistry.

DEFINITIONS/ACRONYMS

g - grams

conc. - concentrated

ppt - precipitate

ul - microliter, lambda

ug - microgram

Methods Blank - deionized distilled water (treated the same as a sample in process).

LRB - Laboratory Record Book

RESPONSIBLE STAFF

Cognizant Scientist

Technician/Analyst

(Note: Except where responsibility is specifically assigned to a Cognizant Scientist, the Analyst may perform all work.)

Author	Date	Project Mgr.	Date	QAD Representative	Date
NL Wynoff		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
BM Gillespie		PF Salter		ALL ORIGINAL SIGNATURES ON FILE	
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PNL TECHNICAL PROCEDURE

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Reagents

All chemicals used are reagent grade unless otherwise specified. The water used is deionized or distilled water.

2.1 Pu-242 tracer. Use appropriate activity as specified by the Cognizant Scientist. The tracer activity generally is selected to be similar to that expected for the isotopes to be measured in the sample. The tracer shall be directly obtained from a certified source, or shall be made from a NIST-traceable standard or other certified standard if a NIST-traceable standard is not available. The method for preparing a tracer solution of known activity from a standard shall be determined by the Cognizant Scientist, as it is dependent on the standard. The tracer preparation method shall be recorded in the secondary Calibrations/Standards LRB located in Room 8, 329 Building. The activity and purity of any tracer solution prepared by the ACL shall be checked against an independent NIST-traceable source by alpha proportional counting (PNL-ALO-460 and PNL-ALO-461) for activity, and by alpha energy analyses (PNL-ALO-469) for purity (i.e., checked that the tracer contains only the expected isotopes). The tracer check data shall be recorded in the secondary Calibrations/Standards LRB. If a commercially or NIST prepared, certified tracer is used, it may be checked against an independent standard for activity and purity in the same manner, at the direction of the Cognizant Scientist. If a ^{242}Pu tracer is not available, a ^{236}Pu tracer may be used.

2.2 Am-243 tracer. Use appropriate activity as specified by a Cognizant Scientist. The tracer activity generally is selected to be similar to that expected for the isotopes to be measured in the sample. The tracer shall be directly obtained from a certified

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source, or shall be made from a NIST-traceable standard or other certified standard if a NIST-traceable standard is not available. The method for preparing a tracer solution of known activity from the standard shall be determined by the Cognizant Scientist, as it is dependent on the standard. The tracer preparation method shall be recorded in the secondary Calibrations/Standards LRB located in Room 8, 329 Building. Alternatively, the activity and purity of a prepared tracer solution shall be checked against an independent NIST-traceable source by alpha proportional counting (PNL-ALO-460 and PNL-ALO-461) for activity, and by alpha energy analyses (PNL-ALO-469) for purity (i.e., checked that the tracer contains only the expected isotopes). The tracer check data also shall be recorded in the secondary Calibrations/Standards LRB.

- 2.3 Fe carrier, 10 mg/ml - Dissolve 18.08 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in H_2O . Dilute to 250 ml with water. (Note: another ferric salt may be used or another concentration as long as the required mgs of Fe^{+3} are added to the sample as directed in Section 4.)
- 2.4 Sr carrier (holdback carrier), 10 mg/ml - Dissolve 18.10 g SrCl_2 in water. Dilute to 1 liter with water. (Note: Another strontium salt may be used or another concentration as long as the required mgs of Sr^{+2} are added to the sample as directed in Section 4.0.)
- 2.5 Cs carrier (holdback carrier), 10 mg/ml - Dissolve 12.67 g CsCl in water. Dilute to 1 liter with water. (Note: Another cesium salt may be used or another concentration as long as the required mgs of Cs^{+1} are added to the sample as directed in Section 4.0.)
- 2.6 Ca carrier, 10 mg/ml - Dissolve 6.93 g CaCl_2 in water. Dilute to 250 ml with water. (Note: Another calcium salt may be used or another concentration as long as the required mgs of Ca^{+2} are added to the sample as directed in Section 4.0.)
- 2.7 conc. NH_4OH .
- 2.8 50% NH_4OH (ammonium hydroxide) - 50 ml water and 50 ml conc. NH_4OH .
- 2.9 5% NH_4OH - 95 ml water and 5 ml conc. NH_4OH .
- 2.10 6 M HCl (hydrochloric acid) - 50 ml water and 50 ml conc. HCl .
- 2.11 9 M HNO_3 (nitric acid) - 44 ml water and 56 ml conc. HNO_3 .
- 2.12 10 M HCl - 17 ml water and 83 ml conc. HCl .
- 2.13 0.1 M NH_4I in 10 M HCl - 7.1 g NH_4I dissolved in 66 ml of water. Dilute to 500 ml with conc. HCl . This solution shall be made fresh weekly. Record the date of preparation on the bottle.

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- 2.14 Conc. HNO_3 .
- 2.15 NaNO_2 (sodium nitrite).
- 2.16 Conc. H_2SO_4 (sulfuric acid).

3.0 Equipment and Supplies

- 3.1 Centrifuge tubes - Normally, 50-ml plastic screw-cap tubes are used. Larger tubes or glass tubes may be used, e.g., when sample analysis is scaled up.
- 3.2 Centrifuge for tubes from 3.1. The centrifuge is operated at the highest, safe speed possible.
- 3.3 50 ml pyrex beaker or appropriate size beaker.
- 3.4 Ion exchange resin column that will hold 5 ml resin bed or appropriate size column to handle scaled-up analysis.
- 3.5 Anion exchange resin - Dowex 1 X 8 (50-100 mesh).
- 3.6 Hot plate.
- 3.7 Muffle furnace.
- 3.8 Filter - glass microfiber or membrane, $\leq 1.5 \mu\text{m}$ effective particle size retention.
- 3.9 Filter apparatus for a filter from 3.8.

4.0 Chemical Procedure

Quality Control (QC)

Samples are spiked with tracers to determine recovery. The tracers used are traceable to NIST or other certified commercial source (See Section 2). Analytical counting quality control is addressed in the Counting Procedure, PNL-ALO-469. Two quality control options (A and B) are defined. Option A shall be used unless a Statement of Work (SOW) written by the client defines Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) requirements. If CERCLA requirements are specified, Option B shall be used. The Cognizant Scientist will recognize the need to use Option B when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional quality control samples may be requested by the client in an Analytical Request Form (ARF) or a SOW. The Cognizant Scientist will convey the additional requirements to the Analyst through the TI or the ARF.

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- A. At a minimum, a methods blank sample shall be analyzed with every sample set (up to 20 samples, but usually 6-8 samples).
- B. For all SOWs written by Westinghouse Hanford Company (WHC) for CERCLA requirements that request analysis, employ a minimum of one sample duplicate and one method blank per every sample set (up to 20 samples of similar matrix, but usually 6-8 samples). Spikes (i.e., tracers) are added to every sample, including blanks, as part of the analysis procedure as a means of quantification.
- 4.1 If there are large amounts of Fe expected as determined by the Cognizant Scientist by visually inspecting the sample solution, the Cognizant Scientist shall specify that the following calcium oxalate precipitation (ppt) separation be performed. If not, proceed to Step 4.2.
- 4.1.1 If tracer has not been added in a sample digestion procedure, do so now. The activity of each tracer added is specified by the Cognizant Scientist and is normally (but not necessarily) equal to the activity expected in the sample. Add Pu-242 tracer; if Am analysis is also requested, also add Am-243 tracer.
- Note: Record exact volume and calibrated activity of Pu-242 and, if required, Am-243 tracers in the LRB or Data Sheet.
- 4.1.2 If sample is not highly acidic (i.e., $\text{pH} \leq 2$), add 6M HCl or 9M HNO_3 until pH is ≤ 2 as determined by pH paper. Add the amount of Ca^{+2} carrier specified by the Cognizant Scientist. Generally this is 100 mg Ca^{+2} carrier, but may vary depending on the amount of Ca^{+2} anticipated to be in the sample. Record the amount of Ca^{+2} carrier added on the Data Sheet or LRB.
- 4.1.3 Add oxalic acid to make sample saturated, and heat to dissolve. The sample is considered saturated when a few grains/crystals of oxalic acid persist in the sample solution after heating for at least 10 minutes. If a small amount (few grains) of undissolved oxalic acid persists after this time, ignore it. If there is a significant amount of oxalic acid solids present after this time (if in doubt ask the Cognizant Scientist), filter the solution, wash ppt with H_2O , save the filtrate and discard the ppt.
- 4.1.4 Adjust pH to 2.8-3.0, using NH_4OH and measuring pH with a sensitive pH paper whose range is centered near pH 3.0. If pH 3.0 is exceeded, adjust pH to 3.0 or less with 6M HCl. Readjust pH to 2.8-3.0 with NH_4OH .

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Note: The solution should be green with cloudy white calcium oxalate ppt. If the solution turns orange, $\text{Fe}(\text{OH})_x$ is forming. Causes may be that the solution is too basic or that there is not enough oxalic acid to chelate all the Fe. Contact Cognizant Scientist for assistance.

Note: Typically, conc. or 50% NH_4OH is used initially and 5% NH_4OH as pH 2.8 is approached.

- 4.1.5 If white calcium oxalate does not form, add 2-4 drops of the Ca carrier solution to the sample. When white ppt forms at the drops, make sample acidic with 6M HCl, and add additional Ca carrier per instructions from the Cognizant Scientist. Readjust to pH 2.8-3.0 with NH_4OH . Document amount of Ca carrier added on the Data Sheet or LRB.
 - 4.1.6 Heat until solution is hot (but not boiling) and then at least 5 minutes more to let ppt become more crystalline. Filter and wash ppt with H_2O . Discard filtrate solution.
 - 4.1.7 Add 10 mg Fe carrier to ppt, and dry under heat lamp.
 - 4.1.8 Muffle overnight at 500°C (not less than 8 hours). Let cool.
 - 4.1.9 Dissolve ppt in HCl (6M or more). Make basic with NH_4OH to ppt rust-colored, gelatinous $\text{Fe}(\text{OH})_x$. Centrifuge at least 5 minutes, and discard solution.
 - 4.1.10 If ppt is mixed with a white or cream-colored ppt, repeat Step 4.1.9 until ppt is not mixed with white ppt.
 - 4.1.11 Dissolve ppt in a minimum (a few drops) of 6M HCl and continue at Step 4.5 (do not add more Fe solution).
 - 4.2 If a tracer was not added before oxalate ppt steps, leaching, or evaporation, add it now. The activity of each tracer added is specified by the Cognizant Scientist and is normally equal to activity expected in the sample. Add Pu-242 tracer; if Am analysis is also requested, also add Am-243 tracer.
- Note: Record exact volume and calibrated activity of Pu-242 and, if required, Am-243 tracers.
- 4.3 If the volume of the sample, water or leachate solution is >20 ml, evaporate it down to <5 ml in an appropriate size beaker. Transfer the sample quantitatively to a plastic centrifuge tube with 6M HCl.

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If the sample is ≤ 5 ml, dilute sample aliquot in plastic centrifuge tube to 10 ± 2 ml with water.

- 4.4 If sample is not highly acidic (i.e., $\text{pH} \leq 2$), add 6M HCl or 9M HNO_3 until pH is ≤ 2 .
- 4.5 Add 10 mg Fe carrier. Add 5 mg Sr carrier and 5 mg Cs carrier (holdback carriers).
- 4.6 Make sample basic ($\text{pH} > 7$) with 50% NH_4OH (about 2 squirts). Visually check for the presence of a rust-colored ppt ($\text{Fe}(\text{OH})_x$) c. with pH paper. Mix well. Centrifuge at least 5 minutes and discard supernate.
- 4.7 Dissolve ppt with a few drops of 6 M HCl.
- 4.8 Add .5 ml H_2O , 5 mg Sr carrier and 5 mg Cs holdback carriers.
- 4.9 Again, make sample basic with NH_4OH (See Step 4.6). Mix well. Centrifuge at least 5 minutes and discard supernate.
- 4.10 Dissolve ppt with .5 ml 9 M HNO_3 .
- 4.11 Add a microspatula tip (about 10 ± 5 ug) of NaNO_2 (sodium nitrite) and allow to sit overnight.
- 4.12 Prepare a 5 ml anion resin column with Dowex 1 X 8 (50-100 mesh). Equilibrate the column by pass 25 ml of 9 M HNO_3 through the column.
- 4.13 Pass the sample solution through the column. If Am analysis has been requested, label a 50 or 100 ml beaker with "Am" and the sample ID, and collect the effluent in this beaker.

Wash column with 5 ml of 9 M HNO_3 , allowing it to drain into the Am fraction. Continue Am separation according to Am procedure, PNL-ALO-467.

If not interested in the Am fraction, discard effluent and the 5 ml HNO_3 wash.
- 4.14 Wash column with 30 ml 9 M HNO_3 .
- 4.15 When the 9 M HNO_3 wash drains to the top of resin bed, rinse column walls above resin bed with a small volume (< 10 ml) of 10 M HCl. Repeat this 2 times, after wash has drained to the top of the resin bed.

Note: This converts over to the Cl system gradually.

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If using the 30 ml column and its detachable reservoir, when the 9 M HNO_3 wash drains out of the reservoir, detach the reservoir and rinse it with water.

Note: This eliminates the HNO_3 that may cause slight gas pressure between the column and the reservoir if mixed with the HCl in the following steps.

- 4.16 Wash column with 50 ml of 10 M HCl by passing solution through column. Discard wash solutions.
- 4.17 Note the date of preparation on the NH_4I solution to ensure its freshness (i.e., <7 days old). Elute Pu with 25 ml of 0.1 M NH_4I in 10 M HCl into a 50 ml beaker labeled with "Pu" and the sample ID. Allow column to drain completely and save solution in 50 ml beaker.

Note: The NH_4I solution must have been made within 7 days.

- 4.18 To the eluted sample solution, add .10 ml conc. HNO_3 .
- 4.19 Evaporate to dryness on hot plate (set at .2).
- 4.20 If the solution is separated sufficiently as determined by a Cognizant Scientist and does not need another column clean-up, then proceed to Step 4.26. This decision is based on the nature of original sample, and the color and amount of residue present in the beaker at the end of Step 4.19. If another clean-up is determined to be required, then proceed with Steps 4.21-4.25.
- 4.21 Dissolve in about 5 ml 9 M HNO_3 and remove from hot plate and cool.
- 4.22 Add a microspatula tip (about 10 ± 5 ug) of NaNO_2 (sodium nitrite). Let stand overnight.
- 4.23 Prepare a 5 ml anion resin column with Dowex 1 X 8 (50-100 mesh). Equilibrate the column with 25 ml of 9 M HNO_3 by passing the solution through the column.
- 4.24 Pass the sample solution through the column. Wash column with 50 ml 9 M HNO_3 by passing solution through the column.
- 4.25 Repeat Steps 4.15 through 4.20.
- 4.26 Dissolve sample in 500 lambda conc. H_2SO_4 . Remove from hot plate and cool. Go to the electroplating procedure, PNL-ALO-468.

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5.0 Specific Qualification

NIST-traceable alpha-emitting isotopes are used as tracers for this process to determine recoveries or yields. Thus, this procedure is self-qualifying as defined in PNL-MA-70, PAP-70-901.

6.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with the Act Now ~~Directive 89.1~~ established records management practices.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-467, FINAL AMERICIUM SEPARATION AFTER INITIAL SEPARATION FROM PLUTONIUM BY ANION EXCHANGE

APPLICABILITY

This procedure describes two methods for making a final separation of americium from other alpha-emitting radionuclides after an initial separation from plutonium and other interferences as described in PNL-ALO-466. The default method is a separation of actinides from interfering lanthanides by co-precipitation followed by ion exchange. The optional method is a simple oxalate co-precipitation. The separated Am is then precipitation-plated according to PNL-ALO-496 or electroplated onto a metal plating disk according to PNL-ALO-468. Americium is then measured by alpha energy analysis (AEA) according to PNL-ALO-469.

DEFINITIONS

- conc - concentrated
- Duplicate - a replicate aliquot of a sample which is brought through the entire sample preparation and analysis process to document the precision of the method.
- Reagent blank - an artificial sample designed to monitor the introduction of contamination into the sample preparation and analysis process; it is treated like a "real sample" as it is carried through the appropriate steps of a process.
- Blank spike - a reagent blank to which a known amount of the analyte of interest is added.
- Matrix spike - a replicate sample to which a known amount of the analyte of interest is added.
- ppt - precipitate
- λ - lambda, equals 1 microliter

Author <i>N. L. Wynhoff</i> NL Wynhoff	Date 1-12-93	Project Mgr. <i>KJ Kuhl-Klinger</i> KJ Kuhl-Klinger	Date 1/13/93	PQ Representative <i>TL Ehler</i> TL Ehler	Date 1/19/93
Technical Reviewer <i>SK Fadeff</i> SK Fadeff	Date 1/20/93	Line Mgr. <i>AG King</i> AG King	Date 1/19/93	Other _____ Date _____	
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PNL TECHNICAL PROCEDURE

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

PROCEDURE

Pre-requisite: Only personnel trained in this procedure may perform the work. Personnel training records are kept in the section office.

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method; or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within +/-10% of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is +/-50% in the next digit located beyond the last one stated.

2.0 Reagents

All reagents are prepared from analytical reagent grade chemicals. Deionized water, with an electrical resistance of >16 megohms-cm is used throughout this procedure. Concentrations are not critical and need only be within +/-10% of stated values.

8 M HNO₃ - 50 ml concentrated nitric acid diluted to 100 ml with water.

2 M HNO₃ - 12.5 ml concentrated nitric acid diluted to 100 ml with water.

Ca carrier, 10 mg/ml - Dissolve 6.24 g CaCO₃ in approximately 50 ml 8 M HNO₃. Dilute to 250 ml with water. (Note: Another calcium salt may be used or another concentration as long as the required mgs of Ca⁺² are added to the sample as directed.)

oxalic acid.

conc NH₄OH - concentrated ammonium hydroxide, 14.5 M.

50% NH₄OH - 50 ml water and 50 ml concentrated ammonium hydroxide.

5% NH₄OH - 95 ml water and 5 ml concentrated ammonium hydroxide.

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6 M HCl - 50 ml concentrated hydrochloric acid diluted to 100 ml with water.

Fe carrier, 10 mg/ml - Dissolve 18.08 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in H_2O . Dilute to 250 ml with water. (Note: another ferric salt may be used or another concentration as long as the required mgs of Fe^{+3} are added to the sample as directed.)

2 M HNO_3 saturated with ascorbic acid - Make this solution up just prior to use. Add solid ascorbic acid to 2 M HNO_3 until no more will dissolve and some solid ascorbic acid remains.

9 M HCl - 75 ml concentrated hydrochloric acid diluted to 100 ml with water.

4 M HCl - 33 ml concentrated hydrochloric acid diluted to 100 ml with water.

2 M NH_4SCN -0.1 M formic acid - 15.22 g NH_4SCN + 400 λ 90% formic acid diluted to 100 ml with water. (90% formic acid = 23.26 M)

1 M NH_4SCN -0.1 M formic acid - 7.61 g NH_4SCN + 400 λ 90% formic acid diluted to 100 ml with water.

2 M HCl - 17 ml concentrated hydrochloric acid diluted to 100 ml with water.

conc HNO_3 - concentrated nitric acid, 16 M.

conc HCl - concentrated hydrochloric acid, 12 M.

conc H_2SO_4 - concentrated sulfuric acid, 18 M.

oxalic acid, sat. - oxalic acid dissolved in 100 ml of water until saturated.

3.0 Equipment

Hot plate/stirrer.

Filter - glass microfiber, $\leq 1.5 \mu\text{m}$ effective particle size retention.

Filter apparatus.

Wash bottles, plastic.

Forceps.

Pipetters.

Small spatulas or scoops.

Transfer pipets, plastic or glass.

pH paper, fine range, centered around pH 3.0.

Heat lamp.

Muffle furnace.

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Centrifuge tubes, conical - 50 ml, plastic screw-cap or glass, or appropriate size.

Centrifuge.

EIChroM Tru-Spec columns.

EIChroM prefilter columns.

EIChroM TEVA-Spec columns.

beakers - 30 ml, 50 ml, 150 ml, or appropriate size.

4.0 Quality Control Instructions

4.1 All quality control (QC) data shall be maintained as hard copy and available for easy reference or inspection.

4.2 Two QC options are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a SOW, and these may be conveyed to the analyst through a Test Instruction (TI).

- (a) Employ a minimum of one reagent blank and one blank spike per sample batch (20 samples or less). Run duplicate or matrix spike analysis upon client request.
- (b) For all SOWs written by a client to meet CERCLA requirements that request analysis, employ a minimum of one reagent blank per sample batch (20 samples or less) to determine if contamination is occurring. Run one duplicate sample and one blank spike (NIST traceable, if possible) per batch (20 samples or smaller). A matrix spike or laboratory control sample may be analyzed with a batch of samples if so directed by the client.

4.3 Volume Calibration: Critical volume measurements, as indicated in the procedure, shall be made with automatic pipets or equivalent. A performance check of the automatic pipet shall be completed prior to use. This consists of pipetting and weighing at least three aliquots of deionized water, equal to the volume being used, into a container on the balance. The average delivery weight is converted to volume by multiplying the weight by the reciprocal of the density as it applies to the ambient temperature. This calculated delivery volume shall be acceptable for 7 days.

5.0 Oxalate Precipitation

This procedure defines two options. The default option is given in Sections 5.0 and 6.0. The second option, Section 7.0, shall only be used if specified by the Cognizant Scientist.

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- 5.1 Evaporate the 9 M HNO_3 Am fraction from the step 4.13 of plutonium procedure PNL-ALO-466 to syrup. Do not go to dryness as that makes dissolution difficult. Dissolve the sample in 2 M HNO_3 .
- 5.2 Unless directed by a Cognizant Scientist, to perform the oxalate precipitation, continue the analysis beginning with step 6.1. (Typically, the Cognizant Scientist will specify the oxalate precipitation [Section 5.3 - 5.13] if the sample is a soil sample and if an oxalate precipitation was not done at the beginning of the plutonium procedure, PNL-ALO-466, Section 4.1.)
- 5.3 If silica is present (cloudy solution) filter the sample through a glass fiber filter. Wash the filter with 2 M HNO_3 .
- 5.4 Add the amount of Ca carrier specified by the Cognizant Scientist. Generally this is 100 mg Ca carrier, but may vary depending on the amount of Ca anticipated to be in the sample. Make an informal note of the amount of Ca carrier added. (This amount is not a part of the sample calculation.)
- 5.5 Add oxalic acid to make sample saturated, and heat to dissolve. The sample is considered saturated when a few grains/crystals of oxalic acid persist in the sample solution after heating for at least 10 minutes. If a small amount (few grains) of undissolved oxalic acid persists after this time, ignore it. If there is a significant amount of oxalic acid solids present after this time (if in doubt ask the Cognizant Scientist), filter the solution, wash ppt with H_2O , save the filtrate and discard the ppt.
- 5.6 Adjust pH to 2.8-3.0, using various concentrations of NH_4OH and HCl , as appropriate, and measuring pH with fine range pH paper.
- NOTE: Typically, conc. or 50% NH_4OH is used initially for pH adjustment, followed by 5% NH_4OH as pH 2.8 is approached.
- NOTE: The solution should be green with a cloudy white calcium oxalate ppt. If the solution turns orange, $\text{Fe}(\text{OH})_x$ is forming. Causes may be that the solution is too basic or that there is not enough oxalic acid to chelate all the Fe. Contact Cognizant Scientist for assistance.
- 5.7 If white calcium oxalate does not form, add 2-4 drops of the Ca carrier solution to the sample. When white ppt forms at the drops, make sample acidic ($\text{pH} < 2.5$) with HCl , and add additional Ca carrier per instructions from the Cognizant Scientist. Readjust to pH 2.8-3.0 with NH_4OH . Make an informal note of the amount of Ca carrier added. (This amount is not a part of the sample calculation.)

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- 5.8 Heat until solution is hot (but not boiling) and then at least 5 minutes more to let ppt become more crystalline. Filter and wash ppt with H_2O . Discard filtrate solution.
- 5.9 Add 10 mg Fe carrier to ppt, and dry under heat lamp.
- 5.10 Muffle overnight at $500^{\circ}C$ (not less than 8 hours). Let cool.
- 5.11 Dissolve ppt in HCl (6 M or higher). Make basic with 50% or conc NH_4OH to ppt rust-colored, gelatinous $Fe(OH)_x$. Centrifuge at least 5 minutes, and discard solution.
- 5.12 If ppt is mixed with a white or cream-colored ppt, repeat Step 5.10 until ppt is not mixed with white ppt.
- 5.13 Dissolve ppt in a minimum (a few drops) of 2 M HNO_3 .

6.0 Extraction Chromatography

- 6.1 If silica is present (cloudy solution) filter the sample through a glass fiber filter. Wash the filter with 2 M HNO_3 .
- 6.2 While mixing the solution add dropwise a 2 M HNO_3 solution saturated with ascorbic acid (made just prior to use) until the solution shows a bluish color. The addition of ascorbic acid is continued until the bluish color goes away. For blanks, 10 mg of iron carrier needs to be added before this step is carried out.
- 6.3 Remove the frit on top of an EIChroM Tru-Spec column with small tweezers and discard it. Place a tuft of glass wool in its place. Start the column by breaking off the plastic tip on the bottom of the column. Condition the column with two 5 ml portions of 2 M HNO_3 .
- 6.4 Load the sample on the column.
- 6.5 Wash the column with 20 ml 2 M HNO_3 in aliquots and discard.
- 6.6 Wash the column with 5 ml of 9 M HCl and discard.
- 6.7 Wash an EIChroM prefilter column with 5 ml of H_2O and discard. Place the EIChroM prefilter column after the Tru-Spec column.
- 6.8 Elute the Am with 20 ml of 4 M HCl and collect.
- 6.9 Evaporate to dryness.

NOTE: The lanthanides are included in this fraction and if they are prevalent they will cause degradation of the peaks obtained with AEA. If the lanthanides are known to be of

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low concentration the Cognizant Scientist may direct that the analysis proceed to step 6.16. If the lanthanide concentration is unknown proceed with the La-Am separation, steps 6.10-6.16.

6.10 Add 1 ml of 2 M NH_4SCN -0.1 M formic acid to the sample. Mix well and allow to stand 30 minutes or longer to assure solution of the sample.

6.11 Prepare an EIChroM TEVA-Spec column by washing the column with 3 ml of H_2O followed by 5 ml of 2 M NH_4SCN -0.1 M formic acid.

NOTE: Evaporate the NH_4SCN wash to dryness and save until the analysis is completed.

6.12 Transfer the sample to the TEVA-Spec column. Rinse the sample container with four 0.5 - 1 ml portions of 2 M NH_4SCN -0.1 M formic acid, adding the rinses to the column.

6.13 Wash the column with 13 ml of 1 M NH_4SCN -0.1 M formic acid. Add the first 5 ml of wash in 1 ml portions and the remaining 8 ml as the column reservoir capacity allows. The eluent contains the lanthanides. Evaporate to dryness and save until analysis completed.

6.14 Place an EIChroM pre-filter column that has been washed with 5 ml H_2O under the TEVA-Spec column so that the eluent from the TEVA-Spec column will pass through the pre-filter column. Elute the Am with 15 ml of 2 M HCl , collecting the eluent in a 150 ml beaker.

NOTE: The decomposition of NH_4SCN can cause vigorous foaming so use a 150 ml beaker to prevent boil-overs.

6.15 Add one ml of conc HNO_3 , cover with a watch glass and warm slowly for 1 - 2 minutes. The NH_4SCN can cause foaming and spattering as it decomposes. Remove watch glass and evaporate to near dryness slowly. Add 1 ml conc HNO_3 and 3 ml conc HCl and evaporate to dryness. Repeat this addition and evaporation up to 4 times to destroy NH_4SCN residues. Add 1 ml conc HNO_3 and evaporate to dryness.

6.16 Go to the precipitation plating procedure, PNL-ALO-496, using the option which does not plate uranium.

As an alternative, if so directed by a Cognizant Scientist, dissolve the sample in 500% conc H_2SO_4 . Remove from the hot plate, cool and continue with the electroplating procedure, PNL-ALO-468. Count and calculate according to PNL-ALO-469.

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7.0 Alternate Final Oxalate Separation

If instructed by a Cognizant Scientist, use this option instead of Sections 5.0 and 6.0. This option requires that all calcium has been separated from the sample. Any amount of calcium above the two milligrams added in step 7.3, below, will drastically reduce the electroplating yield.

7.1 Evaporate the 9 M HNO_3 Am fraction from the step 4.13 of Pu procedure, e.g., PNL-ALO-466, to low volume (approx 1 ml).

7.2 Transfer to a centrifuge tube with water and dilute to about 10 ml.

7.3 Add 10 - 20 mg Fe carrier and 2 mg Ca carrier. Add 100 - 150 mg oxalic acid. Place in hot water bath to dissolve.

NOTE: All the oxalic acid may not dissolve.

7.4. Adjust pH to 2.8-3.0, using various concentrations of NH_4OH and HCl , as appropriate, and measuring pH with fine range pH paper.

NOTE: Typically, conc. or 50% NH_4OH is used initially and 5% NH_4OH as pH 2.8 is approached.

NOTE: The solution should be green with cloudy white calcium oxalate ppt. If the solution turns orange, $\text{Fe}(\text{OH})_3$ is forming. Causes may be that the solution is too basic, that is, $\text{pH} \geq 3.5$, or that there is not enough oxalic acid to chelate all the Fe. Contact Cognizant Scientist for assistance.

7.5 Let stand 5 minutes or more in a hot water bath to let the ppt become more crystalline.

7.6 Centrifuge. Discard supernate.

7.7 Dissolve ppt with a minimum amount of conc HNO_3 . Dilute to about 5 to 10 ml with water. Add 1 ml saturated oxalic acid solution.

7.8 Repeat steps 7.4, 7.5 and 7.6.

7.9 Wash ppt with water. Repeat step 7.6. This step may be repeated to remove any remaining solid oxalic acid.

7.10 Dissolve ppt with conc HNO_3 and transfer to a small beaker (typically 30 or 50 ml). Take to dryness on a hot plate.

7.11 Dissolve in 500 μ l conc H_2SO_4 . Remove from the hot plate, cool and continue with the electroplating procedure, PNL-ALO-468. (As an

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alternative to this step, if so directed by a Cognizant Scientist, go to the precipitation plating procedure, PNL-ALO-496.) Count and calculate according to PNL-ALO-469.

8.0 Specific Qualification

None required.

9.0 Records

Records will be maintained and controlled so as to conform to requirements of the ACL Quality Assurance Plan, MCS-033. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with established records management practices.

10.0 References

EIChroM Industries, Inc., 8205 S. Cass Ave. Suite 107, Darien, IL 60559. Product Literature.

Davis, T. M., Analysis of Americium in Soil and Bottom Sediment. Procedure DARC-0007, Radiochemistry Laboratory, Dosimetry and Analytical Services Section, Argonne National Laboratory.

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-468.1 R0
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A.

Document Number: PNL-ALO-468 Revision Number: 0

Document Title: Procedure for Electroplating Plutonium,
Americium and Uranium onto Counting Disks

Document's Original Author: NL Wynoff

Effective Date
of ICN: 5/11/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 3 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert TL Ehlert Date: 5/7/92

Approval Authority: AG King AG King Date: 5/7/92

Other Approvals: BM Gillespie B. M. Gillespie Date: 5/11/92

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-468, PROCEDURE FOR ELECTROPLATING PLUTONIUM, AMERICIUM AND URANIUM ONTO COUNTING DISKS

APPLICABILITY

This procedure is used to electroplate Pu, Am or U onto counting disks for alpha energy analysis (AEA). Solutions first go through respective separations for purification before being electroplated out of a sulfuric acid matrix, unless they are pure radionuclide standard or tracer solutions. This procedure was developed by PNL Radioanalytical Scientists, and is based on over 10 years experience in Pu, Am and U analysis of a broad spectrum of sample types.

DEFINITIONS/ACRONYMS

ul - microliter, lambda
conc. - concentrated

RESPONSIBLE STAFF

Cognizant Scientist
Technician/Analyst

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.

Author	Date	Project Mgr.	Date	QAD Representative	Date
NL Wynoff		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Li e Mgr.	Date	Other	Date
BM Gillespie		PF Salter		ALL ORIGINAL SIGNATURES ON FILE	
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- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Chemical Reagents

All chemicals used shall be reagent grade unless otherwise specified. The water used shall be deionized or distilled.

2.1 0.02% thymol blue indicator solution - 0.05 g dissolved in 20-25 ml water and 36 μ l 6 M NaOH, with stirring and heat if necessary. Dilute to 250 ml with water.

2.2 50% NH_4OH - 50 ml water and 50 ml conc. NH_4OH . This solution shall be made within a week of use. Other concentrations lower than 50% may be used for better control of neutralization. Record the date of preparation on the bottle.

2.3 Ethanol.

2.4 Conc. NH_4OH .

3.0 Supplies and Equipment

3.1 Electroplating Apparatus. Consists of a power supply, electrical leads, plating cell and platinum strip electrodes.

3.2 Metal Plating Disks.

4.0 Chemical Procedure and Plating

4.1 To a prepared sample (dissolved in 500 lambda conc. H_2SO_4), add 3 ml H_2O . Let stand 1/2 hour.

Note: A prepared sample is one that has been through a separation procedure such as PNL-ALO-466 or other preparatory procedure as designated by the Cognizant Scientist, TI or ARF.

4.2 Add approximately 4 (2-6) drops of 0.02% thymol blue indicator.

4.3 Note that the NH_4OH solution is fresh (i.e., <7 days old). Drop-wise, add NH_4OH solution until color changes to yellow-orange-gold (pink gone, orange almost gone, but not greenish).

Note: 50% NH_4OH solution usually works well. Lower concentrations may be used for better control of neutralization. It shall be made within a week of use.

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- 4.4 Remove disk cover from a 7/8" (22 mm) polished metal plating disk which has the sample identification (ID) engraved on the back. Wash with ethanol and wipe with a Kimwipe or equivalent to remove adhesive. Let dry.
- 4.5 Mount sample disk in electroplating cell.
- 4.6 Quantitatively transfer sample to cell with H₂O and fill cell to near the top (to within 1/4"-1/2" of the top of the vial as visually determined).
- 4.7 Electroplate at 1 amp for 1 hour.
- 4.8 20 seconds before finishing, add 1-2 ml conc. NH₄OH.
- 4.9 Wash electrodes with H₂O while removing them, and turn power off. Remove sample solution from cell.
- 4.10 Wash electroplated disk with water, then with ethanol. Let dry.
- 4.11 Store sample disks in cardboard AEA holders labeled with sample identification in the Counting Room in the 329 Laboratory (Room 16A) or in Room 4B if there is insufficient space in Room 16A.

5.0 Specific Qualifications

In this procedure, radioactive tracers are used to determine recoveries or yields. The requirements, identified in PNL-MA-70, PAP-70-901, for the procedure to be "self-qualifying" are met by the use of the tracers.

6.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with the Act Now Directive 89.1 established records management practices.

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INTERIM CHANGE NOTICE
(ICN)

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A. Document Number: <u>PNL-AL0-469</u> Revision Number: <u>0</u> Document Title: <u>Counting Procedure for Alpha Spectrometry</u> Document's Original Author: <u>NL Wynhoff</u>		Effective Date of ICN: <u>08/05/91</u> Change Requested By: <u>JH Kaye</u>
B. Action: <u>Replaces ALL pages including Exhibit 1.</u>		
C. Effect of Change: These changes will have no impact on data or calculations, and will provide more meaningful information for monitoring detector performance.		
D. Reason for Change/Description of Change Under sections 4.1.2 - 4.1.7 and 4.2.1 of PNL-AL0-469, detectors were determined to be out of control even though only small changes in gain occurred. This happened because 1) the regions of interest used for determining counting rate were in fixed locations, 2) the regions of interest were too narrow and 3) a ± 5 channel restriction on peak shift is unnecessarily stringent. The following changes have been made - 1) The region of interest is now defined relative to the peak channel (channel with the highest counting rate). 2) The region of interest is now widened to cover the entire peak. 3) Only the Pu-239 alpha peak at 5.157 MeV is now monitored for control charting. 4) An additional parameter, full width at half-maximum (FWHM) is now monitored. 5) Gross, rather than net, counting rates are now monitored. See attached for Description of Change.		
E. Approval Signatures (Please Sign and Date)	Type of Change: (Check (/) one) () Minor Change ☒ Major Change	
Process Quality QA Department Concurrence: <u>GT Gende</u> Date: <u>7/1/91</u> Approval Authority: <u>Jim L. L...</u> Date: <u>7/8/91</u> Other Approvals: <u>B.M. D...</u> Date: <u> / / </u> : _____ Date: <u> / / </u>		

D. Description of Change

1) Replace 4.1.2 with the following:

- 4.1.2 Locate the middle spectral peak, corresponding to 5.157 MeV alpha particles from the control source due to decay of Pu-239. Record the channel number of the peak channel (the channel with the highest number of counts) in the Detector Control Check section of the AEA Detector Control Log (Exhibit 1) for that detector.

Define the region of interest (ROI) for this peak as follows:

Locate the lowest channel in the valley between this peak and the higher energy peak. This is the upper limit of the ROI. Do the same for the lower limit of the ROI.

Example - Determination of Region of Interest for Control Data

channel	counts	channel	counts
323	20	365	215
324	9	366	95
325	19	367	48
326	15	368	13
327	14	369	5
328	22	370	1
329	27	371	3
330	32...	372	3

The region of interest includes channels 324 - 370.

Integrate the total number of counts in this region and divide by the live time in minutes to determine the counting rate. Record this value in the Detector Control Check section of the AEA Detector Control Log.

2) Delete 4.1.3 and 4.1.4

3) Renumber 4.1.5 as 4.1.3 and replace the text with the following:

- 4.1.3 After a total of 10 control counts have been recorded, compute the average gross cpm and the standard deviation for the Pu-239 peak in the control source using the ROI as defined above, and record in the AEA Detector Control Log (Exhibit 1) for that detector in the Reference Control section.

4) Renumber 4.1.6 and 4.1.7 as 4.1.4 and 4.1.5, respectively.

5) Add the following as 4.1.6:

4.1.6 The FWHM is defined as follows:

Divide the gross number of counts in the peak channel by two. Look on the high energy side of the peak and determine which channel is closest to this value. Do the same on the low energy side of the peak. The difference between these channels is the FWHM. Record this value in the Reference Control section of the AEA Detector Control Log.

Example - Peak channel = 1891 counts $1891/2 = 946$ counts

channel	counts	channel	counts
305	743	316	1723
306	940	317	1409
307	985	318	957
308	1178	319	535
309	1231	320	261
310	1455	321	99
311	1553	322	45
312	1882...	323	20

The FWHM = channel 318 - channel 306 = 12 channels

Note - Although this method is only an approximation, it is adequate for control charting purposes and will allow determination of changes in resolution which are large enough to have a significant effect on the results.

- 4.1.7 For any subsequent control count, if the FWHM changes by five or more channels from the previous value, repeat the control count two more times. If the FWHM value for either of these counts is still five or more channels different from the previous value, the detector is out of control, this shall be so posted and a DR shall be filed per PNL-MA-70, PAP-70-1502. A Cognizant Scientist will evaluate the system and determine the appropriate action. Spectra for all samples analyzed since the last good FWHM control measurement shall be evaluated by the Cognizant Scientist to determine if recounting or recalculation is needed.

6) Replace the first two sentences of 4.2.1 with the following:

- 4.2.1 After each control source count, the location of the peak channel for the Pu-239 peak is recorded in the Detector Control Check section of the AEA Detector control log and compared with the most recent previously recorded value. If this peak location is more than five channels from its previous location, the detector is out of control and a DR shall be filed per PNL-MA-70, PAP-70-1502.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-469, COUNTING PROCEDURE FOR ALPHA SPECTROMETRY

APPLICABILITY

This procedure is applicable to the operations of the Alpha Energy Analysis (AEA) counting spectrometer systems located in the 329 Building. This procedure is applied to the analyses of alpha emitting radionuclide samples prepared in accordance with PNL-ALO-468 or other sample preparation procedure designated by the Cognizant Scientist. This procedure was developed by PNL Radioanalytical Scientists, and is based on over 10 years experience in radionuclide determination by AEA.

DEFINITIONS/ACRONYMS

d/c - disintegrations per count, an efficiency factor
cpm - counts per minute
dpm - disintegrations per minute (concentration term)
bkg - background
ROI - region of interest

RESPONSIBILITIES

Cognizant Scientist
Technician/Analyst

(Note: Except where responsibility is specifically assigned to a Cognizant Scientist, the Analyst may perform all work.)

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

Author	Date	Project Mgr.	Date	QAD Representative	Date
NL Wynhoff		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
PF Salter		PF Salter		Original Signatures on File	
GG Brodaczynski					
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- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Alpha Spectrometry Counting System Description

AEA spectrometers are used to identify isotopes and measure concentrations of alpha-emitting radionuclides in electroplated samples.

The AEA spectrometers use silicon-charged particle detectors housed in chambers which can be evacuated. Samples are electrodeposited on metal counting disks. The disks are centered on a pedestal directly below the detector in the chamber. The active area of each detector is normally about 450 mm². They operate at about +100 volts bias or less. After the sample has been positioned, the chambers are evacuated to minimize spectral degradation from alpha-particle scattering in air.

A counting system consists of several detectors/chambers with their associated preamplifiers, amplifiers and high-voltage power supplies. The amplified output from these detectors is digitized by an analog to digital converter (ADC).

