Analytical Chemistry Laboratory Department

ANALYTICAL CHEMISTRY
LABORATORY (ACL)
PROCEDURE COMPENDIUM

Volume 3: Inorganic Instrumental
Methods

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Approved for Use
and Application by

A. G. King
Department Manager

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-MA-599-Vol.3-1

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A.

Document Number: See Attachment Revision Number: _____

Document Title: See Attachment

Document's Original Author: See Attachment

Effective Date
of ICN: 12 / 23 / 92

Change Requested by:
AG King

B. Action: Place the attached procedures in PNL-MA-599 manual, Volume 3. Place this ICN and attachment with the Table of Contents.

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

D. Reason for Change/Description of Change:

Incorporates the procedures from PNL-MA-597 manual into PNL-MA-599 manual by changing the procedure numbers. This eliminates the need for maintaining two sets of technical procedures. Procedural references in these procedures have been updated. See attachment for the procedures to be incorporated into PNL-MA-599 manual, Volume 3.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

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

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

Other Approvals: _____ Date: / /

: _____ Date: / /

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New Doc#	Rev.	Author	Document Title	Old Doc#
PNL-ALO-223	0	MC Burt	Oxygen to metal ratio Thermogravimetry	2-30.5
PNL-ALO-224	0	MC Burt	Weight loss upon ignition	2-30.7
PNL-ALO-229	0	MC Burt	Uranium by Automated Potentiometric Titration	2-30.8
PNL-ALO-231	0	FE Holt	Separation of carbon from soil/sediment/sludge samples	7-40.16
PNL-ALO-233	0	MC Burt	Plutonium Purification by Ion Exchange	2-30.9
PNL-ALO-237	0	MC Burt	Total Nitrogen by fusion and Gas Chromatography	2-40.7
PNL-ALO-238	0	MC Burt	Water by constant voltage Coulometry	2-40.11
PNL-ALO-240	0	MC Burt	Carbon and Sulfur by Combustion and infrared absorption	4-30.4 & 2-40.19
PNL-ALO-241	0	MC Burt	Total nitrogen by fusion and gas chromatography	4-30.6
PNL-ALO-242	0	RW Stromatt	Surface Chloride and Fluoride using swab test	4-30.8
PNL-ALO-243	0	RW Stromatt	Water leachable chloride and Fluoride in cloth and other materials	4-40.3
PNL-ALO-244	0	MW Goheen	Vacuum Outgas of intrinsic Germanium Detector dewars	7-30.1
PNL-ALO-245	0	MW Goheen	Gas mixing	7-30.4
PNL-ALO-246	0	SJ Bos	Mass spectrometer isotopic analysis of gases	7-40.4
PNL-ALO-247	0	JJ McCown	Analysis of metals, metal alloys and metal compounds by x-ray fluorescence	7-40.6

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PNL-ALO-249	0	DL Baldwin	Hydrogen in Zircaloy by inert gas fusion/gas chromatography	7-40.10
PNL-ALO-250	0	RF Keough	Determination of hydrogen in metals by the inert gas fusion method	7-40.11
PNL-ALO-251	0	RF Keough	Determination of oxygen in metals by the inert gas fusion method	7-40.12
PNL-ALO-254	0	MC Burt	Impurity separation by liquid-liquid extraction	7-40.19
PNL-ALO-255	1	MC Burt	Spectrophotometric determination of reduced and total iron in glass with 1,10 phenanthroline	7-40.20
PNL-ALO-256	0	MC Burt	Determination of free acid in uranium/plutonium solutions	7-40.22
PNL-ALO-257	0	MC Burt	Density of solutions	7-40.23
PNL-ALO-258	0	MW Goheen	Isotopic analysis of Krypton and xenon in FFTF cover gas	7-40.28
PNL-ALO-259	0	RF Keough	Determination of hydrogen by combustion	7-40.31
PNL-ALO-260	0	MW Goheen	Mass spectrometer isotopic analysis of lithium	7-40.32
PNL-ALO-261	0	MW Goheen	Mass spectrometer isotopic analysis of cesium	7-40.33
PNL-ALO-262	0	MW Goheen	Mass spectrometer isotopic analysis of lanthanide series elements	7-40.35
PNL-ALO-263	0	RF Keough	Operation of gas chromatographs	7-40.44

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PNL-ALO-265	0	PK Melethil	Determination of total sodium on filters by flame atomic emission	7-40.46
PNL-ALO-266	1	RW Sanders	Procedures and quality control for energy dispersive x-ray fluorescence spectroscopy using the BFP approach with the KEVEX 0810A system	7-40.48
PNL-ALO-267	0	FE Holt	Operation of the Canberra model 20 multichannel analyzer	7-40.51
PNL-ALO-283	1	ED Jenson	Solids analysis: Microprobe analysis	HTA-3-5
PNL-ALO-284	0	MW Goheen	Quantitative analysis of gas samples	7-40.18 & HTA-4-34

PNL-MA-599 ANALYTICAL CHEMISTRY LABORATORY (ACL) PROCEDURE COMPENDIUM
Volume 3: Inorganic Instrumental Methods

April 5, 1993

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HWVP-2	0	0	FLUORIDE BY ELECTRODE	6/21/88
PNL-ALO-211	0	2	DETERMINATION OF ELEMENTS BY INDUCTIVELY COUPLED ARGON PLASMA ATOMIC EMISSION SPECTROMETRY	8/19/91
PNL-ALO-212	1	0	DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY	12/04/92
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PNL-ALO-223	0	0	OXYGEN TO METAL RATIO THERMOGRAVIMETRY	06/21/88
PNL-ALO-224	0	0	WEIGHT LOSS UPON IGNITION	06/21/88
PNL-ALO-225	0	1	MEASUREMENT OF pH IN AQUEOUS SOLUTION	03/04/92
PNL-ALO-226	0	2	AMMONIA (NITROGEN) IN AQUEOUS SAMPLES	08/25/92
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PNL-ALO-228	0	0	DETERMINATION OF HYDROXYL (OH ⁻) AND ALKALINITY OF AQUEOUS SOLUTIONS, LEACHATES AND SUPERNATES	03/07/92
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PNL-ALO-231	0	0	SEPARATION OF CARBON FROM SOIL/SEDIMENT/SLUDGE SAMPLES	06/17/88
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PNL-ALO-237	0	0	TOTAL NITROGEN BY FUSION AND GAS CHROMATOGRAPHY	06/21/88
PNL-ALO-238	0	0	WATER BY CONSTANT VOLTAGE COULOMETRY	06/21/88
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PNL-ALO-244	0	0	VACUUM OUTGAS OF INTRINSIC GERMANIUM DETECTOR DEWARs	08/02/88
PNL-ALO-245	0	0	GAS MIXING	08/02/88
PNL-ALO-246	0	0	MASS SPECTROMETER ISOTOPIC ANALYSIS OF GASES	03/29/88
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PNL-ALO-254	0	0	IMPURITY SEPARATION BY LIQUID-LIQUID EXTRACTION	08/08/88
PNL-ALO-255	0	0	SPECTROPHOTOMETRIC DETERMINATION OF REDUCED AND TOTAL IRON IN GLASS WITH 1,10 PHENANTHROLINE	03/05/91
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PNL-ALO-259	0	0	DETERMINATION OF HYDROGEN BY COMBUSTION	05/01/89
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PNL-ALO-261	0	0	MASS SPECTROMETER ISOTOPIC ANALYSIS OF CESIUM	05/08/89
PNL-ALO-262	0	0	MASS SPECTROMETER ISOTOPIC ANALYSIS OF LANTHANIDE SERIES ELEMENTS	05/19/89
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PNL-ALO-267	0	0	OPERATION OF THE CANBERRA MODEL 20 MULTICHANNEL ANALYZER	02/28/91
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PNL-ALO-282	0	2	DETERMINATION OF URANIUM CONCENTRATION/ISOTOPIC COMPOSITION USING ICP-MS	10/28/91
PNL-ALO-283	0	0	SOLIDS ANALYSIS: MICROPROBE ANALYSIS	07/01/87
PNL-ALO-284	0	0	QUANTITATIVE ANALYSIS OF GAS SAMPLES	06/15/88
PNL-ALO-285	0	1	TOTAL CYANIDE BY REMOTE MICRODISTILLATION AND ARGENTOMETRIC TITRATION	02/03/93
PNL-ALO-286	0	0	MEASUREMENT OF HYDROGEN AND NITROUS OXIDE IN AIR	03/08/93
PNL-ALO-290	0	0	DETERMINATION OF pH IN SOIL SAMPLES	03/03/93

PNL TEST PROCEDURE

TITLE: 7-40.7, SOLUTIONS ANALYSIS: CARBON

1.0 APPLICABILITY

This procedure provides instructions for the analysis of aqueous solutions for total organic carbon, inorganic carbon and total carbon using the UV light catalyzed oxidation method.

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

- Carbon analyzer (procedure based on Dohrmann DC80 total organic carbon analyzer).
- Hypodermic syringes (25, 50, 250 and 1000 ul).
- Carbon standards (10, 400 and 2000 ug/ml carbon) in aqueous solutions of potassium acid phthalate -- The 2000 ug/ml standard is purchased from the manufacturer or prepared as follows: dissolve 425 (± 1) mg NBS SRM-84 potassium acid phthalate in 15 M or better deionized water as determined by the deionizer readout, add 0.1 ml concentrated phosphoric acid and dilute the solutions to 100 ml. The 10 and 400 ug/ml standards are prepared by diluting the 2000 ug/ml standard. The 10 ug/ml standard should be prepared fresh the day it is used.
WARNING: Because of the potential for biodegradation of the standard, it is to be stored in a refrigerator to minimize the biodegradation process. Before use, the solution shall be checked visually; and if any precipitation is observed, a new 2000 ug/ml standard shall be prepared.
- Oxidizing reagent (2 to 3.5 wt% $K_2S_2O_8$ in 0.2 vol% concentrated H_3PO_4).

Concurrence		Date		Approved		Date	
				<i>J. H. Town</i>		3/31/88	
Prepared by		Date		QAD Concurrence		Date	
<i>Robert W. Hornett</i>		3/31/88		<i>B. E. Thridge</i>		3/31/88	
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PNL TEST PROCEDURE

4.2 Method

Total carbon is determined by injecting the sample into an acidic oxidizing reagent that flows through an ultraviolet light catalyzed reactor. All the carbon is converted to CO₂, which is measured by a nondispersive infrared detector. Detector response is converted electronically to carbon concentration in the sample. Total organic carbon is determined by acidifying the sample, purging the CO₂ from the solution, and injecting the inorganic carbon-free sample into the analyzer.

Inorganic carbon can be measured indirectly by subtracting the results of the total organic carbon from the results of the total carbon measurement. A direct determination of inorganic carbon is made by injecting the sample into the analyzer after replacing the oxidizing solution with acid or turning off the ultraviolet light in the analyzer and allowing the reactor solution to cool.

4.3 Calibration

Perform the following steps according to the instrument's operating manual (see Section 5.0).

- Step 1) Turn on detector and reaction module power, UV lamp, pump, and oxygen. Allow detector current to stabilize.
- Step 2) Set the instrument to the appropriate range: 1-ml for the 10 ppm calibration, 200-ul for 400 ppm or 40 ul for 2000 ppm.
- Step 3) Inject the standard into the instrument and depress START immediately. When the determination is completed, the READY light will glow.
- Step 4) Repeat the determinations until two successive results are within 1% relative.
- Step 5) Depress the CALIBRATE switch.

4.4 Sample Analysis

- Step 1) Set the instrument to the concentration range used for the calibration (Section 4.3).
- Step 2) To determine total carbon inject the sample (sample volume is set according to instrument range used) and press START as in Section 4.3.
- Step 3) To determine inorganic carbon turn off the UV lamp and wait 10 minutes, inject sample as in Step 2 and press START.

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PNL TEST PROCEDURE

Step 4) To determine total organic carbon place about 5-ml (or less) in test tube and acidify with concentrated phosphoric acid. Place a drop of the acidified solution on pH indicator paper; if the pH is $\leq$ than about 3 continue as follows otherwise add more acid and repeat acidity check. Place the sample on the external sparger, and bubble gas through the sample 5-min. Then inject the sample and press START.

Step 5) If a dilution is used it may be necessary to determine a diluent blank.

4.5 Calculations

If an undiluted sample is analyzed, record the instrument readout, R. If a diluted sample is analyzed, use the following equations.

$$C = \frac{V_2}{V_1} [R - \frac{(V_2 - V_1)}{V_2} B]$$

where, C = carbon concentration, ppm
V₂ = final volume, ml
V₁ = initial volume, ml
R = carbon reading in sample, ppm
B = carbon reading in blank, ppm

4.6 Records

Records will be controlled according to PAP-1701. Laboratory notebooks will be controlled according to PAP-1704.

4.7 Procedure Qualification

None required. This procedure is self-qualifying due to its dependence on analytical standards.

5.0 REFERENCES

- Dohrmann DC80 Total Organic Carbon Analysis System Equipment Manual, XERTEX, Dohrmann, Santa Clara, CA.

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PNL TEST PROCEDURE

TITLE: HWVP-2; FLUORIDE ION IN AQUEOUS SAMPLES

1.0 APPLICABILITY

This procedure is applicable for the analyses of fluoride ion concentration in aqueous samples using the fluoride specific ion electrode.

2.0 DEFINITIONS

Total Ionic Strength Adjustor (TISAB) - Solution to provide a constant background ionic strength, decomplex fluoride and adjust solution pH.

3.0 RESPONSIBLE STAFF

Responsible Scientist
Cognizant Staff

4.0 PROCEDURE

4.1 Summary of method

An aliquot of the sample is mixed with TISAB and the fluoride ion determined using the specific fluoride ion electrode using the known addition method.

4.2 Specific Qualification

4.2.1 A RESPONSIBLE SCIENTIST shall supervise the individual performing the analyses.

4.2.2 The COGNIZANT STAFF shall follow this procedure in performing the analyses.

4.3 Reagent

4.3.1 Fluoride Standard Solution (1.0 ml = 1.0 mg F)

Dissolve 2.210 ± 0.005 g of sodium fluoride in water and dilute to 1 liter. Store in a polypropylene bottle. Or purchase a certified 1.00 g/L fluoride standard solution.

Concurrence <i>D. L. Widrig</i>		Date 6/21/88		Approved <i>J. J. McCown</i>		Date 6/21/88	
Prepared by D. L. Widrig		Date 6/21/88		QAD Concurrence <i>L. J. Ethridge</i>		Date 6/21/88	
Procedure No. HWVP-2		Revision No. 0		Effective Date 6/21/88		Page 1 of 5	

PNL TEST PROCEDURE

4.3.2 100 ppm Fluoride Standard With TISAB III

Pipet 25 ml of 1000 ppm fluoride standard solution into a 250 ml volumetric flask. Add 25 ml of TISAB III solution into the flask and dilute to volume with demineralized water. Store this solution in a polypropylene bottle.

4.3.3 10 ppm Fluoride Standard With TISAB III

Pipet 25 ml of 100 ppm fluoride standard from 4.3.2 into a 250 ml volumetric flask. Add 25 ml of TISAB III solution into the flask and dilute to volume with demineralized water. Store this solution in a polypropylene bottle.

4.3.4 TISAB III

A commercially available buffering mixture containing acetic acid, NaCl, and CDTA used to decomplex fluoride ion.

4.4 Sample Logging Procedure

4.4.1 COGNIZANT STAFF shall log the sample onto the sample log sheet. Series of similar liquid samples which require no special sample preparation except sample dilution can be logged under one laboratory serial number since the customer's sample identification maintains traceability. Samples which require a sample weighing or unique sample preparation (e.g. fusion) shall be logged with separate laboratory serial number.

4.4.2 For each laboratory serial number, prepare a "Report of Analysis" card (Exhibit 1) which uniquely identifies each customer's sample. Any analysis which requires weighing the sample or unique sample preparation (e.g. fusion) shall have the data written on the back of the analysis card. These entries shall be dated and signed by the COGNIZANT STAFF performing the analysis.

4.5 Calibration and Analyses of Sample

4.5.1 Turn the slope thumbwheel switches to read about -56.0. If the instrument had been used previously for fluoride analysis, do not change setting from previous values.

4.5.2 If the SET BLANK button is lit, press to turn it off.

4.5.3 Turn STD thumbwheel switches to read 10.0.

4.5.4 Set the mode switch KA10.

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PNL TEST PROCEDURE

- 4.5.5 For setting blank correction, place the electrode in 2.5 ml of distilled water. Add 250 microliter of TISAB. Allow the reading to stabilize. Press the CLEAR/READ MV button.
- 4.5.6 Press SET CONC button. The display may be unstable.
- 4.5.7 Pipet 250 microliter of 10 ppm standard fluoride into blank. Allow time for reading to stabilize.
- 4.5.8 Press SET BLANK button. The button light will turn on.
- 4.5.9 Rinse the electrode, blot dry and place 2.5 ml of 10 ppm standard into the disposable beaker. Add 250 microliter of TISAB to the beaker. Press CLEAR/READ MV button.
- 4.5.10 Allow time for reading to stabilize. Press SET CONC button.
- 4.5.11 Pipet 250 microliter of 10 ppm standard to the beaker. If reading is not $10.0 \pm .1$ ppm, adjust the thumbwheel switches so the display reads 10.00 ppm.
- 4.5.12 Run the .1, 1.0 and 10 ppm solution. Record these values in the notebook located at this station.
- 4.5.13 Fluoride concentration in the sample is measured by pipetting 2.5 ml sample into a disposable beaker. Add 250 microliter of TISAB. Place the electrode in the sample and press the CLEAR/READ MV button.
- 4.5.14 Allow time for reading to stabilize. Press SET CONC button. The display may be unstable if the fluoride concentration in the sample is very low.
- 4.5.15 Pipet 250 microliter of the 10 ppm standard into the sample cup.
- 4.5.16 Allow the reading to stabilize. Record the sample concentration from the display.

4.6 Calculation

The ORION RESEARCH microprocessor Ionalyzer/901 calculates the results automatically. The formula for calculating these results is given in the ORION operation manual.

4.7 Reporting Results

Upon completion of the analysis the COGNIZANT STAFF shall tabulate the values to be reported onto the front of the "Report of

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PNL TEST PROCEDURE

Analysis" card. These entries shall be signed and dated by the COGNIZANT STAFF. The RESPONSIBLE SCIENTIST shall review the results for acceptability and document this review by signing and dating the "Report of Analysis" card. The "Report of Analysis"

card shall be xeroxed and the xeroxed copy submitted to the customer. The original "Report of Analysis" card shall be retained in the laboratory for at least one year.

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PNL TEST PROCEDURE

Battelle

Pacific Northwest Laboratories

BNW ANALYTICAL LABORATORY - 3720 BLDG.

REPORT OF ANALYSIS

Serial No.				<div style="display: flex; justify-content: space-between;"> <div><u>CONSTITUENT</u></div> <div><u>ANALYSIS</u></div> </div>
Sample Of				
Source				
For	Sampling Date	Time	AM PM	
Submitted By				
Remarks				
Date Reported		Time	AM PM	
Analyst			Report Approved	

A-1700-165 (7-79)

EXHIBIT 1

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HWVP-2	0	6/21/88	5	5

INTERIM CHANGE NOTICE
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<p>A. Document Number: <u>PNL-ALO-211.2</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Determination of Elements by Inductively Coupled Argon Plasma Atomic Emissions Spectrometry</u></p> <p>Document's Original Author <u>JJ Wagner</u></p>	<p>Effective Date of ICN: <u>2/23/93</u></p> <hr/> <p>Change Requested by: <u>RM Nipper</u></p>
<p>B. Action: <u>Replace pages 15 & 16 with the attached pages 15 & 16.</u></p>	
<p>C. Effect of Change: <u>This change will give a more accurate records requirement resource.</u></p>	
<p>D. Reason for Change/Description of Change: Reason: 1. <u>Deletes inaccurate information.</u></p> <p>Description: 1. <u>Replaced: PNL-MA-70, PAP-70-1701 with the Analytical Chemistry Lab (ACL) Quality Assurance Plan (QAP) MCS-033.</u></p> <p> 2. <u>Replaced: "LRB's will be used in accordance with the ACT Now Directive 89.1" with "LRB's will be used in accordance with established records management practices."</u></p>	
<p>E. Approval Signatures: (Please Sign and Date)</p> <p>QP Concurrence: <u>TL Ehlert</u> <u>TL Ehlert</u> Date: <u>2/23/93</u></p> <p>Approval Authority: <u>AG King</u> <u>AG King</u> Date: <u>2/23/93</u></p> <p>Other Approvals: <u>JJ Wagner</u> <u>JJ Wagner</u> Date: <u>2-23-93</u></p> <p style="margin-left: 40px;"><u>(FOR JJ WAGNER)</u> Date: _____</p>	<p>Type of Change (Check (✓) one) (✓) Minor Change () Major Change</p>

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TITLE: PNL-ALO-211, DETERMINATION OF ELEMENTS BY INDUCTIVELY COUPLED ARGON PLASMA ATOMIC EMISSION SPECTROMETRY

APPLICABILITY

This procedure is applicable for determining the concentration of inorganic analytes in aqueous samples and leachates from solids (for example, soils and sediments). The methodology is comparable to EPA Method 200.7 CLP-M. Solid samples shall be subjected to an appropriate dissolution procedure before analysis, such as PNL-ALO-101.

DEFINITIONS/ACRONYMS

Batch: A group of samples of similar matrix prepared at the same time.

RESPONSIBLE STAFF

Cognizant Scientist
Technician/Analyst

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified as follows : 1) a tolerance limit may be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- a. Unless otherwise specified, all values for measurements stated in the methods, such as volume, weight, time, etc., are approximate values. The actual measurements used, however, shall be within 10% of the stated value.

Author <i>Deezy Logan</i>	Date 3-27-91	Project Mgr. <i>B.M. Gillespie</i>	Date 3/27/91	QAD Representative <i>CK Gerke</i>	Date 3/27/91
Technical Reviewer <i>Mike Allen</i>	Date 3/27/91	Line Mgr. <i>Jim Luther</i>	Date 3-27-91	Other	Date
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- b. When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 0.5 of the least significant digit. The maximum number of significant figures for this method is three.
- c. All class "A" glass pipets shall be considered sufficiently accurate (1% or better) for use without verification, provided that a visual inspection of the pipet reveals no evidence of breaks or chips to the glass tip or other obvious damage.
- d. Mechanical or electronically operated pipets shall be verified by the user, before and after single or repetitive deliveries, by weighing at least one aliquot of water. The equivalent volume determined by the weight of the aliquot measured shall be within the manufacturers stated accuracy, typically 0.8% or better, for volumes greater than 500 μL .

2.0 Summary of Method

ICP-AES is a technique for the simultaneous or sequential multi-analyte determination of inorganic analytes in solution. The basis of the method is the measurement of atomic emission by an optical-spectroscopic technique. Aqueous or solubilized solutions of solid samples are nebulized and the aerosol that is produced is transported to a plasma torch where excitation occurs. Characteristic atomic-line emission spectra is produced by a radio frequency inductively coupled argon plasma (ICP). The spectra is dispersed by a grating spectrometer and intensities of the lines monitored by photomultiplier tubes. Photocurrents from the photomultiplier detector tubes are processed by a computer system.

3.0 Interferences

3.1 Several types of interference effects may lead to inaccuracies in the determination of trace inorganic analyte concentrations.

3.1.1 Spectral interferences can be classified as 1) overlap of a spectral line from another element, 2) unresolved overlap of molecular band spectra, 3) background contribution from continuum or recombination phenomena, and 4) background contribution from stray light by intense line emission of elements present in high concentrations.

3.1.1.1 Overlap interference will be minimized using a computer calculated adjustment of the analyte data, based upon the measured intensity of the interfering element.

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- 3.1.1.2 Unresolved overlap of molecular band spectra may require use of an alternate analyte wavelength.
- 3.1.1.3 Background contribution from continuum, recombination phenomena or from stray light shall be corrected, provided the resulting adjustment does not degrade the accuracy of the analysis. The correction can be made by applying background correction adjustment to the analyte data when an appropriate wavelength region can be found on either or both sides of the analytical wavelength. An alternate technique of applying a background correction adjustment, similar to overlap interference correction method, can be made if the offending analyte can be identified and quantified.
- 3.1.2 Physical interferences are considered to be effects associated with sample nebulization and transport processes.
 - 3.1.2.1 Interference effects caused by viscosity and surface tension can be reduced by the use of a peristaltic pump in the nebulizer sample delivery system.
 - 3.1.2.2 Interference effects caused by sample concentrations of total dissolved solids greater than 5,000 mg/L (0.5 wt%) can be reduced by an appropriate dilution of the sample.
 - 3.1.2.3 Nebulizer effects caused by salt buildup at the tip of the nebulizer can be reduced by using water saturated argon aerosol.
 - 3.1.2.4 Nebulizer argon aerosol flow rates can be stabilized by using a mass flow controller for improved instrument performance.
- 3.1.3 Chemical interferences are not normally pronounced with the ICP technique. When observed, their effect can be reduced by careful selection of operating conditions, such as incident power, carrier argon flow rates, by buffering of the sample, by matrix matching, or by standard addition procedures.

4.0 Apparatus

- 4.1 ICP-AES system: Analytical system composed of sample nebulization system, optical dispersion system, computer control, calculation software, and associated ancillary equipment (for example, electronic

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power supplies, RF power generator and gas flow controls, etc.). Thermo Jarrell Ash Corp. model ICP-61 or equivalent (eg. Applied Research Laboratory ICP model 3580).

- 4.2 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.
- 4.3 Micropipet: Calibrated, manual or electronically operated, ranging from 5 to 10,000 μ L, as required.
- 4.4 Autosampler: (Optional) Thermo Jarrell Ash, or equivalent system.

5.0 Reagents and Standards

- 5.1 Water: Water of sufficient quality, similar to ASTM Type II reagent water, shall be used for preparing standards and samples, such that calibration blanks and sample blanks will produce concentrations at or below instrument detection limits for all analytes of interest.
- 5.2 Acids: All acids used in the preparation of standards and sample processing shall be ultra-high purity grade or redistilled acids of sufficient quality such that calibration blanks and sample preparation blanks produce concentrations at or below the instrument detection limit for all analytes of interest.

5.2.1 Hydrochloric acid, concentrated.

5.2.2 Hydrochloric acid, (1+1): Add 500 mL concentrated HCl to approximately 400 mL water and dilute to 1 liter.

5.2.3 Nitric acid, concentrated.

5.2.4 Nitric acid, (1+1): Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter.

- 5.3 Standard stock solutions: Stock standard solutions, Sections 5.3.1 through 5.3.25, are needed to support CERCLA requirements and additional stock standard solutions, Sections 5.3.26 through 5.3.45, are needed for general laboratory support.

Preferred: Purchase certified aqueous stock standards from a supplier and verify by comparison with second standard.

Alternative: Prepare stock standard solutions from reagent grade materials (dried for one hour at 105°C unless otherwise specified) as described below. Reagent stock solutions prepared as specified

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below remain stable for at least one year from date of preparation. All stock reagents shall be kept at room temperature to prevent precipitation.

- 5.3.1 Aluminum solution, stock (1000 mg/L):
Dissolve 1.000 g of aluminum metal in an acid mixture of 40 mL of (1+1) HCl and 10 mL of concentrated HNO₃ in a beaker. Warm gently to effect dissolution. When solution is complete, transfer quantitatively to a liter flask, add 10 mL of (1+1) HCl and dilute to 1000 mL with water.
- 5.3.2 Antimony solution, stock (1000 mg/L):
Dissolve 2.669 g K(SbO)C₄H₄O₆ in water, add 10 mL (1+1) HCl and dilute to 1000 mL with water.
- 5.3.3 Arsenic solution, stock (1000 mg/L):
Dissolve 1.320 g of As₂O₃ in 100 mL of water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO₃ and dilute to 1000 mL with water.
- 5.3.4 Barium solution, stock (1000 mg/L):
Dissolve 1.516 g BaCl₂ (dried at 250°C for 2 hours) in 100 mL reagent water with 20 mL (1+1) HCl. Dilute to 1000 mL with water.
- 5.3.5 Beryllium solution, stock (100 mg/L):
Do not dry. Dissolve 1.966 g BeSO₄·4H₂O in water, add 10 mL concentrated HNO₃ and dilute to 1000 mL with water.
- 5.3.6 Boron solution, stock (1000 mg/L):
Do not dry. Dissolve 5.716 g anhydrous H₃BO₃ in water and dilute to 1000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly sealed and store in a desiccator to prevent the entrance of atmospheric moisture.
- 5.3.7 Cadmium solution, stock (1000 mg/L):
Dissolve 1.142 g CdO in a minimum amount of (1+1) HNO₃. Heat to increase rate of dissolution. Add 10 mL of concentrated HNO₃ and dilute to 1000 mL with water.
- 5.3.8 Calcium solution, stock (1000 mg/L):
Suspend 2.498 g CaCO₃, dried at 180°C for 1 hour, in water and dissolve cautiously with a minimum amount of (1+1) HNO₃. After effervescence subsides, add 10 mL concentrated HNO₃ and dilute to 1000 mL with water.

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- 5.3.9 Chromium solution, stock (1000 mg/L):
Dissolve 1.923 g of CrO_3 in water. When solution is complete acidify with 10 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.10 Cobalt solution, stock (1000 mg/L): Dissolve 1.000 g of cobalt metal in a minimum amount of (1+1) HCl and dilute to 1000 mL with water.
- 5.3.11 Copper solution, stock (1000 mg/L):
Dissolve 1.252 g CuO in a minimum amount of (1+1) HNO_3 . Add 10 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.12 Iron solution, stock (1000 mg/L):
Dissolve 1.430 g Fe_2O_3 in a warm mixture of 50 mL (1+1) HCl and 20 mL of concentrated HNO_3 . Cool, add an additional 5 mL of concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.13 Lead solution, stock (1000 mg/L):
Dissolve 1.599 g $\text{Pb}(\text{NO}_3)_2$ in a minimum amount of (1+1) HNO_3 . Add 10 mL of concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.14 Magnesium solution, stock (1000 mg/L):
Dissolve 1.658 g MgO in a minimum amount of (1+1) HNO_3 . Add 10 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.15 Manganese solution, stock (1000 mg/L):
Dissolve 1.000 g of manganese metal in the acid mixture, 50 mL concentrated HCl and 10 mL concentrated HNO_3 , and dilute to 1000 mL with water.
- 5.3.16 Molybdenum solution, stock (1000 mg/L):
Dissolve 2.043 g $(\text{NH}_4)_2\text{MoO}_4$ in water and dilute to 1000 mL.
- 5.3.17 Nickel solution, stock (1000 mg/L):
Dissolve 1.000 g of nickel metal in 50 mL hot concentrated HNO_3 , cool and dilute to 1000 mL with water.
- 5.3.18 Potassium solution, stock (1000 mg/L):
Dissolve 1.907 g KCl , dried at 110°C , in water. Dilute to 1000 mL with water.
- 5.3.19 Selenium solution, stock (1000 mg/L):
Do not dry. Dissolve 1.727 g H_2SeO_3 (actual assay 94.6%) in water and dilute to 1000 mL with water.

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- 5.3.20 Silicon solution, stock (1000 mg/L):
Do not dry. Dissolve 10.1189 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in approximately 500 mL water. Add 20 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.21 Silver solution, stock (1000 mg/L):
Dissolve 1.575 g AgNO_3 in 100 mL of water and 20 mL concentrated HNO_3 . Dilute to 1000 with water.
- 5.3.22 Sodium solution, stock (1000 mg/L):
Dissolve 2.542 g NaCl in water. Add 20 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.23 Thallium solution, stock (1000 mg/L):
Dissolve 1.303 g TlNO_3 in water. Add 20 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.24 Vanadium solution, stock (1000 mg/L):
Dissolve 2.297 g NH_4VO_3 in a minimum amount of concentrated HNO_3 . Heat to increase rate of dissolution. Add 20 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.25 Zinc solution, stock (1000 mg/L):
Dissolve 1.245 g ZnO in a minimum amount of dilute HNO_3 . Add 50 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.26 Bismuth solution, stock (1000 mg/L):
Dissolve 1.1148 g Bi_2O_3 in a minimum amount of concentrated HNO_3 . Add 50 mL concentrated HNO_3 and dilute to 1000 with water.
- 5.3.27 Cerium solution, stock (1000 mg/L):
Dissolve 3.9126 g $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in water. Dilute to 1000 with water.
- 5.3.28 Dysprosium solution, stock (1000 mg/L):
Dissolve 1.1477 g Dy_2O_3 in a minimum amount of hot concentrate HCl . Add 50 mL concentrated HCl and dilute to 1000 with water.
- 5.3.29 Europium solution, stock (1000 mg/L):
Dissolve 1.1579 g Eu_2O_3 in a minimum amount of hot concentrate HCl . Add 50 mL concentrated HCl and dilute to 1000 with water.

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- 5.3.30 Gadolinium solution, stock (1000 mg/L):
Dissolve 1.1526 g Gd_2O_3 in a minimum amount of hot concentrate HCl. Add 50 mL concentrated HCl and dilute to 1000 with water.
- 5.3.31 Lanthanum solution, stock (1000 mg/L):
Dissolve 1.1728 g La_2O_3 in a minimum amount of hot concentrate HCl. Add 50 mL concentrated HCl and dilute to 1000 with water.
- 5.3.32 Lithium solution, stock (1000 mg/L):
Dissolve 5.3243 Li_2CO_3 in a minimum amount of concentrate HCl. Add 50 mL concentrated HCl and dilute to 1000 with water.
- 5.3.33 Neodymium solution, stock (1000 mg/L):
Dissolve 1.1664 Nd_2O_3 in a minimum amount of concentrate HCl. Add 50 mL concentrated HCl and dilute to 1000 with water.
- 5.3.34 Phosphorus solution, stock (1000 mg/L):
Dissolve 4.3937 g KH_2PO_4 in water. Dilute to 1000 with water.
- 5.3.35 Rhenium solution, stock (1000 mg/L):
Dissolve 1.000 g Re powdered metal in a minimum amount of concentrated HNO_3 . Add 50 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.36 Rhodium solution, stock (1000 mg/L):
Dissolve 1.000 g Rh powdered metal in a minimum amount of Hot concentrated H_2SO_4 . Dilute to 1000 mL with water.
- 5.3.37 Ruthenium solution, stock (1000 mg/L):
Dissolve 1.6332 g RuO_4 in water. Dilute to 1000 with water.
- 5.3.38 Strontium solution, stock (1000 mg/L):
Dissolve 1.6849 $SrCO_3$ in a minimum amount of concentrate HCl. Add 50 mL concentrated HNO_3 and dilute to 1000 with water.
- 5.3.39 Tellurium solution, stock (1000 mg/L):
Dissolve 1.2507 g TeO_2 in a minimum amount of concentrated HNO_3 . Add 50 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.40 Thorium solution, stock (1000 mg/L):
Dissolve 1.138 g ThO_2 in a minimum amount of concentrated HNO_3 . Add 50 mL concentrated HNO_3 and dilute to 1000 mL with water.

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- 5.3.41 Titanium solution, stock (1000 mg/L):
Dissolve 1.000 g Ti powdered metal in a minimum amount of dilute (1:1) H_2SO_4 . Dilute to 1000 mL with water.
- 5.3.42 Tungsten solution, stock (1000 mg/L):
Dissolve 1.7942 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in water. Dilute to 1000 with water.
- 5.3.43 Uranium solution, stock (1000 mg/L):
Dissolve 1.1344 g UO_2 in a minimum amount of concentrated HNO_3 . Add 50 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.44 Yttrium solution, stock (1000 mg/L):
Dissolve 1.270 g Y_2O_3 in a minimum amount of Hot concentrated HCl . Add 50 mL concentrated HNO_3 and dilute to 1000 mL with water.
- 5.3.45 Zirconium solution, stock (1000 mg/L):
Place 1.000 g powdered metal Zr in a covered platinum dish and dissolve the metal using 5 mL of water and 1 mL of HF . Once dissolved, the fluoride is removed by adding 1 to 2 mL of sulfuric acid (cold) and evaporating to dryness. Add 5 mL of water and 5 mL concentrated HNO_3 and dissolve the residue in platinum dish. Transfer all of the solution to a 1000 mL volumetric flask. Add 95 mL of concentrated HNO_3 and dilute to 1000 mL with water.

- 5.4 Multianalyte working standards: Following are examples of multianalyte working standards, other analyte combinations may be required as governed by the Statement of Work from the client, with the analysis protocol transmitted to the analyst via Test Instructions. Prepare multianalyte standard solutions by combining and diluting accurately measured volumes of stock solutions. Transfer the multianalyte standard solutions to a clean, labeled, teflon (or polyethylene) bottle. Multianalyte working standards are to be prepared as needed and initially verified using quality control standards. Multianalyte working standards shall be preserved in two percent (by volume) nitric acid or other appropriate preservation as deemed appropriate by the cognizant scientist. All standards shall be stored at room temperature to avoid precipitation. Multianalyte working standards shall be prepared every six months (or more frequently) unless stability can be verified using quality control standards. Record all standards and pipet checking information on Data Sheets or in LRB (project dependent).

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5.4.1 Standard solution #1: (Calibration Blank) 2% v/v HNO₃.
[See 5.5.1].

5.4.2 Multianalyte standard solution #2: (14 elements)

500 µg/mL Mg
250 µg/mL Na
200 µg/mL Fe
50 µg/mL Pb
20 µg/mL Co, Cr, Cu, Ni, Zn, Zr
10 µg/mL Ba, Mo, Sr, Ti
(In 2% v/v HNO₃).

5.4.3 Multianalyte standard solution #3: (10 elements)

500 µg/mL Al, Ca, K
200 µg/mL Si
100 µg/mL P
20 µg/mL B, Li
10 µg/mL Cd, Mn, Na
(In 2% v/v HNO₃).

5.4.4 Multianalyte standard solution #4: (6 elements)

50 µg/mL Dy, Nd, Ru, Th
20 µg/mL Eu, La
(In 2% v/v HNO₃).

5.4.5 Multianalyte standard solution #5: (8 elements)

50 µg/mL As, Ce, Gd, Sb, Te
20 µg/mL V
10 µg/mL Y
1 µg/mL Be
(In 2% v/v HNO₃).

5.4.6 Standard solution #6: (1 element)

500 µg/mL U
(In 2% v/v HNO₃).

5.4.7 System Performance Check Standard: (4 elements)

10 µg/mL Cu, Li, Mn, Zn
(In 2% v/v HNO₃).

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5.4.8 Interference Check Standard (ICS): (16 elements)

500 µg/mL Al, Ca, Mg
200 µg/mL Fe
1 µg/mL Ag, Cd, Ni, Pb, Zn
0.5 µg/mL Ba, Be, Co, Cr, Cu, Mn, V
(In 2% v/v HNO₃).

5.4.9 Instrument Detection Limit Check Standard (IDL): (22 elements)

For each analyte of interest, dilute an accurately measured aliquot of stock reagent and combine together into one solution such that the final concentration will be within three to five times the estimated instrument detection limit for each analyte. Following is an example of a multianalyte standard solution containing all the analytes specified per protocols defined by EPA Method 200.7.

1500 µg/L K
800 µg/L As
375 µg/L Se
300 µg/L Mg, Pb, Tl
250 µg/L Al, Sb
150 µg/L Ni
100 µg/L Ca, Cr, Na, Zn
50 µg/L Co, Fe, V
25 µg/L Ag, Ba, Be, Cd, Cu, Mn
(In 2% v/v HNO₃).

5.4.10.1 Sample Spiking Stock Concentrate (Part 1 of 2): (16 elements)

200 µg/mL As, Ba, Se, Tl
50 µg/mL Co, Mn, Ni, Pb, Sb, V, Zn
25 µg/mL Cu
20 µg/mL Cr
5 µg/mL Ag, Be, Cd
(In 2% v/v HNO₃).

5.4.10.2 Sample Spiking Stock Concentrate (Part 2 of 2): (2 elements)

200 µg/mL Al
100 µg/mL Fe
(In 2% v/v HNO₃).

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5.4.11 Midrange Calibration Verification Standard: Prepare a midrange calibration verification check standard. (23 elements)

25 µg/mL Al, Ca, K, Mg
13 µg/mL Na
20 µg/mL Fe
2.5 µg/mL As, Pb, Sb, Se, Tl
1.0 µg/mL Co, Cr, Cu, Ni, V, Zn
0.5 µg/mL Ag, Ba, Cd, Mn, Sr
0.1 µg/mL Be
(In 2% v/v HNO₃).

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical calibration curve while the method blank (or preparation blank) may be used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing. Method blank correction requirements shall be governed by the Statement of Work from the client, with the analysis protocol transmitted to the analyst via Test Instructions.

5.5.1 The calibration blank shall be prepared by diluting 20 mL of concentrated HNO₃ to 1000 mL with water. The calibration blank is used for instrument calibration (zero concentration standard) and flushing the system between standards and between samples.

5.5.2 The method blank (or preparation blank) must contain all reagents and in the same amounts as used in processing the samples. The method blank shall be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6.0 Calibration

6.1 The system shall be calibrated for each analyte of interest following the manufacturer's recommended calibration procedure provided in the instrument reference manual (See 11.0) and using the Calibration Standards described in Section 5.4 and 5.5. Calibration parameters shall be established and recorded; the performance of the calibration verification standards shall determine the calibration frequency per Section 6.2.

6.2 The Midrange Calibration Verification Standard shall be used to check the working calibration curve daily. The responses for all analytes of interest shall all be within $\pm 10\%$ of the initial calibration values. If this condition is not satisfied, verification shall be repeated. If the results are still greater than $\pm 10\%$ a new

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7.0 Quality Control

7.1 All quality control data shall be maintained and available for easy reference or inspection.

7.2 Minimum quality control requirements.

Note: the statements in Section 6.0 relate to all analytes which are to be reported for a sample group. That is, if all analytes defined in the Statement of Work from the client or in the Test Instructions are to be reported, then verification standards, etc. must exist for all analytes.

7.2.2 All measurements must be within the instrument's linear range where interference correction factors are valid. If they are higher than the linear range covered by the correction factors, the samples shall be diluted, and reanalyzed. Alternatively, a sample measurement of an analyte that exceeds the calibration range may be quantified without dilution provided that an analyte standard of higher concentration than the sample is shown to be linear, within the tolerance limits of Section 6.2 and, the analyte being measured shall not interfere with other analyte measurements in the sample.

7.2.3 The total dissolved solids concentration for a sample must be less than 5,000 mg/L. If it is more concentrated then the sample shall be diluted and reanalyzed.

7.2.4 Analyze a minimum of one method blank for each batch of samples prepared.

7.2.5 Analyze at least one calibration verification standard for every sample batch or more frequently. If results of the calibration verification standard are not within the control boundaries (± 10 percent), the Cognizant Scientist shall determine the corrective action. All samples bracketed by a verification standard that falls outside of control boundaries shall be flagged on the data reports and corrective action documented with the data. Validation of the data is the responsibility of the Technical Group Leader or his designee.

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- 7.2.6 Additional quality control (i.e., duplicates, spikes, additional method or matrix blanks, tighter tolerances, holding times, etc.) is governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the Analytical Request Form (ARF), the project Statement of Work, or the sample analysis Test Instruction (TI).
- 7.2.7 A Quality Control Chart of Mn/Cu-RATIO measurements, using the System Performance Check Standard, shall be maintained and readily available for viewing. Initially the upper control limit (UCL) and lower control limit (LCL), and mean shall be determined by measuring the system performance check standard once a day for a minimum of seven days. The UCL and LCL are determined using three times the standard deviation above and below the mean, respectively. The System Performance Check Standard shall be measured daily prior to calibration using Intensity mode. If the Mn/Cu Ratio falls outside the UCL or LCL it must be re-measured. Failure the second time shall require corrective action as determined by the Cognizant Scientist.
- 7.3 Quality Control for clients requesting compliance with Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) requirements.
- 7.3.1 Analyses shall be performed per protocols defined in Appendix A. Also, all definitions/acronyms (e.g. Sample Delivery Group, SDG) shall be consistent with USEPA CLP SOW 788 [Reference 11] usage. These QC requirements are summarized:

Sample Preparation QC Requirements

- . Spike Sample Analysis (S) - one for every group of samples of a similar matrix type (e.g. water, soil) or for each Sample Delivery Group, whichever is more frequent.
- . Duplicate Sample Preparations - one duplicate for every group of samples of a similar matrix type (e.g. water, soil) or for each Sample Delivery Group, whichever is more frequent
- . Method Blanks or Preparation Blank (PB) - one per Sample Delivery Group or with each batch of samples digested, whichever is more frequent

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- . Interference Check Sample (ICS) - analyzed at the beginning and end of each analysis run or a minimum of twice per 8 hours, whichever is more frequent, but not before Initial Calibration Verification. Analysis results for the ICS must fall within the control limit of $\pm 20\%$ of the true value
- . Instrument Detection Limit (IDL) - determined within 30 days of the start of contract and quarterly thereafter
- . Interelement Corrections - determined prior to the start of contract analyses and at least annually. Correction factors for spectral interference due to Al, Ca, Fe, and Mg shall be determined at all wavelengths used for each analyte reported. Determination must also be performed ~~in~~ if any adjustment was made that may affect the Interelement Corrections
- . Linear Range Analysis (LRA) - determined quarterly. Analytical results must be within $\pm 5\%$ of the true value
- . Multiple dilutions of samples shall be made so that all analytes fall within the calibration range.

7.3.2 Additional quality control requirements shall be governed by the Statement of Work from the client, with the analysis protocol transmitted to the Analyst via Test Instructions.

8.0 Analysis Method

Sample collection, preservation, and preparation are not within the scope of this procedure. However, it is important that samples be collected and preserved in order to maintain sample integrity. The applicability of sample preparation schemes, such as PNL-ALO-101 or PNL-ALO-102, for specific matrices shall be demonstrated by analyzing spiked samples or relevant standard reference material, or by use of other qualifying techniques.

Note 1: Aqueous samples which have been properly preserved (i.e. stabilized at pH < 2) and leachates/digestates from solid samples shall be kept at room temperature to prevent precipitating.

Note 2: Non-acidified samples and solids shall be refrigerated at 4°C ($\pm 2^\circ\text{C}$), radioactivity levels permitting.

Note 3: All samples are to be analyzed within the holding times specified (i.e. CLP SOW 7/88 Section II or the governing SOW)

8.1 Analyze aqueous samples by inserting the sample uptake tube of the instrument into the aqueous sample and initiating an analytical cycle

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by entering the appropriate commands using the instrument's computer keyboard. After a few minutes, the system will display the concentration of all the analytes on the video display terminal, produce a printed copy of the analyte data, and record the analytical results onto magnetic media (floppy disk).

8.2 If the concentration of any of the analytes exceed the calibration range, dilute the sample with an appropriate quantity of acidified water (e.g. 2% v/v HNO_3) and reanalyze.

8.3 Refer to the computer calculated concentration data readout for analyte concentrations.

8.3.1 Aqueous samples: Apply all preparation and analysis dilution factors and report results in mg/L or ppm (or $\mu\text{g/L}$ for CERCLA).

8.3.2 Solid samples: Determine the percent solids using procedure PNL-ALO-504. Calculate and report the concentration in mg/Kg on a dry weight basis:

$$\text{Concentration (mg/Kg)} = (C * V) / (W * (P/100))$$

Where:

C = mg/L analyte in the measured solution
(corrected for all analysis dilutions).

V = Final volume after sample preparation (L)

W = Weight of wet sample (Kg)

P = Percent solids (%)

9.0 Specific Qualifications:

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and quality control standards according to PNL-MA-70, PAP-70-901.

10.0 Records:

Records will be maintained and controlled so as to conform to requirements of ~~PNL ML 70, PAP 70-1701~~ the Analytical Chemistry Lab (ACL) Quality Assurance Plan MCS-033. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with the ~~Act Now Directive 89.1~~ established records management practices.

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8.3 Refer to the computer calculated concentration data readout for analyte concentrations.

8.3.1 Aqueous samples: Apply all preparation and analysis dilution factors and report results in mg/L or ppm (or µg/L for CERCLA).

8.3.2 Solid samples: Determine the percent solids using procedure PNL-ALO-504. Calculate and report the concentration in mg/Kg on a dry weight basis:

$$\text{Concentration (mg/Kg)} = (C * V) / (W * (P/100))$$

Where:

C = mg/L analyte in the measured solution
(corrected for all analysis dilutions).

V = Final volume after sample preparation (L)

W = Weight of wet sample (Kg)

P = Percent solids (%)

9.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and quality control standards according to PNL-MA-70, PAP-70-901.

10.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-ML-70, PAP-70-1701. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with the Act Now Directive 89.1.

11.0 References

EPA Test Method 200.7 CLP-M: "Inductively Coupled Plasma-Atomic Emission Spectroscopy Method for Trace Element Analysis of Water and Wastes" (SOW 3/90: ILM01.0);

ICAP 61 Operator's Manual. January 1988. Thermo Jarrell Ash Corporation. Part Number 125791-01.

USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, SOW 788.

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APPENDIX A

SECTION I

GENERAL QA/QC PRACTICES

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases must also be adhered to. For additional guidelines regarding these general laboratory procedures, see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

SECTION II

SPECIFIC QA/QC PROCEDURES

The quality assurance/quality control (QA/QC) procedures defined herein must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Contractor must also follow these procedures.

NOTE: The cost of performing all QA/QC procedures specified in this Statement of Work is included in the price of performing the bid lot, except for duplicate, spike, and laboratory control sample analyses, which shall be considered separate sample analyses.

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The primary function of the QA/QC program is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by EPA EMSL-Las Vegas. The Contractor can expect to analyze two samples per calendar quarter during the contract period.

The Contractor must perform and report to SMO and EMSL/LV as specified in Exhibit B quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this contract. All the IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Contractor must also report, as specified in Exhibit B, linearity range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this Statement of Work, the term "analytical sample" is used in discussing the required frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit G. As the term is used, analytical sample includes all field samples, including Performance Evaluation samples, received from an external source, but it also includes all required QA/QC samples (matrix spikes, analytical/post-digestion

spikes, duplicates, serial dilutions, LCS, ICS, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB, CCV/CCB). A "frequency of 10%" means once every 10 analytical samples. Note: Calibration verification samples (ICV/CCV) and calibration verification blanks (ICB/CCB) are not counted as analytical samples when determining 10% frequency.

In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their QA/QC analysis must be analyzed under the same operating and procedural conditions.

If any QC measurement fails to meet contract criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Contractor must report all QC data in the exact format specified in Exhibits B and H.

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as described in this Exhibit:

1. Instrument Calibration
2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)
3. CRDL Standards for AA (CRA) and ICP (CRI)
4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
5. ICP Interference Check Sample (ICS) Analyses
6. Spike Sample Analysis (S)
7. Duplicate Sample Analysis (D)
8. Laboratory Control Sample (LCS) Analysis
9. ICP Serial Dilution Analysis (L)
10. Instrument Detection Limit (IDL) Determination
11. Interelement Corrections for ICP (ICP)
12. Linear Range Analysis (LRA)
13. Furnace AA QC Analyses

1. Instrument Calibration

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis must be given in the raw data.

Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be within $\pm 5\%$ of the true value. Each standards concentration and the calculations to show that the $\pm 5\%$ criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary.

The $\pm 5\%$ criteria does not apply to the atomic absorption calibration standard at the CRDL.

Calibration standards for AA procedures must be prepared as described in Exhibit D.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification and blank check; resloping is acceptable as long as it is immediately preceded and immediately followed by CCV and CCB. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.

2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

a. Initial Calibration Verification (ICV)

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses (in Exhibit E), the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used for analysis. For CN, the initial calibration verification standard must be distilled. The Initial Calibration Verification for CN serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV. The values for the initial and subsequent continuing calibration verifications shall be recorded on FORM II-IN for ICP, AA, and cyanide analyses, as indicated.

b. Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions
2. NBS SRM 1643a
3. A Contractor-prepared standard solution

TABLE 1. INITIAL AND CONTINUING CALIBRATION VERIFICATION CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	% of True Value (EPA Set)	
		Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for a Case of samples received.

Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it as well as the difference in time between the CCV and the analytical sample immediately preceding it may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of preceding 10 analytical samples or all analytical samples analyzed since the last good calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP, AA and cyanide as indicated.

3. CRDL Standards for ICP (CRI) and AA (CRA)

To verify linearity near the CRDL for ICP analysis, the Contractor must analyze an ICP standard (CRI) at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.

To verify linearity near the CRDL for AA analysis, the Contractor must analyze an AA standard (CRA) at the CRDL or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the Initial Calibration Verification.

Specific acceptance criteria for the two standards will be set by EPA in the future. In the interim, the Contractor must analyze and report these Standards on FORM II(PART 2)-IN.

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses

a. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours

during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run. The results for the calibration blanks shall be recorded on FORM III-IN for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the calibration blank result exceeds the IDL, the result must be so reported in ug/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the CRDL (Exhibit C), terminate analysis, correct the problem, recalibrate, verify the calibration and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration blank.

b. Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch¹ of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM III-IN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

- 1) If the absolute value of the concentration of the blank is less than or equal to the Contract Required Detection Limit (Exhibit C), no correction of sample results is performed.
- 2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.
- 3) If the concentration of the blank is below the negative CRDL, then all samples reported below 10x CRDL associated with the blank must be redigested and reanalyzed.

¹A group of samples prepared at the same time.

The values for the preparation blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples on FORM III-IN for ICP, AA, and cyanide analyses.

5. ICP Interference Check Sample (ICS) Analysis

To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Samples must be obtained from EPA (EMSL/LV) if available and analyzed according to the instructions supplied with the ICS.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of $\pm 20\%$ of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all contract specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

If the ICP Interference Check Sample is not available from EPA, independent ICP Check Samples must be prepared with interferent and analyte concentrations at the levels specified in Table 2-Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample. The mean value and standard deviation must be established by initially analyzing the Check Samples at least five times repetitively for each parameter on FORM IV-IN. Results must fall within the control limit of $\pm 20\%$ of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the Interference Check Sample analyses must be recorded on FORM IV-IN for all ICP parameters.

TABLE 2. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(ng/L)	Interferents	(ng/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

6. Spike Sample Analysis (S)

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps (i.e., CN-). At least one spike sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.²

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see section 7, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

The analyte spike must be added in the amount given in Table 3-Spiking Levels for Spike Sample Analysis, for each element analyzed. If two analytical methods are used to obtain the reported values for the same element within a Sample Delivery Group (i.e. ICP, GFAA), spike samples must be run by each method used.

²EPA may require additional spike sample analysis, upon Project Officer request, for which the Contractor will be paid.

If the spike recovery is not at or within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on FORMs I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

For flame AA, ICP, and CN analyses, when the pre-digestion/pre-distillation spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, a post-digestion/post-distillation spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. Results of the post-digestion/post-distillation spike must be reported on FORM V(PART 2)-IN. Note: No post digest spike is required for Hg.

In the instance where there is more than one spike sample per matrix and concentration per method per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix, level, and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

$$\% \text{Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

Where, SSR - Spiked Sample Result
SR - Sample Result
SA - Spike Added

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive or negative) must be reported on FORM V-IN for ICP, AA and cyanide analyses, as indicated.

The units for reporting spike sample results will be identical to those used for reporting sample results in FORM I-IN (i.e., ug/L for aqueous and mg/Kg dry weight basis for solid).

TABLE 3. SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS

Element	For ICP/AA (ug/L)		For Furnace AA (ug/L)		Other ⁽¹⁾ (ug/L)
	Water	Soil ⁽²⁾	Water	Soil	
Aluminum	2,000	*			
Antimony	500	500	100	100	
Arsenic	2,000	2,000	40	40	
Barium	2,000	2,000			
Beryllium	50	50			
Cadmium	50	50	5	5	
Calcium	*	*			
Chromium	200	200			
Cobalt	500	500			
Copper	250	250			
Iron	1,000	*			
Lead	500	500	20	20	
Magnesium	*	*			
Manganese	500	500			1
Mercury					
Nickel	500	500			
Potassium	*	*			
Selenium	2,000	2,000	10	10	
Silver	50	50			
Sodium	*	*			
Thallium	2,000	2,000	50	50	
Vanadium	500	500			
Zinc	500	500			100
Cyanide					

NOTE: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

¹Spiking level reported is for both water and soil/sediment matrices.

²The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

*No spike required.

7. Duplicate Sample Analysis (D)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.³ Duplicates cannot be averaged for reporting on FORM I-IN.

Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. EPA may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group (i.e., ICP, GFAA), duplicate samples must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where, RPD = Relative Percent Difference
S = First Sample Value (original)
D = Second Sample Value (duplicate)

The results of the duplicate sample analyses must be reported on FORM VI-IN in ug/L for aqueous samples and mg/Kg dry weight basis for solid original and duplicate samples. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x CRDL (Exhibit C). A control limit of ($\pm$) the CRDL must be used for sample values less than 5x CRDL, and the absolute value of the control limit (CRDL) must be entered in the "Control Limit" column on FORM VI-IN.

If one result is above the 5x CRDL level and the other is below, use the $\pm$ CRDL criteria. If both sample values are less than the IDL, the RPD is not calculated on FORM VI-IN. For solid sample or duplicate results < 5x CRDL, enter the absolute value of the CRDL, corrected for sample weight and percent solids, in the "Control Limit" column.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on FORMs I-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix, concentration, and method in the SDG. The percent difference data will be used by EPA to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to FORM VI-IN at a later date based on these precision results.

³EPA may require additional duplicate sample analyses, upon Project Officer request, for which the Contractor will be paid.

8. Laboratory Control Sample (LCS) Analysis

Aqueous and solid Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration Verification Solutions may be used). One aqueous LCS must be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group, or for each batch of aqueous samples digested, whichever is more frequent. An aqueous LCS is not required for mercury and cyanide analysis.

The EPA-provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be prepared and analyzed for every group of solid samples in a Sample Delivery Group, or for each batch of samples digested, whichever is more frequent.

All LCS results and percent recovery (%R) will be reported on FORM VII-IN. If the percent recovery for the aqueous LCS falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

9. ICP Serial Dilution Analysis (I)

Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not at or within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

where, I - Initial Sample Result

S - Serial Dilution Result (Instrument Reading x 5)

In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix and concentration in the Sample Delivery Group. Serial dilution results and "E" flags must be reported on FORM IX-IN.

10. Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed under this contract, the instrument detection limits (in ug/L) must be determined for each instrument used, within 30 days of the start of contract analyses and at least quarterly (every 3 calendar months), and must meet the levels specified in Exhibit C.

The Instrument Detection Limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-5x the instrument manufacturer's suggested IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined IDL for an instrument must always be used as the IDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

IDLs must be reported for each instrument used on FORM X-IN submitted with each data package. If multiple AA instruments are used for the analysis of an element within a Sample Delivery Group, the highest IDL for the AAs must be used for reporting concentration values for that Sample Delivery Group. The same reporting procedure must be used for multiple ICPs.

11. Interelement Corrections for ICP

Before any field samples are analyzed under this contract, the ICP interelement correction factors must be determined prior to the start of contract analyses and at least annually thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. Results from interelement correction factors determination must be reported on FORM XI(PART 1)-IN and FORM XI(PART 2)-IN for all ICP parameters.

12. Linear Range Analysis (LRA)

For all ICP analyses, a linear range verification check standard must be analyzed and reported quarterly (every 3 calendar months) for each element on FORM XII-IN. The standard must be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard must be within $\pm 5\%$ of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

13. Furnace Atomic Absorption (AA) QC Analyses

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1-Furnace AA Analysis Scheme ("MSA Tree") will be required for quantitation. (These procedures do not replace those in Exhibit D of this SOW, but supplement the guidance provided therein.)

- a. All furnace analyses must fall within the calibration range. In addition, all analyses, except during full methods of Standard Addition (MSA), will require duplicate injections. The absorbance or concentration of each injection must be reported in the raw data as well as the average absorbance or concentration values and the relative standard deviation (RSD) or coefficient of variation (CV). Average concentration values are used for reporting purposes. The Contractor must be consistent per method and SDG in choosing absorbance or concentration to evaluate which route is to be followed in the MSA Tree. The Contractor must also indicate which of the two is being used if both absorbance and concentration are reported in the raw data. For MSA analysis, the absorbance of each injection must be included in the raw data. A maximum of 10 full sample analyses to a maximum 20 injections may be performed between each consecutive calibration verifications and blanks. For concentrations greater than CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the analytical sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value reported on FORM I-

IN with an "M". The "M" flag is required for the analytical spike as well as the sample. If the analytical spike for a sample requires an "M" flag, the flag must be reported on FORM I- IN for that sample.

- b. All furnace analyses for each analytical sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike¹ will be required to be at a concentration (in the sample) 2x CRDL. This requirement for an analytical spike will include the LCS and the preparation blank. (The LCS must be quantitated from the calibration curve and corrective action, if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85-115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses (see item 6, this section), will then determine how the sample will be quantitated, as follows:

- 1) If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.
- 2) If the spike recovery is greater than or equal to 40% and the sample absorbance or concentration is less than 50% of the "spike"⁵, report the sample results to the IDL. If the spike recovery is less than 85% or greater than 115%, flag the result with a "W".
- 3) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is at or

¹Analytical Spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

⁵"Spike" is defined as [absorbance or concentration of spike sample] minus [absorbance or concentration of the sample].

between 85% and 115%, the sample must be quantitated directly from the calibration curve and reported down to the IDL.

- 4) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

c. The following procedures will be incorporated into MSA analyses.

- 1) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.
- 2) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

- 3) For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.
- 4) Spikes must be prepared such that:
 - a) Spike 1 is approximately 50% of the sample absorbance or concentration.
 - b) Spike 2 is approximately 100% of the sample absorbance or concentration.
 - c) Spike 3 is approximately 150% of the sample absorbance or concentration.
- 5) The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data. The results must be reported on FORM VIII-IN. Reported values obtained by MSA must be flagged on the data sheet (FORM I-IN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.
- 6) If the correlation coefficient (r) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, report the results on FORM I-IN from the run with the best "r" and flag the result with a "+" on FORM VIII-IN and FORM I-IN.

Figure 1
FURNACE ATOMIC ABSORPTION ANALYSIS SCHEME

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-212, DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

APPLICABILITY

This procedure is applicable for determining the concentration of several inorganic anions (i.e., F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , and SO_4^{2-}) in aqueous samples and leachates from solids (e.g., soils and sediments). The methodology is comparable to EPA Method 300.0. Solid samples shall be subjected to an appropriate leaching procedure prior to analysis, such as PNL-ALO-103 or PNL-ALO-108.

DEFINITIONS/ACRONYMS

Batch - group of samples of similar matrix prepared and analyzed as a set.

Cal - calibration standard used to initially calibrate the ion chromatograph (IC).

Ver - calibration verification check standard used to verify the initial calibration. The Ver standard is obtained/prepared from a source that is independent from the Cal standard.

RESPONSIBLE STAFF

Cognizant Scientist
Technician/Analyst

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

Author <i>MW Urie</i> MW Urie	Date 12-4-92	Project Mgr. <i>TY Hosaka</i> TY Hosaka	Date	QP Representative <i>TL Ehlert</i> TL Ehlert	Date 12/4/92
Technical Reviewer <i>MC Burt</i> MC Burt	Date 12/4/92	Line Mgr. <i>AG King</i> AG King	Date 12/6/92	Other	Date
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- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Summary of Method

Ion chromatography is a rapid, multi-ion method for analyzing anions in a small volume (typically 5 mL) of sample solution. The method utilized in this procedure is based on separation of the anions on an anion exchange column, suppression of eluent conductivity by a cation exchange membrane, and conductimetric detection of the separated anions as they pass through a small conductivity cell. The increase in conductivity caused by each anion is recorded and the anion concentrations are determined by comparison with detector responses from standard solutions. The anions are identified by their retention time, the time required for the anion peak to appear following injection.

Ion chromatography is an evolving technique which often requires operational modifications for optimal performance for unusual matrices. In the interest of introducing changes or modifications in a timely manner, the changes will be documented in the sample records when such changes are of a non-permanent nature and documented by ICN when the changes are to be permanent. When required by the client, notification of such changes will be made in writing.

3.0 Interferences

- 3.1 Substances with retention times that are similar to and overlap those of the anion of interest can cause interference. It is difficult to correct or compensate for interference caused by such substances without changing analytical conditions, such as column, eluent, etc.
- 3.2 Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution can be used to solve most of this type of interference problems.
- 3.3 The water dip or negative peak which elutes near (and can interfere with) the fluoride peak can be eliminated by the addition of the equivalent of 1 mL of 100X concentrated eluent to 100 mL of each standard or sample.
- 3.4 Method interferences may be caused by contamination in the reagent water, reagents, glassware, and other sample processing apparatus

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that lead to discrete artifacts or elevated baseline in ion chromatograms.

- 3.5 Samples and reagent solutions that contain particles larger than 0.45 can damage columns and flow apparatus. Filtration may be required for visually turbid samples.
- 3.6 Retention time is affected by concentration. Late eluting anions, such as nitrate and sulfate, exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration can reduce resolution or lead to misidentification.
- 3.7 Weak organic acids (e.g., formic, acetic) can coelute with the fluoride and chloride. A weaker eluent or a gradient elution program is required to eliminate this type of interference.
- 3.8 Maintain the maximum separator column loading below 400 $\mu\text{g/mL}$ (for all anions), since nonlinear response can result from exceeding the column capacity.

4.0 Apparatus

- 4.1 Ion chromatograph system: Analytical system complete with ion chromatograph and all required accessories including analytical columns, compressed air, detector, and recorder/plotter (Dionex 2000 series, or equivalent). A data system is recommended for peak integration.
- 4.2 Balance: Analytical, capable of weighing to the nearest 0.001 g.
- 4.3 Anion separator column: Dionex IonPac AS4A, or equivalent.
- 4.4 Anion guard column: Dionex IonGuard AG4A, or equivalent.
- 4.5 Anion suppressor column: Dionex AMMS, or equivalent.
- 4.6 Conductivity detector: 6 μL volume, Dionex, or equivalent.
- 4.7 Micropipet: 5 to 10,000 μL , as required.
- 4.8 Autosampler: (Optional) Dionex, low-volume, pressure delivery, or equivalent.

5.0 Reagents and Standards

Guidelines for the preparation of standards and reagents are given below. The cognizant scientist may implement changes when required; such changes will be documented in the sample record.

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- 5.1 Deionized water: Water shall be used for sample, standard and reagent dilutions such that no anions above the method detection limit are found in it.
- 5.2 Eluent solution (0.00175 M NaHCO_3 + 0.00185 M Na_2CO_3): Dissolve 0.588 g sodium bicarbonate (NaHCO_3) and 0.784 g sodium carbonate (Na_2CO_3) in water and dilute to 4.00 L.
- 5.3 Suppressor regeneration solution (0.025 N H_2SO_4): Dilute 2.8 mL of concentrated sulfuric acid with water to 4.0 L.
- 5.4 Stock standard solutions (1000 mg/L): Preferred: Procure certified aqueous stock standards from a supplier and verify by comparison with a second standard. Alternative: Prepare stock standard solutions from reagent grade materials as described below. Solid sources used for standard preparation will be stored in a dessicator when not being used. Dilute working standards should be prepared from stock standard solutions as needed [See Sections 5.5 and 6.3]. All anion stock standard solutions must be stored under refrigerated conditions.
 - 5.4.1 Bromide (1000 $\mu\text{g Br}^-/\text{mL}$): Dissolve 0.1286 g sodium bromide (NaBr) in water and dilute to 100.0 mL.
 - 5.4.2 Chloride (1000 $\mu\text{g Cl}^-/\text{mL}$): Dissolve 0.1649 g sodium chloride (NaCl) in water and dilute to 100.0 mL.
 - 5.4.3 Fluoride (1000 $\mu\text{g F}^-/\text{mL}$): Dissolve 0.2210 g sodium fluoride (NaF) in water and dilute to 100.0 mL.
 - 5.4.4 Nitrate (1000 $\mu\text{g NO}_3^-/\text{mL}$): Dissolve 0.1371 g sodium nitrate (NaNO_3) in water and dilute to 100.0 mL.
 - 5.4.5 Nitrite (1000 $\mu\text{g NO}_2^-/\text{mL}$): Dissolve 0.1499 g sodium nitrite (NaNO_2) in water and dilute to 100.0 mL.
 - 5.4.6 Phosphate (1000 $\mu\text{g PO}_4^{3-}/\text{mL}$): Dissolve 0.1263 g monobasic sodium phosphate (NaH_2PO_4) in water and dilute to 100.0 mL.
 - 5.4.7 Sulfate (1000 $\mu\text{g SO}_4^{2-}/\text{mL}$): Dissolve 0.1479 g sodium sulfate (Na_2SO_4) in water and dilute to 100.0 mL.
- 5.5 Multianalyte working standards: For each analyte of interest, prepare calibration standards at a minimum of three concentration levels by adding accurately measured volumes of one or more of the stock standards and diluting to the appropriate volume with water. Deionized water [See Section 5.1] is used as a blank. The standards should define the working range of the detector. Standards should be made every two weeks or as required, based on

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results from the calibration verification check standards [See Section 6.3]. All anion working standards must be stored under refrigerated conditions.

Calibration & Verification Standards Preparation Guideline

	F ⁻ (μg/mL)	Cl ⁻ (μg/mL)	NO ₂ ⁻ (μg/mL)	Br ⁻ (μg/mL)	NO ₃ ⁻ (μg/mL)	PO ₄ ⁻³ (μg/mL)	SO ₄ ⁻² (μg/mL)
Cal 1	0.25	0.25	0.5	0.25	0.5	0.5	0.5
Cal 2	0.50	0.50	1.0	0.50	1.0	1.0	1.0
Cal 3	1.00	1.00	5.0	1.00	5.0	5.0	5.0
Cal 4	2.50	2.50	10.0	2.50	10.0	10.0	10.0
Cal 5	5.00	5.00	20.0	5.00	20.0	20.0	20.0
Cal 6	7.50	7.50	30.0	7.50	30.0	30.0	30.0
Ver H	6.00	6.00	25.0	6.00	25.0	25.0	25.0
Ver M	4.00	4.00	15.0	4.00	15.0	15.0	15.0
Ver L	1.50	1.50	5.0	1.50	5.0	5.0	5.0

The Ver H, M and L are the high-, mid- and low-range calibration verification check standards which are prepared from secondary stock aqueous standards or solids as described in Step 5.4.

Note: The calibration (Cal) and calibration verification check standards (Ver) shall be obtained and/or prepared from different sources.

6.0 Calibration

- 6.1 The system shall be calibrated for each anion of interest using the Calibration Standards from Section 5.5. Calibration parameters shall be established and recorded; the performance of the calibration verification check standards shall determine the calibration frequency per Section 6.3. The same injection volume will be used on samples analyzed using this calibration curve.
- 6.2 Using injections of each calibration standard [Section 5.5, Calibration Standards], tabulate the peak height or peak area response against concentration. The results shall be used to prepare a calibration curve for each analyte. This becomes the working calibration curve.
- 6.3 The working calibration curve shall be verified each working day or whenever the anion eluent is changed, and after at least every 10 samples. The responses and retention times for analytes shall be within ±10% (±15% for F⁻ and Cl⁻ retention times) of the verification standard's nominal values. If this condition is not satisfied, the verification run shall be repeated. If the results

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are still greater than $\pm 10\%$ ($\pm 15\%$ for F^- and Cl^- retention times), new calibration curves may need to be generated.

NOTE: It is possible that a sample matrix may affect analyte quantitation in a reversible manner. The interpretation of the cognizant scientist can override the need for recalibration if operations such as column cleanup will recover calibration quality.

7.0 Quality Control

7.1 All quality control data shall to be maintained and available for easy reference or inspection.

7.2 Minimum quality control requirements.

7.2.1 Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest calibration standard.

7.2.2 When appropriate, analyze a minimum of one method blank per sample group (typically 10 samples) or one for each batch of samples prepared, whichever is more frequent.

7.2.3 Analyze at least one calibration verification check standard prior to beginning sample analyses after every 10 samples, and at the end of the analysis run. If results of the calibration verification check standard is not within the control boundaries established [See Section 6.3], the Cognizant Scientist shall determine the corrective action. All samples within the previously analyzed sample group shall be flagged on the data reports and the corrective action documented with the data. Validation of the data is the responsibility of the Technical Group Leader or Cognizant Scientist.

7.2.4 Additional quality control (i.e., duplicates, spikes, additional system or matrix blanks, etc.) is governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the Analytical Request Form (ARF), the project Statement of Work, or the sample analysis Test Instruction (TI).

7.3 Quality Control for clients requesting compliance with Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) requirements.

7.3.1 Samples and standards shall be analyzed per protocols defined by EPA 300.0. These QC requirements are:

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Sample Preparation QC Requirements

- Duplicate Sample Preparations - one per 10 samples or per batch of similar matrix, whichever is smaller.
- Method Blanks - one per 10 samples or per batch of similar matrix, whichever is smaller.
- Matrix Spikes - one per 10 samples or per batch of similar matrix, whichever is smaller.
- Matrix Spike Duplicates - one per 20 samples or per batch of sample matrix, whichever is smaller.

Anion Analysis QC Requirements

- At a minimum, a four point calibration shall be used in the initial calibrating for each analyte.
- A calibration verification check sample shall be run before analyses begin, after every 10th sample, and at the end of the analysis run.
- A deionized water blank shall be run after each calibration verification check sample is run.
- Multiple dilutions of samples shall be made so that all analytes fall within their instrument calibration range.

7.3.2 Additional quality control requirements shall be governed by the Statement of Work from the client, with the analysis protocol transmitted to the Analyst via Test Instructions.

8.0 Analysis Method

8.1 Sample collection and preservation: All samples shall be refrigerated at 4°C ($\pm 2^\circ\text{C}$), radioactivity levels permitting, and analyzed within the hold times specified either by EPA Method 300.0 (i.e., 48 hours for NO_2^- , NO_3^- , and PO_4^{3-} and 28 days for the other anions) or the governing SOW.

8.2 Solids preparation: Solids (e.g., soils and sediments) shall be prepared according to PNL-ALO-103 or PNL-ALO-108 as directed by the TI, ARF, or SOW. If no direction is provided, the Cognizant Scientist shall determine the appropriate solid preparation method. The applicability of other sample preparation techniques for like or other matrices shall be demonstrated by analyzing spiked samples

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and/or relevant standard reference materials. Solid sample leachates shall be refrigerated at 4°C (±2°C), radioactivity levels permitting, and analyzed within the holding times specified.

- 8.3 Load and inject an aliquot of the sample. Record the resulting peak height or area.

NOTE: For all injections within a batch, the size of the sampling loop should be the same for calibration, verification, and sample analyses.

NOTE: The experience of the Cognizant Scientist should be weighed heavily in the interpretation of chromatograms; specifically peak shapes, retention times, overlapped peaks and detector responses.

- 8.4 If the response of the peak exceeds the calibration range, dilute the sample with an appropriate quantity of water and reanalyze.
- 8.5 If the resulting chromatogram fails to produce adequate resolution or if identification of specific anions is questionable, the sample may be spiked, if possible, with an appropriate quantity of standard and reanalyzed.
- 8.6 Refer to the separate calibration curves for each anion of interest [See Section 6]. Compute sample concentration by comparing sample peak response with the standard curve.

8.6.1 Aqueous samples: Apply all dilution factors and report results in µg/mL.

8.6.2 Solid samples: Determine the percent solids using procedure PNL-ALO-504. Apply all dilution factors to the leachate. Calculate and report the concentration in mg/kg on a dry weight basis:

$$\text{Concentration (mg/kg)} = (C * V) / (W * (P/100))$$

Where:

C = µg/mL anion in the measured solution (corrected for any analysis dilution)

V = Final volume after sample preparation (L)

W = Weight of wet sample (kg)

P = Percent solids (%).

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9.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and quality control standards according to PNL-MA-70, PAP-70-901.

10.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with established records management practices.

11.0 References

EPA Test Method 300.0. September, 1991. "The Determination of Inorganic Anions in Water by Ion Chromatography," EPA-600/4-84-017.

ASTM Standard Test Method D4327-84. 1984. "Anions in Water by Ion Chromatography."

AI450 Software Reference Manual. July 1990, or later version. Dionex Corp. Document 034039, Revision 05 or higher.

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INTERIM CHANGE NOTICE
ICN

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<p>A. Document Number: <u>PNL-ALO-213.1</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Mercury in Water, Solids and Sludges By</u> <u>Manual Cold Vapor Technique</u></p> <p>Document's Original Author <u>JJ Wagner</u></p>	<p>Effective Date of ICN: _____</p> <p>Change Requested by: <u>RM Nipper</u></p>
<p>B. Action: <u>Replace pages 11 & 12 with the attached pages 11 & 12.</u></p>	
<p>C. Effect of Change: <u>This change will give a more accurate records requirements resource.</u></p>	
<p>D. Reason for Change/Description of Change: Reason: 1. <u>Deletes inaccurate information.</u></p> <p>Description: 1. <u>Replaced: PNL-MA-70, PAP-70-1701 with Analytical Chemistry Lab (ACL) Quality Assurance Plan (QAP) MCS-033.</u></p> <p>2. <u>Replaced: "LRB's will be used inaccordance with the ACT Now Directive 89.1" with "LRB's will be used in accordance with established records management practices."</u></p>	
<p>E. Approval Signatures: (Please Sign and Date)</p>	<p>Type of Change (Check (✓) one) (✓) Minor Change () Major Change</p>
<p>QP Concurrence: <u>TL Ehlert</u> <i>TL Ehlert</i> Date: <u>2/13/93</u></p> <p>Approval Authority: <u>AG King</u> <i>AG King</i> Date: <u>2/17/93</u></p> <p>Other Approvals: <u>MW Urie</u> <i>MW Urie</i> Date: <u>2/12/93</u></p> <p>: _____ Date: _____</p>	

PNL TECHNICAL PROCEDURE

TITLE: PNL-AO-213, MERCURY IN WATER, SOLIDS, AND SLUDGES BY MANUAL COLD VAPOR TECHNIQUE

APPLICABILITY

This procedure is applicable for determining the concentration of total mercury (organic and inorganic) in water, soils, sediments and sludge type materials. The methodology is comparable to CLP SOW 788 Methods 245.1 and 245.5.

DEFINITIONS

Batch: A group of samples of similar matrix prepared at the same time.

RESPONSIBLE STAFF

**Cognizant Scientist
Technician**

PROCEDURE

1.0 Summary of Method

- 1.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a single pass system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded.
- 1.2 The method detection limit is 0.01 $\mu\text{g Hg}$. Using the nominal sample sizes of 50 mL for waters and 0.2 g for soils/sludges, the detection limits are 0.2 $\mu\text{g/L}$ and 0.05 mg/Kg, respectively.

Author <i>MWJhu</i>	Date <i>3/27/91</i>	Project Mgr. <i>B. N. Gellgren</i>	Date <i>3-26-91</i>	QAD Representative <i>G. K. K.</i>	Date <i>3/26/91</i>
Technical Reviewer <i>Radumanabhan Melethil</i>	Date <i>3/27/91</i>	Line Mgr. <i>[Signature]</i>	Date <i>3-26-91</i>	Other	Date
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2.0 Interferences

- 2.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide have been shown to have no effect on recovery of mercury from spiked samples.
- 2.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have been shown to have no effect on recovery of mercury from spiked samples.
- 2.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate. Care must be taken to assure that free chlorine, which absorbs radiation of 253 nm, is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent.
- 2.4 Samples containing high concentrations of oxidizable organic materials may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate used in the digestion.
- 2.5 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or airborne mercury contamination.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified via the following: 1) a tolerance limit is stated with a measurement value, or 2) the following system of tolerances shall be in effect:

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL.

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- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

4.0 Apparatus

- 4.1 Atomic Absorption Spectrophotometer: Any atomic absorption unit having an open sample presentation area for mounting the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.
- 4.2 Mercury hollow cathode lamp or electrodeless discharge lamp (EDL).
- 4.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable; multi-pen is recommended.
- 4.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing (1" O.D. x 4.5" length). The ends are ground perpendicular to the longitudinal axis and quartz windows (1" O.D. x 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.
- 4.5 Compressed Air: Regulated, industrial grade.
- 4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.
- 4.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.
- 4.8 Drying Tube: Containing magnesium perchlorate; typically 20 g in tube 6" long by 3/4" diameter.
- 4.9 Pipets: Calibrated, with disposable tips, sized from 5 to 1000 μL , as required.

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- 4.10 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

5.0 Reagents

- 5.1 Sulfuric Acid (H_2SO_4), Concentrated: Reagent grade of low mercury content as indicated by absence of mercury in the preparation blank.

- 5.2 Nitric Acid (HNO_3), Concentrated: Reagent grade of low mercury content as indicated by the absence of mercury in the preparation blank.

Note: If a high reagent blank is obtained, it may be necessary to purify the nitric acid by distillation.

- 5.3 Hydrochloric Acid (HCl), 0.5 N: Add 20 mL of concentrated HCl carefully to 400 mL of water then dilute to 500 mL.

- 5.4 Stannous Chloride Solution: Add 25 g SnCl_2 to 250 mL of 0.5 N HCl .

Note: A 10% solution of stannous sulfate in 0.5 N H_2SO_4 may be used in place of SnCl_2 . However, this mixture is a suspension and requires continuous stirring during use.)

- 5.5 Sodium Chloride-Hydroxylamine Hydrochloride Solution: Dissolve 12 g of NaCl and 12 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in water and dilute to 100 mL.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

- 5.6 Potassium Permanganate Solution: 5% solution, w/v. Dissolve 5 g of KMnO_4 in 100 mL of distilled water.

- 5.7 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of $\text{K}_2\text{S}_2\text{O}_8$ in 100 mL of distilled water.

- 5.8 Stock Mercury Standard Solution: Dissolve 0.1354 g of mercuric chloride (HgCl_2) in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL. [1 mL - 1 mg Hg].

- 5.9 Working Mercury Standard Solution: Make successive dilutions of the stock mercury standard solution [See 5.8] to obtain a working standard containing 0.1 $\mu\text{g/mL}$. This working standard, as well as

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the dilutions of the stock mercury standard solution, shall be prepared fresh daily. Acidity of the working standard shall be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. [1 mL - 1 μ g Hg].

6.0 Quality Control

6.1 All quality control data shall be maintained and available for easy reference or inspection.

6.2 Minimum quality control requirements

6.2.1 A minimum of four calibration standards and one measurement blank are required for calibration [See section 7.2.1].

6.2.2 Samples shall be redigested and reanalyzed if they are more concentrated than the highest standard which is within the calibration range.

6.2.3 At least one quality control standard shall be analyzed with each batch/group of samples, or at a minimum, once during daily operation. A sample batch/group contains ≤ 20 samples. If the result of the QC standard is not within 80% to 120% of the mean value, the Cognizant Scientist shall determine and document the corrective action. Validation of the data is the responsibility of the technical group leader.

6.2.4 It is not necessary that all standards be digested in like manner to the samples. For calibration verification, undigested mid-range verification standards shall be analyzed every 10-15 samples. If the verification standard does not agree to within 85% to 115% of the mean value, the Cognizant Scientist shall determine and document the corrective action. Validation of the data is the responsibility of the technical group leader.

5.2.4 Additional quality control (e.g., duplicates, spikes, additional system blanks or matrix blanks, tighter tolerances, hold time requirements, etc.) is governed by the analytical requirements of the project or specific analysis requested. These additional QC requirements are provided by the Analytical Request Form (ARF) or the project Statement of Work (SOW) and transmitted to the analyst via Test Instructions (TI).

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6.3 Quality control for clients requesting compliance with CERCLA requirements. Note: All definitions/acronyms (e.g. Sample Delivery Group, SDG) shall be consistent with USEPA CLP SOW 788 [Reference 10] usage.

6.3.1 A minimum of four calibration standards and one blank are required for the calibration of the atomic absorption system [See 7.2.1].

6.3.2 A minimum of one methods blank, one duplicate and one matrix spike shall be prepared and analyzed for every sample batch of similar matrix type. Spikes shall be added at the time of sample preparation.

6.3.2.1 The methods blank shall be a water sample processed through each preparation and analysis step. Note: If the methods blank is not $\leq$ the requested detection limit (from the SOW, ARF, or TI), then all samples in the batch associated with the methods blank shall be prepared and analyzed again.

6.3.2.2 The duplicate samples shall have a relative percent difference (RPD) control limit less than or equal to the required precision (from the SOW, ARF or TI) if the sample values are $>5x$ the requested detection limit. If no required precision is given, the RPD shall be $\leq 20\%$.

Note: If the sample values are $<5x$ the requested detection limit, a control limit of $\pm$ the detection limit shall be used. This criterial also applies if one result is $>5x$ and one $<5x$.

Note: If the RPD is outside control limits, flag all samples in the batch/group with an asterisk (*).

$$\text{Note: } RPD = \frac{|S - D|}{(S + D)/2} * 100$$

Where, S = Original sample value
D = Duplicate sample value

6.3.2.3 The matrix spike is added to a replicate sample prior to any preparation or analysis. The spike, which is prepared from the stock, is added in such manner as to add $0.1 \mu\text{g Hg}$ to the replicate.

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Note: Spike recoveries shall be within the limits of 75% to 125%. If this recovery is not met, then the results for each sample in the batch/group shall be flagged with an "N". In the event the sample results exceed the spike by 4x no flag is necessary.

$$\text{Note: \%Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} * 100$$

Where, SSR = Spiked Sample Results
SR = Sample Results
SA = Spike Added

Note: The units for reporting the spike sample results shall be identical to those used for reporting the sample results (i.e., $\mu\text{g/L}$ for aqueous and mg/Kg dry weight basis for solids).

- 6.3.3 An initial calibration verification standard (ICV) shall be analyzed immediately following calibration.
Note: The ICV result shall be within $\pm 20\%$ of the true value. If the measurement is outside the limit, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

- 6.3.4 At a minimum, a continuing calibration verification (CCV) standard shall be analyzed at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent.

Note: The CCV is made from the stock standard and diluted to a concentration at or near the mid-range of the calibration curve.

Note: The CCV result shall be within $\pm 20\%$ of the true value. If the measurement is outside the limit, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

- 6.3.5 A calibration blank shall be analyzed after the ICV, after each CCV, and after the last sample in a set of samples being analyzed. A calibration blank sample is a blank ($0.0 \mu\text{g/L Hg}$) sample made up exactly like the methods blank of the calibration standards. The calibration blank sample is not digested.

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Note: If the absolute value of the calibration blank sample exceeds the requested detection limit (from the SOW, ARF or TI), the analysis is terminated, the problem corrected, the instrument recalibrated, and all analytical samples analyzed since the last good calibration blank are to be redigested and reanalyzed.

7.0 Analysis Method

Caution: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass must be included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as, equal volumes of 0.1 N KMnO_4 and 10% H_2SO_4 , or 0.25% iodine in a 3% KI solution.

7.1 Sample collection, preservation, and handling.

Sample collection and field preservation is not within the scope of this procedure. However, it is important, whenever possible, that the samples be collected and preserved properly in order to maintain sample integrity. Once received, the samples should be preserved according to the steps below.

7.1.1 If not already treated at the time of collection, aqueous samples shall be preserved by acidification with nitric acid to a pH of 2 or lower.

7.1.2 Samples shall be refrigerated at 4°C ($\pm 2^\circ\text{C}$), radioactivity levels permitting, and analyzed within the holding times specified (i.e., by either Appendix A or the governing SOW/TI).

7.1.3 The soil/sediment/solid samples shall be analyzed without drying. A separate percent solids determination (e.g., procedure PNL-ALO-504) is required.

7.2 Calibration standard preparation

7.2.1 Transfer 0.0, 0.5, 1.0, 5.0 and 10 mL aliquots of the working mercury solutions [See 5.9] containing 0.0 to $1.0\ \mu\text{g}$ Hg to a series of sample analysis bottles (e.g., 300 mL BOD or equivalent).

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7.2.2 When processing aqueous samples, add enough distilled water to each bottle to make a total volume of 50 mL, then proceed to step 7.3.2.

7.2.3 When processing soil/sediment/solid samples, add enough distilled water to each bottle to make a total volume of 5 mL, then proceed to 7.4.2.

7.3 Aqueous sample digestion

7.3.1 Transfer 50 mL [V_a] of sample, or an aliquot [V_a] diluted to 50 mL, containing not more than $1.0 \mu\text{g Hg}$, to a sample analysis bottle.

7.3.2 Mix thoroughly and add 5 mL of conc. H_2SO_4 [See 5.1]. Mix and add 2.5 mL of conc. HNO_3 [See 5.2].

7.3.3 Add 15 mL of KMnO_4 solution [See 5.6] to each bottle and allow to stand at least 15 minutes.

Note: Some samples may require additional KMnO_4 [See 2.3, for example]. If this is necessary, add additional portions of KMnO_4 until the purple color persists for at least 15 minutes.

7.3.4 Add 8 mL of $\text{K}_2\text{S}_2\text{O}_8$ solution [See 5.7] to each bottle, mix thoroughly, and heat for 2 hours in a water bath maintained at 95°C .

7.3.5 Cool and proceed to 7.5.

7.4 Soil/Sediment/Solid sample digestion

7.4.1 Weigh a representative 0.2 g portion of wet sample [W_s] and place in the bottom of a sample analysis bottle.

7.4.2 Mix thoroughly and add 5 mL of conc. H_2SO_4 [See 5.1]. Mix and add 2.5 mL of conc. HNO_3 [See 5.2].

7.4.3 Heat for 2 minutes in a water bath at 95°C . Remove and allow the sample to cool.

7.3.4 Add 50 mL distilled water and 15 mL of KMnO_4 solution [See 5.6] to each bottle and allow to stand at least 15 minutes.

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Note: Some samples may require additional KMnO_4 [See 2.3, for example]. If this is necessary, add additional portions of KMnO_4 until the purple color persists for at least 15 minutes.

7.4.5 Add 8 mL of $\text{K}_2\text{S}_2\text{O}_8$ solution [See 5.7] to each bottle, mix thoroughly, and return to the water bath for 30 minutes.

7.4.6 Cool and proceed to 7.5

7.5 Calibration and Analysis

7.5.1 Process each standard [See 7.2.1] through 7.5.2 to 7.5.6. Construct a standard curve by plotting absorbance peak height (mm) versus Hg content (μg). An alternate approach is to perform a linear regression to establish Hg concentration based on absorbance peak height [Use in 7.5.7].

