1 of 3

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
 (METHODS AS OF MARCH 1990)

APPENDIX A3-R

S. C. Goheen
 M. McCulloch
 J. L. Daniel

May 1993

Prepared for
 the U.S. Department of Energy
 under Contract DE-AC06-76RLO 1830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Pacific Northwest Laboratory
 Richland, Washington 99352

1993

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A3-R
Table of Contents

PNL-325: Radionuclides

Appendix Number	Lab Number	Method Name	Analytes
A3-R.10	PNL-SP-31	Sample Preparation for Gross Alpha Analysis	Alpha
A3-R.20	RSD-51-DEQ13, Rev.0	Instrumental Counting of Cores by Gamma Spectrometry	Gamma
A3-R.30	HTA-4-22, Rev. 3	Solutions Analysis: Preparation of Alpha Sources by Direct Evaporation	Alpha
A3-R.40	HTA-4-4, Rev. 4	Solutions Analysis: Liquid Scintillation	Alpha, Beta
A3-R.50	PNL-SP-34	Alpha Counting Procedure	Alpha
A3-R.60	HTA-4-6, Rev. 4	Solutions Analysis: Alpha Counting	Alpha
A3-R.70	HTA-4-5, Rev. 4	Solution Analysis Alpha Spectrometry	Alpha
A3-R.80	RSD-51-DEQ 14 Rev. 0	Instrumental Neutron Activation Analysis of Briney Groundwaters and Core Samples by Gamma Spectrometry	Gamma
A3-R.90	PNL-SP-32	Sample Preparation for Gross Beta Analysis	Beta
A3-R.100	HTA-4-8, Rev. 4	Solutions Analysis: Beta Counting	Beta

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A3-R
Table of Contents

PNL-325: Radionuclides				
Appendix Number	Lab Number	Method Name	Analytes	
A3-R.110	HTA-4-23, Rev. 3	Solutions Analysis: Preparation of Beta Sources by Direct Evaporation	Beta	
A3-R.120	PNL-SP-25	Beta Counting Procedure	Beta	
A3-R.130	HTA-4-9, Rev. 4	Solutions Analysis: Gamma Spectrometry	Gamma	
A3-R.140	RSD-51-DEQ 10 Rev. 0	Counting Procedure and Quality Control for Gamma Spectrometry	Gamma	
A3-R.160	HTA-4-15, Rev. 5	Separation of Plutonium by Solvent Extraction Prior to Measurement of Alpha Counting	Pu	
A3-R.170	PNL-040/ESSA-12	Determination of Plutonium, Americium, and Curium in Solid and Liquid Samples	Pu, Am, Cm	
A3-R.180	PNL-MA-597-2-30.6 Rev. 0	Isotope Composition of Plutonium and Uranium by Mass Spectrometry	Pu, U	
A3-R.190	HTA-4-13, Rev. 6	Separation of Americium-241 and Curium-244 by Anion Exchange Prior to Measurement by Alpha Counting	241Am, 244Cm	
A3-R.200	HTA-4-14, Rev. 5	Separation of Neptunium by Cation Exchange and Solvent Extraction Prior to Measurement by Alpha Counting	237Np	

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A3-R
Table of Contents

PNL-325: Radionuclides			Method Name	Analytes
Appendix Number	Lab Number			
A3-R.210	RSO-51-DEQ-2 Rev. 1		Chemical Separation and Analysis Procedure for Uranium (²³⁴ U, ²³⁵ U)	Isotopic U
A3-R.220	RDS-51-DEQ-3 Rev. 1		Chemical Separation and Analysis Procedure for Thorium (²³⁴ Th, ²³² Th, ²³⁰ Th, ²²⁸ Th)	Isotopic Th
A3-R.230	RSD-51-DEQ-4 Rev. 1		Chemical Separation and Analysis Procedure for Radium (²²⁶ Ra, ²²⁴ Ra)	Isotopic Ra
A3-R.250	RSD-51-DEQ-8 Rev. 1		Chemical Separation and Analysis Procedure for Polonium (²¹⁰ Po)	²¹⁰ Po
A3-R.260	PNL-MA-597-7-40.39 Rev. 0		Determination of ⁹⁹ Tc	⁹⁹ Tc
A3-R.270	PNL-SP-47		Determination of Technetium-99 by Resin Method for Solid and Liquid Samples	⁹⁹ Tc
A3-R.290	HTA-4-12, Rev. 4		Separation of Technetium by Cation Exchange and Solution Extraction Prior to Measurement by Beta Counting	⁹⁹ Tc
A3-R.300	HTA-4-17, Rev. 4		Solutions Analysis: Carbon-14 by Distillation Prior to Measurement by Liquid Scintillation Counting	¹⁴ C

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A3-R
Table of Contents

PNL-325: Radionuclides

Appendix Number	Lab Number	Method Name	Analytes
A3-R.310	PNL-SP-33	Liquid Scintillation Counting Procedure	^{14}C , ^3H , ^{32}P
A3-R.320	PNL-110	Radionuclide Separation and Analysis Procedure for Carbon-14	^{14}C
A3-R.330	PNL-MA-597-7-40.26 Rev. 2	Separation of Iodine-129 by Solvent Extraction and Distillation from Chloride Solutions Prior to Measurement by Gamma (X-Ray/Counting)	^{129}I
A3-R.340	PNL-SP-49	Radionuclide Separation and Analysis Procedure for Iodine-129	^{129}I
A3-R.350	PNL-MA-597-7-40.17 Rev. 2	Separation of Iodine-129 by Cation Exchange and Distillation Prior to Measurement by Gamma (X-Ray) Counting	^{129}I
A3-R.360	PNL-SP-39A	Determination of Strontium-90 by ^{90}Y Decay Method	^{90}Sr
A3-R.370	HTA-4-11, Rev. 5	Separation of Strontium-90 by Cation Exchange Prior to Measurement by Beta Counting	^{90}Sr
A3-R.380	PNL-SP-38	Determination of ^{59}Ni and ^{63}Ni in Solid and Liquid Samples	^{59}Ni , ^{63}Ni

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A3-R
Table of Contents

PNL-325: Radionuclides

Appendix Number	Lab Number	Method Name	Analytes
A3-R.390	PNL-MA-597-7-40.15 Rev. 6	Selenium-79 by Ion Exchange and Distillation Separation Prior to Measurement by Liquid Scintillation Counting	⁷⁹ Se
A3-R.400	HTA-4-21, Rev. 3	Separation of Tin-126 by Anion Exchange Prior to Measurement by Gamma Counting	¹²⁶ Sn
A3-R.410	HTA-4-40, Rev. 1	Separation of Cesium Prior to Measurement of Cs-135 by Mass Spectrometry and Gamma Spectrometry	¹³⁵ Cs
A3-R.420	PNL-SP-30	Radionuclide Separation and Analysis Procedure for Tritium	³ H
A3-R.430	HTA-4-16, Rev. 3	Solutions Analysis: Uranium by Laser-Excited Fluorescence	Total U
A3-R.440	HTA-4-36, Rev. 2	Separation of Uranium from Brine Solutions by Ion Exchange	Total U
A3-R.450	PNL-SP-24	Counting Procedure for Alpha Spectrometry	Alpha-Single Isotope
A3-R.460	PNL-091	Total Strontium in Test Wells and Water Samples (Oxalate-Nitric Acid Method)	Total Sr

HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A3-R
Table of Contents

PNL-325: Radionuclides

<u>Appendix Number</u>	<u>Lab Number</u>	<u>Method Name</u>	<u>Analytes</u>
A3-R.480	WHC-053-1	Laboratory Procedure for Measurement of Physical and Rheological Properties of Solutions, Slurries, and Sludges	Physical Properties, Rheology
A3-R.490	HTA-4-10, Rev. 0	Solutions Analysis: Cesium Stripping for Gamma Spectrometry	Gamma

PNL TECHNICAL PROCEDURE

Title: SAMPLE PREPARATION FOR GROSS ALPHA ANALYSIS

1.0 Applicability

This procedure is applicable to the samples received for gross alpha analysis.

2.0 Definitions

dpm-disintegrations per minute (a concentration term)
pCi-picocuries (2.22 dpm, a concentration term)
LRB-Laboratory Record Book

3.0 Responsible Staff

3.1 Service Manager

3.2 Scientist

3.3 Technician

4.0 Procedure

Prerequisite = Personnel trained in this procedure may perform the work.
Perform all ether work under a hood.

4.1 Liquid Samples

4.1.1 Transfer a 100 ml aliquot into a 150 ml beaker, (do this in duplicate) and acidify with 5 ml of concentrated HNO₃.

4.1.2 Evaporate the solutions on a hot plate to a few mls (do not evaporate dry).

4.1.3 Add 5 ml of 9M HNO₃ to each sample. Add two stainless steel stirring bars and 3 drops of RuCl₃ carrier solution.

4.1.4 Add a volume of diethyl ether approximately the same as the aqueous layer volume. Place the beaker on an air-powered stirrer and stir 10 minutes. Avoid too rapid a stirring action that may splash out some of the sample.

Prepared by <i>J. K. King</i>	Date 9-17-87	Approved (SECTION MGR) <i>[Signature]</i>	Date 9-17-87
QAD Concurrence <i>S. L. English</i>	Date 9-17-87	Effective Date SEP 17 1987	
Procedure No. PNL-SP-31	Revision No. 0	Page <u>1</u> of <u>2</u>	

PNL TECHNICAL PROCEDURE

4.1.5 Turn off the air to the stirrer and allow the phases to separate. Then transfer the ether layer into a labeled second 150 ml beaker that has been prechecked for fit in the steam bath. If any aqueous solution accompanies the ether decant the ether to a third labeled 150 ml beaker and separate the aqueous portion. Combine the ether fractions.

4.1.6 Add distilled water to the combined ether layers to bring the beaker about 3/4 full. Evaporate the ether on a steam bath. Concentrate the aqueous layer to a few ml's on a hot plate. Quantitatively transfer the remaining aqueous solutions to flamed 1 1/2" counting dishes. Evaporate the solutions under a heat lamp and flame gently to dry.

4.1.7 Count the alpha activity (refer to procedure PNL-SP-34).

4.1.8 Calculate total alpha activity:

$$T\alpha = \frac{(\text{net c/m}) \times (d/c) \times (0.45045)}{\text{Volume (l)} \times (\text{yield})}$$

$$= \text{net c/m} \times 16.74 \text{ pCi/l for}$$

$$d/c=2.601, \text{ yield}=0.700, \text{ volume}=0.100 \text{ l.}$$

4.2 Solid Samples

4.2.1 Weigh the sample as received and select an appropriately sized aliquot for analysis in duplicate.

4.2.2 Leach the sample aliquots three times with hot 6N HCL and combine the leachates.

4.2.3 Evaporate the leachates to a few ml's on a hot plate. Add excess concentrated HNO₃ and continue the evaporation to convert the salts to the nitrate form.

4.2.4 Complete the separation as in steps 4.1.2. + 4.1.7.

4.2.5 Calculate the total alpha activity:

$$T\alpha = \frac{(\text{net c/m}) \times (d/c) \times (0.45045)}{\text{Aliquot wt (gm)} \times (\text{yield})}$$

$$= \frac{(\text{net c/m}) \times (1.674)}{\text{Aliquot wt (gm)}} \text{ pCi/gm}$$

$$\text{where } d/c=2.601, \text{ yield}=0.700$$

TITLE: INSTRUMENTAL COUNTING OF CORES BY GAMMA SPECTROMETRY

1.0 OBJECTIVE

This procedure describes a method for instrumental counting for radionuclides ^{238}U , ^{235}U , ^{230}Th , ^{226}Ra , ^{210}Pb , ^{232}Th , and ^{40}K in cores by gamma spectrometry. Using known amounts of liquid and solid reference standards, an efficiency or disintegration per count (DPC) factor for each radionuclide is established to calculate concentrations ($\mu\text{g/g}$ or dpm/g) in cores. The procedure also describes the method of gamma measurement and data reduction for the radionuclides.

2.0 APPLICABILITY

When this procedure is selected for implementation by a QA plan prepared and approved in accordance with PNL-MA-60, this procedure is applicable to the instrumental counting of cores by gamma spectrometry.

This procedure is applicable to the Project Manager, and trained and qualified personnel within the "Disequilibrium Study of Natural Radionuclides" Program and/or the Chemical Technology Department of PNL, who will be performing instrumental counting of cores by gamma spectrometry.

3.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)
 ng - nanograms (10^{-9} grams)
 μg - micrograms (10^{-6} grams)
 $t_{1/2}$ - half-life
 LRB - Laboratory Record Book
 LTC - Large Tuna Can
 STC - Small Tuna Can
 TC - Tuna Can
 DPC - Disintegrations Per Count
 SBX - Shatter Box
 LEPD - Low Energy Photon Detector

4.0 RESPONSIBILITIES

4.1 Project Manager

- Assures that the work is performed by qualified personnel. Maintains personnel training of procedures described in this text.

Approved (Project/Program Manager)		Approved (Line Manager)	
J. C. Lau <i>JC Lau</i>		N. A. Wogman <i>N. A. Wogman</i>	
Prepared by	Technical Review		QA Review
JC Lau <i>JC Lau</i>	<i>[Signature]</i>		<i>[Signature]</i>
Procedure No.	Revision No.	Date Issued	Page <u>1</u> of <u>18</u>
RSD-51-DEQ 13	0	5/20/85	

PNL TEST PROCEDURE FOR SRP

- Reviews and maintains all data
- Approves deficiency and nonconformance reports
- Prepares a report on results
- Assures that the work is done according to applicable procedures
- Assures that all required equipment, chemicals, reagents and glasswares are available to comply with procedures

4.2 Cognizant Test Personnel

- Conduct separations according to this procedure
- Comply with laboratory record keeping procedures and data reduction practices
- Report completed results to the Project Manager or cognizant scientist
- Initiate deficiency and nonconformance reports

4.3 QA Representative

- Reviews and approves deficiency and nonconformance report
- Approves waivers from this procedure prior to departure from it

5.0 PROCEDURE

5.1 Equipment and Materials

- Large "tuna can" (LTC) made of aluminum, 5.9 cm diameter X 2.8 cm height, 220 gm usable capacity.
- Small "tuna can" (STC) made of aluminum, 3.4 cm diameter X 2.4 cm height, 80 gm usable capacity.
- Tuna can sealer for LTC and STC, to seal can airtight.
- Lucite holder for LTC and STC on detectors
- Shatterbox (SBX) to pulverize rock chips into fine powder. Made by Spex Industries Inc., Metuchen, NJ
- Mettler PC 4400 electrobalance. Suitable for material from 1 to 1000 grams.

Procedure No.
RSD-51-DEQ 13

Revision No.

Date Issued
5/20/85

Page 2 of 18

PNL TEST PROCEDURE FOR SRP

- Miscellaneous laboratory materials: weighing paper, plastic bags, hammer, pipettes, stirring rod, 8 oz plastic jars
- Low energy photon detectors (LEPD) No. D389 and No. D447 plus counting system
- High efficiency Ge(Li) or intrinsic Ge detector plus counting system
- Coincidence-noncoincidence Ge(Li)-NaI(Tl) detectors plus counting system
- Coincidence-noncoincidence NaI(Tl)-NaI(Tl) multidimensional detectors plus counting system
- PDP 11/44 computer for data reduction and storage of gamma-ray spectra
- Versatec printer (VP) for hard copy printout of data calculation and gamma-ray spectra
- Magnetic storage device (MSD) for computer storage of data reduction and gamma-ray spectra
- Radionuclide standards (^{238}U , ^{235}U , ^{230}Th , ^{226}Ra , ^{210}Pb , ^{232}Th , ^{228}Ra , ^{228}Th , ^{40}K) for LTC and STC
- Eppendorf micropipettes for STC and LTC radionuclide standard preparation
- Reference Rock Standard - IAEA S-7, S-8 (uranium ore) and NBS Rocky Flats soil SRM 4353

5.2 Radionuclide Standards in Tuna Cans

5.2.1 Preparation

- Weigh ~75 gm for STC and/or 210 gm for LTC of pure Al_2O_3 powder using the PC 4400 Mettler balance.
- Pipette a known concentration of liquid standard evenly over the Al_2O_3 , and let it air-dry in a hood.
- Stir the dry Al_2O_3 powder for about 15-30 minutes with a disposable plastic rod or disposable tongue depressor to assure the mixture is homogeneous.
- Pour the Al_2O_3 quantitatively into the tuna can (LTC or STC) and seal the can with a can sealer with 1-1/2" setting for STC and 3" setting for LTC.

Procedure No.	Revision No.	Date Issued	Page <u>3</u> of <u>18</u>
RSC-51-DEF 12		5/20/85	

PNL TEST PROCEDURE FOR SRP

- Label the can with an LRB number and dpm of radionuclide and place it in a clear plastic bag. Table 1 shows the activity (dpm) spiked for each standard in STC.
 - Make sure the LRB contains all pertinent information on the production of each TC standard such as; can LRB identification no. (ID), activity in can, weight of matrix and liquid standard ID no.
- A. Balance shall be calibrated prior to use in accordance with PAP-1201, Calibration.

5.2.2 Disintegration Per Count (DPC) Factors for STC

In all cases so far, STC has been used for instrumental counting. The LTC is included in the previous text because of the possibility of future use.

- Place the bagged STC onto an appropriate lucite holder and detector. Detectors used for counting are: (1) low energy photon detector (LEPD) No. D389 and D447. (2) Coincidence-noncoincidence Ge(Li)-NaI(Tl) "Diode I". (3) Multidimensional NaI(Tl)-NaI(Tl) counting systems. Count the can on each detector for sufficient time to achieve $\leq 1\%$ statistical counting error for the desired photopeak.
- Use the peak integration method (see section 5.5.2) and obtain net cpm $\pm 1 \sigma$ error for the desired photopeak.
- Divide the dpm $\pm \sigma_1$ error (spiked in the can) by the net cpm $\pm \sigma_2$ error and obtain the DPC factor $\pm \sigma_3$ error, as follows:

$$DPC \pm \sigma_3 = \frac{dpm}{cpm} \pm \frac{dpm}{cpm} \left[\left(\frac{\sigma_1}{dpm} \right)^2 + \left(\frac{\sigma_2}{cpm} \right)^2 \right]^{1/2}$$

Usually the errors associated with the standard and DPC factors are small ($\leq 2\%$). Table 2 lists the DPC factors for the radionuclides used in measurements and the system background for each counting system.

- A. All radionuclide counters shall be calibrated in accordance with PAP-1201, prior to use.
- B. All hand calculations shall be performed, documented, and reviewed in accordance with PAP-301.

PNL TEST PROCEDURE FOR SRP

TABLE 1. Liquid Standard Reference Material used
for Calibration and Determining DPC Factors

<u>Radionuclide</u>	<u>T 1/2</u>	<u>PNL. No.</u>	<u>S.T.C. No.</u>	<u>Concentration (dpm) in STC</u>
238U	4.51 X 10 ⁹ y	50037-129-0	5347-16-1	1.190 X 10 ⁵
235U	7.13 X 10 ⁸ y	50037-129-0	5347-16-1	5409
230Th	7.52 X 10 ⁴ y	50037-131-1	5347-18-1	8.00 X 10 ⁴
226Ra	1600 y	3368-147-0	5347-19-1	2.20 X 10 ⁴
210Pb	22.3 y	50037-127-0	5347-19-1	8.23 X 10 ⁴
232Th	1.39 X 10 ¹⁰ y	50037-133-0	5347-17-1	5.10 X 10 ⁴
228Ra	5.76 y	50037-133-0	5347-17-1	5.10 X 10 ⁴
40K*	1.28 X 10 ⁹ y	50690-42-3	5347-151-2	7.48 X 10 ³

*KCl analytical grade solid is used.

PNL TEST PROCEDURE FOR SRP

Radionuclide	$T_{1/2}$	Detector Type	γ -peak (Isotope) keV	Sys. Bkg. (c/m)	*DPC (efficiency-1) STC
^{238}U	$4.51 \times 10^9 \text{y}$	389 LEPD	63.3 (234Th)	0.049	322.6
			92.6 (234Th)	0.13	256.5
^{230}Th	$7.52 \times 10^4 \text{y}$	447 LEPD	63.3 (234Th)	0.064	379.2
			92.6 (234Th)	0.20	288.3
^{226}Ra	1600 y	389 LEPD	67.8 (230Th)	0.017	2770
			67.8 (230Th)	0.02	3349
^{226}Ra	1600 y	447 LEPD	186 (226Ra)	0.100	604.3
			295 (214Pb)	0.017	227.5
^{210}Pb	22.3 y	447 LEPD	352 (214Pb)	0.037	154.8
			186 (214Pb)	0.127	653.1
^{235}U	$7.13 \times 10^8 \text{y}$	389 LEPD	295 (214Pb)	0.039	247.5
			352 (214Pb)	0.069	167.1
^{210}Pb	22.3 y	389 LEPD	186 (226Ra)	0.110	567.4
			295 (214Pb)	0.097	97.15
^{210}Pb	22.3 y	447 LEPD	352 (214Pb)	0.005	161.1
			Conc. (214Pb)	270	2.01
^{210}Pb	22.3 y	447 LEPD	Conc. (214Pb)	0.24	29.7
			46.5 (210Pb)	0.073	342.0
^{210}Pb	22.3 y	447 LEPD	46.5 (210Pb)	0.028	421.8
			163.4 (235U)	0.01	353.4
^{210}Pb	22.3 y	447 LEPD	205.4 (235U)	0.01	491.7

TABLE 2. Radionuclide data and detector disintegrations per count (DPC) factors for various radionuclides in small tuna can (STC)

PNL TEST PROCEDURE FOR SRP

Radionuclide	T _{1/2}	Detector Type	Y-peak (Isotope) keV	Sys. Bkg. (c/m)	*DPC (efficiency-1) STC
232Th 228Ra	1.39 x 10 ¹⁰ y 5.76 y	447 LEPD	163.4 (235U)	0.03	389.6
			205.4 (235U)	0.01	500.0
		389 LEPD	129.2 (228Ac)	0.015	761.4
			338.2 (228Ac)	0.01	490.6
224Ra	3.66 d	447 LEPD	129.2 (228Ac)	0.020	890.1
			338.2 (228Ac)	0.040	540.6
		"1" Ge(Li)-NaI(Tl)	338 (228Ac)	0.25	393.3
			911 (228Ac)	0.26	389.3
			969 (228Ac)	0.048	663.5
		389 LEPD	239 (212Pb)	0.110	73.5
			300 (212Pb)	0.002	1640
			239 (212Pb)	0.219	80.9
40K	1.28 x 10 ⁹ y	447 LEPD	300 (212Pb)	0.009	1774
			239 (212Pb)	1.57	57.2
		"1" Ge(Li)-NaI(Tl)	300 (212Pb)	0.080	1472
			727 (212Bi)	0.040	1405
			583 (208Tl)	0.12	875
		Multidimensional NaI(Tl)-NaI(Tl)	583 (208Tl)	0.26	291
			+Conc. (208Tl)	0.124	17.95
			+Conc. (40K)	35.0	27.83
		Multidimensional NaI(Tl)-NaI(Tl)			

* DPC's are approximate values and depend on geometry. They are periodically checked.
DPC = 1/efficiency. The higher the DPC value, the lower the efficiency. 186 keV γ of 226Ra has contribution from 185.6 keV γ of 235U, which is corrected.
† Coincidence peak.

TABLE 2. Radionuclide data and detector disintegrations per count (DPC) factors for various radionuclides in small tuna can (STC)

PNL TEST PROCEDURE FOR SRP

5.2.3 Verification of DPC Factors

Soil Reference standards, NBS Rocky Flats soil SRM 4353 and IAEA uranium ore number S-7 are used for verification of DPC factors. These are pulverized and homogenized reference standards.

- Take a known amount (note in LRB) of the reference standard and mix thoroughly with Al_2O_3 to obtain total weight of 75 gm for STC and 210 gm for LTC.
- Pour the reference standard plus Al_2O_3 into the STC/LTC and seal the can with a can sealer. Count the can under the same conditions as the radionuclide standard in Section 5.2.2.
- Use peak integration method (Section 5.5.2) and obtain net $cpm \pm 1 \sigma$ error for the desired photopeaks.
- Multiply the net $cpm \pm \sigma_4$ error by the $DPC \pm \sigma_3$ factor from Section 5.2.2 and calculate the $dpm \pm \sigma_5$ for the reference standards.

$$dpm \pm \sigma_5 = (cpm) \times (DPC) \pm (cpm) (DPC) \left[\left(\frac{\sigma_4}{cpm} \right)^2 + \left(\frac{\sigma_3}{DPC} \right)^2 \right]^{1/2}$$

Table 3 shows the comparison of experimental results with certified dpm/gm values of NBS Rocky Flats soil. In all cases the agreement is excellent ($\pm \leq 3\%$).

Table 3. Comparison of Our Values with the Certified Values of NBS Rocky Flats Soil No. SRM 4353

	Certified (dpm/gm)	PNL Value (dpm/gm)
U-238	2.33 ± 0.12	2.30 ± 0.10
Th-230	2.65 ± 0.13	<3
Ra-226	2.57 ± 0.17	2.65 ± 0.10
Pb-210	---	2.73 ± 0.10
Ra-228	4.20 ± 0.20	4.20 ± 0.12
Th-228	4.24 ± 0.20	4.30 ± 0.12
K-40	43.3 ± 4.2	36.3 ± 2.0

PNL TEST PROCEDURE FOR SRP

- IAEA uranium ore standard is certified to have 0.527% content of natural U_3O_8 , which gives 3310 dpm/gm of ^{238}U . This IAEA standard is in equilibrium with its chain members (^{230}Th , ^{226}Ra and ^{210}Pb) and is used as an internal control during the experiment.
- A. Balance shall be calibrated in accordance with PAP-1201 prior to use.
- B. Hand calculations shall be performed, documented, and reviewed in accordance with PAP-301.

5.3 Core Sample Preparation Procedure

- Weigh a known amount (100-200 gm) of core on a Mettler balance. Record the weight in LRB. Place the core in a heavy duty large plastic bag (16" X 21") and give several rolls. Place the rolled up bag into another heavy duty large plastic bag and again give several rolls. Then wrap it in 2 layers of ultraclean heavy duty terry cloth towel.
- Place the towel bundle between two stainless steel plates. Strike the plate with a hammer several times until the core is broken into small fragments of 1/2" to 1" size.
- Transfer the fragments onto a clean plastic sheet and then into a clean stainless steel shatter box unit. Run the shatter box for 1-2 minutes. The fragments are pulverized into a fine powder.
- Transfer the powder into a clean 16" X 21" plastic bag. Transfer the powder from the bag into a large plastic jar. Cap the jar and label it. Shake the jar for about 5-10 minutes to ensure complete homogeneity of sample.
- Weigh 75 gm for STC or 210 gm for LTC of sample on tared weighing paper using the PC 4400 Mettler balance. Note the weight in LRB and transfer the sample into a STC or LTC. Level the powder evenly. Measure height of sample in can (this height should be very close to the height of the 75 gm/210 gm of Al_2O_3 used in the standard STC/LTC).
- Seal the STC or LTC with a can sealer. Label the can with LRB number, weight of sample, height of sample in can and seal in a clean plastic bag. Make sure LRB also contains all the above STC sample preparation information.
- A. Balance shall be calibrated in accordance with PAP-1201 prior to use.

Procedure No.	Revision No.	Date Issued	Page <u>9</u> of <u>18</u>
RSD-51-DEQ 13		5/20/85	

PNL TEST PROCEDURE FOR SRP

5.4 Counting of Core Samples

- Prior to counting canned core samples, count standards ^{238}U , ^{230}Th , ^{226}Ra , ^{210}Pb , ^{232}Th , and ^{40}K (Section 5.2.1) and reference standards (IAEA) (uranium ore) and NBS Rocky Flats soil SRM 4353 (Section 5.2.3) on the same detectors on which the core samples are to be counted. Take a system background of the detector for 1000-2000 minutes. Also assure that the detectors are in control (see Counting Procedure and Quality Control for Gamma Spectrometry (RSD-51-DEQ 10) using control standards.
 - Calculate the DPC's for each detector and verify if the new DPC's are within the experimental error of the DPC factors listed in Table 2. If the values differ significantly, use reference standards to recheck detector control.
 - Place the STC in a lucite holder. Count the core sample in a holder on LEPD No. D389 or D447, coincidence-noncoincidence Ge(Li)-NaI(Tl) "Diode I" and NaI(Tl)-NaI(Tl) multidimensional counting systems, under the same geometry conditions as that of standards.
- A. All radionuclide counters shall be calibrated in accordance with PAP-1201 prior to use.

5.4.1 Counting and Data Acquisition and Storage

Exhibit 1 shows a typical counting sheet for a sample and detector. The essential information on the counting sheets is as follows:

Header

Detector Identification ("Diode")

Computer file name reference for samples ("Ref")

Sampling reference date ("SRD/EOB")

Detector calibration ("Gain keV/CH")

Number of channels used in MCA memory ("# Chnls")

Parameter set in computer ("PARM IN")

Description

Computer magnetic storage sequence number Spectrum No.) for each individual sample count

Procedure No.

Revision No.

Date Issued

Page 10 of 18

RSD-51-DEQ 13

5/20/85

PNL TEST PROCEDURE FOR SRP

Run #

Weight of sample

Date counted

Time of start of count (Min, Sec)

Detector shelf or holder (geometry)

Comments

Percent dead time

Pile up rejector ON/OFF (optional)

Live time/Pre-set count

Elapsed time

Procedure

- Acquire data in analyzer. Note start time of count and all necessary parameters noted above. Length of counts for samples range between 200 to 2000 minutes. After counting, record live time and elapsed time on counting sheet (Exhibit 1). Set the analyzer to output mode for data transfer to PDP 11/44 computer and transfer the data.
- Store the data on a floppy disk and print out the raw data (hard copy) via Versatec Printer. The data can be plotted by PDP 11/44 Computer for peak identification and intensity.

5.5 Data Reduction

5.5.1 Preparation of Library for Radionuclides

A library for the radionuclides of interest is prepared for each detector before executing calculations on the raw data for final values.

- Identify the photopeaks in a gamma spectrum and select the photopeaks of interest for each radionuclide. Identify the peak channel, lower and upper integration limits and Compton background channels for each side of the peak (see Section 5.5.2 and Figure 1). Background channels can be on one side of the peak if the other side is not suitable due to interference peaks. Identify the DPC factors for

Procedure No.

RSD-51-DEQ 13

Revision No.

Date Issued

5/20/35

Page 11 of 18

PML TEST PROCEDURE FOR SRP

each photopeak for the detector used plus 1 σ interference correction for any radionuclide and the system background plus error for the detector used (see Section 5.5.3).

- Tabulate all the above information in the order called for in preparing the library. Exhibit 2 shows a typical example of the library used for LEPD No. 389.

5.5.2 Gamma Peak Analysis Procedure

Use the "SUM" program to calculate the final results (dpm/g) of sample. The procedures for calculating net counts per minute and errors in the "SUM" program are as follows:

Net Count Rate (cpm, 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 (R).

Figure 1. An idealized diagram of a gamma photopeak on a Compton continuum

This technique can be explained by using a simplified diagram of a gamma photopeak and a Compton continuum (Figure 1).

$$N \pm 1\sigma_N \text{ error} = T - C \pm \left[\frac{n^2}{4} \left(\frac{t_1}{n_1^2} + \frac{t_2}{n_2^2} \right) + T \right]^{1/2}$$

where

N = net counts

PML TEST PROCEDURE FOR SRP

T = total counts in n channels of photopeak

$$= \sum_{i=1}^n C (\text{counts})_i$$

t_1 = total counts in n_1 channels of Compton continuum

t_2 = total counts in n_2 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:

$$R \pm \sigma_R = \frac{N}{CT (\text{min})} \pm \frac{\sigma_N}{CT (\text{min})}$$

5.5.3 System Background

System background is comprised of the counting data due to the radionuclides occurring naturally in and around the gamma detector. Perform gamma peak analysis procedure (Section 5.5.2) on a spectrum acquired from a "background" (without the sample) count, and store the information in the library (Section 5.5.1). Subtract the system background net cpm from the sample net cpm.

5.5.4 Final Value (dpm/g)

Correct the sample net cpm to the sample reference date (SRD) by the decay factor. The decay factor is $e^{(\lambda \Delta t)}$, where Δt equals the time between the SRD and the midtime of the count. Usually, because of equilibrium conditions in the core samples, there is no need for a decay correction as the $t_{1/2}$ of each parent radionuclide is very long ($>10^5$ y). Multiply the corrected cpm (same as net cpm) by the DPC factor and divide by the weight of sample used. The equation is as follows.

$$\text{Radionuclide Activity in sample (dpm/g)} = \frac{(\text{Net cpm in Sample})(\text{DPC})}{\text{Wt. of Sample}}$$

PNL TEST PROCEDURE FOR SRP

Propagate the error at each step by the simple propagation method below. The error is mostly due to the counting statistics of the sample count. The errors in standards and DPC values are usually small ($\leq 2\%$). An example of the propagation of errors is as follows.

$$\frac{(A \pm \sigma A)(B \pm \sigma B)}{(C \pm \sigma C)} = \frac{A \times B}{C} \pm \sigma$$

$$\text{Where } \sigma = \frac{A \times B}{C} \left[\left(\frac{\sigma A}{A} \right)^2 + \left(\frac{\sigma B}{B} \right)^2 + \left(\frac{\sigma C}{C} \right)^2 \right]^{1/2}$$

- Record final results in summary sheets shown in Exhibit 3.

- A. All hand calculations from step 5.5 shall be performed, documented and reviewed in accordance with PAP-301.

5.6 Data Records

All sample preparations for each sample are referenced by the ID number which describes the LRB, page and sample number.

All spectral data for gamma spectrometry are recorded and filed. Spectra are stored on magnetic disk and a hard copy of each spectrum and calculation is stored in a binder notebook.