3.0 Use of the Counting Systems

Alpha sources (standards and samples) are loaded into chambers for counting by the following steps:

- 3.1 Turn the bias voltage of the detector slowly off (takes at least 1 minute). When the bias is off, gradually release the chamber vacuum. Open the chamber. Place the source in the center of the pedestal of the chamber. Close and evacuate the chamber. Wait about 1 minute. Slowly turn the bias voltage to the setting for that detector (takes at least 1 minute). The setting for that detector may be written on or adjacent to the voltage control knob for ready reference. The setting shall also be recorded in the Counting Equipment Maintenance Log in the 329 Laboratory Counting Room (Room 16A) for reference.

Note: On some systems, bias and vacuum are controlled by switches. Turn the switch to vent, and wait for the voltage and vacuum

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to go to zero. Open the chamber, place the source in the center of the pedestal of the chamber. Close the chamber. Turn the switch to "pump"; when chamber is evacuated, voltage will slowly rise to the correct setting for the detectors. Both voltage and vacuum are indicated on a gauge for these systems and are pre-set.

3.2 When the voltage has stabilized (at least 5 seconds), clear the timer of the multichannel analyzer and clear the memory storage unit. Start the count. If the required count time is not specified in this procedure, it will be specified by a Cognizant Scientist. Record the counter number, date and time of count, and the source or sample identification in the LRB or Data Sheet.

3.3 When the count has been completed, record the count time in the LRB or Data Sheet. Turn the multichannel analyzer output control to select the fraction of memory where the spectrum is stored. Transfer the contents of the memory to computer files to which the counter number, start date and time of count, sample/source ID, file name and count time have been entered. Print a hard copy. The hard copy is filed in Room 8 or Room 22, 329 Building (see Section 6).

Note: A hard copy of the counting data alone is acceptable when there are computer malfunctions. In this case, the Analyst shall record onto the printed hard copy the counter number, date and time of count, the source or sample ID, and the count time.

3.4 Slowly reduce the detector bias voltage to zero. Release the chamber vacuum and return the source to its holder.

Note: On some systems, bias and vacuum are controlled by switches (See information in Step 1).

3.5 If the detector is not to be immediately used for another sample count, a background count is usually started. Place a new, ethanol-rinsed, background disk on the pedestal. Close and evacuate the chamber, set the detector bias voltage and begin a background count (preset count time to -800,000 sec).

3.6 Spectral peaks are integrated per instructions from a Cognizant Scientist. For example, the regions of interest may be specified as the peak channel plus the next 5 channels of higher energy and the 9 channels of lower energy (standard 15-channel region). Any backgrounds used in sample calculations shall be based on regions.

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having the same number of channels integrated. Calculations are recorded on the computer hard copy or on a Data Sheet and filed with the spectra hard copy.

4.0 Counter Performance Tests and Quality Control

Control of alpha detector and counting system performance is established by measuring National Institute of Standards Technology (NIST)-traceable electroplated alpha-emitting isotope sources. Other commercially-available Certified sources may be used if NIST sources are not available. These isotopes fall in the energy range from 3.0 to 9.0 MeV, and shall be periodically used as control sources (See Sections 4.1, 4.2, 4.3) and, when needed, to obtain the counting efficiencies of the alpha detectors and counting systems.

Control of system performance shall be reestablished when a new detector is put in operation, when control source analysis warrants it (See Sections 4.1 and 4.2), or when a Cognizant Scientist determines that the replacement of an electronic component makes it necessary.

4.1 Counter Control Checks

When instruments are in nearly continuous use, a periodic check (at least once a month) of performance shall be made. If the instrument is not used for an extended period (a few weeks), these checks may be discontinued until operations are again started. Control checks shall be made as follows. All calculations for control checks are recorded on Data Sheets and filed with the hard copy of the alpha energy spectra (counting data). These files are kept in Room 8, 329 Building. In addition, an AEA Detector Control Log (Exhibit 1) is kept in the Counting Room (16A), 329 Building.

- 4.1.1 A NIST or other Certified control source containing ^{238}Pu , ^{239}Pu and ^{242}Pu is counted on each detector per instructions given in Section 3.0. Each detector shall always be checked with the same control source as shown below. Controls shall be counted at least 60 min.

<u>Control #</u>	<u>Detector Assigned that Source</u>
#1/5	C1, C5, C9, 05
#2/6	C2, C6, C10, 06
#3/7	C3, C7, C11, 07
#4/8	C4, C8, C12, 08

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- 4.1.2 Locate the middle spectral peak, corresponding to 5.157 MeV alpha particles from the control source due to decay of Pu-239. Record the channel number of the peak channel (the channel with the highest number of counts) in the Detector Control Check section of the AEA Detector Control Log (Exhibit 1) for that detector.

Define the region of interest (ROI) for this peak as follows:

Locate the lowest channel in the valley between this peak and the higher energy peak. This is the upper limit of the ROI. Do the same for the lower limit of the ROI.

Example - Determination of Region of Interest for Control Data

channel	counts	channel	counts
323	20	365	215
324	9	366	95
325	19	367	48
326	15	368	13
327	14	369	5
328	22	370	1
329	27	371	3
330	32...	372	3

The region of interest includes channels 324 - 370.

Integrate the total number of counts in this region and divide by the live time in minutes to determine the counting rate. Record this value in the Detector Control Check section of the AEA Detector Control Log.

- 4.1.3 After a total of 10 control counts have been recorded, compute the average gross cpm and the standard deviation for the Pu-239 peak in the control source using the ROI as defined above, and record in the AEA Detector Control Log (Exhibit 1) for that detector in the Reference Control section.
- 4.1.4 For control purposes, any subsequent counter control check shall be recorded on the AEA Detector Control Log for that detector and in the Control Check Section. The counter control check shall be within 2% of the mean value or within

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± 2 standard deviations of the mean, whichever is the larger limit for each peak.

- 4.1.5 If a counter control check is not within the established control limits recorded on the Detector Control Log, the detector is out of control for any use that requires use of a d/c factor. Post a sign on the instrument: "Do Not Use Detector # X Until a Cognizant Scientist has Reevaluated the Detector d/c." File a Deficiency Report (DR) per PNL-MA-70, PAP-70-1502. A Cognizant Scientist will evaluate the system and determine a new d/c or determine if repairs are required. If a determination of the need for repairs is made, this evaluation and any repairs made will be documented in the Counting Equipment Maintenance Log and on the DR. Spectra for all samples analyzed since the last good counter control check shall be evaluated by the Cognizant Scientist for the need to recount. These samples shall be recounted as determined by the Cognizant Scientist or as required by the client.

4.1.6 The FWHM is defined as follows:

Divide the gross number of counts in the peak channel by two. Look on the high energy side of the peak and determine which channel is closest to this value. Do the same on the low energy side of the peak. The difference between these channels is the FWHM. Record this value in the Detector Control check section of the AEA Detector Control Log.

Example - Peak channel = 1891 counts $1891/2 = 946$ counts

channel	counts	channel	counts
305	743	316	1723
306	940	317	1409
307	985	318	957
308	1178	319	535
309	1231	320	261
310	1455	321	99
311	1553	322	45
312	1882...	323	20

The FWHM = channel 318 - channel 306 = 12 channels

Note - Although this method is only an approximation, it is adequate for control charting purposes and will allow

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determination of changes in resolution which are large enough to have a significant effect on the results.

- 4.1.7 For any subsequent control count, if the FWHM changes by five or more channels from the previous value, repeat the control count two more times. If the FWHM value for either of these counts is still five or more channels different from the previous value, the detector is out of control, this shall be so posted and a DR shall be filed per PNL-MA-70, PAP-70-1502. A Cognizant Scientist will evaluate the system and determine the appropriate action. Spectra for all samples analyzed since the last good FWHM control measurement shall be evaluated by the Cognizant Scientist to determine if recounting or recalculation is needed.

4.2 Energy Calibration

- 4.2.1 After each control source count, the location of the peak channel for the Pu-239 peak is recorded in the Detector Control Check section of the AEA Detector control log and compared with the most recent previously recorded value. If this peak location is more than five channels from its previous location, the detector is out of control and a DR shall be filed per PNL-MA-70, PAP-70-1502. The Cognizant Scientist shall determine if adjustments or repairs are required, and reestablish control of the detector. This evaluation and any repairs made will be documented in the Counting Equipment Maintenance Log and on the DR. Spectra for all samples analyzed since the last good counter control check shall be evaluated by the Cognizant Scientist for the need to recount. These samples shall be recounted as determined by the Cognizant Scientist or as required by the client.
- 4.2.2 Using at least the ^{238}Pu and the ^{242}Pu peak locations, the gain and zero offset shall be calculated by graphing alpha energy on the Y axis and channel number on the X axis or by linear regression. The gain is the slope of the line expressed as KeV/channel and the zero offset is the Y axis intercept in KeV or MeV. This graph or calculation shall be filed with the hard copy of the Counter Control Check counting data in Room 8, 329 Building. The information from this source analysis is used to calculate peak location for other alpha-emitting radionuclides.

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4.3 Background Measurements

- 4.3.1 Determine the backgrounds by counting a new, ethanol-rinsed, stainless steel disk using the same counting procedure outlined in Section 3.0. A background count shall be taken for at least 200,000 sec. Backgrounds shall be determined at least monthly for each detector when the instruments are in continual use. If the instrument is not used for an extended period (>1 month), the background checks may be discontinued until standard/sample counting is restarted for that detector system.
- 4.3.2 Using peak locations from the control count and a standard 15-channel region (peak channel + next 5 channels of higher energy and next 9 channels of lower energy), the gross background count shall be calculated for each region of interest. The region of interest is defined by the alpha energy of the radioisotopes being analyzed.
- 4.3.3 Before using a detector for sample analysis, a Cognizant Scientist compares the current background with sample detection limit requirements and determines if the detector is suitable for the measurement. If the background is too high to achieve the requested detection limit, a different, lower-background detector shall be used, and/or the high-background detector shall be replaced with a new detector.

4.4 Disintegrations Per Count (d/c) Measurement

The d/c of a detector is determined only when required by a specific analysis. It is not required when the samples are spiked with an alpha-emitting tracer isotope as in PNL-ALO-466. The frequency of d/c determinations shall be specified in the analysis procedure that requires the d/c value or if a TI requires that it be determined.

The d/c of each detector is determined using a ^{238}Pu - ^{239}Pu source electroplated on a stainless steel disk. The source is checked for accuracy against ^{239}Pu sources prepared from a NIST Reference Standard or other Certified standard. All standards/sources information is documented in one of two Calibration Standards Notebook(s): 1) the primary Calibration/Standards Notebook located in Room 10A, 329 Building, which contains data/information on all primary standards/reference materials; and 2) the secondary Calibrations/Standards Notebook located in Room 8, 329 Building, which contains all data related to preparation and verification of

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secondary standards, sources and tracers, and any re-checks of the primary standards.

A d/c determination is made by following the subsequent steps:

- 4.4.1 Count a standard alpha source containing ^{238}Pu - ^{239}Pu , and save the spectrum per instructions in Section 3.0. Count the source for a sufficient count time to accumulate at least 10,000 counts in each spectral peak.
- 4.4.2 Locate the spectral peak corresponding to the alpha particles from ^{239}Pu (5.157 MeV) and from ^{238}Pu (5.499 MeV). Integrate all the counts in each peak.
- 4.4.3 Use a recent background spectrum for the detector (within 1 month) to determine the background cpm for the same spectral regions that were integrated in Step 2. Determine the net cpm for each peak by subtracting the background cpm from the gross cpm. Sum the total net cpm of both peaks and record in the secondary Calibration Standards Notebook.
- 4.4.4 Calculate the detector d/c as follows:

$$\text{d/c} = \frac{\text{dpm of standard source}}{\text{net cpm}}$$

Record the value on the AEA Detector Control Log with the date of determination.

4.5 Radionuclide Standards and the Tracer Method

- 4.5.1 The alpha tracer method is an alternative to determining activity using d/c's. Isotopic standard solutions (tracers) of several long-lived alpha-emitting radionuclides are added to trace the radiochemical recovery or yield during chemical preparation and separation processes. Known activities of NIST-traceable standards or other Certified standards are used to prepare and cross-check tracer solutions. All secondary standards/tracers and their preparation and verification information are recorded in the secondary Standards/Calibrations Notebook located in Room 8, 329 Building. Traceability to primary standards is provided by recorded reference to the appropriate information in the

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primary Standards/Calibration Notebook located in Room 10A, 329 Building.

- 4.5.2 When the tracers used are alpha particle emitters, the alpha spectrometry measurement will simultaneously record count peaks corresponding to the alpha particle energies of the tracers and the other isotopes being measured.
- 4.5.3 Since the counting efficiency of the silicon-charged particle detectors is independent of alpha particle energy in the range of energies being measured, the relative net cpm of the tracer and each isotope is in proportion to the relative disintegration rates which are present at the time of the count.

5.0 Sample Counting and Data Reduction

- 5.1 Count the samples according to instructions in Section 3.0. Locate and integrate spectral regions for the isotopes of interest, including tracers.
- 5.2 Integrate the same spectral regions for the detector background spectrum taken most recently (within 1 month).

Note: The "same region" means the same region relative to the peak channel. So, if the region in the sample count is the peak channel +5 channels and -9 channels, then the background region is the peak channel from its associated control count +5 and -9.

- 5.3 Determine the net counts in each peak (i.e., each analyte or tracer):

$$\text{net analyte counts} = \text{peak counts} - \frac{(\text{bkg counts} \times \text{sample count time})}{\text{bkg count time}}$$

If using ad/c in calculations, calculate net cpm:

$$\text{net cpm} = \frac{\text{peak counts}}{\text{sample counttime}} - \frac{\text{bkg counts}}{\text{bkg count time}}$$

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5.4 Calculate analyte activity as follows:

Using Tracer:

$$\text{analyte activity} = \frac{\text{net analyte counts} \times \text{dpm for tracer added}}{B \times \text{net tracer counts}}$$

Using Efficiency:

$$\text{analyte activity} = \frac{\text{net analyte cpm} \times \text{d/c factor}}{B}$$

where B = factor or factors to account for sample volumes, yield as determined by tracer, dilutions, weights, leach solution volumes and any other factors needed to produce the appropriate reporting units. These factors shall be documented as part of the project record. Analyte activity shall be reported in the units requested by the TI or ARF. If specific units are not requested, activity shall be reported as the Cognizant Scientist directs (usually Ci/L or Ci/g).

6.0 Data Storage

AEA Control and Background Spectra and Calculations are stored in the "AEA Control and Background" files in Room 8, 329 Building until data are reported to the Analytical Chemistry Laboratory (ACL) Sample Monitoring Operation (SMO) or to the client. After that time, the data and supporting documentation are stored in Room 22, 329 Building.

7.0 Specific Qualification

NIST-traceable alpha-emitting isotopes are used as standards to control this instrument. Thus, this procedure is self-qualifying as defined in PNL-MA-70, PAP-70-901.

8.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with the Act Now Directive 89.1.

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-470.2 R0
Page 1 of 1

A.

Document Number: PNL-ALO-470 Revision Number: 0

Document Title: Procedure for Maintaining Control of Germanium Spectrometers Used for Gamma-Ray Spectroscopy

Document's Original Author: EA Lepe1

Effective Date
of ICN: 5/7/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 6 with 1 through 5 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert

Date: 5/7/92

Approval Authority: AG King

Date: 5/7/92

Other Approvals: _____

Date: 1/1

:

Date: 1/1

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-AL0-470.1
Page 1 of 1

A. Document Number: <u>PNL-AL0-470</u> Revision Number: <u>0</u> Document Title: <u>Procedure for Maintaining control of Germanium Spectrometers</u> Document's used for <u>Gamma-Ray Spectroscopy</u> Original Author: <u>E. A. Lepel</u>		Effective Date of ICN: <u>4/24/91</u> Change Requested By: <u>E. A. Lepel</u>
B. Action: Please replace page 1 with the attached page.		
C. Effect of Change: To allow coverage of the multidimensional (MDA) counting systems by this procedure. The MDA systems consist of NaI (TI) detectors.		
D. Reason for Change/Description of Change Reason for change: To allow coverage of the multidimensional (MDA) counting systems by this procedure. The MDA systems consist of NaI (TI) detectors. Description of change: See attached		
E. Approval Signatures (Please Sign and Date)	Type of Change: (Check (/) one) () Minor Change ☒ Major Change	
Process Quality OSAR Department Concurrence: <u>GRG ete, DE</u> Date: <u>4/10/91</u> Approval Authority: <u>[Signature]</u> Date: <u>4/11/91</u> Other Approvals: <u>[Signature]</u> Date: <u>4/12/91</u> : <u>B.M. [Signature]</u> Date: <u>4/15/91</u>		

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-470, PROCEDURE FOR MAINTAINING CONTROL OF GERMANIUM SPECTROMETERS USED FOR GAMMA-RAY SPECTROSCOPY

SCOPE

This procedure is to be used to assure the reliability and stability control of Germanium and Sodium Iodide Spectrometers used for gamma-ray spectroscopy. This will be assured by the periodic counting of "control check standards" in which specific peak areas are monitored. The reproducibility of the count data is a measure of the instrument stability and reliability. The periodic gamma counting of calibration control check standards, automated transfer of spectra from analyzers to data manipulation computers, the ability to retrieve and display control parameters as a function of time (possibly years), and archival storage of data for each counting system provide not only a measure of assurance of instrument stability but also accuracy and precision of each gamma spectrometer. This procedure was developed by PNL Scientists, and reflects over 10 years of experience in gamma-ray spectroscopy of a wide variety of samples.

APPLICABILITY

This procedure is implemented to assure quality and is approved and written to conform with PNL-MA-70.

This procedure is applicable to the Counting Room Manager and trained and qualified personnel within the Analytical Chemistry Laboratory and Nuclear Chemistry Department of PNL.

This procedure is primarily intended to assure that the gamma spectrometry equipment is maintained in control and in proper working condition.

DEFINITIONS/ACRONYMS

dpm - disintegrations per minute (activity term)

ng - nanograms (10^{-9} grams)

ug - micrograms (10^{-6} grams)

tl/2 - half-life

LRB - Laboratory Record Book

CTL - Control

Author	Date	Project Mgr.	Date	QAD Representative	Date
EA Lepel		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
KH Abel		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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- 2.1 The control check standard for each gamma-ray detection system is listed in Tables 1 and 2. The control check source standards are identified by LRB reference numbers. Each control check source standard is mounted either on a plastic holder which fits onto the detector or an aluminum card which is placed in a specific shelf of a card holder. Using the control check source and geometry specified for the detector, count the source for the time required to yield specific integrated gamma-ray peaks of <5% relative error ($\leq 1\%$ relative error, preferably) from counting statistics, per Sections 5.2.1-5.2.4 of PNL-ALO-464. The count times are listed in Table 2.
- 2.2 The accumulated spectrum is then transferred to the computer, the peaks integrated, resolution checked, and the calibration listed on the user's computer terminal. This is accomplished by using the control program (See Section 3.0).
- 2.3 The control program (CTL) stores the spectral data by date and the detector identification onto magnetic media. The program will then print and plot all values necessary to determine if the detector system is within control values based on 2 and 3 sigma ranges.

3.0 The Control (CTL) Program

The Control (CTL) program is used to track the consistency of a diode. The CTL program is also used to transfer an accumulated spectrum to the computer from a specific multichannel analyzer and performs the required data reduction and interpretation. This is done by typing CTL "X" at the ">" prompt, where X is the identification of the detector. After pressing Enter (or Return on the keyboard terminal), the program will transfer the data to the computer, integrate specific peak areas, check the resolution, and list the energy calibration on the computer terminal. The program then will print and plot the "Detector Reliability" Chart.

3.1 Computer Methodology

The CTL program assumes that for a particular diode its control source standard has been counted. CTL will transfer the spectrum into the computer and integrate the peaks according to the library ANTI.LIB or SING.LIB (depending on how the detector is configured with respect to coincidence-noncoincidence). The results of the integration (in counts per minute) are compared against a saved average, with a report and plot being generated.

The average activity (in cpm) for an area of interest (as designated by the SUM library) is calculated as follows:

Until 10 control check spectra are recorded, the average is used to determine the "goodness" of the latest control check spectrum. Once 10 control check spectra have been completed and accepted by the

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- Count - to acquire data via digitized pulses from radioactive sources in gamma spectrometer systems
- Control Source - aliquot of mixed radioactive source contained in counting geometry
- Diode - Detector - Part of the gamma detector system which includes the actual detector crystal in a metal cylindrical housing and its immediate electronics up to the preamplifier.

RESPONSIBLE STAFF

Counting Room Manager
Analysts

PROCEDURE

1.0 Equipment and Materials

Detectors - intrinsic germanium (IG) detector, lithium drifted germanium detector [Ge(Li)], low-energy photon detector (LEPD), multidimensional detector

Associated Electronics - preamplifier, amplifier, analog-to-digital converter (ADC), pulse pile-up rejector, multichannel analyzer, CAMAC interface, DEC PDP 11/44 computer, DEC μ VAX, or PC

Mixed radioactive control source containing at least two of these radioisotopes: ^{241}Am , ^{137}Cs , or ^{60}Co .

2.0 Gamma Spectrometry Control Procedure

This procedure defines the means for providing detector reliability and stability information to the system user. The primary method for monitoring gamma spectrometer system performance is the "detector reliability" chart. Each instrument must be checked routinely using radioactive sources to ensure that the stability, efficiency, and resolution of each detector is within a specified calibration range. The frequency of the calibration control check counts are based on the usage of the detector. When the detectors are in use, calibration control check counts are taken at least bi-monthly (two times a month) or as specified in a project-specific Statement of Work (SOW), Technical Project Plan (TPP) or Quality Assurance Project Plan (QAPjP). The proper standards and methods used for the calibration control check must be matched to the particular counting system being used. Graphing the control counting data (appropriate decay corrections must be made for the radioactive sources) readily determines that the detector system is operating properly and also provides a permanent record that aids in measuring instrument reliability.

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FIGURE 1. An Illustration of the FWHM Valve

The resolution (R) is calculated as follows:

$$R = \frac{\Delta\text{CH}(\gamma \text{ peak KeV})}{\text{CH}_C}$$

Where:

ΔCH = channel width at half max ($1/2 h$) in channels

CH_C = channel number at centroid of peak

and ΔCH is calculated by determining i and f fractional channel numbers by calculating the slope between channels in which the half max count lies between.

This resolution is checked as described in Section 3.2.

4.0 Records

Records will be maintained and controlled so as to conform to requirements of PAP-70-1701. Laboratory Record Books (LRBs) and Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~Act Now Directive 89.1~~ established records management practices.

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analyst, they determine the average for the detector. The average stays fixed from then on to guard against creeping or abnormal changes that could go unnoticed with a running average. The latest 50 control check spectra are kept in memory, and subsequent control check spectra are consecutively written over the top of the oldest. The plot uses the average as the center line, with the dotted lines on either side representing 2 sigma from the average and the next solid lines representing 3 sigma from the average.

3.2 CTL "Detector Reliability" Chart

The "Detector Reliability" chart shows the activities and resolution of the measured control source photopeaks as calculated by the CTL program. The chart is reviewed by the Counting Room Manager or Cognizant Staff to see if the activities and resolution of the latest counts are within 3 sigma of the standard deviation of the mean computed using the first 10 "good" control check spectra obtained for the control check source/standard. If the values are acceptable, the chart is signed and stored beside the detector system in a plastic folder which is readily visible. If the observed values are out of the 3 sigma range, the user will check the control check source/standard and geometry and rerun the control check source (per Section 2) to see if positioning or just a statistical variation was responsible [for 99.7% confidence (3 sigma), three in a thousand should fall outside the limits]. If the observed values are still outside the 3 sigma range, a Deficiency Report (DR) shall be issued per PNL-MA-70, PAP-70-1502, and the user will consult an instrument technician and/or engineer to determine and repair the problem. The response shall be documented on the Control Chart and/or Instrument Log and on the DR. Another CTL count of the control check sources shall then be made per Section 2 to see if all observed data are within the 3 sigma control value. All samples counted on that detector between the last good CTL counted and the bad CTL counted shall be checked for validity by cross calibration to another detector and/or recounted on that detector when the control check standard spectra shows all activities again within the 3 sigma range. The Counting Room Manager shall maintain copies of the Detector Reliability Charts which cover the full cycle of 50 entries for each detector system.

3.3 Photopeak Resolution (FWHM) Calculation

The FWHM (full-width, half-maximum) is a measure of the peak sharpness. In gamma spectrometry, clearly resolved peaks are Gaussian in shape, provided the electronic components are adjusted correctly. The simplest method used to calculate the FWHM of a peak is by a graphical method; however, numerical methods are required in order to do this by computer. An illustration of the FWHM is shown in Figure 1.

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TABLE 2: Control Source Parameters for Use With Germanium Spectrometers

DETECTOR IDENTIFICATION	CONTROL SOURCE	LENGTH OF TIME	POSITION	CTL PROGRAM "SUM" LIBRARY USED
BNW	50690-27-2	600s	W/holder	Sing. Lib
E	50690-27-3	600s	3" setting	Anti. Lib
* EE	50690-117-1	6000s	3" setting	Anti. Lib
G	50690-27-3	600s	w/holder	Sing. Lib
H	50690-117-7	600s	w/holder	Sing. Lib
I	50690-27-6	600s	w/holder ctl setting	Anti. Lib
* II	50690-117-2	6000s	w/holder ctl setting	Anti. Lib
J	50690-27-4	600s	w/holder phosphors closed	Anti. Lib
* JJ	50690-117-3	600s	w/holder phosphors closed	Anti. Lib
K	50690-27-5	600s	w/holder	Sing. Lib
L	50690-27-1	600s	w/holder	Sing. Lib
N	50690-117-6	600s	shelf #5	Sing Lib.
R	50690-117-8	400s	shelf #4	Sing Lib.
389	4491-58-1(pellet)	6000s	w/holder	389. Lib
447	3368-87-10(pellet)	6000s	w/holder	447. Lib

* Actually the detector is identified by the single numeric character. The two digit character is used when transferring the spectrum to the computer.

**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-471.1 R0
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A.

Document Number: PNL-ALO-471 Revision Number: 0

Document Title: Determination of Low Concentration of
¹⁰⁶Ru in Ground Water by Direct Counting on Dual Large
Sodium Iodide Detectors with
Coincidence/Anticoincidence Multidimensional Analysis

Document's Original Author: EA Lepe1

Effective Date
of ICN: 5/7/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 15 with 1 through 14 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

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E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehler

Date: 5/7/92

Approval Authority: AG King

Date: 5/7/92

Other Approvals: _____

Date: 1/1

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-471, DETERMINATION OF LOW CONCENTRATION OF ^{106}Ru IN GROUND WATER BY DIRECT COUNTING ON DUAL LARGE SODIUM IODIDE DETECTORS WITH COINCIDENCE/ANTICOINCIDENCE MULTIDIMENSIONAL ANALYSIS

SCOPE

This procedure describes a method for measuring (or determining a lower limit of detection) extremely minute amounts of ^{106}Ru in ground water by direct counting on large sodium-iodide coincidence/anticoincidence gamma-ray spectrometers. The sample volume should be at least 1.5 liters and can be as large as 4 liters provided appropriate standards are prepared and counted. A lower limit of detection (LLD) of 6 picoCuries per liter (pCi/L) of ^{106}Ru (at 2 sigma) can be achieved in the presence of up to 500 pCi/L of ^{60}Co concurrent with up to 100 pCi/L of ^{214}Bi and a counting time of .1 day. For samples containing no more than 50 pCi/L of ^{60}Co along with 50 pCi/L of ^{214}Bi , a LLD of 2 pCi/L of ^{106}Ru can be achieved at the 95% level of confidence.

APPLICABILITY

This procedure is implemented to assure quality and is approved and written to conform with PNL-MA-70.

This procedure is applicable to the Counting Room Manager and trained and qualified personnel within the Analytical Chemistry Laboratory and Nuclear Chemistry Department of PNL.

This procedure is primarily intended to assure that the samples are counted on the gamma spectrometry equipment in the proper manner and that the data reduction is performed appropriately.

DEFINITIONS/ACRONYMS

- Laboratory Record Book - LRB
- Multidimensional Analysis (MDA) - a term referring to a gamma-ray system of analysis in which two large sodium-iodide crystals count single gamma-rays and coincidence gamma-rays. Counts from gamma-rays detected in only one of the detectors are stored in the corresponding x or y axis of the data storage array. Counts from gamma-rays detected in both detectors simultaneously are stored in the x and y portion of the data storage array. Photopeaks arising from events in one detector only are represented as areas on an x

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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
KH Abel		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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or y axis while photopeaks arising from events in both detectors simultaneously are represented as volumes in three dimensions (XYZ). In addition, large plastic scintillators which also detect gamma-rays surround these two detectors and are in anticoincidence (whenever a pulse from the plastic scintillator is detected, the counting system is gated off for a predetermined length of time).

- Lower Limit of Detection (LLD) - in total counts is defined as: The square root of two times the total counts of interference. System background and Compton from all contributing radionuclides are included in the interference. For purposes of this procedure, 2σ confidence (i.e., two standard deviation) means that samples containing the amount of activity represented by the LLD will yield positive results 95% of the time (be categorized as above the LLD); and 5% of samples containing this amount of activity will be categorized as below the LLD. False positive results will occur for 2.50% of samples containing no ^{106}Ru . The LLD in total counts can be converted into pCi/L by multiplying or dividing by all appropriate factors as described in the body of this text.
- Clean - a term that means free of radioactivity, at least free from smearable radioactivity.
- D/C Factor (disintegrations per count) - the inverse of counting efficiency which is in counts per disintegration.
- Decay Characteristics - decay characteristics of ^{106}Ru , ^{106}Rh , ^{60}Co , ^{214}Bi , and other radionuclides can be found in Lederer and Shirley. For purposes of this procedure, ^{106}Ru is the radionuclide referred to although ^{106}Rh (daughter of ^{106}Ru) is the radionuclide actually emitting the gamma rays used to measure the activity. Since the half-life of ^{106}Ru is long (372.6 days) and the half-life of ^{106}Rh is short (29.8 seconds), secular equilibrium of ^{106}Ru - ^{106}Rh is reached within a few minutes, i.e., the activity of ^{106}Rh is "equal to" the activity of ^{106}Ru within a few minutes after a sample containing ^{106}Ru has been collected. In secular equilibrium, the half-life of ^{106}Ru governs the decay of both radionuclides. The energies of the two coincident gamma rays used to measure ^{106}Ru (^{106}Rh) are 511.8 keV and 621.8 keV.
- Radon daughter(s) - Both ^{222}Rn and ^{220}Rn are found in the atmosphere from the decay of primordial uranium and thorium, respectively. The half-life of ^{220}Rn is only 55.6 seconds and its activity (and the activity of its daughters) found in a laboratory atmosphere is generally significantly less than that of ^{222}Rn (and daughters) which has a 3.8235 day half-life. Bi-214 has a 19.8 minute half-life and is generally the major interference from atmospheric contamination.

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RESPONSIBLE STAFF

Counting Room Manager
Cognizant Staff Members/Analysts

PROCEDURE

1.0 Equipment and Materials

- A container in which the samples will be counted. The container should be of low density material such as plastic and should be about 11 inches to 12 inches in diameter and contain not less than 1.5 liters and not more than 4 liters. A Tupperware pie storage container is one acceptable container, and directions are given for this container. If some other container is used, then adjust the directions appropriately.
- Plastic bags (19" x 21" polyethylene are adequate) in which to place each sample to facilitate keeping the sample container free of radioactive contamination.
- Plastic tape (1" wide) or electricians tape (about .75" wide) or some other tape appropriate for taping the lid to the container.
- Impulse heat sealer to seal the plastic bags.
- Disposable plastic gloves, scissors, knife or scalpel, marking pens, writing pens (black ink), and a LRB should be available.
- One MDA counting system, with detectors of sufficient size to produce the desired results, and associated electronics. The system used for developing this procedure consist of two 12" diameter by 8" thick NaI(Tl) detectors with 4" thick sodium iodide (non Tl activated) "light pipes" which shield the detectors from primordial radioactivity in the photomultiplier tubes. These detectors are contained within a plastic scintillator anticoincidence shield which is 40" in diameter and 48" in length. Four inches of borated paraffin surrounds the plastic, and all is contained within a lead shield with 4" thick walls. High voltage supplies, amplifiers, ADC's, coincidence electronics, live timers, multichannel analyzer, printers, etc., comprise the operating MDA systems. Data reduction is performed by computer using the appropriate data reduction program which has been verified by hand calculation.

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2.0 Sample Preparation

If new containers are not used, the sample counting containers are prepared by thoroughly rinsing with deionized water, drying, and then sealing in individual plastic bags to keep them free of radioactive contamination.

A work station free of radioactive contamination is required. A clean bench (or clean paper or plastic placed on a bench) will suffice if reasonable care is taken. If the samples are radioactive, it may be necessary to determine the net weight of the samples while they are contained in a plastic bag. The following procedure keeps cross-contamination to a minimum. The average weight of an empty container, tape, and bag can be determined by individually taping, bagging, and weighing a few (3-5) empty containers. If the difference in weight is less than 10 grams, the average can be used for the tare weight for an entire set of containers (since 10 grams or less is an acceptable uncertainty for the weight or volume if the sample weight is 2000 grams or more). Typically, this uncertainty will be no more than one or two grams. Alternatively, a container can be tared, the sample added, and the sample weight read directly. In either case, the pertinent information shall be recorded in an LRB.

Specific gravity information will be supplied for each sample by the sampling organization and will be used to determine the volume based on the net weight of each sample. A specific gravity of 1.00 will be used if no specific gravity information is supplied.

Prepare a clean place to put each sample once it has been cleanly bagged. Remove each sample from its protective bag(s) in a manner that will not transfer contamination from one sample to another or to the clean section to which the sample is to be transferred. Transfer the sample into a clean polyethylene bag in such a manner that no contamination will be transferred to the outside of the clean bag. This can be accomplished if working alone by the following two steps.

Step 1: Ascertain that at least one hand is free of radioactivity i.e., "clean." Open the bag with a clean hand (disposable plastic gloves work well, and replacing gloves goes more quickly if two gloves are kept on each hand, replacing the outer one whenever it becomes potentially contaminated). Transfer the sample into the bag with the other hand (this other hand should be relatively clean also, so as not to cross-contaminate the sample container). Considerable care must be taken to make sure the sample container does not touch any part of the outside of the clean bag into which it is being transferred.

Step 2: Seal the bag using an impulse sealer as close to the container as practical. This bag is the protection that the counting system has from contamination that may be on the sample

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container (and the system's protection in case some sample should accidentally leak from the sample container). Once the samples have been cleanly transferred into clean bags and sealed, place an additional bag around each sample to help keep radon and radon daughters from contaminating the inner bag. The outer bag is to be removed just prior to placing the sample into the counting chamber. Allow the samples to stay in the bag for 24 hours or more in order for radon daughters to have time to undergo significant decay. The samples are typically counted overnight (1000 to 1400 minutes). The count may consist of one long count or a series of short counts. The advantage of the shorter counts is that the possibility of gain shifting is reduced during the counting interval. The sample is again placed into a protective bag(s) upon removal from the counting chamber. This outer protective bag helps keep radioactive contamination from coming into contact with the inner (counting system protection) bag in case a recount is necessary.

3.0 Multidimensional Analysis (MDA) Spectrometry Procedure

Counting and data reduction including error analysis and LLD calculations are performed in the manner prescribed for gamma-ray spectrometry with sodium iodide detectors. For coincidence counting, the peaks are actually volumes, but since all algorithms are identical for areas or volumes, peak areas are used in this procedure. A brief general description follows.

3.1 Energy Calibration

The gamma-ray spectrometer is calibrated for energy by adjusting the analyzer amplifier gain and ADC zero to achieve the desired peak locations. Cobalt-60 and ^{137}Cs are typically used for this operation with the 661.7 keV peak from cesium being located in channel 14 and the peak from the sum of the 1173.2 keV and the 1332.5 keV gamma-rays of cobalt located mid-way between channels 50 and 52 (other radionuclides can be used if one well resolved photopeak below one MeV and one well resolved photopeak above two MeV are present in the spectrum).

Gain and/or zero shift during a count can radically change the number of counts in channels used to measure any particular radionuclide as well as the Compton contribution of any radionuclide to other areas. Gain and/or zero shift can sometimes be monitored by using the gamma-ray information obtained from counting the sample. Whenever this is not adequate, other radioactive sources must be placed into the counting chamber and used to ascertain that gain and zero are within acceptable limits. Gain and zero must be checked at sufficient intervals to ascertain that they are within acceptable limits. The Compton correction factors are derived by counting an aliquot of the appropriate

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radionuclide at a different time. It is necessary that gain and zero are set properly and are stable throughout a counting interval.

Acceptable limits can be established by counting appropriate radioactive sources at the correct gain and zero and counting them again with the gain and/or zero set slightly off and the efficiency and Compton factors compared to that obtained with correct settings. The gain and zero must be controlled such that they are acceptably close to the correct settings both before and after a sample is counted. If the temperature cannot be controlled to within a degree or two, extra caution should be used and measurements shall be made to assure that gain and/or zero are acceptably stable during a counting interval. If a computer controls data acquisition, then data can be transferred automatically periodically and the results combined algebraically. A bias error rather than a statistical error in the results may occur if gain or zero is consistently different during sample counting relative to what it was during standard counting.

- 3.2 Calibration Control Checks - counting a radioactive source that contains certain radionuclides periodically and determining that the results are consistent is referred to as "running controls" or "control checks". Controls shall include at least one coincidence gamma-emitting radionuclide and one or more single gamma-emitting radionuclide. Cobalt-60 and ^{137}Cs can be used for control or other suitable radionuclides. It is not necessary that the control be a "standard" nor that it be in the same geometry as the samples being counted. It is necessary that the control be in a stable geometry and be counted in the same geometry each time. See PNL-ALO-470, Procedure for Maintaining Control of Germanium Spectrometers Used for Gamma-ray Spectroscopy. The information from at least one control check taken before the samples and standards are counted and at least one control check taken after the samples and standards are counted shall be recorded.

3.3 System Background

A system background shall be determined. The background can be determined by counting a blank (as nearly identical as practical to that of the sample except that radioactivity is absent) for the same length of time as the sample. Alternatively, one or more backgrounds with counting intervals different, but longer than that used for the samples may be taken and the results adjusted for the difference in counting intervals according to standard practices.

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3.4 Efficiency Calibration and Compton Interference Corrections

Radioactive standards shall be traceable to Nationally Recognized Standards (i.e., NIST or equivalent) and prepared as identical as possible to the samples in volume, shape, and medium. Counting efficiency in counts per disintegration is determined by counting a standard of known disintegration rate and then determining the number of net counts per disintegration. A standard of each radionuclide of interest (i.e., ^{106}Ru) shall be prepared and counted either before, during, or after the period of time in which sample analyses are being performed. In addition, aliquots of ^{60}Co and ^{214}Bi in similar geometries shall be counted to determine the interference corrections. It is recommended that these standards and interference correction samples be counted before (or near) the beginning of the sample analysis period to avoid the need for recounting samples in the event of a system failure that cannot be repaired. The activity in the standards must not be so high that significant dead time or pulse pileup or any other problems occur due to the activity. The standards shall be counted for sufficient time so that 1σ statistical errors relevant to the peak counting efficiency and Compton areas are less than 2%.

Gross peak areas are determined by summing the counts in the channels selected for each radionuclide. The selection of channels is generally made after observing the spectra produced by counting the radionuclides of interest. Enough channels shall be used to represent more than half the total peak area. About 80% of the total peak area is generally sufficient to obtain the major portion of the peak area and not include too great an amount of interference. The channels used for determining the peak area for a standard shall be used for determining that peak area for each sample.

Net peak areas shall be determined in order to calculate the activity of each radionuclide they represent. Counts from the system background and counts from Compton produced by other radionuclides shall be subtracted from the gross peak areas to obtain the net peak area. For standards containing only one radionuclide, the only interference is system background.

Compton interference shall be quantified in order to make corrections. Compton correction factors are determined from the spectra of each standard by measuring the ratio of the net counts in the channels used to measure ^{106}Ru to the net counts in the channels used to measure each radionuclide that is causing interference; and using this ratio to determine the counts in the channels for the sample by measuring the counts in the channels used to measure each interfering radionuclide and multiplying by the ratio determined from the appropriate standard. Compton correction factors can be determined for each radionuclide's effect

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on each of the areas used to measure all radionuclides observed in sample spectra.

When more than one radionuclide contributes to the Compton and if they are mutually interfering, an iterative process can be used to calculate the net counts for each interfering radionuclide and the net counts for ^{106}Ru (or least squares matrix inversion, or any other appropriate method can be used).

Samples shall be positioned in the counting chamber in the same stable and reproducible geometry in which the standards are counted. The length of counting interval is mandated by the activity of radionuclides in each sample and the uncertainty or LLD that is desired. For samples with very low ^{106}Ru activity such as is expected in ground water, total counting times of 1000 to 1400 minutes may be required (shorter counting times may produce acceptable LLD's for samples that have little interference). Data reduction is performed after the counting interval has ended.

3.5 Sample and Standards Counting

After verifying that the detector system to be used is in control by checking the "Detector Reliability Chart" (See PNL-ALO-470), the basic sample counting/data acquisition procedure is as follows:

3.5.1 Position

Position the sample in the detector system using the appropriate sample holder for the required geometry.

3.5.2 Analyzer Start-Up

Clear the analyzer memory. Start the analyzer counting and record the date and time on a "Counting Sheet," or record directly into memory, if appropriate. A typical counting sheet is shown in Figure 1. Fill in known information on the counting sheet. Initial the sheet with the individual's initials who started the count, and sign the bottom of the sheet. The signature at the bottom is only required once for each Counting Sheet.

