General

Los Alamos
NATIONAL LABORATORY

memorandum

Chemical Science and Technology
Responsible Chemistry for America

CST-3, Analytical Quality and Chemical
Information Management
Los Alamos, New Mexico 87545

To/MS: Holders of LA-10300-M
From/MS: Margaret A. Gautier, Editor
Symbol: CST-3/97-213
Date: February 19, 1997

SUBJECT: OCTOBER 1996 UPDATES AND ADDITIONS

The Analytical Quality and Chemical Information Management Group (CST-3) of Los Alamos National Laboratory is continuing the publication of its analytical procedures. Besides this cover memo, enclosed in this packet you will find the following items:

- update instructions,
- Document Acknowledgment Sheet, and
- shrink-wrapped updates and additions.

Please incorporate the updates and additions into your manual by following the update instructions. Then, on the Document Acknowledgment Sheet, fill in the date of receipt and any address changes or corrections to be made. Also, please fill in the question about your Internet access and any comments you may have on our plan, as described below, to move to electronic distribution. Return the sheet to CST-3.

THIS WILL BE YOUR LAST HARD-COPY UPDATE. Because of on-going budget constraints as well as the rapid growth in the Internet, we have decided to publish LA-10300, to be renamed "Analytical Chemistry: Techniques and Quality Assurance," only in electronic format. Currently we are developing our internal system to allow analysts to obtain electronically only those procedures they are responsible for instead of receiving an entire set of manuals. In other words, we are moving from a manual-based, hard-copy system to a procedure-based, electronic system. Development of this internal distribution system takes precedence and it may be some time, possibly a year, before we are able to fully duplicate unclassified portions for external distribution. Unfortunately, because of classification concerns, we cannot allow direct access to our internal system. For this reason, we have agreed to periodically "publish" our procedures externally, as time permits, on the server found at the Research Library at Los Alamos National Laboratory.

http://lib-www.lanl.gov

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We are currently converting our procedures as "pdf" files using Adobe Acrobat. While some browsers may read these automatically, most people will need to download free software (Adobe Acrobat Reader) to view the files. Your local computer personnel should be able to help you if you have problems. The free software is currently available off our Library server at

http://lib-www.lanl.gov/pubs/la-pubs.htm

However, please remember that it will be up to a year or more before the external system is fully operational; the URL addresses may have changed by then. When we have the external system ready, we will send you notification with further details.

If you have any questions regarding the procedures or update instructions, or if I may be of any further assistance, please feel free to contact me.

UPDATE INSTRUCTIONS
LA-10300-M, REVISION 8 (October 1996)

Volume I:

(1) Replace the existing white title page (rev. March 1995) with the new one (rev. October 1996).

General Information

(2) Replace the table of contents (pages GI-1 through GI-21) with the revised version.

Radiobioassay Chemistry

(3) Replace the table of contents (pages R-1 and R-2) with the revised version.

(4) Replace ***page 1 and 2 only*** of procedure R290. This procedure has been retired.

Industrial Hygiene Chemistry

(5) Replace the table of contents (pages IH-1 through IH-3) with the revised version.

(6) Replace ***page 1 and 2 only*** of procedures IH273 and IH345. These procedures have been retired.

Volume II:

(7) Replace the existing white title page (rev. March 1995) with the new one (rev. October 1996).

Environmental Chemistry

(8) Replace the table of contents (pages E-1 through E-5) with the revised version.

Environmental Inorganic Chemistry

(9) Replace ***page 1 and 2 only*** of procedures EI105, EI125, EI130, EI135, EI140, EI145, EI160, EI170, EI175, EI190, EI195, EI200, EI205, EI210, and EI520. All of these procedures have been retired.

(10) Replace procedure EI735 with the revised version.

Volume III:

(11) Replace the existing white title page (rev. March 1995) with the new one (rev. October 1996).

Waste Water Chemistry

(12) Replace the table of contents (pages WW-1 through WW-5) with the revised version.

Waste Water Inorganic Chemistry

(13) Replace procedure WI230 with revised version.

(14) Replace ***page one and two only*** of procedure WI260. This procedure has been retired.

(15) Replace procedures WI270, WI320, and WI340 with revised versions.

(16) Replace ***page one and two only*** of procedure WI428. This procedure has been retired.

(17) Replace procedures WI460, WI529, WI530, and WI630 with revised versions.

(18) Replace ***page one and two only*** of procedure WI640. This procedure has been retired.

(OVER)

(19) Replace procedures WI650, WI660, and WI670 with revised versions.

(20) Replace *page one and two only* of procedure WI680. This procedure has been retired.

(21) Replace procedures WI681, WI685, and WI690 with revised versions.

Volume IV:

(22) Replace the existing white title page (rev. March 1995) with the new one (rev. October 1996).

Quality Control

(23) Replace the table of contents (pages QC-1 through QC-5) with the revised versions.

Quality Control Inorganic Chemistry

(24) Replace procedure QCI100 with revised version

(25) Insert new procedure QCI115 after QCI110.

(26) Replace procedures QCI120, QCI135, QCI140, QCI170, QCI180, QCI190, QCI200, QCI210, and QCI220 with revised versions.

Quality Control Organic Chemistry

(27) Insert new procedure QCO122 after QCO120.

(28) Replace procedures QCO130, QCO210, QCO220, QCO250, and QCO260 with revised versions.

Quality Control Radiochemistry

(29) Replace procedure QCR100 with revised version.

(30) Insert new procedure QCR105 after QCR100.

(31) Replace procedures QCR110, QCR120, and QCR130 with revised versions.

(32) Insert new procedure QCR138 after QCR130.

(33) Replace procedures QCR140, QCR150, and QCR160 with revised versions.

(34) Insert new procedure QCR165 after QCR160.

(35) Replace procedures QCR170, QCR180, QCR190, QCR200, QCR210, QCR220, QCR230, QCR240, QCR250, QCR260, and QCR270 with revised versions.

(36) Replace *page one and two only* of procedure QCR180. This procedure has been retired.

Quality Control Intercomparison Studies

(37) Replace procedures QCS100 and QCS110 with revised versions.

(38) Insert new procedure QCS120 after QCS110.

(39) Replace procedures QCS130, QCS140, and QCS150 with revised versions.

(40) Insert new procedure QCS170 after QCS150.

(41) Replace procedures QCS180, QCS200, QCS220, QCS230, and QCS240 with revised versions.

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Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance

Los Alamos
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Los Alamos, New Mexico 87545

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ALPHA1 Computer Code 09/87

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CR380 Calibrating the HPGe Detector Systems . . . . . In Progress

CR390 Performance Verification for the HPGe Detector Systems 10/93

CR400 Standard Analysis for the HPGe Detector Systems 10/93

CR410 Operating the Tennelec LB5100 Gross Alpha/Beta
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CR420 Data Reduction for the Tennelec LB5100 Gross Alpha/Beta Gas-Flow Proportional Counting System 10/93

CR430 Operating the NaI(Tl) Well Crystal Counting System . . . . . In Progress

CR450 Calibrating the Oxygen Sensor for the Gamma-Counting Facility . . . . . In Progress

CR500 Operating the Tennelec LB4000 . . . . . In Progress

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Quality Control Analytical Procedures - Inorganic

QCI100 Beryllium and Lead for Vegetation Ash— QC Sample Preparation 07/95

QCI105 Electrical Conductivity/Resistivity of Water 11/93

QCI110 TCLP Elements for Water and Soil— QC Sample Preparation . . . . . Retired

QCI115 Mercury on Tubes—QC Sample Preparation 06/95

QCI120 Oil and Grease in Water—QC Sample Preparation 06/95

QCI130 TCA in Urine—QC Sample Preparation . . . . . In Progress

QCI135 Trace Elements in Bulk Materials—QC Sample Preparation 09/95

QCI140 Trace Elements on Filter Media—QC Sample Preparation 03/95

QCI150 Trace Elements in Solvent—QC Sample Preparation . . . . . Retired

QCI160 Trace Elements in Urine—QC Sample Preparation . . . . . In Progress

QCI170 Trace Elements in Nitric Acid—QC Sample Preparation 03/95

QCI180 Trace Elements in Hydrochloric Acid— QC Sample Preparation 03/95

QCI190 Trace Elements in Water—QC Sample Preparation 01/95

QCI200 Trace Elements for Water and Soil (Mercury by TCLP)—QC Sample Preparation 07/95