7.5.2 Treating each sample individually, add 6 mL of $\text{NaCl-NH}_2\text{OH}\cdot\text{HCl}$ solution [See 5.5] to reduce the excess permanganate.

Note: It may be necessary to add additional reductant in 6 mL increments until KMnO_4 is completely reduced.

7.5.3 By partially inserting the sparge tube into the analysis bottle, purge the bottle head space for at least 1 minute and then add 5 mL of SnCl_2 [See 5.4]. Immediately attach the analysis bottle to the aeration apparatus which has been previously adjusted for a constant flowrate of 1 L/min.

7.5.4 Allow sample to stand quietly without manual agitation. The absorbance will increase and reach a maximum within 30 seconds.

7.5.5 As soon as the recorder pen levels off (approximately 1 minute), transfer the sparge tube to the standby analysis bottle which contains 5 mL conc. H_2SO_4 [See 5.1], 2.5 mL conc. HNO_3 [See 5.2], and 50 mL water.

7.5.6 Continue the aeration until the absorbance returns to its minimum value.

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7.5.7 Measure and record the peak height of the sample from the recorder chart and obtain the Hg content [C] from the standard curve constructed in 7.5.1.

7.6 Calculation of Hg concentration.

7.6.1 Aqueous samples

$$\text{Hg } (\mu\text{g/L}) = (C * 1000) / V_a$$

Where: C = μg Hg in sample aliquot
 V_a = Volume of aliquot in mL

7.6.2 Soil/Sediment/Solid samples

$$\text{Hg (mg/Kg)} = C / (W_s * P_s)$$

Where: C = (μg Hg in sample aliquot) * 1000
 W_s = (Weight of aliquot in g) * 1000
 P_s = (Percent Solids in %) / 100

8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and quality control standards as per PNL-MA-70, PAP-70-901.

9.0 Records

Records will be maintained and controlled so as to conform to requirements of ~~PNL MA 70, PAP 70-1701~~ Analytical Chemistry Lab (ALC) Quality Assurance Plan (QAP) MCS-033. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with ~~the ACT NOW Directive 89.1~~ established records management practices.

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10.0 References

Koop, J.F., Longbottom, M.C. and Lobring, L.B. "Cold Vapor Method for Determining Mercury", AWWA, vol. 64, p. 20, Jan. 1972.

Standard Method for the Examination of Water and Wastewater 14th Edition, p. 156 (1975).

USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, SOW 7/88; Methods 245.1 and 245.3.

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-214.1 R1
Page 1 of 1

A.

Document Number: PNL-ALO-214 Revision Number: 1

Document Title: Arsenic (Atomic Absorption, Furnace Technique)

Document's Original Author: MW Urie

Effective Date
of ICN: 5/11/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 7 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert

Date: 5/7/92

Approval Authority: AG King

Date: 5/17/92

Other Approvals: PK Melethil

Date: 5/18/92

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-214, ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

APPLICABILITY

This procedure is applicable for determining the concentration of arsenic in wastes, mobility-procedure extracts, soils, and ground water. The methodology is comparable to CLP SOW 788 Method 206.2. All samples must be subjected to an appropriate dissolution/digestion procedure prior to analysis as specified by the cognizant scientist or in Test Instructions (TI) or Analytical Request Form (ARF).

DEFINITIONS

Batch: A group of samples of like matrix prepared at the same time.

Modifier: A substance added to the furnace to alter the atomization characteristics of either the analyte or interfering matrix. Modifiers are employed to separate analyte and matrix in time allowing reduction of matrix interferences on the measurement of the analyte atomization signal profile. Modifiers may be added as a liquid to the sample solution, injected into the furnace or incorporated in the argon gas stream during the pretreatment, atomization or the clean-out steps.

RESPONSIBLE STAFF

Cognizant Scientist
Technician

PROCEDURE

1.0 Summary of Method

- 1.1 Following the dissolution of the sample, a representative sample aliquot and modifier are placed, by means of an automatic sampler, into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The

Author	Date	Project Mgr.	Date	QAD Representative	Date
MW Urie		TE Jones		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
JK Melethil		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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absorption of lamp radiation during atomization is proportional to the arsenic concentration.

- 1.2 The method detection limit for As is 1 mg/Kg for soils and 10 $\mu\text{g/L}$ for waters. Typical instrument detection limits (IDL) for As is 1 $\mu\text{g/L}$ in the analysis solution.

2.0 Interferences

- 2.1 Elemental arsenic and many of its compounds (e.g., arsenic chloride) are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spiked samples and relevant standard reference materials should be processed to determine if the chosen dissolution procedure is appropriate.
- 2.2 Caution must be employed during the selection of times and temperature for the drying and charring cycles. A palladium or other acceptable modifier (e.g., Nickel) should be added to all digestates prior to analysis to minimize volatilization losses during drying and charring.
- 2.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction is required to avoid erroneous results. Phosphorus and aluminum can cause interferences when using deuterium background correction. Zeeman background correction can be useful in these situations.
- 2.4 The analyte may not be completely volatilized during atomization, causing potential memory effects. This situation can be minimized by operating the furnace at 2500-2600°C immediately after atomization.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following: 1) a tolerance limit is stated with a measurement value, or 2) the following system of tolerances shall be in effect:

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL.

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- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

4.0 Apparatus and Materials

- 4.1 Atomic absorption spectrophotometer: Double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, provisions for simultaneous background correction, and interfacing with a computer and/or strip-chart recorder. Example: Perkin-Elmer 5100 AA Spectrophotometer with AS60 autosampler, deuterium lamp background correction, and P-E 7300 computer.
- 4.2 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): An EDL provides better sensitivity for the analysis of As.
- 4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls. Example: Perkin-Elmer HG600.
- 4.4 Pipets: Calibrated, with disposable tips, sized from 5 to 1,000 μL , as required.
- 4.5 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g. (Optional)

5.0 Reagents

- 5.1 Deionized water: Deionized water of sufficient quality, similar to ASTM Type II reagent water, shall be used for preparing samples, standards, and reagent dilutions. Calibration and sample blanks will produce concentrations at or below instrument detection limits.
- 5.2 Concentrated nitric acid (HNO_3): Ultrex grade.
- 5.3 Arsenic standard stock solution (1,000 mg/L): Preferred: Procure a certified aqueous standard from a supplier and verify by comparison with a second standard. Alternative: Dissolve 1.320 g of arsenic trioxide (As_2O_3 , analytical reagent grade or equivalent) in 100 mL of water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 , dilute to 1000.0 mL, and verify by comparison with a second standard.

Caution: Arsenic compounds are extremely toxic and should be handled with care.

- 5.4 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis.

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Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3 at 1% of final volume and dilute with water to volume.

- 5.5 Palladium modifier solution (1000 $\mu\text{g/mL}$ Pd in HNO_3): Preferred: Procure a certified Pd solution from a supplier. Alternative: Dissolve 0.100 g palladium wire in a minimum volume of aqua regia and evaporate to near dryness, add 5 mL of concentrated HNO_3 , warm until dissolution is complete, dilute to 100 mL; or dissolve 0.167 g palladium chloride (PdCl_2) in 5 mL of concentrated HNO_3 , evaporate to near dryness, repeat with 5 mL of concentrated HNO_3 , and dilute with water to 100 mL.

- 5.7 Argon purge gas: Industrial-grade

6.0 Quality Control

- 6.1 All quality control data shall be maintained and available for easy reference or inspection.

6.2 Minimum quality control.

- 6.2.1 The system shall be calibrated following manufacturer's recommended calibration procedure which is in the instrument reference manual (see Section 10.0). Calibration parameters shall be established and recorded each day of operation.
- 6.2.2 Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest calibration standard.
- 6.2.3 Employ a minimum of one method blank per sample group (typically 20 samples) or one for each batch of samples digested, whichever is more frequent.
- 6.2.4 Analyze at least one verification check standard or one quality control standard every 8 to 12 samples. If the results of the verification or QC standard are not within 80% to 120% of their mean value, the cognizant scientist shall determine the corrective action. All samples within the previously analyzed sample group shall be flagged on the data reports and the corrective action documented with the data. Validation of the data is the responsibility of the technical group leader.
- 6.2.5 Additional quality control (i.e., duplicates, spikes, duplicate matrix spikes, multiple injections, additional system or matrix blanks, tighter tolerances, holding times, etc.) shall be governed by the analytical requirements of the project or specific analyses requested. Specific QC

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requirements are provided by the Analytical Request Form (ARF), the project Statement of Work (SOW), or the sample analysis Test Instruction (TI).

6.3 Quality control for clients requesting compliance with CERCLA requirements.

6.3.1 Analyze samples per protocol detailed in Appendix A. Use Figure 1 of Appendix A to establish quantitation method to be used; that is, either direct calibration or method of standard addition. Also, all definitions/acronyms (e.g. Sample Delivery Group, SDG) shall be consistent with USEPA CLP SOW 788 [Reference 10] usage.

6.3.2 Any additional quality control requirements shall be governed by the Statement of Work (SOW) from the client with the analysis protocol transmitted to the analyst via Test Instructions (TI).

7.0 Analysis Method

Sample collection, preservation and preparation is not within the scope of this procedure. However, it is important, whenever possible, that the samples be collected and preserved properly in order to maintain sample integrity. The applicability of sample preparation schemes, such as PNL-ALO-101, for specific matrices shall be demonstrated by analyzing spiked samples or relevant standard reference materials, or by the use of other qualifying techniques.

7.1 The 193.7 nm wavelength line and a background correction system shall be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.2 Furnace parameters suggested by the manufacturer in the reference manual (see Section 10.0) should be employed as guidelines. The furnace parameters used shall be optimized and remain constant throughout batch analyses. All parameters shall be recorded with the data.

----- Guidelines for furnace settings -- P-E 5100

<u>Step</u>	<u>Temp(°C)</u>	<u>Time(sec)</u>
Drying	150	15-30
Charring	1100	30-180
Atomization	2400	1-5
Cleaning	2500	1-2
Cool down	20	1-10

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Note: Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters may be confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

- 7.3 Inject measured μL -aliquots of sample and modifier solution (typically, 20 μL of sample and 5 μL of modifier) into the furnace and atomize. If the concentration found is greater than the highest standard, the sample shall be diluted in the same acid matrix and reanalyzed. Note: Multiple injections improve precision and help detect furnace pipetting errors.
- 7.4 Analyze a verification standard or a QC standard after every 8 to 12 samples. Note: Verification standards help monitor the life and performance of the graphite tube. An RSD for duplicate injections of mid-range standards exceeding 10% or an instrument response <70% of the manufacturer's recommendation as stated in the reference manual (see Section 10.0), shall be investigated and corrective action, if required, documented.
- 7.5 Calculation of arsenic concentration: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphase samples must be appropriately qualified (e.g., $\mu\text{g/mL}$ aqueous phase). Document the method used.

8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and quality control standards.

9.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~ACT NOW Directive 89.1~~ established records management practices.

10.0 References

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PNL TECHNICAL PROCEDURE

USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, SOW788, Method 206.2

Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

SW-846, Method 7060, 3rd Edition.

Perkin-Elmer Atomic Absorption Spectrophotometer Reference Manual, Model 5100, Volume 1 and Volume 2.

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-215.2 R1
Page 1 of 1

A.

Document Number: PNL-ALO-215 Revision Number: 1

Document Title: Selenium (Atomic Absorption, Furnace Technique)

Document's Original Author: MW Urie

Effective Date
of ICN: 5/26/92

Change Requested by:
TE Jones / TG Walker

B. Action:

Replace pages 1 through 7 due to new format.

C. Effect of Change:

Deleting ACT 89.1 and replacing with established records management practices.

Brings procedure into compliance.

Changes in concentrations and volume due to typographical errors.

Due to errors produced by ICN No. PNL-ALO-215.1; corrections have been made to Section 7.2.

D. Reason for Change/Description of Change:

Section 9.0: Change "ACT NOW Directive 89.1" to "established records management practices" because ACT NOW Directive 89.1 is no longer in existence.

Section 5.5: Change "3000 $\mu\text{g/L}$ " to "3000 mg/L," "2000 $\mu\text{g/L}$ " to "2000 mg/L," and "5 $\mu\text{g/L}$ " to "5 μl ."

Section 7.2: Add: "Furnace parameters suggested by the manufacturer in the reference manual, should be employed as guidelines." due to omission by above ICN.

Section 7.2: Delete: "The furnace parameters used shall be recorded with the data" with "." due to errors in the above ICN.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert *TL Ehlert* Date: 5/20/92

Approval Authority: AG King *AG King* Date: 5/21/92

Other Approvals: MW Urie *MW Urie* Date: 5/26/92

: _____ Date: 1/1

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-AL0-215.1
Page 1 of 8

A. Document Number: <u>PNL-AL0-215</u> Revision Number: <u>1</u> Document Title: <u>Selenium (Atomic Absorption, Furnace Technique)</u> Document's Original Author: <u>M. W. Urie</u>		Effective Date of ICN: <u>4/8/91</u> Change Requested By: <u>M. W. Urie</u>
B. Action: Replace existing sections with changed sections as described in Section D of this ICN. Replace affected pages.		
C. Effect of Change: This change adds clarity to sections which are not currently consistent with other approved AA procedures for CERCLA clients.		
D. Reason for Change/Description of Change Reason: Although approved, this procedure is not compatible with other, more recent, AA procedures. This ICN has been requested by CERCLA clients and is required to continue CERCLA support. Description: See attached		
E. Approval Signatures (Please Sign and Date)		Type of Change: (Check (☒) one) (☐) Minor Change (☒) Major Change
Process Quality QA/R -Department Concurrence: <u><i>G. Gerke</i></u> Approval Authority: <u><i>[Signature]</i></u> Other Approvals: <u><i>B. M. Gillespie</i></u>		Date: <u>3/21/91</u> Date: <u>3/29/91</u> Date: <u>4/2/91</u> Date: <u>1/1</u>

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-215, SELENIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

APPLICABILITY

This procedure is applicable for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water. The methodology is comparable to CLP SOW 788 Method 270.2. All samples shall be subjected to an appropriate dissolution/digestion procedure prior to analysis as specified by the cognizant scientist or in Test Instructions (TIs) or Analytical Request Forms (ARFs).

DEFINITIONS

Batch: A group of samples of like matrix prepared at the same time.

Modifier: A substance added to the furnace to alter the atomization characteristics of either the analyte or interfering matrix. Modifiers are employed to separate analyte and matrix in time allowing reduction of matrix interferences on the measurement of the analyte atomization signal profile. Modifiers may be added as a liquid to the sample solution, injected into the furnace or incorporated in the argon gas stream during pretreatment, atomization or the clean-out step.

RESPONSIBLE STAFF

Cognizant Scientist
Technician

PROCEDURE

1.0 Summary of Method

- 1.1 Following the dissolution/digestion of the sample, a representative sample aliquot and modifier are placed, by means of an automatic sampler, into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization is proportional to the selenium concentration.

Author MW Urie <i>MW Urie</i> 5/26/91	Date 5/26/91	Project Mgr. BM Gillespie	Date	QAD Representative GK Gerke	Date
Technical Reviewer P. Melethil	Date	Line Mgr. PF Salter	Date	Other ALL ORIGINAL SIGNATURES ON FILE	Date
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PNL TECHNICAL PROCEDURE

- 1.2 The method detection limit for Se is 0.5 mg/kg for soils and 5 µg/L for water. Typical instrument detection limit (IDL) for Se is 2 µg/L in the analysis solution.

2.0 Interferences

- 2.1 Elemental selenium and many of its compounds (e.g., selenium chloride) are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Spiked samples and relevant standard reference materials should be processed to determine if the chosen dissolution procedure is appropriate.
- 2.2 Care must be employed in selecting the drying and charring step times, temperatures and temperature ramps. A palladium, or other acceptable analyte modifier (e.g., platinum), and magnesium nitrate should be added to all digestates prior to analysis to minimize volatilization losses during drying and charring. Magnesium nitrate has been shown to assist in spreading the Pd-Se compounds more evenly in the furnace which reduces diffusion time of the analyte in the magnesium oxide matrix. Magnesium thus serves to sharpen the analyte peak shape during atomization and increases analytical precision.
- 2.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction is required to minimize erroneous results. High iron and cobalt can cause interferences when using deuterium background correction. Zeeman background correction can be useful in these situations.
- 2.4 The analyte may not be completely volatilized during atomization; potentially causing memory effects. This situation can be minimized by operating the furnace at 2500-2600°C immediately after atomization.
- 2.5 Selenium analysis suffers interference from chloride (>800 mg/L) and sulfate (>200 mg/L). The addition of palladium nitrate such that the final concentration is about 0.1% palladium will lessen this interference.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following: 1) a tolerance limit is stated with a measurement value, or 2) the following system of tolerances shall be in effect:

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PNL TECHNICAL PROCEDURE

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL.
- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

4.0 Apparatus and Materials

- 4.1 Atomic absorption spectrophotometer: Double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-900 nm, provisions for simultaneous background correction, and interfacing with a computer and/or strip-chart recorder. Example: Perkin-Elmer 5100 AA Spectrophotometer with AS60 autosampler, deuterium lamp background correction, and IBM PS/2 computer.
- 4.2 Selenium hollow cathode lamp, or electrodeless discharge lamp (EDL): An EDL provides better sensitivity for the analysis of Se.
- 4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls. Example: Perkin-Elmer HGA 600
- 4.4 Pipets: Calibrated, with disposable tips, sized from 5 to 1,000 μ L, as required.
- 4.5 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g. (Optional)

5.0 Reagents

- 5.1 Deionized water: Deionized water of sufficient quality, similar to ASTM Type II reagent water, shall be used for preparing samples, standards, and reagent dilutions. Calibration and sample blanks will produce concentrations at or below instrument detection limits.
- 5.2 Concentrated nitric acid: (HNO_3): Ultrex grade.
- 5.3 Selenium standard stock solution: (1,000 mg/L): Preferred: Procure a certified aqueous standard from NIST or equivalent supplier and verify by comparison with a second standard.

Alternative: Dissolve 0.3453 g of selenous acid (analytical reagent grade, assay 94.6% H_2SeO_3 , or equivalent) in water, dilute to 200.0 mL, and verify by comparison with a second standard.

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PNL TECHNICAL PROCEDURE

Caution: Selenium and its compounds are extremely toxic and should be handled with care.

- 5.4 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3 at 1% of final volume and dilute with water to volume.

- 5.5 Palladium nitrate - magnesium nitrate mixed modifier solution

Preferred: Mix equal volumes of 3000 $\mu\text{g/L}$ mg/L of certified aqueous Pd standard in HNO_3 and 2000 $\mu\text{g/L}$ mg/L of $\text{Mg}(\text{NO}_3)_2$. A 5 $\mu\text{g/L}$ μl volume of this solution is added to each sample, corresponding to masses of 15 μg of Pd (32.5 μg PdNO_3) and 10 μg of $\text{Mg}(\text{NO}_3)_2$.

Alternate source for palladium: Dissolve 0.300 g Pd wire in a minimum volume of aqua regia and evaporate to dryness, add 5 mL of concentrated HNO_3 , warm until dissolution is complete, dilute to 100.0 mL; or dissolve 0.5001 g palladium chloride (PdCl_2) in 5 mL of concentrated HNO_3 , evaporate to near dryness, repeat with 5 mL of concentrated HNO_3 , and dilute with water to 100.0 mL.

- 5.6 Argon purge gas: Industrial-grade argon or a mixture of argon-hydrogen (95-5%)

6.0 Quality Control (QC)

- 6.1 All QC data shall be maintained and available for easy reference or inspection.

- 6.2 Minimum QC.

6.2.1 The system shall be calibrated following manufacturer's recommended calibration procedure which is in the instrument reference manual (see Section 10.0). Calibration parameters shall be established and recorded each day of operation.

6.2.2 Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest calibration standard.

6.2.3 Employ a minimum of one method blank per sample group (typically 20 samples) or one for each batch of samples digested, whichever is more frequent.

6.2.4 Analyze at least one verification check standard or one QC standard every 8 to 12 samples. If the results of the verification or QC standard are not within 80% to 120% of their mean value, the cognizant scientist shall determine

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PNL TECHNICAL PROCEDURE

the corrective action. All samples within the previously analyzed sample group shall be flagged on the data reports and the corrective action documented with the data. Validation of the data is the responsibility of the technical group leader.

Note: Verification standards help monitor the life and performance of the graphite tube. An RSD for duplicate injections of midrange standards exceeding 10%, or an instrument response <70% of the manufacturer's recommendation as stated in the reference manual (see Section 10.0), shall be investigated and corrective action, if required, documented.

- 6.2.5 Additional QC (i.e., duplicates, matrix spikes, duplicate matrix spikes, multiple injections, additional system or matrix blanks, tighter tolerances, and holding times, etc.) shall be governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the ARF, the project Statement of Work (SOW), or the sample analysis TI.

6.3 QC for clients requesting compliance with CERCLA requirements.

- 6.3.1 Analyze samples per protocol detailed in Appendix A. Use Figure 1 of Appendix A to establish the quantitation method to be used; that is, either direct calibration or method of standard addition. Also, all definitions/acronyms (e.g., sample delivery group, [SDG]) shall be consistent with USEPA CLP 788 (see Section 10.0) usage.

- 6.3.2 Any additional QC requirements shall be governed by the SOW from the client with the analysis protocol transmitted to the analyst via TI.

7.0 Analysis Method

Sample collection, preservation and preparation is not within the scope of this procedure. However, it is important that samples be collected and preserved properly in order to maintain sample integrity. The applicability of sample preparation schemes, such as Procedure PNL-ALO-101, for specific matrices shall be demonstrated by analyzing spiked samples or relevant standard reference materials, or by the use of other qualifying techniques.

- 7.1 The 196.0 nm wavelength line and a background correction system shall be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters. These are located in the instrument reference manual (see Section 10.0).

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PNL TECHNICAL PROCEDURE

- 7.2 Furnace parameters suggested by the manufacturer in the reference manual, should be employed as guidelines. ~~The furnace parameters used shall be recorded with the data~~ with "The furnace parameters used shall be optimized and remain constant throughout batch analyses. All parameters shall be recorded with the data."

Suggested furnace settings --- P-E 5000 or 5100

Step	Temp (*C)	Ramp Time(sec)	Hold Time(sec)
Drying #1	90	1	15
Drying #2	150	10	15
Charring	800	10	30
Cool Down #1	30	1	15
Atomization	2100	0	5
Cleaning	2500	1	2
Cool Down #2	20	10	5

Note: Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters may be confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

- 7.3 Inject measured μL -aliquots of sample and modifier solution (typically, 20 μL of sample and 5 μL of modifier) into the furnace and atomize. If the concentration found is greater than the highest standard, the sample shall be diluted in the same acid matrix and reanalyzed. Note: Multiple injections improve precision and help detect furnace pipetting errors.
- 7.4 Calculate the selenium concentration: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors shall be taken into account. Concentrations reported for multiphase samples shall be appropriately qualified (e.g., $\mu\text{g/mL}$ aqueous phase).

8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and QC standards as per PNL-MA-70, PAP-70-901.

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PNL TECHNICAL PROCEDURE

9.0 Records

Records will be maintained and controlled so as to conform to requirements of Manual PNL-MA-70, Procedure PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~ACT NOW Directive 89.1~~ established records management practices.

10.0 References

USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, SOW 788, Method 270.2.

Gaskill, A. Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

SW-846, Method 7740, 3rd Edition.

Perkin-Elmer Atomic Absorption Spectrophotometer Reference Manual, Model 5100, Volume 1 and 2.

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**INTERIM CHANGE NOTICE
(ICN)**

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Page 1 of 1

A.

Document Number: PNL-ALO-216 Revision Number: 0

Document Title: Bismuth (Atomic Absorption, Furnace Technique)

Document's Original Author: MW Urie

Effective Date
of ICN: 05/21/92

Change Requested by:
TE Jones / TG Walker

B. Action:

Replace pages 1 through 7 due to new format.

C. Effect of Change:

Deleting ACT 89.1 and replacing with "established records management practices".
Brings procedure into compliance.

Change in concentration and volume due to typographical errors.

D. Reason for Change/Description of Change:

Section 9.0: Change "ACT NOW Directive 89.1" to "established records management practices" because the ACT NOW Directive 89.1 is no longer in existence.

Section 5.5: Change "3000 $\mu\text{g/L}$ " to "3000 mg/L," "2000 $\mu\text{g/L}$ " to 2000 mg/L" and "5 $\mu\text{g/L}$ " to "5 μl ."

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert

Date: 5/20/92

Approval Authority: AG King

Date: 5/21/92

Other Approvals: _____

Date: 1 1

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Date: 1 1

INTERIM CHANGE NOTICE
(ICN)

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Page 1 of 8

A. Document Number: <u>PNL-AL0-216</u> Revision Number: <u>0</u> Document Title: <u>Bismuth (Atomic Absorption, Furnace Technique)</u> Document's Original Author: <u>M. W. Urie</u>		Effective Date of ICN: <u>4/8/91</u> Change Requested By: <u>M. W. Urie</u>
B. Action: Replace existing sections with changed sections as described in Section D of this ICN. Replace affected pages.		
C. Effect of Change: This change adds clarity to sections which are not currently consistent with other approved AA procedures for CERCLA clients.		
D. Reason for Change/Description of Change Reason: Although approved, this procedure is not compatible with other, more recent, AA procedures. This ICN has been requested by CERCLA clients and is required to continue CERCLA support. Description: See attached		
E. Approval Signatures (Please Sign and Date)	Type of Change: (Check (/) one) () Minor Change (X) Major Change	
Process Quality QA Department Concurrence: <u>G. Geste</u> Date: <u>3/29/91</u> Approval Authority: <u>[Signature]</u> Date: <u>3/29/91</u> Other Approvals: <u>B. M. Dilemari</u> Date: <u>4/29/91</u> : _____ Date: <u>1/1</u>		

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-216, BISMUTH (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

APPLICABILITY

This procedure is applicable for determining the concentration of bismuth in wastes, mobility-procedure extracts, soils, and ground water. The methodology is comparable to CLP SOW 788 graphite furnace techniques for analysis of metals. All samples shall be subjected to an appropriate dissolution/digestion procedure prior to analysis as specified by the cognizant scientist or in Test Instructions (TIs) or Analytical Request Forms (ARFs).

DEFINITIONS

Batch: A group of samples of like matrix prepared at the same time.

Modifier: A substance added to the furnace to alter the atomization characteristics of either the analyte or interfering matrix. Modifiers are employed to separate analyte and matrix in time allowing reduction of matrix interferences on the measurement of the analyte atomization signal profile. Modifiers may be added as a liquid to the sample solution, injected in to the furnace or incorporated in the argon gas stream during pretreatment, atomization or the clean-out step.

RESPONSIBLE STAFF

Cognizant Scientist
Technician

PROCEDURE

1.0 Summary of Method

- 1.1 Following the dissolution/digestion of the sample, a representative sample aliquot and modifier are placed, by means of an automatic sampler, into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization is proportional to the bismuth concentration.

Author MW Urie	Date	Project Mgr. BM Gillespie	Date	QAD Representative GK Gerke	Date
Technical Reviewer PK Melethil	Date	Line Mgr. PF Salter	Date	Other ALL ORIGINAL SIGNATURES ON FILE	Date
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PNL TECHNICAL PROCEDURE

- 1.2 The method detection limit for Se is 1.0 mg/kg for soils and 10 µg/L for water. Typical instrument detection limit (IDL) for Bi is 5 µg/L in the analysis solution.

2.0 Interferences

- 2.1 Care must be employed in selecting the drying and charring step times, temperatures and temperature ramps. A palladium, or other acceptable analyte modifier (e.g., platinum), and magnesium nitrate should be added to all digestates prior to analysis to minimize volatilization losses during drying and charring. Magnesium nitrate has been shown to assist in spreading the Pd-Se compounds more evenly in the furnace which reduces diffusion time of the analyte in the magnesium oxide matrix. Magnesium thus serves to sharpen the analyte peak shape during atomization and increases analytical precision.
- 2.2 In addition to the normal interferences experienced during graphite furnace analysis, bismuth analysis can suffer from nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction (Zeeman or deuterium lamp) is required to minimize erroneous results.
- 2.3 The analyte may not be completely volatilized during atomization; potentially causing memory effects. This situation can be minimized by operating the furnace at 2300-2600°C immediately after atomization.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit is stated with the measurement value, or 2) the following system of tolerances shall be in effect:

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; and 369 mL means 369.0 ± 0.5 mL.
- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

4.0 Apparatus and Materials

- 4.1 Atomic absorption spectrophotometer: Double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-900 nm, provisions for simultaneous

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PNL TECHNICAL PROCEDURE

background correction, and interfacing with a computer and/or strip-chart recorder. Example: Perkin-Elmer 5100 AA Spectrophotometer with AS60 autosampler, deuterium lamp background correction, and IBM PS/2 computer.

- 4.2 Bismuth hollow cathode lamp, or electrodeless discharge lamp (EDL): An EDL provides better sensitivity for the analysis of Bi.
- 4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls. Example: Perkin-Elmer HGA 600
- 4.4 Pipets: Calibrated, with disposable tips, sized from 5 to 1,000 μL , as required.
- 4.5 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g. (Optional)

5.0 Reagents

- 5.1 Deionized water: Deionized water of sufficient quality, similar to ASTM Type II reagent water, shall be used for preparing samples, standards, and reagent dilutions. Calibration and sample blanks will produce concentrations at or below IDLs.

- 5.2 Concentrated nitric acid: (HNO_3): Ultrex grade.

- 5.3 Bismuth standard stock solution: (1,000 mg/L): Preferred: Procure a certified aqueous standard from NIST or equivalent supplier and verify by comparison with a second standard.

Alternative: Dissolve 1.000 g of bismuth metal in a minimum volume of 1:1 HNO_3 -water, dilute to 1000.0 mL with water, and verify by comparison with a second standard.

- 5.4 Bismuth working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3 at 1% of final volume and dilute with water to volume.

- 5.5 Palladium nitrate - magnesium nitrate mixed modifier solution:

Preferred: Mix equal volumes of 3000 $\mu\text{g/L}$ mg/L of certified aqueous Pd standard in HNO_3 and 2000 $\mu\text{g/L}$ mg/L of $\text{Mg}(\text{NO}_3)_2$. A 5 $\mu\text{g/L}$ μL volume of this solution is added to each sample, corresponding to masses of 15 μg of Pd (32.5 μg PdNO_3) and 10 μg of $\text{Mg}(\text{NO}_3)_2$.

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PNL TECHNICAL PROCEDURE

Alternate source for palladium: Dissolve 0.300 g Pd wire in a minimum volume of aqua regia and evaporate to dryness, add 5 mL of concentrated HNO_3 , warm until dissolution is complete, dilute to 100.0 mL; or dissolve 0.5001 g palladium chloride (PdCl_2) in 5 mL of concentrated HNO_3 , evaporate to near dryness, repeat with 5 mL of concentrated HNO_3 , and dilute with water to 100.0 mL.

5.6 Argon purge gas: Industrial-grade argon or a mixture of argon-hydrogen (95-5%).

6.0 Quality Control (QC)

6.1 All QC data shall be maintained and available for easy reference or inspection.

6.2 Minimum QC.

6.2.1 The system shall be calibrated following manufacturer's recommended calibration procedure in the instrument reference manual (See Section 10.0). Calibration parameters shall be established and recorded each day of operation.

6.2.2 Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest calibration standard.

6.2.3 Employ a minimum of one method blank per sample group (typically 20 samples) or one for each batch of samples digested, whichever is more frequent.

6.2.4 Analyze at least one verification check standard or one QC standard every 8 to 10 samples. If the results of the verification or QC standard are not within 80% to 120% of their mean value, the cognizant scientist shall determine the corrective action. All samples within the previously analyzed sample group shall be flagged on the data reports and the corrective action documented with the data. Validation of the data is the responsibility of the technical group leader.

Note: Verification standards help monitor the life and performance of the graphite tube. An RSD for duplicate injections of midrange standards exceeding 10%, or an instrument response <70% of the manufacturer's recommendation as stated in the reference manual (see Section 10.0), shall be investigated and corrective action, if required, documented.

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PNL TECHNICAL PROCEDURE

6.2.5 Additional QC (i.e., duplicates, matrix spikes, duplicate matrix spikes, multiple injections, additional system or matrix blanks, tighter tolerances, and holding times, etc.) shall be governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the ARF, the project Statement of Work (SOW), or the sample analysis TI.

6.3 QC for clients requesting compliance with CERCLA requirements.

6.3.1 Analyze samples per protocol detailed in Appendix A. Use Figure 1 of Appendix A to establish the quantitation method to be used; that is, either direct calibration or method of standard addition. Also, all definitions/acronyms (e.g., sample delivery group, [SDG]) shall be consistent with USEPA CLP 788 (see Section 10.0) usage.

6.3.2 Any additional QC requirements shall be governed by the SOW from the client with the analysis protocol transmitted to the analyst via TI.

7.0 Analysis Method

Sample collection, preservation and preparation is not within the scope of this procedure. However, it is important, whenever possible, that the samples be collected and preserved properly in order to maintain sample integrity. The applicability of sample preparation schemes, such as Procedure PNL-ALO-101, for specific matrices shall be demonstrated by analyzing spiked samples or relevant standard reference materials, or by the use of other qualifying techniques.

7.1 The 223.1 nm wavelength line and a background correction system shall be employed. Follow the manufacturer's suggestions in the instrument reference manual (see Section 10.0) for all other spectrophotometer parameters.

7.2 The furnace parameters used shall be optimized and remain constant throughout batch analyses. All parameters shall be recorded with the data.

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PNL TECHNICAL PROCEDURE

Suggested furnace settings --- P-E 5000 or 5100

Step	Temp(°C)	Ramp Time(sec)	Hold Time(sec)
Drying #1	90	1	15
Drying #2	150	10	15
Charring	850	10	30
Cool Down #1	30	1	15
Atomization	2000	0	5
Cleaning	2300	1	2
Cool Down #2	20	10	5

Note: Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters may be confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

- 7.3 Inject measured μL -aliquots of sample and modifier solution (typically, 20 μL of sample and 5 μL of modifier) into the furnace and atomize. If the concentration found is greater than the highest standard, the sample shall be diluted in the same acid matrix and reanalyzed. Note: Multiple injections improve precision and help detect furnace pipetting errors.
- 7.4 Calculate the bismuth concentration: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors shall be taken into account. Concentrations reported for multiphase samples shall be appropriately qualified (e.g., $\mu\text{g/mL}$ aqueous phase).

8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and QC standards as per Manual PNL-MA-70, Procedure PAP-70-901.

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PNL TECHNICAL PROCEDURE

9.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~ACT NOW Directive 89.1~~ established records management practices.

10.0 References

USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, SOW 788, Graphite Furnace Methods.

Standard Methods for Examination of Water and Wastewater, 1986, 16th Edition, Method 303a.

Perkin-Elmer Atomic Absorption Spectrophotometer Reference Manual, Model 5100, Volume 1 and 2.

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**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-217.1 R0

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A.

Document Number: PNL-ALO-217 Revision Number: 0

Document Title: Lead (Atomic Absorption, Furnace
Technique)

Document's Original Author: JM Robbins

Effective Date
of ICN: 05/21/92

Change Requested by:
TE Jones / TG Walker

B. Action:

Replace pages 1 through 9 due to new format.

C. Effect of Change:

Deleting ACT 89.1 and replacing with established records management practices.

Brings procedure into compliance.

Change in matrix modifier volume due to a typographical error.

D. Reason for Change/Description of Change:

Section 9.0: Change "ACT NOW Directive 89.1" to "established records management practices" because ACT NOW Directive 89.1 is no longer in existence.

Section 5.5: Change "10 µl" to "5 µl" due to typographical error.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert

Date: 5/20/92

Approval Authority: AG King

Date: 5/21/92

Other Approvals: _____

Date: 1/1

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-217, LEAD (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

APPLICABILITY

This procedure is applicable for determining the concentration of lead in wastes, mobility-procedure extracts, soils, and ground water. The methodology is comparable to CLP Method 239.2 in SOW 788 or SOW 390. All samples shall be subjected to an appropriate dissolution/digestion procedure prior to analysis as specified by the cognizant scientist or in Test Instructions (TIs) or Analytical Request Forms (ARFs).

DEFINITIONS

Batch: A group of samples of like matrix prepared at the same time.

Modifier: A substance added to the furnace to alter the atomization characteristics of either the analyte or interfering matrix. Modifiers are employed to separate analyte and matrix in time allowing reduction of matrix interferences on the measurement of the analyte atomization signal profile. Modifiers may be added as a liquid to the sample solution, injected into the furnace or incorporated in the argon gas stream during the pretreatment, atomization or the clean-out steps.

RESPONSIBLE STAFF

Cognizant Scientist Technician

PROCEDURE

1.0 Summary of Method

- 1.1 Following the dissolution/digestion of the sample, a representative sample aliquot and modifier are placed, by means of an automatic sampler, into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization is proportional to the lead concentration.

Author	Date	Project Mgr.	Date	QAD Representative	Date
JM Robbins		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
JM Barsoum		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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PNL TECHNICAL PROCEDURE

- 1.2 The method detection limit for Pb is 0.3 mg/Kg for soil and 3 $\mu\text{g/L}$ for water. Typical instrument detection limit (IDL) for Pb is 1 $\mu\text{g/L}$ in the analysis solution.

2.0 Interferences

- 2.1 Spiked samples and relevant standard reference materials should be processed to determine if the chosen dissolution procedure is appropriate.
- 2.2 Care must be employed in selecting the drying and charring step times, temperatures and temperature ramps. A palladium, or other acceptable analyte modifier (e.g., platinum), and magnesium nitrate should be added to all digestates prior to analysis to minimize volatilization losses during drying and charring. Magnesium nitrate assists in spreading the Pd-Pb compounds more evenly in the furnace reducing diffusion time of the analyte in the Mg oxide matrix (Slavin et al., 1982; Jackson and Qiao, 1990). Magnesium thus serves to sharpen the analyte peak shape during atomization and increases analytical precision.
- 2.3 Pb analysis is affected by sodium chloride (Welz et al., 1988b). Use of an argon-hydrogen gas mixture (95-5%) during temperature ramp to 1000°C eliminate interferences from chloride by evolving it as HCl during the charring step (Shrader, et al., 1988; Rettberg and Beach, 1989; Gilchrist et al., 1990). Presence of hydrogen also enhances reduction of Pd to the metal which is necessary for Pb stabilization (Voth-Beach and Shrader, 1987). Use of this argon-hydrogen gas mixture lowers the appearance temperature of Pb, requiring a modification of the temperature programming of the pyrolysis and atomization steps (Ni Zhe-ming and Shan Xiao-quan, 1987). Use of the new fork platform design can improve Pb recoveries in high salt matrices (Zhang Li et al., 1990).

Dammonium phosphate has been used as a matrix modifier in the presence of high chloride; it increases atomization temperature of Pb by binding it as a less volatile lead phosphate. This allows the removal of most salt interferences during the char step (Slavin and Manning, 1979).

- 2.4 Lead may condense at cool ends of the graphite furnace during atomization; potentially causing memory effects in subsequent analyses. This situation can be minimized by operating the furnace at 2500-2650°C immediately after atomization or enhancing removal of Pb by use of an argon (99%) and freon (1%) gas mixture in the clean-out step (Welz and Schlemmer, 1988).

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PNL TECHNICAL PROCEDURE

2.5 Potential Zeeman effect background overcorrection in lead analysis can occur at the 283.3 nm wavelength in the presence of platinum, osmium and tin. If the more sensitive 217 nm wavelength is chosen copper, antimony, nickel and iron can cause background overcorrection in Zeeman mode (Slavin and Carnrick, 1988). The 217 nm line for Pb should be avoided when deuterium arc background correction is used, as this line is subject to high background interference.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following: 1) a tolerance limit is stated with a measurement value, or 2) the following system of tolerances shall be in effect:

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL.
- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

4.0 Apparatus and Materials

- 4.1 Atomic absorption spectrophotometer: Double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-900 nm, provisions for simultaneous background correction, and interfacing with a computer and/or strip-chart recorder. Example: Perkin-Elmer 5100 AA Spectrophotometer with AS60 autosampler, deuterium lamp of Zeeman effect background correction, and IBM PS/2 computer.
- 4.2 Lead hollow cathode lamp or electrodeless discharge lamp: Electrodeless discharge lamps (EDL) are generally preferred as they have greater lamp output and longer life than hollow cathode lamps (HCL). Lead EDL lamps provide the same sensitivity and detection limit as lead HCL lamps.
- 4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls. Example: Perkin-Elmer HGA 600
- 4.4 Pipets: Calibrated, with disposable tips, sized from 5 to 1,000 μ L, as required.

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- 4.5 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g. (Optional)

5.0 Reagents

- 5.1 Deionized water: Deionized water of sufficient quality, similar to ASTM Type II reagent water, shall be used for preparing sample, standards, and reagent dilutions. Calibration and sample blanks shall produce concentrations at or below IDLs.

- 5.2 Concentrated nitric acid (HNO₃): Ultrex grade.

- 5.3 Lead standard stock solution (1,000 mg/L): Preferred: Acquire a certified aqueous standard from NIST or an equivalent supplier and verify by comparison with a second standard.

Alternatives: Dissolve 1.000 g of lead (Johnson Matthey or equivalent) in a minimum amount of concentrated HNO₃ and dilute to 1 L, using deionized distilled water. The analyst may alternatively use 0.7992 g of Pb(NO₃)₂ diluted with 2% HNO₃ to 500 mL.

Caution: Lead and its compounds are toxic and should be handled with care.

- 5.4 Lead working standards: Prepare dilutions of the stock standard solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO₃ at 1% of final volume and dilute with water to volume.

- 5.5 Palladium nitrate - magnesium nitrate mixed modifier solution: Preferred: Mix equal volumes of 3000 mg/L of a Pd standard (Inorganic Ventures, Inc. or equivalent) in HNO₃ and 2000 mg/L of Mg(NO₃)₂ (Merck, Suprapure or equivalent), respectively. It is suggested that modifier may be made up in batch by combining 30 mL of 5,000 mg/L Pd standard, 20 mL of DDI water and 50 mL of 2000 mg/L of Mg(NO₃)₂.

A ~~10~~ 5 µL volume of this solution is added to each sample, corresponding to masses of 15 µg of Pd (32.5 µg PdNO₃) and 10 µg of Mg(NO₃)₂ (Schlemmer and Welz, 1986 and Welz et al., 1988a,b). The amount of Mg(NO₃)₂ used may be increased from 10 µg (Schlemmer and Welz, 1986 and Welz et al., 1988) to 50 µg, as higher concentrations have been shown to improve peak shape for Pb analysis (Bozsai et al., 1990).

Alternative source for palladium: Dissolve 0.300 g Pd wire in a minimum volume of aqua regia and evaporate to dryness, add 5 mL

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of concentrated HNO_3 , warm until dissolution is complete, dilute to 100 mL; or dissolve 0.5001 g palladium chloride (PdCl_2) in 5 mL of concentrated HNO_3 , evaporate to near dryness, repeat with 5 mL of concentrated HNO_3 , and dilute with water to 100.0 mL.

- 5.6 Argon purge gas: Industrial-grade argon. When chloride interference is suspected, the use of a mixture of argon-hydrogen (95-5%) is recommended.

6.0 Quality Control (QC)

- 6.1 All QC data shall be maintained and available for easy reference or inspection.

6.2 Minimum QC.

- 6.2.1 The system shall be calibrated following manufacturer's recommended calibration procedure which is in the instrument reference manual (see Section 10.0). Calibration parameters shall be established and recorded each day of operation.
- 6.2.2 Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest calibration standard.
- 6.2.3 Employ a minimum of one method blank for each sample delivery group or batch of samples digested.
- 6.2.4 Analyze at least one verification check standard or one QC standard every 8 to 12 samples. If the results of the verification or QC standard are not within 80% to 120% of their mean value, the cognizant scientist shall determine the corrective action. The instrument must be recalibrated, the calibration verified, and all analytical samples analyzed since the last good calibration verification must be reanalyzed for the analytes affected. This corrective action taken shall be documented with the data. Validation of the data is the responsibility of the technical group leader.

Note: Verification standards help monitor the life and performance of the graphite tube. An RSD for duplicate injections of midrange standards exceeding 10% or an instrument response <70% of the manufacturer's recommendation as stated in the reference manual (see Section 10.0), shall be investigated and corrective action, if required, documented.

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- 6.2.5 Additional QC (i.e., duplicates, matrix spikes, duplicate matrix spikes, multiple injections, additional system or matrix blanks, tighter tolerances, and holding times, etc.) shall be governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the ARF, the project Statement of Work (SOW), or the sample analysis TI.
- 6.3 QC for clients requesting compliance with Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) requirements.
- 6.3.1 Analyze samples per protocol detailed in Appendix A. Use Figure 1 of Appendix A to establish the quantitation method to be used; that is, either direct calibration or method of standard addition. Also, all definitions/acronyms (e.g. Sample Delivery Group, [SDG]) shall be consistent with USEPA CLP SOW 788 (Reference 10) usage.
- 6.3.2 Any additional QC requirements shall be governed by the SOW from the client with the analysis protocol transmitted to the analyst via TI.

7.0 Analysis Method

Sample collection, preservation and preparation is not within the scope of this procedure. However, it is important that samples be collected and preserved properly in order to maintain sample integrity. The applicability of sample preparation schemes, such as Procedure PNL-ALO-101, for specific matrices shall be demonstrated by analyzing spiked samples or relevant standard reference materials, or by the use of other qualifying techniques.

- 7.1 The 283.3 nm wavelength line and a background correction system shall be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters. These are located in the instrument reference manual (see Section 10.0).
- 7.2 Furnace parameters suggested by the manufacturer in the reference manual should be employed as guidelines. The furnace parameters used shall be optimized and remain constant throughout batch analyses. All parameters shall be recorded with the data.

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PNL TECHNICAL PROCEDURE

Suggested graphite furnace program settings P-E 5000 or 5100

Step	Temp(°C)	Ramp Time(sec)	Hold Time(sec)
Drying #1	90	1	15
Drying #2	130	10	10
Charring	1000	10	20
Cool down #1	30	1	15
Atomization	2100	0	5
Cleaning	2600	1	5
Cool down #2	20	1	5

Note: Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters may be confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

The char step can be removed from the furnace program when analyzing low salt matrices while using Zeeman background correction to decrease sample analysis time (Slavin et al., 1989)

- 7.3 Inject measured μL -aliquots of sample and modifier solution (typically, 20 μL of sample and 5 μL of modifier) into the furnace and analyze for lead following graphite furnace program. If the concentration found is greater than the highest standard, the sample shall be diluted in the same acid matrix and reanalyzed. Note: Multiple injections improve precision and help detect furnace pipetting errors.
- 7.4 Calculate the lead concentration: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors shall be applied prior to reporting results. Concentrations reported for multiphase samples shall be appropriately qualified (e.g., $\mu\text{g/L}$ aqueous phase or mg/Kg for solids).

8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and QC standards as per Manual PNL-MA-70, Procedure PAP-70-901.

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PNL TECHNICAL PROCEDURE

9.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~ACT NOW Directive 89-1~~ established records management practices.

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Bozsai, G., Schlemmer, G. and Grobensi, Z. 1990. Determination of arsenic, cadmium, lead and selenium in highly mineralized waters by graphite-furnace atomic-absorption spectrometry. Talanta

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Schlemmer, G. and Welz, B. 1986. Palladium and magnesium nitrates, a more universal modifier for graphite furnace atomic absorption spectrometry. Spectro. Acta. 41B: 1157- 1165.

Shrader, D. E., Beach, L. M. and Rettberg, T. M. 1988. Graphite furnace AAS: Application of reduced palladium as a chemical modifier. J. of Res. Natl. Bureau of Stds. 93: 450-452.

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Welz, B. and Schlemmer, G. 1988. The use of freon as an alternate gas in graphite furnace atomic absorption spectrometry. At. Spectrosc. 9: 81-83.

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APPENDIX A

SECTION I

GENERAL QA/QC PRACTICES

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases must also be adhered to. For additional guidelines regarding these general laboratory procedures, see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

SECTION II

SPECIFIC QA/QC PROCEDURES

The quality assurance/quality control (QA/QC) procedures defined herein must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Contractor must also follow these procedures. NOTE: The cost of performing all QA/QC procedures specified in this Statement of Work is included in the price of performing the bid lot, except for duplicate, spike, and laboratory control sample analyses, which shall be considered separate sample analyses.

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The primary function of the QA/QC program is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by EPA EMSL-Las Vegas. The Contractor can expect to analyze two samples per calendar quarter during the contract period.

The Contractor must perform and report to SMO and EMSL/LV as specified in Exhibit B quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this contract. All the IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Contractor must also report, as specified in Exhibit B, linearity range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this Statement of Work, the term "analytical sample" is used in discussing the required frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit G. As the term is used, analytical sample includes all field samples, including Performance Evaluation samples, received from an external source, but it also includes all required QA/QC samples (matrix spikes, analytical/post-digestion

spikes, duplicates, serial dilutions, LCS, ICS, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, IGV/ICB, CCV/CCB). A "frequency of 10%" means once every 10 analytical samples. Note: Calibration verification samples (IGV/CCV) and calibration verification blanks (ICB/CCB) are not counted as analytical samples when determining 10% frequency.

In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their QA/QC analysis must be analyzed under the same operating and procedural conditions.

If any QC measurement fails to meet contract criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Contractor must report all QC data in the exact format specified in Exhibits B and H.

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as described in this Exhibit:

1. Instrument Calibration
2. Initial Calibration Verification (IGV) and Continuing Calibration Verification (CCV)
3. CRDL Standards for AA (CRA) and ICP (CRI)
4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
5. ICP Interference Check Sample (ICS) Analyses
6. Spike Sample Analysis (S)
7. Duplicate Sample Analysis (D)
8. Laboratory Control Sample (LCS) Analysis
9. ICP Serial Dilution Analysis (L)
10. Instrument Detection Limit (IDL) Determination
11. Interelement Corrections for ICP (ICP)
12. Linear Range Analysis (LRA)
13. Furnace AA QC Analyses

1. Instrument Calibration

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis must be given in the raw data.

Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be within $\pm 5\%$ of the true value. Each standards concentration and the calculations to show that the $\pm 5\%$ criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary.

The $\pm 5\%$ criteria does not apply to the atomic absorption calibration standard at the CRDL.

Calibration standards for AA procedures must be prepared as described in Exhibit D.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification and blank check; resloping is acceptable as long as it is immediately preceded and immediately followed by CCV and CCB. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.

2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

a. Initial Calibration Verification (ICV)

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses (in Exhibit E), the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used for analysis. For CN, the initial calibration verification standard must be distilled. The Initial Calibration Verification for CN serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV. The values for the initial and subsequent continuing calibration verifications shall be recorded on FORM II-IN for ICP, AA, and cyanide analyses, as indicated.

b. Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions
2. NBS SRM 1643a
3. A Contractor-prepared standard solution

TABLE 1. INITIAL AND CONTINUING CALIBRATION VERIFICATION CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	<u>% of True Value (EPA Set)</u>	
		Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for a Case of samples received.

Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it as well as the difference in time between the CCV and the analytical sample immediately preceding it may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of preceding 10 analytical samples or all analytical samples analyzed since the last good calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP, AA and cyanide as indicated.

3. CRDL Standards for ICP (CRI) and AA (CRA)

To verify linearity near the CRDL for ICP analysis, the Contractor must analyze an ICP standard (CRI) at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.

To verify linearity near the CRDL for AA analysis, the Contractor must analyze an AA standard (CRA) at the CRDL or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the Initial Calibration Verification.

Specific acceptance criteria for the two standards will be set by EPA in the future. In the interim, the Contractor must analyze and report these Standards on FORM II(PART 2)-IN.

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses

a. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours

during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run. The results for the calibration blanks shall be recorded on FORM III-IN for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the calibration blank result exceeds the IDL, the result must be so reported in ug/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the CRDL (Exhibit C), terminate analysis, correct the problem, recalibrate, verify the calibration and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration blank.

b. Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch¹ of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM III-IN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

- 1) If the absolute value of the concentration of the blank is less than or equal to the Contract Required Detection Limit (Exhibit C), no correction of sample results is performed.
- 2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.
- 3) If the concentration of the blank is below the negative CRDL, then all samples reported below 10x CRDL associated with the blank must be redigested and reanalyzed.

¹A group of samples prepared at the same time.

The values for the preparation blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples on FORM III-IN for ICP, AA, and cyanide analyses.

5. ICP Interference Check Sample (ICS) Analysis

To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Samples must be obtained from EPA (EMSL/LV) if available and analyzed according to the instructions supplied with the ICS.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of $\pm 20\%$ of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all contract specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

If the ICP Interference Check Sample is not available from EPA, independent ICP Check Samples must be prepared with interferent and analyte concentrations at the levels specified in Table 2-Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample. The mean value and standard deviation must be established by initially analyzing the Check Samples at least five times repetitively for each parameter on FORM IV-IN. Results must fall within the control limit of $\pm 20\%$ of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the Interference Check Sample analyses must be recorded on FORM IV-IN for all ICP parameters.

TABLE 2. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

6. Spike Sample Analysis (S)

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps (i.e., CN-). At least one spike sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.²

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see section 7, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

The analyte spike must be added in the amount given in Table 3-Spiking Levels for Spike Sample Analysis, for each element analyzed. If two analytical methods are used to obtain the reported values for the same element within a Sample Delivery Group (i.e. ICP, GFAA), spike samples must be run by each method used.

²EPA may require additional spike sample analysis, upon Project Officer request, for which the Contractor will be paid.

If the spike recovery is not at or within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on FORMs I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

For flame AA, ICP, and CN analyses, when the pre-digestion/pre-distillation spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, a post-digestion/post-distillation spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. Results of the post-digestion/post-distillation spike must be reported on FORM V(PART 2)-IN. Note: No post digest spike is required for Hg.

In the instance where there is more than one spike sample per matrix and concentration per method per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix, level, and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

$$\% \text{Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

Where, SSR - Spiked Sample Result
SR - Sample Result
SA - Spike Added

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive or negative) must be reported on FORM V-IN for ICP, AA and cyanide analyses, as indicated.

The units for reporting spike sample results will be identical to those used for reporting sample results in FORM I-IN (i.e., $\mu\text{g/L}$ for aqueous and mg/Kg dry weight basis for solid).

TABLE 3. SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS

Element	For ICP/AA (ug/L)		For Furnace AA (ug/L)		Other ⁽¹⁾ (ug/L)
	Water	Soil ⁽²⁾	Water	Soil ⁽²⁾	
Aluminum	2,000	*			
Antimony	500	500	100	100	
Arsenic	2,000	2,000	40	40	
Barium	2,000	2,000			
Beryllium	50	50			
Cadmium	50	50	5	5	
Calcium	*	*			
Chromium	200	200			
Cobalt	500	500			
Copper	250	250			
Iron	1,000	*			
Lead	500	500	20	20	
Magnesium	*	*			
Manganese	500	500			1
Mercury					
Nickel	500	500			
Potassium	*	*			
Selenium	2,000	2,000	10	10	
Silver	50	50			
Sodium	*	*			
Thallium	2,000	2,000	50	50	
Vanadium	500	500			
Zinc	500	500			100
Cyanide					

NOTE: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

¹Spiking level reported is for both water and soil/sediment matrices.

²The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

*No spike required.

7. Duplicate Sample Analysis (D)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.³ Duplicates cannot be averaged for reporting on FORM I-IN.

Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. EPA may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group (i.e., ICP, GFAA), duplicate samples must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where, RPD - Relative Percent Difference
S - First Sample Value (original)
D - Second Sample Value (duplicate)

The results of the duplicate sample analyses must be reported on FORM VI-IN in ug/L for aqueous samples and mg/Kg dry weight basis for solid original and duplicate samples. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x CRDL (Exhibit C). A control limit of ($\pm$) the CRDL must be used for sample values less than 5x CRDL, and the absolute value of the control limit (CRDL) must be entered in the "Control Limit" column on FORM VI-IN.

If one result is above the 5x CRDL level and the other is below, use the $\pm$ CRDL criteria. If both sample values are less than the IDL, the RPD is not calculated on FORM VI-IN. For solid sample or duplicate results < 5x CRDL, enter the absolute value of the CRDL, corrected for sample weight and percent solids, in the "Control Limit" column.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on FORMs I-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix, concentration, and method in the SDG. The percent difference data will be used by EPA to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to FORM VI-IN at a later date based on these precision results.

³EPA may require additional duplicate sample analyses, upon Project Officer request, for which the Contractor will be paid.

8. Laboratory Control Sample (LCS) Analysis

Aqueous and solid Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration Verification Solutions may be used). One aqueous LCS must be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group, or for each batch of aqueous samples digested, whichever is more frequent. An aqueous LCS is not required for mercury and cyanide analysis.

The EPA-provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be prepared and analyzed for every group of solid samples in a Sample Delivery Group, or for each batch of samples digested, whichever is more frequent.

All LCS results and percent recovery (%R) will be reported on FORM VII-IN. If the percent recovery for the aqueous LCS falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

9. ICP Serial Dilution Analysis (L)

Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not at or within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

where, I - Initial Sample Result

S - Serial Dilution Result (Instrument Reading x 5)

In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix and concentration in the Sample Delivery Group. Serial dilution results and "E" flags must be reported on FORM IX-IN.

10. Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed under this contract, the instrument detection limits (in ug/L) must be determined for each instrument used, within 30 days of the start of contract analyses and at least quarterly (every 3 calendar months), and must meet the levels specified in Exhibit C.

The Instrument Detection Limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-5x the instrument manufacturer's suggested IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined IDL for an instrument must always be used as the IDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

IDLs must be reported for each instrument used on FORM X-IN submitted with each data package. If multiple AA instruments are used for the analysis of an element within a Sample Delivery Group, the highest IDL for the AAs must be used for reporting concentration values for that Sample Delivery Group. The same reporting procedure must be used for multiple ICPs.

11. Interelement Corrections for ICP

Before any field samples are analyzed under this contract, the ICP interelement correction factors must be determined prior to the start of contract analyses and at least annually thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. Results from interelement correction factors determination must be reported on FORM XI(PART 1)-IN and FORM XI(PART 2)-IN for all ICP parameters.

12. Linear Range Analysis (LRA)

For all ICP analyses, a linear range verification check standard must be analyzed and reported quarterly (every 3 calendar months) for each element on FORM XII-IN. The standard must be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard must be within $\pm 5\%$ of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

13. Furnace Atomic Absorption (AA) QC Analyses

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1-Furnace AA Analysis Scheme ("MSA Tree") will be required for quantitation. (These procedures do not replace those in Exhibit D of this SOW, but supplement the guidance provided therein.)

- a. All furnace analyses must fall within the calibration range. In addition, all analyses, except during full methods of Standard Addition (MSA), will require duplicate injections. The absorbance or concentration of each injection must be reported in the raw data as well as the average absorbance or concentration values and the relative standard deviation (RSD) or coefficient of variation (CV). Average concentration values are used for reporting purposes. The Contractor must be consistent per method and SDG in choosing absorbance or concentration to evaluate which route is to be followed in the MSA Tree. The Contractor must also indicate which of the two is being used if both absorbance and concentration are reported in the raw data. For MSA analysis, the absorbance of each injection must be included in the raw data. A maximum of 10 full sample analyses to a maximum 20 injections may be performed between each consecutive calibration verifications and blanks. For concentrations greater than CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the analytical sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value reported on FORM I-

IN with an "M". The "M" flag is required for the analytical spike as well as the sample. If the analytical spike for a sample requires an "M" flag, the flag must be reported on FORM I- IN for that sample.

- b. All furnace analyses for each analytical sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike¹ will be required to be at a concentration (in the sample) 2x CRDL. This requirement for an analytical spike will include the LCS and the preparation blank. (The LCS must be quantitated from the calibration curve and corrective action, if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85-115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses (see item 6, this section), will then determine how the sample will be quantitated, as follows:

- 1) If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.
- 2) If the spike recovery is greater than or equal to 40% and the sample absorbance or concentration is less than 50% of the "spike"⁵, report the sample results to the IDL. If the spike recovery is less than 85% or greater than 115%, flag the result with a "W".
- 3) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is at or

¹Analytical Spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

⁵"Spike" is defined as [absorbance or concentration of spike sample] minus [absorbance or concentration of the sample].

between 85% and 115%, the sample must be quantitated directly from the calibration curve and reported down to the IDL.

- 4) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

c. The following procedures will be incorporated into MSA analyses.

- 1) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.
- 2) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

- 3) For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.
- 4) Spikes must be prepared such that:
 - a) Spike 1 is approximately 50% of the sample absorbance or concentration.
 - b) Spike 2 is approximately 100% of the sample absorbance or concentration.
 - c) Spike 3 is approximately 150% of the sample absorbance or concentration.
- 5) The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data. The results must be reported on FORM VIII-IN. Reported values obtained by MSA must be flagged on the data sheet (FORM I-IN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.
- 6) If the correlation coefficient (r) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, report the results on FORM I-IN from the run with the best "r" and flag the result with a "+" on FORM VIII-IN and FORM I-IN.

Figure 1
FURNACE ATOMIC ABSORPTION ANALYSIS SCHEME

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-218, ICP AND IC DATA CALCULATIONS FOR SST SAMPLES

APPLICABILITY

This procedure addresses the data manipulations required to produce the data report provided to the Analytical Laboratory Operations (ALO) Project Support Office (PSO) for inductively coupled plasma atomic emission spectroscopy (ICP) and ion chromatography (IC) analyses using Lotus 1-2-3 spreadsheet programs. Calculations involve simple algebraic steps to incorporate sample weights and dilutions involved in sample preparation steps. All calculations are easily verified by hand calculations.

Although such calculations are usually incorporated in software packages packages supplied by the instrument vendor, such software packages have not been installed on the current ICP and IC instrumentation in the 325 Building.

DEFINITIONS

None

RESPONSIBLE STAFF

Inorganic Task Leader
Technical Staff
ALO Project Support Clerk

PROCEDURE

1.0 ICP Analyses

- 1.1 Background: ICP provides analyses of solutions. Primary analytical data are reported in units of $\mu\text{g/ml}$. Generally, data must be processed to account for the sample preparation methodology. Solid samples must go through some type of dissolution process. Liquid samples may require dilution or pre-concentration prior to analysis.
- 1.2 Primary analytical data (in units of $\mu\text{g/ml}$) from the instrument report are entered into the spreadsheet template. This data is checked for transcription accuracy by both the enterer and verifier, as per PNL-MA-70, PAP-70-1101.

Author <i>M. W. Lue</i>	Date <i>8/17/90</i>	Project Mgr. <i>2 E. Jones</i>	Date <i>8/15/90</i>	QAD Representative <i>CK Gerbe</i>	Date <i>8/17/90</i>
Technical Reviewer <i>2 E. Jones</i>	Date <i>8/15/90</i>	Line Mgr. <i>[Signature]</i>	Date <i>8/17/90</i>	Other	Date
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PNL TECHNICAL PROCEDURE

- 1.3 The Inorganic Task Leader or their designee processes the primary analytical data through a Lotus 1-2-3 program. The approach used is described in Attachment 1.
- 1.4 The Inorganic Task Leader reviews the final data report and signs the data report.
- 1.5 The data report provided to the ALO-PSO includes the primary analytical data report (instrument print-out), instrument blank data, estimated detection and quantitation limits, and the resolved analytical data for the sample.

2.0 IC Analyses

- 2.1 Background: IC provides analyses of solutions. Primary analytical data are reported in units of $\mu\text{g/ml}$. Generally, data must be processed to account for the sample preparation methodology. Solid samples must go through some type of dissolution process. Liquid samples may require dilution or pre-concentration prior to analysis.
- 2.2 Primary analytical data and sample preparation information are entered into the spreadsheet template. The data/information is checked for transcription accuracy by both analyst and reviewer, as per PNL-MA-70, PAP-70-1101.
- 2.3 The Inorganic Task Leader or their designee processes the primary analytical data through the Lotus 1-2-3 program. The calculations are described in Attachment 2.
- 2.4 The Inorganic Task Leader reviews the final data report, including data transcription accuracy, and signs the report.
- 2.5 The data report provided to the ALO-PSO includes the primary analytical data report (instrument print-out), instrument blank data, estimated detection limits, and the resolved analytical data for the sample.

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ICP CALCULATIONS

Calculations to support the generation of the final ICP reports are performed within a LOTUS 123 spreadsheet. The raw analytical data (in $\mu\text{g/mL}$) is obtained from the computer generated output of the ICP system and the sample preparation data is obtained from the "Sample Prep Data Sheet". These data are keyed into an ICP template; templates are available for acid leached, water leached and fused sample sets. The calculations below (identified as A thru S) accompany ICP CALCULATION KEYS 1-5.

General Information:

The "boxed" areas in the ICP CALCULATION KEYS 1,2 & 5 are sample analysis information/data and worksheet data which has been keyed into the spreadsheet template. This data is verified by both the enterer and verifier.

The Sample ID is generally the sample log number and for the calculation explanations below the last digit identifies the sample number (e.g., 89-0621a3 is Sample 3).

For the spike control and blank, the results are many times expressed in wt%. This is actually a wt% equivalence with the spike control assuming a nominal 1 g sample weight and the blank using an average sample weight of samples 1 & 2. The data is presented in the same units for comparison purposes.

For calculation of dilution factors it has been assumed that 1 mL of water equals 1 g.

Key 2A: Spike Dilution Factor for Samples 3 & 4

$$\text{Spike Dilution} = \frac{(\text{Makeup Vol mL})}{(\text{Spike Vol mL})}$$

Key 2B: Preparation Dilution Factors for Samples 1,2,3 & 5

For Acid/Water Leached Samples

$$\text{Prep Factor} = \frac{(\text{Makeup Vol mL}) + (\text{Sample Wt g})}{(\text{Sample Wt g})}$$

For Fused Samples

$$\text{Prep Factor} = \frac{(\text{Makeup Vol mL})}{(\text{Sample Wt g})} * \frac{(\text{X mL}) + (\text{Y mL})}{(\text{X mL})}$$

Where: X mL = Dil: Smpl mL (or volume of Makeup Vol sampled)
Y mL = Dil: Vol mL (or volume of Diluent added)

Key 2C: Weight % Factor for Samples 1,2,3 & 5

$$\text{Wt\% Factor} = (\text{Prep Factor}) * (\text{ICP Dilution}) * 0.0001$$

Key 2D: Weight % Factor for Sample 4

$$\text{Wt\% Factor} = (\text{Makeup Vol mL}) * (\text{ICP Dilution}) * 0.0001$$

Key 2E: Element Weight % for Samples 1 thru 5 (except Bi)

$$\text{Weight \%} = ((\text{Conc}) - (\text{Blank})) * (\text{Wt\% Factor})$$

Where: Conc = The measured $\mu\text{g/mL}$ concentration of each element [See Key 1]
Blank = Average of last 10 system blanks [See Key 5]

Key 2F: Bismuth Weight % for Samples 1 thru 5

$$\text{Weight \%} = \frac{(\text{Conc Bi } \mu\text{g/mL}) * (\text{Wt\% Factor})}{(\text{ICP Dilution})}$$

Note: Bi is analyzed in sequential mode and the $\mu\text{g/mL}$ concentration of the prepared base solution is entered from a worksheet. That is, the ICP dilution factor and blank have already been incorporated

Key 3G: Weight Percent Reported

Logical Test Only -- For Initial solution [G1] and Diluted solution [G2]

If Wt% < (DL * Wt% Factor) Then Report "<DL"
If Wt% > (DL * Wt% Factor) and < (QL * Wt% Factor)
Then Report Weight % within parentheses
If Wt% > (QL * Wt% Factor) Then Report Weight %

Key 3H: Percent Difference -- For Serial Dilutions Only

$$\% \text{ Dif} = \frac{(G1 - G2)}{G1} * 100$$

Where: G1 = Wt% of Initial solution
G2 = Wt% of Diluted solution

Note: Both G1 and G2 must be above (QL * Wt% Factor)
before value reported

Key 3I: Detection Limit -- DL (μg/mL)

This data is input from the "blank" Standards file. It represents 3 times the standard deviation of the last 10 blanks analyzed. [See Key 5]

Key 3J: Quantitation Limit -- QL (μg/mL)

This data is input from the "blank" Standards file. It represents 10 times the standard deviation of the last 10 blanks analyzed. [See Key 5]

Key 4K: Average Wt% for Samples 1 & 2

$$\text{Average Wt\%} = \frac{(\text{Sample 1 [G1]}) + (\text{Sample 2 [G1]})}{2}$$

Note: Both Sample 1 & 2 must be above (DL * Wt% Factor),
otherwise no average is reported.

Key 4L: Relative Percent Difference -- RPD

$$RPD = \left| \frac{(\text{Sample 1 [G1]}) - (\text{Sample 2 [G1]})}{((\text{Sample 1 [G1]}) + (\text{Sample 2 [G1]})) / 2} \right| * 100$$

Note: Both Sample 1 & 2 must be above (DL * Wt% Factor), otherwise no RPD is reported.

Key 4M: Spike Added to Sample 3 -- (Wt% Equivalence Sample 3)

$$\text{Wt\% Spike Added} = \frac{(\text{Spike True Value}) * (\text{Spike Vol mL})}{(\text{Sample 3 Wt g})}$$

Note: Spike True Value is obtained from the base ICP template [See Key 5]

Key 4N: Percent Spike Recovery from Sample Matrix

$$\% \text{ Rec} = \frac{(\text{Wt\% Sample 3}) - (\text{Ave Wt\% Sample 1\&2})}{(\text{Wt\% Spike Added})} * 100$$

Key 4P: Measured Spike Control (µg/mL)

$$\mu\text{g/mL} = (\text{Conc} - \text{Blank}) * \text{Spike Dilution} * \text{ICP Dilution}$$

Where: Conc = The measured µg/mL concentration of each element [See Key 1]
Blank = Average of last 10 system blanks [See Key 5]

Note: P1 is the Initial solution and P2 is the Diluted solution

Key 4Q: Percent Difference for Serial Dilutions of Spike Control 4

Same as "H" above except P1 & P2 are substituted for G1 & G2

Key 4K: Spike Std (µg/mL)

Stock spike standard concentration as "given" in base ICP template -- [See Key 5]

Key 4S: Percent Recovery for Spike Control

$$\% \text{ Rec} = \frac{\text{Spike Control [P1]}}{\text{Spike Std}} * 100$$

ICP CALCULATION KEY 1

Date: 11/13/89 thru 11/14/89
Project: SST
Procedure: PNL-SP-7
M&TE: WA55672

Data Entry By: _____
Data Verified By: _____

File: icp0621a

Sample ID:	89-0621a1	89-0621a2	89-0621a3	89-0621a4	89-0621a4	89-0621a5
ICP Run #	1795	1796	1797	1818	1798	1816
(ug/mL) Ag	0.0229	0.0186	0.0268	0.0008	0.0032	-0.0010
Al	1.0147	0.9927	1.0280	0.0767	0.1068	0.0356
As	0.0162	0.0210	0.2929	1.5332	0.3942	0.0056
B	0.0650	0.0465	0.0508	0.0765	0.0296	0.0399
Ba	0.0122	0.0116	0.3287	1.5620	0.3085	0.0029
Be	0.0002	0.0002	0.0081	0.0381	0.0079	0.0000
Cd	0.7240	0.7062	0.7141	0.6813	0.1524	0.6490
Ce	0.0077	0.0046	0.0200	0.0565	0.0176	0.0098
Co	0.0509	0.0409	0.0564	-0.0290	0.0241	-0.0440
Cr	-0.0700	-0.0990	-0.0030	0.3501	0.0669	-0.0750
Cu	0.6986	0.6732	0.7387	0.1683	0.0386	0.0107
Dy	0.0247	0.0196	0.0607	0.2122	0.0442	0.0227
Fe	0.0027	-0.0010	0.0000	-0.0020	0.0031	0.0029
K	16.3020	15.8830	16.3700	0.4682	0.1034	0.0446
La	0.3335	0.2352	0.2275	0.3171	0.1086	0.5362
Li	0.0635	0.0585	0.0611	-0.0010	0.0048	0.0010
Mg	0.0167	0.0106	0.0132	0.0472	0.0159	0.0678
Mn	0.1623	0.1599	0.1608	0.1473	0.0317	0.1393
Mo	0.0628	0.0513	0.1419	0.4036	0.0810	0.0104
(ug/mL) Na	-0.0360	-0.0410	-0.0400	-0.0230	-0.0410	-0.0300
Nd	81.7450	78.9430	82.0510	0.5672	0.2143	0.6174
Ni	0.0281	0.0238	0.0333	-0.0040	0.0145	-0.0180
Ni	0.0198	0.0188	0.1035	0.4067	0.0866	0.0000
P	13.8820	13.8480	14.3850	0.0009	-0.0630	0.2147
Pb	0.9476	0.9625	1.0475	0.4229	0.0961	0.0276
Re	0.0129	0.0129	0.0132	-0.0040	0.0142	0.0036
Rh	-0.0200	-0.0270	-0.0290	-0.0140	0.0260	-0.0170
Ru	-0.0280	-0.0330	-0.0310	-0.0070	0.0043	-0.0040
Sb	0.2651	0.4614	0.4682	0.5366	0.3678	0.1267
Se	0.0696	-0.0070	0.3257	1.3044	0.3716	0.0151
Si	0.5745	0.4129	0.7129	0.6767	0.1561	0.5206
Sr	0.1754	0.1697	0.1757	0.0026	0.0006	0.0022
Te	0.0000	-0.0010	0.0095	0.0036	0.0379	-0.0050
Th	-0.0150	-0.0300	-0.0250	-0.0120	0.0304	-0.0330
Ti	0.0081	0.0075	0.0084	0.0062	0.0042	0.0049
Tl	-0.5370	-0.0920	0.6088	1.2332	0.6368	-0.4490
U	0.3414	0.1530	0.2454	-0.3130	0.0216	-0.4860
V	0.0000	0.0000	0.0791	0.3858	0.0776	-0.0020
Zn	0.0810	0.0770	0.1589	0.4076	0.0834	0.0210
Zr	0.7200	0.0100	0.0131	0.0000	0.0027	0.0001
(ug/mL) Bi	40.7900	15.9700	76.6600	-0.4100		-0.2900

ICP CALCULATION KEY 2

Date: 11/13/89 thru 11/14/89
Project: SST
Procedure: PNL SP-7

Analyst: _____
Reviewer: _____

File: icp0621a
Reported: 03/29/90

Sample Log#	89-0621a1	89-0621a2	89-0621a3	89-0621a4	89-0621a4	89-0621a5
ID	S1 5x	S1 7x	S2 5x	S2 7x	SP+S3 5x	SP+S3 7x
Prep Type	Acid	Acid	Acid	Acid	Acid	Acid
Sample Wt-g	1.061		1.018		1.050	
Makeup Vol-ml	250.0		250.0		250.0	
Dil: Smp/ML						
Dil: Vol-ml						
Prep Factor	236.60		246.65		239.07	
Spike ID						
Spike Vol-ml						
Spike Dilution						
ICP Dilution	5.00		5.00		5.00	
Wt% Factor	0.11830		0.12333		0.11954	
ICP Run #	1795		1796		1797	
Weight %						
Ag	0.0024		0.0019		0.0029	
Al	0.1147		0.1169		0.1175	
As	-0.0006		-0.0000		0.0325	
B	0.0050		0.0029		0.0033	
Ba	0.0013		0.0013		0.0392	
Be	0.0000		0.0000		0.0009	
Ca	0.0856		0.0870		0.0853	
Cd	0.0006		0.0002		0.0021	
Ce	0.0003		-0.0009		0.0010	
Co	-0.0133		-0.0174		-0.0054	
Cr	0.0822		0.0826		0.0879	
Cu	0.0023		0.0018		0.0066	
Dy	-0.0002		-0.0006		-0.0005	
Fe	1.9282		1.9584		1.9565	
K	0.0358		0.0252		0.0236	
La	0.0005		0.0062		0.0063	
Li	0.0014		0.0007		0.0010	
Mg	0.0191		0.0194		0.0192	
Mn	0.0073		0.0072		0.0169	
Mo	-0.0039		-0.0047		-0.0044	
Na	9.6653		9.7302		9.8027	
Nd	0.0014		0.0010		0.0021	
Ni	0.0015		0.0015		0.0115	
P	1.6212		1.6859		1.6983	
Pb	0.1100		0.1165		0.1231	
Re	0.0006		0.0006		0.0006	
Rh	-0.0112		-0.0125		-0.0124	
Ru	-0.0048		-0.0056		-0.0052	
Sb	0.0308		0.0563		0.0554	
Se	0.0021		-0.0073		0.0327	
Si	0.0657		0.0486		0.0830	
Sr	0.0207		0.0209		0.0209	
Te	-0.0037		-0.0039		-0.0026	
Th	-0.0059		-0.0080		-0.0072	
Ti	0.0007		0.0006		0.0007	
Tl	-0.0961		-0.0453		0.0399	
U	0.0124		-0.0103		0.0010	
V	-0.0003		-0.0003		0.0091	
Zn	0.0092		0.0091		0.0187	
Zr	0.0020		0.0009		0.0012	
Bi	0.9651		0.3939		1.8327	

ICP CALCULATION KEY 3

G1		G2		H						I		J	
Samp Log#:		89-0621a1		89-0621a2		89-0621a5							
Dilution:		5.80		5.00		1.00							
Wt% Factor:		0.11830		0.12333		0.02415							
ICP Run #		1795		1796		1816						DL QL	
	(Wt %)	(Wt %)	%Dif	(Wt %)	(Wt %)	%Dif	(Wt% *)	(Wt% *)	%Dif	(ug/mL)	(ug/mL)		
Ag	(0.0024)			(0.0019)			<DL			0.0126	0.0419		
Al	0.1147			0.1169			<DL			0.0886	0.2953		
As	<DL			<DL			<DL			0.1567	0.5223		
B	<DL			<DL			<DL			0.0718	0.2395		
Ba	0.0013			(0.0013)			<DL			0.0033	0.0112		
Be	<DL			<DL			<DL			0.0004	0.0012		
Ca	0.0856			0.0870			0.0157			0.0017	0.0058		
Cd	<DL			<DL			(0.0002)			0.0060	0.0201		
Ce	<DL			<DL			<DL			0.2083	0.6942		
Co	<DL			<DL			<DL			0.3038	1.0128		
Cr	0.0822			0.0826			(0.0002)			0.0065	0.0218		
Cu	(0.0023)			<DL			<DL			0.0177	0.0589		
Dy	<DL			<DL			<DL			0.0163	0.0545		
Fe	1.9282			1.9584			0.0010			0.0067	0.0222		
K	<DL			<DL			(0.0122)			0.4545	1.5150		
La	(0.0065)			(0.0062)			<DL			0.0435	0.1448		
Li	<DL			<DL			0.0015			0.0138	0.0462		
Mg	0.0191			0.0194			0.0034			0.0012	0.0038		
Mn	0.0073			0.0072			0.0002			0.0021	0.0069		
Mo	<DL			<DL			<DL			0.0717	0.2391		
Na	9.6653			9.7302			0.0138			0.1494	0.4979		
Nd	<DL			<DL			<DL			0.1056	0.3519		
Ni	<DL			<DL			<DL			0.0173	0.0578		
P	1.6212			1.6859			<DL			0.6388	2.1295		
Pb	0.1100			0.1165			<DL			0.0909	0.3028		
Re	<DL			<DL			<DL			0.0164	0.0547		
Rh	<DL			<DL			<DL			0.3368	1.1227		
Ru	<DL			<DL			<DL			0.0354	0.1180		
Sb	<DL			<DL			<DL			0.6341	2.1135		
Se	<DL			<DL			<DL			0.1113	0.3710		
Si	0.0657			0.0486			0.0121			0.0560	0.1867		
Sr	0.0207			0.0209			(0.0000)			0.0011	0.0036		
Te	<DL			<DL			<DL			0.0809	0.2696		
Th	<DL			<DL			<DL			0.1847	0.6157		
Ti	<DL			<DL			<DL			0.0090	0.0300		
Tl	<DL			<DL			<DL			2.6893	8.9644		
U	<DL			<DL			<DL			1.7634	5.8779		
V	<DL			<DL			<DL			0.0084	0.0279		
Zn	0.0092			0.0091			0.0004			0.0046	0.0153		
Zr	(0.0020)			<DL			<DL			0.0088	0.0292		
Bi	0.9651			0.3939			<DL			N/A	N/A		

* Methods blank - average sample weight used to calculate wt%.

03/29/90

ICP CALCULATION KEY 4

K	L	M	G1	G2	H	N	P1	P2	Q	R	S	
	89-0621a1 89-0621a2 Average		Spike Added	89-0621a3 5.00 Spike+ Sample	Spike+ Sample		<Sample ID> <Dilution>	89-0621a4 1.00 Spike Control	89-0621a4 5.00 Spike Control		Spike STD	
	(Wt %)	RPD	(Wt %)	(Wt %)	(Wt %)	% Dif	% Rec	(ug/mL)	(ug/mL)	% Dif	(ug/mL)	% rec
Ag	0.0021	20.0%		(0.0029)								
Al	0.1158	1.9%		0.1175								
As	N/A		0.0388	(0.0325)			83.8%	74.3	91.7	23.4%	80.0	92.9%
B	N/A			<DL								
Ba	0.0013	1.3%	0.0388	0.0392			97.7%	76.7	75.6	1.5%	80.0	95.9%
Be	N/A		0.0010	0.0009			97.6%	1.9	1.9	1.7%	2.0	93.2%
Ca	0.0863	1.7%		0.0853								
Cd	N/A		0.0010	(0.0021)			211.8%	3.1	3.6	16.0%	2.0	156.4%
Ce	N/A			<DL								
Co	N/A		0.0097	<DL			-55.9%	15.1	6.0	60.1%	20.0	75.6%
Cr	0.0824	0.4%	0.0039	0.0879			141.2%	8.1	8.6	6.7%	8.0	101.3%
Cu	N/A		0.0048	(0.0066)			137.1%	10.2	9.6	5.7%	10.0	101.8%
Dy	N/A			<DL								
Fe	1.9433	1.6%		1.9565								
K	N/A			<DL								
La	0.0063	5.4%		(0.0063)								
Li	N/A			<DL								
Mg	0.0193	1.4%		0.0192								
Mn	0.0073	1.7%	0.0097	0.0169			99.0%	19.8	19.7	0.5%	20.0	98.9%
Mo	N/A			<DL								
Na	9.6977	0.7%		9.8027								
Nd	N/A			<DL								
Ni	N/A		0.0097	0.0115			119.2%	19.6	19.6	0.3%	20.0	98.2%
P	1.6536	3.9%		1.6983								
Pb	0.1132	5.7%	0.0097	0.1231			101.5%	19.9	19.2	3.6%	20.0	99.5%
Re	N/A			<DL								
Rh	N/A			<DL								
Ru	N/A			<DL								
Sb	N/A		0.0097	<DL			572.0%	26.1	89.3	241.4%	20.0	130.7%
Se	N/A		0.0388	(0.0327)			84.5%	61.6	78.6	27.6%	80.0	76.9%
Si	0.0572	30.0%		0.0830								
Sr	0.0208	0.8%		0.0209								
Te	N/A			<DL								
Th	N/A			<DL								
Ti	N/A			<DL								
Tl	N/A		0.0388	<DL			102.9%	47.1	88.8	88.7%	80.0	58.8%
U	N/A			<DL								
V	N/A		0.0097	0.0091			94.2%	18.8	18.4	2.3%	20.0	94.1%
Zn	0.0092	1.1%	0.0097	0.0187			97.6%	19.9	19.8	0.5%	20.0	99.5%
Zr	N/A			(0.0012)								
Bi	0.6795	84.1%		1.8327								

03/29/90

ICP CALCULATION KEY 5

File: icp0621a

Last STD1 Run = 1820

STATS*****					Spike	
Run#	Ave[10] (ug/mL)	Std Dev	3x SD	10x SD	Std B-1	(ug/mL)
Ag	0.0029	0.0042	0.0126	0.0419	Ag	
Al	0.0452	0.0295	0.0886	0.2953	Al	
As	0.0212	0.0522	0.1567	0.5223	As	80.00
B	0.0230	0.0239	0.0718	0.2395	B	
Ba	0.0009	0.0011	0.0033	0.0112	Ba	80.00
Be	0.0002	0.0001	0.0004	0.0012	Be	2.00
Ca	0.0006	0.0006	0.0017	0.0058	Ca	
Cd	0.0028	0.0020	0.0060	0.0201	Cd	2.00
Ce	0.0480	0.0694	0.2083	0.6942	Ce	
Co	0.0423	0.1013	0.3038	1.0128	Co	20.00
Cr	0.0034	0.0022	0.0065	0.0218	Cr	8.00
Cu	0.0052	0.0059	0.0177	0.0589	Cu	10.00
Dy	0.0042	0.0054	0.0163	0.0545	Dy	
Fe	0.0029	0.0022	0.0067	0.0222	Fe	
K	0.0305	0.1515	0.4545	1.5150	K	
La	0.0085	0.0145	0.0435	0.1448	La	
Li	0.0047	0.0046	0.0138	0.0462	Li	
Mg	0.0005	0.0004	0.0012	0.0038	Mg	
Mn	0.0009	0.0007	0.0021	0.0069	Mn	20.00
Mo	0.0030	0.0239	0.0717	0.2391	Mo	
Na	0.0450	0.0498	0.1494	0.4979	Na	
Nd	0.0160	0.0352	0.1056	0.3519	Nd	
Ni	0.0069	0.0058	0.0173	0.0578	Ni	20.00
P	0.1778	0.2129	0.6388	2.1295	P	
Pb	0.0181	0.0303	0.0909	0.3028	Pb	20.00
Re	0.0078	0.0055	0.0164	0.0547	Re	
Rh	0.0743	0.1123	0.3368	1.1227	Rh	
Ru	0.0125	0.0118	0.0354	0.1180	Ru	
Sb	0.0045	0.2114	0.6341	2.1135	Sb	20.00
Se	0.0519	0.0371	0.1113	0.3710	Se	80.00
Si	0.0183	0.0187	0.0560	0.1867	Si	
Sr	0.0005	0.0004	0.0011	0.0036	Sr	
Te	0.0310	0.0270	0.0809	0.2696	Te	
Th	0.0350	0.0616	0.1847	0.6157	Th	
Ti	0.0026	0.0030	0.0090	0.0300	Ti	
Tl	0.2753	0.8964	2.6893	8.9644	Tl	80.00
U	0.2367	0.5878	1.7634	5.8779	U	
V	0.0028	0.0028	0.0084	0.0279	V	20.00
Zn	0.0028	0.0015	0.0046	0.0153	Zn	20.00
Zr	0.0028	0.0029	0.0088	0.0292	Zr	

IC CALCULATIONS

Calculations to support the generation of the final IC reports are performed within a LOTUS 123 spreadsheet. The raw analytical data (in $\mu\text{g/mL}$ or ppm) and sample preparation data are keyed into an IC spreadsheet template and both a raw data report and final report are generated. The calculations below (identified as A thru F) accompany the IC CALCULATION KEY.

General Information:

The "boxed" areas in the IC CALCULATION KEY are sample information and worksheet analysis data which is keyed into the spreadsheet template. This data/information is verified by both the analyst and reviewer.

Calculated mg/kg values are calculated and displayed to 3 significant digits only.

At the current time, the "measured" (not the true) spike control values are used to calculate the spike added to the sample (in mg/kg) and the percent spike recovery. Difficulties have arisen in the longterm stability of the multi-anion control standard which has prompted this decision.

Key A: Dilution factors for Samples 1,2,3 & 5 (blank)

$$\text{Samp Dil} = \frac{(\text{Vol mL}) + (\text{Wt gm})}{(\text{Wt gm})}$$

Key B: Dilution factor for Spike Control, Sample 4

$$\text{Samp Dil} = \frac{(\text{Vol mL})}{(\text{Spike mL})}$$

Key C: Concentration for Samples 1 thru 5 (blank)

$$\text{Sample } \underline{X} \text{ (mg/kg)} = (\mu\text{g/mL Sample } \underline{X}) * (\text{Samp Dil Sample } \underline{X})$$

Key D: Relative Percent Difference between Sample 1 & 2

$$RPD = \left| \frac{(S1 - S2)}{(S1 + S2) / 2} \right| * 100$$

Where: S1 = mg/kg concentration of sample 1
S2 = mg/kg concentration of sample 2

Key E: Spike added to Sample 3 [Sample 3 mg/kg equilalency]

(Sample 4 [μ g/mL]) * (Spike mL) * (Samp Dil Sample 3)

Key F: Percent Spike Recovery (based on measured spike control)

$$\begin{aligned} \% \text{ Spk Rec} &= S3 - ((S1 + S2)/2) \\ \% \text{ Spk Rec} &= \frac{\quad}{S3 \text{ Spk}} \end{aligned}$$

Where: S3 = mg/kg concentration of sample 3
S2 = mg/kg concentration of sample 2
S1 = mg/kg concentration of sample 1
S3 Spk = mg/kg spike added

Analyst: _____

Reviewer: _____

Subject: SST IC Results
Method: PNL-MA-599 7-40.8
M&TE: WA94483
Method: PNL-MA-599 7-40.7
M&TE: WA64102

Sample: 90-0716 File: ic0716

Sample:	90-0716	File:	ic0716
Sample:	90-0716	04/03/90	
Spk	2230	2290	2.7%
Spk	1500	1450	3.4%
Spk	12300	11600	5.9%
Spk	235000	226000	3.9%
Spk	27600	28500	3.2%
Spk	14000	13500	3.6%
Spk	993	936	5.9%
Spk	456	396	14.1%
Spk	2230	2290	2.7%
Spk	1500	1450	3.4%
Spk	12300	11600	5.9%
Spk	235000	226000	3.9%
Spk	27600	28500	3.2%
Spk	14000	13500	3.6%
Spk	993	936	5.9%
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Spk	456	396	14.1%
Spk	2230	2290	2.7%
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Spk	993	936	5.9%
Spk	456	396	14.1%
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Spk	1500	1450	3.4%
Spk	12300	11600	5.9%
Spk	235000	226000	3.9%
Spk	27600	28500	3.2%
Spk	14000	13500	3.6%
Spk	993	936	5.9%
Spk	456	396	14.1%
Spk	2230	2290	2.7%

- (a) The spike's measured concentration has been used to calculate the quantity of spike added in mg/kg.
- (b) The % spike recovery is valid only if the spike level is over 20% of the sample's base value.
- (c) The average Wt-gm of Sample 1 & 2 is used to calculate blank in mg/kg.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-219, ANTIMONY (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

APPLICABILITY

This procedure is applicable for determining the concentration of antimony in wastes, mobility-procedure extracts, soils, and ground water. The methodology is comparable to CLP Method 204.2 in SOW 788. All samples shall be subjected to an appropriate dissolution/digestion procedure prior to analysis as specified by the cognizant scientist or in Test Instructions (TIs) or Analytical Request Forms (ARFs).