3.5.3 Analyzer Shutdown

Stop the multichannel analyzer from acquiring data. Record the elapsed time and initials of the Analyst changing the count on the count sheet. If the Analyst is different than in 3.5.2, the Analyst also signs at the bottom of the sheet. This signature at the bottom is only done once on each Counting Sheet.

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3.5.4 Data Transfer and Storage

If the counting system is controlled by a PC, the data will be automatically transferred to a magnetic storage device when the system is stopped. If the counting system is a separate entity, transfer the spectral data from the analyzer to the data acquisition computer system, and store the data on a magnetic storage device (hard disk, floppy disk, etc.). If the sample and counting parameters are not transferred, they will be added via keyboard from the counting sheet.

3.5.5 Data Identification

The following parameters shall accompany the spectral data, on a hard copy printout from a printer or in the associated file stored on a magnetic storage device:

- a. Identification (sample description with a unique id).
- b. Computer file name (if on computer) unique to the particular sample.
- c. Start time of the count.
- d. Date and time of sample collection.
- e. Live time of count (actual time the MCA is free to accept pulses). This should be determined by the MCA and transferred within the spectra.
- f. Real time of count (the actual duration of count in regular clock time).
- g. Sample mass and/or volume.

3.5.6 Data Analysis

Use a gamma-ray data reduction program to analyze the individual spectra and calculate the final concentration values. The calculated values may be verified by hand calculations, if necessary. The program used is "MDA" for multidimensional analysis.

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4.0 Calculations

4.1 The calculational Methodology used to calculate activity in pCi per liter is illustrated below.

$$\text{Activity} = \frac{(\text{gross counts} - \text{background counts} - \text{Compton counts}) \times \text{D/C factor} \times \text{decay correction}}{\text{length of count in minutes} \times \text{volume in liters} \times 2.22}$$

Where: 2.22 = disintegrations per minute per pCi

D/C factor = 1 divided by the counting efficiency in counts per disintegration

$$\text{Decay correction} = e^{-\lambda t}$$

where λ = the natural log of 2 divided by the half-life in minutes (may be called decay constant)

t = minutes from mid point of sampling to mid point of count (this is an approximation but is quite accurate where sampling and counting times are short relative to the half-life).

Example for calculation of activity:

volume of sample = 3.500 liters

length of count = 1038 minutes

decay time from mid point of sample collection to mid point of count = 5040 minutes.

Gross counts in ^{106}Ru channels = 3980 system background = 291

Gross counts in ^{60}Co channels = 103856 system background = 41

Gross counts in ^{214}Bi channels = 31927 system background = 1023

Subtract the appropriate system background from each gross

counts left in ^{106}Ru channels = 3689
 counts left in ^{60}Co channels = 103815
 counts left in ^{214}Bi channels = 30904
 Compton factor ^{106}Ru effect on ^{60}Co = 0.00131
 Compton factor ^{106}Ru effect on ^{214}Bi = 0.04770
 Compton factor ^{60}Co effect on ^{106}Ru = 0.02134
 Compton factor ^{60}Co effect on ^{214}Bi = 0.2257
 Compton factor ^{214}Bi effect on ^{60}Co = 0.00987
 Compton factor ^{214}Bi effect on ^{106}Ru = 0.2022

Compton correction factors are applied to the value for "counts left after background subtraction" until a net or temporary net has been determined for each radionuclide. Note that the temporary net values should be used in the equations at the first opportunity. The "counts left after subtracting background" is the value from which to subtract the Compton counts.

$$\text{Temporary Net } ^{214}\text{Bi} = 30904 - (3689 \times .04770) - (103815 \times .22570) = 7297.$$

$$\text{Temporary Net } ^{60}\text{Co} = 103815 - (7297 \times .00987) - (3689 \times .00131) = 103738.$$

$$\text{Temporary Net } ^{106}\text{Ru} = 3689 - (7297 \times .20220) - (103738 \times .02134) = -.222$$

Retain the new values for each of the radionuclides and repeat the exercise, ie.:

$$\text{Temporary Net } ^{214}\text{Bi} = 30904 - (-.222 \times .04770) - (103738 \times .22570) = 7490.$$

$$\text{Temporary Net } ^{60}\text{Co} = 103815 - (7490 \times .00987) - (-.222 \times .00131) = 103741.$$

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$$\text{Temporary Net } ^{106}\text{Ru} = 3689 - (7490 \times .20220) - (103741 \times .02134) = -39.3$$

Retain the new values for each of the radionuclides and repeat once more, ie.:

$$\text{Net } ^{214}\text{Bi} = 30904 - (-39.3 \times .04770) - (103741 \times .22570) = 7492.$$

$$\text{Net } ^{60}\text{Co} = 103815 - (7492 \times .00987) - (-39.3 \times .00131) = 103741.$$

$$\text{Net } ^{106}\text{Ru} = 3689 - (7492 \times .20220) - (103741 \times .02134) = -39.7$$

Three or more iterations will be performed. Using these net values and the appropriate Compton factors, the Compton interference can be calculated as follows:

$$^{214}\text{Bi Compton} = 7492. \times .20220 = 1515.$$

$$^{60}\text{Co Compton} = 103741. \times .02134 = 2214.$$

$$\text{Total Compton interference} = 1515 + 2214 = 3729.$$

The values necessary for calculations have now been determined, and the activity of ^{106}Ru in pCi/L can be determined:

$$\text{Gross counts (} ^{106}\text{Ru)} = 3980$$

$$\text{System background counts} = 291$$

$$\text{Compton interference} = 3729$$

$$\text{Net counts} = 3980 - 291 - 3729 = -40.$$

$$\text{D/C factor} = 220$$

$$\text{Length of count (min)} = 1038$$

$$\text{Volume (in liters)} = 3.5$$

$$\text{Decay time (min)} = 5040$$

$$\text{Decay constant} = 1.293 \times 10^6 \text{ minute}^{-1}$$

$$\text{Decay correction} = e^{\lambda t} = e^{(1.293 \times 10^6 \text{ minute}^{-1}) (5040 \text{ minutes})}$$

$$\text{Activity} = \frac{(\text{gross counts} - \text{background counts} - \text{Compton counts}) \times \text{D/C factor} \times \text{decay correction}}{\text{length of count in minutes} \times \text{volume in liters} \times 2.22}$$

$$\text{Activity} = \frac{(3980. - 291. - 3729.) \times 220. \times 1.0065}{1038. \times 3.500 \times 2.22}$$

$$\text{Activity} = -1.10 \text{ pCi/L of } ^{106}\text{Ru of sample}$$

4.2 The uncertainty is calculated as follows:

$$\begin{aligned} \text{Uncertainty (in total counts)} &= \text{the square root of (gross counts plus interference)} \\ &= \text{the square root of } (3980. + 291. + 3729.) = 89.44 \end{aligned}$$

Uncertainty (in pCi/L) is determined by multiplying or dividing the value in total counts by the appropriate factors as in the example for determination of activity listed above. This uncertainty is at 1 σ confidence (68%); simply multiply by two to get 2 σ confidence.

The uncertainty (in pCi/L) for this example is:

$$\text{Uncertainty} = \frac{(\text{Uncertainty in total counts}) \times \text{D/C factor} \times \text{decay correction}}{\text{length of count in minutes} \times \text{volume in liters} \times 2.22}$$

$$\text{Uncertainty} = \frac{89.7 \times 220. \times 1.0065}{1038. \times 3.500 \times 2.22} = 2.46 \text{ pCi/L of } ^{106}\text{Ru at } 1 \sigma$$

4.3 The LLD for ^{106}Ru in the sample used for the example shown above is calculated as follows:

The LLD for ^{106}Ru (in total counts) is:

$$\text{LLD} = \text{the square root of (two times (total counts in system background + total counts Compton))}$$

$$= \text{the square root of } 2(291. + 3729.) = 89.67, \text{ this value is in total counts}$$

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* this value in total counts can be converted into picocuries per liter by multiplying or dividing by all the factors used to calculate the activity in the example above.

$$LLD = \frac{89.7 \times 220. \times 1.0065}{1038. \times 3.500 \times 2.22}$$

$$LLD = 2.46 \text{ pCi/L of } ^{106}\text{Ru of sample (10')}$$

If the sample and the system background are counted for different lengths of time, then a correction must be made for that difference in activity calculations, uncertainty calculations, and LLD determinations (see ASTM standards). Equations can be worked out to handle whatever method is chosen and data reduction by computer can be utilized.

5.0 Sample Storage and Disposal

The samples shall be returned to WHC for disposal. These samples are rather large and will take up significant space in the counting laboratory and the number of samples in the counting laboratory should be minimized.

6.0 Potential Interference and Recommended Precautions

If significant quantities of other interfering radionuclides are present, the LLD will increase. Likewise, if ^{60}Co and/or ^{214}Bi are present in larger quantities, the LLD will be higher.

Measurements may be made on samples having activity as high as a few microcuries of ^{106}Ru (per sample) provided the total activity of all radionuclides in the sample is no more than a few microcuries. If samples with higher activity are counted, care should be used to ascertain that pulse pileup or some other electronic malady does not cause erroneous results to be obtained.

The major interferences in the samples measured during development of this procedure were ^{60}Co and ^{214}Bi . Radon (and effectively, its short half-life daughters) can generally be removed by sparging with argon or helium if necessary to meet detection limit requirements, but the improvement would be rather small for these samples since cobalt is the larger contributor. If the counting can be performed about two weeks or longer after sampling, radon daughter interference will be reduced through radioactive decay and escape of the gaseous radon. For wells with low ^{60}Co activity, radon daughters become the major interference but are typically low enough to allow detection limits of 3 pCi of ^{106}Ru per liter to be achieved (even at the 2σ confidence level). Potassium-40 (if present) will contribute slightly to the ruthenium peak. The potassium peak area should be monitored and a correction made if necessary.

Radon daughter contamination from radon and daughters in the atmosphere should be controlled by keeping the samples in at least one extra

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plastic bag while they are awaiting counting and removing it immediately before placing the sample into the counting chamber. If a sample must be counted soon after it has been taken or prepared for counting (i.e., soon after it has been placed into the primary plastic bag that is required before placing the sample into the counting chamber), a 2-hour period should elapse before starting the count to allow time for short half-life radon daughters to decay by about an order of magnitude. These radionuclides deposited on the outside of the sample container may produce a different Compton spectrum than that from the solution located inside the container and lead to erroneous results.

Continual vigilance for any other radionuclides that might contribute to the ruthenium peak area is always recommended. It goes without saying that the instrumentation must be maintained in good, reliable working condition and the system maintained free of contamination (especially ^{106}Ru).

The system background may vary slightly due to various primary and secondary effects from cosmic radiation. This should not be significant at the level of activity in these samples if the electronics are maintained properly. The background due to radon daughters is another matter and could be significant if not kept under control. Again, a bias may occur if some consistent pattern is inadvertently developed.

7.0 Specific Qualifications

This procedure utilizes radiochemical standards for control, and as such meets the definition to be self-qualifying per PNL-MA-70, PAP-70-901.

8.0 Records

Records shall be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books and Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with ~~Act Now Directive 89-1~~ established records management practices.

9.0 References

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ASTM: E-181-82, Standard General Methods for Detector Calibration and Analysis of Radionuclides; D-2459-72, Standard Test Method for Gamma Spectrometry of Water; D-3085-75, Standard Practice for Measurement of Low-level Activity in Water; and D-3649-78, Standard Practice for Gamma-Ray Spectrometry.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-472, REV.0, DETERMINATION OF ^{93m}Nb AND ^{94}Nb

APPLICABILITY

This procedure is used for the analysis of ^{93m}Nb and ^{94}Nb in aqueous samples, such as water and aqueous leachate or dissolved samples. Separation is accomplished by precipitation of hydrated niobium pentoxide ("niobic acid") which is collected by filtration and converted to Nb_2O_5 in air. Yield (or recovery) is determined from the ^{95}Nb tracer by gamma-ray spectroscopy. ^{94}Nb and ^{93m}Nb activities are both determined by gamma spectroscopy. A low energy photon detector is used to measure the x-rays produced from the internal transition decay from the 30.4 keV state of ^{93m}Nb . One limitation to this procedure is the incomplete separation of Nb from Sb. A cognizant scientist will need to evaluate the results in terms of the amount of ^{93m}Nb and ^{125}Sb present and the required sensitivity for ^{93m}Nb .

DEFINITIONS

dpm - disintegrations per minute
d/c - disintegrations per count, an efficiency factor
conc - concentrated
ppt - precipitate
keV - kilo electron volt
std - standard

RESPONSIBLE STAFF

Cognizant Scientist
Analyst

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified. A tolerance limit can be stated with a measurement value

Author N. L. Lynhoff <i>N. L. Lynhoff</i>	Date 6/27/91	Project Mgr. B. M. Gillespie <i>B. M. Gillespie</i>	Date 7-15-91	QAD Representative G. K. Gerke <i>G. K. Gerke</i>	Date 7/11/91
Technical Reviewer C. W. Thomas <i>C. W. Thomas</i>	Date 6-28-91	Line Mgr. J. M. Latkovich <i>J. M. Latkovich</i>	Date 7-12-91	Other	Date
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given in a method. If a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Reagents

All chemicals used are reagent grade unless otherwise specified. The water used is deionized or distilled water.

2.1 conc HCl

2.2 3 M HCl - (1:4 dilution of conc HCl with water)

2.3 conc HF

2.4 conc HNO₃

2.5 9 M HNO₃

2.6 Co carrier, 10 mg/ml - Dissolve 24.7 g Co(NO₃)₂ · 6H₂O in 50 to 100 ml water. Heat if necessary. Cool to about room temperature. Dilute to 500 ml with water. (Note: Another cobalt salt may be used or another concentration as long as the required mg of Co⁺² are added.)

2.7 Sb (holdback) carrier, ~20 mg/ml - Dissolve 20 g SbCl₃ in 50-100 ml of 3 M HCl. Heat if necessary. Cool to about room temperature. Dilute to 500 ml with 3 M HCl. (Note: Another antimony salt may be used or another concentration as long as the required mg of Sb⁺³ are added.)

2.8 Nb carrier, 10 mg/ml - In a Teflon beaker dissolve 14.3 g Nb₂O₅ in 50 ml conc HF. Heat if necessary. Cool to about room temperature. Dilute to 1 liter with water. Store in Teflon or polyethylene. (Note: Another niobium compound may be used or another concentration as long as the required mg of Nb⁺⁵ are added.)

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2.9 ^{95}Zr - ^{95}Nb tracer - Use appropriate activity as specified by a cognizant scientist.

2.10 conc NH_4OH

3.0 Supplies

3.1 Teflon beaker, 250 ml or other appropriate size

3.2 50 or 100 ml plastic centrifuge tube

3.3 pH paper, gross range, pH 2 to 10

3.4 250 ml pyrex or kimax beaker, or other appropriate size

3.5 Hot plate/magnetic stirrer

3.6 Teflon stir bar

3.7 Filter apparatus for filter from Sec. 3.8

3.8 Filters - glass microfibre, 4.7 or 5.5 cm diameter, 1.6 μm effective particle size retention or better

3.9 Mylar sheet, nominal thickness 5/10,000 in.

3.10 Pressure sensitive tape (e.g., Scotch Magic Mending)

3.11 Cardboard filter holder, nominal dimensions 6.2 cm x 8.2 cm with a centered 3.8 cm diameter hole

3.12 Small plastic bag, such as a 6 1/4 in. x 3 1/8 in. baby bottle bag

3.13 Heat sealer

3.14 Filters - membrane, 4.7 cm diameter, any pore size, for use only in preparing the tracer std (Sec. 4.3)

4.0 Chemical Procedure

Except where responsibility is specifically assigned to a cognizant scientist, the analyst may perform all work.

All pertinent data (e.g., aliquot volumes) observations, and calculations will be recorded in a project record in a manner traceable to the sample.

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When an added volume is a feature of the general calculation, the automatic pipette must have had an acceptable performance check before use on the day the volume is pipetted. To performance check a pipette, pipet and weigh at least three aliquots of D.I. water equal to the volume being used, into a tared container. Weigh and determine the net weight of water. Calculate the average, standard deviation and % standard deviation. The weights must agree to within $\pm 3\%$ of the measured volume or a different pipette shall be checked and used. Correct the weight measured and the standard deviation for temperature effects on the actual delivered volume using the formulas:

$$\text{avg. weight (g)} \times \text{volume factor (ml/g)} = \text{volume (ml)}$$

$$\text{std deviation (g)} \times \text{volume factor (ml/g)} = \text{std deviation (ml)}$$

The value of the volume factor is dependent on the ambient temperature and is found in the Relative Density and Volume of Water table (Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, and Exhibit 1). The data and this calculation shall be recorded in the Pipet Calibration Logbook.

4.1 Chemical Separation

- 4.1.1 Place an aliquot of sample, as specified by the cognizant scientist and documented in a project record, in a plastic centrifuge tube. If the sample is not highly acidic (i.e., $\text{pH} \leq 2$), add conc or 9M HNO_3 until the pH is ≤ 2 .

Note: Record the exact volume (and std deviation) of the sample aliquot.

- 4.1.2 Add 10 mg Co (holdback) carrier, ~20 mg Sb (holdback) carrier, and 200 mg Nb carrier.

Note: 20 mg of Sb holdback carrier substantially reduces the amount of any interfering ^{125}Sb present in the ^{94}Nb sample gamma spectrum. Increasing the amount of Sb holdback carrier would further reduce the amount of ^{125}Sb present in the ^{94}Nb sample spectrum, if needed.

- 4.1.3 Add the amount of ^{95}Zr - ^{95}Nb tracer specified by the cognizant scientist.

Note: Record the exact volume (and std deviation) and identification of the tracer added.

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- 4.1.4 Make sample strongly basic ($\text{pH} \geq 9$) with conc NH_4OH , mixing well. Check the pH with pH paper.

Note: A white ppt forms.

- 4.1.5 Centrifuge at least 4 minutes and discard supernate.

- 4.1.6 Dissolve the ppt with 2 to 5 ml of conc HF (or with additional conc HF, if required). Add 10 mg of Co carrier and 20 mg of Sb carrier.

- 4.1.7 Add 50 ml of conc HNO_3 to a 250 ml glass beaker (Pyrex or Kimax) and then quantitatively transfer the sample in HF solution to this beaker using conc HNO_3 as the rinse solution. Add additional conc HNO_3 to make a total volume of at least 150 ml in the beaker.

Note: If the sample solution in HF (from step 4.1.6) has a volume of $>10\text{ml}$ (read from a scale on a centrifuge tube), scale up the beaker size and volumes of conc HNO_3 proportionately.

- 4.1.8 Heat the solution while stirring with a teflon stir bar, without boiling (setting of about 3 to 4). Continue heating and stirring the solution until the solution has evaporated to half or less of its original volume and the white niobic acid (i.e., $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$) ppt has formed. Cool to about room temperature (until beaker is cool to the touch).

Note: Do not let it evaporate to dryness.

- 4.1.9 Transfer to a plastic centrifuge tube with conc HNO_3 and centrifuge at least 4 minutes. Discard the supernate. Record this date and time as the Nb separation time.

Note: The ppt should not be left in contact with air for an extended time since NbO_x may form and is insoluble in HF.

- 4.1.10 Rinse the ppt 3 times with water, centrifuging and discarding the supernate after each wash.

- 4.1.11 Repeat steps 4.1.6 through 4.1.8 one time.

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- 4.1.12 Filter cooled solution (from repeat of step 4.1.8), using a tared glass microfibre filter. Thoroughly rinse the filter with H₂O. Discard filtrate.

Note: Record tare weight of filter.

- 4.1.13 Air dry the filter (heat lamp may be used for low heat). Weigh dry filter and ppt and record the weight. Calculate the ppt weight.

4.2 Sample Mounting For Counting

- 4.2.1 Place filter face down on a piece of Mylar (i.e., ppt against the Mylar) that is supported by a clean (new) paper towel.
- 4.2.2 Tape the filter to the mylar, completely covering and sealing the filter with tape.
- 4.2.3 Cut excess tape/mylar from around the filter leaving sufficient to overlap the edges of the hole in the cardboard holder.
- 4.2.4 Tape the filter to the bottom of the cardboard such that the ppt is centered in the hole and visible from the top through the Mylar.
- 4.2.5 Write the sample identification and "Nb" (to indicate analysis) on the taped back of the filter and on the face of the cardboard mount.

Note: An alternative to steps 4.2.1 through 4.2.4 may be used as long as the order of layers is cardboard holder, mylar, and ppt on filter centered in the hole of the holder and the sample is completely sealed.

- 4.2.6 Heat seal the cardboard holder into a plastic bag or flat-seal the plastic bag with tape.

Note: For some gamma detector shelf-holders, a full-sized cardboard holder in a plastic bag may not fit. It may be necessary to trim ~1 mm off both ends of the cardboard holder (producing 6.2 cm x 8.0 cm dimensions) before sealing it in a plastic bag.

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4.3 Preparation of ^{95}Zr - ^{95}Nb Tracer Standard for Yield Determination

4.3.1 On a membrane filter, draw a 3.8 cm circle, approximately centered.

4.3.2 With a calibrated pipette, stipple an appropriate aliquot of ^{95}Zr - ^{95}Nb tracer (as specified by a cognizant scientist) onto the filter. The drops should be distributed as uniformly and symmetrically as practical within the circle. Air dry the filter.

Note: Record the tracer identification and exact volume (and std deviation) pipetted.

4.3.3 Mount the standard for counting according to Sec. 4.2. Label " ^{95}Zr - ^{95}Nb " and with the tracer identification and the exact volume pipetted. This is the tracer std.

5.0 Gamma Counting Procedure

5.1 Count the sample and the tracer std (prepared in Sec. 4.3) on a high resolution Ge detector. From these counts the yield is determined from the ^{95}Nb peak at 766 keV and the ^{94}Nb is determined from the 703 keV and/or 872 keV peaks. The 724 keV and/or 757 keV peaks of ^{95}Zr are also usually determined (see Sec. 6.1.1). The detectors are typically operated at a nominal gain of 1 keV/channel.

5.2 Remove the sample from the plastic bag and count it on an LEP detector. $^{93\text{m}}\text{Nb}$ decays by internal transition from the 30.4 keV state producing Nb x-rays at 17 keV. The detectors are typically operated at 0.2 keV/channel.

Note: Samples are counted in a standard geometry with the ppt centered over the face of the detector. If a holder does not prevent actual contact with the face of the detector, be sure a Mylar cover is placed between the sample and the detector face to protect the detector from inadvertent contamination. When counting on an LEP detector, the ppt must be facing the detector face.

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6.0 Calculation Procedure

6.1 ⁹⁵Nb Yield Calculation

The ⁹⁵Nb tracer yield is used to correct the ⁹⁴Nb and ^{93m}Nb for processing losses.

- 6.1.1 For the count of the tracer std, the net dpm of ⁹⁵Nb and ⁹⁵Zr are calculated using the following equation. The ⁹⁵Nb is calculated from the net cpm (i.e., the background-corrected count rate) of the 766 keV gamma ray and the ⁹⁵Zr from the net cpm of the 724 keV and/or the 757 keV gamma rays.

$$\text{dpm} = (\text{net cpm})(d/c)$$

where: d/c = disintegrations per count, an efficiency factor for the specific gamma ray energy and specific counting geometry.

- 6.1.2 Since ⁹⁵Nb ($t_{1/2} = 35$ d) is shorter-lived than its parent ⁹⁵Zr ($t_{1/2} = 64$ d), the tracer std count must be decay-corrected to the time of the separation of Nb from Zr (the Nb separation time from Sec. 4.1.9) according to the following equation:

$$A_N = \frac{A_Z^0 (\lambda_N)}{(\lambda_N - \lambda_Z)} (e^{-\lambda_Z t} - e^{-\lambda_N t}) + A_N^0 e^{-\lambda_N t}$$

where: A_N = activity (dpm) of ⁹⁵Nb in tracer std at the time of the Nb separation

A_Z^0 = the initial activity (dpm) of ⁹⁵Zr in the tracer std

λ_N = the decay constant for ⁹⁵Nb

λ_Z = the decay constant for ⁹⁵Zr

t = the time from the tracer std count (initial activity) to the Nb separation time

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A_N^0 = the initial activity (dpm) of ^{95}Nb in the tracer std.

6.1.3 The fractional yield of ^{95}Nb is calculated using the following equation:

$$^{95}\text{Nb Yield} = \frac{(\text{sample net dpm})(e^{\lambda_N T})(C)}{(\text{net dpm in tracer})}$$

where:

- λ_N = the decay constant for ^{95}Nb
- T = the decay time between Nb separation time and the time the sample was counted
- C = a factor to account for any differences between the aliquot of tracer added to the sample and that evaporated as the tracer std

sample net dpm is from Sec. 6.1.1
net dpm in tracer is from Sec. 6.1.2.

6.2 ^{94}Nb Calculation

Calculate the ^{94}Nb in the sample using the net cpm (i.e., the background-corrected count rate) of the 703 keV and/or the 872 keV gamma rays, using the following equation:

$$^{94}\text{Nb} = \frac{(\text{net cpm})(d/c)(B)}{(\text{Nb-95 yield})}$$

where: d/c = disintegrations per count, an efficiency factor for the specific gamma ray energy and specific counting geometry

B = a factor or factors to account for sample volumes, dilutions, aliquots, weights and any other factors needed to produce the appropriate reporting units. These factors shall be documented as part of the project records.

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6.3 ^{93m}Nb Calculation

Calculate the ^{93m}Nb in the sample using the net cpm (i.e., the background-corrected count rate) of the 17 keV x-rays, using the following equation:

$$^{93m}\text{Nb} = \frac{(\text{net cpm})(d/c)(B)}{(\text{Nb-95 yield})(\text{SSA})}$$

where: d/c = disintegrations per count, an efficiency factor for the specific gamma ray energy and specific counting geometry

B = a factor or factors to account for sample volumes, dilutions, aliquots, weights and any other factors needed to produce the appropriate reporting units. These factors shall be documented as part of the project records.

SSA = self absorption factor, a factor to correct for count rate losses due to absorption and scatter of the 17 keV x-rays within the Nb₂O₅ ppt and thus not measured by the detector.

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RELATIVE DENSITY AND VOLUME OF WATER

The mass of one cubic centimeter of water at 4° C is taken as unity.
The values given are numerically equal to the absolute density in grams per milliliter.

(Smithsonian Tables, compiled from Various Authors.)

Temp. °C.	Density.	Volume.	Temp. °C.	Density.	Volume.
-10	0.99815	1.00186	+35	0.99406	1.00598
-9	843	157	36	371	633
-8	809	131	37	336	669
-7	802	108	38	299	706
-6	912	088	39	262	743
-5	0.99930	1.00070	40	0.99224	1.00782
-4	915	055	41	186	821
-3	958	012	42	147	861
-2	970	031	43	107	901
-1	979	021	44	066	943
+0	0.99987	1.00013	45	0.99025	1.00985
1	993	007	46	0.98982	1.01028
2	997	003	47	940	072
3	999	001	48	896	116
4	1.00000	1.00000	49	852	162
5	0.99999	1.00001	50	0.98807	1.01207
6	997	003	51	762	254
7	993	007	52	715	301
8	988	012	53	669	349
9	981	019	54	621	398
10	0.99973	1.00027	55	0.98573	1.01448
11	963	037	60	324	705
12	952	048	65	059	979
13	940	060	70	0.97781	1.02270
14	927	073	75	489	576
15	0.99913	1.00087	80	0.97183	1.02899
16	897	103	85	0.96865	1.03237
17	880	120	90	534	590
18	862	138	95	192	959
19	843	157	100	0.95838	1.04343
20	0.99823	1.00177	110	0.9510	1.0515
21	802	198	120	0.9434	1.0601
22	780	221	130	0.9352	1.0693
23	756	244	140	0.9264	1.0794
24	732	268	150	0.9173	1.0902
25	0.99707	1.00293	160	0.9075	1.1019
26	691	320	170	0.8973	1.1145
27	654	347	180	0.8866	1.1279
28	626	375	190	0.8750	1.1429
29	597	405	200	0.8628	1.1590
30	0.99567	1.00433	210	0.850	1.177
31	537	466	220	0.837	1.195
32	505	497	230	0.823	1.215
33	473	530	240	0.809	1.236
34	440	563	250	0.794	1.259

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-473, NICKEL SEPARATION FROM RADIOACTIVE SOLUTIONS

APPLICABILITY

This procedure describes the method for separating nickel from a complex mixture in solution, electroplating it on a disk, and preparation for liquid scintillation counting. It is useful for the separation of ^{59&63}Ni for subsequent determination by counting methods. Stable nickel is used as a carrier and is determined by ICP-OES or equivalent. The procedure is summarized in a flow chart (Attachment 1).

The procedure was developed for use with highly radioactive tank samples but can be applied to other sample types. Variations in the radioactive isotopes present and the radioactive Ni concentration will be factors used to determine aliquot size, amount of carrier added, and the number of times individual separation steps should be repeated. Because stable Ni is used as a yield monitor, the amount of Ni in the original sample may need to be determined in order to calculate Ni recovery. Large amounts of Ni (e.g., >5mg) may cause absorption and quenching problems with counting techniques. NOTE: Variation in sample types should be tested before use to assure applicability of the procedure.

DEFINITIONS

- LEPS - low energy photon spectroscopy
- LSC - liquid scintillation counter
- gm - grams
- mL - milliliter
- conc - concentrated
- M - molar
- Duplicate - a replicate aliquot of a sample which is brought through the entire sample preparation and analysis process to document the precision of the method.

Author <i>RS Strebin</i> RS Strebin	Date 4-23-92	Project Mgr. <i>TE Jones</i> TE Jones	Date 4/23/92	QAD Representative <i>TL Ehlert</i> TL Ehlert	Date 4/23/92
Technical Reviewer <i>J. H. Kaya</i> J. H. Kaya	Date 4/23/92	Line Mgr. <i>AG King</i> AG King	Date 4/24/92	Other	Date
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- Reagent blank - an artificial sample designed to monitor the introduction of contamination into the sample preparation and analysis process; it is treated like a "real sample" as it is carried through the appropriate steps of the process.
- Blank spike - a reagent blank to which a known amount of analyte of interest is added.
- Matrix spike - a replicate sample to which a known amount of analyte of interest is added.

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

PROCEDURE

Prerequisite: Only personnel trained in this procedure may perform the work. Personnel training records are kept in the ACL office.

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method; or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is $\pm 50\%$ in the next digit located beyond the last one stated.

2.0 Reagents

All reagents are prepared from analytical reagent grade chemicals. Deionized water, with an electrical resistance of >16 megohms-cm is used throughout this procedure. Concentrations are not critical and need only be within $\pm 10\%$ of stated values.

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Holdback carrier: use a suite of carriers defined by the cognizant scientist to accommodate the nature of the sample. Suggested carriers include: Ba, Sr, Zn, Co, La, Cs, Zr, Mn, Cr, Re, Ru, Y, and Sb. The chemical form of these metals is not important as long as the compound is readily soluble. Usually they are prepared to make individual solutions of 1 to 10 mg/mL.

Standardized nickel carrier solution of approximately 1 or 2 mg/mL in 1 to 2M HNO_3 . This may be a standard prepared commercially or in house from a suitable nickel salt, as specified by the cognizant scientist.

^{63}Ni , use a certified ^{63}Ni standard from NIST or other certified vendor.

5M NaOH - 20 gm NaOH diluted to 100 mL with water.

0.5M NaOH - 10 mL 5M NaOH diluted to 100 mL with water.

conc HCl - concentrated hydrochloric acid, 12M.

0.1M HCl - 0.83 mL concentrated hydrochloric acid diluted to 100 mL.

6M HCl - 50 mL concentrated hydrochloric acid diluted to 100 mL with water.

9M HCl - 75 mL concentrated hydrochloric acid diluted to 100 mL with water.

Saturated NH_4Cl - 30 gm diluted to 100 mL with water, keep undissolved material in container to assure saturation.

conc NH_4OH - concentrated ammonium hydroxide, 14.5M.

1M NH_4 Citrate - 22.6 gm dibasic ammonium citrate, $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$, diluted to 100 mL with water.

DMG saturated ethanol - 1% Dimethylglyoxime in ethanol, keep undissolved material in container to assure saturation.

Aerosol solution - 0.5% solution in water (a surfactant).

conc HNO_3 - concentrated nitric acid, 16M.

8M HNO_3 - 50 mL conc HNO_3 diluted to 100 mL.

2 volume % HNO_3 - 2 mL concentrated nitric acid diluted to 100 mL.

H_2O_2 - 30% solution.

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conc H_2SO_4 - concentrated Sulfuric Acid, 18M.

Ultima Gold LSC cocktail - liquid scintillation cocktail sold by Packard Instrument Company (or equivalent).

Ethanol, Absolute.

Thymol blue indicator.

pH 7 water - adjust deionized water pH with 0.5M NaOH to pH 7.

3.0 Equipment

Vortex stirrer

Centrifuge

Centrifuge tubes, plastic, 50 mL

Ion exchange resin, AG1 X 8 100-200 mesh chloride form, or equivalent

Transfer pipets, plastic and glass

Glass wool

Glass stirring rods

Ion exchange columns, 1.5 X 20 cm, plastic disposable

Protective gloves, assorted sizes

Dropper bottles, 125-mL with syringe control

Pipetter, adjustable, 0.1 and 1 mL

Graduated cylinders, 10-mL, 50-mL, 100-mL

Beakers: 50, 100, 250, and 500 mL

Syringes

Disposable 5 mL plastic beakers

Electrodeposition cells

Plating discs, 7/8 inch diameter polished metal disc

Disc holder

Pt electrodes

Wash bottles, plastic

Hot plates

Heat lamps

Scintillation vial, low potassium glass, 7 & 20 mL size

20 mL plastic screw cap bottles

4.0 Quality Control Instructions:

4.1 All quality control (QC) data shall be maintained as hard copy and available for easy reference or inspection.

4.2 Two QC options are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a SOW, and these will be conveyed to the analyst through a Test Instruction (TI).

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- (a) Employ a minimum of one reagent blank and one reagent blank spike per sample batch (20 samples or less). Run duplicate and spike sample analysis upon client request.
- (b) For all SOWs written by a client to meet CERCLA requirements that request analysis, employ a minimum of one methods blank per sample batch/set (20 samples or less) to determine if contamination is occurring. Run one duplicate sample for every 20 samples or for each set, whichever is smaller. A spike sample or standard (NIST traceable if possible) shall be employed for every 20 samples analyzed or per every set of samples, whichever is smaller. A matrix spike duplicate and/or laboratory control sample may be analyzed with a set/batch of samples if so directed by a TI.

4.3 Volume Calibration: Critical volume measurements, as indicated in the procedure, shall be made with automatic pipets or equivalent. A performance check of the automatic pipet shall be completed prior to use. This consists of pipetting and weighing at least three aliquots of deionized water, equal to the volume being used, into a container on the balance. The average delivery weight is converted to volume by multiplying the weight by the reciprocal of the density as it applies to the ambient temperature. This calculated delivery volume shall be acceptable for 7 days.

5.0 Separation Procedure

- 5.1 Add 1 to 5 mg of each holdback carrier specified by the cognizant scientist to each 50 mL centrifuge tube needed for each sample in the analysis set. Add nickel carrier to each 50 mL centrifuge tube and to a yield monitor vial (to be used to calibrate the nickel concentration) using a calibrated pipet. Cap the yield monitor vial and save for Step 8.3.

NOTE: Record Ni carrier volume and other pertinent information on the analyses sheet (see Attachment 2).

- 5.2 Add ^{63}Ni to the blank spike and to the matrix spike (if one is to be processed) using a calibrated pipet.
- 5.3 Measure an appropriate sample aliquot, as determined by the cognizant scientist, with a calibrated pipet and place in the 50 mL plastic centrifuge tube. Measure the activity of each sample and record for reference (if appropriate). Allow the mixture to set overnight if possible.

NOTE: Measuring the sample activity here and elsewhere in this procedure is intended to be done qualitatively with a portable Geiger-Mueller detector, with gamma spectrometry, or other suitable technique, as determined by the cognizant scientist.

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- 5.4 Add 5M NaOH drop-wise, stirring after each addition. Test the pH when the first sign of precipitation occurs. Use 0.5M NaOH and various concentrations of HCl to adjust the pH to 7-8. Use wide range pH paper (pH 2-10) and narrow range pH paper (pH 6-8) as appropriate to measure the pH. Use a stirring rod to transfer a trace of the sample to the pH paper (save the rod, if desired, for reuse on the same sample). Centrifuge 10 minutes on high, collect the supernate in a separate vessel. Add 5 mL of pH 7 water to the precipitate, stir, centrifuge and add the supernate to the previous fraction. Measure the activity of the supernate to assess the separation, then discard it.
 - 5.5 Add an additional 1 mg Cs carrier and 1 mg Sr carrier (or as specified by the cognizant scientist) to the precipitate, then dissolve the precipitate in a minimum of 5M HCl. Repeat Step 5.4.
 - 5.6 Steps 5.4 and 5.5 may be repeated up to 4 times as decided by the cognizant scientist. When the activity separated (the supernate in Step 5.4) is low, as determined by the cognizant scientist, continue to Step 5.7.
 - 5.7 Dissolve the precipitate in approximately 4-6 drops (or minimum amount needed) of 1M HCl with swirling, make sure the sample is in solution. Add 4 drops additional 1M HCl, dilute to 5 mL with water and stir. Add 12 mL of saturated NH_4Cl , stir and warm in a water bath until the sample is heated. Add rapidly with swirling 5 mL of conc NH_4OH . Allow the mixture to stand 10-20 minutes. Centrifuge on high for 10 minutes, save the supernate. To the precipitate add 2 mL conc NH_4OH and 2 mL water, stir, centrifuge 10 minutes and combine and save the supernates. Measure the activity of the phases to assess the separation. Discard the precipitate.
- NOTE:** It is critical that the soluble Ni-ammonia complex be formed at this step.
- 5.8 Mix approximately 2 mg of Fe carrier with 1 mL water. Using a dropper add the carrier to the sample drop-wise while stirring on a mixer. Stir until the iron hydroxide precipitate coagulates. Centrifuge 10 minutes on high setting, decant and save the supernate. Add about 1 mL conc NH_4OH and about 1 mL water to the precipitate, stir, centrifuge 10 minutes and combine the supernates. Save the supernates. Measure the activity of the phases to assess the separation, if appropriate.
 - 5.9 Step 5.8 can be repeated up to 4 times as determined by the cognizant scientist. When the precipitate has insignificant or no detectable activity go on to Step 5.10.

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- 5.10 Add 3 mL 1M $\text{NH}_4\text{Citrate}$ to the combined supernates and stir. Let stand at least 15 minutes for the complexing reactions to take place. Add 15 mL of DMG saturated ethanol--a large red precipitate (NiDMG) should form. Heat in a water bath to near boiling then remove. Place the tube in an ice bath until colorless DMG crystals begin to precipitate. Centrifuge on high setting 10 minutes. Decant the supernate until precipitate starts to pour off, then re-centrifuge and decant supernate. Save the precipitate. A few drops of aerosol solution may be added to control the precipitate. To the tube containing the precipitate add 3 mL water and 1 mL conc NH_4OH , use a few drops of aerosol solution to control the precipitate and to remove precipitate adhering to the tube walls. Stir, centrifuge on high setting for 10 minutes, decant the supernate and save. If the precipitate starts to pour off, re-centrifuge and then decant off the supernate.
- 5.11 To the precipitate add 5 mL water then 1 mL of conc HNO_3 with stirring. Warm if necessary to dissolve the precipitate. Add 3 mL of 1M $\text{NH}_4\text{Citrate}$ and stir. Add 3 mL conc NH_4OH and stir. Add 15 mL DMG saturated ethanol and stir. Place the tube in an ice bath until colorless DMG crystals form on the red NiDMG . Centrifuge on high setting for 10 minutes, decant the supernate. If the precipitate starts to pour off, recentrifuge and then decant off the supernate. Use a few drops of aerosol solution to control the precipitate and to remove precipitate adhering to the tube walls. Save the precipitate.
- 5.12 To the tube containing the Ni precipitate, add 3 mL water and 1 mL conc NH_4OH . Use a few drops of aerosol solution to control the precipitate and to remove precipitate adhering to the tube walls. Stir, centrifuge on high setting for 10 minutes, decant the supernate. If the precipitate starts to pour off, recentrifuge and then decant off the supernate. Combine all the supernates from Steps 5.10 through 5.12 and evaporate to dryness; save until analysis is completed.
- 5.13 To the precipitate (red Ni-DMG) add 1 mL water then dissolve the precipitate in 1-2 mL of conc HNO_3 . Transfer the solution quantitatively to a 50 mL beaker. (Recommended sequence: rinse the tube with four 1 mL portions of conc HNO_3 transferring the rinses to the beaker; rinse the tube with 1-3 mL of water and transfer to the beaker.) Place the beaker on a hot plate (setting 3-4) and carefully evaporate to small volume. **DO NOT ALLOW TO GO TO DRYNESS.**

NOTE: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has a boiling point of 137°C and can be lost if the solution goes to dryness. If solution does go dry, continue with procedure.