QCI210 Trace Elements in Water (CN)—QC Sample Preparation 09/95

QCI215 Trace Elements in Water (Minerals and Nutrients) 05/94

QCI220 Trace Elements in Water (NO_2-N)—QC Sample Preparation 08/95

Quality Control Analytical Procedures - Organic

QCO100 Formaldehyde on Tubes—QC Sample Preparation 09/94

QCO110 Herbicides on Soil—QC Sample Preparation 10/94

QCO120 Herbicides in Water—QC Sample Preparation 10/94

QCO122 High Explosives on Soil—QC Sample Preparation 03/95

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QCO180 Polychlorinated Biphenyls in Water—QC Sample Preparation 10/94

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QCR130 Cesium-137 in Water—QC Sample Preparation 06/95

QCR138 Gross Alpha and Gross Beta on Filter Media—QC Sample Preparation . 03/95

QCR140 Gross Alpha and Gross Beta on Soil—QC Sample Preparation 08/95

QCR150 Gross Alpha and Gross Beta in Water—QC Sample Preparation 09/95

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QCR165	Radionuclides on Fecal Material—QC Sample Preparation	06/95
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QCR180	Plutonium and Americium in Water—QC Sample Preparation	09/95
QCR190	Plutonium-238 in Urine—QC Sample Preparation	03/95
QCR200	Plutonium-239 in Urine—QC Sample Preparation	03/95
QCR210	Radionuclides on Filter Media—QC Sample Preparation	08/95
QCR220	Radium-226 in Water—QC Sample Preparation	08/95
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QCS150	EPA Blind A and B Performance Evaluation Study	08/95
QCS160	NPDES Study	In Progress
QCS170	NIOSH PAT Program	08/95
QCS180	EPA Plutonium in Water Performance Evaluation Study	09/95
QCS190	EML Quality Assessment Program	In Progress
QCS200	EPA Radionuclides in Milk Intercomparison Study	07/95
QCS210	EPA Radium in Water Performance Evaluation Study	Retired
QCS220	EPA Strontium in Water Performance Evaluation Study	07/95
QCS230	EPA Tritium in Water Performance Evaluation Study	07/95
QCS240	EPA Uranium-Radium in Water Intercomparison Study	06/95
QCS250	EPA Water Pollution Study	In Progress

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Radiobioassay Analytical Procedures

R100 Americium in Urine—Alkaline Earth Phosphate 02/93

R110 Americium and Plutonium in Fecal Samples—
A Screening Procedure 02/93

R120 Cesium-137 in Urine . . . . . Retired

R130 Gross Beta Activity . . . . . Retired

R150 Phosphorus-32 in Urine . . . . . Retired

R160 Polonium-210 in Urine . . . . . Retired

R170 Plutonium in Urine—Alkaline Earth Phosphate Procedure 05/93

R190 Plutonium in Urine—Rapid Method . . . . . Retired

R200 Plutonium in Fecal Samples—RAS 04/93

R210 Thorium in Urine—Colorimetric . . . . . Retired

R230 Tritium (T_2O or TOH)—LS 10/93

R240 Tritium in Urine—Distillation . . . . . Retired

R250 Uranium—Delayed Neutron Counting . . . . . Retired

R260 Uranium in Urine—Anion Exchange and Radiometric . . . . . Retired

R261 Uranium (Isotopic) in Urine—Alkaline Earth Phosphate and Alpha Spectrometry 05/93

R270 Uranium in Urine—Anion Exchange and Colorimetric . . . . . Retired

R280 Uranium-238 Fluorometric . . . . . Retired

R290 Uranium in Urine—ICPMS . . . . . Retired

URANIUM IN URINE — ICPMS

Analyte: Uranium	**Method No.:** R290
Matrix: Urine	**Minimum Detectable Activity:** 0.2 μg/L
Procedure: Inductively coupled plasma mass spectrometry	**Accuracy and Precision:** 98% ± 3%
Effective Date: 09/01/89 to 09/01/95	**Authors:** Michael G. Bell Ernest S. Gladney

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. The urine is directly aspirated into the ICPMS after an initial dilution of 1:1 with 1% low temperature redistilled nitric acid. A standard curve and internal standard are used to compensate for the instrument drift and for variations in nebulization over the course of the analysis.

2. Sensitivity

2.1. The sensitivity of the ICPMS for uranium is 0.2 μg/L in the urine matrix. The standard curve must be made so that the limit of quantification is at 0.1 μg/L.

3. Accuracy and Precision

3.1. Analysis of spiked urine QC samples prepared in 1987 and 1988 using this procedure gave a mean recovery of 106% ± 7%. The data have been published in Source Materials 12.4 and 12.5 and are summarized below.

URANIUM SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

Year	Spike level (μg/L)	Mean ± RSD (%)	Number of samples
1987	8.0	111 ± 2	6
	13.0	100 ± 2	3

URANIUM SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION (cont)			
Year	Spike level (μg/L)	Mean ± RSD (%)	Number of samples
1988	3.0	103 ± 7	9
	13.0	97	1
	31.0	111 ± 5	6
	50.0	102 ± 7	12
	68.0	110 ± 6	6

4. Interferences

4.1. There is no instrumental interference at the high mass range around uranium. The matrix interference is currently under study.

5. Collection and Storage of Samples

5.1. Spike samples with 0.25 mL of low-temperature redistilled nitric acid upon receipt. Refrigerate pending analysis.

6. Apparatus

6.1. Inductively coupled plasma mass spectrometer: VG Plasmaquad or equivalent, equipped with a Gilson model 221 Autosampler.

6.2. Autosampler: Gilson model 221.

6.3. Bottles: 125-mL, high-density linear polyethylene.

6.4. Test tubes: 15-mL, polypropylene.

6.5. Pipettes: 100-, 250-, 500-, and 1000-μL.

6.6. Pipette tips for above pipettes.

7. Reagents

7.1. Nitric acid (concentrated, low-temperature redistilled, LTRD).

7.2. Uranium standard: stock standard (100 mg/L). Spex Industries, Inc., Edison, New Jersey.

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Industrial Hygiene Chemistry Analytical Techniques

Industrial Hygiene Analytical Procedures

IH100 Aliphatic Amines in Air . . . . . Retired

IH110 Anions by Ion Chromatography . . . . . Retired

IH120 Aromatic Amines in Air . . . . . Retired

IH130 Aromatic Amines—A Chemical Spot Test . . . . . Retired

IH135 Arsenic and Gallium on Air Filters—IENA . . . . . Retired

IH140 Asbestos Fibers in Air . . . . . Retired

IH150 Beryllium on Air Filters 05/93

IH155 Breathing Air 04/93

IH160 Cadmium in Urine—Flame AA . . . . . Retired

IH161 Cadmium in Urine—Flameless AA . . . . . Retired

IH170 Cholinesterase in Serum . . . . . Retired

IH180 N,N-Dimethylaminoazobenzene—A Chemical Spot Test . . . . . Retired

IH185 Ethanol in Air 09/93

IH190 Fluoride in Urine . . . . . Retired

IH200 Formaldehyde in Air—Alumina Tube Collection . . . . . Retired

IH210 Formaldehyde in Air—Impinger Collection . . . . . Retired

IH211 Formaldehyde in Air, Water, or Solids 09/93

IH214 Halogens and Sulfur in Liquids—NAA . . . . . Retired

IH220 Metals on Air Filters—NIOSH PAT Samples 03/93

IH230 Mercury in Urine . . . . . Retired

IH240 Metals—General Procedure . . . . . Retired

IH250 Aromatic Nitro-Compounds—A Chemical Spot Test . . . . . Retired

IH260 Organic Solvents in Air—General Procedure 09/93

IH270 Organic Solvents—NIOSH PAT Samples 09/93

IH273 Perchlorate in Waters—Colorimetric . . . . . Retired

IH274 Petroleum Hydrocarbons, Total Recoverable in Soil 04/93

IH275 Petroleum Hydrocarbons, Total Recoverable in Water 04/93

IH280 Phenol in Urine—Gas Chromatography . . . . . Retired

IH290 Phenol in Urine—HPLC . . . . . Retired

IH300 Phenol in Water—HPLC . . . . . Retired

IH310 Polychlorinated Biphenyls (PCBs) in Air . . . . . Retired

IH320 Polychlorinated Biphenyls (PCBs) in Oil . . . . . Retired

IH321 Polychlorinated Biphenyls (PCBs)—Screening by NAA . . . . . Retired

IH330 Polynuclear Aromatic Hydrocarbons in Air—HPLC 09/93

IH340 Polynuclear Aromatic Hydrocarbons in Air—GC 04/93

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Trace Metals in Air Filters . . . . . In Progress