DEFINITIONS

Batch: A set of 20 or fewer samples of like matrix.

Group (sample delivery group): A set of 20 samples or less submitted at the same time.

RESPONSIBLE STAFF

Cognizant Scientist
Technician

PROCEDURE

1.0 Summary of Method

- 1.1 Following the dissolution/digestion of the sample, a representative sample aliquot and modifier are placed, by means of an automatic sampler, into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization is proportional to the antimony concentration.
- 1.2 The reportable detection limit for Sb is 4 mg/Kg for soil and 20 $\mu\text{g/L}$ for water. Typical instrument detection limit (IDL) for Sb is 6 $\mu\text{g/L}$ in the analysis solution.

Author <i>JM Robbins</i> JM Robbins	Date 4-21-92	Project Mgr. <i>TE Jones</i> TE Jones	Date 4/21/92	QAD Representative <i>TL Ehlert</i> TL Ehlert	Date 4/21/92
Technical Reviewer <i>J Wagner</i> J Wagner	Date 4-23-92	Line Mgr. <i>AG King</i> AG King	Date 4/23/92	Other	Date
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2.0 Interferences

- 2.1 Elemental Sb and many of its compounds (e.g., antimony chloride) have relatively high volatility; therefore, samples may be subject to losses of Sb during sample preparation. Spiked samples and relevant standard reference materials should be processed to determine if the chosen dissolution procedure is appropriate.
- 2.2 Care must be employed in selecting the drying and charring step times, temperatures and temperature ramps. A palladium, or other acceptable analyte modifier (e.g., platinum), and magnesium nitrate should be added to all digestates prior to analysis to minimize volatilization losses during drying and charring. Magnesium nitrate has been shown to assist in spreading the Pd-Sb compounds more evenly in the furnace which reduces diffusion time of the analyte in the Mg oxide matrix (Slavin et al., 1982; Jackson and Qiao, 1990). Magnesium thus serves to sharpen the analyte peak shape during atomization and increases analytical precision.
- 2.3 Sb analysis is subject to a relatively high background absorbance in the presence of potassium sulfate which is not completely eliminated by Zeeman background correction (Welz, 1988a). Use of a hydrogen-argon gas mixture in the char step eliminates this interference by driving off the sulfate as H_2SO_4 .

Hydrogen also enhances reduction of Pd which is necessary for Sb stabilization (Rettberg and Beach, 1989). Use of this argon-hydrogen gas mixture lowers the appearance temperature of Sb, requiring a modification of the temperature programming of the pyrolysis and atomization steps (Ni Zhe-ming and Shan Xiao-quan, 1987).
- 2.4 Sb may condense at cool ends of graphite furnace during atomization; potentially causing memory effects in subsequent analyses. This situation can be minimized by operating the furnace at 2650°C immediately after atomization. Alternatively, the use of a transverse heated graphite furnace (with longitudinal a.c. magnet for Zeeman effect background correction), as introduced on the Perkin-Elmer 4100ZL GFAAS instrument, can prevent this condensation phenomena.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following: 1) a tolerance limit is stated with a measurement value, or 2) the following system of tolerances shall be in effect:

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PNL TECHNICAL PROCEDURE

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 369 mL means 369.0 ± 0.5 mL.
- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

4.0 Apparatus and Materials

- 4.1 Atomic absorption spectrophotometer: Double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-900 nm, provisions for simultaneous background correction, and interfacing with a computer and/or strip-chart recorder. Example: Perkin-Elmer 5100 AA Spectrophotometer with AS60 autosampler, deuterium lamp background correction, and IBM PS/2 computer.
- 4.2 Antimony hollow cathode lamp: Electrodeless discharge lamps (EDL) are generally preferred as they have greater lamp output and longer life than hollow cathode lamps (HCL). Sb EDL lamps provide the same sensitivity and detection limit as Sb HCL lamps.
- 4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls. Example: Perkin-Elmer HGA 600
- 4.4 Pipets: Calibrated, with disposable tips, sized from 5 to 1,000 μ L, as required.
- 4.5 Balance: Analytical, capable of minimally weighing to the nearest 0.001 g.

5.0 Reagents

- 5.1 Deionized water: Deionized water of sufficient quality, similar to ASTM Type II reagent water, shall be used for preparing sample, standards, and reagent dilutions. Calibration and sample blanks will produce concentrations at or below IDL.
- 5.2 Concentrated nitric acid (HNO_3): Ultrex grade.
- 5.3 Antimony standard stock solution (1,000 mg/L): Preferred: Acquire a certified aqueous standard from NIST or an equivalent supplier and verify by comparison with a second standard.

Alternative: Dissolve 2.743 g of antimony potassium tartrate (analytical grade), dissolve in deionized water, and dilute to 1 L.

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Caution: Antimony compounds are toxic and should be handled with care.

- 5.4 Antimony working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3 at 2% of final volume, respectively, and dilute to volume with deionized water.
- 5.5 Palladium nitrate - magnesium nitrate mixed modifier solution:
Preferred: Mix equal volumes of 3000 $\mu\text{g/L}$ of a certified aqueous Pd standard in HNO_3 and 2000 $\mu\text{g/L}$ of $\text{Mg}(\text{NO}_3)_2$ (Merck, suprapure or equivalent), respectively. A 5 μL volume of this solution is added to each sample, corresponding to masses of 15 μg of Pd (32.5 μg PdNO_3) and 10 μg of $\text{Mg}(\text{NO}_3)_2$ (Schlemmer and Welz, 1986 and Welz et al., 1988a,b).

Alternative source for palladium: Dissolve 0.300 g Pd wire in a minimum volume of aqua regia and evaporate to dryness, add 5 mL of concentrated HNO_3 , warm until dissolution is complete, dilute to 100.0 mL; or dissolve 0.5001 g palladium chloride (PdCl_2) in 5 mL of concentrated HNO_3 , evaporate to near dryness, repeat with 5 mL of concentrated HNO_3 , and dilute with water to 100.0 mL.

- 5.6 Argon purge gas: Industrial-grade argon or a mixture of argon-hydrogen (95-5%).

6.0 Quality Control

- 6.1 All quality control (QC) data shall be maintained and available for easy reference or inspection.
- 6.2 Minimum QC.
- 6.2.1 The system shall be calibrated following manufacturer's recommended calibration procedure which is in the instrument reference manual (see Section 10.0). Calibration parameters shall be established and recorded each day of operation.
- 6.2.2 Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest calibration standard.
- 6.2.3 Employ a minimum of one method blank per sample group (typically 20 samples) or batch of samples digested.

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6.2.4 Analyze at least one verification check standard or one QC standard every 12 samples, or more frequently. For CERCLA work include a verification standard or a QC standard after every 10 samples. If the results of the verification or QC standard are not within 80% to 120% of their mean value, the cognizant scientist shall determine the corrective action. All samples within the previously analyzed sample group shall be flagged on the data reports and the corrective action documented with the data. Validation of the data is the responsibility of the technical group leader.

Note: Verification standards help monitor the life and performance of the graphite tube. An RSD for duplicate injections of midrange standards exceeding 10%, or an instrument response <70% of the manufacturer's recommendation as stated in the reference manual (see Section 10), shall be investigated and corrective action, if required, documented.

6.2.5 Additional QC (i.e., duplicates, matrix spikes, duplicate matrix spikes, multiple injections, additional system or matrix blanks, tighter tolerances, holding times, etc.) shall be governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements shall be provided by the ARF, the project Statement of Work (SOW), or the sample analysis TI.

6.3 QC for clients requesting compliance with Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) requirements.

6.3.1 Analyze samples per protocol detailed in Appendix A. Use Figure 1 of Appendix A to establish the quantitation method to be used; that is, either direct calibration or method of standard addition.

6.3.2 Any additional QC requirements shall be governed by the SOW from the client with the analysis protocol transmitted to the analyst via TI.

7.0 Analysis Method

Sample collection, preservation and preparation is not within the scope of this procedure. However, it is important that samples be collected and preserved properly in order to maintain sample integrity. The applicability of sample preparation schemes, such as PNL-ALO-101, for specific matrices shall be demonstrated by analyzing spiked samples or relevant standard reference materials, or by the use of other qualifying techniques.

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- 7.1 The 217.6 nm wavelength line and a background correction system shall be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters. These are located in the instrument reference manual (see Section 10.0).
- 7.2 Furnace parameters suggested by the manufacturer in the reference manual should be employed as guidelines. The furnace parameters used shall be recorded with the data.

GUIDELINES: Furnace settings -- P-E 5000 or 5100

<u>Step</u>	<u>Temp(°C)</u>	<u>Ramp Time(sec)</u>	<u>Hold time(sec)</u>
Drying #1	90	1	15
Drying #2	130	10	10
Charring	1000	10	20
Cool down #1	30	1	15
Atomization	2200	0	5
Cleaning	2650	1	5
Cool Down #2	20	1	5

Note: Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters may be confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

- 7.3 Inject measured μL -aliquots of sample and modifier solution as directed by the cognizant scientist into the furnace and atomize. If the concentration found is greater than the highest standard, the sample shall be diluted in the same acid matrix and reanalyzed.
- 7.4 Calculate the antimony concentration: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors shall be applied prior to reporting results. Concentrations reported for multiphase samples shall be appropriately qualified (e.g., $\mu\text{g/L}$ aqueous phase or mg/Kg for solids).

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8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and QC standards as per PNL-MA-70, PAP-70-901.

9.0 Records

Records will be maintained and controlled so as to conform to requirements of Manual PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Data Sheets provide a mechanism for control of most records. LRB will be used in accordance with PNL-MA-68, Section 6.4, LRBs.

10.0 References

Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

Jackson, K.W. and Qiao, H.C. 1990. Effects of charring on particle distribution and atomization characteristics in slurry ETAAS (Sch. Pub. Health. State Univ.. New York, Wadsworth Labs., Albany, N.Y.)

Ni Zhe-ming and Shan Xiao-quan. 1987. The reduction and elimination of matrix interferences in graphite furnace atomic absorption spectrometry. Spectrochim. Acta. 42B: 937-949.

Perkin-Elmer Atomic Absorption Spectrophotometer Reference Manual. 1986. Model 5100, Volume 1 and Volume 2.

Rettberg, T and Beach, L.M. 1989. Peak profile characteristics in the presence of palladium for graphite furnace atomic absorption spectrometry. J. Anal At. Spectro. 4: 427-431.

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Schlemmer, G. and Welz, B. 1986. Palladium and magnesium nitrates, a more universal modifier for graphite furnace atomic absorption spectrometry. Spectro. Acta. 41B: 1157-1165.

USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, SOW 788, Method 204.2.

Welz, B., Schlemmer, G. and Mudakit, J.R. 1988. Palladium nitrate - magnesium nitrate modifier for graphite furnace atomic absorption spectrometry. Part 1. Determination of arsenic, antimony, selenium and thallium in airborne particulate matter*. J. Anal. At. Spectro. 3:93-97.

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APPENDIX A

SECTION I

GENERAL QA/QC PRACTICES

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases must also be adhered to. For additional guidelines regarding these general laboratory procedures, see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

SECTION II

SPECIFIC QA/QC PROCEDURES

The quality assurance/quality control (QA/QC) procedures defined herein must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Contractor must also follow these procedures.

NOTE: The cost of performing all QA/QC procedures specified in this Statement of Work is included in the price of performing the bid lot, except for duplicate, spike, and laboratory control sample analyses, which shall be considered separate sample analyses.

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The primary function of the QA/QC program is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by EPA EMSL-Las Vegas. The Contractor can expect to analyze two samples per calendar quarter during the contract period.

The Contractor must perform and report to SMO and EMSL/LV as specified in Exhibit B quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this contract. All the IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Contractor must also report, as specified in Exhibit B, linearity range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this Statement of Work, the term "analytical sample" is used in discussing the required frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit C. As the term is used, analytical sample includes all field samples, including Performance Evaluation samples, received from an external source, but it also includes all required QA/QC samples (matrix spikes, analytical/post-digestion

spikes, duplicates, serial dilutions, LCS, ICS, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, IGV/ICB, CCV/CCB). A "frequency of 10%" means once every 10 analytical samples. Note: Calibration verification samples (IGV/CCV) and calibration verification blanks (ICB/CCB) are not counted as analytical samples when determining 10% frequency.

In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their QA/QC analysis must be analyzed under the same operating and procedural conditions.

If any QC measurement fails to meet contract criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Contractor must report all QC data in the exact format specified in Exhibits B and H.

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as described in this Exhibit:

1. Instrument Calibration
2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)
3. CRDL Standards for AA (CRA) and ICP (CRI)
4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
5. ICP Interference Check Sample (ICS) Analyses
6. Spike Sample Analysis (S)
7. Duplicate Sample Analysis (D)
8. Laboratory Control Sample (LCS) Analysis
9. ICP Serial Dilution Analysis (L)
10. Instrument Detection Limit (IDL) Determination
11. Interelement Corrections for ICP (ICP)
12. Linear Range Analysis (LRA)
13. Furnace AA QC Analyses

1. Instrument Calibration

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis must be given in the raw data.

Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be within $\pm 5\%$ of the true value. Each standards concentration and the calculations to show that the $\pm 5\%$ criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary.

The $\pm 5\%$ criteria does not apply to the atomic absorption calibration standard at the CRDL.

Calibration standards for AA procedures must be prepared as described in Exhibit D.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification and blank check; resloping is acceptable as long as it is immediately preceded and immediately followed by CCV and CCB. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.

2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

a. Initial Calibration Verification (ICV)

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses (in Exhibit E), the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used for analysis. For CN, the initial calibration verification standard must be distilled. The Initial Calibration Verification for CN serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV. The values for the initial and subsequent continuing calibration verifications shall be recorded on FORM II-IN for ICP, AA, and cyanide analyses, as indicated.

b. Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions
2. NBS SRM 1643a
3. A Contractor-prepared standard solution

TABLE 1. INITIAL AND CONTINUING CALIBRATION VERIFICATION
CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	% of True Value (EPA Set)	
		Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for a Case of samples received.

Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it as well as the difference in time between the CCV and the analytical sample immediately preceding it may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of preceding 10 analytical samples or all analytical samples analyzed since the last good calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP, AA and cyanide as indicated.

3. CRDL Standards for ICP (CRI) and AA (CRA)

To verify linearity near the CRDL for ICP analysis, the Contractor must analyze an ICP standard (CRI) at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.

To verify linearity near the CRDL for AA analysis, the Contractor must analyze an AA standard (CRA) at the CRDL or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the Initial Calibration Verification.

Specific acceptance criteria for the two standards will be set by EPA in the future. In the interim, the Contractor must analyze and report these Standards on FORM II(PART 2)-IN.

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses

a. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours

during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run. The results for the calibration blanks shall be recorded on FORM III-IN for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the calibration blank result exceeds the IDL, the result must be so reported in ug/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the CRDL (Exhibit C), terminate analysis, correct the problem, recalibrate, verify the calibration and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration blank.

b. Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch¹ of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM III-IN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

- 1) If the absolute value of the concentration of the blank is less than or equal to the Contract Required Detection Limit (Exhibit C), no correction of sample results is performed.
- 2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.
- 3) If the concentration of the blank is below the negative CRDL, then all samples reported below 10x CRDL associated with the blank must be redigested and reanalyzed.

¹A group of samples prepared at the same time.

The values for the preparation blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples on FORM III-IN for ICP, AA, and cyanide analyses.

5. ICP Interference Check Sample (ICS) Analysis

To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Samples must be obtained from EPA (EML/LV) if available and analyzed according to the instructions supplied with the ICS.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of $\pm 20\%$ of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all contract specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

If the ICP Interference Check Sample is not available from EPA, independent ICP Check Samples must be prepared with interferent and analyte concentrations at the levels specified in Table 2-Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample. The mean value and standard deviation must be established by initially analyzing the Check Samples at least five times repetitively for each parameter on FORM IV-IN. Results must fall within the control limit of $\pm 20\%$ of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the Interference Check Sample analyses must be recorded on FORM IV-IN for all ICP parameters.

TABLE 2. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

6. Spike Sample Analysis (S)

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps (i.e., CN-). At least one spike sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.²

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see section 7, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

The analyte spike must be added in the amount given in Table 3-Spiking Levels for Spike Sample Analysis, for each element analyzed. If two analytical methods are used to obtain the reported values for the same element within a Sample Delivery Group (i.e. ICP, GFAA), spike samples must be run by each method used.

²EPA may require additional spike sample analysis, upon Project Officer request, for which the Contractor will be paid.

If the spike recovery is not at or within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on FORMs I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

For flame AA, ICP, and CN analyses, when the pre-digestion/pre-distillation spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, a post-digestion/post-distillation spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. Results of the post-digestion/post-distillation spike must be reported on FORM V(PART 2)-IN. Note: No post digest-spike is required for Hg.

In the instance where there is more than one spike sample per matrix and concentration per method per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix, level, and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

$$\% \text{Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

Where, SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive or negative) must be reported on FORM V-IN for ICP, AA and cyanide analyses, as indicated.

The units for reporting spike sample results will be identical to those used for reporting sample results in FORM I-IN (i.e., ug/L for aqueous and mg/Kg dry weight basis for solid).

TABLE 3. SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS

Element	For ICP/AA (ug/L)		For Furnace AA (ug/L)		Other ⁽¹⁾ (ug/L)
	Water	Soil ⁽²⁾	Water	Soil	
Aluminum	2,000	*			
Antimony	500	500	100	100	
Arsenic	2,000	2,000	40	40	
Barium	2,000	2,000			
Beryllium	50	50			
Cadmium	50	50	5	5	
Calcium	*	*			
Chromium	200	200			
Cobalt	500	500			
Copper	250	250			
Iron	1,000	*			
Lead	500	500	20	20	
Magnesium	*	*			
Manganese	500	500			
Mercury					1
Nickel	500	500			
Potassium	*	*			
Selenium	2,000	2,000	10	10	
Silver	50	50			
Sodium	*	*			
Thallium	2,000	2,000	50	50	
Vanadium	500	500			
Zinc	500	500			
Cyanide					100

NOTE: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

¹Spiking level reported is for both water and soil/sediment matrices.

²The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

*No spike required.

7. Duplicate Sample Analysis (D)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.³ Duplicates cannot be averaged for reporting on FORM I-IN.

Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. EPA may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group (i.e., ICP, CFAA), duplicate samples must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where, RPD = Relative Percent Difference
S = First Sample Value (original)
D = Second Sample Value (duplicate)

The results of the duplicate sample analyses must be reported on FORM VI-IN in ug/L for aqueous samples and mg/Kg dry weight basis for solid original and duplicate samples. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x CRDL (Exhibit C). A control limit of ($\pm$) the CRDL must be used for sample values less than 5x CRDL, and the absolute value of the control limit (CRDL) must be entered in the "Control Limit" column on FORM VI-IN.

If one result is above the 5x CRDL level and the other is below, use the $\pm$ CRDL criteria. If both sample values are less than the IDL, the RPD is not calculated on FORM VI-IN. For solid sample or duplicate results < 5x CRDL, enter the absolute value of the CRDL, corrected for sample weight and percent solids, in the "Control Limit" column.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on FORMs I-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix, concentration, and method in the SDG. The percent difference data will be used by EPA to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to FORM VI-IN at a later date based on these precision results.

³EPA may require additional duplicate sample analyses, upon Project Officer request, for which the Contractor will be paid.

8. Laboratory Control Sample (LCS) Analysis

Aqueous and solid Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration Verification Solutions may be used). One aqueous LCS must be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group, or for each batch of aqueous samples digested, whichever is more frequent. An aqueous LCS is not required for mercury and cyanide analysis.

The EPA-provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be prepared and analyzed for every group of solid samples in a Sample Delivery Group, or for each batch of samples digested, whichever is more frequent.

All LCS results and percent recovery (%R) will be reported on FORM VII-IN. If the percent recovery for the aqueous LCS falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

9. ICP Serial Dilution Analysis (I)

Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not at or within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

where, I = Initial Sample Result

S = Serial Dilution Result (Instrument Reading x 5)

In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix and concentration in the Sample Delivery Group. Serial dilution results and "E" flags must be reported on FORM IX-IN.

10. Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed under this contract, the instrument detection limits (in ug/L) must be determined for each instrument used, within 30 days of the start of contract analyses and at least quarterly (every 3 calendar months), and must meet the levels specified in Exhibit C.

The Instrument Detection Limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-5x the instrument manufacturer's suggested IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined IDL for an instrument must always be used as the IDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

IDLs must be reported for each instrument used on FORM X-IN submitted with each data package. If multiple AA instruments are used for the analysis of an element within a Sample Delivery Group, the highest IDL for the AAs must be used for reporting concentration values for that Sample Delivery Group. The same reporting procedure must be used for multiple ICPs.

11. Interelement Corrections for ICP

Before any field samples are analyzed under this contract, the ICP interelement correction factors must be determined prior to the start of contract analyses and at least annually thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. Results from interelement correction factors determination must be reported on FORM XI(PART 1)-IN and FORM XI(PART 2)-IN for all ICP parameters.

12. Linear Range Analysis (LRA)

For all ICP analyses, a linear range verification check standard must be analyzed and reported quarterly (every 3 calendar months) for each element on FORM XII-IN. The standard must be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard must be within $\pm 5\%$ of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

13. Furnace Atomic Absorption (AA) OC Analyses

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1-Furnace AA Analysis Scheme ("MSA Tree") will be required for quantitation. (These procedures do not replace those in Exhibit D of this SOW, but supplement the guidance provided therein.)

- a. All furnace analyses must fall within the calibration range. In addition, all analyses, except during full methods of Standard Addition (MSA), will require duplicate injections. The absorbance or concentration of each injection must be reported in the raw data as well as the average absorbance or concentration values and the relative standard deviation (RSD) or coefficient of variation (CV). Average concentration values are used for reporting purposes. The Contractor must be consistent per method and SDG in choosing absorbance or concentration to evaluate which route is to be followed in the MSA Tree. The Contractor must also indicate which of the two is being used if both absorbance and concentration are reported in the raw data. For MSA analysis, the absorbance of each injection must be included in the raw data. A maximum of 10 full sample analyses to a maximum 20 injections may be performed between each consecutive calibration verifications and blanks. For concentrations greater than CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the analytical sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value reported on FORM I-

IN with an "M". The "M" flag is required for the analytical spike as well as the sample. If the analytical spike for a sample requires an "M" flag, the flag must be reported on FORM I- IN for that sample.

- b. All furnace analyses for each analytical sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike¹ will be required to be at a concentration (in the sample) 2x CRDL. This requirement for an analytical spike will include the LCS and the preparation blank. (The LCS must be quantitated from the calibration curve and corrective action, if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85-115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses (see item 6, this section), will then determine how the sample will be quantitated, as follows:

- 1) If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.
- 2) If the spike recovery is greater than or equal to 40% and the sample absorbance or concentration is less than 50% of the "spike"⁵, report the sample results to the IDL. If the spike recovery is less than 85% or greater than 115%, flag the result with a "U".
- 3) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is at or

¹Analytical Spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

⁵"Spike" is defined as [absorbance or concentration of spike sample] minus [absorbance or concentration of the sample].

between 85% and 115%, the sample must be quantitated directly from the calibration curve and reported down to the IDL.

- 4) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

c. The following procedures will be incorporated into MSA analyses.

- 1) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.
- 2) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

- 3) For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.
- 4) Spikes must be prepared such that:
 - a) Spike 1 is approximately 50% of the sample absorbance or concentration.
 - b) Spike 2 is approximately 100% of the sample absorbance or concentration.
 - c) Spike 3 is approximately 150% of the sample absorbance or concentration.
- 5) The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data. The results must be reported on FORM VIII-IN. Reported values obtained by MSA must be flagged on the data sheet (FORM I-IN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.
- 6) If the correlation coefficient (r) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, report the results on FORM I-IN from the run with the best "r" and flag the result with a "+" on FORM VIII-IN and FORM I-IN.

Figure 1
FURNACE ATOMIC ABSORPTION ANALYSIS SCHEME

**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-220.1 R0
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A.

Document Number: PNL-ALO-220 Revision Number: 0

Document Title: Thallium (Atomic Absorption, Furnace Technique)

Document's Original Author: JM Robbins

Effective Date
of ICN: 05/21/92

Change Requested by:
TE Jones / TG Walker

B. Action:

Replace pages 1 through 8 due to new format.

Make references to microwave digestion upgrade.

C. Effect of Change:

Deleting ACT 89.1 and replacing with established records management practices.

Brings procedure into compliance.

Change in matrix modifier concentration due to a typographical error.

Suggests alternate dissolution procedure.

D. Reason for Change/Description of Change:

Section 2.1: Add the following sentence to end of paragraph as an alternate procedure: "Use of the CLP closed microwave digestion procedure is suggested (EPA-CLP-M 3/90)."

Section 5.5: Due to typographical errors; change "3000 µg/L" to 3000 mg/L" and "2000 µg/L" to "2000 mg/L."

Section 9.0: Change "ACT NOW Directive 89.1" to "established records management practices" because ACT NOW Directive 89.1 is no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert *TL Ehlert* Date: 5/20/92

Approval Authority: AG King *AG King* Date: 5/21/92

Other Approvals: _____ Date: 1 1

: _____ Date: 1 1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-220, THALLIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

APPLICABILITY

This procedure is applicable for determining the concentration of thallium in wastes, mobility-procedure extracts, soils, and ground water. The methodology is comparable to CLP Method 279.2 in SOW 788 or SOW 390. All samples shall be subjected to an appropriate dissolution/digestion procedure prior to analysis as specified by the cognizant scientist or in Test Instructions (Tis) or Analytical Request Forms (ARFs).

DEFINITIONS

Batch: A set of 20 or fewer samples of like matrix.

Group (sample delivery group): A set of 20 samples or less submitted at the same time.

RESPONSIBLE STAFF

Cognizant Scientist
Technician

PROCEDURE

1.0 Summary of Method

- 1.1 Following the dissolution/digestion of the sample, a representative sample aliquot and modifier are placed, by means of an automatic sampler, into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization is proportional to the thallium concentration.
- 1.2 The reportable detection limit for Tl is 2 mg/Kg for soil and 10 $\mu\text{g/L}$ for water. Typical instrument detection limit (IDL) for Tl is 1 $\mu\text{g/L}$ in the analysis solution.

Author	Date	Project Mgr.	Date	QAD Representative	Date
JM Robbins		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
MW Urie		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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PNL TECHNICAL PROCEDURE

2.0 Interferences

- 2.1 Elemental thallium and many of its compounds (e.g., thallium chloride) have relatively high volatility; therefore, samples may be subject to losses of Tl during sample preparation. Spiked samples and relevant standard reference materials should be processed to determine if the chosen dissolution procedure is appropriate. Use of the CLP closed microwave digestion procedure is suggested (EPA-CLP-M 3/90).
- 2.2 Care must be employed in selecting the drying and charring step times, temperatures and temperature ramps. A palladium, or other acceptable analyte modifier (e.g., platinum), and magnesium nitrate should be added to all digestates prior to analysis to minimize volatilization losses during drying and charring. Magnesium nitrate has been shown to assist in spreading the Pd-Tl compounds more evenly in the furnace which reduces diffusion time of the analyte in the Mg oxide matrix (Slavin et al., 1982; Jackson and Qiao, 1990). Magnesium thus serves to sharpen the analyte peak shape during atomization and increases analytical precision.
- 2.3 Tl analysis is affected by sodium chloride at concentrations above 100 mg/L. Addition of 100 μ g of Li, as LiNO_3 , the nitrate reduces chloride interference on Tl to approximately 10% at NaCl levels of 300-600 mg/L. (Welz et al., 1988b). However, in the presence of 0.1% NaCl or KCl even Zeeman correction does not eliminate interferences for Tl.
- Use of an argon-hydrogen gas mixture (95-5%) during temperature ramp to 900°C eliminates interferences from up to 1% chloride. Hydrogen enhances reduction of Pd which is necessary for Tl stabilization (Rettberg and Beach, 1989). Use of this argon-hydrogen gas mixture lowers the appearance temperature of Tl, requiring a modification of the temperature programming of the pyrolysis and atomization steps (Ni Zhe-ming and Shan Xiao-quan, 1987).
- For Chloride concentrations less than 30 μ g the simple solution of elimination of the pyrolysis step and the matrix modifier allowed full recovery of Tl when Zeeman background correction is used (Manning and Slavin, 1988).
- 2.4 Tl may condense at cool ends of graphite furnace during atomization; potentially causing memory effects in subsequent analyses. This situation can be minimized by operating the furnace at 2500-2650°C immediately after atomization. Alternatively, the use of a transverse heated graphite furnace (with longitudinal a.c. magnet for Zeeman effect background correction), as introduced on

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PNL TECHNICAL PROCEDURE

the Perkin-Elmer 4100 GFAAS instrument, can prevent this condensation phenomena.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following: 1) a tolerance limit is stated with a measurement value, or 2) the following system of tolerances shall be in effect:

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL.
- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

4.0 Apparatus and Materials

- 4.1 Atomic absorption spectrophotometer: Double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-900 nm, provisions for simultaneous background correction, and interfacing with a computer and/or strip-chart recorder. Example: Perkin-Elmer 5100 AA Spectrophotometer with AS60 autosampler, deuterium lamp background correction, and IBM PS/2 computer.
- 4.2 Thallium hollow cathode lamp: Electrodeless discharge lamps (EDL) are generally preferred as they have greater lamp output and longer life than hollow cathode lamps (HCL). Thallium EDL lamps provide the same sensitivity and detection limit as thallium HCL lamps.
- 4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls. Example: Perkin-Elmer HGA 600
- 4.4 Pipets: Calibrated, with disposable tips, sized from 5 to 1,000 μ L, as required.
- 4.5 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g. (Optional)

5.0 Reagents

- 5.1 Deionized water: Deionized water of sufficient quality, similar to ASTM Type II reagent water, shall be used for preparing sample, standards, and reagent dilutions. Calibration and sample blanks will produce concentrations at or below IDLs.

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5.2 Concentrated nitric acid (HNO_3): Ultrex grade.

5.3 Thallium standard stock solution: (1,000 mg/L): Preferred: Acquire a certified aqueous standard from NIST or an equivalent supplier and verify by comparison with a second standard.

Alternative: Dissolve 1.303 g of 99.99% thallium nitrate (TlNO_3) Johnson Matthey or equivalent, in deionized water, add 10 mL of concentrated HNO_3 and dilute to 1 L, using deionized water.

Caution: Thallium and its compounds are extremely toxic and should be handled with care.

5.4 Thallium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3 at 1% of final volume and dilute with water to volume.

5.5 Palladium nitrate - magnesium nitrate mixed modifier solution: Preferred: Mix equal volumes of 3000 $\mu\text{g/L}$ mg/L of a certified aqueous Pd standard in HNO_3 and 2000 $\mu\text{g/L}$ mg/L of $\text{Mg}(\text{NO}_3)_2$ (Merck, suprapure or equivalent), respectively. A 5 μL volume of this solution is added to each sample, corresponding to masses of 15 μg of Pd (32.5 μg PdNO_3) and 10 μg of $\text{Mg}(\text{NO}_3)_2$ (Schlemmer and Welz, 1986 and Welz et al., 1988a,b).

Alternative source for palladium: Dissolve 0.300 g Pd wire in a minimum volume of aqua regia and evaporate to dryness, add 5 mL of concentrated HNO_3 , warm until dissolution is complete, dilute to 100.0 mL; or dissolve 0.5001 g palladium chloride (PdCl_2) in 5 mL of concentrated HNO_3 , evaporate to near dryness, repeat with 5 mL of concentrated HNO_3 , and dilute with water to 100.0 mL.

5.6 Argon purge gas: Industrial-grade argon or a mixture of argon-hydrogen (95-5%).

6.0 Quality Control (QC)

6.1 All QC data shall be maintained and available for easy reference or inspection.

6.2 Minimum QC.

6.2.1 The system shall be calibrated following manufacturer's recommended calibration procedure which is in the instrument reference manual (see Section 10.0). Calibration parameters shall be established and recorded each day of operation.

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- 6.2.2 Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest calibration standard.
- 6.2.3 Employ a minimum of one method blank per sample group (typically 20 samples) or batch of samples digested.
- 6.2.4 Analyze at least one verification check standard or one QC standard every 8 to 12 samples. For CERCLA work include a verification standard or a QC standard after every 10 samples. If the results of the verification or QC standard are not within 80% to 120% of their mean value, the cognizant scientist shall determine the corrective action. All samples within the previously analyzed sample group shall be flagged on the data reports and the corrective action documented with the data. Validation of the data is the responsibility of the technical group leader.

Note: Verification standards help monitor the life and performance of the graphite tube. An RSD for duplicate injections of midrange standards exceeding 10%, or an instrument response <70% of the manufacturer's recommendation as stated in the reference manual (see Section 10.0), shall be investigated and corrective action, if required, documented.

- 6.2.5 Additional QC (i.e., duplicates, matrix spikes, duplicate matrix spikes, multiple injections, additional system or matrix blanks, tighter tolerances, holding times, etc.) shall be governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the ARF, the project Statement of Work (SOW), or the sample analysis TI.
- 6.3 QC for clients requesting compliance with Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) requirements.
- 6.3.1 Analyze samples per protocol detailed in Appendix A. Use Figure 1 of Appendix A to establish the quantitation method to be used; that is, either direct calibration or method of standard addition.
- 6.3.2 Any additional QC requirements shall be governed by the SOW from the client with the analysis protocol transmitted to the analyst via TI.

7.0 Analysis Method

Sample collection, preservation and preparation is not within the scope of this procedure. However, it is important that samples be collected and preserved properly in order to maintain sample integrity. The

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applicability of sample preparation schemes, such as PNL-ALO-101, for specific matrices shall be demonstrated by analyzing spiked samples or relevant standard reference materials, or by the use of other qualifying techniques.

- 7.1 The 276.8 nm wavelength line and a background correction system shall be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters. These are located in the instrument reference manual (see Section 10.0).
- 7.2 Furnace parameters suggested by the manufacturer in the reference manual should be employed as guidelines. The furnace parameters used shall be recorded with the data.

Suggested furnace settings -- P-E 5000 or 5100

Step	Temp(°C)	Ramp Time(sec)	Hold Time(sec)
Drying #1	90	1	15
Drying #2	130	10	10
Charring	900	10	20
Cool down #1	30	1	15
Atomization	1800	0	5
Cleaning	2650	1	5
Cool Down #2	20	10	5

Note: Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters may be confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

- 7.3 Inject measured μL -aliquots of sample and modifier solution (typically, 20 μL of sample and 5 μL of modifier) into the furnace and atomize. If the concentration found is greater than the highest standard, the sample shall be diluted in the same acid matrix and reanalyzed. Note: Multiple injections improve precision and help detect furnace pipetting errors.
- 7.4 Calculate the thallium concentration: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors shall be applied prior to reporting results. Concentrations reported for multiphase samples shall be

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appropriately qualified (e.g., $\mu\text{g/L}$ aqueous phase or mg/Kg for solids).

8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and QC standards as per Manual PNL-MA-70, Procedure PAP-70-901.

9.0 Records

Records will be maintained and controlled so as to conform to requirements of Manual PNL-MA-70, Procedure PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with the ~~ACT NOW Directive 89.1~~ established records management practices.

10.0 References

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APPENDIX A

SECTION I

GENERAL QA/QC PRACTICES

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases must also be adhered to. For additional guidelines regarding these general laboratory procedures, see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

SECTION II

SPECIFIC QA/QC PROCEDURES

The quality assurance/quality control (QA/QC) procedures defined herein must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Contractor must also follow these procedures. NOTE: The cost of performing all QA/QC procedures specified in this Statement of Work is included in the price of performing the bid lot, except for duplicate, spike, and laboratory control sample analyses, which shall be considered separate sample analyses.

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The primary function of the QA/QC program is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by EPA EMSL-Las Vegas. The Contractor can expect to analyze two samples per calendar quarter during the contract period.

The Contractor must perform and report to SMO and EMSL/LV as specified in Exhibit B quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this contract. All the IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Contractor must also report, as specified in Exhibit B, linearity range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this Statement of Work, the term "analytical sample" is used in discussing the required frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit G. As the term is used, analytical sample includes all field samples, including Performance Evaluation samples, received from an external source, but it also includes all required QA/QC samples (matrix spikes, analytical/post-digestion

spikes, duplicates, serial dilutions, LCS, ICS, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB, CCV/CCB). A "frequency of 10%" means once every 10 analytical samples. Note: Calibration verification samples (ICV/CCV) and calibration verification blanks (ICB/CCB) are not counted as analytical samples when determining 10% frequency.

In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their QA/QC analysis must be analyzed under the same operating and procedural conditions.

If any QC measurement fails to meet contract criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Contractor must report all QC data in the exact format specified in Exhibits B and H.

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as described in this Exhibit:

1. Instrument Calibration
2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)
3. CRDL Standards for AA (CRA) and ICP (CRI)
4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
5. ICP Interference Check Sample (ICS) Analyses
6. Spike Sample Analysis (S)
7. Duplicate Sample Analysis (D)
8. Laboratory Control Sample (LCS) Analysis
9. ICP Serial Dilution Analysis (L)
10. Instrument Detection Limit (IDL) Determination
11. Interelement Corrections for ICP (ICP)
12. Linear Range Analysis (LRA)
13. Furnace AA QC Analyses

1. Instrument Calibration

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis must be given in the raw data.

Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be within $\pm 5\%$ of the true value. Each standards concentration and the calculations to show that the $\pm 5\%$ criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary.

The $\pm 5\%$ criteria does not apply to the atomic absorption calibration standard at the CRDL.

Calibration standards for AA procedures must be prepared as described in Exhibit D.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification and blank check; resloping is acceptable as long as it is immediately preceded and immediately followed by CCV and CCB. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.

2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

a. Initial Calibration Verification (ICV)

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses (in Exhibit E), the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used for analysis. For CN, the initial calibration verification standard must be distilled. The Initial Calibration Verification for CN serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV. The values for the initial and subsequent continuing calibration verifications shall be recorded on FORM II-IN for ICP, AA, and cyanide analyses, as indicated.

b. Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions
2. NBS SRM 1643a
3. A Contractor-prepared standard solution

TABLE 1. INITIAL AND CONTINUING CALIBRATION VERIFICATION CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	% of True Value (EPA Set)	
		Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for a Case of samples received.

Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it as well as the difference in time between the CCV and the analytical sample immediately preceding it may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of preceding 10 analytical samples or all analytical samples analyzed since the last good calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP, AA and cyanide as indicated.

3. CRDL Standards for ICP (CRI) and AA (CRA)

To verify linearity near the CRDL for ICP analysis, the Contractor must analyze an ICP standard (CRI) at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.

To verify linearity near the CRDL for AA analysis, the Contractor must analyze an AA standard (CRA) at the CRDL or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the Initial Calibration Verification.

Specific acceptance criteria for the two standards will be set by EPA in the future. In the interim, the Contractor must analyze and report these Standards on FORM II(PART 2)-IN.

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses

a. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours

during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run. The results for the calibration blanks shall be recorded on FORM III-IN for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the calibration blank result exceeds the IDL, the result must be so reported in ug/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the CRDL (Exhibit C), terminate analysis, correct the problem, recalibrate, verify the calibration and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration blank.

b. Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch¹ of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM III-IN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

- 1) If the absolute value of the concentration of the blank is less than or equal to the Contract Required Detection Limit (Exhibit C), no correction of sample results is performed.
- 2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.
- 3) If the concentration of the blank is below the negative CRDL, then all samples reported below 10x CRDL associated with the blank must be redigested and reanalyzed.

¹A group of samples prepared at the same time.

The values for the preparation blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples on FORM III-IN for ICP, AA, and cyanide analyses.

5. ICP Interference Check Sample (ICS) Analysis

To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Samples must be obtained from EPA (EML/LV) if available and analyzed according to the instructions supplied with the ICS.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of $\pm 20\%$ of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all contract specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

If the ICP Interference Check Sample is not available from EPA, independent ICP Check Samples must be prepared with interferent and analyte concentrations at the levels specified in Table 2-Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample. The mean value and standard deviation must be established by initially analyzing the Check Samples at least five times repetitively for each parameter on FORM IV-IN. Results must fall within the control limit of $\pm 20\%$ of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the Interference Check Sample analyses must be recorded on FORM IV-IN for all ICP parameters.

TABLE 2. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

6. Spike Sample Analysis (S)

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps (i.e., CN-). At least one spike sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.²

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see section 7, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

The analyte spike must be added in the amount given in Table 3-Spiking Levels for Spike Sample Analysis, for each element analyzed. If two analytical methods are used to obtain the reported values for the same element within a Sample Delivery Group (i.e. ICP, GFAA), spike samples must be run by each method used.

²EPA may require additional spike sample analysis, upon Project Officer request, for which the Contractor will be paid.

If the spike recovery is not at or within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on FORMs I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

For flame AA, ICP, and CN analyses, when the pre-digestion/pre-distillation spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, a post-digestion/post-distillation spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. Results of the post-digestion/post-distillation spike must be reported on FORM V(PART 2)-IN. Note: No post digest spike is required for Hg.

In the instance where there is more than one spike sample per matrix and concentration per method per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix, level, and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

$$\% \text{Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

Where, SSR = Spiked Sample Result
 SR = Sample Result
 SA = Spike Added

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive or negative) must be reported on FORM V-IN for ICP, AA and cyanide analyses, as indicated.

The units for reporting spike sample results will be identical to those used for reporting sample results in FORM I-IN (i.e., ug/L for aqueous and mg/Kg dry weight basis for solid).

TABLE 3. SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS

Element	For ICP/AA (ug/L)		For Furnace AA (ug/L)		Other ⁽¹⁾ (ug/L)
	Water	Soil ⁽²⁾	Water	Soil	
Aluminum	2,000	*			
Antimony	500	500	100	100	
Arsenic	2,000	2,000	40	40	
Barium	2,000	2,000			
Beryllium	50	50			
Cadmium	50	50	5	5	
Calcium	*	*			
Chromium	200	200			
Cobalt	500	500			
Copper	250	250			
Iron	1,000	*			
Lead	500	500	20	20	
Magnesium	*	*			
Manganese	500	500			
Mercury					1
Nickel	500	500			
Potassium	*	*			
Selenium	2,000	2,000	10	10	
Silver	50	50			
Sodium	*	*			
Thallium	2,000	2,000	50	50	
Vanadium	500	500			
Zinc	500	500			
Cyanide					100

NOTE: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

¹Spiking level reported is for both water and soil/sediment matrices.

²The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

*No spike required.

7. Duplicate Sample Analysis (D)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.³ Duplicates cannot be averaged for reporting on FORM I-IN.

Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. EPA may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group (i.e., ICP, GFAA), duplicate samples must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where, RPD = Relative Percent Difference
 S = First Sample Value (original)
 D = Second Sample Value (duplicate)

The results of the duplicate sample analyses must be reported on FORM VI-IN in ug/L for aqueous samples and mg/Kg dry weight basis for solid original and duplicate samples. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x CRDL (Exhibit C). A control limit of ($\pm$) the CRDL must be used for sample values less than 5x CRDL, and the absolute value of the control limit (CRDL) must be entered in the "Control Limit" column on FORM VI-IN.

If one result is above the 5x CRDL level and the other is below, use the $\pm$ CRDL criteria. If both sample values are less than the IDL, the RPD is not calculated on FORM VI-IN. For solid sample or duplicate results < 5x CRDL, enter the absolute value of the CRDL, corrected for sample weight and percent solids, in the "Control Limit" column.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on FORMs I-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix, concentration, and method in the SDG. The percent difference data will be used by EPA to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to FORM VI-IN at a later date based on these precision results.

³EPA may require additional duplicate sample analyses, upon Project Officer request, for which the Contractor will be paid.

8. Laboratory Control Sample (LCS) Analysis

Aqueous and solid Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration Verification Solutions may be used). One aqueous LCS must be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group, or for each batch of aqueous samples digested, whichever is more frequent. An aqueous LCS is not required for mercury and cyanide analysis.

The EPA-provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be prepared and analyzed for every group of solid samples in a Sample Delivery Group, or for each batch of samples digested, whichever is more frequent.

All LCS results and percent recovery (%R) will be reported on FORM VII-IN. If the percent recovery for the aqueous LCS falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

9. ICP Serial Dilution Analysis (L)

Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not at or within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

where, I = Initial Sample Result

S = Serial Dilution Result (Instrument Reading x 5)

In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix and concentration in the Sample Delivery Group. Serial dilution results and "E" flags must be reported on FORM IX-IN.

10. Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed under this contract, the instrument detection limits (in ug/L) must be determined for each instrument used, within 30 days of the start of contract analyses and at least quarterly (every 3 calendar months), and must meet the levels specified in Exhibit C.

The Instrument Detection Limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-5x the instrument manufacturer's suggested IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined IDL for an instrument must always be used as the IDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

IDLs must be reported for each instrument used on FORM X-IN submitted with each data package. If multiple AA instruments are used for the analysis of an element within a Sample Delivery Group, the highest IDL for the AAs must be used for reporting concentration values for that Sample Delivery Group. The same reporting procedure must be used for multiple ICPs.

11. Interelement Corrections for ICP

Before any field samples are analyzed under this contract, the ICP interelement correction factors must be determined prior to the start of contract analyses and at least annually thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. Results from interelement correction factors determination must be reported on FORM XI(PART 1)-IN and FORM XI(PART 2)-IN for all ICP parameters.

12. Linear Range Analysis (LRA)

For all ICP analyses, a linear range verification check standard must be analyzed and reported quarterly (every 3 calendar months) for each element on FORM XII-IN. The standard must be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard must be within $\pm 5\%$ of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

13. Furnace Atomic Absorption (AA) QC Analyses

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1-Furnace AA Analysis Scheme ("MSA Tree") will be required for quantitation. (These procedures do not replace those in Exhibit D of this SOW, but supplement the guidance provided therein.)

- a. All furnace analyses must fall within the calibration range. In addition, all analyses, except during full methods of Standard Addition (MSA), will require duplicate injections. The absorbance or concentration of each injection must be reported in the raw data as well as the average absorbance or concentration values and the relative standard deviation (RSD) or coefficient of variation (CV). Average concentration values are used for reporting purposes. The Contractor must be consistent per method and SDC in choosing absorbance or concentration to evaluate which route is to be followed in the MSA Tree. The Contractor must also indicate which of the two is being used if both absorbance and concentration are reported in the raw data. For MSA analysis, the absorbance of each injection must be included in the raw data. A maximum of 10 full sample analyses to a maximum 20 injections may be performed between each consecutive calibration verifications and blanks. For concentrations greater than CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the analytical sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value reported on FORM I-

IN with an "M". The "M" flag is required for the analytical spike as well as the sample. If the analytical spike for a sample requires an "M" flag, the flag must be reported on FORM E- IN for that sample.

- b. All furnace analyses for each analytical sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike¹ will be required to be at a concentration (in the sample) 2x CRDL. This requirement for an analytical spike will include the LCS and the preparation blank. (The LCS must be quantitated from the calibration curve and corrective action, if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85-115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses (see item 6, this section), will then determine how the sample will be quantitated, as follows:

- 1) If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.
- 2) If the spike recovery is greater than or equal to 40% and the sample absorbance or concentration is less than 50% of the "spike"⁵, report the sample results to the IDL. If the spike recovery is less than 85% or greater than 115%, flag the result with a "W".
- 3) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is at or

¹Analytical Spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

⁵"Spike" is defined as [absorbance or concentration of spike sample] minus [absorbance or concentration of the sample].

between 85% and 115%, the sample must be quantitated directly from the calibration curve and reported down to the IDL.

- 4) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

c. The following procedures will be incorporated into MSA analyses.

- 1) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.
- 2) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

- 3) For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.
- 4) Spikes must be prepared such that:
 - a) Spike 1 is approximately 50% of the sample absorbance or concentration.
 - b) Spike 2 is approximately 100% of the sample absorbance or concentration.
 - c) Spike 3 is approximately 150% of the sample absorbance or concentration.
- 5) The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data. The results must be reported on FORM VIII-IN. Reported values obtained by MSA must be flagged on the data sheet (FORM I-IN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.
- 6) If the correlation coefficient (r) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, report the results on FORM I-IN from the run with the best "r" and flag the result with a "+" on FORM VIII-IN and FORM I-IN.

Figure 1
FURNACE ATOMIC ABSORPTION ANALYSIS SCHEME

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-221.1 R0
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A.

Document Number: PNL-ALO-221 Revision Number: 0

Document Title: Silver (Atomic Absorption, Furnace Technique)

Document's Original Author: SI Barsoum

Effective Date
of ICN: 5/8/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 8 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert TH Ehlert

Date: 5/7/92

Approval Authority: AG King AG King

Date: 5/12/92

Other Approvals: MW Urie MW Urie

Date: 5/8/92

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-221, SILVER (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

APPLICABILITY

This procedure is applicable for determining the concentration of silver in wastes, mobility-procedure extracts, soils, and ground water. The methodology is comparable to CLP Method 272.2 in SOW 788 or SOW 390. All samples shall be subjected to an appropriate dissolution/digestion procedure prior to analysis as specified by the cognizant scientist or in Test Instructions (TIs) or Analytical Request Forms (ARFs).

DEFINITIONS

Batch: A group of samples of like matrix prepared at the same time.

Modifier: A substance added to the furnace to alter the atomization characteristics of either the analyte or interfering matrix. Modifiers are employed to separate analyte and matrix in time allowing reduction of matrix interferences on the measurement of the analyte atomization signal profile. Modifiers may be added as a liquid to the sample solution, injected into the furnace or incorporated in the argon gas stream during the pretreatment, atomization or the clean-out steps.

RESPONSIBLE STAFF

Cognizant Scientist Technician

PROCEDURE

1.0 Summary of Method

- 1.1 Following the dissolution/digestion of the sample, a representative sample aliquot and modifier are placed, by means of an automatic sampler, into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization is proportional to the silver concentration.

Author	Date	Project Mgr.	Date	QAD Representative	Date
SI Barsoum		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
Urie <i>[Signature]</i>	5/8/92	JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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- 1.2 The method detection limit for Ag is 1 mg/Kg for soil and 10 $\mu\text{g/L}$ for water. The typical instrument detection limit (IDL) for Ag is 0.2 $\mu\text{g/L}$ in the analysis solution

2.0 Interferences

- 2.1 Spiked samples and relevant standard reference materials should be processed to determine if the chosen dissolution procedure is appropriate.
- 2.2 Care must be employed in selecting the drying and charring step times, temperatures and temperature ramps. A modifier mixture of palladium and magnesium should be added to all digestates prior to analysis to minimize volatilization losses during drying and charring magnesium nitrate assists in spreading the Pd-Ag compounds more evenly in the furnace reducing diffusion time of the analyte in the Mg oxide matrix. Magnesium thus serves to sharpen the analyte peak shape during atomization and increases analytical precision.
- 2.3 The use of an argon-hydrogen gas mixture (95-5%) during temperature ramp to 900° C has been shown to eliminate interferences from chloride. Hydrogen enhances reduction of Pd which is necessary for analyte stabilization.
- 2.4 Silver may condense at cool ends of the graphite furnace during atomization; potentially causing memory effects in subsequent analyses. This situation can be minimized by operating the furnace at 2500-2650°C immediately after atomization.
- 2.5 If Zeeman background correction was used then high level of phosphates in samples may require that less sensitive 338.3 nm be used to eliminate possible interference from the phosphates band splitting.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following: 1) a tolerance limit is stated with a measurement value, or 2) the following system of tolerances shall be in effect:

- a. When two or more significant figures are specified, the tolerance limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL.
- b. If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

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4.0 Apparatus and Materials

- 4.1 Atomic absorption spectrophotometer: Double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-900 nm, provisions for simultaneous background correction, and interfacing with a computer and/or strip-chart recorder. Example: Perkin-Elmer 5100 AA Spectrophotometer with AS60 autosampler, deuterium lamp of Zeeman effect background correction, and IBM PS/2 computer.
- 4.2 Silver hollow cathode lamp: Electrodeless discharge lamps (EDL) are not available for silver.
- 4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls. Example: Perkin-Elmer HGA 600
- 4.4 Pipets: Calibrated, with disposable tips, sized from 5 to 1,000 μL , as required.
- 4.5 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g. (Optional)

5.0 Reagents

- 5.1 Deionized water: Deionized water of sufficient quality, similar to ASTM Type II reagent water, shall be used for preparing sample, standards, and reagent dilutions. Calibration and sample blanks shall produce concentrations at or below instrument detection limits.
- 5.2 Concentrated nitric acid (HNO_3): Ultrex grade.
- 5.3 Silver standard stock solution (1,000 mg/L): Preferred: Acquire a certified aqueous standard from NIST or an equivalent supplier and verify by comparison with a second standard.

Alternative: Dissolve 1.575 g of 99.99% silver nitrate (AgNO_3), Johnson Matthey or equivalent, in deionized water, add 10 mL of concentrated HNO_3 and dilute to 1 L, using deionized water. Store silver standard in an amber glass bottle as silver is sensitive to light.

- 5.4 Silver working standards: Prepare dilutions of the stock standard solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3 at 5% of final volume to keep silver in solution and dilute with water to volume.

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5.5 Palladium nitrate - magnesium nitrate mixed modifier solution:
Preferred: Mix equal volumes of 3000 mg/L of a certified aqueous Pd standard in HNO_3 and 2000 mg/L of $\text{Mg}(\text{NO}_3)_2$ (Merck, suprapure or equivalent), respectively. A 5 μL volume of this solution is added to each sample, corresponding to masses of 15 μg of Pd (32.5 μg PdNO_3) and 10 μg of $\text{Mg}(\text{NO}_3)_2$.

Alternative source for palladium: Dissolve 0.300 g Pd wire in a minimum volume of aqua regia and evaporate to dryness, add 5 mL of concentrated HNO_3 , warm until dissolution is complete, dilute to 100 mL; or dissolve 0.5001 g palladium chloride (PdCl_2) in 5 mL of concentrated HNO_3 , evaporate to near dryness, repeat with 5 mL of concentrated HNO_3 , and dilute with water to 100.0 mL.

5.6 Argon purge gas: Industrial-grade argon.

Note: When chloride interference is suspected the use of a mixture of argon-hydrogen (95-5%) is recommended.

6.0 Quality Control

6.1 All quality control data shall be maintained and available for easy reference or inspection.

6.2 Minimum quality control.

6.2.1

The system shall be calibrated following manufacturer's recommended calibration procedure which is in the instrument reference manual [see Section 10.0]. Calibration parameters shall be established and recorded each day of operation.

6.2.2

Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest calibration standard.

6.2.3

Employ a minimum of one method blank for each sample delivery group or batch of samples digested.

6.2.4

Analyze at least one verification check standard or one quality control standard every 8 to 12 samples. If the results of the verification or QC standard are not within 80% to 120% of their mean value, the cognizant scientist shall determine the corrective action. The instrument must be recalibrated, the calibration verified, and all analytical samples analyzed since the last good calibration verification must be reanalyzed for the analytes affected. This corrective action

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taken shall be documented with the data. Validation of the data is the responsibility of the technical group leader.

Note: Verification standards help monitor the life and performance of the graphite tube. An RSD for duplicate injections of mid-range standards exceeding 10% or an instrument response <70% of the manufacturer's recommendation as stated in the reference manual (see Section 10), shall be investigated and corrective action, if required, documented.

6.2.5

Additional quality control (i.e., duplicates, matrix spikes, duplicate matrix spikes, multiple injections, additional system or matrix blanks, tighter tolerances, holding times, etc.) shall be governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the Analytical Request Form (ARF), the project Statement of Work (SOW), or the sample analysis Test Instruction (TI).

6.3 Quality control for clients requesting compliance with Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) requirements.

6.3.1

Analyze samples per protocol detailed in Appendix A. Use Figure 1 of Appendix A to establish the quantitation method to be used; that is, either direct calibration or method of standard addition. Also, all definitions/acronyms (e.g. Sample Delivery Group, SDG) shall be consistent with USEPA CLP SOW 788 [Reference 10] usage.

6.3.2

Any additional quality control requirements shall be governed by the Statement of Work (SOW) from the client with the analysis protocol transmitted to the analyst via Test Instructions (TI)

7.0 Analysis Method

Sample collection, preservation and preparation is not within the scope of this procedure. However, it is important that samples be collected and preserved properly in order to maintain sample integrity. The applicability of sample preparation schemes, such as PNL-ALO-101, for specific matrices shall be demonstrated by analyzing spiked samples or relevant standard reference materials, or by the use of other qualifying techniques.

7.1 The 328.1 nm wavelength line and a background correction system shall be employed. Follow the manufacturer's suggestions for all

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other spectrophotometer parameters. These are located in the instrument reference manual (see Section 10.0).

- 7.2 Furnace parameters suggested by the manufacturer in the reference manual should be employed as guidelines. The furnace parameters used shall be optimized and remain constant throughout batch analyses. All parameters shall be recorded with the data.

Suggested graphite furnace program settings P-E 5000 or 5100:

Step	Temp(°C)	Ramp time(sec)	Hold time(sec)
Drying #1	90	10	10
Drying #2	130		10 10
Charring	1000		10 20
Cool down #1	30	5	10
Atomization	1800		0 5
Cleaning	2600		1 5
Cool down #2	20	1	5

Note: Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters may be confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

- 7.3 Inject measured μL -aliquots of sample and modifier solution (typically, 20 μL of sample and 5 μL of modifier) into the furnace and analyze for silver following graphite furnace program. If the concentration found is greater than the highest standard, the sample shall be diluted in the same acid matrix and reanalyzed. Note: Multiple injections improve precision and help detect furnace pipetting errors.
- 7.4 Calculate the silver concentration: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors shall be applied prior to reporting results. Concentrations reported for multiphase samples shall be appropriately qualified (e.g., $\mu\text{g/L}$ aqueous phase or mg/Kg for solids).

8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and quality control standards as per PNL-MA-70, PAP-70-901.

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9.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ACT NOW Directive 89.1 established records management practices.

10.0 References

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APPENDIX A

SECTION I

GENERAL QA/QC PRACTICES

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases must also be adhered to. For additional guidelines regarding these general laboratory procedures, see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

SECTION II

SPECIFIC QA/QC PROCEDURES

The quality assurance/quality control (QA/QC) procedures defined herein must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Contractor must also follow these procedures. NOTE: The cost of performing all QA/QC procedures specified in this Statement of Work is included in the price of performing the bid lot, except for duplicate, spike, and laboratory control sample analyses, which shall be considered separate sample analyses.

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The primary function of the QA/QC program is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by EPA EMSL-Las Vegas. The Contractor can expect to analyze two samples per calendar quarter during the contract period.

The Contractor must perform and report to SMO and EMSL/LV as specified in Exhibit B quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this contract. All the IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Contractor must also report, as specified in Exhibit B, linearity range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this Statement of Work, the term "analytical sample" is used in discussing the required frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit G. As the term is used, analytical sample includes all field samples, including Performance Evaluation samples, received from an external source, but it also includes all required QA/QC samples (matrix spikes, analytical/post-digestion

spikes, duplicates, serial dilutions, LCS, ICS, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB, CCV/CCB). A "frequency of 10%" means once every 10 analytical samples. Note: Calibration verification samples (ICV/CCV) and calibration verification blanks (ICB/CCB) are not counted as analytical samples when determining 10% frequency.

In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their QA/QC analysis must be analyzed under the same operating and procedural conditions.

If any QC measurement fails to meet contract criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Contractor must report all QC data in the exact format specified in Exhibits B and H.

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as described in this Exhibit:

1. Instrument Calibration
2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)
3. CRDL Standards for AA (CRA) and ICP (CRI)
4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
5. ICP Interference Check Sample (ICS) Analyses
6. Spike Sample Analysis (S)
7. Duplicate Sample Analysis (D)
8. Laboratory Control Sample (LCS) Analysis
9. ICP Serial Dilution Analysis (L)
10. Instrument Detection Limit (IDL) Determination
11. Interelement Corrections for ICP (ICP)
12. Linear Range Analysis (LRA)
13. Furnace AA QC Analyses

1. Instrument Calibration

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis must be given in the raw data.

Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be within $\pm 5\%$ of the true value. Each standards concentration and the calculations to show that the $\pm 5\%$ criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary.

The $\pm 5\%$ criteria does not apply to the atomic absorption calibration standard at the CRDL.

Calibration standards for AA procedures must be prepared as described in Exhibit D.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification and blank check; resloping is acceptable as long as it is immediately preceded and immediately followed by CCV and CCB. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.

2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

a. Initial Calibration Verification (ICV)

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses (in Exhibit E), the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used for analysis. For CN, the initial calibration verification standard must be distilled. The Initial Calibration Verification for CN serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV. The values for the initial and subsequent continuing calibration verifications shall be recorded on FORM II-IN for ICP, AA, and cyanide analyses, as indicated.

b. Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions
2. NBS SRM 1643a
3. A Contractor-prepared standard solution

TABLE 1. INITIAL AND CONTINUING CALIBRATION VERIFICATION
CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	<u>% of True Value (EPA Set)</u>	
		Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for a Case of samples received.

Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it as well as the difference in time between the CCV and the analytical sample immediately preceding it may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of preceding 10 analytical samples or all analytical samples analyzed since the last good calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP, AA and cyanide as indicated.

3. CRDL Standards for ICP (CRI) and AA (CRA)

To verify linearity near the CRDL for ICP analysis, the Contractor must analyze an ICP standard (CRI) at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.

To verify linearity near the CRDL for AA analysis, the Contractor must analyze an AA standard (CRA) at the CRDL or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the Initial Calibration Verification.

Specific acceptance criteria for the two standards will be set by EPA in the future. In the interim, the Contractor must analyze and report these Standards on FORM II(PART 2)-IN.

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses

a. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours

during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run. The results for the calibration blanks shall be recorded on FORM III-IN for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the calibration blank result exceeds the IDL, the result must be so reported in ug/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the CRDL (Exhibit C), terminate analysis, correct the problem, recalibrate, verify the calibration and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration blank.

b. Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch¹ of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM III-IN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

- 1) If the absolute value of the concentration of the blank is less than or equal to the Contract Required Detection Limit (Exhibit C), no correction of sample results is performed.
- 2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.
- 3) If the concentration of the blank is below the negative CRDL, then all samples reported below 10x CRDL associated with the blank must be redigested and reanalyzed.

¹A group of samples prepared at the same time.

The values for the preparation blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples on FORM III-IN for ICP, AA, and cyanide analyses.

5. ICP Interference Check Sample (ICS) Analysis

To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Samples must be obtained from EPA (EMSL/LV) if available and analyzed according to the instructions supplied with the ICS.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of $\pm 20\%$ of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all contract specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

If the ICP Interference Check Sample is not available from EPA, independent ICP Check Samples must be prepared with interferent and analyte concentrations at the levels specified in Table 2-Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample. The mean value and standard deviation must be established by initially analyzing the Check Samples at least five times repetitively for each parameter on FORM IV-IN. Results must fall within the control limit of $\pm 20\%$ of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the Interference Check Sample analyses must be recorded on FORM IV-IN for all ICP parameters.

TABLE 2. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

6. Spike Sample Analysis (S)

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps (i.e., CN-). At least one spike sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.²

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see section 7, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

The analyte spike must be added in the amount given in Table 3-Spiking Levels for Spike Sample Analysis, for each element analyzed. If two analytical methods are used to obtain the reported values for the same element within a Sample Delivery Group (i.e. ICP, GFAA), spike samples must be run by each method used.

²EPA may require additional spike sample analysis, upon Project Officer request, for which the Contractor will be paid.

If the spike recovery is not at or within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on FORMs I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

For flame AA, ICP, and CN analyses, when the pre-digestion/pre-distillation spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, a post-digestion/post-distillation spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. Results of the post-digestion/post-distillation spike must be reported on FORM V(PART 2)-IN. Note: No post digest spike is required for Hg.

In the instance where there is more than one spike sample per matrix and concentration per method per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix, level, and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

$$\% \text{Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

Where, SSR - Spiked Sample Result
SR - Sample Result
SA - Spike Added

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive or negative) must be reported on FORM V-IN for ICP, AA and cyanide analyses, as indicated.

The units for reporting spike sample results will be identical to those used for reporting sample results in FORM I-IN (i.e., ug/L for aqueous and mg/Kg dry weight basis for solid).

TABLE 3. SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS

Element	For ICP/AA (ug/L)		For Furnace AA (ug/L)		Other ⁽¹⁾ (ug/L)
	Water	Soil ⁽²⁾	Water	Soil	
Aluminum	2,000	*			
Antimony	500	500	100	100	
Arsenic	2,000	2,000	40	40	
Barium	2,000	2,000			
Beryllium	50	50			
Cadmium	50	50	5	5	
Calcium	*	*			
Chromium	200	200			
Cobalt	500	500			
Copper	250	250			
Iron	1,000	*			
Lead	500	500	20	20	
Magnesium	*	*			
Manganese	500	500			1
Mercury					
Nickel	500	500			
Potassium	*	*			
Selenium	2,000	2,000	10	10	
Silver	50	50			
Sodium	*	*			
Thallium	2,000	2,000	50	50	
Vanadium	500	500			
Zinc	500	500			100
Cyanide					

NOTE: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

¹Spiking level reported is for both water and soil/sediment matrices.

²The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

*No spike required.

7. Duplicate Sample Analysis (D)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.³ Duplicates cannot be averaged for reporting on FORM I-IN.

Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. EPA may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group (i.e., ICP, GFAA), duplicate samples must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where, RPD - Relative Percent Difference
S - First Sample Value (original)
D - Second Sample Value (duplicate)

The results of the duplicate sample analyses must be reported on FORM VI-IN in ug/L for aqueous samples and mg/Kg dry weight basis for solid original and duplicate samples. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x CRDL (Exhibit C). A control limit of ($\pm$) the CRDL must be used for sample values less than 5x CRDL, and the absolute value of the control limit (CRDL) must be entered in the "Control Limit" column on FORM VI-IN.

If one result is above the 5x CRDL level and the other is below, use the $\pm$ CRDL criteria. If both sample values are less than the IDL, the RPD is not calculated on FORM VI-IN. For solid sample or duplicate results < 5x CRDL, enter the absolute value of the CRDL, corrected for sample weight and percent solids, in the "Control Limit" column.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on FORMs I-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix, concentration, and method in the SDG. The percent difference data will be used by EPA to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to FORM VI-IN at a later date based on these precision results.

³EPA may require additional duplicate sample analyses, upon Project Officer request, for which the Contractor will be paid.

8. Laboratory Control Sample (LCS) Analysis

Aqueous and solid Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration Verification Solutions may be used). One aqueous LCS must be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group, or for each batch of aqueous samples digested, whichever is more frequent. An aqueous LCS is not required for mercury and cyanide analysis.

The EPA-provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be prepared and analyzed for every group of solid samples in a Sample Delivery Group, or for each batch of samples digested, whichever is more frequent.

All LCS results and percent recovery (%R) will be reported on FORM VII-IN. If the percent recovery for the aqueous LCS falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

9. ICP Serial Dilution Analysis (L)

Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not at or within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

where, I - Initial Sample Result

S - Serial Dilution Result (Instrument Reading x 5)

In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix and concentration in the Sample Delivery Group. Serial dilution results and "E" flags must be reported on FORM IX-IN.

10. Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed under this contract, the instrument detection limits (in ug/L) must be determined for each instrument used, within 30 days of the start of contract analyses and at least quarterly (every 3 calendar months), and must meet the levels specified in Exhibit C.

The Instrument Detection Limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-5x the instrument manufacturer's suggested IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined IDL for an instrument must always be used as the IDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

IDLs must be reported for each instrument used on FORM X-IN submitted with each data package. If multiple AA instruments are used for the analysis of an element within a Sample Delivery Group, the highest IDL for the AAs must be used for reporting concentration values for that Sample Delivery Group. The same reporting procedure must be used for multiple ICPs.

11. Interelement Corrections for ICP

Before any field samples are analyzed under this contract, the ICP interelement correction factors must be determined prior to the start of contract analyses and at least annually thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. Results from interelement correction factors determination must be reported on FORM XI(PART 1)-IN and FORM XI(PART 2)-IN for all ICP parameters.

12. Linear Range Analysis (LRA)

For all ICP analyses, a linear range verification check standard must be analyzed and reported quarterly (every 3 calendar months) for each element on FORM XII-IN. The standard must be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard must be within $\pm 5\%$ of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

13. Furnace Atomic Absorption (AA) QC Analyses

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1-Furnace AA Analysis Scheme ("MSA Tree") will be required for quantitation. (These procedures do not replace those in Exhibit D of this SOW, but supplement the guidance provided therein.)

- a. All furnace analyses must fall within the calibration range. In addition, all analyses, except during full methods of Standard Addition (MSA), will require duplicate injections. The absorbance or concentration of each injection must be reported in the raw data as well as the average absorbance or concentration values and the relative standard deviation (RSD) or coefficient of variation (CV). Average concentration values are used for reporting purposes. The Contractor must be consistent per method and SDG in choosing absorbance or concentration to evaluate which route is to be followed in the MSA Tree. The Contractor must also indicate which of the two is being used if both absorbance and concentration are reported in the raw data. For MSA analysis, the absorbance of each injection must be included in the raw data. A maximum of 10 full sample analyses to a maximum 20 injections may be performed between each consecutive calibration verifications and blanks. For concentrations greater than CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the analytical sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value reported on FORM I-

IN with an "M". The "M" flag is required for the analytical spike as well as the sample. If the analytical spike for a sample requires an "M" flag, the flag must be reported on FORM I- IN for that sample.

- b. All furnace analyses for each analytical sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike¹ will be required to be at a concentration (in the sample) 2x CRDL. This requirement for an analytical spike will include the LCS and the preparation blank. (The LCS must be quantitated from the calibration curve and corrective action, if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85-115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses (see item 6, this section), will then determine how the sample will be quantitated, as follows:

- 1) If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.
- 2) If the spike recovery is greater than or equal to 40% and the sample absorbance or concentration is less than 50% of the "spike"⁵, report the sample results to the IDL. If the spike recovery is less than 85% or greater than 115%, flag the result with a "W".
- 3) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is at or

¹Analytical Spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

⁵"Spike" is defined as [absorbance or concentration of spike sample] minus [absorbance or concentration of the sample].

between 85% and 115%, the sample must be quantitated directly from the calibration curve and reported down to the IDL.

- 4) If the sample absorbance or concentration is greater than or equal to 50% of the spike and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

c. The following procedures will be incorporated into MSA analyses.

- 1) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.
- 2) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

- 3) For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.
- 4) Spikes must be prepared such that:
 - a) Spike 1 is approximately 50% of the sample absorbance or concentration.
 - b) Spike 2 is approximately 100% of the sample absorbance or concentration.
 - c) Spike 3 is approximately 150% of the sample absorbance or concentration.
- 5) The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data. The results must be reported on FORM VIII-IN. Reported values obtained by MSA must be flagged on the data sheet (FORM I-IN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.
- 6) If the correlation coefficient (r) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, report the results on FORM I-IN from the run with the best "r" and flag the result with a "+" on FORM VIII-IN and FORM I-IN.

Figure 1
FURNACE ATOMIC ABSORPTION ANALYSIS SCHEME

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-222.1 R1

Page 1 of 1

A.

Document Number: PNL-ALO-222 Revision Number: 1

Document Title: Plutonium by automated amperometric titration

Document's Original Author: MC Burt

Effective Date
of ICN: 12 / 23 / 92

Change Requested by:
AG King

B. Action: Place the attached procedure into PNL-MA-599 manual, volume 3.

C. Effect of Change: Incorporates this procedure into PNL-MA-599 manual. -

D. Reason for Change/Description of Change:

- 1) Incorporates this procedure into PNL-MA-599 manual by changing the procedure number. (Old document # 2-30.3, PNL-MA-597).
 - 2) Adds the figures on page 19 which were inadvertantly left out of the last ICN (#2-30.3-RO-1).
-

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert

Date: 12/23/92

Approval Authority: AG King

Date: 12/23/92

Other Approvals: _____

Date: / /

: _____

Date: / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-222, (Replaces 2-30.3), PLUTONIUM BY AUTOMATED AMPEROMETRIC TITRATION

1.0 APPLICABILITY

A solid sample is dissolved either by fusion with sodium bisulfate or by heating in nitric acid with a trace of hydrofluoric acid. The fused sample is dissolved in sulfuric acid, after which the plutonium is oxidized to plutonium(VI) with excess silver(II) oxide and the excess silver(II) is reduced by heating. The nitric acid dissolved sample and other plutonium nitrate solutions are fumed with sulfuric acid to remove the nitrate before the plutonium is oxidized. After the oxidation of plutonium and reduction of excess silver(II), the solution is adjusted to about 6M in sulfuric acid. Excess standardized ferrous ammonium sulfate is added and the excess iron(II) is back-titrated with standard potassium dichromate using an amperometric end-point detection. The indicating electrode is a rotating platinum or gold microelectrode that is used in conjunction with a saturated mercurous sulfate reference electrode as the counter electrode.

- (a) Material Plutonium bearing solids and solutions.
- (b) Range From 5 to 20 mg of plutonium are required for each titration.
- (c) Reliability The pooled relative standard deviation obtained over a one-year period from 44 titrations of 4 solutions of mixed oxide pellets used as control standards was 0.10%. The average percent recovery was 100.061%.
- (d) Interferences Ions that are oxidized by silver(II) and are reduced by iron(II) (such as chromium, manganese, and vanadium) cause a high bias. A 0.1 weight percent positive error will result from 150 μ g of chromium or 100 μ g of manganese per gram of sample. These two constituents of stainless steel are the most probable interferences. Metals precipitated by sulfate may remove some plutonium from solution, causing low results. Iron and uranium do not interfere.

Author	Date	Project Mgr.	Date	QAD Representative	Date
MC Burt	9/8/92	N/A		TL Ehlert	9/8/92
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
	9/8/92	AG King	9/8/92	All original signatures on file	
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With amperometric titrations, the end point is determined from measurements made of the "amperometric" current during the titrations.^{(d)(h)} The amperometric current is generated at constant potential across a rotating platinum or gold microelectrode (indicator electrode) and a saturated mercurous sulfate reference electrode. Values of this current as a function of the amounts of titrant added are plotted, giving two essentially straight lines that intersect at the end point of the titration. The relationship between current and the titrant added is not linear near the end point. Consequently, the current titrant data are extrapolated from the linear portions to the intersection at the end point.

If the substance being titrated is not electroactive at the potential applied to the indicator electrode, no current will flow before the end point except for a small and essentially constant residual current. Then, if the titrant is electroactive at the potential, the amperometric current will increase as the titrant is added after the end point. This is the case when plutonium(VI) is titrated directly with iron(II).

The plutonium(VI) reduction by iron(II) is a slow reaction. As a result, upon addition of iron(II) before the end point, the current will increase quickly and then slowly decay to the residual current, although near the end point the current decays at a faster rate. This characteristic makes it difficult to recognize when the end point is being approached and it results in a time consuming titration if the current is allowed to decay to the residual current after each addition of titrant before the end point. To reduce the time of titration, common practice is to add titrant before the end point without waiting for the current to decay to the residual current and then measure current as a function of titrant added after the end point in the linear portion of the curve. The initial residual current is assumed to be constant up the end point.^(f) Current values are read across a 1000-ohm resistor and are thus read as mV on a digital volt meter.

The initial residual current should be less than 0.2 mV (preferably less than 0.1 mV) so that it is insignificant compared to the current measured at the first data point taken after the end point. This permits the end point to be calculated from only a few data points past the end point instead of drawing a titration curve from several points. If the initial residual current is greater than 0.2 mV, there may be a competing reaction at the surface of the electrode. Usually, letting the indicator electrode soak in the solution a few minutes will allow the residual current to decay to an acceptable level. Persistent high residual currents usually can be eliminated by soaking the indicator electrode in 8M nitric acid overnight.

The problems encountered by the slow plutonium(VI)--iron(II) reaction can be eliminated by a back-titration. A known amount of standardized iron(II) solution in excess of the amount needed to reduce all

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plutonium(IV) is added and the excess is back-titrated with standard potassium dichromate solution.^(c) The chromium(VI)--iron(II) reaction is faster than the plutonium(VI)--iron(II) reaction and thus, the current decays to a constant value faster after each addition of dichromate standard. In this back-titration, the dichromate ion is not electroactive at the potential applied to the indicator electrode and as the titrant is added to react with the excess iron(II), the current decreases towards the residual current. The final titration point taken should be at a current greater than 1 mV to avoid the nonlinearity near the end point. The titration data are linear between 1 and at least 15 mV under the conditions used at PNL.

A slow drift downward in current after each addition of titrant is encountered during the back-titration that may be caused by air oxidation of the excess iron(II). By reading the current at a given time after each addition of titrant, the effect of the drift can be minimized. A better approach, however, is to monitor the amperometric current with a recorder. The recorder gives a continuous readout of the current during the titration and a better estimate can be obtained of the amperometric current when the initial decay has stopped and the drift is minimal. The recorder also permits a better "look" at background noise, which helps in evaluating the performance of the amperometric system.

Another source of current drift is leakage of electrolyte from the reference electrode compartment, in which case the drift can be eliminated by stopping the leakage. This drift is characterized by a linear increase in current with time and it is really a measure of the leak rate from the electrode compartment.

The oxidation of plutonium with argentic oxide is done at room temperature in 0.5N sulfuric acid. Excess argentic oxide is indicated by a blackish-brown color in the solution and a black precipitate. Sufficient time must be allowed for complete oxidation before reducing the excess oxidant, which is done by increasing the acid concentration and heating the solution. The excess is gone when the blackish color and precipitate disappear. The plutonium(VI) should be titrated within a few hours to avoid possible reduction from radiolysis,^(g) although the length of time before reduction could become significant is not known. Using the prescribed conditions, plutonium(VI) solutions have been stable up to at least four hours after the excess oxidant was reduced.

Amperometry is one of two methods used to determine plutonium in mixed oxides.^(a) With both methods, plutonium can be determined without separation from uranium, which is an important advantage over other plutonium methods when analyzing mixed oxides.^(e) The amperometric method is also free of interference from iron, which is useful since iron is a common trace metal in plutonium containing materials.

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2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Analyst

4.0 PROCEDURE

4.1 DISCUSSION

4.2 APPARATUS

- (a) Amperometric End-Point Detector. See Figure 30.3.1.
- (b) Analytical Balance. Readable to at least 0.1 mg.
- (c) Digital Volt Meter, Fluke Model 8860A with IEEE-488 Interface.
- (d) Flasks. Erlenmeyer, fused quartz, 50 ml, with a fused quartz cover glass.
- (e) Magnetic Stirrer.
- (f) Muffle Furnace.
- (g) Hot Plate.
- (h) Reference Electrode, Mercurous sulfate, Brinkman Instruments EA 406.
- (i) Rotating Platinum or Gold Electrode. Brinkman Instruments Control Unit 628-10 and Drive Unit 628-50. Platinum Electrode EA 289/2 or Gold Electrode EA 289/3.
- (j) Digital Buret (2), Brinkman Instruments Model 655 with 5 ml and 1 ml delivery capacity.
- (k) Control Unit, Brinkman Instruments Model 643, to control turntable operation, stirrer and valve operation.
- (l) 10-Place Rotating Turntable, Brinkman Instruments Model 624 with Stirrer 622/1 and spiral stirrer shaft.

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PNL TECHNICAL PROCEDURE

- (m) HP85A Computer with GPIO interface, BCD interface, HPIB interface and I/O ROM Drawer.
- (n) Controlling Software Package.
- (o) Weighing Burets. Drop dispensing bottles, 15, 30 and 60 ml volume, polyethylene.
- (p) Titration Vessels. See Figure 30.3.2.

4.3 REAGENTS

- (a) Acid Mixture. 12M HNO_3 - 0.05M HF.
- (b) Argentic Oxide.
- (c) Ferrous Ammonium Sulfate. Dissolve 7.5 g in 500 ml 1N H_2SO_4 . This solution, approximately 3.5×10^{-2} milliequivalents per gram, must be standardized each day it is used because Fe(II) is gradually oxidized by air (see Subsection 4.6.1).
- (d) Standard Potassium Dichromate, NBS (NIST) 136c or equivalent, for back titration. Dissolve 1.5-1.6 g in 2 liters water. Calculate titer (see 4.8 (f)).
- (e) Sodium Bisulfate
- (f) Sulfuric Acid. 0.5N, 1 N, and 18N.

4.4 STANDARDS

- (a) Calibration Standard. The calibration standard is a solution of plutonium prepared from NBS plutonium metal (SRM 949) or a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ prepared from NBS (NIST) 136c or equivalent. Plutonium metal is dissolved in 6N HCl, fumed to dryness in H_2SO_4 and fused with sodium bisulfate to make the standard composition as near to that of samples as possible. The final concentration of plutonium is about 10 mg Pu/g. Prepare as follows:
 - 1. Take three units of NBS SRM 949f or its replacement and carefully transfer them to a quartz Erlenmeyer flask. Add 6N HCl dropwise to effect dissolution. When dissolution is complete, add 3 or 4 ml 6N H_2SO_4 and evaporate to dryness. Add 10 g sodium bisulfate and fuse at 600C for 1 to 2 h. Dissolve melt in 1N H_2SO_4 and transfer to a tared bottle. Dilute to appropriate volume with 1N H_2SO_4 to give a final

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solution with a concentration of 10 to 11 mg pu/g. Weigh the solution to the nearest 0.1 mg.

2. Encapsulate the standard in 5 ml sealed glass ampules.
3. Calculate the mg of plutonium per gram and the milliequivalents per gram of solution using part (a) of Section 4.8.
4. Dry the $K_2Cr_2O_7$ at 100-110°C for 1-2 hrs. and cool in a dessicator. Weigh 0.8-0.9 g and carefully transfer with approximately 200 ml water to a tared (with cap) 8 oz. glass bottle and weigh the solution to nearest 0.1 mg. Swirl to insure dissolution. Keep the bottle tightly capped when not in use. Appropriate portions are transferred to a 15 ml weighing buret for aliquoting. Calculate titer using part (g) of Section 4.8.

(b) Control Standard. A mixed oxide pellet is used as a control standard. The material has been used in the SALE program and has an established value for both plutonium and uranium. The value established for Pu is $20.16 \pm 0.04\%$ in 1982. It is corrected for isotopic decay. Prepare as follows:

1. Weigh three pellets to the nearest 0.1 mg into a quartz Erlenmeyer. Proceed as per Section 4.7.2 (a) through (e). Transfer to a tared bottle using 1N H_2SO_4 and dilute to give a concentration of approximately 28 mg sample/gram of solution.
2. Weigh solution to the nearest 0.1 mg and calculate concentration using part (b) of Section 4.8.
3. Encapsulate the solution in 5 ml sealed glass ampules.

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.

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- (c) Ceramic tops on hot plates can shatter if etched heavily by caustic. Carefully check such tops before use if they have been exposed to caustic solutions.

4.6 QUALITY CONTROL

4.6.1 Calibration

Calibration involves standardizing the ferrous ammonium sulfate solution [Reagent (c), Section 4.3] with NBS plutonium solution (the calibration standard) or the NIST dichromate standard (section 4.4 (a)). The iron(II) solution is standardized each 8-hr shift during which plutonium analyses are made because iron(II) is slowly oxidized by air. Standardize as follows:

- (a) Weigh to the nearest 0.1 mg three or four 1-g portions of the calibration standard into separate titration vessels.
- (b) Add 10 ml of 0.5N H_2SO_4 and a stirring bar to each vessel. When using dichromate add 10 ml 1N H_2SO_4 and proceed to 4.7.4.
- (c) Proceed at step (b) of Subsection 4.7.3 and continue through Subsection 4.7.4 for each vessel.
- (d) Calculate the results of the standards using Subsection 4.8 (c).
- (e) Calculate the average and relative standard deviation from the results of the titrations.¹

The relative standard deviation should be <0.1%. If it is >0.2%, investigate and correct the problem before continuing with the analysis.

4.6.2 Control

- (a) Weigh to the nearest 0.1 mg two portions of the control standard into separate titration vessels.

One 5 ml ampoule provides enough solution for 2 portions.

¹

The relative standard deviation is defined in Section 1.2 of Volume 1.

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- (b) Proceed at step (a) of Subsection 4.7.3 and continue through Subsection 4.7.4 for each vessel.
- (c) Calculate the results using Subsection 4.8 (d) and plot results on control chart. See MCS-033.
- (d) Systematic error (or bias) is monitored by averaging the control standard results for five days analysis. The data from the current days analysis plus the previous four analyses are averaged as $\bar{X}$.

Bias is defined as $b = \bar{X} - X_a$, where X_a is the accepted value for the control standard.

Percent bias is calculated as follows,

$$\%bias = \frac{b(100)}{X_a}$$

- (e) Record %bias as a deviation from a straight line (zero) on a control chart. Positive or negative trends warrant attention to standards and/or procedure.
- (f) When the procedure has not been used in excess of six months, it shall be necessary to requalify the method. In the absence of NIST traceable standard materials the control material (Section 4.4 (b)) shall be deemed adequate. At a minimum, at least two different solutions (dissolutions) of the control standard shall be analyzed in triplicate with precision (rsd) less than 0.2% and all titration values within the 3 sigma limits assigned to the decay corrected values. These limits are based on historical data.

For the initial requalification of the procedure using NIST dichromate standards (or any requalification after 24 months non-use), six different solutions (dissolutions) of the control standard shall be analyzed in duplicate. The mean value shall be tested to verify that the value is not significantly different from the historical mean value. The standard deviation estimated from 12 measured values shall be used to calculate control limits for the method. (The measured values can be pooled with historical data for establishing control limits if it can be shown that it is appropriate to do so).

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4.6.3 Training

- (a) Refer to MCS-033.
- (b) The analyst shall be trained in the use of the procedure by the responsible scientist. He shall demonstrate qualification by successfully analyzing duplicate reference standards (following calibration) on three successive occasions. Ongoing qualification consists of successful analysis of NBS and reference standards.

4.7 ANALYSIS

Samples already in solution form as the nitrate or chloride are analyzed by starting at Step (f) of Subsection 4.7.1.

4.7.1 Sample Dissolution in Acid (12M HNO₃ - 0.05MHf)

- (a) Add a portion of sample weighed to the nearest 0.1 mg to a 150-ml beaker.

Select an amount of sample to give a plutonium concentration of 3 to 5 mg/ml in a 60-ml volume.

- (b) Add 20 ml of the acid mixture; cover the beaker with a watch glass and heat on a hot plate until dissolution is complete.

If the hot plate has a ceramic top, see Part (c) of Section 4.5.

The solution must be examined carefully to determine if dissolution is complete. It is difficult to detect small amounts of residue in the highly colored solution. Add additional amounts of the acid mixture, if necessary, until the dissolution is complete.

If the solution should evaporate to dryness during the dissolution, add 20 ml of the acid mixture and heat to redissolve the sample.

- (c) Remove the beaker from the hot plate and let the solution cool to room temperature.
- (d) Quantitatively transfer the solution to a tared 60-ml weighing buret using 1M H₂SO₄ to rinse the beaker.

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- (e) Dilute to about 60 ml with 1M H_2O_4 , mix thoroughly, and weigh. Calculate sample concentration, C_s , according to Section 4.8 (b).
- (f) Add an aliquot weighed to the nearest 0.1 mg and containing 5 to 20 mg of plutonium to a titration vessel.
- (g) Add about 0.5 ml of 18N H_2SO_4 and evaporate to dryness on a hot plate.
- (h) Raise the temperature of the hot plate and continue heating until all of the H_2SO_4 is gone; remove the vessel from the hot plate.
- (i) Let the vessel cool to room temperature and then add 10 ml of 0.5N H_2SO_4 , rinsing down the sides of the beaker as the acid is added.
- (j) Swirl the vessel until the residue is completely dissolved.
- (k) Proceed with the oxidation of the plutonium by following Subsection 4.7.3.

4.7.2 Sample Dissolution by Fusion

- (a) Add a portion of sample weighed to the nearest 0.1 mg to a 50-ml quartz Erlenmeyer flask.

Select an amount of sample to give a plutonium concentration of 3 to 5 mg/ml in a 60-ml volume.
- (b) Add 10 to 12 g of sodium bisulfate to the flask and cover with a fused quartz cover glass.
- (c) Place the flask in a muffle furnace and heat at 600°C for one to two hours.
- (d) Remove the flask from the furnace after the furnace has cooled.
- (e) Dissolve the melt in 30 ml of 1N H_2SO_4 , swirling the flask occasionally to aid dissolution.
- (f) Quantitatively transfer the solution to tared 60-ml weighing buret using 1N H_2SO_4 to rinse the flask.

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- (g) Dilute to about 60 ml with 1N H_2SO_4 , mix thoroughly, and weigh. Calculate sample concentration, C_s , according to Section 4.8 (b).
- (h) Add an aliquot weighed to the nearest 0.1 mg and containing 5 to 20 mg of plutonium to a titration vessel and add 0.5N H_2SO_4 to a volume of 10 ml.
- (i) Proceed with oxidation of the plutonium by following Subsection 4.7.3.

4.7.3 Oxidation of Plutonium

- (a) Add a stirring bar to the titration vessel.
- (b) Put the vessel on the magnetic stirrer, and while the solution is being stirred, add 25-mg portions of argentic oxide every 15 to 30 seconds until excess oxide has been added.

Excess argentic oxide is indicated by a brownish-black color in the solution along with a black precipitate. Fused samples (Subsection 4.7.2) require more argentic oxide for complete oxidation than samples dissolved in acid (Subsection 4.7.1).

- (c) Remove the vessel from the stirrer and let the solution stand for at least 30 minutes.