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- 5.14 Wet ash the sample as follows without letting the solution go to dryness (see note in Step 5.13). Rinse the sides of the beaker with 2-4 mL conc HNO_3 and evaporate to small volume, repeat up to 5 times to destroy organic material. Rinse the sides of the beaker with 2-4 mL of conc HNO_3 then add 1-3 mL of 30% H_2O_2 drop-wise as the reaction allows, while evaporating to small volume, repeat up to 5 times. Add 3 times the liquid volume in the beaker as conc HCl and evaporate to near dryness, repeat up to 4 times to transpose to the chloride form. The solution, in small volume, should be light green from the added nickel.
- 5.15 Prepare a column for ion exchange separation as follows. Make up each ion exchange column with 20 mL AG1X8 resin 100-200 mesh and place a small glass wool plug on top of the resin. Wash the column with water until the effluent is clear. Just prior to use wash the column with 15 mL of conc HCl followed by 15 mL of 9M HCl . Do not allow the column to stand overnight with strong acid. The cognizant scientist may specify a smaller column depending on sample concentration. In this case use proportionally reduced volumes.
- 5.16 Add 1 mL of conc HCl to the sample from Step 5.14, then add 2 mL of 9M HCl , mix well and load onto column. Collect all eluent from the column, this is the Ni fraction of the sample. Rinse the beaker with four 3-mL portions of 9M HCl adding each rinse to the column after the previous rinse has gone through. Wash the column with four 5-mL portions of 9M HCl , adding each rinse to the column after the previous rinse has gone through. Combine all the eluents from the column. Evaporate to small volume; do not allow to go to dryness. Elution volumes can be reduced proportionally if smaller columns are used.
- 5.17 Wet ash the sample without letting the solution go to dryness (see note in Step 5.13). Rinse the sides of the beaker with 2-4 mL conc HNO_3 and evaporate to small volume, repeat up to 5 times to destroy organic material. Rinse the sides of the beaker with 2-4 mL of conc HNO_3 then add 1-3 mL of 30% H_2O_2 drop-wise as the reaction allows, evaporate to small volume, repeat up to 5 times. When the organic material is destroyed the solution, in a small volume, should be light green.

NOTE: With direction from the cognizant scientist, the sample may be divided at this point with one part used for electrodeposition (Step 5.18) and another part for LSC (Step 5.19).

- 5.18 To prepare the sample for electrodeposition in preparation for beta and LEPS counting, go to Step 6.1.

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NOTE: If this sample fraction will not be counted by LSC (for yield determination), an alternate method of yield determination should be made as follows. Evaporate the solution just to dryness then perform Steps 8.2 and 8.3. Evaporate the resulting solution just to dryness and continue with Step 6.1. Also, follow direction of note in Step 6.8.

- 5.19 To prepare the sample for liquid scintillation counting, add 3 times the liquid volume in the beaker as conc HCl and evaporate to near dryness, repeat up to 4 times to transpose to the chloride form. Go to Step 8.1.

6.0 Electrodeposition

- 6.1 To the solution from Step 5.18, add 0.5 mL conc H_2SO_4 and 3 mL water, and cool to room temperature.
- 6.2 Add 1-6 drops of thymol blue indicator.
- 6.3 Add 50% NH_4OH (and H_2SO_4 if necessary) until the color just changes to green. The color change is purple to straw to green at neutrality. Low reagent concentrations may be used for better control of neutralization.
- 6.4 Remove disc cover from a 7/8 inch diameter polished metal plating disc which has the sample identification engraved on the back. Wash with ethanol and wipe with a tissue paper to remove adhesive. Let dry. Weigh the disc.
- 6.5 Mount the sample disc in electroplating cell.
- 6.6 Quantitatively transfer sample to cell with water and fill the cell to 1/2 full.
- 6.7 Insert platinum electrode, connect to power supply, and electroplate at 1 amp for 1 hour (± 15 minutes).
- 6.8 Wash electrodes with water while removing them and turn power off. Pour solution from the cell into the sample beaker and evaporate to dryness.

NOTE: Continue the alternate yield determination from Step 5.18 note as follows. Dilute the electrolysis solution to a known volume (e.g., 25 mL) and submit for Ni analysis.

- 6.9 Remove the electroplated disc from the cell and wash disc with water, then wash with ethanol and allow to dry. Weigh the disc. The weight of the Ni plated is an estimate of the recovery.

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- 6.10 Place disc in a labeled holder. The sample is now ready for beta counting. Count the sample on a beta counter. If requested by the cognizant scientist, obtain a beta absorption curve using a range of aluminum foil absorbers.
- 6.11 For LEPS counting (^{59}Ni determination), the disc is wrapped in mylar and sealed with tape. Count the sample on a LEPS counter. NOTE: A x-ray Ni fluorescence peak may interfere with the ^{59}Ni peak on the LEPS spectra. Cognizant scientist must be aware of this possibility.
- 6.12 If the sample is to be counted by the liquid scintillation method carry out the disc strip procedure (Step 7.1).

7.0 Disc Strip Procedure

- 7.1 Place the disc on a hot plate, setting low.
- 7.2 Place 1-2 mL of 8M HNO_3 into a disposable plastic beaker.
- 7.3 Cover the disc with about 0.1 - 0.2 mL 8M HNO_3 and warm. When the Ni deposit starts to dissolve, transfer the liquid to a glass LSC vial using a glass transfer pipet. Repeat up to 6 times or until the visible deposit is removed to quantitatively transfer the Ni to the LSC vial.
- 7.4 Cover the disc with 8M HNO_3 , heat approximately 2 minutes or until the solution is evaporated to no more than half volume. Then transfer the solution to the LSC vial. Repeat until all the 8M HNO_3 solution is used.
- 7.5 Evaporate the solution in the LSC vial to 0.5 mL or less and then add conc HCl drop-wise, with evaporation between additions, until no yellow color forms upon further addition of HCl and the solution is transposed to chloride form.
- 7.6 Add 1 mL of conc HCl and evaporate to dryness under a heat lamp. Repeat using 0.25 - 1 mL conc HCl. Go to Step 8.2.

8.0 Liquid Scintillation Counting

- 8.1 Using small aliquots of 6M HCl (0.1 - 0.5 mL) transfer the sample solution from the beaker (Step 5.19) to an LSC vial using a transfer pipet. Repeat 3-6 times to assure quantitative transfer. Evaporate to dryness under a heat lamp. Add 1 mL of conc HCl and evaporate to dryness under a heat lamp.

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PNL TECHNICAL PROCEDURE

8.2 Add exactly 1 mL (using a calibrated pipet) of 0.1M HCl to the LSC vial and swirl, allow to stand about 30 minutes with occasional swirling to assure dissolution and mixing of the Ni.

8.3 Transfer exactly 0.05 or 0.1 mL of the sample solution in the LSC vial to exactly 10 mL of 2 volume % HNO_3 in a 20 mL poly bottle and seal. In the same manner bring the yield monitor solution to a 10 mL volume with 2 volume % HNO_3 . The samples and yield monitor will be submitted for Ni analysis for yield determination.

For Ni determination submit an ARF. The dilution factors should be given so the data can be reported as concentration. Submit 10 mL of the 2 volume % HNO_3 as a blank.

8.4 Add 9 mL of Ultima Gold LSC cocktail to the LSC vial, seal and mix well. The cognizant scientist may change the amount and type of cocktail.

8.5 The sample is now ready for LSC.

9.0 Calculations

The 6.9 keV Co X-ray peak (from the electron capture decay of ^{59}Ni) counted on the LEP diode is used to calculate ^{59}Ni in the sample using the following equation:

$$^{59}\text{Ni Activity} = \frac{(\text{net cpm})(d/c)(B)}{(\text{Ni yield})(\text{sample volume})}$$

The ^{63}Ni activity is determined from the LSC spectra using the following equation:

$$^{63}\text{Ni Activity} = \frac{(\text{net cpm})(d/c)(B)}{(\text{Ni yield})(\text{sample volume})}$$

WHERE:

net cpm = the gross counts per minute minus the background cpm.

d/c = disintegration per count, an efficiency factor unique to each instrument and isotope; for LSC this will include the quenching effects.

B = factor to account for sample dilutions, and any other factors needed to produce the appropriate reporting units.

yield = is determined by the amount stable Ni recovered relative to the amount added.

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PNL TECHNICAL PROCEDURE

10.0 Specific Qualification

None required.

11.0 References

Bhat, I. S., Iyer, R. S., and Chandramonli, S., Anal. Chem., 48, page 224, (1976).

Pacific Northwest Laboratory. "Determination of ^{63}Ni and ^{59}Ni ," Revision 0 (PNL-ALO-439). PNL-MA-599, Pacific Northwest Laboratory, Richland, Washington.

Idaho National Engineering Laboratory 1982. (Procedure Ni-1-1). Idaho National Engineering Laboratory Analytical Chemistry Branch Procedures, Radiological and Environmental Sciences Laboratory, Idaho.

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Attachment 1. Flow Chart

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Ni-59 AND Ni-63 ANALYSIS
ANALYST SHEET

Procedure PNL-ALO-473

Date Sample Prep Started _____

Nickel Carrier

Volume _____ ml $\pm$ _____ ml Date pipetted _____
Pipet No. _____ Standard ID _____ Concentration _____
Standard Expiration Date _____

Nickel-63 Spike

Volume _____ ml $\pm$ _____ ml Date pipetted _____
Pipet No. _____ Spike ID _____ Spike Conc. _____

Sample Information

Sample ID	Sample Size	Initial Volume	Aliquot Volume	Sample Splits	
				LSC	LEPS

Balance No. _____

Final Sample Aliquot Volume (Step 8.2) _____ ml $\pm$ _____ ml

Pipet No. _____ Date _____

Aliquot for stable Ni determination (Step 8.3) _____ ml $\pm$ _____ ml

Pipet No. _____ Date _____

Final Solution Volume for Ni determination (Step 8.3) _____ ml $\pm$ _____ ml

Pipet No. _____ Date _____

Reference Pipet/Balance Log LRB _____ page(s) _____

Analyst's Signature _____ date _____

Reviewer's Signature _____ date _____

N1ANAL.LOG

INTERIM CHANGE NOTICE
(ICN)

ICN-PNL-ALO-474.1 R0
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A. Document Number: <u>PNL-ALO-474</u> Revision Number: <u>0</u> Document Title: <u>Measurement of Alpha and Beta Act</u> Document's Original Author: <u>J. H. Kaye</u>		Effective Date of ICN: <u>11/04/92</u>
		Change Requested By: <u>S. K. Fadeff</u>
B. Action Replace page 1 and 2 with the attached pages 1 and 2.		
C. Effect of Change Allows monitoring of counter efficiency under the counter control section.		
D. Reason for Change/Description of Change Counter efficiency is calculated by the instrument based on response to the tritium and C-14 standards. It is simpler to monitor these values since they are provided by the instrument and they are a perfectly acceptable method of monitoring counter control. Added to section 1.1 the redlined sections: The instrument response (such as count rate or efficiency)...		
E. Approval Signatures (Please sign and date)	Type of Change: (Check (✓) one) (✓) Minor Change () Major Change	
PQ Department		
Concurrence: <u>TL Ehlert</u>	<u>TL Ehlert</u>	Date: <u>11/4/92</u>
Approval		
Authority: <u>LR Greenwood</u>	<u>LR Greenwood</u>	Date: <u>11/9/92</u>
Other		
Approvals: <u>SG McKinley</u>	<u>SG McKinley</u>	Date: <u>11/11/92</u>
Author: <u>JH Kaye</u>	<u>JH Kaye</u>	Date: <u>11/11/92</u>

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-474 MEASUREMENT OF ALPHA AND BETA ACTIVITY BY LIQUID SCINTILLATION SPECTROMETRY

APPLICABILITY

This procedure describes measurement of alpha and beta activity in liquid samples by liquid scintillation spectrometry. Liquid scintillation spectrometry is used to determine alpha and beta energy and activity according to the nature of photons generated per each radioactive decay. Energy is determined by the amplitude of the photon produced and activity is determined by the frequency of photon production.

The procedure is applicable to any liquid sample which is compatible with standard liquid scintillation cocktail solutions. Quenching considerations may need to be addressed depending on the nature of the sample and method used for calculation of results.

This procedure is applicable to any liquid scintillation counting (LSC) system which incorporates multichannel pulse height analysis capability. A typical system is the Packard Tri-Carb 2260XL system, described in the References Section of this procedure.

DEFINITIONS

Quenching - An interference with the conversion of decay energy to electronic signal in the photomultiplier tubes. Chemical quenching is the absorption of beta decay energy before its conversion to photons. Optical quenching is the attenuation of photons as they pass through the sample medium.

Background - Counts introduced due to radioactivity in the local environment and from cosmic ray interactions.

Cocktail - A solution added to the sample which contains a scintillating medium.

Liquid scintillation spectrometer - a counting instrument which converts radioactive decay events from a liquid sample into light pulses which are stored in different channels according to their amplitude.

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PNL TECHNICAL PROCEDURE

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

PROCEDURE

Prerequisite: Only personnel trained in this procedure may perform the work. Personnel training records are kept in the ACL office.

Many modes of operation of LSC systems are available, and the user shall be familiar with the operation manual for the particular spectrometer to be utilized.

1.0 LSC Performance Evaluation

The system performance is evaluated by performance standard results. These results are plotted on appropriate control charts. The control charts are prepared on the basis of at least 10 control counts of each standard taken over a period of at least three days. Control limits are set at $\pm 3\%$ or $\pm 3s$ (s = standard deviation), whichever is greater.

- 1.1 The instrument response (such as count rate or efficiency) to sealed tritium and ^{14}C standards shall be determined, as well as the response to a sealed blank solution. These standards shall be run prior to each sample set to verify consistent system operation.
- 1.2 After counting these standards, the count rate is recorded on a control chart. If the count rate is within ± 3 sigma, the count rate is considered in control.
- 1.3 If the system is not in control, discontinue sample counting and recount the control standards twice more. If both recounts are in control, counting may continue on any remaining samples of the set. Counting data from samples already analyzed is acceptable. If one or both of the recounts are out of control, sample counting shall cease until the Cognizant Scientist evaluates the system. After corrections, adjustments, or repairs are made, the control standards shall be re-run, or new control charts shall be established, as deemed necessary by the Cognizant Scientist. If the Cognizant Scientist determines the out-of-control condition is limited solely to the control counts, an explanation of this shall be written in the control log for the instrument. Under this circumstance, samples do not need to be re-counted. If the out-of-control condition is not limited to the control standards, then any samples run after the last acceptable control count was taken shall be either re-counted or the results to the client shall be flagged appropriately and a Deficiency Report written.

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2.0 Establishing a Quench Curve

A quench curve may be needed, as determined by the Cognizant Scientist. Quenching usually results from spectrum distortion or interference based on the chemical and/or optical nature of the sample(s). A quench factor on each sample is provided by the instrument which helps determine the necessity of a quench curve.

- 2.1 Prepare a series of standards according to the applicable sample preparation procedure, using the same ratio of aqueous volume to LSC cocktail volume as used in the sample analysis. Record the aqueous volume and LSC cocktail type and volume.
- 2.2 To each standard/cocktail solution, add varying amounts of chloroform or nitromethane, or other suitable quenching agent, as determined by the Cognizant Scientist. Record the standard identification, volume, activity, and quenching agent and volume(s).
- 2.3 Count these samples by liquid scintillation to determine the relationship of count rate and/or peak location to the quenching factor. Maintain records of the analyte quenching behavior for the project and for future reference.

3.0 Sample Counting

- 3.1 Place the samples in the sample holder assembly. The following placement order is preferred: blank, standard, samples, standard, blank; this will provide information on the counter performance during the course of an analytical run.
- 3.2 Log sample positions on a sample log form.
- 3.3 Edit the analysis protocol as necessary and as directed by the Cognizant Scientist. The following items should be printed by the computer or recorded in some other manner:
 - date and time
 - region(s) of interest, lower and upper level values, KeV
 - counting time
 - sample identification
 - counts per minute for the region(s) of interest
 - quench indicating parameter.

4.0 Calculations

Calculate the activities of samples, standards, and blanks in accordance with instructions from the Cognizant Scientist or as required by the pertinent analyte analysis procedure.

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PNL TECHNICAL PROCEDURE

5.0 Records

Records shall be maintained and controlled in conformance with requirements of Manual PNL-MA-70, Procedure PAP-70-1701. The following items need to be kept as hard copy with the sample report.

Sample Log Form - This form provides a record of the location of each sample in the LSC sample changer, and the date the sample set was counted.

LSC Printout Form - This form is printed by the system printer after each sample is counted. It gives the specific sample information as defined in Section 3.3.

Sample spectra and summed region(s) of interest.

If a quench curve was generated, the cocktail type, volume, aqueous volume, standard identification, volume and quench agent volumes need to be recorded. Additionally, the sample log form, LSC printout form and sample spectra need to be recorded and maintained as hard copy. Any conclusions drawn from the quench curve study should also be maintained with the hard copy data.

6.0 Specific Qualifications

None required.

7.0 References

Packard Instrument Company. 1988. Tri-Carb™ Liquid Scintillation Analyzer Model 2260XL Operation Manual.

Packard Instrument Company. 1988. Spectrograph™ Spectrum Analysis Software Package.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-479, (Replaces 7-40.34), TRITIUM IN IRRADIATED CLADDING MATERIALS

1.0 APPLICABILITY

This procedure is intended for measurement of total tritium in the following type of material:

- (a) Material Zircaloy cladding or other metallic materials which are non-volatile at 2600°C.
- (b) Range Sample sizes up to 2 grams and 3/8" maximum dimension. Tritium detection limit approximately one nanocurie per gram of cladding.
- (c) Interferences None.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Discussion

This method for tritium uses the LECO Impulse resistance furnace, model EF-10 in cell 5. A sample is melted in a graphite crucible in the furnace for 2-3 minutes in a flowing stream of 6% hydrogen, balance helium. The gas stream is routed out of cell, through a hot copper oxide column for conversion of tritium gas to water. This water is then collected in a water bubbler trap and the carrier gas is routed back into the cell.

The tritium is measured by liquid scintillation counting. The counting is referenced to an NIST traceable tritium counting standard.

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PNL TECHNICAL PROCEDURE

4.2 Apparatus

- (a) EF-10 furnace, LECO Corp., installed in-cell.
- (b) Apparatus, as shown in figure.
- (c) Graphite sample crucibles, LECO Corp., for use in EF-10.

4.3 Reagents

- (a) Tritium Trap Solution: distilled water.
- (b) Carrier Gas: 6% hydrogen in helium.
- (c) Scintillation cocktail: Beckman Ready-Gel

4.4 Standards

A tritium counting standard is used during the liquid scintillation counting for reference. Standard should be NIST-traceable and decay-corrected.

4.5 Safety

- (a) Observe general laboratory safety rules.

4.6 Analysis

4.6.1 Preliminary

- (a) Samples should be weighed in tared vials in the range of 0.3 to 2.0 grams. Weigh two replicates each. Record in LRB.
- (b) Copper oxide column heater must be turned on and warmed up before use. Temperature of column should be 500-600°C. Record in LRB.
- (c) Carrier gas flow pressure should be 1-3 psi. Carrier gas flow rate should be 200-300 mls/min. This is a moderately vigorous bubbling through the bubbler trap. Record in LRB.
- (d) System should be flushed with carrier gas for several hours to purge of any residual tritium. To check this, run two 1-hour blanks and analyze for tritium. Record in LRB.

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- (e) The copper oxide column may have to be regenerated before use. This must be done if the oxide is 1/2 converted to copper metal. Regenerate by flowing air for several hours through the column with column at full temperature. Record in LRB.
- (f) The EF-10 furnace should be prepared before use if it has sat idle for over 1 month. The upper and lower electrode o-rings should be replaced. The furnace should be leak-checked, using the portable helium leak detector. Possibly the drop chamber o-ring may have to be replaced. Record in LRB.

4.6.2 Sample Analysis

- (a) If sample is solid chunk, then the Auto-Drop chamber should be used. If sample is powdered, then the crucible should be preoutgassed, removed, the sample poured in, the crucible replaced onto the electrode, the system outgassed with the furnace circuit breakers off, then the circuit breakers turned back on and the sample melted. Use tin capsule only as flux!
- (b) Assuming the sample to be a solid chunk, load crucible into electrodes and load sample into Auto-Drop chamber. Start furnace through full cycle.
- (c) After Outgas phase is complete, manually twist Auto-Drop chamber to drop the sample. Do this quickly. The Analyze phase will now begin.
- (d) The current should reach 1.1-1.3 k-amps. Record in LRB. Possibly the time of burn may have to be increased from the standard two minutes. This decision is based upon the melt appearance and will be made by the cognizant scientist and recorded in the LRB. When Analyze phase is complete, press Standby button. Continue collecting tritium for 60 minutes $\pm$ 2 minutes.
- (e) After the first collection is complete in 60 minutes $\pm$ 2 minutes, replace used trap water with fresh trap water and collect for an additional 15 minutes $\pm$ 2 minutes. This completes the collection of the tritium.

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- (f) Each trap solution should be diluted up to 250 ml with distilled water in 250 ml grad cylinder. This may need to be further diluted, possibly 1/2000. Pipet 1 ml into LSC. Mix well and place into scintillation counter for counting. Record in LRB.

4.7 Calculations

$$(a) \text{ Ci/g tritium} = \frac{(A - B) \times C \times D}{E \times F}$$

Where, A = Tritium counted in sample, cpm
B = Tritium counted in blank, cpm
C = Dilution factor, eg., 250
D = Tritium standard, decay-corrected, dpm
E = Tritium standard, cpm
F = 2.22×10^{12} dpm/Ci

4.8 Procedure Qualification

This procedure is considered qualified due to its dependence on analytical standards. It is also considered qualified through the Independent Technical Review process.

5.0 BIBLIOGRAPHY

Saari, C.E., "A Simple and Rapid Method for Determining Tritium in Irradiated Boron Carbide and Getter Materials, "HEDL-TME 77-52, July 1977.

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PNL TECHNICAL PROCEDURE

Figure A-1: Tritium Analysis Apparatus

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-480, (Replaces 7-40.39), DETERMINATION OF ^{99}Tc

1.0 APPLICABILITY

This procedure is applicable to aqueous samples. Solid samples may be analyzed if they are first dissolved or leached by an appropriate method. The cognizant scientist will decide if this procedure is applicable to a specific sample or if a procedure for initial sample preparation or to remove additional interferences is needed.

2.0 DEFINITIONS

ppt - precipitate

dpm - disintegrations per minute

cpm - counts per minute

d/c - an efficiency factor, disintegrations per count

conc - concentrated

i.d. - inner diameter

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 REAGENTS AND SUPPLIES

4.1 Rhenium carrier - Dissolve 12.01 g NH_4ReO_4 in H_2O and dilute to 250 ml with H_2O in a certified volumetric flask. This solution is 33.3 mg Re/ml^2 . Another concentration of Re solution may be used as long as the concentration is well known.

4.2 $^{95\text{m}}\text{Tc}$ and ^{99}Tc tracer solutions - These solutions each have a unique identification number directly traceable to a lab notebook. This notebook and associated files contain records of the source, dilutions and activities of each individual tracer solution. By

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specifying a tracer number and volume, the activity is therefore known.

- 4.3 Dowex 1-X8 resin, Cl form, 200-400 mesh.
- 4.4 6M NH_4NO_3 - 5M HNO_3 solution - Dissolve 720 g NH_4NO_3 in approximately 0.5 liters with H_2O . Add 500 ml conc. HNO_3 ; dilute to 1.5 liters with H_2O .
- 4.5 Fe carrier, 10 mg/ml - Dissolve 18.08 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in H_2O . Dilute to 250 ml. (Note: another ferric salt may be used or another concentration as long as the required mg of Fe_{+3} are added.)
- 4.6 Concentrated NH_4OH .
- 4.7 Tetraphenyl arsonium chloride solution - Dissolve 22.5 g tetraphenyl arsonium chloride in approximately 60ml absolute ethanol. Dilute to approximately 450 ml total volume with water.
- 4.8 Membrane filter, 45 mm diameter, 0.45 μm pore size or 45 mm diameter glass fiber filter.
- 4.9 Counting card, 38 mm diameter opening.
- 4.10 Distilled or deionized water.

5.0 CHEMICAL PROCEDURE

Except where responsibility is specifically assigned to the cognizant scientist, the analyst may perform all work. All pertinent data, observations, and calculations e.g., aliquot volumes, ppt weights and counting data, will be recorded in a project record in a manner traceable to the sample.

5.1 Chemical Separation of the Sample.

- 5.1.1 Place sample in beaker (up to 4 liter). Divide sample among several beakers, if necessary. Add 100 mg rhenium carrier, and $^{95\text{m}}\text{Tc}$ tracer, as specified by the cognizant scientist; divide the carrier and tracer approximately equally among the beakers. Record the sample and tracer volumes and the tracer identification. Stir for 10 minutes.
- 5.1.2 To each beaker add 20ml 200-400 mesh anion resin (Cl form); stir for 20-30 minutes. Filter until resin is very dry. Transfer resin to a beaker using 6M NH_4NO_3 - 5M HNO_3 solution. Use no H_2O .

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- 5.1.3 Repeat step 5.1.2, combining resin. Set solution aside.
- 5.1.4 Add enough 6M NH_4NO_3 · 5M HNO_3 solution to resin to stir well. Stir for 20-30 minutes.
- 5.1.5 Transfer to filtering flask. (Use no H_2). Filter very dry. Save solution. Transfer resin back to beaker using 6M NH_4NO_3 · 5M HNO_3 solution.
- 5.1.6 Repeat steps 5.1.4 and 5.1.5, two times. Combine filtrates.
- 5.1.7 Discard resin. To composite filtrates, add 20-100 mg Fe carrier depending on solution volume; add concentrated NH_4OH until basic. Stir until a rust-colored ppt. forms; filter solution and discard ppt.
- 5.1.8 Add 5 ml of tetraphenyl arsonium chloride solution. Stir for 30 minutes. After 10 minutes check for ppt; if none has formed, add 1 ml additional tetraphenyl arsonium chloride. Continue stirring for 30-60 minutes.
- 5.1.9 When sample has fully precipitated, filter onto a pre-weighed, 45 mm diameter filter. Dry flat under heat lamp; weigh. Calculate and record net precipitate weight.
- 5.1.10 Mount sample, face up, on a 38 mm i.d. cardboard counting card, so that the filter is taped to the underside of the card.

5.2 YIELD DETERMINATION

If $^{95\text{m}}\text{Tc}$ tracer is not used, follow this procedure:

- 5.2.1 Take an aliquot of one sample, a composite aliquot of the set, or the remaining solution from step 5.1.3 of one sample. This aliquot is specified by the cognizant scientist and its identification and volume will be recorded.
- 5.2.2 Add ~ 13000dpm ^{99}Tc , accurately known, per instructions of the cognizant scientist. Record ^{99}Tc tracer number and volume.
- 5.2.3 Prepare according to Section 5.1. This is the ^{99}Tc spiked sample.

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PNL TECHNICAL PROCEDURE

If ^{95m}Tc tracer is used, follow this procedure:

- 5.2.4 Mount a clean membrane filter on a counting card as described in section 5.1.9.
- 5.2.5 Evaporate an aliquot of ^{95m}Tc on the filter, using the same aliquot size used in section 5.1.1. This is the ^{95m}Tc counting standard. Record the identification and volume of the tracer.

6.0 COUNTING AND CALCULATIONS

Normally the Battelle Beta Counting Form is used to record counting data. See Exhibit 1.

- 6.1 Count the samples on a beta counter with no absorber and with a 10 mg/cm^2 absorber. Record the shelf number and the exact absorber thickness. Calculate and record the net cpm (net cpm = gross cpm - background cpm), for each. If the cognizant scientist has specified that a blank sample be analyzed, net cpm may be calculated as net cpm = sample gross cpm - blank gross cpm.
- 6.2 Count a ^{99}Tc counting standard on the same shelf, both with and without the absorber. Calculate and record the net cpm for each and the fraction counted through the absorber. This fraction is the ^{99}Tc term.
- 6.3 If ^{95m}Tc tracer was used, count the ^{95m}Tc counting standard on the same shelf, both with and without the absorber. Calculate and record the net cpm through the 10 mg/cm^2 absorber. This is the ^{95m}Tc term.
- 6.4 If ^{95m}Tc tracer is used, determine yield by gamma counting both the samples and the ^{95m}Tc counting standard, measuring the 204 keV gamma.

$$\text{Yield} = \frac{\text{net cpm in sample}}{\text{net cpm in standard}}$$

- 6.5 If ^{95m}Tc tracer was not used, count the ^{99}Tc spiked sample on the same shelf of the beta counter without the absorber. Calculate the net cpm as specified in Section 6.1.

$$\text{Yield} = \frac{\text{net cpm} \times \text{d/c}}{\text{dpm } ^{99}\text{Tc std added}}$$

where d/c is determined by the cognizant scientist.

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PNL TECHNICAL PROCEDURE

6.6 If ^{95m}Tc tracer is used, the sample calculation is:

$$A = \frac{(\text{net cpm through } 10 \text{ mg/cm}^2) - ({}^{95m}\text{Tc term} \times \text{yield}) \times \text{d/c}}{{}^{99}\text{Tc term} \times B \times \text{yield}}$$

where A = ${}^{99}\text{Tc}$ activity of the sample.

B = factor to account for sample volumes, dilutions or weights and any other factors needed to produce the appropriate reporting units.

d/c is determined by the cognizant scientist.

6.7 If ^{95m}Tc tracer is not used, the sample calculation is:

$$A = \frac{\text{net cpm} \times \text{d/c}}{B}$$

6.8 Per instructions from the cognizant scientist, check the beta absorption curve slopes for the samples (i.e., net cpm through 10 ÷ net cpm with no absorber). If the ratio is too high, it may be advisable to run an absorption curve on the sample to identify and correct for the higher-energy beta component.

7.0 PROCEDURE QUALIFICATION

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally, it is considered qualified because it has received an independent technical review.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-481, (Replaces 7-40.40), GAMMA-RAY SPECTRAL ANALYSIS OF IRRADIATED IRON OR NICKEL CONTAINING ALLOYS (INCLUDING ZIRCALOY-2) BY HIGH RESOLUTION GAMMA SPECTROMETRY FOR USE IN CHARACTERIZING NEUTRON FLUENCE AND SPECTRA

1.0 APPLICABILITY

Gamma spectrometric analysis of irradiated iron containing alloy sample sections is performed using high resolution gamma spectrometry with a high purity germanium detector coupled to a computerized multichannel pulse height analyzer with automated peak analysis, data reduction and an automated sample changer - positioner system (ASC-P) 5.0 (a). Other available gamma spectrometry systems may be used at the discretion of the cognizant scientist. The procedures and methodology used are in accord with those described in references 5.0 (b) and (c). All gamma photopeaks of significant intensity observed are noted and identified but complete analysis may be limited to only those photopeaks of activation products useful in characterizing the neutron fluence and spectra. Mn-54 produced from the fast neutron reaction, Fe-54 (n,p) Mn-54, in the tiny amount of iron alloyed in the Zircaloy-2 is the only activation product normally observed that can be used to estimate the fast neutron ($E \geq 1$ MeV) component of the neutron spectrum. Fe-59, Co-60, Zr-95 and Sb-125 are analyzed, if possible, to use in estimating the absolute and relative differences in the thermal neutron fluences for each sample section.

- (a) **Material** Irradiated Zircaloy-2 and alloys with accurately known iron composition. Most metal alloys with accurately known iron content.
- (b) **Range** 10^{-3} to 10^{15} Bq Mn-54 depending on interferences and relative abundance of other radionuclides. Physical sample size and shape must fit a 0.06 dia x 0.5 in. long cylinder for counting on the ASC-P system.
- (c) **Reliability** The gamma spectrometry systems are calibrated using NBS SRM's. The uncertainty of individual

Author	Date	Project Mgr.	Date	QAD Representative	Date
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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	8/8/88	All original signatures on file	
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spectrometric results is calculated based on total counts, background and interference corrections. This may vary from $\pm 2\%$ to $\pm 50\%$. For alloy samples, the uncertainty in the iron content of the alloy is usually the largest and overriding uncertainty.

- (d) Interferences Any gamma emitting radionuclide present in large excess relative to the nuclides to be measured and any nuclides emitting gammas energies within 10 to 30 keV of energies of interest for the nuclides to be measured.

2.0 DEFINITIONS

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

The results from gamma spectrometric analysis of neutron irradiated iron containing alloys are often used to characterize the neutron fluence and spectrum experienced by the sample. The amount of Mn-54 observed (corrected as appropriate for radioactive decay and burnout) is directly related to the portion of the neutron spectrum with neutron energies greater than 1 MeV. The 312.5 day half-life of Mn-54 limits its direct usefulness to the last 2.5 to 3 years of irradiation with conditions during the last year of irradiation having the largest influence. If it is assumed that the irradiation conditions have remained more or less stable over many years, results based on Mn-54 can be assumed to be valid over a similar period.

There are usually two or more thermal neutron activation products in the sample that can be measured gamma spectrometrically at the same time the Mn-54 is determined. Results from these along with the reactor power history, or more precisely, the operating power history for the samples being measured, can be used to calculate the thermal neutron fluence. Similarly, the Mn-54 results and power history are used to calculate a fast neutron fluence. Derivation of a neutron spectrum and fluence at a dosimetry location is accomplished by spectral adjustment codes. These

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codes start with a calculated or estimated spectral shape, with either a normalized or absolute magnitude. The shape and magnitude are modified to give improved agreement with (or a "best fit" to) the dosimetry measurements 5.0 (d). Adjustment codes currently used by the PNL National Reactor Dosimetry Center (NRDC) include SAND-II 4.0 (e) and FERRET 5.0 (f).

The accuracy of all of the fluence calculations is directly related to the accuracy of the values used for the target nuclide contents in the original material. Since iron is a minor alloy component of Zircaloy-2 (typically 0.12%) the uncertainty in the iron content of the original material can be expected to be on the order of $\pm 20\%$. It follows that the minimum uncertainty in fast fluence values based on Mn-54 results will be of similar or greater order.

If the samples can be analyzed relatively soon (3 - 4 months) after the end of the irradiation, it may be possible to measure Co-58, 70.8 d half-life, produced by the Ni-58 (n,p) Co-58 fast neutron reaction. This would augment the Mn-54 results and add to the accuracy of the final fluence and spectrum determination. Nickel is minor-alloy component of Zircaloy-2 (typically 0.05%).

This procedure is intended for use by knowledgeable persons who understand and appreciate the possible and probable sources of error as well the options to increase the accuracy of the final result.

4.2 APPARATUS

- (a) Gamma spectrometer system with a high resolution HP-Ge or Ge(Li) detector and appropriate associated electronics including but not limited to an integrated programmable computer system with peak search and analysis software tested for accuracy and reliability with known standard spectra. Energy and efficiency calibrations for the system shall have been made using certified NBS Standard Reference Materials (SRMs) issued for this purpose. NBS SRMs used in calibrating the gamma spectrometer systems in the PNL Chemistry and Analysis Labs included SRMs: 4215-F, 4218-D, 4275, 4233-B, 4200-B AND 4207.
- (b) Sample holder vials for the gamma spectrometer system used.
- (c) Analytical balance, capable of weighing to 0.1 mg or better.
- (d) Assorted stainless-steel tongs and precision tweezers.

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- (e) Ultrasonic cleaner with a minimum 1 pint cleaner liquid capacity.
- (f) 30 ml or 50 ml borosilicate glass beakers.
- (g) Large sized (3 ml) polyethylene droppers.
- (h) Portable radiation survey and dose rate measuring instruments.
- (i) Self reading dosimeter pencil and dosimeter finger rings if survey readings indicate a need as defined by the appropriate approved RWP.
- (j) Lead bricks to supply local shadow shielding during sample cleaning and weighing operations. If the radiation dose rates from the samples are too high to allow working in this manner, these operations will need to be done in the Shielded Analytical Laboratory (SAL) and the Dosimeter Sorting Cell using remote handling methods.
- (l) Mainframe computer (Sperry 1100/44 or equivalent) with compatible versions of SAND-II, FERRET and TIMH computer codes 5.0 (e), (f) and (g), with necessary support files and I/O devices in place and working.

4.3 REAGENTS

- (a) Acetone, ACS Analytical Reagent Grade.
- (b) Distilled or deionized water.
- (c) Hydrochloric acid - Hydrofluoric acid mixture: 35:1 prepared from concentrated Reagent Grade Acids.

4.4 STANDARDS

- (a) The National Bureau of Standards (NBS) periodically renews its SRMs for radionuclide detector systems calibration. SRMs are issued as both mixed multiple source standards and single radionuclide standards in sealed point source and calibrated solution configurations. The standards used for system calibration should approximate as nearly as possible the physical characteristics (size, density, thickness) of the samples to be analyzed. Where this is not possible, calculational corrections for the differences must be made. The energy range covered by the standards should overlap the energies of the nuclides analyzed. See reference 4.0 (b) and (c).

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- (b) A "working" control source standard consisting of a sealed source containing relatively long-lived radionuclides with gamma energy peaks at the low, intermediate and high end of the energy range covered by the gamma spectrometer is provided for each detector system. A mixed source containing Am-241, Cs-137 and Co-60 with gamma emission peaks at 59.54, 661.65 and 1332.5 keV, respectively, has been used with good success. The 5.27 year half-life of the Co-60 which has the shortest half-life of the group allows a useful control source life of about 10 years.

4.5 SAFETY

- (a) Observe the general laboratory safety rules.
- (b) Carefully read and adhere to the work practices and equipment requirements specified in the controlling Radiation Work Procedures (RWPs), 86-325-21 Rev. 2 for the Radiochemistry Labs and 86-325-22 Rev. 2 for the main Radiochemistry Counting Rooms.
- (c) Limit use of acetone to minimum volumes needed and confine work to well ventilated areas away from possible ignition sources.
- (d) Use prescribed protective clothing and procedures for handling acids. Clean up any real or suspected spills immediately. HF burns are especially insidious and extra care to avoid and/or minimize contact with HF is justified.

4.6 QUALITY CONTROL

- (a) Daily measurements of the control standard source are made to insure that the gamma spectrometer system is operating properly. Daily "control" plots are made for the net peak areas for the 59.54, 661.65 and 1332.5 gamma energy peaks. Additionally, the peak energies and resolutions measured by the peak analysis program are recorded. Unusual values for any of these parameters, if verified, require resolution and remedial action before the system is used for normal sample analysis.
- (b) Periodically, sources containing known amounts of long-lived radionuclides are measured on the gamma spectrometer systems. These may be NBS SRM sources, other known standards or dosimeters that were previously analyzed on the system being checked or a different system. If the results do not check within expected statistical limits, the problem is resolved before the system is returned to normal use.

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4.7 ANALYSIS

4.7.1 Sample Preparation

- (a) Cleaning: Determine from the sample radiation dose rates whether it is reasonable to clean and weight the samples in a Radiochemistry Laboratory, if not, some of the following steps should be done in the SAL and/or Dosimeter Sorting Cell.
- (b) Each sample should be ultrasonically agitated with two 5 ml to 10 ml volumes of acetone, applied serially, to remove cutting oil and surface debris left by the sectioning process.
- (c) Following a water rinse to remove the acetone, the sample surface should be lightly and uniformly etched using the HCl-HF acid etch solution. The rate and uniformity of the etching process should be carefully monitored and controlled. Ultrasonic agitation, aqueous dilution, heating and/or cooling the solution may be necessary to obtain the desired results.
- (d) As soon as the sample surface has been suitably etched, the sample should be rinsed with distilled water then with acetone or methanol and blotted dry.
- (e) When the sample is completely dry, it should be weighed to the nearest 0.1 mg (0.01 mg if feasible) on a currently certified analytical balance.
- (f) After recording the sample weight, place it in its designated pre-labeled vial.

4.8 CALCULATION

- (a) Samples to be analyzed on the ASC-P system are loaded into special bar code labeled vials which are loaded in batches of ten into numbered cassette trays. Before these can be loaded into the ASC-P system, all pertinent sample identification data, product radionuclide parameters, composition data, tray numbers and vial numbers must be entered into proper files on the ND6620.
- (b) Prepare and assign appropriate disk files and logical unit assignments as indicated in the ND6620/ASC-P Operating Documents and Notes.

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- (c) Use Program "ENTER" to enter the pertinent sample identification data, tray numbers and vial numbers into the "Master/Index" file pair assigned to logical units 1 and 10, respectively.
- (d) Use Program "DOSED" to enter product radionuclide parameters, sample composition data and the dosimeter type/subtype designation into the dosimeter library. This is necessary for any dosimeter type/subtypes not in the current library file.
- (e) Run Program "TEX" to move trays selected for replacement by trays containing samples to be analyzed to the unload/load port of the ASC-P. It may be necessary to run Program "REMAP" in order to synchronize the computer MAP FILE with the actual positions of the sample trays on the sample changer table before "TEX" can be run with reliable results.
- (f) During the execution of "Tex" the trays containing completed samples selected for removal are unloaded and replaced by a tray containing samples to be analyzed on a one for one basis. Care must be taken to make sure that the trays being loaded are loaded in the right orientation (lipped end in) or the changer will jam.
- (g) Run Program "BATED" to enter a BATCH FILE to designate the priority order for analyzing the samples, the counting position or maximum count rate desired for each sample, the activation products (radionuclides) to be analyzed and the gamma energies to be used for their analysis. The activation products requested for analysis and the gamma energies used must correspond exactly with the data in the Dosimeter Library for a given dosimeter type/subtype, see Step (d) above.
- (h) Using the line editor program "APS.EDITOR" see 5.0 (k), edit an existing ASC-P Operation Job Stream File to fit the samples to be analyzed by replacing the Master, Index and tape File names with those set up for the samples to be run.
- (i) Initialize a new tape on tape unit MT0 to record header and spectral data in the ND format or load the existing tape and read the entire directory leaving the tape in position at the end of the last record. See MTINIT command in 5.0 (k).
- (j) Initialize a new tape on tape unit MT1 to record individual analysis results with count, peak analysis and complete spectrum data by loading a new tape and executing Program "TAPE," or load the existing tape and read the entire

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directory leaving the tape in position at the end of the last record as in Step (i).