- 5.7 The project manager shall assure that the following records are processed in accordance with PNL Administration Procedure, PAP-1701, Records Management.

- Hand Calculations
- Laboratory Record Books (LRB)
- Spectral Data

5.8 Documents and Discrepancies

- 5.8.1 Records from this work shall be maintained and stored in accordance with PAP-1701.

- 5.8.2 When deviations from the procedure are found, the responsible staff shall initiate a Deficiency Report in accordance with PAP-1502, Controlling Deviations from QA Requirements and Established Procedures.

Procedure No.

RSD-51-DEO 13

Revision No.

Date Issued

5/20/85

Page 14 of 18

PNL TEST PROCEDURE FOR SRP

5.8.3 If elements of this procedure require a change only for one specific test, a waiver of specific steps is possible prior to any departure from this procedure. The waiver shall be processed in accordance with PAP-1502. The responsible QE shall approve all waivers for procedural changes.

5.8.4 If an incident occurs during this project, the responsible staff shall complete an incident report in accordance with PAP-1503. The responsible QE shall review and approve all incident reports.

6.0 REFERENCED DOCUMENTS

6.1 PNL-MA-60, Quality Assurance Manual for License Related Programs.

6.2 PAP-301, Hand Calculation Documentation and Review.

6.3 PAP-1201, Calibration Control System.

6.4 PAP-1502, Controlling Deviations from QA Requirements and Established Procedures.

6.5 PAP-1503, Incident Reporting.

6.6 PAP-1701, Records Maintenance and Storage in Project Files.

6.7 PAP-1704, Laboratory Record Books.

6.8 RSD-51-DEQ 10, Counting Procedure and Quality Control for Gamma Spectrometry.

Procedure No.

RSD-51-DEQ 13

Revision No.

Date Issued

5/20/85

Page 15 of 18

PNL TEST PROCEDURE FOR SRP

SRD/EOB
EOB 1-1-85 1200

DIODE: D389

PARM IN
GAIN: .2 KeV/Ch

SERIES FILE NAME: Sample 389

CHNLS: 2048

[illegible]

EXHIBIT-1 Typical Counting Sheet

PML TEST PROCEDURE FOR SRP

ISOTOPE	CUORE 309.1 LB: 7	NUCLIDE	PEAK	HLFLIFE	LOW	HIGH	DPC	DPC ERR	BKG	310	311	312	322	323	324	325	S BKG	SB ERR
U-238			317	0.000000	313	321	322.600	1.500000E-02	309	310	311	312	322	323	324	325	0	0.100000
U-238			463	0.000000	458	469	256.500	1.500000E-02	454	455	0	0	0	0	0	0	0	0.100000
Th-230			339	0.000000	336	341	2770.00	2.000000E-02	331	332	333	344	345	346	0	0	0.125000	0.100000
Ra-226			931	0.000000	926	936	604.300	1.500000E-02	920	921	922	930	939	940	0	0	1.700000E-02	0.740000
Pb-214			1476	0.000000	1469	1482	227.500	1.500000E-02	1460	1461	1462	1485	1486	1487	0	0	9.900000E-02	0.100000
Pb-214			1759	0.000000	1751	1766	154.800	1.500000E-02	1741	1742	1743	1767	1768	1769	0	0	2.950000E-02	0.200000
Pb-210			233	0.000000	230	237	342.000	1.500000E-02	226	227	228	239	240	241	0	0	2.000000E-02	0.200000
U-235			817	0.000000	813	822	353.400	2.000000E-02	807	808	809	825	826	827	0	0	6.250000E-02	0.220000
U-235			1027	0.000000	1022	1031	491.700	2.000000E-02	0	1033	1034	1035	0	0	0	0	7.900000E-03	1.33000
Ra-228			1691	0.000000	1686	1696	490.600	1.500000E-02	1682	1683	1684	1698	1699	1700	0	0	4.000000E-03	2.24000
Ra-228			646	0.000000	642	649	761.400	1.500000E-02	637	638	639	0	0	0	0	0	1.530000E-02	0.210000
Ra-224			1194	0.000000	1188	1198	73.5000	1.500000E-02	1182	1183	1193	1200	0	0	0	0	1.100000E-02	0.020000
Ra-224			1500	0.000000	1497	1504	1640.00	2.000000E-02	1490	1491	1492	1506	1507	1508	0	0	9.103000	0.120000
																	2.400000E-02	0.000000

SINGLE STRIPER FACTOR

931 317 0.350000

EXHIBIT-2 A typical example of library used for LEPD No. 389

PNL TEST PROCEDURE FOR SRP

Core Data Summary				Zone (Depth):	
Core Sample ID:	Tuna Can Geometry:	Radionuclide (*Daughter)	Half-life	Y-key	Well ID:
					Tuna Can ID:
Tuna Can Geometry:	Radionuclide (*Daughter)	Half-life	Y-key	Detector Date dpm/gm	Detector Date dpm/gm
238U	(234Th)	4.47 x 10 ⁹ y	63.4		
238U	(234Th)		92.6		
230Th		7.54 x 10 ⁴ y	67.8		
226Ra		1600 y	186.2		
226Ra	(214Pb)		295.0		
226Ra	(214Pb)		351.8		
226Ra	(214Pb)		609.0		
210Pb		22.3 y	46.6		
235U		7.04 x 10 ⁸ y	163.4		
235U			205.4		
232Th	(228Ac)	1.39 x 10 ¹⁰ y			
228Ra	(228Ac)	5.76y	129.2		
228Ra			338.2		
228Ra			911.4		
228Ra			969.0		
228Ra	(212Pb)	3.66 d	238.8		
224Ra			300.0		
224Ra			727.3		
224Ra	(212Bi)		583.1		
224Ra	(208Tl)	1.28 x 10 ⁹ y	1460		
40K					

* Actual radionuclide measured via gamma spectroscopy. If a daughter is in equilibrium with its parent, daughter's t_{1/2} is governed by its parents t_{1/2}.

EXHIBIT-3 Core Summary Sheet

PNL TEST PROCEDURE

TITLE: HTA-4-22, SOLUTIONS ANALYSIS: PREPARATION OF ALPHA SOURCES BY DIRECT EVAPORATION

1.0 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 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

- Deionized water.
- Ammonium hydroxide, reagent-grade, concentrated.
- Disc, 7/8-in. diameter, stainless steel.
- Heat lamp.
- Droppers, plastic.
- Propane torch.
- Hot plate.

4.0 PROCEDURE

Step 1) Pipet the required volume of sample onto a stainless steel disc. Volume should be $\leq 100 \mu\text{L}$ to avoid flow of solution off the edge of the disc while drying. Record the volume on the analytical report to the nearest $1 \mu\text{L}$.

Concurrence NA	Date	Approved	Date 7/2/87
Prepared by AC Lerb	Date 7/1/87	QAD Concurrence B.O. BARNES	Date 6/30/87
Procedure No. HTA-4-22	Revision No. 3	Effective Date JUL 01 1987	Page of 1 2

PNL TEST PROCEDURE

- Step 2) Evaporate the solution to dryness under a heat lamp.
- Step 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.
- Step 4) Heat for a few seconds to dissolve the residue.
- Step 5) Add one drop of ammonium hydroxide to the water on the disc.
NOTE: Do NOT touch the water with the dropper tip.
- Step 6) Evaporate the solution to dryness under the heat lamp.
- Step 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.
- Step 8) Measure the alpha activity on the disc using the Alpha Spectrometry (HTA-4-5) and the Alpha Counting (HTA-4-6) procedures.
- Step 9) Record 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-22	3	JUL 01 1987	2	2

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 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-4-4	Revision No. 4	Effective Date JUL 01 1987	Page of 1 3

PNL TEST PROCEDURE

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-4	4	JUL 01 1987	2	3

PNL TEST PROCEDURE

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

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-4	4	JUL 01 1987	3	3

PNL TECHNICAL PROCEDURE

TITLE: ALPHA COUNTING PROCEDURE

1.0 APPLICABILITY

The objective of this procedure is to communicate both specific and general information regarding the analytical operations of an Alpha 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.

2.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)
ng - nanograms (10^{-9} grams)
 μ g - micrograms (10^{-6} grams)
t_{1/2} - half-life
LRB - Laboratory Record Book

3.0 RESPONSIBLE STAFF

- Service Manager
- Scientist
- Analyst

4.0 PROCEDURE

4.1 Low-Background Alpha Counting System Description

Low-background alpha counters are used to measure low-level concentrations of alpha emitting radionuclide samples.

The alpha counting systems consist of zinc sulfide scintillation counters with photomultipliers, pre-amplifiers, amplifiers, timers and scaler. The sample chambers are shop-made; once the sample is slid under the detector it is jacked up and locked in position next to the scintillator. The counter will operate to pre-set time or pre-set count.

The electronics for the LOW BACKGROUND ALPHA Counting System consists of a high voltage power supply, a high voltage distribution and signal separation unit, amplifiers, discriminators, event counters, and timers. Each counting channel consists of an amplifier and pulse height discriminator combination that are both contained within one single wide NIM module.

Prepared by <i>[Signature]</i>	Date 9-17-87	Approved (SECTION MGR) <i>[Signature]</i>	Date 9-17-87
QAD Concurrence <i>[Signature]</i>	Date 9-17-87	Effective Date SEP 17 1987	
Procedure No. SP-34	Revision No. 0		Page 1 of 5

PNL TECHNICAL PROCEDURE

Each channel's timer and pulse counter are contained within a double wide NIM bin. The high voltage distribution unit takes high voltage to the multiplier photo tubes. Internal to this unit are the anode signal pickoff circuits which separate the alpha signals from the high voltage circuits and deliver them to the amplifiers. Because the alpha pulses are relatively large, a good plateau in count-rate vs high voltage results allowing the high voltage to be chosen for best background. The amplifier gain and discriminator are set to give maximum sensitivity consistent with the lowest back-ground achievable for the set detector parameters.

4.1.1 Electronic Components in Alpha Counters

Scintillation Counters - General Electric 974109G; H. V. Power Supply - John Fluke 412A; Voltage divider-shop made; Nuclear Counters - Canberra 1491; Preamplifier-discrimination - Canberra 813.

4.1.2 Counter Performance Tests

The control source for alpha counting and spectrometry is a secondary $^{238}\text{Pu} + ^{239}\text{Pu}$ standard containing 1218 ± 30 dpm alpha, traceable to the U.S. Bureau of Standards as referenced in LRB 50335-10. The source is electroplated on a stainless steel disk, which is placed in the center of a standard $1\frac{1}{2}$ " stainless steel counting dish. The calibration accuracy has been found to be within $\pm 3\%$. The counting efficiency of all shop made counters has not changed more than 3% from the efficiency established in 1963.

4.2 Geometry Measurement

The efficiency due to geometry of each instrument is measured on a monthly basis using a $^{238}\text{Pu} + ^{239}\text{Pu}$ control source (LRB 50335 - 10) and is recorded in the calibration control book for alpha counting instruments.

1. To establish the geometry, use the 1218 ± 30 dpm alpha counting source. Take the source from its storage holder and place it on a $1\frac{1}{2}$ " dish and place on the pedestal of the instrument being tested. Slide the pedestal into the counter and elevate and lock it.

PNL TECHNICAL PROCEDURE

2. Record the date, voltage setting of the power supply and the length of count (10 minutes) on a Counter Control Data Form (such as but not necessary limited to Exhibit 1) in the section of the control book for alpha counters that is assigned to each counter. Set the counter for a 10-minute counting interval and start the count. When the count interval is completed, record the count registered on the Counter Control Data form.
3. Repeat step 2 for a total of three 10-min counts.
4. Obtain the most recent background counting rate and record it on the Counter Control Data form. Compute the net cpm for each count by subtracting the background from the gross count.
5. Determine the average net c/m for the three counts and record it on the Counter Control (Exhibit 1) form. Determine the geometry using the following formula.

$$\text{Geometry} = \frac{\text{Average Net cpm}}{1218 \pm 30}$$

6. Record the geometry on the Counter Control Data form such as but not limited to (Exhibit 1). The geometry of the system should be within 0.415 and 0.418. If geometry is not within error limits, the instrument should be rechecked and calibrated.

4.3 Counter Control Checks

When instruments are used routinely, a periodic check of performance should be made. If the instrument is not used for an extended period (a few weeks), these checks may be discontinued until the operations are resumed. Control checks are to be made as follows:

PNL TECHNICAL PROCEDURE

1. Count the assigned control source (238+239Pu, LRB5033510) on each counter for 10 minutes. Record the date, high voltage setting, total counts, length of count and most recently measured background cpm in the calibration control notebook. Recount and record ten times. Calculate the net cpm for each count.
2. Compute the mean and standard deviation (σ) and record on the Counter Control Data form (Exhibit 1).
3. If the net cpm of any control count is outside the 1% or 3σ range in step 2 (whichever is larger), recheck the instrument and calibration.

4.4 Alpha Counter Background

1. When a counter is routinely used, a background of the counter should be taken periodically. Place a clean standard 1 1/2" dish on the dish holder for the counter. Take the background preferably for 1000 minutes. Record the date/time of the background count in the calibration control notebook..
2. For each radionuclide measurement, take a background using the same geometry minus the sample. Take the system background counts several times over an extended period of six months to a year.
3. Typical background of the alpha counters is 0.1-0.4 cpm. If the background is outside a 20% range of 3σ range from the average, whichever is higher, recheck the background with another clean S. S. dish. Sometimes high background results when the detector is contaminated following counting high count rate sample or standard or results from unusual radon concentrations in the air. Wait a few hours and let the system stabilize and clean the absorber. Recheck the background.

4.5 Control Count Values with "in control values"

When at least 10 values of the counter control (section 4.3) and background counts (section 4.4) have been accumulated, prepare a control chart and calculate the average $\pm \sigma$ of 10 measurements of counter controls and background counts. The calculations are shown below.

Procedure No. PNL-SP-34	Revision No. 0	Effective Date SEP 17 1987	Page <u>4</u> of <u>5</u>
----------------------------	-------------------	-------------------------------	---------------------------

PNL TECHNICAL PROCEDURE

The Average ($\bar{x}$) & Standard Deviation (σ). Given 10 measurements, the average value $\bar{x}$, and standard deviation (σ), are calculated as shown below

$$\bar{x} = \sum_{i=1}^{10} \frac{(\text{net cpm})_i}{10}$$

$$\sigma = \left[\frac{10 \sum_{i=1}^{10} (\text{net cpm})_i^2 - \left(\sum_{i=1}^{10} \text{net cpm} \right)^2}{10 \times 9} \right]^{1/2}$$

PNL TEST PROCEDURE

TITLE: HTA-4-6, SOLUTIONS ANALYSIS: ALPHA COUNTING

1.0 APPLICABILITY

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

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

- Proportional alpha counter (PAC).
- Ludlum ZnS scintillation alpha counter (SAC).
- Methane gas, commercial-grade, Union Carbide Corporation.
- Disc, 7/8-in. diameter, stainless steel.

4.0 PROCEDURE

4.1 Calibration Standards

The PAC and the SAC are initially calibrated using replicate counting sources prepared from an NBS-calibrated, high-purity, plutonium-239 solution (Radioactivity Standard T-1350). The measured efficiency and limit of error are posted on each PAC. Calibration counting sources are not used routinely to avoid loss of integrity through daily handling. Calibration sources are used only to recalibrate the PAC and the SAC after instrument modification or repair.

Concurrence <i>NA</i>		Date		Approved <i>[Signature]</i>		Date <i>7/2/87</i>	
Prepared by <i>ACLeef</i>		Date <i>7/1/87</i>		QAD Concurrence <i>B.O. BARNES</i>		Date <i>6/30/87</i>	
Procedure No. HTA-4-6		Revision No. 4		Effective Date JUL 01 1987		Page of 1 5	

PNL TEST PROCEDURE

4.2 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 PACs or SACs are initially calibrated using the NBS standard, and limits are defined that must be met on a daily basis. Electroplated sources are more rugged and will retain their integrity even with daily handling.

The following daily control standard count procedure shall be used.

For PACs:

- Step 1) Open counting chamber and insert control counting source provided for the specific PAC.
- Step 2) Close chamber and allow gas to purge for 10 to 15 seconds.
- Step 3) Preset time to 10-minutes.
- Step 4) Press STOP, RESET and START buttons. (Count will stop automatically at the end of 10 minutes.)
- Step 5) Record total counts on daily control data sheet and plot counts per minute on daily control chart. Counts per minute must fall within limits defined on daily control chart.

For SACs:

- Step 1) Open counting chamber and insert control counting source provided for the specific SAC.
- Step 2) Close and lock the chamber.
- Step 3) Preset time for 10 minutes.
- Step 4) Press COUNT button. This will clear the count register and start the count. The count will stop at 10 minutes.
- Step 5) Record total counts on daily control data sheet and plot counts per minute on daily control chart. Counts per minute must fall within limits defined on daily control chart.

4.3 Daily Background Count

For PACs:

- Step 1) Using a clean background disk, repeat Steps 1 to 4 of Section 4.2 above.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-6	4	JUL 01 1987	2	5

PNL TEST PROCEDURE

- Step 2) Record counts per minute on daily control data sheet.
- Step 3) Repeat Steps 1 and 2 except now preset the time to 100 minutes. (This count is normally started at the end of the day shift and is recorded the following morning.)

NOTE: These background counts for 10 minutes and for 100 minutes are used in the sample calculation in Section 4.4, Step 6 for PACs.

For SACs:

- Step 1) Insert a clean background disc in counting chamber.
- Step 2) Close and lock chamber.
- Step 3) Preset time for 900 minutes. (This count is normally started at the end of the day shift and is recorded the following morning.)
- Step 4) Press COUNT button.
- Step 5) Record counts per minute on daily control data sheet.

NOTE: These 900-minute background counts are used in the sample calculations in Section 4.4, Step 6 for SACs.

4.4 Sample Count

For PACs:

- Step 1) Survey prepared sample of counting source using an alpha survey instrument to insure that the alpha activity on the disk is not excessive (~20,000 dpm).
- Step 2) Open counting chamber and insert sample source.
- Step 3) Close chamber and allow the gas to purge 10 to 15 seconds.
- Step 4) Preset desired counting time. (This may vary from 10 to 1000 minutes depending on activity level and counting statistics required.)
- Step 5) Press STOP, RESET and START buttons. (Count will stop automatically at the preset time.)
- Step 6) Record the date counted, PAC efficiency, minutes counted, and total counts; calculate the counts per minute less the background count (Section 4.3, Step 3 for PACs) as outlined in the Alpha Counting Data portion of the Sample Report Card.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-6	4	JUL 01 1987	3	5

PNL TEST PROCEDURE

For SACs:

- Step 1) Survey prepared sample of counting source using an alpha survey instrument to ensure that the alpha activity on the disc is not excessive (~50 dpm). (SACs are low-level counters, hence the lower maximum activity level.)
- Step 2) Open chamber and insert sample disc.
- Step 3) Close and lock chamber.
- Step 4) Preset desired counting time (normally 100 minutes).
- Step 5) Press COUNT button. (Count register will clear and count will stop at preset time.)
- Step 6) Record the date counted, SAC efficiency, minutes counted, and total counts; calculate the counts per minute less the background counts (Section 4.3, Step 5 for SACs) as outlined in the Alpha Counting Data portion of the Sample Report Card.

4.5 Sample Calculations

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

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

where: B = uncertainty in gross alpha counts (B) per minute less background
 c = total sample counts (Section 4.4)
 t_c = counting time of sample (minutes)
 b = total background counts (Section 4.3)
 t_b = counting time of background (minutes)

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

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 4.4, Step 6 for PAC or SAC)

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-6	4	JUL 01 1987	4	5

PNL TEST PROCEDURE

- 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, HTA-4-5, Section 4.0, Step 13)
 α = uncertainty of A (dis/min/mL)
 β = uncertainty of B
f = uncertainty of alpha fraction (from Alpha Spectrometry procedure, HTA-4-5, Section 4.0, Step 13)

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

- 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, HTA-4-5, Section 4.0, Step 13)
B = counts per minute (Section 4.4, Step 6 for PAC or SAC)
F = alpha fraction for a particular isotope (from Alpha Spectrometry procedure, HTA-4-5, Section 4.0, Step 13)
A = dis/min/mL for a particular isotope calculated above.

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-6	4	JUL 01 1987	5	5

PNL TEST PROCEDURE

TITLE: HTA-4-5, SOLUTIONS ANALYSIS: ALPHA SPECTROMETRY

1.0 APPLICABILITY

This procedure provides instructions for measuring the relative abundance of each alpha-emitting radionuclide in a mixture in hydrothermal autoclave water leachate solutions.

This procedure applies to the analysis of aqueous samples by alpha spectrometry as prepared in Procedures HTA-4-7, HTA-4-13, HTA-4-14, HTA-4-15, HTA-4-22 and HTA-4-35 or other procedures as they are developed.

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

- Alpha spectrometer, ORTEC-576.
- Pulse height analyzer, Tracor Northern TN-1750.

3.1 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. See Procedure HTA-4-7 for the electroplating procedure.

As a calibration check, a control standard is 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.

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-4-5	Revision No. 4	Effective Date JUL 01 1987	Page of 1 3

PNL TEST PROCEDURE

If isotopes other than ^{237}Np , ^{239}Pu , and ^{241}Am are observed in the spectrum 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.

4.0 PROCEDURE

An alpha-counting source is first prepared by plating the alpha emitters onto a metal disk (see HTA-4-7, HTA-4-13, HTA-4-14, HTA-4-15, HTA-4-22), and HTA-4-35. Normally all alpha-counting sources are analyzed by alpha spectrometry to: 1) ensure purity of a separated isotope or 2) measure the abundance of 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.

Sample analysis, control standards and background counts are made in a similar manner.

- Step 1) Turn NIM BIN power ON.
- Step 2) Turn Detector voltage OFF.
- Step 3) Turn Pump/Vent valve to Vent.
- Step 4) Remove chamber cover and place control standard (or sample or clean disc (for background count)] in chamber.
- Step 5) Replace chamber cover.
- Step 6) Turn Pump/Vent valve to Pump. Allow it to pump for about 15 seconds before proceeding to Step 7.
- Step 7) Turn Detector voltage ON. Allow system to stabilize for about 1 minute before proceeding to Step 8.
- Step 8) Set Live Time Scan to 0 seconds for sample control counting, sample counting, or background counting. (A 0-second setting will acquire counts until the system is halted by pressing the STOP ACQUIRE switch.)
- Step 9) Press STOP ACQUIRE, ERASE DATA, and START ACQUIRE. To stop data acquisition, press the STOP ACQUIRE switch.
- Step 10) Print out spectra. Time counted is automatically printed with spectral data. Store control standard spectra in the BWIP notebook. Store sample and background counts in the BWIP file.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-5	4	JUL 01 1987	2	3

PNL TEST PROCEDURE

- Step 11) Add eight channels in the peak of each isotope. The exception is ^{237}Np , where 16 channels are added because of the wider range of alpha energies.
- Step 12) Add the same channels from the background count and normalize the background count to the same sample counting time as the sample, using the equation:

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

where: B = background count (normalized to sample counting time)
 C = background count
 D = sample counting time (s)
 E = background counting time (s).

- Step 13) Calculate the fraction of alpha activity for each isotope using the following equation:

$$F \pm f = \frac{(X - B) \pm \sqrt{X + B}}{\Sigma(X - B)}$$

where: F = Alpha fraction
 f = estimated uncertainty in F
 X = counts summed in peak of interest
 B = normalized background count (Step 12)
 $\Sigma(X - B)$ = sum of all observed peaks less normalized background.

- Step 14) Record the alpha fraction (F) and uncertainty (f) on the Sample Data Card and attach the data printout spectrum from Step 10) and file in the BWIP file.

NOTE: Use $F \pm f$ in the calculations for a particular isotope. (See Alpha Counting procedure, HTA-4-6, Section 4.5.)

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-5	4	JUL 01 1987	3	3

~~NOT~~ CONTROLLED
DOCUMENT

PNL ADMINISTRATIVE PROCEDURES FOR SRP

~~COPY NO. #~~

TITLE: • INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF BRINEY GROUNDWATERS
AND CORE SAMPLES BY GAMMA SPECTROMETRY

1.0 OBJECTIVE

This procedure describes the method used to determine major, minor, and trace elements in liquid and solid samples by instrumental neutron activation analysis (INAA). Concentrations of elements are determined by comparative analysis where the specific activities of individual nuclides in a sample are compared to the standard specific activity. Samples and standards are subjected to the same thermal neutron fluence, identical count geometries, and identical peak reduction criteria. The procedures describing the method of gamma spectrometry and data reduction for the activated radionuclides are described in RSD-51-DEQ-10 and RSD-51-DEQ-13.

2.0 APPLICABILITY

When this procedure is selected for implementation by a QA plan prepared and approved in accordance with PNL-MA-60, this procedure is applicable to INAA of liquid and solid samples by gamma spectrometry.

This procedure is applicable to the Project Manager, trained and qualified personnel with the "Disequilibrium Study of Natural Radionuclides" program and/or personnel of the Chemical Technology Department of PNL which will be performing the instrumental neutron activation analysis (INAA) of groundwater and core samples by gamma spectrometry.

3.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)
cpm - counts per minute (concentration term)
dpc - disintegration per count
ng - nanograms (10^{-9} grams)
 μ g - micrograms (10^{-6} grams)
 $t_{1/2}$ - half-life
LRB - Laboratory Record Book

4.0 RESPONSIBILITIES

4.1 Project Manager

- Assures that the work is performed by qualified personnel. Maintains personnel training for procedures described in this text

Approved (Project/Program Manager)		Approved (LINE Manager)	
J. C. Lau <i>J. C. Lau</i>		<i>Neil W. Wynn</i>	
Prepared by		QA Review	
J. C. Lau <i>J. C. Lau</i>		<i>W. Smith</i> 10/10/85	
Procedure No.	Revision No.	Date Issued	Page <u>1</u> of <u>18</u>
RSD-51-DEQ 14	0	7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

- Reviews and maintains all data
- Approves deficiency and non-conformance reports
- Prepares a report on results
- Assures that the work is done according to applicable procedures
- Reviews and complies with laboratory record keeping procedures and practices
- Assures that all required counting equipment, chemicals, reagents and glasswares are available to comply with procedures

4.2 Cognizant Test Personnel

- Conduct gamma spectrometry according to this procedure
- Comply with laboratory record keeping procedures and data reduction practices
- Report completed results to the Project Manager
- Initiate deficiency and non-conformance reports

4.3 QA Representative

- Reviews and approves deficiency and non-conformance reports
- Approves waivers from this procedure prior to departure from it

5.0 PROCEDURE

5.1 Equipment and Materials

- Polyvials 2, 2/5, 2/27 dram polyethylene vials
- Sealer, a small 30W soldering iron
- Mettler H51AR balance, suitable for material from 1 to 200 grams
- Mortar and pestal used for crushing solid samples and/or shatter-box (SBX) (made by Spex Industries Inc., Mutuchen, NJ)
- Miscellaneous laboratory materials: weighing paper, plastic bags, pipettes, solvents

Procedure No	Revision No.	Date Issued	Page <u>2</u> of <u>18</u>
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

- Low energy photon detectors (LEPD) No. D 389 and No. D 447 plus data acquisition system for γ -ray spectrometry
- High efficiency Ge(Li) or intrinsic Ge detectors plus data acquisition system γ -ray spectrometry
- Coincidence-noncoincidence Ge(Li)-NaI(Tl) detectors plus data acquisition system γ -ray spectrometry
- Lucite holders for polyvials geometries
- PDP 11/44 computer for data reduction and storage of gamma-ray spectra
- Versatec printer (VP) for hard copy printout of data (gamma-ray spectra), integrated peaks and decay corrected activities
- Magnetic storage device (MSD) for storage of data reduction and gamma-ray spectra
- Standards: various USGS rock standards and primary liquid and solid standards (ie. BCR-1, GSP-1, AGV-1, PCC-1, BHVO-1 rock standards) and rare earth element (REE), Dy, Mn, Al, Na, Ca, Mg, Au, U, Zn standards
- Research reactor facility: (e.g. TRIGA Reactor at Oregon State University, Corvallis, OR; Washington State University, Pullman, WA; and Westinghouse facility on Hanford site). The reactor facility must supply constant and reproducible thermal neutron fluxes to the samples and standards
- Activation capsules: pneumatic (rabbit tubes) and rotating rack activation tubes

5.2 Preparation of Standards

In this procedure, accurate and reproducible results are obtained by using standard materials which have been previously certified or are traceable to certified standard materials. Because this procedure employs comparative methods to calculate concentrations in samples, the standards are carefully prepared in identical activation and counting geometries as the respective samples.

- Weigh appropriate amounts of each solid and liquid standard (record in LRB) on a Metler balance into a pretared polyvial (2/5 or 2/27 dram).

Procedure No	Revision No.	Date Issued	Page <u>3</u> of <u>18</u>
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

- Seal the polyvial (2/5 or 2/27 dram) and place in a larger polyvial and seal this vial.

5.3 Preparation of Solid Samples

The procedure used to conform as "received" samples to irradiation and counting geometries identical to those of the standard material is described below.

- Homogenize the core samples by: 1) breaking the core into small fragments of 1/2" to 1" size, 2) pulverizing the chips in the shatter box for 1-2 minutes, 3) transferring the powder to a clean plastic jar and shaking for 5-10 minutes.
- Weigh a known amount (0.1-1 gm) of solid sample on a Mettler balance in a preweighed polyvial (2/5 or 2/27 dram). Record the weight in the LRB.
- Seal the polyvial and place it in a 2 dram polyvial and seal this vial.

5.4 Preparation of Liquid Samples

The 2/5 dram polyvial has capacity up to 1 ml. Depending on the trace element of interest and dissolved content in solution (molality of brine water) preparation of liquid samples can be done in one of the following ways.

- Pipette 1 ml or weigh a known volume of solution into a 2/5 dram polyvial. Record the weight in LRB.
- If the solution can be concentrated, take 5 to 10 ml of solution in a 30 ml beaker. Record the original volume. Slowly reduce the volume to about 1 ml under a heat lamp in a hood. Transfer the solution to a preweighed 2/5 dram polyvial. Record the weight in LRB.
- Take a known volume (100 ml to 1 litre) of solution in a beaker. Briney solutions usually contain sufficient Fe^{+3} content, if not, add 10-20 mg of Fe^{+3} carrier. Warm the solution on a hot plate. Slowly add conc. NH_4OH to precipitate Fe^{+} as $\text{Fe}(\text{OH})_3$. Several trace elements such as REE, Sc, U, Th, Ba, Sr, Hf, etc. quantitatively coprecipitate along with the $\text{Fe}(\text{OH})_3$. Filter the $\text{Fe}(\text{OH})_3$ ppt. using a Whatman fine filter paper. Discard the supernate. Dissolve the $\text{Fe}(\text{OH})_3$ ppt. in a few ml of conc. HCl or conc. HNO_3 . Make-up the solution to 5 or 10 ml in a volumetric flask. Take a known volume in a preweighed 2/5 dram polyvial.

Procedure No	Revision No.	Date Issued	Page 4 of 18
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

Record the weight in LRB.

- Seal the 2/5 dram polyvial and place it in a 2 dram polyvial and seal this vial.

A. Balance shall be calibrated in accordance with PAP-1201 prior to use.

5.5 Neutron Irradiation

Research reactor facilities supply a constant thermal neutron flux ($n/cm^2/sec$) to the samples and standards. The facilities which are to be used are operated at Hanford by Westinghouse; Oregon State University, Corvallis, OR; and Washington State University, Pullman, WA. For neutron irradiation, the sample is to be doubly encapsulated and sealed.

The usual sequential INAA procedure consists of two irradiations (a short irradiation of 5 minutes and a long irradiation of 7-8 hours) and four counting intervals to measure about 30 elements in an aliquot (Table 1). Table 2 lists the isotopes, half-life, γ -energy selected, decay interval and possible interference. The use of different decay intervals optimizes the detection sensitivity of the numerous elements.

5.5.1 Short Irradiation

- Place a sample in pneumatic transfer (rabbit) facility of a reactor
- "Shoot" the sample into the rabbit facility for a preset time (1.0-5.0 minutes).
- After irradiation and return from the reactor, remove the sample from the rabbit tube.
- Transfer the irradiated sample vial to a clean, non-irradiated 2-dram polyvial for counting
- After a decay period of about 15 minutes, count the sample on a Ge(Li) detector coupled with a 2048/4096 channel analyzer for a known period (5 minutes) to measure the short-lived isotopes ^{51}Ti , ^{27}Mg , ^{52}V , ^{28}Al and ^{49}Ca (Table 1).
- Wait 3-5 hours to let the short-lived isotopes decay away. Count the sample again to measure ^{165}Dy , ^{56}Mn and ^{24}Na (Tables 1 and 2).

Procedure No	Revision No.	Date Issued	Page <u>5</u> of <u>18</u>
RSD-51-DEQ 14		7/16/85	

TABLE 1. INAA SCHEME

NEUTRON FLUX = 6×10^{12} n/cm²/sec
IRRADIATION I = 5 MINUTES
IRRADIATION II = 8 HOURS

DECAY INTERVAL	ISOTOPES MEASURED
I (1) 15 MINUTES	⁵¹ Ti, ²⁷ Mg, ⁵² V, ²⁸ Al, ⁴⁹ Ca
(2) 3 - 5 HOURS	¹⁶⁵ Dy, ⁵⁶ Mn, ²⁴ Na
II (3) 1 - 3 DAYS	⁴² K
(4) 4 - 7 DAYS	¹⁶⁶ Ho, ¹⁵³ Sm, ¹⁵² Eu, ¹⁷⁷ Lu, ²³⁹ Np(U), ¹⁷⁵ Yb, ¹⁹⁸ Au,
	¹³¹ Ba, ¹⁴⁷ Nd, ¹⁴⁰ La, ²⁴ Na
(5) 40 - 50 DAYS	¹⁸² Ta, ¹⁵² Eu, ¹⁴¹ Ce, ¹⁶⁰ Tb, ²³³ Pa (Th), ⁵¹ Cr, ¹⁸¹ Hf,
	⁸⁵ Sr, ⁹⁵ Zr, ¹³⁴ Cs, ⁵⁸ Co (Ni), ⁴⁶ Sc, ⁸⁶ Rb, ⁵⁹ Fe, ⁶⁵ Zn,
	⁶⁰ Co, ¹²⁴ Sb

PNL ADMINISTRATIVE PROCEDURES FOR SRP

- Record activation time and length, proper neutron flux (reactor power) used, and decay periods for all samples and standards on count data sheet (Exhibit 1).