The black precipitate and color of the solution must persist during the 30-min period. If not, insufficient argentic oxide was added.

- (d) Add sufficient 1N H_2SO_4 to bring the volume of solution to about 20 ml, rinsing the sides of the vessel while adding the acid.
- (e) Place the vessel on the hot plate and heat the solution until all the black precipitate disappear. Thirty minutes is usually sufficient.

If the hot plate has a ceramic top, see Part (c) of Section 4.5.

- (f) Remove the vessel from the hot plate and let it cool to room temperature.
- (g) Rinse down the sides of the vessel with 1N H_2SO_4 , but do not let the volume exceed 25 ml.

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- (h) Proceed with the titration by following Subsection 4.7.4.

2.7.4 Amperometric Titration

The amperometric titration is automatic and is controlled by the program in the Hewlett-Packard 85A Computer. Samples are titrated according to the following procedure after control is given to the computer.

The turntable is rotated and the sample is raised to the up position. Valve 1 opens and admits 10 ml of 18N H_2SO_4 , the stirrer and rotating electrode are turned on. The DVM monitors solution potential for 45 seconds and then reads the base voltage. Buret 1 then adds an initial increment of 1.250 ml of ferrous solution, then alternately reads solution potential and adds ferrous solution in 50 μ l increments until the end set point is reached. After a preset wait time, the voltage is read and two 100 μ l additions of standard potassium dichromate from buret 2 are added with voltage readings taken after set wait times. Upon completion, the stirrer and electrode are turned off and as the vessel is being lowered, Valve 2 opens and the stirrer, electrodes and solution delivery tips are rinsed with water. The turntable then rotates and the process is repeated.

The following steps are required prior to start of titrations.

- (a) Insure that reagent reservoirs are adequately filled (18N H_2SO_4 and rinse H_2O).
- (b) Turn burets to mode 1 and manually discharge two volumes from buret 1 and five volumes from buret 2. Return mode switches to mode 2.
- (c) Insert cassette into HP85, type LOAD "Pu" and press ENDLINE. When program has loaded (small LED below tape goes out), press RUN. The system is left in a standby condition with the program loaded. If this is the situation, all that is necessary is to press RUN.
- (d) The CRT will display "Pu ASSAY PROGRAM" and ask for inputs from the keyboard. All entries are made by typing the appropriate information and pressing ENDLINE.

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1. Option 1 or 2
Press 1 ENDLINE
2. Time for Base Voltage
Press 45 ENDLINE
3. Set Point MV
Press 5 ENDLINE
4. Time for Set Point
Press 25 ENDLINE
5. Time for Data Points
Press 20 ENDLINE
6. Number of Samples
Press (any) number up to 10 ENDLINE
7. Sample Number
Any combination of alpha-numeric characters up to eight characters.
Press (eight) characters ENDLINE
8. Aliquot Number
Any integer up to 99.
Press number ENDLINE

Sample number and aliquot number will keep coming up until the number of samples from step 6 have been identified. The CRT will then display "Start 643".

Prepared samples in titration vessel are placed in the turntable beakers in the order entered into the computer, with number 1 being to the immediate right of the titration head. The turntable may be manipulated manually with switches on the front of the 643 controller with the auto/manual switch in manual position.

9. Place the on/off switch on the end point detector to the on position; turn the I/E switch to the E position and adjust the voltage reading on the DVM to 0.600 V and then turn the switch back to the I position.
10. Insure that the auto/manual switch on the 643 controller is in the "auto" position.

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11. Place the stop/start switch on the 643 controller in the "start" position.

This initiates the titration process. The HP85 will control the titration with the parameters which were input and will send a stop pulse to the controller when the titration is completed.

12. When all titrations are completed, turn the end point detector to the "off" position and press RUN on the HP85. All the other components are left in their present mode.
13. All data pertinent to calculations along with sample number and aliquot number are printed by the computer at the completion of each sample titration.
14. A rubber cover is placed over the tip of the mercurous sulfate electrode for storage.

4.8 CALCULATIONS

- (a) Plutonium metal SRM 949

$$Pu = \frac{MF}{W_{Pu}}$$

where Pu = mg of plutonium per g of solution
 M = wt in mg of plutonium metal used
 F = Purity Factor
 W_{Pu} = wt in g of final solution.

$$C_{Pu} = \frac{MF(2)}{W_{Pu} (239.08)}$$

where C_{Pu} = milliequivalents per g of solution

- (b) Mixed oxide control standard

$$C_s = \frac{W_{\text{sample}}}{W_{\text{solution}}}$$

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where C_s = mg sample per g of solution
 W_{sample} = wt in mg of sample used
 W_{solution} = wt in g of final solution

- (c) Iron Standardization. Calculate the milliequivalents per gram of ferrous ammonium sulfate solution as follows:

$$C_{\text{Fe}} = \frac{W C_{\text{Pu}} + \text{Vol}_{\text{Cr}} + (C_3 - C_{\text{res}}) \left(\frac{C_1}{C_1 - C_2} + \frac{C_2}{C_2 - C_3} \right) C_{\text{Cr}}}{2 \text{Vol}_{\text{Fe}}}$$

where C_{Fe} = milliequivalents per ml of solution
 W = weight in g of plutonium solution taken
 C_{Pu} = milliequivalents per g of plutonium solution
 C_{Cr} = milliequivalents per ml of dichromate solution
 Vol_{Cr} = volume in ml of dichromate solution used
 C_1 = current reading after Fe addition
 C_2 = current reading at first titration point
 C_3 = current reading at second titration point
 C_{res} = residual current
 Vol_{Fe} = volume of iron solution used in titration
 $C_{\text{Cr}_1} = \text{Vol}_{\text{Cr}}/2$
 $C_{\text{Cr}_2} = \text{Vol}_{\text{Cr}}/2$

Note: When calibrating with dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) substitute SC_{Cr} (4.8 (g)) for C_{Pu} .

- (d) Solid Samples. Calculate the concentration of plutonium in mixed oxide and plutonium oxide samples as follows:

$$\text{Pu} = \frac{\text{Vol}_{\text{Fe}} C_{\text{Fe}} - \text{Vol}_{\text{Cr}} + (C_3 - C_{\text{res}}) \left(\frac{C_1}{C_1 - C_2} + \frac{C_2}{C_2 - C_3} \right) C_{\text{Cr}}}{2 (W)_s C_s} \cdot A \cdot 100$$

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where Pu = wt% of plutonium in sample
 Vol_{Fe} = volume of iron solution used in titration
 C_{Fe} = milliequivalent per ml of iron solution
 Vol_{Cr} = volume in ml of dichromate solution used
 C_{Cr} = milliequivalents per ml of dichromate solution
 C₁ = current reading after Fe addition
 C₂ = current reading at first titration point
 C₃ = current reading at second titration point
 C_{res} = residual current
 Cr₁ = Vol_{Cr}/2
 Cr₂ = Vol_{Cr}/2
 W_s = weight in g of sample solution used
 C_s = concentration of sample solution, in mg sample/g solution
 A = Isotopic correction

where
$$A = \frac{239.082 [(0.01B)(240.0538) + (1.00 - 0.01B)(239.0521)]}{239.082}$$

where B = % ²⁴⁰Pu in sample

Note: to calculate mg Pu found, delete W_s, C_s and 100 from the formula.

(e) Solution Samples. Calculate the concentration of plutonium in plutonium solutions as follows:

$$Pu = \frac{Vol_{Fe} C_{Fe} - Vol_{Cr} + (C_3 - C_{res}) \frac{Cr_1}{C_1 - C_2} + \frac{Cr_2}{C_2 - C_3}}{2 (W_s)} \cdot DF \cdot SpG \cdot A$$

where Pu = plutonium concentration in g/P
 Vol_{Fe} = volume of iron solution used in titration
 C_{Fe} = milliequivalents per ml of iron solution
 Vol_{Cr} = volume in ml of dichromate solution used
 C_{Cr} = milliequivalents per ml of dichromate solution
 C₁ = current reading after Fe addition
 C₂ = current reading at first titration point
 C₃ = current reading at second titration point
 Cr₁ = Vol_{Cr}/2
 Cr₂ = Vol_{Cr}/2

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C_{res} = residual current
 W_s = weight in g of sample solution used
 DF = Dilution Factor
 SpG = Specific Gravity of sample solution
 A = Isotopic correction

$$A = \frac{239.082 [(0.01B)(240.0538) + (1.00 - 0.01B)(239.0521)]}{239.082}$$

where

where $B = \% {}^{240}\text{Pu}$ in sample

(f) Chrome titer for back titration.

$$C_{cr} = \frac{WF (10^3)}{V (49.0317)}$$

where C_{cr} = milliequivalents per mL of solution
 W = weight of $\text{K}_2\text{Cr}_2\text{O}_7$, in grams
 V = volume of solution, in mL
 F = purity factor

(g) Chrome titer for Calibration Standard.

$$SC_{cr} = \frac{WF (10^3)}{W_s (49.0317)}$$

where SC_{cr} = Milliequivalents per gram of solution
 W = weight of $\text{K}_2\text{Cr}_2\text{O}_7$, in grams
 W_s = net weight of solution, in grams
 F = purity factor

5.0 BIBLIOGRAPHY

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Figure 30.3.1. Amperometric End-Point Detector

- A - Turntable Beaker
- B - Polyethylene Spacer
- C - Pyrex Titration Vessel

Figure 30.3.2. Titration Vessel

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TITLE: PNL-ALO-223, (Replaces 2-30.5), OXYGEN TO METAL RATIO BY THERMOGRAVIMETRY

1.0 APPLICABILITY

Samples are weighed and then heated to constant weight at 800 to 900°C in an atmosphere of hydrogen-helium saturated with water vapor at 0°C. The O/M is calculated from the difference between the initial and final weights. Procedures for macroanalysis (≥ 0.5 -g samples) and microanalysis (≤ 100 -mg samples) are included in this method.

- (a) Material Uranium oxide and mixed oxide powder and pellets; plutonium oxide derived from burning plutonium metal. Plutonium oxide derived from other sources may contain a variety of impurities that could affect the analysis [see Part (d) below].
- (b) Range All O/M values encountered in the above materials.
- (c) Reliability Standard deviations of 0.001 to 0.003 are normally obtained.
- (d) Interferences Inert impurities that contribute significantly to the weight of a sample and impurities that cause a weight change during the analysis.

The oxygen-to-metal ratio of uranium and plutonium oxides is commonly determined thermogravimetrically. In thermogravimetric methods, an oxide is treated under conditions that are assumed¹ to give stoichiometric oxide by either adding oxygen to or removing oxygen from the sample. The difference between the initial weight of the oxide and the weight at stoichiometry is used to calculate the O/M. The results

¹ The word "assumed" is used in this discussion because it has not been unquestionably substantiated that stoichiometry is reached under the conditions used in thermogravimetric methods. See references (b), (c), (d), (e), and (g) for discussions on the criteria used to establish stoichiometry.

Author	Date	Project Mgr.	Date	QAD Representative	Date
MC Burt	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	6/16/88	All original signatures on file	
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obtained, however, may require correction for impurities present in the samples.

There can be two kinds of interferences from impurities. A weight change caused by impurities that are oxidized, reduced, or that volatilize during analysis produces one kind of interference. Water, which is readily adsorbed by some powders but not by sintered pellets,^{(c)(g)} can cause this kind of interference. The second kind, which is not as significant as the first, is caused by inert impurities. If the concentration of inert impurities is large enough to measurably affect the fractional weight change $[W_2 - W_1 / W_2 - W_1]$, see Section 4.8A], then a bias in the result will occur. Bias from impurities can be a particular problem when analyzing plutonium dioxide. Oxide produced from the low temperature calcination of plutonium salts, particularly from oxalate, may contain many undefined and volatile impurities that would make a reliable determination of O/M difficult to achieve.

Two thermogravimetric methods, which have been used by laboratories associated with the production of mixed oxide fuel for the FFTF are the Lyon and Chikalla methods. Lyon's original method involves a two-step heating cycle in which the oxide is first heated in air at 750°C to produce hyperstoichiometric oxide and is then heated to constant weight at 700°C in hydrogen to reduce the oxide to a composition assumed to be stoichiometric (O/M = 2.000).^(a) Various modifications in Lyon's method have been made; however, Lyon's basic concept has remained. The Chikalla method, developed by Chikalla and McNeilly,^(d) is a one-step method in which the oxide is adjusted to a composition assumed to be stoichiometric whether the initial O/M is hypo- or hyperstoichiometric. In this method, the oxide is heated to constant weight at 800°C in hydrogen-helium that has been saturated with water vapor at 0°C.

The question of equivalency of these methods has been raised from time-to-time. For example, the O/M results from a round robin held in 1969 fell into two distinct groups and a conclusion drawn was that bias between methods existed.^(f) To determine if that conclusion was true, a study was made at HEDL in which three of the methods used were compared. The study showed that those methods are equivalent, at least to within 0.003 O/M units, and that the grouping of O/M values resulted from something other than method bias.^(g)

The equivalency of 0.003 O/M units suggested by the HEDL study was probably more of an indication of variation from materials used in the study than from methods. Two batches of mixed oxide pellets were used. The ranges in standard deviation for the two batches were 0.003 and 0.0007.^(g) These ranges indicate that one batch was more uniform in O/M from pellet to pellet than the other batch. Difference in uniformity between batches of materials has been seen often in the analysis of samples. Since the macro O/M apparatus at PNL (Figure 30.5.1) can handle up to 30 pellets in one furnace loading, quite often samples from

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several pellet batches are loaded at the same time. It is not unusual to find that some of those batches have very small standard deviations while others have relatively large standard deviations. Also, the examination of results from the analysis of control standards for a recent 16-month period supports this observation.

The standard used is a mixed oxide pellet that has been adjusted to stoichiometry and is thereafter treated as a sample during each sample run [see Section 4.7A, Part (b) and Subsection 4.7B]. Thus, its weight before and after ignition should change only if the conditions of ignition change to give a composition other than stoichiometry. This assumes, of course, that between analyses the composition of the pellet does not change. The pellet must also be protected from an inadvertent weight change caused by chipping or contamination. Over a 16-month period, five pellets were used as control standards and the pooled standard deviation involving 548 before- and after-weighings was 0.000065 g, which is equivalent to 0.0011 O/M units. For the five pellets, the standard deviations ranged from 0.000042 g (O/M = 0.0007) to 0.000077 g (O/M = 0.0013).

This O/M method is a modified Chikalla method. The method as written has procedures for both macro and microanalyses. Samples weighing from 0.5 g to several grams and between 50 and 100 mg are taken for macro and microanalysis respectively. Both procedures have provisions to eliminate water interference during analysis of powders. These procedures have been compared and they give equivalent results. For the past several years, however, the procedure for macroanalyses has been used exclusively; the micro procedure is retained in this written method for information and for possible future use.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0A PROCEDURE: A - MACROANALYSIS

4.1A DISCUSSION

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PNL TECHNICAL PROCEDURE

4.2A APPARATUS

- (a) Analytical Balance. Substitution-weighing type, single pan, readable to at least 0.1 mg. A semimicro balance, readable to 0.01 mg. is used. This balance is a Mettler AE-163 (Electronic Analytical Balance) modified for glove box use. It has a Digitec Printer (Model 961) that provides a printout containing 5 digits for sample identification and 8 digits for weight. With this balance all weighings are made to 0.01 mg.
- (b) O/M Macroanalysis Apparatus. Figure 30.5.1.
1. Boats, fused silica, about 10-mm o.d. x 7-mm high, flat bottom.
 2. Bubbler, located at the exit end of the furnace tube to prevent back-diffusion of air into the tube.
 3. Drying tube.
 4. Flowmeter, capable of controlling the gas flow from 300 to 1000 ml/min.
 5. Furnace tube, fused silica.
 6. Ice-bath bubbler, used to saturate gas with water vapor at 0°C. A dewar flask containing ice is placed around the bubbler.
 7. Temperature controller, Honeywell Pyrovane.
 8. Tube furnace, capable of sustained operation at 900°C.

4.3A REAGENTS

- (a) Argon. Prepurified grade or equivalent.¹ Helium (high purity grade) may be used instead.
- (b) Helium-Hydrogen Mixture. 6% hydrogen, prepared from prepurified grade or equivalent gases.⁽¹⁾
- (c) Ice. Crushed.

¹

Matheson Gas Data Book, The Matheson Co., Inc., East Rutherford, NJ, 4th Ed., 1966.

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(d) Magnesium Perchlorate. Anhydrous, for the drying tube.

4.4A STANDARDS

Materials of known O/M for use as calibration and control standards are not available. A balance weight and a mixed oxide pellet are used for calibration and control purposes. These standards must be stored in a clean, dry, and closed container and handled carefully to prevent a change in weight.

- (a) Calibration Standard. 1- g weight, NBS Class S.
- (b) Control Standard. A mixed oxide pellet that has been adjusted to stoichiometry using Subsection 4.7.1A or 4.7.2A.

4.5A 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.
- (c) Precautions are required to avoid fires when operating a furnace in a glove box.

4.6A QUALITY CONTROL

Because of a lack of O/M standards, this method cannot be calibrated and controlled in the same manner as other analytical methods. Calibration and control are limited primarily to controlling the integrity of the balance.

4.6.1A Calibration

The analytical balance is maintained under a routine maintenance and calibration schedule [see Part (a), PNL-ALO-052]. Check the calibration of the balance at least once with each set of weighings as follows:

- (a) Adjust the zero reading of the balance.
- (b) Place the 1-g calibration standard on the pan.
- (c) If the weight reads 1.0000 ± 0.0001 g, the calibration is satisfactory; if not, investigate and resolve the problem before continuing with the analysis.

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4.6.2A Control

The control standard is analyzed with each set of samples by following Subsection 4.7.1A or 4.7.2A. Plot both the initial and final weight on the control chart and determine control status.¹ Since the oxide pellet is initially stoichiometric, both weights should be equal within the limits of weighing error, unless the conditions of the analysis have changed to give a composition other than stoichiometry.

4.7A ANALYSIS

This section contains two procedures: the first is for samples that contain little, if any, water and that do not sorb water readily; the second is for samples that contain amounts of water or that readily sorb water. Sintered, high density pellets typify materials suitable for the first procedure, whereas powders and low density (high open porosity) pellets are materials suitable for the second procedure.

4.7.1A Pellets.

- (a) Prepare the O/M macroanalysis apparatus (Figure 30.5.1) as follows:
 1. Adjust the flow rate of helium-hydrogen from 300 to 500 ml/min.
 2. Adjust valves so that the gas passes through the ice-bath bubbler.
 3. Turn on the furnace and adjust the temperature to 900°C.
- (b) Determine the tare weights (W_t) of the boats to the nearest 0.1 mg after heating to constant weight under the above conditions.¹

¹ Instructions for preparing control charts and the criteria that establish when a method is out of control are found in the laboratory quality assurance manual, Volume 1.

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- (c) Place the samples in the boats and weigh (W_1) to the nearest 0.1 mg at room temperature.⁽¹⁾

The sample must be a whole pellet or pieces of a pellet. The minimum weight of a piece should be 0.2 g and a sufficient amount of sample should be taken to give a total weight of at least 0.5 g. The most desirable weight is between 1 and 2 g.

- (d) Place the boats containing the samples into the furnace tube and heat for a minimum of 6 hr under the conditions given in Step (a).

Heating for 6 hr should be sufficient for a 1- to 2-g sample to reach constant weight.

- (e) Remove the furnace tube containing the boats and samples from the furnace to allow rapid cooling to room temperature.

The samples must remain in the helium-hydrogen atmosphere during cooling to prevent oxidation of the sample material.

- (f) Remove the boats containing the samples from the furnace tube and weigh (W_2) to the nearest 0.1 mg.⁽¹⁾

Steps (d) and (f) can be repeated to assure that constant weight is obtained. The difference in W_2 should not exceed 0.2 mg.

4.7.2A Powders.

- (a) Determine the tare weights (W_T) of the boats to the nearest 0.1 mg after heating for 1 hr at 900°C in dry argon (<20 ppm H_2O) at a flow rate of 300 ml/min.¹

Use the O/M macroanalysis apparatus (Figure 30.5.1). The argon must bypass the ice-bath bubbler.

¹

If the balance used has the capability, weigh to the nearest 0.01 mg.

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PNL TECHNICAL PROCEDURE

- (b) Add from 1 to 2 g of sample to a boat and dry the sample in the thermogravimetric apparatus by heating at 150°C for 1 hr in dry argon flowing at 300 ml/min.
- (c) Remove the furnace tube from the furnace and allow to cool to room temperature.
- (d) Quickly weigh the boat and sample (W_1) to the nearest 0.1 mg.⁽¹⁾
- (e) Prepare the O/M apparatus as follows:
 - 1. Adjust the flow rate of the helium-hydrogen from 300 to 500 ml/min.
 - 2. Adjust the valves so that the gas passes through the ice-bath bubbler.
 - 3. Turn on the furnace and adjust the temperature to 900°C.
- (f) Place the boat and sample into the furnace tube and heat a minimum of 6 hr under the above conditions.

Heating to a 1- to 2-g sample for 6 hr should be sufficient for the sample to reach constant weight.
- (g) Cool to 150°C and adjust the proper valves so that the helium-hydrogen bypasses the ice-bath bubbler.

While cooling to 150°C, the sample must remain in the helium-hydrogen to prevent oxidation of the sample material.
- (h) Keep the samples at 150°C for approximately 20 minutes.

The time required to dry the gas and the gas lines leading to the furnace tube (Figure 30.5.1) can be reduced to less than 20 min by increasing the flow rate of the gas by a factor of 3.

¹ If the balance used has the capability, weigh to the nearest 0.01 mg.

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- (i) Remove the furnace tube from the furnace and allow to cool to room temperature.
- (j) Quickly weigh boat and sample (W_2) to the nearest 0.1 mg.¹

Steps (f) through (j) can be repeated to assure that constant weight is obtained. The difference in W_2 should not exceed ± 0.2 mg.

4.8A CALCULATION

Calculate the O/M according to the following equation. All weights are expressed in grams.

$$O/M = 2.000 - \frac{(W_2 - W_1)F}{(W_2 - W_T)}$$

where W_2 = final weight of sample and boat

W_1 = initial weight of sample and boat

$F = \frac{\text{formula weight of metal oxide}}{15.999}$

W_T = tare weight of boat.

Unless otherwise instructed, report results to the nearest 0.001 O/M units.

4.0B PROCEDURE: B - MICROANALYSIS

4.1B DISCUSSION

4.2B APPARATUS

- (a) Electrobalance. Cahn RG Automatic.
- (b) Ice-Bath Bubbler. Used to saturate gas with water vapor at 0°C. A Dewar flask containing ice is placed around the bubbler.

¹

If the balance used has the capability, weigh to the nearest 0.01 mg.

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- (c) Radiant Heater. Duel Elliptical, Research Incorporated, Model E2-5-3.
- (d) Recorder. Stripchart, 1-mV full scale. 0.5-sec response. A two-pen recorder is used to record weight and temperature.
- (e) Temperature Programmer. F&M, Model 240.
- (f) Vacuum Pump. Capable of pumping to a pressure of 100 millitorr or less.

4.3B REAGENTS

- (a) Helium-Hydrogen Mixture. 6% hydrogen, prepurified grade or equivalent.¹
- (b) Ice. Crushed.

4.4B STANDARDS

Materials of known O/M for use as calibration or control standards are not available. Balance weights and a fragment of mixed oxide pellet are used for calibration and control purposes. These materials must be stored in a clean, dry, and closed container and handled carefully to prevent a change in weight.

- (a) Calibration Standard. 5-mg weight, NBS Class M.
- (b) Control Standard.
 - 1. 50-mg weight, NBS Class M.
 - 2. Mixed oxide pellet fragment that has been adjusted to stoichiometry using Section 4.7B.

4.5B 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.

¹

Matheson Gas Data Book, The Matheson Co., Inc., East Rutherford, NJ, 4th Ed., 1966.

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- (c) Precautions are required to avoid fires when operating a furnace in a glove box.

4.6B QUALITY CONTROL

Because of a lack of O/M standards, this method cannot be calibrated and controlled in the same manner as other analytical methods. Calibration and control are limited primarily to controlling the integrity of the balance.

4.6.1B Calibration

Calibrate the electrobalance according to the procedure found in the manufacturer's instruction manual.¹ The calibration is checked whenever the balance is out of control or maintenance problems occur.

4.6.2B Control

- (a) Weigh the 50-mg standard at least once in each 8-hr shift during which the balance is used. Plot the weight on the control chart and determine control status.²
- (b) Analyze the pellet fragment with each set of samples by following Section 4.7B. Record the weight of the fragment at Steps (f) and (h). Plot both weights on the control chart and determine control status.⁽²⁾ Since the oxide fragment is stoichiometric, both weights should be equal within the limits of weighing error, unless the conditions of the analysis have changed to give a composition other than stoichiometry.

4.7B ANALYSIS

This microanalysis procedure is used for powders and fragments of pellets and it can be used for samples that contain water or that readily sorb water. See Figure 30.5.2.

¹ Instruction Manual, RG Automatic Electrobalance, Cahn Instrument Co., Paramount, California.

² Instructions for preparing control charts and the criteria that establish when a method is out of control are found in the laboratory quality assurance manual, Volume 1.

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- (a) Evacuate the balance system to 100 millitorr or less and backfill it to atmospheric pressure with helium-hydrogen saturated with water vapor at 0°C.

When helium-hydrogen is specified in the following steps, its saturation with water vapor at 0°C is implied.

- (b) Heat the empty balance pan (left pan) at 100°C and record the weight.

This is the tare weight.

- (c) Turn off the heater; allow it to cool for 5 min and remove the hangdown tubes that surround both the left and right balance pans.

- (d) Add 50 to 100 mg of sample to the left pan and weights to the right pan until the weight on the left pan exceeds the weight on the right pan by less than 10 mg.

Samples weighing as little as 2 mg can be used, but a loss of precision results.

- (e) Replace both hangdown tubes; evacuate the system to 100 millitorr and back-fill it to atmospheric pressure with helium-hydrogen.

- (f) Heat the sample at 100°C for several minutes and weigh the sample (W_1).

The sample weight is equal to the sum of the following weights: the weights on the right pan, the weight equivalent to the reading of the mass dial, and the weight indicated by the recorder pen on the chart. See the Instruction Manual of the Cahn RG Automatic Electrobalance for detailed weighing instruction.¹

- (g) Increase the temperature to 800°C using manual temperature control and let the weight stabilize.

Usually about 30 min are required for the weight to stabilize.

¹

Instruction Manual, RG Automatic Electrobalance, Cahn Instrument Co., Paramount, California.

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- (h) Shut off the heater and allow the sample to cool to 100°C; weigh the sample (W_2).

See note at Step (f).

The indicated weight at 800°C is unreliable because of turbulence effects caused by temperature gradients near the sample. Thus, the final weighing is made at 100°C.

4.8B CALCULATION

Calculate the O/M according to the following equation. All weights are expressed in milligrams.

$$O/M = 2.000 - \frac{(W_2 - W_1)F}{(W_2 - W_T)}$$

where W_2 = final weight of sample plus tare weight

W_1 = initial weight of sample plus tare weight

$F = \frac{\text{formula weight of oxide}}{15.999}$

W_T = tare weight.

Unless otherwise instructed, report results to the nearest 0.001 O/M unit.

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FIGURE 30.5.1. O/M Macroanalysis Apparatus

FIGURE 30.5.2. O/M Microanalysis Apparatus

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-224, (Replaces 2-30.7), WEIGHT LOSS UPON IGNITION

1.0 APPLICABILITY

Weight loss is determined by measuring the change in weight of a sample when heated to constant weight at 950°C in air.

- (a) Material Plutonium dioxide powder, prepared by calcining plutonium salts at temperatures below 950°C.
- (b) Range The smallest weight loss that can be determined depends upon the sensitivity of the balance used for the weight measurement and the weight of sample taken.
- (c) Reliability For 1-g samples the relative standard deviation is 1.2 and 6% for weight losses of 2.5 and 0.5%, respectively.
- (d) Interferences None are anticipated.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Analyst

4.0 PROCEDURE

4.1 DISCUSSION

The primary purpose of this method is to determine the weight change in plutonium dioxide when heated at 950°C. Normally a loss in weight occurs. A secondary purpose can be the adjustment of a plutonium oxide sample to a relatively stable composition prior to analysis, particularly with respect to its water content. Oxide prepared from calcining plutonium salts at low temperatures, particularly plutonium oxalate, will readily sorb significant

Author	Date	Project Mgr.	Date	QAD Representative	Date
MC Burt	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	6/16/88	All original signatures on file	
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quantities of water if exposed to a moist atmosphere.^(a) Ignition above 800°C makes the oxide relatively stable and its composition begins to approach stoichiometry above 900°C.^(b)

This analytical procedure is simple and it incorporates standard laboratory practices relating to gravimetric analyses. It can be used for determining weight loss of other materials, although conditions such as temperature may require adjustment.

4.2 APPARATUS

- (a) Analytical Balance. Readable to at least 0.1 mg.
- (b) Muffle Furnace. Capable of sustained operation at 950°C with the temperature controlled to $\pm 10^\circ\text{C}$.
- (c) Platinum Crucibles. 5-ml capacity.

4.3 REAGENTS

None required.

4.4 STANDARDS

None required.

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.
- (c) Precautions are required to avoid fires when operating a furnace in a glove box.

4.6 QUALITY CONTROL

4.6.1 Calibration

The analytical balance is maintained under a routine maintenance and calibration schedule. See the general quality assurance requirements (Volume 1, Section 4.0).

4.6.2 Control

Control is not established in the usual way. Instead, instructions for handling plutonium dioxide samples are

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included to provide for control and uniform handling of samples. Special precautions in handling samples to prevent changes in composition before analysis are necessary because plutonium dioxide can readily sorb or desorb water.

- (a) The requester should schedule the shipment of plutonium dioxide samples to the laboratory so that the analysis can be started immediately upon receipt of the samples in the laboratory.
- (b) The weight of a sample aliquot is obtained immediately after the sample container is opened. Only one sample container is opened at a time.

4.7 ANALYSIS

Samples are ignited (heated) in an air atmosphere. Constant weight, as used in this procedure, is defined as a maximum difference of 0.2 mg between weighings made after two successive ignitions.

- (a) Transfer 1 g of sample to a crucible that has been tared to constant weight at $950 \pm 25^{\circ}\text{C}$ and immediately proceed to Step (b).

This step is done in a dry atmosphere; however, do not open the sample container until a tared crucible is ready for use so that sample can be added to the crucible immediately upon opening the container. Excessive exposure of the sample to the dry atmosphere may cause a loss of water if moisture is present in the sample.

Larger amounts of sample may be used should be ignited material be required for other analyses.

- (b) Weigh the crucible and sample to the nearest 0.1 mg without delay.
- (c) Place the crucible in a cold or warm (about 110°C) furnace.

Loss by spattering may occur when a moisture-laden sample is placed into a hot furnace.

A dry atmosphere is not required for Steps (c), (d), and (g).

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- (d) Heat the sample at 110°C for 30 min and then raise the temperature to $950 \pm 25^\circ\text{C}$; hold the sample at this temperature for 1 hr.
- (e) Remove the crucible from the furnace and let it cool to room temperature.

Cooling must be done in a dry atmosphere to prevent the resorption of water as the sample cools.

- (f) Weigh the crucible and sample to the nearest 0.1 mg.
- (g) Replace the crucible in the furnace at 950°C for 20 min; repeat Steps (e) and (f).

Constant weight should be obtained. If not, repeat this step until constant weight is obtained.

4.8 CALCULATION

Calculate the percent weight loss as follows:

$$\text{Weight Loss} = \frac{S - B}{S - C} \times 100$$

where Weight Loss = wt percent

S = weight in g of preignited sample plus tared crucible

B = weight in g of ignited sample plus crucible

C = weight in g of tared crucible.

Unless otherwise instructed, report results to the nearest 0.1 wt percent. Note: If a weight gain occurs, report the result as a weight gain.

5.0 BIBLIOGRAPHY

- (a) J. T. Byrne, C. E. Caldwell, R. L. Delnay, J. D. Moseley, and F. L. Oetting. Measurements Involved in Shipping Plutonium Oxide, RKFP-502, August (1965).
- (b) J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps, and C. F. Metz. Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Material, LA-4622, p. 145, March (1971).

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INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-225.1 R0
PAGE 1 OF 1

<p>A. Document Number: <u>PNL-ALO-225</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Measurement of pH in Aqueous Solutions</u></p> <p>Document's Original Author: <u>MC Burt</u></p>	<p>Effective Date of ICN: <u>1/20/93</u></p> <hr/> <p>Change Requested by: <u>MC Burt</u></p>
<p>B. Action:</p> <p style="margin-left: 40px;">Replace pages 1 through 3 with the attached 1 through 3.</p>	
<p>C. Effect of Change:</p> <p style="margin-left: 40px;">Brings procedure into compliance.</p> <p style="margin-left: 40px;">Increases the number of buffers available for use and the number required for calibration. Will better define slope of calibration curve.</p>	
<p>D. Reason for Change/Description of Change:</p> <p style="margin-left: 40px;"><u>Reason:</u></p> <p style="margin-left: 40px;">Act NOW Directive 89.1 no longer in existence.</p> <p style="margin-left: 40px;">Improve accuracy of pH measurement by better definition of slope of calibration curve.</p> <p style="margin-left: 40px;"><u>Description:</u></p> <p style="margin-left: 40px;">Delete ACT NOW Directive 89.1 from the Records Section (2.0).</p> <p style="margin-left: 40px;">Increase number of buffers available for use in Section 1.3.</p> <p style="margin-left: 40px;">Increases minimum number of buffers required for calibration in Section 1.5.1.</p> <p style="margin-left: 40px;">See strikeout and redline changes in text.</p>	
<p>E. Approval Signatures: (Please Sign and Date)</p> <p>QP Concurrence: <u>TL Ehlert</u> <i>TL Ehlert</i></p> <p>Approval Authority: <u>AG King</u> <i>AG King</i></p> <p>Other Approvals: <u>SG McKinley</u> <i>SG McKinley</i></p> <p style="margin-left: 100px;">: <u>MW Urie</u> <i>MW Urie</i></p>	<p>Type of Change (Check (✓) one) (✓) Minor Change () Major Change</p> <p>Date: <u>1-20-93</u></p> <p>Date: <u>1-20-93</u></p> <p>Date: <u>1-28-93</u></p> <p>Date: <u>1-28-93</u></p>

PNL TECHNICAL PROCEDURE

PNL-ALO-225 MEASUREMENT OF pH IN AQUEOUS SOLUTIONS

APPLICABILITY

This method is applicable to aqueous samples, leachates and supernates which do not contain suspensions or colloids and which do not have high ionic strength.

- Material-Aqueous samples, leachates and supernates.
- Range-From 0 to 14.
- Reliability-With proper standardization, ± 0.1 pH unit.
- Interferences-Temperature effects pH measurement, therefore, calibration and measurement shall be done at the same temperature. Some electrodes exhibit a sodium error at pH greater than 10. (Special low sodium error electrodes are available.)

DEFINITIONS

N/A

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

PROCEDURE

1.1 Discussion

pH is measured by determining the activity of hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. Because of the difficulty of using the hydrogen electrode, a glass electrode is commonly used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. There are many types of electrodes available including specialized electrodes for specific applications. The most commonly used are combination electrodes; that is, both the reference and indicating electrodes are in a single probe. Also several types of liquid junctions are available for the reference electrode with

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MW Urie		AG King		ALL ORIGINAL SIGNATURES ON FILE.	
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the quartz type being very common. Special electrodes are also available for pH values over 10 and below 1.

1.2 Apparatus

- pH meter (electrometer)
- Indicating (glass) and reference electrode, or combination pH electrode
- Suitable beakers, 20-50 mL
- Teflon coated stir bars
- Magnetic stirrer

1.3 Reagents

pH buffer solutions, 4,7,10. Commercially available certified buffers. Additional buffers are available for use when required.

1.4 Standards

pH buffer solutions (see reagents).

1.5 Quality Control

1.5.1 Standardization. Because of the different capabilities of different pH meters in use only minimum requirements can be specified. Manufacturers instructions shall be followed for calibration of the meters using standard buffers. A minimum of ~~two one~~ buffer shall be used and calibration checked with a different buffer. Where possible two buffers shall be used and calibration checked with a third.

1.5.2 Control. Control is established by measuring within ± 0.1 pH units a buffer not used for calibration before beginning analysis, after every 10th sample and at the end of the analysis run.

1.6 Analysis

1.6.1 Instrument set up.

1.6.1.1 Follow manufacturers operating instructions for set up and calibration of pH meter using buffer solutions as specified.

NOTE: To avoid contamination of buffer solutions do not return used solutions to the container.

1.6.1.2 Immerse electrode(s) in buffer solution not used for calibration and, with stirring, allow reading to

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equilibrate. It shall read within ± 0.1 pH units of its stated value. If not, recalibrate.

1.6.2 Sample analysis.

1.6.2.1 Sample shall be at the same temperature as the buffer solutions (normally ambient temperature). Put sufficient sample to immerse the electrode tip and reference junction into a clean beaker, add stirring bar and stir continuously.

1.6.2.2 Allow sufficient time for reading to stabilize. Stirring shall not be so vigorous that air is entrained into the sample. Record reading.

1.6.2.3 Remove electrode from sample, rinse electrode with water. Repeat measurement.

Glass electrodes are fragile and care must be taken to not scratch or break the electrodes. Electrodes shall be replaced when manufacturer specified maintenance procedures do not return it to satisfactory operation.

Electrodes shall be stored according to manufacturers instructions when not in use.

1.7 Calculations

None.

2.0 RECORDS

Records shall be maintained and controlled so as to conform to requirements of the ACL QA Plan, MCS-033. ~~Manual PNL MA-70, Procedure PAP-70-1701, "Records System."~~ Laboratory Record Books (LRBs), or worksheets, which are approved by the Technical Group Leader, provide a mechanism for control of data and records. ~~LRBs shall be used in accordance with the ACT NOW Directive 89-1.~~

3.0 REFERENCES

Instruction manual for meter used.

Standard Methods for the Examination of Water and Wastewater, 1985, 16th Edition.

American Public Health Association, Washington, D.C. 20005. Bates, R.G. 1973, Determination of pH, Theory and Practice, 2nd Ed. John Wiley & Sons, New York, New York.

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-226.2 R0

Page 1 of 1

A.

Document Number: PNL-ALO-226 Revision Number: 0

Document Title: Ammonia (Nitrogen) in Aqueous Samples

Document's Original Author: MC Burt

Effective Date
of ICN: 8 / 25 / 1992

Change Requested by:
MC Burt

B. Action:

Replace pages 1 through 6.

C. Effect of Change:

Will require use of different source compounds for calibration and control standards.

D. Reason for Change/Description of Change:

Separate source for calibration and control standards, see redline in section 5.2.

Primary calibration solution is stable for 3 months and need only be diluted rather than redissolved within the 3 month period, see redline in section 7.0.

Additional reference, see section 10.0.

To clarify and correct typos change 10 to 10ml in section 4.5, 100 to 250mL in section 5.4, 6.3 to 5.3 and delete as per 8.3 in section 7.3

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☐ Minor ☒ Major

Process

Quality Department: TL Ehler *TL Ehler*

Date: 8/25/92

Approval Authority: AG King *AG King*

Date: 8/25/92

Other Approvals: PK Melethil *PK Melethil*

Date: 8/25/92

: _____ Date: 1 / 1

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-226.1 R0
Page 1 of 1

A.

Document Number: PNL-ALO-226 Revision Number: 0

Document Title: Ammonia (Nitrogen) in Aqueous
Samples

Document's Original Author: MC Burt

Effective Date
of ICN: 5/11/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 6 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert TL Ehlert

Date: 5/7/92

Approval Authority: AG King AG King

Date: 5/12/92

Other Approvals: PK Melethil PK Melethil

Date: 5/11/92

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-226, AMMONIA (NITROGEN) IN AQUEOUS SAMPLES

APPLICABILITY

This procedure is applicable to the determination of nitrogen as ammonia in aqueous samples: leachates, ground waters, surface waters and waste samples.

DEFINITIONS

None.

RESPONSIBLE STAFF

Cognizant Scientist
Technician

PROCEDURES

1.0 Summary of Method

1.1 Following pH adjustment to above 11, a hydrophobic gas permeable membrane electrode measures the dissolved ammonia in a known volume of sample. The electrode response is calibrated over a range of several decades with standard solutions.

1.2 The method is applicable over the range of 0.03 to 1400 mg NH₃-N/L.

2.0 Interferences

2.1 Amine compounds are a direct interference. Mercury and silver can interfere by complexing with ammonia. If interferences are determined to be present in sufficient quantity to require a separation, a distillation procedure is documented on pp. 377-378 of Ref. (1).

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Melethil		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

- 3.1 Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within +10% of the stated value.
- 3.2 When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

4.0 Apparatus and Materials

- 4.1 Electrometer, a pH meter with expanded millivolt scale reading between -700 and +700 mV or a specific ion meter.
- 4.2 Ammonia selective electrode. Orion Model 95-12 or equivalent.
- 4.3 Volumetric flasks, 100 mL and 250 mL.
- 4.4 Magnetic stirrer and stir bars.
- 4.5 Pipets, 10, with disposable tips, 100, 250, 1000 μ L and 10mL.
- 4.6 Balance, analytical, capable of weighing to 0.0001 g.
- 4.7 Beaker, 20 mL.

5.0 Reagents

- 5.1 Deionized water to be used for sample, standard and reagent dilutions. ASTM Type II (ASTM D193) or equivalent.

- 5.2 ~~Primary Standard, NH_4Cl , Reagent grade. Dry at 100°C for two hours. Dissolve 0.9548 g in water, add 0.5 ml conc. HCl , and dilute to 250 mL. 1 mL = 1 mg N = 1.22 mg NH_3 . This solution shall be made fresh daily.~~

~~Primary Standard, $(\text{NH}_4)_2\text{SO}_4$, Reagent grade or better. Dry at 100°C for one hour. Dissolve 1.1795 g in water and dilute to 250 mL. 1 mL = 1 mg N = 1.22 mg NH_3 . This solution is stable for three months.~~

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5.3 Control Standard, NH_4Cl , Reagent grade. Dry at 100°C for two hours. Dissolve 0.1-0.2 g in water, add 0.5 ml conc. HCl , and dilute to 250 mL. Calculate concentration according to 8.1. This solution shall be made fresh daily.

5.4 NaOH , 6 N. Dissolve 60 g NaOH in 100 mL water, cool and dilute to 100 250 mL.

6.0 Quality Control

All quality control data shall be maintained and available for easy reference or inspection.

6.1 The analytical system shall be calibrated on a daily basis using freshly prepared standards.

6.2 A freshly prepared control standard shall be analyzed with each group of samples (20 samples or less).

6.3 A reagent blank shall be analyzed with each group of samples (20 or less) to insure that contamination is not occurring.

6.4 After each sample is analyzed a known spike shall be added as a further test for possible interferences and to check proper electrode operation.

6.5 Additional quality control (i.e., duplicates, duplicate matrix spikes, etc.) shall be governed by the analytical requirements of the project or as provided by the Analytical Request Form (ARF), the project Statement of Work (SOW), or the sample Test Instruction (TI).

7.0 Analysis Method

Because of the volatility of ammonia only freshly prepared ~~acidified~~ ~~diluted~~ standard solutions shall be used.

Prepare a series of standard solutions with concentrations of 1000, 100, 10, 1, and 0.1 mg $\text{NH}_3\text{-N/L}$ by making successive 10 mL to 100 mL dilutions of the stock primary calibration standard solution.

Follow directions on page 4 of the ammonia electrode instruction manual, Ref. (2), to set up the electrode for use.

7.1 Test the electrode for proper function as follows:

7.1.1 Put 10 mL water and a stir bar in a 20 mL beaker. Place on magnetic stirrer and immerse electrode tip. Do not stir so

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rapidly that air bubbles are trapped under the electrode tip. Add 250 μ L of 6N NaOH.

- 7.1.2 Add 100 μ L of 1000 mg/L standard solution. When a stable reading is displayed, record the electrode potential in millivolts.
- 7.1.3 Add 1000 μ L of 1000 mg/L standard solution. When a stable reading is displayed, record the electrode potential in millivolts.
- 7.1.4 The difference between the first and the second potential readings should be in the range of -54 to -60 millivolts. If it is not, refer to the troubleshooting section of the electrode manual.
- 7.1.5 Remove electrode from the solution. Rinse tip with water.

7.2 Standard Solution Measurement

- 7.2.1 Starting with the lowest concentration, pipet 10 mL of standard solution into the beaker and stir. Immerse the electrode tip and pipet 250 μ L of 6 N NaOH into the solution. Wait for a stable reading and record. Low standards (and samples) may take as long as 5-10 minutes to stabilize, with higher concentrations equilibrating more rapidly.
- 7.2.2 Rinse the electrode with water and repeat step 7.2.1 for all the standard solutions.
- 7.2.3 Plot the standard curve using semilogarithmic paper. Plot ammonia concentration in mg $\text{NH}_3\text{-N/L}$ on the log axis and potential in millivolts on the linear axis. A regression curve may also be generated with the logarithm of the concentration used for the X-Axis Data and the mV reading for the Y-Axis Data.

7.3 Control Standard

Make a 10 mL to 100 mL dilution of the control standard prepared in step ~~6-3~~ 5.3 and analyze it per step 7.4.. Determine the results as per 8.2 and the recovery is calculated. ~~as per 8.3~~ Recovery on the control standard shall be within $\pm 10\%$ of its make up value or the analyses shall be repeated. If still out, make a new control standard. If results are still unacceptable, see the Cognizant Scientist for resolution.

7.4 Sample Analysis and Spike Addition

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- 7.4.1 Pipet 10 mL of sample into the beaker, stir and immerse electrode tip.
- 7.4.2 Pipet 250 μ L of 6 N NaOH into the sample; confirm pH $\geq$ 11 using pH paper.
- 7.4.3 After stabilization record the millivolt reading.
- 7.4.4 Add 100 μ L of 100 mg/L standard solution as a spike for solutions reading up to 10 mg/L. For samples greater than 10 mg/L use 100 μ L of 1000 mg/L standard solution. Record millivolt reading after stabilization.
- 7.4.5 Rinse electrode tip with water.
- 7.4.6 Calculate samples according to 8.2 or 8.4 and spike recoveries according to 8.3. Spike recovery shall be 80-120%. If recovery is outside range repeat analyses. If still out see Cognizant Scientist to resolve problem.

NOTE: If the electrode is not to be used for over one week it should be disassembled and rinsed inside and out with distilled water, dried and reassembled. For overnight or weekly storage it should be immersed in 1000 mg/L standard solution (no NaOH added).

8.0 Calculations

8.1 Control Standard

$$C = \frac{W (1000) (1000)}{3.819 V}$$

Where: C = concentration in mg NH_3 -N/L
W = weight NH_4Cl used, in grams
V = make up volume, in mL

8.2 Sample Concentration

Results are read directly from the calibration curve for liquid samples, or by the use of the regression equation.

$$C = A*B$$

Where: A = dilution factor, if used
B = concentration from calibration curve
C = concentration in mg NH_3 -N/L

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8.3 Spike recoveries are calculated as follows

$$R = \frac{(T+V)*C - B*T}{A} * 100$$

Where:

- R = per cent recovery
- C = concentration from curve for sample plus spike in mg NH₃-N/L
- A = concentration of spike in mg NH₃-N/L times the volume of added spike in L
- B = concentration from curve for sample in mg NH₃-N/L
- V = volume of added spike, in L
- T = volume of sample, in L

8.4 Calculations for solid samples

$$D = \frac{C*L}{W}$$

Where:

- D = mg NH₃-N/kg of solid sample
- C = concentration of liquid sample, from curve, in mg NH₃-N/L
- L = volume of leach solution, in L
- W = weight of solid sample, in kg

9.0 Records

Records shall be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books shall be used in accordance with the ACT NOW Directive 89.1 established records management practices.

10.0 References

1. Standard Methods for the Examination of Water and Wastewater. 16TH Edition pp. 384-386. American Public Health Association, Washington, D.C. 20005.
2. Orion Research Incorporated Instruction Manual, Model 95-12 Ammonia Electrode
3. ASTM Annual Standard, Water and Environmental Technology, 1992 Volume 11.01, D 1426 Test Method B, p.331, American Society for Testing and Materials, 1916 Race St., Philadelphia, PA. 19103.

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-227.1 R0
Page 1 of 1

A.

Document Number: PNL-ALO-227 Revision Number: 0

Document Title: Determination of CR(VI) in Aqueous Samples

Document's Original Author: MC Burt

Effective Date
of ICN: 5/7/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.
Replace pages 1 through 7 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
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Type of Change: (Check one):

X Minor Major

Process

Quality Department: TL Ehlert

Date: 5/7/92

Approval Authority: AG King

Date: 5/7/92

Other Approvals: JM Robbins

Date: 5/7/92

:

Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-227, DETERMINATION OF CR(VI) IN AQUEOUS SAMPLES

APPLICABILITY

This procedure measures Cr(VI) colorimetrically in any aqueous sample; ie., leachates, ground waters, etc.

DEFINITIONS/ACRONYMS

Sample batch is defined as 20 or fewer samples with the same basic matrix, ie., soils, water, sludge, etc.

RESPONSIBLE STAFF

Group Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Summary of Method

1.1 The procedure measures only hexavalent chromium which forms a reddish-violet complex with diphenylcarbazide in acid solution. Concentration is determined by measuring absorbance of solutions at 540 nm spectrophotometrically and comparing to a series of known standards.

1.2 The detection limit is 2ug Cr (VI).

2.0 Interferences

2.1 The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury react with the reagent but at much lower intensities. Concentrations as high as 200 mg/L can be tolerated. Iron interferes above 5 mg/L and may be corrected for by using the standard addition method. See Cognizant Scientist.

Author	Date	Project Mgr.	Date	QAD Representative	Date
MC Burt		TE Jones		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
Robbins		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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2.2 Vanadium also interferes but concentrations up to ten times that of chromium will not cause problems.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

3.1 Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.

3.2 When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

4.0 Quality Control

All quality control data shall be maintained and available for easy reference or inspection.

Two quality control options (4.1 and 4.2) are defined below. Option 4.1 shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option 4.2 shall then be followed. The analyst will recognize the need to use option 4.2 when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a Statement of Work (SOW), and these will be conveyed to the analyst through a TI.

4.1 Employ a minimum of one method blank per sample batch to determine if contamination is occurring. Duplicate analyses shall be done upon client request. A known spike aliquot shall be added to one sample in each sample batch to insure that the procedure is working properly and to check for interferences.

4.2 For all SOWs written by WHC for CERCLA protocol requests for analysis, employ a minimum of one method blank per sample batch to determine if contamination is occurring. Analyze at least one duplicate sample per sample batch. A duplicate sample is a second sample taken through the entire sample-preparation and analytical process. At least one matrix spike and control standard sample shall be employed for every sample batch to insure that the procedure is working properly.

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PNL TECHNICAL PROCEDURE

5.0 Apparatus and Materials

- 5.1 150 ml beakers.
- 5.2 100 ml volumetric flasks.
- 5.3 pH meter.
- 5.4 500 ml volumetric flasks.
- 5.5 Spectrophotometer, capable of measuring absorbance at 540 nm and scanning from 400 to 700nm. The HP 8451A Diode Array Spectrophotometer is used.
- 5.6 1 cm spectrophotometric cuvettes.
- 5.7 Teflon covered stir bars.
- 5.8 Calibrated pipets, 2, 5, and 10 ml. Other sizes as may be required.

6.0 Reagents

- 6.1 ASTM Type II water (ASTM D1193) To be used for sample, standard, and reagent dilutions.
- 6.2 H₂SO₄, 6 N Dilute 17 ml concentrated H₂SO₄ to 100 ml
- 6.3 Buffer solutions, pH 4 and 7
- 6.4 Primary standard, K₂Cr₂O₇, NIST 136c. Dissolve 70.73 mg in H₂O and dilute to 500 ml. This gives a 50 µg/ml solution which is stable for one year. A dilution is made daily for standardization by pipeting 10 ml of 50 µg/ml solution into a 100 ml volumetric flask. Bring to volume with water and mix well.
- 6.5 Secondary standard (used as control), Reagent grade K₂Cr₂O₇, EM or Bakers Analyzed Reagent. Make up same as (6.4).
- 6.6 1,5-Diphenylcarbazide Dissolve 250 mg in 50 ml acetone. Store in brown bottle. Discard when the solution becomes darkened.
- 6.7 Acetone, reagent grade.

7.0 Standard Curve Preparation

- 7.1 Calibrate pH meter with buffer solutions according to the manufacturers instructions.

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PNL TECHNICAL PROCEDURE

- 7.2 Pipet 0, 2, 10, and 20 ml of diluted standard into 150 ml beakers containing a stir bar. This gives 0, 10, 50, and 100 μg Cr(VI).
 - 7.3 Add water to each beaker to bring volume to approximately 50 ml.
 - 7.4 Adjust pH of solution to 1.0 ± 0.3 by adding 6 N H_2SO_4 dropwise to stirred solution.
 - 7.5 Transfer solutions to 100 ml volumetric flasks, add 2 ml diphenylcarbazide, bring to volume and mix well. Let stand 5-10 minutes for color development.
 - 7.6 Measure absorbance according to steps 9.1 and 9.3 for each standard solution.
 - 7.7 Scan the highest standard according to step 9.4 and include the scan as part of the analysis record.
 - 7.8 Subtract blank (0) absorbance and plot μg Cr (abscissa) vs. net absorbance (ordinate) on linear graph paper. Draw a straight line best fit of the data. No data point shall deviate from the line by more than 10% of its value or it shall be repeated.
 - 7.9 Calculate the slope according to step 10.2.
- 8.0 Sample Analysis
- Concentration of Cr (VI) varies between samples and sample types and sample volumes are sometimes limited. Therefore no definitive guide to sample size can be given. Some samples also contain components which cause premature color fading, turbidity and partial wavelength interference. Compromises sometimes therefore have to be made with sample size.
- 8.1 A control standard is carried through steps 8.2 to 8.4 for each group of samples as required by 4.2. For the control standard, add 5 or 10 ml of the solution prepared in 6.5. Recovery should be within $\pm 10\%$ of the expected value. If not, repeat analysis; if still out contact cognizant Scientist to correct problem. The calibration blank serves as the reagent blank. Additional blanks may be submitted with samples.
 - 8.2 Add approximately 40 ml water to a 150 ml beaker containing a stir bar. Immerse the pH electrode and adjust the pH to 1.0 ± 0.3 with 6 N H_2SO_4 . Add 2 ml diphenylcarbazide solution, then using calibrated pipets, add sample in 2 to 10 ml portions, maintaining the pH at 1.0, until color appears in the proper intensity (ABS = .2 - .9). Record volume sample used.

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If after addition of approximately 40 ml sample no color develops and sufficient sample is available, use 50 ml of sample instead of water and proceed as before.

In general only blanks or samples very low in Cr(VI) would require sample sizes in excess of 50 ml.

- 8.3 Transfer solution quantitatively to a 100 ml volumetric flask, bring to volume and mix well.
- 8.4 Wait 5-10 minutes and measure absorbance according to steps 9.1 to 9.3. For each sample complete step 9.4 and include copy of scan as part of the analysis record.

Some samples may fade or change color in less than 5 minutes. Analysis shall then be repeated and the absorbance measured immediately.

If sample scan shows a baseline deflection, draw a line from the baseline at approximately 440 nm to the baseline at approximately 630 nm. Net absorbance is then measured from the peak top to the intersect of the new baseline at 540 nm.

- 8.5 Select one sample from each batch, treat as described above and add 5 or 10 ml of the control standard from step 6.5 as a spike.

Calculate spike recovery as per step 10.6. Spike recovery shall be 80-120%.

9.0 Absorbance Measurement

The 8451A is controlled by a touchpad keyboard on the front of the instrument. Upon turn-on the instrument performs a series of self tests to insure proper operation. Refer to the operators manual if any of these tests fail. The instrument shall warm up for about one hour before making measurements.

- 9.1 To set the required wavelength press labeled keys LAMBDA,5,4,0, EXECUTE.

This sets the spectrometer to measure at 540 nm.

- 9.2 Place a cuvette containing distilled water as reference solution into the spectrophotometer. Press labeled keys REFERENCE,1,0,EXECUTE. The reference needs to be run only once.
- The '1,0' instructs the instrument to integrate the absorbance reading for 10 seconds. This instruction must be given for each measurement.

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10.5 To calculate control standard

$$\%Rec = \frac{C * 100}{B}$$

Where %Rec = per cent recovery of control standard
C = ug Cr from curve
B = ug Cr taken (concentration * ml taken)

10.6 To calculate spike recovery

$$\%Rec = \frac{(C - R) * 100}{A}$$

Where %Rec = per cent recovery of added spike
C = ug Cr in sample plus added spike (from curve)
R = ug Cr found in sample without spike (step 10.3)
A = ug Cr added as spike (concentration * ml taken)

10.7 To calculate micrograms Cr/g for leaches of solid materials

$$T = \frac{CB}{VW}$$

Where T = micrograms Cr/g
C = micrograms Cr from curve
V = volume sample, in ml
W = weight solid sample, in grams (Indicate whether solid sample is wet or dry weight).
B = volume (or weight) water used in leach (1g=1ml)

note: ug Cr/g = mg Cr/kg

11.0 Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~ACT NOW Directive 89.1~~ established records management practices.

12.0 References

Standard Methods for the Examination of Water and Wastewater. 16th Edition pp.201-204. American Public Health Association, Washington D.C. 20005

HP 8451A Diode Array Spectrophotometer Operator's Manual, Hewlett Packard Corp.

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Chromium, Hexavalent

Cr ⁶⁺

Version 1.0

Applicability/Scope: Part of weekly analysis of industrial wastewater in compliance with the Industrial wastewater discharge permit No. 4, issued to Hewlett-Packard, Corvallis by the City of Corvallis.

Method originator / date:

James M. Robbins

September 1, 1990

Preparation of standard solutions:

Stock solutions:

Dilute 25 mL of a 1000 µg/mL Cr atomic absorption standard (as K₂Cr₂O₇) to 500 mL in a volumetric flask to yield a 50 µg/mL Cr ⁶⁺ standard solution. Transfer to a 500 mL narrow mouth LDPE bottle (Nalgene). Alternatively dissolve 141.4 mg of K₂Cr₂O₇ in distilled water and dilute to 1000 mL to make a 50 µg/mL Cr ⁶⁺ standard solution.

Dilute 50 mL of Cr ⁶⁺ standard solution to 500 mL in a volumetric flask to yield a 5 µg/mL Cr ⁶⁺ standard solution. Standard solutions are very stable and can be used as standards for over six months. Store with lid tightly sealed to prevent evaporation of solution. Evaporation rate through polyethylene is approximately 1% a year ().

Working Standards:

Prepare working standard solutions daily using the 5 µg/mL Cr ⁶⁺ standard solution. Transfer 8, 4, 2, and 1 mL of this standard to separate 100 mL volumetric flasks. Add 50 mL of 0.3 N H₂SO₄ and dilute to volume with distilled water. Procedure yields working standards containing 0.40, 0.20, 0.10 and 0.05 µg/mL Cr ⁶⁺, respectively. Prepare blank containing 50 mL of 0.3 N H₂SO₄ and dilute to 100 mL volume with distilled water.

Reagent preparation:

Sulfuric acid (H₂SO₄), 0.30 N: Transfer 8.3 mL of concentrated H₂SO₄ to a clean one liter clean HDPE wide mouth bottle containing 1000 mL of distilled water. Mix well to yield a 0.3 N H₂SO₄ solution with an acidity of approximately pH 0.52.

Diphenylcarbazide solution: Dissolve 0.5 mg of 1,5-diphenylcarbazide(1,5-diphenylcarbohydrazide) in 100 mL of acetone. Store in a 125 mL narrow mouth brown plastic bottle. Discard when solution becomes discolored.

Buffer, pH 2.0: Dissolve contents of five pHydrion buffer capsules in 500 mL of distilled water in a volumetric flask. Transfer to a labelled 500 mL wide mouth HDPE bottle.

Apparatus and glassware:

HP 8450A UV/VIS spectrometer
Adsorption cells, 1-cm (matched pair)
pH meter and electrode
Funnel
Glass beaker
Volumetric flask 100 mL
filter paper, Whatman #44, 15 cm diameter.

Interferences:

Presence of Fe and Cu at concentrations greater than one ppm can cause color development with 1,5-diphenylcarbazide resulting in a positive interference in Cr^{6+} (Standard Methods, 1989). Large excesses of Hg, Y and hexavalent Mo can also cause minor interferences. Measure Fe and Cu concentration by atomic absorption to determine if such an interference can occur. For these rare cases the removal of interferents with Cupferron using a CHCl_3 liquid-liquid extraction described in Standard Methods (1989) is recommended.

Instrument calibration:

Measure balance for the two precleaned 1-cm absorption cells after filling them with distilled water. Measure absorbances of standards and calculate regression equation relating concentration and absorbance.

Analysis procedure:

Filter approximately 100 mL of wastewater through a Whatman #44 filter into a 125 mL beaker. Transfer 500 μL of solution to a 10 mL volumetric flask, dilute to volume and reserve for fluoride analysis. If filtrate is turbid it will be necessary to use a finer filter such as 0.2 nm Nucleopore or millipore type filter disks.

Transfer 50 mL of filtered wastewater into a labelled 100 mL volumetric flask. Dilute to volume with 50 mL of 0.3 N H_2SO_4 . Prepare working standards and a blank containing as described in standard preparation section. Pipet 2 mL of 1,5-diphenylcarbazide solution to each volumetric flask and allow lavender color to develop for 10 min. Transfer portion of the solution to a 1-cm adsorption cell and measure absorbance at 540 nm using a HP 8450A UV/VIS spectrometer. Use second 1-cm adsorption filled with distilled water as a reference. Color complex is stable for at least 2 hours. Calibrate pH meter with pH 2.0 buffer and check acidity of sample solution to ensure it is within pH of 1.0-1.3.

Calculations:

Determine concentration of Cr^{6+} in sample solutions from regression equation describing calibration curve of concentration vs absorbance for the Cr^{6+} standards. If all absorbance values for samples are below that of the lowest standard then sample concentrations can be determined by solving the equation:

$$Y = M(X) + B$$

where Y is equal to concentration of in solution, M is the slope (concentration/absorbance) and B is the concentration intercept of the blank absorbance. Since the sample was diluted 1:1 using H_2SO_4 , the Cr^{6+} concentration in the original wastewater sample is obtained by multiplying the Cr^{6+} concentration (mg/L) by two.

Safety considerations:

Hexavalent chromium is highly toxic and its solutions should be handled with care. Cell membranes are readily permeable to Cr^{6+} but not Cr^{3+} . Once adsorbed Cr^{6+} is reduced to Cr^{3+} and bound in a wide number of coordinate complexes with biomolecules. Manifestations of local Cr exposure include skin and mucous membrane irritation and chronic ulcerations. Systemic effects include bronchial asthma and renal and liver disfunction. Research on occupationally exposed workers indicates Cr is very slowly eliminated from human tissues over a period of several decades (Tsalev and Zaprianov, 1983). Concentrated Cr^{6+} solutions should be treated as a toxic waste and disposed of by HP health and safety department personnel.

PNL TECHNICAL PROCEDURE

PNL-ALO-228 DETERMINATION OF HYDROXYL (OH^-) AND ALKALINITY OF AQUEOUS SOLUTIONS, LEACHATES AND SUPERNATES

APPLICABILITY

This method is applicable to aqueous samples which may contain any or all of the titratable bases; carbonate, bicarbonate and hydroxyl.

- Material-Aqueous samples, leachates, supernates with a $\text{pH} > 7$.
- Range-From 0 to (by dilution) any required concentration.
- Reliability-Dependent on the complexity and make up of the sample. For samples containing only hydroxyl, accuracy and precision are $< \pm 5\%$ or better.
- Interferences-Borates, phosphates, silicates, other bases or any hydrolyzable ions which may be present.

DEFINITIONS

N/A

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

PROCEDURE

1.0 DISCUSSION

Aqueous samples are titrated potentiometrically versus a standardized strong acid. The titration curve is plotted automatically by the titrator and inflection points are marked. Samples containing only hydroxide will have a typical strong base, strong acid 'S' shaped curve with an inflection point near neutral pH (7). Depending on components present, samples containing carbonate, bicarbonate and hydroxyl or interferences will have two or more inflection points and the shape of the curve will vary depending on concentration of the various components. All equivalence points within the specified ranges will be assumed to be due to carbonate, bicarbonate and hydroxyl. With complex samples containing interferences this may be an

Author MC Burt <i>McBurt</i>	Date 3/5/92	Project Mgr. TE Jones <i>TE Jones</i>	Date 3/5/92	QAD Representative GK Gerke <i>TK Ewert</i>	Date 3/5/92
Technical Reviewer Urie <i>Urie</i>	Date 3/5/92	Line Mgr. AG King <i>A. King</i>	Date 3/7/92	Other	Date
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PNL TECHNICAL PROCEDURE

complex samples containing interferences this may be an erroneous assumption. Hydroxyl and bicarbonate do not coexist in the same solution.

1.1 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

- Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 APPARATUS

- Recording automatic potentiometric titrator, Brinkmann 636 or equivalent.
- Digital buret compatible with titrator, 5 or 10 mL capacity.
- Beakers, 30 or 50 mL.
- Electrode, combination pH.
- Stir bars, teflon coated.
- Pipets, as required. Performance checked unless glass pipets are used.
- Magnetic stirrer.
- Volumetric flasks, 1000, 500, 100 mL.

3.0 REAGENTS

- 3.1 pH buffer solutions, 4, 7, 10. Use commercially available certified buffers.
- 3.2 0.1 N HCl. Dilute 8.3 mL of concentrated reagent to 1 liter. Standardize versus 0.1 N NaOH.
- 3.3 0.1 N NaOH. Weigh 4.0 g NaOH, dissolve in deionized water and make to volume in 1000 mL volumetric flask. Standardize versus primary standard grade potassium acid phthalate.

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- 3.4 0.1 N $\text{KHC}_8\text{H}_4\text{O}_4$. Baker Analyzed Reagent, Primary Standard grade or equivalent or NIST material. Dry reagent at 120°C for two hours. Cool and weigh 20.4 g and transfer to a 1000 mL volumetric flask. Dissolve in deionized water and make to volume. Calculate concentration according to Section 7.1.1.
- 3.5 0.02 N HCl. Dilute 100 mL of standardized 0.1 N HCl to 500 mL.
- 3.6 Sodium carbonate, ACS reagent grade.
- 3.7 Sodium bicarbonate, ACS reagent grade.

4.0 STANDARDS

The solution of potassium acid phthalate is stable and if kept tightly stoppered may be kept for one year from preparation date. The HCl solutions are also stable if properly stored but shall be performance checked. The NaOH solution is stable if properly stored but shall be discarded when carbonate precipitate begins to form.

- 4.1 An aliquot of the standardized NaOH is titrated versus the HCl used to verify its concentration each day titrations are performed.
- 4.2 A freshly prepared control standard of sodium carbonate and sodium bicarbonate is titrated each day titrations are performed. This control is not required if the sample contains only hydroxyl, which is ascertained from the shape of the titration curve. Dissolve 0.53 g of dried sodium carbonate and 0.84 g of dried sodium bicarbonate in deionized water and make to 100 mL. This gives a solution 0.1 N in carbonate and 0.1 N in bicarbonate. Concentrations are calculated according to Section 7.1.4 and 7.1.5.

5.0 QUALITY CONTROL

- 5.1 Standardization. At least three aliquots of potassium acid phthalate are titrated versus 0.1 N NaOH according to Section 6.2 and calculated according to Section 7.1.2. The agreement between replicates shall be within 0.005 N, if not, repeat analysis. The average value is used as the titer value. Three aliquots of the 0.1 N HCl are titrated versus the NaOH according to Section 6.2 and the results calculated according to Section 7.1.3. Agreement between replicates shall be within 0.005 N. If the calculated values are not within the specified values repeat the replicate titrations. If the values are still not within the specified values see Cognizant Scientist before proceeding. The average value is used as the titer value. Depending on the samples to be titrated, either the 0.1 N HCl or the diluted 0.02 N HCl is used in the buret. See Cognizant Scientist.

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- 5.2 Control. An aliquot of the carbonate-bicarbonate solution is titrated if the sample(s) contain those components. Results shall be within 0.01 N of the make up value. Should the sample contain only hydroxyl as determined by the titration curve shape, the NaOH is the control.

6.0 ANALYSIS

6.1 Instrument Set Up

- 6.1.1 Follow manufacturers instruction manual for proper set up of the Brinkmann titrator. On turn on the display will indicate all '8's and then display 36 0.000. Enter date as ddmmyy, then press ENTER followed by 100 G0. This is the electrode calibration mode. The display then reads C 25.000. Press '25' (or current temperature if not 25°C) ENTER,G0. The display will then read PH.
- 6.1.2 Immerse the electrode in pH 10 buffer, start the magnetic stirrer, enter the pH of the solution and press ENTER.
- 6.1.3 When the display again reads PH, remove the buffer and replace with pH 4 buffer. Enter '4' and press ENTER.
- 6.1.4 When display again reads PH, press G0. The calibration data is then printed. The display will read G0. Press G0, then 101 G0.
- 6.1.5 Replace the buffer solution with pH 7 buffer and press MEASURE. If the reading is not within ± 0.1 repeat steps a-c. Measurement is stopped by pressing '5'.
- 6.1.6 Pressing 101 loaded a built-in program which will titrate pH versus volume with automatic inflection point marking, proper heading, volume titrant used to endpoint and pH at each end point printed out. The titrator is now ready for operation.

6.2 Sample Analysis

The volume of sample to be used in the titration is a function of the concentration of titratable components. Sample volume may range from a few microliters to 30 or more milliliters. The amount of sample used needs to be large enough to make the initial pH in the titration vessel greater than 9, but not so large as to exceed the volume of the titrant buret. With most samples this will require trial and error to determine optimal sample size. For most leachate and supernate samples the 0.02 N HCl is appropriate. For higher concentration samples the 0.1 N HCl is required. This selection is made by the Cognizant Scientist.

- 6.2.1 Put 20-25 mL of water into the titration vessel and immerse the electrode and titrant tip. Pipet 100 μ L of sample into the vessel.

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- 6.2.2 Press the MEASURE key. If the pH reading is not above 9 continue adding sample until it is above 9 (or 10). If after the addition of approximately 5-10 mL the pH is still not above 9 a much larger sample will probably be required. Press the '5' key to stop measurement.
- 6.2.3 Remove electrode and tip from solution and rinse. Pour out solution and rinse beaker. Pipet 20-30 mL of sample into the beaker and immerse electrode and tip. Press MEASURE. If the pH is still below 10 there is no hydroxyl present and the sample may be titrated. pH measurement is stopped by pressing '5'.
- 6.2.4 Titration is initiated by pressing GO. The titration is automatic and inflection points will be marked as the titration progresses. At the completion of the titration the pH of the inflection (end)point(s) and volume of titrant used will be printed.
- 6.2.5 Raise the electrode and rinse with water. Pour the sample out and rinse the beaker with water. Proceed to the next sample.
- 6.2.6 When analyses are completed the electrode shall be stored according to the manufacturers instructions. Titrants and standards shall be tightly stoppered to prevent evaporation and contamination.

7.0 CALCULATIONS

7.1 Standardization

7.1.1 Potassium acid phthalate

$$N = \frac{g \ 1000}{M \ V}$$

Where,

N = normality
g = weight used, in grams
M = gram molecular weight, 204.23
V = volume, mL

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7.1.2 NaOH

$$N_1 = \frac{N V}{V_1}$$

Where,

 N_1 = normality of NaOH N = normality of potassium acid phthalate V = volume of potassium acid phthalate used, mL V_1 = volume of NaOH used, mL

7.1.3 HCl

$$N_2 = \frac{N_1 V_1}{V_2}$$

Where,

 N_2 = normality of HCl N_1 = normality of NaOH V_2 = volume of HCl, mL V_1 = volume of NaOH, mL

7.1.4 Sodium Bicarbonate

$$N_b = \frac{g}{M} \frac{1000}{V}$$

Where,

 N_b = normality of NaHCO_3 g = weight used, in grams M = gram molecular weight, 84.00 V = volume, mL

7.1.5 Sodium Carbonate

$$N_c = \frac{(2) g}{M} \frac{1000}{V}$$

Where,

 N_c = normality of Na_2CO_3 g = weight used, in grams M = gram molecular weight, 105.99 V = volume, mL

PNL TECHNICAL PROCEDURE

7.2 Samples

$$N_s = \frac{N_1 V_1}{V_s}$$

Where,

N_s = normality of sample
 N_1 = normality of HCl
 V_1 = volume of HCl, mL
 V_s = volume of sample, mL

Samples with strong acid-strong base 'S' shaped titration curves may be calculated with this formula and the results reported as hydroxyl concentration. Samples with strong acid-weak base curves and/or multiple end points will be calculated using Section 7.2 and the following scheme. End points in the range of 8.0-8.6 are designated 'P' and end points in the range of 4.2-4.8 are designated 'T'. Normalities are calculated using the above formula for 'P' and 'T' values and the alkalinity is derived from the following relationship.

<u>Titration Result</u>	<u>Hydroxyl Normality</u>	<u>Carbonate Normality</u>	<u>Bicarbonate Normality</u>
P = 0	0	0	T
P < 1/2T	0	2P	T-2P
P = 1/2T	0	2P	0
P > 1/2T	2P-T	2(T-P)	0
P = T	T	0	0

8.0 RECORDS

Records shall be maintained and controlled so as to conform to requirements of Manual PNL-MA-70, Procedure PAP-70-1701 "Records System." Laboratory Record Books (LRBs), or worksheets approved by the Technical Group Leader provide a mechanism for control of data and records. LRBs shall be used in accordance with the ACT NOW Directive 89.1.

9.0 REFERENCES

Instruction Manual for Brinkmann 636 Titroprocessor, Brinkmann Instruments, Cantiague Road, Westbury, NY.

Standard Methods for the Examination of Water and Wastewater, 1985, 16th Edition, American Public Health Association, Washington, D.C. 20005.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-229, (Replaces 2-30.8), URANIUM BY AUTOMATED POTENTIOMETRIC TITRATION

1.0 APPLICABILITY

Uranium is reduced to U(IV) by excess Fe(II) in strong phosphoric acid and sulfamic acid. Excess Fe(II) is selectively oxidized by nitric acid in the presence of Mo(VI) catalyst. The U(IV) is titrated using standard potassium dichromate solution to a potentiometric end point. Vanadium (IV) solution is added before the titration to sharpen the end point.

- (a) Material Uranium bearing materials, solid and solution.
- (b) Range Twenty to 30 mg is the preferred amount of uranium for each titration, however, as little as 5 mg may be successfully titrated.
- (c) Reliability Relative standard deviations from 0.025 to 0.10% are obtained for a variety of sample materials.
- (d) Interferences The method is insensitive to large concentrations of diverse ions often present in uranium samples. Tc, Ru, Os and halides interfere and may be removed by fuming with H_2SO_4 . Mo interferes in the presence of nitrate, which is removed by fuming with sulfuric acid. As, Sb, and Sn interfere if present in reduced form; the interference is removed by preoxidizing the sample and/or the contaminated reagent. V, Mn, Pd, Ag, Ir, Pt, Hg, and Au interfere and may be removed by ion exchange or liquid-liquid extraction.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Analyst

Author	Date	Project Mgr.	Date	QAD Representative	Date
McBurt	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
OP Amacker Jr.	6/17/88	JJ McCown	6/16/88	All original signatures on file	
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4.0 PROCEDURE

4.1 DISCUSSION

The titrimetric determination of uranium following ferrous ion reduction was first described by Davis and Gray.^(a) Up to 300 mg of uranium was reduced to U(IV) by an excess of Fe(II) in strong phosphoric acid in the presence of sulfamic acid. The excess Fe(II) was selectively oxidized by nitric acid in the presence of Mo(VI) catalyst. The U(IV) was titrated to a colorimetric end point using barium diphenylamine sulphonate indicator and standard potassium dichromate titrant. The reaction was very sluggish near the end point.

The titration sensitivity and end point were improved by Cherry's use of an amperometric end point detection.^(b) The method was further improved by the discovery at the New Brunswick Laboratory (NBL) that V(IV) added prior to the final titration sufficiently sharpened the end point to allow a potentiometric titration.^(c) Additional studies at NBL have characterized interferences, applicability to uranium product materials and scrap, and methods of automation. Several automation efforts involving volumetric^{(c)(j)} and electrometric^(k) titrations have been reported.

This procedure has been modified to allow the titration of 20 to 30 mg of uranium. Modifications include aliquoting of sample by weight, reducing volume of solution titrated by a factor of 3, increasing the time for the reduction to 60 seconds and diluting with a vanadyl sulfate--sulfuric acid solution. These modifications reduce the volume of liquid waste produced, which is important when plutonium is associated with the uranium. In addition, this modified method allows easy coordination of sample dissolution with the plutonium amperometric method when mixed oxide samples are involved (see Method PNL-ALO-222).

The conditions required to reduce uranium quantitatively and to oxidize Fe(II) selectively are quite specific. Careful attention must be given to solution volumes, reagent concentrations, reaction times, and reaction temperatures. For example, a sample volume of less than 3 ml is necessary to maintain the required phosphate concentration for the initial uranium reduction. Solution volumes and reaction times can be controlled more precisely using computer controlled dispensing devices and sample preparation stations. The system currently in use at PNL consists of a modified Metrohm 624 turntable and a Hewlett-Packard 85A control computer coupled with control hardware. The modified turntable has two titration stations, one for titration and the other for the oxidation state adjustment chemistry. Included is an air driven magnetic stirrer used in the pretreatment steps so

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that nothing contacts the sample solution and thus needs rinsing prior to titration. Each sample is prepared at station one and rotated to station two for the potentiometric titration.

To maximize precision a Brinkmann E636 Titroprocessor is used to perform the titration. This instrument measures the rate of potential change per unit of titrant addition and slows down the addition rate near the end point. The titration curve is plotted and the exact end point is determined and marked by the instrument. Once the vanadyl sulfate solution is added, the titration must be completed within five minutes.

Special care is taken in storing the standard solutions. The dichromate titrant dispensed by the digital buret is protected from evaporation and dust by a wine fermentation lock attached to the reservoir of the buret. Air entering the reservoir (and leaving when the room temperature increases) passes through a dichromate solution of the same concentration as in the reservoir. The uranium NBS 960 calibration standard is stored in tightly capped and taped glass bottles.

Solid samples are dissolved by fusion with sodium bisulfate at 600°C, followed by dissolution of the salt cake in 1N sulfuric acid. The sulfate solution is then analyzed directly for uranium. Solutions containing high-level nitrates or halides must be fumed with sulfuric acid first to remove the interferences.

A small positive bias, which is reasonably constant, is associated with the analysis. This bias is apparently caused by cumulative oxidation state changes in the vanadyl sulfate solution. To prevent air oxidation of the V(IV) to V(V) in the vanadyl sulfate solution, the solution is made 1N in sulfuric acid.⁽¹⁾ The bias is determined by the analysis of the uranium metal standard.

4.2 APPARATUS

- (a) Bottle. Dropping, polyethylene, 60-ml, Nalge 2411, used as weighing buret.
- (b) Bottle. Dropping, polyethylene, 30-ml, Nalge 2411, used as weighing buret.
- (c) Bottle. Washing, Teflon, 500-ml.
- (d) Titrator. Metrohm (Brinkmann) E636 equipped with an E635 buret and a 5-ml buret readable to 0.001 ml.
- (e) Electrode. Platinum, Brinkmann EA-202.

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- (f) Electrode. Reference, saturated calomel, Brinkmann EA-404.
- (g) Hewlett-Packard 85 with IEEE-488 interface.
- (h) Hewlett-Packard 3488A Control/Switch unit.
- (i) Metrohm (Brinkmann) 624 turntable modified to have two titration stations with a magnetic stirrer built into one raise/lower head.
- (j) Reagent addition valves, all Teflon, electrically operated.
- (k) Modified 100 ml titration beakers. Top flared to fit snugly in plastic turntable beaker.

4.3 REAGENTS

- (a) Oxidizing Acid. 8M HNO_3 , 0.24M sulfamic acid, and 0.4% ammonium molybdate. Dissolve 3.2 g of ammonium molybdate in 200 ml of distilled water and dissolve 18.8 g of sulfamic acid in 200 ml of distilled water. Combine both solutions and add, with stirring, 400 ml of 15.7M HNO_3 . Replace with freshly prepared reagent after one week.
- (b) Potassium Dichromate Titrant. Prepare as follows:

Weigh about 6.8-7.0 g of NBS potassium dichromate into a calibrated 2-ℓ volumetric flask. Dilute to volume and mix thoroughly. Calculate the titer (mg U/ml of solution equivalent) using Part (a) of Section 4.8.
- (c) Reducing Acid. 11.8M phosphoric acid, 0.09M ferrous sulfate, 0.17M sulfuric acid. Dissolve 25.2 g of ferrous sulfate heptahydrate in 200 ml of distilled water. Add, with stirring, 9 ml of 18M H_2SO_4 . Dilute to 1-ℓ with pre-oxidized 14.8M H_3PO_4 . The H_3PO_4 is pre-oxidized by adding 10 drops of 4% potassium dichromate per 4-ℓ of H_3PO_4 . Replace with freshly prepared reagent after one week.
- (d) Sulfamic Acid. 1.7M. Dissolve 33.0 g of sulfamic acid in 200 ml of distilled water.
- (e) Sulfuric Acid. 1N and 18M (96%).
- (f) Vanadyl Sulfate. 0.008M in 1N sulfuric acid. Dissolve 5.6 g of purified vanadyl sulfate dihydrate in about 2 liters of distilled water. Add, with stirring, 98 ml of 18M H_2SO_4 . Cool and dilute to 3.5 liters with distilled water. Store in glass or Teflon bottle.

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Reagents are dispensed by gravity from vessels located on top of the glove box. Feed lines should be flushed with fresh reagents prior to sample analysis. The valves are controlled from the HP3488A. To actuate (open) a valve, press CLOSE (to close relay which opens the valve), press the three digit channel number, then press EXECUTE. To close the valve press OPEN (to open the relay), press the channel number, then press EXECUTE. Channel numbers are:

100 SULFAMIC ACID
101 REDUCING ACID
102 OXIDIZING ACID
103 STIRRER (AIR)
104 VANADYL SOLUTION
105 RINSE
106 STIRRER (ELEC)
107 BEAKERS UP
108 BEAKERS DOWN
109 ROTATE TURNTABLE

The dichromate delivery line requires flushing with two buret volumes (10 ml) to clear any air bubbles which may have formed. This should be done immediately before titrations begin if the system has not been used for more than eight hours.

4.4 STANDARDS

(a) Calibration Standard. The calibration standard is a solution having about 30 mg U/g of solution prepared from uranium metal. Prepare the standard as follows:

1. Cut off an appropriate size piece of NBS SRM 960 uranium metal. Immerse in warm 8M HNO_3 until the metal becomes shiny and all traces of oxide are removed. Rinse three times in distilled water, rinse with acetone, and dry in a vacuum dessicator.

The weight of metal (size of piece) taken and the weight of final solution (Step 2) should produce a uranium concentration of about 30 mg/g.

2. Weigh the piece to the nearest 0.1 mg and dissolve it in a minimum amount of 8M HNO_3 . Add an approximately equal volume of 1M H_2SO_4 and evaporate over low (approximately 100°C) heat to a moist residue. (This step may be repeated if a large volume of 8M HNO_3 was used for metal dissolution.) Dissolve the moist residue in a minimum volume of 1N H_2SO_4 .

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3. Transfer the solution quantitatively with 1N H_2SO_4 to a tared glass container of appropriate volume. Weigh the container and solution and calculate the uranium concentration using Part (b) of Section 4.8.
4. Transfer aliquots of the standard to 30-ml plastic dropping bottles for dispensing as required.

(b) Control Standard. A mixed oxide pellet is used as a control standard. The material has been used in the SLE program and has an established value for both plutonium and uranium. The value established for U is $67.81 \pm 0.16\%$ in 1982. The same material is used for Method PNL-ALO-222. Prepare the standard as follows:

1. Weigh three pellets to the nearest 0.1 mg into a quartz Erlenmeyer. Proceed as per Section 4.7.1 (a) through (e). Transfer to a tared bottle using 1N H_2SO_4 and dilute to give a concentration of approximately 28 mg sample/gram of solution.
2. Weigh solution to the nearest 0.1 mg and calculate concentration using part (b) of Section 4.8, Method PNL-ALO-222.
3. The solution is stored in 5 ml break seal ampules. One ampoule is sufficient for duplicate titrations.

4.5 SAFETY

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

4.6 QUALITY CONTROL

4.6.1 Calibration

Calibration is made by analyzing at least three, but preferably four, aliquots of the calibration standard during each 8-hr shift in which uranium analyses are made. Take from 20 to 30 mg of uranium and analyze by following Subsection 4.7.2. Calculate the calibration correction using Part (c) of Section 4.8.

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4.6.2 Control

Control is established by obtaining satisfactory results on the control sample. Control requirements are as follows:

- (a) Analyze the control standard by following Subsection 4.7.2 and calculate the results using Part (d) 1 of Section 4.8.
- (b) Plot the results of the control sample on the control chart and determine control status.¹
- (c) The control standard is analyzed at least once during each 8-hr shift in which samples are analyzed. If possible, two control standards are analyzed. They should be separated in time such that one is analyzed at the beginning of the shift and the other in the middle or later part of the shift.
- (d) Systematic error (or bias) is monitored by averaging the control standard results for five days analyses. The data from the current days analysis plus the previous four analyses are averaged as $\bar{X}$.

Bias, b , is defined as $b = \bar{X} - X_a$, where X_a is the accepted value for the control std.

Percent bias is calculated as follows,

$$\% \text{ Bias} = \frac{b(100)}{X_a}$$

- (e) Record % Bias as a deviation from a straight line (zero) on a control chart. Positive or negative trends warrant attention to standards and/or procedure.

¹ Instructions for preparing control charts and the criteria that establish when a method is out of control are found in the Laboratory Quality Assurance Manual, Volume 1.

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4.6.3 Training

- (a) Refer to MCS-033.
- (b) The analyst shall be trained in the use of the procedure by the responsible scientist. He shall demonstrate qualification by successfully analyzing duplicate reference standards (following calibration) on three successive occasions. Ongoing qualification consists of successful analysis of NBS and reference standards.

4.7 ANALYSIS

4.7.1 Sample Dissolution by Fusion

- (a) Add a portion of sample weighed to the nearest 0.1 mg to a 50-ml quartz Ernlmeyer flask.

Select an amount of sample to give a uranium concentration of about 12-15 mg/ml in a 60-ml volume.
- (b) Add 10 g of fused sodium bisulfate to the flask and cover with a quartz cover glass.
- (c) Place the flask in a muffle furnace and heat a 600°C for 1 to 2 hr.
- (d) Let furnace cool and remove flask(s).
- (e) Dissolve the melt in 30 ml of 1N H₂SO₄, swirling the flask occasionally to aid dissolution.
- (f) Quantitatively transfer the solution to a tared 60-ml dropping bottle using 1N H₂SO₄ to rinse the flask.
- (g) Dilute to about 60 ml with 1N H₂SO₄, mix thoroughly, and weigh. Calculate sample concentration, C_s, according to Section 4.8(b) Method PNL-ALO-222.

4.7.2 Sample Preparation, System Set Up

- (a) Weigh, to the nearest 0.1 mg, aliquots of sample containing 20 to 30 mg of uranium into 100-ml beakers containing stir bars and proceed as follows:

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1. For sample solutions containing low-level nitrate and no chloride, proceed to Step (b).
 2. For sample solutions containing high-level nitrate and chloride, evaporate to dryness and fume. Let cool, add 2 ml of 1N H_2SO_4 to dissolve the residue and proceed to Step (b).
- (b) Place 100 ml beakers in plastic turntable beakers in proper order beginning with the position to the right of the preparation station.

Up to ten samples may be placed on the turntable but up to fifty sample identification/aliquot numbers may be entered into the computer prior to start. New samples are then placed on the turntable as analyses are completed.

- (c) The analysis is performed automatically and is controlled by the program in the HP85A. Samples are analyzed according to the following procedure after control is given to the computer.

The turntable is rotated and the first sample is raised to the up position in the first station. Two ml of 1.7 M sulfamic acid is added, the magnetic stirrer is turned on for 10 sec and turned off. Twenty-five ml of reducing acid is added and the stirrer turned on. After a 60-sec wait five ml of oxidizing acid is added. The solution turns brown black and then clears. A wait of 260 sec after addition of oxidizing acid is required to allow for clearing and completion of the oxidation (180 sec after clearing).

The beaker is then lowered and rotated to the next station for titration while the next sample is positioned for preparation. The samples are raised and the preceding steps repeated in station one. In station 2 forty-five ml of vanadyl solution is added and the stirrer turned on. Following a 10-sec wait the computer instructs the 636 titro processor to begin titration. The 636 is fully programmed to perform the titration and communicates volume of titrant used and end point potential to the HP85A upon completion of the titration. When both stations have completed their operations, the beakers are lowered and the electrodes/delivery tip in station two are rinsed

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automatically. The turntable rotates and the process is repeated until all samples are completed.

- (d) The E636 is programmed by use of a program card. Instructions are as follows:
1. Turn on instrument and E635 buret.
 2. The instrument will briefly read all "8"s and then 36 0.00000. This is for entry of date. Depress digit keys (example) 70984 ENTER for 7 September 1984.
 3. Display will then show "ENGO", depress "GO" key and display will show "CARD".
 4. Slide the program card fully into the slot and slowly withdraw.
 5. Press 37, "MOD", 2, then "ENTER".
 6. The instrument is now ready to operate.
- (e) The operating program is loaded into the HP85A by inserting the proper cassette into the machine, typing LOAD "UA" and pressing ENDLINE. When the program has loaded (small LED below tape goes out), press RUN.
- (f) The CRT will display Uranium Assay System. Press CONT to start. The CRT will ask for keyboard inputs. All entries are made by typing the appropriate information and pressing ENDLINE.
1. How many samples?
Press any number up to 50, ENDLINE
 2. Sample identification?
Any combination of alpha-numeric characters up to eight characters, ENDLINE
 3. Aliquot numbers?
Any integer up to 99, ENDLINE

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Query 2, 3 will be repeated until all samples from query 1 have been identified. The system will wait until CONT is pressed before beginning the analysis.