IH350 Trichloroacetic Acid in Urine . . . . . Retired

Instrument Procedures

IH800 Gas Chromatography and Mass Spectrometry—
General Procedure . . . . . Retired

IH810 Infrared Spectroscopy—General Procedure . . . . . Retired

PERCHLORATE IN WATERS — COLORIMETRIC

Analyte: Perchlorate	**Method No.:** IH273
Matrix: Water	**Detection Limit:** 0.2%
Procedure: Colorimetric	**Accuracy and Precision:** Qualitative
Effective Date: 08/18/92 to 09/01/95	**Author:** Daryl Knab

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure and Source Material 11.1 for proper waste disposal practices.

1. Principle of Method

1.1. Perchlorate precipitates with methylene blue to form an observable purple precipitate. The current method is only qualitative, but a quantitative colorimetric procedure could be developed from it. The precipitate will not coagulate below about 0.2% (2000 ppm). This level is adequate for detecting ClO_4^- when dismantling duct work.

2. Accuracy and Precision

2.1. The procedure is qualitative.

3. Interferences

3.1. Color and turbidity interfere with this method.

4. Collection and Storage of Samples

4.1. Collect and store non-acid samples in polyethylene bottles at 4°C. Filter all samples.

4.2. Complete analysis within 6 months.

5. Apparatus

5.1. Transfer pipette: 5-mL, disposable.

5.2. Pipette: 25- and 250-μL, Eppendorf.

5.3. Hot-water bath.

5.4. Test tubes: 50-mL, glass.

5.5. Filter syringe: 10-mL, 0.45-μ, and 25-mm.

6. Reagents

6.1. Methylene blue. Dissolve 100 mg of methylene blue in approximately 100 mL of water.

6.2. Perchlorate solution (2000 μg/L). Dilute 250 μL of perchloric acid (70%, 12 M) in approximately 100 mL of water.

7. Calibration and Standards

7.1. None currently used.

8. Procedure

8.1. Pipette 10 mL of water into a tube and 10 mL of the perchlorate solution into a second tube. With a filter syringe, add 10-mL aliquots of sample to two additional tubes. Add 25 μL of perchloric acid to one of the samples.

8.2. Add 2 drops of methylene blue solution to each tube, mix well, and let stand for approximately 20 min.

8.3. The presence of perchlorate is indicated by the blue methylene blue solution turning lavender. If a color change is observed, but no precipitate coagulates on stirring after 20 min, place the solutions in a hot-water bath for approximately 10 min. Let cool for approximately 20 min and check for a visible precipitate. If no precipitate is visible, the solution contains less than 2000 ppm perchlorate.

8.4. Visually compare the sample with the blank and the standard. Check to see that the spike sample formed a precipitate to determine if interferences are present.

9. Calculations

9.1. This is a qualitative determination which indicates whether perchlorate is present above the 0.2% level.

9.2. Prepare serial dilutions to estimate the concentration of a sample that actually contains perchlorates.

10. Proper Waste Disposal Practices

10.1. Discard all solutions in the acid waste system.

THALLIUM IN URINE – ICPMS

Analyte: Thallium	**Method No.** IH345
Matrix: Urine	**Sensitivity:** 0.2 μg/L
Procedure: Inductively coupled plasma mass spectrometry (ICPMS)	**Accuracy and Precision:** 98% ± 5%
Effective Date: 09/01/89 to 09/01/95	**Authors:** Michael G. Bell Ernest S. Gladney

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. The urine is directly aspirated into the Inductively Coupled Plasma Mass Spectrometer (ICPMS) after an initial dilution of 1:1 with 1% low-temperature redistilled (LTRD) nitric acid.

1.2. A standard curve and internal standard are used to compensate for the instrument drift and variations in nebulization over the course of the analysis.

2. Sensitivity

2.1. The sensitivity of the ICPMS for thallium is 0.2 μg/L in the urine matrix. The standard curve is prepared so that the limit of quantification is at 0.1 μg/L.

3. Accuracy and Precision

3.1. Analysis by ICPMS of spiked urine QC samples prepared between 1988 and 1990 using this procedure gave a mean recovery of 98% ± 5%. The data are published in Source Material 12.4. to 12.6. and are summarized below.

THALLIUM SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION			
Year	Spike Level (μg/L)	Mean ± RSD (%)	Number of Samples
1988	15.0	93 ± 2	4
	23.0	98 ± 3	8
	40.0	97 ± 4	4
	77.0	98 ± 4	8
1989	15.0	98 ± 3	13
	40.0	96 ± 2	10
1990	15.0	104 ± 17	4
	40.0	102 ± 16	4

4. Interferences

4.1. There is a lack of instrumental interference at the high-mass range around thallium. The matrix interference is currently under study.

5. Collection and Storage of Samples

5.5. Spike the samples with 0.25 mL of LTRD hydrochloric acid upon receipt. Refrigerate the samples pending analysis.

6. Apparatus

6.1. Inductively Coupled Plasma Mass Spectrometer: VG Plasmaquad or equivalent, equipped with a Gilson Model 221 Autosampler.

6.2. Bottles: 125-mL, high-density, linear polyethylene.

6.3. Test tubes: 15-mL, polypropylene.

6.4. Pipettes: 100-, 250-, 500-, and 1000-μL.

6.5. Pipette tips for above pipettes.

7. Reagents

7.1. Nitric acid (LTRD).

7.2. Hydrochloric acid (LTRD).

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Environmental Chemistry Analytical Techniques

Environmental Analytical Procedures - Inorganic

EI100 Arsenic in Water and Soil Extracts—Graphite Furnace AA 05/93

EI105 Barium in Water and Soil Extracts—Flame AA . . . . . Retired

EI120 Cadmium in Water and Soil Extracts—Graphite Furnace AA 05/93

EI125 Calcium in Water and Soil Extracts—Flame AA . . . . . Retired

EI130 Chromium in Oil, Water, and Soil Extracts—Flame AA . . . . . Retired

EI135 Chromium in Water and Soil Extracts—Graphite Furnace AA . . . . . Retired

EI140 Copper in Water and Soil Extracts—Flame AA . . . . . Retired

EI145 Iron in Water and Soil Extracts—Flame AA . . . . . Retired

EI150 Lead in Water and Soil Extracts—Graphite Furnace AA 05/93

EI160 Magnesium in Water and Soil Extracts—Flame AA . . . . . Retired

EI165 Mercury in Water—Cold Vapor AA . . . . . In Progress

EI170 Nickel in Water and Soil Extracts—Flame AA . . . . . Retired

EI175	Potassium in Water and Soil Extracts—Flame AA	Retired
EI185	Selenium in Water and Soil Extracts—Graphite Furnace	05/93
EI190	Silver in Water and Soil Extracts—Flame AA	Retired
EI195	Sodium in Water and Soil Extracts—Flame AA	Retired
EI200	Thallium on Filters—Graphite Furnace AA	Retired
EI205	Thallium in Water and Soil Extracts—Graphite Furnace AA	Retired
EI210	Zinc in Water and Soil Extracts—Flame AA	Retired
EI300	Barium in Soils—Acid Digestion and ICPAES	Retired
EI400	Anions in Water and Waste Water—IC	06/92
EI520	pH of Soil	Retired
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EI730	Mercury in Environmental Materials—Cold Vapor Gold Film Analyzer	10/90
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EI735	Sample Preparation for Spectrochemical Analyses of Total Recoverable Elements (EPA Method 200.2)	10/95
EI790	Water (Bound and Unbound) in Geological Matrices—High Temperature Coulometry	Retired