5.5.2 Long Irradiation

- Transfer to reactor operations personnel all labeled samples and standards in 2 dram polyvials.
- After the long irradiation (about 8 hours) and appropriate decay period (1-2 days), transport the samples and standards from the reactor to the laboratory in approved radioactive shipping containers and under approved DOT regulations.
- Transfer the samples into clean preweighed 2/5 dram polyvials. Record the weight in LRB. Seal the 2/5 dram polyvial and place it in a clean 2 dram polyvial.

5.6 Counting Scheme

- Tables 1 and 2 shows the counting scheme during short and long irradiations and their decay intervals. The samples are mostly counted on Ge(Li) detector (25% efficiency, FWHM 1.8 keV for 1332 keV γ of ^{60}Co) coupled with a 2048/4096 channel analyzer.
- In cases (after long irradiation), where the sensitivity of an element is poor or not feasible by the normal Ge(Li) counting, then count the sample on coincidence-noncoincidence Ge(Li)-NaI(Tl) counting system. Figure 1 shows a typical coincidence-noncoincidence spectra of a USGS BCR-1 geological standard counted after 50 days decay interval. As is obvious from Figure 1, the compton background in the non-coincidence mode is about 10 times lower than the background in the coincidence mode, thus increasing their sensitivity by an order of magnitude.
- Figure 2 summarizes the mode of measurement of 43 elements by sequential INAA using normal Ge(Li) counting and coincidence-noncoincidence counting. If needed, greater sensitivity for Ba, Sr, U and REE can be achieved by radiochemical neutron activation analysis (RNAA). The procedure for measuring REE in groundwaters by RNAA is outlined in Chemical procedure RSD-51-DEQ-9.
- Record irradiation time and length, neutron fluence (reactor power), start of count time count lengths, counting geometries (shelf), and dead times on the counting sheet (Exhibit 2).

Procedure No	Revision No.	Date Issued	Page <u>8</u> of <u>18</u>
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

FIGURE 1. Coincidence and Noncoincidence Gamma-Ray Spectra of Neutron-Irradiated BCR-1

Procedure No

RSD-51-DEQ 14

Revision No.

Date Issued

7/16/85

Page 9 of 18

THE ELEMENTS

																0	He
																IIIA	Ne
																IVA	F
																VA	O
																VIA	N
																VIIA	C
																VIIIA	B
																	Al
																IB	Si
																IIB	P
																	Cl
																	Ar
																	Kr
																	Br
																	Se
																	As
																	Ge
																	Sb
																	Sn
																	Te
																	I
																	Xe
																	Rn
																	Po
																	Bi
																	Pb
																	Tl
																	Hg
																	Cd
																	In
																	Zn
																	Cu
																	Ni
																	Co
																	Fe
																	Mn
																	Cr
																	V
																	Ti
																	Zr
																	Hf
																	Ta
																	W
																	Re
																	Os
																	Ir
																	Pt
																	Au
																	Hg
																	Tl
																	Pb
																	Bi
																	Po
																	At
																	Rn
																	Fr
																	Ra
																	Ac
																	Th
																	Pa
																	U
																	Np
																	Pu
																	Am
																	Cm
																	Bk
																	Cf
																	Es
																	Fm
																	Md
																	No
																	Lr

43 ELEMENTS

- INAA Ge (LI)
- INAA COINCIDENCE - NONCOINCIDENCE
- RNAA, REE, Ba, Sr, U

FIGURE 2. Mode of Measurements of 43 Elements

PNL ADMINISTRATIVE PROCEDURES FOR SRP

- A. All counters shall be calibrated in accordance with PAP-1201 prior to use.

5.7 Counting

Exhibit 1 is used for short counting and Exhibit 2 is used for counting following a long irradiation.

- Exhibits 1 and 2 show a typical counting sheet used for a sample and detector. The essential information included on the counting sheets are as follows:

Header

Detector Identification ("Diode")

Computer file name reference for samples ("Ref")

Sampling reference date ("EOB")

Detector calibration ("Gain in keV/Ch")

Number of channels used in MCA memory ("No. Chnls")

Parameter set stored in the computer ("PARM IN")

Description

Computer magnetic storage sequence number (Spectrum No.) for each individual sample count

Run No.

Weight of sample

Date of count

Start time of count (Min, Sec)

Detector shelf or holder (geometry)

Comments

Percent dead time of ADC

Pile up rejector ON/OFF (optional)

Procedure No	Revision No.	Date Issued	Page <u>11</u> of <u>18</u>
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

-Live time/Pre-set count time

Elapsed time

- For details of the counting systems, see the procedure on counting and Quality Control by gamma spectrometry (RSD-51-DEQ 10). Also see the review article on "Neutron Activation Analysis of Geological Materials" by Laul (1979).
- Based on the peak-to-Compton (P/c) ratio, comparison of the counting modes is made. Normal Ge(Li) counting is favored for most radio-nuclides. The spectrum obtained in the non-coincidence mode is favored for ^{51}Cr , ^{58}Co (^{58}Ni), ^{65}Zn , ^{124}Sb , ^{86}Rb , ^{85}Sr , ^{95}Zr , and the LEPD counting is favored for low energy gamma emitters such as ^{153}Sm and ^{147}Nd .
- Depending on the activity level present, select the best count mode to optimize the detection sensitivity of the individual radio-nuclides. Generally, counting by normal Ge(Li) and coincidence-noncoincidence Ge(Li)-NaI(Tl) systems is adequate to achieve the desired sensitivities. Whenever possible, make 2-3 counts of the sample on each counting system.
- Label all spectra with proper identifications as specified in Exhibit 2.

A. All counting systems shall be calibrated in accordance with PAP-1201, Calibration.

5.8 Calculations

Most of the calculations are performed by a PDP 11/44 computer using the code CANGAS. The principle for gamma peak analysis in CANGAS is outlined by Laul et al. (1979). The general procedure in gamma peak analysis is as follows.

5.8.1 Gamma Peak Analysis Procedure

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).

Procedure No	Revision No.	Date Issued	Page <u>12</u> of <u>18</u>
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

Figure 3. An idealized diagram of a gamma photopeak on a Compton continuum

This technique can be explained by using a simplified diagram of a gamma photopeak and a Compton continuum (Figure 3).

$$N \pm 1\sigma_N \text{ error} = T - C \pm \left[\frac{n^2}{4} \left(\frac{t_1}{n_1^2} + \frac{t_2}{n_2^2} \right) + T \right]^{1/2}$$

where

T = total counts in n channels of photopeak

$$= \sum_{i=n_1}^n (\text{counts})_i$$

t_1 = total counts in n_1 channels of Compton continuum

t_2 = total counts in n_2 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:

$$R \pm \sigma_R = \frac{N}{CT (\text{min})} \pm \frac{\sigma_N}{CT (\text{min})}$$

Procedure No	Revision No.	Date Issued	Page 13 of 18
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

5.8.2 Concentration of an Element in Sample

The concentration of an element is determined by the comparative method with the known standard. Consider an example of a ^{140}La calculation. After the net cpm under a photopeak of 1597 KeV γ is calculated for sample and standard, their activities are decay corrected to the time of irradiation. The concentration of La in the sample is given as follows.

$$\begin{aligned} \text{Conc. of La } (\mu\text{g/l}) \\ \text{in sample} &= \frac{\text{Conc. of La in Std. } (\mu\text{g}) \times (\text{net c/m } ^{140}\text{La})_{\text{sample}} e^{\lambda t_1}}{(\text{net c/m } ^{140}\text{La})_{\text{std}} e^{\lambda t_2} \times (\text{wt})_{\text{sample}}} \end{aligned}$$

$$\text{where } \lambda = \ln 2 / t_{1/2} = 0.693 / 40.2 \text{ hr} = .0172 / \text{hr}$$

t_1 = Count time of sample — irradiation time (hours)

t_2 = Count time of standard — irradiation time (hours)

(WT) sample = weight or volume of sample analyzed.

Errors reported are mainly due to counting statistics of the sample and standard. For example, from the activities in the sample and standard, the associated error is as follows.

$$\text{Sample Activity} = A_1 \pm \sigma_1 \quad \text{where } \sigma_1 = (A_1)^{1/2}$$

$$\text{Standard Activity} = A_2 \pm \sigma_2 \quad \text{where } \sigma_2 = (A_2)^{1/2}$$

$$\text{Ratio} = \frac{A_1 \pm \sigma_1}{A_2 \pm \sigma_2}$$

$$\text{Error} = \frac{A}{A_2} \pm \frac{A_1}{A_2} \left[\left(\frac{\sigma_1}{A_1} \right)^2 + \left(\frac{\sigma_2}{A_2} \right)^2 \right]^{1/2}$$

The errors are propagated at each step.

A. Hand calculations shall be performed, documented and reviewed in accordance with PAP-301, Hand Calculation Doc. and Review.

5.8.3 Accuracy of Standards

In a comparative method, the efficiency or DPC of a detector is not important as long as the sample and standard are counted

Procedure No	Revision No.	Date Issued	Page <u>14</u> of <u>18</u>
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

under identical conditions. However, the absolute concentration of an element in a sample depends entirely on the accuracy of the certified or reported concentrations of elements in the standard. The standards used here are USGS reference geological standards such as BCR-1, W-1, G-2, AGV-1, BHVO-1, PCC-1, and GSP-1. The element concentrations in these geological standards vary over three orders of magnitude. The results obtained in our laboratory for these geological reference standards agree within 5% of the recommended values reported by Flanagan (1973).

The BCR-1 is routinely used as a control for accuracy and precision in the NAA experiments on a variety of geological matrices.

5.9 Data Records

All sample preparation and chemistry used for each sample is referenced by an identification number which describes the LRB, page and sample number.

Gamma spectrometry: All spectral data (SD) are recorded and filed under each well site zone. Spectra are stored on magnetic disks by SD number.

5.10 The Project Manager shall assure that the following records are processed in accordance with PNL Administrative Procedure, PAP-1701, Records Management

- Hand Calculations
- Laboratory Record Books (LRB)
- Spectral Data

5.11 Documents and Discrepancies

5.11.1 Records from this work shall be maintained and stored in accordance with PAP-1701.

5.11.2 When deviations from the procedure are found, the responsible staff shall initiate a Deficiency Report in accordance with PAP-1502, Controlling Deviations From QA Requirements and Established Procedures. The QAO Representative shall review and approve all Deficiency Reports.

Procedure No	Revision No.	Date Issued	Page <u>15</u> of <u>1</u>
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

5.11.3 If elements of this procedure require a change only for one specific test, a waiver of specific steps is possible prior to any departure from this procedure. The waiver shall be processed in accordance with PAP-1502. The responsible Q.E. shall approve all waivers for procedural changes.

5.11.4 If an incident occurs during this project, the responsible staff shall complete an incident report in accordance with PAP-1503. The responsible Q.E. shall review and approve all incident reports.

6.0 REFERENCED DOCUMENTS

- 6.1 PNL-MA-60, Quality Assurance Manual for License Related Programs
- 6.2 PAP-301, Hand Calculation Documentation and Review
- 6.3 PAP-1201, Calibration Control System
- 6.4 PAP-1502, Controlling Deviations from QA Requirements and Established Procedures
- 6.5 PAP-1503, Incident Reporting
- 6.6 PAP-1702, Records maintenance and Storage in Project Files
- 6.7 PAP-1704, Laboratory Record Books
- 6.8 Laul, J. C., E. A. Lepel, W. C. Weimer and N. A. Wogman. 1982. "Precise Trace Rare Earth Analysis by Radiochemical Neutron Activation." Journal of Radioanalytical Chemistry, 69, p. 181-196.
- 6.9 Laul, J. C. 1979. "Neutron Activation of Geological Materials." Review Article in Atomic Energy Review, 17, p. 603-694.
- 6.10 Flanagan, F. J. 1973. "1972 Values for International Geochemical Reference Sample." Geochim. Cosmochim. Acta, 37, p. 1189-1200.
- 6.11 Laul, J. C., C. L. Wilkerson and V. L. Crow. 1979. "Computer Methodology and its Applications to Geological and Environmental Matrices." Proceedings on Computers in Activation Analysis and Gamma-ray Spectroscopy, DOE Symposium Series, 49, P 840-856.
- 6.12 RSD-51-DEQ 10, Counting Procedure and Quality Control for Gamma Spectrometry.
- 6.13 Lederer, C. M., J. M. Hollander and I. Perlman. 1967. Table of Isotopes, 6th ed., John Wiley, New York, 594 p.

Procedure No	Revision No.	Date Issued	Page <u>16</u> of <u>18</u>
RSD-51-DEQ 14		7/16/85	

PNL ADMINISTRATIVE PROCEDURES FOR SRP

Det. NaI/Ge(Li) _____

C. F. Gain _____

Calibration _____

Power = _____

LT = _____

Ref. # _____

Shelf =

[illegible]

EXHIBIT 1 - Typical Counting Sheet

Procedure No

RSD-51-DEQ 14

~~Revision No.~~

Date Issued

7/16/85

Page 17 of 18

PNL ADMINISTRATIVE PROCEDURES FOR SRP

SRD/EOB
EOB 1-1-85 1200

DIODE: D389

PARM IN
GAIN: .2 KeV/Ch
CHNLS: 2048

SERIES FILE NAME: Sample 389

[illegible]

EXHIBIT 2 - Typical Counting Sheet

PNL TECHNICAL PROCEDURE

TITLE: SAMPLE PREPARATION FOR GROSS BETA ANALYSIS

1.0 APPLICABILITY

This procedure is applicable to the samples received for gross beta analysis.

2.0 DEFINITIONS

dpm - disintegration per minute (concentration term)
pCi - picocuries (2.22 dpm, a concentration term)
LRB - Laboratory Record Book

3.0 RESPONSIBILITIES

Laboratory Manager
Scientist
Technician

4.0 PROCEDURE

Prerequisite: Personnel trained in this procedure may perform the work.

4.1 Sample Preparation

4.1.1 Liquid Samples

4.1.1.1 Transfer a 100-ml aliquot into a 150-ml beaker (do this in duplicate) and evaporate on a hot plate until the volume is reduced to a few mls.

4.1.1.2 Quantitatively transfer the remaining aqueous solutions to flamed 1" counting dishes with distilled water. Evaporate the solutions under a heat lamp until the dishes are dry.

4.1.1.3 Count the beta activity (refer to procedure PNL-SP-25).

Prepared by <i>[Signature]</i>	Date 9-17-87	Approved (SECTION MGR) <i>[Signature]</i>	Date 9-17-87
QAD Concurrence <i>[Signature]</i>	Date 9-17-87	Effective Date SEP 17 1987	
Procedure No. PNL-SP-32	Revision No. 0	Page 1 of 2	

PNL TECHNICAL PROCEDURE

4.1.1.4 Calculate the total beta activity :

$$T\beta = \frac{(\text{net c/m}) (d/c) \times (0.45045)}{\text{volume (l.)} \times (\text{yield})}$$

$$= \text{net c/m} \times 9.312 \text{ pCi/l}$$

where d/c=1.78(as ^{106}Ru), yield=0.861, volume=0.1002

4.1.2 Solid Samples

4.1.2.1 Weigh the sample as received and select an appropriately sized aliquot for analysis in duplicate.

4.1.2.2 Leach the sample aliquots three times with hot 6 M HCL and combine the leachates.

4.1.2.3 Evaporate the leachates to a few mls on a hot plate. Add excess conc. HNO_3 and continue the evaporation to convert the salts to the nitrate form.

4.1.2.4 Quantitatively transfer the remaining nitric acid solutions to flamed 1" counting dishes with dilute nitric acid. Evaporate the solutions under a heat lamp until the dishes are dry.

4.1.2.5 Count the beta activity (refer to procedure PNL-SP-25).

4.1.2.6 Calculate the total beta activity:

$$T\beta = \frac{(\text{net c/m}) \times (d/c) \times (0.45045)}{\text{Aliquot wt (gm)} \times (\text{yield})}$$

$$= \frac{(\text{net c/m}) \times (0.9312)}{\text{Aliquot wt (gm)}} \text{ pCi}$$

where d/c=1.78 (as ^{106}Ru), Yield=0.861

PNL TEST PROCEDURE

TITLE: HTA-4-8, SOLUTIONS ANALYSIS: BETA COUNTING

1.0 APPLICABILITY

This procedure applies to the analysis of hydrothermal test solutions by beta counting prepared using Procedures HTA-4-11, HTA-4-12, HTA-4-23 or other procedures that require beta counting.

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

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

4.0 PROCEDURE4.1 Method

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. Beta counts for a given isotope are converted to disintegrations by comparison to standard sources of the same isotope.

Concurrence <i>NA</i>	Date	Approved <i>[Signature]</i>	Date <i>7/2/87</i>
Prepared by <i>A.C. Leaf</i>	Date <i>7/1/87</i>	QAD Concurrence <i>B.O. BARNES</i>	Date <i>6/30/87</i>
Procedure No. HTA-4-8	Revision No. 4	Effective Date JUL 01 1987	Page of 1 3

PNL TEST PROCEDURE

4.2 Calibration Standards

Calibration standards of the isotope being counted are prepared on stainless steel beta-counting dishes. Standards are to be NBS or NBS-traceable whenever possible. Replicate standard sources are counted, and the counting data and efficiency are recorded in the beta notebook.

4.3 Control Standards

Control standards are sources of $^{90}\text{Sr-Y}$ (high beta energy) and ^{99}Tc (low beta energy) that are counted daily to ensure control of BPCs. Each source is counted at least 10 times when the BPCs are initially calibrated, and 2σ limits are defined that must be met on a daily basis. Control standards are prepared using Procedure HTA-4-23.

The following daily control standard count procedure shall be used.

- Step 1) Open shield door and place $^{90}\text{Sr-Y}$ control source on Shelf 1.
- Step 2) Close shield door and preset counting time for 10 minutes.
- Step 3) Press STOP, RESET and START buttons. (Count will stop automatically at the end of 10 minutes.)
- Step 4) Record total counts on daily control data sheet; plot counts per minute less background (Section 4.4, Step 2) on daily control chart. (Counts per minute must fall within limits defined on control chart.) Data Sheets and Control Charts are located in the beta notebook.
- Step 5) Repeat Steps 1 through 4 using ^{99}Tc daily control standard.

4.4 Daily Background Count

- Step 1) Using a clean background dish, repeat Steps 1 through 3 of Section 4.3 above.
- Step 2) Record counts per minute on daily control data sheet in the beta notebook.
- Step 3) Repeat Step 1 of Section 4.4 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 notebook.)

4.5 Sample Count

- Step 1) Survey the prepared sample counting source using beta survey instrument to ensure that beta activity is not excessive

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-8	4	JUL 01 1987	2	3

PNL TEST PROCEDURE

(<2000 counts per minute on GM). If the 2000 c/m is exceeded, adjust as required using sample preparation procedure.

- Step 2) Open shield door and place sample source on Shelf 1; close shield door.
- Step 3) Preset desired counting time. (This may vary from 10 to 100 minutes depending on activity levels.)
- Step 4) Press STOP, RESET and START buttons. (Count will stop automatically at the end of preset counting time.)
- Step 5) Record the date counted, BPC efficiency for isotope counted, minutes counted and total counts; calculate counts per minute less the background count as outlined in the beta counting data portion of the analytical report.
- Step 6) 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 Step 5

C = dilution factor or volume factor to correct to 1 mL

D = BPC disintegrations/count as posted on counter for specific isotope (see beta notebook for standard counts and calculations).

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-8	4	JUL 01 1987	3	3

PNL TEST PROCEDURE

TITLE: HTA-4-23, SOLUTIONS ANALYSIS: PREPARATION OF BETA SOURCES BY
DIRECT EVAPORATION

1.0 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 HTA-4-8.

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

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

4.0 PROCEDURE

- Step 1) Pipet the required volume of sample into a stainless steel dish. Volume should be 1000 μ L to avoid overflow of the solution from the dish. Record the volume on the analytical report.
- Step 2) Evaporate the solution to dryness under a heat lamp.
- Step 3) Measure the beta activity using Procedure HTA-4-8, "Solutions Analysis: Beta Counting."
- Step 4) Record counting data and calculations on the cognizant scientist's copy of the analytical report.

Concurrence NA	Date	Approved JPLC Town	Date 7/2/87
Prepared by AC Leahy	Date 7-1-87	QAD Concurrence B.O. BARNES	Date 6/30/87
Procedure No. HTA-4-23	Revision No. 3	Effective Date JUL 01 1987	Page of 1 2

PNL TEST PROCEDURE

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-23	3	JUL 01 1987	2	2

PNL TECHNICAL PROCEDURE

TITLE: BETA COUNTING PROCEDURE

1.0 APPLICABILITY

This Standard Operating Procedure (SOP) is applicable to the operations of the Beta Counting Systems located in the 329 Bldg. Analytical Support Laboratory as they are applied to the analyses of Beta emitting radionuclide samples. The objective of this procedure is to communicate both specific and general information regarding the analytical operations of an 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.

2.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)
 ng - nanograms (10^{-9} grams)
 μ g - micrograms (10^{-6} grams)
 t_{1/2} - half-life
 LRB - Laboratory Record Book

3.0 RESPONSIBLE STAFF

3.1 Service Manager
 3.2 Scientist
 3.3 Analyst

4.0 PROCEDURE

4.1 Low-Background Beta Counting System Description

Low-background Beta counters are used to measure low-level concentrations of Beta emitting radionuclide samples.

The beta counting systems consist of end-window gas-flow proportional counters, pre-amplifiers, amplifiers, timers and scalars. The 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.

Prepared by <i>S. English</i>	Date 9-17-87	Approved (SECTION MGR) <i>[Signature]</i>	Date 9-17-87
QAD Concurrence <i>S. English</i>	Date 9-17-87	Effective Date SEP 17 1987	
Procedure No. PNL-SP-25	Revision No. 0		Page 1 of 8

PNL TECHNICAL PROCEDURE

There are two low-background beta counting systems. One uses a commercial Spectrum Sciences "Low Beta" detection system. It has an end window about one inch in diameter. The detector is a short flat cylindrical chamber made of plastic with larger cylindrical chambers above and below it to provide background reduction. The second one is shop-made low-background system. It uses hemispherical steel detection chambers with end windows about 2 inches in diameter. This system is extremely shielded with inches of pre-world war II battleship steel to further lower the ambient background level. Four primary detectors are surrounded by several proportional cosmic shield detectors that are about a meter long and 5 cm in diameter. These shield detectors provide the background reduction signal.

Also available are two "regular" beta counters that use approximately hemispherical detector chambers with end windows about 1 3/8 inches in diameter. These are housed in 2-inch thick lead shields. The "regular" beta counters have high background and are not normally used for low activity samples. The shop-made systems have low background (<1 cpm each) and are used for low activity samples. The shop-made system has been used continuously for over 20 years, with modifications made only to update the associated electronics.

The current electronics in the low background systems are NIM modular units, with detached pre-amplifiers mounted near the detectors. Amplifiers are operated with pole-zero adjustments set to minimize the occurrences of double count registration caused by large pulses at the normal operating voltages. Amplifier gain is set near maximum to permit detector operation at lower high voltage settings, whereby there are no occurrences of saturated pulses at the pre-amplifier output from the sample beta particles. A short shaping time constant (between 0.5 and 2 microseconds) permits the amplifiers to minimize occurrences of double count registration and pulse pile-up losses at high count rates. A pulse height discriminator is set approximately 25% above the maximum voltage of ambient electronic noise pulses as determined using an oscilloscope. A block diagram of a low-background system is shown in Figure 1.

Procedure No. PNL-SP-25	Revision No. 0	Effective Date SEP 17 1987	Page <u>2</u> of <u>8</u>
----------------------------	-------------------	-------------------------------	---------------------------

PNL TECHNICAL PROCEDURE

4.1.1 Electronic Components in Beta Counters

The following electronic components are currently being used. They may be replaced with components of equal or better quality.

- Low Background Shop-made system: H.V. power supply - Canberra 3105, Preamplifier - Canberra 2006, Amplifier - Canberra 2012, Discriminator - ORTEC 550, Anti-coincidence Gate - RIDL 32-3 (Cosmic Guard), Scaler Timer - Canberra 2071.
- Low Background Commercial System: Spectrum Sciences Model number 9500.
- "Regular" Beta Counter: HV power supply - Ortec 459, preamplifier - Ortec 142PC, amplifier - Ortec 571, Discriminator - Ortec 550, counter/timer - Ortec 776.

4.1.2 Counter Performance Tests

The shop-made beta systems were originally calibrated in 1959 and the control of the instruments have been maintained by counting reference sources since that time. Originally, the control sources were U.S. Bureau of Standards (U.S.B.S.) calibrated Ra DEF (210Pb and daughters) electrodeposited on thick silver discs. In 1963, the instrument control sources were changed to 90Sr + 90y tracers mounted on the standard type of dish routinely used for sample mounts. We use two sizes of this standard type of dish. The standard dishes are described in Figure 2 (A and B). Also shown in Figure 2 is the surface area of various quantities of precipitates of three densities. The count rate for the new 90Sr-90y control dishes was evaluated initially using instruments that had been checked daily with the original control sources. After the normal count rate for the new sources had been established by daily counting of both the old and new control sources, use of the original sources was discontinued. The disintegration rate for the 90Sr + 90y solution used to prepare these sources was determined at the HEDL standards laboratory by using a 4 π beta counting technique with weightless sources mounted on essentially weightless films. The accuracy of that calibration was evaluated by cross comparison with other stock solutions of 90Sr + 90y. The calibration accuracy was found to be within $\pm 2\%$. At present these control sources are still in use. The counting efficiency of all shop made counters has not changed more than 3% from the efficiency established in 1963.

Procedure No.
PNL-SP-25

Revision No.
0

Effective Date
SEP 17 1987

Page 3 of 8

PNL TECHNICAL PROCEDURE

4.2 Geometry Measurement

The efficiency due to geometry of each instrument is measured on a monthly basis using the ^{90}Sr + ^{90}Y control sources and is recorded in the calibration control book for beta counting instruments.

4.2.1 To establish the geometry, use ^{90}Sr + ^{90}Y Source No. 17 (28312 dpm on 6/14/63 from Standards Laboratory Record No. R-149). Take the source from its storage holder and place it on the one-inch dish holder assigned to the instrument being tested. Slide the one-inch dish holder into the front slot of low background counters.

4.2.2 Record the date, voltage setting of the power supply and the length of count (10 minutes) on a Counter Control Data Form (Exhibit 1) in the section of the control book for beta counters that is assigned to each counter. Set the counter for a 10-minute counting interval and start the count. When the count interval is completed, record the count registered on the Counter Control Data form.

4.2.3 Repeat step 2 for a total of three 10-minute counts.

4.2.4 Obtain the most recent background counting rate from the calibration control book and record it on the Counter Control Data form. Compute the gross cpm and net cpm for each count.

4.2.5 Determine the average net c/m for the three counts and record it on the Counter Control form (Exhibit 1). Determine the geometry using the following formula.

$$\text{Geometry} = \frac{\text{Average Net cpm}}{(28312) e}$$

where λ = decay constant for ^{90}Sr ; $\ln 2/T_{1/2} = 2.40 \times 10^{-2}/\text{year}$
and t = (Count date - 6/14/63)(years)

- Using ^{90}Sr $t_{1/2}$ of 28.88 years, the activity of Control Standard Source No. 17 has decayed from 28312 dpm at 6/14/63 to 17103 dpm at 6/14/84.

PNL TECHNICAL PROCEDURE

- 4.2.6 Record the geometry on the Counter Control Data form (Exhibit 1). The geometry of the shop-made system should be within 0.538 and 0.560 (Average = 0.549). If geometry is not within error limits, the instrument should be rechecked and calibrated.

4.3 Voltage Plateau Measurement of Beta Counter

- 4.3.1 Slide control $^{90}\text{Sr} + ^{90}\text{Y}$ source No.17 (R-149) for the instrument into the front slot of the counter. Set the timer to make 2 minute counts. Note the current setting for the instrument's high voltage supply. Lower the high voltage about 300 volts below the current setting, to the nearest setting that is a multiple of 50 volts. Record the voltage setting, date and time on the first line of the count data section of the form and start the first count. When it is complete, record the length of count and the registered total counts on that line.
- 4.3.2 Increase the high voltage setting by 50 volts and take another count, recording the voltage setting, time, length of count and total counts on the next line of the form.
- 4.3.3 Repeat step 2, increasing the high voltage in 50 volt increments, until any one of the following has occurred.
- The voltage reaches 2100 volts
 - The voltage is 400 volts above the original setting for the instrument
 - The count rate first changes very slowly with voltage increase and then increases by a factor of two or more (end of voltage plateau).
- 4.3.4 Lower the voltage setting to the setting used on the first line of the plateau data. Remove the source from the instrument. Place a clean one-inch counting dish on the holder and slide it into the instrument. Take a series of 2-minute background counts at each voltage setting used in the plateau and record the data in the calibration notebook.

PNL TECHNICAL PROCEDURE

- 4.3.5 Obtain net cpm (gross cpm - background cpm) for each voltage and compare the net cpm versus voltage settings. Use 100 V/inch and a cpm scale that permits about 1% change per minor division. (Only data including the plateau region need to be plotted as the highest and lowest voltage settings may be off-scale.)
- 4.3.6 Estimate the width of the voltage plateau. It should be about 150 V in width for stable performance. Measure the slope of the voltage plateau. The slope should not change more than 3% of cpm per 100 volts.
- 4.3.7 The operating voltage is normally from 1/3 to 1/2 of the voltage span between the lower and upper ends of the plateau region. Compare the normal voltage setting in normal use with this criterion. If the normal voltage setting is not in this area of the plateau, examine the previous plateau which is also located in the beta control book. If the operating point has changed significantly, recheck the instrument and calibration.

4.4 Counter Control Checks

When instruments are used routinely, a periodical check of performance should be made. If the instrument is not used for an extended period (a few weeks), these checks may be discontinued until the operations are resumed. Control checks are to be made as follows.

- 4.4.1 Count the assigned control source ($^{90}\text{Sr} + ^{90}\text{Y}$, No.17 R-149) for each counter for about 10 minutes. Record the date, high voltage setting, total counts, length of count and most recently measured background cpm in the calibration control notebook. Recount and record ten times. Calculate the net cpm for each count.
- 4.4.2 Compute the mean and standard deviation (σ) and record on the Counter Control Data form (Exhibit-1). Since the source for the shop-made system contains about 9000 c/m, the gross counts for 10 min. counting is about 90,000 counts. The

Procedure No. PNL-SP-25	Revision No. 0	Effective Date SEP 17 1987	Page <u>6</u> of <u>8</u>
----------------------------	-------------------	-------------------------------	---------------------------

PNL TECHNICAL PROCEDURE

statistical error in 90,000 counts at the 2σ confidence level is 0.65%. Thus, 1% variability in total counts is satisfactory for control purposes.

- 4.4.3 If the net cpm of any control count is outside the 1% or 3σ range in step 2 (whichever is larger), recheck the instrument, plateau and calibration.

4.5 Beta Counter Background

- 4.5.1 When a counter is routinely used, a background of the counter should be taken periodically. Place a clean standard one-inch dish on the dish holder for the counter. Slide the holder in the beta counter. Take the background preferably for 1000 minutes. Record the date/time of the background count in the calibration control notebook.
- 4.5.2 For each radionuclide measurement, take a background using the same geometry minus the sample. Take the system background counts several times over an extended period of six months to a year.
- 4.5.3 Typical background of a low-background beta counter lies between 0.3-1.0 cpm. If the background is unusually high, recheck the background with another clean S.S. disk and/or filter paper. Sometimes, high background results when the detector is contaminated following counting high count rate sample or standard or a contaminated absorber has been used. Wait for a few hours and let the system stabilize and clean the absorber. Recheck the background.

4.6 Control Count Values with "in control values"

- 4.6.1 When at least 10 values of the counter control (section 4.4) and background counts (section 4.5) have been accumulated, prepare a control chart and calculate the average $\pm \sigma$ of 10 measurements of counter controls and background counts. The calculations are shown below.

PNL TECHNICAL PROCEDURE

The Average ($\bar{x}$) + Standard Deviation (σ). Given 10 measurements, the average value $\bar{x}$, and standard deviation (σ), are calculated as shown below

$$\bar{x} = \frac{1}{N} \sum_{i=1}^{10} x_i$$

and

$$\sigma = \frac{\sum_{i=1}^{10} (x_i - \bar{x})^2}{N-1}^{1/2} \quad \text{where } N = 10$$

Once the control chart is set up with the first ten counts, only one count is done each time a control check is made (bi-monthly).

1. If the net cpm of any control count (after the initial first 10 counts) is outside the 2% or 5 σ range in step 1 (whichever is larger), refer to the responsible scientist for action to be taken.

4.6.2 Maintain the control charts each time a counter check or background is determined.

4.7 COUNTING SAMPLES

Since specific sample preparation and counting procedures vary greatly depending on the matrices involved and the analyses desired, specific step by step radioanalytical procedures shall be prepared to cover the samples analyzed.

4.7.1 Generic Counting Procedures

1. Place the sample on a counting dish and then place the dish onto the dish holder. Slide the dish holder into the counter.
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 beta counter control notebook. All data shall be recorded in the sample LRB or directly on the data printer output.

Procedure No. PNL-SP-25	Revision No. 0	Effective Date SEP 17 1987	Page 8 of 8
----------------------------	-------------------	-------------------------------	-------------

PNL TEST PROCEDURE

TITLE: 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 (~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 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.)