- (g) All data pertinent to calculation along with sample identification will be printed by the HP85 at the completion of each sample titration. When all titrations are completed press RUN. All components may be left in their present mode.
- (h) Calculate solid samples using 4.8.1 and liquid samples using 4.8.2.

4.8 CALCULATION

Calculate the titer of the dichromate titrant, the uranium concentration in samples, and the calibration correction using the appropriate equations below.

- (a) Dichromate Titer.

$$T_v = \frac{W_v(119.019)(f)(1000)}{V_v(49.0317)}$$

where T_v = volume titrant titer, mg U/ml solution
 W_v = weight of dichromate in g
 V_v = volume of solution in ml
 f = purity factor of the potassium dichromate
119.019 = equivalent weight natural uranium
49.0137 = equivalent weight potassium dichromate.

- (b) Uranium Concentration in Calibration Standard.

$$U_{cs} = \frac{W_{std}f}{W_1 - W_2}$$

where U_{cs} = concentration of U in mg/g of solution
 W_{std} = weight of U metal in mg
 W_1 = weight of container and solution in g
[Step 3, Section 4.4(a)]
 W_2 = tare weight of container.

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f = purity factor of the uranium

(c) Calibration

$$R = \frac{(T_v V_x) A}{U_{cs} W_a}, \quad \bar{R} = \frac{R_1 + R_2 + \dots R_n}{n}$$

where R = recovery of uranium in standard

T_v = volume titrant titer

V_x = volume in ml of dichromate titrant used

A = atomic weight of uranium divided by 238.038

U_{cs} = Concentration of U in mg/g of solution

W_a = weight in g of aliquot taken

$\bar{R}$ = average of n values of R, used for calibration correction.

(% Recovery = $R \times 100$)

(d) Uranium Concentration in Samples.

4.8.1 Solid Samples

$$\text{Uranium} = \frac{(T_v V_x)(A)(100)}{W_a C \bar{R}}$$

where Uranium = concentration of U in sample as weight percent

T_v = volume titrant titer

V_x = volume in ml of dichromate used

A = atomic weight of U in sample divided by 238.038

W_a = weight in g of sample aliquot taken

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C = concentration of sample in solution, mg
sample/g of solution

$\bar{R}$ = average recovery of uranium in standard.

Unless otherwise instructed, report results to the nearest 0.01%.

4.8.2 Liquid Samples

$$\text{Uranium} = \frac{(T_v V_x)(A)(DF)D}{W_a \bar{R}}$$

where Uranium = concentration of U in sample as g U/l

DF = Dilution Factor, if diluted, otherwise use 1.

D = Density of Sample, g/cc

T_v = volume titrant titer

V_x = volume in ml of dichromate used

$\bar{A}$ = atomic weight of U in sample divided by 238.038

W_a = weight in g of sample aliquot taken

$\bar{R}$ = average recovery of uranium in standard.

Unless otherwise instructed, report results to the nearest 0.01 g/l.

5.0 BIBLIOGRAPHY

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-231, (Replaces 7-40.16), SEPARATION OF CARBON FROM SOIL/SEDIMENT/SLUDGE SAMPLES

1.0 Applicability

This procedure applies to the preparation of soil/sediment/sludge samples by dissolution, oxidation and evolution of carbon dioxide in apparatus in the shielded cells prior to the measurement of total carbon and/or C-14 using follow-on procedures PNL-ALO-230, PNL-ALO-415 and/or PNL-ALO-444.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant scientist and technician.

4.0 PROCEDURE

4.1 Equipment and Materials

- Sulfuric acid, 4M - prepare by diluting 220 (± 5) ml of concentrated, reagent-grade sulfuric acid to 1000 (± 1) ml with deionized, Type II water.
- Sulfuric acid, 1M - prepare by diluting 55 (± 5) ml of concentrated, reagent-grade sulfuric acid to 1000 (± 1) ml with deionized, Type II water.
- Potassium persulfate, (potassium peroxydisulfate), crystals, reagent-grade.
- Sodium hydroxide, .6M - prepare by dissolving 24 (± 0.1)g of reagent-grade NaOH in 1000 ml of deionized, Type II water.
- Silver nitrate, 2M - prepare by dissolving 34 (± 0.1)g of reagent-grade AgNO_3 in 100 ml of deionized, Type II water.
- Ascarite[®] for the absorption of CO_2 from air.

Author	Date	Project Mgr.	Date	QAD Representative	Date
FE Holt	6/17/88	N/A		LJ Ethridge	6/17/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	6/17/88	All original signatures on file	
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- Glass apparatus as per Figure 1.
- Drying tube, single bulb, 150 mm long, Corning 7775 or equivalent.
- Wheaton double-sidearm Celstir flask, 100 ml size, modified as per diagram.
- Drierite-filled column.
- Hot plate and water bath.
- 35 ml screw-cap glass vials.

4.2 Sample Analysis

This procedure involves the acid dissolution/oxidation of soils, sediments or sludge samples to release carbon present in all carbon-containing compounds. The heated sulfuric acid/persulfate solution oxidizes all carbon compounds to CO_2 , which then evolves from solution. The released CO_2 is trapped in a caustic trap solution. The solution is removed and transferred to another laboratory for further processing.

Step 1) Set up the dissolution and trap apparatus up to but not including the caustic trap shown in Figure 1.

- NOTES: a) The Ascarite-filled tube is required only if the distillate will be analyzed for total carbon.
- b) The poly insert cup shown in Figure 1 is required only when specified by the cognizant Scientist.

Step 2) Add 40 ml of 4M H_2SO_4 , 5g of potassium persulfate and 100 (± 10) μl of AgNO_3 to the dissolver flask.

Step 3) Add 60 ml of 1M H_2SO_4 to the acid scrubber trap.

Step 4) Establish an air flow of 50-100 cc/min through the system.

Step 5) Heat the water bath to approximately 90°C.

Step 6) Add 15.0 (± 0.1) ml of 0.6M NaOH to the caustic trap.

Step 7) Weigh out an amount of sample material specified by the cognizant Scientist to the nearest 0.0001 g.

Step 8) Stop air flow and connect the caustic trap and remaining parts of the system together.

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- Step 9) Close the system and re-establish the air flow rate of 50-100 cc/min.
- Step 10) Briefly open the dissolver flask and add the weighed sample to the dissolver solution. Quickly close the flask to re-establish the air flow.
- Step 11) Sparge and heat the sample and solution for one hour.
- Step 12) After one hour, stop the air flow, let the flask cool, and remove the caustic trap.
- Step 13) Transfer the caustic trap solution to a 35 ml, screw-cap vial and remove from the cell for further preparation.

4.3 Records

Records will be maintained and controlled so as to conform to requirements of MCS-033.. Laboratory notebooks and analytical report cards provide a mechanism for control of most records. ~~Laboratory record book will be used in accordance with PAP-1704.~~

4.4 Procedure Qualification

None required. This procedure is considered qualified due to its dependence on well understood chemical principals. Additionally it is considered qualified because it has an Independent Technical Review.

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FIGURE 1

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-233, (Replaces 2-30.9), PLUTONIUM PURIFICATION BY ION EXCHANGE

1.0 APPLICABILITY

The oxidation state of plutonium is chemically adjusted to +4 after which it is loaded on the ion exchange resin. Impurities are washed from the column with 8 N HNO₃ and finally the plutonium is eluted with dilute HCl. After evaporation, fuming in H₂SO₄ and dissolution the sample is ready for assay analysis.

- (a) Material Plutonium oxide, mixed oxide materials and plutonium/uranium solutions.
- (b) Range From 5 to 20 mg of plutonium is required.
- (c) Reliability Recovery based on NBS 949 and reference standards from 28 samples show an average recovery of 99.96%.
- (d) Interferences There are no interferences to this procedure.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Analyst

4.0 PROCEDURE

4.1 DISCUSSION

Plutonium is efficiently and quantitatively separated from impurities by anion exchange in nitric acid medium. This separation is made possible with a high degree of selectivity by

Author	Date	Project Mgr.	Date	QAD Representative	Date
MC Burt	6/15/88	N/A		LJ Ethridge	6/16/88
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OP Amacker, Jr.	6/17/88	JJ McCown	6/16/88	All original signatures on file	
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the ability of plutonium(IV), to the exclusion of most elements, to form an anionic hexanitrate complex $[\text{Pu}(\text{NO}_3)_6]^{-2}$ which is readily absorbed on Dowex-1 anion exchange resin. The plutonium must be in the Pu(IV) oxidation state since Pu(III) and Pu(VI) are not quantitatively absorbed on the resin. Plutonium and only a few elements such as Pd, In, Pt, Np(IV), Au, and Th are strongly absorbed on Dowex-1 resin, while other impurities are either weakly absorbed or unabsorbed. The unabsorbed or weakly absorbed elements are removed from the resin by washing with sufficient quantities of 8 N HNO_3 , although some impurities, especially uranium, require more washing than others for complete removal. Plutonium is retained on the resin column and quantitatively eluted with 0.36 N HCl -0.01N HF solution.

4.2 APPARATUS

- (a) Adjustable pipet, 0-5 ml and tips.
- (b) Resin, AG 1-X4 100-200 mesh.
- (c) Columns, glass (see Figure 1).
- (d) Quartz wool.
- (e) Titration vessels (see PNL-ALO-222).
- (f) 50 ml beakers.
- (g) Hot plate.

4.3 REAGENTS

- (a) Ferrous Sulfate, 0.1 M. Dissolve 7.5g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 250 ml distilled water containing 1.5 ml concentrated H_2SO_4 .
- (b) Eluting solution, 0.36 N HCl -0.01N HF . Add 30 ml of HCl and 7-8 drops of HF to 500 ml distilled water, dilute to 1 liter and mix well.
- (c) Nitric acid, 1.5 N.
- (d) Nitric acid, 8 N.
- (e) Nitric acid, 15 N.
- (f) Sulfuric acid, 6 N.

4.4 STANDARDS

Duplicate aliquots of either NBS 949 or the reference standard (see PNL-ALO-222) are carried through the entire procedure with each group of samples. Recovery should be within the limits set for the reference standard (see PNL-ALO-222) and should be >99.9% for the NBS 949.

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PNL TECHNICAL PROCEDURE

4.5 SAFETY

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

4.6 QUALITY CONTROL

This procedure is a preparation step prior to plutonium assay. Calibration and control procedures as discussed in PNL-ALO-222 apply.

4.7 ANALYSIS

Sample must be in liquid form prior to ion exchange purification. See Section 4.7.1 and 4.7.2 of PNL-ALO-222 for dissolution procedures.

4.7.1 COLUMN PREPARATION

- (a) Place a small quartz wool plug in the column tip.
- (b) Add resin slurry to within 5-10 mm of column shoulder.
- (c) Wash with several column volumes of 8 N HNO_3 . Stir to remove air bubbles if necessary.

4.7.2 ANALYSIS

- (a) Weigh sufficient sample into a 50 ml beaker to give 10 mg plutonium and evaporate to dryness.
- (b) Rinse beaker sides with 2 ml 1.5 N HNO_3 and swirl to dissolve sample.
- (c) When sample is dissolved add 1 ml 0.1 M FeSO_4 and swirl.
Solution will turn a bluish color indicating Pu^{+3} .
- (d) Add 3 ml 15 N HNO_3 and swirl.
Solution will turn a greenish color indicating Pu^{+4} .
- (e) Dilute to 20-25 ml with 8 N HNO_3 .

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- (f) Add solution to prepared columns in 5-10 ml increments allowing the column to empty prior to each addition.
- (g) Rinse beaker twice with 8 N HNO_3 and add to column.
- (h) Wash column with 30 ml 8 N HNO_3 in 5-10 ml increments allowing the column to empty before each addition.
- (i) Place clean titration vessels (PNL-ALO-222) under the columns and elute with 30 ml 0.36 N HCl -0.01N in 5-10 ml increments. Allow the column to empty prior to each addition.
- (j) Add 1 ml 6 N H_2SO_4 and evaporate to dryness.
- (k) Samples are ready for plutonium assay. Add a stir bar and 10 ml 0.5 N H_2SO_4 , allow residue to dissolve and proceed to PNL-ALO-222, Section 4.7.3 (b).

4.8 CALCULATIONS

None required.

5.0 BIBLIOGRAPHY

C. E. Pietri, B. P. Freeman and J. R. Weiss, "The Quantitative Ion Exchange Separation of Plutonium from Impurities," NBL-298, (1981).

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-237, (Replaces 2-40.7), TOTAL NITROGEN BY FUSION AND GAS CHROMATOGRAPHY

1.0 APPLICABILITY

Powdered or small pieces of sample are fused at about 2600°C in a graphite crucible. The nitrogen is released in its elemental form and it is measured by gas chromatography, which is based upon the differences in thermal conductivity of gases.

- (a) Material Uranium oxide and mixed oxide powder and pellets; plutonium dioxide or any solid material.
- (b) Range From 5 to 2500 μ g of nitrogen can be determined in a 0.3 to 1 g sample
- (c) Reliability A pooled relative standard deviation of 12% was obtained from the analysis of 22 standards with the amount of nitrogen taken for analysis ranging between 5 and 300 μ g. A pooled recovery of 97% was obtained.
- (d) Interferences Nitrogen from the atmosphere will enter the nitrogen analyzer if the sample is improperly loaded and this will cause a high result. Ammonia, nitrates, and other nitrogen-containing compounds from extraneous sources will cause high results.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Analyst

4.0 PROCEDURE

Author	Date	Project Mgr.	Date	QAD Representative	Date
MC Burt	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	6/16/88	All original signatures on file	
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4.1 DISCUSSION

In this method, the sample is fused at 2600°C in a graphite crucible to release nitrogen in all forms as elemental nitrogen gas. Thus, total nitrogen is determined with this method.

The nitrogen analyzer used has an impulse furnace in which an electrical current is passed through the graphite crucible, heating the crucible and sample material to a high temperature. A stream of helium carries the nitrogen and other gases formed by the fusion from the furnace, through scrubbers to remove interfering gases, and into a column of molecular sieve where the nitrogen is separated. The concentrated nitrogen is then carried from the molecular sieve by helium into a gas chromatograph for measurement. Helium is used also to flush air from the furnace prior to heating and to purge the system of interfering gases released during the outgassing of the crucible.

The analyzer has two impulse furnaces, one of which is a remote furnace housed in an inert atmosphere glovebox. This remote furnace is used in the analysis of materials containing plutonium.

During fusion any oxygen present in the sample material combines with carbon from the crucible to form carbon monoxide and any combined hydrogen present is converted to elemental hydrogen. These interfering gases are converted to carbon dioxide and water when carried by the helium through a heated column of rare earth and copper oxide. The carbon dioxide is removed later from the gas stream by Ascarite and the water by Anydron. The molecular sieve used to concentrate the nitrogen also helps to separate interfering gases.

The gas chromatograph has a thermoconductivity cell that detects differences in the thermal conductivity of gases. The cell consists of a pair of matched thermistors used in two legs of a Wheatstone bridge. The reference thermistor is kept in a helium environment having constant pressure, flow, and temperature. The measure thermistor is kept under the same conditions as the reference except for the gas composition, which varies as nitrogen is carried into the measure thermistor by the helium carrier gas. The nitrogen causes the temperature of the measure thermistor to change because of the difference in thermal conductivity between helium and nitrogen. The change in temperature causes the Wheatstone bridge to become unbalanced, and through the electronic system, the degree of imbalance is converted into a readout on the digital voltmeter. The readout is also coupled to a digital

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PNL TECHNICAL PROCEDURE

integrator that is set to automatically integrate the nitrogen peak. The integrator is more sensitive than the voltmeter and the timing for integration of the nitrogen peak is less critical with the integrator.

4.2 APPARATUS

- (a) Analytical Balance. Capable of weighing to 1.0 mg.
- (b) Digital Integrator. Autolab Minigrator, Spectra Physics Corp.
- (c) Graphite Crucible, LECO #767-277 or equivalent.
- (d) Nitrogen Analyzer. LECO UO14 sp Nitrogen Determinator, Model #857-034.
- (e) Remote Furnace. LECO, Model 875-492.
- (f) Tin Capsule. LECO #501-059 or equivalent.

4.3 REAGENTS

- (a) Anydrone. LECO #501-171 or equivalent.
- (b) Ascarite. 20-30 mesh, LECO #183-001, or equivalent.
- (c) Ascarite. 8-20 mesh, LECO #501-166 or equivalent.
- (d) Helium. Ultra-high purity, 99.995%
- (e) Molecular Sieve. 5A, 20-30 mesh.
- (f) Phosphorus Pentoxide. LECO #765-278 or equivalent.
- (g) Rare Earth Oxide. LECO #501-170 or equivalent.
- (h) Sulfur Absorber. LECO #763-770 or equivalent.

4.4 STANDARDS

- (a) Calibration Standard. Steel standards are used to calibrate the digital integrator and mixed uranium-plutonium oxide blends are used to prepare a calibration curve.
 - 1. The following stainless steel standards are used: NBS SRM 346 and 133, and LECO #501-551, #501-552, and #501-533.
- (b) Control Standard. None required (see Subsection 4.6.1).

4.5 SAFETY

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

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PNL TECHNICAL PROCEDURE

(b) Observe the general laboratory safety rules.

4.6 QUALITY CONTROL

4.6.1 Calibration

(a) Prepare the instrument for analysis. The analyzer must conform to the following:

1. Be sure that the water supply to the electrode coolant circulator has been shut off and disconnected; then turn on the electrode coolant circular power switches.
2. "DVM ON" switches must be on.
3. "AUX FURN ON" indicator must be on.
4. The "FUNCTION SWITCH" switch must be in the "OPERATE" position.
5. The two circuit breakers at the rear of the analyzer must be on.
6. The "STD-BY" indicator must be green.
7. The "HELIUM BLANKET" indicator must be off.
8. The furnace must be empty and closed.
9. The "OVEN INDICATOR" must be cycling on and off and the oven temperature must be approximately 45°C.
10. The helium regulator must be set for 40 psig (2.8 kg/cm²).
11. The helium outlet valves at the back of the analyzer must be opened.
12. Both the "MEASURE FLOW" and the "REFERENCE FLOW" rotometers must indicate the approximate flows.
13. The digital integrator must be on with the controls set as follows:

PW = 10
SS = 700

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PNL TECHNICAL PROCEDURE

All other settings are left at their default values.

14. The furnace selection valves and control plug must be set for the furnace to be used:

Internal
External

Furnace on Analyzer
Remote Furnace in Glovebox

- (b) Turn the "FUNCTION SELECT" switch to the "DVM ZERO" and adjust the DVM zero if necessary.
- (c) Depress the "STD-BY" switch. Turn the "FUNCTION SELECT" switch to the "OPERATE" position for approximately 30 sec. Then turn the "FUNCTION SELECT" switch to the "INTEG CHECK" position and note the time; at the end of 1 min note the reading.

The DVM reading must not change more than ± 0.001 during this period. If it does, refer to the Electronic Checkout in the Instruction Manual (Section 4.0).

- (d) Turn the function select switch to Bridge. Adjust the DVM to read 000, by turning the screw marked Bridge, on the front of the Analyzer. Push the Shift button, then the Slope button on the integrator. The integrator should read 500, if not adjust the bridge accordingly.
- (e) Depress the "STD-BY" switch. Turn the "FUNCTION SELECT" switch to the "OPERATE" position.
- The "STD-BY" indicator should turn green.
- (f) Open the furnace.

The remote furnace is operated pneumatically by the toggle switch on the glovebox face.

The "PURGE" indicator will turn white and the "STD-BY" indicator will go off.

Inspect the interior of the upper electrode cavity with a mirror and flashlight to make sure that no deposits of graphite or other material are present.

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PNL TECHNICAL PROCEDURE

Also inspect the lower electrode. The bottom interior of the lower cup must be free from all metal or graphite particles. A small argon gas jet is ideal for cleaning the bottom interior of the lower electrode. Clean the electrodes using the proper brush, being careful to prevent scratching of the electrodes or the "O" rings.

Do not insert your fingers or any metallic object near the safety thermostat mounted on the outside of the upper electrode. When power is applied, there is 115 V on these connections.

- (g) Place a LECO crucible on the lower electrode assembly using the tweezers.

To avoid contamination, do not touch the crucible with your fingers.

- (h) Close the furnace.

The "PURGE" indicator will turn green.

The furnace must be kept closed at all times except when cleaning the interior of the furnace or loading the crucible. The furnace must be cleaned before each analysis.

- (i) Depress the "OUT-GAS" switch.

The "OUT-GAS" indicator will be white during the out-gas period and the "PURGE" indicator will be off.

The crucible current value is indicated on the "FURNACE POWER" meter and during out-gas the value should be greater than or equal to 1100 A. If not, refer to the procedure for adjusting fusion current described in the Installation Section of the Instruction Manual.

- (j) The following procedure will compensate for a normal nitrogen blank:

1. Repeat Steps (d) through (h).
2. The "OUT-GAS" indicator must be green.

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PNL TECHNICAL PROCEDURE

3. The empty out-gassed crucible must be left in the furnace.

Do not put a sample into the crucible at this time.

4. Set the digital integrator to "RUN" and simultaneously depress the "ANALYZE" switch.

The "ANALYZE" indicator will turn white and the "OUT-GAS" indicator will go off.

When the digital value for the nitrogen peak at 110 to 130 sec has been integrated, record the value and set the integrator to "STD-BY."

5. Repeat this procedure with a minimum of three crucibles to establish the proper crucible blank value.

- (k) The following describes the procedure for calibration of the analyzer.

1. Repeat Steps (d) through (f).
2. Place a steel calibration standard of a weight between 0.300 and 0.699 g into the loading head.

Be sure to handle the sample only with tweezers.

The sample form must be such that it can be contained in a cylinder 6 mm in dia and 8-mm high.

3. Close the furnace.
4. Depress the "OUT-GAS" switch.
5. Push the "SAMPLE DROP" button after the "OUT-GAS" indicator turns green.

This lets the standard fall into the crucible.

6. Turn the digital integrator to "RUN" and simultaneously depress the "ANALYZE" switch.

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PNL TECHNICAL PROCEDURE

The "OUT-GAS" indicator will go off and the "ANALYZE" indicator will turn white.

The crucible current value may be slightly lower than during out-gas (approximately 30 A lower). If the current is considerably lower, the sample may not have fallen into the crucible--check the loading head cavity.

7. Record the integrated value for the nitrogen peak at 110 to 130 sec and set the integrator to "STD-BY."
8. Repeat this procedure with a minimum of two standards.
9. Calculate the $\mu\text{g N}/1000$ counts for the three results after subtracting the crucible blank value and calculate the average.

The average must agree to within $\pm 5\%$ of the previous average. If not, determine the source of the problem before proceeding.

- (1) Determine a calibration factor for sample analysis and prepare a calibration curve by repeating 1 through 7 of Step (k), using a mixed-oxide calibration standard instead of a steel standard at 2. The mixed oxide is placed into a tin capsule; the capsule is pinched flat and folded and then it is placed into the loading head.

1. Analyze at least five portions of the mixed oxide standard to provide calibration points ranging between 10 and 300 μg of nitrogen.

The amounts of standard taken should be between 0.20 and 0.60 g.

2. Determine a tin capsule blank using an empty capsule at Step (k) 2; make at least three determinations and calculate an average blank.
3. Subtract the average blank from each standard readout and calculate an average $\mu\text{g N}/1000$ counts for the five results. This value is the calibration factor used in the equation of Section 11.0.

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PNL TECHNICAL PROCEDURE

A new calibration factor is not required each time nitrogen analyses are made, although at least one standard must be analyzed to check the factor during each 8-hr shift in which analyses are made. The method is in calibration if the result falls within $\pm 5\%$ of the factor. A new factor must be determined if two consecutive results fall outside $\pm 5\%$.

4. Prepare a calibration curve to check for linearity by plotting the five net readouts versus μg of nitrogen using linear graph paper.

4.6.2 Control

Control is not established.

4.7 ANALYSIS

- (a) Repeat Steps (d) through (f) of Subsection 4.6.
- (b) Place a sample into the loading head.

The sample form must be such that it can be contained in a cylinder 6 mm in dia and 8-mm high.

Weight powdered samples (0.2 to 0.6 g) in tin capsules; flatten and roll the capsule. Whole pellets and chunks of pellets (<1.5 g) need not be encapsulated.

Contamination of samples with nitrogen from air can be eliminated by weighing in an argon atmosphere.

- (c) Close the furnace.
- (d) Depress the "OUT-GAS" switch.
- (e) Push the "SAMPLE DROP" button after the "OUT-GAS" switch turns green.

This lets the sample fall into the crucible.

- (f) Set the digital integrator to "RUN" and simultaneously depress the "ANALYZE" switch.

The "OUT-GAS" indicator will go off and the "ANALYZE" indicator will turn white.

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PNL TECHNICAL PROCEDURE

The fusion current should be between 1100 and 1200 A, which requires the highest transformer setting possible without causing crucible breakdown.

If current drops to zero during analysis, discard the result and repeat the analysis.

Record the integrated value for the nitrogen peak that occurs at 110 to 130 sec and set the integrator to "STD-BY."

4.5 CALCULATION

Calculate the concentrate of nitrogen in the sample using the following equation:

$$\text{Nitrogen} = \frac{(A - B)F}{W}$$

where nitrogen = nitrogen content in $\mu\text{g/g}$

A = nitrogen counts determined from the digital integrator divided by 1000

B = average crucible blank plus tin capsule blank (as appropriate) in digital integrator counts divided by 1000

F = calibration factor in $\mu\text{g N}$ per 1000 counts [See Step (1) 3 of Subsection 4.6.1]

W = sample weight in g.

Unless otherwise instructed, report results to two significant figures. Report results $10 \mu\text{g/g}$ as $<10 \mu\text{g/g}$.

5.0 BIBLIOGRAPHY

- (a) Instruction Manual. U014 sp Nitrogen Determinator, Model #875-034, Laboratory Equipment corp., St. Joseph, Michigan (1974).
- (b) Instruction Manual. Autolab Minigrator, Spectra Physics Corp., Mountain View, California.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-238, (Replaces 2-40.11), WATER BY CONSTANT VOLTAGE COULOMETRY

1.0 APPLICABILITY

Water is released from the sample by heating. A carrier gas sweeps the water into an electrolytic cell containing phosphorus pentoxide to absorb the water. A potential applied across the cell causes the absorbed water to be electrolyzed. The total current is integrated and displayed digitally as micrograms of water.

- (a) Material Any solid material.
- (b) Range From five to several thousand micrograms of water per measurement.
- (c) Reliability Relative standard deviation: about 20% for 20 to 40 μg of water and 2 to 5% for $> 100 \mu\text{g}$. Over a two-month period, 17 sodium tartrate standards containing from 300 to 1000 μg of water were analyzed, and the recovery varied from 95 to 101% with a relative standard deviation of 2%.
- (d) Interferences Hydrogen, alcohols, and amines will give a high bias. Other materials can coat the inside of the cell, making it inactive.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Analyst

4.0 PROCEDURE

Author	Date	Project Mgr.	Date	QAD Representative	Date
MC Burt	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	6/16/88	All original signatures on file	
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4.1 DISCUSSION

The operation of the water analyzer is based upon the coulometric electrolysis of water.^(b) As the sample is heated, the evolved water is carried in a stream of dry nitrogen into an electrolytic cell where the water is absorbed by phosphorus pentoxide. The phosphorus pentoxide, which coats two parallel platinum wires, becomes conductive as the water is absorbed. When a potential is applied across the wires, the water is electrolyzed, which in turn allows more water to be absorbed. The process continues until all of the evolved water has been electrolyzed. The total current is integrated automatically and displayed digitally as micrograms of water. Built-in safeguards prevent the electrolytic cell from being overloaded by excessive amounts of water.

Liquids and solids entrained in the gas stream as well as ammonia and other basic substances that react with phosphorus pentoxide can cause malfunction of the electrolytic cell. Alcohols, glycols, and similar substances respond as water and cause a high bias. Further, the level and variability of the humidity can cause a bias when samples susceptible to adsorbing or desorbing water are analyzed. If the water analyzer is located where the humidity is not controlled, precautions may be required to protect samples from water adsorption and to prevent errors in the analyses caused by variable blanks. If the analyzer is located where the humidity is controlled at a very low level, precautions may be required to prevent samples from desorbing water.

The temperature at which water is completely evolved depends upon the material being analyzed. Studies have shown that water evolves from uranium and plutonium oxides in at least two temperature ranges: up to 200°C and between 200 and 400°C.^{(c)(g)} Two additional ranges (400 to 600°C and 600 to 800°C) were observed by Michaelson^(c) with a powder blend of UO_2 -1% PuO_2 . For sintered mixed oxide (25% PuO_2) pellets, Vance^(g) observed a two-range evolution which was completed below 400°C. Although experimental work at HEDL has not specifically confirmed Vance's observation, we believe that it is substantially correct.

WHC's experimental work^(e) did show a release of water from sintered mixed oxide pellets between 400 and 500°C. That release, however, occurred because hydrogen was present in the pellets and reacted with available oxygen to form water. Since no evidence was found that hydrogen reacts below 400°C, a temperature of 400°C should be low enough to avoid hydrogen interference and yet high enough to remove water completely as observed by Vance.

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PNL TECHNICAL PROCEDURE

4.2 APPARATUS

- (a) Analytical Balance. Readable to 0.01 mg.
- (b) Gas Flowmeter. Capable of measuring a flow rate up to 150 ml/min.
- (c) Platinum Boat. 1- by 3- by 0.5-cm. Platinum boats are used instead of the nickel boats supplied with the water analyzer because nickel is more apt to have an oxide coating that can react with hydrogen to form water (see Section 3.0).
- (d) Water Analyzer. DuPont Model 902H Moisture Evolution Analyzer.

4.3 REAGENTS

- (a) Magnesium Perchlorate. Anhydrous, for the gas dryer supplied with the water analyzer.
- (b) Nitrogen. Prepurified grade or equivalent.¹

4.4 STANDARDS

- (a) Calibration Standard. Not available.
- (b) Control Standard. Sodium tartrate dihydrate (15.6% water), crystals, weighing from 1 to 7 mg.

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

The analyzer is precalibrated electronically by the manufacturer. However, recalibration is necessary at least twice each year and whenever maintenance problems

¹ Matheson Gas Data Book, The Matheson Co., Inc., East Rutherford, New Jersey, 4th Ed., 1966.

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PNL TECHNICAL PROCEDURE

occur. Follow the manufacturer's recommended procedure for calibration.

4.6.2 Control

The control standard is analyzed at least once in each 8-hr shift during which water analyses are made. Analyze the control standard as follows:

- (a) Weigh to the nearest 0.01 mg between 1 and 7 mg of sodium tartrate dehydrate.

Using cloudy crystals may lead to low results; therefore, use only very clear crystals.

- (b) Analyze the sodium tartrate by following Subsection 10.1 with the following exception: use 125°C instead of the stated temperature at Steps (b), (d), (i), and (o).

Heating above 150°C will cause sodium tartrate to decompose, resulting in a high bias.

- (c) Calculate the percent water using Part (c) of Section 4.8. The control limits are 14.0 to 17.2%. If the result is outside these limits, investigate and correct the problem before analyzing samples.

4.7 ANALYSIS

4.7.1 Constant Rate Procedure

This procedure is used for samples containing over 50 μg of water. These samples are usually powders such as uranium and plutonium oxides.

- (a) Adjust the nitrogen flow rate to 100 ml/min at 5 psig.

The flow rate adjustment is not critical. Because the cell current is integrated as a function of time, the total water present is independent of the carrier-gas flow rate. However, a flow rate less than 150 ml/min is recommended.

- (b) Set the temperature controller at 400°C.

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PNL TECHNICAL PROCEDURE

Other temperatures may be required for a particular analysis. The temperature used at this step must be used at Steps (d), (i), and (o) also.

- (c) Place an empty platinum boat in the oven.
- (d) Start the timer and heat at 500°C until a constant count rate from the integrator is maintained over a 10-min period.

The system must be dried sufficiently at this step to permit adjustment of the analyzer to zero at Step (e). The count rate that indicates sufficient drying is determined by experience.

- (e) Zero the instrument at a count rate of 0.6 $\mu\text{g}/\text{min}$.

Consult the manufacturer's operation manual for instructions on how to zero the analyzer.

- (f) Turn off the timer and set the integrator to zero.

- (g) Remove the boat when the oven reaches room temperature.

- (h) Replace the boat in the oven after about 10 sec and turn on the timer.

The time interval between removal and replacement of the boat should be held constant for both the blank and the sample runs.

- (i) Heat at 400°C until the count rate of the integrator decreases to a constant rate of 0.6 $\mu\text{g}/\text{min}$.

- (j) Record the integrator reading (R_b) and the time (T_b) required to complete Step (i).

If the analyzer is not used in a controlled environment, the blank will vary from day-to-day, particularly if the humidity varies. Therefore, it is recommended that blanks be determined periodically during the day.

- (k) Stop the timer and reset the integrator to zero.

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PNL TECHNICAL PROCEDURE

- (l) Remove the boat when the oven reaches room temperature.

The time interval between removal and replacement of the boat should be held constant for both the blank and the sample runs.

- (m) Add a sample weighed to the nearest 1 mg (W_s) to the boat.

For uranium dioxide powder, a minimum sample size of 0.5 g is recommended. The sample size required for plutonium dioxide will vary because the water content of that oxide can vary considerably. Sample size for other materials will also vary according to water content.

- (n) Replace the boat in the oven.

- (o) Heat at 400°C until the count rate of the integrator decreases to a constant rate of 0.6 $\mu\text{g}/\text{min}$.

Samples may be heated at temperatures up to 800°C. A blank must be determined at measurement temperature.

- (p) Record the integrator reading (R_s) and the time (T_s) required to complete Step (o).

The reading and time are R_c and T_c respectively when a control standard is analyzed.

- (q) Stop the timer and reset the integrator to zero.

- (r) Repeat Steps (l) through (q) for subsequent sample analyses.

4.7.2 Constant Time Procedure

This procedure is used for samples containing less than 50 μg of water. These samples are usually sintered pellets.

- (a) Follow Steps (a) through (h) of Subsection 4.7.1.
(b) Heat at 400°C for 5 min.

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(c) Record the integrator reading (R_b).
If the analyzer is not used in a controlled environment, the blank will vary from day-to-day, particularly if the humidity varies. Therefore, with samples containing less than 30 μg of water, it is recommended that a blank be determined between each sample analysis.

(d) Stop the timer and reset the integrator to zero.

(e) Remove the boat when the oven reaches room temperature.

The time interval between removal and replacement of the boat should be held constant for both the blank and the sample runs.

(f) Add a sample weighed to the nearest 1 mg (W_s) to the boat.

Whole pellets are usually taken for analysis.

(g) Replace the boat in the oven.

(h) Heat at 400°C for 5 min.

(i) Record the integrator reading (R_s).

(j) Stop the timer and reset the integrator to zero.

(k) Repeat Steps (e) through (j) for subsequent sample analyses.

4.8 CALCULATION

Calculate the micrograms of water per gram of sample and the weight percent of water in the control standard using the appropriate equations below.

(a) Sample, Constant Rate Procedure (Subsection 4.7). Calculate the concentration of water in the sample as follows:

$$\text{Water}_s = \frac{R_s - (B)(T)_s}{W_s}$$

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where $\text{Water}_s = \mu\text{g water/g sample}$
 $R_s = \mu\text{g water from sample measurement}$
 $B = R_b/T_b$ [see Step (j), Subsection 4.7.1]
 $T_s = \text{min required for sample measurement}$
 $W_s = \text{sample weight in g.}$

Unless otherwise instructed, report results to the nearest whole number below 100 $\mu\text{g/g}$ and to two significant figures for results $\geq 100 \mu\text{g/g}$.

- (b) Sample, Constant Time Procedure (Subsection 4.7.2). Calculate the concentration of water in the sample as follows. Unless otherwise instructed, report results to the nearest whole number.

$$\text{Water}_s = \frac{R_s - R_b}{W_s}$$

where $\text{Water}_s = \mu\text{g water/g sample}$
 $R_s = \mu\text{g water from sample measurement}$
 $R_b = \mu\text{g water from blank measurement}$
 $W_s = \text{sample weight in g.}$

- (c) Control Standard. Calculate the concentration of water in the control standard as follows:

$$\text{Water}_c = \frac{R_c - (B)(T_c)}{(W_c)(10^4)}$$

where $\text{Water}_c = \text{wt\% water in control standard}$
 $R_c = \mu\text{g water from control standard measurement}$
 $B = R_b/T_b$ [see Step (j), Subsection 4.7.2]
 $T_c = \text{min required for control standard measurement}$
 $W_c = \text{control standard weight in g.}$

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5.0 BIBLIOGRAPHY

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- (b) F. A. Keidel. "Determination of Water by Direct Amperometric Measurement," Anal. Chem., 31, 2043 (1959).
- (c) J. G. Michaelson. Determination of Water in Plutonium and Uranium Oxides by Electrolysis, HW-83487, May (1964).
- (d) Operation and Maintenance Manual. Solids Moisture Analyzer, Model 26-321 AMA, 992212-008, Consolidated Electrodynamics Corp., Monrovia, California (1968).
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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-240, (Replaces 4-30.4, & 2-40.19), CARBON AND SULFUR BY COMBUSTION AND INFRARED ABSORPTION

1.0 APPLICABILITY

Samples are ignited with a tungsten accelerator between 1600° and 1700°C in a stream of oxygen. The carbon and the sulfur, as their oxides, are swept from the furnace into an infrared detector. The oxides absorb a portion of the infrared radiation and this absorption is used to measure simultaneously the amount of those gases evolved from the sample.

- (a) Material Stainless steels and other alloys or metals.
- (b) Range From 5 to over 1000 µg of carbon or sulfur per analysis.
- (c) Reliability Relative standard deviations of 3 and 4 percent were obtained for carbon and sulfur, respectively, at a concentration of 0.1 weight percent over a six-month period. An average recovery of 98 percent was obtained for both elements.
- (d) Interferences Interferences are not expected. Care must be taken, however, to avoid extraneous carbon and sulfur contamination of sample and equipment.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

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4.1 DISCUSSION

In the analysis of materials for carbon and sulfur, a separation of these elements from the matrix material is necessary prior to their measurement. Separation is done by evolving the carbon and sulfur as gaseous compounds that are measured by one of several available techniques.

In this method a commercially available analyzer is used that simultaneously determines carbon and sulfur as their oxides using infrared absorption. The analyzer consists of an induction generator and furnace, a measurement system, a balance, and control console. The analyzer system is microprocessor controlled. A second analyzer was modified for glove box use and is available for use also.

With this analyzer, induction heating is used for rapid combustion of the sample in the presence of flowing oxygen, which carries the gaseous combustion products from the furnace into the measuring part of the analyzer. The combustion is done at 1600° to 1700°C using tungsten as an accelerator. About 97% of the carbon is released as carbon dioxide and the remaining carbon forms carbon monoxide. The sulfur is oxidized to sulfur dioxide and trioxide, more than 90% of which is the dioxide and the carbon monoxide is oxidized to carbon dioxide.

The measurement system consists of two cells (one each for carbon and sulfur) which contain an IR source, a chopper motor, a wavelength filter and IR detector. The filter selectively passes only the proper wavelength into the cell and as the combustion gases pass a proportional amount of the energy is absorbed by the product gases (CO₂ or SO₂) thus reducing the energy received at the detector. This change in output is integrated over time and electronically converted to percent carbon and sulfur.

The determinator provides a printout of the weight percent of carbon and sulfur in the sample. The sample weight is electronically transferred from the balance to the determinator to provide the data needed to print out carbon and sulfur concentrations in the sample. The analyzer also provides automatic compensation for a system blank.

Because the sulfur trioxide produced cannot be measured by infrared absorption, it is important that analytical conditions be maintained as constant as possible to ensure a reproducible sulfur dioxide to trioxide ratio. Calibration compensates for sulfur trioxide and thus 100% recovery of sulfur is obtained. Frequent calibration checks are important to avoid biased results.

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PNL TECHNICAL PROCEDURE

Calibration is performed using LECO or NBS certified standards. Calibration is checked each day samples are analyzed by analysis of a LECO or NBS standard (see instruction manual for operational technique for calibration).

4.2 APPARATUS

(a) Analyzer. CS-44 Carbon-Sulfur system, LECO Model 784-600, including:

1. Control Console, LECO 780-300,
2. Determinator, LECO 781-200,
3. Induction generator, LECO 777-400, HF-100,
4. Auto Loader, LECO 773-601.

(b) Crucibles. LECO 528-081 or equivalent.

(c) Scoop. With a volume of about 0.25 cm³.

4.3 REAGENTS

(a) Accelerator (Tungsten). LECO 763-266 (Lecocel) or equivalent.

(b) Anhydron.

(c) Ascarite.

(d) Iron. Granular, LECO 501-673 or equivalent.

(e) Oxygen. Ultra high purity grade or equivalent.

(f) Platinized Silca Gel, LECO 501-587.

4.4 STANDARDS

(a) Calibration Standard. Steel standard, LECO 501-503. This standard is certified to contain 0.187 and 0.0181 weight percent carbon and sulfur respectively. The certification includes "uncertainties" of 0.005 and 0.004 for the carbon and sulfur respectively. Other steel standards can be used as long as their carbon and sulfur values are certified by NBS or LECO.

(b) Control Standard. None required (see Subsection 4.6).

4.5 SAFETY

(a) Care must be taken to avoid contact with high frequency induction leads to prevent burns and electrical shocks.

(b) When using the glove box unit be aware that plutonium-bearing materials are radioactive and toxic. Precautions

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PNL TECHNICAL PROCEDURE

are required to avoid the contamination of the laboratory and personnel.

- (c) Observe the general laboratory safety rules.

4.6 QUALITY CONTROL

4.6.1 Calibration

The instrument is calibrated according to the instructions on page 44 of the LECO Instruction Manual.

The calibration is stored in the microprocessor memory and recalibration is required only when checks show a drift or part replacement (cells, etc.) has occurred.

4.6.2 Control

Control is not established, although the calibration procedure does provide a degree of control.

4.7 ANALYSIS

Care must be taken to avoid contamination of the crucibles and samples with extraneous carbon and sulfur.

- (a) The analyzer must conform to the following conditions:

1. Power switch on (normally left in this position).
2. Induction generator on.
3. Oxygen Regulator set at 33 to 37 psig.

- (b) Prepare a crucible by adding one scoop of the accelerator (Lecocel) and about one-half to two-thirds of a scoop of iron.

- (c) Place the crucible on the balance pan.

The balance will tare automatically.

- (d) Add 0.5 to 1.0 g of sample to the crucible and press the Enter button.

The sample may be in any form (solid piece, turnings, chips, etc.). It should be thoroughly degreased in acetone and air dried.

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PNL TECHNICAL PROCEDURE

The sample weight is automatically transferred to the Determinator. A weight can be placed into the Determinator manually using the key board. See Instruction Manual.

- (e) Place the sample identification number into the analyzer by pressing ID Code and then the required digits.
- (f) Place the crucible on the autoloader and press the analyze key on the control console.

As many as eight samples may be placed on the autoloader and up to 50 weights and identification numbers in the memory stack.

- (g) Repeat Steps (b) through (f) for each additional sample.

Samples are automatically advanced and analyzed.

- (h) When analyses are completed, shutdown the analyzer as follows:

1. Turn off the induction generator.
2. Close the oxygen regulator.

The analyzer may be left in this condition.

3. Change the Anydrone and Ascarite in the columns in the Determinator after every 8 hr of use.

4.8 CALCULATION

The weight percents of carbon and sulfur are printed out at the completion of each analysis. By moving the decimal point 4 places to the right, the weight percent is changed to parts per million (ppm) if required. Report no more than three significant figures.

5.0 BIBLIOGRAPHY

Instruction Manual, Manual 200-319, CS-344 Carbon-Sulfur System, Model 784-600 LECO Corp., St. Joseph, Michigan.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-241, (Replaces 4-30.6), TOTAL NITROGEN BY FUSION AND GAS CHROMATOGRAPHY

1.0 APPLICABILITY

Small pieces of sample are fused at about 2600°C in a graphite crucible. The nitrogen is released in its elemental form and it is measured by gas chromatography, which is based upon the differences in thermal conductivity of gases.

- (a) Material 300 series stainless steels and other alloys.
- (b) Range From 0.00001% to 0.5% nitrogen can be determined in a 1-g sample.
- (c) Reliability Relative standard deviations of 5 to 10 percent are expected at concentration levels of 0.001 to 0.02 percent nitrogen.
- (d) Interferences Nitrogen from the atmosphere will enter the nitrogen analyzer if the sample is improperly loaded and this will cause a high result. Ammonia, nitrates, and other nitrogen containing compounds from extraneous sources will cause high results.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

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PNL TECHNICAL PROCEDURE

4.0 PROCEDURE

4.1 DISCUSSION

In this method, the sample is fused at 2600°C in a graphite crucible to release nitrogen in all forms as elemental nitrogen gas. Thus, total nitrogen is determined with this method.

The nitrogen analyzer used has an impulse furnace in which an electrical current is passed through the graphite crucible, heating the crucible and sample material to a high temperature. A stream of helium is used to carry the nitrogen and other gases formed by the fusion from the furnace, through scrubbers to remove interfering gases, and into a column of molecular sieve where the nitrogen is separated. The concentrated nitrogen is then carried from the molecular sieve by helium into a gas chromatograph for measurement. Helium is used also to flush air from the furnace prior to heating and to purge the system of interfering gases released during the outgassing of the crucible.

During the fusion, any oxygen present in the sample material combines with carbon from the crucible to form carbon monoxide and any combined hydrogen present is converted to elemental hydrogen. These interfering gases are converted to carbon dioxide and water when carried by the helium through a heated column of rare earth and copper oxides. The carbon dioxide is removed later from the gas stream by Ascarite and the water by Anhydrone. The molecular sieve used to concentrate the nitrogen also helps to separate interfering gases.

The gas chromatograph has a thermoconductivity cell that detects differences in the thermal conductivity of gases. The cell consists of a pair of matched thermistors used in two legs of a Wheatstone bridge. The reference thermistor is kept in a helium environmental having constant pressure, flow, and temperature. The measure thermistor is kept under the same conditions as the reference except for the gas composition, which varies as nitrogen is carried into the measure thermistor by the helium carrier gas. The nitrogen causes the temperature of the measure thermistor to change because of the difference in thermal conductivity between helium and nitrogen. The change in temperature causes the Wheatstone bridge to become unbalanced, and through the electronic system, the degree of imbalance is converted into a readout on the digital volt meter. That readout is calibrated in terms of micrograms of nitrogen.

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4.2 APPARATUS

- (a) Nitrogen Analyzer LECO TN-114 Nitrogen Determinator, Model 782-700.
- (b) Graphite Crucibles, LECO #775-053.

4.3 REAGENTS

- (a) Anhydrone. LECO 501-171 or equivalent.
- (b) Ascarite. 20 to 30 mesh, LECO 183-001 or equivalent.
- (c) Helium. 99.99% or better.
- (d) Compressed Air or Nitrogen (for pneumatics).
- (e) Copper Oxide. LECO 501-170 or equivalent.

4.4 STANDARDS

- (a) Calibration Standards. NBS SRM steel standards and/or available LECO standards are used for calibration. LECO 501-551, 501-552 and 501-646 are currently on supply.
- (b) Control Standard. None required.

4.5 SAFETY

Observe the general laboratory safety rules.

4.6 QUALITY CONTROL

4.6.1 Calibration

The instrument is calibrated according to the instructions on page 46 of the LECO instruction manual. The calibration is stored in microprocessor memory and calibration is checked each time samples are analyzed by running a standard. Calibration is required when checks show a drift from accepted values or when maintenance or part replacement has occurred.

4.6.2 Control

Control is not established, although the standard check provides a degree of control.

4.7 ANALYSIS

Care must be taken to avoid contamination of crucibles and samples with nitrogen containing substances.

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PNL TECHNICAL PROCEDURE

The nitrogen analyzer uses the same furnace as the oxygen analyzer. The selector switch must be set to NITROGEN. The two valves in the flow lines must also be set to NITROGEN (these are located on the hood wall next to the analyzer).

(a) The Analyzer must conform to the following conditions:

1. Power switch on (normally left on).
2. Furnace power on.
3. He regulator set at 40 psig ± 4 .
4. Pneumatic supply set at 40 psig.
5. Auto/Manual switch in AUTO position.

(b) Prepare a sample by cutting the appropriate size (generally <1/gram) and cleaning and drying it.

(c) Place the weighing pan on the balance. It will automatically tare.

(d) Place the sample on the pan. When the weight stabilizes push the ENTER key.

Up to 50 sample weights may be entered.

(e) Push the LOADER CONTROL switch on the furnace, and place the sample in the loading hole.

(f) Push the LOADER CONTROL switch again. The lower electrode will open. Discard any electrode and clean the upper and lower electrodes with the brush.

(g) Place a new crucible on the lower electrode and press the LOADER CONTROL switch.

- The lower electrode will close and the analysis will automatically begin.
- The printer will print % nitrogen upon completion of the analytical cycle.

(h) Continue at step (e) if more than one weight was put in the weight stack initially.

The operator should familiarize himself with pages 36-53 of the LECO Instruction Manual before operating the instrument.

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PNL TECHNICAL PROCEDURE

4.8 CALCULATION

There are no calculations to perform.

5.0 BIBLIOGRAPHY

Instruction Manual, 782-700 System, TN-114 Nitrogen Analyzer, LECO Corp., St. Joseph, Michigan.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-242, (Replaces 4-30.8), SURFACE CHLORIDE AND FLUORIDE USING SWAB TEST

1.0 APPLICABILITY

One square foot of surface is swabbed alternately with wet and dry gauze pads to remove soluble halides. The pads (swabs) are washed free of the halides by passing water through them in a hypodermic syringe. The wash water (test solution) is analyzed for chloride by constant current coulometry and for fluoride by ion selective electrode potentiometry.

- (a) Material Water-soluble chloride and fluoride on metal surfaces.
- (b) Range The detection limits per test are about 5 μg chloride and 0.3 μg fluoride in the swabs, which correspond to 0.035 and .0002 μg per square inch over a once square foot of surface for chloride and fluoride respectively.
- (c) Reliability Pads spiked with known amounts of chloride and fluoride were analyzed with the following results:

<u>μg Cl</u>	<u>RSD</u>	<u>% Recovery</u>
50	12	104
500	6	100
<u>μg F</u>		
5	4	91
50	2	95

- (d) Interferences Bromide, iodide, sulfide, and other ions that form insoluble silver compounds are measured as chloride. Variations in pH and ionic strength between standards and test solutions adversely affect the fluoride measurement. Therefore, a buffering solution is used to control those variables.

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PNL TECHNICAL PROCEDURE

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

This method is based upon dissolving water-soluble chloride and fluoride from the surfaces of cladding components by swabbing alternately with wet and dry gauze pads. The pads are washed free of the halides and then the concentrations of those halides in solution are measured.

The lower limits of the techniques used to measure the concentrations in the final solution are about 0.2 and 0.02 $\mu\text{g/ml}$ of chloride and fluoride respectively. Under the conditions of this method, the detection limits are equivalent to 0.035 and 0.002 μg per square inch chloride and fluoride, respectively, when one square foot of surface is swabbed. These lower limits for surface concentrations are 14 and 250 times below the established specification limit for surface chloride and fluoride of 0.5 μg per square inch. Thus, this method is more than adequate for determining if cladding components meet the surface chloride and fluoride specification.

A commercially available chloride analyzer is used to measure the chloride content of the final solution [Section 5.0(a)]. The instrument electrolytically generates silver ions at constant current from a silver electrode. Insoluble silver chloride is formed until all of the chloride has been precipitated. The end point is detected by the amperometric indication of the excess silver ions across an indicator electrode pair, and the generating current is shut off automatically at a pre-set increment of indicator current. Since the rate of generating silver ion is constant, the amount of chloride precipitated is proportional to the time required for the titration according to Faraday's law [Section 5.0(c)].

¹ Specification limit established for cladding components for the Fast Flux Test Facility (FFTF).

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The fluoride content of the final solution is measured with the fluoride-selective electrode, which is highly specific for fluoride and which responds linearly on a semi-log plot over a fluoride concentration range of 19 mg/ml to about 0.2 $\mu\text{g/ml}$ Section 5.0(b) and (d). The electrode responds, however, to fluoride ion activity and not concentration; therefore, it must be calibrated with fluoride standards to relate response to concentration.

To ensure the reliability of the fluoride measurement, the solution matrix of the calibration standards must be the same as that used for the samples. This is necessary because the ionic strength, complexation, and the pH of solutions affect the electrode response. Thus, variations in these conditions between standards and samples will bias the measurement. Therefore, the calibration standards and sample solutions are prepared in the buffering solution.

4.2 APPARATUS

- (a) Automatic chloride titrator, Aminco-Cotlove, American Instrument Co.
- (b) Fluoride ion selective electrode/reference combination, Orion 96-09.
- (c) Forceps, 25-cm. Rinse thoroughly with deionized or distilled water and store in plastic bags.
- (d) Gauze pads, 7.6 x 7.6 - cm, 12-ply (Johnson and Johnson Steripads or equivalent). The pads must be washed before use to remove chloride and fluoride contamination. Prepare as follows;
 - 1. Remove 100 gauze pads from their envelopes and place them in a 2000 ml beaker.
 - 2. Add deionized or distilled water until the pads are covered.
 - 3. Boil the gauze pads eight to ten hours changing the water every hour.
 - 4. Set up the drying tube (Item q, Section 4.2) with the pull up screen near the bottom of the tube.
 - 5. Using clean forceps place the pads on the screen in the tube (the tube will hold more than 1000 pads).

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6. Cover the top of the tube with tissue paper. Turn on the vacuum supply to the tube to remove the residual water from the tube and pads for a few seconds. (The cover on the tube filters the air passing through as the water is removed).
 7. Turn off the vacuum supply to the tube. Remove the cover and slowly add 1-pt acetone to the tube allowing the acetone to flow down the tube to soak all the pads.
 8. Turn on the vacuum, and pour an additional pint of acetone over the pads.
 9. Replace the cover, and continue pulling air through the tube until the pads are dry. The pads will be dry when water no longer condenses on the outside of the glass drying tube.
 10. Remove four pads and check their chloride and fluoride contents according to the procedure beginning at section 10.2. If the total chloride and fluoride found in the pads are equal to or less than 5 and 0.3 μg respectively, the pads are adequately clean. If not, repeat steps 2 to 9 (in Step 3, boil for an additional 3 hours changing the water each hour).
 11. Place two pads in each of the 1 and 8 oz. plastic bottles.
 12. Add 7 ml of deionized or distilled water to the 1 oz. bottles and place caps on all bottles.
- (e) Graduated cylinders, 25 ml.
- (f) Hypodermic syringe, 30 ml.
- (g) Magnetic stirrer.
- (h) Magnetic stir bar, 0.8 cm long.
- (i) Digital pH/mV meter, Beckman Model 4500 or equivalent.
- (j) Parafilm M, American Can Company.
- (k) Plastic or rubber gloves. Rinse the outside of the gloves thoroughly with deionized or distilled water. Some types of gloves do not need to be rinsed, but this must be determined for each type and lot.

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PNL TECHNICAL PROCEDURE

- (l) Plastic bags, polyethylene, about 15- by 24-cm.
- (m) Plastic bottles and caps, polyethylene, 1 and 8 oz. These bottles must be leached or rinsed with deionized or distilled water before use.
- (n) Plastic ruler, flexible.
- (o) Plastic beaker, 8 ml.
- (p) Wash bottle.
- (q) Drying tube, for gauze pads. A vertical glass tube, 60-cm long by 6-cm o.d., with an 8-mm o.d. outlet at the bottom connected to a vacuum system that draws air down the tube. An aspirator flask is placed in the vacuum line so that the acetone and any residual water will be trapped in the flask. A coarse circular plastic screen (with about 7-mm holes) attached to 2 stiff wires is used to draw the pads up the tube.

4.3 REAGENTS

- (a) Acetone, ACS reagent grade.
- (b) Deionized or distilled water chloride-free ($<0.1 \mu\text{g/ml}$).
- (c) Nitric-acetic acid solution, 1M HNO_3 - 4M acetic acid containing 20 to 30 $\mu\text{g Cl/ml}$ of solution. Prepare by adding 20 to 30 ml of the 1 mg/ml chloride standard to each liter of the nitric-acetic acid solution. Mix thoroughly.
- (d) Gelatin solution. See Operations Manual for the chloride titrator [Reference (c), Section 5.0].
- (e) Silver cleaning paste. See Operations Manual for chloride titrator. [Reference (c), Section 5.0].
- (f) Total Ionic Strength Adjustment Buffer (TISAB). Add 57 ml of glacial acetic acid, 58 g of sodium chloride and 2 g of 1,2-cyclohexylene dinitrilo tetraacetic acid (cyclohexane diamine tetraacetic acid) to 500 ml of deionized water in a 1-l beaker. Stir to dissolve and cool to room temperature. Adjust the solution pH to 5.3 ± 0.2 with 5M NaOH (about 150 ml), which has been prepared with deionized water. Transfer the solution to a 1-l volumetric flask and dilute to volume with deionized water.

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PNL TECHNICAL PROCEDURE

4.4 STANDARDS

(a) Calibration Standards

1. Chloride standard, 2000 $\mu\text{g/ml}$. Dissolve 1.6485 g of sodium chloride, previously dried at 110°C , in deionized water and dilute to 1 l with deionized water. A commercial standards of 1000 $\mu\text{g Cl/ml}$ ($\pm 0.5\%$) is satisfactory.
2. Fluoride standards. Prepare a stock solution of 100 $\mu\text{g F/ml}$ by dissolving 0.2210 g of sodium fluoride, previously dried at 100°C , in deionized water and diluting to 1 l. A commercial standard of 100 $\mu\text{g F/ml}$ ($\pm 0.5\%$) is satisfactory. Prepare a set of calibration standards of 10, 1.0, 0.20, 0.05 and 0.01 $\mu\text{g F/ml}$ by appropriate dilutions of the stock solution.

(b) Control Standard. None required (see Subsection 4.6).

4.5 SAFETY

Observe the general laboratory safety rules.

4.6 QUALITY CONTROL

4.6.1 Calibration

(a) Chloride Titrator. Calibration involves the determination of a calibration blank and a calibration factor. Base values are determined for both by making at least nine measurements of each over a period of three working days or more. The base value is the average value obtained. The base values are used in calculations.

1. Calibration blank. Determine the blank by following Subsection 10.3 using 5.00 ml of deionized water at Step (c) in place of sample. At least three blanks shall be determined at the start of each 8-hr shift during which chloride titrations are made. If the average of the three blanks is within ± 1.0 sec. of the base value, proceed with Part 2. If not, investigate and correct the problem before proceeding.

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2. Calibration factor. Determine the calibration factor by following Subsection 10.3, using 50.0 μ l of the calibration standard and 5.00 ml of deionized water at Step (c) instead of a sample solution. The calibration factor shall be determined at least once each month during which chloride titrations are made. If the result is not within $\pm 1\%$ of the base value, investigate and correct the problem before proceeding with samples.
- (b) Fluoride electrode. The fluoride electrode shall be calibrated within 2 hr of making fluoride measurements because the calibration may drift with time. Calibrate the electrode as follows:
1. Assemble the electrode apparatus.
 2. Turn on the stirrer and adjust it to a moderate speed.
 3. Rinse the electrode with deionized or distilled water, pipet 100 ml of TISAB and 1.00 ml of 0.01 μ g F/ml standard into the 8-ml plastic beaker, place the electrode in the solution and let it soak until a stable reading is obtained.
 4. Remove the standard solution from the beaker and rinse the beaker with deionized or distilled water. Repeat Step 3. The reading should stabilize within 5 min and it must agree within 2 mV of the reading in Step 3. If so, record the reading; if not, repeat Step 3.
 5. Repeat Step 4 with the 0.05, 0.20, 1.0, and 10 μ g F/ml calibration standards (in that order) and record these readings.
 6. Plot the calibration readings from Steps 4 and 5 on 3-cycle semi-log graph paper with fluoride concentration on the log scale.

4.6.2 Control

Control is not established.

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PNL TECHNICAL PROCEDURE

4.7 ANALYSIS

Extreme care shall be taken to prevent extraneous chloride and fluoride contamination of reagents and equipment. Wash (test) solutions shall be analyzed for fluoride within 2 hr of preparing the calibration curve because the fluoride calibration may drift with time.

4.7.1 Removal of Chloride and Fluoride from Surface

One test will require 4 pads; 2 wet ones in the 1-oz bottle and 2 dry ones in the 8-oz bottle. The person doing this work must wear pre-washed plastic or rubber gloves.

- (a) Measure a test area of about 1 ft².

For large, flat surfaces this can be done with a template. On other surfaces, the area measurement can be done using the plastic ruler.

- (b) Remove a wet pad from the 1-oz bottle and swab the test surface firmly; place the pad in an empty 8-oz bottle.

If the surface being swabbed is not horizontal, care must be taken to avoid excess water from the pad running out of the test area and being lost.

- (c) Swab the area next with a dry pad and place this pad in the 8-oz bottle containing the first (wet) pad.

- (d) Repeat Steps (b) and (c) with new wet and dry pads.

- (e) Record the area of the surface tested in square inches and describe the test area. The 8-oz bottle containing these pads should be labelled with this information.

4.7.2 Separation of Chloride and Fluoride from Pads

The graduated cylinders and syringe used in this Subsection must be reserved for this analysis. When not in use the cylinders should be filled with deionized or distilled water and the syringe should be stored in a covered bottle.

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- (a) Remove the 4 pads from the bottle [Subsection 4.2(d)] with clean forceps and place them in the 30-ml syringe.
- (b) Rinse the bottle with about 5 ml of deionized or distilled water and pour the rinse into the syringe.
- (c) Insert the plunger into the syringe and squeeze the water into a clean 25-ml graduated cylinder.
- (d) Remove the plunger and add sufficient deionized water to the syringe so that 25 ml will be collected.
- (e) Replace the plunger and squeeze the water into the same graduated cylinder (Step c).
- (f) Dilute to volume with deionized water, cover the cylinder with Parafilm and mix thoroughly.

4.7.3 Chloride Measurement

If the silver electrodes are not bright, start at Step (a); otherwise start at Step (b).

- (a) Clean the silver electrodes with silver cleaning paste and wash thoroughly with deionized or distilled water.

The first one or two chloride measurements made after this cleaning step may not be satisfactory. Clean only if necessary.

- (b) Pipet 1.00 ml of the HNO_3 -acetic acid solution containing chloride into a clean 10-ml titration cell.

Because this chloride constitutes a significant blank, the amount of acid to improve the sensitivity of the titration by providing sufficient chloride to exceed the solubility product of silver chloride. Otherwise, a significant error occurs when titrating a few micrograms of chloride.

- (c) Pipet 5.00 ml of sample solution from Subsection 4.7.2, Step (f) into the titration cell.

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PNL TECHNICAL PROCEDURE

- (d) Add 3 or 4 drops of the gelatin solution.
- (e) Rinse the electrodes with deionized or distilled water.
- (f) Place the titration cell into position on the chloride titrator.
- (g) Begin stirring by turning the titrate switch to the "1" position.
- (h) Set the timer counter to zero.
- (i) Set the adjustable (red) pointer on the meter-relay 10 divisions above the indicator (black) pointer.

The Operations Manual for the chloride titrator has instructions for initially setting the indicator pointer.

- (j) Begin the titration by turning the titrate switch to the "2" position.
- (k) Record the time when the counter stops.

This is the titration time for the sample (T_s), calibration standard (T_{st}) or calibration blank (T_{cb}), depending upon what is being determined.

4.7.4 Fluoride Measurement

- (a) Prepare the electrode for the fluoride measurement by following Steps 1 and 2 of Part (b), Subsection 4.6.1 and then rinse the electrode with deionized water.
- (b) Pipet 1.00 ml of sample solution and 1.00 ml of TISAB into the 8-ml plastic beaker.
- (c) Place the electrode into the solution and record the mV reading after a stable reading is obtained.
- (d) Obtain the fluoride solution concentration ($\mu\text{g/ml}$) from the calibration curve.

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PNL TECHNICAL PROCEDURE

4.8 CALCULATION

Calculate the chloride calibration factor and the concentration of chloride and fluoride on the sample using the appropriate equations below.

(a) Chloride Calibration Factor.

$$F = \frac{Cl}{T_{st} - T_{cb}}$$

where F = calibration factor, μg of chloride per sec

Cl = μg of chloride added from the chloride standard [Step 2 of Part (a), Subsection 4.6.1]

T_{st} = titration time of standard [Step (k) of Subsection 4.7.3]

T_{cb} = titration time of calibration blank [Step (k)].

(b) Concentration of Chloride on Surface of Sample.

$$C_a = \frac{F(T_s - T_{cb})V}{SA}$$

where C_a = μg chloride per in.^2 of surface

F = calibration factor

T_s = titration time of sample [Step (k) of Subsection 4.7.3]

T_{cb} = titration time of calibration blank

A = sample aliquot, normally 5.00 ml

S = area of test in in.^2

V = total volume of solution collected, usually 25.0 ml.

Unless otherwise instructed, report results to two significant figures.

(c) Concentration of Fluoride on Surface of Sample.

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$$F = \frac{F_a V}{a S}$$

where F_a = $\mu\text{g F/in.}^2$ of surface
 F_s = $\mu\text{g F/ml}$ from Step (d), Subsection 4.7.4
 S = area of test in in.^2
 V = total volume of solution collected,
usually 25.0 ml.

Unless otherwise instructed, report results to two significant figures.

5.0 BIBLIOGRAPHY

- (a) E. Cotlove, H. W. Tranthan, and R. L. Bowman, "An Instrument and Method for Rapid, Accurate, and Sensitive Titrations of Chloride in Biologic Samples," J. Lab. Clin. Med., 51, 461 (1958).
- (b) M. S. Frank and J. W. Ross, Jr., "Electrode for Sensing Fluoride Ion Activity in Solution," Science, 154, 1553 (1966).
- (c) Operations Manual, Aminco-Cotlove Automatic Chloride Titrator, Instruction No. 951, American Instrument Co., Inc., Silver Springs, MD.
- (d) G. A. Rechnitz. "Ion-Selective Electrode," Chem. Eng. News, 45, 153, June 12 (1967).

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-243, (Replaces 4-40.3), WATER LEACHABLE CHLORIDE AND FLUORIDE IN CLOTH AND OTHER MATERIALS

1.0 APPLICABILITY

This method is for the determination of water soluble chloride and fluoride in their ionic form leached from materials such as cloth, paper, sponge, etc. The sample is immersed in a minimum amount of water which is gently boiled for 30 minutes. The water is analyzed for chloride by constant current coulometry with an amperometric end point for fluoride by ion selective electrode potentiometry.

- (a) Material Water soluble ionic chloride and fluoride on or in water immersible material.
- (b) Range The detection limits per test are about 0.1 $\mu\text{g/ml}$ chloride and 0.01 $\mu\text{g/ml}$ fluoride in the leach water solution. The actual concentration range for the chloride and fluoride depends on sample material size and configuration.
- (c) Reliability There is no estimate of reliability for most of the samples. However, chloride and fluoride added to cloth samples can be recovered to within $\pm 15\%$ (relative) of the amount added for as little as 50 μg of chloride and 5 μg of fluoride.
- (d) Interferences Bromide, iodide, sulfide, and other ions that form insoluble silver salts are measured as chloride. Variations of pH and ionic strength between standard and test solutions as well as the presence of ions complexing fluoride can affect the fluoride result; and therefore, a buffering solution is used to control these variables.

Author	Date	Project Mgr.	Date	QAD Representative	Date
RW Stromatt	9/19/88	N/A		LJ Ethridge	9/19/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	9/19/88	All original signatures on file	
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PNL TECHNICAL PROCEDURE

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

Water soluble ionic chloride and fluoride are removed from a sample by leaching in gently boiling water for 30 minutes. The leach solution is then analyzed for the chloride and fluoride.

Samples for this analysis include gloves, plastic bags, plastic sheet, rags, tape, sponges, solid objects, etc. The sensitivity required for the analysis will likely be set by the requester. Since the actual sensitivity depends on the volume of water required to cover the sample, it is important to devise a configuration of sample and water container to satisfy the requester's sensitivity requirements. For example, if the specification for a plastic sheet were $0.5 \mu\text{g}/\text{in.}^2$, it would be desirable to have the detection limit be $0.2 \mu\text{g}/\text{in.}^2$. This means that a plastic sheet with 100-in.^2 total area would have to be leached in 200 ml of water.

Results are reported as $\mu\text{g}/\text{in.}^2$ and/or $\mu\text{g}/\text{g}$. Usually, the requester wants the result for plastic sheet, tape and other non-porous materials such as solid metal objects in terms of $\mu\text{g}/\text{in.}^2$. Results for porous materials such as cloth are usually reported as both $\mu\text{g}/\text{in.}^2$ and $\mu\text{g}/\text{g}$. Results for porous material such as sponge, for which a surface area cannot be measured, are reported as $\mu\text{g}/\text{g}$. For non-porous material such as plastic sheet, one should consider both sides of the sheet in the surface area calculation. On the other hand, for porous material such as cloth, the surface area used would be one side only, since chloride on the outer surface of a piece of cloth lying on a steel surface can diffuse to the inner or contact surface.

4.2 APPARATUS

- (a) Automatic chloride titrator, Aminco-Cotlove American Instrument Co.

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- (b) Balance, top loading, capable of weighing to the nearest 0.01 g.
- (c) Fluoride Electrode, ion selective/reference combination, Orion 96-09.
- (d) Magnetic stirrer and stir bars.
- (e) Digital pH/mV Meter, Beckman Model 450C or equivalent.
- (f) Plastic beaker, 8 ml.

4.3 REAGENTS

- (a) Deionized or distilled water, chloride-free ($<0.1 \mu\text{g/ml}$).
- (b) Gelatin solution, see Operations Manual for the chloride titrator [Reference (c), Section 5.0].
- (c) Nitric-acetic acid solution, 1M HNO_3 -4M acetic acid containing 20 to 30 $\mu\text{g Cl/ml}$ of solution. Prepare by adding 20 to 30 μl of the 1 mg/ml chloride standard to each liter of the nitric-acetic acid solution. Mix thoroughly.
- (d) Silver cleaning paste, see Operations Manual for the chloride titrator. [Reference (c), Section 5.0].
- (e) Total ionic strength adjustment buffer (TISAB). Add 57 ml of glacial acid, 58 g of sodium chloride and 2 g of 1, 2-cyclohexylene dinitrilo tetra-acetic acid (cyclohexane diamine tetraacetic acid) to 500 ml of deionized water in a 1-l beaker. Stir to dissolve and cool to room temperature. Adjust the solution pH to 5.3 ± 0.2 with 5 M NaOH (about 150 ml), which has been prepared with deionized water. Transfer the solution to a 1-l volumetric flask and dilute to volume with deionized water.

4.4 STANDARDS

- (a) Calibration Standards. Stock solutions of 1000 $\mu\text{g/ml}$ chloride and 100 $\mu\text{g/ml}$ fluoride with accuracy of $\pm 0.5\%$ are obtained from commercial sources. Prepare a set of calibration standards of 10.0, 1.00, 0.20, 0.05, and 0.01 $\mu\text{g F/ml}$ by appropriate dilutions of the stock solution.

4.5 SAFETY

Observe the general laboratory safety rules.

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4.6 QUALITY CONTROL4.6.1 Calibration

- (a) Chloride titrator. Calibration involves the determination of a calibration blank and calibration factor. Base values are determined for both making at least nine measurement of each over a period of three working days or more. The base value is the average value obtained. The base values are used in calculations.
1. Calibration blank. Determine the blank by following Subsection 4.7.2 using 5.00 ml of deionized or distilled water at Step (c) in place of sample. At least three blanks shall be determined at the start of each 8-hr shift during which chloride titrations are made. If the average of three blanks is within ± 1.0 sec of the base value, proceed with Part 2. If not, investigate and correct the problem before proceeding.
 2. Calibration factor. Determine the calibration factory by following Subsection 4.7.2, using 50.0 μ l of the calibration standard and 5.00 ml of deionized or distilled water at Step (c) instead of a sample solution. The calibration factor shall be determined at least once each month during which chloride titrations are made. If the result is not within $\pm 1\%$ of the base value, investigate and correct the problem before proceeding with samples.
- (b) Fluoride electrode. The fluoride electrode shall be calibrated within 2 hr of making fluoride measurements because the calibration may drift with time. Calibrate the electrode as follows:
1. Assemble the electrode apparatus.
 2. Turn on the stirrer and adjust it to a moderate speed.
 3. Rinse the electrode with deionized or distilled water, pipet 1.00 ml of TISAB and 1.00 ml of 0.01 μ g F/ml standard into the crucible, place the electrode in the

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PNL TECHNICAL PROCEDURE

solutions and let it soak until a stable reading is obtained.

4. Remove the standard solution from the crucible and rinse the crucible with deionized or distilled water. Repeat Step 3. The reading should stabilize within 5 min and it must agree to within 2 mV of the reading in Step 3. If so, record the reading; if not, repeat Step 3.
5. Repeat Step 4 with the 0.05, 0.20, 1.0, and 10.0 $\mu\text{g F/ml}$ calibration standards (in that order) and record these readings.
6. Plot the calibration readings from Steps 4 and 5 on 3-cycle semi-log graph paper with fluoride concentration on the log scale.

4.6.2 Control

Control is not established.

4.7 ANALYSIS

Extreme care shall be taken to prevent extraneous chloride and fluoride contamination of reagents and equipment. Leach test solutions shall be analyzed for fluoride within 2 hr of preparing the calibration curve because the fluoride calibration may drift with time.

4.7.1 Leaching Procedure

- (a) Weigh the sample into a clean pre-weighed beaker.

The sample size and beaker volume should be selected to allow the maximum size sample with a minimum leach water volume. In preparing the sample, use care not to contaminate it. Tools to prepare the sample such as knives, scissors and forceps should be washed free of halides and should be handled with care. Washed rubber or plastic gloves should be used if the sample must be handled by hand.

- (b) Add just enough deionized or distilled water to cover the sample and place a watch glass on the beaker.

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- (c) Heat the water to a gentle boil and continue boiling for 30 min.

Porous samples should be stirred and compressed with a glass rod several times during the leach operation.

- (d) Allow the leach water to cool, wash condensate on the watch glass into the beaker and weigh the beaker with sample and water.
- (e) Carefully stir the leach solution and compress porous samples to assure a homogeneous leach solution for the subsequent chloride and fluoride measurements.

4.7.2 Chloride Measurement

If the silver electrodes on the chloride titrator are not bright, start at Step (a); otherwise start at Step (b).

- (a) Clean the silver electrodes with silver cleaning paste and wash thoroughly with deionized or distilled water.

The first one or two chloride measurements made after this cleaning step may not be satisfactory. Clean only if necessary.

- (b) Pipet 1.00 ml of the HNO_3 -acetic acid solution containing chloride into a clean 10-ml titration cell.

Because this chloride constitutes a significant blank, the amount of acid solution added must be accurately pipetted. Chloride is added to improve the sensitivity of the titration by providing sufficient chloride to exceed the solubility product of silver chloride. Otherwise, a significant error occurs when titrating a few micrograms of chloride.

- (c) Pipet 5.00 ml of sample solution from Step (e), Subsection 4.7.1, into the titration cell.
- (d) Add 3 drops of the gelatin solution.

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- (e) Rinse the electrodes with deionized or distilled water.
- (f) Place the titration cell into position on the chloride titrator.
- (g) Begin stirring by turning the titrate switch to the "1" position.
- (h) Set the timer counter to zero.
- (i) Set the adjustable (red) pointer on the meter-relay 10 divisions above the indicator (black) pointer.

The Operations Manual for the chloride titrator has instructions for initially setting the indicator pointer.

- (j) Begin the titration by turning the titrate switch to the "2" position.
- (k) Record the time when the counter stops.

This is the titration time for the sample (T_s), calibration standard (T_{st}) or calibration blank (T_{cb}), depending upon what is being determined.

4.7.3 Fluoride Measurement

The fluoride measurement shall be made within 2 hr of calibration because calibration tends to drift with time.

- (a) Make the measurement by following Steps 1 through 4 of Part (b), Subsection 4.6.1, using 1.00 ml of the leach solution from Step (e), Subsection 4.7.1, instead of calibration standard at Step 3.
- (b) From the electrode mV reading, obtain $\mu\text{g F/ml}$ in the leach solution of the calibration curve.

4.8 CALCULATION

Calculate the chloride calibration factor and the concentration of chloride and fluoride in or on the sample using the appropriate equations below.

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(a) Chloride Calibration Factor

$$F = \frac{Cl}{T_{st} - T_{cb}}$$

where F = calibration factor, μg of chloride per sec

Cl = μg of chloride added from the chloride standard [Step 2 of Part (a), Subsection 4.6.1].

T_{st} = titration time of standard [Step (k) of Subsection 4.7.2].

T_{cb} = titration time of calibration blank [Step 1 of Part (a), Subsection 4.6.1].

(b) Concentration of Chloride on Surface of Sample.

$$C_a = \frac{F(T_s - T_{cb})V}{SA}$$

where C_a = μg chloride per in.^2 of surface

F = calibration factor

T_s = titration time of sample [Step (k) of Subsection 4.7.2]

T_{cb} = titration time of calibration blank

A = sample aliquot, normally 5.00 ml

S = surface area of test in in.^2

V = total volume of leach solution, which is the difference in weights of the beaker and its contents at Steps (a) and (d) of Subsection 4.7.1.

¹ The specific gravity of the solution is assumed to be 1.0.

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PNL TECHNICAL PROCEDURE

(c) Concentration of Chloride in Sample.

$$C_w = \frac{F(T_s - T_{cb})V}{WA}$$

where C_w = μg chloride per g of sample

F = calibration factor

T_s = titration time of sample

T_{cb} = titration time of calibration blank

V = total volume of leach solution [see Part (b), Section 4.8]

A = sample aliquot, normally 5.00 ml

W = weight of sample in g.

(d) Concentration of Fluoride on Surface of Sample.

$$F_a = \frac{F_c V}{S}$$

where F_a = μg fluoride per in.^2 of surface

F_c = μg fluoride per ml of leach solution

S = surface area of test in in.^2

V = total volume of leach solution [see Part (b), Section 4.8].

(e) Concentration of Fluoride in Sample.

$$F_w = \frac{F_c V}{W}$$

where F_w = μg fluoride per g of sample

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PNL TECHNICAL PROCEDURE

F_c = μg fluoride per ml of leach solution

V = total volume of leach solution [see Part (b) of Section 4.8]

W = weight of sample in g.

Unless otherwise instructed, report all results to two significant figures.

5.0 BIBLIOGRAPHY

- (a) E. Cotlove, H. W. Trantham, and R. L. Bowman. "An Instrument and Method for Rapid, Accurate, and Sensitive Titrations of Chloride in Biologic Samples," J. Lab. Clin. Med., 51, 461 (1958).
- (b) M. S. Frank and J. W. Ross, Jr. "Electrode for Sensing Fluoride Ion Activity in Solution," Science, 154, 1553 (1966).
- (c) Operations Manual, Aminco-Cotlove Automatic Chloride Titrator, Instructions No. 951, American Instrument Co., Inc., Silver Springs, MD.
- (d) G. A. Rechnitz. "Ion-Selective Electrode," Chem. Eng. News., 45, 153, June 12 (1967).

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-244, (Replaces 7-30.1), VACUUM OUTGAS OF INTRINSIC GERMANIUM DETECTOR DEWARS

1.0 APPLICABILITY

This procedure is for vacuum cleanup of the Intrinsic Germanium Detector Dewars used at the Fast Flux Test Facility (FFTF) for Fuel Failure Monitoring. After prolonged usage, air in-leakage into the vacuum chambers of the Dewar flasks decreases the resolution of the detectors and increases the use of liquid nitrogen. The way to rejuvenate the Dewar is to vacuum outgas the Dewar and the getter materials in the vacuum chambers to remove as much gas as possible.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE

Cognizant scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

Richardson valves for connecting the Dewar vacuum valves. Obtain these from FFTF Engineering.

Vacuum system with vacuum gauges.

Heating system such as an air wand heater.

Temperature controller.

4.2 Performance Check

None required.

Author	Date	Project Mgr.	Date	QAD Representative	Date
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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	8/2/88	All original signatures on file	
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4.3 Vacuum Outgassing

Remove the covers over the two valves on the vacuum chambers on the Dewar. One valve is under a small aluminum cover secured with two machine bolts on the detector end of the cold finger and the other valve is covered with a slip fit cap. Install the Richardson valves on to the Dewar valves. Use a little high vacuum grease on the 'O' rings. Connect the outlets on the valves to a vacuum rack and check for leaks. Leak checking can be done simply by observing vacuum gauges and/or watching pressure rise after the initial pump down.

Before opening the Dewar valves, insure that the Richardson valves are connected to the roughing system on the vacuum rack. The Dewar may be at or close to atmospheric pressure and opening to the high vacuum system could damage or trip out the pumps.

Open the Dewar valves by inserting and engaging the Richardson valves and turning the Dewar valves one and a half turns counterclockwise. Note the pressure rise if any. When the pressure is below about 0.1 Torr switch to the high vacuum pump. Do another simple leak check. If the Dewar appears to have a large leak rather than just a high gas load problem, use a helium leak detector to locate the leak.

When the Dewar is at a reasonable vacuum (gauge pressure of $10E-5$ Torr), it is ready for heating. Insert a heat wand into neck of the Dewar. Use a ring stand to hold the wand steady and do not touch the Dewar neck. Connect the wand to the building air supply and establish an air flow of at least one scfm through the wand and into the Dewar. Connect the wand to a heater control. Be sure to put the thermocouple into the neck of the Dewar about half-way down. Then set the controller for about one hundred degrees celsius and turn the heat control on. Watch the pressure during the warm up period. The pressure usually goes up to the $10E-4$ Torr range (gauge reading).

Heat the Dewar overnight or over a weekend. Usually the pressure will drop back into the $10E-5$ range while the Dewar is still warm. Cool the Dewar by simply turning off the power to the wand and increasing the air flow.

When the Dewar is cooled the valves can be closed. Insert the Richardson valves into the Dewar valves and turn one and a half turns clockwise until the seats are set fairly firmly without excessive force.

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PNL TECHNICAL PROCEDURE

4.4 Calculations

None needed in the procedure.

4.5 Records

None needed.

4.6 Procedure Qualification

None required. This is a cleaning procedure. The Dewar flasks are checked for acceptability by the customer.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-245, (Replaces 7-30.4), GAS MIXING

1.0 APPLICABILITY

The procedure describes the methods used to mix gases. Gas tags of various isotopic enrichments of xenon and/or krypton are prepared by this method for use in various experiments for fuel or control rod breach locators at the Fast Flux Test Facility (FFTF) or similar facilities. Gas mixtures of most permanent gases can be blended by variations of the procedure.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

High vacuum/gas rack.

Capacitance manometer.

Various gases such as xenon and krypton as needed.

Various gas cylinders for containing mixed gases.

Rotary mixer.

Gas regulators (leak tight) for high pressure gas cylinders.

Thermometer.

Author	Date	Project Mgr.	Date	QAD Representative	Date
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4.2 Performance Check

An occasional check of the proper operation of the pumps and electronics should be made. This can be done by observing readouts and checking set up points such as the zero and span on the capacitance manometer. A reasonable operational check of the manometer can be made by venting and checking the reading against atmospheric pressure. This will expose the vacuum surfaces to air and water and should be done only when it doesn't interfere with the operation of the system. The pressure heads can be calibrated by the vendor or checked against a calibrated head. For most work calibration is not necessary. The usual mixture is made by ratios and if possible the mixture is analyzed prior to use. Most mixes made in the mass spectrometry laboratories have been within a percent or two of the desired composition.

NOTE: Anyone blending gases should be familiar with vacuum equipment, use of compressed gases and the proper use of liquid nitrogen. Further an understanding of the physical chemistry gas laws is required to make gas blends.

4.3 Gas Mixing

A mixture is made by blending pure gases one at a time into a volume (gas cylinder) at calculated pressures until the total pressure for the blend is reached. In this case the volume of the cylinder should be large compared to the connecting lines. The cylinder after removal from the blending rack, must be rotated to mix the gases. The higher the pressure, the longer the rotation. If possible rotate for four hours or longer. Two hours has been sufficient in cases where the blends were made up on an emergency basis. Most gas blends are analyzed by an appropriate method such as gas mass spectrometry to insure that the blend is as specified by the customer or laboratory need. Occasionally, blends are made which are beyond the capability of the laboratory to analyze. In these cases particular care is taken to insure that the pressure and volume measurements are as precise as possible.

Mixtures of condensible gases such as xenon and krypton can be 'frozen' into cylinders with little loss of the valuable gases. This method is used for making 'gas tags'. The isotopically differing starting gases used for the mixes are bled into known volumes to calculated pressures in the vacuum/gas rack and then condensed into a cylinder cooled by liquid nitrogen. The mixture

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must be blended by rotating or otherwise agitated. Gas tags are usually rotated for four hours or more. Gas tags are always analyzed for species content and isotopic distribution.

Care must be used to exclude air by always pumping connecting lines out before the blending operations. The vacuum pumps must be valved off before blending to protect the pumps and avoid losses of valuable gases.

4.4 Calculations

Calculations are usually performed by a hand calculator. The calculations usually involve simple percentage or PVT relations of the ideal gas laws. The calculations are recorded in the appropriate books or binders.

4.5 Records

Records will be maintained and controlled so as to conform with the requirements of MCS-033. Laboratory Record Books and Analytical Reports provide a mechanism for control of most records. ~~Laboratory record book will be used in accordance with PAP-70-1704.~~

4.6 Procedure Qualification

None required. The methods used are those presented in many general chemistry and physical chemistry text books. The ideal gas laws are followed by the permanent gases involved in most gas blending operations.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-246, (Replaces 7-40.4), MASS SPECTROMETER ISOTOPIC ANALYSIS OF GASES

1.0 APPLICABILITY

The analytical method described there applies to the isotopic analysis of gases. Samples requiring this analysis include fission gases and gas tags. This procedure could apply if a backup is needed to analyze FFTF cover gas samples. Other samples can be analyzed with the use of appropriate calibration.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant scientist.

4.0 PROCEDURE

4.1 Equipment and Materials

Magnetic sector mass spectrometer.

Mass spectrometer sample inlet with a molecular leak.

High vacuum/gas separation racks.

Electron bombardment source.

Electron multiplier of faraday cup detectors.

Computer control and data collection system.

Natural occurring gases are used as isotopic reference gases. All gases used as reference standards will be supplied by commercial vendors and shall be research grade or better.

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NOTE: Persons operating this equipment should be fully trained in its use prior to any attempt to analyze samples.

4.2 Performance Check

A performance check is made periodically (usually monthly) to ensure that the instrument response is within 1% of the reference values.

The ANALYST shall perform the following steps unless otherwise specified.

- 4.2.1 Attach a cylinder of natural reference standard gas to the vacuum rack.
- 4.2.2 Evacuate the connecting lines between the cylinder of standard gas and the mass spectrometer's inlet system.
- 4.2.3 Close the valves to the vacuum pumps and allow 50 to 100 microns of natural reference gas into the mass spectrometer's inlet.
- 4.2.4 Introduce the sample into the ion source of the mass spectrometer.
- 4.2.5 Determine which isotope has the highest concentration and adjust signal strength to 90% of full scale for this isotope.
- 4.2.6 Analyze the gas for isotope abundance using the computer control system.
- 4.2.7 Print out a report and compare the isotopic ratios to the accepted values. All isotopic ratios should be within 1% of the accepted values.
- 4.2.8 A copy of the report printout showing the isotopic ratios, from the performance check, will be permanently attached to the laboratory record book, used to record this analysis.
- 4.2.9 Repeat Steps 4.2.1 to 4.2.8 for the next gas to be analyzed.

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4.3 Sample Analysis

The ANALYST shall perform the following steps unless otherwise specified.

- 4.3.1 Attach the cylinder containing the sample gas to the vacuum rack.
- 4.3.2 Evacuate the connecting lines between the sample cylinder and the mass spectrometer's inlet system.
- 4.3.3 Close the valves to the vacuum pumps and allow 50 to 100 microns of sample gas into the mass spectrometer's inlet.
- 4.3.4 Introduce the sample into the ion source of the mass spectrometer.
- 4.3.5 Determine which isotope has the highest concentration and adjust signal strength to 90% of full scale for this isotope.
- 4.3.6 Analyze the gas for isotope abundance using the computer control system.
- 4.3.7 Print out a report and compare the isotopic ratios for each cycle. The ratios should be similar and should not drift up or down.
- 4.3.8 Repeat Steps 4.3.1 to 4.3.7 for the next gas to be analyzed.

4.4 Calculations

Calculations are performed by the computer at the end of each analysis. The control system stops on each isotope to be measured as it steps through its routine. Five cycles are usually run. A cycle consists of measuring voltage output for each mass up and down in a stepping mode. At the end of the analysis routine, isotopic voltage measurement are averaged and isotopic ratios are calculated. Calculations are checked for accuracy during the performance check.

4.5 Records

Records will be maintained and controlled so as to conform with the requirements of MCS-033. Laboratory Record Books and Analytical Report forms provide a mechanism for control of most records. ~~Laboratory record books will be used in accordance with PAP 1704.~~

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PNL TECHNICAL PROCEDURE

4.6 Procedure Qualifications

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

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-247, (Replaces 7-40.6), ANALYSIS OF METALS, METAL ALLOYS AND METAL COMPOUNDS BY X-RAY FLUORESCENCE

1.0 APPLICABILITY

This procedure describes the identification and analysis of various elements within metals, metal alloys and metal compounds using x-ray fluorescence spectrometry. The elements in a sample are bombarded by x-rays, exciting atoms which emit characteristic x-rays from each element. The emitted x-rays are measured by a Si-Li detector and an electronic counting system which present counts versus energy spectra.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

4.2 APPARATUS

4.3 REAGENTS

4.4 STANDARDS

Standards will be NBS or equivalent. Standards will be run in the same manner as samples: see Section 4.7.

4.5 SAFETY

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PNL TECHNICAL PROCEDURE

4.6 QUALITY CONTROL

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.