- (k) Double check to see that all pertinent files are current, run Programs "MLIST" and "BLIST" to list the current Map and Batch File contents on the Versatec printer. Run Program "SUM" to list the Master/Index Files contents and check this listing against the original input data lists for sample identification, weight, designated dosimeter type/subtype, etc., correct any errors at this time.
- (l) Start analysis of samples on the ASC-P system by starting the appropriate Job Stream, (File edited in Step (h) above) see reference 5.0 (k) and ND6620/ASC-P Documents and Notes.
- (m) The ND6620/ASC-P system automatically calculates the sample results in disintegrations per second (dps per mg of target element at the end of irradiation (EOI) if the original sample data were correctly entered into the system files. The results for each radionuclide analyzed are recorded in the Master/Index Files pair and can be extracted in a printed report by executing Program "REPORT" and responding to the program prompts to produce the type and detail of report desired.
- (n) The dps/mg results are converted to saturated reaction rates using the power history and TIMH code for input into the SAND-II and FERRET codes, 5.0 (g), (e) and (f) to derive "best fit" neutron fluence and spectral characterization values at the dosimeter location.

4.9 DOCUMENTATION

- (a) Samples not analyzed using the ASC-P system are normally loaded into the cap of a 'Wig-L-Bug' plastic vial with the sample held centered against the inside surface of the cap by cotton packed in the body of the vial.
- (b) Sample holders designed to hold the sample in calibrated positions at a number of different fixed sample to detector distances for the different gamma spectrometers are used to select an optimum analysis position for the sample.
- (c) The sample is counted for a preset time period based on the desired counting statistics, sample activity, and practical considerations.

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- (d) Depending on which gamma spectrometer system is used, a computerized peak search and analysis is performed on the collected gamma spectrum and the net gamma photopeak areas of interest are extracted for further calculations. In one system it is possible to input sample and radionuclide parameter data into files which can be used in a program called FCALC which will combine these data and the gamma spectrometry data and calculate results in units of dps/mg at EOI, the same as ND6620/ASC-P results.
- (e) When only the net gamma photopeak areas of interest are available, the results in dps/mg at EOI are calculated using an electronic calculator or personal computer spreadsheet program.

The dps/mg at EOI is calculated using the following equation:

$$\text{dps/mg at EOI} = \frac{(\text{NP}) \times (1/\text{E}) \times \exp(\ln 2) \times (\text{T}) / (\text{t})}{(\text{LTS}) \times (\text{WT}) \times (\text{COMP}) \times (\text{gss}) \times (\text{g/d}) \times (\text{RSC})}$$

where:

NP = Net gamma photopeak counts (at the designated energy) from the peak analysis

1/E = Reciprocal of the detection efficiency (gammas/count)

T = Elapsed time between the EOI and start of count

t = Half life of product measured in same units as T

LTS = Live time counted in seconds

WT = Weight of sample specimen in milligrams

COMP = Fractional composition of the target element in the sample

gss = Correction for gamma self-shielding by the sample

g/d = Gamma yield or gammas emitted per disintegration

RSC = Random summing correction

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NOTE: See 5.0 (b), (c), (h), (i) and (j) for detailed explanations of the factors used above plus correction for sample decay during count which is negligible for count time « than the half-life.

5.0 BIBLIOGRAPHY

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- (c) Standard General Methods for Detector Calibration and Analysis of Radionuclides, ASTM, E 181-82, Annual Book of ASTM Standards, Vol. 12.02.
- (d) FTR Dosimetry Handbook, HEDL MG-166, A1.3 Appendix A1, March 1983.
- (e) McElroy, W. N., S. Berg, and T. Crocket. A Computer-Automated Iterative Method of Neutron Flux Spectra Determined by Foil Activation, AFWL-TR-67-41, Vol. I-IV, Air Force Weapons Laboratory, Kirkland AFB, NM, July 1967.
- (f) Schmittroth, F. A., Ferret Data Analysis Code, HEDL-TME 79-40, Hanford Engineering Development Laboratory, Richland, WA, September 1979.
- (g) Bourquin, R. D., TIMH - A Computer Program for the Determination of Fluence with a Varying Flux, BNWL-1492, Pacific Northwest Laboratory, Richland, WA, August 1970.
- (h) Standard Method for Determining Fast-Neutron Flux Density by Radioactivation of Iron, ASTM, E 263-82, Annual Book of ASTM Standards, Vol. 12.02.
- (i) Standard Method for Measuring Thermal Neutron Flux by Radioactivation Techniques, ASTM, E 262-77, Annual Book of ASTM Standards, Vol. 12.02.
- (j) Standard Method for Determining Fast-Neutron Flux by Radioactivation of Nickel, ASTM, E 264-82, Annual Book of ASTM Standards, Vol. 12.02.

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- (k) ND6600 Data Acquisition and Processing System Operator's Manual, Nuclear Data Instrumentation, Golf and Meacham Roads, Schaumburg, IL, 60196.
- (l) ND6620, ASC-P, CSC AND 5TI Documentation and notes, kept with the ND6620/ASC-P System in Room 209, 325 Bldg.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-483, (Replaces 7-40.50), PLUTONIUM - RAPID PROCEDURE FOR URINE

1.0 APPLICABILITY

If there is no DTPA in the sample the actinide elements along with other metals can be concentrated as a group from the urine using an alkaline phosphate precipitation step and the precipitate is dissolved in acid and wet ashed. If there is DTPA in the sample, the sample must be wet ashed to destroy all organics including the DTPA, the wet ashing procedure is also valid for general use. The plutonium species are converted to the Pu (IV) state using NaNO_2 in which form Pu is adsorbed onto an anion-exchange column. Trivalent actinides pass through the column. Iron and thorium are removed using 8M HNO_3 and 9M HCl . Isotopes of Pu are measured following additional separation by Electrodeposition, Procedure PNL-ALO-485 and Alpha Energy Analysis, Procedure PNL-ALO-469.

2.0 DEFINITIONS

LRB	Laboratory Record Book
AEA	Alpha Energy Analysis
Reagent Blank	Analysis performed without any sample matrix material under analytical conditions identical to the actual sample analysis.
Matrix Blank	Analysis performed using blank sample matrix material under analytical conditions identical to the actual sample analysis.
Matrix Spike	Analysis performed using blank sample matrix with known amounts of the appropriate spike, under analytical conditions identical to the actual sample analysis. Note: If natural blank matrix is not available for spikes or blanks, artificial urine may be used in its place.
Sample Batch	A group of samples analyzed in parallel up to 12 samples.

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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LR Greenwood	7/17/92	AG King	7/21/92	All original signatures on file	
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3.0 RESPONSIBLE STAFF

Cognizant Scientist A chemist or other scientist familiar with this procedure and having an in-depth knowledge of the chemistry taking place.

Analyst An individual who has been trained in the use of this procedure.

4.0 REAGENTS AND STANDARDS

All reagents are prepared from analytical reagent grade chemicals. Deionized (DI) water, with an electrical resistance of >16 megaohms-cm is used throughout this procedure. Concentrations are not critical and need only be within $\pm 10\%$ of stated values. Replace all lab-prepared reagents annually, unless otherwise specified, or otherwise decided by the cognizant scientist.

- 16M HNO_3 - concentrated Nitric Acid
- 8M HNO_3 - Add 500 mls of concentrated (16M) Nitric Acid to 500 mls DI water
- 2M HNO_3 - Add 125 ml concentrated Nitric Acid to 875 ml DI water
- 12M HCl - concentrated Hydrochloric Acid
- 9M HCl - Add 750 ml concentrated Hydrochloric Acid to 250 mls of DI water
- NaNO_2 - Sodium Nitrite
- H_2SO_4 - concentrated Sulfuric Acid
- 30% H_2O_2 - concentrated hydrogen peroxide
- AG-1, X-8, 50-100 mesh chloride-form anion-exchange resin
- 2-octanol
- NH_4I - Ammonium Iodide
- NH_4OH - concentrated Ammonium Hydroxide
- Ca Carrier (50 mg Ca^{+2}/ml)

Weigh 100g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ into a 500 ml beaker. Add DI water until volume is about 200 ml. When dissolved, bring volume to 300 ml. Filter through Whatman No. 2 filter paper (or equivalent as

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determined by cognizant scientist) and collect filtrate in a labelled 500 ml screw cap bottle.

- Phosphate Solution (300 mg PO_4^{-3} /ml)

Weigh 140g $(\text{NH}_4)_2\text{HPO}_4$ into a 500 ml beaker. Add DI water until volume is about 200 ml. Heat gently and stir until salt is completely dissolved. Cool and bring volume to 300 ml. Filter through glass wool two times and store in labelled 500 mL screw cap bottle.

- Eluting Solution (NH_4I in 9M HCl)

Add 1g NH_4I to 100 ml 9M HCl, stir. Store in a labelled screw-cap bottle. **Note:** This solution shall be prepared fresh each day it is needed in the amount that will be used.

4.1 Internal Standards

- ^{242}Pu , 20 to 100 dpm/ml traceable to NIST.
- ^{243}Am and ^{233}U standards if Am, U and Cm are to be determined, 20 to 100 dpm/ml each traceable to NIST.
- Standard preparations shall be documented.

4.2 Spike Standards

- ^{239}Pu , 10 to 50 dpm/ml traceable to NIST.
- ^{241}Am , ^{238}U , about 10 to 50 dpm/ml each isotope traceable to NIST, to be used if Am, U and Cm are to be determined.
- Standard preparations shall be documented.

5.0 EQUIPMENT AND MATERIALS

- Centrifuge
- Centrifuge tubes, plastic, 50 mls. (for example: Nalgene, Oak Ridge type, Nalgene catalog No. 3118-0050)
- Ion exchange resin: AG-1 X-8, 50-100 mesh, chloride form
- Transfer pipettes, 5.0 ml plastic
- Glass wool
- Glass stirring rods

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- Ion exchange columns for the phosphate precipitation method. The columns shall be made from 5.0 ml plastic disposable pipettes, or equivalent, with the top 1/4 inch removed. A small piece of glass wool is placed in the bottom tip of the column, is lightly compressed, and is rinsed with DI water to eliminate all bubbles. A total resin volume of $0.7 \pm .1$ ml AG-1 X-8, 50-100 mesh, chloride form resin is added to the columns as a slurry and rinsed with DI water. A small plug of glass wool shall be placed on top of the resin bed. The resin is converted to the nitrate form by washing it with 5 ml of 8M HNO_3 .
- Ion exchange columns for the wet ash method. For up to 5 ml of resin use the small disposable column (0.7x15 cm), for greater than 5 ml of resin use the large size disposable column (1.5x20 cm). The resin is added to the column as a slurry and rinsed with DI water. A small plug of glass wool shall be placed on top of the resin bed.
- Rubber gloves, assorted sized
- Hot water bath
- Pyrex or equivalent glass beakers
- Pyrex or equivalent crystallizing dishes
- Dropper bottles with syringe control
- Pipetter, adjustable, 100 lambda to 1 mL
- Graduated cylinders - Class A, certified
- Protective gloves
- Hot plate or electric griddle
- Beaker tongs
- 3" plastic funnels
- Filter paper, Whatman No. 2 or equivalent as determined by cognizant scientist

6.0 QUALITY CONTROL INSTRUCTIONS

Yield monitors (carriers and tracers) and QC spikes may be prepared by the Analytical Laboratory.

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Prepare a minimum of one reagent blank, one matrix blank, and one matrix spike per sample batch, or as directed by the statement of work.

One time procedural variations are allowed if deemed necessary by the professional judgement of the cognizant scientist to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require documented approval by the cognizant scientist and verbal notification of Internal Dosimetry including the sample numbers. The variation in procedure shall be recorded in the LRB or on a data sheet. Reported data shall be flagged to indicate a deviation in procedure along with an explanation of the deviation specifics.

A copy of all quality control data and instructions shall be maintained in the LRB or on a data sheet and be available for easy reference or inspection.

7.0 VOLUME CALIBRATION

Except where noted, all sample volumes used in this procedure are given to within $\pm 10\%$. Critical volume measurements shall be made with calibrated or certified pipetters and glassware. These latter measurements are identified by the fact that notation shall be made in the LRB or on a data sheet regarding the volumes measured and calibration or glassware used.

When an added volume is a feature of the general calculation, a performance check of the automatic pipette shall be completed before and after each sample set for each volume to be measured. Pipet and weigh at least three aliquots of DI water equal to the volume being used, into a container in the balance. Determine the average weight. Correct the weight measured for temperature effects on the actual delivered volume using the formula:

$$\text{measured weight(g)} / d(\text{g/ml, density}) = \text{volume (ml)}$$

The value for d is dependent on the ambient temperature and is found in the temperature versus water density table in the Handbook of Chemistry and Physics (see reference 8 and Exhibit A). Record all data in the LRB or on a data sheet.

8.0 PROCEDURE

The cognizant scientist, with consultation from the requesting organization, must decide which chemical processing procedure to use on the sample. The precipitation procedure (9.0) is applicable for up to 300 ml sample size if DTPA is not present. The wet ash procedure (10.0) is applicable for all cases for up to 3000 ml of urine and must be used if DTPA is present in the sample.

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9.0 PRECIPITATION PROCEDURE (No DTPA present)

- 9.1 Measure the total sample volume using an appropriately sized Class A certified graduated cylinder. Note the sample volume and state Class A cylinder plus the date and time of sample receipt, ALO number, and client's name in the LRB or on a data sheet.
 - 9.1.1 Take the total sample or up to a 300 ml aliquot (measure with graduated cylinder) and put into a 600 ml beaker containing a stirring bar. Record the sample volume taken. Using 30 ml of conc. HNO_3 , rinse the sample container well then add the acid to the sample, repeat the rinse with 10-20 ml of 8M HNO_3 and add to the sample, repeat. Add a magnetic stir bar and stir while adding the spikes, steps 9.13 and 9.14.
 - 9.1.2 If volume is less than 300 ml, make up to 300 ml with DI water.
 - 9.1.3 With a calibrated pipete, add 20-25 dpm of ^{242}Pu Internal Standard to all samples, reagent blanks, matrix blanks, and matrix spikes (hereafter collectively called samples). Record the volume added and standard identification in the LRB or on a data sheet.
 - 9.1.4 Using a calibrated pipete, add 10 dpm of ^{239}Pu spike to the matrix spike solution. Record the volume added and standard identification in the LRB or on a data sheet.
- 9.2 Add 2 drops of 2-octanol, and 500 lambda of calcium carrier (50 mg Ca^{+2}). Stir for approximately 5 minutes.
- 9.3 Heat at $\sim 90^\circ\text{C}$ for approximately 2 hours in a water bath.
- 9.4 Let cool for about 15 minutes, add 2.5 ml of phosphate solution.
- 9.5 Form the precipitate by adding 50 ml of conc. NH_4OH and stir for 5 minutes.
- 9.6 Remove stir bar and allow precipitate to settle for 1 hour. Samples may be centrifuged to avoid the 1 hour settling period.
- 9.7 Electrodeposition cells, procedure PNL-ALO-485, and ion exchange columns, section EQUIPMENT AND MATERIALS, may be prepared at this time.
- 9.8 Decant and temporarily hold the supernate until analyses are completed and results are approved. Transfer the precipitate to a 50 ml centrifuge tube, and spin for 5-20 minutes until a clear

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supernatant is obtained. Decant supernate into previously saved supernate solution.

- 9.9 Dissolve the precipitate in 10 ml conc. HNO_3 and transfer back to the original beaker. Rinse the tube twice (5 ml each rinse) with conc. HNO_3 , adding the rinses to the sample.
- 9.10 Boil the sample down (hot plate on high setting) to about 10 ml and slowly add 3 ml of H_2O_2 , continue to boil to dryness heating until evolution of fumes stop.
- 9.11 Repeat the ashing cycle (step 9.10) 2-5 times, adding 5 ml of conc. HNO_3 and 3 ml of H_2O_2 , until the material is almost pure white. On the last cycle, the beaker is removed from the hot plate just as it is going dry to facilitate dissolution of the residue in the next step.
- 9.12 Dissolve the sample in nominally 25 ml of 8M HNO_3 keeping the total volume to a minimum (up to 50 ml). Place on a hot plate and boil for 2 to 3 minutes. Cool and add approximately 100 mg NaNO_2 , mix and wait for at least 10 minutes (waiting one hour to overnight is acceptable). If undissolved salts remain, centrifuge or filter. Pass the sample solution through a prepared column at a rate of approximately 1 drop every 2 seconds, saving the eluant in a 500 ml beaker labelled for Am/Cm and U if these analyses are requested. Save the filter and eluant until all procedures have been completed and data checked for report to customer.
- 9.13 Wash the beaker with three-2 ml portions of 8M HNO_3 adding each wash to the column. Wash the column with three-2 ml portions of 8M HNO_3 followed by six 2-ml portions of 9M HCl . Collect all these column washings and save in the same labelled beaker used in step 9.12 for possible Am/Cm and U analysis.
- 9.14 Wash the column with two-5 ml portions of the eluting solution containing NH_4I in HCl (500 mg NH_4I per 50 ml 9M HCl made fresh daily or as needed) and collect this Pu-fraction (the entire two-5 ml portions) in a 50 ml beaker labelled with the sample identification.
- 9.15 Add 5 ml conc. HNO_3 and 3 ml H_2O_2 to the sample solution and boil to near dryness. Repeat this step until iodine color is gone, or up to 3 times, using 1 ml of conc. HNO_3 and 0.5 ml of H_2O_2 . Take the beaker off the hot-plate, cool and carefully add about 1 ml of conc. H_2SO_4 . Heat this solution until dense white fumes of H_2SO_4 evolve and the volume is about 0.5 ml, cool beaker for 5-10 minutes.

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KEY POINT: Solution must be colorless at this stage. If not, add a few drops of 30% H_2O_2 and heat again until dense white fumes of H_2SO_4 appear.

- 9.16 For electrodeposition and AEA measurements: Go to section 4.5.8 of procedure PNL-ALO-485.

10.0 WET ASH PROCEDURE, DTPA PRESENT

10.1 Measure the total sample volume using an appropriately sized Class A certified graduated cylinder. Note the sample volume and Class A plus the date and time of sample receipt, ALO number, and client's name in the LRB or on a data sheet. Place the sample in an appropriately sized container that will hold the entire sample. Rinse the graduated cylinder with 10-20 ml of 8M HNO_3 and add to the sample, repeat.

10.2 Using conc. HNO_3 equal to 10% of the sample volume, rinse the sample container well then add to the sample. Repeat the rinse with 10-20 ml of 8M HNO_3 then with 10-20 ml of water.

10.3 Add a magnetic stir bar and stir samples. Stir while adding spikes (as outlined in steps 10.4 and 10.5 below) and for at least 10 minutes more. Stirring may continue during evaporation.

10.4 With a calibrated pipette, add 20-25 dpm of ^{242}Pu Internal Standard to all samples, reagent blanks, matrix blanks, and matrix spikes (hereafter collectively called samples). Record the volume added and standard identification in the LRB or on a data sheet.

NOTE: If DTPA is present in the samples, DTPA needs to be added to the reagent blank, matrix blank and matrix spike. The requesting organization will supply the DTPA and advise as to the amount.

10.5 Using a calibrated pipette, add 10 dpm of ^{239}Pu spike solution to the matrix spike solution. Record the volume added and standard identification in the LRB or on a data sheet.

10.6 Stir for at least 10 minutes following the addition of the spikes.

10.7 Depending on the sample size, the cognizant scientist will decide on the container or container sizes to use for the evaporation. For very large samples up to 3 crystallizing dishes may be used, or one to three appropriately sized beakers. The containers should be filled no more than 1/2 full.

10.8 Evaporate the samples at the 5-6 setting (high if controlled boiling occurs) on a hot plate. Add 5-6 drops of octanol before

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evaporation begins and additionally as needed to control foaming (up to 1 ml) if the sample was divided into multiple containers, the sample must be combined into one appropriately sized beaker when the sample volume has evaporated to no less than 1/4 inch depth in the container. Use 3-5 rinses of 5-15 ml portions of conc. HNO_3 to rinse the individual containers into the one evaporation container. Continue the evaporation to low volume. The stir bar should be removed before the sample has begun to decompose.

- 10.9 Wet ash the sample with repeated additions of 5-10 ml portions of con HNO_3 and 3 ml portions of H_2O_2 , and evaporate to small volume. Repeat the additions as necessary. To remove sample from the sides of the beaker add 10-20 ml of con HNO_3 , cover with a watch glass and reflux. Evaporate to dryness and continue heating until evolution of fumes stop, 3 ml portions of H_2O_2 may be added as the sample goes to dryness to assist the ashing process. (When the sample is first taken to dryness, if organic material has not been destroyed, the sample may ignite; this should be avoided. If the sample starts to turn really dark, a little water can be added to stop charring). Add 5-10 ml portions of con HNO_3 and 3-6 ml portions of H_2O_2 as needed, and evaporate to dryness and continue heating until evolution of fumes stop and the salt does not become whiter with continued heating. Repeat as necessary up to 5 times. The wet ash process is not specific and the amounts of individual reagents and the order of addition can be varied to give a final, almost clear-white residue of salts. On the last evaporation to dryness heat on hot plate set to high until NOX fumes cease to be evolved (up to one hour).
- 10.10 If a large amount of salt is present and the cognizant scientist decides, aqua regia may be added to reduce the amount of NH_4NO_3 . Add 5 ml of conc HNO_3 and 15 ml of conc HCl to the sample and evaporate to dryness. Repeat if necessary. Add 5-15 ml of con HNO_3 and evaporate to dryness to assure the removal of chloride. The salt may also be reduced by heating on a hot plate on high for as much as 1 hour.
- 10.11 Add 5-25 ml conc HNO_3 to the sample, cover the beaker with a watch glass and reflux the sides of the beaker for 5-10 minutes, then remove the watch glass and evaporate just to dryness. Remove from the hot plate and cool.
- 10.12 Dissolve the residue in a minimum (up to 300 ml) of 8M HNO_3 . Heat to aid dissolution, however, the salt must stay in solution upon cooling to room temperature. To determine the amount of acid to add, remove a one ml aliquot of the solution and add 8M HNO_3 until the solution is clear. Use this value to calculate the amount of acid needed to dissolve the total sample. Add the removed aliquot

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back to the sample. The solution must be clear at this time; if not, consult the cognizant scientist. Undissolved material will make the ion-exchange columns drip very slow, the solution may be filtered. If this is done, filter the solution through a glass fiber filter, wash the filter with 5-ml of water then 5-ml of conc HNO_3 and save the filter until good recovery is assured.

- 10.13 Add 100 mg of NaNO_2 and allow to stand one hour (overnight is satisfactory). If salting out occurs, add additional 8M HNO_3 and warm to redissolve.

NOTE: Some hexavalent Pu may be formed in the wet ash process. The reduction to quadravalent Pu is slow and allowing the solution to set overnight facilitates the reduction.

- 10.14 Prepare the ion exchange column. The column size shall be decided by the cognizant scientist. Use either a small or large diameter disposable column, the small column will hold up to 5 ml of resin. For a sample size (the volume from step 10.12) up to 300 ml, use 5 ml of resin. For a sample size (the volume from step 10.12) up to 2000 ml, use 15 ml of resin. Slurry the proper amount of resin into the column, wash the sides of the column with DI H_2O and drain, washing all the resin off the sides of the column. Place a small glass wool plug on top of the resin. Add with water covering the resin to avoid an air pocket. Wash the column with 10 or 20 ml of DI H_2O .

NOTE: The cognizant scientist may change the resin volume in fractions or multiples of the 5 ml size. All column reagents are then multiplied by that fraction or multiple.

- 10.15 Pass 25 ml (5 ml column volume) or 75 ml (15 ml column volume) of 8M HNO_3 through the column.
- 10.16 Pass the sample solution through the column. Rinse the sample beaker 4 times with 5 ml portions of 8M HNO_3 , adding each rinse to the column. If Am analysis has been requested, label a beaker with "Am" and the sample ID, and collect the effluent in this beaker.
- 10.17 Wash the column with 5 ml (5 ml column volume) or 15 ml (15 ml column volume) of 8M HNO_3 , allowing it to drain into the Am fraction.
- 10.18 Wash the column with 30 ml (5 ml column volume) or 90 ml (15 ml column volume) 8M HNO_3 in aliquots. Discard the effluent.
- 10.19 When the 8M HNO_3 wash drains to the top of the resin bed, rinse the column walls above the resin bed with a small volume (<10 ml)

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of 9M HCl. Repeat this 2 times after wash has drained to the top of the resin bed. If using a column with a detachable reservoir, when the 8M HNO₃ wash drains out of the reservoir, detach the reservoir and rinse it with water. Discard the effluent.

- 10.20 Wash the column with 50 or 150 ml (respective to the 5 ml or 15 ml column volume) of 10M HCl by passing the solution through the column in aliquots. Discard the effluent.
- 10.21 Elute Pu with 25 or 75 ml (respective to the 5 ml or 15 ml column volume) of eluting solution (0.1M NH₄I in 9M HCl) into a beaker labeled with "Pu" and the sample ID.
- 10.22 Add 5 ml conc HNO₃ and 3 ml H₂O₂ to the sample solution and boil to near dryness. Repeat this step until iodine color is gone or up to 3 times, using 1 ml of conc HNO₃ and 0.5 ml of H₂O₂. The solution must be colorless at this stage.
- 10.23 Cool, then slowly add 1 ml conc H₂SO₄. Heat until dense white fumes of H₂SO₄ evolve and the volume is reduced to about 0.5 ml. Cool beaker.
- 10.24 For electrodeposition and AEA measurements, go to Section 4.5.8 of procedure PNL-ALO-485.

11.0 CALCULATIONS

- 11.1 After electrodeposition and alpha energy analysis, the ²³⁸Pu and ²³⁹⁺²⁴⁰Pu activities can be calculated from the following equations. The superscript 23x refers to calculations performed for the measurement of ²³⁸Pu individually and the measurement of ²³⁹⁺²⁴⁰Pu together.

$$\text{net } ^{23x}\text{Pu c/m} = \text{peak } ^{23x}\text{Pu c/m} - \text{background c/m}$$

$$\text{dpm for added } ^{242}\text{Pu tracer} = (\text{ml } ^{242}\text{Pu spike}) \times (\text{dpm/ml } ^{242}\text{Pu std} \times)$$

$$\text{sample d/c} = (\text{dpm } ^{242}\text{Pu added}) / (\text{gross c/m } ^{242}\text{Pu tracer} - \text{background c/m})$$

$$^{23x}\text{Pu activity (dpm/L)} = (\text{net } ^{23x}\text{Pu c/m}) \times \text{sample (d/c)/sample vol. (L)**}$$

*Provided by the Analytical Laboratory

**Use aliquot volume if an aliquot of the original sample was taken.

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- 11.2 The uncertainty in the Pu content determination is due to the error associated with measuring the tracer volume and its dpm/ml, the original sample volume and the variation from counting by the alpha spectrometry system.

$$U = \sqrt{[Vt^2 + Cd^2 + Vs^2 + Ct^2 + Cs^2 + Cbt^2 + Cbs^2]}$$

VT = %Error in measuring volume of tracer

Cd = %Error in establishing dpm of tracer

Vs = %Error in measuring the sample volume

Ct = %Error associated in measuring the gross counts of tracer which equals ($\sqrt{\text{gross tracer counts}}$)

Cs = %Error associated with measuring the gross counts of analyte ($\sqrt{\text{gross analyte counts}}$)

Cbt = %Error in measuring the tracer background count ($\sqrt{\text{tracer background count}}$)

Cbs = %Error in measuring the analyte background count ($\sqrt{\text{analyte background count}}$)

12.0 EMERGENCY REPORTING

- 12.1 Report activities immediately by telephone to PNL Exposure Evaluator (376-2222).

BE SURE TO INCLUDE:

Individuals' name and payroll number
Volume of sample received

Volume of sample analyzed
Sample date and sequence number if more than one sample/date

- 12.2 Document the following in the LRB or on a data sheet:

- Date and time sample was received at PNL.
- Date and time results reported and name of the person taking message.
- QC data results, tracer and radiochemical recovery.

- 12.3 Mail a copy of the sample ID and analytical results to Internal Dosimetry (A3-60) within 2 working days after analysis is completed.

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13.0 SAMPLE DISPOSAL

Unused sample portions and sample counting disks shall be kept for 30 days after the report is submitted to Internal Dosimetry. Then, excess urine samples may be disposed by flushing down a toilet, provided the analysis results show less than 1×10^4 pCi/l (100 dpm/ml). Sample counting disks can be disposed of as general lab waste if the alpha activity is less than 100 pCi/g. Otherwise, the samples shall be disposed of using approved procedures.

14.0 SPECIFIC QUALIFICATIONS

None required.

15.0 REFERENCES

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RELATIVE DENSITY AND VOLUME OF WATER

The mass of one cubic centimeter of water at 4°C is taken as unity.
The values given are numerically equal to the absolute density in grams per milliliter.

(American Tables, compiled from Various Authorities.)

Temp. °C.	Density.	Volume.	Temp. °C.	Density.	Volume.
-10	0.999816	1.000184	-1.5	0.999916	1.000084
-9	999	157	0	999	000
-8	998	100	1	998	000
-7	997	100	2	997	000
-6	996	099	3	996	000
-5	995	099	4	995	000
-4	994	098	5	994	000
-3	993	097	6	993	000
-2	992	096	7	992	000
-1	991	095	8	991	000
0	990	094	9	990	000
1	989	093	10	989	000
2	988	092	11	988	000
3	987	091	12	987	000
4	986	090	13	986	000
5	985	089	14	985	000
6	984	088	15	984	000
7	983	087	16	983	000
8	982	086	17	982	000
9	981	085	18	981	000
10	980	084	19	980	000
11	979	083	20	979	000
12	978	082	21	978	000
13	977	081	22	977	000
14	976	080	23	976	000
15	975	079	24	975	000
16	974	078	25	974	000
17	973	077	26	973	000
18	972	076	27	972	000
19	971	075	28	971	000
20	970	074	29	970	000
21	969	073	30	969	000
22	968	072	31	968	000
23	967	071	32	967	000
24	966	070	33	966	000
25	965	069	34	965	000

3100

EXHIBIT A

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-485, (Replaces 7-40.53), ELECTRODEPOSITION PROCEDURE

1.0 APPLICABILITY

This procedure is the final preparation for most samples requiring analysis by alpha spectrometry. Solutions containing alpha emitting nuclides are electrodeposited and are resolved by alpha spectrometry. (See procedure PNL-ALO-469, Alpha Energy Analysis.)

The actinides are plated onto stainless steel or platinum disks by cathodic deposition of their hydrated oxides. The capability of the alpha spectrometer to resolve the alpha energies of the radioisotopes present depends on the suitability of the previous separation procedure(s) and the ability to prevent spectral degradation due to electrodeposited contaminants. The most common contaminant, iron, is a constituent of laboratory dust. Samples must always be protected, as much as possible, from airborne dust and other sources of contaminants.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist- A chemist or other scientist familiar with this procedure, who has an in-depth knowledge of the chemistry taking place, and who has been assigned by the Group Leader.

Technician- An individual trained and certified in the use of this procedure.

4.0 PROCEDURE

4.1 Description

The sample is wet-ashed with nitric acid and hydrogen peroxide. After adding sulfuric acid to the nitric acid, the sample is heated until white sulfur trioxide fumes are evolved. After

Author	Date	Project Mgr.	Date	QAD Representative	Date
SK Fadeff	12/10/90	N/A		GK Gerke	12/7/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LR Greenwood	12/4/90	HH Van Tuyl	12/7/90	All original signatures on file	
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cooling, the sample solution is adjusted to the proper pH with ammonium hydroxide, using thymol blue indicator. The sample is electrodeposited on a polished, stainless steel or platinum disk. The electrodeposition is quenched after the appropriate time with ammonium hydroxide. The disks are removed from the cell, rinsed, dried, and submitted for counting by procedure PNL-ALO-469.

4.2 Reagents

All reagents are prepared from analytical reagent grade chemicals, unless otherwise specified. Deionized (DI) water must have an electrical resistivity of greater than 16 megohm-cm when obtained. Replace lab-prepared reagents annually, unless otherwise specified. Concentrations are not critical and may be within $\pm 10\%$ of stated values.

- Acetone
- Ammonium hydroxide (NH_4OH)- concentrated, 15M. Replace if cloudiness appears.
- 3M Sulfuric acid ($3\text{M H}_2\text{SO}_4$) - carefully and slowly pour 83 mL of 18M H_2SO_4 into approximately 350 mL of chilled DI water in a beaker. Stir, let cool. Dilute to 500 mL with DI water. Store in a polyethylene bottle.
- Beaker washing solution, pH 2.2:
 - To a 1-L beaker, add approximately 900 mL of DI water.
 - Add 3 M H_2SO_4 dropwise with thorough stirring to a pH of 2.2 ± 0.1 , checking with pH indicator strip or paper. Wait about 15 seconds for a pH strip to respond fully (because ion concentrations are low in the water). If the pH goes too low (too acidic), add ammonium hydroxide dropwise and stir thoroughly, checking the pH as before.
 - Rinse a 1-L polyethylene bottle with DI water and drain.
 - Transfer the washing solution to the bottle. DO NOT RINSE THE BEAKER INTO THE BOTTLE. Label the bottle.
 - Store the bottle tightly capped away from strong acids and bases. Check the pH of the washing solution weekly, or with each set of samples if its use is less frequent. Adjust back to $\text{pH } 2.2 \pm 0.1$ if necessary, or discard. The bottle may be refilled.

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- Hydrochloric acid (HCl) - concentrated, 12M
- Hydrogen peroxide (H₂O₂) - 30%
- Nitric acid (HNO₃)- concentrated, 16M.
- 8M Nitric acid (8M HNO₃)- Add 500 mL of concentrated nitric acid to 500 mL of DI water and mix well.
- Sulfuric acid (H₂SO₄) - concentrated, 18M (95-98%).
- Thymol blue, 0.1% solution (pH indicator)- Dissolve 0.1 g of dye- (thymolsulfonphthalein, sodium salt) in 100 mL of DI water.

4.3 Equipment and Materials

- Beakers- Pyrex glass, 500 and 1000 mL
- Cell bases- stainless steel, threaded to accept the cell reservoir
- Cell covers- hard Teflon
- Cell reservoirs- Nalgene, one ounce, polyethylene, narrow-mouth bottles with bottoms cut off.
- Disk holders- cardboard, for transport and storage.
- Disks- stainless steel, type 304, 1 1/16-inch diameter, 0.015-inch thick, polished on one side.
- Electrodeposition unit principal components:
 - Power supplies- low voltage, direct current, adjustable
 - Electrical current- indicator lamps, one for each cell;
 - Cell- current meter (ammeter), for each cell;
 - Current adjustment knob.
 - Electrical wires with clips, two per cell.
 - Racks to hold electrodeposition cells.
- Electrodes- platinum, 1/16-inch wire, approximately 3.5 inches long with one end bent.
- Engraver or scribe
- Hot plate
- Kimwipes or equivalent
- Pen- felt-tip, fine point, permanent ink
- Pipets- transfer, polyethylene, disposable, with tips cut approximately 1/2-inch long to fit platinum electrodes
- Ruler- 6-inch or 12-inch
- Stirring rods- glass
- Tape
- Test papers- pH indicator paper or strips, narrow range that includes pH 2.2, sensitive to 0.1 pH increments.
- Tweezers
- Watch glasses
- Graduated cylinders- 1000 mL

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4.4 Quality Control Instructions

- 4.4.1 One time procedural variations are allowed if deemed necessary by the professional judgement of the cognizant scientist to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require documented approval by the cognizant scientist. Internal Dosimetry shall be notified verbally (including sample numbers) of the variation within one day of approval and note of the variation will be made in the LRB. The affected data in the final data report shall be flagged such that a variation of procedure is known to have occurred.
- 4.4.2 A copy of all quality control data and instructions shall be maintained and available for easy reference or inspection.

4.5 Sample Preparation

Solution volumes added to the sample are approximate but within 10% of the specified value.

- 4.5.1 While preparing the sample(s) starting at step 4.5.2, ready the electrodeposition cells as follows:
- 4.5.1.1 Check that disk is flat. Engrave or scribe the sample identification and other necessary information, such as isotope or sequence number on the rough-edged (unpolished) side of stainless steel disks. Write the previously engraved, unique disk identification number on the disk holder.
- 4.5.1.2 Clean the unmarked (polished) side of the disk with a few drops of acetone and a Kimwipe. Wipe clean to remove grease and dirt.
- 4.5.1.3 Place the disk with the unmarked side up in the center of the cell base. If the disk is not centered, the cell will leak.
- 4.5.1.4 Inspect the bottom of the cell reservoir (that part which contacts the disk) for the absence of burrs, nicks, and scratches. Screw the reservoir into the cell base and tighten. Label the reservoir with the sample identification using the felt-tip pen.

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4.5.1.5 Pour at least 10 mL of DI water into the cell. Let the cell stand for at least 30 minutes to check for any possible leak. If no leak is detected, this cell is ready for use.

4.5.1.6 If the cell leaks, disassemble it. Wipe dry the cell base, outside threads of the cell reservoir, and disk. Re-center the disk in the cell base and assemble the cell again. Check for leaks as before. If the cell leaks again, try replacing the reservoir before checking for leaks.

4.5.2 Add 5-10 mL of conc. HNO_3 to the sample solution (or dried sample residue). Evaporate the solution just to dryness, DO NOT BAKE.

4.5.3 NOTE: Fresh H_2O_2 reacts vigorously with the evolution of gas. Replace the source H_2O_2 if only minimal reaction is noticed.

CAUTION: The recommended way to prevent sample loss due to splattering is to add HNO_3 first and then add H_2O_2 .

Wet-ash the residue with small additions (a few drops to 1 mL) of conc. HNO_3 and 30% H_2O_2 .

4.5.4 Evaporate the solution just to dryness and inspect the residue. Repeat the wet-ashing a few more times if the sample is still colored. Notify the cognizant scientist for possible additional purification if wet-ashing still results in discoloration.

4.5.5 With the beaker off the hot plate, rinse the beaker sides with 2-3 mL of concentrated HNO_3 from a squirt bottle. Slowly add 1 mL of concentrated H_2SO_4 down the sides of the beaker.

4.5.6 Return the beaker to the hot plate set at a higher heat to produce white, dense fumes from the H_2SO_4 . The final volume should be about 0.5 mL.

NOTE: Some samples look dark colored after addition of concentrated H_2SO_4 and heating. Repeat previous wet-ashing steps (steps 4.5.2 to 4.5.6) if necessary, until colorless.

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4.5.7 Monitor the beaker continuously to preclude evaporation to dryness. Should any sample evaporate to complete dryness, remove the beaker from the hot plate, cool, then repeat section 4.5.5. and 4.5.6. The final volume should be about 0.5 mL.

4.5.8 Cool the sample beaker. Carefully wash the sides of the beaker with about 3 mL of DI water. Give the beaker a swirling motion then let it cool for about 3 minutes.

4.5.9 Add 1 or more drops of 0.1% thymol blue indicator to obtain a color intense enough to see clearly. Add concentrated ammonium hydroxide dropwise carefully and swirl the beaker gently to mix sample and reagents. Continue the addition of ammonium hydroxide until a slightly pink color is observed. For better control of acidity adjustment, more dilute solutions of NH_4OH may be used.

NOTE: The optimum pH is 2.2. The preferred pH range is 2.1 to 2.4. The thymol blue indicator gives a salmon-pink to straw color in the preferred range. Thymol blue is pink below pH 1.9 and yellow above pH 2.6.

4.5.10 The pH should be about 2.2. Check with pH paper or strip. If the solution becomes too basic (pH too high), add 3M H_2SO_4 dropwise, swirling the beaker gently.

4.5.11 At this time, if the electrodeposition cell from step 4.5.1.5 has not leaked, pour out the water.

4.5.12 Transfer the sample solution from section 4.5.10 to the electrodeposition cell. Wash the walls of the beaker with a few drops of the beaker washing solution. Swirl the beaker and pour the washing into the cell.

4.5.13 Repeat the beaker washings using 1 to 2 mL of the beaker washing solution at a time until the volume of the solution in the cell is about 10 mL. Carefully swirl the cell to mix the contents.

4.5.14 Place the pre-space Pt-electrode into the cell. (The spacing of the platinum electrode (anode) from the disk (cathode) is about 4 mm (3/16 in.)).

4.5.15 Attach the electrode clips: positive (red wires) go on the platinum electrode and negative (black wires) on the stem of the cell base.

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4.5.16 Place a small beaker or a watch glass under the cell base stem, in case a leak develops during the electrodeposition.

4.5.17 Adjust the current to about 1.1 ampere (A) for the cell. Repeat sections 4.5.14 through 4.5.18 for each cell. The light bulbs for all cells in use should burn with approximately equal intensity.

CAUTION: Make sure the platinum electrode does not contact the disk.

4.5.18 The current may rise slightly soon after starting the electrodeposition. Therefore, ensure that the current to each cell has not exceeded 1.2 A about ten minutes after starting. Electroplate for 30-60 minutes.

4.5.19 CAUTION: Do not turn the power off until the next step has been performed on the cell for the corresponding power supply.

To terminate electrodeposition, add at least 1 mL of concentrated NH_4OH to the cell, without interrupting the current flow. Allow the cell contents to mix for at least 30 seconds. Turn the power off.

4.5.20 Remove the electrode clips. Lift the platinum electrode and cap from the cell and pour the electrolyte into the original beaker. Rinse cell and electrode with DI water and pour into the same beaker. Save the beaker until the analysis results from counting are known.

4.5.21 Disassemble the cell and remove the disk from the cell base. Rinse the disk with DI water, then acetone. Set the disk with its marked side down on a paper towel and let air dry.