Concurrence NA		Date		Approved <i>[Signature]</i>		Date 7/2/87	
Prepared by ACH		Date 7/1/87		QA Concurrence B.O. BARNES		Date 6/30/87	
Procedure No. HTA-4-9	Revision No. 4	Effective Date JUL 01 1987		Page 1		of 4	

PNL TEST PROCEDURE

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 limited 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.
- 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-9	4	JUL 01 1987	2	4

PNL TEST PROCEDURE

4.4 Sample Count - ND-66

The ND-66 gamma spectrometer usually will be used only for counting ^{126}Sn as prepared using Procedure HTA-4-21.

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

$$A = \frac{(B)(C)(D)}{(E)(F)}$$

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 .

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-9	4	JUL 01 1987	3	4

PNL TEST PROCEDURE

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-9	4	JUL 01 1987	4	4

NOT CONTROLLED
DOCUMENT
COPY NO. ~~2~~

PNL TEST PROCEDURE FOR SRP

TITLE: COUNTING PROCEDURE AND QUALITY CONTROL FOR GAMMA SPECTROMETRY

1.0 OBJECTIVE

This procedure describes methods employed to insure that the gamma spectrometry results obtained for briney groundwaters and core samples are accurate and reproducible. Although gamma spectrometry is a relatively straightforward method used to determine gamma 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. Periodical gamma counting of control standards, automated transfer of spectra from analyzers to data manipulation computers, 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 of reliability and credibility to the accuracy and precision of each gamma spectrometer.

2.0 APPLICABILITY

When this procedure is selected for implementation by a QA plan prepared and approved in accordance with PNL-MA-60, this procedure is applicable to the Counting Procedure and Quality Control for Gamma Spectrometry.

This procedure is applicable to the Project Manager, and trained and qualified personnel within the "Disequilibrium Study of Natural Radionuclides" program and/or the Chemical Technology Department of PNL who will be performing the determination of radionuclides in groundwater and core samples using gamma spectrometry.

This procedure is primarily intended to assure that gamma spectrometry equipment is maintained and in proper working condition.

3.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)
ng - nanograms (10^{-9} grams)
 μ g - micrograms (10^{-6} grams)
 $t_{1/2}$ - half-life
LRB - Laboratory Record Book
CTL - Control

Approved (Project/Program Manager) J. C. Lau <i>J. C. Lau</i>		Approved (Line Manager) N. A. Wogman <i>N. A. Wogman</i>	
Prepared by J. C. Lau <i>J. C. Lau</i>	Technical Review <i>[Signature]</i>		QA Review <i>[Signature]</i>
Procedure No. RSD-51-DEQ 10	Revision No. 0	Date Issued 5-22-85	Page <u>1</u> of <u>21</u>

PML TEST PROCEDURE FOR SRP

4.0 RESPONSIBILITIES

4.1 Project Manager

- Assures that the work is performed by qualified personnel. Maintains personnel training of procedures described in this text
- Reviews and maintains all data
- Approves deficiency and non-conformance reports
- Prepares a report on results
- Assures that the work is done according to applicable procedures
- Reviews and complies with laboratory record keeping procedures and practices
- Assures that all required counting equipment, chemicals, reagents and glasswares are available to comply with procedures

4.2 Cognizant Test Personnel

- Conduct gamma spectrometry according to this procedure
- Comply with laboratory record keeping procedures and data reduction practices
- Report completed results to the Project Manager
- Initiate deficiency and non-conformance reports

4.3 QA Representative

- Reviews and approves deficiency and non-conformance reports
- Approves waivers from this procedure prior to departure from it

5.0 PROCEDURE

5.1 Equipment and Materials

- Radioactive standard sources - ^{57}Co , ^{60}Co , ^{85}Sr , ^{88}Y , ^{109}Cd , ^{113}Sn , ^{137}Cs , ^{203}Hg
- High voltage supplies
- Detectors - NaI(Tl) , Ge(Li) , Intrinsic, Low-energy photon detector (LEPD)

Procedure No.
RSD-51-DEQ 10

Revision No.

Date Issued
5-22-85

Page 2 of 21

PNL TEST PROCEDURE FOR SRP

- Pre-amplifiers, amplifiers, analog-to-digital converters (ADC), pulse pile-up rejectors, multichannel analyzers
- Mixed radioactive standard source - ^{241}Am , ^{137}Cs , ^{60}Co

5.2 Gamma Spectrometry Quality Assurance Procedures

5.2.1 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 counting geometry is not too critical. If the gamma spectrum is simple, then the NaI(Tl) detector, being more sensitive, can count more samples per time than the solid state diode detectors for a given accuracy. In general, for a given energy, the NaI(Tl) detector will be about 10-20 times more sensitive than the solid state detector. However, the solid state detector (diode) will have a much improved resolution of gamma energies.

Gamma-ray spectrometers must be calibrated so that the peak energies appear at identifiable energy levels and then absolute efficiencies can be calculated. This is accomplished using NBS calibration standards with accurately known disintegration rates. A typical standard that has been used here is a mixed radioisotope Standard Reference Material, 4216-D, containing ^{57}Co , ^{60}Co , ^{85}Sr , ^{88}Y , ^{109}Cd , ^{113}Sn , ^{137}Cs , and ^{203}Hg , all with known branching ratios for radioactive decay and easily recognizable (interference free) gamma energies. This SRM standard (4216-D) is ideally suited for determining the calibration, resolution 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.

5.2.2 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.

Procedure No. RSD-51-DEQ 10	Revision No.	Date Issued 5-22-85	Page <u>3</u> of <u>21</u>
--------------------------------	--------------	------------------------	----------------------------

PML TEST PROCEDURE FOR SRP

The NaI(Tl) detectors are scintillators which require a photomultiplier closely coupled optically to the detector to change the light pulses seen 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.

B. Power Supply

Each detector requires a stable high voltage supply. Generally, about 1250 volts, on the photomultiplier, or about 2500-4000 volts on the semiconductor type detectors are used.

C. Preamplifier

The preamplifier is a very stable, linear pulse amplifier used mainly for conditioning the detector signal 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 of 1 to 10.

D. Amplifiers

The modern amplifier has two functions: 1) to provide a gain of about 1000 at 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 systems should 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

Procedure No. RDS-51-DEQ 10	Revision No.	Date Issued 5-22-85	Page <u>4</u> of <u>21</u>
--------------------------------	--------------	------------------------	----------------------------

PML TEST PROCEDURE FOR SRP

to allow the first channel to correspond to 0 KeV. Changing the zero setting affects the gain setting a bit so it is necessary to readjust both the gain and zero each time changes are made.

The discriminator controls are for eliminating excessive noise counts. Most of our instruments operate with the upper discriminator at maximum setting and the lower discriminator set to eliminate low energy noise signals. Normally these controls are initially set and require no further adjustment.

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 which may or may not correspond to a real radioisotope.

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.

Procedure No. RDS-51-DEQ 10	Revision No.	Date Issued 5-22-85	Page <u>5</u> of <u>21</u>
--------------------------------	--------------	------------------------	----------------------------

PNL TEST PROCEDURE FOR SRP

5.3 Counting Systems

5.3.1 The multidimensional sodium iodide system

A schematic diagram of the detector with necessary electronics is shown in Figure 1. The electronic components are listed with their manufacture model numbers. These, equivalents, or superior components are to be used.

A mixed ^{60}Co and ^{137}Cs standards (Table 1) is used for control determinations for each of the four multidimensional counting systems. Each standard is housed in a 1" X 6" diameter pvc housing and absorbed onto Al_2O_3 powder.

5.3.2 Low Energy Photon Detectors (LEPD)

The two intrinsic Ge diodes, D389 and D447, and their associated electronic components are diagramed in Figure 2. The electronic components are listed with their manufacture model numbers. These, equivalents, or superior components are to be used.

Natural uranium standards, O.I.E.A.7 (Table 1), are used for control standards. Each standard is in a pellet geometry enclosed in plastic to prevent detector contamination.

5.3.3 Conventional Ge(Li) (or Intrinsic Ge) Detector

Diode "L" is used for measuring the gamma energy spectrum between 25-2000 KeV. This diode and its associated electronic components are diagramed in Figure 3. The electronic component configuration is shown with listed manufacture model numbers. These components, equivalents, or superior models are to be used with this detector.

A mixed ^{241}Am , ^{60}Co , and ^{137}Cs standard (Table 1) 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".

5.3.4 Coincidence-Noncoincidence Ge(Li)-NaI(Tl) Detector

Detection applicability of this system is like that for the standard Ge(Li) types (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 diagramed in Figure 4. The

PML TEST PROCEDURE FOR SRP

TABLE 1. Control Standards for Gamma Spectrometry

PML Control STD. No.	Detector(s)	Radionuclides (γ-peak energy)	t _{1/2}	Origin (cross ref.) NBS SRM No.	PML No.	Ref. date	dpm/ml or g ¹	dpm/std
50690-27-1	L, M	241Am (59.5)	432 y	Amersham (AM 2.44)	4491-101-0	1/2/84	6.20 x 10 ⁵	3.72 x 10 ⁵
50690-27-2	O, 8NW	137Cs (661.8)	30.17 y	(SRM No. 4216-0)	1892-136-0	1/2/84	2.09 x 10 ⁷	5.23 x 10 ⁵
50690-27-3	Mixed	60Co (1174)	5.27 y	(SRM No. 4216-0)	3368-54-0	1/2/84	7.48 x 10 ⁶	1.50 x 10 ⁶
50690-27-4	J, E	60Co (1332.5)						
50690-27-5	K							
50690-27-6	I, H							
5591-58-1	389	238U (63.2)	4.47 x 10 ⁹ y	0.1.E.A.-7	4491-58-1	-	3.313 x 10 ³	5.014 x 10 ⁴
		230Th (67.4)					3.313 x 10 ³	5.014 x 10 ⁴
		226Ra (186.2)					3.313 x 10 ³	5.014 x 10 ⁴
		210Pb (46.5)					3.313 x 10 ³	5.014 x 10 ⁴
3368-87-10	447	238U (63.2)	4.47 x 10 ⁹ y	0.1.E.A.-7	3368-87-10	-	3.313 x 10 ³	5.014 x 10 ⁴
		230Th (67.4)					3.313 x 10 ³	5.014 x 10 ⁴
		226Ra (186.2)					3.313 x 10 ³	5.014 x 10 ⁴
		210Pb (46.5)					3.313 x 10 ³	5.014 x 10 ⁴
6408-27-13P	M-D SYSTEMS	137Cs (661.8)	30.17 y	(SRM No. 4216-0)	N-067-500	1/11/77	9.982 x 10 ⁴	*4.991 x 10 ⁴
6408-27-10P	P-4	Mixed			N-066-250	8/7/75	1.028 x 10 ⁵	*2.056 x 10 ⁴
6408-27-12P	P-5	60Co (1174.)	5.27 y	(SRM No. 4216-0)				
6408-27-14P	P-8	60Co (1332.5)						
	*P-9							

*The multi-dimensional system (M-D SYSTEMS) - P-9 uses a lower activity dpm/std.

†Natural U standard is in dpm/gm, 241Am-137Cs-60Co standard is in dpm/ml.

Procedure No.
RSD-51-DEQ 10

Revision No.

Date Issued
5-22-85

Page 7 of 21

PML TEST PROCEDURE FOR SRP

FIGURE 1. Multidimensional System Electronic Block Diagram of a Gamma-Gamma Multidimensional Spectrometer System

PNL TEST PROCEDURE FOR SRP

FIGURE 2. Low Energy Photon Detector Electronic Block Diagram for Diodes 'D389' and 'D447'.

PML TEST PROCEDURE FOR SRP

FIGURE 3. Conventional Ge(Li) Detector Electronic Block
Diagram for Diode 'L'.

PML TEST PROCEDURE FOR SRP

FIGURE 4. Anticoincidence-Coincidence Electronic Block Diagram for Diode 'I'.

PNL TEST PROCEDURE FOR SRP

electronic component configuration is shown with listed manufacturer model numbers. These components, equivalents, or superior models are to be used with this detector.

The control standard of ^{241}Am , ^{60}Co , ^{137}Cs (Table 1) is similar to that used with standard Ge(Li) detectors.

5.4 Gamma Spectrometer Control Procedure

The primary method for monitoring counting instrument performance is the control chart. Each instrument must be checked routinely using NBS traceable radioactive standards to insure that the stability, efficiency, and resolution of each detector is within a specified range. Background counts should be taken periodically. The proper standards and methods used for calibration must be matched to the particular instrument being used. Graphing the control counting data (appropriate decay corrections must be made for the standard) readily determines that the instrument is operating properly and also provides a permanent record that aids in measuring instrument reliability.

5.4.1 The control standards for each gamma detection instrument are listed in Table 1. Using the calibration source and geometry specified for the detector, count the source for the time required to yield specific integrated gamma peaks of $\leq 1\%$ counting statistics. This time normally requires 10-20 minutes.

5.4.2 The accumulated spectrum can be transferred to the computer, the peaks integrated, resolution checked, and calibration listed by using the command: CTL/CTL and then CTL "detector ID."

5.4.3 The control program (CTL) stores the spectral data by date and detector identification on magnetic storage. The program will print and plot all values necessary to determine if the detector system is within control values based on 5 and 10 sigma ranges.

5.5 The Control Program

This program incorporates CANGAS (Computer ANALysis for GAMMA-ray Spectrometry), DMN (Date MaNipulation), and LIMAN (LIBrary MAintenance) programs. Basically, the program is based on the principle of manual selection of a photopeak area and Compton background channels for previously identified photopeaks (Laul, et al. 1979). For control purposes, the gamma photopeaks listed in Table 1 for each detector system are used. The library which defines each photopeak area and Compton background channels for each detector is stored for automatic

Procedure No.

RSD-51-DEQ 10

Revision No.

Date Issued

5-22-85

Page 12 of 21

PML TEST PROCEDURE FOR SRP

retrieval by the control program. Because photopeak efficiencies and resolutions are checked over long periods of time, this library is not changed, thus allowing for each control test to be subjected to constant parameters of peak integration.

- A. All radionuclide counters shall be calibrated in accordance with PAP-1201 prior to use.

5.6 Computer Methodology

- The control program, CTL, is used to track the consistency of a diode. CTL assumes that for a particular diode, its 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 are compared against a saved average with a report and plot are generated.

The average for an area of interest (as designated by the library) is calculated as follows:

- First control run - No average. It is accepted. Until 10 "good" controls are recorded, the average used to determine the "goodness" of the latest spectrum is the average of all "good" controls previously accepted. Once 10 controls have been accepted, they make up the average. 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 controls are kept in memory and subsequent controls 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 5 sigma from the average and the next solid lines representing 10 sigma from the average.

5.6.1 CTL User's Guide

CTL is used to perform the tasks of the detector reliability system. It is made up of three different programs.

- A. CTL - Moves spectrum from diode to disk similar to the Mov command. To run, type: CTL DIODE where diode is the name of the diode to be moved. Immediately before or immediately after typing this, the diode must be triggered to send the information. If the diode puts the live time in channel 0, no questions are asked; if the live time is not in channel 0, the user is asked to enter the live time. The spectrum is written to a DMN type file named CTL.TMP.

Procedure No. RSD-51-DEQ 10	Revision No.	Date Issued 5-22-85	Page <u>13</u> of <u>21</u>
--------------------------------	--------------	------------------------	-----------------------------

2 of 3

PNL TEST PROCEDURE FOR SRP

- B. CT1 - This program takes the spectrum found in CTL.TMP or spectrum file name entered in command line and integrates the results in a manner similar to SUM. It requires a library called ANTI.LIB for an anticoincidence spectrum and a library called SING.LIB for a normal or single spectrum. This library is a SUM type library. CT1 writes the results of the integration to a file called CT1.RES.

CT1 can be run in two ways: It is automatically started by CTL if CTL is run just previously or it can be started manually by typing CT1 (File name).

It expects to find the spectrum being integrated in the file CTL.TMP if automatically started by CTL or if a filename is not specified. If a filename is specified, this spectrum will be integrated. It expects the necessary library in ANTI.LIB if it is an anticoincidence spectrum, or SING.LIB if it is a single spectrum. If it is diode D389, it will use library 389.LIB. If it is diode D447, it will use 447.LIB.

When CT1 is done, it writes the spectrum to a file called DIODE.SPC (where DIODE is the name of the diode). This file can then be written to floppy: PRM can be run against it, etc.

The results of the integration are stored on a magnetic device in the file CT1.RES:1 for use by CT2.

- C. CT2 - This program takes the results generated by CT1 (located in file CT1.RES) and does the required limit checks on the data. If the new spectrum is within required limits, peak counts and errors information are added to the historical data file being maintained for the diode (located in DIODE.CTL where DIODE is the name of the diode). If the spectrum is out of limits at any or all regions, error messages are written to the terminal and the data are not added to the historical file. A report and plot of the data are produced. Currently, 50 previous results are stored.

5.6.2 Operating Instructions - (Where DIODE is the name of the diode being transferred.) The diode must be triggered to send the spectrum.

- If live time is requested, the user will be questioned. If a subsequent program cannot be properly initiated, the user will be asked to manually start it. When it is time

PNL TEST PROCEDURE FOR SRP

to produce a report and when it is time to produce a plot, the user will be asked if it is all right to print (plot).

- If a spectrum to be "controlled" already exists on disk, the user must put it in the CTL directory, or have the required library in his directory. To run the spectrum, CT1 must be invoked:

5.6.3 CT1 Filename

- Where filename is the name of the spectrum file, CT1 will integrate the spectrum as described above and automatically invoke CT2 to check, report, plot, and store the results.
- If the integration results are already in disk, they must be entered into a file called CT1.RES:1 or CT2 must be invoked with the filename specified (see analyst for proper format). These results can then be checked, reported, plotted, and stored by CT2 by typing CT2 filename.

5.6.4 CT2 Filename

- Where filename is not specified, the results are in CT1.RES:1. If the results are under some other name, it must be specified. If the filename starts with an O, it is assumed to be a file of filenames to be run against CT2. If a file of filenames is processed, no results are printed.

5.7 Calculations

Pertinent calculations performed in the control program determine the net count rate, N , net count rate uncertainty, σ_N , and the peak resolution (FWHM) of each photopeak prespecified in the control library. Additionally, these count rate values are decay corrected to a reference time and they and the resolution values are compared to previous "in control" values.

Most of the calculations are performed by a PDP 11/44 computer. The principle of gamma peak analysis is outlined by Laul et al. (1979) and is as follows:

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).

Procedure No. RSD-51-DEQ 10	Revision No.	Date Issued 5-22-85	Page <u>15</u> of <u>21</u>
--------------------------------	--------------	------------------------	-----------------------------

PNL TEST PROCEDURE FOR SRP

This technique can be explained by using a simplified diagram of a gamma photopeak and a Compton continuum (Figure 5).

Figure 5. An idealized diagram of a gamma photopeak on a Compton continuum

$$N \pm 1 \sigma_N \text{ error} = T - C \pm \left[\frac{n^2}{4} \left(\frac{t_1}{n_1^2} + \frac{t_2}{n_2^2} \right) + T \right]^{1/2}$$

where

N = net counts
 T = total counts in n channels of photopeak

$$= \sum_{i=n_1}^n C (\text{counts})_i$$

t_1 = total counts in n_1 channels of Compton continuum

t_2 = total counts in n_2 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:

PNL TEST PROCEDURE FOR SRP

$$R \pm \sigma_R = \frac{N}{CT \text{ (min)}} \pm \frac{\sigma_R}{CT \text{ (min)}}$$

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

In all cases this calculation is performed; generally the system's background count rate is insignificant when counting control standards with activities listed in Table 1. The system backgrounds and their uncertainties are obtained from long (≥ 1000 min) background counts.

A. Hand calculations shall be performed, documented, and reviewed in accordance with PAP-301.

5.8 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 6.

Figure 6. An Illustration of the FWHM Value

Procedure No. RSD-51-DEQ 10	Revision No.	Date Issued 5-22-85	Page <u>17</u> of <u>21</u>
--------------------------------	--------------	------------------------	-----------------------------

PNL TEST PROCEDURE FOR SRP

The resolution is calculated as follows:

$$R = \frac{\Delta CH(\text{KeV})(Y \text{ peak KeV})}{CH_C}$$

where

ΔCH = channel width at half max ($1/2 h$)

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. For example, assume channels identified as 3 and 4 and channels 7 and 8 bracket the half max count height, $1/2 h$, as in Figure 6. Since two points define a line

$$y = mx + b$$

where

m = slope

x = channel fraction

b = intercept $\equiv$ counts in channel 3 or 7

y = $1/2 h$

then

$$y = m_i x_i + b_i$$

and

$$y = m_f x_f + b_f$$

and

$$\Delta CH = |(CH_3 + x_i) - (CH_7 + x_f)| = |(3 + x_i) - (7 + x_f)|$$

An example of the calculations above is shown below by assuming the gross counts in $CH_3 = 220$, $CH_4 = 350$, $CH_5 = 500$, $CH_7 = 340$, and $CH_8 = 200$

PNL TEST PROCEDURE FOR SRP

then

$$h = 500$$

$$1/2h = 250$$

$$m_i = \frac{220 - 350}{3 - 4} = 130$$

$$m_f = \frac{340 - 200}{7 - 8} = -140$$

$$x_i = \frac{y - b_i}{m_i} = \frac{250 - 220}{130} = 0.231$$

$$x_f = \frac{250 - 340}{-140} = 0.643$$

$$\Delta CH = |(3 + 0.231) - (7 + 0.643)| = 4.412$$

finally

$$R = \frac{\Delta CH}{CH_C} (\gamma \text{ KeV}) = \frac{4.412}{2665} 1332.5 = \underline{\underline{2.21 \text{ KeV}}}$$

A. Hand calculations shall be performed, documented, and reviewed in accordance with PAP-301.

5.9 Intercomparison of Control Count Values with "in control values"

Initially, the control program establishes the average $\pm$ standard deviation of each peak count rate and resolution.

5.9.1 Establishing the average $\pm$ standard deviation (σ) given 10 measurements. The average value, $\bar{x}$ is given below

and

PNL TEST PROCEDURE FOR SRP

$$\bar{x} = \frac{\sum_{i=1}^{10} x_i}{N}$$

$$\sigma = \left[\sum_{i=1}^{10} \frac{(x_i - \bar{x})^2}{N-1} \right]^{1/2} \quad \text{where } N = 10$$

5.9.2 Using the calculation procedures in section 5.7, the control values, x_s , are determined and compared to $\bar{x}$ values. The difference, D , is calculated based on the standard deviation of the "in control" values as follows.

$$D = |x_s - \bar{x}|$$

and the fractional difference, $\frac{D}{\bar{x}}$ is compared with the standard deviation of the "in control" deviations by

$$\sigma \text{ deviations} = \frac{D/\bar{x}}{\sigma}$$

where σ deviations "in control" are $\leq 10 \sigma$.

5.10 The Project Manager shall assure that the following records are processed in accordance with PNL Administrative Procedure, PAP-1701, Records Management

- Hand Calculations
- Laboratory Record Books (LRB)
- Spectral Data

5.11 Documents and Discrepancies

5.11.1 Records from this work shall be maintained and stored in accordance with PAP-1701.

Procedure No. RSD-51-UEQ 10	Revision No.	Date Issued 5-22-85	Page <u>20</u> of <u>21</u>
--------------------------------	--------------	------------------------	-----------------------------

PNL TEST PROCEDURE FOR SRP

5.11.2 When deviations from the procedure are found, the responsible staff shall initiate a Deficiency Report in accordance with PAP-1502, Controlling Deviations From QA Requirements and Established Procedures. The QAO Representative shall review and approve all Deficiency Reports.

5.11.3 If elements of this procedure require a change only for one specific test, a waiver of specific steps is possible prior to any departure from this procedure. The waiver shall be processed in accordance with PAP-1502. The responsible Q.E. shall approve all waivers for procedural changes.

5.11.4 If an incident occurs during this project, the responsible staff shall complete an incident report in accordance with PAP-1503. The responsible Q.E. shall review and approve all incident reports.

6.0 REFERENCED DOCUMENTS

- 6.1 PNL-MA-60, Quality Assurance Manual for License Related Programs
- 6.2 PAP-301, Hand Calculation Documentation and Review
- 6.3 PAP-1201, Calibration Control System
- 6.4 PAP-1502, Controlling Deviations from QA Requirements and Established Procedures
- 6.5 PAP-1503, Incident Reporting
- 6.6 PAP-1701, Records Maintenance and Storage in Project Files
- 6.7 PAP-1704, Laboratory Record Books
- 6.8 RSD-51-DEQ 13, Instrumental Counting of Cores by Gamma Spectrometry
- 6.9 Lail, J. C., C. L. Wilkerson and V. L. Crow. 1979. "Computer Methodology and Its Applications to Geological and Environmental Matrices". Proceedings on Computers in Activation Analysis and Gamma-Ray Spectrometry. DOE Symposium Series 49, p. 840-856.

Procedure No.
RSD-51-DEQ 10

Revision No.

Date Issued
5-22-85

Page 21 of 21

PNL TEST PROCEDURE

TITLE: HTA-4-15, SEPARATION OF PLUTONIUM BY SOLVENT EXTRACTION PRIOR TO MEASUREMENT BY ALPHA COUNTING

1.0 APPLICABILITY

This procedure can be used to separate plutonium from other alpha emitting radionuclides in liquid leachate samples. The Pu is then measured by alpha counting using 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

- Aluminum nitrate, 1 M in 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 (± 1) 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 (± 1) mL with deionized water; mix thoroughly.
- Hydrochloric acid, 1 M -- Dilute 83 (± 1) mL of concentrated reagent-grade hydrochloric acid to 1000 (± 1) mL with deionized water; mix thoroughly.
- Centrifuge, clinical.
- Cold spot heater.

Concurrence <div style="text-align: center; font-size: 1.5em;">NA</div>	Date	Approved <div style="text-align: center;"> </div>	Date <div style="text-align: center; font-size: 1.5em;">7/2/87</div>
Prepared by <div style="text-align: center; font-size: 1.5em;">A. Cheaf</div>	Date <div style="text-align: center; font-size: 1.5em;">7/1/87</div>	QAD Concurrence <div style="text-align: center; font-size: 1.5em;">B. O. BARNES</div>	Date <div style="text-align: center; font-size: 1.5em;">6/30/87</div>
Procedure No. HTA-4-15	Revision No. 5	Effective Date JUL 01 1987	Page of 1 3

PNL TEST PROCEDURE

- 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.

4.0 PROCEDURE

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.

- Step 1) To a 2 dram vial add a volume ($\pm 1\%$) of test solution specified by the cognizant scientist. Record the volume on the analytical report card.
- Step 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.
- Step 3) Evaporate the solution in the vial to dryness using a heat lamp.
- Step 4) Remove from the heat and allow to cool for at least 10 minutes.
- Step 5) Add 1 (± 0.01) mL of 2 M nitric acid.
- Step 6) Heat for 20 (± 1) minutes at 90 (± 5) $^{\circ}\text{C}$ in the 1/2 in. deep heat block.
- Step 7) Remove the heat and cool for at least 10 minutes.
- Step 8) Add 1 (± 0.01) mL of 2 M sodium nitrate dropwise; swirl frequently while adding.
- Step 9) Allow the reaction to subside for 5 minutes; swirl frequently.
- Step 10) Heat for 15 minutes at 90 (± 5) $^{\circ}\text{C}$ in the 1/2 in. deep heating block.
- Step 11) Remove from the heating block and allow to cool for at least 10 minutes.
- Step 12) Add 2 (± 0.02) mL of 0.5 M TTA in xylene.
- Step 13) Cap the vial tightly and mix by vortexing 3 minutes.
- Step 14) Centrifuge for ~1 minute to separate the phases.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-15	5	JUL 01 1987	2	3

PNL TEST PROCEDURE

- Step 15) Transfer most of the TTA phase (top) to a clean 2-dram vial.
- Step 16) To the vial containing the TTA phase add:
- 1 (± 0.01) mL of 1 M hydrochloric acid
 - 100 (± 10) μ L of 2 M sodium nitrate.
- Step 17) Cap the vial and vortex for 3 minutes.
- Step 18) Centrifuge for about 1 minute to separate the phases.
- Step 19) Mount 1 (± 0.01) mL of the TTA phase on a stainless steel counting disc using the cold spot heater.
- Step 20) Rinse the pipet with xylene and add the rinse to the disc.
- Step 21) Heat the disc on the hot plate on high heat to burn off the organic residue.
- Step 22) Count the plutonium using the Alpha Counting (HTA-4-6) and Alpha Spectrometry (HTA-4-5) analysis procedures. Record as specified in the referenced 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-15	5	JUL 01 1987	3	3

WORKING DOCUMENT IS IN THE LABORATORY

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 O. P. Amacker, Jr.	Date 6/17/88	Approved J. J. McCown	Date 6/16/88
Prepared by W. Y. Matsumoto	Date 6/15/88	QAD Concurrence L. J. Ethridge	Date 6/16/88
Procedure No. 2-30.6	Revision No. 0	Effective Date 6/21/88	Page of 1 10

PNL TEST PROCEDURE

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

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	2	10

PNL TEST PROCEDURE

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.

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	3	10

PNL TEST PROCEDURE

- (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.

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	4	10

PNL TEST PROCEDURE

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.

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	5	10

PNL TEST PROCEDURE

- (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.

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	6	10

PNL TEST PROCEDURE

- (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.

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	7	10

PNL TEST PROCEDURE

- (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.

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	8	10

PNL TEST PROCEDURE

- (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.

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	9	10

PNL TEST PROCEDURE

- (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

- (a) Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides [(U,Pu)O₂], C. 698, American Society for Testing and Materials (ASTM), Philadelphia, PA (1972).
- (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).

Procedure No.	Revision No.	Effective Date	Page	of
2-30.6	0	6/21/88	10	10

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 <i>[Signature]</i>	Date 7/2/87
Prepared by ACLeh	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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-13	6	JUL 01 1987	2	3

PNL TEST PROCEDURE

- 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-13	6	JUL 01 1987	3	3

PNL TEST PROCEDURE

TITLE: HTA-4-14, SEPARATION OF NEPTUNIUM BY CATION EXCHANGE AND SOLVENT EXTRACTION PRIOR TO MEASUREMENT BY ALPHA COUNTING

1.0 APPLICABILITY

This procedure can be used for separating ^{237}Np from other alpha emitting radio-nuclides in liquid leachate samples. Following the separation, the ^{237}Np is 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

- Cation exchange resin, Dowex-50[®] (or AG-50W[®]), X-8, 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 (± 0.05) g of ceric sulfate [$\text{H}_4\text{Ce}(\text{SO}_4)_4$] 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.

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

Concurrence <i>NA</i>	Date	Approved <i>[Signature]</i>	Date <i>7/2/87</i>
Prepared by <i>AC Lee</i>	Date <i>7/1/87</i>	QAD/Concurrence <i>B.O. BARNES</i>	Date <i>6/30/87</i>
Procedure No. HTA-4-14	Revision No. 5	Effective Date JUL 01 1987	Page of 1 4

PNL TEST PROCEDURE

- Sodium nitrite, 2 M — Dissolve 13.8 (± 0.1) g of sodium nitrite in 100 (± 1) 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 with deionized water; mix thoroughly.
- Hydroxylamine hydrochloride, 5 M — Dissolve 34.8 (± 0.1) g of hydroxylamine hydrochloride in 100 (± 1) mL of deionized water; mix thoroughly.
- Ferrous ammonium sulfate, 0.1 M — Dissolve 3.9 (± 0.1) g of ferrous ammonium sulfate in 100 (± 1) mL of deionized water plus 1 (± 0.1) mL of 1 M hydrochloric acid; mix thoroughly. NOTE: Prepare just prior to use.
- Xylene, reagent-grade, (FLAMMABLE).
- Thenoyltrifluoroacetone (TTA), 0.5 M in xylene — Dissolve 111 (± 1) g of TTA salt in 1000 (± 1) 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.

4.0 PROCEDURE

The neptunium is separated from other radioactive species by cation exchange of NpO_2^+ followed by solvent extraction of Np^{+4} into thenoyltrifluoroacetone in xylene. The neptunium activity is measured by alpha counting and alpha spectrometry.