4.7 ANALYSIS

Done per operating instructions in the Operations Manuals for the KEVEX 770/8000 System.

- 4.7.1 Samples of metals and alloys are placed on the instrument sample turntable in one of 16 numbered positions. The names of the samples and the position number are entered into the system computer in a Names file which becomes a part of the Matrix record.
- 4.7.2 Elements of interest are identified to the computer software "Toolbox" package and the system identifies those secondary x-ray targets best used for a measurement.
- 4.7.3 Conditions are put into the software per the guidance in 4.7.2 and saved in the matrix set up for the respective samples or sample types.
- 4.7.4 Data is collected by exposing the sample to x-rays under the conditions set up previously, i.e., kv, ma, time, range, atmosphere.
- 4.7.5 Following data collection the data is checked visually, peaks are identified and a method of analysis is chosen from the methods available in "Toolbox." Many metals and alloys are analyzed using only 1 secondary target for exposure and using a "Fundamental Parameters" mathematical model for quantitation by a standardless program "ASAP".

For samples requiring more than 1 target for measuring elements of interest in order to use "ASAP" a 1 element standard must be measured by each set of conditions for each target used on the unknown.

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If the samples are the same thickness and shape as available standards, analyses can also be performed using a "Match" routine, an "Exact" routine or a "Least Squares" routine. All of these methods are in the "Toolbox" software and require the measurement of 1 or more standards under the same conditions as the sample.

4.8 CALCULATION

Done per operating instructions in the Operations Manuals for the KEVEX 770/8000 system.

Calculations are done by PDP computer built into the KEVEX system. A number of calculational options are provided in the "Toolbox" software and the choice is dependent upon the sample type and the customers requirements. Normally, the calculations involve:

- 1) Identifying peaks present
- 2) Performing an integration of the peaks to get c/s.
- 3) Calculating the concentration of the elements from the c/s data using either comparisons with data from standards or a standardless routine with mathematical corrections for absorption, efficiency, etc.

4.9 DOCUMENTATION

Records will be controlled according to MCS-033 .
~~Laboratory Record Books shall be controlled according to PAP-70-1704.~~

4.10 EQUIPMENT AND MATERIALS

- KEVEX 770/8000 X-Ray Fluorescence System.
- Helium gas--high purity not required. Used a sweep gas to remove air.
- Plastic sample holders.
- Mylar sheets.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-249, (Replaces 7-40.10), HYDROGEN IN ZIRCALOY BY INERT GAS FUSION/GAS CHROMATOGRAPHY

1.0 APPLICABILITY

A sample is melted within two minutes in a furnace in an inert carrier gas stream. The released gas is swept out of the shielded cell and to a gas chromatograph. Hydrogen is measured by thermal conductivity.

- (a) Material Zirconium and Zirconium alloys. Applicable to any other metals which will melt at 2600°C.
- (b) Range Sample sizes up to 2 grams and 3/8 in. maximum dimension. Hydrogen quantities from 5-10 μg (5 ppm) and up.
- (c) Reliability System recovery is verified with NBS SRM 352, 353, 354. Approximately $\pm 20\%$ at $\leq 20 \mu\text{gH}$, $\pm 10\%$ at $20 \mu\text{g}$ -50 μgH , $\pm 5\%$ at $\geq 50 \mu\text{gH}$.
- (d) Interference None.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

This procedure uses the Inert Gas Fusion method identical to a commercial LECO Hydrogen Analyzer. A sample is fused at 2600°C in

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argon carrier gas in an EF-10 Resistance Furnace is a shielded cell. A LECO XK-10 controls the furnace and carrier gas flow. Released gases are swept out of cell through purification columns, through a gas flow splitter directly into a gas chromatograph for measurement by thermal conductivity detector (see Figure).

Results obtained by the Inert Gas Fusion method agree with those obtained by the ASTM Vacuum Extraction method.

4.2 APPARATUS

- (a) EF-10 furnace, LECO Corp.
- (b) EF-10 Controller, LECO Corp.
- (c) Apparatus, as shown in figure.
- (d) Gas chromatograph, with thermal conductivity detector, Perkin Elmer Sigma 300 or equivalent.
- (e) Graphite sample crucibles, LECO Corp, for use in EF-10.

4.3 REAGENTS

- (a) Magnesium Perchlorate, moisture absorbent.
- (b) Schutze Reagent, LECO Corp., $\text{CO} \rightarrow \text{CO}_2$ conversion.

4.4 STANDARDS

Three hydrogen in titanium standards are available from NBS:

- (a) SRM 352, 47 ppm H_2
- (b) SRM 353, 98 ppm H_2
- (c) SRM 354, 215 ppm H_2

4.5 SAFETY

- (a) Observe the general laboratory safety rules.

4.6 QUALITY CONTROL

Analysis of the NBS standard first determines the calibration factor per use in calculations. Subsequent analyses of standards checks for proper operation of the system and proper recoveries. Recovery of NBS standards should be ± 10 -20%, depending upon the range.

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4.7 ANALYSIS

4.7.1 Instrument Preparation

- (a) If furnace has been idle for 1-2 months or more, the electrode O-rings (both upper and lower) are changed. Place light grease on each O-ring.
- (b) Check Purification column containing Anhydrone/Schutze Reagent. Replace reagents if necessary, particularly Schutze.
- (c) Dust Trap/Column on side of in-cell furnace must be checked. For hydrogen analysis, it should be thin (1/2 in.) tube filled only with glass wool. (For other analyses, i.e., fission gas, this may be fat column filled with hot copper/copper oxide.)
- (d) Check complete gas flow path from supply (argon, helium, etc.) to XK-10, into the cell and furnace, out of cell, through purification columns, into the GC, and to the gas return line to the cell. Also check path from V-3 to XK-10 and return to cell.
- (e) Check argon regulator on cylinder (set at 12-15 psi) and set Gas Miser switch to OPERATE.
- (f) Tools for the handling of samples and crucibles must be clean and totally free of grease. Bring in new tools if necessary.
- (g) When all is ready, turn on coolant circulator in Room 200, then activate XK-10 POWER ON and GAS FLOW switches.
- (h) Close EF-10 electrodes and put XK-10 to STANDBY. Set V-3 to [GC] position and V-5 to [H₂] position.
- (i) The final check should be leak checking by the Deadhead method. Switch V-5 to Ar position, and close V-3 to stop exit flow from the furnace. The flow at FM-3 should decrease to 1.0 or less. If not, a leak is indicated and must be repaired.

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(j) Gas Chromatograph conditions:

Column Temp.: 40°C
Detector Current: N₂/Ar position (push RESET)

(k) Recorder settings:

Scale: 0.1 V. full scale

(l) Valves - There are two important valves used during the procedure:

G.C. Carrier Gas Selection Valve, V-5 (at rear of G.C.)

Deadhead Valve, V-3 (on "From Furnace" gas line, right face of cell)

1. During all times other than actually running a sample, the GC Carrier Selection Valve, V-5, is set to [Ar] position, to allow pure argon carrier gas through the column and detector. At the start of a sample analysis (after electrodes are closed and air flushed from lines), the valve is set to [H₂] position, for carrier gas from the furnace.
 2. The Deadhead Valve, V-3, is usually set for gas flow from furnace to XK-10 and back to cell for normal operation. For a leakcheck test, performed several times throughout the day, the valve is set to the Deadhead position (half-way, no-flow position), allowing no gas flow, thus pressurizing the furnace gas lines to about 6-7 psig for a leak check.
- (m) All gas flows should be checked. Typical flowrates for each flowmeter (FM) should be as follows:

FM - 2	Through GC	10 - 15 sccm
FM - 3	To Furnace	100 - 130 sccm
FM - 5B	Bypass back to cell through flow-spitter	90 - 115 sccm

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PNL TECHNICAL PROCEDURE

- NOTES: 1) Use V-6 to adjust flow split.
2) Flowrate through #2 plus #5B should equal #3.
3) Flowrate through #2 should be ~10% of #3.

(n) Check that recorder trace is stabilized and adjust to +20% of scale using the ZERO control.

4.7.2 Sample Preparation

All samples must be cleaned according to the following procedure, then weighed:

- 1) Ultrasonically clean each sample separately 30 sec in reagent-grade toluene.
- 2) Ultrasonically clean 30 sec in reagent-grade methanol.
- 3) Rinse thoroughly in distilled water.
- 4) Dry, place in peanut vial.

Weight each sample to ± 0.0001 g and record weight in notebook.

4.7.3 General Daily Procedure

After all the above preparations have been completed, the instrument is ready for analyses. The operating procedure is nearly identical for the analysis of blanks, standards, and samples.

The following general procedure should be strictly carried out in the given order:

- (a) Three to five crucible blanks are run first until the blank signal peak height decreases to a consistent 10-20 chart divisions (mV's).
- (b) NBS hydrogen standards (47, 98, 215 ppm) are run.
- (c) At this point, the calibration factor (% recovery) must be calculated for each standard and checked before going on to samples. If at

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PNL TECHNICAL PROCEDURE

least the two higher standards check out to 100% $\pm 10\%$ recovery, then the samples may be begun. If not, rerun blanks, standards, and check for leaks.

- (d) Finally the samples may be started. A standard and/or blank should be run periodically (every 5-6 samples) throughout the day. If a very high sample is encountered, a double or triple 215 ppm standard should be run.
- (e) The last run of the day should be a 98 or 215 ppm standard or blank, depending upon whether the samples are high or low - run a standard if latest samples are ≥ 25 mV, run a blank if samples are ≤ 25 mV.

4.7.4 The operating procedure is nearly identical for the blanks, standards, and samples. It is as follows:

- (a) Clean electrodes and insert crucible with two tin flux discs.
- (b) Set furnace tap setting to give about 1.2 Ka current (tap = 6 or 7).
- (c) Activate XK-10 AUTO SEQUENCE. When current comes on, stall the program for two minutes for extra outgas of crucible. Then let cycle continue until OUTGAS goes off. Activate STANDBY.
- (d) Switch circuit breakers in back of XK-10 to OFF.

NOTE: Samples are manually loaded into the crucible because their size is generally too large for the Autodrop system and the possibility of picking up grease contamination in the chamber (the chamber cannot be cleaned).

- (e) Open electrodes and drop sample into crucible. Be certain that sample does not extend above top of crucible.
- (f) Activate AUTO SEQUENCE (with circuit breakers off!) to start analysis sequence and purge the chamber of air. When OUTGAS light goes off, stall the cycle.

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- (g) Switch V-3 for gas flow to the GC, switch V-5 to the $[H_2]$ position and start the recorder chart drive. Turn circuit breakers back ON. Set EF-10 tap setting for current of 1.0-1 Ka; usually 4 or 5 depending on the sample size.
- (h) Verify that GC (and Minigrator if used) are set to attenuation of 1. Verify that flow indicators on FM-2, FM-3, and FM-5B are within specs (see Step 1.13).
- (i) When GC baseline has stabilized (about 1 minute), continue the AUTO SEQUENCE cycle.
- (j) When "Heat" cycle is complete and furnace turns off, press STANDBY, and allow GC chromatogram to finish.
- (k) When complete, switch V-3 back to normal position and V-5 to [Ar].
- (l) Open electrodes, remove crucible, observe for any sign of incomplete burn, etc. Then dispose of crucible.
- (m) Electrodes must be thoroughly cleaned between analyses.

4.8 CALCULATIONS

(a) Measurements

Always measure peak height (ignore shoulder on rear side of peak).

- (b) Determine the avg blank to use in calculations (1 chart division = 1 mV). Throw out high blank values.

(c) Standards

- 1) Must use ug H in each calculation

$$\text{ug H} = \text{Std conc (ug/g)} \times \text{Std wt (g)}$$

e.g.:

$$98 \text{ ug/g} \times 0.230 \text{ g} = 22.5 \text{ ug H}$$

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- 2) Calculate new calibration factor (sensitivity):

$$\frac{(\text{PkHt} - \text{Blank})}{\text{Std ug H}} = \text{mV/ug}$$

- 3) Calculate % Recovery:

$$\frac{(\text{PkHt} - \text{Blank}) \times 100}{\text{Cal. Factor} \times \text{Std ug H}}$$

e.g.

$$\frac{(40.5 \text{ div} - 15 \text{ div}) \times 100}{1.09 \times 22.5 \text{ Std ug H}} = 103.9\% \text{ recovery}$$

NOTE: If the results are = 100% ± 20%, then the Cal. Factor is good. If it is off, a new Cal. Factor may need to be determined. The normal Cal. factor has been 1.09 mV/ug.

- (d) Samples

$$\frac{(\text{PkHt} - \text{Blank})}{\text{Cal. Fac.} \times \text{smp l wt(g)}} = \text{ppm H in sample}$$

e.g.

$$\frac{(51 \text{ div} - 15 \text{ div})}{1.09 \times 0.9804 \text{ g}} = 33.7 \text{ ppm H}$$

- (e) If you have any doubts about any particular result, i.e., odd peak, air, poor burn, etc., then asterisk * the result and state your concern. This is important to do.

5.0 BIBLIOGRAPHY

Operation Manual Procedure for LECO XK-10
Operation Manual for LECO EF-10
Operation Manual for Perkin-Elmer Sigma 300 Gas Chromatograph
Operation Procedure for LECO RH-1

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FIGURE 1. Schematic for Hydrogen in Zircaloy

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-250, (Replaces 7-40.11), DETERMINATION OF HYDROGEN IN METALS
BY THE INERT GAS FUSION METHOD

1.0 APPLICABILITY

Metallic samples are melted with a flux in a stream of argon. Hydrogen is evolved and swept by the argon through a chromatographic column to a thermal conductivity detector where it is measured.

- (a) Material Non-volatile metals such as steels, titanium, copper and scandium.
- (b) Range 2 to 1000 wppm of hydrogen.
- (c) Reliability Blank and calibration checks performed with each set of samples.
- (d) Interferences Possible instrument damage from volatile metals, e.g., zinc and mercury.

2.0 DEFINITIONS

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

This method is based on the use of the Laboratory Equipment Company (LECO) model RH-1SP hydrogen determinator; an instrument designed specifically for measuring hydrogen in metals.

Author	Date	Project Mgr.	Date	QAD Representative	Date
RF Keough	8/10/88	N/A		LJ Ethridge	8/10/88
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N/A		WC Weimer	8/9/88	All original signatures on file	
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4.2 APPARATUS

- (a) Balance, capable of measuring to 10 ug.
- (b) LECO RH-1SP Hydrogen Determinator
- (c) Graphite crucibles

4.3 REAGENTS

- (a) Standard metals, tracable to the National Bureau of Standards as to hydrogen content.
- (b) Tin Flux
- (c) Acetone, reagent grade
- (d) toluene, reagent grade

4.4 STANDARDS

Standard metals, tracable to the National Bureau of Standards as to hydrogen content.

4.5 SAFETY

- (a) Observe the general laboratory safety rules
- (b) Touch used crucibles with caution; they may be hot.

4.6 QUALITY CONTROL

Standards and blanks are run before and during each set of samples. They are run by the same procedure as the samples. For a single sample, a total of at least 4 blanks plus standards will be run. For a set of six samples, at least 8 blanks plus standards will be run. All samples will be run at least in duplicate if sufficient material is available.

4.7 ANALYSIS

4.7.1 Sample Preparation

Preparation depends on the specific sample and the needs of the sample originator. Most samples must be cut to a suitable size. This can be done with snips or a hack saw in most cases. All tools must be free

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PNL TECHNICAL PROCEDURE

of rust, grease and paint. A final surface cleaning with toluene or acetone in an ultrasonic bath is generally employed to remove grease or finger oils.

4.7.2 Analytical Procedure

- (a) Weight the sample (or standard) to within 0.5%. Maximum weight is 1 gram.
- (b) Place the sample in the LECO loading chamber and push the slide in.
- (c) Place a crucible containing a pellet of tin on the pedestal, then raise the crucible into position.
- (d) Push the OFF GAS button.
- (e) When the green light comes on, rotate the sample chamber to drop the sample into the crucible.
- (f) Push the ANALYZE button.
- (g) When the green light comes on again, the digital display will lock and the micrograms of hydrogen found in the sample will be indicated.
- (h) Remove and discard the used crucible. Repeat the procedure with more samples, standards or blanks.

4.8 CALCULATIONS

$$(a) \quad \text{wppm Hydrogen} = \frac{(H - B)(T)}{(W)(F)}$$

where,

H = hydrogen found in the sample (μg)
B = Hydrogen found in blank (μg)
T = True micrograms of hydrogen in standard
W = Weight of sample in grams
F = Hydrogen found in standard (μg)

5.0 BIBLIOGRAPHY

NONE

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-251, (Replaces 7-40.12), DETERMINATION OF OXYGEN IN METALS BY THE INERT GAS FUSION METHOD

1.0 APPLICABILITY

A sample contained in a graphite crucible with nickel flux is heated by passing low voltage current through the graphite crucible in a stream of flowing argon. As the sample melts and alloys with the flux, carbon from the crucible reacts with oxygen in the sample to form carbon monoxide gas. The carbon monoxide is swept by the argon through a purification system and into an optical cell where the attenuation of an infrared light beam provides a measure of carbon in the sample. An integrator, calibrated in micrograms of oxygen, converts the analog detector response to a digital readout.

- (a) Material Non-volatile metals such as steels, titanium, copper and vanadium.
- (b) Range 5 to 1000 wppm of oxygen.
- (c) Reliability Blanks and calibration checks run with each set of samples.
- (d) Interferences Volatile metals such as zinc and mercury may damage the instrument.

2.0 DEFINITIONS

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

Author	Date	Project Mgr.	Date	QAD Representative	Date
RF Keough	10/8/88	N/A		LJ Ethridge	8/10/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	8/9/88	All original signatures on file	
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PNL TECHNICAL PROCEDURE

4.1 DISCUSSION

This method is based on the use of the Laboratory Equipment Company (LECO) model RO-116 oxygen determinator; an instrument designed specifically for measuring oxygen in metals.

4.2 APPARATUS

LECO Oxygen analyzer RO-116
Tweezers
Wire cleaning brush
Graphite crucibles
Balance, capable of measuring to 10 μ g

4.3 REAGENTS

- (a) Nickel coils for flux
- (b) Metal standards, certified by the National Bureau of Standards as to hydrogen content
- (c) Acetone, reagent grade
- (d) Toluene, reagent grade

4.4 STANDARDS

LECO oxygen standards. One gram pieces of metal containing various certified oxygen contents.

4.5 SAFETY

- (a) Observe the general laboratory safety rules
- (b) Handle used crucibles with caution; they may be hot

4.6 QUALITY CONTROL

Standards and blanks are run before and during each set of samples by the same procedure as the samples. For a single sample a total of at least 4 blanks plus standards will be run. For a set of six samples, at least 8 blanks plus standards will be run. All samples will be run at least in duplicate if sufficient material is available.

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PNL TECHNICAL PROCEDURE

4.7 ANALYSIS

4.7.1 Sample Preparation

- (a) Use clean metal snips or hacksaw to cut samples as necessary to reduce the weight or size.
- (b) Clean and degrease samples by ultrasonic cleaning in reagent grade grease solvent (acetone or toluene) followed by drying in air or vacuum.

4.7.2 Oxygen Measurement

- (a) Press the Loader Control switch one time. The sample drop mechanism will open. Load the weighed sample into the sample drop mechanism.
- (b) Press the Loader Control switch again. The electrodes will open. Remove any used crucible and clean the electrodes. Place a new crucible on the electrode and put one half of a nickel coil into the crucible.
- (c) Press the Loader Control switch again. The instrument will run the analysis and display μg of oxygen found on the printer.

4.8 CALCULATIONS

$$\text{wppm Oxygen} = \frac{(O - B)(T)}{(W)(F)}$$

where,

O = oxygen found in the sample (μg)
B = oxygen found in blank (μg)
T = true micrograms of oxygen in standard
W = weight of sample in grams
F = oxygen found in standard (μg)

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-254, (Replaces 7-40.19), IMPURITY SEPARATION BY LIQUID-LIQUID EXTRACTION

1.0 APPLICABILITY

Solutions containing uranium and plutonium are extracted with TBP (Tri-Butyl Phosphate) in Hexane. The resulting U-Pu free solutions may be analyzed for impurities by ICP-AES without interferences. Elemental impurity recoveries are determined by adding known amounts of the impurities of interest to starting solutions.

- (a) Material Solutions containing U/Pu.
- (b) Range 0 - ~400 g/l HM.
- (c) Reliability Four liquid/liquid contacts reduces U/Pu to <100 ug/ml.
- (d) Interferences N/A.

2.0 DEFINITIONS

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

Determination of impurities in uranium and or plutonium bearing solutions requires separation due to their extremely complex emission spectra. The liquid/liquid extraction technique removes the interferences completely while leaving most impurity elements in the aqueous phase for subsequent ICP-AES measurement. Most

Author	Date	Project Mgr.	Date	QAD Representative	Date
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PNL TECHNICAL PROCEDURE

common metal impurities have reported recoveries of 80-100% except Si which is approximately 50%. One element of particular interest, Gd, has a recovery in the 80-100% range.

Sample acidity is adjusted to ~3 N HNO_3 and mixed with an equal volume of 30% TBP. The organic phase is separated and discarded and the procedure repeated. Two additional contacts are made after adjustment of the aqueous phase to ~4 N HNO_3 . The aqueous phase is evaporated to remove residual organics and finally diluted for analysis.

Elements of particular interest may be added to separate samples in known amounts prior to separation as a check for recovery.

4.2 APPARATUS

- (a) Hot plate.
- (b) Pipet, Eppendorf type, 100 λ , 200 λ , 1000 λ with disposable tips.
- (c) Glass vials, 8 ml with caps.
- (d) Transfer pipet with fine glass tip.

4.3 REAGENTS

- (a) Tri-Butyl Phosphate.
- (b) Hexane.
TBP/Hexane mixture is 30 v/o.
- (c) Ultrex grade concentrated HNO_3 .
- (d) Deionized water.
- (e) 3N HNO_3 made with Ultrex acid.

4.4 STANDARDS

Elemental spikes may be added to samples as required. Solutions used are Spex Industry standard solutions at 1000 ug/ml or dilutions thereof.

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PNL TECHNICAL PROCEDURE

4.5 SAFETY

- (a) Plutonium bearing materials are radioactive and toxic. Precautions are required to avoid contamination of the laboratory and personnel.
- (b) Observe general laboratory safety rules.
- (c) Samples containing uranium only may be extracted in a hood.

4.6 QUALITY CONTROL

Control is established by requirements of particular analyses. Elemental spikes and/or multi-level spikes may be used as required.

4.7 PROCEDURE

4.7.1 Pipet 1 ml sample into an 8 ml vial.

Labeled vials are used for spikes as required. A blank is also carried through the procedure.

The acid concentration of the sample needs to be known
PNL-ALO-256.

4.7.2 Extraction

- (a) Adjust acid concentration to ~3N with Ultrex concentrated HNO_3 or H_2O as required. Adjust volume to 2 ml (see step 4.8).
- (b) Add an equal volume of 30% TBP-Hexane.
- (c) Shake for 60 seconds and let phases separate for 2 minutes.
- (d) Remove organic layer (top) with transfer pipet and discard.
- (e) Repeat steps 4.7.2 (c) and (d).
- (f) Add 100 μ l Ultrex HNO_3 to aqueous layer.
- (g) Repeat steps 4.7.2 (c) and (d) twice. After the second contact remove the aqueous layer (bottom) with a fine tip transfer pipet and put it in a clean labeled 8 ml vial.

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PNL TECHNICAL PROCEDURE

(h) Place on hot plate and evaporate to ~1/2 ml. Cool and make up to 5 ml with deionized water.

Sample is now ready for ICP-AES analysis. Further dilutions may be required as per ICP procedure.

4.8 CALCULATIONS

To calculate volume concentrated Ultrex HNO_3 required to adjust a one ml sample to 3N in a final volume of 2 ml.

The concentrated HNO_3 is added as required then 3N HNO_3 is added to bring sample to 2 ml.

$$V = \frac{3-SC}{12.8},$$

where,

V = volume Ultrex concentrated HNO_3 required
SC = acid concentration of sample

Note: If sample is >3N acid an appropriate water dilution should be made.

5.0 BIBLIOGRAPHY

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-255, (Replaces 7-40.20), SPECTROPHOTOMETRIC DETERMINATION OF REDUCED AND TOTAL IRON IN GLASS WITH 1,10 PHENANTHROLINE

1.0 APPLICABILITY

This method is an adaptation (a) of a method of Begheijn (b) for the determination of reduced iron in rock, soil and clay. The method eliminates the need for platinum ware and allows the measurement of both ferrous and total iron on the same sample.

(a)	Material	Pulverized glasses containing ferrous and ferric iron.
(b)	Range	0 to 10% Fe.
(c)	Reliability	Calibration checks performed with each analytical run.
(d)	Interferences	Possible interference from Cd, Hg, Zn.

2.0 DEFINITIONS

3.0 RESPONSIBLE STAFF

Cognizant Scientist,
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

A glass sample is dissolved in a mixture of HF and H₂SO₄, diluted with buffer, colorimetric reagents added, and spectrophotometric measurement of color intensity made. Following reduction of Fe(III), color intensity is again measured and Fe(II) and total iron concentrations determined from the calibration curve.

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4.2 APPARATUS

- (a) Spectrophometer, capable of measuring at a wavelength of 510 nm.
- (b) 1 cm spectrophotometer cells
- (c) Analytical balance, capable of weighing to 0.1 mg or better.
- (d) Teflon beaker
- (e) Magnetic stir bars
- (f) 150 ml beakers
- (g) 100 ml volumetric flasks, class A
- (h) Pipets as required, performance checked
- (i) pH meter with combination electrode
- (j) Magnetic stirrer

4.3 REAGENTS

- (a) O-phenanthroline 0.25 w/v solution. Dissolve 500 mg in 200 ml distilled H₂O.
- (b) Potassium Acid Phthalate 0.5 M (KHP). Dissolve 102.1 g in 1 liter distilled H₂O.
- (c) Boric Acid 4 w/v solution. Dissolve 40 g in 1 liter distilled H₂O.
- (d) Hydroquinone.
- (e) HF, concentrated reagent.
- (f) H₂SO₄, concentrated reagent.
- (g) NH₄OH, concentrated reagent.
- (h) pH buffer, pH 4.0 or 7.0.
- (i) HCl, concentrated reagent.

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PNL TECHNICAL PROCEDURE

4.4 STANDARDS

- (a) Fe stock solution. Current issue AA or ICP single element standard solutions which are traceable to NIST and contain 1000 μg Fe/ml shall be used. NIST single element standard solutions issued at 10,000 μg Fe/ml may also be used with appropriate dilution. A second solution from a separate source is used as a control check. Both solutions (1000 μg /ml) are diluted by measuring 10 ml (plus 1 ml HCl) into a 100 ml volumetric flask and bringing to volume with distilled water. This solution contains 100 μg (0.1 mg) Fe/ml.
- (b) Control Standard. A well characterized glass, designated WV 202 has been supplied by PNL MCC for use as a control standard. An aliquot of this material shall be analyzed with each sample batch. Other control standards may also be analyzed as required by a customer.

4.5 SAFETY

- (a) Observe the general laboratory safety rules.
- (b) Concentrated HF and H_2SO_4 are extremely hazardous and great care should be exercised in their use.
- (c) Samples containing plutonium should be dissolved in a glove box. Applicable Radiation Work Procedures (RWP) shall be followed when working with radioactive solutions.

4.6 QUALITY CONTROL

4.6.1 Calibration. Calibration curve is made by adding 0, 1, 2, 3, 4 and 5 ml of the diluted (100 μg Fe/ml) standard along with 0.5 ml of concentrated H_2SO_4 and 1.5 ml of concentrated HF to 150 ml beakers containing:

- Stir bar
- 25 ml of boric acid solution
- 10 ml of KHP buffer solution
- 4 ml of o-phenanthroline solution
- 2 ml of concentrated NH_4OH solution

The standards, including the blank, are carried through the analytical procedure, starting at 4.7.2 (skip step b and e) and 4.7.3 (skip step a).

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PNL TECHNICAL PROCEDURE

Note: Reagent addition may be made with unchecked pipets and/or/ graduated cylinders as tolerances within $\pm 10\%$ are adequate.

Plot the measured absorbance on the ordinate versus mg Fe. A straight line should be produced and the calculated slope shall be 0.52 ± 0.04 mg Fe/absorbance unit.

If this requirement is not met, a new calibration curve shall be made.

4.6.2 Control. The provided control standard shall be carried through the analytical procedure on each day that samples are analyzed. The ferrous/ferric ratio on WV 202 shall be 0.204 ± 0.014 . An aliquot (2, 3 or 4 ml) of the control check solution is also carried through the same procedure as the calibration standards after the calibration curve is completed. Recovery on the control check shall be $\pm 10\%$ of expected value. If these requirements are not met the analysis shall be repeated. See Cognizant Scientist if repeat values are unacceptable.

4.7 ANALYSIS

4.7.1 Dissolution

- (a) Weigh to 0.1 mg approximately 25 mg of powdered glass into a Teflon beaker.
- (b) Add 0.5 ml of concentrated H_2SO_4 and wet the sample.
- (c) Carefully add 1.5 ml of concentrated HF and slowly mix the two liquids by tipping and rolling the beaker.
- (d) When dissolution is complete, add 10 ml of boric acid solution.

4.7.2 Adjustments

- (a) Calibrate pH meter with pH buffer solution.
- (b) Transfer the dissolved sample to a 150 ml beaker containing:

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PNL TECHNICAL PROCEDURE

- a stir bar
- 15 ml of boric acid solution
- 10 ml of KHP buffer solution
- 4 ml of o-phenanthroline solution
- 2 ml of concentrated NH_4OH .

- (c) Immerse the pH electrode in the solution and while stirring adjust the pH to between 3.3 and 3.5 by adding dropwise NH_4OH or H_2SO_4 as required.
- (d) Transfer to a labeled 100 ml volumetric flask and make to volume with distilled water.
- (e) After mixing let stand 1 hour.

4.7.3 Measurement

- (a) Measure absorbance at 510 nm versus the reagent blank and record the result. (For ferrous iron.)

If absorbance is above 0.9 make a dilution and remeasure. Dilution is made by adding 4 ml of O-phenanthroline and 10 ml of the prepared sample solution to a 100 ml volumetric flask and diluting to volume. This solution is then remeasured.

- (b) Add 20 mg of hydroquinone crystals to the remaining solution from step 4.7.3(a), shake and let stand for 1 hour.
- (c) Measure the absorbance at 510 nm versus the reagent blank and record the results. (For total iron.)

Follow the same dilution technique as in 4.7.3 (a) if absorbance is greater than 0.9.

- (d) Calculate and report results.

4.8 CALCULATIONS

- (a) Ferrous Iron

$$\% \text{ Fe(II)} = \frac{(A_1)(S)(100)(DF)}{S_w}$$

where,

$\% \text{ Fe(II)}$ = percent ferrous iron in original sample

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PNL TECHNICAL PROCEDURE

A_1 = absorbance from step 4.7.3(a)

S = slope of calibration curve in mg Fe/absorbance unit from step 4.6.1

DF = dilution factor, if used

S_w = weight of sample used, in mg

(b) Total Iron

$$\% \text{ Fe(tot)} = \frac{(A_2)(S)(100)(DF)}{S_w}$$

where,

$\% \text{ Fe(tot)}$ = percent total iron in original sample

A_2 = absorbance from step 4.7.3(c)

S = slope of calibration curve in mg Fe/absorbance unit from step 4.6.1

DF = dilution factor, if used

S_w = weight of sample used, in mg

(c) Ferrous/Ferric Ratio

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

where,

A = ratio of ferrous iron to ferric iron

B = percent of ferrous iron from 4.8(a)

C = percent of ferric iron from 4.8(b)

5.0 RECORDS

Records shall be maintained and controlled so as to conform to requirements of PNL-Ma-70, MCS-033. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for

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PNL TECHNICAL PROCEDURE

control of most records. ~~Laboratory Record Books shall be used in accordance with the ACT NOW Directive 89-1.~~

6.0 REFERENCES

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-256, (Replaces 7-40.22), DETERMINATION OF FREE ACID IN URANIUM/PLUTONIUM SOLUTIONS

1.0 APPLICABILITY

Solutions containing hydrolyzable ions (Pu and U) are titrated to an equivalence end point in a solution of ammonium oxalate. The oxalate ion forms a complex with U-Pu to reduce their interference in the titration. An automatic potentiometric titrator is used to record the titration curve.

- (a) Material Acid solutions containing Pu-U.
- (b) Range 0-16 M HNO_3 , 0-400 g/l HM.
- (c) Reliability Reproducibility with the PNL prepared standards is within ± 0.02 molar units.
- (d) Interferences Ions which form equilibria with hydrogen and hydrolyzable ions not complexed by oxalate.

2.0 DEFINITIONS

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

The determination of free acid in solutions containing hydrolyzable ions (Plutonium and uranium) has been especially difficult and many techniques and methods have been tried with varying degrees of success. (a,b,c,d,e,f) A study was undertaken at Hanford in 1984 to determine which technique worked best at heavy metal concentrations up to 400 g/l and acid concentrations

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PNL TECHNICAL PROCEDURE

of 0.1 M to 6 M. A series of standards was prepared and a satisfactory method developed. (g)

4.2 APPARATUS

- (a) Automatic potentiometric titration system, Brinkmann Instruments Model 636 or 672 titroprocessor.
- (b) Combination electrode, Orion Model 81-02.
- (c) Pipets, Eppendorf, adjustable 25 μ l to 100 μ l with disposable tips.
- (d) Magnetic stirrer.
- (e) Stir bars, teflon covered.
- (f) Repipet, adjustable volume.

4.3 REAGENTS

- (a) Ammonium Oxalate solution, 0.15 M.
- (b) Standardized NaOH, approximately 0.1 N.
- (c) Standardized HNO₃ for spike, 1 N and 6 N.

4.4 STANDARDS

- (a) Uranyl nitrate standard, 300 g/l U and approximately 3 N HNO₃.
- (b) PNL prepared U-Pu standard series. (g)

4.5 SAFETY

- (a) Plutonium bearing materials are radioactive and toxic. Precautions are required to avoid contamination of the laboratory and personnel.
- (b) Observe general laboratory safety rules.
- (c) Follow manufacturers instructions for operation of titrator.

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PNL TECHNICAL PROCEDURE

4.6 QUALITY CONTROL

- 4.6.1 Calibration. Calibration shall include, but not be limited to, titration of standard nitric acid solutions versus standardized sodium hydroxide.
- 4.6.2 Control shall be established by a TBD method probably involving PNL prepared U-Pu acid standards and/or a uranyl nitrate standard.

4.7 ANALYSIS

- 4.7.1 Set up titration system according to manufacturers instructions including calibration of electrode with pH 4 and/or pH 7 buffers. Do not change instrument settings once optimum conditions are established.
- 4.7.2 Analyze standard acid (300 g/l U, 2.71 M H^+) as per 4.7.3.
- 4.7.3 Titration of sample using complexant.
- (a) Add 20 ml of oxalate solution to titration vessel containing stirring bar.
 - (b) Immerse electrode and delivery tip in solution and start stirrer.
 - (c) Pipet sample into vessel and initiate titration. A measured acid spike may be added prior to sample addition to check recovery. Frequency of spike addition to be determined.
 - (d) After titration is complete remove electrode and delivery tip and rinse with distilled water.

Rinse titration vessel and proceed to next sample.
 - (e) Record volumes of sample added, spike (if used), volume of titrant consumed to end point (from titroprocessor).
- 4.7.4 For samples requiring titration to a different pH end-point with no complexant added complete the following steps:
- (a) Add 10 ml of deionized water.

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PNL TECHNICAL PROCEDURE

- (b) Immerse electrode and delivery tip in solution and start stirrer.
- (c) Pipet sample into vessel and titrate to the specified pH end-point.
- (d) Complete steps (d) and (e) of 4.7.3.

4.8 CALCULATIONS

(Calculations may be performed by the titrator after insertion of appropriate information.)

Formulas used are as follows:

$$N_a = \frac{(V_b)(N_b)}{V_s}$$

where,

N_a = Normality of acid (sample)

V_b = Volume standard base used, in ml

N_b = Normality of standard NaOH

V_s = Volume sample used, in ml

The volume of base used for the titration as given by the titrator is the amount required to titrate to the inflection (equivalence) point. A recording of the shape of the curve (pH or mV vs volume base) is also produced.

If an acid spike is used the calculation becomes:

$$N_a = \frac{(V_b - V_{bs})(N_b)}{V_s}$$

$$\text{where } V_{bs} = \frac{N_{sp} V_{sp}}{N_b} = \text{Volume Standard base to titrate spike}$$

where, N_{sp} = Normality of spike

where, V_{sp} = Volume spike used, in ml

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5.0 BIBLIOGRAPHY

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-257, (Replaces 7-40.23), DENSITY OF SOLUTIONS

1.0 APPLICABILITY

Solutions to be measured are inserted into a small U-shaped tube vibrating at a fixed frequency. Change of frequency is directly proportional to solution density and is electronically converted to a digital readout.

- (a) Material Any solution including those with particulates.
- (b) Range 0.5 g/cc to 2.5 g/cc with proper calibration.
- (c) Reliability The system will measure density to ± 0.0001 g/cc.
- (d) Interferences None.

2.0 DEFINITIONS

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

The measurement is based on the change of the natural frequency of a hollow oscillator when filled with liquids or gases of different mass (density). The oscillator is a U-shaped glass tube supported at the open ends and electronically excited in an undamped harmonic fashion. The direction of the oscillation is

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N/A		WC Weimer	8/9/88	All original signatures on file	
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perpendicular to the plane of the tube and is thus influenced or changed by the introduction of a liquid or gas other than air. It is essential that no air bubbles be trapped in the tube during liquid sample introduction. Utilizing the simple relationship between density of the sample and natural frequency of the filled oscillator it is possible to calculate the density of liquids or gases. The DMA 45 electronically makes the calculations and displays the density digitally to four decimal places.

4.2 APPARATUS

- (a) Mettler Paar Model DMA 45 Digital Density Meter.
- (b) 2 ml plastic syringes.

4.3 REAGENTS

- (a) Acetone.
- (b) Distilled water.

4.4 STANDARDS

Distilled water and air are used as calibrating materials. Presently no other standards are available.

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. Calibration is performed at ambient temperature according to the equipment manual. Calibration should be performed if ambient temperature varies more than 1°C from a calibrated temperature.
- 4.6.2 Control. Control is established by measuring the density of distilled water at ambient temperature. It should agree with handbook values to within ± 0.0001 g/cc.

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4.7 ANALYSIS

Turn on instrument and allow approximately two hours for warm up.

- (a) Fill syringe with distilled water at ambient temperature, insert syringe into inlet port so that it fits snugly and push plunger slowly until all liquid is expended.

The first 1 ml will rinse the cell and clear it of air bubbles.

- (b) Wait 20-30 sec until reading stabilizes, then wait for five consecutive readings without change before recording result.

The instrument calculates density and updates the reading every four seconds.

- (c) Remove syringe from port and let liquid drain out. Rinse cell with distilled water until effluent is clear, then rinse with acetone and finally, force air through the cell until the meter reads 0.0015 or less.

The unit is now ready for the next sample.

4.8 CALCULATION

There are no calculations to be made as the instrument reads directly in grams/cc.

5.0 BIBLIOGRAPHY

Instruction Manual, Calculating Digital Density Meter, Anton Paar K. G., Graz, Austria.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-258, (Replaces 7-40.28), ISOTOPIC ANALYSIS OF KRYPTON AND XENON IN FFTF COVER GAS

1.0 APPLICABILITY

The method applies to the isotopic analysis of krypton and xenon tag gases in argon gas. Samples requiring this analysis are tag gases trapped from the argon cover gas at FFTF in gas tag sample traps (GTST). Samples with krypton and xenon concentrations as low as 0.01 ppb can be analyzed using appropriate concentration techniques. Krypton and xenon in gases other than argon can be analyzed with slight changes in the separation techniques.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Magnetic sector mass spectrometer.
- Mass spectrometer sample inlet.
- High vacuum/gas separation racks.
- Gas tag sample trap (GTST).
- Small charcoal trap (SCT).
- GTST valve controller panel.
- GTST and SCT temperature control panel.
- Inlet and/or rack valve control panel.

Author	Date	Project Mgr.	Date	QAD Representative	Date
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N/A		JJ McCown	6/17/88	All original signatures on file	
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- Computer control and data collection system.
- Naturally occurring krypton and xenon for isotopic reference gases.
- Helium or neon, used in the separation process, is analyzed prior to use.

NOTE: Anyone operating this equipment should be fully trained in its use prior to any attempt to analyze samples.

4.2 Performance Check

Performance is checked monthly when instrument is in use.

The ANALYST shall perform the following steps unless otherwise specified.

- 4.2.1 Attach a cylinder of natural reference standard gas to the auxiliary inlet.
- 4.2.2 Evacuate the auxiliary inlet and connecting lines.
- 4.2.3 Close the valves to the vacuum pumps and allow natural reference gas into the mass spectrometer's inlet. A pressure of 0.03 to 0.05 Torr of reference gas is usually sufficient to do the performance check.
- 4.2.4 Introduce the sample into the ion source of the mass spectrometer.
- 4.2.5 Determine which isotope has the highest concentration and adjust signal strength to about 90% of full scale (highest attenuation on the particular electrometer in use) for this isotope.
- 4.2.6 Analyze the gas for isotopic abundance using the computer control system.
- 4.2.7 Print out a report and compare the isotopic ratios to the accepted values. All isotopic ratios should be within 2% of the accepted values.
- 4.2.8 The report printout from the performance check will be placed in the loose leaf notebook containing standards data and saved for at least 4 years. The notebooks are located in the mass spectrometer laboratories in the 325 Building.

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PNL TECHNICAL PROCEDURE

4.2.9 Repeat step 4.2.1 to 4.2.8 for the next element to be analyzed.

4.3 Gas Tag Sample (GTST) Processing

Cover gas samples are collected at FFTF in the GTST and then transported to the gas tag laboratory for further processing and analyses. Tag gases are separated from other gases by trapping on charcoal, purging and pumping while holding the traps at specified temperatures.

NOTE: All temperatures are $\pm 10^{\circ}\text{C}$. All times are ± 5 minutes. All flow rates are $\pm .1$ liters.

The ANALYST shall perform the following steps unless otherwise specified.

4.3.1 Connect the GTST to the shielded rack and pump out the connecting lines. Observation of the vacuum gauges will give an indication of leaks in the connections and valves on the GTST.

4.3.2 As requested, obtain a sample of gas from the grab sampler on the GTST cart. Mount a counting chamber on the sampling port and pump out all lines connecting the counting chamber to the grab sampler. Open the electrical valve (2) on the cart keeping the line valve (1) closed. Valves 3, 4 and 5 are also kept closed. Pump the connecting line to a pressure in the 10-6 Torr range. Close the vacuum pump valves then open the hand operated valve on the grab sampler. Allow the gas to expand into the counting chamber. Record the pressure reading of the manometer and sampling data from the cover gas sample. Close the valves on the counting chamber and grab sampler then pump out the lines. Close the valves to sampling port and manometer head.

4.3.3 Isolate the SCT and the GTST sides of the vacuum/gas rack. Establish helium flow or neon flow-through the GTST bypass valve (3) and through the vacuum/gas rack to purge any residual air out of the lines. At the same time, cool the GTST to -100°C for neon or to -80°C for helium purging.

4.3.4 Purge the GTST with helium or neon for one hour. Close the GTST bypass valve, open the GTST inlet valve (5) first then open the GTST outlet valve (4). At the same time, bake the SCT at 300 to 350°C for about twenty minutes. Pump on the SCT with the high vacuum pump during the bake out.

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4.4 Sample Transfer

- 4.4.1 After about 55 minutes of flushing the GTST, cool the small charcoal trap (SCT) to -150°C.
- 4.4.2 Continue the helium flow through the GTST. Start the flow of helium through the SCT. If neon was used for purging, change to helium prior to this step.
- 4.4.3 Heat the GTST to +150°C. This will cause the sample to transfer to the SCT
- 4.4.4 Allow the transfer to continue for about 1 hour.
- 4.4.5 Stop the helium flow by closing the exhaust valve first then the SCT outlet valve and then the SCT inlet valve.

4.5 Pumping Cycle

- 4.5.1 Increase the temperature of the SCT to about -70°C.
- 4.5.2 Open the rough vacuum valve. Open the SCT outlet valve evacuating the SCT to a pressure of less than 0.05 Torr.
- 4.5.3 Close the rough vacuum valve and open the high vacuum valve.
- 4.5.4 Pump on the sample until a pressure of approximately 2×10^{-7} Torr (ion gauge reading) is reached while holding the trap at about -70°C. The pumping cycle will take about one hour.

4.6 GTST Bakeout

- 4.6.1 Establish argon flow to about 2 liters/minute through the GTST.
- 4.6.2 Heat the GTST to 325°C and hold for about 40 minutes.
- 4.6.3 Cool the GTST back to room temperature while continuing the Ar flow.
- 4.6.4 Close the GTST outlet valve allowing the Ar to pressurize the GTST to above atmospheric pressure.
- 4.6.5 Close the GTST inlet valve.
- 4.6.6 Flush out the grab sample cylinder by opening the inlet and outlet valves.

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PNL TECHNICAL PROCEDURE

4.6.7 Close the grab sample cylinder outlet valves then the inlet valves.

4.7 Sample Collection

4.7.1 Close the vacuum pumps the mass spectrometer inlet valves.

4.7.2 Open the transfer line valve.

4.7.3 Collect the sample for about 20 minutes by heating the SCT to about +150°C.

4.8 Sample Analysis

The ANALYST shall perform the following steps unless otherwise specified.

4.8.1 Introduce the sample into the ion source of the mass spectrometer.

4.8.2 Set the electron multiplier power supply duodial to 190 or 280 and set the variable molecular leak to 130, 140, or 150. Use settings that give a reasonable ion beam intensity from the sample. Measure the total voltages for krypton and xenon. Record the data in the mass spectrometer run book.

4.8.3 Determine which isotope has the highest concentration and adjust signal strength to approximately 90% of full scale on the highest range of the electrometer (10 volt range for the NBS parametric electrometer) for this isotope. Repeat this step for each element prior to isotopic analysis.

4.8.4 Analyze the gas for krypton and xenon isotopic abundance using the computer control system.

4.8.5 Print out the report and compare the isotopic ratios for each cycle. Look for argon interference in the 80/84 krypton ratio and check for instrument drift (unexpected magnetic or high voltage drift) before pumping out the sample.

4.8.6 The report printout will be placed in loose leaf notebooks containing sample analysis. The notebooks are located in the mass spectrometer laboratories in the 325 building.

NOTE: More detailed operating instructions are available in the mass spectrometer operating guides and manuals.

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PNL TECHNICAL PROCEDURE

4.9 Calculations

Calculations are performed by the computer at the end of each element's analysis. The control system stops at each mass and measures the voltage as it steps through the routine. Five cycles are usually run. A cycle consists of measuring each mass up and down the masses selected for the element, in a stepping mode. Each mass is measured at least 10 times. Isotopic ratios are calculated from the measurements for each cycle. Then the five or more cycles are averaged. Calculation are checked when the calibration is checked.

4.10 Records

Records will be maintained and controlled to conform with the requirements of MCS-033. Laboratory record books and analytical report forms provide a mechanism for control of most records. ~~Laboratory record books will be used in accordance with PAP-1704.~~

4.11 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally it is considered qualified because it has Independent Technical Review.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-259, (Replaces 7-40.31), DETERMINATION OF HYDROGEN BY COMBUSTION

1.0 APPLICABILITY

This procedure is intended for the measurement of hydrogen at the percent level in such various materials as hydrides of the transition metals and organic materials. For trace levels of hydrogen in metals, the inert gas fusion method is recommended.

2.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

3.0 SAFETY

This procedure involves no special safety hazards other than the obvious ones of working with a red hot furnace.

4.0 PROCEDURE

4.1 Definitions

None

4.2 Equipment and Materials

The apparatus (Figure 1) consists primarily of:

- a tube furnace operated at 800-900°C
- a quartz furnace tube about 25 mm diameter
- a 50 mm plug of copper oxide wool in the quartz tube
- a quartz boat of 10-20 cc volume
- a water trap weighing less than 150 grams when loaded with magnesium perchlorate desiccant
- a supply of dry air flowing at a constant 150 cc/min.

Author	Date	Project Mgr.	Date	QAD Representative	Date
R.F. Keough	5/25/89	N/A		LJ Ethridge	5/30/89
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	5/31/89	All original signatures on file	
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PNL TECHNICAL PROCEDURE

4.3 Performance Checks

The analyst and apparatus shall be checked by means of analysis of a standard sample. The standard analysis shall agree to within 4% of the expected value before any samples are analyzed.

4.4 Blank Determination

- 1) Heat the tube furnace to 800 C while passing air through the water trap in 150 cc/m to dry and condition the apparatus.
- 2) Remove and weigh the trap to the nearest milligram. Record M&TE used in measurements.
- 3) Reattach the trap to the apparatus. Open and quickly insert an empty, dry boat. Immediately close the system and resume air flowing at 150 cc/min.
- 4) After 2 hours reweigh the trap to determine weight gain. This is the blank. It must be less than 10 mg and will typically be about 1 mg.

4.5 Sample/Standard Analysis

- 1) Weigh 0.1 to 4 grams of sample to the nearest milligram. Sample size should be adjusted to contain about 50 mg of hydrogen. If practical, sample particle size should be less than 3-4 mm diameter to speed oxidation. Most types of samples must be protected from unnecessary air exposure by weighing in closed vials.
- 2) Weigh the water trap and attach it to the apparatus.
- 3) Transfer the sample to a quartz boat and quickly insert the boat in the furnace tube and immediately close the tube.
- 4) Allow air to flow over the sample for two hours, converting it to oxide and sweeping the resulting water into the trap.
- 5) After two hours of oxidation at 800 C, stop the gas flow and reweigh the water trap.
- 6) If the sample is of an untested material, reconnect the water trap to the apparatus and flow gas for another hour. Reweigh the trap to confirm that no additional water was produced by the extended heating.

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PNL TECHNICAL PROCEDURE

5.0 CALCULATIONS

The weight percent hydrogen in the sample is:

$$\% = \frac{(W_s - W_b) (2) (A) (10000)}{(C) (B) (R)}$$

Where: W_s = Weight of water from sample (grams)
 W_b = Weight of water from blank (grams)
 A = Atomic weight of hydrogen (1.008)
 B = Molecular weight of water (18.016)
 C = Sample weight (grams)
 R = Percent standard recovery

Combining numerical constants;

$$\% \text{ hydrogen} = \frac{1119 (W_s - W_b)}{(C) (R)}$$

6.0 RECORDS

A laboratory notebook will be the recording mechanism for all data relating to this analysis. ~~The notebook will be used in accordance with the Act Now Directive 89-1 of MS 4.3.~~

7.0 PROCEDURE QUALIFICATION

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

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APPARATUS FOR DETERMINATION HYDROGEN

FIGURE 1

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-260, (Replaces 7-40.32), MASS SPECTROMETER ISOTOPIC ANALYSIS OF LITHIUM

1.0 APPLICABILITY

This method describes the isotopic analysis of lithium. Lithium or salts of lithium dissolved in dilute nitric or hydrochloric acid can be run using this method. The isotopic ratio, Atom % and Weight % are determined.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

Thermal ionization magnetic sector mass spectrometer.

Thermal ionization source.

Electron multiplier or Faraday cup detectors.

Computer control and data collection system.

Bake-out system for vacuum outgassing filament assemblies.

Triple filament hats.

High purity rhenium filament ribbon. (0.001" thick and 0.030" wide.)

Spot Welder.

Heat Lamp.

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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	5/3/89	All original signatures on file	
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PNL TECHNICAL PROCEDURE

Hermetically sealed terminals.

Lithium standard (NIST interim 9).

NOTE: Anyone operating this equipment should be fully trained in its use prior to any attempt to analyze samples.

4.2 Performance Check

A standard is run each day lithium samples are run.

The ANALYST shall perform the following steps unless otherwise specified.

- 4.2.1 Prepare filaments for triple filament hats using high purity rhenium, hermetically sealed terminals, and spot welder. Clean the filament hat assembly in acetone or alcohol and dry under a heat lamp. Put the filament hat assembly into the bake-out. Pump the bell jar down and then outgas the filaments at about 2000 degrees centigrade. (White hot appearance.)
- 4.2.2 Carefully remove or lower the center filament away from the two side filaments in the filament assembly.
- 4.2.3 Place a drop of the standard solution between the two side filaments. Five to ten microliters will be needed. Dry the sample via a heat lamp until all water is removed. Carefully install the center filament.
- 4.2.4 Close the valves to the vacuum pumps and analyzer section of the instrument. Vent the source region with dry air. Open the source flange. Remove the previous filament hat and insert the sample. Connect the center filament to the electrical leads. Don't connect the side filaments. Close the vent valve and source flange.
- 4.2.5 Pump the source down. Use the rough pump down to about 0.20 Torr and then the turbomolecular pump.
- 4.2.6 When the source ion gage shows that the pressure is $2E-6$ Torr or lower, open the analyzer valve.

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PNL TECHNICAL PROCEDURE

- 4.2.7 Set the mass via the computer to seven, turn on the high voltage and slowly turn up the electrical current to the center filament. Observe the electrometer (Cary or NIST) for indication of ions reaching the detector. Watch the signal to observe growth and stability. When a strong (30 or 10 volt range on the electrometer) signal that is growing or dying slowly is obtained, check the centering on the mass positions and then run sample via the computer control.
- 4.2.8 Print out a report and compare the average isotopic ratio to the accepted value. The average isotopic ratio should be within 1% of the accepted value.
- 4.2.9 The report will be stored in the laboratory files.

4.3 Sample Analysis

The ANALYST shall perform the following step unless otherwise specified.

- 4.3.1 Prepare filaments for triple filament hats using high purity rhenium. Clean the filament hat assemblies in acetone or alcohol and dry under a heat lamp. Put the filament hat assemblies into the bakeout. Pump the bell jar down and then outgas the filaments at about 2000 degrees centigrade. (White hot in appearance).
- 4.3.2 Lower or remove the center filament. Place a drop of the sample solution between the two side filaments. Five to ten microliters will be needed. Dry the sample via a heat lamp until all water is removed. Carefully reinstall the center filament.
- 4.3.3 Close the valves to the vacuum pumps and analyzer section of the instrument. Vent the source region with dry air. Open the source flange. Remove the previous filament hat and insert the sample. Connect the center filament to the electrical leads. Don't connect the side filaments. Close the vent valve and source flange.
- 4.3.4 Pump the source down. Use the rough pump down to about 0.200 Torr and then the turbomolecular pump.
- 4.3.5 When the source ion gage shows that the pressure is $2E-6$ Torr or lower, open the analyzer valve.

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PNL TECHNICAL PROCEDURE

4.3.6 Set the mass via the computer to seven or six, turn on the high voltage and slowly turn up the electrical current to the center filament. Observe the electrometer (Cary or NIST) for indication of ions reaching the detector. Check both mass six and mass seven. Select the mass with the higher signal and watch the signal to observe growth and stability. When a strong (30 or 10 volt range on the electrometer) signal that is growing or dying slowly is obtained, check the centering on the mass positions and then run sample via the computer control.

4.3.7 Print out a report. Check the ratios for consistency. There should be no apparent increase or decrease of ratios during the run. Changes should be random. If there is a trend, check peak settings and source controls and then rerun the sample. If the problem persists try another sample loading. If the problem still persists check with the cognizant scientist for help.

4.4 Calculations

Calculations are performed by the computer at the end of each analysis. The control system stops on each isotope to be measured as it steps through the routine. Nine cycles are usually run. A cycle consists of measuring each mass up and down in a stepping mode. At the end of the analysis routine isotopic voltage measurements are averaged and isotopic ratios are calculated. Calculation are checked for accuracy during the performance check.

4.5 Records

Records will be maintained and controlled so as to conform with the requirements of MCS-033. Laboratory record books and analytical report forms provide a mechanism for control of most records. ~~Laboratory record book will be used in accordance with the Act Now Directive 89-1 of Management Guide 4.3.~~

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 independent technical review.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-261, (Replaces 7-40.33), MASS SPECTROMETER ISOTOPIC ANALYSIS
OF CESIUM

1.0 APPLICABILITY

This method describes the isotopic analysis of cesium. Cesium or salts of cesium dissolved in dilute nitric or hydrochloric acid can be run using this method. Atom %, weight %, and the isotopic ratios are determined.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

Thermal ionization magnetic sector mass spectrometer.

Thermal ionization source.

Electron multiplier or Faraday cup detectors.

Computer control and data collection system.

Bake-out system for vacuum outgassing filament assemblies.

Triple or single filament hats.

High purity rhenium ribbon. (0.001" thick and 0.030" wide).

Spot welder.

Sample loading unit, used to evaporate a sample solution on a filament by passing an electrical current through the filament.

Author	Date	Project Mgr.	Date	QAD Representative	Date
MW Goheen	5/3/89	N/A		LJ Ethridge	5/4/89
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	5/3/89	All original signatures on file	
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PNL TECHNICAL PROCEDURE

Hermetically sealed terminals.

Rubidium NIST standard.

NOTE: Anyone operating this equipment should be fully trained in its use prior to any attempt to analyze samples.

4.2 Performance Check

A rubidium standard is run each day cesium samples are run. Natural cesium is monoisotopic, therefore no natural standard is available. Rubidium is used because it is similar to and thermally emits very much like cesium.

The ANALYST shall perform the following step unless otherwise specified.

- 4.2.1 Prepare single filaments for filament hats using high purity rhenium, hermetically sealed terminals, and the spot welder. Install the filaments in hats. Clean the filament hat assemblies in acetone or alcohol and dry under a heat lamp. Put the filament hat assemblies into the bake-out. Pump the bell jar down and then outgas the filaments at about 2000 degrees centigrade. (White hot in appearance.) Outgassed carbonized rhenium filaments can also be used. The carbonization has no affect on the thermal emission of cesium.
- 4.2.2 Place a drop of the standard solution on the filament. Five to ten microliters will be needed. Dry the standard with 0.5 amps of current until all water is removed.
- 4.2.3 For the C.E.C. 12-60 mass spectrometer: Close the valves to the vacuum pumps and analyzer section of the instrument. Vent the source region with dry air. Open the source flange. Remove the previous filament hat and insert the sample. Connect the filament to the electrical leads. Close the vent valve and source flange.
- 4.2.4 Pump the source down. Use the rough pump down to about 0.200 Torr and then the turbomolecular pump.
- 4.2.5 When the source ion gage shows that the pressure is $2E-6$ Torr or lower, open the analyzer valve.

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PNL TECHNICAL PROCEDURE

- 4.2.6 For the Nuclide Corporation 12-90-3S mass spectrometer: Remove the vacuum lock carriage from the instrument via the vacuum lock. Remove the previous sample hat. Install the standard on the ion source and reinstall the vacuum lock carriage in the vacuum lock.
- 4.2.7 Set the mass via the computer to 85, turn on the high voltage and slowly turn up the electrical current to the center filament. Observe the electrometer (Cary or NIST) for indication of ions reaching the detector. Watch the signal to observe growth and stability. When a strong (30 or 10 volt range on the electrometer if possible) signal that is growing or dying slowly is obtained, check the centering on the mass positions and then run the standard via the computer control.
- 4.2.8 Print out a report and compare the average isotopic ratio to the accepted value. The average isotopic ratio should be within 1% of the accepted value.
- 4.2.9 The report will be stored in the laboratory files.

4.3 Sample Analysis

The ANALYST shall perform the following steps unless otherwise specified.

- 4.3.1 Prepare single filaments for filament hats using high purity rhenium, hermetically sealed terminals, and the spot welder. Install the filaments in hats. Clean the filament hat assemblies in acetone or alcohol and dry under a heat lamp. Put the filament hat assemblies into the bake-out. Pump the bell jar down and then outgas the filaments at about 2000 degrees centigrade. (White hot in appearance.) Outgassed carbonized rhenium filaments can also be used. The carbonization has no affect on the thermal emission of cesium.
- 4.3.2 Place a drop of the sample solution on the filament. Five to ten microliters will be needed. Dry the sample with 0.5 amps of current until all water is removed. Use care. Cesium salts evaporate very readily.

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PNL TECHNICAL PROCEDURE

- 4.3.3 For the C.E.C. 12-60 mass spectrometer: Close the valves to the vacuum pumps and analyzer section of the instrument. Vent the source region with dry air. Open the source flange. Remove the previous filament hat and insert the sample. Connect the vent valve and source flange.
- 4.3.4 Pump the source down. Use the rough pump down to about 0.200 Torr and then the turbomolecular pump.
- 4.3.5 When the source ion gage shows that the pressure is $2\text{E}-6$ Torr or lower, open the analyzer valve.
- 4.3.6 For the Nuclide Corporation 12-90-3S mass spectrometer: Remove the vacuum lock carriage from the instrument via the vacuum lock. Remove the previous sample hat. Install the sample on the ion source and reinstall the vacuum lock carriage into the vacuum lock.
- 4.3.7 Set the mass via the computer to 133 or 137, turn on the high voltage and slowly turn up the electrical current to the center filament. Observe the electrometer (Cary or NIST) for indication of ions reaching the detector. Watch the signal to observe growth and stability. When a strong (30 or 10 volt range on the electrometer if possible) signal that is growing or dying slowly is obtained, check the centering on the mass positions and then run the sample via the computer control.
- 4.3.8 Print out a report. Check the ratios for consistency. There should be no apparent increase or decrease of the ratios during the run. Changes should be random. If there is a trend, check peak settings and source controls and then rerun the sample. If the problem persists try another sample loading. If the problem still persists check with the cognizant scientist for help.
- 4.3.9 Calculations

Calculations are performed by the computer at the end of each analysis. The control system stops on each isotope to be measured as it steps through the

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PNL TECHNICAL PROCEDURE

routine. Nine cycles are usually run. A cycle consists of measuring each mass up and down in a stepping mode. At the end of the analysis routine isotopic voltage measurements are averaged and isotopic ratios are calculated. Atom % and mass % are then calculated for each isotope from the isotopic ratios. Calculations are checked for accuracy during the performance check.

4.3.10 Records

Records will be maintained and controlled so as to conform with the requirements of MCS-033 .. Laboratory record books and analytical report forms provide a mechanism for control of most records. ~~Laboratory record books will be used in accordance with Act Now Directive 89-1 of Management Guide 4.3.~~

4.3.11 Procedure Qualification

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

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-262, (Replaces 7-40.35), MASS SPECTROMETER ISOTOPIC ANALYSIS OF LANTHANIDE SERIES ELEMENTS

1.0 APPLICABILITY

This method describes the isotopic analysis of the lanthanide series elements neodymium, samarium, gadolinium, europium, and etc. Neodymium and most other lanthanides can be run using this method. Atom %, Weight % and the isotopic ratios are determined.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

Thermal ionization magnetic sector mass spectrometer.

Thermal ionization source.

Electron multiplier and/or Faraday cup detectors.

Computer control and data collection system.

Bakeout system for vacuum outgassing filament assemblies.

Triple or single filament hats.

High purity rhenium ribbon. (0.001 inch thick and 0.030 inch wide).

Benzene or trans-2-butene.

Spot welder.

Author	Date	Project Mgr.	Date	QAD Representative	Date
MW Goheen	5/6/89	N/A		LJ Ethridge	5/16/89
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	5/18/89	All original signatures on file	
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PNL TECHNICAL PROCEDURE

Sample loading unit, used to evaporate a sample solution on a filament by passing an electrical current through the filament.

Hermetically sealed terminals.

High purity naturally occurring neodymium.

Chloroplatinic acid 0.05 g/ml in 0.02 M sucrose solution.

Note: Anyone operating this equipment should be fully trained in its use prior to any attempt to analyze samples.

4.2 Performance Check

A natural neodymium is run each day samples are run. Natural neodymium or other lanthanide is used as the standard since NIST does not have certified standards available.

The ANALYST shall perform the following step unless otherwise specified.

4.2.1 Prepare single filaments for filament hats using high purity rhenium, hermetically sealed terminals and the spot welder. Install the filaments in hats. Clean the filament hat assemblies in acetone or alcohol and dry under a heat lamp. Put the filament hat assemblies into the bakeout. Pump the bell jar down and then outgas the filaments at about 2000 degrees centigrade, (white hot in appearance). The rhenium filaments are then carbonized by heating for approximately 90 minutes at about 1600 degrees centigrade in benzene or trans-2-butene at a pressure of about 5×10^{-4} Torr. The conditions for carbonization must be found for the particular bell jar setup. The filaments when carbonized properly will be quite fragile and break very easily and must be handled carefully.

4.2.2 Place a drop of the standard solution on the filament. Ten microliters is usually needed. Add 5 μ l of the chloroplatinic acid. Dry the solution with 1.0 amps of current until all water is removed. Increase the amperage to 1.2 to 1.5 until a matt gray platinum overplate is produced.

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- 4.2.3 For the C.E.C. 12-60 mass spectrometer: Close the valves to the vacuum pumps and analyzer section of the instrument. Vent the source region with dry air. Open the source flange. Remove the previous filament hat and insert the sample. Connect the filament to the electrical leads. Close the vent valve and source flange.
- 4.2.4 Pump the source down. Use the rough pump down to about 0.200 Torr and then use the turbomolecular pump.
- 4.2.5 When the source ion gage shows that the pressure is $2\text{E}-6$ Torr or lower, open the analyzer valve.
- 4.2.6 For the Nuclide Corporation 12-90-3S mass spectrometer: Remove the vacuum lock carriage from the instrument via the vacuum lock. Remove the previous sample hat. Install the standard on the ion source and reinstall the vacuum lock carriage in the vacuum lock.
- 4.2.7 Set the mass via the computer to 142 for neodymium, turn on the high voltage and slowly turn up the electrical current to the center filament. For other lanthanides use an appropriate high abundance mass position. Observe the electrometer (Cary or NIST) for indication of ions reaching the detector. Watch the signal to observe growth and stability. When a strong (30 or 10 volt range on the electrometer if possible) signal that is growing or dying slowly is obtained, check the centering on the mass positions and then run the standard via the computer control.
- 4.2.8 Print out a report and compare the average isotopic ratios to the accepted values. The average isotopic ratios should be within 1% or 2% of the accepted values.
- 4.2.9 The report will be stored in the laboratory files.

4.3 Sample Analysis

The ANALYST shall perform the following step unless otherwise specified.

- 4.3.1 Prepare single filaments for filament hats using high purity rhenium, hermetically sealed terminals and the spot welder. Install the filaments in hats. Clean the filament hat assemblies in acetone or alcohol and dry under a heat lamp. Put the filament hat assemblies into the bakeout. Pump the

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PNL TECHNICAL PROCEDURE

bell jar down and then outgas the filaments at about 2000 degrees centigrade, (white hot in appearance). The rhenium filaments are then carbonized by heating for approximately 90 minutes at about 1600 degrees centigrade in benzene or trans-2-butene at a pressure of about 5×10^{-4} Torr. The conditions for carbonization must be found for the particular bell jar setup. The filaments when carbonized properly will be quite fragile and break very easily and must be handled carefully.

- 4.3.2 Place a drop of the sample solution on the filament. Ten microliters is usually needed. Add 5 μ l of the chloroplatinic acid. Dry the solution with 1.0 amps of current until all water is removed. Increase the amperage between 1.2 and 1.5 until a matt gray platinum overplate is produced.
- 4.3.3 For the C.E.C. 12-60 mass spectrometer. Close the valves to the vacuum pumps and analyzer section of the instrument. Vent the source region with dry air. Open the source flange. Remove the previous filament hat and insert the sample. Connect the filament to the electrical leads. Close the vent valve and source flange.
- 4.3.4 Pump the source down. Use the rough pump down to about 0.200 Torr and then use the turbomolecular pump.
- 4.3.5 When the source ion gage shows that the pressure is $2E-6$ Torr or lower, open the analyzer valve.
- 4.3.6 For the Nuclide Corporation 12-90-3S mass spectrometer: Remove the vacuum lock carriage from the instrument via the vacuum lock. Remove the previous sample hat. Install the sample on the ion source and reinstall the vacuum lock carriage into the vacuum lock.
- 4.3.7 Set the mass via the computer to 145 or 146 for neodymium, turn on the high voltage and slowly turn up the electrical current to the center filament. Observe the electrometer (Cary or NIST) for indication of ions reaching the detector. Watch the signal to observe growth and stability. When a strong (30 or 10 volt range on the electrometer if possible) signal that is growing or dying slowly is obtained, check the centering on the mass positions and then run the sample via the computer control.

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PNL TECHNICAL PROCEDURE

4.3.8 Print out a report. Check the ratios for consistency. There should be no apparent increase or decrease of the ratios during the run. Changes should be random. If there is a trend, check peak settings and source controls and then the rerun sample. If the problem persists try another sample loading. If the problem still persists check with the cognizant scientist for help.

4.4 Calculations

Calculations are performed by the computer at the end of each analysis. The control system stops on each isotope to be measured as it steps through the routine. Nine cycles are usually run. A cycle consists of measuring each mass up and down in a stepping mode. At the end of the analysis routine isotopic voltage measurements are averaged and isotopic ratios are calculated. Atom % and mass % are then calculated for each isotope from the isotopic ratios. Calculations are checked for accuracy during the performance check.

4.5 Records

Records will be maintained and controlled so as to conform with the requirements of MCS-033. Laboratory record books and analytical report forms provide a mechanism for control of most records. ~~Laboratory record book will be used in accordance with the Act Now Directive 89-1 of Management Guide 4.3.~~

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 independent technical review.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-263, (Replaces 7-40.44), OPERATION OF GAS CHROMATOGRAPHS

1.0 APPLICABILITY

This procedure details the operation of the gas chromatographs and the associated gas handling system used for analysis of reactor cover gas (argon) by ASTM C997-83.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment

Figure 1 shows the apparatus and the connections between the units. Major components are:

- Gas chromatograph with thermistor type TC detector. Gow-Mac #570.
- Gas chromatograph with flame ionization type detector. Gow-Mac #580.
- High purity argon, air and hydrogen supplies.
- Standard gas mixture in argon for calibration.
- Vacuum pump for operation of 0.001 psia.
- Gas sampling system or manifold.
- Digital manometer, 0-100 psia range.

Author	Date	Project Mgr.	Date	QAD Representative	Date
RF Keough	10/2/89	N/A		GK Gerke	10/3/89
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	10/2/89	All original signatures on file	
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PNL TECHNICAL PROCEDURE

4.2 Startup

- 4.2.1 Open the plug valve blocking the exit of gas from the TCD chromatograph. This allows carrier gas to flow through the system.
- 4.2.2 Turn on the detector power to this chromatograph with the front panel switch. Allow an hour for warm up.
- 4.2.3 Turn on the power to the FID chromatograph; the switch is on the rear of the instrument. Allow an hour for warm up.
- 4.2.4 Turn on the gas purifier and vacuum pump by turning on the "power strip" under the table. It will take 30 minutes for the purifier to warm up.
- 4.2.5 Connect the sample cylinder to the gas manifold.
- 4.2.6 After everything has warmed up, adjust the argon flow to the FID chromatograph to 35 cc/m using the valve on the lower front panel.
- 4.2.7 Open the hydrogen valve on the hydrogen generator and open the outlet valve on the compressed air regulator.
- 4.2.8 Allow 5 minutes for the lines to flush then push the "ignite" button on the FID chromatograph for 5 seconds to light the detector flame.

4.3 Measurement of Oxygen Hydrogen and Nitrogen

- 4.3.1 Evacuate the entire gas system with all manifold valves open except the standard gas valve. Backfill with argon to about 20 psia. Close the toggle valve to isolate the FID chromatograph.
- 4.3.2 Evacuate the manifold with the sampling valve in the "up" position then backfill with sample (or standard if doing a calibration). Adjust the pressure to 18 ± 0.3 psia.
- 4.3.3 With the recorder and associated signal conditioner set to give a full scale response to 0.02 mV, switch the sampling valve to the down (analyze) position.
- 4.3.4 Record the peaks, if any, for oxygen, hydrogen and nitrogen. Adjust sensitivity, if necessary, to capture the full peak.

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PNL TECHNICAL PROCEDURE

4.3.5 Repeat the analysis once. Repeat with the standard gas to calibrate the instrument.

4.4 Measurement of Hydrocarbons

4.4.1 Open the toggle valve on the gas manifold to allow sample flow to the FID chromatograph.

4.4.2 Evacuate the manifold while the sampling valve on the chromatograph is in the counter-clockwise position. Backfill with sample (or standard) gas via the manifold to 15 ± 0.2 psia via the manifold.

4.4.3 With the recorder on the 1 mV scale, switch the sampling valve. The single peak will appear on the recorder in about 10 seconds.

4.4.4 Repeat if sample is available. Repeat with standard gas to calibrate the instrument.

4.5 Calculations

Over the range of interest 0-200 ppm oxygen, and nitrogen, 0-10 ppm hydrogen and hydrocarbons, the concentration is proportional to peak height. Therefore, for each impurity the concentration in the sample is:

$$\text{Concentration} = \frac{(\text{sample peak ht})(\text{conc in std})}{\text{std peak ht}}$$

These calculations should be made in the laboratory record book. Normally all concentrations are given in parts per million by volume (vppm).

4.6 Notes

4.6.1 Helium overlaps the hydrogen peak so samples taken in the Gas Tag Sample Trap (GTST) are not analyzed for hydrogen since they contain at least 100 ppm of helium.

4.6.2 The FID chromatograph is set up to measure all hydrocarbon gases in one peak to give "total hydrocarbons". While it would be easy to separate the various hydrocarbons, that is not desired for the FFTF samples this procedure is primarily intended to accommodate.

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5.0 RECORDS

A laboratory record book will be the recording mechanism for all data relating to this technical procedure. ~~The record book will be used in accordance with PAP 70-1704.~~

6.0 PROCEDURE QUALIFICATION

Not required. This procedure is considered self qualifying due to its dependence on standards and blanks analyzed with each sample or set of samples.

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FIGURE 1

GAS CHROMATOGRAPH SYSTEM

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-265, (Replaces 7-40.46), DETERMINATION OF TOTAL SODIUM ON FILTERS
BY FLAME ATOMIC EMISSION

1.0 APPLICABILITY

This procedure describes the operation of a flame atomic emission spectrometer for the analysis of total sodium on FFTF air filters.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment

A flame atomic emission spectrometer with air and fuel supply (e.g. Perkin-Elmer 306)
Sodium-free distilled water
A Sodium Standard (e.g. conc. 2 $\mu\text{g/mL}$)
Two-inch burner head

4.2 Start-up

4.2.1 Turn on the instrument and set the following conditions:
EM CHOPPER: ON
FUNCTION: EM
RANGE: VIS

4.2.2 Position the burner head in the optical path so that it is slanted at an angle; secure in place.

4.2.3 Adjust the gas flows so that the fuel and oxidizer levels yield a flame with minimal luminosity.

Author	Date	Project Mgr.	Date	QAD Representative	Date
PK Melethil	6/18/90	N/A		GK Gerke	6/21/90
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RF Keough	6/20/90	WC Weimer		All original signatures on file	
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PNL TECHNICAL PROCEDURE

4.2.4 Set the monochromator to the emission line of Sodium. This should be about 590 nm.

4.2.5 Zero the spectrometer output using Sodium-free water.

4.2.6 Add 5-ml Na-free water to each filter.

4.2.7 Optimize wavelength selection using the Sodium standard to achieve maximum emission. Adjust the gain as needed for standardization (e.g. for a 2 ug/mL standard, adjust maximal emission to read 10.0). This yield I (std).

4.3 Measurement

4.3.1 Aspirate the sample into the flame and record the emission intensity, I (samples).

4.3.2 Flush the system with Na-free water between samples and at the end of the run.

4.4 Calculations

As the instrument has been standardized, the total ug Na on the filter, T, may be calculated as:

$$T = I(\text{sample})/I(\text{std}) \times 5S$$

where I = Emission intensity, and
S = concentration of standard in $\mu\text{g/mL}$

In practice, the standardization procedure and sample preparation have been designed to allow the direct readout of total micrograms of sodium per filter from the spectrophotometer.

5.0 RECORDS

The results are recorded directly on forms provided by FFTF and immediately transmitted to FFTF work control by telephone and a record copy delivered to in-house data entry personnel.

6.0 PROCEDURE QUALIFICATION

Not required. This procedure is considered to be self-qualifying as a standard and blanks are run with each set of samples.

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-266, (Replaces 7-40.48), PROCEDURES AND QUALITY CONTROL FOR ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY USING THE BFP APPROACH WITH THE KEVEX 0810A SYSTEM

1.0 APPLICABILITY

This procedure describes energy dispersive x-ray fluorescence (EDXRF) spectroscopy for a variety of sample matrices. Twenty-four elements are typically determined in one-to-two minutes. The backscatter fundamental parameter (BFP) approach corrects for sample matrix effects without prior knowledge of the (usual) major sample components like hydrogen, oxygen, and carbon.

The procedure is an x-ray fluorescence analytical method applicable to a wide variety of solid and liquid samples including geologicals, biologicals, glasses, salts, metals, slurries, and brines. It is also well suited to the analysis of filter samples. Elements normally reported are Al, Si, P, S, Cl, K, Ca, (Ti or Zr secondary target); Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Se, As, Br, Rb, Pb, (only Zr secondary target); Sr, Y, Zr, Nb, Mo, U (only Ag secondary target); Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, and Ce (only Gd secondary target).

1.1 Principles of Method

An atom fluoresces when it is excited and then immediately reverts to a stable configuration through electron transitions with energy loss to the atomic system. The energy loss, in this case, is usually one or more high energy photons, or x-rays, which are characteristic of the transitions among the inner shell electrons of the atom. The x-ray photons are detected, tabulated by energy and stored in a spectrum. The element masses or concentrations are calculated from the net peak areas of the spectrum using libraries of fundamental constants and single element sensitivities (calibration factors).

Atoms in the sample are excited through a 2-step process. A

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PNL TECHNICAL PROCEDURE

primary target is bombarded with electrons to produce bremsstrahlung radiation which in turn irradiates one of several secondary targets (excitation sources). The bremsstrahlung radiation stimulates the excitation source to produce x-rays which are in turn directed at the sample. The x-rays that irradiate the sample cause atoms in the sample to become excited and the reversion to the stable state produces new x-rays (fluorescence) characteristic of the sample atoms.

The x-rays are detected by a solid state lithium drifted silicon (Si(Li)) detector connected to a multichannel analyzer which provides counts per channel or peaks for subsequent data analysis.

The calculation of element concentrations from EDXRF peak intensities is generally complicated by sample self absorption and emission of secondary x-rays from the sample. These matrix effects are corrected by fundamental parameter calculations which require knowledge of all major element concentrations in the sample. Because hydrogen, carbon, oxygen, and other light elements are the major variable components of liquid, biologic, and geologic materials and are not directly observed in ordinary EDXRF analysis, they are estimated by use of the incoherent and coherent backscatter intensities.

Additional information on the computer calculations is in the Supplemental Information section at the end of this procedure.

1.2 Limitations

Samples must be reasonably homogeneous and be prepared to cover the sensitive area of the x-ray beam. Mono-energetic excitation must be used to generate the discrete incoherent and coherent backscatter peaks. The geometry of the sample chamber must be controlled to ensure that virtually all the observed backscatter comes from the sample. The latter two limitations are met by using only the excitation sources and equipment specified in this procedure.

Because of the versatility of the instrumentation and software, the spectroscopist (analyst) has the prerogative of whether to dilute or concentrate samples and to vary the counting parameters of live time and tube current. These variations have only a simple linear effect on the calibration curve. A variance must be requested and documented from the cognizant scientist if the tube voltage is changed because the effect to the calibration curve is no longer linear and thereby requires a new curve.

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PNL TECHNICAL PROCEDURE

1.3 Safety Requirements

Radiation protection instruction is required and provided annually for all qualified operators of the EDXRF in accordance with PNL-MA-6, Radiation Protection because the EDXRF is classed as a Radiation Generating Device (RGD). Documentation of training is maintained in accordance with PNL Administrative Procedure PAP-70-201, Indoctrination and Training. Radioactive or radioactive-contaminated samples may be analyzed, consistent with the current Radiation Work Permit and if the radioactivity is non-smearable or the samples are packaged to be non-smearable.

2.0 DEFINITIONS

Calibration standard - a National Institute of Standards and Technology (NIST) traceable preparation of single or multiple pure elements on a thin film.

Matrix standard - a NIST, NIST-traceable, United States Geological Survey (USGS), or equivalent certified standard reference material.

Sample group - a set of samples, usually no more than 16, of any matrix.

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment

4.1.1 Hardware

KEVEX Subsystem 0810A - See 0810A Instruction Manual

This is a commercial x-ray fluorescence excitation and detection subsystem that is used to perform X-Ray Energy Spectroscopy. This unit contains a water-cooled tungsten-x-ray tube, sample chamber with multiple sample positions, a series of secondary targets (typically Ti, Cu, Zr, Mo, Sn, and Gd), a cryogenically-cooled Li drifted Si detector, preamplifier, and microprocessor. The system can

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be operated in vacuum, helium, or air. The system configuration is such that no inadvertent scatter from the shielding impinges on the detector window.

KEVEX High Voltage Generator - See KEVEX, Interlock System for the KEVEX High Voltage Generator, in Instruction Manual - High Voltage Generator 80 kV 80 mA (milliamps), Serial No. 105.79.

This commercial unit provides the tube voltage and anode current to the tungsten-x-ray tube in the Kevex Sub-system 0810A and is controlled by the central electronics of the 0810A. Voltage range extends from 10 kV to 80 kV and the anode current range is 0 to 80 mA.

KEVEX 4620 Detector Bias Supply - This unit supplies high voltage (typically 1000 V) to the detector.

Canberra Jupiter Computer System (includes the following equipment).

- Canberra Series 80 Multichannel Analyzer - see Series 80 Multichannel Analyzer Operators Manual Version 1.0, June 1978.
- This commercial unit contains a microprocessor that is interfaced with the main PDP-11/34A computer. This unit allows user keyboard interaction with spectrum acquisition sequence and provides visual surveillance of the acquisition via the video terminal. The unit is capable of controlling and storing four separate spectra simultaneously and can be operated in a hands-on mode or remotely by the PDP-11/34A computer.
- Canberra Model 8623 PHA/LTC - See PHA/LTC Model 8623 Operating Manual, March 1981.
- Four of these units are interfaced with the Series 80. Each unit includes an ADC, pile-up rejector, amplifier, baseline control, and gain control.
- Digital RX01, floppy disc drive - interfaced to main computer. See User's Manual RX8/RX11 EK-RX01-OP.001, November 1976.
- Digital RL01 - (2), hard disc drive - interfaced to main computer. See RL01 Disk Subsystem User's Guide EK-RL01-UG-002, April 1978.

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- Digital PDP-11/34A, 112K computer - operating system RSX-11A.V.4.0. See PDP-11/34A Users Manual, EK 11039-UG-001 (1977) plus KY11-LB Operators Manual.
- Digital VT-102 - (2), terminal, interfaced to PDP-11/34A. See Digital VT-102, Video Terminal Users Guide, EK-VT102-UG-003.
- Versatec, fast printer/plotter, interfaced to PDP-11/34A. See Operation and Maintenance Manual 1110, Series Manual Edition No. 3, April 1978.

4.1.2 Software

The following computer programs are active in the PDP-11/34A computer in both source and task code. Hard copies and floppy disc storage are maintained in 3708 and 329 Buildings. All computer software shall be controlled in accordance with the PNL Software Control Procedures (SCPs), reference PNL-MA-70, Volume I, Procedures for Quality Assurance Program.

Program MCA (Multichannel Analyzer); code residence - DL1:[10,11], installed [1,54]. Listings described in C1-SE-422-1, Canberra FT 8673 Subroutine (November 1979).

Description: This program provides control and monitoring functions for:

Secondary Target	(0810A)
Live Time	(Series 80 MCA)
Sample Changer	(0810A)
High Voltage	(High Voltage Generator)
Tube Current	(High Voltage Generator)
Spectrum Storage	(Jupiter.DL0:DL1:DX1:DX_)
Provides and Records:	target used, live time, clock time, current, voltage, sample series name.

Program XRF (X-Ray Fluorescence); code residence - DL1:[10,11], installed [1,54]. Listings described in C1-SE-422-1, Fortran Callable Subroutines. X-Ray Fluorescence presents an option menu to the user and defines and provides to MCA all pertinent information required for the EDXRF spectrum acquisition and storage sequence.

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Program DTP (Disc to Printer/Plotter); code residence -DL1:[6,14], installed [1,54]. Program DTP presents an option menu for spectrum manipulation. It provides two types of plots, hard copies of digital data, and transfers spectrum from one unit to another.

Program SAP3 (Spectrum Analysis Program); code residence - DL1:[6,14]. The SAP3 program performs the dual functions of automatic spectrum analysis and quantitative interpretation of energy dispersive x-ray fluorescence (EDXRF) data.

Program XAD (X-Ray Spectra Addition). Program XAD generates a composite spectrum by splicing a Ti secondary source generated spectrum and a Zr secondary source spectrum.

Program SXR (Sponsor X-Ray Analysis Report). This program provides the analyte concentrations and supporting information necessary to the sponsor.

4.2 Sample Tracking

When the samples are received from the sponsor, the sponsor is requested to complete an accompanying EDXRF analysis request form (see attachment A). Receipt acknowledgement and inspection shall be performed at this time, and shall be documented on the Chain-of-Custody form. Receipt inspection shall include checking sample containers and sample shipping containers for presence/absence of custody seals, locks, evidence tape, and container breakage. The condition of the containers shall be recorded on the Chain-of-Custody form, which shall be completed per PNL-MA-567, procedure AD-4, "Sediment Sample Chain-of-Custody."

The identity of samples received with an accompanying Chain-of-Custody form shall be verified prior to signing and dating the form. A copy of the signed Chain-of-Custody form shall be given to the individual delivering the samples or sent to the sample originator. Any necessary subdividing of samples is performed prior to receipt in the EDXRF Laboratory.

Sponsor, date received, work package number, number and type of samples, and a short statement as to EDXRF analyses required shall be recorded in the Sample Receipt Record Book Laboratory Record Book (LRB) along with a code referencing the appropriate LRB where a detailed record of the analysis is presented. For example, an entry of 50281-76 in the Sample Receipt Record Book indicates that the analysis write-up can be located in (LRB) BNW-50281 on page 76.

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After sample and matrix standard preparation described in 4.3, the samples shall be logged into the Operational LRB Record Book designated specifically for this purpose. Entries consist of EDXRF analysis series name, counting parameters, sample position in the changer, and the sponsor-given name for each sample.

4.3 Sample Preparation (General)

Solid samples are usually pelletized directly from 180 to 1500 mg of the dry sample in a 3.2-cm-diameter, 27,000-kg laboratory press. Sample material which cannot be readily pressed into a self-supporting pellet (wafer) may be analyzed directly by supporting it on or between thin plastic films such as polypropylene, mylar, parafilm, or common tape. Liquid samples can be processed directly, in open cells or in polypropylene packets, or can be concentrated into cellulose powder or to the solid residue. Filter samples generally can be mounted on 35-mm slides and analyzed directly. Samples must be prepared to fill the sensitive area viewed by the x-ray detector. (See Attachment B)

4.4 Analysis of Samples

4.4.1 Verify or set gain on PHA/LTC for Series 80 MCA. Refer to Series 80 Manual (2-40) and Canberra 8623 PHA/LTH Operating Manual, March 1981, for set-up procedures.

For secondary targets of Ti, Zr, and Ag:

Gain:	25 eV/channel
Resolution:	182 eV at 6.4 KeV
Timing Counter:	12 μ sec
Bias:	-1000 V

For secondary target of Gd:

Gain:	50 eV/channel
Resolution:	182 eV at 6.4 KeV
Timing Counter:	12 μ sec
Bias:	-1000 V

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4.4.2 Solid Samples

This procedure can be applied to sediments, clays, rocks, fly ash, salts, coal, leaves, bone, tissue, or evaporated brines and residues. If the average atomic number of the sample is such that the dead time exceeds 40% even with current reductions, dilution with SiO_2 or cellulose will be required. If cellulose is used, particle size corrections (PNL-4173, The SAP3 Computer Program for Quantitative Multielement Analysis by Energy Dispersive X-Ray Fluorescence, page 60) will be required.

1. Prepare representative, homogeneous samples less than 150 mesh (use 200 to 1000 mg).
2. Press into self-supporting wafer.
3. Support wafer on 35-mm slide as to cover detector sensitive area.
4. Place USGS or NIST matrix standard in Position #1 of sample changer.
5. Fill remaining positions with unknowns.
6. Close shielding on x-ray subsystem.
7. Apply and verify vacuum.
8. Set KEVEX 0810A and KEVEX High Voltage generator in computer control mode.
9. Activate program MCA.
Type: M C A ↓ on TT0:
10. Activate program XRF
Type: X R F ↓ on TT3:
11. Provide XRF with necessary information for data acquisition and storage.

Targets Ti, Zr, Ag, Gd - defaults

*Live Time Ti = 500 sec defaults
 Zr = 1500 sec defaults
 Ag = 750 sec defaults
 Gd = 750 sec defaults

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Tungsten Tube Voltage (kV)	Ti	20 default
	Zr	40 default
	Ag	45 default
	Gd	70 default
*Tube Current (milliamps)	Ti	10 default
	Zr	20 default
	Ag	20 default
	Gd	20 default

* Samples may be counted at greater than but not less than 60% live time. Vary the anode current and change the live time as necessary. Both of these functions affect the calibration curve linearly and thus require only a time adjustment to the concentration of the matrix standard in Position #1.

Number of Samples	Options 1 to 17; default
Series Name	Accepts 5 alphanumeric inputs
Inputs -	Program places the first initial of target in front of input.

Designate Spectra Storage.

Option -	DL1:[100,10]
	DL0:[100,10]
	DX1:[100,10]
	DX0:[100,10]

End of Acquisition.

4.4.3 Powder Samples

Material that cannot be readily pressed into self-supporting wafers may be analyzed by supporting it between thin film such as polypropylene or parafilm. The procedure is the same as for solid samples except the option to correct for absorption of the thin film must be used. See PNL-4173, page 29.