4.5.22 Write the sample identification on the disk holder. Assure that the labeled disk is placed in the appropriate position of the disk holder. Record the date of electrodeposition and initials of analyst on the disk holder. The disk is now ready to submit for counting in an alpha spectrometer Procedure PNL-AL0-469.

4.5.23 Obtain counting time length from the cognizant scientist and write it on the card holder and in the LRB. Take the disk(s) in the holder to the counting room.

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- 4.5.24 Discard the plastic cell reservoir. Clean the Teflon cell cap and steel cell base in water with detergent. Rinse with tap water, then DI water.
- 4.5.25 Rinse the platinum electrodes with water, then soak in 8M HNO_3 , preferably overnight. Rinse with DI water and dry.

NOTE: If the electrodes need to be used again promptly, replace the overnight soaking with 20 to 30 minutes of heating in hot, concentrated nitric acid. Do not add any other acid.

4.6 Electrodeposition Rerun

- 4.6.1 If the cognizant scientist decides, after evaluating the alpha spectrometry results, that a sample should be replated, do one of the following as directed:

- If only the sample on the counted disk is to be used, go to section 4.6.2.
- If both the sample on the disk and the solution in the beaker from section 4.5.23 are to be used, go to section 4.6.3.
- If only the sample in the beaker from section 4.5.23 is to be used, go to section 4.6.4.

4.6.2 Disk Only--

- 4.6.2.1 Transfer the counted disk into a clean, labeled, 100-mL beaker, electrodeposited side up. Add approximately 10 mL of concentrated nitric acid. Place a watch glass over the beaker. Heat the beaker on a hot plate until the disk is clear and shiny (usually takes 10 to 15 minutes).
- 4.6.2.2 Remove the disk from the the beaker with Teflon-coated or stainless steel tweezers. Rinse the disk with concentrated HNO_3 into the beaker. Rinse the disk with DI water into the beaker.
- 4.6.2.3 If the cognizant scientist wants the stripped disk to be recounted to verify removal of the actinide, rinse the disk with acetone, but not into the beaker. Let the disk dry. Resubmit the disk for alpha spectrometry.

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4.6.2.4 Continue with section 4.5.5

4.6.3 Disk and Solution from section 4.5.23.

4.6.3.1 Perform section 4.6.2

4.6.3.2 Transfer the solution from section 4.6.2.2 into the beaker containing the solution from section 4.5.20. Rinse the emptied beaker with 8M HNO_3 and add to the other beaker.

4.6.3.3 If necessary, acidify the sample with a small amount of concentrated HNO_3 . Evaporate the sample to near dryness on a hot plate. Let the beaker cool. Note qualitatively the amount of salts present.

4.6.3.4 Measure and add 3mL of concentrated HNO_3 and 9 mL of concentrated HCl .

NOTE: This ratio of these acids produces aqua regia, which decomposes the ammonium ion.

Gently heat the beaker on a hot plate until the bubbling and foaming subsides, then heat to near dryness.

4.6.3.5 Note qualitatively the amount of salts now present and compare with that in section 4.6.3.3. If nearly all are not gone, repeat section 4.6.3.4.

4.6.3.6 Continue with section 4.5.1 of this procedure or at the appropriate step of the procedure specified by the cognizant scientist.

4.6.4 Solution Only (from 4.5.23)

4.6.4.1 If necessary, acidify the sample with a small amount of HNO_3 (concentrated). Evaporate the sample to near dryness. Let the beaker cool.

4.6.4.2 Continue with Section 4.6.3.4.

5.0 REFERENCES

Talvitie, N.A., Electrodeposition of Actinides for Alpha Spectrometric Determination, Anal. Chem. 44:280-283, 1972.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-486, (Replaces 7-40.56), TOTAL STRONTIUM - RAPID ANALYSIS FOR URINE

1.0 APPLICABILITY

Strontium is concentrated from urine using a modified version of the alkaline phosphate precipitation method described by Horwitz, et. al.¹ Actinides as well as strontium are co-precipitated along with calcium ammonium phosphate. The precipitate is then dissolved and passed through a strontium specific resin. Strontium is loaded onto the resin and eluted with deionized water and is counted by beta and gamma spectrometry. Procedures PNL-ALO-463 (B counting) and PNL-ALO-267 (gamma counting with NaI).

2.0 DEFINITIONS

- LRB - Laboratory Record Book
 - Reagent Blank - Analysis performed without any sample matrix material under analytical conditions identical to the actual sample analysis.
 - Matrix Blank - Analysis performed using blank sample matrix material under analytical conditions identical to the actual sample analysis.
 - Matrix spike - Analysis performed using blank sample matrix with known amounts of the appropriate spike, under analytical conditions identical to the actual sample analysis.
- Note: If natural blank matrix is not available for spikes or blanks, artificial urine may be used in its place.
- Sample Batch - A group of samples analyzed in parallel of up to 20 samples.

Author	Date	Project Mgr.	Date	QAD Representative	Date
RS Strebin	7/22/92	N/A		TL Ehlert	7/22/92
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LR Greenwood	7/22/92	AG King	7/22/92	All original signatures on file	
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3.0 RESPONSIBLE STAFF

Cognizant Scientist - a chemist or other scientist familiar with this procedure and having an in-depth knowledge of the chemistry taking place.

Analyst - an individual who has been trained in the use of this procedure.

4.0 PROCEDURE

4.1 Reagents

All reagents are prepared from analytical reagent-grade chemicals. Deionized (DI) water, with an electrical resistance of >16 megohm-cm is used throughout this procedure. Concentrations are not critical and need only be within $\pm 10\%$ of stated values. Replace lab-prepared reagents annually, unless otherwise specified.

- . $16M$ HNO_3 - concentrated Nitric Acid
- . $3M$ HNO_3 - 189 mL conc. HNO_3 / liter

Add 189 mL of conc. Nitric Acid to 500 mL DI water in a 1000 mL beaker. Bring volume to 1000 mL with DI water and pour into a labelled one-liter polyethylene bottle.

- . Phosphate Solution (300 mg PO_4^{-3} /mL)

Weigh 140 g $(NH_4)_2HPO_4$ into a 500 mL beaker. Add DI water until the volume is about 200 mL. Heat gently and stir until salt is completely dissolved. Cool and bring volume to 300 mL. Filter through glass wool two times and store in labelled 500 mL screw cap bottle.

- . Ca Carrier (50 mg Ca^{+2} /mL)

Weigh 100g $Ca(NO_3)_2 \cdot 4H_2O$ into a 500 mL beaker. Add DI water until volume is about 200 mL. When dissolved, bring volume to 300 mL. Filter through Whatman No. 2 filter paper or equivalent and collect filtrate in a labelled screw cap bottle.

- . Eluting Solution (DI water).
- . Spike Solution Sr-90: 2000 to 3000 dpm/ml traceable to NIST. The preparation shall be documented.

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- . Tracer - Sr-85 ~1000 dpm/mL. Measure and record value used.
- . 2-octanol
- . NH_4OH - concentrated ammonium hydroxide
- . SR-SPEC resin - Eichrom Industries, Inc.

Resin is commercially available as SR-SPEC material from Eichrom Industries, 1801 Maple Ave. Evanston, IL 60201; phone number (708) 491-4958.

- . $2\text{M Al}(\text{NO}_3)_3$

Weigh 750.3 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ into a 1500 mL beaker. Add deionized water until volume is approximately 900 mL. Dissolve salt, warm to room temperature, and dilute to 1000 mL. Purify solution by passing it through a 1/4 inch i.d. column filled to 5 cm with BIO-RAD Anion Exchange resin AG 1-X8, 100-200 mesh or equivalent resin.

- . Column Feed Solution: 2M HNO_3 - $0.5\text{M Al}(\text{NO}_3)_3$

Pour 500 mL $2\text{M Al}(\text{NO}_3)_3$ (purified) into a 2000 mL volumetric flask. Add 250 mL conc. HNO_3 . Bring to 2000 mL volume with deionized water.

4.2 Equipment and Material

- . Centrifuge
- . Centrifuge tubes, 50 mL
- . Ion exchange columns: disposable, 5.0ml polyethylene pipets.
- . Glass wool
- . Cotton
- . Rubber Gloves - assorted sizes
- . Hot water bath
- . Glass beakers, 50, 500, 1000, and 1500 mL
- . Pipetter, adjustable 100 μL to 1mL
- . Pipetter, adjustable 1mL to 5mL

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- . Graduated cylinders - 100 mL
- . Graduated cylinder, 500ml Class A, Certified
- . Beaker tongs
- . Magnetic stirring hot plates
- . 5-mL Volumetric flasks (class A, certified)
- . 2000 mL Volumetric flasks (class A, certified)
- . Teflon or glass coated magnetic stirring bars
- . 15 mL. screw cap vials with polyseal closures
- . .5 dram screw cap vials
- . Beta dishes heated on hot plate for about 10 minutes or until dish darkens

4.3 Quality Control Instructions

Yield monitors (tracers) and QC spikes shall be prepared by the Analytical Laboratory and shall be distributed appropriately for use during sample analysis.

- 4.3.1 Prepare a minimum of one reagent blank and one matrix blank and one matrix spike per sample batch or as directed by the statement of work.
- 4.3.2 One time procedural variations are allowed if deemed necessary by the professional judgement of the cognizant scientist to accommodate variation in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variation in procedure shall require documented approval by the cognizant scientist and verbal notification of Internal Dosimetry, including sample numbers. The variation in procedure shall be recorded in the LRB or on a data sheet. Reported data shall be flagged to indicate a deviation in procedure along with an explanation of the deviation specifics.
- 4.3.3 A copy of all quality control data and instructions shall be maintained in the LRB or on a data sheet and be available for easy reference or inspection.

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4.4 Sample Preparation

Except where noted, all sample volumes used in this procedure are given to within +/-10%. Critical volume measurements shall be made with calibrated or certified pipetters and glassware. These latter measurements are identified by the fact that notation shall be called for and documented in the LRB or on a data sheet regarding the calibration or glassware used.

When an added volume is a feature of the general calculation, a performance check of the automatic pipette shall be completed before and after each sample set for each volume to be measured. Pipet and weigh at least three aliquots of D.I. water equal to the volume being used, into a container in the balance. Calculate the average weight. Correct the weight measured for temperature effects on the volume (or density) using the formula:

$$\text{measured weight (g)} / d \text{ (g/ml)} = \text{volume (ml)}$$

The value of d is dependent on the ambient temperature and is found in the temperature versus density conversion table in the Handbook of Chemistry and Physics (see exhibit A). Record all data in the LRB or on a data sheet.

- 4.4.1 Measure the total sample volume using an appropriately sized Class A certified graduated cylinder. Note the volume measured and Class A cylinder plus the date and time of sample receipt, CML number, and client's name in the LRB or on a data sheet.

Take the total spot sample, or a 300 mL aliquot measured with a Class A graduated cylinder, and put into a nominally 500 mL beaker containing a large (at least 2 inches) stirring bar. Record the sample volume taken in the LRB or on a data sheet.

- 4.4.1.1 If the volume is less than 300 mL, make up to 300 mL with DI water.

- 4.4.1.2 Using a calibrated pipete, add about 400 dpm of Sr-85 yield monitor to all samples, reagent blanks, matrix blanks, and matrix spikes (hereafter collectively called samples). Also add the same amount to a yield control sample consisting of about 3ml DI H₂O; bring to a 5ml volume with DI H₂O using a class A volumetric flask. Set this latter solution aside for gamma counting and beta counting. Record the volume

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of ^{85}Sr yield monitor measured and identification in the LRB or on a data sheet.

- 4.4.1.3 Add about 200 dpm of Sr-90 spike solution to the matrix spike solution using a calibrated pipete. Record the volume measured and standard identification in the LRB or on a data sheet.
- 4.4.2 Place sample on a magnetic stirrer and add 2 drops of 2-octanol, 30 mL conc. HNO_3 (add very slowly), and then 2 mL of Ca carrier solution. Stir for 5 minutes.
- 4.4.3 Heat at approximately 90 degrees C for 2 hours in a water bath. Leave in up to 3 hours if time is available.
- 4.4.4 Transfer the yield control sample (from step 4.4.1.2) to screw cap bottle. Using a calibrated pipet, measure 2 ml into a 2 ml screw cap bottle for gamma counting. Perform gamma count according to procedure PNL-ALO-267. Using a calibrated pipet, plate 2 ml of the yield control sample (from step 4.4.1.2) onto a beta counting dish. Proceed with procedure PNL-ALO-463 (beta counting procedure). Count the yield control sample on each regular beta counter for 30 minutes.
- 4.4.5 Return the sample beaker to the stirrer and stir for approximately 5 minutes.
- 4.4.6 Continue stirring while adding 10 mL of phosphate solution.
- 4.4.7 While rapidly stirring, form the precipitate by very slowly adding 55 mL of concentrated NH_4OH . Continue stirring for approximately another 5 minutes.
- 4.4.8 Allow calcium-ammonium phosphate to settle for approximately five minutes.
- 4.4.9 While stirring, add 1 mL of calcium carrier and mix the solution well. Allow the precipitate to settle for approximately five minutes.
- 4.4.10 Repeat 4.4.9. Remove the stir bar then allow the precipitate to settle for at least 1 hour. Leave overnight if time is available.
- 4.4.11 Decant and retain the supernate until analyses are completed and reported. Transfer the precipitate to a

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50 mL centrifuge tube and spin for 5 to 10 minutes or until a clear supernate is obtained. Decant and discard the supernate.

- 4.4.12 Dissolve the precipitate with 5 mL of conc. HNO_3 and transfer back to the original beaker. Rinse the centrifuge tube with another 5 mL of conc. HNO_3 and transfer the rinse to the original beaker. Cover the beaker with a watch glass.
- 4.4.13 Transfer the beaker to a hot plate and evaporate the sample to dryness. Continue heating until evolution of fumes stop. The beaker is then removed from the hot-plate and allowed to cool for 2 to 5 minutes.
- 4.4.14 Add 5 mL of concentrated HNO_3 cover with a watch glass and repeat section 4.4.13 until residue is pure white (usually 3 cycles total).
- 4.4.15 Dissolve the white residue completely with 10 mL. of column feed solution ($0.5\text{M Al(NO}_3)_3$ - 2M HNO_3).
- 4.4.16 Prepare a resin column using a 5-mL polyethylene disposable pipet with the top half centimeter removed. Place a small portion of cotton or glass wool at the tip of the column and lightly compress. Wash the column with DI water. Add 600 lambda of Sr-SPEC resin (Soaked in 3M HNO_3 or H_2O) to the column. Place a small portion of the glass wool on top of the column bed. Wash the column with 2 mL of 3M HNO_3 , followed by 2 mL of $0.5\text{M Al(NO}_3)_3$ - 2M HNO_3 .
- 4.4.17 Pass the analyte solution from section 4.4.15, one mL at a time through the column. Collect the effluent in an appropriately marked beaker or poly bottle.
- 4.4.18 Wash the analyte solution beaker with 2 mL of column feed solution ($0.5\text{M Al(NO}_3)_3$ - 2M HNO_3) and pass one mL at a time through the column. Collect the effluent in the same beaker or bottle as used in step 4.4.17.
- 4.4.19 Pass 2 mL of 3M HNO_3 (500 lambda at a time) through the column. This removes the column feed solution from the column. Collect the effluent in the same beaker or bottle as in step 4.4.17.
- 4.4.20 Elute Sr from the column with 5 mL (1 mL at a time) DI water. Collect the eluant in a certified, Class A 5 mL volumetric flask labelled with the sample identification.

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Record time sample elution started. Make the volume to 5mL with DI water. Add a stir-bar and stir on magnetic stirrer or parafilm the top and shake well. Transfer to 15 mL vial for pipetting.

- 4.4.21 Using a calibrated pipette, plate 2 mL of the eluant on the beta counting dish and dry under heat lamp.
- 4.4.22 Using a calibrated pipette, measure 2 ml of the sample solution into a 1/2 dram glass vial. Count the sample for gamma activity according to Procedure PNL-ALO-267.
- 4.4.23 Send beta plates to counting room for beta counting, Procedure PNL-ALO-463.

Note: Beta counting shall be performed within 3 hours of the separation (Step 4.4.20) to avoid the need for ⁹⁰Y correction.

5.0 CALCULATIONS

The ^{89&90}Sr recovery is determined by the yield of the ⁸⁵Sr. Strontium-85 is determined by gamma spectrometry; Strontium is determined by beta counting. Due to the need for rapid 89 & 90 data reporting, no check is made for ⁸⁹Sr.

The value d/c is disintegrations per count and is determined using known standards and is unique for each detector. The determination of this value is found in the beta counting procedure PNL-ALO-463.

⁸⁵Sr yield = (cpm ⁸⁵Sr obtained from separation)/(cpm ⁸⁵Sr yield control added)

The corrected background count based on ⁸⁵Sr interference = ((100% beta counts of the ⁸⁵Sr beta plate spike)-(instrument background c/m*minutes ⁸⁵Sr spike counted))*(⁸⁵Sr yield for the sample)+(background c/m * min. sample is counted)

net ^{89&90}Sr beta = sample counts - corrected background counts

^{89&90}Sr dpm/sample = ((net ^{89&90}Sr beta counts)/(minutes sample counted)) x d/c x 5/2 / (⁸⁵Sr yield of sample)

decay correction for ⁹⁰Sr C = (Co/2) e exp (0.693((days from Co calib.)/365.25d/y)(28.5y))) where Co equals the original ⁹⁰Sr concentration and C equals ⁹⁰Sr concentration on the count day.

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The factor (5/2) corrects for the dilution when the sample was split for the gamma and beta analyses.

6.0 EMERGENCY REPORTING

Report activities immediately by telephone to PNL Exposure Evaluator (376-2222). Be sure to include:

1. Individual's name and payroll number
2. Volume of sample received
3. Volume of sample analyzed.
4. Sample date and sequence if one of multiple samples.

Document the following in the LRB or on a data sheet:

1. Date and time sample received at PNL
2. Date and time results reported and name of person taking message
3. QC data results, tracer and radiochemical recovery.

Mail a copy of the sample I.D. and analytical results to Internal Dosimetry, A3-60, within 2 working days after analysis is completed.

7.0 WASTE DISPOSAL

Unused sample portions are to be kept for 30 days after the report is submitted to Internal Dosimetry. Then excess samples may be disposed of by flushing down a toilet, provided the analysis results (including ^{85}Sr) show less than 7×10^3 pCi/L (15 dpm/mL). Otherwise, the sample must be disposed of using approved procedures for contaminated liquids.

8.0 SPECIFIC QUALIFICATION

None.

9.0 REFERENCES

1. Horwitz, E. P., Dietz, M. L., Nelson, D. M., LaRossa, J. J., and Fairman, W. D., "Concentration and Separation of Actinides from Urine Using a Supported Bifunctional Organophosphorus Extractant," Analytica Chimica Acta, 238 (1990) 263-271.
2. Horwitz, E. P., Dietz, M. L., and Fisher, D. E., "Separation and Preconcentration from Biological and Environmental Samples by Extraction Chromatography Using a Crown Ether," Analytical Chemistry, Vol. 63, No. 5 (1991).
3. Maiti, T., Experimental work recorded in LRB or on a data sheet #53497, pgs 39-44, 1990.

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4. Relative Density and Volume of Water, p. 2198, Handbook of Chemistry and Physics, 44th Edition, Chemical Rubber Publishing Co.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-487, (Replaces 7-40.63), TRITIUM IN URINE BY THE METHOD OF STANDARD ADDITION-RAPID AND NORMAL PROCEDURES

1.0 APPLICABILITY

This procedure is applicable to the measurement of tritium (H-3) in urine. Following sample preparation using this procedure, procedure PNL-ALO-488 is used for liquid scintillation counting of the samples.

2.0 DEFINITIONS

- dpm - Disintegrations per minute, number of atoms which undergo radioactive decay in one minute
- pCi/L - PicoCuries per liter, a radioactivity concentration term. One picoCurie/L equals 2.22 dpm per liter
- LRB - Laboratory Record Book
- LSC - Liquid Scintillation Counter
- ALO log number - A number assigned by the Analytical Laboratory Operations, as defined in Procedure PNL-ALO-010
- ARF - Analytical Request Form
- NIST/SRM - National Institute of Standards and Technology/Standard Reference Material
- Sample set - Any group of samples of 20 or less. At least two blanks and one "spiked" blank shall be processed along with each sample set.
- Spiked sample/blank - A sample/blank to which a radioisotope (i.e. H-3) has been added.

Author	Date	Project Mgr.	Date	QAD Representative	Date
JH Kaye	10/11/90	N/A		GK Gerke	10/12/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LR Greenwood	10/11/90	HH Van Tuyl	10/11/90	All original signatures on file	
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3.0 RESPONSIBLE STAFF

Cognizant Scientist - a chemist or other scientist familiar with this procedure and having an in-depth knowledge of the chemistry and counting methods involved.

Analyst - an individual who is qualified in the use of this procedure, and for whom this has been documented in the analyst's qualification training records. An analyst shall be considered qualified when 3 spiked samples have been analyzed by this procedure for which the results agree within $\pm 10\%$ of the known values.

4.0 PROCEDURE

4.1 General

For each analysis, two aliquots of a sample are pipetted directly into separate scintillator solutions. To one of these a known amount of H-3 standard is added. These are transferred to the sample changer of a liquid scintillation counter for 1 to 24 hours before counting is begun. This waiting period allows temperature equilibrium to be reached and the decay of excitation within the plastic vials. When the samples are counted, the counting rate of the spiked sample, containing a known amount of H-3, is compared to that of the unspiked sample. This approach, known as the method of standard additions, allows determination of the amount of H-3 in a sample without knowledge of quenching parameters and counting efficiency.

4.2 Reagents

- Low tritium blank water, e.g., Montana deep well water (< 2 dpm H-3))
- Scintillation cocktail - Packard Opti-Fluor
- Tritium standard (spike) - Water containing a known amount of tritium, the activity of which shall be traceable to NIST. Specific information on this standard shall be recorded in the LRB for Bioassay Sample Analysis
- D.I. water, >16 megohms-cm resistance

4.3 Equipment and Materials

- Surgeon's gloves, rubber, various sizes
- Automatic pipet (fixed or adjustable) for pipetting 50 μ L and 4 mL aliquots.
- 25 mL plastic scintillation vials

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- Pipet, Class A certified
- Graduated cylinder, Class A certified, 50, 100, 250 mL, 1L, and 2L
- 0-25 mL Repipet (accuracy $\pm 1\%$ full scale, reproducibility $\pm 0.1\%$ full scale) attached to bottle of scintillation cocktail, set to deliver a nominal volume of 19 mL
- Kimwipes
- Microbalance, capable of weighing to ± 0.1 mg.
- Vortex stirrer
- Disposable filter unit with 0.45 micron cellulose filter

Note: Filter unit may consist of either one or two pieces. If it is one piece, put a coat of vacuum grease around the connection between the filter and reservoir. If it is two pieces, it should have a rubber gasket between the filter and reservoir. If not, use same procedure as for the one piece unit.

- 50-ml graduated, conical centrifuge tube with cap

4.4 Safety Precautions

Urine samples may contain harmful micro-organisms in addition to radioactivity. Rubber gloves, checked for air leaks, shall be worn at all times until samples are ready for counting. Gloves shall be discarded after each sample set. If an analyst suffers a puncture wound at any time when working with these samples, he/she shall immediately stop work, get surveyed and report to First Aid.

4.5 Analysis

For each sample set, at least two blanks shall be analyzed. Each sample in the set shall be run in duplicate. Each duplicate analysis shall consist of one unspiked and one spiked aliquot of sample. Assign each sample a number, which shall be cross-referenced in the LRB to the ALO log number and client's name. For those samples which are spiked, record the amount of spike added. Label the blanks BK1 and BK2.

NOTE: Example of Vial Labelling- for a set consisting of two samples:

For first sample

1a	(unspiked aliquot)
1b	(duplicate)
1a + 50	(aliquot with 50 lambdas H-3 spike)
1b + 50	(duplicate with 50 lambdas H-3 spike)

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For second sample

2a
2b
2a + 50
2b + 50

For blanks

BK1
BK2

- 4.5.1 Note the date the sample was received, ALO log number, and client's name in the LRB. For emergency and expedite samples, note the time of sample receipt.

NOTE 1: Steps 4.5.2 and 4.5.3 are unnecessary if an adequate amount of washed activated charcoal is on hand.

- 4.5.2 Wash up to 500 ml of activated charcoal a minimum of three times with twice the volume of deionized water each time. Stir the charcoal well each time before decanting off the black-colored liquid.
- 4.5.3 Distribute the charcoal onto large watchglasses and dry in a drying oven set below 100 F. Alternatively, spread the charcoal onto a sheet of aluminum foil and place on a hotplate at a setting of 3, until dry.
- 4.5.4 Put 25-30 ml of charcoal into a 50-ml graduated, conical centrifuge tube. Add a minimum of 25 ml of urine. Cap and shake vigorously.
- 4.5.5 Let stand a minimum of 1 hour, or until the urine looks colorless (except for the black color from the charcoal particles).
- 4.5.6 Centrifuge for a minimum of 5 minutes.
- 4.5.7 Pour the centrifuged urine through a 0.45 micron filter in a disposable filter unit.
- 4.5.8 Pour the filtered urine into a labeled beaker.
- 4.5.9 Put 19 mL (± 2 mL) scintillation cocktail into each vial with Repipet apparatus, and label as shown above.

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4.5.10 NOTE: A performance check of the automatic pipetter shall be completed before and after each sample set. Pipet and weigh at least 3 aliquots of 50 μ l and 3 of 4 mL of D.I. water into a container in the microbalance. Measure ambient temperature and use temperature vs density table (see reference (c)) to determine delivered volume of aliquots. The 4 ml aliquot must agree to within $\pm 1\%$ of the pipetted volume; the 50 μ l aliquot must agree to within $\pm 2\%$ of the pipetted volume. If this is not the case, repair or discard the pipetter. Record all data in the pipet record LRB.

4.5.11 Pipet 4 mLs of sample 1 with a 4 mL automatic pipet into scintillation vials 1a, 1b, 1a + 50, 1b + 50. Repeat for each sample. Mix each vial by shaking by hand or using a vortex stirrer for 1 minute or until solution is clear, whichever comes first.

NOTE: Fresh samples which show evidence of precipitation or varying degrees of cloudiness shall be stirred for 20 sec before and during aliquotting. Samples older than 30 days will not be stirred.

4.5.12 Pipet 4 mLs of blank (low tritium distilled water) into the scintillation vials marked BK1 and BK2 with 4 mL automatic pipet and mix each for 20 seconds with the vortex stirrer or hand shaking.

NOTE: The method used to determine that the activity of the blank is < 2 dpm in tritium shall be documented in the Bioassay LRB.

4.5.13 Pipet 50 μ l of H-3 spike solution into vials 1a + 50, 1b + 50, etc.. Mix thoroughly with a vortex stirrer or shaking by hand for 20 sec and wipe outside of all vials with Kimwipes to remove smudges and fingerprints.

4.5.14 Package all vials, survey, and take to the counting room for LSC counting.

4.5.15 Count samples as follows: Emergency and Priority - 10 minutes unspiked, 1 minute spiked; Routine - 30 minutes unspiked, 1 minute spiked. Spiked or hot samples may also be counted with a preset of 1% (2σ)

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counting statistics. Count blanks for 30 minutes. Document counting results by taping final report summary or copy in Bioassay LRB. Store original LSC counting printout in a 3-ring binder specifically designated for the Bioassay Program.

- 4.5.16 Measure the remaining volume of each sample using an appropriately sized Class A graduated cylinder. Note the cylinder lot number and volume (add the 16 ml from the previous sampling) in the LRB.

4.6 Calculations

4.6.1 Tritium Activity in Sample

The tritium activity in the sample (sa) is given by:

dis/min/mL H-3 (sa) =

$$\frac{\text{net c/min (sa)} \times \text{mL (std)} \times \text{dis/min/mL (std)}}{(\text{c/min (sa+std)} - \text{c/min (sa)}) \times \text{mL (sa)}}$$

where

net c/min (sa) = c/min (sample) - c/min (blank)

c/min (sa+std) = c/min (sample + std)

dis/min/mL (std) = H-3 activity per mL of standard, decay corrected to time of count

The result in pCi/L is given by

pCi/L = dis/min/mL x 450.45

4.6.2 Uncertainty in Tritium Estimate

Since the counting rate of the sample with spike added will be much higher than without, the uncertainty in the tritium estimate will be dominated by the uncertainty in the net counting rate of the unspiked sample.

Let G = gross counts in sample = c/min (sample) x t (sample)

where t (sample) = counting time of sample (w/o spike)

Let B = counts in blank = c/min (blank) x t (blank)

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where $t(\text{blank})$ = counting time of blank

Let $k = t(\text{sample})/t(\text{blank})$ = counting time factor

Let N = net counts in sample

$$N = G - Bk$$

$$\text{uncertainty in net counts (sa)} = \sqrt{G + Bk^2(1\sigma)}$$

Let U = uncertainty in H-3 estimate (1σ)

$$U = \text{dis/min/mL H-3 (sa)} \times \frac{\sqrt{G + Bk^2}}{N}$$

- 4.6.3 Record liquid scintillation counting results in the LRB. Record dis/min/mL and/or pCi/L results and uncertainties on the analytical report form.

4.7 Emergency and Normal Reporting

- 4.7.1 Report results immediately (Emergency samples only) by telephone to PNL Exposure Evaluator (376-2222). Be sure to include:

Individual's name and P.R. number
Volume of urine received and analyzed

- 4.7.2 Document the following in the LRB:

1. Date (and time for emergency and expedite) sample(s) was (were) received at PNL
2. Date and time results were called in and name of client taking message
3. Counting results for each sample, spiked sample and blank

- 4.7.3 Mail a copy of the sample I.D. and analytical results to Internal Dosimetry (A3-60) within 2 working days after analysis is completed for emergency samples and within 5 working days for all other samples.

4.8 Archiving and Storage

Save 25 mL (± 5 mL) of each sample in a labelled scintillation counting vial for a period of 30 days or until another sample from the same individual is received.

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4.9 Sample Disposal

Disposal of excess and archived samples by flushing down a toilet is only permitted if the H-3 activity is less than $2 \times 10^{-4} \mu\text{Ci/ml}$ (PNL MA-8, Section 12, Liquid effluents) and it is known that no other activity is present. If this is not the case, dispose of the samples as radioactive liquid waste. All human excreta has been found to be nonradioactive according to the criteria in PNL-MA-6, Section 7.3, namely, less than 100 pCi/mL alpha and 400 pCi/mL beta/gamma activity.

5.0 REFERENCES

- (a) Beckman LS8000 Series, "Liquid Scintillation System - Operations, Installation, and Maintenance Manual," 1977. Beckman Instruments Inc., Fullerton, CA.
- (b) United Technologies/Packard 4000 Series, Liquid Scintillation Counting, Model 4430 Operation Manual, REV. A, 1983.
- (c) Relative Density and Volume of Water, p 2198, Handbook of Chemistry and Physics, 44th Ed., Chemical Rubber Publishing Co.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-488 (replaces 7-40.64); LIQUID SCINTILLATION COUNTING
PROCEDURE FOR MEASUREMENT OF TRITIUM IN URINE BY METHOD OF STANDARD
ADDITIONS

1.0 APPLICABILITY

This procedure is applicable to the measurement of tritium in urine samples by liquid scintillation counting, utilizing the method of standard additions. It is written specifically for the Beckman Model LS-8000 system in 329 building; however, it is applicable to other LSC systems with minor alterations. For emergency or expedite samples, a backup counter will be used in Building 325. (See Procedure PNL-ALO-490, Rev. 0)

2.0 DEFINITIONS

- dpm - disintegrations per minute, number of atoms which undergo radioactive decay in one minute
- pCi/L - picoCuries per liter, a radioactivity concentration term. One picoCurie/L equals 2.22 dpm per liter
- LRB - Laboratory Record Book
- LSC - Liquid Scintillation Counting

3.0 RESPONSIBLE STAFF

Cognizant Scientist - A chemist or other scientist familiar with this procedure and having an in-depth knowledge of the principles involved and the instrument being used.

Analyst - An individual who is qualified in the use of this procedure, and for whom this has been documented in the analyst's qualification training records. An analyst shall be considered qualified when 3 spiked samples have been analyzed by this procedure for which the results agree within $\pm 10\%$ of the known (spiked) values.

Author	Date	Project Mgr.	Date	QAD Representative	Date
JH Kaye	10/11/90	N/A		GK Gerke	10/12/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LR Greenwood	10/11/90	HH Van Tuyl	10/11/90	All original signatures on file	
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4.0 DESCRIPTION OF SYSTEM

The LSC system in 329 building is designed for counting ^3H , ^{14}C , ^{32}P and other beta-emitters. However, virtually all alpha, beta, x-ray, positron, and gamma emitters, properly prepared, can be counted by LSC methods.

The Beckman model LS-8000 is a two-channel spectrometer with a 300-sample capacity. The instrument utilizes microprocessor technology and is equipped with a Graphic Display, ten factory-installed counting programs (Library Programs) in an unalterable memory, keyboard with program editing feature, and an interrupt function. The system is provided with a Teletypewriter for data readout, a Bar Graph Display, and a Random Coincidence Monitor.

5.0 INTERNAL STANDARDIZATION COUNTING METHOD

An internal standardization counting method is utilized for measurement of tritium in urine because it allows measurement of the tritium activity without the need to determine quenching parameters. In this method, one aliquot of sample is counted directly, and an identical aliquot is counted after spiking with a known amount of the radionuclide to be determined, in this case tritium. A blank is also counted so that the net counting rate of the unspiked sample can be determined. The tritium activity is then calculated as described in Procedure PNL-ALO-487.

6.0 COUNTER PERFORMANCE TESTING

Sealed ^3H , ^{14}C and blank standards (Beckman Nos. H277092, C277066 and B11080, respectively) shall be counted before and after each set of samples. The counting rates of the ^3H , ^{14}C and blank standards shall be recorded in the LSC notebook and plotted on the control charts which will be maintained in the LSC notebook. These counting rates shall be compared with previous counting data to document satisfactory system operation. The standards and their certification are:

C277066 = $\pm 10\%$ (NBS Benzoic Acid/Carbon-14 standard #4925)
H277092 = $\pm 10\%$ (NBS Toluene/Tritium standard #4947)
B11080 = $\pm 25\%$ (pure toluene in POPOP)

Control charts shall be set up and maintained as per reference (c) (see Attachment A), utilizing counting data for the above standards. Criteria described in this reference shall be used to determine that the method is in control or the action to be taken if this is not the case.

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7.0 SAMPLE COUNTING PROCEDURES

- 7.1 Transfer the blank, spiked and unspiked sample counting vials into the automatic sample changer. Allow a minimum of one hour for stabilization prior to counting samples.
- 7.2 Recall the operator's number and check that the required counting times are specified as per Procedure PNL-ALO-487, and that the lower and upper limit values for CH 1 and CH 2 are the same as in Attachment B of this procedure. Modify the program as necessary. This program will be automatically printed out with the data and becomes part of the hard copy record of the measurements.
- 7.3 Start the automatic counting procedure.
- 7.4 Hard copy printouts of the data include the sample position number, count rate (in counts per minute), counting uncertainty, counting time and elapsed time since the automatic counting sequence was started. Original or copies of the printouts of the counting data shall be transferred to the Bioassay LRB. The sample position number shall be referenced to the corresponding sample in the LRB.

8.0 CALCULATIONS

Calculations for tritium in urine by the standard additions method are included in Procedure PNL-ALO-487.

9.0 REFERENCES

- (a) Beckman LS 8000 Series, "Liquid Scintillation System - Operations, Installation and Maintenance Manual," 1979. Beckman Instruments, Inc., Fullerton, CA.
- (b) 566321 Liquid Scintillation Standards Set, Beckman Instruments, Inc., Fullerton, CA 92634, September 1972.

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ATTACHMENT A

7.0 QUALITY CONTROL

7.1 CONTROL ANALYSES

Control data include items identified in Section 7.2 and specific requirements of analytical procedures. Results shall be documented in data records, which may be commingled with sample data (e.g., in a LRB). Actions taken to regain control shall be documented in data records.

7.2 STATISTICAL PRACTICES

Statistical practices used to treat analytical measurements are given below. Definitions of the statistical terms used are found in MCS-033.

(a) Control Charts - Prepare control charts according to the following procedure:

1. Obtain a group of at least nine measurements over a period of at least three working days.
2. Calculate the average () for the group.
3. Calculate the standard deviations.
4. Calculate the upper control limit (UCL) and the lower control limit (LCL) as follows:
$$UCL = + 3s$$
$$LCL = - 3s$$
5. Prepare a control chart to plot measurements obtained against the order in which the measurements were obtained, with control lines corresponding to, UCL and LCL.
6. Plot each measurement from the standard in the order obtained.

(b) Method Out of Control - The following criteria establish when a method is out of control. When that happens, the problem shall be investigated and the steps taken to bring the method back into control shall be documented in the data records. Samples shall not be analyzed using a method that is out of control.

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1. If a point falls outside a control limit, immediately run another standard. If the second measurement falls outside, the method is out of control.
 2. If the second standard falls within the control limits, run a third standard. The measurements from this third standard determines whether the method is in or out of control.
 3. If consecutive standard values plotted on the control chart begin to drift toward a control limit, the method may be going out of control and the situation shall be investigated and recorded in LSC notebook.
- (c) Outlying Observations - When evaluating a series of measurements and one (or more) value appears to deviate significantly from the other values, a decision must be made about how to treat the outlier(s). The outlier shall be discarded if it can be substantiated that the outlier resulted from a specific error. Justification for discarding the outlier shall be documented in the LSC notebooks. Otherwise, the outlier shall be included with the series of measurements. The outlier shall be documented in the data records as being suspect.

7.3 LIMITS OF ERROR

Limits of error for all measurements made during an analysis shall be specified in some manner. If a limit is not stated with a measurement value, then the following system of limits of error shall be in effect:

- (a) When two or more significant figures are specified, the limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g ($4.5E+2$) means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL. (The example of 450 g is included to show that zeros before the decimal point are not considered to be significant figures).
- (b) If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

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ATTACHMENT B

00668

PROG	1	USER	1
CNT CH	12	1 TIMES	
CSS		1 TIMES	
SCR	=2/1		
AQC	=NO		
RCM	=NO		
CALC	=	1	
PST	=	100.00 MIN	
QCF	=	0 H#	
CH 1		1.00 2 SIGMA %	
		.0 LSR	
		.0 BKG	
		.00 2 SIGMA B	
		0 LL	
		397 UL	
CH 2		1.00 2 SIGMA %	
		.0 LSR	
		.0 BKG	
		.00 2 SIGMA B	
		180 LL	
		397 UL	

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-489, (Replaces 7-40.65, & HTA-4-35), SOLUTIONS ANALYSIS:
AMERICIUM AND CURIUM ISOTOPES BY CATION AND ANION EXCHANGE
SEPARATION

1.0 APPLICABILITY

This procedure applies to the preparation of aqueous samples, including brine, for the determination of americium and curium isotopes.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst - See 5.5

4.0 QUALITY CONTROL REQUIREMENTS

For all QA level I and II projects, a spiked sample (spiked matrix), and a methods blank (simulated sample matrix solution) will be processed with every separation group, or as directed in a Request for Analytical Services (RFAS) or Test Instructions (TI).

Project specific quality control, if different from above will be specified in a TI or RFAS.

5.0 PROCEDURES

5.1 Equipment and Materials

- Nitric acid, 1 M -- Dilute 63 (±1)mL of concentrated reagent-grade acid (HNO_3) to 1000 (±1)mL with deionized water; mix thoroughly.
- Nitric acid, 1.85 M -- Dilute 117 (±1)mL of concentrated reagent-grade acid to 1000 (±1)mL with deionized water; mix thoroughly.
- Nitric acid, 8 M -- Dilute 506 (±1)mL of concentrated reagent-grade acid to 1000 (±1)mL with deionized water, mix thoroughly.

Author	Date	Project Mgr.	Date	QAD Representative	Date
AE Kozelisky/TC Maiti	11/15/90	N/A		GK Gerke	11/20/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
BM Gillespie	11/10/90	LR Greenwood	11/20/90	All original signatures on file	
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- Pipet, glass, serological, disposable, Kimble 72120, 10 mL x 1/10 mL, with top removed.
- Ion exchange resin, AG-50W®, X-8, 200 to 400 mesh, or equivalent, H⁺ form. Prepare by mixing in a volume of deionized water about 5 times the volume of the resin. Allow resin to settle until only suspended fines remain. Decant the water to remove the fines. Repeat the mixing, settling, and decanting two or three times. Store resin in deionized water.
- Cation column, 3mL -- Prepare cation column of AG-50W®, X-8, 200 to 400 mesh, H⁺ form resin. Fill the tip of a glass pipet with cotton to $\approx$ Mark 9, or about $\frac{1}{2}$ -inch. Measure a volume of 3 mL above the cotton and mark. Fill the pipet to the mark with the resin.
- Anion exchange resin, AG-1®, X-4, 100 to 200 mesh, or equivalent, Cl⁻ form. Prepare by mixing in a volume of deionized water about 5 times the volume of the resin. Allow resin to settle until only suspended fines remain. Decant the water to remove the fines. Repeat the mixing, settling, and decanting two or three times. Store resin in deionized water.
- Anion column, 500 μ L ($\pm$ 50 μ L) -- Prepare anion column of AG-1®, X-4, 100 to 200 mesh, Cl⁻ form resin. Remove the top of the bulb from a 7.5-mL plastic dropper. Place a small cotton ball into the tip of the dropper and tamp lightly. Measure a volume of 500 μ L above the cotton and mark. Fill the dropper to the mark with the resin.
- Hydroxylamine Hydrochloride, 5 M -- Dissolve 34.8 ($\pm$ 0.1) g of hydroxylamine hydrochloride in 100 ($\pm$ 1)mL of deionized water; mix thoroughly. Prepare fresh every two weeks.
- Vials, 15-mL, 35-mL, glass.
- Droppers, 7.5-mL, plastic.
- Stir bar, glass, 1/2-inch.
- Heat lamp, infrared.
- Disk, 7/8-inch, stainless steel.
- Heating Block.
- Hot plate.