Environmental Analytical Procedures—Organic

EO400	Polychlorinated Biphenyls (PCBs) in Oil: Solvent Extraction—GC/ECD	03/93
EO410	Polychlorinated Biphenyls (PCBs) in Soil: Solvent Extraction—GC/ECD	03/93
EO420	Polychlorinated Biphenyls (PCBs) in Swipes: Solvent	

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EO430	Polychlorinated Biphenyls (PCBs) in Water: Solvent Extraction—GC/ECD	03/93
EO500	Semivolatile Organics in Solid Matrices: Solvent Extraction—GC/MS	05/93
EO530	Semivolatile Organics in Aqueous Matrices: Solvent Extraction—GC/MS	05/93
EO700	Volatile Organic Compounds: Thermal Desorption of Air Sampling Tubes—GCMS	04/94
EO720	Volatile Organic Compounds in Soil and Sediment: Capillary Column Technique—GC/MS (EPA SW846 Method 8260)	05/93
EO730	Volatile Organic Compounds in Water: Precision Dynatech Autosampler Capillary Column Technique—GC/MS (EPA SW846 Method 8260)	05/93

Environmental Analytical Procedures — Radiochemical

ER100	Gross Alpha and Beta Activity in Environmental Matrices—Gas-Flow Proportional Counting	04/92
ER110	Americium-241 in Environmental Matrices (Greater than 2-Gram Samples)—Alpha Spectrometry	02/93
ER120	Americium-241 in Environmental Matrices (Less than 2-Gram Samples)—Alpha Spectrometry	08/92
ER130	Gamma-Ray-Emitting Nuclides in Environmental Matrices—Instrumental Method	04/93
ER140	Qualitative Gamma-Ray Scan of Environmental Matrices	04/93
ER150	Gross Gamma in Environmental Matrices	06/93
ER160	Plutonium in Environmental Matrices—Alpha Spectrometry	04/93
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ER170 Radium-226 in Geologicals—Gamma-Ray Spectrometry 04/91

ER180 Radium-226 in Water—Radon Emanation 04/93

ER190 Strontium-90 in Environmental Matrices 10/93

ER200 Thorium-230 in Geologicals—Alpha Spectrometry 05/91

ER210 Tritium in Environmental Matrices—Distillation and LS 10/93

ER230 Uranium-235/Uranium-238 Ratio in Geologicals and Natural Waters—RTNA . . . . . Retired

ER240 Uranium in Air Filters—DNA . . . . . Retired

ER250 Uranium in Biological Matrices—DNA . . . . . Retired

ER260 Uranium in Geologicals—DNA . . . . . Retired

ER270 Uranium in Water—DNA . . . . . Retired

ER290 Total Uranium and $^{235}U/^{238}U$ Ratio in Water—ICPMS 02/91

ER300 Depleted Uranium in Soils—IENA . . . . . Retired

ER320 Uranium in Environmental Matrices—KPA 10/93

Mobile Laboratory Analytical Techniques

Mobile Laboratory Analytical Procedures—Organic

MLO274 Petroleum Hydrocarbons, Total Recoverable in Soil—Mobile Laboratory Method 04/93

MLO410 Polychlorinated Biphenyls (PCBs) in Soil—Mobile Laboratory Method 03/93

MLO500 Semivolatile Organics in Solid Matrices: Solvent Extraction-GC/MS—Mobile Laboratory Method 04/93

MLO510 Extraction of Semivolatile Organic Analytes in Solid Matrices for Analysis by GC/MS—Mobile Laboratory Method 04/93

MLO720 Volatile Organic Compounds in Soil Sediment—
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Mobile Laboratory Analytical Procedures—Radiochemical

MLR100 Gross Alpha/Beta Screening of Silicates—
Mobile Laboratory Method 02/93

MLR200 Gross Gamma Screening of Silicates—
Mobile Laboratory Method 02/93

MLR300 Gross Tritium Analysis of Silicates—
Mobile Laboratory Method 02/93

MLR400 Gross Moisture Analysis of Silicates—
Mobile Laboratory Method 02/93

BARIUM IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Barium	**Method No.:** EI105
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 100 μg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** 100% ± 1.0% RSD
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 208.1 and SW-846 method 7080.

1.2. Barium in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to Ba in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

2. Accuracy and Precision

2.1. The determination of barium in four in-house quality control samples (400 μg/L) over a three-month period had a mean of 397.5 μg/L and a relative standard deviation (RSD) of 1.0%.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences can be controlled by the addition of KCl, a matrix modifier, to all samples and standards at high concentration levels (1.0%).

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. Potassium chloride. Matrix modifier for all samples and standards.

6.5. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

CALCIUM IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Calcium	**Method No.:** EI125
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 25 mg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** not determined
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 215.1 and SW-846 method 7140.

1.2. Calcium in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to Ca in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis.

2. Accuracy and Precision

2.1. The accuracy and precision of the method for in-house quality control samples has not yet been determined.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences can be controlled by the addition of KCl, a matrix modifier, to all samples and standards at high concentration levels (0.1%).

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. Potassium chloride. Matrix modifier for all samples and standards.

6.5. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

CHROMIUM IN OIL, WATER, AND SOIL EXTRACTS — FLAME AA

Analyte: Chromium	**Method No.:** EI130
Matrix: Oil, water, waste water, and soil extracts	**Detection Limit:** 1.0 mg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** 100% ± 4.0% RSD
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 218.1 and SW-846 method 7190.

1.2. Chromium in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to Cr in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis. In oil, methyl isobutyl ketone is used as the solvent for samples and standards.

2. Accuracy and Precision

2.1. The determination of chromium in 27 in-house quality control samples (18.6 μg/L) over a 9-month period had a mean of 17.8 μg/L and a relative standard deviation (RSD) of 4.0%.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences are matrix dependent and can be corrected by the addition of matrix modifiers. Refer to the Perkin-Elmer (PE) Analytical Methods for AAS for appropriate modifier.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double deionized water.

6.4. Methyl isobutyl ketone (MIBK).

6.5. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

CHROMIUM IN WATER AND SOIL EXTRACTS — GRAPHITE FURNACE AA

Analyte: Chromium	**Method No.:** EI135
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 1.0 μg/L
Procedure: Graphite furnace atomic absorption	**Accuracy and Precision:** 94% ± 0.9% RSD
Effective Date: 09/25/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.6 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 218.2 and SW846 method 7190.

1.2. Chromium in solution may be readily determined by graphite furnace atomic absorption spectroscopy. The method is applicable to Cr in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis.

2. Accuracy and Precision

2.1. The determination of chromium in 23 in-house quality control samples (18.6 μg/L) over an 8-month period had a mean of 17.4 μg/L and a relative standard deviation (RSD) of 0.9%.

3. Collection and Storage of Samples.

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within 6 months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. Periodically clean the work area, including the bench top, to eliminate environmental contamination. Use acid-washed sample cups in the autosampler.

4.2. Chemical interferences can be controlled by the addition of a matrix modifier to all samples and standards. Refer to Perkin-Elmer chart 0993-8199 Rev. D (11/89), or to the PE *Methods of Analysis for AAS*, for the appropriate matrix modifier.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. To control this problem, use disposable sterile 50-mL polypropylene centrifuge tubes in the sample digestion steps.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile prolypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption instrument: equipped with a Zeeman graphite furnace or equivalent.

5.6. Required gas for the above instrument is ultrapure argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

6.5. Appropriate matrix modifier for all samples, standards, and QCs.

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water, waste water, and soil extracts, take a 50-mL aliquot from an acid-preserved sample containing not more than

COPPER IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Copper	**Method No.:** EI140
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 10 μg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** 100% ± 2.1% RSD
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 220.1 and SW-846 method 7210.

1.2. Copper in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to Cu in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

2. Accuracy and Precision

2.1. The determination of copper in 20 in-house quality control samples (21.9 μg/L) over a 9-month period had a mean of 21.2 μg/L and a relative standard deviation (RSD) of 2.1%.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences are matrix dependent.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

7.1.4. Allow the sample to cool and dilute to 50 mL with ASTM Type I water.

IRON IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Iron	**Method No.:** EI145
Matrix: Water, waste water, and soil extracts	**Detection Limits:** 20 μg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** 100% ± 8.7% RSD
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 236.1 and SW-846 method 7380.