4.4.4 Liquid Samples

Brines, process waste streams, and oils may be analyzed by injecting the liquids directly into 33-mm polyethylene cells fitted with 0.006-mm polypropylene x-ray windows. Samples are excited in a He environment. Use the same libraries as solid samples and the same options as powdered samples.

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4.4.5 Aqueous Samples

For analysis of trace elements in water samples the following steps are used to prepare the sample.

1. Weigh 100 to 200 mg of micro-crystalline cellulose into a narrow 50 ml Teflon beaker.
2. Pipet or weigh 10 to 40 ml of the water sample into the beaker. Record volume/wt.
3. Place beaker into laminar-flow hood to evaporate to dryness. Note: this step may require 2 to 7 days to complete.
4. Break cellulose pad and mix in beaker.
5. Transfer to alumina mortar and grind.
6. Place teflon film on both surfaces of die to avoid contamination in case the water sample was acidified. Transfer ground cellulose to 1 1/4 inch die and press into wafer.
7. Weigh resultant wafer. Record volume/wt.
8. Perform EDXRF analysis by normal procedure for solid samples.
9. Multiply results (ppm) by weight (in grams) of wafer and divide by ml of sample. Report results in ug element/ml water sample.

$$\text{ug/ml element} = \frac{\text{ppm} \times \text{gm sample}}{\text{Volume in ml}}$$

4.4.6 Procedure for Steels

Samples may be analyzed as solid disks, lathe or drill turnings, or as pellets prepared from the turnings. Radioactive steels may also be analyzed. The procedure is the same as for liquid samples except the metal only option is used. The analytical method is described in detail in 1982, Anal. Chem. 54:1782-1786 and in PNL-4173, page 28.

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4.4.7 Aerosol Loaded Filters

Filter samples can generally be mounted on 35 mm slide holders and analyzed without any further sample preparation. The setup for the acquisition phase with the exception of anode current is the same as for solid samples. The anode current is set as follows:

Ti	15 mamps
Zr	30 mamps
Ag	35 mamps
Gd	30 mamps

Quantitative interpretation for filters is the same as for other samples except for dividing by calculated weight. Results are given in mass of element/cm². If the sponsor requires the analyte concentration to be in ppm, the weight of the aerosol deposit in measurements/cm² and the assurance that the deposit is both uniform across the filter and large enough to fill the sensitive beam area must be provided. Having these assurances, the mass information can be input and the program will output percent or ppm analyte concentrations.

4.5 Quantitative Interpretation of Acquired Spectra

The basic method is described below. Modifications to the basic method may be performed as needed according to the sample type as described above.

Type: R U N S A P 3

Program execution and user options are described, with examples, in PNL-4173, pages 26-32.

Requires the use of libraries

TZ2010.LIB for Ti Target
Z1AgV1.LIB for Zr Target
SKBROK.LIB for Ag Target
AMGL1B.LIB for Gd Target

Options Used: Save Paper
 Float Energy Scale
 Divide by Calculated Weight

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Determine Thickness from Scatter
Subtract Blank
Save Sponsor Report File

Energy Calibrate Refer to PNL-4173, page 31.

Live Time Refer to PNL-4173, page 32.

Data Set Refer to PNL-4173, page 32.

The series name designates target [Z] zirconium
" " " " sponsor [R S] Ron Sanders
" " " " month [07] July
" " " " set [1] 1st set

For example, Z R S 0 Z 1 0 1 through Z R S 0 Z 1 1 Z is interpreted as 1st to 17th sets of samples for sponsor RS, excited with Zr Target on the 1st of July.

SAP3 OUTPUT - Described in detail, with examples, in PNL-4173, pages 68-78.

Sponsor Report. Refer to PNL-4173, page 31.

Type: R U N [1 0 , 1 2] S X R

This program allows the operator to output a report with all associated information (Method, Standard, Sample Name, Series Names, etc.) plus the quantitative interpretation of the spectrum. Output includes all peak analysis information, matrix correction factors and element concentrations, uncertainties and detection limits.

4.6 Calculations of Uncertainty

The uncertainty calculations are completely described in Nielsen, K. K., "X-Ray Spectrum," 1978, 7:15-22, and "SAP3," PNL-4173, pp. 47-50. Because of the importance of these calculations, they are outlined here.

The standard error in the peak area, S_n , is estimated for a peak occurring at integral channel locations as

$$S_n = [N + B (1 + \frac{B}{k (b_1 + b_2)})]^{1/2}$$

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where

N = the partial net peak area

B = the background area beneath N

b_1, b_2 = the counts in the two channels used to define the background

k = number of channels used in the smoothing function prior to peak analysis

When interfering peaks are encountered, element concentrations are corrected by a simple product of the peak overlap coefficients (in units of mass/mass) and the concentrations of the interfering element. In such cases, the uncertainty of the peak area is increased by uncertainty of the overlap correction as

$$S_n = [S_n^2 + S_o^2 f (A_o/A_n)]^{1/2}$$

where S_o is the uncertainty in the peak area used to analyze the interfering element, f is the peak overlap coefficient, and A_o and A_n are the respective absorption correction factors for the interfering and primary element peaks.

The uncertainty in element concentrations, S_c , is determined from the peak area uncertainty by using the same form of equation used to relate peak areas to elemental quantities.

$$S_c = \frac{S_n \cdot Y \cdot A_o \cdot P \cdot E}{T \cdot K}$$

where Y = the normalization factor used to alter concentration unit (1 unless sample is diluted)

A_o = the self absorption correction factor

P = the particle size correction factor (diluted samples)

E = the enhancement correction factor

T = the analysis live-time

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K = the element calibration factor (x-ray intensity per unit element mass).

The above equations give the 1-sigma statistical precision of the element concentrations due to counting statistics only, and thus represent the maximum confidence that can be placed in the results.

Systematic sources of errors such as calibration error, or other source of errors are not addressed by this calculation. The SAP3 program provides an option for the user to insert an estimate of other source of error into the formula. When entered, this error is combined with the above estimate of random error as:

$$S_c = C[(S_c/C)^2 + \epsilon^2]^{1/2}$$

where C = the element concentrations

ϵ = the fractional error to be combined with the peak statistical error.

5.0 QUALITY CONTROL REQUIREMENTS

5.1 Conditions

There must be a data library for each type of support matrix (blank) for each excitation source. Samples and standards must be prepared to cover the sensitive beam area and adhere to the geometry conditions for proper backscatter.

The EDXRF system, i.e., the equipment and software, must be operated by trained analysts. Documented professional experience may be substituted for training. Knowledge of PNL-4173 will be acquired by the issuance of a documented reading assignment and briefings by the cognizant scientist. Annual recertification is required by means of a conceptual test which will be maintained and posted near the EDXRF machine. Training is documented and records are maintained in accordance with PNL-MA-70, PAP-201, "Indoctrination and Training."

5.2 Calibration

5.2.1 Thin Films

Conduct the EDXRF calibration as specified in PNL-4173, using the thin film calibration standards for each excitation source. Follow the analytical procedure or system software instructions to run the thin film standards.

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Calibrate the system the first time the system or method is used, after any significant modification to the equipment or software, and for each new element and excitation source.

Thin film standards are used for the determination of intensity in count/min/ $\mu\text{g}(\text{element})/\text{cm}^2$ versus element energy in KeV. The standards are typically produced by vapor deposit of the elements on mylar or polycarbonate substrate and are available from Micro Matter, Eastsound, Washington. The supplier provides certification of traceability to the U.S. National Institute of Standards and Technology.

5.2.2 Matrix Standards

A matrix standard is analyzed in position number 1 to obtain factors to adjust the calibration curve for the matrix effect. The matrix standard must have a matrix similar to the sample group and be prepared in a similar fashion with similar materials. Following the analytical procedure or system software instructions, the matrix standard will be run and the correction factors applied. Documentation is maintained with the sample analyses.

5.3 Library Preparation

The data required for a new library include a set of thin-film standard spectra and one or more spectra from samples of known composition and thickness (g/cm^2).

The thin-film sensitivities or calibration factors of the spectrometer using the intended excitation source and intensity are determined by analyses of thin-film single element standards of all elements to be included in the library. The resulting sensitivities are plotted logarithmically as a function of x-ray energy and the data smoothed to remove the uncertainties in the individual element standards. The smoothed data is entered into the library.

The incoherent and coherent scatter peak calibration constants are determined, in accordance with PNL-4173, for a given excitation source and for a given x-ray system by analysis of one or more samples of known thickness and composition. Pellets of cellulose or carbon, or thin sheets of aluminum provide suitable samples of simple composition.

A data library for the blank of the intended sample mounting is also determined from an analysis of the desired blank configuration. This information corrects for the attenuation of x-rays by the support materials.

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A data library for the system blank, or background contribution is also prepared.

Prior to routine use of the library, the set of standards is analyzed using the new library with various options to check the accuracy of the various calibrations and make any refinements that are indicated.

5.4 Quality Control Data

The quality control samples described below are analyzed with each sample group.

A. Matrix Standards

A matrix standard, which shall be different from the one used for calibration, shall also be analyzed as part of the sample group.

Standards must have an approximate matrix match (e.g., rock vs. rock, tissue vs. tissue) to the sample group, and be prepared to approximate the sample size.

Analyze at least one matrix standard, in addition to the one analyzed at the beginning of each sample group, for each group of analyses.

If the matrix standard analysis equals or exceeds the control action limit, re-run the matrix standard one or two times. If two of the three analyses equal or exceed the control action limit, stop sample analysis and correct the problem. (See Section 5.8 below.) The matrix standard will be counted before and after sample analysis run. Concentrations of the sample and matrix standard must compare within errors, or sample analysis will be stopped and reprocessed.

Matrix standards are examined for deterioration, such as warping or holes, prior to each use and not used if any adverse changes are detected.

B. Duplicates

Run one duplicate analysis per sample group to determine the analytical precision. If the duplicate sample results are outside the control limits, the group leader must determine the corrective action, including rendering a judgement on the validity of the data. If the samples are not to be re-run, then all the data for the samples associated with that duplicate sample, i.e., all the samples in that sample group or the samples that preceded the suspect duplicate, must be flagged.

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5.5 Program Dependent Quality Control Data

Generation of the quality control data specified in this section is dependent on the technical nature of the program.

A. Spikes

When matrix standards are unavailable or unsuitable, analyze one duplicate spiked sample per sample group. The spike shall include the major analytes of interest. If each spike recovery is not at or within the limits of 75 - 125%, based upon the thin film standard as described on page 19 of PNL-4173, the spike will be redone and the corrective measures documented in the LRB.

B. Lab Control Samples

Analyze one lab control sample per sample group. The lab control sample shall be prepared from certified material and it must have a matrix (e.g., solid or aqueous) similar to the matrix of the sample group. If the percent recovery falls outside the control limits, re-run the lab control sample one or two times. If two of the three analyses equal or exceed the control action limit, stop sample analysis and correct the problem. The samples associated with that lab control sample, i.e., all the samples in the sample group or that preceded the suspect lab control sample, must be reanalyzed. The group leader must determine if the samples to be reanalyzed must be reprocessed in total as well.

C. Preparation Blanks

A preparation blank shall be prepared and analyzed for those occasions when the sample must be diluted or its mechanical strength enhanced by addition of other materials. If the preparation blank results are outside the control limits, the group leader must determine the corrective action, including rendering a judgement on the validity of the data.

5.6 Data Reports and Control Charts

- A. Reports to the client shall be reviewed and signed by the analyst and a technically qualified reviewer. Reports shall be submitted to the group leader for review and transmission to the client. The group leader may act as the technical reviewer.
- B. Analytical Laboratory Operations (ALO) will establish the required control chart procedures and assure that the charts are maintained in the laboratory on a regular basis. To establish the control chart initially, the first time the

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system is used, send the first ten results from matrix standards to ALO Data Quality to calculate limits for the control chart. Thereafter submit all (non-calibration) matrix standard analysis data to ALO.

- C. Analytical results from duplicates for each sample group or run shall be reported to the Manager, Analytical Data Quality, ALO.

5.7 Precision and Accuracy

In collaboration with the EDXRF group leader, the Analytical Data Quality (ADQ) office will utilize the QC data provided from Section 5.4 above to determine the precision and accuracy initially for each sample matrix.

This information is used to prepare a control limit chart for a set of similar matrix samples. This is accomplished by the determination of the standard deviation, based on ten acquisitions, of selected analytes represented by the matrix standards. The control limit chart is then based on +/- three times the standard deviation for the selected analytes. The data accumulated on these matrix standards during the routine analysis is then compared to the control limit chart.

5.8 Sample Analyses Control

If the routine analysis of the matrix standards show that the procedure is out of control (results equal or exceed control chart action limits), the condition shall be corrected, and the start up instrument calibration procedure applied. All samples that were analyzed since the last acceptable matrix standard or duplicate analysis shall be re-analyzed and the earlier analytical data declared void.

6.0 REFERENCES

1. Nielson, K. K. 1978. "Applications of Direct Peak Analysis to Energy-Dispersive X-Ray Fluorescence Spectra." X-Ray Spectrum 7:15-22.
2. Nielson, K. K., and R. W. Sanders. 1982. The SAP3 Computer Program for Quantitative Multi-element Analysis by Energy-Dispersive X-Ray Fluorescence. PNL-4173, Pacific Northwest Laboratory, April 1982, 120 pp.
3. Covell, D. F. 1959. "Determination of Gamma-Ray Abundance Directly from Total Absorption Peak." Anal. Chem. 31:1785-1790.

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4. Sanders, R. W., K. B. Olsen, and W. C. Weimer. 1983. "Multielement Analysis of Unweighted Oil Samples by X-Ray Fluorescence Spectrochemistry with Two Excitation Sources." Anal. Chem. 55 12:1911-1914.
5. McMaster, W. H., N. K. Delrande, J. H. Mallett, and J. H. Hubbell, "Compilation of X-Ray Cross Sections." UCRL-50174, Sec. II, Rev. 1, (1969).
6. Nielson, K. K., S. R. Garcia. 1977. "Use of X-Ray Scattering in Absorption-Correction for X-Ray Fluorescence." Adv. X-Ray Anal. 20:497-506.
7. Nielson, K. K., R. W. Sanders, and J. C. Evans. 1982. "Analysis of Steels by Energy-Dispersive X-Ray Fluorescence with Fundamental Parameters." Anal. Chem. 54 11:1782-1786.
8. PNL-MA-6, Radiation Protection (latest version)
9. PNL-MA-70, Quality Assurance Manual (latest version)
10. Kevex 0810A Instruction Manual
11. Canberra Series 80 Multichannel Analyzer Operators Manual, Version 1.0, June, 1978.
12. PNL-MA-567, Procedures for Ground-Water Investigations, AD-4, "Sediment Sample Chain-of-Custody."

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Supplemental Information

Introduction

The SAP3 program analyzes x-ray fluorescence spectra for selected peak areas and calculates element concentrations from the resulting data. It computes net peak areas by a background-independent method and uses them to calculate element masses or concentrations from a library of sensitivities and fundamental constants. The calculations require no user interaction after initial selection of options and entry of the analysis live time.

General Considerations

SAP3 uses thin-film spectrometer sensitivities, with mathematical corrections for three types of matrix effects, i.e., self-absorption, enhancement, and particle-size effects. The corrections permit analyses of thin, intermediate or thick samples without corresponding calibrations or standards. The matrix corrections require a complete definition of sample constituents. For metal alloys, this definition can often be determined from the fluorescent peaks in the spectrum. For geological, biological, or other materials containing significant quantities of oxygen, carbon, or other light elements not observed in the EDXRF spectrum, the remainder of the sample matrix is defined from the incoherent and coherent backscatter peaks. The contribution to the backscatter by the observed elements is first determined, and the remainder is attributed to two "representative light elements", whose masses are used in the matrix correction calculations. The SAP3 program is thus unique from other fundamental parameter methods in its ability to perform matrix corrections without any prior knowledge of major sample constituents.

In estimating sample thickness, the program assumes that the observed mass is spread over the sensitive area viewed by the detector. Samples therefore must be either sufficiently large to cover the sensitive area, or be infinitely thin or thick to conform to the fundamental parameter calculations used in the program.

The geometry of the sample chamber must be such that virtually all observed backscatter comes from the sample rather than from the sample chamber or other system components and monoenergetic excitation is required to give discretely measurable incoherent and coherent backscatter peaks.

Suitable precautions should always be taken to verify the sample preparation method with a standard reference material.

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Plastic supporting films should also be characterized for their absorption and scatter characteristics, as well as impurity contents, prior to use in sample mounting.

Library Preparation and Calibration Curve

The generalized calibration is based on a set of thin-film sensitivities, which are stored in a library disk file and used for all sample matrices and thicknesses. Peak overlap factors are also determined from the thin-film standards, and are stored in the library for calculating peak overlap corrections.

The peak analysis and elemental concentration sections of the SAP3 program uses arrays of fundamental physical parameters of x-ray energies, mass absorption coefficients, cross sections, fluorescence yields, absorption edge, and jump ratios to perform the matrix corrections for relating net peak intensities to element concentrations. These arrays are read into the computer from a disc file when the SAP3 program is initiated. Each excitation source has its own unique disk file or library. The thin film sensitivities or calibration factors of the spectrometer using the intended excitation source is also part of the library. The complete library preparation procedure is detailed and explained in PNL-4173, pages 5 through 24.

Peak Analysis Method

The method of peak analysis is described in detail in "Nielsen, K. K. 1978. Application of Direct Peak Analysis to Energy-Dispersive X-Ray Fluorescence Spectra. X-Ray Spect. 7:15-22" and in "Nielsen, K. K., and R. W. Sanders. 1982. The SAP3 Computer Program for Quantitative Multielement Analysis by Energy-Dispersive X-Ray Fluorescence," PNL-4173, Pacific Northwest Laboratory Report to U.S. Department of Energy, pp 43-50.

The method is a modified Covell (Covell, D. F. 1959, Anal. Chem.) approach for direct peak analysis that is applied to x-ray fluorescence spectra. It is background independent and provides acceptable precision, and minimizes errors from instrumental gain shifts, sum peaks, and peak overlap. The peak analysis process:

- smooths the raw spectral data using a 5-point algorithm,
- determines accurate energy/ channel scale using an observed scatter peak and a known spectral peak,
- finds peak centers in terms of channel number using the energy/channel scale and known x-ray peak energies, or, optionally, through comparisons to a correlation spectrum,
- finds the window for each peak from its energy using a linear width versus energy relationship,
- computes window boundaries by successively adding and

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subtracting the appropriate width from the energy peak and interpolating to the exact window boundaries and their corresponding intensities, and f) integrates the net peak area using Covell's method.

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ATTACHMENT A

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ANALYSIS REQUEST FORM

INSTRUCTIONS:

1. Please submit completed form with samples, QA section must be specific.
2. Sample designation can be up to 25 characters.
3. Leave form with samples in the sample receiving area, or send form with samples to:

R.W. Sanders PB-08
3708 bldg./300 area
Battelle Pacific Northwest Laboratories
P.O. Box 999
Richland, Wa 99352

4. All prepared samples and residual sample material will be disposed of unless you specify otherwise under "Special Instructions".

GENERAL INFORMATION:

Name: _____ Ph: _____
Plant Mail: _____
Work Package: _____
SOW: _____
RFAS: _____
Sponsor: _____

What QA/QC requirements are imposed on this analysis?(sponsor or other)

Date Results are needed: _____

Today's Date: _____

Brief Description of sample material: _____

Analyze these samples qualitatively/quantitatively (circle one) for the following elements:

XRFA:

AAS:

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(continued)

ATTACHMENT A

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ANALYSIS REQUEST FORM

SPECIAL INSTRUCTIONS:

- () Samples need refrigeration.
- () Other requirements:
- () Return residual sample material. Yes() No()
to:
- () Send prepared samples. Yes() No()
to:
- () Send ___ analysis report(s).
- () Other comments and/or instructions:

Author: _____ date: _____

Activity Manager: _____ date: _____

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ATTACHMENT B

ILLUSTRATION OF SENSITIVE AREA VIEWED BY THE X-RAY DETECTOR

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-267, (Replaces 7-40.51), OPERATION OF THE CANBERRA MODEL 20 MULTICHANNEL ANALYZER

1.0 APPLICABILITY

This procedure describes the use of the Canberra Model 20 MCA which is connected to a NaI(Tl) well detector in Room 3B, 329 Bldg. The procedure's only purpose is to measure the ^{85}Sr gamma ray peak at 514 KeV, before and after a chemical separation per Procedure PNL-ALO-486.

2.0 DEFINITIONS

LRB Laboratory Record Book
MCA Multichannel Analyzer
NAI(Tl) Sodium Iodide, Thallium activated crystal
ROI Region of Interest

3.0 RESPONSIBLE STAFF

Cognizant Scientist - A chemist or other scientist familiar with this procedure who has an in-depth knowledge of this equipment.

Analyst - An individual who has been trained and certified in the use of this procedure.

4.0 PROCEDURE

4.1 Equipment and Materials

- Canberra Model 20 MCA
- High Voltage Power Supply set to ~ 1100 volts
- NaI(Tl) well Xtl
- > 1/2 dram glass cup set inside the NaI(Tl) well to avoid crystal contamination in the event of sample leaks
- Cs-137 "Control" source, ~ 4000 d/m in sealed, 1/2 dram, screw-cap vial

Author	Date	Project Mgr.	Date	QAD Representative	Date
FE Holt	2/28/91	N/A		GK Gerke	2/28/91
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
MR Weiler	2/28/91	LR Greenwood	2/28/91	All original signatures on file	
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4.2 Quality Control

The only purpose of this procedure is to obtain the ratio

counts ^{85}Sr after chemical processing,
counts ^{85}Sr before chemical processing

so a simple plot of a sealed Cs-137 control source vs. date will confirm that the equipment is functioning properly. Follow instructions in Attachment A of Procedure PNL-ALO-490. Count the control source for 10 minutes and plot the Area (total counts in ROI #2 less 3 channels on either side of the peak). If the Areas fall within the $\pm 3\sigma$ boundaries, and the peak channel number is between channels 329 and 333 the equipment is in control. The control source shall be counted before and after each set of samples processed for their $^{89+90}\text{Sr}$ contents.

4.3 System Description and Controls

Figures 1 through 4 with accompanying text illustrate and describe the basic features of the counting system.

Figure 1. NaI System Setup

The Series 20's front panel is illustrated in Figure 2. The key numbers refer to the text following the figure.

Figure 2. Front Panel

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1. The display is an 18 cm CRT screen (measured diagonally).
2. Below the display and to its right are a number of keys. Most of the keys are labeled with two functions. These are called hard keys.
3. The INTENSITY control varies the display's brightness for comfortable viewing. The control also turns the Series 20 ON and initializes the unit when it is turned clockwise.
4. The numeric keys 1 through 5, are called soft keys; their labels, shown on the display's bottom line, change with the function being defined.
5. The INDEX key in the lower right corner of the front panel moves the cursor to the start of the next ROI, if any, otherwise it has no function. The two horizontal arrow keys control cursor movement. The two vertical arrows control the display's Vertical Full Scale and some parameter entries.

HARD AND SOFT KEYS

The Series 20 uses two types of function key: the "hard" key and the "soft" key. Pressing the MENU/EXIT hard key (one with a permanently defined function) to the right of the display will show a line of soft keys (keys with the changeable function definitions) at the bottom of the screen.

Soft key labels are automatically displayed on the line above the first five numeric keys. These key labels change according to the current function.

A hard key function is activated by pressing its key. A soft key function is activated by pressing the numeric key just below the appropriate label.

In the reference (Operator's Manual) the hard keys are shown in boldface type in a box outline.

(COLLECT)

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The soft keys are shown with the function name enclosed in a dashed outline.

(STATUS)

INITIAL DISPLAY

A few seconds after the power is applied, the display in Figure 3 will appear on the screen.

(1)	(2)	(3)
CL= 0 CTS= 0	MEM 1/1 VFS 64	FROM 2 TO 4095 INTG= 0
<hr/>		
<div>STATUS PAGE</div>	<div>COMPUTE TIME</div>	<div>EXECUTE TASK S1</div>
		PSET(L)= 1000 ELAP(L)= 0
(4)	(5)	(6)
<hr/>		
		(7)

Figure 3. Initial Display

1. CL = the Cursor's location in the spectrum
CTS = the COUNTS at the cursor's location.
ROI# = current ROI number, if any, otherwise not shown.
2. MEM = current memory group.
VFS = the display's Vertical Full Scale.
Status = Series 20's current status; if idle, nothing is shown.
3. FROM-TO = low and high channels of current ROI, if any, otherwise of display's current limits.

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INTG* = Integral (total number of counts) in the current ROI, if any, otherwise of the channels in the current display.
AREA* = Integral minus the averaged background of the current ROI, if any, otherwise not shown.

STATUS PAGE

If you press the STATUS PAGE soft key (the numeral 1), the display will change to show a list of the current data acquisition and EIA parameters. If you want to see the current calibration parameters (the calibration equation), press the ECAL key.

Figure 4 shows the Status Page with the default parameters. The Status Page always shows the last parameter values entered. The clock and calendar show the current time and date; they are not reset by power off.

CANBERRA SERIES 20 V2802-A3

PRESET LIVETIME= 1000 SECONDS

MODE: IDLE TAGWORD= 0

CURRENT COMPUTE FUNCTION
F1= shown on Model 2802 only

AMP	SCA	ADC	EIA	CLOCK
GAIN ~1130	LLD 0.322%	GAIN 4096	BAUD 2400	DA/MO/YR 22/02/91
INPUT NEG	ULD 110.0%	PHA ADD	LENGTH 7	TIME 12:45
SHAPING SLOW		OFFSET 0	PARITY EVEN	
		ZERO 0%		

[AMP] [SCA] [ADC] [EIA] [CLOCK]

Figure 4. The Status Page

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4.4 Checking and Adjusting Gain

Prior to counting the control source, it is necessary to check and, if necessary, adjust the gain of the amplifier via the analyzer keys. This is done as follows:

- 4.4.1 Check the gain by placing a sealed Cs-137 source into the well of the NaI(Tl) detector and counting for a sufficient period that the peak center can be estimated reasonably accurately.
- 4.4.2 The center of the Cs-137 662 keV gamma ray peak should be between channels 329 and 333. If this is the case, no gain adjustment is needed -- proceed to 4.4.
- 4.4.3 If the amplifier gain needs adjustment, do the following:

From the MAIN MENU, press key 1 (STATUS PAGE).

From the sub-menu which appears, press key 1 (AMP).

From the sub-menu which appears, press key 5 (GAIN).

The current value of the amplifier gain will be displayed, along with the range of acceptable values. To change the value, use the number keys to enter the value desired, then press key ENTER.

Press key 1 (COLLECT) to clear the current spectrum, initiate counting and display the spectrum.

Continue to adjust the gain as necessary until the center channel of the Cs-137 662 keV peak is between channels 329 and 333.

Return to the main menu by pressing key MENU/EXIT.

4.5 Operating the Counter-Control Source

- 4.5.1 An automatic sequence of steps, S1, are incorporated into the counting system to obtain the control counts.
- 4.5.2 Set the glass sleeve into the NaI(Tl)'s well and place the sealed source marked "Control" inside that.

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- 4.5.3 Press Menu/Exit once or twice until you obtain
MENU ANALYZE EXECUTE at the
bottom of the screen.
- 4.5.4 Press the #3 under Execute
- 4.5.5 Press #1 under S1. The ROI channels for the 662 KeV peak are from 279 to 406. Put in 1, only, program starts.
- 4.5.6 The analyzer will clear data from the screen, set live time to 600 seconds, and count for that period of time.
- 4.5.7 Plot the Area (upper right corner of screen) onto the control chart provided. The counts must be within the $\pm 3s$ boundaries and the peak channel shall be between channels 329 and 333.

4.6 Operating the Counter-Sample Count and Standard Count

- 4.6.1 Set the glass sleeve into the NaI(Tl)'s well and place the sample or standard source inside that.
- 4.6.2 Press Menu/Exit once or twice until you obtain
MENU ANALYZE EXECUTE at the
bottom of the screen.
- 4.6.3 Press the #3 under Execute
- 4.6.4 Press #2 under S2. The ROI channels for this peak at 514 KeV are from 202 to 310, enter Number, 1, enter, program starts.
- 4.6.5 The analyzer will clear the data from the screen, set live time to 3600 seconds and count for that period of time. The peak channel counts shall be between channels 283 and 261.
- 4.6.6 Record the Area of the count on the analytical card, labeling it sample count or standard count. The ratio of the sample count/standard count is the fractional recovery of the method and is used in the calculations of Procedure PNL-ALO-486, Section 5.0.

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5.0 References

Series 20 Multichannel Analyzer - Operator's Manual, Canberra Industries.

ATTACHMENT A

QUALITY CONTROL

CONTROL ANALYSES

Control data include items identified in Section 7.2 and specific requirements of analytical procedures. Results shall be documented in data records, which may be commingled with sample data (e.g., in a LRB). Actions taken to regain control shall be documented in data records.

STATISTICAL PRACTICES

Statistical practices used to treat analytical measurements are given below. Definitions of the statistical terms used are found in Section 4.0, MCS-033.

(a) Control Charts - Prepare control charts according to the following procedure:

1. Obtain a group of at least nine measurements over a period of at least three working days.
2. Calculate the average () for the group.
3. Calculate the standard deviations.
4. Calculate the upper control limit (UCL) and the lower control limit (LCL) as follows:

$$UCL = + 3s$$

$$LCL = - 3s$$

5. Prepare a control chart to plot measurements obtained against the order in which the measurements were obtained, with control lines corresponding to , UCL and LCL.
6. Plot each measurement from the standard in the order obtained.

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- (b) Method Out of Control - The following criteria establish when a method is out of control. When that happens, the problem shall be investigated

ATTACHMENT A - CONTINUED

and the steps taken to bring the method back into control shall be documented in the data records. Samples shall not be analyzed using a method that is out of control.

1. If a point falls outside a control limit, immediately run another standard. If the second measurement falls outside, the method is out of control.
2. If the second standard falls within the control limits, run a third standard. The measurements from this third standard determines whether the method is in or out of control.
3. If consecutive standard values plotted on the control chart begin to drift toward a control limit, the method may be going out of control and the situation shall be investigated and recorded in LSC notebook.

- (c) Outlying Observations - When evaluating a series of measurements and one (or more) value appears to deviate significantly from the other values, a decision must be made about how to treat the outlier(s). The outlier shall be discarded if it can be substantiated that the outlier resulted from a specific error. Justification for discarding the outlier shall be documented in the LSC notebooks. Otherwise, the outlier shall be included with the series of measurements. The outlier shall be documented in the data records as being suspect.

LIMITS OF ERROR

Limits of error for all measurements made during an analysis shall be specified in some manner. If a limit is not stated with a measurement value, then the following system of limits of error shall be in effect:

- (a) When two or more significant figures are specified, the limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g ($4.5E+2$)

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means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL. (The example of 450 g is included to show that zeros before the decimal point are not considered to be significant figures.)

- (b) If a single significant figure is specified, the actual measurement shall be within $\pm 5\%$ of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

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**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-270.4 R0
Page 1 of 1

A.

Document Number: PNL-ALO-270 Revision Number: 0

Document Title: Total Cyanide in Waters, Solids or
Sludges

Document's Original Author: MW Urie

Effective Date
of ICN: 5/12/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 17 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert *TL Ehlert*

Date: 5/7/92

Approval Authority: AG King *AG King*

Date: 5/7/92

Other Approvals: TE Jones *TE Jones*

Date: 5/12/92

: _____ Date: 1/1

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-270.2

Page 1 of 2

A. Document Number: <u>PNL-ALO-270</u> Revision Number: <u>0</u>		Effective Date of ICN: <u>11/01/91</u>
Document Title: <u>TOTAL CYANIDE IN WATER SOLIDS &</u> Document's <u>SLUDGES</u> Original Author: <u>MW URIE</u>		Change Requested By: <u>MW URIE</u>
B. Action REPLACE PAGE 3-17 Delete Page 18		
C. Effect of Change CHANGE IS TO PROVIDE CONSISTENCY OF LABELING PRACTICES & ALLOW OTHER DOCUMENTATION (e.g. MA-70 & ANALYTICAL CHEMISTRY LABORATORY QA PLAN MCS033) TO BE THE GOVERNING DOCUMENTS ON STANDARDS LABELING.		
D. Reason for Change/Description of Change Reason: Provide for consistency in labeling standards and working solutions. Description: Step 5.10 changed to Stock Standard cyanide solution from Stock Cyanide solution. Step 5.11 changed to Intermediate working cyanide solution from Intermediate standard cyanide solution and stock standard cyanide solution from stock cyanide solution. Delete last sentence. That is, "Record Date of Preparation on Bottle." is to be deleted. Continued on page 2.		
E. Approval Signatures (Please sign and date)	Type of Change: {Check (✓) one} ☐ Minor Change ☒ Major Change	
Process Quality Department: GK GERKE <u>[Signature]</u> , <u>QE</u>	Date: <u>11/13/91</u>	
Approval Authority: AG KING <u>[Signature]</u>	Date: <u>11/14/91</u>	
Other Approvals: BM GILLESPIE <u>[Signature]</u>	Date: <u>11/18/91</u>	
:	Date: <u> </u> / <u> </u> / <u> </u>	

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-270.2
Page 2 of 2

Step 5.12 changed to Working cyanide solution from Working standard cyanide solution and to intermediate working cyanide solution from intermediate standard cyanide solution. Delete last sentence. That is, "Record Date of Preparation on Bottle." is to be deleted.

Step 6.3.2.3 changed to Stock Standard from Stock and to Intermediate Working CN solutions from Intermediate CN Solutions.

Step 7.3.1.1 Changed to working cyanide solution from working standard.

Step 7.3.2.1 Changed to intermediate working cyanide solution from intermediate standard solution.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-270, TOTAL CYANIDE IN WATERS, SOLIDS OR SLUDGES

APPLICABILITY

This procedure is applicable for determining the concentration of cyanide in waters, soils, and sludges. The methodology is comparable to CLP SOW 788 Method 335.2 distillation and colorimetric technique for the analysis of cyanide.

DEFINITIONS/ACRONYMS

Total Cyanide: Cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

RESPONSIBLE STAFF

Cognizant Scientist
Technician/Analyst

PROCEDURE

1.0 Summary of Method

- 1.1 The cyanide, as hydrocyanic acid (HCN), is released from cyanide complexes by means of a reflux-distillation operation and is absorbed in a scrubber containing sodium hydroxide (NaOH) solution. The cyanide ion in the absorbing NaOH solution is then measured colorimetrically.
- 1.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone reagent and the absorbance is read at 620 nm, or on the addition of pyridine-barbituric acid reagent and the absorbance is read at 578 nm.

Author	Date	Project Mgr.	Date	QAD Representative	Date
MW Urie		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
TE Jones		PF Salter		ALL ORIGINAL SIGNATURES ON FILE	
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2.0 Interferences

- 2.1 Interferences are eliminated or reduced by using the distillation procedure described in Section 7.2.
- 2.2 Sulfides have an adverse effect on the colorimetric measurement. The presence of sulfides is determined by testing the distillate with lead acetate test paper.
- 2.3 To obtain comparable color intensities for samples and standards containing the same concentrations of cyanide, it is important to maintain the same salt content for the samples and standards.

3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

4.0 Apparatus

- 4.1 Reflux distillation apparatus (such as shown in Figure 1): The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber should be a Fisher-Milligan scrubber, or equivalent.
- 4.2 Spectrophotometer: Suitable for measurements at 620 nm or 578 nm with a 1.0 cm cell or larger.
- 4.3 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.
- 4.4 Filter apparatus and filters (Whatman 42, or equivalent).
- 4.5 Lead-acetate test paper.

5.0 Reagents and Standards

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- 5.1 Deionized water: Deionized water of sufficient quality, similar to ASTM Type II reagent water shall be used for preparing standards, samples, and reagent dilutions. Calibration and sample blanks shall produce concentrations at or below the instrument detection limits.
- 5.2 Sodium hydroxide solution (1.25 N): Dissolve 50 g of reagent NaOH in water, and cool to room temperature. Dilute to 1.0 L with water.
- 5.3 Sulfamic acid (0.4 N): Dissolve 40 g of H_2NSO_3 in 500 mL of water and dilute to 1.0 L with water.
- 5.4 Concentrated sulfuric acid (H_2SO_4): Reagent grade.
- 5.5 Magnesium chloride solution: Dissolve 510 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 500 mL of water and dilute to 1.0 L with water.
- Note: The use of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is an acceptable alternative except for EPA-CLP analysis (dissolve 60 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 500 mL DIW and dilute to 1.0 L with water).
- 5.6 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-aminobenzalrhodanine in 100 mL of acetone.
- 5.7 Manual spectrophotometric reagents:
- 5.7.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1.0 L water. Refrigerate this solution.
- 5.7.2 Chloramine-T solution: Dissolve 1.0 g of white, water-soluble chloramine-T in 100 mL water and refrigerate until ready to use. Prepare fresh weekly. Record date of preparation on the bottle of solution.
- 5.7.3 Color-reagent: One of the following may be used:
- 5.7.3.1 Pyridine-barbituric acid solution: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of conc. HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with water and mix. This reagent is stable for approximately six months if stored in a cool, dark place. Record date of preparation on bottle.

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5.7.3.2 Pyridine-pyrazolone solution: Pour solution 5.7.3.2.1 through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper, pour solution 5.7.3.2.2, collecting the filtrate in the same container as filtrate from 5.7.3.2.1. Mix until the filtrates are homogeneous. The mixed reagent develops a pink color, but this does not affect the color production with cyanide if used within 24 hours of preparation. Record date and time of preparation on the bottle.

5.7.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.

5.7.3.2.2 3,3'-Dimethyl-1,1'-diphenyl [4,4'-bi-pyrazolin]-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

5.7.4 For non-EPA-CLP analyses, HACH chemicals may be used instead of the reagents in 5.7.1, 5.7.2 and 5.7.3. The HACH chemicals are Cyaniver™ cyanide reagents for the colorimetric determination of cyanide using the pyridene-pyrazolone method (HACH Cyanide Reagent Powder Pillows #14049-69, #14040-69 and #14041-69).

5.8 Hydrochloric acid (2.4 N): Add 200 mL of concentrated HCl (reagent grade) to 700 mL of water, cool to near room temperature, and dilute to 1.0 L.

5.9 Hydrochloric acid (0.024 N): Add 1 mL of 2.4 N HCl to 70 mL of water, cool to room temperature, and dilute to 100 mL.

5.10 Stock standard cyanide solution (1 mL = 1 mg CN⁻): Dissolve 2.51 g KCN and 2 g KOH in 500 mL of water and dilute to 1000.0 mL. Standardize with 0.0192 N AgNO₃ solution using the rhodanine indicator. (1 mL AgNO₃ solution is equivalent to 1 mg CN⁻ in stock cyanide solution).

5.11 Intermediate standard working cyanide solution (1 mL = 100 ug CN⁻): Dilute 10.0 mL of stock cyanide solution to 100.0 mL with water. Prepare fresh daily. ~~Record date of preparation on bottle.~~

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- 5.12 Working standard cyanide solution (1 mL = 10 ug CN⁻): Dilute 10.0 mL of intermediate working standard cyanide solution to 100.0 mL with water. Prepare fresh daily. Record date of preparation on bottle.
- 5.13 Standard silver nitrate solution (0.0192 N): Weigh 3.2647 ± 0.0002 g crushed AgNO₃, which has been dried to a constant weight at 40°C, dissolve in water, and dilute to 1000.0 mL.

5.14 Cadmium carbonate (powdered).

6.0 Quality Control

- 6.1 All quality control data shall to be maintained and available for easy reference or inspection.
- 6.2 Minimum quality control requirements.
- 6.2.1 A minimum of three calibration standards and one measurement blank are required for spectrophotometer calibration [See Section 7.3]
- 6.2.2 Samples shall be diluted, and reanalyzed, if they are more concentrated than the highest standard which is within the calibration range.
- 6.2.3 At least one quality control standard shall be analyzed with each group of samples or, at a minimum, once during daily operation. If the results of the QC standard are not within 80% to 120% of the mean value, the Cognizant Scientist shall determine the corrective action. All samples analyzed since the previous QC standard shall be flagged on the data reports and corrective action documented with the data. Validation of the data is the responsibility of the technical group leader.
- 6.2.4 It is not imperative that all standards be distilled in like manner to the samples. However, at least one mid-range verification check standard per every 10-15 samples shall be distilled and compared to the calibration curve to ensure the distillation technique is reliable. If the distilled standard does not agree to within 85% to 115% of the undistilled standard, the Cognizant Scientist shall determine the corrective action. All samples analyzed since the previous verification check standard shall be flagged on the data reports and corrective action documented with the data. Validation of the data is the responsibility of the Technical Group Leader.

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6.2.5 Additional quality control (i.e., duplicates, spikes, additional system or matrix blanks, tighter tolerances, holding times, etc.) is governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the Analytical Request Form (ARF), the project Statement of Work (SOW), or the sample analysis Test Instruction (TI).

6.3 Quality control for clients requesting compliance with CERCLA requirements.

6.3.1 A minimum of three calibration standards and one matrix blank are required for the calibration of the spectrophotometer (See Section 7.3). One calibration standard shall be at the required detection limit (from the SOW, TI, or ARF).

6.3.2 A minimum of one methods blank, one duplicate, one matrix spike and a matrix spike duplicate shall be prepared and analyzed for every sample batch/group of similar matrix type. A sample batch/group is ≤ 20 samples. Spikes shall be added at the time of sample preparation.

6.3.2.1 The methods blank shall be a water sample processed through each sample preparation and analysis step. If the methods blank is not $\leq$ the requested detection limit (from the SOW, TI, or ARF), then the samples must be prepared and analyzed again.

6.3.2.2 The relative percent difference between the duplicate samples must be less than or equal to the required precision per the SOW, TI, or ARF if the sample values are greater than 5x the requested detection limit (from SOW, TI, or ARF). If no required precision is given, then the relative percent difference shall be $\leq 20\%$. If the sample value is less than 5x the requested detection limit, then the difference between duplicates must be within $\pm$ the detection limit. If one result is above the 5x value and one below, use the $\pm$ detection limit criteria. If duplicate sample results are outside these control limits, flag all data with an asterisk (*) for the sample batch/group associated with that duplicate analysis in the data report.

6.3.2.3 The spike and matrix spike duplicate are added to two replicates of a sample prior to any preparation or analysis. A field blank sample may not be

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selected for spike analysis. The spikes are added to the samples such that the concentration of the spike in the sample shall be 100 $\mu\text{g/L}$. Spikes shall be prepared from the Stock Standard or Intermediate Working CN solutions (See Sections 5.10 and 5.11).

6.3.2.3.1 Spike recoveries shall be at or within the limits of 75% to 125%.

Note: For calculational purposes, when a measured sample concentration is < the detection limit, the sample concentration value used is 0.

6.3.2.3.2 If this recovery is not met for the spike or spike duplicate, all data in the sample batch/group must be flagged with the letter "N" in the data report, unless the sample concentration exceeds the spike concentration by a factor of four or more. In that event, the data need not be flagged.

6.3.2.3.3 If the recovery is not met and the sample concentration does not exceed the spike concentration by a factor of four, a post-distillation spike must be performed. Spike an unspiked aliquot of the distilled sample solution at 2x the indigenous level or 2x the required detection limit, whichever is greater, using one of the prepared standard solutions (Section 5). Prepare and analyze in accordance with Section 7.4.2. Report results as "post-distillation spike sample result, spike added and % recovery" in the data report.

6.3.3 An initial calibration verification standard (ICV) shall be procured from the EPA or a certified solution obtained from a source independent from the instrument calibration standards. It shall be at a concentration other than those used for instrument calibration, but within the calibration range.

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NOTE: This standard must be distilled with the samples to be analyzed. At least one ICV shall be prepared for each batch of samples to be analyzed. The ICV also serves as the Laboratory Control Sample.

This standard is to be analyzed immediately following the calibration of the spectrophotometer. The measured value must be at or within 85% to 115% of the true value. If the measurement is outside of this limit, then the analysis must be terminated, the problem corrected, the instrument recalibrated and the calibration reverified.

6.3.4 At a minimum, a continuing calibration verification (CCV) standard (made from the original instrument calibration standard source) diluted to a concentration at or near the mid-range of the calibration curve must be analyzed at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The continuing calibration verification standard must be at or within 85% to 115% of the true value. If the CCV standard is greater than these limits, the analysis must be stopped, the problem corrected, the instrument recalibrated, and a reanalysis of all analytical samples analyzed since the last good CCV be conducted. The CCV is not distilled.

6.3.5 A calibration blank sample shall be analyzed after every CCV sample and after the last sample analyzed in the set of samples being analyzed. The calibration blank sample is the blank solution made up as part of the calibration standards (See Section 7.3). If the absolute value of the calibration blank sample exceeds the requested detection limit (from the SOI, TI, or ARF), the analysis is terminated, the problem corrected, the instrument recalibrated and a reanalysis of all analytical samples analyzed since the last good calibration blank sample conducted. The calibration blank sample is not distilled.

7.0 Analysis Method

The CN Analysis Worksheet is used to record information required to construct calibration curves and to calculate reportable results (See Figure 2).

7.1 Sample collection and preservation

Sample collection and field preservation is not within the scope of this procedure. However, it is important, whenever possible, that the samples be collected and preserved properly in order to maintain sample integrity. Once received, the samples should be preserved according to the steps below.

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- 7.1.1 If not already treated at the time of collection, aqueous samples shall be preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH >12) upon receipt.
- 7.1.2 Oxidizing agents such as chlorine decompose most of the cyanides. At the time of field sampling, test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.
- 7.1.3 Samples shall be refrigerated at 4°C ($\pm 2^\circ\text{C}$), radioactivity levels permitting, and analyzed within the holding times specified (i.e., either Appendix A or the governing SOW).

7.2 Distillation

- 7.2.1 The distillation procedure for the water, solid and sludge samples is identical except for the sampling procedure.

NOTE: For samples analyzed to EPA-CLP requirements, a laboratory control standard equivalent to the initial calibration verification standard (See Section 6.3.3) must be prepared and distilled with each batch of samples.

- 7.2.1.1 Water sample - Transfer 500 mL of sample [V^s], or an aliquot of liquid sample [V^s] diluted to 500 mL with water, to the boiling flask containing boiling chips.
- 7.2.1.2 Solid or sludge sample - Weigh a representative 1.00- to 5.00-g portion of sample [W^s] and transfer it to the boiling flask containing boiling chips. Add 500 mL of water; shake or stir to disperse the sample.
- 7.2.2 Measure 50 mL of the sodium hydroxide solution (5.2) into the absorber tube. It may be necessary to dilute with water to obtain an adequate depth of liquid in the absorber.
- 7.2.3 Connect the vacuum to the distillation apparatus and adjust the flow so that between 1 to 2 bubbles of air per second enter the boiling flask.

Note: The bubble rate will not remain constant after the reagents have been added and while heat is applied. Therefore, the air rate must occasionally be adjusted

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to prevent the solution in the boiling flask from backing up into the air inlet.

- 7.2.4 If the sample is known (or suspected) to contain high nitrate or nitrite concentrations, add 50 mL of the sulfamic acid solution through the air inlet tube. Allow the air flow to mix the sample for at least 3 minutes. Record the addition of sulfamic acid.
- 7.2.5 Once the sample is mixed, slowly and carefully add 25 mL of the concentrated sulfuric acid through the air inlet tube. Thoroughly wash the air inlet tube with water.
- 7.2.6 Add 20 mL of magnesium chloride solution through the air inlet tube and wash down with water. (Note: For non-CLP samples, if magnesium sulfate is being used instead of magnesium chloride, add 60 mL of magnesium sulfate solution in the same manner.) Again, allow the air flow to mix the sample for at least 3 minutes.
- 7.2.7 Heat the solution to boiling and reflux for at least one hour. Continue to adjust the air flow during the entire reflux period to prevent the solution from backing up into and overflowing from the air inlet tube. Turn off heat and, continuing the air flow, allow the flask to cool for at least 20 minutes. After cooling, disconnect/close off vacuum and disconnect absorber tube.
- 7.2.8 Quantitatively transfer the absorber solution from the absorber tube to a 250 mL volumetric flask by washing with water. Dilute to volume [V^a] with water.
- 7.2.9 If the sample distillate is suspected to contain sulfides, verify the presence of sulfide by placing a drop of distillate on lead acetate test paper. In the presence of sulfide, the test paper will darken. Sulfide-containing distillates should be treated by adding cadmium carbonate until the distillate solution does not darken the lead acetate paper. Yellow cadmium sulfide will precipitate if the sample contains sulfide. Filter the distillate solution through dry filter paper into a dry beaker and use the filtrate as the sample to be analyzed.

7.3 Calibration of the Spectrophotometer

- 7.3.1 Calibration of Spectrophotometer when using HACH chemicals to prepare sample distillates and standards for colorimetric analysis:

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- 7.3.1.1 Prepare a minimum of three standards and a blank by pipetting suitable volumes of the working cyanide solution standard into 25 mL disposable beakers containing 5 mL of sodium hydroxide solution. Add water to bring volume to approximately 15 mL.

Standards Preparation Guideline

mL Standard	Conc. $\mu\text{g/L}$
0.0	Blank
0.05	20
0.10	40
0.25	100
0.50	200
0.75	300

- 7.3.1.2 Proceed with Steps 7.4.1.2 to 7.4.1.7. The absorbance readings obtained are used to construct a standard calibration curve of absorbance vs. concentration (See Figure 2).
- 7.3.2 Calibration of Spectrophotometer when NOT using HACH chemicals to prepare sample distillates and standards for colorimetric analysis (this option must be followed for samples requiring compliance with CERCLA requirements):
- 7.3.2.1 Prepare a minimum of 3 standards and a blank by pipetting suitable volumes of the intermediate standard working cyanide solution into 100 mL volumetric flasks to which 20 mL of the NaOH solution (Section 5.2) has already been added. Note: One calibration standard must be at the required detection limit (from the SOW, TI, or ARF). Dilute to 100 mL with water.

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Standards Preparation Guideline

mL standard	Prep. Conc., $\mu\text{g/L}^*$	Meas. Conc., $\mu\text{g/L}^*$
0	Blank	Blank
0.02	20	10
0.05	50	25
0.10	100	50
0.25	250	125
0.50	500	250
0.75	750	375

*The prep. conc. is the concentration in the 100 mL flask; the meas. concentration is the concentration in the final solution used to obtain absorbance readings.

- 7.3.2.2 Proceed with Steps 7.4.2.1 to 7.4.2.4. The absorbance readings obtained are used to construct a standard calibration curve of absorbance vs. concentration (See Figure 2). Concentrations are the Measured Concentration, not the Preparation Concentration.

7.4 Colorimetric Determination of Cyanide

- 7.4.1 Colorimetric Determination of Cyanide using HACH chemicals for sample and standards preparation:

- 7.4.1.1 Pipet 15.0 mL of solution [V^b] from the 250 mL volumetric flask to a disposable beaker.
- 7.4.1.2 Using a pH meter, add 2.4 N HCl drop-wise to a pH between 9 and 10. Using 0.024 N HCl, continue to adjust the solution to a pH near 7 to 7.5.
- Caution:** Addition of dilute HCl should be added drop-wise very carefully so as to maintain pH as close to 7 as possible.
- 7.4.1.3 Transfer the solution, quantitatively, to a clean 25.0 mL stoppered graduated cylinder. Dilute to volume [V^c] with water, then stopper and mix thoroughly.
- 7.4.1.4 Add the contents of one Cyaniver™3 Cyanide Reagent Pillow; then stopper and shake for 30 seconds. Allow the sample to stand for 30 seconds.

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- 7.4.1.5 Add the contents of one Cyaniver™4 Cyanide Reagent Pillow; then stopper and shake for 10 seconds. Proceed immediately to Step 7.4.6.
- 7.4.1.6 Add the contents of one Cyaniver™5 Cyanide Reagent Pillow; then stopper and shake vigorously for 15 seconds. If cyanide is present, a pink color will develop and turn blue within a few minutes. Allow at least 30 minutes for the color to develop.
- 7.4.1.7 Transfer a portion of the solution to a 1.0 cm spectrophotometer cell and read the absorbance at 620 nm.
- 7.4.2 Colorimetric Determination of Cyanide when NOT using HACH chemicals to prepare sample distillates and standards for colorimetric analysis (this option must be followed for samples requiring compliance with CERCLA requirements):
- 7.4.2.1 Withdraw 50 mL of the distillate or standard solution [V^b] from the flask (Step 7.2.8 or 7.3.2.1, respectively) and transfer to a 100 mL beaker.
- 7.4.2.2 Add 15.0 mL of sodium dihydrogenphosphate solution (Step 5.7.1) to the beaker from 7.4.2.1 and mix. Check the pH with a pH meter. If the pH is not approximately 7-7.5, adjust the solution pH with 0.024 N HCl or 2.4 N HCl, depending on the magnitude of adjustment needed.
- Caution: Addition of dilute HCl should be added drop-wise very carefully so as to maintain a pH as close to 7 as possible.
- 7.4.2.3 Transfer solution quantitatively to a 100 mL volumetric flask. Do NOT dilute to volume. Flask should be no more than 85% full.
- 7.4.2.4 Color development:
- 7.4.2.4.1 Pyridine-barbituric acid method: Add 2 mL of choramine-T (Step 5.7.2) to flask from 7.4.2.3 and mix. After 1-2 minutes, add 5 mL of pyridine-barbituric acid solution (Step 5.7.3.1) and mix. Dilute to volume [V^c] with water and mix again. Allow the color to

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develop for at least 8 minutes and then read absorbance at 578 nm in a 1 cm cell within 15 minutes from color development.

7.4.2.4.2

Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (Step 5.7.2) and mix. After 1-2 minutes, add 5 mL of pyridine-pyrazolone solution (Step 5.7.3.2) and mix. Dilute to volume [V^c] with water and mix again. After at least 40 minutes, read absorbance at 620 nm in a 1 cm cell.

NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

7.5 Calculations

7.5.1 From the absorbances measured from the calibration standards (Section 7.3), construct a standard calibration curve of absorbance vs. concentration. An alternate approach is to determine the slope and intercept (e.g., by a linear regression analysis).

7.5.2 From the absorbances measured from the analysis solutions, use the calibration curve (or fit equation) to obtain the cyanide concentration [C^s] in $\mu\text{g/L}$.

7.5.3 Calculation of CN^- concentration in samples:

C^s = Measured CN concentration ($\mu\text{g/L}$) in V^c solution
 V^a = Final volume (mL) of absorber solution
 V^b = Aliquot (mL) of absorber solution taken for colorimetric measurement
 V^c = Final volume (mL) of colorimetric measurement solution
 V^s = Volume (mL) of water sample
 W^s = Weight (g) of solids/sludges; wet weight for sludges, dry weight for solids
%S = Percent solids from Procedure PNL-ALO-504.

7.5.3.1 Water samples

$$\mu\text{g/L CN}^- = C^s * (V^c/V^b) * (V^a/V^s)$$

7.5.3.2 Solid samples

$$\mu\text{g/g (mg/kg) CN}^- = C^s * (V^c/V^b) * (V^a/W^s)$$

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7.5.3.3 Sludge samples - reported on dry weight basis

$$\text{mg/g CN}^- = C^s * (V^c/V^b) * V^a * (100 / (\%S * W^s))$$

8.0 Specific Qualifications

This procedure is self-qualifying due to dependence on analytical standards, calibrations, and quality control standards per PNL-MA-70, PAP-70-901.

9.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with the Act New Directive 89.1 established records management practices.

10.0 References

USEPA Contract Laboratory Program, SOW 788, Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, Method 335.2.

SW-846, Method 9010, 3rd Edition

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Figure 1. Cyanide Distillation Apparatus

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Figure 2. CN Analysis Worksheet

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INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-271.4
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<p>A. Document Number: <u>PNL-ALO-271</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Procedure for Analysis of Free Cyanide in Water and Solid Sample Leachates</u></p> <p>Document's Original Author: <u>KH Pool</u></p>		<p>Effective Date of ICN: <u>12/03/92</u></p> <p>Change Requested by: <u>PK Melethil</u> <i>[Signature]</i></p>							
<p>B. Action:</p> <p style="text-align: center;">Replace pages 6 and 7 with the attached pages 6 and 7.</p>									
<p>C. Effect of Change:</p> <p style="text-align: center;">None. However procedure incorporates flexibility to minor changes.</p>									
<p>D. Reason for Change/Description of Change:</p> <p><u>Reason:</u></p> <p>Use of eluant in place of 0.02 N NaOH as a diluent so as to improve matrix matching.</p> <p><u>Description:</u></p> <p>Added:</p> <p>4.3.1 "Eluent may be used in place of 0.02 N NaOH", following standards preparation guideline.</p> <p>4.4.1, dilute the sample with 0.02 N NaOH or eluent appropriately,...</p> <p>See redline changes in text of the procedure.</p>									
<p>E. Approval Signatures (Please sign and Date)</p> <table style="width: 100%; border: none;"><tr><td style="width: 50%; border: none; vertical-align: top;">QP Department Concurrence: <u>TL Ehlert</u> <i>[Signature]</i></td><td style="width: 50%; border: none; vertical-align: top;">Type of Change (Check (✓) one) (✓) Minor Change () Major Change</td></tr><tr><td style="border: none; vertical-align: top;">Approval Authority: <u>AG King</u> <i>[Signature]</i></td><td style="border: none; vertical-align: top;">Date: <u>12/3/92</u></td></tr><tr><td style="border: none; vertical-align: top;">Other Approvals: <u>MW Urie</u> <i>[Signature]</i></td><td style="border: none; vertical-align: top;">Date: <u>12/10/92</u></td></tr><tr><td style="border: none; vertical-align: top;">Author Approval: <u>KH Pool</u> <i>[Signature]</i></td><td style="border: none; vertical-align: top;">Date: <u>12-3-92</u></td></tr></table>		QP Department Concurrence: <u>TL Ehlert</u> <i>[Signature]</i>	Type of Change (Check (✓) one) (✓) Minor Change () Major Change	Approval Authority: <u>AG King</u> <i>[Signature]</i>	Date: <u>12/3/92</u>	Other Approvals: <u>MW Urie</u> <i>[Signature]</i>	Date: <u>12/10/92</u>	Author Approval: <u>KH Pool</u> <i>[Signature]</i>	Date: <u>12-3-92</u>
QP Department Concurrence: <u>TL Ehlert</u> <i>[Signature]</i>	Type of Change (Check (✓) one) (✓) Minor Change () Major Change								
Approval Authority: <u>AG King</u> <i>[Signature]</i>	Date: <u>12/3/92</u>								
Other Approvals: <u>MW Urie</u> <i>[Signature]</i>	Date: <u>12/10/92</u>								
Author Approval: <u>KH Pool</u> <i>[Signature]</i>	Date: <u>12-3-92</u>								

**INTERIM CHANGE NOTICE
(ICN)**

ICN - PNL-ALO-271.3 R0
Page 1 of 1

A.

Document Number: PNL-ALO-271 Revision Number: 0

Document Title: Procedure for Analysis of Free
Cyanide in Water and Solid Sample Leachates

Document's Original Author: KH Pool

Effective Date
of ICN: 5/8/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 10 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert

Date: 5/7/92

Approval Authority: AG King

Date: 5/17/92

Other Approvals: MW Urie

Date: 5/18/92

:

Date: 1/1

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~~ICN-PNL-ALO-271.1~~
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A. Document Number: <u>PNL-ALO-271</u> Revision Number: <u>0</u> Document Title: <u>Procedure for Analysis of Free Cyanide in Water and</u> <u>Document's Solid Sample Leachates</u> Original Author: <u>Karl H. Pool</u>		Effective Date of ICN: <u>10/14/91</u> Change Requested By: <u>P. K. Melethil</u>
B. Action: Replace entire procedure with the pages attached.		
C. Effect of Change: The following changes have been made to allow operations using a Pulsed Electrochemical Detector (PED) from Dionex for radioactive samples. The details are appended. No significant changes are expected. The new procedure will allow operation of either an amperometric or electrochemical detector, in the pulsed mode.		
D. Reason for Change/Description of Change The current procedure imposes restrictions on the use of equivalent detector and chromatography hardware.		
E. Approval Signatures (Please Sign and Date)	Type of Change: {Check (☒) one} (☐) Minor Change (☒) Major Change	
Process Quality OS&R Department Concurrence: <u>GK George, DE</u> Date: <u>7/24/91</u> Approval Authority: <u>[Signature]</u> Date: <u>7/18/91</u> Other Approvals: <u>B. M. Dillipuri</u> Date: <u>7/17/91</u> : _____ Date: <u>1/1</u>		

Changes

Add to Definitions/Acronyms section:

Batch: A group of samples of like matrix prepared at the same time.

Change section 3.1.1 to read:

- 3.1.1 Ion chromatograph (IC) fitted with amperometric or pulsed amperometric detector (PAD) or equivalent system e.g. pulsed electrochemical detector.

Change section 3.3 to read:

3.3 Stock Standards and Titration Reagents

All chemicals are Reagent Grade unless otherwise noted. Smaller volumes of solutions, at the same concentrations, may be prepared if waste generation can be reduced.

Change section 3.3.3 to read:

- 3.3.3 Working standard cyanide solution (1 mL $\approx$ 5.0 μ g CN): Dilute 10.0 mL of intermediate cyanide solution to 100.0 mL with water [Exact concentration is 0.10 x concentration of intermediate standard cyanide solution concentration from 3.3.2.] Prepare fresh daily. Record date of preparation on container.

Change section 4.2.3 to read:

- 4.2.3 Hook up electrical leads from potentiostat module to cell and from potentiostat to recorder/integrator as directed in the Appendix (Attachment I) when using a Dionex PAD system. Manufacturer's guidelines should be followed for other similar hardware.

Change section 4.2.4 to read:

- 4.2.4 Set the working electrode potential to 0.0 (zero) volts, and output range to 20 nA. Use manufacture recommended settings for other detector systems.

Change section 4.2.5 to read:

- 4.2.5 The chromatography-detector system may be configured as indicated in the following block flow diagram:

Dionex AG6 guard column and Dionex AS6 separator column, or equivalent are used.

Change section 4.2.7 to read:

- 4.2.7 The following conditions are used in operation of the IC: 100 μ L or 200 μ L sample loop; eluent flow rate 1.0 mL/min. Any changes in operating conditions shall be recorded in the LRB used with this procedure and reported to the client, if requested.

(Note: The retention time for cyanide is approximately 7 minutes using the chromatographic conditions specified.)

Change section 4.3.1 to read:

- 4.3.1 A series of working standards may be prepared by diluting the second IC standard cyanide solution (3.3.4) with 0.02 N NaOH to 100.0 mL according to the following guideline:

Change section 4.3.3 to read:

- 4.3.3 The operator shall either prepare a standard curve by plotting chromatographic peak heights (or peak areas) of standards versus cyanide concentration in the standards or use a calculator or a computer to fit the response of the detector (peak height or peak area) to the concentration of the analyte. The method used for calibration shall be explicitly stated in the LRB and reported to the client, if requested.

Change section 4.4.1 to read:

- 4.4.1 Inject standards and samples and refer to the standard curve generated in 4.3.3 to determine the concentration of cyanide in the samples. If the concentration found is greater than the highest standard used, dilute the sample with 0.02 N NaOH appropriately, document what dilution was made, and rerun.

Note: Samples containing visible particulate will be filtered through a 0.45 μ m filter. This will prevent the autosampler transfer line from being plugged.

Change section 5.0 to read:

5.0 Calculations

The concentration of free cyanide in the sample is determined by comparison to the calibration curve (4.3.3) and multiplied by appropriate dilution factors (if any).

Change section 6.3.2 to read:

- 6.3.2 A minimum of one calibration (method) blank, one duplicate, and one matrix spike shall be prepared and analyzed for every sample batch of similar matrix type. Spikes shall be added at the time of sample preparation.

Change section 6.3.4 to read:

- 6.3.4 At a minimum, a continuing calibration verification (CCV) standard, from the original instrument calibration standard source at a concentration at or near the mid-range of the calibration curve, shall be analyzed at a frequency of at least 20% during an analysis run. The continuing calibration verification standard must be at or within 90% to 110% of the true value. If the CCV standard is outside of these limits, analyze a second calibration standard (from 6.3.1) that will bracket the previous sample response before analyzing the calibration blank sample. The sample value immediately preceding the CCV plus the sample values following the bracketing standard shall be normalized to the new response. This high frequency of CCV analysis is to compensate for the fact that the PAD sensitivity tends to drift with time.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-271, PROCEDURE FOR ANALYSIS OF FREE CYANIDE IN WATER AND SOLID SAMPLE LEACHATES

APPLICABILITY

This procedure is applicable to the determination of free cyanide in drinking, surface and saline waters, domestic and industrial wastes and extracts/leachates of soils. Free cyanide is determined by direct injection through a 0.45 um syringe filter into a properly fitted ion chromatograph/amperometric detector instrument system. Chromatographic peak heights or areas are compared to those obtained from matrix matched standards. The working range of the method is 0 to 0.05 mg CN⁻/L. Higher level samples must be diluted to fall within the working range. This procedure was developed by PNL Analytical Chemists for measuring free CN in groundwater and soil.

DEFINITIONS/ACRONYMS

Free cyanide is defined as that portion of the total cyanide in a sample that is not strongly complexed by iron, cobalt, silver, gold, or nickel.

This definition of free cyanide is philosophically justifiable in the context of toxicity, which is the ultimate consideration of the Environmental Protection Agency (EPA). The measurement of free cyanide, as defined here, is a good measure of liquid sample toxicity, since the tightly bound cyanide complexes of metals such as Fe, Co, Ni, Ag, and Au are much less toxic to aquatic life than cyanide derived from simple salts, e.g., KCN, and weaker complexes such as those of zinc and cadmium.

Batch: A group of samples of like matrix prepared at the same time.

RESPONSIBLE STAFF

Cognizant Scientist
Technician/Analyst

Author	Date	Project Mgr.	Date	QAD Representative	Date
KH Pool		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
MW Urie <i>[Signature]</i> 5/8/92		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within +10% of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Sample Handling and Preservation

- 2.1 All bottles shall be rinsed with deionized water (ASTM Type II) prior to use to remove soluble material from containers (performed in the field).
- 2.2 Oxidizing agents such as chlorine decompose most of the cyanides. At the time of field sampling, test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume (performed in the field).
- 2.3 Aqueous samples are preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH >12) at the time of collection (performed in the field).
- 2.4 Soil samples are prepared and preserved in accordance with PNL-ALO-107.
- 2.5 Samples shall be stored at 4°C($\pm 2^\circ\text{C}$) and shall be analyzed within 14 days of sample receipt into the analytical laboratory.

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PNL TECHNICAL PROCEDURE

3.0 Apparatus, Reagents and Supplies

3.1 Apparatus

- 3.1.1 Ion chromatograph (IC) fitted with amperometric or pulsed amperometric detector (PAD) or equivalent system e.g. pulsed electrochemical detector.
- 3.1.2 Ten (10) mL microburet.
- 3.1.3 Analytical balance capable of accurately weighing to 0.0001 g.
- 3.1.4 0.45 μ m syringe filter apparatus and filters.

3.2 Reagents

All chemicals are Reagent Grade unless otherwise noted.

- 3.2.1 Chromatographic eluent - 0.5 M sodium acetate + 0.1 M NaOH + 0.5% (v/v) ethylenediamine. To a 2.0 liter volumetric flask, add 136.1 ± 0.5 g sodium acetate trihydrate, 16.0 ± 0.5 g 50% NaOH and 10.0 ± 0.2 mL ethylenediamine. Dissolve in deionized water and bring to volume. Transfer to eluent reservoir.
- 3.2.2 ASTM Type II water. This water is to be used for sample, standard and reagent dilution.
- 3.2.3 Tank of inert gas for sparging, such as He (Industrial Grade).

3.3 Stock Standards and Titration Reagents

All chemicals are Reagent Grade unless otherwise noted. Smaller volumes of solutions, at the same concentrations, may be prepared if waste generation can be reduced.

- 3.3.1 Stock cyanide solution (1 mL = 1 mg CN^-): Dissolve 2.51 g of KCN and 2 g KOH in 500 mL water and dilute to 1000.0 mL with water. Standardize with 0.0192 N AgNO_3 . (See 4.1)
- 3.3.2 Standard cyanide solution, intermediate (1 mL = 50 μ g CN^-): Dilute 5.00 mL of stock cyanide solution (3.3.1) to 100.0 mL with water. [Exact concentration is 0.05 x concentration from 4.1.4.] Prepare fresh daily. Record date of preparation on solution container.

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3.3.3 Working standard cyanide solution (1 mL = 5.0 μg CN): Dilute 10.0 mL of intermediate cyanide solution to 100.0 mL with water [Exact concentration is 0.10 x concentration of intermediate standard cyanide solution concentration from 3.3.2.] Prepare fresh daily. Record date of preparation on container.

3.3.4 Second IC standard cyanide solution: Prepare fresh daily by diluting 10.0 mL of working standard cyanide solution (3.3.3) to 250.0 mL with 0.02 N NaOH. This solution has a nominal cyanide concentration of 0.20 mg CN⁻/L. [Exact concentration is 0.04 x the working standard CN solution concentration from 3.3.3.] Record date of preparation on solution container.

3.3.5 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO₃ crystals and drying to constant weight at 40°C. Weigh out 3.2647 ± 0.0002 g of dried AgNO₃, dissolve in distilled water, and dilute to 1000.0 mL. Titer: 1 mg CN⁻/mL AgNO₃.

3.3.6 Rhodanine indicator: Dissolve 20 ± 1 mg of p-dimethylaminobenzalrhodanine in 100 ± 5 mL of acetone.

3.3.7 Sodium hydroxide solution, 0.25 N: Dissolve 10.0 ± 0.5 g of NaOH in water and dilute to 1.00 ± 0.05 liter.

3.3.8 Sodium hydroxide solution, 0.02 N: Dissolve 0.80 ± 0.05 g of NaOH in water and dilute to 1.00 ± 0.05 liter.

4.0 Procedure

4.1 Standardization of Stock Cyanide Solution

4.1.1 Fill micro buret (3.1.2) with standard silver nitrate solution (3.3.5).

4.1.2 To a 100 mL Erlenmeyer flask, add 25 mL of 0.25 N NaOH and pipet 5.00 mL of stock cyanide solution (3.3.1) into flask with the 25 mL 0.25 N NaOH. Add 2-3 drops of rhodanine indicator (3.3.6) and titrate with AgNO₃ until the first change in color from yellow to brownish-pink. Record the volume of AgNO₃ titrant used (V_A mL) in a Laboratory Record Book (LRB) or Data Sheet.

4.1.3 Repeat Steps 4.1.1 and 4.1.2 except do not add any cyanide to the titration mixture. This is the titration blank.

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Record volume of AgNO_3 needed to produce the same indicator color change (V_B mL) in a LRB or Data Sheet.

- 4.1.4 Calculate the concentration of cyanide in the stock cyanide solution as follows and record in LRB or Data Sheet:

$$\text{mg CN}^-/\text{L} = (V_A - V_B) \times 200$$

4.2 Ion Chromatographic/Amperometric Equipment Set-Up

- 4.2.1 Set up the chromatograph and detector according to instrument manufacturer's instructions. (The directions given here refer to Dionex equipment, but equivalent systems are commercially available.) Refer to the instrument operators manual for details of preparation and operation of the chromatographic system (See references).
- 4.2.2 Repolish the silver working electrode in the amperometric detector module. Reassemble cell using the thin gasket and fill the reference compartment with eluent (3.2.1). Directions are given in the Appendix (Attachment I).
- 4.2.3 Hook up electrical leads from potentiostat module to cell and from potentiostat to recorder/integrator as directed in the Appendix (Attachment I) when using a Dionex PAD system. Manufacturer's guidelines should be followed for other similar hardware.
- 4.2.4 Set the working electrode potential to 0.0 (zero) volts, and output range to 30 nA. Use manufacturer recommended settings for other detector systems.
- 4.2.5 The chromatography-detector system may be configured as indicated in the following block flow diagram:

Dionex AG6 guard column and Dionex AS6 separator column, or equivalent are used.

NOTE: No suppressor is used.

The guard and separator columns should be Dionex® AG6 and AS6, respectively, or equivalent.

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- 4.2.6 Degas the eluent using an inert gas sparge (helium preferred) for 10 to 15 minutes.
- 4.2.7 The following conditions are used in operation of the IC: 100 μ L or 200 μ L sample loop; eluent flow rate 1.0 mL/min. Any changes in operating conditions shall be recorded in the LRB used with this procedure and reported to the client, if requested.

(Note: The retention time for cyanide is approximately 7 minutes using the chromatographic conditions specified.)

4.3 Standards Preparation and Analysis

- 4.3.1 A series of working standards may be prepared by diluting the second IC standard cyanide solution (3.3.4) with 0.02 N NaOH to 100.0 mL according to the following guideline:

<u>mL Second IC Standard Cyanide Solution Taken</u>	<u>Concentration (μg CN⁻/L)</u>
0	Blank (0)
2.00	4.0
5.00	10.0
10.0	20.0
25.0	50.0

Eluent may be used in place of 0.02 N NaOH.

- 4.3.2 Load a standard or blank into the sample loop of the chromatograph. Immediately switch to "inject" position and activate event marker. Once the chromatogram is developed (approx. 10 min), load and inject the next standard or blank. After the blank and all standards have been run, proceed to 4.3.3.
- 4.3.3 The operator shall either prepare a standard curve by plotting chromatographic peak heights (or peak areas) of standards versus cyanide concentration in the standards or use a calculator or a computer to fit the response of the detector (peak height or peak area) to the concentration of the analyte. The method used for calibration shall be explicitly stated in the LRB and reported to the client, if requested.

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4.4 Sample Analysis

- 4.4.1 Inject standards and samples and refer to the standard curve generated in 4.3.3 to determine the concentration of cyanide in the samples. If the concentration found is greater than the highest standard used, dilute the sample with 0.02 N NaOH or eluent appropriately, document what dilution was made, and rerun.

Note: Samples containing visible particulate will be filtered through a 0.45um filter. This will prevent the autosampler transfer line from being plugged.

- 4.4.2 If sensitivity has changed by more than 10% as indicated by an associated increase or decrease in chromatographic peak height to the standard, normalize the sample results obtained immediately preceding and immediately after the standard accordingly. If sensitivity has changed by less than 10%, normalization of sample results is not necessary. (See Section 6.3.4 for samples requiring compliance with CERCLA requirements.)

5.0 Calculations

The concentration of free cyanide in the sample is determined by comparison to the calibration curve (4.3.3) and multiply by appropriate dilution factors (if any).

6.0 Quality Control

- 6.1 All quality control data shall be maintained and available for easy reference or inspection.

- 6.2 Minimum quality control requirements.

6.2.1 A minimum of three calibration standards and one measurement (matrix) blank are required for IC calibration (See Section 4.3).

6.2.2 Samples shall be diluted with 0.02 N NaOH, and reanalyzed, if they are more concentrated than the highest standard which is within the calibration range.

6.2.3 Additional quality control (i.e., duplicates, spikes, additional system or matrix blanks, etc.) is governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the Analytical Request Form (ARF), the project

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- 6.3 Quality control for clients requesting compliance with Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) requirements.
- 6.3.1 A minimum of three calibration standards and one matrix blank are required for the calibration of the IC-PAD system (See Section 4.3). One calibration standard shall be at the required detection limit (per SOW, TI, or ARF).
- 6.3.2 A minimum of one calibration (method) blank, one duplicate, and one matrix spike shall be prepared and analyzed for every sample batch of similar matrix type. Spikes shall be added at the time of sample preparation.
- 6.3.2.1 The methods blank shall be a water sample processed through each sample preparation and analysis step. If the methods blank is not $\leq$ the requested detection limit (from the SOW, TI or ARF), then the samples must be prepared and analyzed again.
- 6.3.2.2 The relative percent difference between the duplicate samples must be less than or equal to the required precision per the SOW, TI or ARF if the sample values are greater than 5x the requested detection limit (from SOW, TI, or ARF). If no required precision is given, then the relative percent difference shall be $\leq 20\%$. If the sample value is less than 5x the requested detection limit, then the difference between duplicates must be within $\pm$ the detection limit. If one result is above the 5x value and one below, use the $\pm$ detection limit criteria. If duplicate sample results are outside these control limits, flag all data for the sample batch/group associated with that duplicate analysis in the data report with an asterisk.
- 6.3.2.3 The spike and matrix spike duplicate are added to two replicates of a sample prior to any preparation or analysis. A field blank sample may not be selected for spike analysis. The spikes are added at a level to be determined by the Cognizant Scientist, based on results from a total CN analysis of the sample and/or expected free CN content of the sample. Spikes shall be prepared from the Stock or Intermediate CN solutions (See Sections 3.3.1 and 3.3.2). Spike recoveries shall be at or within the limits of 75% to 125%. If this recovery is not met for the spike or spike

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duplicate, all data in the sample batch/group must be flagged in the data report with the letter "N".

- 6.3.3 As an independent source for a free CN standard is not available, the standard used is cross-checked by titrating with AgNO_3 (See Section 4.1).
- 6.3.4 At a minimum, a continuing calibration verification (CCV) standard, from the original instrument calibration standard source at a concentration at or near the mid-range of the calibration curve, shall be analyzed at a frequency of at least 20% during an analysis run. The continuing calibration verification standard must be at or within 90% to 110% of the true value. If the CCV standard is outside of these limits, analyze a second calibration standard (from 6.3.1) that will bracket the previous sample response before analyzing the calibration blank sample. The sample value immediately preceding the CCV plus the sample values following the bracketing standard shall be normalized to the new response. This high frequency of CCV analysis is to compensate for the fact that the PAD sensitivity tends to drift with time.
- 6.3.5 A calibration blank sample shall be analyzed after every CCV sample and after the last sample analyzed in the set of samples being analyzed. The calibration blank sample is the 0.02N NaOH solution used to make up the calibration standards. If the absolute value of the calibration blank sample exceeds the requested detection limit (from the SOW, TI or ARF), the analysis is terminated, the problem corrected, the instrument recalibrated and a reanalysis conducted of all analytical samples analyzed since the last good calibration blank sample.
- 6.3.6 Additional quality control (i.e., duplicates, spikes, additional system or matrix blanks, etc.) is governed by the analytical requirements of the project or specific analyses requested. Specific QC requirements are provided by the Analytical Request Form (ARF), the project Statement of Work (SOW), or Sample Analysis Test Instruction (TI).
- 6.3.7 Samples shall be diluted with 0.02 N NaOH, and reanalyzed, if they are more concentrated than the highest standard which is within the calibration range.

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7.0 Specific Qualifications

This procedure is self-qualifying due to the dependence on analytical standards, calibrations and quality control standards as per PNL-MA-70, PAP-70-901.

8.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRBs) and Analytical Data Sheets provide a mechanism for control of most records. LRBs will be used in accordance with ~~the Act Now Directive 89-1~~ established records management practices.

9.0 References

Pool, K. H. 1989. "FY89 WHC SOW ED9517-B, Final Report: Develop and Demonstrate an Analytical Procedure for Measuring Total, Complexed and Free Cyanide in Groundwater and Soil."

Dionex Ionchrom/Pulsed Amperometric Detector Operator's Manual. 1986.

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INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-272.2 R0
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A.

Document Number: PNL-ALO-272 Revision Number: 0

Document Title: Spectrophotometric Determination of
Hydrazine Concentration Using LAMBDA-1 UV/Vis
Spectrophotometer

Document's Original Author: KH Pool

Effective Date
of ICN: 5/8/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.
Replace pages 1 through 8 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehlert TE Ehlert

Date: 5/7/92

Approval Authority: AG King AG King

Date: 5/7/92

Other Approvals: MC Burt MC Burt

Date: 5/8/92

: _____ Date: 1/1

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-272.1

Page 1 of 1

A. Document Number: <u>PNL-ALO-272</u> Revision Number: <u>0</u> Document Title: <u>Spectrophotometric Determination of Hydrazine</u> Document's Original Author: <u>SIMON BARSOUM</u>		Effective Date of ICN: <u>5/14/91</u> Change Requested By: <u>Simon Barsoum</u>
B. Action: 1-Insert the following note below step 9.2.5: to reduce the waste volume, a minimum of 3 calibration standards may be used. * 2-Insert the following note below step 9.3.5.2.2: to reduce the waste volume, a minimum of 2 standard additions may be used. 3-Revise the 2nd sentence in step 9.1.1 to read: If the ph of the received samples is not 8 or below then samples shall be acidified as such.		
C. Effect of Change: -For 1 and 2 above no analytical impact. -For 3 to avoid the possibilities of obtaining false negative results.		
D. Reason for Change/Description of Change -For 1 and 2 to reduce the volume of the waste generated without affecting the analytical validity of data generated. -For 3 adding excess acid to a sample of unknown matrix may diminish the hydrazine content of the sample. Experimentally, I had found this to be true, simply because an aqueous solution of hydrazine is a diacid-base. * - Replace Pages 5, 6, 7, and 8 with the attached.		
E. Approval Signatures (Please Sign and Date) QSA Department Concurrence: <u>CS Bebe, DE</u> Approval Authority: <u>[Signature]</u> Other Approvals: <u>MC BURT McBurt TECH. REVIEWER</u> : <u>[Signature]</u>	Type of Change: (Check () one) (X) Minor Change () Major Change Date: <u>1/21/91</u> Date: <u>1/21/91</u> Date: <u>1/21/91</u> Date: <u>1/23/91</u>	

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-272, SPECTROPHOTOMETRIC DETERMINATION OF HYDRAZINE CONCENTRATION USING LAMBDA-1 UV/Vis SPECTROPHOTOMETER

APPLICABILITY

This procedure is applicable for determining the concentration of hydrazine in aqueous waste, boiler water, and groundwater.

DEFINITIONS

P-DAB: P-Dimethylaminobenzaldehyde
P-DABAZ: P-Dimethylaminobenzalazine

RESPONSIBLE STAFF

Cognizant Scientist
Technician/Analyst

PROCEDURE

1.0 Summary of Method

- 1.1 P-DAB, in a solution mixture of methanol and hydrochloric acid, reacts with the hydrazine present in an acidified sample to form P-DABAZ. This product is yellow colored, absorbs at 458 nm, and its absorbance is quantitatively proportional to the hydrazine content of the sample.
- 1.2 The linear dynamic range for this method is from a detection limit of 5 $\mu\text{g/l}$ up to 200 $\mu\text{g/l}$. Higher concentrations of hydrazine can also be determined after appropriate dilutions.

2.0 Interferences

Aromatic amines, turbidities, and colors that absorb at or near 458 nm.

Author	Date	Project Mgr.	Date	QAD Representative	Date
S Barsoum		TE Jones		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
Burt		JM Latkovich		ALL ORIGINAL SIGNATURES ON FILE	
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3.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- (a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- (b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

4.0 Apparatus and Materials

4.1 LAMBDA-1 UV/Vis spectrophotometer with 50 mm cell.

4.2 Calibrated analytical balance capable of accurately weighing to the nearest 0.0001 g.

4.3 Glassware

- 100 ml volumetric flask
- 200 ml volumetric flask
- 500 ml volumetric flask
- 1000 ml volumetric flask
- 200 ml amber glass bottle
- 50 ml stoppered graduate cylinders
- class "A" glass pipettes of 5, 10, 25, and 50 ml
- performance-checked micro pipettes of 1000, 500, and 10 μL

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): water is to be used for sample, standard, and reagents dilutions.

5.2 Concentrated hydrochloric acid (HCl): ULTREX Grade (specific gravity of 1.19).

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- 5.3 Methanol (CH_3OH), reagent grade
- 5.4 P-Dimethylaminobenzaldehyde [$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CHO}$], reagent grade
- 5.5 Hydrazine Dihydrochloride ($\text{NH}_2\text{NH}_2 \cdot 2\text{HCl}$), reagent grade

6.0 Safety Precautions

- 6.1 Read the Material Safety Data Sheets (MSDS) for the P-DAB and the hydrazine Dihydrochloride prior to performing procedure.
- 6.2 Hydrazine Dihydrochloride is a mutagen. Handle with caution: wear gloves, dust mask and use the fume hood.
- 6.3 Comply with the applicable radiation zone regulations when working on radioactive samples.

7.0 Quality Control

- 7.1 The required minimum quality control is as follows:
 - 7.1.1 The spectrophotometer shall be operated in accordance with the manufacturer's instruction for operation.
 - 7.1.2 Micro pipette performance check must be performed on all the micro pipettes prior to analysis as follows: using water at room temperature, pipette and accurately weigh the dispensed volume. Repeat and record this measurement 3 times then calculate the mean and obtain the % error. If this value exceeds 1% the micro pipette shall not be used.
 - 7.1.3 If the sample's hydrazine content is more than $200 \mu\text{g/l}$, it shall be diluted appropriately to obtain a concentration reading within the calibration range.
 - 7.1.4 At least one verification check standard shall be employed for every 3 to 5 samples. If the results do not fall within 80 to 120% of the mean value for the check standard, recalibration or other corrective action shall be taken, and the data will be discarded and the analysis shall be repeated.
 - 7.1.5 At least one spike of 3 times the detection limit shall be employed for every 6 to 10 samples.
 - 7.1.6 If chemical interferences are suspected by an unacceptably low spike recovery then the standard addition method shall be used to quantitate the hydrazine.

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7.1.7 If samples are turbid or highly colored, they shall be diluted appropriately, then analyzed by the standard addition method since there is no known approach to eliminate the turbidity or the coloration without diminishing the hydrazine content.

8.0 Reagents and Standards Solution Preparations

8.1 Stock Hydrazine Solution of 100 mg/L

Dissolve 0.1640 g of hydrazine Dihydrochloride in a mixture of 50 ml water and 5 ml hydrochloric acid in a 500 ml volumetric flask. Dilute to the mark with water. A fresh stock solution of this concentration shall be made once a month.

8.2 Working Stock Hydrazine Solution of 500 μ g/l

Using a calibrated micropipette transfer 2500 μ L of the above stock solution into a 500 ml volumetric flask and dilute to the mark with water. This working stock solution shall be made fresh daily.

8.3 P-DAB Solution

Dissolve 2.0000 g of P-DAB in a mixture of 100 ml methanol and 10 ml hydrochloric acid. The final volume of this solution is 110 ml. Keep this solution in a dark bottle and in a dark location. This solution shall be prepared daily.

8.4 Blank Solution

Transfer 5 ml of concentrated hydrochloric acid into a dry and clean 500 ml volumetric flask and dilute to the mark with water.

8.5 Standard Solutions

Add 1 ml of concentrated hydrochloric acid and 20 ml water to 6 dry and clean 100 ml volumetric flasks. Transfer 1, 2, 5, 10, 20, 40 ml of the hydrazine working stock solution prepared in 8.2 into these volumetric flasks and dilute to the mark with water to obtain the standards of the following concentrations respectively: 5, 10, 25, 50, 100, 200 μ g/l.

8.6 Standard Addition Solution

Transfer 80 ml of the working hydrazine stock solution prepared in 8.2 into a dry, clean 200 ml volumetric flask, dilute to the mark with water. This solution is 200 μ g/l hydrazine.

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8.7 Hydrazine Spiking Solution

Transfer 5 ml of the stock hydrazine solution prepared in 8.1 into a dry, clean 10 ml volumetric flask, dilute to the mark with water. This solution is 50 mg/l hydrazine.

9.0 Analysis Method

9.1 Sample Preparation

9.1.1 Samples should be acidified upon collection with 1 ml of hydrochloric acid for each 100 ml of sample. If the pH of the received samples is not between 1 and 3 then samples shall be acidified as such.

9.1.2 Keep the samples refrigerated at 4°C ($\pm 2^\circ\text{C}$).

9.2 Calibration

9.2.1 Add 50 ml of the blank prepared in 8.4 and each of the standards prepared in 8.5 to graduate cylinders with stoppers. Then add 10 ml of P-DAB solution prepared in 8.3. Cap and invert the cylinders several times for thorough mixing and allow to stand for at least 15 minutes, but no longer than 60 minutes.

9.2.2 Power the LAMBDA-1 spectrophotometer by pressing ON/OFF button (right rear corner of the instrument). The wavelength window (front center panel) starts to count down from 90 to 40 then it climbs up to 400 nm and remains there (this is a self-test and should the wavelength drop below 40 nm reinitiate this test by turning the instrument OFF, then back ON. Allow a minimum of 15 minutes for the instrument to warm up.

9.2.3 When the wavelength reading is at 400 nm, switch to Vis position (lower right front corner of the instrument) press the following in order: C/E, 0 (i.e., zero), SAFEMEM, then key in 458 and press GOTO λ . The wavelength of 458 will be displayed.

9.2.4 After a minimum of 15 minutes has passed for step 9.2.1, rinse the 50 mm cell with the blank solution several times. The cell is then filled, capped, cleaned and wiped dry and placed in the center of the sample holder and the cover closed. Press Mode several times until you see the ABS light come on. Wait 10 seconds, then press AUTOZERO.

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- 9.2.5 Empty the cell and rinse twice with the first standard solution. The cell is then filled, capped, cleaned and wiped dry and placed in the center of the sample holder and the cover closed. Wait 10 seconds and record the absorbance reading in the LRB. Repeat this step for the remainder of the standards.
- 9.2.6 Plot absorbances vs. concentrations in $\mu\text{g/l}$, and calculate the slope by linear regression (see Calculation section). The reciprocal of the slope obtained will be the C factor on the instrument.
- 9.2.7 Key in the C factor value then press enter (blue button). Then press AUTOCONC. Verify that the C factor is entered by pressing and holding AUTOCONC. The reading should be displayed in the right front digital read-out. (You may store this value by pressing 1, enter (blue button), SAFEMEM. To recall, just press 1 then SAFEMEM).

NOTE: The concentration of the hydrazine in the samples can also be interpolated from the calibration curve established using the absorbance readings of the samples.

9.3 Sample Analysis

- 9.3.1 To a 50 ml aliquot of sample, add 10 ml of P-DAB solution prepared in 8.3 in a graduate cylinder, cap it, and invert it several times, then let it stand for a minimum of 15 minutes, but no longer than 60 minutes. Wash the cell twice with this solution then fill and cap it. Wipe the outside surface dry, and place it in the center of the cell holder. Close the cover, wait 10 seconds until the reading is stabilized. This is the concentration of the sample in $\mu\text{g/l}$. Multiply concentration by the appropriate dilution factor, if dilution was made.
- 9.3.2 Perform a standard check. If the concentration reading deviates from the true value by more than $\pm 20\%$, recalibration is necessary.
- 9.3.3 Take 10 μl of the 50 mg/l hydrazine prepared in 8.7 and dilute it to the 50 ml mark with the sample to obtain 10 $\mu\text{g/l}$ spike level. Add 10 ml of P-DAB solution prepared in 8.3. Mix well in stoppered graduate cylinder and let sit for 15 minutes before taking any instrumental readings. If % spike recovery was found to be outside the acceptable level, indicative of chemical interferences, then the standard addition method shall be utilized to quantitate the hydrazine content of the sample.