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5.2 Calibration of Equipment and Volume Determination

Recorded volumes shall be determined on a calibrated balance. The volume dispensed shall be determined as follows:

Dispense an aliquot and record the weight, then tare the balance. Repeat four more times. Record the temperature. Average the weights and multiply by the volume factor (Ref. 1) for the recorded temperature. Record the pipet number, volume dispensed, the weights, temperature, volume factor, and calculation in the LRB. The result of the calculation yields the determined dispensed volume and is recorded on the Analytical Report form.

The balance is performance checked prior to any volume determination on a daily-as-used basis, per PAP-70-1201.

5.3 Separation

The americium and curium isotopes are separated from other radionuclides by loading onto a cation exchange resin column and washing brine as well as Cs^{137} and Sr^{90} from the column with 1.85 M nitric acid. The americium, curium, and plutonium are eluted from the column with 8 M nitric acid. The plutonium is removed by loading onto an anion exchange column while the americium plus curium pass through. The americium and curium isotopes are then measured and resolved by alpha counting and alpha spectrometry.

Recoveries are estimated at $94\% \pm 2\%$. Data from Am^{241} plus brine recovery tests are located in notebook HEDL-N-3472, pp. 52-53. Normally the sample calculation does not include any bias correction.

The volumes in this procedure do not require a tolerance due to their non-critical nature. Manufacturer's specifications meet this procedure.

- 1) To a 15-mL vial the ANALYST shall add up to 1 mL of sample. Record the sample volume on the analytical report. Add 200 μL of 5 M hydroxylamine hydrochloride.
- 2) Place the vial in a 90°C ($\pm 5^\circ\text{C}$) heating block and heat for 35-45 minutes. Cool for 10 minutes.
- 3) Add 5.0 mL of 1.85 M HNO_3 to the 15-mL vial.
- 4) Using a plastic dropper, mix the solution in the 15-mL vial from Step 3. Carefully transfer the solution, 1-mL at a time, to the 3mL cation in glass column by slowly running the solution down the side of the glass. Allow each 1-mL portion

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to drain completely before adding the next. **DO NOT DISTURB** the resin bed. Collect the effluent as waste in a 35-mL vial.

- 5) Wash the 15-mL vial with six 5-mL portions of 1.85 M HNO_3 and transfer the solution slowly into the column. Allow each portion to drain completely before adding the next. Collect the effluent as waste in a 35-mL vial.
- 6) Elute the americium and curium isotopes with five 2-mL portions of 8 M HNO_3 . Allow each 2-mL portion to drain completely before adding the next. Collect the effluent in a 15-mL vial.
- 7) Heat the 15-mL vial containing the americium and curium for 15 (± 2) minutes at 80°C ($\pm 5^\circ\text{C}$). Cool for at least 10 minutes.

NOTE: This step must be performed just prior to loading onto the anion column.

- 8) Wash the 500 μL anion column with 2 mL of 8 M HNO_3 just prior to use. Collect as waste in a 35-mL vial.
- 9) Using a plastic dropper, slowly transfer the americium plus curium solution from Step 7 to the anion column. Collect the effluent containing the americium and curium in a 35-mL vial.
- 10) Wash the 15-mL vial with four 1-mL portions of 8 M HNO_3 and transfer the solution to the column. Collect the effluent in the 35-mL vial containing the americium and curium (Step 9).
- 11) Evaporate the americium and curium solution to dryness (normally overnight under a heat lamp). Cool for 10 minutes.
- 12) Add 500 μL of 1 M HNO_3 to the dry residue in the 35-mL vial. Cap tightly. Record the volume added on the analytical report.
- 13) Swirl to dissolve the residue. Rotate the vial several times to ensure that all residue from all of the glass surface is dissolved.
- 14) Centrifuge for at least 1 minute to bring the solution to the bottom of the vial.
- 15) Add a small stir bar and stir for 1 minute.
- 16) Plate an aliquot, preferably 100 μL , of the solution onto a 7/8-inch stainless steel disc. Record the volume on the analytical report.
- 17) Evaporate the solution to dryness under a heat lamp.

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- 18) Add a few drops of deionized water to the disc to cover the dried residue.
- 19) Evaporate to dryness under a heat lamp.
- 20) Place the disc on a hot plate and heat on high until the organic residue is burned off.
- 21) Count the americium and/or curium isotopes using Alpha Counting and Alpha Spectrometry procedures.

5.4 Records

Records will be maintained and controlled to conform with requirements of PNL-MA-70, MCS-033. ~~Laboratory Record Books (LRB's) shall be used in accordance with ACT NOW 89-1.~~

LRB's and analytical report cards provide a mechanism for control of most records.

5.5 Analyst Qualification

The analyst shall be trained on this procedure before being qualified to perform the procedure on samples. The COGNIZANT SCIENTIST, or their designee, shall train the analyst. The procedure shall be performed on at least three standards. Recovery should be $95 \pm 5\%$. Qualification shall be determined by the COGNIZANT SCIENTIST or their designee.

6.0 REFERENCES

1. Relative Density and Volume of Water, page 2198, Handbook of Chemistry and Physics, 44th Edition, Chemical Rubber Publishing Co.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-490, (Replaces 7-40.66), LIQUID SCINTILLATION COUNTING
PROCEDURE FOR PACKARD MODEL 4430 IN 325 BUILDING

1.0 APPLICABILITY

This procedure is applicable to the operation of the liquid scintillation counting system located in the 325 Building.

Other PNL Test Procedures reference this procedure. Other Test Procedures which reference this procedure include:

Procedure PNL-ALO-487 for tritium in urine
Procedure PNL-ALO-479 for tritium in irradiated cladding
Procedure PNL-ALO-482 for carbon-14 in liquids, soils, and sludges

2.0 DEFINITIONS

- dpm - Disintegrations per minute, number of atoms which undergo radioactive decay in 1 minute
- pCi/l - Pico curies per liter, a radioactivity concentration term. One picocurie/l equals 2.2 DPM PER LITER
- $t_{1/2}$ - Half life
- LRB - Laboratory Record Book
- LSC - Liquid Scintillation Counting
- cpm - Counts per minute
- SIS - Spectral Index of Sample

3.0 RESPONSIBLE STAFF

Cognizant Scientist - A chemist or other scientist familiar with this procedure and having an in-depth knowledge of the principles involved and the instrument being used.

Author	Date	Project Mgr.	Date	QAD Representative	Date
DL Baldwin	12/4/90	N/A		GK Gerke	12/4/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LR Greenwood	11/29/90	HH Van Tuyl	11/30/90	All original signatures on file	
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PNL TECHNICAL PROCEDURE

Analyst-

An individual who is qualified in the use of this procedure, and for whom this has been documented in the analyst's qualification training records. An analyst shall be considered qualified when 3 spiked samples have been analyzed by this procedure for which the results agree within $\pm 10\%$ of the expected (spiked) values.

4.0 PROCEDURE

4.1 Liquid Scintillation Counting (LSC) System Description

The LSC system is designed for counting ^3H , ^{14}C , ^{32}P , and other beta-emitters. However, virtually all alpha, beta, x-ray, positron, and gamma emitters, properly prepared, can be counted with good efficiency.

The Packard Model 4430 (located in 325 Bldg, Room 326) is a three region, micro-processor based, multi-user liquid scintillation counter. The system uses cassettes for sampling, storage and handling which may be pre-programmed to select any of 15 user programs stored in system memory. Sample capacity is 300 samples.

The detector consists of two opposed photomultiplier tube assemblies, shielded by 2" of lead to reduce the effects of external radiation. Up to three energy regions are set across the spectrum to form the regions of analysis. The entire spectrum of the radionuclide accumulates during sample measurements. The displayed and printed data are from the regions of interest.

The LSC system is intended for use by analysts experienced with the methodology of in-vitro diagnostic radioassay, radioimmunoassay, and radiochemistry procedures which require nuclear counting by liquid scintillation techniques.

4.1.1. Components in the LSC System

The LSC system is a Packard Model 4430, M&TE No. WA82507. The 300-sample conveyor sample changer is housed in a light-protected compartment, as are the photomultiplier tubes and operator/program selection towers. Circuit boards are emplaced outside at the base of the sample compartment.

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4.1.2. Counter Quench Correction

The system is equipped with an external standardization method for quench correction in which a high-energy gamma source ^{226}Ra can be automatically positioned near the sample vial to produce a continuum of Compton recoil electrons which can excite solvent molecules that will eventually transfer the energy of excitation to solute molecules to produce photons. If quenching is present in the sample, the resulting Compton pulse height distribution is affected in the same manner as the photons induced in the scintillator by decay of the radioactive sample. The true quench level of the sample is expressed as a shift in the Compton edge of the sample relative to an unquenched sample. The model 4430 analyzes the sample spectrum to provide a measure of the sample quenching. A "Spectral Index of Sample" (SIS) is calculated and is directly related to the quenching of the sample.

Samples counted with a SIS number are subjected to quench correction in order to determine actual sample activity-disintegrations per minute (dpm)- regardless of quenching in the sample. Quenched standards, which contain the same isotope as the sample (or one with similar decay properties) but whose activity is known, are prepared or purchased and counted to determine count rates -- counts per minute (cpm). SIS numbers are measured for each standard and a quench curve generated which relates the counting efficiency of each standard to its corresponding SIS number.

4.1.3 Internal Standardization Counting Method

As an alternative to generating a curve with quenched standards and applying an appropriate correction factor to compensate for quenching effects, an internal standardization counting method may be used. In this approach, which is utilized for measurement of tritium in urine, one aliquot of sample is counted directly and an identical aliquot is counted after spiking with a known amount of the radionuclide being determined. This method permits measurement of sample radioactivity without the need to determine quenching parameters.

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PNL TECHNICAL PROCEDURE

5.0 COUNTER PERFORMANCE TESTING

Sealed ^3H , ^{14}C , and blank unquenched Packard standards shall be counted before and after each set of samples. The counting rates of ^3H , ^{14}C , and blank standards shall be recorded in the LSC notebook and plotted on control charts which shall be maintained in the LSC notebook. Control charts shall be set up and maintained as per procedure PNL-ALO-488, Revision 0; Attachment A. These counting rates shall be compared with previous counting data to document satisfactory system operation. The standards and their certification are:

1. ^3H Unquenched Standard: 255,300 dpm, January 28, 1985, I.D. No. 416 (NIST Reference Material: Toluene, NIST Reference Number: 4947, NIST Concentration Uncertainty: $\pm 0.82\%$).
2. ^{14}C Unquenched Standard: 111,700 dpm, March 1, 1985, I.D. No. 275 (NIST Reference Material: n-Hexadecane, NIST Reference Number: 4222, NIST Concentration Uncertainty: $\pm 3.0\%$).
3. Background Unquenched Standard: April 1985.

If the counting rates for the ^3H or ^{14}C sealed standards either before or after the samples are counted are outside the Control Limits (± 3 sigma), the counting data for the samples shall not be used. The cause of the problem shall be determined and resolved, and the samples shall be recounted.

6.0 COUNTING PROCEDURES

- 6.1 Insert the blank and sample counting vials. Allow a minimum of 1 hour for stabilization prior to counting samples.
- 6.2 Recall the program number and display the program summary to check that the required units are in the program. Modify the program as necessary to achieve required counting statistics for the sample set as specified by the relevant procedure. This modification is automatically printed out with the data. For tritium in urine, counting times are specified in procedure PNL-ALO-487, Revision 0.

Check the program summary to insure that the channel limits and counting times are the same as in Attachment A of this procedure.

For use with other PNL Test Procedures, specific conditions of counting may be described in the applicable Test Procedure. Otherwise, general counting conditions are listed here, as follows:

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<u>Isotope</u>	<u>Count Time</u>	<u>Region A</u>	<u>Region B</u>	<u>Region C</u>
^3H	10 min.	0-19	2-19	19-2000
^{14}C	10 min.	0-156	2-156	156-2000

These general conditions may be overwritten by a specific Test Instruction.

- 6.3 Start the automatic counting procedure.
- 6.4 Transfer copies of the printouts of the counting data to the appropriate LRB (the LRB for bioassay samples for tritium in urine).

The printout contains the program summary, sample positions, count rates (cpm), uncertainty, counting time, and elapsed time since the sequence was initiated. The sample position number shall be referenced to the corresponding sample in the LRB.

7.0 CALCULATIONS

See Procedure PNL-ALO-487 for tritium in urine.
See Procedure PNL-ALO-479 for tritium in irradiated cladding.
See Procedure PNL-ALO-482 for carbon-14 in liquids, soils, and sludges.

8.0 REFERENCE

Packard Model 4430, 4000 Series Liquid Scintillation Counting, Operation Manual, 1983, Packard Instruments.

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ATTACHMENT A

PROGRAM 3 = 4

20/06/89 21:50

REGION A: LL-UL= 0- 19 LCR = 0 BKG = .00 % 2 SIGMA = 1.0

REGION B: LL-UL= 2- 19 LCR = 0 BKG= .00 % 2 SIGMA = 1.0

REGION C: LL-UL= 19-2000 LCR = 0 BKG= .00 % 2 SIGMA = 1.0

TIME = 10.00 K = 1.000 QIP = SIS

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-491, (Replaces 7-40.74), ANALYSIS FOR TRITIUM IN GAS

1.0 APPLICABILITY

This procedure is intended for measurement of total tritium in gas samples. The measurement can provide either tritium concentration or absolute quantity. Measurement of the tritium is by Liquid Scintillation Counting (LSC). Gas samples are generally provided in some type of stainless steel sampler container with inlet and outlet valves at each end to allow a flowthrough purge.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant Scientist - a chemist or other scientist familiar with this procedure and having an in-depth knowledge of the chemistry.

Analyst - an individual who is qualified in the use of this procedure, and for whom this has been documented in the analyst's qualification training records.

4.0 PROCEDURE

4.1 Preparations

4.1.1 The system shall be set up as shown in Figure 1. The following parameters shall be set:

Sweep Gas Composition	1000 $\pm$ 100 ppm H ₂ in UHP He
Flowrate	100 $\pm$ 10 cc/min ² STP
CuO Bed Temp	500 $\pm$ 10 degC
Bubbler volume	80 ml $\pm$ 5 ml
Bubbler Liquid	Distilled water

Author	Date	Project Mgr.	Date	QAD Representative	Date
DL Baldwin	10/7/91	N/A		GK Gerke	10/8/91
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- 4.1.2 Must assure that the CuO is well regenerated by the flushing of air through it while at temperature. Shall regenerate every other sample analysis. Use a source of clean air, such as a small diaphragm pump. Flowrate is not critical. Do not use building air. With CuO at full temperature, purge air through for at least two hours, possibly overnight in preparation for analysis.
- 4.1.3 System must also be flushed well, at least two hours, to reduce system tritium background. The regeneration with air (see section 4.1.2) will also help to reduce background. Switch to sweep gas (0.1% H₂ in He) for 60 minutes to simulate sample, collect tritium in bubblers, and measure tritium by LSC to determine system tritium background.

4.2 Analysis

- 4.2.1 When all is ready, connect gas sampler to system with all valves closed. Sampler may have swagelok or VCR fittings. Sampler may be connected to the system with short (1") sections of Tygon tubing.
- 4.2.2 Sample pressure and temperature and cylinder volume must be known beforehand from customer if tritium concentration is requested. If these parameters are not known, then absolute quantity of tritium in the sampler is determined. At the least, customer shall provide information as to whether gas sample is greater than or less than 760 torr.
- 4.2.3 If sampler is pressurized, open sampler cylinder outlet valve first, very slowly, to relieve pressure through bubblers. When pressure is relieved and flow drops to near zero, slowly open sampler inlet valve and gas supply to establish flow through entire system.
- 4.2.4 If sampler is under-pressurized, open sampler cylinder inlet valve, with gas supply on, first until sampler is pressurized, noted by observing drop in flow. Then slowly open sampler outlet valve to bubblers to establish system flow. When opening any valves, always carefully watch bubbler water level so that water is not sucked back.
- 4.2.5 Establish flow of sweep gas at 100 $\pm$ 10 cc/min. Flow for 60-90 minutes for any sampler under 300 cc volume. For larger volumes, Cognizant Scientist shall determine flowrate and time required, inform analyst, and record in LRR.

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- 4.2.6 At end of period, disconnect water bubblers. Close sampler outlet valve first, then inlet valve in order to pressurize sampler cylinder with inert gas. Disconnect from system.
- 4.2.7 At the direction of the Cognizant Scientist, a gas sampler may periodically be checked for retained HTO (tritiated water) on internal surfaces. For this measurement, fresh water is placed into the bubblers, and the sampler is heated with tape heater to 120°C. Either 0.1% H₂ in He or moisture-containing room air is used as sweep gas, under direction of the Cognizant Scientist. Steps 4.2.1 through 4.2.6 are repeated. Record information in LRB.

4.3 Tritium Measurement

- 4.3.1 The bubbler contents are transferred to two 100 ml vol flasks. Rinse each bubbler into 100 ml vol flasks with distilled water, keeping the 1st and 2nd bubbler solutions separate and identified. Dilute to volume mark with distilled water. Mix and identify.
- 4.3.2 The bubbler solutions may have to be diluted in preparation for liquid scintillation counting. Each bubbler solution shall undergo two different dilution levels. A typical dilution would be as follows:

Dilution #1	25 μ l into 50 ml vol flask
Dilution #2	100 μ l into 50 ml vol flask

Record dilution information into LRB. Pipettes shall be gravimetrically calibrated daily prior to use and calibration recorded into LRB.

- 4.3.3 Liquid scintillation counting is performed according to PNL Test Procedure PNL-ALO-490, latest revision, "Liquid Scintillation Counting Procedure for Packard Model 4430 in 325 Building". Typically, 1000 μ l aliquots of the dilutions are added to 12 ml of the scintillation cocktail. Sample, standards, and blanks shall be prepared identically.

5.0 CALCULATIONS

5.1 Gas Sample Volume

- 5.1.1 Volume of gas in the sampler cylinder must be calculated. This is generally determined to STP.

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PNL TECHNICAL PROCEDURE

$$\text{gas volume, cm}^3 \text{ STP} = \frac{P}{T} \times \frac{V}{x} \times \frac{273}{760}$$

where

- P = gas sample pressure, mm Hg
- V = cylinder volume, cm³
- T = sample temperature at time of sampling, °K.

5.2 Tritium Calculation

5.2.1 Sample result may be calculated in a variety of units, typically in Ci/m³. Any other units and calculations should be determined by Cognizant Scientist and recorded in LRB.

$$\text{Ci/m}^3 \text{ STP} = \frac{(A-B)}{E} \times \frac{C}{x} \times \frac{D}{F} \times 10^6$$

where

- A = Tritium in sample, cpm
- B = Tritium in blank, cpm.
- C = Dilution factor
- D = Tritium counting efficiency factor (dpm/cpm)
- E = 2.22 x 10¹² dpm/Ci
- F = Gas sample volume, cm³STP, see 5.1.1.

5.2.2 Alternatively, the result may be calculated in absolute quantity, such as mCi, as follows:

$$\text{mCi (STP)} = \frac{(A-B)}{E} \times \frac{C}{x} \times \frac{D}{F}$$

where

- A = Tritium in sample, cpm
- B = Tritium in blank, cpm.
- C = Dilution factor
- D = Tritium counting efficiency factor (dpm/cpm)
- E = 2.22 x 10⁹ dpm/mCi

6.0 RECORDS

All sample identification, specific conditions and parameters for each sample shall be recorded into LRB. Also all sample volumes, dilution volumes and counting results shall be recorded into LRB. Calculations are made directly into LRB.

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PNL TECHNICAL PROCEDURE

Figure 1: Apparatus for Analysis of Tritium in Gas

DL Baldwin
7/3/91

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-492, (Replaces 7-40.75), TRITIUM/HELIUM MEASUREMENT IN LITHIUM CERAMICS BY HIGH TEMPERATURE VACUUM EXTRACTION/INDUCTION HEATING

1.0 APPLICABILITY

This procedure is applicable to the measurement of total tritium and helium in irradiated lithium ceramics or irradiated beryllium. It is applicable to any material which can be melted at 1800°C. The apparatus for this procedure exists in 325 bldg, room 416 and is shown in Figure 1.

2.0 DEFINITIONS

LRB - Laboratory Record Book maintained in room 416, 325 bldg for this work.

LSC - Liquid Scintillation Counter.

3.0 RESPONSIBLE STAFF

Cognizant Scientist - a chemist or other scientist familiar with this procedure and having an in-depth knowledge of the chemistry.

Analyst - an individual who is qualified in the use of this procedure, and for whom this has been documented in the analyst's qualification training records.

4.0 PROCEDURE

Lithium ceramics (the oxide, aluminate, silicate, zirconate, or other material, such as beryllium) are analyzed by the same extraction method. Pellets or sub-sections are heated in covered graphite crucibles, in a vacuum, until melted. Two hydrogen spikes are added to isotopically swamp and carry the tritium. All H and T is oxidized to water and condensed in the cryogenic trap. A He-3 spike is added for isotopic dilution of the released He-4. Two gas samples are then taken for analysis by the method of mass spectrometry/isotope dilution.

Author	Date	Project Mgr.	Date	QAD Representative	Date
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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
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PNL TECHNICAL PROCEDURE

4.1 Equipment

- 4.1.1 The extraction manifold is shown in Figure 1.
- 4.1.2 MKS Baratron Capacitance Manometers, Category I calibration. Calibration shall be maintained, through factory calibration, on a yearly basis.
- 4.1.3 Lecture bottle of Preparation-Grade Hydrogen Gas.
- 4.1.4 Chromel-Alumel thermocouple, Category I calibration.
- 4.1.5 He-3 gas in lecture bottle for spike preparation.

4.2 Preparations

- 4.2.1 Prepare two 500 cc hydrogen injections, injection 1 and injection 2. The copper oxide furnace must be cool and manifold must be leak tight. Note and record atmospheric pressure from MKS display into LRB. Attach tygon tubing from hydrogen cylinder (outside the hood) to port G on manifold. Evacuate manifold\tygon up to hydrogen cylinder (cylinder valve closed). Evacuate down to at least 0.100 torr. Close main vacuum valve A and crack open hydrogen cylinder valves B and C to back-fill hydrogen to atmospheric pressure ± 10 torr. Note and record final pressure and room temperature into LRB.
- 4.2.2 He-3 spike must be prepared beforehand. At least the day before, have up to three 75 cc He-3 spikes made in 325 bldg Mass Spec lab, filled to 20 ± 1 torr pressure. Mass Spec lab must record the pressure to ± 0.1 torr and temperature to ± 0.1 deg and date of preparation. Do not use after one week storage.
- 4.2.3 Connect He-3 cylinder onto port D on manifold. Connect two empty 75 cc sample cylinders onto ports E and F on manifold. Wrench firmly. Attach air-dried glass cryogenic tritium trap onto manifold.
- 4.2.4 Power on to copper oxide, 50% for temp of 1200°F. Allow time for heatup of copper oxide. Have liquid nitrogen available. Open valve to LEPEL Induction Generator cooling water, power on LEPEL main switch, power on oscillator filament, and power on to quartz chamber cooling water.
- 4.2.5 Outgas crucible and lid, while evacuating (vacuum valve A

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PNL TECHNICAL PROCEDURE

open), at ~60% power on LEPEL Induction Generator. Heat until 0.05 Torr is reached. Power off and allow to cool at least 5 minutes. Open system to air.

4.2.6 Load sample into graphite crucible with lid. Place in Tantalum basket. Place into quartz extraction chamber. Mount quartz chamber in position on manifold.

4.2.7 Evacuate through valve A to system pressure of at least 0.0050 Torr. Open sample cylinders 1 and 2 for evacuation. Load LN2 dewar around water trap. If .0050 Torr system pressure can be achieved, then system is leak-tight. Close Sample Cylinders 1 and 2. Close vacuum valve A.

4.3 Extraction

4.3.1 When all is ready, double-check all above valves. All valves, A, B, C, D, E, F, and G shall be closed. Place LN2 dewar around tritium cold trap. Power on Lepel at 0% power (GRID = 45%), and open hydrogen Spike 1, valve B. Complete the following heating time table:

Power Level	Time
=====	=====
0%	2 min
10%	4 min
15%	4 min
20%	4 min
25%	4 min
30%	3 min
35%	3 min
40%	3 min
Power Off	

4.3.2 Record into LRB the following type of data using the example below:

Power Level	Time	Power Output	System Pressure	Comments
30%	3 min	5.2 kV	34 torr	Still no residue
40%	3 min	5.9 kV	35 torr	Black residue

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PNL TECHNICAL PROCEDURE

4.4 Sampling

- 4.4.1 After 20 minutes, or when system pressure reaches minimum plateau, about 1 Torr, open He-3 spike cylinder, valve D, then open Hydrogen Spike 2, valve C.
- 4.4.2 After 30 more minutes, or when system pressure again reaches minimum plateau, generally about 4-5 Torr, tritium collection is complete. Record system pressure.
- 4.4.3 Open Sample Cylinders 1 and 2, valves E and F. Allow 1 minute for equilibration. Close sample cylinders. Record system pressure in notebook. Helium sampling is complete.

4.5 Measurement

- 4.5.1 Remove LN2 dewar flask from cryogenic trap. Open system to air by opening valve G. Remove cryogenic water and place in beaker of room temp water to thaw collected water. Let come to room temp. For periodic information on % recovery of collected water, weigh trap several times and record stable weight.
- 4.5.2 Disconnect sample cylinders from manifold. Survey, label with sample ID, remove from lab and give to Mass Spec Lab for analysis.
- 4.5.3 Add 30-50 cc distilled water to warmed cryogenic trap, and transfer to 100 ml vol flask with additional water. Dilute to mark and mix. Label with sample ID.
- 4.5.4 Label a black, poly-lined lid vial as archive with sample ID and store about 15 ml.
- 4.5.5 Routinely perform two dilutions, as follows. Pipettes must be gravimetrically calibrated daily prior to use. Any change in these dilution levels must be specified by Cognizant Scientist and recorded into LRB.

For dilution A, pipet 25 ± 0.2 ul into 50 ml flask and dilute to mark with distilled water. Mix.

For dilution B, pipet 100 ± 0.5 ul into 50 ml flask and dilute to mark with distilled water. Mix.

- 4.5.6 Prepare LSC vials with 12 ± 0.2 ml Packard Ultima Gold cocktail. Depending upon tritium concentration, under

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PNL TECHNICAL PROCEDURE

direction of Cognizant Scientist, perform the following. Record into LRB. Any change must be specified by Cognizant Scientist and recorded into LRB.

A) Add 1000 ul distilled water. For both dilutions A and B, add 25 ± 0.2 ul of sample. Mix. or

B) Add no additional water. Pipette 1000 ± 1 ul of dilution A into cocktail for sample A and 1000 ± 1 ul dilution B into cocktail for sample B. Mix.

4.5.7 Set into Packard Scintillation counter for measurement. See PNL Technical Procedure PNL-ALO-490 for operation of liquid scintillation counter.

4.5.8 Remove quartz chamber from manifold and lift out sample crucible. Determine if sample is melted and record results.

4.5.9 If analysis of lithium ceramic, then some deposit on quartz chamber has retained some percentage of tritium, generally $7 \pm 1\%$ of total. Measure periodically by diluting quartz chamber rinse solution (see section 5.0.1) and count by liquid scintillation counting to determine amount retained.

5.0 CLEANING OF QUARTZ FURNACE CHAMBER

5.0.1 The quartz furnace chamber must be cleaned after each use. Add water and dilute acid to quartz chamber and allow to sit at least one hour. Deposit on chamber wall may require wire brush cleaning for complete removal of deposition.

5.0.2 Rinse well after cleaning and allow to air dry.

6.0 CALCULATIONS

Count data (in CPM) is obtained from printout from liquid scintillation counter. The results, calculated in Ci or Ci/g, are calculated as follows:

$$\text{tritium (Ci/g)} = \frac{(\text{cpm}_{\text{spl}} - \text{cpm}_{\text{blk}}) \times \text{d/c} \times \text{DF}}{2.22 \times 10^{12} \times \text{wt(g)} \times \text{R}}$$

where

cpm_{spl}	=	counts per minute of sample
cpm_{blk}	=	counts per minute of blank
d/c	=	dpm/cpm, counting efficiency
DF	=	dilution factor
wt	=	sample weight in g

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PNL TECHNICAL PROCEDURE

R = correction factor for percentage retained
on quartz wall.

Record raw data, calculations, and final results into LRB.

7.0 RECORDS

All sample identification, specific conditions and parameters for each sample shall be recorded into room 416, 325 bldg LRB, as well as the specific equation to be used for calculations. Results shall be recorded into LRB. Calculations are made directly into LRB.

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Figure 1: Schematic of Apparatus for Total Tritium and Helium Analysis of Solids by High Temperature Vacuum Extraction

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-495, NICKEL SEPARATION FROM RADIOACTIVE SOLUTIONS USING CHROMATOGRAPHY

APPLICABILITY

This procedure describes the method for separating nickel from a complex mixture in solution using column precipitation chromatography and ion exchange. It is useful for the separation and purification of ^{59&63}Ni for subsequent determination by counting methods. Stable nickel is used as a carrier and is determined by weight, or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) or equivalent.

The procedure was developed for use with highly radioactive Hanford tank samples but can be applied to other sample types. Variations in the radioactive isotopes present and the radioactive Ni concentration will be factors used to determine aliquot size and, amount of carrier added. Because stable Ni is used as a yield monitor, the amount of Ni in the original sample may need to be determined in order to calculate Ni recovery. Large amounts of Ni (e.g., >5mg) may cause absorption and quenching problems with counting techniques. These may be corrected with appropriate calibration curves constructed at the direction of the Cognizant Scientist. An option of Co separation by anion exchange may be used if ⁶⁰Co concentration is high.

NOTE: Specific sample matrices (other than single shell tanks (SST), and double shell tanks (DST)) may need to be tested with this procedure to assure its applicability.

DEFINITIONS

- LEPS - low energy photon spectroscopy
- LSC - liquid scintillation counter
- gm - grams
- mL - milliliter
- conc - concentrated
- M - molar

Author <i>RS Strebin</i>	Date <i>2-8-93</i>	Project Mgr. <i>S. K. Fackoff</i>	Date <i>2/5/93</i>	PQ Representative <i>TL Ehlert</i>	Date <i>3/2/93</i>
Technical Reviewer <i>CO Harvey</i>	Date <i>3/2/93</i>	Line Mgr. <i>AG King</i>	Date <i>3/2/93</i>	Other	Date
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PNL TECHNICAL PROCEDURE

- Duplicate - a replicate aliquot of a sample which is brought through the entire sample preparation and analysis process to document the precision of the method.
- Reagent blank - An artificial sample designed to monitor the introduction of contamination into the sample preparation and analysis process; it is treated like a "real sample" as it is carried through the appropriate steps of the process.
- Blank spike - a reagent blank to which a known amount of analyte of interest is added.
- Matrix spike - a replicate sample to which a known amount of analyte of interest is added.

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

PROCEDURE

Prerequisite: Only personnel trained in this procedure may perform the work. Personnel training records are kept in the ACL office.

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method; or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is $\pm 50\%$ in the next digit located beyond the last one stated.

2.0 Reagents

All reagents are prepared from analytical reagent grade chemicals. Deionized water, with an electrical resistance of >16 megohms-cm is used

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Ultima Gold LSC cocktail - liquid scintillation cocktail sold by Packard Instrument Company (or equivalent).

Ethanol, Absolute.

Thymol blue indicator.

NH₄Citrate wash solution - 15 mL 1 M NH₄Citrate diluted to 100 mL adjusted to pH 8.5-9 with NH₄OH.

Basic Buffer Solution - Water adjusted to pH 8.5-9 with NH₄OH. One drop of conc NH₄OH in 100 mL of water will buffer to pH 8.5-9.

Dimethylglyoxime (DMG) - Solid Reagent.

Dimethylglyoxime (DMG) - Saturated Ethanol - Add sufficient DMG (2-3 gm) to 50 mL ethanol with mixing. Let stand overnight the solution is saturated when solid DMG is still present.

Tartaric Acid - Solid reagent.

NaHSO₄ - Solid reagent.

Microthene - Trade mark for 50 mesh polyethane powder.

Ethanol - Absolute reagent.

3.0 Equipment

Vortex stirrer

Centrifuge

Centrifuge tubes, plastic, 50 mL

Ion exchange resin, AG1 x 8 100-200 mesh chloride form, or equivalent

Transfer pipets, plastic and glass

Glass wool

Glass stirring rods

Ion exchange columns, plastic disposable (Isolab/QS-NP or equivalent)

Protective gloves, assorted sizes

Dropper bottles, 125 mL with syringe control

Pipetter, adjustable, 0.1 and 1 mL

Graduated cylinders, 10 mL, 50 mL, 100 mL

Beakers: 50, 100, 250, and 500 mL

Syringes

Disposable 5 mL plastic beakers

Electrodeposition cells

Plating disks, 7/8 inch diameter polished metal disc

Plating disks, 7/8 diameter Pt

Disc holder

Pt electrodes

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throughout this procedure. Concentrations are not critical and need only be within $\pm 10\%$ of stated values.

Holdback carrier: use a suite of carriers defined by the Cognizant Scientist to accommodate the nature of the sample. Suggested carriers for SST and DST include: Sr, Co, La, Cs, and Y. The chemical form is not important as long as the compound is readily soluble. Usually they are prepared to make individual solutions of 1 to 10 mg/mL. A combined carrier mix can be made which can then be added to each sample.

Standardized nickel carrier solution of approximately 10 mg/mL in 1 to 2M HNO_3 . This may be a standard prepared commercially or in house from a suitable nickel salt, as specified by the Cognizant Scientist.

^{63}Ni , use a certified ^{63}Ni standard from NIST or other certified vendor.

5M NaOH - 20 gm NaOH diluted to 100 mL with water.

0.5M NaOH - 10 mL 5M NaOH diluted to 100 mL with water.

conc HCl - concentrated hydrochloric acid, 12M.

0.1M HCl - 0.83 mL concentrated hydrochloric acid diluted to 100 mL.

6M HCl - 50 mL concentrated hydrochloric acid diluted to 100 mL with water.

9M HCl - 75 mL concentrated hydrochloric acid diluted to 100 mL with water.

conc NH_4OH - concentrated ammonium hydroxide, 14.5M.

dilute NH_4OH - 5 mL conc NH_4OH diluted to 100 mL with water.

50% NH_4OH - 50 mL conc NH_4OH diluted to 100 mL with water.

1M $\text{NH}_4\text{Citrate}$ - 22/6 gm dibasic ammonium citrate, $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$, diluted to 100 mL with water.

conc HNO_3 - concentrated nitric acid, 16M.

8M HNO_3 - 50 mL conc HNO_3 diluted to 100 mL.

3M HNO_3 - 18.75 mL conc HNO_3 diluted to 100 mL with water.

2 volume % HNO_3 - 2 mL concentrated nitric acid diluted to 100 mL.

H_2O_2 - 30% solution.

conc H_2SO_4 - concentrated Sulfuric Acid, 18M.

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5.0 DMG Column Preparation

- 5.1 Add 0.5 gm DMG to a beaker and add 50 mL ethanol, stir and heat as needed to aid dissolution. This will be called the DMG-ETOH mix.

NOTE: This preparation is enough to fill 10 columns. If more than 10 columns are required, the reagent volumes will need to be proportionately increased.

- 5.2 To a beaker containing 4 gm Microthene add 5-10 mL of DMG-ETOH mix and evaporate with heating and stirring until the mix is a slurry. Repeat the additions of the DMG-ETOH mix until all the DMG-ETOH mix from step 5.1 has been added and the mix is a thick slurry.

- 5.3 To the slurry add dropwise in 5 mL aliquots with vigorous stirring, 20 mL of basic buffer solution.

NOTE: If more buffer is added, the slurry will separate into phases. This will be called DMG-MIC mix.

- 5.4 Prepare a small disposable column by removing the bottom frit, replacing it with a glass wool plug, and attaching a stopcock to the bottom of the column. Transfer the DMG-MIC to the column until the column has been filled to 3 mL. When loading the column keep a head of liquid over the microthene bed. Excess liquid is drained off as the DMG-MIC is added. When the bed is filled to 3 mL carefully drain the liquid to just over the top of the bed (~1 mm) then carefully slide the frit that was removed from the bottom of the column to the top of the bed leaving a small gap between the frit bottom and the bed.

- 5.5 Wash the prepared column with 30-50 mL of basic buffering solution. The column is read for use.

6.0 Separation Procedure

- 6.1 Using a performance tested pipet, add nickel carrier (amount directed by Cognizant Scientist) to each of the following:

- centrifuge tube (or appropriate size beaker) for each sample
- Plastic LSC vial for a yield monitor (to be used to calibrate the nickel concentration)
- two glass LSC vials (for LSC blanks)
- two glass LSC vials for LSC ^{63}Ni standards

Cap the yield monitor vial and save for step 10.3.

NOTE: Record Ni carrier volume and other pertinent information on the analysis sheet (see Attachment 1).

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Wash bottles, plastic
Hot Plates
Heat lamps
Scintillation vial, low potassium glass, 7 & 20 mL size
20 mL plastic screw cap bottles
Filter holder, 50 mL polysulfone filter funnel with stainless steel support screen (Gelman 4203/4204) or equal
Suction flask
Tuffryn membrane filter, HT 200, 25 mm diameter or equal
Petri dish

4.0 Quality Control Instructions

- 4.1 All quality control (QC) data shall be maintained as hard copy and available for easy reference or inspection.
- 4.2 Two QC options are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a SOW, and these may be conveyed to the analyst through a Test Instruction (TI).
- (a) Employ a minimum of one reagent blank and one blank spike per sample batch (20 samples or less). Run duplicate and matrix spike analysis upon client request.
 - (b) For all SOWs written by a client to meet CERCLA requirements that request analysis, employ a minimum of one reagent blank per sample batch (20 samples or less) to determine if contamination is occurring. Run one duplicate sample blank and one blank spike (NIST traceable if possible) per batch (20 samples or smaller). A matrix spike or laboratory control sample may be analyzed with a batch of samples if so directed by the client.
- 4.3 Volume Calibration: Critical volume measurements, as indicated in the procedure, shall be made with automatic pipets or equivalent. A performance check of the automatic pipet shall be completed prior to use. This consists of pipetting and weighing at least three aliquots of deionized water, equal to the volume being used, into a container on the balance. The average delivery weight is converted to volume by multiplying the weight by the reciprocal of the density as it applies to the ambient temperature. This calculated delivery volume shall be acceptable for 7 days.

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6.2 Using a calibrated pipet, add ^{63}Ni (amount directed by Cognizant Scientist) to each of the following:

- blank spike
- matrix spike (if one is to be processed)
- two glass LSC vials identified above for LSC ^{63}Ni standards

Save the LSC ^{63}Ni standards for step 9.6, skip step 10.3 with the LSC blank vials.

NOTE: Record ^{63}Ni volume, activity and identification on the analysis sheet (see Attachment 1).

6.3 Measure an appropriate sample aliquot, as determined by the Cognizant Scientist, with a calibrated pipet (or by other suitable means) and place in the 50 mL plastic centrifuge tube containing the Ni carrier. Large aqueous samples may be evaporated to small volume in a beaker, in this case the Ni carrier should be added to the sample before evaporation. The Cognizant Scientist may decide to add holdback carriers at this point. Measure the activity of each sample and record for reference (if appropriate).

NOTE: Record sample size on the analysis sheet (see Attachment 1).

NOTE: Measuring the sample activity here and elsewhere in this procedure is intended to be done qualitatively with a portable Geiger-Mueller detector, with gamma spectrometry, or other suitable technique, as determined by the Cognizant Scientist. These qualitative measurements are not permanent records.

NOTE: Basic samples (such as tank drainable fluids) are acidified with conc HCl. When basic tank fluids are acidified a precipitate may form. Centrifuge the precipitate, wash twice with 6M HCl and combine the washes with the sample. Discard the washed precipitate.

6.4 If directed by the Cognizant Scientist, concentrate large samples, (e.g., >5 mL) by iron hydroxide precipitation. Go on to step 6.5 if concentration is not needed. Add 0.1-2 mg Fe carrier to the sample, stir. Add 5M NaOH drop-wise, stirring after each addition. Test the pH when the first sign of precipitation occurs. Use 0.5M NaOH and various concentrations of HCl to adjust the pH to 7-8. Use wide range pH paper (pH 2-10) and narrow range pH paper (pH 6-8) as appropriate to measure the pH. Transfer a trace of the sample (with a stirring rod for example) to the pH paper (save the rod, if desired, for reuse on the same sample). Centrifuge 10 minutes on high setting, collect the supernate in a separate vessel. Add 5-10 mL of pH 7 water to the precipitate, stir, centrifuge and discard the supernate (the Cognizant Scientist may determine to skip this wash step). Dissolve the precipitate in approximately 4-6 drops (or

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minimum amount needed) of 6M HCl with swirling, make sure the sample is in solution. Dilute to 1-5 mL with water.