Step 1) To a 2-dram vial, add up to 1 (± 0.01) mL of test solution plus an equal volume of 2 M nitric acid. Record the sample volume on the analytical report.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-14	5	JUL 01 1987	2	4

PNL TEST PROCEDURE

- Step 2) Add 100 (± 10) μL of 0.1 M ceric sulfate; swirl to mix.
- Step 3) Heat for 5 (± 1) minutes at 65°C ($\pm 5^\circ\text{C}$) in heating block.
- Step 4) Remove from heating block, and allow to cool for 5 minutes or longer.
- Step 5) Add 200 (± 20) μL of 2 M sodium nitrite; swirl to mix.
- Step 6) Heat for 15 (± 2) minutes at 90°C ($\pm 5^\circ\text{C}$) in heating block.
- Step 7) Remove from heat, and allow to cool for 10 minutes or longer.
- Step 8) Prepare a 2 (± 0.1) mL column of Dowex-50, X-8, 200 to 400 mesh, H^+ form resin.
- Step 8.1) Cut off the top of a 7-mL plastic dropper.
- Step 8.2) Fill the tip with a small ball of cotton to support the resin.
- Step 8.3) Measure a 2 (± 0.1) mL volume above the cotton plug.
- Step 8.4) Mark the column at the 2-mL volume.
- Step 8.5) Add a slurry of resin to the column until the settled bed of resin is to the mark.
- Step 9) Transfer the solution from Step 7 onto the prepared resin column. Collect the column effluent in a 2-dram vial.
- Step 10) Rinse the vial from Step 7 with five 1 (± 0.01) 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 Step 9. Discard the column.
- Step 11) Evaporate the column effluent to dryness under a heat lamp.
- Step 12) To the residue in the vial, add 1 (± 0.01) mL of 0.5 M hydrochloric acid plus 200 (± 20) μL of 5 M hydroxylamine hydrochloride; swirl to mix.
- Step 13) Heat for 20 (± 2) minutes at 90°C ($\pm 5^\circ\text{C}$) in heating block.
- Step 14) Remove from heating block.
- Step 15) Add 100 (± 10) μL of 0.1 M ferrous ammonium sulfate; swirl to mix.
NOTE: Ferrous ammonium sulfate must be prepared just prior to use.
- Step 16) Heat for 10 (± 1) minutes at 90°C ($\pm 5^\circ\text{C}$) in heating block.
- Step 17) Remove from heating block and cool for 10 minutes or longer.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-14	5	JUL 01 1987	3	4

PNL TEST PROCEDURE

- Step 18) Add 1 (± 0.01) mL of 0.5 M TTA in xylene. Cap the vial tightly.
- Step 19) Mix for 3 (± 0.5) minutes, using a vortex mixer.
- Step 20) Centrifuge for 1 minute to separate phases.
- Step 21) Plate 500 (± 10) μ L of the TTA-xylene phase on a 7/8-in. stainless steel disc, using the cold-spot heater.
- Step 22) Heat the disc on the hot plate at high heat to burn off organic residue.
- Step 23) Count the neptunium using the Alpha Counting (HTA-4-6) and Alpha Spectrometry (HTA-4-5) 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-14	5	JUL 01 1987	4	4

PNL TEST PROCEDURE

TITLE: CHEMICAL SEPARTATION AND ANALYSIS PROCEDURE FOR URANIUM (^{238}U , ^{235}U , ^{234}U)

1.0 APPLICABILITY

This procedure describes a method for the chemical separation and determination of uranium (^{238}U , ^{235}U , ^{234}U) radionuclides in groundwaters or cores.

When this procedure is selected for implementation by a QA Plan prepared and approved in accordance with PNL-MA-60, this procedure is applicable to the Chemical Separation and Analysis of Uranium.

2.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)

ng - nanograms (10^{-9} grams)

μg - micrograms (10^{-6} grams)

$t_{1/2}$ - half-life

LRB - Laboratory Record Book

3.0 RESPONSIBLE STAFF

Project Manager
Cognizant Test Personnel

4.0 PROCEDURE

Due to the diverse nature of sample matrices and wide range of sample concentrations that can be encountered, plus ever changing tolerance limits for measured values and qualitative and quantitative acceptance criteria (depending upon the particular situation at hand), it is not feasible to write one all encompassing procedure to cover in detail, all of the possible variables required to perform a separation. The following procedure describes a specific approach to the separation and analyses of U isotopes, plus gives as an example very specific step by step instructions for a given generic situation. As real life situations arise, the radioanalytical chemist will write and implement detailed radioanalytical test intructions (RTI) which will be specific to the problems/needs at hand. These RTIs will be written in accordance with PNL-SP-29 and will give complete results traceability as required by PNL-MA-60, as well as provide sufficient information such that results can be replicated by qualified analytical personnel.

Concurrence C. W. Thomas	Date 1-29-87	Approved R. L. Brodzinski	Date
Prepared by C. Lau	Date 1/29/87	QAD Concurrence S. L. English	Date
Procedure No. J-51-DEQ 2	Revision No. 1	Effective Date	Page 1 of 7

PNL TEST PROCEDURE

4.1 Special Equipment

- . Vacuum Filtration Apparatus
- . Anion Exchange Column and appropriate resins
- . Tracer standardized and traceable to a certified standard
- . Calibrated pipette(s)

4.2 Uranium Separation From Groundwater

The schematic diagram of a basic Uranium Separation Scheme is shown in Figure 1. A diagram of this nature is not required in RTIs, however such diagrams are encouraged in this project. Basic step by step instructions detailed below constitute an example of the information which should be present in the procedure section of an RTI.

- 4.2.1 Check the acidity of water brought from the field. Record as found pH. If the pH is >2 , add more conc. HCl until the pH is <2 . Record the amount added in LRB and let sample equilibrate for a few hours. Take two different sized aliquots of solution. Record aliquot sizes and identify each with an unique sample subnumber. Oxidize the sample if necessary using an appropriate oxidizing agent and record agent and amount added. Always add the same amounts of reagents to each sample; even if this may be excessive to the smaller aliquot. (This is important because the reagent blank contributions will be determined using standard additions method between the two different aliquots.) Add ^{233}U tracer to each aliquot and record amount and tracer identification number in LRB.
- 4.2.2 Heat the solutions. A yellow to brown solution indicates that ferrous is oxidized to the ferric state (Fe(II) to Fe(III)). If the solution is not yellow add Fe(III) carrier and let equilibrate. Record amount of Fe(III) carrier added. Precipitate ferric hydroxide, co-precipitating U hydroxides using base. Record base and amount added in LRB.
- 4.2.3 Collect $\text{Fe}(\text{OH})_3$ ppt and dissolve with 10N HCl. Load the solution onto an anion exchange column (chloride form) which has been pre-equilibrated with 10NHCL.
- 4.2.4 Wash the ion-exchange resin with 5 column volumes of 10N HCl.
- 4.2.5 Elute U and Fe with 1 to 3 column volumes of 0.1N HCl, followed by 0.1N HNO_3 , followed by 0.1N HCL, followed by 0.1N HNO_3 .

Procedure No.	Revision No.	Effective Date	Page 2 of 7
RSD-51-DEQ 2	1		

PNL TEST PROCEDURE

Flow Scheme of Uranium Separation

Figure 1.

Procedure No. RSD-51-DEQ 2	Revision No. 1	Effective Date	Page 3 of 7
-------------------------------	-------------------	----------------	-------------

PNL TEST PROCEDURE

Evaporate the solution on a hot plate to < 20 ml and transfer to a small beaker. Add about 10 ml concentrated HNO_3 and take solution to dryness. Add about 10 ml concentrated HNO_3 and take solution to dryness a second time to insure chloride ions are removed.

4.2.6 Prepare ammonium nitrate solution (ANS) by dissolving 80 g of NH_4NO_3 in 100 ml of 5M HNO_3 . Take 10 ml of ANS in a small beaker and equilibrate with equal volume of ether using a magnetic stirrer. Discard the ether phase. Use the equilibrated ANS for the following ether extraction steps.

4.2.7 Ether Extraction - Perform ether extraction by adding 1 ml of ANS. Dissolve the U and Fe residue obtained in 4.2.5, in 1 ml of ANS. Add 2-3 ml of ethyl ether, a drop of Ru and mix vigorously (extract). Uranium goes into the ether phase and Fe stays in the aqueous phase. Ruthenium's dark color (Figure 1) helps distinguish the ether from the aqueous phase.

4.2.8 After extraction, slowly evaporate the ether. Then evaporate the aqueous solution to dryness. Label the beaker with sample number and cover with parafilm. The sample is now in the form for mass-spectrometric analysis (see 4.4).

4.3 Uranium Separation From Cores

When cores are being analyzed, the RTI will include the few additional steps listed below.

4.3.1 Fusion of Core - Transfer a weighed core aliquot to a 50 ml crucible. Add 10 g Na_2O_2 and 10-15 g of Na_2CO_3 . Heat the crucible over a flame until the peroxide/carbonate and core sample forms a clear melt. Cool crucible.

4.3.2 In a 250 ml beaker dissolve the fusion cake using about 50 ml of distilled water and minimal HNO_3 . Add minimal concentrated HCl until the solution is clear.

(In some cases fusion of the core may not be necessary. In which case, an RTI which details leaching with acid steps will be used.)

4.3.3 Follow the RTI described in section 4.2.

4.4 Analysis of ^{238}U , ^{235}U , ^{234}U , and ^{233}U by Mass Spectrometry

See 4.5 for performance check of mass spectrometer.

4.4.1 Remove the parafilm and evaporate the solution (if any) to a volume of about 50 μl .

4.4.2 Prepare a Rhenium (Re) mass spectrometer filament by heating it in a vacuum at 2000°C for 1 hour.

Procedure No.	Revision No.	Effective Date	Page 4 of 7
RSD-51-DEQ 2	1		

PNL TEST PROCEDURE

- 4.4.3 Pipette approximately 2 μ l aliquot from step 4.4.1 onto the prepared Re filament from step 4.4.2. Evaporate the solution to dryness under a heat lamp.
- 4.4.4 Load the Re filament into a three-stage mass spectrometer coupled with an ion pulse-counting detection system. The MS is computer controlled and is routinely used to measure the uranium atom ratios.
- 4.4.5 Increase the filament temperature until the ion intensity of ²³⁸U reaches a count rate of 10⁶/sec. The analysis and magnetic scanning of 238, 236, 235, 234 and 233 masses is controlled by the computer to achieve optimum sensitivity for each mass. The data collection continues until the intensity falls to two-thirds of the initial ion intensity.
- 4.4.6 Increase the filament temperature again until the initial ion intensity is restored and data collection is restored. This procedure assures that all scans have approximately equal statistical weight.

4.5 Stability and Quality Control of Mass Spectrometer (MS)

Prior to analyzing the sample, the stability of MS and associated electronic instruments are checked by analyzing a NBS natural uranium assay standard (NBS, U-950b). The long-term bias correction, which is typically 0.2% per mass unit for uranium, is applied to the measured isotope ratios of the sample.

- 4.5.1 Tracer (²³³U) - Uranium-233 is absent in the naturally occurring uranium. Thus it is ideal to use ²³³U as a tracer in the procedure for the chemical yield determination.

The ²³³U tracer was obtained from Oak Ridge National Laboratory (ORNL) as U₃O₈ with an ORNL assay of 99.9986 atom percent ²³³U. This material was calibrated with four separate gravimetric base solutions of NBS-950a gravimetric standard uranium. The average of the assay obtained from the four NBS standards yielded a value of 0.9965 $\pm$ 0.0007 g/l or 99.56 μ g/ml of ²³³U in the solution used as ²³³U spike. Its further dilution was made in such a manner that 100 λ (0.10 ml) aliquot yields 20.1 ng of ²³³U tracer.

Procedure No.	Revision No.	Effective Date	Page 5 of 7
RSD-51-DEQ 2	1		

PNL TEST PROCEDURE

The ratios of other uranium isotopes in the ^{233}U tracer are measured by the same MS used for sample analysis at PNL. These ratios are shown below.

<u>Isotopic Ratio</u>	<u>Value</u>
$^{234}\text{U}/^{233}\text{U}$	$(3.46 \pm 0.11) \times 10^{-6}$
$^{235}\text{U}/^{233}\text{U}$	$(4.00 \pm 1.00) \times 10^{-7}$
$^{236}\text{U}/^{233}\text{U}$	$(9.95 \pm 0.20) \times 10^{-6}$
$^{238}\text{U}/^{233}\text{U}$	$(8.00 \pm 1.00) \times 10^{-7}$

The contribution from these ratios due to ^{233}U spike in the sample is insignificant as compared to the actual ratios measured in the sample. Thus, the blank correction due to the ^{233}U tracer is negligible.

4.6 Example of M.S. Analysis

Exhibit 1 shows a typical print-out of atom percent $\pm 1\sigma$ error for ^{234}U , ^{235}U , ^{236}U and ^{238}U , and $^{233}\text{U}/^{238}\text{U}$ ratio with $\pm 1\sigma$ error. Samples in which the $^{233}\text{U}/^{238}\text{U}$ ratio was not obtained, were not spiked with ^{233}U (20.1 ng) tracer. These unspiked samples can be used to determine isotopic ratios. Identification No. 5348-60-1 refers to LRB, page No. and sample 1 (see step 4.2.8). For illustration, consider the example of 5438-60-1 and 5438-60-2 samples, which are brine waters from Zone 9 of J. Friemmel Well No. 1. Sample 60-2 was spiked with 20.1 ng ^{233}U tracer while sample 60-1 was not spiked.

Procedure No.	Revision No.	Effective Date	Page 6 of 7
RSD-51-DEQ 2	1		

PNL TEST PROCEDURE

Exhibit 1

Typical Print-Out From Mass Spectrometer Analysis

Sample Number		Atom Percents $\pm 1\sigma$ Error				Atom Ratio
Customer	A&NR	U-234	U-235	U-236	U-238	$^{233}\text{U}/^{238}\text{U}$
5348-65-4	76574	.0069 $\pm .0001$	.7103 .0009	.0002 .0000	99.2826 .0009	
5348-60-1	76575	.0090 $\pm .0001$	.7141 .0014	.0002 .0000	99.2767 .0014	
5348-60-2	76576	.0088 $\pm .0001$	.7136 .0027	.0004 .0000	99.2772 .0027	0.01058 0.00005
5348-65-2	76577	.0067 $\pm .0001$	.7104 .0008	.0000 .0000	99.2828 .0008	
5348-65-3	76578	.0068 $\pm .0001$	.7101 .0006	.0002 .0000	99.2829 .0006	0.003421 0.000006
5348-65-1	76579	.0068 $\pm .0001$	.7114 .0007	.0000 .0000	99.2818 .0007	0.003414 0.000005

Procedure No.
RSD-51-DEQ 2

Revision No.
1

Effective Date

Page 7 of 7

INDEPENDENT TECHNICAL REVIEW (ITR)
REPORT

DESIGNEE: J. C. Lane

Procedure No. RSD-51-DEQ2 Rev. 1

All of the required reviews have been received. ☒ Yes ☐ No

All comments have been satisfactorily resolved. ☒ Yes ☐ No

The document fulfills its requirements and objectives. ☒ Yes ☐ No

Summary of controversial resolutions or minority opinions: None

Reviewers/background :

- 1) C. W. Thomas / Technical
- 2) M. R. Smith / Technical
- 3) S. L. English / QA
- 4) _____ / _____

Enclosures: A before review copy of the procedure.
All closed out Document Review Records (DDR)
A final copy of the final document resulting from the ITR
resolutions.

Designee: Delash Date: 1/22/97
QA Representative: S. L. English Date: 1-30-97
Line Manager: R. B. Boudy Date: 1/30/97

PACIFIC NORTHWEST LABORATORIES DOCUMENT REVIEW RECORD <u>LTR</u>	TITLE <u>CHEMICAL SEPARATION AND ANALYSIS</u> <u>PROCEDURE FOR URANIUM (235, 238, 239 U)</u>		Page of	
	Document No. <u>PSD-51-PHQ 2</u>	Rev. No. <u>1</u>	DA Ltr.	Draft Date <u>1/27/87</u>

This document is being submitted for your review, concurrence or comments. Since this review is controlled, a response is required from all reviewers. Therefore, please return the DRR with or without comments to:

Name: J. C. LAUL Location: 329/300 By: 1/30/87

Additional Instructions:

Department	Reviewer	Signature/ Date	Department	Reviewer	Signature/ Date
Chem. Sciences	C.W. Thomas		Chem. Sci.	<i>[Signature]</i>	1-29-87
Chem. Sciences	M.R. Smith				
C.A.	S.L. ENGLISH				

CONCUR (X) CONCUR, BUT WITH COMMENTS () DO NOT CONCUR ()

No.	Comments, Justification & Recommendations	Resolution (justify if not in agreement)
Concur with Resolution <u>N/A</u>		Comments Resolved by <u>N/A</u> Date <u>1/30/87</u>

PACIFIC NORTHWEST LABORATORIES DOCUMENT REVIEW RECORD <u>ITR</u>	TITLE <u>Chemical Separation and Analysis</u> <u>of Procedure For Uranium</u> (234, 235, 238U)		Page 1 of 1
	Document No. <u>RSD-51-DEQ2</u>	Rev. No. <u>1</u>	Draft Date <u>1/27/87</u>

This document is being submitted for your review, concurrence or comments. Since this review is controlled, a response is required from all reviewers. Therefore, please return the DRR with or without comments to:

Name: J. C. LAUL Location: 329/300 By: 1/30/87

Additional Instructions:

Department	Reviewer	Signature/ Date	Department	Reviewer	Signature/ Date
Chem. Services	M. R. Smith	<i>[Signature]</i> 1/29/87			

CONCUR (X) CONCUR, BUT WITH COMMENTS () DO NOT CONCUR ()

No.	Comments, Justification & Recommendations	Resolution (justify if not in agreement)
	change 5.29 in Sec. 4.6 line 5 to 4.2.8	done
Concur with Resolution		Date
		Comments Resolved by <i>[Signature]</i> Date <u>1-29-87</u>

rec'd 1-29-87

rel'd 1-29-87

PACIFIC NORTHWEST LABORATORIES DOCUMENT REVIEW RECORD ITR	TITLE <i>CHEMICAL SEPARATION AND ANALYSIS</i> <i>PROCEDURE FOR URANIUM (238U, 235U, 239U)</i>		Page 1 of 2	
	Document No. <i>RSD-51-DEF 2</i>	Rev. No. <i>1</i>	DA Ltr.	Draft Date <i>1/29/87</i>

This document is being submitted for your review, concurrence or comments. Since this review is controlled, a response is required from all reviewers. Therefore, please return the DRR with or without comments to:

Name: J. C. LAUL Location: 329/300 By: 1/30/87

Additional Instructions:

Department	Reviewer	Signature/ Date	Department	Reviewer	Signature/ Date
Chem Sciences	C. W. THOMAS				
Lab Sciences	M. R. SMITH				
QA	S. L. ENGLISH				

CONCUR () CONCUR, BUT WITH COMMENTS () DO NOT CONCUR ☒

No.	Comments, Justification & Recommendations	Resolution (justify if not in agreement)
* ①	Wrong forms were used.	used new forms
2	Recommend you delete reference to SRP from title block at top. & ref. to QA Dept in 3.0	OK, done
* ③	4.2.1 Last sentence: The exhibit (Figure 1) allows you to use ^{238U} or ^{235U}	have taken out reference to both.
Concur with Resolution <i>S. L. English</i>		Comments Resolved by <i>McLaur</i>
Date <i>1-30-87</i>		Date <i>1-29-87</i>

DOCUMENT REVIEW RECORD - CONTINUATION				
Document No.	Revision No.	DA No.	Draft Date	Page of
RSD-51-DEQ-2	1		1-27-87	2 2
No.	Comments, Justification & Recommendations	Resolution (justify if not in agreement)		
④	Figure 1: identifies ²³⁴ Th, whereas text refers to only ²³² U. Delete reference to <u>40 mg Carrier</u> , it doesn't match text. "Perform Extraction (see Text)". Text doesn't really tell you how to perform extraction.	Have taken off reference to " ²³⁴ Th" see 4.2.2. Changed 4.2.7 Specific details of the 'normal' extraction are not required. If an unusual extraction procedure is used, where the results may be affected, the details/method will be specified.		
5	4.2.5 (pg 7) line #2 Delete reference to 10 ml HNO ₃ or add "about".	added "about"		
⑥	4.2.7 This section is not clear.	This has been cleared up.		
7	4.4.5 Did you forget to include 234?	Yes, I have included 234.		
⑧	4.6 2 nd sentence is not a sentence and doesn't make sense	Fixed.		
⑨	4.6 line 5. "(see step 5.2.9)" is incorrect	Step 5.2.9 changed to step 4.2.8.		
S.L. English 1-29-87				

PNL TEST PROCEDURE

TITLE: CHEMICAL SEPARATION AND ANALYSIS PROCEDURE FOR THORIUM (^{234}Th , ^{232}Th , ^{230}Th , ^{228}Th)

1.0 APPLICABILITY

When this procedure is selected for implementation by a QA plan prepared and approved in accordance with PNL-MA-60, this procedure is applicable to the chemical separation and analysis of thorium radionuclides in groundwaters or cores. Following chemical separations, thorium isotopic ratios are obtained using alpha and beta spectrometry. Based on the known spike added in the procedure, absolute ^{234}Th , ^{232}Th , and ^{228}Th concentrations and/or activities are determined.

2.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)
ng - nanograms (10^{-9} grams)
 μg - micrograms (10^{-6} grams)
 $t_{1/2}$ - half-life
LRB - Laboratory Record Book

3.0 RESPONSIBLE STAFF

Project Manager
Cognizant Test Personnel

4.0 PROCEDURE

Due to the diverse nature of sample matrices and wide range of sample concentrations that can be encountered, plus ever changing tolerance limits for measured values and qualitative and quantitative acceptance criteria (depending upon the particular situation at hand), it is not feasible to write one all encompassing procedure to cover, in detail, all of the possible variables. The following procedure describes a specific approach to the separation and analyses of Th isotopes, plus gives as an example of specific step by step instructions for a given generic situation. As real life situations arise, the radioanalytical chemist will write and implement detailed radioanalytical test instructions (RTI) which will be specific to the problems/needs at hand. These RTI's will be written in accordance with PNL-SP-29 and will give complete results traceability as required by PNL-MA-60, as well as provide sufficient information such that results can be replicated by qualified analytical personnel.

Concurrence	Date	Approved	Date
C.W. Thomas	1-29-87	R.L. Brodzinski	
Prepared by	Date	QAD Concurrence	Date
J.C. Lau	1-29-87	S.L. English	
Procedure No.	Revision No.	Effective Date	Page 1 of 9
RSD-51-DEQ 3	1		

PNL TEST PROCEDURE

4.1 Special Equipment

- Vacuum Filtration Apparatus
- Anion Exchange Column and appropriate resins
- Electroplating Cell, 1 inch Stainless Steel Electroplating Disk, Voltage Supply (0-25 Volt, 0-2 Ampere), Platinum Electrodes
- Calibrated pipette(s)

4.2 Thorium Separation From Groundwater

The schematic diagram of the Thorium Separation Procedure is shown in Figure 1. A diagram of this nature is not required in RTIs, however such diagrams are encouraged in this project. Basic step by step instructions detailed below constitute an example of the information which should be present in an RTI.

- 4.2.1 Check the acidity of water brought from the field. If the pH is greater than 2, add more conc. HCl until the pH is ≤ 2 . Let the sample equilibrate for a few hours. Take two aliquots ranging in volume from 3.5-50 liters for analysis. Add 3-5 ml 5% NaOCl solution to each aliquot. Add tracer to one of the solutions. Record amount added and the particular isotope. The other solution is left unspiked.
- 4.2.2 Let the solution equilibrate overnight. A yellow-to-brown solution color indicates that ferrous iron is oxidized to ferric state ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$). If it does not turn yellow, there is not enough iron in the water, add about 40 mg of Fe^{2+} carrier and let equilibrate for ≥ 2 hours. Add slowly, conc. NH_4OH until a pH of about 8 is obtained. Ferric hydroxide precipitates quantitatively co-precipitating U and Th as hydroxides. Record date/time of separation in LRB. Let the $\text{Fe}(\text{OH})_3$ precipitate settle for a few hours to overnight.
- 4.2.3 Collect $\text{Fe}(\text{OH})_3$ ppt by filtering through a glass fiber filter (millipore AP 20 or equivalent) using a vacuum filtering apparatus. Dissolve the $\text{Fe}(\text{OH})_3$ ppt in about 20 ml 10N HCl. Load the solution onto an anion exchange column (Dowex AG 1-X8, 50-100 mesh chloride form) that has been pre-equilibrated with 100 ml 10N HCl.
- 4.2.4 Wash the column with about 250 ml of 10N HCl. Collect the effluent which contains thorium in a 400 ml beaker. Iron and U stay on the column, while Th passes through the column. Save the Th fraction.

Procedure No.	Revision No.	Effective Date	Page 2 of 9
RSD-51-DEQ 3	1		

PNL TEST PROCEDURE

FLOW SCHEME OF THORIUM SEPARATION

Figure 1

PNL TEST PROCEDURE

- 4.2.5 Evaporate the thorium solution to a low volume (~20 ml) on a hot plate. Add about 10 ml conc. HNO_3 and heat the solution to remove the chloride ions. Repeat the HNO_3 addition process 2-3 times until the solution is colorless. Take the residue up in 9N HNO_3 .
- 4.2.6 Load the solution onto an ion-exchange column (AG 1-X8, 50-100 mesh, 2 cm dia. X 15 cm height) that has been preequilibrated with 9N HNO_3 . Thorium stays on the column while U and Fe impurities pass through the column. Wash the column with about 200 ml 9N HNO_3 . Elute Th with 250-300 ml 10N HCl into a beaker.
- 4.2.7 Evaporate the solution to a low volume (~20 ml) on a hot plate. Add conc. HNO_3 several times as in step 4.2.5 to completely remove the chloride ions. The solution is converted to HNO_3 medium. Evaporate the solution to near dryness. Add 500 μl (0.50 ml) conc. H_2SO_4 and 4 ml distilled water. Add three drops of Thymol blue indicator. Add dropwise NH_4OH until the solution color turns into a straw gold. This is an electroplating solution for Th.
- 4.2.8 Electroplating Steps - Prepare a polished 1-inch stainless steel (SS) disk for electroplating. Label back of disk with scribing tool using the LRB No., page and sample number identification. Clean polished surface with ethanol (95%) and dry.
- 4.2.9 Assemble electroplating cell with 1-inch SS disk in place. Check for leaks using distilled water. If there is no visible leak, discard water and transfer the pH adjusted electroplating solution (containing Th in step 4.2.7) to the electroplating cell.
- 4.2.10 Electroplate for about 2-4 hours at 1 Ampere current using a platinum electrode (strip) as an anode (positive) and the 1-inch SS disk as the cathode (negative). Thorium is electroplated on the SS disk. Record the start and end time of electroplating in LRB. After two hours, discard the solution, rinse off the platinum electrode with distilled water. Remove the 1-inch SS disk and wash with distilled water, then with alcohol and air dry. Count the sample using a beta detector for ^{234}Th and alpha detector for ^{232}Th , ^{230}Th and ^{228}Th radionuclides.

4.3 Thorium Separation From Core

A few additional steps are required to measure thorium in solids. Addition of these dissolution steps constitutes a separate RTI. Generally, only ^{232}Th and ^{230}Th radionuclides are to be measured in cores. Consequently thorium-228 ($t_{1/2} = 1.91 \text{ y}$) is often used as a tracer (note in LRB). However ^{229}Th may be used as a tracer also.

Procedure No.	Revision No.	Effective Date	Page 4 of 9
RSD-51-DEQ 3	1		

PNL TEST PROCEDURE

4.3.1 Fusion of Core - Transfer a weighed core aliquot (1-10 grams) to a 50 ml platinum or zirconium crucible. Add 10 gm Na_2O_2 and about 10 gm of Na_2CO_3 . Slowly heat the crucible on a bunsen burner until the Na_2O_2 and Na_2CO_3 start melting. Increase and maintain the heat until there is a clear melt. The crucible is red hot at this stage. After the clear melt is achieved, turn off the burner. Let the crucible cool and place it in a 250 ml beaker, and cover it with a watch glass.

4.3.2 Add about 50 ml of distilled water and 1-2 ml conc. HNO_3 to the crucible. The reaction is vigorous and the fused mass starts decomposing. After the reaction subsides, transfer the contents to the beaker and wash off the crucible with distilled water. Add slowly, conc. HCl until the solution is clear.

4.3.3 Combine the solution from steps 4.3.1 and 4.3.2. Add 5-10 ml HCl until the pH is about 1 (check the pH paper). Add 40 mg of Fe^{+++} carrier and a known amount of ^{228}Th and ^{233}U tracers (note in LRB) to the solution. Heat the solution to near boiling on a hot plate. Cool the solution to room temperature. Add slowly, conc. NH_4OH until a pH of about 8 is obtained. The ferric hydroxide $\text{Fe}(\text{OH})_3$ precipitate quantitatively coprecipitates Th and U as hydroxides. Let the $\text{Fe}(\text{OH})_3$ precipitate settle for a few hours to overnight.

4.3.4 Follow the RTI outlined in steps from 4.2.3 to 4.2.10, under Section 4.2.

4.4 Counting of ^{232}Th , ^{230}Th and ^{228}Th Radionuclides by Alpha Spectrometry

See Counting Procedure and Quality Control for Alpha Spectrometry for generalized details concerning the detector principal limitations, supporting electronics, calibration procedures and alpha spectral analysis.

PNL TEST PROCEDURE

4.4.1 Table 1 lists pertinent nuclear data used in this procedure for determining the activity (disintegration per minute, dpm) of ^{232}Th , ^{230}Th and ^{228}Th .

TABLE 1. Thorium-232, 230 and 228 Radionuclide Data

Isotope	Half-Life	α -Decay Energy (MeV) and Intensity	Approximate Channel Region*
^{232}Th	1.40×10^{10} y	3.95 (24%) - 4.01 (76%)	124 - 170
^{230}Th	7.52×10^4 y	4.62 (24%) - 4.68 (76%)	250 - 294
^{228}Th	1.91 y	5.34 (28%) - 5.43 (71%)	370 - 414
^{229}Th	7340 y	4.84 (58%) - 5.05 (7%)	320 - 350

*Channel regions correspond to 1024 channel multi-channel analyzers (MCA) calibrated with a 3.1 MeV offset and 5.8 KeV/Ch.

Radiochemical yield, geometry and efficiency corrections are made using a ^{230}Th tracer of known disintegration rate (Note in LRB). Absolute activities or concentrations are obtained for ^{234}Th , ^{232}Th and ^{228}Th in this manner. The ^{230}Th concentration in the sample is determined by normalizing the ^{232}Th and ^{228}Th concentrations from the alpha spectrum of the unspiked sample.

4.4.2 Tracer - The ^{230}Th and ^{229}Th tracers, used in this work are calibrated sources and their activities are cross calibrated with NBS traceable ^{239}Pu , ^{240}Pu and ^{242}Pu standards.

4.5 Counting of ^{234}Th by Beta Spectrometry

See Procedure and Quality Control for Beta Counting. The ^{234}Th ($t_{1/2} = 24.1$ d) activity is measured via its daughter $^{234\text{m}}\text{Pa}$ ($t_{1/2} = 1.18$ m) which emits a beta with an energy of 2.29 MeV (β_{max}). The counting is done on a low background (≤ 1 cpm) gas proportional beta counter equipped with anticoincidence shields. Because the ^{228}Th isotope is present, which has β emitting daughter isotopes (e.g. ^{212}Pb and ^{212}Bi), a 54 mg/cm² aluminum absorber is used to eliminate alphas and weak energy beta interferences.

Procedure No. RSD-51-DEQ 3	Revision No. 1	Effective Date	Page 6 of 9
-------------------------------	-------------------	----------------	-------------

PNL TEST PROCEDURE

4.6 Data Records

Chemistry: The thorium sample is identified by the LRB, page and sample number. Under the sample number in the LRB, the sample description, aliquot, tracer amount and peculiarities observed (if any) during chemical separations are recorded. Time of $\text{Fe}(\text{OH})_3$ separation (step 5.2.2) is noted in the LRB.

Alpha Spectrometry: All spectral data are recorded and filed under each well site and zone sampled. Additionally, spectra are stored on magnetic disks by LRB No., page and sample No.

Beta Spectrometry: Counting data are recorded and filed under the title of well site and zone sampled. Background count rate data and standard count data are also recorded. See procedure for Counting and Quality Control for Beta Spectrometry.

All analyses are accompanied with title, sample identification, detector identification, date counted, time counted (minutes). Other necessary data, such as aliquot, tracer quantity, separation times, and electroplating data are referenced using sample ID number in the LRB.

4.7 Printout and Spectra

Exhibits 1 and 2 show a typical example of printout and spectra for ^{232}Th , ^{230}Th and ^{228}Th isotopes. The regions (channel width) of interest are shown in exhibit 1. The integrated peaks and calculations are documented in traceable form and located in the appropriate LRB.

PNL TEST PROCEDURE

26 THREE 1.00-11 T. 33-00-1-00 2000. 2000.

Sample ID..... 1991-003474-031

• of COUNCILS..... 1934

STATUS 1.0..... 0000

DATE RECEIVED.....

CAL INFORMATION..... 5-8 SEARCH

THE END 1-12-54 at 10423120

CHARTER..... 1/15/71 to 10/23/72

(C-80 NUMBERED INDEX TYPED

LIVE GROW TIME.... 160 Hours of Runtime, 3 Seasons (10127.00 min.)

SLATED TIME..... (60 Hours of Rotation) Summer (1817.75 Hrs.)
(600 Hrs = 0.0000)

FLUX CONNECTION... 8-4700

DATA CORRECTION....	0.0000	0.0000	0.0000	0.0000	0.0000
---------------------	--------	--------	--------	--------	--------

LE 1247..... 2.0000 grams

[illegible]

EXHIBIT 1

Raw Printout Data. Regions Are
Marked for 232Th, 230Th and 228Th

[illegible]

PNL TEST PROCEDURE

Procedure No. RSD-51-DEQ 3	Revision No. 1	Effective Date	Page 9 of 9
-------------------------------	-------------------	----------------	-------------

PNL TEST PROCEDURE

TITLE: CHEMICAL SEPARATION AND ANALYSIS PROCEDURE FOR RADIUM (^{228}Ra , ^{226}Ra , ^{224}Ra)

1.0 APPLICABILITY

This procedure describes a method for the chemical separation and analysis of radium (^{228}Ra , ^{226}Ra , ^{224}Ra) radionuclides in groundwaters or cores. When this procedure is selected for implementation by a QA plan prepared and approved in accordance with PNL-MA-60, this procedure is applicable to the chemical separation and analysis of radium.

2.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)
ng - nanograms (10^{-9} grams)
 μg - micrograms (10^{-6} grams)
 $t_{1/2}$ - half-life
LRB - Laboratory Record Book
LVWS - Large Volume Water Sampler
SD no. - Sample Designation No.