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9.3.4 If the sample to be analyzed is turbid, or yellow colored, then the standard addition method shall also be utilized.

9.3.5 Standard Addition Method

9.3.5.1 Instrument in ABS mode, take the absorbance reading for 50 ml of sample (or diluted sample) + 10 ml of P-DAB after 15 minutes of reaction time. This absorbance will be the Y-axis intercept for the standard addition plot.

9.3.5.2 Perform the following four standard additions:

9.3.5.2.1 25 µg/l addition. Transfer 6.25 ml of 200 µg/l hydrazine into a graduate cylinder and dilute to 50 ml mark with the sample (or diluted sample) then add 10 ml of P-DAB. Cap the cylinder, invert several times and let it stand for a minimum of 15 minutes. Obtain the absorbance reading and record.

9.3.5.2.2 Repeat the above step for 50, 100, and 150 µg/l additions by transferring 12.5 and 25 ml of the 200 µg/l and 15 ml of the 500 µg/l.

9.3.5.3 Plot absorbance vs. additions concentrations in µg/l. Interpolate for X axis intercept, this will be the concentration of the sample. Multiply it by the dilution factor if sample was diluted.

10.0 Calculations

10.1 Spike Recovery

The percent spike recovery is calculated from the following formula:

$$\% \text{ Spike Recovery} = \frac{\text{SpSa} - \text{Sa}}{\text{SP}} \times 100$$

where:

SpSa = the concentration of the spiked sample in µg/l
Sa = the concentration of the sample in µg/l
Sp = the spike level in µg/l

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10.2 Slope by Linear Regression

Plotting the absorbances on Y axis and the concentration in $\mu\text{g/l}$ on the X axis, the slope is calculated from the following relationship:

$$m = \frac{\sum (X \cdot Y)}{\sum (X^2)}$$

where:

m = the slope

x = the absorbances

y = the concentration in $\mu\text{g/l}$

11.0 Records

Control of the Laboratory Record Book and all of the analytical sheets conform to the requirements of PNL-MA-70, PAP-70-1701 and shall be in accordance with ~~Act Now Directive 89.1~~ established records management practices.

12.0 References

1990 Annual Book of ASTM Standards Vol 11.01 (D1385-88).

1989 Annual Book of ASTM Standards Vol. 14.01 (E275-83).

1983 Perkin-Elmer. LAMBDA-1 UV/Vis Spectrophotometer Condensed Operating Directions.

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INTERIM CHANGE NOTICE
(ICN)

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A.

Document Number: PNL-ALO-280 Revision Number: 0

Document Title: Inductively Coupled Plasma-Mass
Spectrometric (ICP-MS) Analysis

Document's Original Author: EJ Wyse

Effective Date
of ICN: 5/14/92

Change Requested by:
TE Jones

B. Action:

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 12 due to new format.

C. Effect of Change:

Brings procedure into compliance.

D. Reason for Change/Description of Change:

ACT NOW Directive 89.1 no longer in existence.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one):

☒ Minor ☐ Major

Process

Quality Department: TL Ehler TL Ehler

Date: 5/7/92

Approval Authority: AG King AG King

Date: 5/7/92

Other Approvals: DW Koppelaar DW Koppelaar

Date: 5/14/92

: _____ Date: 1/1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-280, INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRIC (ICP-MS) ANALYSIS

APPLICABILITY

This procedure is applicable to the receiving and handling of samples, the operations of the ICP-MS VG Plasmaquad (PQ), and the reporting of analytical results. Controlling software for this instrument is VG supplied (latest version). Although some specific and general information regarding the analytical operations of the VG Plasmaquad are described below, this procedure is not written to replace VG supplied operations and PlasmaQuad instruction manuals. Specific analytical procedures are described which include sufficient information to allow a skilled operator to repeat the analyses performed using this instrument.

When this procedure is approved in accordance with Manual PNL-MA-70, this procedure is applicable for the analysis by ICP-MS.

DEFINITIONS/ACRONYMS

MATRIX MATCH - Add to the calibrating standards any major matrix components present in the samples.

LRB - Laboratory Record Book

AMU - atomic mass unit

RSD - Relative Standard Deviation

TUNE SOLUTION - A solution containing 100 ppb Mg, In, Pb for the purpose of tuning the instrument and establishing a mass response curve. Any solution containing 50 - 500 ppb of a low, medium, and high mass element can be used alternatively as a TUNE SOLUTION.

RESPONSIBILITIES

Analyst
Cognizant Scientist

Author	Date	Project Mgr.	Date	QAD Representative	Date
EJ Wyse		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
DW Koppenaal		PF Salter		ALL ORIGINAL SIGNATURES ON FILE	
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PROCEDURE

1.0 RECEIPT AND HANDLING OF SAMPLES

1.1 Receiving Samples

Upon receipt, samples are logged into a LRB designated for that purpose. Information logged includes the number of samples, sample identification, date received and from whom, blanks and standards included (if any), and sample and/or standard preparation, if necessary. Additional information logged may include specific instructions for analysis (e.g., a memo, DSI, Analytical Request Form [ARF], Test Instruction [TI], or Statement of Work [SOW]), and the work order number, if available at the time of log-in.

1.2 Preparation

1.2.1 Dissolution

If the samples to be analyzed were received as a solid, they must be dissolved for conventional ICP-MS analysis. (This is not necessary for laser ablation ICP-MS.) Dissolution procedures vary greatly between sample types, but the chosen procedure (or designated in a TI, ARF or SOW) is always described in its entirety in the sample log-in LRB.

1.2.2 Dilution

If the elements of concern are in sufficiently high concentration (>500ppb), dilution is usually necessary. If the elements of concern are below this concentration, or are in a matrix that is expected to dramatically diminish the elements' response signal, dilution may not be necessary. Dilutions are usually made by volume (rather than by weight) with calibrated pipets; preferred ultimate matrix is 1.0% HNO₃. The dilutions are described in detail in the designated LRB.

Example: 10X dilution: 8.5 mLs 5% HNO₃ + 1.0 mL sample + 0.5 mL 1 ppm In

1.2.3 Internal Standard

An appropriate internal standard (e.g., In) is added to both samples and standards for semi-quantitative as well as quantitative analyses. For quantitative analysis, it is used to correct for instrument drift and matrix effects. For semi-quantitative analysis, it is used as a reference standard. The internal standard concentration is determined by the operator based on that specific analysis, but is typically 10-200 ppb. The internal standard chosen depends on the elements of concern and the sample matrix. It is

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crucial that the samples do not contain the internal standard selected, and that there are no interferences from other element isotopes, molecular ion species, or matrix effects. For example, In-115 would not be appropriate as an internal standard for Sn analysis, because Sn has an isotope at 115.

1.2.4 Standard Preparation

Standards chosen depend on the elements of concern, and are typically prepared with element concentrations in the same approximate range as that of the samples. For best quantitative results, at least two different concentrations of the same element shall be prepared and run to generate a calibration curve (rather than a simple ratio) for the calculation of results. Standards prepared for analysis are dilutions of NBS or other recognized primary standards, or dilutions of prepared stock solution standards traceable to said primary standards, and are listed and described in a separate LRB designated for that purpose. This "Standards LRB" shows the traceability of all of the standards used in analysis from how they were made (pipet calibration and stock solution preparation information) back through information regarding all of the primary standards used (Lot Number, concentration, matrix, etc.).

1.3 Procedure File and Sample Analysis Identification

When it is time for the samples to be analyzed, a procedure file is set up with a unique identification number for that analysis run. The number is four digits long, followed by a letter, and each digit has a specific meaning:

Example: Procedure File #8c15a

1st digit: Designates the year of analysis (1988)

2nd digit/letter: Designates the month of analysis
(1-9 = Jan-Sep; a-c = Oct-Dec)

3rd & 4th digits: Designates the date of analysis (01-31)

5th letter: Designates the analysis procedure number (set of samples) of that date (a-g = first-seventh analysis)

6th digit: Designates the sample in that procedure (set).

For the example listed above, it is the first analysis run on December 15, 1988. Individual samples are numbered as well, meaning the sixth sample run in Procedure File #8c15a is designated 8c15a6.

The sample ALO number is cross referenced in the ICP-MS log-in LRB with the analysis procedure number (set of samples analyzed that

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day) and the sample in that procedure (samples in set are numbered consecutively).

2.0 INSTRUMENT OPERATION

The following procedures are to be used in conjunction with the VG Plasmaquad Operating and User's Manuals. The procedures below assume that the instrument is operating and functioning normally.

2.1 Instrument Maintenance

The ICP/MS shall be maintained on a daily basis. The ANALYST must ascertain that the individual instrument components are clean before beginning an analysis procedure. The following is a general description of the expected periodic maintenance (see VG Plasmaquad User's Manual):

Clean sample, skimmer cone; torch, elbow	Daily
Clean spray chamber	Weekly or biweekly (depends on sample history)
Clean ion lens stack	Semi-annually/as needed
Clean quadrupole	ONLY when necessary (See SCIENTIST)
Change roughing pump oil	Semi-annually
Change channeltron	As needed

2.2 Tuning the Instrument

The ICP/MS is tuned by aspirating the TUNE SOLUTION and manually adjusting the lens voltages for optimal sensitivity. The element in the TUNE SOLUTION having the middle mass (e.g., indium at 115 amu) is typically tuned first, with the low and high masses being tuned subsequently to obtain approximately equivalent signal response for each analyte mass.

2.2.1 Instrument Response and Precision Check: TUNEIR

The instrument response and precision are evaluated by running the TUNE SOLUTION five consecutive times using the isotope ratio procedure TUNEIR in IR SCAN found under SCAN ACQUIRE. TUNEIR hard copies must be signed and dated by the ANALYST, and logged in a notebook designated for that purpose. (NOTE: The TUNEIR is not a calibration, but rather an indication of the instrument's sensitivity, stability, and overall performance. The maintenance of

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these records are helpful in reviewing trends in performance over a period of time.)

2.3 Program Descriptions

Numerous programs and their subroutines are used for analysis, depending on the type of results the operator or sponsor wishes to obtain. A brief description of each program and its uses are described below.

2.3.1 Element Menu Definition Program

This program is used to define the elements (isotopes) to be analyzed, either for isotope ratio or multi-element work. This program also defines the run conditions for acquiring the data, either range scanning or peak jumping. Follow VG PlasmaQuad Software Manual to select the elements of interest.

The Element Menu Program also sets scan parameters such as the number of channels, sweeps, length of dwell time, and mass regions which will be skipped.

2.3.2 Multi Element Analysis Procedure Definition Program

This Program defines the order and type of samples to be run. Constructing and upgrading procedures are clearly described in the VG PlasmaQuad Software Manual. Standards, their preparation and their certification shall be documented in the LRB.

2.3.3 Isotope Ratio Analysis Procedure Definition Program

This program is identical to the multi-element analysis program with the exception that the number of ratios to be performed is requested instead of the Conc File name.

The measurement of isotopic ratios on the VG PlasmaQuad shall be carried out in a similar manner to quantitative analysis, i.e., the sample shall be compared to a well defined isotopic standard. The standards, their preparation and their certification shall be documented in the LRB. Specific details of the isotopic ratio program procedures are described in the VG PlasmaQuad Software Manual.

2.3.4 Acquire Programs

Three acquisition programs are addressed through Survey Acquire, Scan Acquire and Peakjump Acquire programs.

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2.3.4.1 Survey Acquire

Survey Acquire is typically used for short qualitative or semi-quantitative analyses. Scan parameters can be altered, but neither an element menu nor an element procedure is necessary for survey acquire.

Semi-quantitative calculations are also performed under survey acquire. For semi-quantitative analysis, an internal standard is added to each sample; calculations are performed based on the concentration of the internal standard.

Mass calibration is also performed under survey acquire. See 2.3.7 for details.

2.3.4.2 Scan Acquire

Scan Acquire is used when a common element menu and element procedure is desired for running a consecutive series of samples. An element procedure is necessary for quantitative analysis; scan acquire is therefore the most efficient acquire program to use for this capability in that an element procedure is requisite for acquisition.

2.3.4.3 Peakjump Acquire

Peakjumping Acquire does not scan, but as the name implies, it jumps from pre-selected isotopes and spends a pre-selected dwell on each individual isotope mass. This method of acquiring is useful when isotopes of interest are spaced across a wide mass range. Longer dwell per amu and fast acquisition times make peakjumping ideal for small sample volumes and for minimizing detection limits.

2.3.5 Calculations Program

With the exception of semi-quantitative calculations (see 2.3.4.1), the calculations program includes all calculation types whether they be multi-element, isotope ratio, standard addition, or isotope dilution.

2.3.5.1 Multi-Element Calculation Program

When performing multi-element calculations, appropriate response files must be used. For very precise and accurate data output, calibration curves which incorporate standard concentrations in the range of the sample concentrations are necessary. In addition, when samples have significant amounts of dissolved solids (e.g., brines), standards which are in similar matrices must be used to account for ionization factors, oxide interferences, and sample introduction (nebulization) efficiencies.

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2.3.5.2 Isotope Ratio Calculation Program

Isotope ratio calculations must include standards which have certifiable isotopic abundance ratios. Interference corrections must be considered when sample matrices are highly variable. All sample isotopic concentrations must also be in the range of the standard concentrations used in order to account for the dead time differences between predominant versus less predominant isotopes. When considering low mass isotopes, it is very important to consider the quadrupole sensitivity. In general, the response curves near the low and high masses can be checked using standards.

2.3.5.3 Standard Addition Program

The standard addition program enables sample concentrations from single isotopes to be calculated using the standard addition technique. If quantitative analysis cannot be achieved directly, then using the qualitative values, process samples by standard addition.

2.3.5.4 Isotope Dilution Program

In this calculation, a specific isotope of an element is added to the sample. Knowing the concentration of this isotope and assuming normal isotopic abundances of the element(s) of concern, the concentrations are calculated. This is a very accurate method for determining elemental concentrations because quenching effects, interference corrections, and unforeseen matrix effects can be accounted for. In the event samples do not have compositions with normal isotopic ratios, isotopic abundances of each analyte of interest must first be determined.

2.3.6 Utility Program

The system utilities are designed to simplify the use of the data system, to provide flexibility in data manipulation, and to enable the operator to define this system configuration. Spectral interference corrections are input through the utilities program via Edit Database. Data manipulation and system configuration procedures are detailed in the VG PlasmaQuad Software Manual. Because spectral interferences other than isobaric interferences can be incorporated by using the Edit Database option, it is important that the ANALYST qualifies these "special" interferences in the final report (Section 3).

2.3.7 Mass Calibration

Before the results are calculated, the ANALYST must first review a sample spectrum to ensure that the peaks observed correspond to their respective masses, i.e., that the instrument is properly mass

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calibrated. Mass calibration is performed under Survey Acquire, and should be done if the peaks observed appear to be shifted from center mass. If the instrument is operating properly, mass calibration should not have to be necessary on a regular basis, but rather only periodically; it should be done if more than 0.5 amu off peak center in accordance with the VG PlasmaQuad Software Manual.

Mass calibration is usually performed only when the instrument has been cleaned or repaired. Documentation of instrument maintenance is in the instrument maintenance log. The new mass calibration parameters are written to file and also are in each sample analysis file and printed as a part of the header for each sample file.

3.0 ANALYSIS PROCEDURES

- 3.1 Tune machine as described in 2.2. An instrument response of less than 1 million counts/second/ppm is not acceptable for analysis. The instrument must be shutdown, cleaned and/or adjusted for better sensitivity.
- 3.2 In the Procedure Definition Program, call Element Menu and define elements and their isotopes for analysis. If qualitative scan is desired, call survey acquire and proceed directly to Section 3.5.
- 3.3 In the Procedure Definition Program, call Multi-Element Procedure Definition (ME PROC DEF) for elemental analysis; call Isotope Ratio Procedure Definition (IR PROC DEF) if isotopic ratio analysis is to be performed.

3.3.1 Multi-Element Procedure

Define Blanks, Standards, and Samples with uniquely identifiable names, as described in 1.3. Define the element file (defined in Element Menu Program). For standards, enter the appropriate concentrations for the standard's elements and create the Response File. If an internal standard is to be used, input the element symbol and mass of the internal standard. The internal standard, if used, must be present in all solutions at the same concentration.

3.3.2 Isotope Ratio Procedure

Define Blanks, Standards, and Samples with uniquely identifiable names, as described in 1.3. Define the isotopic ratio to be investigated.

- 3.4 Quit Procedure Definition Files and call Acquire Programs
- 3.5 Call Scan Acquire subroutine for analyses with pre-defined procedure definitions; otherwise call Survey Acquire and input element menu and define run parameters. Aspirate the sample; once it is

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ascertained that the sample has entered the plasma, commence scanning.

- 3.6 After acquiring data, each of the mass spectra will be automatically stored on a magnetic device under files defined in the procedure definition file. The files can be retrieved as raw data or integrated data (counts/sec/mass unit).

3.7 Perform Calculations

- 3.7.1 Under Survey Acquire: For semi-quantitative analyses, the default response curve is used to calculate the results based on the internal standard concentration. Input the internal standard concentration, the analysis procedure or the sample file identification, and commence calculations. For better semi-quantitative accuracy, a response curve can be generated using a standard solution containing low, medium, and high mass elements; see VG PlasmaQuad Software Manual for details.
- 3.7.2 Under Calculations: For multi-element analyses, reference material is used to calibrate the mass responses of the samples. For each of the elements, a mass response curve is generated from the responses of the reference materials; at least two different concentrations of each element that are similar in concentration to that of the samples should be analyzed to generate a proper calibration curve. An R^2 value for each curve is reported; an R^2 value of less than 0.9 is unacceptable, and the results for that element shall either be omitted in the final report, or reported as suspect.

4.0 INTERFERENCES AND MATRIX EFFECTS

4.1 Spectral Interferences

Spectral interferences are usually few in number and, in most cases, small in relative magnitude. Interference factors for normal day-to-day operations are accessed by analyzing various concentrations of single element solutions for each of the elements to be addressed. Only those interferences $>0.1\%$ for elements common at higher concentrations and $>1\%$ for less common elements shall be reported in the final results summary. For more details on interpreting interferences, refer to the VG PlasmaQuad Software Manual.

4.2 Acid Concentration

Acid concentration can have effects on the accuracy of the data by causing quenching of the analytical signal. For standard "ICP/MS"

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analyses, in which the calibration standards are in dilute acid, the samples should be diluted to acid strengths of similar concentration. In cases where the acid concentration is greater than 5% and dilution is not an acceptable solution due to loss of signal, then calibration standards can be made with acid concentrations which approximate the samples (± 10 relative percent); see 4.3. However, if the internal standard used is similar in chemical properties to the element(s) of interest, the quenching effect on the internal standard will be representative of the effect on the samples, and matrix matching will then be unnecessary.

4.3 Matrix Matching

Solutions with high levels of dissolved solids should be analyzed against "matrix matched" calibrating standards, because increasing dissolved solids tend to depress (or quench) the analytical signal. The simplest way to avoid matrix matching is by dilution. However, if this is not acceptable, then the matrix effects must be accessed by spiking the matrix with an appropriate standard and observing the effect on the elements of that standard. If the effects are not acceptable, as determined by the qualified ANALYST and the customer, then matrix matched standards (e.g. digested geologic material) must be employed.

5.0 REPORTING AND ARCHIVING RESULTS

The precision and accuracy are assessed for each data set.

5.1 Quantitative Analysis

If the check standard results are accurate, and the RSD of the results are acceptable ($<10\%$), the results are tabulated and reported as requested. Results having RSD's of 10-50% are reported preceded by the RSD value; results having RSD's greater than 50% shall be reported as semiquantitative values. Elements by which the check standard results differ by 10-50% are either normalized, or reported as being suspect; elements by which the check standard results differ by $>50\%$ may be normalized, but the results should be reported as suspect.

5.2 Semi-quantitative Analysis

Semi-quantitative analysis is reported in the same format as quantitative analysis, but without the constraints on accuracy; values should be designated as semi-quantitative, with associated errors as being -50% to +100%. Precision between runs should be the same as for quantitative analysis.

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5.3 Reporting Results

The tabulated results, along with any documentation requested in the statement of work, are arranged in report format with a cover letter to the customer. The final report is signed by the ANALYST and reviewed by SCIENTIST on the basis of accuracy and technical adequacy.

Copies of the report, as well as the output of the results summary, the procedure listing, the element menu, the raw data, and all other computer output are assimilated and filed in a folder and cabinet designated for that purpose in 3708 Bldg., Room 108.

5.4 Archiving

At least once every two months, the raw data (found in directory C:\RAWDATA on the computer) is backed up onto a mass storage device (MSD) for every sample run since the last backup took place. The MSD is then labelled appropriately and stored. This MSD is stored in a file cabinet in room 3708 Bldg., Room 108 designated for this purpose.

6.0 REFERENCES

VG Plasmaquad Software Manual.

VG Plasmaquad Operation Manual.

7.0 RECORDS

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with the ~~ACT NOW Directive 89.1~~ established records management practices.

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INTERIM CHANGE NOTICE
ICN

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<p>A. Document Number: <u>PNL-ALO-281</u> Revision Number: <u>0</u></p> <p>Document Title: <u>ICP/MS Determination of ⁹⁹Tc</u></p> <p>Document's Original Author: <u>EJ Wyse</u></p>	<p>Effective Date of ICN: <u>1/04/93</u></p> <p>Change Requested By: <u>EJ Wyse</u></p>								
<p>B. Action:</p> <p>Replace pages 1 through 4 with the attached pages 1 through 6.</p> <p>Implement changes as specified on attached sheets.</p>									
<p>C. Effect of Change:</p> <p>The change addresses the possibility of a Ru interference: how to identify, and how to make the necessary correction if one exists. Cognizance of this potential interference is required if accurate results are to be obtained.</p>									
<p>D. Reason for Change/Description of Change:</p> <p>Reason: Current procedure (Rev. 0) doesn't address the possibility of a Ru interference and how to make a correction if an interference exists.</p> <p>Description: See redline and strike-out changes in Section 1.0, 5.0, and 7.0.</p>									
<table border="1" style="width: 100%; border-collapse: collapse;"><tr><td style="width: 65%; vertical-align: top; padding: 5px;"><p>E. Approval Signatures: (Please Sign and Date)</p></td><td style="width: 35%; vertical-align: top; padding: 5px;"><p>Type of Change (Check (✓) one)</p><p>() Minor Change (✓) Major Change</p></td></tr></table>		<p>E. Approval Signatures: (Please Sign and Date)</p>	<p>Type of Change (Check (✓) one)</p> <p>() Minor Change (✓) Major Change</p>						
<p>E. Approval Signatures: (Please Sign and Date)</p>	<p>Type of Change (Check (✓) one)</p> <p>() Minor Change (✓) Major Change</p>								
<table style="width: 100%;"><tr><td style="width: 65%;">QP Concurrence: <u>TL Ehlert</u> <i>TL Ehlert</i></td><td style="width: 35%;">Date: <u>1/4/93</u></td></tr><tr><td>Approval Authority: <u>AG King</u> <i>AG King</i></td><td>Date: <u>1-14-93</u></td></tr><tr><td>Other Approvals: <u>EJ Wyse</u> <i>EJ Wyse</i></td><td>Date: <u>1/6/93</u></td></tr><tr><td><u>DW Koppenaal</u> <i>DW Koppenaal</i></td><td>Date: <u>1/8/93</u></td></tr></table>		QP Concurrence: <u>TL Ehlert</u> <i>TL Ehlert</i>	Date: <u>1/4/93</u>	Approval Authority: <u>AG King</u> <i>AG King</i>	Date: <u>1-14-93</u>	Other Approvals: <u>EJ Wyse</u> <i>EJ Wyse</i>	Date: <u>1/6/93</u>	<u>DW Koppenaal</u> <i>DW Koppenaal</i>	Date: <u>1/8/93</u>
QP Concurrence: <u>TL Ehlert</u> <i>TL Ehlert</i>	Date: <u>1/4/93</u>								
Approval Authority: <u>AG King</u> <i>AG King</i>	Date: <u>1-14-93</u>								
Other Approvals: <u>EJ Wyse</u> <i>EJ Wyse</i>	Date: <u>1/6/93</u>								
<u>DW Koppenaal</u> <i>DW Koppenaal</i>	Date: <u>1/8/93</u>								

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-281 - ICP/MS DETERMINATION OF ^{99}Tc

APPLICABILITY

This procedure is applicable to the determination of ^{99}Tc in aqueous, acidified samples, using ICP/MS techniques. Samples in other physical forms or matrices should be digested, fused, leached or otherwise prepared to result in an aqueous matrix, preferably acidified with HNO_3 to an acid content not exceeding 5% vol/vol. This procedure is applicable to the determination of ^{99}Tc at concentrations ≥ 10 ppt (170 pCi/L), in solution.

This procedure shall be applied in accordance with PNL-ALO-280 (Inductively Coupled Plasma Mass Spectrometric (ICP/MS) Analysis) and PNL-MA-70.

DEFINITIONS/ACRONYMS

amu - atomic mass unit

acps - area counts per second (units of integrated ICP/MS signal intensity)

ARF - analytical request form

CERCLA - Comprehensive Environmental Response, Compensation, and Liability Act

cps - counts per second (units of ICP/MS signal intensity)

ICP/MS - inductively coupled plasma mass spectrometry

IP - ionization potential, in units of electron volts (eV)

m/z - mass (in amu) divided by charge

NIST - National Institute of Standards Technology

PNL - Pacific Northwest Laboratory

ppb - parts per billion ($\mu\text{g/L}$)

ppt - parts per trillion (ng/L)

RSD - Relative Standard Deviation

Author	Date	Project Mgr.	Date	QAD Representative	Date
EJ Wyse		BM Gillespie		GK Gerke	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
DW Koppenaal		PF Salter		ALL ORIGINAL SIGNATURES ON FILE	
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SOW - statement of work

TI - test instruction

TP - Test Procedure

TUNE SOLUTION - A solution containing 100 ppb Mg, In, Pb for the purpose of tuning the ICP/MS instrument. Any solution containing 50 - 500 ppb of at least one low, medium, and high mass element can be used alternatively as a TUNE SOLUTION.

PROCEDURE

- 1.0 Define ELEMENT MENU in instrument operations software to include m/z 99 (Tc), 101, 102, 104 (Ru), and the amu of the designated internal standard(s); the minimum scanned mass range should include m/z 95 through 106 (see PNL-ALO-280, 2.3.1 and 3.2). Stipulate data acquisition in either scanning, peak jumping, or single ion monitoring mode depending on anticipated ⁹⁹Tc concentration, other analytes to be determined, and possible interferences that may require monitoring and correction. Name, save and record ELEMENT MENU with all operational parameters.
- 2.0 Define ANALYSIS PROCEDURE as described in PNL-ALO-280, 3.3 and 1.3. Run duplicate sample acquisitions in all cases (sample volume permitting). Number and frequency of standards, blind standards, spiked samples, and blanks shall be in accordance with the default QUALITY CONTROL procedures given below (8.0), or as specified in governing TI, SOW, or ARF instructions. Name, save and record ANALYSIS PROCEDURE.
- 3.0 Start up ICP/MS instrument, allow 30 minute warm-up period, and perform instrument response and precision check using TUNEIR analysis procedure as specified in PNL-ALO-280, 2.2 and 3.1. Verify adequate instrument response and stability (criterion: response $\geq 1 \times 10^6$ acps/ppm for tune elements In or Pb; stability $\leq 7\%$ RSD concentration/isotope ratio precision for tune elements Mg, In, and Pb). Save and archive TUNEIR data and results.
- 4.0 Prepare samples by adding appropriate level and type of INTERNAL STANDARD as specified in PNL-ALO-280, 1.2.3. Internal standard elements/isotopes should be judiciously chosen based on proximity in mass range and ionization potential to Tc (m/z 99 and 7.28 eV, respectively). Candidate internal standards for this determination include Rh (m/z 103; IP 7.46 eV) and In (m/z 113,115; IP 5.79 eV).
- 5.0 Standards solutions shall be prepared, using dilutions of previously prepared stock calibration standards, to yield standard concentrations that bracket the anticipated sample concentrations. During analysis, if a sample concentration exceeds two times that of the maximum concentration standard, a dilution shall be made of the sample so that it

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is within the calibration standard range; if it is below that of the minimum concentration standard and above 100 ppt, a standard containing an appropriate lower concentration of ^{99}Tc (e.g., 500 ppt) shall be prepared and analyzed. Internal standards shall be added to the standard solutions in exact concentration and form as the samples, in accordance with 4.0 above. Stock calibration standards that are available for use in this determination are the following:

52433-43: 12.56 ppb ^{99}Tc (BNW LRB 52433, p 43)
52433-47: 98.74 ppb ^{99}Tc (BNW LRB 52433, p 47)
52433-48D: NIST SRM 3.759E4 kBq/g soln (59.27 ppm ^{99}Tc [BNW LRB 52433, p 48])
53960-17: 49.86 ppb ^{99}Tc (BNW LRB 53960, p 17)
53960-28: 49.01 ppb ^{99}Tc (BNW LRB 53960, p 28)

Working standards shall be prepared fresh weekly, at minimum.

- 6.0 Prepared samples and standards shall be analyzed by ICP/MS according to ICP/MS Procedure PNL-ALO-280, 2.3.4 and 3.5, the instrument operating manuals, and SOPs for this instrument.
- 7.0 Calculation of the acquired data shall be performed via instrument software in accordance with PNL-ALO-280, 3.7. Calibration curves shall be constructed using standards intensity and concentration data; linear/quadratic regression fitting shall be performed using this data. Identity and number of standards, type of fit, and regression coefficients shall be stored in CALCULATION PROCEDURE RESPONSE files and output with data results. Ru correction: It is essential to determine the extent (if any) that Ru contributes to the response at m/z 99. One of the problems in doing so is that if Tc does exist in the sample, it is possible that any Ru that coexists is fission product Ru, and as such will have a different isotopic abundance than natural Ru. If the Ru is natural, its contribution at m/z 99 can be accurately calculated and subtracted out; if it instead proves to be from unnatural origins, the interference must be estimated and the results qualified to indicate the resulting uncertainty.

7.1 Correcting the Natural Ru: Natural isotopic abundance for Ru is determined by measuring the relative intensities at m/z (99), 101, 102, and 104; natural isotopic abundances for these isotopes is (12.7%), 17.1%, 31.6%, and 18.6% respectively.

NOTE: When using m/z 102 and 104 to make this determination, the Pd contribution at m/z 102 and 104 must also be considered. This can be calculated using the response at 105 amu).

If the Ru present appears to be natural based on the responses from these isotopes, the interference correction is calculated in the following manner:

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7.1.1 The Ru contribution at 99 amu can be calculated by multiplying the response at 101 amu (the integrated counts) by 0.7427 (the abundance ratio of Ru 99/101).

7.1.2 A ruthenium-based technetium correction factor (TCF) is then calculated which indicates the percentage at 99 amu due to technetium; this is calculated by subtracting the ⁹⁹Ru contribution from the response at 99 amu (integrated counts), and dividing the difference by the uncorrected response at 99 amu (integrated counts).

7.1.3 The original calculated Tc value is then multiplied by the TCF to obtain the corrected ⁹⁹Tc result.

7.2 Correcting for Fission Product Ru: As previously explained, if the isotopic abundance of Ru proves not to be from natural origins, the interference must be estimated and the results qualified to indicate the resulting uncertainty. To estimate the result and the uncertainty, the following parameters must be considered: 1) the relative concentrations of Ru and apparent Tc (e.g., is the response at m/z 101, 102, and 104 insignificant compared to the response at m/z 99), and 2) the response at m/z 99 from similar samples that do not appear to contain or are known not to contain any technetium. An TCF may still be calculated (as described in 7.1.1-3 above), but should be judiciously applied to results where the isotopic abundance of the Ru present is demonstrated to be other than natural. Regardless of the apparent precision and accuracy of the analysis, the uncertainty of the estimated results will necessarily be at least 15%, and probably higher in most cases.

7.3 Reporting Uncertainties. Reporting of the results shall be in accordance with PNL-ALO-280, 5.3, and shall include the uncertainty of the results, which are based on deviations between values obtained from analytical runs as well as those obtained from different elemental isotopes. When estimating an uncertainty for a given result, the relative versus absolute uncertainties (related to the TCF) must be considered. For example, an uncorrected Tc value of 1.0 has a calculated (absolute) uncertainty of 5% (0.05 ppb). The TCF is calculated at 0.20, making the corrected Tc result 0.20 ppb. The absolute uncertainty in this example is still 0.05 ppb, therefore the relative uncertainty of the corrected ⁹⁹Tc result is 0.05/0.20, or 25%. As stated in 7.2, a result that was corrected by estimating the contribution at 99 amu from fission product ruthenium will have a corresponding uncertainty of not less than 15%.

7.4 Examples

7.4.1 Example 1. The following data was obtained:

Integrated counts are m/z 99 = 1000*

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101 - 171
102 - 316
104 - 186
105 - 2

*Originally calculated to be 0.10 ppb ⁹⁹Tc (before correction). The Ru in this example appears to be natural based on relative isotopic abundance for m/z 101, 102, and 104. The contribution at m/z 99 is therefore 171 * 0.7427 = 127. The TCF is then calculated to be (1000-127)/1000 = 0.873. The TCF is then multiplied by the original ⁹⁹Tc value (0.10 ppb) to obtain a corrected ⁹⁹Tc result of 0.087 ppb.

7.4.2 Example 2. The following data was obtained:

Integrated counts at m/z 99 - 1000*
101 - 22
102 - 61
104 - 74
105 - 21

*Originally calculated to be 0.10 ppb ⁹⁹Tc (before correction). The Ru in this example does not appear to be natural. Four other samples in this batch of 10 had similar responses at m/z 101, 102, 104, and 105, but did not have any measurable response over background at mass 99. It would appear that all of the response at mass 99 could be attributed to ⁹⁹Tc. An estimated 15 - 20% uncertainty would be attributed to the final result: 0.10±0.02 ppb.

7.4.3 Example 3. The following data was obtained:

Integrated counts at m/z 99 - 100*
101 - 64
102 - 35
104 - 27
105 - 21

*Originally calculated to be 0.010 ppb ⁹⁹Tc (before correction). The Ru in this example does not appear to be natural. This was the only sample that appeared to contain any measurable response at m/z 99 - 105. Although a 1 ppt detection limit for ⁹⁹Tc had been obtained for the analysis, the final result in this example would have to be <0.01 ppb, due to the uncertainty of the relative abundances of Ru and/or Tc present at 99 amu.

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8.0 Quality Control

All analysis and quality control data shall be maintained and available for easy reference or inspection.

Two quality control options are defined. Option A shall be used unless a SOW written by WHC defines CERCLA protocols. Option B shall then be followed. The analyst will recognize the need to use Option B when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a Statement of Work (SOW), and these will be conveyed to the analyst through a TI.

- A. Employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Run duplicate analysis upon client request. A spiked sample or standard (NIST traceable) shall be periodically employed to ensure that correct procedure is followed and that all equipment is operating properly.
- B. For all SOW's written by WHC for CERCLA protocol requests for analysis, employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Run one duplicate sample for every 20 samples or for each set, whichever is smaller. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A spike sample or standard (NIST traceable) shall be run for every 20 samples analyzed or per every set of samples, whichever is smaller.

9.0 Results

ICP/MS results are normally reported in weight/volume concentration units, typically as ppb or ppt. Radiometric concentrations can alternatively be computed/reported, using the calculation below for results in pCi/L units:

$$[^{99}\text{Tc}], \text{ pCi/L} = ([^{99}\text{Tc}], \text{ ppt} * 1 \times 10^{-9} * A * \ln 2) / AW * t_{1/2} * C$$

where:

$$\begin{aligned} AW &= 99 \text{ g/mole;} \\ t_{1/2} &= 6.72 \times 10^{12} \text{ sec;} \\ A &= 6.023 \times 10^{23} \text{ atoms/mole; and} \\ C &= 0.037 \text{ dps/pCi} \end{aligned}$$

which reduces to:

$$[^{99}\text{Tc}], \text{ pCi/L} = [^{99}\text{Tc}], \text{ ppt} * 16.95$$

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INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-282.2

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A. Document Number: PNL-ALO-282 Revision Number: 0

Document

Title: DETER OF URANIUM CONC/ISOTOPIC COM-

Document's POSITION USING ICP/MS

Original Author: EJ WYSE

Effective

Date of ICN: 10/28/91

Change

Requested By: EJ WYSE

B. Action

REPLACE ALL PAGES

C. Effect of Change

PAGE SEVEN ADDED TO PROCEDURE

D. Reason for Change/Description of Change

PAGE SEVEN INADVERTENTLY LEFT OFF OF ICN-PNL-ALO-282.1

E. Approval Signatures

(Please sign and date)

Type of Change: {Check (✓) one}

☒ Minor Change

☐ Major Change

Process Quality

Department: GK GERKE [Signature]

Date: 11/5/91

Approval

Authority: AG KING [Signature]

Date: 10/28/91

Other

Approvals: BM GILLESPIE [Signature]

Date: 10/28/91

:

Date: / /

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-282.1
Page 1 of 1

A. Document Number: <u>PNL-ALO-282</u> Revision Number: <u>0</u> Document Title: <u>Determination of Uranium Concentration/Isotopic Composition</u> Document's Original Author: <u>E.J. Wyse</u> Using ICP/MS		Effective Date of ICN: <u>10/14/91</u> Change Requested By: <u>E.J. Wyse</u>
B. Action: Replace all pages.		
C. Effect of Change: Gives conditions for assuming natural isotopic abundance to get total uranium activity in the absence of measurable U-234. (U-234 is not always observed, yet accounts for ~50% of the total activity of natural uranium.)		
D. Reason for Change/Description of Change The current procedure does not consider the possibility that data may not be acquired for U-234; if [U]<200 ppb (natural abundance U), U-234 will not be observed. This needs to be addressed (i.e. how data should be calculated and reported). Description: Section 10.1 was added as depicted in redline.		
E. Approval Signatures (Please Sign and Date)	Type of Change: () Minor Change (Y) Major Change	
QS&R Department Concurrence: <u>Altthridge for GK Herke</u> Approval Authority: <u>[Signature]</u> Other Approvals: <u>B.M. [Signature]</u>		Date: <u>6/27/91</u> Date: <u>6/24/91</u> Date: <u>6/21/91</u> Date: <u>1/1</u>

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-282 - DETERMINATION OF URANIUM CONCENTRATION/ISOTOPIC COMPOSITION USING ICP/MS

APPLICABILITY

This procedure is applicable to the determination of uranium concentration and/or isotope ratio composition in aqueous, acidified samples, using ICP/MS techniques. Samples in other physical forms or matrices should be digested, fused, leached or otherwise prepared to result in an aqueous matrix, preferably acidified with HNO₃ to an acid content not exceeding 5% vol/vol. This procedure is applicable to the determination of total uranium and/or uranium isotopes (²³⁸U, ²³⁵U, ²³⁴U, and ²³⁶U) at concentrations ≥ 10 ppt for each isotope of interest.

This procedure shall be applied in accordance with PNL-ALO-280 (Inductively Coupled Plasma Mass Spectrometric (ICP/MS) Analysis) and PNL-MA-70.

DEFINITIONS/ACRONYMS

amu - atomic mass unit

acps - area counts per second (units of integrated ICP/MS signal intensity)

ARF - analytical request form

CERCLA - Comprehensive Environmental Response, Compensation, and Liability Act

cps - counts per second (units of ICP/MS signal intensity)

ICP/MS - inductively coupled plasma mass spectrometry

IP - ionization potential, in units of electron volts (eV)

m/z - mass (in amu) divided by charge

Author	Date	Project Mgr.	Date	QAD Representative	Date
EJ Wyse	9/17/90	BM Gillespie	9/19/90	GK Gerke	9/19/90
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
DW Koppenaar	9/17/90	PF Salter	9/20/90	original signatures on file	
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NIST - National Institute of Standards Technology

PNL - Pacific Northwest Laboratory

ppb - parts per billion ($\mu\text{g/L}$)

ppt - parts per trillion (ng/L)

RSD - Relative Standard Deviation

SOW - statement of work

TI - test instruction

TP - Test Procedure

TUNE SOLUTION - A solution containing 100 ppb Mg, In, Pb for the purpose of tuning the ICP/MS instrument. Any solution containing 50 - 500 ppb of at least one low, medium, and high mass element can be used alternatively as a TUNE SOLUTION.

PROCEDURE

- 1.0 Define ELEMENT MENU in instrument operations software to include the uranium isotopes of interest (see PNL-ALO-280 2.3.1 and 3.2). Stipulate data acquisition in either scanning, peak jumping, or single ion monitoring mode depending on anticipated uranium concentration, other analytes to be determined, and possible interferences that may require monitoring and correction. Name, save and record ELEMENT MENU with all operational parameters.
- 2.0 If only total uranium concentration determinations are required, skip this instruction and proceed to 3.0 below. Otherwise, define ISOTOPE RATIO ANALYSIS PROCEDURE as described in PNL-ALO-280 3.3.2, 2.3.3, 1.3, and the ICP/MS instrument software manual. Uranium isotope ratios shall be chosen with ^{238}U chosen as the denominator in each instance. Each sample shall be run five times consecutively for suitable isotope ratio statistics. Number and frequency of standards, blind standards, spiked samples, and blanks shall be in accordance with the default QUALITY CONTROL procedures given below (9.0), or as specified in governing TI, SOW, or ARF instructions. Name, save and record ISOTOPE RATIO ANALYSIS PROCEDURE.

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- 3.0 Define MULTI-ELEMENT ANALYSIS PROCEDURE as described in PNL-ALO-280 3.3.2, 2.3.3, 1.3, and the ICP/MS instrument software manual. Identify samples (including appropriate dilution factors) and the standards (including appropriate ^{238}U concentrations) for the purpose of determining the ^{238}U concentrations in the samples; by knowing this as well as the isotope ratio, the activity of each isotope and the total uranium concentration can be determined.
- 4.0 Start up ICP/MS instrument, allow 30 minute warm-up period, and perform instrument response and precision check using TUNEIR analysis procedure as specified in PNL-ALO-280 2.2 and 3.1. Verify adequate instrument response and stability (criterion: response $\geq 1 \times 10^6$ acps/ppm for tune elements In or Pb; stability $\leq 7\%$ RSD concentration/isotope ratio precision for tune elements Mg, In, and Pb). Save and archive TUNEIR data and results.
- 5.0 Prepare samples by adding appropriate level and type of INTERNAL STANDARD as specified in PNL-ALO-280 1.2.3. Internal standard elements/isotopes should be judiciously chosen based on proximity in mass range and ionization potential to U (m/z 234-238 and 6.08 eV, respectively). Candidate internal standards for this determination include Bi (m/z 209; IP 7.29 eV) or Th (m/z 232; IP 6.95 eV).
- 6.0 Standard concentration and isotope ratio solutions shall be prepared, using dilutions of previously prepared stock calibration standards. The concentrations of total U standards shall bracket the anticipated sample concentrations. Isotope ratio standards shall be selected or prepared with isotope ratios as close as feasible to those of samples but yet allowing for acquisition of statistically significant count levels for all isotopes. During total uranium concentration determinations, if a sample concentration exceeds two times that of the maximum concentration standard, a dilution shall be made of the sample so that it is within the calibration standard range; if it is below that of the minimum concentration standard and above 100 ppt, a standard containing an appropriate lower concentration of uranium (e.g., 500 ppt) shall be prepared and analyzed. Internal standards shall be added to the concentration standard solutions in exact concentration and form as the samples, in accordance with 5.0 above. Stock calibration standards that are available for use in this determination are the following:

52433-43: 10.12 ppb uranium (BNW LRB 52433, p 43)

52433-46: 999.4 ppb uranium (BNW LRB 52433, p 46)

NIST SRM 3164: 10,000 ppm uranium

Working standards shall be prepared fresh weekly, at minimum.

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- 7.0 Prepared samples and standards shall be analyzed by ICP/MS under the SCAN ACQUIRE (using either IR SCAN (for isotope and concentration determination) or ME SCAN (concentration only determination)) instrument programs according to ICP/MS Procedure PNL-ALO-280 2.3.4 and 3.5, the instrument operating manuals, and SOPs for this instrument.
- 8.0 Calculation of the isotope ratios as well as the ^{238}U concentrations shall be performed via instrument software in accordance with PNL-ALO-280 3.7. Isotope ratio and/or concentration calculations will be performed as a part of data acquisition in 7.0 above. Total uranium calibration curves shall be constructed using standards intensity and concentration data; linear/quadratic regression fitting shall be performed using this data. Identity and number of standards, type of fit, and regression coefficients shall be stored in CALCULATION PROCEDURE RESPONSE files and output with data results. Reporting of the results shall be in accordance with PNL-ALO-280 5.3, and shall include the uncertainty of the results, which are based on deviations between values obtained from analytical runs.

9.0 QUALITY CONTROL

All analysis and quality control data shall be maintained and available for easy reference or inspection.

Two quality control options are defined. Option A shall be used unless a SOW written by WHC defines CERCLA protocols. Option B shall then be followed. The analyst will recognize the need to use Option B when a Chain-of-Custody (COC) defines a Test Instruction. Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a Statement of Work (SOW), and these will be conveyed to the analyst through a TI.

- A. Employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Run duplicate analysis upon client request. A spiked sample or standard (NIST traceable) shall be periodically employed to ensure that correct procedure is followed and that all equipment is operating properly.
- B. For all SOW's written by WHC for CERCLA protocol requests for analysis, employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Run one duplicate sample for every 20 samples or for each set, whichever is smaller. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A spike sample or standard (NIST traceable) shall be run for every 20 samples analyzed or per every set of samples, whichever is smaller.

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10.0 RESULTS

ICP/MS results are normally reported in weight/volume concentration units, typically as ppb or ppt. Before radiometric concentrations for individual isotopes can be determined, their individual isotopic weight/volume concentrations must first be calculated in the following manner:

$$\begin{aligned} [^{234}\text{U}] \text{ in sample} &= ^{234}\text{U}/^{238}\text{U} * [^{238}\text{U}] \\ [^{235}\text{U}] \text{ in sample} &= ^{235}\text{U}/^{238}\text{U} * [^{238}\text{U}] \\ [^{236}\text{U}] \text{ in sample} &= ^{236}\text{U}/^{238}\text{U} * [^{238}\text{U}] \end{aligned}$$

Radiometric concentrations can alternatively be computed/reported, using the calculation below for results in pCi/L units:

$$[\text{U isotope}], \text{ pCi/L} = ([\text{U isotope}], \text{ ppt} * 1 \times 10^{-9} * A * \ln 2) / (AW * t_{1/2} * C)$$

where:

$$AW = 238, 235, 234, 236 \text{ g/mole};$$

$$\begin{aligned} t_{1/2} : \quad ^{238}\text{U} &= 1.410 \times 10^{17} \text{ seconds} \\ ^{235}\text{U} &= 2.222 \times 10^{16} \text{ seconds} \\ ^{234}\text{U} &= 7.700 \times 10^{12} \text{ seconds} \\ ^{236}\text{U} &= 7.391 \times 10^{14} \text{ seconds} \end{aligned}$$

$$A = 6.02 \times 10^{23} \text{ atoms/mole; and}$$

$$C = 0.037 \text{ dps/pCi}$$

which reduces to:

$$\begin{aligned} \{^{234}\text{U}\}, \text{ pCi/L} &= [^{234}\text{U}], \text{ ppt} * 6.26 \\ \{^{235}\text{U}\}, \text{ pCi/L} &= [^{235}\text{U}], \text{ ppt} * 0.00216 \\ \{^{236}\text{U}\}, \text{ pCi/L} &= [^{236}\text{U}], \text{ ppt} * 0.0647 \\ \{^{238}\text{U}\}, \text{ pCi/L} &= [^{238}\text{U}], \text{ ppt} * 0.000336 \end{aligned}$$

Total uranium activity is computed from the sum of these data:

$$\{^T\text{U}\}, \text{ pCi/L} = \{^{234}\text{U}\} + \{^{235}\text{U}\} + \{^{236}\text{U}\} + \{^{238}\text{U}\}$$

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10.1

If the concentration of uranium in the solution being analyzed is less than 200 ng/mL (ppb), then a natural isotopic abundance can be inferred using the $^{235}\text{U}/^{238}\text{U}$ ratio and observing the following criteria:

Column A: The concentration of uranium in the solution being analyzed.

Column B: The maximum allowable variation between the total uranium concentration calculated using ^{235}U and the total uranium concentration calculated using ^{238}U .

A (ng/mL)	B (%)
100-200	-5
50-100	-10
10-50	-15

The PQ software will calculate the total uranium concentration from the response of each isotope (U-235, U-238, and U-234 if possible), i.e., there will be as many total uranium values as there are isotopes. For low uranium concentrations, only the values from U-235 and U-238 will be obtained. The PQ software algorithm calculates each result based on natural isotopic abundance; these values should theoretically be identical. To calculate the percent difference between the U-235 value and the U-238 value with respect to the U-238 value (being the predominant isotope and therefore more accurate at low concentrations), the following equation is used:

$$\% \text{ difference (with respect to U-238)} = \frac{[^{235}\text{U value}] - [^{238}\text{U value}]}{[^{238}\text{U value}]} \times 100$$

The result should be compared with those listed in Column B to determine whether or not the observed variation falls within the specified allowable range for natural isotopic abundance.

If the natural isotopic abundance is inferred, data shall be marked or indicated as calculated.

If the concentration of uranium is less than 10 ppb or the above criteria cannot be met, natural abundance cannot be assumed, and only the activity due to ^{238}U can be reported. The result will be flagged and noted that it does not account for the activity of other isotopes.

If the samples do not meet the above criteria, the uranium in the samples is either depleted or enriched, and, as such, the activity from individual isotopes must be calculated. If the uranium concentration is too low to either observe the presence of or to establish adequate

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statistics on the ^{234}U concentration, the final uranium activity results shall contain only the contribution from the isotopes observed; the result will be flagged and noted that it does not account for the activity of ^{234}U .

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PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-283, (Replaces HTA-3-5), SOLIDS ANALYSIS:
MICROPROBE ANALYSIS

1.0 APPLICABILITY

This procedure establishes the techniques for electron microprobe analysis of irradiated and unirradiated solids. This procedure applies to the analysis of solid samples using the electron microprobe.

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

- Electron microprobe, shielded, MAC Model 450 with R-Theta stage and associated transfer cask.
- Electron microprobe, nonshielded, ETEC Autoprobe® or equivalent.

4.0 PROCEDURE

Samples for microprobe analysis may be either irradiated (therefore radioactive) or nonirradiated (therefore nonradioactive). In general, radioactive samples are examined in the shielded electron microprobe, while nonradioactive samples are examined in an unshielded instrument. Most steps in the procedure are the same; those that differ are called out separately.

*Autoprobe is a registered trademark of ETEC (formerly), currently Perkin-Elmer Corporation, Palo Alto, California.

Author	Date	Project Mgr.	Date	QAD Representative	Date
ED Jenson	07/1/87	N/A		BO Barnes	06/30/87
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	07/02/87	All original signatures on file	
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A small sample of the solid material is mounted in resin or similar mounting material; the mount is cut to expose the sample, and the surface is polished. The polished surface is examined in the electron microprobe by impinging a finely focused electron beam on the sample and examining the emitted x-rays, electrons, or absorbed beam current. Variations in composition and topography are studied by observing variations in current absorbed or x-rays emitted from the sample while rastering the beam over the sample surface. An enlarged area of the image surface can be displayed on a CRT screen. Elements in phases of interest may be identified by analyzing x-ray spectra from the intersection of those areas and the electron beam. The distribution of selected elements may be observed by displaying a signal with intensity proportional to the concentration of the element or by displaying "dot maps" where each x-ray detected generates one dot on the CRT. Quantitative analysis may be done by determining x-ray generation rate and comparing the count rate to standards.

4.1 Sample Preparation

4.1.1 Loading Radioactive Samples

- Step 1) Mount sample in a cylindrical plastic mount 1.25 in. in diameter.
- Step 2) Cut mount at right angles to the cylinder, exposing the sample.
- Step 3) Polish the cut surface through at least 1 μm .
- Step 4) Prepare a montage of the polished surface at $\sim 20\times$.
- Step 5) Carbon coat the polished surface with $\sim 200 \text{ \AA}$ carbon in a carbon evaporator.
- Step 6) Insert the sample in the stage and place a small drop of silver paint or conductive carbon at the interface between the stage lip and the polished surface.
- Step 7) Retract the stage in the cask body. Cap the face and transfer the assembly to the shielded electron microprobe.

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- Step 8) Load the stage into the shielded electron microprobe by removing the face plate, rolling the cask forward to interface to the column, and sliding the stage into the column using the protruding push rod.
- Step 9) Press the EVACUATE button to evacuate the air from the column.

4.1.2 Loading Nonradioactive Samples

- Step 1) Mount the sample in a cylindrical plastic mount, using either an 0.75-in. or a 1.25-in. diameter mount, as specified by the cognizant scientist.
- Step 2) Cut the mount to expose the sample.
- Step 3) Polish the sample through at least 1 μm .
- Step 4) Prepare a montage of the sample at $\sim 20\times$.
- Step 5) Carbon coat the sample and count with ~ 200 Å of carbon.
- Step 6) Deliver the mounted sample to the cognizant scientist.
- Step 7) Insert the sample into a holder, using the appropriate springs and backing plate.
- Step 8) Load the holder containing the sample into the stage.
- Step 9) Press the EVACUATE button to evacuate the air from the column.

4.2 Operating Conditions

Operating conditions vary considerably depending on the type of analysis to be performed. Therefore, specifying parameter settings will not result in optimum analysis conditions. Operation manuals for the instrument used in the examination assist in the selection of appropriate parameters. In general, an accelerating potential between 10 and 25 kV and sample currents between 1 and 10,000 nA are

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appropriate. Scanning rates, counting times, time constants, grid bias, aperture sizes, beam diameter, pulse height analyzer lower and upper limits, detector voltages, detector types, detector gas and flow rates, wavelength settings for peak and background determinations, and appropriate standards, must be chosen by the cognizant scientist to optimize the data for the specific use intended.

4.3 Analyses

4.3.1 Quantitative Analysis

For quantitative analysis, appropriate computer codes are available to drive either microprobe in the data collection process. These codes collect data in the desired areas (points, lines, or area scans) and then reduce the data to percent composition and location. These data are stored on discs or cassettes or are dumped to the printer, as appropriate.

Calibration of the system shall be done for quantitative analysis by determining the count rate on elements or compounds of well known composition under as nearly the same conditions as used for the determination on the sample. Exceptions may occur if the beam conditions are too high and may damage the standard. In this case the sample current used on the sample will be measured on the standard support ring (steel), then reduced to a safe value for the standard. The standard value to be used will be the product of the determined value multiplied by the ratio of the two samples current measurements on the support ring. If a standard is required that is not present in the standard ring an adjacent element or near by element may be used as an approximation provided no absorption edges lie between the elements used. The approximate composition is given by the ratio of count rate on the sample divided by the count rate on the standard.

4.3.2 Qualitative Analysis

Qualitative analysis using a nonshielded microprobe is usually done with energy-dispersive spectra. Photographic recording of the resulting spectral displays are a means of conveying the data so generated.

Qualitative analysis using the shielded electron microprobe uses wavelength scans over predetermined ranges of x-ray wavelength. These data are output onto chart paper and are analyzed manually.

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PNL TECHNICAL PROCEDURE

4.3.3 Elemental Distributions

Images of the surface or elemental distributions using either area (dot maps or rate meter displays) or linear (line profiles) display modes are recorded photographically.

4.4 Records

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

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TITLE: PNL-ALO-284, (Replaces 7-40.18 & HTA-4-34), QUANTITATIVE ANALYSIS OF GAS SAMPLES

1.0 APPLICABILITY

This procedure describes the mass spectrometer techniques for the quantitative determination of atoms, molecules or isotopes in gas mixtures. The method is applicable to gases that are permanent gases (noncondensable at room temperature). Condensible gases may adsorb to the walls of the vacuum lines and chambers. Some reactive gases which may react with or chemisorb to the vacuum walls are very difficult to analyze.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant Scientist.
Analyst.

4.0 PROCEDURE

4.1 Equipment and Materials

- Gas mass spectrometer.
- Mass spectrometer inlet.
- High vacuum/gas rack.
- Capacitance manometer.

Calibration gases pure and mixtures. Natural occurring gases (xenon, krypton, etc.) for isotopic analyses. Many calibration mixtures can be purchased, other mixtures which are not available commercially or can not be purchased in a reasonable time frame must be prepared on a gas mixing rack. For general work pure gases of the best quality available are usually used. Trace level impurities in gases used for standards can be corrected for by obtaining calibration data on the impurity gases.

Author	Date	Project Mgr.	Date	QAD Representative	Date
MW Goheen	6/15/88	N/A		LJ Ethridge	6/16/88
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		JJ McCown	6/15/88	All original signatures on file	
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NOTE: Anyone operating this type of equipment should be fully trained prior to any attempt to analyze samples.

4.2 Performance Check and/or Calibration

A performance check should be made to ensure that the instrument is responding properly for the particular sample to be analyzed. Usually a standard, working standard or pure gas is used for this check. The frequency depends on the particular instrument and type of sample to be analyzed. The timing could be monthly or daily as determined by the cognizant scientist.

Calibration is done when a major change occurs, ie., (filament replacement--refocus, etc.). For mixture analysis, calibration is checked whenever the measured inlet pressure differs by more than 20 percent from the total of the analyzed partial pressures. Differences can be from condensible constituents such as water in the sample mixtures. Calibration factors for seldom encountered gases are run as determined by the cognizant scientist.

The Analyst shall perform the following steps unless otherwise specified.

- 4.2.1 Install a cylinder or bulb of the calibration gas on the vacuum/gas rack of the mass spectrometer.
- 4.2.2 Evacuate the connecting lines between the bulb/cylinder and all inlet lines.
- 4.2.3 Close the valves to the vacuum pumps and obtain a sample sized for the particular calibration. Record the reading of the manometer in the mass spectrometer diary book or log books.
- 4.2.4 Introduce the sample into the mass spectrometer.
- 4.2.5 On a timing sequence after the inlet valve is opened, scan or peak step through the mass spectra of interest.
- 4.2.6 Identify and measure the recorded peaks. Make corrections for interferences from background, moleculars fragments and multiple ionizations.
- 4.2.7 Calculate sensitivity/calibration factors from the measured isotopes, atoms, molecular ions, or ion fragments. Record the factors in the mass spectrometer operating guide book or in the appropriate log book.

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4.3 Sample Analysis

The Analyst shall perform the following steps unless otherwise specified.

- 4.3.1 Attach the cylinder/bulb containing the sample gas to the vacuum rack.
- 4.3.2 Evacuate the connecting lines containing the sample gas to the vacuum rack.
- 4.3.3 Close the valves to the vacuum pumps and obtain a sample sized for the particular calibration.
- 4.3.4 Introduce the sample into the ion source of the mass spectrometer.
- 4.3.5 On a timing sequence after the inlet valve is opened, scan or peak step through the mass spectra of interest.
- 4.3.6 Identify and measure the mass peaks. Make corrections for interferences from background, molecular fragments and multiple ionizations.

4.4 Calculations

Calculate the amount of each gas or isotope of interest. For gas mixture analysis, normalize the gases present in the mixture to volume or mole percent. At present this calculation is done by hand. The calculation could be done on a control and data reduction computer.

4.5 Records

Records will be maintained and controlled so as to conform with the requirements of MCS-033. Laboratory Record Books and Analytical Report forms provide a mechanism for control of most records. ~~Laboratory Record Books will be used in accordance with PAP-1704.~~ File a copy of the report and also file the recorder chart of computer print out (if any).

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 independent technical review.

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INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-285.1 R0

PAGE 1 OF 1

<p>A. Document Number: <u>PNL-ALO-285</u> Revision Number: <u>0</u></p> <p>Document Title: <u>Total Cyanide by Remote Microdistillation and Argentometric Titration</u></p> <p>Document's Original Author: <u>KH Pool</u></p>		<p>Effective Date of ICN: <u>03/05/93</u></p> <p>Change Requested by: <u>KH Pool</u></p>
<p>B. Action:</p> <p>Replace pages 1 through 6 with the attached pages 1 through 7.</p>		
<p>C. Effect of Change:</p> <p>The change will give more accurate descriptions and results.</p>		
<p>D. Reason for Change/Description of Change:</p> <p><u>Reason:</u></p> <p>To describe the operational details actually used in applying this procedure.</p> <p><u>Description:</u></p> <ol style="list-style-type: none">1) Description of sample pretreatment to provide more relevant details. See Section 3.8, 4.4, and 4.5.2) Results calculation description. See Sections 6.2 and 6.3.3) Miscellaneous clarifications in language; editorial in nature. <p>See redline and strikeout throughout the procedure.</p>		
<p>E. Approval Signatures: (Please Sign and Date)</p> <div style="display: flex; justify-content: space-between; align-items: flex-start;"><div style="width: 60%;"><p>QP Concurrence: <u>TL Ehlert</u> <i>TL Ehlert</i></p><p>Approval Authority: <u>AG King</u> <i>AG King</i></p><p>Other Approvals: <u>SG McKinley</u> <i>SG McKinley</i></p><p style="margin-left: 20px;">: <u>SA Bryan</u> <i>SA Bryan</i></p></div><div style="width: 35%; text-align: right;"><p>Type of Change (Check (✓) one) () Minor Change (✓) Major Change</p><p>Date: <u>3/5/93</u></p><p>Date: <u>3/5/93</u></p><p>Date: <u>3/5/93</u></p><p>Date: <u>3-8-93</u></p></div></div>		

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-285, Total Cyanide by Remote Microdistillation and Argentometric Titration

APPLICABILITY

This procedure provides a method for determining total cyanide in waste tank matrices where the concentration of total cyanide is greater than approximately 0.1 weight percent. The detection limit for this procedure is approximately 20 µg cyanide.

DEFINITIONS

Batch - A group of samples of similar matrix treated and distilled at the same time. A batch can not exceed (N-4) samples, where N is the number of available spaces in the heating block used. For analyses performed in support of Single Shell Tank (SST) characterization, all samples are to be analyzed in duplicate. Therefore, the maximum number of samples that would constitute a batch when working with SST samples will be (N-3)/2. Where N is the number of available spaces in the heating block used.

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst/Technician

PROCEDURE

1.0 Equipment and Materials

- 1.1 Micro-Distillation Tubes (Lachat® part no. 1700-001 or equivalent)
- 1.2 Temperature controlled heating block designed to accommodate at least 5 Micro-Distillation tubes simultaneously
- 1.3 Micro-Distillation Tube Assembler/Disassembler (MDTA/D)
- 1.4 Pipets (adjustable or fixed volume)
- 1.5 Disposable pipet tips
- 1.6 Repipetor, 500 mL
- 1.7 Analytical four place balance
- 1.8 Buret, 10 mL, readable to nearest 0.02 mL
- 1.9 Magnetic stirrer
- 1.10 Vials, glass, 15 mL

Author	Date	Project Mgr.	Date	PQ Representative	Date
KH Pool		SG McKinley		TL Ehlert	
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
SA Bryan		AG King		ALL ORIGINAL SIGNATURES ON FILE	
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- 1.11 Stir bars, glass
- 1.12 Ice cream cartons (sample transfer containers)
- 1.13 Drug cartons (secondary containment vessels)
- 1.14 Tissue or Kleenex® (secondary containment vessel packing)
- 1.15 Silicone grease

2.0 Reagents

- 2.1 0.0192 N AgNO₃ solution (Titer: 1.00 mg CN⁻/mL): Weigh 3.2647 ± 0.0002 g crushed primary standard grade (99.9% or better) AgNO₃ which have been dried to constant weight at 40°C, dissolve in deionized water (DIW), and dilute to 1000 mL. Alternatively a certified AgNO₃ solution from a commercial source may be used.
- 2.2 Sample pretreatment solution: Acid form EDTA and Ethylenediamine. Dissolve 5.0 grams acid form EDTA and 5.0 grams Ethylenediamine in Deionized Water (DIW) to a total volume of 100 mL.
- 2.3 Releasing solution: 7.11 M H₂SO₄ + 0.79 M MgSO₄: Dissolve 47.5 g MgSO₄ (anhydrous) in approximately 150 mL of DIW. Add 350 g concentrated H₂SO₄ slowly to avoid overheating to the point of boiling. Dilute to 500 mL final total volume. Filter, if undissolved solids persist.
- 2.4 Deionized water, greater than 15 megohm, as indicated by the deionizer meter readout.
- 2.5 Rhodanine Indicator Solution: Dissolve 0.02 g of p-dimethylaminobenzalrhodanine in 100 mL of acetone.
- 2.6 Stock Standard CN⁻ spiking solution(s): K₄Fe(CN)₆ and/or Na₂NiFe(CN)₆ dissolved in the sample pretreatment solution. Concentration ~1mg CN⁻/mL.
- 2.7 0.25 M NaOH solution: Dissolve 10.0 ± 0.2 gram Reagent grade NaOH pellets in 1.0 liter of DIW.

3.0 Predistillation Preparation

- 3.1 Unpackage the required number of micro-distillation tubes to complete the batch. Verify that the sealed upper portion of each tube contains approximately 1.5 mL of vendor supplied sodium hydroxide trap solution.
- 3.2 Label the upper and lower halves of each micro-distillation tube with the appropriate sample identification information. Every batch will consist of samples, a duplicate sample, spike, a control sample, and a methods blank. For QC requirements, see Section 7.0. Label the required number of 15 mL glass vials

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needed to transfer the distillates out of the hot cell. Place a disposable glass stir bar in each vial. Place the vials in secondary containment to keep them externally free of radioactive contamination.

- 3.3 Lightly grease the joint where the upper and lower portions of each tube join. Use silicon grease.
- 3.4 Turn on the power to the heat block. Allow at least 30 minutes for the unit to warm up. Verify that the temperature of the heating block is 128 ± 3 degrees C, using a calibrated thermometer or thermocouple. Record actual temperature on a bench sheet (see Exhibit 1).
- 3.5 Perform a balance performance check in accordance with PNL-ALO-052.
- 3.6 Check and document the delivery of all pipets that will be used both in-cell and out. Document the checks on the bench sheet.
- 3.7 Pipet or weigh the appropriate amount of spike solutions into the lower parts of the appropriate micro-distillation tubes prior to introducing them into the hot cells. The appropriate amounts will be provided by the Cognizant Scientist. Place the lower tube sections into an ice cream carton to keep them upright while they are being transferred into the cells.
- 3.8 Weigh approximately 0.5 g sample (nearest 0.1 mg) into a tared scintillation vial. Add approximately 5 g pretreatment solution (nearest 0.1 mg) to the vial along with a magnetic stir bar. Record weights of sample and pretreatment solution. Stir the sample + pretreatment solution mixture in the capped vial vigorously for approximately 30 minutes to dissolve the alkali-nickel-ferrocyanide compounds.

4.0 Distillation

- 4.1 Transfer the still separated micro-distillation tube sections into the hot cell.
- 4.2 Place the upper tube sections in the large holding block in a logical sequential order.
- 4.3 Place the bottom tube sections in the small holding block in logical order.
- 4.4 Weigh approximately 1 g of sample/pretreatment solution mixture (Section 3.8) into the appropriate lower tube section and record the weight on the bench sheet. The weight of mixture taken should

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be measured to the nearest milligram or better. Weigh approximately 100 mg (or other quantity as suggested by the Cognizant Scientist) of as received sample material into the appropriate lower tube sections and record the data on the bench sheet.

- 4.5 Fill the lower tube section to the flange with sample pretreatment solution. ~~Agitate by drawing and expelling the contents of each lower tube section into the disposable pipet tip to facilitate sample dissolution. Be sure to use a new pipet tip for each sample to avoid cross contamination. CAUTION: It is important that solids, either from sample or spiking material, be completely dissolved before proceeding to the next step. Continue the agitation procedure until no visible solids remain then agitate at least three more times for good measure.~~
- 4.6 Using the MDTA/D, add 0.6 mL 0.5 mL of the $\text{H}_2\text{SO}_4/\text{MgSO}_4$ releasing solution to the lower tube section. Seal the upper and lower tube sections together. NOTE: This sealing operation must be done as quickly as possible to minimize the potential loss of HCN. Place the sealed tubes in the heating block.
- 4.7 Allow the heating/distillation process to proceed for at least 30 minutes but no longer than 40 minutes.
- 4.8 Using the MDTA/D, disconnect the lower portions of the tubes from the upper and discard the lower section. The elapsed time between the removal of a tube from the heat block and parting the upper and lower sections should be minimized to prevent the potential "suck-back" of distillate into the lower tube sections. Failure to minimize the time interval may result in low recoveries.
- 4.9 With each upper tube section, hold horizontally and rotate slowly to rinse the walls with the distillate. Tap the tube section on a firm hard surface (e.g., the hot cell floor) to ensure that all of the trap solution is in the lower portion just above the semi-permeable membrane. Break the upper tube section in the location pre-scored by the manufacturer. Transfer the distillate into a prelabeled 15 mL glass vial. Rinse each half of the upper tube section with approximately 5 mLs of 0.25 M NaOH (squeeze bottle) and add the rinses to the glass vial.
- 4.10 Transfer the glass vials containing the distillates and rinses out of the hot cell and to the fume hood where the titrations are to be done.

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PNL TECHNICAL PROCEDURE

5.0 Titrations

For each sample:

- 1) Fill a clean 10 mL buret with 0.0192 N AgNO_3 .
- 2) While stirring the sample by means of magnetic stirrer and stirbar, add 3 drops of Rhodanine indicator to the vial.
- 3) Continue stirring sample and titrate to the first permanent appearance of a "salmon" color. Record the volume of AgNO_3 used on the bench sheet.

6.0 Calculations

6.1 Since the titer of 0.0192 N AgNO_3 is 1.00 mg CN^- /mL, the volume of the titrant used (in mL) is numerically equal to the mg CN^- in the distillate. Therefore,

$$\text{mg CN}^- \text{ found} = (\text{mL AgNO}_3 \text{ used to titrate} - (\text{mL AgNO}_3 \text{ used to titrate distillate}))$$

6.2 Let:

W_1 = weight (g) sample taken (Section 3.8)

and

W_2 = weight (g) pretreatment solution taken (Section 3.8)

$$\text{Then, the weight fraction of sample in mixture} = \frac{W_1}{W_1 + W_2} = X$$

For samples and blank spikes:

$$\% \text{ CN}^- = \frac{\text{mg CN}^- \text{ found}}{(W_s)(X) \times 10^3} \times 100$$

where: W_s = weight (g) mixture (Section 4.4) taken.

2) ~~For samples, standards and/or blank spikes;~~

$$\% \text{ CN}^- = \frac{\text{mg CN}^- \text{ found}}{\text{mg sample taken}} \times 100$$

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6.3 Spiked Samples

$$\text{Spike recovery (\%)} = \frac{[V_{sp} - V_B - \frac{(W_s)(X)}{1000} \times \frac{A}{100}]}{W_{sp}} \times 100$$

where: V_{sp} = mL AgNO_3 used to titrate spiked sample distillate

V_B = mL AgNO_3 used to titrate blank distillate

W_{sp} = weight (mg) of CN^- in added spike

W_s = weight (g) mixture (Section 4.4) taken

A = % CN^- found for unspiked sample

3) ~~Spiked samples:~~

$$\text{Spike Recovery (\%)} = \frac{A}{(V_{sp} - \frac{W_s}{W_{sp}} \times 100)} \times 100$$

where, V_{sp} = mL AgNO_3 used to titrate ~~spiked sample distillate~~

W_{sp} = weight (mg) of CN^- in spike

W_s = weight (mg) of sample included in the spiked sample

A = % CN^- found for unspiked sample

7.0 Quality Assessment

Each analytical session (distillation + titration) shall include as a minimum: one blank, one spiked sample, one sample duplicate, and one spiked blank a.k.a. control sample. For SST samples, all samples will be analyzed in duplicate.

The preparation/method blank and control sample represent known performance indicators for this procedure and may render the analytical session suspect. Evidence of contamination in the blank and/or control sample recovery falling outside 80-120% warrant immediate corrective action. Notify the Cognizant Scientist immediately when one or both of these situations occur.

Sample spike recoveries should fall within 80-120%. When this recovery limit is exceeded contact the Cognizant Scientist.

The relative percent difference (RPD) for duplicate samples shall not exceed 15%, if the cyanide content of the is ≥ 10 times the method detection limit.

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PNL TECHNICAL PROCEDURE

The Cognizant Scientist is responsible for investigating all incidents of QC failure and directing appropriate corrective action.

8.0 Records

Records will be maintained and controlled so as to conform to requirements of the Analytical Chemistry Laboratory Quality Assurance Plan, MCS-033.

9.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

- a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.
- b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

10.0 References

Winters, W.I., 'Analytical Methods for Determining Cyanide in Hanford Nuclear Waste,' RHO-SD-WM-TI-315, Rockwell Hanford Operations, Richland, WA, September, 1987.

'Micro-Dist Distillation System Reference and Methods Manual,' Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218, December 28, 1989.

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Total Cyanide

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Shielded Analytical Laboratory
Bench Sheet

Project Id.:

Project No.:

Temperature of Heating Block: _____ °C

Tube No.

Contents

Volume 0.0192 M AgNO₃
to titrate

Balance check:

Pipet Delivery check(s):

Analyst:

Date:

Reviewer:

Date:

Procedures Used:

____ PNL-ALO-101, Acid Digestion for Metals Analysis
____ PNL-ALO-102, Fusion of Hanford Tank Waste Solids
____ PNL-ALO-103, Water Leach of Sludges, Soils, and Other Solid Samples
____ PNL-ALO-104, Extraction Procedure Toxicity
____ PNL-ALO-106, Acid Digestion for Preparation of Samples for
Radiochemical Analysis
____ PNL-ALO-107, Leach Procedure for Preparing Sludges, Soils and Other
Solid Samples for Free Cyanide Analysis
____ PNL-ALO-108, Aqueous Leach of Sludges, Soils and Other Solid Samples
for Anion Analysis
____ PNL-ALO-330 Hexadecane Extracts for Volatile Organic Compounds
____ PNL-ALO-504, Percent Solids Determination of Soils/Sludges/Solids
____ PNL-ALO-120, Procedure for Extraction of Single Shell Tank Samples
for the Analysis of Semivolatile Organic Compounds
____ PNL-ALO-130, Procedure for the Receipt and Inspection of Single
Shell Tank (SST) Samples
____ WHC-053-1, Laboratory Procedure for Measurement of Physical and
Rheological Properties of Solutions, Slurries and
Sludges
____ 7.40.9 Laboratory Procedure for the Physical Characterization of
Fluids
____ 7.40.16 Separation of Carbon from Soil/Sediment/Sludge Samples
____ 7.40.24 Measurement of Carbon-14 in Zircaloy Cladding Crud Layer
____ 7.40.25 Distillation of Caustic Trap Solutions for C-14 Separation
____ 7.40.29 Specific Gravity of Highly Radioactive Solutions
____ 7.40.30 Bulk Density of Highly Radioactive Free-Flowing Granular
Solids
____ 7.40.34 Tritium in Irradiated Cladding Materials
____ 7.40.36 Analysis of Solid Samples for Carbonate by Use of
Coulometrics Model 5011 Coulometer.
____ 7.40.37 Determination of Carbon in Solids Using the Coulometrics
Carbon Dioxide Coulometer
____ 7.40.42 Determination of Carbon-14 in Radioactive Liquids, Soils,
and Sludges
____ 7.40.47 Determination of TC, TOC and TIC in Radioactive Liquids,
Soils, and Sludges by Hot Persulfate Method
____ Other _____

M&TE Used:

____ Cell 2 Balance 360-06-01-016 Mettler AE 160
____ Cell 6 Balance 362-06-01-038 Mettler AE 200
____ Counter Balance 360-06-01-024 Sartorius R 200D
____ Corning pH meter Model 240 S/N 6629

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-286, Measurement Of Hydrogen And Nitrous Oxide In Air

APPLICABILITY

This procedure is suitable for the measurement of hydrogen and nitrous oxide in air over the range of approximately 1 percent to 5 ppm. Minor modifications can expand the range to higher levels. Application to matrices other than air may require additional modifications. This procedure was prepared especially for samples of SY-101 tank atmosphere which are delivered in 75 cc metal cylinders at a pressure of 10-14 psia.

DEFINITIONS

PSIA: Pounds per square inch, absolute.

RESPONSIBLE STAFF

Cognizant Scientist
Analyst

PROCEDURE

1.0 Equipment

1.1 Gas Chromatograph. Thermal conductivity type. Ideally, a chromatograph should be set up for each analyte to save time and manipulations. For hydrogen, a molecular sieve column preconditioned at 300° is used with dry, CO₂-free air as the carrier gas. For nitrous oxide, a Haysep-S column preconditioned at 120° C is used with helium as the carrier gas.

- Standard Gas Mixes in air, oxygen or nitrogen.
- Gas sampling/diluting system or manifold.
- Volumetric Gas Syringes. Capacities of 0.1 to 500 cc.

2.0 Sample Preparation

Samples must be pressurized to at least 20 psia to permit valid sampling. This results in a dilution for which a correction must ultimately be made. A Sample Pressurization Table is provided for convenience in making quantitative dilutions (Exhibit 1). The table assumes that the samples are in 75 cc metal cylinders and that the existing 25cc gas manifold (#M-1) is used. Recalibration and revision of the table will be necessary if the volume of either is changed.

Author <i>R.F. Keough</i> RF Keough	Date <i>3/8/93</i>	Project Mgr. <i>M.W. Goheen</i> MW Goheen	Date <i>3-8-93</i>	QP Representative <i>TL Ehlert</i> TL Ehlert	Date <i>3/8/93</i>
Technical Reviewer <i>SJ Bos</i> SJ Bos	Date <i>3/8/93</i>	Line Mgr. <i>AG King</i> AG King	Date <i>3-9-93</i>	Other N/A	Date
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PNL TECHNICAL PROCEDURE

- 2.1 Connect the sample cylinder to the gas manifold, as in Exhibit 1, and adjust the pressure in the manifold to 13.0 psia with valve number 2. Open valve number 1 and read the pressure. Add air to bring the cylinder pressure up to 2 or 3 times the initial pressure and into the 20-30 psia range. Use Exhibit 2 for guidance. Record the dilution multiple.

3.0 Hydrogen Measurement

- 3.1 Prepare two or more working (dilute) standards from a commercial hydrogen standard or from pure (99+%) gas by dilution with air.
- 3.2 Inject a known volume of the working standards into the chromatograph and record the resulting hydrogen peaks.
- 3.3 Inject the same volume of the diluted samples into the chromatograph and record the resulting hydrogen peaks. There is generally insufficient sample for replicates.
- 3.4 After concluding the sample analyses, run a replicated standard to assure that there has been negligible drift in instrument response.

4.0 Nitrous Oxide Measurement

- 4.1 Prepare two or more working (dilute) standards from a commercial nitrous oxide standard or from pure (99+%) gas by dilution with air.
- 4.2 Inject a known volume of the working standards into the chromatograph and record the resulting nitrous oxide peaks.
- 4.3 Inject the same volume of the diluted samples into the chromatograph and record the resulting nitrous oxide peaks.
- 4.4 After concluding the sample analyses, run a replicate standard to assure that there has been negligible drift in instrument response.

ACCEPTANCE CRITERIA

The data is presumed to be valid if the standards measured before and after the samples are in agreement to within $\pm 5\%$.

CALCULATIONS

- 1.) For both analytes, plot the concentration (generally ppm) of the standards versus their observed peak heights.
- 2.) From the plot, read the measured ppm of the samples corresponding to their peak heights.

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PNL TECHNICAL PROCEDURE

- 3.) Correct for the sample dilution (pressurization) by multiplying the measured ppm by the dilution factor; generally 2x or 3x.

RECORDS

A record book will be the recording mechanism for data relating to this procedure. The record book will be used in accordance with established records management practices.

PROCEDURE QUALIFICATION

Not Required. This procedure is considered to be self qualifying due to its dependence on standards analyzed with each sample or set of samples.

REFERENCES

None.

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CYLINDER/MANIFOLD CONNECTION

SAMPLE PRESSURIZATION TABLE

OBSERVED PSIA	INITIAL PSIA	2X INITIAL PSIA	3X INITIAL PSIA
9.7	8.60	17.20	25.80
9.8	8.73	17.47	26.20
9.9	8.87	17.73	26.60
10.0	9.00	18.00	27.00
10.1	9.13	18.27	27.40
10.2	9.27	18.53	27.80
10.3	9.40	18.80	28.20
10.4	9.53	19.07	28.60
10.5	9.67	19.33	29.00
10.6	9.80	19.60	29.40
10.7	9.93	19.87	29.80
10.8	10.07	20.13	30.20
10.9	10.20	20.40	30.60
11.0	10.33	20.67	31.00
11.1	10.47	20.93	31.40
11.2	10.60	21.20	31.80
11.3	10.73	21.47	32.20
11.4	10.87	21.73	32.60
11.5	11.00	22.00	33.00
11.6	11.13	22.27	
11.7	11.27	22.53	
11.8	11.40	22.80	
11.9	11.53	23.07	
12.0	11.67	23.33	
12.1	11.80	23.60	
12.2	11.93	23.87	
12.3	12.07	24.13	
12.4	12.20	24.40	
12.5	12.33	24.67	
12.6	12.47	24.93	
12.7	12.60	25.20	
12.8	12.73	25.47	
12.9	12.87	25.73	
13.0	13.00	26.00	
13.1	13.13	26.27	
13.2	13.27	26.53	
13.3	13.40	26.80	
13.4	13.53	27.07	
13.5	13.67	27.33	
13.6	13.80	27.60	
13.7	13.93	27.87	
13.8	14.07	28.13	
13.9	14.20	28.40	
14.0	14.33	28.67	
14.1	14.47	28.93	
14.2	14.60	29.20	
14.3	14.73	29.47	
14.4	14.87	29.73	
14.5	15.00	30.00	
14.6	15.13	30.27	
14.7	15.27	30.53	

SOURCE OF THE SAMPLE PRESSURIZATION TABLE

The sample pressurization process is as follows:

The pressure in the 25 cc manifold is adjusted to 13 psia via valve #2.

With valve #2 closed, valve #1 is opened and the "observed psia" is noted. From the table the "initial psia" in the sample cylinder is determined.

Valve two is then opened to allow air to pressurize the sample cylinder. It is convenient to pressurize to either x or 3X as in the table but any pressure in the 20-30 psia range could be used with manual dilution calculated.

The general equation governing the system of cylinder and manifold is:

$$(P_c)(V_c) + (P_m)(V_m) = (P_{c'}) (V_{c'}) + (P_{m'}) (V_{m'})$$

where:

P_c	=	initial pressure in cylinder
$P_{c'}$	=	pressure in cylinder after valve #1 is opened (this is the "observed psia" and is equal to $P_{c'}$)
P_m	=	initial pressure in manifold (set at 13 psia)
$P_{m'}$	=	pressure in manifold after valve #1 is opened (this is the "observed psia" and is equal to $P_{c'}$)
V_c	=	volume of sample cylinder (75 cc)
V_m	=	volume of manifold (25cc)

Rearranging and substituting the fixed volume values:

$$P_c = \frac{75P_{c'} + 25P_{m'} - 25P_m}{75}$$

Reducing further:

$$P_c = 1.333P_{c'} - 4.33$$

To work an example: Assume a sample cylinder is opened into the manifold containing 13 psia (as the procedure requires). Assume the pressure reading changes to 10.1 psia. Substituting in the reduced equation (above), the initial pressure in the cylinder would have been:

$$P_c = (1.333)(10.1) - 4.33 = 9.13 \text{ psia}$$

This is the value given in the table. Note that a dilution to 2X would not give the 20 psia required for the analysis so dilution to 3X, or 27.4 psia would probably be used. If the sample were diluted to 22 psia for example, the dilution is simply $22/9.13 = 2.42X$.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-290, DETERMINATION OF pH IN SOIL SAMPLES

APPLICABILITY

This procedure is derived from EPA SW-846 Method 9045 and is approved for measuring pH in soils after leaching with water or a dilute calcium chloride solution.

Interferences - Temperature affects pH measurement, therefore, calibration and measurement shall be performed at ambient temperature. If electrodes become coated with substances from the sample matrix during measurement which do not rinse off easily, follow electrode manufacturer's instructions for cleaning and conditioning electrodes.

DEFINITIONS

Calcareous - Containing calcium or calcium carbonate.

RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

PROCEDURE

This procedure measures pH of soil leachate. Water or dilute calcium chloride is used as the leachate depending on whether or not the soil is calcareous or non-calcareous. Calcareous soils are recognized by the presence of white deposits of CaCO_3 and/or NaHCO_3 . The Cognizant Scientist will make the determination as to sample type. For discussion of pH measurement see Bates, et.al. or PNL-ALO-225.

1.0 APPARATUS

- pH meter (electrometer)
- Indicating (glass) and reference electrode, or combination pH electrode

Author <i>MC Burt</i> MC Burt	Date 3/3/93	Project Mgr. <i>J. Hosaka</i> J. Hosaka	Date 3/17/93	PQ Representative <i>TL Ehlert</i> TL Ehlert	Date 3/16/93
Technical Reviewer <i>MW Urie</i> MW Urie	Date 3/18/93	Line Mgr. <i>A. King</i> AG King	Date 3/18/93	Other	Date
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PNL TECHNICAL PROCEDURE

- Suitable beakers, 20-50 mL
- Teflon coated stir bars
- Magnetic stirrer
- Volumetric flask, 500 mL
- Volumetric flask, 1 liter

2.0 REAGENTS

- High purity water, (Deionized), with pH of 6-7.
- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, ACS Reagent grade or equivalent.
- Stock calcium chloride solution (CaCl_2), 2.0 M. Dissolve 147g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in high purity water, cool, dilute to 500 mL and mix well.
- Calcium chloride (CaCl_2), 0.01 M. Dilute 5.0 mL of stock 2.0 M CaCl_2 to 1 liter with high purity water. If the pH of this solution is not between 5 and 6.5, adjust the pH by adding $\text{Ca}(\text{OH})_2$ or 1:10 HCl.

3.0 STANDARDS

Commercially available certified buffers at pH values of 4.0, 7.0, and 10.0. Other certified buffers are available and may be used as required.

4.0 QUALITY CONTROL

- 4.1 Standardization. Because of the different pH meters which may be used, only minimum requirements can be specified. Manufacturer's instructions shall be followed for calibration of the meters using standard buffers. A minimum of two buffers shall be used for the calibration.
- 4.2 Control. Control is established by measuring, within ± 0.1 pH units of the certified value, a buffer not used for calibration. This step shall be performed prior to beginning analysis, after every 10th sample, and at the end of the analytical run.
- 4.3 Quality Control. A method blank shall be analyzed with each sample group (typically 10 samples) or for each batch of samples prepared, whichever is more frequent. One sample from each sample group or batch of ten samples shall be analyzed in duplicate. If pH values of duplicate samples vary by more than 1 pH unit, notify the Cognizant Scientist for corrective action/resolution as required.

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PNL TECHNICAL PROCEDURE

5.0 ANALYSIS

5.1 Instrument Set Up

- 5.1.1 Follow manufacturer's operating instructions for set up and calibration of pH meter using buffer solutions as specified.

Note: To avoid contamination of buffer solutions do not return used solutions to the container.

- 5.1.2 Immerse electrode(s) in buffer solution not used for calibration and, with stirring, allow reading to equilibrate. It shall read within ± 0.1 pH units of its stated value. If not, recalibrate.

5.2 Sample Analysis

- 5.2.1 Sample preparation of non-calcareous soils. Weigh soil into a suitable beaker and add high purity water in a ratio of one mL water to one gram of sample. Sufficient sample and water to allow immersion of the electrode is required. Stir several times over a 30 minute period and let stand undisturbed for about an hour to allow settling of particulates. Measure as per steps 5.2.3.1 through 5.2.3.3.
- 5.2.2 Sample preparation of calcareous soils. Weigh soil into a suitable beaker, add 2 mL 0.01 M CaCl_2 (step 2.0) solution per gram of soil and stir several times over a 30 minute period. Let stand undisturbed for about 30 minutes to allow settling of particulates. Measure as per steps 5.2.3.1 through 5.2.3.3.
- 5.2.3 Sample Measurement
- 5.2.3.1 Sample shall be at the same temperature as the buffer solutions (normally ambient temperature). Immerse the electrode(s) into the solutions deep enough to ensure electrical contact.
- 5.2.3.2 Without stirring allow the meter reading to stabilize. Record reading. Remove electrode(s) from solution, rinse with water and repeat measurement. Record reading. Repeat measurements shall agree within ± 0.1 pH unit. If not, see Cognizant Scientist for resolution.

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PNL TECHNICAL PROCEDURE

For calcareous soils report as "soil pH measured in 0.01 M CaCl_2 ."

- 5.2.3.3 Remove electrode(s) from sample, and rinse with water. Glass electrodes are fragile and care must be taken to not scratch or break the electrodes. Electrodes shall be replaced when manufacturer's specified maintenance procedures do not return it to satisfactory operation.

Electrodes shall be stored according to manufacturer's instructions when not in use.

6.0 CALCULATIONS

None.

7.0 SPECIFIC QUALIFICATIONS

This procedure is self-qualifying due to dependence on the use of calibration standards. It is based on standard, well understood methods. See PNL-MA-70, PAP-70-901.

8.0 RECORDS

Records shall be maintained and controlled so as to conform to requirements of the Analytical Chemistry Laboratory Quality Assurance Plan, MCS-033. Record Books, or worksheets/benchsheets, provide a mechanism for control of data and records.

9.0 REFERENCES

Instruction manual for meter used.

Bates, R.G. 1973, Determination of pH, Theory and Practice, 2nd Ed. John Wiley & Sons, New York, N.Y.

US EPA Test Methods for Evaluating Solid Waste-Physical/Chemical Methods; SW846, Method 9045

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