1.2. Iron in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to Fe in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

2. Accuracy and Precision

2.1. The determination of iron in 24 in-house quality control samples (99 μg/L) over a 9-month period had a mean of 107.3 μg/L and a relative standard deviation (RSD) of 8.7%.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences are matrix dependent.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

7.1.4. Allow the sample to cool and dilute to 50 mL with ASTM Type I water.

MAGNESIUM IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Magnesium	**Method No.:** EI160
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 250 μg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** not determined
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 242.1 and SW-846 method 7050.

1.2. Magnesium in solution may be readily determined by atomic absorption spectroscopy. The method is simple and rapid and is applicable to Mg in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

2. Accuracy and Precision

2.1. The accuracy and precision of the method for in-house quality control samples has not yet been determined.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences can be controlled by the addition of KCl, a matrix modifier, to all samples and standards at high concentration levels (0.1%).

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. Potassium chloride. Matrix modifier for all samples and standards.

6.5. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

NICKEL IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Nickel	**Method No.:** EI170
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 15μg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** 100% ± 5% RSD
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 249.1 and SW-846 method 7520.

1.2. Nickel in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to Ni in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

2. Accuracy and Precision

2.1. The determination of nickel in 15 in-house quality control samples (800 μg/L) over a 9-month period had a mean of 841 μg/L and a relative standard deviation (RSD) of 5%.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences are matrix dependent.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

7.1.4. Allow the sample to cool and then dilute to 50 mL with ASTM Type I water.

POTASSIUM IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Potassium	**Method No.:** EI175
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 2 mg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** not determined
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 258.1 and SW-846 method 7610.

1.2. Potassium in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to K in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis.

2. Accuracy and Precision

2.1. The accuracy and precision of the method for in-house quality control samples has not yet been determined.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences are matrix dependent and can be corrected by the addition of matrix modifiers. Refer to Perkin-Elmer (PE) Analytical Methods for AAS for appropriate modifier.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

SILVER IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Silver	**Method No.:** EI190
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 10 μg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** 100% ± 1.2% RSD
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 272.1 and SW-846 method 7760.

1.2. Silver in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to Ag in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis.

2. Accuracy and Precision

2.1. The determination of silver in 88 in-house quality control samples (500 μg/L) over a 9-month period had a mean of 0.494 μg/L and a relative standard deviation (RSD) of 1.2%.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences are matrix dependent.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

7.1.4. Allow the sample to cool and dilute to 50 mL with ASTM Type I water.

SODIUM IN WATER AND SOIL EXTRACTS — FLAME AA

Analyte: Sodium	**Method No.:** EI195
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 2 mg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** not determined
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 273.1 and SW-846 method 7770.

1.2. Sodium in solution may be readily determined by atomic absorption spectroscopy (AAS). The method is simple and rapid and is applicable to Na in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis.

2. Accuracy and Precision

2.1. The accuracy and precision of the method for in-house quality control samples has not yet been determined.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences are matrix dependent and can be corrected by the addition of matrix modifiers. Refer to the Perkin-Elmer (PE) Analytical Methods for AAS for appropriate modifier.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

THALLIUM ON FILTERS — GRAPHITE FURNACE AA

Analyte: Thallium	**Method No.:** EI200
Matrix: Filters	**Detection Limit:** 5.0 μg/L
Procedure: Graphite furnace atomic absorption	**Accuracy and Precision:** 100% ± 1.0% RSD
Effective Date: 09/30/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. Thallium in solution may be readily determined by graphite furnace atomic absorption spectroscopy. The method is applicable to Tl on filters. Samples are acid-leached or prepared by total digestion with concentrated nitric acid.

2. Accuracy and Precision

2.1. The determination of thallium in 6 in-house quality control samples (84.6 μg/L) over an 8-month period had a mean of 84.3 μg/L and a relative standard deviation (RSD) of 1.0%.

3. Collection and Storage of Samples.

3.1. There are no special requirements for filters sealed in their containers.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. Periodically clean the work area, including the bench top, to eliminate environmental contamination. Use acid-washed sample cups in the autosampler.

4.2. Chemical interferences can be controlled by the addition of a matrix modifier to all samples and standards. Refer to Perkin-Elmer chart 0993-8199 Rev. D (11/89), or to the PE *Methods of Analysis for AAS*, for the appropriate matrix modifier.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. To control this problem, use sterile disposable 50-mL polypropylene centrifuge tubes or 15-mL polypropylene tubes in the sample digestion steps.

5. Apparatus

5.1. Polypropylene tubes: 15- and 50-mL, sterile polypropylene, with caps.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. An automatic sample shaker.

5.5. Perkin-Elmer 5000 atomic absorption instrument: equipped with a Zeeman Graphite Furnace or equivalent.

5.6. Required gas for the above instrument is ultrapure argon.

5.7. Hot plate with aluminum heating block drilled to hold centrifuge tubes.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Double-deionized water.

6.3. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

6.4. Appropriate matrix modifier for all samples, standards, and QCs.

6.5. Secondary standards for making the appropriate standard curves.

7. Sample Preparation Procedure

7.1. Place filters in 15-mL polypropylene tubes and add 10 mL of 1% nitric acid, LTRD or Ultrex grade, and put caps on securely.

7.1.1. Samples should include a blind QC, customer blank filter, and an extraction blank.

7.1.2. Put samples on the shaker for a minimum of 4 h for extraction.

7.1.3. Add the sample and standards to acid-cleaned sample cups.

THALLIUM IN WATER AND SOIL EXTRACTS — GRAPHITE FURNACE AA

Analyte: Thallium	**Method No.:** EI205
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 5.0 μg/L
Procedure: Graphite furnace atomic absorption	**Accuracy and Precision:** 100% ± 1.0% RSD
Effective Date: 09/30/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.6 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 279.2 and SW846 method 7841.

1.2. Thallium in solution may be readily determined by graphite furnace atomic absorption spectroscopy. The method is applicable to Tl in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis.

2. Accuracy and Precision

2.1. The determination of thallium in 6 in-house quality control samples (84.6 μg/L) over an 8-month period had a mean of 84.3 μg/L and a relative standard deviation (RSD) of 1.0%.

3. Collection and Storage of Samples.

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within 6 months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. Periodically clean the work area, including the bench top, to eliminate environmental contamination. Use acid-washed sample cups in the autosampler.

4.2. Chemical interferences can be controlled by the addition of a matrix modifier to all samples and standards. Refer to Perkin-Elmer chart 0993-8199 Rev. D (11/89), or to the PE *Methods of Analysis for AAS*, for the appropriate matrix modifier.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. To control this problem, use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption instrument: equipped with a Zeeman graphite furnace or equivalent.

5.6. Required gas for the above instrument is ultrapure argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μhmo/cm conductivity).

6.5. Appropriate matrix modifier for all samples, standards, and QCs.

6.6. Secondary standards for making the appropriate standard curves.

ZINC IN WATER AND SOIL EXTRACTS – FLAME AA

Analyte: Zinc	**Method No.:** EI210
Matrix: Water, waste water, and soil extracts	**Detection Limit:** 5.0 μg/L
Procedure: Flame atomic absorption	**Accuracy and Precision:** 100% ± 4.0% RSD
Effective Date: 09/23/91 to 09/01/95	**Authors:** Michael G. Bell Barbara J. Hemberger

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure and Source Material 12.5 for proper waste disposal practices.

1. Principle of Method

1.1. This procedure is based on Environmental Protection Agency (EPA) method 289.1 and SW-846 method 7950.

1.2. Zinc in solution may be readily determined by atomic absorption spectroscopy. The method is simple and rapid and is applicable to Zn in drinking, surface, and saline waters and in domestic and industrial wastes.

1.3. Drinking water free of particulate matter may be analyzed directly. Ground water, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis.

2. Accuracy and Precision

2.1. The determination of zinc in nine in-house quality control samples (66 μg/L) over a nine-month period had a mean of 67.2 μg/L and a relative standard deviation (RSD) of 4.0%.