3.0 RESPONSIBLE STAFF

- Project Manager
- Cognizant Test Personnel
- QAD Representative

4.0 PROCEDURE

Due to the diverse nature of sample matrices and the wide range of sample concentrations that can be encountered, plus ever changing tolerance limits for measured values and qualitative and quantitative acceptance criteria (depending upon the particular situation at hand), it is not feasible to write one all-encompassing procedure to cover in detail, all of the possible variables required to perform a separation. The following procedure describes a specific approach to the separation and analyses of Ra isotopes, plus gives as an example very specific step by step instructions for given generic situation. As real life

Concurrence	Date	Approved	Date
Prepared by J. C. Lau	Date	QAD Concurrence	Date
Procedure No. RSD-51-DEQ-4	Revision No. 1	Effective Date	Page 1 of 13

PNL TEST PROCEDURE

situations arise, the radionanalytical chemist shall write and implement detailed radionanalytical test instructions (RTI) which will be specific to the problems/needs at hand. These RTIs shall be written in accordance with PNL-SP-29 and shall give complete results traceability as required by PNL-MA-60, as well as provide sufficient information such that results can be replicated by qualified analytical personnel.

4.1 SPECIAL EQUIPMENT

- Large Volume Water Sampler (LVWS)
- Vacuum Filtration Apparatus

4.2 Radium Radionuclides (^{228}Ra , ^{226}Ra , ^{224}Ra) In $\text{Al}_2\text{O}_3\text{-BaSO}_4$ Adsorption Beds Using LVWS on Site

See procedure on Groundwater Field Sampling using Large Volume Water Sampler (LVWS) on site (RSD-51-DEQ-1). The use of LVWS is primarily made to pre-concentrate radium radionuclides. The preparation of $\text{Al}_2\text{O}_3\text{-BaSO}_4$ adsorption beds, assembly of the LVWS and its operation are described in detail in the procedure of Groundwater Field Sampling (RSD-51-DEQ-1). Only pertinent information is discussed here. The detailed step by step instructions listed below constitute an example of the information which should be present in an RTI.

4.2.1 Field Operation - A schematic diagram of the sampling train using LVWS in the field is shown in Figure 1. The groundwater is collected from the well head by a hose in 10-30 gallon plastic containers. If the water is spiked with a known activity of ^{133}Ba tracer, note the amount (dpm) in LRB. In series, the water is pumped through a prefilter such as RTI (Balston Type 54/50) using a 1/2 H.P. centrifugal pump. The water enters the inlet of the LVWS and goes through several glass fiber filters such as (millipore AP20) in parallel and then through two 1/4" thick $\text{Al}_2\text{O}_3\text{-BaSO}_4$ adsorption beds (8" diameter) in sequence. The outflow water goes through the water meter which records the amount of water pumped through the LVWS. (Note the meter reading in LRB.) The water outflow rate is kept at 1-2 gallons per minute. Note the time (start-finish) in LRB when the experiment is complete.

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DEQ-4	1		2	13

PNL TEST PROCEDURE

FIGURE 1. A schematic diagram of groundwater sampling using LVWS in the field

Procedure No.

RSD-51-DEQ-4

Revision No.

1

Effective Date

Page of

3

13

PNL TEST PROCEDURE

- 4.2.2 The LVWS is disassembled by unscrewing the top nuts from the bolts. The $\text{Al}_2\text{O}_3\text{-BaSO}_4$ sorption beds (No. 1,2) are removed and transferred to separate plastic bags and sealed with tape and properly labeled. The $\text{Al}_2\text{O}_3\text{-BaSO}_4$ sorption beds are brought to the laboratory.
- 4.2.3 Laboratory Operation - In the LRB, log each sample by (1) assigning a sample designation number (LRB No., page No., sample No.); (2) sampling date-time (start-finish); (3) water gallons pumped through LVWS; (4) bed numbers; and (5) zone and well site.
- 4.2.4 Transfer each $\text{Al}_2\text{O}_3\text{-BaSO}_4$ sorption bed to a clean pyrex dish and dry the beds under a heat lamp. Mix each sorption bed thoroughly for homogeneity and weigh it. Record the total weight of each bed in LRB.
- 4.2.5 Take a known weight (note in LRB) and transfer quantitatively to a small tuna can (STC) or large tuna can (LTC) made of thin aluminum. Seal the can with a hydraulic sealer and label the can.
- 4.2.6 Count samples for ^{228}Ra , ^{226}Ra and ^{224}Ra radionuclides using low energy photon detector (LEPD), Ge(Li) detector, and coincidence/noncoincidence $\text{Ge(Li)}\text{-NaI(Tl)}$ counting systems using gamma counting procedure RSD-51-DEQ-10.

The disintegration per count (DPC) factors or geometry efficiency for the various gamma-ray energies of ^{228}Ra , ^{226}Ra , ^{224}Ra and ^{133}Ba are established for the different counting systems using standards of known activity (dpm) in identical matrix such as $\text{Al}_2\text{O}_3\text{-BaSO}_4$.

Table 1 lists the DPC factors for: (1) small tuna can (STC), (2) large tuna can (LTC), (3) $\text{Ba} + \text{Ra(SO}_4\text{)}$ precipitation method, and (4) direct counting of a known (e.g., 200 ml) aliquot in a plastic bottle, on (a) LEPD "389" and "447", detectors, (b) Ge(Li) detector "L", (c) coincidence-noncoincidence $\text{NaI(Tl)}\text{-NaI(Tl)}$ detector.

4.3 Radium-228 and ^{226}Ra Analysis by BaSO_4 precipitation Method

Similar to Section 4.2 above, the detailed instructions listed below constitute an example of an RTI. Figure 2 shows the flow diagram of $\text{Ra} + \text{Ba(SO}_4\text{)}$ precipitation method.

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DEQ-4	1		4	13

PNL TEST PROCEDURE

TABLE 1. Radionuclide data and detector efficiencies used for ^{228}Ra , ^{228}Ac , and ^{232}Th radionuclides

Radioisotope	$T_{1/2}$	Detector (Type)	γ -Peak (Isotope) KeV	Sys. Eff.- (C/H)	Geometry factor, $\text{gpc} \cdot \text{efficiency}^{-1}$		
					SLC	LTC	200 ml
^{228}Ra	5.76 y	389 LEPD	129 (228Ac) 338 (228Ac)	0.014 0.006	761.4 490.6	1227 884.4	900
		447 LEPD	129 (228Ac) 338 (228Ac)	0.019 0.040	890.1 540.6	---	---
		I Ge(Li)-NaI(Tl)	338 (228Ac) 911 (228Ac) 969 (228Ac)	0.25 0.26 0.048	393.3 389.3 663.6	574.1 545.1 896.2	---
		L Ge(Li)	338 (228Ac)	0.036	---	243	---
^{226}Ra	1600 y	389 LEPD	186 (226Ra) 295 (214Pb) 352 (214Pb)	0.100 0.017 0.037	604.3 227.5 154.8	---	1320
		447 LEPD	186 (226Ra) 295 (214Pb) 352 (214Pb)	0.127 0.039 0.069	653.1 247.5 167.1	---	1260
		I Ge(Li)-NaI(Tl)	186 (226Ra) 295 (214Pb) 352 (214Pb)	0.110 0.097 0.005	567.4 97.15 161.1	---	---
		L Ge(Li)	186 (226Ra)	0.372	---	420	---
				270	2.01	2.07	
				0.24	29.7	34.1	

PNL TEST PROCEDURE

TABLE 1. Radionuclide data and detector efficiencies used for ^{224}Ra , ^{226}Ra , and ^{133}Ba radionuclides (continued)

Radionuclide	$T_{1/2}$	Detector (Type)	γ -Peak (Isotope) KeV	Sys. Bkg. (C/M)	Geometry Factor, a IPC (efficiency)=1		
					STC	LTC	BaSO ₄ 200 ml
^{224}Ra	3.66 d	389 LEPD	239 (212Pb)	0.110	73.5		
			300 (212Pb)	0.002	1640		
		447 LEPD	239 (212Pb)	0.219	80.9		
			300 (212Pb)	0.009	1774		
		I Ge(Li)-NaI(Tl)	239 (212Pb)	1.57	57.2		
			300 (212Pb)	0.080	1472		
			727 (212Pb)	0.040	1405		
			583 (208Tl)	0.12	875		
			†583 (208Tl)	0.26	291		
			Coln. (208Tl)	0.124	17.95	17.35	
^{133}Ba	10.7 y	389 LEPD	303 (133Ba)	---	298.9		64.1
			356 (133Ba)	0.012	105.2		
		447 LEPD	303 (133Ba)	---	327.1		
			356 (133Ba)	0.030	114.1		
		I Ge(Li)	356 (133Ba)	---			42.4
		I Ge(Li)-NaI(Tl)	303 (133Ba)	---	198		
			356 (133Ba)	---	66.34		

a IPC are approximate values and depend on geometry. They are periodically checked. IPC = 1/Efficiency.

The higher the IPC value, the lower the efficiency.

STC = Small Tuna Cans with ~75 grams of BaSO₄-Al₂O₃ resin

LTC = Large Tuna Cans with ~210 grams of BaSO₄-Al₂O₃ resin

BaSO₄ = Precipitation method

200 ml = Direct counting of an aliquot

† Coincidence Peak

PNL TEST PROCEDURE

Flow Scheme of Ba + Ra (^{228}Ra + ^{226}Ra) Precipitation Method

Water
Sample

↓ Heat
Add ^{133}Ba Tracer
↓ Heat

↓ Add 50-100 mg Ba carrier
Add 9M H_2SO_4
↓

Ba, Ra (SO_4) ppt.

↓ Filter on Glass Fiber
Dry the ppt.
↓ Mount on Counting Card

Ba, Ra (SO_4) ppt.

↓ Allow ^{228}Ac Ingrowth
Wait ~ 30 hours
↓ Before Counting

Count on LEPD and Ge(Li) Detectors
 ^{228}Ra (^{228}Ac) = 129 and 338 keV γ
 ^{226}Ra = 186 keV γ
 ^{133}Ba = 356 keV γ for Chemical Yield

↓ Record Results of
Radium Analysis

FIGURE 2. Schematic diagram of Ba-Ra(SO_4) precipitation method

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DEQ-4	1		7	13

PNL TEST PROCEDURE

- 4.3.1 Take a known volume of water (note in LRB) in a beaker. Add Conc. HCl to adjust to pH 2. Heat the solution to near boiling on a hot plate. Add a known amount of Ba carrier (50-100mg) and ^{133}Ba tracer carrier to the solution (note in LRB). Heat the solution.
- 4.3.2 Add slowly a few ml 9 M H_2SO_4 to precipitate $\text{BaSO}_4 + \text{RaSO}_4$. $\text{Ba}(\text{SO}_4)$ coprecipitates RaSO_4 quantitatively. The precipitation is slow. Cool the solution and allow the precipitate to settle for $\geq$ one hour.
- 4.3.3 Filter the precipitate using a glass fiber filter and a vacuum filtration apparatus. Record date and time of filtration and sample designation in LRB.
- 4.3.4 Dry the precipitate (plus filter) under a heat lamp and mount it on a cardboard holder. Cover the ppt. with mylar and seal with scotch tape. Label the cardboard with LRB number, page number, and sample number.
- 4.3.4 ^{228}Ra ($t_{1/2} = 5.76$ y) decays to ^{228}Ac ($t_{1/2} = 6.13$ hr) which emits gamma energies of 129 KeV and 338 KeV. Wait for about 30 hours to let ^{228}Ac grow into secular equilibrium with ^{228}Ra . Count the sample on LEPD and Ge(Li) detector for 129 and 338 KeV of ^{228}Ac , 186 KeV of ^{226}Ra and 356 KeV of ^{133}Ba . The gamma peaks are very well resolved. Use the ^{133}Ba 356 KeV peak for chemical yield determination. The DPC factors for these gamma energies are listed in Table 1.

4.4 Direct Counting of 200 ml aliquot

When ^{226}Ra and/or ^{228}Ra activity in water is high, direct counting of an aliquot (about 200 ml) is possible.

As in the above sections, the instructions listed below constitute an example of a RTI. Take an aliquot of water in a nalgene bottle (record in LRB), cap it and label it. Count the aliquot bottle on the LEPD system. Use 338 KeV gamma for ^{228}Ra and 186 KeV gamma for ^{226}Ra . The DPC factors for 338 and 186 KEV gammas for LEPD are listed in Table 1.

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DE0-4	1		8	13

PNL TEST PROCEDURE

4.5 Radium-226 via ^{222}Rn by De-emanation Scintillation Method

$^{226}\text{Ra} \leftrightarrow \alpha$	$^{222}\text{Rn} \leftrightarrow \alpha$	$^{218}\text{Po} \leftrightarrow \alpha$	$^{214}\text{Pb} \leftrightarrow \beta$
1600 y	3.82 d	3.0 m	26.8 m
$^{214}\text{Bi} \leftrightarrow \beta$	$^{214}\text{Po} \leftrightarrow \alpha$	^{210}Pb	
19.7 m	2×10^4 s	22.3y	

Radium-226 sensitivity by ^{222}Rn measurement is about 100 times better than by the methods described earlier. When secular equilibrium exists between ^{222}Rn and its daughters, for every disintegration of ^{222}Rn , three alphas are emitted. The detection efficiency of alpha by alpha scintillation detector is much higher when compared to gamma spectrometry. For details of apparatus, counting, and operation of the de-emanation scintillation method, see Chemical Separation and Analysis Procedure for Radon (RSD-51-DEQ 5). Only a brief description is made here.

Figure 3 shows the schematic view of ^{222}Rn measurement by the de-emanation scintillation method, and is discussed below.

- Transfer the water into a 50 ml glass bubbler (gas purge bottle). Connect the bubbler to the Rn system (Figure 3). Attach a He supply to bubbler, and purge for 30 minutes to let existing Rn escape. After purging, seal the bubbler by closing V1 and V2 valves (Figure 3). Note the volume and end-time of purging in LRB. Store the bubbler for about two weeks to let ^{222}Rn grow in secular equilibrium with ^{226}Ra . Follow steps outlined in the Rn procedure number RSD-51-DEQ 5.
- Purge radon gas for about a known interval (15-20 minutes) using He as a carrier at a flow rate of 100-125 cc/min. collect Rn gas in a charcoal trap that is cooled in a liquid N₂ bath.
- After Rn collection, heat the charcoal and purge with He gas, and collect Rn in an evacuated scintillation cell.
- Count the sample collection cell for alpha scintillation (RSD-51-DEQ 5) in a counting system. If possible, make 2 or 3 counts to follow the $t_{1/2}$ of ^{222}Rn .

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DEQ-4	1		9	13

PNL TEST PROCEDURE

FIGURE 3. Schematic view of ^{222}Rn (^{226}Ra via ^{222}Rn) measurement by deemanation scintillation method

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DEO-4	1		10	13

PNL TEST PROCEDURE

4.6 Radium (^{228}Ra , ^{226}Ra) Radionuclide Analysis of Cores by Instrumental Counting

When necessary, the cores are pulverized by a shatter box. The powder is homogenized. Take a known amount (100-200 gm) in a small or large tuna can (STC or LTC). (Record the weight in LRB). Seal the can with a lid using a can sealer. Label the can with LRB number, page number, and sample number. Wait for about two weeks to let ^{222}Rn and its daughters grow in equilibrium with ^{226}Ra . For the desired sensitivity, where necessary, count the sample on LEPD, coincidence-noncoincidence Ge(Li)-NaI(Tl), and multidimensional NaI(Tl)-NaI(Tl) counting system. The DPC factors for ^{226}Ra (186 KeV γ) and ^{228}Ra (338 KeV γ) are shown in Table 1.

4.7 Radium-226 via ^{222}Rn in Cores by Dissolution Method

The RTI procedure detailed below is coupled with U and Th separations in cores. See Chemical Separation and Analysis procedures for U and Th (RDS-51-DEQ 2 and RSD-51-DEQ 3) and appropriate RTIs.

4.7.1 Take a few gm salt core (note in LRB) in a beaker and add distilled water. Warm the solution on a hot plate overnight. Most of the salt core dissolves. Filter the solution through a glass fiber filter into another beaker. Dry the residue on a filter paper under a heat lamp.

4.7.2 Fusion of Residue - Transfer the residue to a 50 ml Zr or platinum crucible. Add 10 gm Na_2O_2 and 10-15 gm of Na_2CO_3 (the weight mixture may vary depending on the size of sample). Slowly heat the crucible on a bunsen burner until Na_2O_2 and Na_2CO_3 starts melting. Increase and maintain the heat until there is a clear melt. Let the crucible cool and place it in a beaker, and cover it with a watch glass.

If Step 4.7.1 is not needed then fuse a known aliquot of sample with Na_2O_2 and Na_2CO_3 as in Step 4.7.2. If fusion step is not necessary, perform leaching with acid (HNO_3 or HCl).

4.7.3 Add distilled water to the crucible. The reaction is vigorous and the fused mass starts decomposing. After the reaction subsides, transfer the contents to the beaker and

PNL TEST PROCEDURE

wash off the crucible with distilled water. Add slowly Conc. HCl until the solution is clear.

4.7.4 Combine the solutions from Steps 4.7.1 and 4.7.3. Add 5-10 ml HCl until the pH is ≤ 1 . Take a known volume of solution in a glass bubbler (note the volume and time in LRB). Wait for about two weeks to let ^{222}Rn grow into secular equilibrium with ^{226}Ra . Follow steps as outlined in Section 4.5.

4.7.5 If U and Th are to be separated, add 40-100 mg of Fe^{+++} carrier and a known amount of ^{228}Th or ^{229}Th and ^{233}U tracers (note the tracer amount in LRB) to the solution. Heat the solution to near boiling, cool it, and add slowly Conc. NH_4OH until a pH of about 8 is obtained. The ferric hydroxide $\text{Fe}(\text{OH})_3$ precipitate quantitatively co-precipitates Th and U as hydroxides, while the solution contains Ra. Follow Step 4.5.

4.8 Calculation of DPC factors from Standards and Data for Samples

The DPCs listed in Table 1 under each of the geometries used for gamma spectrometric measurements are obtained by using known ^{228}Ra , ^{226}Ra , and ^{224}Ra (^{228}Th) standard (Table 2 concentrations). Radium-226 measurements by the ^{222}Rn de-emanation procedure also incorporate the ^{226}Ra standards listed in Table 2 for assessment of disintegration rate per count (see ^{222}Rn Analysis Procedure, RSD-51-DEQ 5) factors.

The standards used in this work are certified NBS standards. These standards are periodically checked for reproducibility of the DPC factors (Table 1) for radium radionuclides on the various gamma counting systems used. Using the DPC values for a specific counting system used, the calculations are documented in LRB or traceable formats.

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DEQ-4	1		12	13

PNL TEST PROCEDURE

TABLE 2. Standard reference material used for Calibration and Determining DPC Factors

Radionuclide	$T_{1/2}$	(Reference Date)	PNL No.	Concentration ^a (dpm/ml)
226Ra (226Ra)	1.91 yr	NBS SRM No. 4206 (10/11/82)	1892-72-1 1892-72-500 (1:500 Dilution) 50037-133-0	2.097 x 10 ⁵ 419.4 3.09 x 10 ⁴
226Ra	5.76 yr	NBS SRM No. 4339 (4/12/83)	N-117-0 N-117-20A (1:20 Dilution) 50037-110-0	4.322 x 10 ⁵ 2.161 x 10 ⁵ 169.4
226Ra	1600 yr	NBS SRM No. 4950E (4/84)	50037-111-0	8.920
226Ra	1600 yr	NBS SRM No. 49530 (4/84)	4491-76-1	4.992 x 10 ⁴
133Ba	10.7 yr	NBS SRM No. 4251B (12/8/83)		

^a All standards have errors $\pm 3\%$.

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DEQ-4	1		13	13

PNL TEST PROCEDURE

TITLE: CHEMICAL SEPARATION AND ANALYSIS PROCEDURE FOR POLONIUM (^{210}Po)

1.0 APPLICABILITY

This procedure describes a method for the chemical separation of polonium (^{210}Po) radionuclide in groundwaters. Following chemical separations, ^{210}Po is determined by alpha spectrometry. Based on the known ^{208}Po spike added in the procedure, absolute ^{210}Po concentration is determined.

When this procedure is selected for implementation by a QA plan prepared and approved in accordance with PNL-MA-60, this procedure is applicable to the chemical separation and analysis by alpha spectrometry for ^{210}Po in groundwaters.

2.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)

ng - nanograms (10^{-9} grams)

μg - micrograms (10^{-6} grams)

$t_{1/2}$ - half-life

LRB - Laboratory Record Book

3.0 RESPONSIBLE STAFF

Project Manager

Cognizant test personnel

4.0 PROCEDURE

Because of the diverse nature of the groundwater sample matrices and wide range of radionuclide concentration encountered in field sampling as well as the sensitivity and accuracy requirements for this program, it is not feasible to establish a single fixed sampling protocol and analytical procedure that will be universally suitable. To prepare procedures that fit specific samples, the radioanalytical chemist will write and implement detailed radioanalytical test instructions (RTI) that are in accordance with PNL-SP-29 and will give complete traceability of results as required by PNL-MA-60. The following procedure is a sample of a practical RTI that provides sufficient detail that the results can be replicated by a qualified analytical chemist.

Concurrence	Date	Approved	Date
Prepared by	Date	QAD Concurrence	Date
J. C. Lau			
Procedure No.	Revision No.	Effective Date	Page of
RSD-51-DEQ-8	1		1 5

PNL TEST PROCEDURE

4.1 Special Equipment

- Vacuum Filtration Apparatus, Filter Paper, Glass Fiber (millipore AP20 or equivalent), pH Paper. Thermometer (0-150°C)
- Reagents - 20 mg/ml Fe⁺³ Solution
- Tracer - 208Po (~20 dpm)
- One-inch Silver Disk, Black Krylon Spray

4.2 Polonium Separation From Groundwater

Process samples as soon as possible after sampling to prevent the ingrowth of 210Po from 210Bi and 210Pb present in the sample. The schematic diagram of the polonium separation procedure is shown in Figure 1. The details of the polonium procedure are as follows.

- 4.2.1 Check the acidity of water brought from the field. If the pH is greater than 2, add conc. HCl until the pH is less than 2. Let the sample equilibrate for a few hours to overnight. Take 1-10 liter(s) (note the volume in LRB) of water in a beaker. Add about 10 ml of conc. HNO₃ to the water. Place a teflon covered stir bar in the beaker. Heat and stir the solution on a hot plate.
- 4.2.2 If needed add 20-50 mg of Fe⁺⁺⁺ carrier. Add a known activity of 208Po tracer (~20 dpm) to the sample (note the tracer amount in LRB). Stir and heat the solution to near boiling. Cool the solution. Add slowly, conc. NH₄OH until a pH of about 9 is obtained. Let the Fe(OH)₃ ppt settle for a few hours to overnight.
- 4.2.3 Collect Fe(OH)₃ ppt by filtering through a glass fiber filter using a vacuum filtering apparatus. Dissolve the Fe(OH)₃ in 10-20 ml conc. HCl in a 400 ml beaker. If Fe(OH)₃ is abnormal in color (not brown), repeat the Fe(OH)₃ precipitation as in step 4.2.2 to give a brown precipitate. Otherwise, repetition of Fe(OH)₃ may not be necessary. Dissolve the Fe(OH)₃ ppt in a few ml of conc. HCl in a beaker. Heat the solution slowly to near dryness.

Procedure No.	Revision No.	Effective Date	Page	of
RSD-51-DEQ-5	1		2	5

PNL TEST PROCEDURE

Flow Scheme of Polonium Separation

FIGURE 1. Schematic Diagram of Polonium Separation

PNL TEST PROCEDURE

- 4.2.4 Dissolve the residue in 300 ml to 1 liter of 0.4N HCl depending on the quantity of residue and add about 100 mg ascorbic acid. Add a teflon covered magnetic stirring bar.
- 4.2.5 Prepare a 7/8" silver disk by spraying one side with rapid drying enamel. Polish the unpainted side with metallographic Al₂O₃ (or silver polish) and rinse with distilled water. Suspend the disk in the solution (from step 4.2.4) by hanging from a pyrex hook fixed to a watch glass.
- 4.2.6 Heat the solution to 75°-95°C. Keep the solution stirring with a magnetic stir bar. Polonium deposits onto the silver disk in 3-6 hours. Remove the disk and rinse with distilled water and dry. Note the time of completion of plating in LRB.

- 4.3 Alpha Counting - Count the ²¹⁰Po sample in an alpha spectrometer equipped with a surface barrier alpha detector.

See Counting Procedure and Quality Control for Alpha Spectrometry for details of calibration and alpha spectral analysis (RSD-51-DIS-11).

The alpha peaks of ²¹⁰Po at 5.305 MeV and ²⁰⁸Po at 5.115 MeV are resolved. Calibration of the instrument is about 10 KeV/channel.

- 4.4 Calculations - Table 1 lists the pertinent nuclear data used in this procedure for determining the activity disintegration per minute (dpm) of ²¹⁰Po.

Table 1. Polonium-210, 208; Bismuth-210; and Lead-210 Radionuclide Data.

Radionuclide	Half-Life	α -Decay Energy (MeV)	Approximate Channel Region*
²¹⁰ Po	138.38 days	5.304	364-391
²⁰⁸ Po	2.898 years	5.115	330-363
²¹⁰ Bi	5.01 days		
²¹⁰ Pb	22.3 years		

- * Channel regions correspond to 1024 channel multichannel analyzers calibrated with a 3.1 MeV zero offset and 5.8 keV/channel.

PNL TEST PROCEDURE

Radiochemical yield, geometry and efficiency corrections are made using ^{208}Po tracer of known disintegration rate. (Record in LRB). Normal calculations often include correction for ingrowth of ^{210}Po from ^{210}Bi and ^{210}Pb in the sample, between the time of sample collection and the polonium separation time. All the data acquisition and calculations are performed in a traceable format.

Procedure No.
RSD-51-DEQ-8

Revision No.
1

Effective Date

Page 5 of 5

WORKING DOCUMENT IS IN THE LABORATORY

WORKING DOCUMENT IS IN THE LABORATORY

PNL TEST PROCEDURE

TITLE: HTA-4-12, SEPARATION OF TECHNETIUM BY CATION EXCHANGE AND SOLUTION EXTRACTION PRIOR TO MEASUREMENT BY BETA COUNTING

1.0 APPLICABILITY

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

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

- 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, 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.

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

Concurrence <i>NA</i>	Date	Approved <i>[Signature]</i>	Date <i>7/2/87</i>
Prepared by <i>AC Leary</i>	Date <i>7/1/87</i>	QAD Concurrence <i>B.O. BARNES</i>	Date <i>6/30/87</i>
Procedure No. HTA-4-12	Revision No. 4	Effective Date JUL 01 1987	Page of 1 3

PNL TEST PROCEDURE

- Beta-counting dishes.
- Pancake probe, P-11.
- Heat lamp.

4.0 PROCEDURE

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 HTA-4-8.

- Step 1) Prepare a 500 (± 50) μL column of AG-50W, X-8, 100 to 200 mesh, H^+ form, cation-exchange resin.
- Step 2) Accurately pipet up to a 1-mL portion of the test solution into a 2-dram vial. Record the volume taken on the analytical report to the nearest 0.01 mL.
- Step 3) Add to the solution 100 (± 10) μL of 0.1 M sodium dichromate; swirl to mix.
- Step 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.
- Step 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 4.
- Step 6) Wash the ion-exchange column with 1 (± 0.01) mL of deionized water. Collect effluent in the vial from Step 4. Discard the ion-exchange column in the dry radioactive waste.
- Step 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.
- Step 8) Add 5.0 (± 0.1) mL of hexone; cap the vial tightly.
- Step 9) Mix the solution on the vortex mixer for 3 minutes.
- Step 10) Centrifuge for 1 to 2 minutes to separate phases.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-12	4	JUL 01 1987	2	3

PNL TEST PROCEDURE

- Step 11) Transfer most of the hexone phase (top layer) to a 2-dram vial containing 1 (± 0.1) mL of deionized water, 500 (± 50) μL of 10 M sodium hydroxide, 100 (± 10) μL of 1 M tartaric acid, and 100 (± 10) μL of 0.1 M sodium dichromate; cap the vial tightly.
- Step 12) Mix the solution on the vortex mixer for 3 minutes.
- Step 13) Centrifuge for about 1 minute to separate phases.
- Step 14) Repeat Steps 11, 12, and 13.
- Step 15) Pipet the desired amount of the hexone phase onto a stainless steel beta-counting disc.
- Step 16) 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 ct/min with the probe directly on the count; if not acceptable, repeat Step 15 with an adjusted volume of hexone.
- Step 17) Measure the technetium activity using the Beta Counting (HTA-4-8) procedure. Record counting data volumes and calculations on the analytical report.

4.1 Records

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

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-12	4	JUL 01 1987	3	3

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>J. H. Crown</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

- Anhydrene,® 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 Anhydrene to a depth of ~10 cm. Use a cotton plug to hold the Anhydrene 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.

®Anhydrene 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-17	4	JUL 01 1987	2	4

PNL TEST PROCEDURE

- 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-17	4	JUL 01 1987	3	4

PNL TEST PROCEDURE

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-17	4	JUL 01 1987	4	4

PNL TECHNICAL PROCEDURE

TITLE: LIQUID SCINTILLATION COUNTING PROCEDURE

1.0 APPLICABILITY

This procedure is applicable to the operation of the liquid scintillation counting system located in the 329 Building.

2.0 DEFINITIONS

dpm - disintegrations per minute (concentration term)

pCi/l - picocuries per liter (concentration term)

$t_{1/2}$ - half-life

LRB - Laboratory Record Book

LSC - Liquid Scintillation Counting

3.0 RESPONSIBLE STAFF

Laboratory Manager

Scientist

Technician

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 329 Bldg. 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.

Prepared by <i>[Signature]</i>	Date 9-17-87	Approved (SECTION-MGR) <i>[Signature]</i>	Date 9-17-87
QAD Concurrence <i>[Signature]</i>	Date 9-17-87	Effective Date SEP 17 1987	
Procedure No. PNL-SP-33	Revision No. 0		Page 1 of 4

PNL TECHNICAL PROCEDURE

The LSC system is intended for use by operators experienced with the methodology of in vitro diagnostic radiassay, radioimmunoassay, and nuclear chemistry procedures which require nuclear counting of certain reagents with particular energy bands by liquid scintillation techniques.

4.1.1 Components in the LSC System

The LSC system is a Beckman LS-8000, serial number 7804114. The 300-sample conveyor sample changer is housed in a refrigerated compartment, as are the photomultiplier tubes and operator/program selection towers. Circuit boards are emplaced outside at the base of the refrigerated compartment.

4.1.2 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

PNL TECHNICAL PROCEDURE

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.

4.1.3 Counter Performance Tests

Sealed ^3H , ^{14}C and blank standards (Beckman Nos. H277092, C277066 and B11080, respectively) are counted before and after each set of samples and the count rates are compared with previously recorded counts to verify consistent system operation.

H277092 = $\pm 10\%$
B11080 = $\pm 25\%$

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 with each sample set and the record of these count rates (corrected for ^3H decay) is compared with previously recorded ^3H count rates.

4.2 Geometry Measurement

The geometry of the LSC system is fixed and depends on the smooth operation of the sample changer and the pedestal on 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. Verification of correct placement of the counting vials must be determined from the counter performance tests summarized in 4.1.3 above.

Procedure No. PNL-SP-33	Revision No. 0	Effective Date SEP 17 1987	Page <u>3</u> of <u>4</u>
----------------------------	-------------------	-------------------------------	---------------------------

PNL TECHNICAL PROCEDURE

This will be done as follows:

1. Insert the blank and spike counting vials behind the operator's command tower.
2. Recall the operator's number and print a program summary to verify that the required units are in the program. Modify the program if necessary to achieve required counting statistics for the sample set. This modification is automatically printed out with data.
3. Start the automatic count procedure.
4. Compare the printed data for the blank and spike sample with data previously obtained for other sample sets.
5. If spike count rates are within $\pm 10\%$ of the decayed concentration and background count rates are within $\pm 30\%$ of the previously recorded backgrounds, count the sample set.
6. Discontinue counting the sample set if spike count rates are not within $\pm 10\%$ and/or background count rates are not within $\pm 25\%$. Consult the Beckman service representative. Any data collected is disqualified and samples are recounted after equipment is repaired or samples may be prepared again and analyzed.

Procedure No. PNL-SP-33	Revision No. 0	Effective Date SEP 17 1987	Page <u>4</u> of <u>4</u>
----------------------------	-------------------	-------------------------------	---------------------------

WORKING DOCUMENT IS IN THE LABORATORY

PNL TEST PROCEDURE

TITLE: 7-40.26, SEPARATION OF IODINE-129 BY SOLVENT EXTRACTION AND DISTILLATION FROM CHLORIDE SOLUTIONS PRIOR TO MEASUREMENT BY GAMMA (X-RAY) COUNTING (replaces HTA-4-42, Rev. 1)

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.

Concurrence	Date	Approved	Date
		J. J. McCown <i>J. J. McCown</i>	6/15/88
Prepared by	Date	QAD Concurrence	Date
A. C. Leaf <i>A. C. Leaf</i>	6/15/88	L. J. Ethridge <i>L. J. Ethridge</i>	6/16/88
Procedure No.	Revision No.	Effective Date	Page of
7-40.26	2	6-15-88	1 10

PNL TEST PROCEDURE

- 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.
- Still, see selenium still, Figure HTA-14-18.1. Procedure HTA-4-18.
- 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 larger beaker cover to

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	2	10

PNL TEST PROCEDURE

avoid loss of filters due to air currents. Record the tare weight on the Analytical Report Form. See HTA-1-1, Figure HTA-1.1.3.

- 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	3	10

PNL TEST PROCEDURE

- 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	4	10

PNL TEST PROCEDURE

- 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.
- 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	5	10

PNL TEST PROCEDURE

- 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.
- 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	6	10

PNL TEST PROCEDURE

- 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 HTA-4-9.
- 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.

4.3 Preparation of I-129 Standards

See Procedure 7-40.17. Use standards prepared in Procedure 7-40.17 and d/c Factor calculated in Procedure 7-40.17.

4.4 Calculations

4.4.1 Counts in Spectrum from Sample Count

Gamma spectrometer energy vs. channel number is 1 keV/channel

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

D

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	7	10

PNL TEST PROCEDURE

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.

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		

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	8	10

PNL TEST PROCEDURE

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.