- 6.5 Add 1 mL of 1 M $\text{NH}_4\text{Citrate}$ to the sample and stir well. Add conc NH_4OH to the sample dropwise to pH 8-9, the pH is not critical as long as it is at least pH 8 and <pH 10. The sample will turn from a green color to a blue color. The sample is ready for the DMG column.
- 6.6 Add the sample to the column in 1 mL aliquots and adjust the column flow rate to approximately 1 drop per 2 seconds. The Ni reaction with the DMG gives a red Ni-DMG precipitate band on the column. Discard the effluent.
- 6.7 Wash the column with 20 mL of $\text{NH}_4\text{Citrate}$ wash solution added in 1 mL aliquots for the first 5 mL then in 3 mL aliquots. The wash volume may be increased by the Cognizant Scientist. Discard the effluent.

NOTE: A portion of the eluent may be counted as directed by the Cognizant Scientist to assess the separation.

- 6.8 Strip the Ni from the column with 30 mL of 3 M HNO_3 added in 1-5 mL aliquots. Save the eluent. If further separation from ^{60}Co is needed as determined by the Cognizant Scientist, go to step 7.0.
- 6.9 Set up a filter apparatus with a Tuffryn membrane filter in place. Record the weight of the filter.
- 6.10 To the eluent from step 6.8, add 0.7 gm tartaric acid and stir well. Add 1 mL DMG Saturated Ethanol. Add conc NH_4OH dropwise to pH 8-9. Red Ni-DMG will precipitate. Allow to stand for 1 hour for precipitation to complete.
- 6.11 Filter the solution. Wash the Ni-DMG precipitate with 10 mL water. Carefully remove the filter and place on a petri dish. Dry at 100-120 degrees C for 1 hr or to constant weight. Record the weight of the filter plus Ni-DMG. Ni-DMG contains 20.32 percent nickel. If an electrodeposited mount for LEPS counting for ^{59}Ni is requested by the Cognizant Scientist go to step 6.14.
- 6.12 Wrap the filter with mylar and tape closed at the back. The sample is ready for LEPS counting for ^{59}Ni .

NOTE: The sample may be gamma counted to determine the presence of ^{60}Co .

- 6.13 After LEPS counting cut the tape off the sample and place the filter and mylar in a weighed LSC vial.

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NOTE: Record the weight of the vial on the analysis sheet (see Attachment 1).

- 6.14 Muffle the sample overnight at 500 deg C. Cool and weigh the vial. The ashed weight is NiO.

NOTE: Record the weight on the analysis sheet (see Attachment 1).

- 6.15 Dissolve the NiO with a minimum of aqua regia (3 parts conc HCl - 1 part conc HNO₃). Evaporate the dissolved Ni to near dryness. Add one mL of conc HCl and evaporate to dryness, repeat 1-2 times to convert to HCl. The sample is ready for liquid scintillation counting preparation, step 10.2. If the Cognizant Scientist determines that the sample needs further ⁶⁰Co separation, go to step 7.0. If the Cognizant Scientist decides the sample is to be electroplated for ⁵⁹Ni determination, go to step 8.0.

7.0 Ion Exchange Separation of ⁶⁰Co

- 7.1 Add Co carrier (0.01 - 0.1 mg as determined by the Cognizant Scientist). Add 3 times the liquid volume in the beaker as conc HCl and evaporate to near dryness, repeat the additions of conc HCl up to 2 times to transpose to the chloride form. Evaporate the solution to near dryness. The solution, in small volume, should be yellow from the added nickel.

NOTE: Ni(NO₃)₂·6H₂O has a boiling point of 137°C and can be lost if the solution goes to dryness; NiCl₂ is not volatile.

- 7.2 Prepare a column for ion exchange separation as follows. Make up each ion exchange column with 2 mL AG1X8 resin 100-200 mesh and place a small glass wool plug on top of the resin. Wash the column with water until the effluent is clear. Just prior to use, wash the column with 3 mL of conc HCl followed by 3 mL of 9M HCl. Do not allow the column to stand overnight with strong acid. The Cognizant Scientist may specify a larger column depending on sample considerations, in this case use proportionally changed volumes.

- 7.3 To the sample from step 7.1, add 1 mL of conc HCl then add 2 mL of 9M HCl, mix well and load onto the column. Collect all eluent from the column, this is the Ni sample. Rinse the beaker with three 1-mL portions of 9M HCl adding each rinse to the column after the previous rinse has gone through. Wash the column with five 2-mL portions of 9M HCl, adding each rinse to the column after the previous rinse has gone through. Combine all the eluents from the column and evaporate to dryness (as NiCl₂ is not volatile).

NOTE: Co will give a green colored band on the top of the column.

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- 7.4 As determined by a Cognizant Scientist for a DMG mount for ^{59}Ni determination dissolve the sample in 15-30 mL of 3M HNO_3 and go to step 6.8, for electrodeposition add 1 mL of water and go to step 8.0 or for LSC go to step 10.1.

8.0 Electrodeposition

- 8.1 Add 0.5 mL of conc H_2SO_4 , rinse the sides of the beaker with 2-4 mL conc HNO_3 and evaporate to H_2SO_4 fumes, repeat up to 3 times to destroy organic material. Rinse the sides of the beaker with 2-4 mL of conc HNO_3 then add 1-3 mL of 30% H_2O_2 dropwise as the reaction allows, evaporate to small volume, repeat up to 3 times. When the organic material is destroyed the solution, in a small volume, should be light yellow in color from the Ni carrier.
- 8.2 Add 3 mL water to the sample and stir to dissolve or mix, then add 1-6 drops of thymol blue indicator.
- 8.3 Add 50% NH_4OH (and H_2SO_4 if necessary) until the color just changes to green. The color change is purple to straw to green at neutrality. Low reagent concentrations may be used for better control of neutralization.
- 8.4 Weigh a clean Pt plating disk and record the number of the disk and the weight. Remove disc cover paper from a 7/8 inch diameter polished metal plating disc and use as a support for the Pt disk in the electrodeposition cell.
- 8.5 Mount the Pt disk and the backing disk in the electroplating cell.
- 8.6 Quantitatively transfer the sample to the electrodeposition cell with water and fill the cell to 1/2 full.
- 8.7 Insert platinum electrode, connect to power supply, and electroplate at 1 amp for 1 hour (± 15 minutes). Connect the black lead to the bottom of the cell, connect the red lead to the Pt electrode.
- 8.8 Wash electrodes with water while removing them and turn power off. Pour solution from the cell into the sample beaker and evaporate to dryness.
- 8.9 Remove the electroplated disk from the cell and wash disk with water, then wash with ethanol and allow to dry. Weigh the disk. The weight of the Ni plated is an estimate of the recovery.

NOTE: Record weight on analysis sheet (see Attachment 1).

- 8.10 Place disk in a labeled holder. The sample is now ready for beta counting. Count the sample on a beta counter. If requested by the

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Cognizant Scientist, obtain a beta absorption curve using a range of aluminum foil absorbers to determine beta purity.

- 8.11 For LEPS counting (^{59}Ni determination), wrap the disk in mylar and seal with tape. Count the sample on a LEPS counter per procedure PNL-ALO-494.

NOTE: An x-ray Ni fluorescence peak will interfere with the ^{59}Ni peak on the LEPS spectra. A correction factor based on a calibration curve is used to correct for this interference.

- 8.12 If the sample is to be counted by the liquid scintillation method for ^{63}Ni carry out the disk strip procedure (step 9.0).

9.0 Disk Strip Procedure

- 9.1 Place the disk on a hot plate, setting low.
- 9.2 Place 1-2 mL of 8M HNO_3 , or 6M HCl into a disposable plastic beaker.
- 9.3 Cover the disk with about 0.1 - 0.2 mL acid and warm. When the Ni deposit starts to dissolve, transfer the liquid to a glass LSC vial using a glass transfer pipet. Repeat up to 6 times or until the visible deposit is removed to quantitatively transfer the Ni to the LSC vial.
- 9.4 Cover the disk with the acid, heat approximately 2 minutes or until the solution is evaporated to no more than half volume. Then transfer the solution to the LSC vial. Repeat until all the acid solution (step 9.2) is used. If HNO_3 was used, go to step 9.5; if HCl was used, evaporate to dryness and go to step 10.2.

NOTE: The disk may be counted on a beta counter to determine that the sample was removed.

- 9.5 Evaporate the solution in the LSC vial to 0.5 mL or less and then add conc HCl dropwise, with evaporation between additions, until no yellow color forms upon further addition of HCl and the solution is transposed to chloride form.
- 9.6 Add 1 mL of conc HCl and evaporate to dryness under a heat lamp. Repeat using 0.25 - 1 mL conc HCl . Go to step 10.2.

10.0 Liquid Scintillation Counting

- 10.1 Using small aliquots of 6M HCl (0.1-0.5 mL) transfer the sample solution from the beaker (step 7.4) to an LSC vial using a transfer pipet. Repeat 3-6 times to assure quantitative transfer. Evaporate

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to dryness under a heat lamp. Add 1 mL of conc HCl and evaporate to dryness under a heat lamp.

- 10.2 Add exactly 1 mL (using a calibrated pipet) of 0.1M HCl to the LSC vial and swirl, allow to stand about 30 minutes with occasional swirling to assure dissolution and mixing of the Ni.

NOTE: Record volume on the analysis sheet (see Attachment 1).

- 10.3 Transfer exactly 0.05 or 0.1 mL of the sample solution in the LSC vial to exactly 10 mL of 2 volume % HNO_3 in a 20 mL poly bottle and seal. In the same manner add exactly 10 mL of 2 volume % HNO_3 to the yield monitor solution. The samples and yield monitor will be submitted for Ni analysis by ICP-OES for yield determination.

NOTE: Record the calibrated volumes on the analysis sheet (see Attachment 1).

For Ni determination submit an Analytical Request Form. Submit 10 mL of the 2 volume % HNO_3 as a blank.

- 10.4 Add 10 mL of Ultima Gold LSC cocktail to the LSC vial, seal and mix well. The Cognizant Scientist may change the amount and type of cocktail.

- 10.5 The sample is now ready for the LSC.

11.0 Pt Disk Cleaning Procedure

- 11.1 Place the Pt disks into a small beaker, cover with 8M HNO_3 and heat to steaming. Discard the solution and rinse the disks with water. This step may be repeated.

- 11.2 Add 5-10 gm NaHSO_4 (hydrated form if available) to cover the disks, and heat on a hot plate on high for 1-8 hours, cool.

- 11.3 Dissolve the NaHSO_4 flux in water with heating and discard the solution.

- 11.4 Cover the disks with 8M HNO_3 and heat to steaming. Rinse Pt disks until acid free with water then dry.

- 11.5 Beta count the Pt disks. The number side is the bottom of the disk. The Cognizant Scientist will determine if the disks can be used or if they should be recleaned.

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12.0 Calculations

The 6.9 keV Co X-ray peak (from the electron capture decay of ^{59}Ni) counted on the LEP diode is used to calculate ^{59}Ni in the sample using the following equation:

$$^{59}\text{Ni Activity} = \frac{(\text{net cpm} - \text{cpm due to } ^{63}\text{Ni fluor}) (d/c) (B)}{(\text{Ni yield}) (\text{sample volume})}$$

The ^{63}Ni activity is determined from the LSC spectra using the following equation:

$$^{63}\text{Ni Activity} = \frac{(\text{net cpm}) (d/c) (B) (\text{vol corr})}{(\text{Ni yield}) (\text{sample volume})}$$

Where:

net cpm = The gross counts per minute minus the background cpm.

cpm due to ^{63}Ni fluor = ^{63}Ni fluorescence correction:

$$[(1.7793 \times 10^{-4} \text{ cpm}/(\text{dpm } ^{63}\text{Ni} * \text{mg Ni})) (\text{mg Ni on disk}) (^{63}\text{Ni activity (dpm)})]$$

d/c = disintegration per count, an efficiency factor unique to each instrument and isotope; for LSC this will include the quenching effects.

B = Factor to account for sample dilutions, and any other factors needed to produce the appropriate reporting units.

yield = is determined by the amount stable Ni recovered relative to the amount added.

sample volume correction = a fraction of sample is take for ICP analysis, this factor corrects for the fraction (volume total/volume for LSC analysis), see steps 10.2 and 10.3.

$1.7793 \times 10_4 \text{ cpm}/(\text{dpm } ^{63}\text{Ni} * \text{mg Ni}) =$ is a constant derived from experimental data which is used to calculate the fluorescence of stable Ni due to ^{63}Ni . The records for it's derivation are located in LRB #53293, page 38. The Cognizant Scientist may use a different factor as more experimental data are obtained.

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13.0 Specific Qualification

None required.

14.0 Records

Records will be maintained and controlled so as to conform to requirements of the Analytical Chemistry Lab (ACL) Quality Assurance Plan, MCS-033. Laboratory Record Books (LRB's) and analytical data sheets provide a mechanism for control of most records. LRB's will be used in accordance with established records management practices.

15.0 References

Bhat, I. S., Iyer, R. S., and Chandramonli, S., Anal. Chem., 48, page 224, (1976).

Pacific Northwest Laboratory. "Nickel Separation from Radioactive Solutions: PNL-ALO-473, PNL-ALO-599, Pacific Northwest Laboratory, Richland, Washington.

Tests, C. D. Desideri, M. A. Meli, C. Roselli, Radioactivity and Radiochemistry "Extraction Chromatography in Radioecology" Vol. 2, No. 4, pages 46-55, (1991).

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-496, PRECIPITATION PLATING OF ACTINIDES FOR HIGH-RESOLUTION ALPHA SPECTROMETRY

APPLICABILITY

This procedure is applicable for any sample which would otherwise be electroplated for Alpha Energy Analysis, AEA. Although most samples must be subject to a separation procedure prior to this precipitation, small aliquots of fused diluted hot cell samples may be plated without separation. The actinides are precipitated as fluorides with a small mass of Ce or Nd, nominally 100 micrograms, which will not cause a significant reduction of resolution. The procedure accommodates substantial quantities of common interferences such as Al, Fe, Ti, and Zr since they form strong fluoro complexes.

DEFINITIONS

- conc - concentrated
- Duplicate - a replicate aliquot of a sample which is brought through the entire sample preparation and analysis process to document the precision of the method.
- Reagent blank - an artificial sample designed to monitor the introduction of contamination into the sample preparation and analysis process; it is treated like a "real sample" as it is carried through the appropriate steps of the process.
- Blank spike - a reagent blank to which a known amount of the analyte of interest is added.
- Matrix spike - a replicate sample to which a known amount of the analyte of interest is added.

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

Author <i>RS Strebin</i> RS Strebin	Date 11/14/93	Project Mgr. <i>KJ Kuhl-Klinge</i> KJ Kuhl-Klinge	Date 11/14/93	PQ Representative <i>TL Ehler</i> TL Ehler	Date 1/19/93
Technical Reviewer <i>NL Wynhoff</i> NL Wynhoff	Date 1-19-93	Line Mgr. <i>AG King</i> AG King	Date 1/19/93	Other	Date
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PROCEDURE

Prerequisite: Only personnel trained in this procedure may perform the work. Personnel training records are kept in the ACL section office.

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method; or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is $\pm 50\%$ in the next digit located beyond the last one stated.

2.0 Reagents

All reagents are prepared from analytical reagent grade chemicals. Deionized water, with an electrical resistance of >16 megohms-cm is used throughout this procedure. Concentrations are not critical and need only be within $\pm 10\%$ of stated values.

Cerous nitrate - solid reagent or known concentration solution

Neodymium nitrate - solid reagent or known concentration solution

Cerous nitrate solution - A solution containing 0.5 mg/mL of cerium in 0.2 M HNO_3

Neodymium Nitrate solution - A solution containing 0.5 mg/mL of neodymium in 0.2 M HNO_3

Carbon Suspension - Fume in 5 mL of conc H_2SO_4 a 47-mm GA-6 Metrice1 filter or equivalent. Cool the suspension and dilute to 50 mL with water.

Substrate Suspension - Dilute 10 mg of cerium or neodymium as a nitrate solution and 20 mL of conc hydrochloric acid to 400 mL with water. Add with stirring 10 mL of conc HF and dilute to 500 mL with water. Add 2-3 mL of carbon suspension and stir well. Store in a plastic bottle.

conc H_2SO_4 - concentrated sulfuric acid, 18 M

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conc HF - concentrated hydrofluoric acid, 48%

conc HCl - concentrated hydrochloric acid, 12 M

3 M HCl - 25 mL conc HCl diluted to 100 mL

20 % TiCl_3 - 20 % reagent titanium trichloride

0.1 % safranine O - 0.01 g safranine O diluted to 10 mL with water

3.0 Equipment

Vortex stirrer

Heat lamp

Glass and plastic graduate cylinders

Centrifuge tubes, plastic, 50 mL

Filter holder, 50 mL polysulfone filter funnel with
stainless steel support screen (Gelman 4203/4204) or equal

Suction flask

Tuffryn membrane filter, HT 200, 25 mm diameter or equal

Petre dish

47-mm GA-6 MetriceI filter (Gelman Instrument Co., Ann Arbor, MI) or
equivalent

4.0 Quality Control Instructions

4.1 All quality control (QC) data shall be maintained as hard copy and
available for easy reference or inspection.

4.2 Two QC options are defined below. Option A shall be used unless a
Statement of Work (SOW) written by a client defines CERCLA
requirements. Option B shall then be followed. Additional QC
samples may be requested by a client in an Analytical Request Form
(ARF), TPP or a SOW, and these may be conveyed to the analyst
through a Test Instruction (TI).

(a) Employ a minimum of one reagent blank and one blank spike
per sample batch (20 samples or less). Run duplicate or
matrix spike analysis upon client request.

(b) For all SOWs written by a client to meet CERCLA requirements
that request analysis, employ a minimum of one reagent blank
per sample batch (20 samples or less) to determine if
contamination is occurring. Run one duplicate sample and
one blank spike (NIST traceable, if possible) per batch (20
samples or smaller). A matrix spike sample may be analyzed
with a batch of samples if so directed by the client.

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PNL TECHNICAL PROCEDURE

- 4.3 Volume Calibration: Critical volume measurements, as indicated in the procedure, shall be made with automatic pipets or equivalent. A performance check of the automatic pipet shall be completed prior to use. This consists of pipetting and weighing at least three aliquots of deionized water, equal to the volume being used, into a container on the balance. The average delivery weight is converted to volume by multiplying the weight by the reciprocal of the density as it applies to the ambient temperature. This calculated delivery volume shall be acceptable for 7 days.

5.0 Procedure

- 5.1 Sample preparation. If the sample is a column eluent add 0.5 mL of conc H_2SO_4 and 1 mL of conc HNO_3 and evaporate to H_2SO_4 fumes. If the sample is an aliquot of a fused sludge go directly to step 5.2.
- 5.2 Dilute the sample to 10 mL with 3 M HCl and hold at near boiling for 5 minutes. Transfer the solution to a 50 mL plastic centrifuge tube using water as a rinse for the tube. The total volume should be no more than 15 mL.
- 5.3 If uranium is not to be determined or if uranium is to be determined separately from the other actinides go to step 5.9. If uranium is to be determined along with all the actinides go to step 5.4.
- 5.4 For the determination of all actinides add one drop of 0.1% safranine O, and 1-3 drops of 20% $TiCl_3$ and stir.

NOTE: The $TiCl_3$ should produce a permanent strong violet color, if not, iron is probably present and a few more drops of $TiCl_3$ must be added to produce a permanent violet color or the reduction and precipitation of uranium will be incomplete.

- 5.5 Add 0.1 mL of 0.5 mg/mL Ce or Nd with stirring.

NOTE: Resolution of alpha spectra is decreased by the presence of as little as 100 micrograms of any other absorbing material. Soil contains about 75 micrograms of the light lanthanides in a 1 gm average soil sample, and in those cases the Ce or Nd carrier may be eliminated.

- 5.6 Add 5 mL of conc HF solution with stirring, and allow to stand for 30 minutes.

NOTE: The violet color changes to light green and any slight turbidity from insoluble compounds of quadravalent Ti clear up.

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5.7 Mount a 25 mm 0.2 micron tuffrin filter on the stainless steel support in a polysulfone twist lock funnel attached to a vacuum system. Apply the vacuum and add 2-4 mL of distilled water. As the filter goes dry, add the following in order.

- a. 5 mL of substrate suspension, after vigorous stirring.
- b. The sample, after vigorous vortex stirring.
- c. Two 4 mL water rinses of the centrifuge tube.

5.8 Dry the filter under a heat lamp. Place the filter in a holder and submit for alpha spectrometry, PNL-ALO-469. The filter contains all actinides.

NOTE: The final residue will not be visible. If a visible precipitate is present consult the Cognizant Scientist.

5.9 For the determination of all actinides without uranium and for the determination of uranium separately add 0.1 mL of 0.5 mg/mL Ce or Nd with stirring.

NOTE: Resolution of alpha spectra is decreased detectably by the presence of as little as 100 micro grams of any other absorbing material. Soil contains about 75 micro grams of the light lanthanides in a 1 gm average soil sample, and in those cases the Ce or Nd carrier may be eliminated.

5.10 Add 5 mL of conc HF solution with stirring, and allow to stand for 30 minutes.

5.11 Mount a 25 mm 0.2 micron tuffrin filter on the stainless steel support in a polysulfone twist lock funnel attached to a vacuum system. Apply the vacuum and add 2-4 mL of distilled water. As the filter goes dry, add the following in order. If uranium is to be determined separately place a plastic test tube inside the vacuum system suction flask to collect the sample solution from step b, this solution is the uranium fraction which will be saved for step 5.15.

- a. 5 mL of substrate suspension, after vigorous stirring.
- b. The sample, after vigorous vortex stirring (save filtrate if uranium is requested)
- c. Two 4 mL water rinses of the centrifuge tube.

5.12 Dry the filter under a heat lamp. Place the filter in a holder and submit for alpha spectrometry, PNL-ALO-469. This filter will contain all the actinides except uranium.

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PNL TECHNICAL PROCEDURE

- 5.13 For the determination of uranium after removal of other actinides use the uranium fraction saved from step 5.11 b. Add one drop of 0.1% safranine O, and 3 drops of 20% TiCl_3 and stir.
- 5.14 Add 0.1 mL of 0.5 mg/mL Ce or Nd with stirring and allow to stand for 30 minutes.
- 5.15 Mount a 25 mm 0.2 micron tuffrin filter on the stainless steel support in a polysulfone twist lock funnel attached to a vacuum system. Apply the vacuum and add 2-4 mL of distilled water. As the filter goes dry, add the following in order.
- 5 mL of substrate suspension, after vigorous stirring.
 - The sample, after vigorous vortex stirring.
 - Two 4 mL water rinses of the centrifuge tube.
- 5.16 Dry the filter under a heat lamp. Place the filter in a holder and submit for alpha spectrometry, PNL-ALO-469. This filter contains the uranium.

6.0 Specific Qualifications

None required.

7.0 Records

All data and test results shall be maintained as hard copy as required by the Quality Assurance Plan, MCS-033.

8.0 References

Idaho National Engineering Laboratory. "RESL Analytical Chemistry Branch Procedures Manual". EG & G Idaho, Inc.

Sill, C. W. and Williams, R. L., Analytical Chemistry, 53, 412, (1981)

Hindman, Forest D. Analytical Chemistry, 55, 2461, (1983)

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-497, Rev. 0; Determination of Sr-90 in Y-90

1.0 Applicability

This procedure provides instruction for determining Sr-90 in concentrated Y-90 product and is valid only when Sr-89 is absent from the material from which the yttrium was separated. Sr-85 tracer is used for the determination of yield. From this value and the Y-90 concentration, the Sr-90 to Y-90 ratio can be calculated. A correction must be made for the contribution of Sr-85 to the sample beta count.

2.0 Definitions

None

3.0 Responsible Staff

Hot cell Technician
Cognizant Scientist
Analyst/Technician

4.0 Quality Control

4.1 Tolerances

All measurements in this procedure unless otherwise stated are $\pm 10\%$.

4.2 Separation Evaluation

The presence of residual yttrium in the separated strontium may be evaluated by Beta absorption measurements. A 136.5 mg/cm^2 absorber will absorb essentially all the Betas from Sr^{90} but only ~50% of those from Y^{90} .

5.0 Procedure

5.1 Materials and Special Equipment

Strontium carrier - 10mg/mL - Dissolve $2.42\text{g Sr}(\text{NO}_3)_2$ in 100 mL deionized (DI) water

Concurrence	Date	Approved	Date
A. G. King	12/16/92	L. S. Kellogg	12-15-92
Prepared by	Date	QAD Concurrence	Date
C. O. Harvey	12/15/92	T. L. Ehlert	12/18/92
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Iron Carrier - 10mg/mL - Dissolve 6.27g $\text{Fe}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ in 100 mL
DI water
Dilute ammonium hydroxide approx. 0.5M
Strontium-85 tracer
Syringe and syringe filter (maximum pore size - 0.45 μM)

5.2 Sr-90 Analysis Kit Preparation

5.2.1 To a 2 dram vial labeled #1 add the following:

500 μL DI water.
200 μL 10/mg/mL Sr carrier.
100 μL 10mg/mL iron carrier.

and the quantity of Sr-85 tracer (specified by the
cognizant scientist) cap vial and mix.

5.2.2 To a separate vial add 500 μL of dilute ammonium hydroxide.

5.2.3 Deliver these vials along with an empty capped vial
labeled #2 to the mini-hotcell operator.

5.3 Tracer Mount Preparation

At the same time the Sr-85 tracer is being added to vial #1, add
exactly the same amount to a beta dish which contains enough water
to cover the bottom. Dry under a heat lamp, submit to counting
room for beta and gamma counting, as per PNL-ALO-431 and
PNL-ALO-451.

Determine the net beta cpm and calculate the Sr-85 514 Kev net
gamma peak area by manual subtraction of background or the cpm
from an "enback" calculation of the gamma count.

5.4 Separation

5.4.1 Mini-hotcell technician - to the vial labeled #1
(containing the tracer) add the sample aliquot and mix by
swirling the vial. Add the contents of the NH_4OH vial to
vial #1 and swirl. Allow the precipitate (ppt) to
coagulate. Filter the sample into vial #2 using a syringe
filter. Deliver the filtrate to the laboratory.

5.4.2 Lab Analyst - to vial #2 add 100 μL iron carrier, swirl,
allow precipitate (ppt) to coagulate (if no ppt forms, add
dilute NH_4OH until it forms), centrifuge.

5.4.3 Using a disposable dropper, transfer the supernate to a
clean vial and repeat step 5.4.2 two more times.

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PNL TECHNICAL PROCEDURE

- 5.4.4 After the second repeat instead of centrifuging, filter into a beta dish using a syringe filter. (this maximizes the amount of sample plated without mounting any of the ppt).
- 5.4.5 Dry under heat lamp. If after some time, the dish appears to still not be dry, remove from under lamp and see if the liquid in the dish crystallizes on cooling. If it does, continue to the next step. If not, replace under heat lamp and complete drying.
- 5.4.6 After the sample is dry, transfer the dish to a cold hot plate. Turn the hot plate to high setting and heat until essentially all the solids in the dish have vaporized.
- 5.4.7 Remove dish from hot plate and submit to counting room for beta and gamma counting.
- 5.4.8 Calculate net beta cpm and gamma cpm or peak area in the same way as the tracer mount (Step 5.3).

6.0 Calculations

$$Sr-90 (dpm/mL) = [SB - \frac{TB}{TG} (SG)] \frac{(E) (TG)}{(V) (SG)}$$

Where:

SB = Beta cpm of the sample.
SG = Gamma cpm, of the 514 Kev peak area, from the sample.
TB = Beta cpm of tracer mount.
TG = Gamma cpm, of the 514 Kev peak area, from the tracer mount.
E = Counter efficiency factor (d/c) for Sr90.
V = Volume of sample.

7.0 Records

Records shall be maintained and controlled so as to conform with requirements of PAP-70-1701. Laboratory notebooks and analytical data sheets provide a mechanism for control of most records.

8.0 Procedure Qualification

Not required. This procedure is considered self-qualifying because of the use of a tracer and the calibration of the equipment used.

9.0 References

None.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-499, SEPARATION OF ACTINIDES BY EXTRACTION CHROMATOGRAPHY AND ION EXCHANGE

APPLICABILITY

This procedure allows for the sequential separation of Am with U, Th, Pu, and Np. It is applicable for up to 10 gm soil leachates or aqueous samples. It can be used for qualitative identification of actinides, or with tracers, can be used for quantitative analysis. After the initial group separation by hydroxide precipitation, Sr and Tc fractions are obtained which can be analyzed after further cleanup.

DEFINITIONS

- conc - concentrated
- Duplicate - a replicate aliquot of a sample which is brought through the entire sample preparation and analysis process to document the precision of the method.
- Reagent blank - an artificial sample designed to monitor the introduction of contamination into the sample preparation and analysis process; it is treated like a "real sample" as it is carried through the appropriate steps of a process.
- Blank spike - a reagent blank to which a known amount of the analyte of interest is added.
- Matrix spike - a replicate sample to which a known amount of the analyte of interest is added.
- ppt - precipitate

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

PRE-REQUISITE

Author RS Strebin	Date 2-3-93	Project Mgr. KJ Kuhl-Kruger	Date 2/2/93	PQ Representative TL Ehlert	Date 2/1/93
Technical Reviewer NL Wynhoff	Date 2-2-93	Line Mgr. AG King	Date 2/3/93	Other	Date
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PNL TECHNICAL PROCEDURE

PRE-REQUISITE

Only personnel trained in this procedure may perform the work. Personnel training records are kept in the section office.

TOLERANCES

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method; or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is $\pm 50\%$ in the next digit located beyond the last one stated.

QUALITY CONTROL

1. All quality control (QC) data shall be maintained as hard copy and available for easy reference or inspection.
2. Two QC options are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. Additional QC samples may be requested by a client in an Analytical Request Form (ARF), SOW, or Technical Project Plan (TPP) and these may be conveyed to the analyst through a Test Instruction (TI).
 - (a) Employ a minimum of one reagent blank and one blank spike per sample batch (20 samples or less). Run duplicate or matrix spike analysis upon client request.
 - (b) For all SOWs written by a client to meet CERCLA requirements that request analysis, employ a minimum of one reagent blank per sample batch (20 samples or less) to determine if contamination is occurring. Run one duplicate sample and one blank spike (NIST traceable, if possible) per batch (20 samples or smaller). A matrix spike may be analyzed with a batch of samples if so directed by the client.
3. Volume Calibration: Critical volume measurements, as indicated in the procedure, shall be made with automatic pipets or equivalent. A performance check of the automatic pipet shall be completed prior to use. This consists of pipetting and weighing at least three aliquots of

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deionized water, equal to the volume being used, into a container on the balance. The average delivery weight is converted to volume by multiplying the weight by the reciprocal of the density as it applies to the ambient temperature. This calculated delivery volume shall be acceptable for 7 days.

SPECIFIC QUALIFICATION

None required.

EQUIPMENT

Hot plate/stirrer
Filter - glass microfiber, $\leq 1.5 \mu\text{m}$ effective particle size retention, to fit filter apparatus
Filter apparatus, disposable
Wash bottles, plastic
Forceps
Pipetters
Small spatulas or scoops
Transfer pipets, plastic or glass
pH paper, fine range, centered around pH 3.0, and broad range
Heat lamp
Centrifuge tubes, 50-100 ml, plastic or appropriate size
Centrifuge
Eichrom Tru-Spec pre-packed columns
Eichrom Tru-Spec resin
Beakers - 30 ml, 50 ml, 150 ml, or appropriate size
Bio-Rad disposable 25ml columns or equivalent
Bio-Rad disposable column stopcocks or equivalent
Small plastic columns, Iso-Lab QS-NP or equivalent

SPIKES

- ^{242}Pu : For use as a general Plutonium spike in cases where Pu is being measured but ^{237}Np is not to be determined or is to be determined separately.
- ^{244}Pu : Specialized Pu spike for Mass-spec recovery and as carrier.
- ^{243}Am - ^{239}Np : For use as a general Americium spike in determination of ^{241}Am . It is also used for determination of ^{237}Np by way of its ^{239}Np daughter.
- ^{152}Eu : A Gamma emitter useful as an Am chemistry tracer, when directed by a Cognizant Scientist.

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PNL TECHNICAL PROCEDURE

REAGENTS

To the extent possible, prepare all reagents in volumes which will be consumed in the procedure operation for waste minimization purposes.

All reagents are prepared from analytical reagent grade chemicals. Deionized water, with an electrical resistance of >16 megohms-cm is used throughout this procedure. Concentrations are not critical and need only be within $\pm 10\%$ of stated values.

Saturated ascorbic acid: Take 3g ascorbic acid and add to 20ml 2M HNO_3 . Prepare just prior to use.

0.1M Ammonium Bioxalate: 1.2 gm ammonium oxalate plus 0.9 gm oxalic acid dissolved in 100mL water.

Sodium nitrite: NaNO_2 solid reagent.

1.5 M HNO_3 : 9.4mL conc HNO_3 diluted to 100mL with water.

2M HNO_3 : 13ml conc HNO_3 diluted to 100ml with water.

0.025M HNO_3 : 0.15ml conc HNO_3 diluted to 100ml with water.

8M HNO_3 : 50ml conc HNO_3 diluted to 100ml with water.

0.1M NH_4I conc HCl : Add 0.288g NH_4I to 20ml conc HCl and mix on vortex. Make 15mL for every sample. I_2 forms readily, therefore make the solution just prior to use.

4M HCl : 33ml conc HCl diluted to 100ml water.

Fe carrier, 10 mg/ml: Dissolve 18.08 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in H_2O . Dilute to 250ml with water. (Note: Another ferric salt may be used or another concentration as long as the required mgs of Fe^{+3} are added to the sample as directed.)

conc HNO_3 : Concentrated nitric acid, 16 M.

conc HCl : Concentrated hydrochloric acid, 12 M.

conc H_2SO_4 : Concentrated sulfuric acid, 18 M.

conc NH_4OH : Concentrated ammonium hydroxide, 14.5M.

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PNL TECHNICAL PROCEDURE

PROCEDURE

1.0 Sample Pre-Treatment

- 1.1 Take appropriate size aliquot of leachate, or aqueous sample (i.e. up to 2g or up to 10g soil equivalent for small or large column respectively) as directed by a Cognizant Scientist and add it to a centrifuge tube that is a minimum of twice the volume of the aliquot. Samples may be evaporated to reduce volume.

Note: Record exact volume or weight of sample and it's identification number on the Data Sheet (Exhibit 1) or equivalent.

- 1.2 Add radionuclide tracers as directed by the Cognizant Scientist. If sample does not contain at least 10mg of Fe, add 10mg Fe carrier.

Note: Record tracer isotope and identification number and exact volume on the Data Sheet (Exhibit 1) or equivalent.

- 1.3 Add conc NH_4OH to sample with stirring until red-brown precipitate forms and continue to add until solution is $>\text{pH } 7$.

- 1.4 Centrifuge and collect supernate. Save the supernate for Sr and Tc analysis if requested.

- 1.5 Add conc HNO_3 dropwise to the precipitate with stirring until all the precipitate has gone into solution.

- 1.6 Repeat steps 1.3, 1.4, and 1.5 up to 5 times. The last time use the minimum acid necessary to dissolve the precipitate in step 1.5. The removed radioactivity of ^{137}Cs may be used as an indicator of the number of times to repeat.

- 1.7 Add, to the solution, an approximately equal volume of 1.5M HNO_3 .

- 1.8 Add saturated ascorbic acid to solution dropwise. The ascorbic acid will appear to make the solution turn blue momentarily. Continue addition until further addition ceases to cause this effect.

- 1.9 Sample is now ready for addition to the Tru-Spec column.

2.0 Actinide Group Purification

For a 2gm soil sample or less proceed on to step 2.2, for a 2-10 gm soil equivalent start with step 2.1.

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PNL TECHNICAL PROCEDURE

2.1 Large Tru-Spec Column Preparation

- 2.1.1 Take a 25ml Bio-rad disposable column and break the tip off, fill the column to the 10-12ml mark, (printed on side of column) with Eichrom Tru-Spec resin.
- 2.1.2 Fill the column to the top with milli-Q water, cap and mix vigorously until all the resin is suspended in water, add more resin if necessary to give 10mL of settled resin.
- 2.1.3 Allow column to settle by letting stand, add a frit to the top of the column and push down gently to resin bed top. Drain water and wash with 15mL water.
- 2.1.4 Wash column with 20ml 2M HNO_3 ; column is now ready for use.
- 2.1.5 Proceed on to step 2.3.

2.2 Small Tru-Spec Column Preparation

- 2.2.1 Break the tip off an Eichrom Tru-Spec disposable column and allow the water to drain
- 2.2.2 Wash the column with 10ml 2M HNO_3 ; column is now ready to use.
- 2.2.3 Proceed on to step 2.3.

2.3 Add sample to column. Note that the column may change color. This is a matrix effect and should not affect the performance of the column.

2.4 Wash the small column with 20ml of 2M HNO_3 or wash the large column with 100ml 2M HNO_3 . Discard the wash.

2.5 Column is now ready to elute.

- a. In the case of a large column, elute the actinides with 100ml 0.025M HNO_3 followed by 100ml 0.1M ammonium Bioxalate into a beaker.
- b. In the case of a small column, elute the actinides with 30ml 0.025M HNO_3 followed by 30ml 0.1M ammonium Bioxalate, into a beaker.

2.6 Add 5ml conc HNO_3 and 0.5ml conc H_2SO_4 and evaporate by heat until dense fumes of sulfuric acid are produced and sample volume is less than 1ml.

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PNL TECHNICAL PROCEDURE

2.7 Add 1-5ml of conc HNO_3 and evaporate to H_2SO_4 fumes, repeat until the solution is clear, up to 5 times.

3.0 Actinide Separation By Anion Exchange

3.1 Take a 5ml disposable column and break the tip off. Replace the tip with a Bio-rad column stopcock, fill the column with 3mL Dowex 1-8x 100-200 mesh anion exchange resin. Rinse once with water and gently put column frit onto resin bed top. Fill reservoir with water and let drain, adjusting the flow rate to 1-2ml per minute.

3.2 Take the sample from step 2.7, add 5ml conc HNO_3 and evaporate to near dryness.

3.3 Add 15ml 2M HNO_3 and 100 μg Fe carrier to the sample, stir, and add 0.5ml saturated ascorbic acid. Bring sample to 8M HNO_3 by addition of 5ml conc HNO_3 .

3.4 Add 25mg NaNO_2 to the sample and gently heat until brown fumes no longer evolve.

3.5 Add three 5mL aliquots of 8M HNO_3 to anion column prepared in step 3.1. Column is now ready for sample. The column should change to a dark brown color as it is washed with the nitric acid.

3.6 Add the sample to the column collecting the effluent in a 50ml beaker. Save. This is the Am/U fraction.

Note: The Np/Am separation time is the time the sample is added to the column. Record this on the Data Sheet (Exhibit 1) or equivalent.

3.7 Wash the column with 25ml 8M HNO_3 in 5mL aliquots. Combine the wash with that from step 3.6, Am/U fraction.

3.8 Wash the column with 25ml conc HCl . This is the Th fraction.

3.9 Wash the column with 15ml 0.1M NH_4I -conc HCl . This is the Pu fraction ready for electrodeposition or precipitation plating.

3.10 Wash the column with 15ml 4M HCl . This is the Np fraction ready for electrodeposition or precipitation plating.

CALCULATIONS

Yields for Am/U, Th, and Pu are determined by Alpha Energy Analysis (AEA) along with the analytes. Yield for Np is determined by Gamma Energy Analysis (GEA) of ^{239}Np .

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PNL TECHNICAL PROCEDURE

RECORDS

Records will be maintained and controlled so as to conform to requirements of the ACL Quality Assurance Plan, MCS-033. Analytical data sheets provide a mechanism for control of most records.

REFERENCES

Eichrom Industries, Inc. 8205 S. Cass Ave Suite 107, Darien IL, 60559; Product Literature.

Concentration and Separation of Actinides from Urine Using a Supported Bifunctional Organophosphorus Extractant. E. Philip Horwitz, Mark L. Dietz, Donald M. Nelson, Jerome J. LaRosa, and William D. Fairman Anal. Chim. Acta 238 (1990) 263-271.

New Chromatographic Materials for Actinide, Lanthanide, and Strontium Analysis in Biological, Environmental, and Radioactive Waste Samples. E. Philip Horwitz, Mark L. Dietz, and Renato Chiarizia. (To be published.)

Analysis of Plutonium in Soil, Bottom Sediment, and Plants, Procedure DARC-0008, Radiochemistry Laboratory, Dosimetry and Analytical Services Section, Argonne National Laboratory.

Analysis of Americium in Soil and Bottom Sediment, DARC-0007, Radiochemistry Laboratory, Dosimetry and Analytical Services Section, Argonne National Laboratory.

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Check if used:

plating: _____

Dates

PNL-ALO-469, AEA: _____

Started:

Completed: _____

Am-243/Np-239

Pipette No. _____ Volume _____ +/- _____ Date Pipetted _____

Spike ID _____ Spike Activity _____

Np-237 - to blank spike

Pipette No. _____ Volume _____ +/- _____ Date Pipetted _____

Spike ID _____ Spike Activity _____

Np-237 - to matrix spike

Pipette No. _____ Volume _____ +/- _____ Date Pipetted _____

Spike ID _____ Spike Activity _____

Balance Number _____ Temperature (if weighing liquid samples) _____

[illegible]

Sample Volumes (if a pipet was used for small aqueous samples)

Used for _____
Pipette No. _____ Volume _____ +/- _____ Date Pipetted _____

Am/Np Separation Date and Time: _____

Analyst _____ Date _____

Reviewer	Date
----------	------

**DATE
FILMED**

10 / 5 / 93

END