3. Collection and Storage of Samples

3.1. Preserve samples with nitric acid (HNO_3) at a pH <2.0. Complete analysis within six months.

4. Interferences

4.1. Contamination is of prime concern during sample preparation. The work area, including the bench top, should be periodically cleaned to eliminate environmental contamination.

4.2. Chemical interferences are matrix dependent.

4.3. Silica from the glassware will grow into the sample solution during and following sample processing. Use sterile disposable 50-mL polypropylene centrifuge tubes in the sample digestion steps to control this problem.

5. Apparatus

5.1. Centrifuge tubes: 50-mL, sterile polypropylene.

5.2. Rainin pipettes with disposable tips.

5.3. Wash bottles: 125-mL, polypropylene, screw tops.

5.4. Hot plate: with aluminum heating block drilled to hold centrifuge tubes.

5.5. Perkin-Elmer 5000 atomic absorption spectrometer or equivalent.

5.6. Gases for the above instrument: air, acetylene, nitrous oxide, argon.

6. Reagents

6.1. Nitric acid (low-temperature redistilled acid, LTRD).

6.2. Hydrochloric acid (low-temperature redistilled acid, LTRD).

6.3. Double-deionized water.

6.4. ASTM Type I water (>10 MΩ/cm resistivity, <0.1 μmho/cm conductivity).

7. Sample Preparation Procedure

7.1. To determine total recoverable elements in water or waste water, take a 50-mL aliquot from an acid-preserved sample containing not more than 0.25% (wt/vol) total solids. Place the aliquot in a sterile disposable 50-mL polypropylene centrifuge tube.

7.1.1. Add 500 μL of LTRD HNO_3 and 250 μL of Ultrex or LTRD HCl to each sample.

7.1.2. Heat on a hot plate without boiling (approximately 85°C) until the final volume is reduced to 5-10 mL.

7.1.3. Loosely cover the tube with the cap and reflux for 30 min.

7.1.4. Allow the sample to cool and dilute to 50 mL with ASTM Type I water.

PH OF SOIL

Analyte: H^+	**Method No.:** EI520
Matrix: Soil	**Sensitivity:** 0.1 pH unit
Procedure: pH electrode	
Effective Date: 06/02/89 to 09/01/95	**Author:** Eric Nickell Ernest S. Gladney Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. Hydronium ions in dried soil samples are solvated using repeated agitation.

1.2. $[H^+]$ is quantified with a combined pH electrode.

2. Sensitivity

2.1. Sensitivity is 0.1 pH unit.

3. Accuracy and Precision

3.1. Precision is ±0.1 pH unit.

4. Interferences

4.1. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH <1, may give incorrectly high pH measurements.

4.2. Temperature fluctuations will cause measurement errors.

4.3. Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can either be cleaned with an ultrasonic bath or washed with detergent, rinsed several times with water, placed briefly in 1:10 HCl so that the lower third of the electrode is submerged, and thoroughly rinsed with water.

5. Collection and Storage of Samples

5.1. Samples must be dried and either ground or sieved for proper soil particle washing by distilled water.

5.2. Samples should be analyzed as soon after collection as possoble.

6. Apparatus

6.1. pH meter: portable, Leeds and Northrup (Cat. no. 7417) or equivalent.

6.2. Centrifuge tubes: 50-mL plastic, disposable.

6.3. Combined pH electrode: rugged construction.

6.4. Analytical balance.

6.5. Corner of styrofoam centrifuge tube holder cut to fit balance pan.

6.6. Spatula.

6.7. Ringstand with small clamp.

6.8. Wash bottle and waste beaker.

6.9. Thermometer: range 10-30°C.

6.10. Tubing for air line.

6.11. Volumetric flasks: 2-L and 1-L.

7. Reagents

7.1. Stock buffer solutions for electrode calibration. The suggested pH range is 4.0- 11.0.

7.2. Distilled, deionized water.

7.3. Primary standard buffer salts. Available from the National Institute of Standards and Technology (NIST) for use where extreme accuracy is necessary. Preparation of reference solutions from these salts requires special precautions and handling, such as low-conductivity water, drying ovens, and carbon-dioxide-free purge gas.

7.4. Secondary standard buffers. Prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions, validated by comparison with NIST standards, are recommended for routine use.

SAMPLE PREPARATION FOR SPECTROCHEMICAL ANALYSES OF TOTAL RECOVERABLE ELEMENTS (EPA METHOD 200.2)

Analyte: Trace metals	**Method No.:** EI735
Matrix: Various	
Effective Date: 01/01/91	**Author:** Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. This method provides sample preparation procedures for the determination of total recoverable elements in ground waters, surface waters, drinking water supplies, wastewaters, sediments, sludges, and solid waste samples, and it applies to the following elements:

Analyte		Chemical Abstracts Services Registry Numbers
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6

Analyte		Chemical Abstracts Services Registry Numbers
Lead	(Pb)	7439-92-1
Lithium	(Li)	9439-93-2
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica	(SiO_2)	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

1.2. Samples prepared by this method can be analyzed by (1) inductively coupled plasma–atomic emission spectrometry (ICPAES), United States Environmental Protection Agency (EPA) Method 200.7, (2) inductively coupled plasma–mass spectrometry (ICPMS), EPA Method 200.8, and (3) direct aspiration flame atomic absorption (FAA) using the EPA 200-series methodology given in "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020, March 1983. Samples may also be analyzed by the stabilized temperature platform furnace atomic absorption (ETVAA) technique. See the above analytical methodology for selection of the appropriate method for the determination of a specific analyte.

1.3. This method is suitable for the preparation of aqueous samples containing silver concentrations up to 0.2 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, prepare succeeding smaller, well- mixed aliquots until the analysis solution contains <0.2 mg/L silver.

1.4. Solid and aqueous samples are prepared in a similar manner for analysis. Metals and toxic elements are extracted from either solid samples or the solid portion of aqueous samples by refluxing the sample for 30 min in a mixture of nitric and hydrochloric acids. After extraction, the solubilized analytes are diluted to specified volumes with deionized distilled water. Diluted samples are to be analyzed by mass and/or atomic spectrometry methods within 72 h after preparation.

2. Definitions

2.1. Total recoverable. The concentration of analyte determined to be in either a solid sample or an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid.

3. Interferences

3.1. Contamination is of prime concern during sample preparation. The work area, including the bench top and fume hood, should be periodically cleaned to eliminate environmental contamination.

3.2. Chemical interferences are matrix dependent.

3.3. Silica from the glassware will grow into the sample solution during and following sample processing. To reduce silica contamination, analyze the sample as soon as possible after final dilution. A laboratory reagent blank can be used to monitor the effect.

4. Sample Collection and Preservation

4.1. For the determination of total recoverable elements in aqueous samples, acidify with 1:1 nitric acid at the time of collection to a pH of <2. The sample should not be filtered before analysis.

NOTE: Samples that cannot be acid-preserved at the time of collection because of sampling limitations or transport restrictions should be acidified with nitric acid to a pH of <2 upon receipt in the laboratory (normally, 3 mL of 1:1 nitric acid per liter of sample is sufficient for most ground, surface, and drinking- water

samples). Following acidification, the sample should be held for 16 h before withdrawing an aliquot for sample processing.

4.2. Solid samples usually require no preservation before analysis other than storage at 4°C.

5. Apparatus

NOTE: For the determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust. A clean laboratory work area, designated for trace-element sample handling, must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching or (2) depleting element concentrations through adsorption processes. All reuseable labware (such as glass, quartz, polyethylene, or Teflon.) including the sample containers should be cleaned before use. Labware should be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with water, and soaked for 4 h in a mixture of dilute nitric and hydrochloric acid, followed by rinsing with water, American Society for Testing and Materials (ASTM) Type I water, and oven drying. *Chromic acid must not be used for the cleaning of glassware.*

5.1. Volumetric flasks.

5.2. Graduated cylinders.

5.3. Centrifuge tubes: glass.

5.4. Pipettes: assorted sizes.

5.5. Centrifuge tubes: 50-mL, polyethylene.

5.6. Mash bottle: one-piece stem, polyethylene bottle with screw closure, 500-mL.

5.7. Micropipette: Rainin, various sizes.

5.8. Balance: analytical, capable of accurately weighing to 0.1 mg.

5.9. Hot plate: Corning PC100 or equivalent.

5.10. Centrifuge: steel cabinet with guard bowl, electric timer, and brake.

6. Reagents

6.1. Reagents may contain elemental impurities that might affect analytical data. High-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade.