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

$$A = \sqrt{B^2 + C^2 + D^2 + E^2 + F^2 + G^2 + H^2 + I^2}$$

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	9	10

PNL TEST PROCEDURE

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.

4.5 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.26	2	6-15-88	10	10

WORKING DOCUMENT IS IN THE LABORATORY

PNL TEST PROCEDURE

TITLE: 7-40.17, SEPARATION OF IODINE-129 BY CATION EXCHANGE AND DISTILLATION PRIOR TO MEASUREMENT BY GAMMA (X-RAY) COUNTING (replaces HTA-4-41, Rev. 1)

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.

Concurrence		Date	Approved		Date
			J. J. McCown		6/15/88
Prepared by		Date	QAD Concurrence		Date
A. C. Leaf		6/15/88	L. J. Ethridge		6/16/88
Procedure No.	Revision No.	Effective Date	Page	of	
7-40-17	2	6-15-88	1	10	

PNL TEST PROCEDURE

- 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 HTA-14-18.1. Procedure HTA-4-18.
- 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	2	10

3 of 3

PNL TEST PROCEDURE

- 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 (see HTA-1-1, Figure HTA-1.1.3).
- 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 (I_2) 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 ($\pm 1\%$) 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.
- Step 6) Stir until the solution clears.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	3	10

PNL TEST PROCEDURE

- 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.
- 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	4	10

PNL TEST PROCEDURE

- 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 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	5	10

PNL TEST PROCEDURE

- Step 29) Wash the vial with 3 to 4 mL of methanol 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.
- 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 HTA-4-9.
- Step 40) Calculate the I-129 concentration in the sample using Section 4.4, Calculations. Record sample counting data

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	6	10

PNL TEST PROCEDURE

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 HTA-4-9, 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

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

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

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

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

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	7	10

PNL TEST PROCEDURE

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.

<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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	8	10

PNL TEST PROCEDURE

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 $\pm$ 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.

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

B = the % counting standard deviation calculated above in Section 4.4.6

C = standard deviation of standard I-129 solutions (0.3%)*

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	9	10

PNL TEST PROCEDURE

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.

4.5 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.17	2	6-15-88	10	10

WORKING DOCUMENT IS IN THE LABORATORY

PNL TEST PROCEDURE

TITLE: HTA-4-11, SEPARATION OF STRONTIUM-90 BY CATION EXCHANGE PRIOR TO MEASUREMENT BY BETA COUNTING

1.0 APPLICABILITY

This procedure can be used for separating ^{90}Sr from other beta emitting radio-nuclides in liquid leachate samples. Following the separation, the ^{90}Sr is measured by beta counting using the HTA-4-8 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

- 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, 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.

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

Concurrence <i>NA</i>	Date	Approved <i>[Signature]</i>	Date <i>7/2/87</i>
Prepared by <i>A. Chey</i>	Date <i>7/1/87</i>	QAD Concurrence <i>B.O. BARNES</i>	Date <i>6/30/87</i>
Procedure No. HTA-4-11	Revision No. 5	Effective Date JUL 01 1987	Page of 1 4

PNL TEST PROCEDURE

- Ion-exchange column (made from 4-mm glass tubing with a 5-m: reservoir).
- Flasks, 10-mL, volumetric.
- Vials, 2-dram, 15 mL.
- Dishes, 1.125-in. diameter, stainless steel.
- Dropper, plastic.

4.0 PROCEDURE

The ^{90}Sr is separated from other radioactive species by selective elution from a cation exchange resin using 2-methylactic 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. The technique of Roberts (1961) is used.

- Step 1) Prepare a 300 (± 20) μL column of AG-50W, X-8, 200 to 400 mesh, NH_4^+ form, ion-exchange resin.
- Step 2) To the column, accurately add up to 500 (± 10) μL of test solution. Record the volume used on the analytical report.
- Step 3) Wash the resin column with 500 (± 10) μL of deionized water. Collect effluent in vial from Step 2.
- Step 4) Wash the resin column with three 1 (± 0.01) mL portions of 0.2 M hydrofluoric acid. Collect effluent in vial from Step 2.
- Step 5) Wash the resin column with four 1 (± 0.01) mL portions of 0.7 M methylactic acid. Collect effluent in vial from Step 2. Cap the vial and discard in the radioactive liquid waste.
- Step 6) Elute strontium with 3.5 (± 0.1) mL of 1.0 M methylactic acid; collect the effluent in a 2-dram vial containing 400 (± 10) μL of 8 M nitric acid.
- Step 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.
- Step 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 7. Discard the 2 dram vial and dropper in the dry radioactive waste.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-11	5	JUL 01 1987	2	4

PNL TEST PROCEDURE

- Step 9) Wash the resin column with three 1 (± 0.01) mL portions of 0.7 M methyl-lactic acid. Record time (T_0) and date that the last drop leaves the column on the analytical report. Collect the effluent in the vial from Step 7. Cap the waste vial and discard in the radioactive liquid waste.
- Step 10) Elute the strontium with 3.5 (± 0.05) mL of 1.0 M methyl-lactic acid. Collect in a 10-mL volumetric flask.
- Step 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.
- Step 12) Accurately pipet the volume required onto a stainless steel beta-counting disc. Record volume on the analytical report.
- Step 13) Dry under a lamp until completely dry.
- Step 14) Immediately count the activity on the disc for 10 minutes using the Beta Counting (HTA-4-8) procedure. Record time (T_1) and date that the count is started on the analytical report.
- Step 15) Recount the beta dish in 3 to 4 days for 10 minutes. Record time (T_2) and date that the count is started on the analytical report.
- Step 16) 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

$$C = e^{-\frac{\ln 2 \times (\Delta T_1)}{64}} \quad \Delta T_1 \text{ is time elapsed from } T_0 \text{ to } T_1 \text{ hours}$$

$$D = e^{-\frac{\ln 2 \times (\Delta T_2)}{64}} \quad \Delta T_2 \text{ is time elapsed from } T_0 \text{ to } T_2 \text{ in hours}$$

- Step 17) Calculate the ^{90}Sr disintegrations per minute per milliliter (dis/min/mL) using the following equation. Record the calculation results on the analytical report.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-11	5	JUL 01 1987	3	4

PNL TEST PROCEDURE

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

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

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

$$Y = {}^{90}\text{Y} \text{ equilibrium count rate from Step 16 (ct min)}$$

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

$$V = \text{volume correction factor to correct activity to 1 mL}$$

$$V_A = \text{volume of sample from Step 2 (mL)}$$

$$V_B = \text{volume of sample pipetted into counting disc in Step 12 (mL)}$$

$$10 = \text{volume from Step 11 (mL)}$$

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-11	5	JUL 01 1987	4	4

WORKING DOCUMENT IS IN THE LABORATORY

PNL TEST PROCEDURE

TITLE: 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 ^{79}Se measured using liquid scintillation counting (Procedure HTA-4-4).

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 notebook and record the mg/mL of selenium on the container used for storing the selenium carrier.
- Nitric acid, 0.5 M -- Prepare by diluting 32 (± 1) mL of reagent-grade 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.

Concurrence N/A	Date	Approved <i>J. M. Town</i>	Date 4/27/88
Prepared by <i>A. Chish</i>	Date 4-27-88	QAD Concurrence <i>L. H. Hridge</i>	Date 4/27/88
Procedure No. 7-40.15	Revision No. 6	Effective Date 4/29/88	Page of 1 11

PNL TEST 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 + Br₂ saturated -- Prepare by adding -100 μ L of reagent-grade bromine 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 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.
- Hydroxylamine hydrochloride, 25 wt% -- Prepare by dissolving 25 ($\pm$ 1) g of the reagent-grade material in deionized water, dilute to 100 ($\pm$ 1) mL, and mix.
- Sodium hydroxide, 0.3 M -- Prepare by dissolving 12 ($\pm$ 0.1) g of reagent-grade NaOH in 1000 ($\pm$ 1) mL of deionized water.
- Methanol, reagent-grade.
- Nitric acid, 69% to 71%, reagent-grade.
- Beaker, 400-mL, Pyrex.
- Deionized water.
- Ice.
- Vial, 2-dram, glass, screw-cap.
- Vial, 35-mL, glass, screw-cap.
- Vial, liquid scintillation, Packard 6001018.
- Selenium still (see Figure 1).
- Variac, 1.5-ampere output, 0 to 140 volts.
- Heating mantle, 50-mL, round bottom.

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

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

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	2	11

PNL TEST PROCEDURE

Figure 1. Selenium Still

- 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 corer. Each filter must be dried at 110°C to 120°C for at least 30 minutes, cooled and

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	3	11

PNL TEST PROCEDURE

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.
- Beaker covers, 3 in. and 4 in. or other suitable carriers for filters.

4.2 Selenium Separation

Selenium-79 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 ^{79}Se is measured using liquid scintillation counting.

The ANALYST shall perform the following steps unless otherwise specified.

Step 1) To a 2-dram vial the ANALYST shall add a volume ($\pm 1\%$) of test solution specified by the COGNIZANT SCIENTIST, 2000 (± 20) μL of selenium carrier, and 500 (± 5) μL of 0.5 M nitric acid saturated with bromine; mix thoroughly.

Step 1a) For fused samples the ANALYST shall add to a 35 mL screw-cap vial up to 20 mL of the fused samples solution, 2000 (± 20) μL of selenium carrier, and 20 (± 1) μL of bromine; mix thoroughly and allow to stand 10 (± 1) minutes.

Step 1b) To the vial add 10 (± 1) mL of 25 w/o hydroxylamine hydrochloride and mix.

Step 1c) Heat until the black selenium metal precipitates; cool.

Step 1d) Centrifuge for 5 (± 1) minutes.

Step 1e) Carefully remove the supernatant liquid. Leave as much of the selenium metal as possible.

Step 1f) To the selenium metal add 500 (± 5) μL of concentrated nitric acid.

Step 1g) Heat until the selenium metal dissolves.

Step 1h) Add 5 mL of bromine water to the vial. Proceed to Step 2.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	4	11

PNL TEST PROCEDURE

- 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 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.
- Step 3) Transfer the solution from Step 1 or Step 1h 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 1h 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.
- Step 7) Adjust the heating mantle such that the still bottom is in the mantle.
- Step 8) Place a 35-mL vial containing 5 (± 0.1) mL of deionized water 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 exit is below the water in the vial.
- Step 9) Connect the still 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 -120°C . Continue distillation for about 35 minutes. The solution in the still should be pale yellow when distillation is complete.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	5	11

PNL TEST PROCEDURE

- Step 11) Turn off the variac and allow to cool for 2 to 3 minutes. Then remove the heater from the still. Remove the vial containing the distillate and turn off the nitrogen flow.
- Step 12) To the distillate in the 35-mL vial add 10 (± 0.2) mL of hydroxylamine hydrochloride.
- Step 13) Place the vial under a heat lamp or in a heating mantle 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.
- Step 14) Centrifuge the vial containing the selenium metal for about 5 minutes.
- Step 15) Using a glass 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 methanol, and swirl the precipitate.
- Step 17) Centrifuge for 5 minutes. Remove the methanol wash using a glass transfer pipet.
- Step 18) Warm the vial to remove residual methanol.
- Step 19) Add 500 (± 50) μ L of 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 w/o 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 plastic dropper transfer the black selenium metal onto the center of the filter.
- Step 25) Wash the vial with 3 to 4 mL of methanol and transfer the residual selenium metal to the filter.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	6	11

PNL TEST PROCEDURE

- 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 suitable carrier, such as a beaker cover, 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 filters due to air currents.
- Step 28) Remove the filter plus selenium metal from the oven and allow to cool 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.
- 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 to the dissolved selenium.
- Step 33) Add 14 mL of Altex CP liquid scintillation cocktail 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 ^{79}Se activity using Procedure HTA-4-4. Since no ^{79}Se standard is available for calibrations, a ^{14}C standard is used. Carbon-14 and ^{79}Se have similar maximum and average beta energies which makes the ^{14}C standards acceptable for the measurement of ^{79}Se . 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.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	7	11

PNL TEST PROCEDURE

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.

4.3 Blank (Background) Solution Preparation

Step 1) Prepare ^{79}Se 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).

Step 2) Label the vial cap as " ^{79}Se Blank." Count the " ^{79}Se Blank" with the samples and standards as described in Procedure HTA-4-4.

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 μL ^{14}C standard solution.

Step 2) Label the vial cap as " ^{79}Se Standard." Count this with the samples and backgrounds using HTA-4-4.

4.5 Calculations

4.5.1 Yield Calculations

$$Y = \frac{A-B}{2C}$$

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/millimeter. See Selenium Carrier, Section 4.1

4.5.2 Standard Disintegration/Count Factor (d/c)

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

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	8	11

PNL TEST PROCEDURE

- where, A - Disintegrations/count (d/c) factor used in subsequent sample calculations
- B - Disintegrations/minute of ^{14}C used in the standard in Section 4.4
- C - Counts/minute in standard from liquid scintillation counting data
- D - Counts/minute in ^{79}Se blank prepared in Section 4.3

4.5.3 Quench Factor

A series of ^{14}C standards are made up containing different amounts of Se carrier, from 0 to 20 mg. No quenching was observed from 0 to 12 mg Se. Above 12 mg, a linear reduction in count rate was observed. See BNW-52626, pages 14-19. From the table below, obtain the quench factors to be used in the calculations of d/m/mL Section 4.5.4.

<u>mg Se recovered*</u>	<u>Quench Factor</u>
12 or less	1.0
13	0.98
14	0.96
15	0.94
16	0.92
17	0.90
18	0.88
19	0.86
20	0.83

*A-B from 4.5.1

4.5.4 Sample Disintegrations/Minute/Milliliter (d/m/mL)

$$S = \frac{(A-B)(C)}{(D)(E)(F)}$$

- where, S - The sample ^{79}Se d/m/mL
- A - The ^{79}Se counts/minute obtained from The liquid scintillation counting data
- B - The ^{79}Se "blank" counts/minute obtained from the liquid scintillation counting data

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	9	11

PNL TEST PROCEDURE

- 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

4.5.5 Sample Disintegration/Minute/Gram (d/m/g)

If a fused sample is being analyzed the calculation becomes:

$$S = \frac{(A-B)(C)(G)}{(D)(E)(F)(H)}$$

- where,
- S - The sample ⁷⁹Se d/m/g
 - A - The ⁷⁹Se counts/minute obtained from liquid scintillation counting data
 - B - The ⁷⁹Se "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
 - G - Volume the fused soil sample was dissolved in
 - H - The weight of the soil sample is grams

4.5.6 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory Record Books shall be used in accordance with PAP-1704.

Procedure No.	Revision No.	Effective Date	Page	of
7-40.15	6	4/29/88	10	11

PNL TEST PROCEDURE

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.

Procedure No.

7-40.15

Revision No.

6

Effective Date

4/29/88

Page of

11 11

INTERIM CHANGE NOTICE (ICN)

ICN No. HTA-4-21-1

Page 1 of 1

A. Doc. No. HTA-4-21 Rev. No. 3 Doc. Title Separation of Tin-126 by Anion Exchange Prior to Measurement by Gamma Counting
Document's Author A.C. Leaf
Requested by K.S. Webster Date Issued 09/03/87

B. Type of Change Approvals:

Minor Change

QAD Concurrence

LE Thomas

Date 8-31-87

Approval

Authentic for J. McCann

Date 8/31/87

Major Change

QAD Concurrence

Date

Approval

Date

Reviews,

Date

Approvals & Dates

C. Reason for Change:

To correct a typographical error.

D. Description of Change:

SECTION 4

Step 1: Change $500(\pm 0.05)\mu\text{L}$ to $500(\pm 5)\mu\text{L}$

PNL TEST PROCEDURE

TITLE: 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 HTA-4-9.

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.
- 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.

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

Concurrence NA	Date	Approved <i>[Signature]</i>	Date 7/2/87
Prepared by AC Lush	Date 7/1/87	QAD/Concurrence B.O. BARNES	Date 6/30/87
Procedure No. HTA-4-21	Revision No. 3	Effective Date JUL 01 1987	Page of 1 3

PNL TEST PROCEDURE

- 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 (± 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) 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.
- 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-21	3	JUL 01 1987	2	3

PNL TEST PROCEDURE

- 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 HTA-4-9.
- 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-21	3	JUL 01 1987	3	3

order of magnitude
1000 required for us
then for us
us quality

PNL TEST PROCEDURE

TITLE: 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 HTA-4-9.

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 (± 1) mL of concentrated Ultrex nitric acid to 500 (± 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 HTA-4-24, "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.

Concurrence NA	Date	Approved <i>[Signature]</i>	Date 7/2/87
Prepared by ACL	Date 7/1/87	QAD Concurrence B. S. BARNES	Date 6/30/87
Procedure No. HTA-4-40	Revision No. 1	Effective Date JUL 01 1987	Page of 1 3

PNL TEST 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) μL portions of 1.5 M nitric acid followed by one 500 (± 5) μL 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 HTA-4-9, "Solution Analysis: Gamma Spectrometry."
- Step 9) Calculate the Cs-135 activity using the following equation:

$$\text{Cs-135 disintegrations/minute/gram fuel} = \frac{(A) (B) (C) (G)}{(D) (E) (F)}$$

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-40	1	JUL 01 1987	2	3

PNL TEST PROCEDURE

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 30.6 HEDL-MG-28, Vol. 2, Rev. 2; 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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-40	1	JUL 01 1987	3	3

PNL TECHNICAL PROCEDURE

TITLE: RADIONUCLIDE SEPARATION AND ANALYSIS PROCEDURE FOR TRITIUM

1.0 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. Methods which describe initial radionuclide separation and radionuclide purification are given.

2.0 DEFINITION

dpm - Disintegrations per minute (concentration term)
cpm - Counts per minute (concentration term)
DPC - Disintegrations per count (i.e., 1/efficiency factor)
pCi - picocuries (2.22 dpm, a concentration term)
LRB - Laboratory Record Book

3.0 RESPONSIBLE STAFF

- Laboratory Manager
- Cognizant Test Personnel

4.0 PROCEDURES

Prerequisites: Personnel trained in this procedure may perform the work.

4.1 Sample Preparation

4.1.1 Liquid Samples

Measure total sample volume and archive aliquots for ^3H and ^{14}C . Dilute to known volume with low-tritium background water if required by the presence of additional radionuclides.

Prepared by <i>T. Kibler</i>	Date 9-17-87	Approved (SECTION MGR) <i>[Signature]</i>	Date 9-17-87
QAD Concurrence <i>S. L. English</i>	Date 9-17-87	Effective Date SEP 17 1987	
Procedure No. PNL-SP-30	Revision No. 0		Page <u>1</u> of <u>3</u>

PNL TECHNICAL PROCEDURE

4.1.2 Solid or Sludge Samples

- 4.1.2.1 Weigh sample as received, archive aliquots for ^3H and ^{14}C (no special preparation) transfer to tared beaker and dry under heat lamp. Determine dry to wet weight ratio.
- 4.1.2.2 Measure gross activity in sample using GM meter and record in LRB. (Record GM # & calib)
- 4.1.2.3 Leach sample three times with hot 6 M HCl and combine leachates.
- 4.1.2.4 Measure residual activity with GM meter and record in LRB.
- 4.1.2.5 If residual activity is 15% or less, use the exact percent for the leaching efficiency in calculation. If residual activity is greater than 15%, add residue to platinum dish and fuse with Na_2CO_3 . Dissolve fused salt with 6 M HCl, filter, add solution to combined leachates in Step 4.1.2.3 and dilute to known volume. Measure residual activity and use this to determine yield. Formula for yield:

$$\text{Yield} = 1 - \frac{\text{remaining activity}}{\text{original activity}}$$

4.1.3 Soil Samples

- 4.1.3.1 Weigh sample as received and place in an appropriate distillation flask. Distill the interstitial water and water of hydration from the soil.
- 4.1.3.2 To the distillate add appropriate holdback carriers, make basic with Na_2CO_3 and distill a second time. Measure the volume and dilute to known volume for preparation of counting solutions.

4.2 Tritium Analysis

- 4.2.1 To a sample aliquot from the sample preparation add appropriate holdback carriers, make it basic with Na_2CO_3 and distill.
- 4.2.2 To the first distillate, add appropriate holdback carriers, make basic with Na_2CO_3 and re-distill.
- 4.2.3 To prepare sample aliquots for counting, thoroughly mix 4 ml aliquots of distillate from 4.2.2 with 19 ml of scintillator solution in liquid scintillation counting vials. Prepare in duplicate.

Procedure No. PNL-SP-30	Revision No. 0	Effective Date SEP 17 1987	Page <u>2</u> of <u>3</u>
----------------------------	-------------------	-------------------------------	---------------------------

PNL TECHNICAL PROCEDURE

- 4.2.4 Prepare blank (background) solutions from 4 ml aliquots of low-tritium background water thoroughly mixed with 19 ml of scintillator solution in liquid scintillation counting vials. Prepare in duplicate.
- 4.2.5 Prepare standard solutions from calibrated tritium solution (NBS traceable) and low-tritium background water thoroughly mixed with 19 ml of scintillator solution in liquid scintillation counting vials. Prepare two standards of different specific activities.
- 4.2.6 Count all samples in the liquid scintillation spectrometer for 100 minutes or 2 σ counting statistics, whichever comes first.
- 4.2.7 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.

4.3 Calculations

$$DPC = \frac{\text{dpm in standard}}{\text{net cpm in standard}}$$

³H concentration as prepared for counting:

$$pCi/2 = \frac{(\text{net cpm in sample}) (DPC) (0.45045)}{0.004}$$

PNL TEST PROCEDURE

TITLE: HTA-4-16, SOLUTIONS ANALYSIS: URANIUM BY LASER-EXCITED FLUORESCENCE

1.0 APPLICABILITY

This procedure applies to the laser-excitation fluorimetry method of determining uranium concentration in test solutions.

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

- 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.
- Analytical balance, 0.1-mg resolution.
- Micropipets, replaceable plastic tip, Eppendorff-type.
- Magnetic stirrer with magnetic stir bar for sample cell (optional).
- Fluorescence enhancement buffer, FLURAN, Scintrex Ltd, Concord, Ontario, Canada.
- Uranium standard, NBS SRM 960.
- Deionized water, greater than 10-megohm resistance, as indicated by the deionizer meter readout.

Concurrence	NA	Date	Approved	<i>[Signature]</i>	Date	7/2/87
Prepared by	<i>[Signature]</i>	Date	QAD Concurrence	B.O. BARNES	Date	6/30/87
Procedure No.		Revision No.	Effective Date		Page	of

PNL TEST PROCEDURE

4.0 PROCEDURE

4.1 Calibration

Calibration is performed as part of the determination using the standard addition technique described in Section 4.2. The standard is prepared by dissolving about 10 g (record actual weight to the nearest 0.1 mg) of NBS SRM 960 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 0.5 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. The high-range standard is prepared by accurately diluting the 100 $\mu\text{g/mL}$ solution 1-to-100 with 0.1 N HNO_3 , giving a nominal 1 $\mu\text{g/mL}$ solution; and the low-range standard is prepared by diluting the 1 $\mu\text{g/mL}$ solution 1-to-10 or 11, giving a nominal 0.1 $\mu\text{g/mL}$ solution. The bottles used to store the two working trace-level standards are conditioned by repeatedly adding freshly prepared standards over a period of time until the standards' concentrations stabilize. This may require several weeks.

4.2 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 that the solution matrix quenching effect on the added uranium is the same as on the sample uranium should be valid.

4.3 Sample Analysis

- Step 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.
- Step 2) Place the cell in its holder on the cell compartment door.
- Step 3) Pipet 5 mL of deionized water into the sample cell and 10 μL of sample into the deionized water. Stir the solution with the pipet tip and close the door.
- Step 4) Turn on the photomultiplier tube (PMT) with the PMT switch.
CAUTION: NEVER open the door with the PMT switch on.

PNL TEST PROCEDURE

- Step 5) Zero the meter with the BALANCE control. If the meter goes off-scale, there may be too much uranium or acid. Dilution or neutralization may be required, after which the meter can be zeroed upon repeating this step. If not, sample purification may be required. The method of purification will depend on the sample.
- Step 6) Turn off the PMT, open the door, and pipet 500 μL of FLURAN into the sample. Stir the solution by working the plunger several times. Alternately, a magnetic stir bar can be placed in the cell and the cell removed to a magnetic stirrer.
- Step 7) Return the cell to its compartment (if removed), close the cell door, and turn on the PMT. Record the meter reading (R_1). If the reading is too low, add more sample to the cell (if the sample matrix does not cause a zero shift). A large initial balance adjustment in Step 5 should indicate this problem. Otherwise, the procedure must be repeated, starting at Step 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 2.
- Step 8) Turn off the PMT and open the cell door. Add sufficient standard (0.1 $\mu\text{g/mL}$ for the low range or 1 $\mu\text{g/mL}$ for the high range) to cause an increase in meter reading of about the same amount as the sample reading. Use enough standard to give at least 0.05 meter units. NOTE: Do these steps rapidly to prevent significant solution temperature changes that affect fluorescent intensity. Record the meter reading (R_2).
- Step 9) Calculate the results according to Section 4.4.

4.4 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).

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-16	3	JUL 01 1987	3	4

PNL TEST PROCEDURE

4.5 Data Recording

- 4.5.1 The identity of the sample is entered on an analytical report card along with a serial number. The serial number may be the analysis requester's identification number or the analytical laboratory's assigned laboratory number for that sample.
- 4.5.2 Meter reading values R_1 and R_2 are recorded on the buff part of the analytical report card.
- 4.5.3 Results are calculated on the analytical report card using the equation in Section 4.4.
- 4.5.4 The analysis results are recorded on the Results section of the card and the white copy is sent to the analysis requester.
- 4.5.5 The buff section of the card is filed in the designated repository file.

4.6 Records

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

PNL TEST PROCEDURE

TITLE: 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 HTA-4-24, Step 1) through Step 6).
- Vials, 20-mL, borosilicate glass (leached per Procedure HTA-4-24, 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.
- 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 HTA-4-16, since any uranium in the acid is collected on the ion-exchange column and will

Concurrence <i>NA</i>	Date	Approved <i>[Signature]</i>	Date <i>7/2/87</i>
Prepared by <i>George E. Meadows</i>	Date <i>7/1/87</i>	QAD Concurrence <i>B.O. BARNES</i>	Date <i>6/30/87</i>
Procedure No. HTA-4-36	Revision No. 2	Effective Date JUL 01 1987	Page of 1 4

PNL TEST PROCEDURE

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 (HTA-4-16). This procedure separates the uranium on an ion exchange column while the brine solution is eluted with a 10 M 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 (HTA-4-16). 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.

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

• AG-1 is a registered trademark of Bio-Rad Laboratories, Richmond, California.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-36	2	JUL 01 1987	2	4

PNL TEST PROCEDURE

- 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 (± 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 (± 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 (± 0.04) mL of 0.2 M nitric acid.
- Step 14) Prewash each column with 1.0 (± 0.01) mL of 10 M hydrochloric acid.
- Step 15) Load the samples on the column, using a polyethylene dropper to transfer the liquid.
- Step 16) Rinse the sample vials with 4 (± 0.04) mL of 10 M HCl and wash the columns with the 10 M rinse solution.
- Step 17) Wash the column with 1.5 (± 0.03) mL of 4 M hydrochloric acid.
- Step 18) Wash the column with 1 (± 0.02) mL of 8 M nitric acid.
- Step 19) Label the 2-dram vials with sample identification.
- Step 20) Remove the 35-mL vials and dispose of the vials and solutions.

Procedure No.

HTA-4-36

Revision No.

2

Effective Date

JUL 01 1987

Page of

3

4

PNL TEST PROCEDURE

- Step 21) Place the 2-dram vials under the columns (from Step 19).
- Step 22) Elute the uranium with 2 (± 0.02) mL of 0.2 M HNO_3 into the 2-dram vials.
- Step 23) Place the 2-dram vials under a heat lamp and evaporate to dryness.
- Step 24) Remove the vials and cool.
- Step 25) Add 500 (± 0.05) μL of 0.1 M hydrochloric acid (or a volume specified by the cognizant scientist) to each vial. Record the added volume on the analytical report form.
- Step 26) Mix the contents of the vials.
- Step 27) Determine the uranium content using Procedure HTA-4-16.

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.

Procedure No.	Revision No.	Effective Date	Page	of
HTA-4-36	2	JUL 01 1987	4	4

PNL TECHNICAL PROCEDURE

TITLE: COUNTING PROCEDURE FOR ALPHA SPECTROMETRY

1.0 APPLICABILITY

This procedure is applicable to the operations of the Alpha Energy Analysis (AEA) counting spectrometer systems located in the 329 Bldg. Analytical Service Center, as they are applied to the analyses of alpha emitting radionuclide samples.

2.0 DEFINITIONS

CPM - counts per minute
dpm - disintegrations per minute (concentration term)
ng - nanograms (10^{-9} grams)
 μ g - micrograms (10^{-6} grams)
t_{1/2} - half-life
LRB - Laboratory Record Book

3.0 RESPONSIBILITIES

3.1 Service Manager
Scientist
Analyst

4.0 PROCEDURE

4.1 Alpha Spectrometry Counting System Description

AEA spectrometers are used to measure low level concentrations of alpha emitting radionuclides in electroplated samples.

The AEA spectrometers use silicon surface-barrier diode detectors housed in chambers which can be evacuated. Samples are electro-deposited on stainless steel 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. After the sample has been positioned, the chambers are evacuated to minimize spectral degradation from alpha particle scattering in air.

Prepared by <i>[Signature]</i>	Date 9-17-87	Approved (SECTION MGR) <i>[Signature]</i>	Date 9-17-87
QAD Concurrence <i>[Signature]</i>	Date 9-17-87	Effective Date SEP 17 1987	
Procedure No. PNL-SP-24	Revision No. 0		Page 1 of 14

PNL TECHNICAL PROCEDURE

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). In some systems the converter has been set to digitally offset the spectrum so that channel zero of the system memory storage unit corresponds to about 3 MeV. In others, a biased amplifier serves this purpose. The memory storage unit of each system is subdivided into quadrants or octants and the digitized signals from each detector in the system are routed to the appropriate subsection of the memory by a signal multiplexing and processing unit. The memory units normally have 4096 channels; system 1 uses octant storage with each spectrum stored in 512 channels; systems 2 and 3 use quadrant storage with each spectrum stored in 1024 channels. Signal multiplexer/processor units of several designs are employed, but the purpose of each of them is to route the signals from the detector to the correct portion of memory, without introducing any counts into other portions of memory. Another design parameter is the minimization of electronic noise cross-talk which can cause a loss of resolution in a single detector from the addition of components from the other detectors. With these systems, the registration of spectral counts for all detectors within the system is started and stopped simultaneously by a single timer. The amplifier gain and conversion gain of the ADC are adjusted to give about 10 keV/channel for system 1 and about 5.8 keV/channel for system 2 and 3. Thus, the instruments normally store the spectral region from about 3 to 8.1 MeV in one octant or 3 to 8.9 MeV in one quadrant of memory for each detector. When a detector in the system is unused, it is maintained evacuated and with a bias of 15 volts on the detector to reduce electronic noise. A block diagram showing the components of system 1 is show in Figure 1.

4.2 Electronic Components in AEA Spectrometers

The electronic equipment listed below is presently being used. However, equivalent or better equipment can be substituted.

Procedure No. PNL-SP-24	Revision No. 0	Effective Date SEP 17 1987	Page <u>2</u> of <u>14</u>
----------------------------	-------------------	-------------------------------	----------------------------

PNL TECHNICAL PROCEDURE

- System 1:** Detector Bias Power Supply - ORTEC 210
Preamplifiers - ORTEC 125
Amplifiers - Canberra 814, ORTEC 472
ADC - Northern NS 621
Multiplier Controller - Northern NS 459B
Memory Storage Unit - Packard 45
Printer - MDS 1200
Timer, Live Time Corrector - Shop-made
Signal Interface Unit - Ship-made
- System 2:** Detector Bias Power Supply - ORTEC 210
Preamplifier - ORTEC 125
Amplifier - ORTEC 451
Signal Processor - ORTEC 4671
Multiplexer Controller - ORTEC 714
Dual Sum and Invert Amplifier - ORTEC 433A
Biased Amplifier - ORTEC 408A
Multichannel Analyzer (ADC + Memory Unit) - ORTEC 6240
Printer - Versatec
- System 3:** Quad Alpha Spectrometer (4 Detectors with Bias Supply + Vacuum Chambers + Preamplifiers + Amplifiers) - Canberra 7404
Multichannel Analyzer - Canberra 35
Printer - Versatec

4.3 Counter Performance Tests and Quality Control

The alpha detector and counting systems are standardized by measuring various NBS traceable electroplated alpha emitting isotopes. These isotopes fall in the energy range from 3.0 to 6.0 MeV and are periodically used to obtain the counting efficiencies of the alpha detectors and counting systems.

4.3.1. Geometry Measurement

The geometry (efficiency) of each detector is determined using a ^{238}Pu + ^{239}Pu source electroplated on a stainless steel disk. The source is cross-calibrated against ^{239}Pu sources prepared from an NBS Reference Standard, using alpha proportional counters. All standard(s) and their preparation are documented in the appropriate calibration standards notebook #BNW-51413 or its predecessors and in BNW-50335.

PNL TECHNICAL PROCEDURE

Geometry determinations are to be made by the following steps:

1. Use Standard No. 50335-10 or similar type source. Turn the bias voltage of the diode slowly off. When the bias is off, slowly release the chamber vacuum. Open the chamber. Place the source in the center of the pedestal of the chamber. Close and evacuate the chamber. Slowly turn the bias voltage to the setting for the diode. The setting can be written on or adjacent to the voltage control knob for ready reference and shall be written in the calibration record book located adjacent to the instrument.
2. When the voltage has stabilized a few seconds, clear the timer of the multi-channel analyzer, clear the memory storage unit. Preset the timer for a 30-minute count. Start the count. Record the counter number, date and time of count, the source identification, and length of count in the count record calibration book.
3. When the count has been completed, turn the multi-channel analyzer output control to select the fraction of memory where the spectrum is stored. Print the contents of the memory. Label and attach the printed spectrum to the count record sheet. If a computer analysis of the alpha particle spectrum is desired, place a magnetic tape cassette in the recorder. Set the multi-channel analyzer to output to magnetic tape and read out the spectrum.
4. Slowly reduce the detector bias voltage to zero. Release the chamber vacuum and return the source to its holder. If the detector is not to be immediately used, close the chamber, evacuate, and slowly increase the bias voltage to 15 V.