6.1.1. Nitric acid (concentrated, sp. gr. 1.41).

6.1.2. Nitric acid (1:1). Dilute 500 mL of concentrated nitric acid to 1000 mL with ASTM Type I water.

6.1.3. Hydrochloric acid (concentrated, sp. gr. 1.19).

6.1.4. Hydrochloric acid (1:4). Dilute 200 mL of concentrated hydrochloric acid to 1000 mL with ASTM Type I water.

6.2. Water. For all sample preparation and dilutions, ASTM Type I water is required. Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7. Calibration and Standards

7.1. Micropipettes should be calibrated quarterly at 10%, 50%, and 100% of maximum volume.

8. Procedure

8.1. Sample preparation for aqueous samples.

8.1.1. To determine total recoverable elements in water or wastewater, take a 100-mL aliquot from a well-mixed, acid-preserved sample containing not more than 0.25% (w/v) total solids, and transfer it to a 250-mL Griffen beaker. If total solids are greater than 0.25%, reduce the size of the aliquot by a proportionate amount.

8.1.2. Add 1 mL of concentrated nitric acid and 0.5 mL concentrated hydrochloric acid. Heat on a hot plate until the volume has been reduced to approximately 1–20 mL, ensuring that the sample does not boil. Evaporation time for 100 mL of sample at 85°C is approximately 1.5 h.

8.1.3. Cover the beaker with a watch glass, reflux for 30 min (very slight boiling may occur), and allow to cool.

8.1.4. Dilute to 50 mL volume with ASTM Type I water. Centrifuge the sample or allow it to stand overnight to separate insoluble material.

8.1.5. The sample is now ready for analysis by either ICPAES or direct-aspiration flame and ETVAA spectroscopy. For analyses by ICPMS, pipette 20 mL of the prepared solution into a 50-mL volumetric flask and dilute to volume with ASTM Type I water. Analyses should be performed within 72 h of the completed preparation.

8.2. Sample preparation for solid samples.

8.2.1. To determine total recoverable elements in solid samples (sludge, soils, sediments), thoroughly mix the sample to achieve homogeneity and accurately weigh a 1.0 ± 0.01 g portion of the sample.

8.2.2. Transfer the aliquot to a 250-mL Phillips beaker. Add 4 mL of 1:1 nitric acid and 10 mL of 1:4 hydrochloric acid.

8.2.3. Cover with a watch glass, heat on a hot plate at 95°C, and gently reflux for 30 min (very slight boiling may occur). Allow the sample to cool.

8.2.4. Dilute to volume with ASTM Type I water. Centrifuge the sample or allow to stand overnight to separate insoluble material.

8.2.5. The sample is now ready for analysis by either ICPAES or direct-aspiration flame and ETVAA spectroscopy. For analysis by ICPMS, pipette 10 mL into a 50-mL volumetric flask and dilute to volume with ASTM Type I water. Analyses should be performed within 72 h of the completed preparation.

8.2.6. Determine the percent solids in the sample for use in calculations and for reporting data on a dry-weight basis.

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

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Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance

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WI480 Residual Chlorine in Water—Amperometric Titration 03/93

Titrimetry

WI500 Alkalinity in Water and Waste Water 09/91

WI510 Chemical Oxygen Demand in Water and Waste Water—Titration . . . . Retired

WI520 Halides in Waste Water and RCRA Waste . . . . . Retired

WI529 Sulfite in Water and Wastewater—Titrimetry 10/95

WI530 Total Cations in Water and Wastewater—Ion Exchange and Potentiometric Titration 10/95

Miscellaneous

WI600 Ash of Organic Waste Material . . . . . Retired

WI610 Corrosivity of Solution Toward Steel 03/93

WI620 EP Toxicity Extraction . . . . . Retired

WI630 Flash Point—Pensky-Martens Closed-Cup Tester 10/95

WI640	Heat Capacity of Combustible Materials	Retired
WI650	Inorganic Toxicity Characteristic Leaching Procedure (TCLP)	10/95
WI660	Oil and Grease (Total Recoverable)	10/95
WI670	Specific Gravity of Water and Wastewater	10/95
WI680	Trace Metal Digestion—Drinking Water, Surface Water, and NPDES Effluents	Retired
WI681	Preparation of Aqueous Samples for Spectrochemical Analysis—FAAS and ICPOES	10/95
WI685	Preparation of Aqueous Samples for Spectrochemical Analysis—GFAAS and ICPMS	10/95
WI690	Preparation of Sediment, Sludge, and Soil Samples for Spectrochemical Analysis—FAAS and ICPOES	10/95
WI691	Preparation of Sediment, Sludge, and Soil Samples for Spectrochemical Analysis—GFAAS and ICP-MS	08/93
WI700	Trace Metal Digestion—Sludge	Retired
WI710	Viscosity	In Progress

Waste Water Analytical Procedures - Radiochemical

WR100	Americium-241 in Waste Water—Instrumental Gamma-Ray Spectrometry Using a Ge(Li) Detector	03/93
WR110	Americium-241 in Waste Water and Filter Cake—Instrumental Gamma-Ray Spectrometry Using a NaI Detector	03/93
WR120	Cesium-137 in Waste Water—Instrumental Gamma-Ray Spectrometry Using a Ge(Li) Detector	03/93
WR130	Cesium (Radioactive) in Waste Water—Phosphomolybdate Procedure	Retired

WR140 Gamma Activity in Waste Water—Gamma Spectrometry with Lithium-Drifted Germanium Detector 03/93

WR150 Gross Alpha, Beta, and Gamma Activity in Waste Water, Soil, Filter Cake, and Organic Materials—Gas Flow Proportional Counting 03/93

WR160 Gross Gamma Activity in Liquid Waste Water—NaI Detector . . . . . Retired

WR170 Plutonium, Americium, and Uranium in Waste Water and Filter Cake—Aluminum Nitrate/Aliquat-336 Procedure . . . . . Retired

WR180 Plutonium, Americium, and Uranium in Waste Water and Filter Cake—Neodymium Fluoride Coprecipitation 04/93

WR190 Strontium-89 and Strontium-90 in Waste Water—Ion Exchange 04/93

WR200 Tritium in Waste Water and Oil—Liquid Scintillation Counting 03/93

CHEMICAL OXYGEN DEMAND IN WATER AND WASTEWATER — AUTO ANALYZER OR MANUAL

Analyte: Chemical oxygen demand	**Method No.:** WI230
Matrix: Water and wastewater	**Range:** 10–500 mg/L
Procedure: Automated colorimetry	**Detection Limit:** 10 mg/L
	Accuracy and Precision: 97% ± 4% RSD
Effective Date: 04/29/86	**Author:** Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure and Source Material 11.5 for proper waste disposal practices.

1. Principle of Method

1.1. The sample is refluxed with hot sulfuric acid and a known excess of potassium dichromate to oxidize organic matter. The amount of Cr^{+3} formed is directly proportional to the concentration of organic matter originally present.

2. Accuracy and Precision

2.1. Auto analyzer procedure.

2.1.1. The determination of chemical oxygen demand (COD) in 15 United States Environmental Protection Agency (EPA) WP782/4 reference samples (232 ± 35 mg/L) over a period of 4 months gave a mean of 225 mg/L (97% recovery) and a relative standard deviation (RSD) of 4%.

2.1.2. Nine COD samples spiked at 40 mg/L over a period of 4 months gave an average recovery of 100% with an RSD of 11%. The recoveries ranged from 88% to 110%.

2.2. Manual procedure.

2.2.1. The determination of COD in 26 EPA WP782/4 reference samples (232 ± 35 mg/L) over a period of 8 months gave a mean of 220 mg/L (95% recovery) and an RSD of 14%.

2.2.2. Thirty-one COD samples spiked at 40 mg/L over a period of 4 months gave an average recovery of 96% with an RSD of 9.5%. The recoveries ranged from 78% to 120%.