PNL TECHNICAL PROCEDURE

5. Locate the spectral regions corresponding to the alpha particles from ^{239}Pu (5.157 MeV, 5.14 MeV, 5.107 MeV - unresolved) and from ^{238}Pu (5.499 MeV, 5.456 MeV, 5.358 MeV - unresolved). For each spectral region integrate the counts in a sufficient number of channels to account for at least 99% of all counts in the spectrum. (Normally about 20 channels for system 1 and 40 channels for systems 2 and 3 for each isotope). Record the identification data, gross counts and length of count in LRB. Calculate gross cpm and record in LRB.

6. Use a recent background spectrum for the detector (taken with a clean new disk in the chamber) to determine the background cpm for the same spectral regions that were integrated in step 5. Subtract the background cpm from the gross cpm for each peak from step 5. Record the background date/time and cpm and the net cpm in the calibration notebook. Sum the total net cpm of both peaks and record.

7. Calculate the standard deviation of the net cpm as follows:

$$\text{S.D.} = \sqrt{C_g/t_s + C_b/t_b} \quad 1/2$$

where

S.D. = the standard deviation of the net cpm

C_g = the gross cpm for both plutonium peaks

C_b = the background cpm for both plutonium peaks

t_s = the length of the standard count (normally 30 minutes), minutes

t_b = the length of the background count (normally overnight to several days), minutes

PNL TECHNICAL PROCEDURE

8. Calculate the detector efficiency (Eff.) as follows:

$$\text{Eff.} = \frac{\text{net cpm}}{1218 \text{ dpm}}$$

Record in Calibration notebook.

9. Calculate the standard deviation (σE) of the detector efficiency as follows:

$$\sigma E = E \frac{\text{S.D.}^2}{\text{net cpm}} + \frac{30^2}{1218}^{1/2}$$

Record σE Calibration notebook.

4.3.2 Counter Control Checks

When instruments are in nearly continuous use, a periodic check (6 months) of performance should 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 are to be made as follows.

1. For each detector, use the assigned calibrated disk source L identified in the Calibration Log Book containing about 400 dpm of an electrodeposited, long-lived alpha particle emitting radionuclide such as ^{242}Pu . Turn the detector bias voltage slowly to zero volts. Slowly release the chamber vacuum. Open the chamber and center the source assigned to the detector on the pedestal. Close the chamber, evacuate and slowly adjust the detector bias voltage to the setting written adjacent to, or on, the control knob in the LRB.
2. Clear the multi-channel analyzer timer and memory storage unit. Set the timer for an interval, sufficient to store at least 10,000 counts in the alpha peak spectral region desired. (normally about 2 hours). Initiate the count.

PNL TECHNICAL PROCEDURE

3. Record the counting data on a Count Record Sheet (Exhibit 1). Record the source and detector identification data, the time of the count, and length of the count. When the count is completed, set the multi-channel analyzer to output the memory contents for the detector to the printer, and print the spectrum. (Only that portion of the spectrum that includes the peak of the desired alpha particle energy, need be printed). If computer analysis of the spectral data is desired, switch the multi-channel analyzer output to the magnetic tape storage device and record the spectrum on magnetic tape. Slowly turn down the detector bias voltage to zero, release the vacuum and remove the standard. Close the chamber. Evacuate and slowly set the detector bias to 15 volts until the next count is to be taken.
4. Locate the spectral region corresponding to the alpha particles from the radionuclide standard (4.903 MeV and 4.863 MeV, unresolved - for ^{242}Pu). Integrate the counts registered in a sufficient number of channels to include at least 99% of the peak area (about 20 channels for system 1 and 40 channels each for system 2 and 3). Always use the same number of channels and the same spectral region (channel numbers the same as this will permit the detection of a significant change of gain, zero offset, or loss of resolution). Record the control standard and instrument identification, the date and time of the count, and gross cpm of the peak on Control Data Form such as Exhibit 1. Calculate the gross cpm.
5. Use a recent (<1 month) background spectrum for the detector to determine the background cpm for the same spectral regions. Calculate and record the background cpm $\pm 1\sigma$ and the net cpm $\pm 1\sigma$ on the Counter Background Form such as Exhibit 2.

PNL TECHNICAL PROCEDURE

6. After a total of 10 control counts have been recorded, compute the average cpm ($\bar{x}$) and the standard deviation (σ) as follows.

$$\bar{x} = \sum_{i=1}^{10} \frac{x_i}{10} \quad (4)$$

$$\sigma = \sqrt{\sum_{i=1}^{10} \frac{(x_i - \bar{x})^2}{9}} \quad (5)$$

7. For control purposes, any subsequent count should be within 2% of the mean value or $\bar{x} \pm 2\sigma$ whichever is the larger limit.
8. If a count is not within the control limits, make a count to test the gain and zero settings and adjust the amplifier gain and multichannel analyzer zero as necessary. Then repeat steps 1-5. If the subsequent count is not within the limits, check the resolution of the spectral region. If there is a significant loss of resolution, repair the instrument as necessary. Then, check the instrument for calibration and efficiency as outlined in steps from sections 5.3.1 and this section.

4.3.3. Background Measurements

Determine the backgrounds using the same counting procedure outlined in steps 1-3 of section 5.3.2, for counter control checks, except that an unused clean stainless steel disk is substituted for the control source disk. Record the date and time of the background count and the length of count time in the Calibration Records log. Compare the current background cpm with the previous background cpm. Integrate the spectral regions of interest from the

PNL TECHNICAL PROCEDURE

printout. If computer analysis of data is desired, the spectrum may also be stored on magnetic tape. If a computer analyses is used on an unknown, it should also be done on a standard to verify results.

4.3.4. Gain and Zero Adjustment Test

Gain and zero adjustments are made using a source of radio-nuclide(s) that emit alpha particles of widely separated energies. A count of the source will produce two or more alpha spectral peaks. The peaks with the highest and lowest energies are used in the calculation as follows.

1. Record and print the spectrum. For example, a source of mixed ^{238}Pu , ^{239}Pu and ^{242}Pu can be used. Count long enough to get at least 10,000 counts in each peak.

2. Locate the lowest and highest of the expected alpha peaks. In the case of ^{238}Pu , ^{239}Pu and ^{242}Pu , there will be three peaks at channels corresponding to the weighted average (W) of the emission energies for each isotope. That is,

$$\begin{aligned}\text{for } ^{238}\text{Pu: } W &= 0.72 (5.499) + 0.28 (5.456) + \\ &0.0009 (5.358) \\ &= 5.492 \text{ MeV}\end{aligned}$$

$$\begin{aligned}\text{for } ^{239}\text{Pu: } W &= 0.733 (5.157) + 0.151 (5.145) + \\ &0.115 (5.107) \\ &= 5.144 \text{ MeV}\end{aligned}$$

$$\begin{aligned}\text{and for } ^{242}\text{Pu: } W &= 0.76 (4.903) + 0.24 (4.863) \\ &= 4.893 \text{ MeV}\end{aligned}$$

3. Determine the channel number of the centroids of the highest and lowest peaks (the 5.492 MeV peak for ^{238}Pu and the 4.893 MeV peak for ^{242}Pu). The centroid can be determined by inspection to an accuracy of ± 1 channel for system 1 and ± 2 channels for systems 2 and 3. The centroid channel normally will have the largest number of counts. To verify, integrate the counts in the

PNL TECHNICAL PROCEDURE

three channels on each side of the channel which is the apparent centroid. Compare the total counts in these two regions. In one region has more counts than the other, move the apparent centroid one channel in the direction of the side with the larger count. Again integrate three channels on each side of the new apparent centroid. If the count is larger on the same side as previously shift the centroid one channel again, and repeat the process. If the count is larger on the opposite side of the new centroid, the correct location may be between two channels. In that case, the count of the region with the higher count is recorded. The region with the lower count is shifted to include the centroid channel dropping the channel furthest from the centroid; then it is integrated. Take the ratio of the region containing the higher counts to the region containing the lower counts in each case. The case which has a ratio closest to 1.0 can be assumed to have the correct centroid.

4. When the centroids for the peaks have been determined, the gain of the instrument (keV/channel) can be calculated as follows:

$$\text{Gain (G)} = \frac{1000 (W_1 - W_2)}{(C_1 - C_2)}$$

where

W_1 = Weighted average energy of highest energy peak,
MeV

W_2 = Weighted average energy of lowest energy peak,
MeV

C_1 = Centroid channel number of highest energy peak

C_2 = Centroid channel number of lowest energy peak

PNL TECHNICAL PROCEDURE

5. When the gain has been determined, the energy displacement corresponding to channel zero can be calculated as follows.

$$\text{Displacement (D)} = W_2 - \frac{G(C_2)}{100G}, \text{ MeV}$$

where

W_2 , G and C_2 are as above.

When G and D have been determined, record them in the Calibration notebook, and compare them with the previously established gain and zero settings for the instrument. If either has changed by more than 1%, readjust the instrument, and recheck.

4.3.5 Radionuclide Standards

- Isotopic standard solutions of several long-lived uranium decay chain radionuclides are added to trace the radio-chemical recovery during chemical separation processes. Known activities are used to trace the recovery of each radionuclide separation. National Bureau of Standards (NBS) or traceable to NBS standards are used to trace each radio-nuclide. All prepared standards are documented in the appropriate level II standards calibrations LRB or other suitable log.
- Since 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.
- Since the counting efficiency of the silicon surface barrier diodes 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. Thus, it is not necessary to

PNL TECHNICAL PROCEDURE

use a counter efficiency factor in calculations because the counter efficiency is common to both the net cpm of the tracer and the other isotopes. The radiochemical recovery need not be used because it is also a common factor for all isotopes, and cancels out in the equations when relative count rates are used. However, the chemical yield should be calculated as a cross-check for chemical separation of thorium and polonium. To compute the dpm of one isotope, take the ratio of the dpm of tracer added to the net observed cpm of that tracer and multiply by the net cpm of the isotope being measured.

- This technique has the advantage that small gain shifts or resolution changes can be automatically compensated for by taking the same numbers of channels in each peak, or channels corresponding to the same fraction of the total peak count, and adjusting the location of the spectral band for each peak to maintain the high energy end point of the predetermined bank width the same number of channels from the peak centroid.

4.4.1 Counting Procedure for Radionuclides in Samples

1. Slowly lower the detector bias voltage to zero volts. Slowly release the chamber vacuum. Center the disk on the pedestal of the chamber (disks are stainless steel for thorium isotopes and silver for polonium isotopes). Evacuate the chamber. Slowly increase the detector bias voltage to the setting.
2. Clear the timer and memory storage unit. Set the timer for a counting interval of at least 1000 minutes. Initiate the count. Record the sample identification, isotope identification, the detector identification, the date and time that the count started and the counting interval on a alpha spectrometry count record form such as Exhibit 3.

PNL TECHNICAL PROCEDURE

3. When the count is complete, switch the multichannel analyzer to output the spectrum from the analyzer memory to the printer. Print the spectrum. Attach the printed spectrum to the alpha spectrometry count record sheet. If computerized data reduction is desired, switch the multichannel analyzer to output the spectrum to a magnetic tape storage unit and store the spectrum on magnetic tape.
4. Slowly reduce the detector bias voltage to zero volts and slowly release the chamber vacuum. Remove the sample. If no additional sample spectrum is to be taken with the detector, evacuate the chamber and slowly increase the detector bias voltage to 15 volts.

4.4.2 Data Reduction

The activities of each isotopes are normally measured using counting systems 2 and 3. The spectral regions corresponding to the alpha particle emissions of all significant peaks from each isotope are integrated. The number of channels used is somewhat variable because of the sample-to-sample variability of spectral resolution, depending on the thickness and density of the electrodeposited source. Normally about 40 channels are integrated for each peak. Since the background count is normally extremely small for these detectors, it is possible to adjust the band width and its location by examining the spectrum. The integrated band is normally positioned so that the centroid of the peak (see 5.3.4 for a description of the location of peak centroids) is about 30% band width below the upper band extremity. This position is used for all isotopes.

1. Locate and integrate spectral regions. If a preprogrammed computerized integration is to be used, the programmed channel band locations must be checked with the printed copy of the spectrum. If the programmed locations are not optimum for the spectrum, the integration should be done manually or the programmed band locations should be adjusted.

PNL TECHNICAL PROCEDURE

2. Integrate the same spectral regions for the detector back-ground spectrum taken most recently and calculate the back-ground cpm for each.
3. Subtract the background cpm from the gross cpm to yield the net cpm for each peak.
4. Calculate the chemical yield (recovery) as follows.

$$\text{Chemical Yield (y)} = \frac{(\text{net cpm tracer}) (\text{DPC})}{(\text{dpm tracer added})}$$

where DPC is disintegration per count (1/Efficiency) for the counting system.

5. Calculate the dpm/L of isotopes in the sample (A) by multiplying with the DPC and dividing by the yield and volume, which is as follows.

$$\text{isotopes (dpm/L)} = \frac{(\text{net cpm}) \times (\text{DPC})}{(\text{yield}) \times (\text{volume})}$$

WORKING DOCUMENT IS IN THE LABORATORY

PNL TEST PROCEDURE

TITLE: WHC-053-1, Laboratory Procedure for Measurement of Physical and Rheological Properties of Solutions, Slurries and Sludges.

1.0 APPLICABILITY

This procedure will be used to measure the following physical properties of solutions, slurries, and sludges:

- Density or Specific Gravity
- pH of solutions
- Physical Appearance
- Settling Rate
- Shear Strength
- Shear Stress versus Shear Rate
- Vol% Centrifuged Solids
- Vol% Settled Solids
- Wt% Dissolved Solids
- Wt% Centrifuged Solids
- Wt% Total Oxides
- Wt% Total Solids
- Yield Stress

This procedure is applicable to samples that are homogenous and representative of the bulk sample with the exception of the sample used for shear strength. If not homogenous, the sample will be mixed and the procedure documented in the appropriate Laboratory Record Book (LRB).

2.0 DEFINITIONS

- Apparent Viscosity - Viscosity of a fluid defined as a ratio of the shear stress (at a particular shear rate) and the shear rate.
- Density or Specific Gravity - Density is the mass per unit volume and Specific Gravity is the ratio of the density of the sample and a reference material.
- Interstitial Solution - The solution contained within the original sludge sample.
- Newtonian - A fluid with no yield stress and a viscosity that is independent to shear rate.
- Non-Newtonian - A fluid whose viscosity varies with shear rate.

Concurrence <i>L.C. By</i>		Date 2/7/89		Approved <i>E. J. Wheelwright</i>		Date 2-7-89	
Prepared by <i>R.D. Scheele</i>		Date 2/6/89		QAD/Concurrence <i>L.C. By</i>		Date 2-9-89	
Procedure No. WHC-053-1		Revision No. 0		Effective Date 2-7-89		Page 1 of 11	

PNL TEST PROCEDURE

- pH - pH is $-\log [H^+]$. pH is applicable to aqueous solutions or slurries only.
- Physical Appearance - The physical state (solid, liquid, sludge, slurry), color, and consistency.
- Rheogram/Flow Curve - A plot of a fluid's shear response as the shear rate is increased from zero to a maximum shear rate and then returned to zero. A plot of ~~shear stress versus~~ shear rate.
- Sludge - Wet solids having little or no standing liquid, i.e. mud-like.
- Slurry - A thin mixture of solids and solution.
- Solution - A liquid phase containing dissolved material.
- Solids Settling Rate - the rate at which the solids in a homogenized sample settle.
- Vol% Settled Solids - the percentage of the volume of the sample that the settled solids occupy.
- Vol% Centrifuged Solids - the percentage of the volume of the sample that the solids occupy after being centrifuged for a specific time and force.
- Wt% Total Oxides - the percentage of the mass of the sample that remains after converting all non-volatile elements to oxides. Some volatile elements such as cesium might be lost in this process.
- Wt% Centrifuged Solids - the percentage of the mass of the sample that the solids occupy after being centrifuged.
- Wt% Dissolved Solids - the percentage of the mass of sample that is dissolved in the aqueous portion of the sample.
- Wt% Total Solids - the percentage of the mass of the sample that remains after removing all free water by drying at $110 \pm 5^\circ\text{C}$ for 24 h.
- Yield Stress - The minimum stress required to initiate fluid movement.

3.0 RESPONSIBLE STAFF

Staff responsible for implementing this procedure are:

- Analyst
- Cognizant Scientist

PNL TEST PROCEDURE

4.0 PROCEDURE for Measurement of Physical and Rheological Properties

4.1 General Requirements

The COGNIZANT SCIENTIST is responsible for preparing the test instructions to implement each step of this procedure and supplying the analyst with the test instructions. Because of the nature and diversity of samples that will be analyzed using this procedure, the COGNIZANT SCIENTIST is responsible for assuring that the test instructions satisfy the requirements of this procedure and provide a unique sample or container identifier to insure sample traceability and control.

All measurements will be made at the temperature specified ($\pm 4^{\circ}\text{C}$) in the test instructions or at ambient temperature if unspecified. Temperature will be measured using a calibrated thermocouple or RTD and digital thermometer or a mercury thermometer. If the test instructions specify a temperature, a constant temperature bath/circulator will be used.

The results of all measurements will be recorded in the appropriate LRB or on the test instructions. A copy of the test instructions sheet will be entered into the LRB. The LRB will be supplied and maintained by the COGNIZANT SCIENTIST. The ANALYST may also record information in the LRB.

In addition to the M & TE list required by PAP-70-1201, the calibrated instrumentation used will be recorded in the LRB or on the test instructions.

4.2 Procedure for Physical Appearance Measurement

This procedure will be used to observe some general physical properties for solutions, sludges, and slurries.

4.2.1 Equipment and Materials

None

4.2.2 Determination of Physical Appearance

Describe the sample in terms of its physical state (solution, slurry, or sludge), its color, particle size, its ability to hold its shape, and any other observable physical characteristics.

The ANALYST'S ability to observe these properties may be limited by work location. For example if the sample is located in the 325A shielded facility, the actual color and the observed color may be different due to the yellow leaded glass used in the shielded cell observation windows. The properties observed in

Procedure No.	Revision No.	Effective Date	Page	of
WHC-053-1	0	2-7-89	3	11

PNL TEST PROCEDURE

this procedure are qualitative not quantitative and are thus subjective based on the ANALYST'S experience.

4.3 Procedure for Settling Rate and Vol% Settled Solids Measurement

4.3.1 Equipment and Materials

- 15 or 50 mL Graduated Plastic Centrifuge Tube with Cap
- Analytical Balance, 2-place (minimum sensitivity)
- Plastic Rod or Plastic Spatula
- Centrifuge

4.3.2 Determination of Solids Settling Rate and Vol% Settled Solids

Label and weigh the centrifuge tube to be used. Determine the cm/mL for the centrifuge tube by measuring the distance between the 3 and 13 mL graduations for the 15 mL tube or between the 10 and 20 mL graduations for the 50 mL tube. Calculate cm/mL.

Transfer the sample to the preweighed, labeled centrifuge tube and seal. Reweigh and determine the sample mass by difference. Measure the volume of the total sample using the graduations on the centrifuge tube. Begin the settling rate measurements on a Monday or Tuesday and no later than 1 h after the start of the working day. Record the start time and the times that all succeeding measurements are taken. Allow the solids in the sample to settle for 1 h and measure the total sample and the solids volumes. Monitor the solids and total sample volumes at the end of hour two and every two hours after that until the end of the working day. Measure the total sample and solids volumes at the end of the working day. Measure the total sample and solids volumes at the beginning of the next working day. Measure every two hours until no change is observed between three successive measurements.

Volumes will normally be measured to ± 0.2 mL when using the 15 mL centrifuge cone and to ± 1 mL when using the 50 mL centrifuge cone. The recommended sample volumes are 10 mL for the 15 mL tube and 30 mL for the 50 mL tube.

Present the settling rate as the solids height versus time. The solids height will be calculated by multiplying the solids volume by the height of 1 mL.

Calculate Vol% Settled Solids by dividing the solids volume by the total volume and multiplying by 100%.

Some samples may stick to the side of the centrifuge tube. Centrifuge these samples briefly to drive them to the bottom of the tube to measure the sample volume. If the centrifuging causes separation of the solids and liquid, shake or blend with a plastic rod or spatula or as directed by the COGNIZANT

Procedure No. WHC-053-1	Revision No. 0	Effective Date 2-7-89	Page 4	of 11
----------------------------	-------------------	--------------------------	-----------	----------

PNL TEST PROCEDURE

SCIENTIST before beginning the settling procedure. Reweigh the tube and sample and calculate the new sample weight by difference.

The upper solids level may be difficult to determine because of different solids settling rates. The solids volume will be defined as the uppermost volume in which solids are present or the solids-solution interface is the point at which the sample becomes opaque.

4.4 Procedure for Density or Specific Gravity Measurement

This procedure will be used to measure the density or specific gravity of sludges, solutions, and slurries. This procedure will refer only to the measurement of density. If the user desires specific gravity, divide the measured density by the density of the reference material.

4.4.1 Equipment and Materials

- Graduated Plastic Centrifuge Tube with Cap
- Centrifuge
- Analytical Balance, 2-place (minimum sensitivity)
- Volumetric Flask (Option for Solutions)

4.4.2 Determination of Density

Transfer the sample to a preweighed, labeled centrifuge tube and seal. Reweigh and calculate the sample mass by difference. As an alternative to a new sample, the sample from 4.3.2 may be used. The sealed centrifuge tube will be centrifuged for 1 h at $\geq \sim 1000$ gravities. Measure the total volume of sample using the graduations of the centrifuge tube.

Calculate the density by dividing the sample mass by the sample volume. The sample mass will normally be measured to ± 0.02 g and the sample volume will normally be measured to ± 0.2 mL for the 15 tube or ± 1 mL for the 50 mL tube. The recommended sample volumes are 10 and 30 mL for the 15 and 50 mL centrifuge tubes, respectively.

With sludge samples the solids will often slope because of the centrifuging, the volume of the sample will be the average of the high and low volumes observed for the sample.

An alternative method for determining a solution's density will be to transfer a sample into a preweighed, labeled volumetric flask. Determine the sample mass by difference. This alternative method is preferable to the use of a graduated centrifuge tube because of increased accuracy for the volume measurement. The volume of a volumetric flask will normally be known to ± 0.04 mL.

Procedure No.	Revision No.	Effective Date	Page	of
WHC-053-1	0	2-7-89	5	11

PNL TEST PROCEDURE

4.5 Procedure for Determination of Vol%, Wt% and Densities of Centrifuged Solids and Supernate

This procedure will be used for determining the vol%, wt%, and the densities of centrifuged solids and centrifuged supernates for sludges and slurries.

4.5.1 Equipment and Materials

- Graduated Plastic Centrifuge Tube with Cap
- Clinical Centrifuge
- Analytical Balance, 2-place (minimum sensitivity)
- Jar (Recommend minimum volume which will contain supernate)
- Transfer Pipet and tips

4.5.2 Determination of Vol%, Wt%, and Densities of Centrifuged Solids and Supernate.

Transfer sample to a preweighed, labeled centrifuge tube and reweigh. Calculate the mass of the sample by difference. The sample and tube from Part 4.4 may be used as the centrifuged sample. Centrifuge the sample for 1 h at ~1000 gravities. Measure the total sample and solids volume using the centrifuge tube graduations. The recorded solids volume will be the average of the high and low solids volume measurements. Supernate volume is total sample volume less the solids volume. Volume is normally measured to ± 0.2 or ± 1 mL for the 15 and 50 mL centrifuge tubes, respectively.

The vol% centrifuged solids is the solids volume divided by the total volume multiplied by 100%. The vol% centrifuged supernate is 100% - vol% solids.

To determine the wt% centrifuged solids, decant or transfer with a pipet the centrifuged supernate into a labeled, preweighed jar. Measure the mass of the centrifuge tube and solids. Calculate the centrifuged solids mass by difference. Weigh the recovered centrifuged supernate and jar and calculate the mass of the centrifuged supernate by difference.

The wt% centrifuged solids is the solids' mass divided by the total sample mass multiplied by 100%. The wt% centrifuged supernate is the mass of the supernate divided by the total sample mass multiplied by 100%. The centrifuged solids density is the mass of the solids divided by the solids volume and the centrifuged supernate density is the supernate's mass divided by its volume.

Procedure No. WHC-053-1	Revision No. 0	Effective Date 2-7-89	Page 6	of 11
----------------------------	-------------------	--------------------------	-----------	----------

PNL TEST PROCEDURE

4.6 Procedure for Determination of Wt% Total Solids, Wt% Dissolved Solids, and Wt% Total Oxides.

This procedure will be used for determining the wt% total solids, wt% dissolved solids, and wt% total oxides in solutions, sludges, and slurries.

4.6.1 Equipment and Materials

- Ceramic Crucibles
- Glass Vials
- Analytical Balance, 2-place
- Desiccator Containing Dry Indicating Desiccant
- Muffle Furnace (100 to >1000°C)
- Drying Oven

4.6.2 Determination of Wt% Total Solids, Wt% Dissolved Solids, and Wt% Total Oxides.

Transfer sample to preweighed, labeled crucible or vial and weigh. Use crucible for samples for which total oxides will be determined and use vials for samples for which only wt% solids are to be determined. Calculate the sample mass by difference. Place sample in desiccator at least overnight to remove free liquid and to prevent splattering in the oven; an alternate method for removing free liquid, such as using a heat lamp, may be designated by the COGNIZANT SCIENTIST. When the free liquid has evaporated, transfer sample and container to 105 ± 5°C drying oven or furnace. Hold at temperature for 24 h. Remove the dried samples and containers and place in the desiccator to cool to room temperature; should take at least 1 h. Reweigh the dried sample and container. Determine residual sample weight by difference. The mass of the sample will normally be measured to ± 0.02 g.

The wt% total solids is the residual mass divided by the initial sample mass multiplied by 100%. For solutions the wt% dissolved solids is the residual mass divided by the initial sample mass multiplied by 100%. For slurries or sludges with interstitial solutions that are recoverable using centrifugation, the wt% dissolved solids is the weight fraction dissolved solids in the centrifuged supernate times the weight fraction centrifuged supernate in the sludge/slurry (determined using procedure found in 4.5) times 100%.

Place the sample and crucible from wt% total solids procedure into the furnace. Do not perform this procedure with the glass vials. Heat the furnace to >1000°C and hold for 30 min between 1000 and 1050°C. Turn off the furnace and cool to 150°C. Transfer the crucibles using tongs to the desiccator and cool to room temperature; should take 1 to 2 h. Once cool weigh the

Procedure No.	Revision No.	Effective Date	Page	of
WHC-053-1	0	2-7-89	7	11

PNL TEST PROCEDURE

burned samples and crucibles. Determine the residual oxide mass by difference. Consider that volatile elements may also be lost.

The wt% total oxide is the residual oxide mass divided by the initial sample mass multiplied by 100%.

4.7 Procedure for Determining pH

This procedure will be used for determine the pH of a solution or slurry.

4.7.1 Equipment and Materials

- pH Meter and Electrode
- pH 4, 7 and 10 Buffers
- Plastic beakers or vials

4.7.2 Determination of pH

Standard Laboratory procedure will be used to measure the pH of solutions or slurries. A pH meter, calibrated (in mv) on a yearly basis, will be used. The electrode will be calibrated daily prior to use using a two standard method taking into account the temperature of the standards and samples. The electrode calibration will be done using pH buffers that are traceable to the manufacturers lot number. The expiration date for the buffers used in the check must not have lapsed. The electrode will be prepared for use and stored in accordance with the manufacturer's directions.

Sufficient sample will be added to a beaker or vial to cover the sensing portion of the electrode. Remove the probe from the storage solution, rinse with deionized (DI) water, and blot dry with a tissue. Insert the probe into the sample. Once the reading has stabilized, record the pH value and rinse the electrode with DI water. After the last sample has been rinsed and blotted, return it to its storage fluid.

The pH meter must have an accuracy of ± 0.02 pH units. Data will normally be reported to the nearest 0.1 pH unit.

4.8 Procedure for Determination of Shear Stress vs Shear Rate and Yield Stress

This procedure will be used for determining the shear stress versus shear rate, yield stress, and shear strength for solutions, sludges, and slurries.

4.8.1 Equipment and Materials

- Haake RV100 Viscometer
- MV I or MV II Sensor

Procedure No. WHC-053-1	Revision No. 0	Effective Date 2-7-89	Page 8	of 11
----------------------------	-------------------	--------------------------	-----------	----------

PNL TEST PROCEDURE

- MV Beaker
- Certified Newtonian Viscosity Standards
- Constant Temperature Bath/Circulator

4.8.2 Performance Requirements

Performance checks of the viscometer will be performed monthly or within 31 days of measurement using Certified Newtonian Viscosity standards traceable to the manufacturer's lot number. The viscometer used must have a demonstrated accuracy of $\pm 10\%$ in apparent viscosity measurements.

The data will be generated following the instructions provided in Instruction Manual Rotovisco RV100. The data will be in the form of a rheogram or flow curve, which is a plot of shear stress as a function of shear rate.

4.8.3 Measurement of Shear Stress vs Shear Rate and Yield Stress

Select and install the Sensor. Adjust the temperature setting for the constant temperature circulator to the desired level. Install the temperature control shroud. Transfer the sample by weight into the viscometer beaker. If the MV I Rotor is used transfer 40 mL or if the MV II Rotor is used transfer 55 mL. The weight transferred equals the density times the volume. After the coolant in the shroud reaches the desired temperature, stir the sample, and install the sample and beaker in the viscometer. Allow the sample to remain in position for 5 min to bring the sample to temperature. Obtain a rheogram. Adjust the temperature controller to the next temperature. Once the temperature of the coolant in the shroud reaches the desired level, equilibrate for 5 min before obtaining a rheogram. Repeat as necessary to obtain rheograms at the temperatures of interest.

It is important that the time between installation of the sample and beaker in the viscometer and the acquisition of the rheogram be minimized to minimize the effects of any solids settling.

To calculate apparent viscosity, measure the shear stress (from the y axis) of the sample at a selected shear rate (from the x axis) and divide the shear stress by shear rate.

The fluid yield stress is obtained from the rheogram. A rheogram for a material with a yield stress will have two portions to it. The first appears as a nearly vertical line beginning at the origin and running up the ordinate. This line forms an angle, β , with the ordinate. This portion of the rheogram is recording the behavior of the material as it acts like a solid or gel. When sufficient force is transmitted to the material to break the gel or make it yield, the rheogram will angle sharply to the right, and from then on the behavior of the material as a fluid will be recorded. This sharp angle

Procedure No.	Revision No.	Effective Date	Page	of
WHC-053-1	0	2-7-89	9	11

PNL TEST PROCEDURE

that is recorded as the material becomes fluid is the yield point. The height of this break measured in Pascals along the ordinate is the value of the material's yield stress.

Some samples exhibit a creeping transition from solid to liquid behavior. This creep is recorded as a rounded yield point that is more difficult to identify. In cases where creep is exhibited, the yield point is defined as the intersection of a tangent drawn along the solid portion of the rheogram with a tangent drawn along the fluid portion of the rheogram.

Yield stress data is normally reported with a degree of precision of ± 0.1 Pa.

4.9 Procedure for Determination of Shear Strength

This procedure will be used to measure the shear strength of sludge samples. Shear strength is a semi-quantitative/qualitative/relative measure of the force that is required to move the material. No calibration standards are currently available to calibrate the shear vane.

4.9.1 Equipment and Materials

- Haake RV 100 Viscometer
- Shear Vane

4.9.2 Measurement of Shear Strength

Install shear vane into the viscometer. Position sample beneath the shear vane. Raise the sample slowly using the lab jack centering the shear vane in the sample. Submerge the vane with at least 3 mm of sample above and below the vane. Based on the appearance of the sample, the COGNIZANT SCIENTIST or ANALYST will select the stress scale and the shear rate. Obtain the rheogram. Note: Shear Strength is dependent on sample history. The sample should be disturbed as little as possible before measurement or should be allowed to age for at least 2 days before shear strength is determined.

The size and geometry of the sample is important when measuring shear strength. Try to select a sample geometry with a diameter of at least 4 shear vane diameters and a depth such that there is at least 3 mm of sample above and below the shear vane. The shear vane should be located at least two shear vane diameters away from the container walls.

The rheogram should show a peak at the beginning, level off, and finally drop off. The shear strength is calculated by taking the peak torque in fraction of full-scale reading on the chart, multiplying by $\% \gamma$, multiplying by the full scale γ , and dividing

Procedure No. WHC-053-1	Revision No. 0	Effective Date 2-7-89	Page 10 of 11
----------------------------	-------------------	--------------------------	---------------

PNL TEST PROCEDURE

by the surface area of the shear vane fins. The shear strength is reported in dynes/cm².

5.0 Quality Assurance

Work performed using this technical procedure will meet Impact Level II requirements as described in PNL-MA-70. All data generated using this procedure will be recorded on test instructions or directly in a LRB. The completed test instructions will later be entered into the appropriate LRB.

Changes to the test instructions can be made only by the COGNIZANT SCIENTIST and will be documented by crossing out the original information with a single line, and recording, initialling, and dating the changes. Major changes will be made by revision of the test instruction.

Procedure No. WHC-053-1	Revision No. 0	Effective Date 2-7-89	Page 11	of 11
----------------------------	-------------------	--------------------------	------------	----------

WORKING DOCUMENT IS IN THE LABORATORY

**DATE
FILMED**

3 / 9 / 94

END