3. Interferences

3.1. Traces of organic material from sampling bottles, glassware, the atmosphere, or reagents may cause gross positive error. Rinse all glassware with 20% H_2SO_4 to reduce contamination.

3.2. Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step. Minimize this loss by cooling the culture tube during addition of the sulfuric acid solution.

3.3. Chlorides are quantitatively oxidized by dichromate and represent a positive interference. The complexation of the chlorides by the addition of mercuric sulfate eliminates this interference.

3.4. Nitrite exerts a COD of 1.1 mg of oxygen per mg of nitrite. This interference is usually insignificant because of low nitrite levels.

3.5. Reduced inorganic species, such as iron and sulfide, are oxidized quantitatively under test conditions.

3.6. Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent.

4. Collection and Storage of Samples

4.1. Collect samples in glass bottles and immediately acidify to pH <2 with concentrated H_2SO_4. Store at 4°C.

4.2. Analyze biologically active samples as soon as possible.

4.3. Mix well those samples containing visible particulates to permit removal of representative aliquots.

5. Apparatus

5.1. Sampler IV: equipped with a 40-slot sample carousel and a 40/h, 3:1 sampling cam. Technicon or equivalent, Tarrytown, New York.

5.2. Proportioning pump: Technicon or equivalent, Tarrytown, New York.

5.3. COD manifold: equipped with pump tubes, mixing coils, and double delay coil. Technicon or equivalent, Tarrytown, New York.

5.4. Colorimeter: equipped with 600-nm filter and 50- by 1.5-mm flow cell. Technicon or equivalent, Tarrytown, New York.

5.5. Dual-pen strip-chart recorder: Technicon or equivalent, Tarrytown, New York.

5.6. Spectrophotometer: Spectronic 88, Bausch and Lomb or equivalent, Rochester, New York.

5.7. Pipettes: class A, volumetric, various sizes.

5.8. Pipettes: 2500-μL, Rainin electronic digital or equivalent.

5.9. Flasks: class A, volumetric, various sizes.

5.10. Culture tubes: Kimble or equivalent glass disposable, 16- by 100-mm, with Teflon-lined caps. VWR Scientific, Los Alamos, New Mexico.

5.11. Oven: capable of maintaining constant heat of 150°C.

5.12. Hach COD reactor: catalog no. 45600-00, Hach Co. or equivalent, Loveland, Colorado (alternate).

5.13. Hach COD digestion reagent vials: low range, Hach Co. or equivalent, Loveland, Colorado (alternate).

6. Reagents

6.1. Sulfuric acid (concentrated, reagent-grade).

6.2. Silver sulfate (reagent-grade, crystal or powder).

6.3. Mercuric sulfate (reagent-grade, powder).

6.4. American Society for Testing and Materials (ASTM) Type I water.

6.5. Digestion solution. Dissolve 10.216 g of potassium dichromate ($K_2Cr_2O_7$) in 500 mL of ASTM Type I water in a 1-L volumetric flask. **Cautiously** add 167 mL of concentrated H_2SO_4 and 33.3 g of $HgSO_4$. Bring volume to about 900 mL and heat and stir on magnetic stirrer to dissolve. Cool and dilute to volume with ASTM Type I water.

6.6. Catalyst solution. Dissolve 22 g of Ag_2SO_4 in a 9-lb bottle of concentrated sulfuric acid (2200 mL). Stir for several hours on magnetic stirrer until dissolved.

6.7. Wash solution (50% H_2SO_4). Cautiously add 500 mL of concentrated H_2SO_4 to about 400 mL of ASTM Type I water in a 1-L volumetric flask. Set in an ice water bath. Mix, cool, and dilute to volume with ASTM Type I water.

6.8. Glassware wash (20% H_2SO_4). Cautiously add 200 mL of concentrated H_2SO_4 to about 700 mL of ASTM Type I water. Cool and dilute to volume with ASTM Type I water.

6.9. Diluent (0.2% H_2SO_4). Add 2.0 mL of concentrated H_2SO_4 to about 900 mL of ASTM Type I water. Dilute to 1 L. Make fresh each run.

6.10. Brij-35 (30% solution). Technicon or equivalent, Tarrytown, New York.

6.11. Reagent water. Add 1.0 mL of Brij to 500 mL of ASTM Type I water.

7. Calibration and Standards

7.1. COD stock standard A (20 g/L). Dissolve 17.00 g of National Institute of Standards and Technology (NIST) standard potassium acid phthalate (previously dried for 2 h at 105°C and stored in a desiccator jar) in approximately 500 mL of ASTM Type I water. Dilute to 1 L and refrigerate. This standard is stable for 6 months.

7.2. COD stock standard B (2000 mg/L). Dilute 10 mL of stock standard A to 100 mL with diluent (0.2% H_2SO_4).

7.3. Working standards. Dilute the following volumes of stock standard B to 100 mL with diluent (0.2% H_2SO_4).

Stock Standard B (mL)	COD (mg/L)
1.25	25
2.5	50
5.0	100
7.0	140
10.0	200
15.0	300
20.0	400
25.0	500

7.4. Auto analyzer procedure.

7.4.1. Set the base line to zero using the base-line control knob on the colorimeter while pumping 50% H_2SO_4 instead of sample and with all pump tubes in their respective reagents. Set the highest-concentration standard to 100 on the chart paper using the **std. cal.** knob. Lower-concentration standards should read at 80, 60, 40, and 20 respectively. Record chart reading of standards in a Laboratory notebook.

7.5. Manual procedure.

7.5.1. Set the wavelength to 600 nm and adjust the blank reading to zero on the spectrophotometer. Read absorbence of standards and record in a Laboratory notebook or appropriate bench sheets.

8. Procedure

8.1. Digestion procedure.

8.1.1. To culture tubes (that have been rinsed with 20% H_2SO_4, ASTM Type I water, and air dried), add 2.5 mL of ASTM Type I water blank, standard, or sample with a Rainin 2500-μL electronic pipette. Reset the pipette to 1500 μL and add 1.5 mL of digestion solution to each tube. **Carefully** add 3.5 mL of catalyst solution down the side of the tube so that the acid forms a layer on the bottom of the tube. To prevent loss of volatile components, do not allow the layer to mix before capping the tube. Cap the tube tightly and let cool 5-10 min. Mix on a vortex mixer to mix the layers. Sample load must include at least 10% spikes, 10% duplicates, and

10% quality control samples. To spike a sample, add 1 mL of stock standard B to 50 mL of sample. The concentration of the spike is 40 mg/L.

8.1.2. Place all tubes, samples, blanks, and standards in an oven at 150°C. Heat for 2 h. Remove from oven and let cool to room temperature.

8.1.3. Alternate using Hach COD reagent vials (0–150 mg/L range). To each COD reagent vial, add one of the following: 2000 μL of ASTM Type I water, standard, or sample. Cap tightly. Mix with vortex mixer. Place up to 25 vials in COD reactor set for 150°C for 2 h. Include a blank, four standards, and a laboratory control standard with each batch of 25 vials. Remove vials, invert, and let cool to room temperature.

8.2. Auto analyzer procedure.

8.2.1. Turn on the colorimeter, heating bath, and recorder and allow to warm up for 30 min. Use 50% H_2SO_4 in the wash receptacle.

8.2.2. Attach the COD manifold in line between the pump and colorimeter. Attach air lines to the segmenter tubes on the pump. Stretch the pump tubes across the brackets. Snap the platen into place. The pump will turn on automatically. Place reagent lines in the glassware wash solution and allow the system to wash for 20 min.

8.2.3. Place lines into the proper reagents and allow the pump to run until a steady base line is achieved. Set the base line to zero. Check the system for uniform bubble pattern, leaks, and adequate reagent supply.

8.2.4. Rinse all glassware and sample cups used in preparation of reagents, standards, and sample dilutions with glassware wash solution before use.

8.2.5. Run samples undiluted. Dilution adjustment may be necessary as evident on strip-chart output. Samples reading < 10 on the chart should be rerun at higher concentrations if possible.

8.2.6. Load the carousel. Place duplicate sample aliquots next with a QC and blank every 10 samples. The last two positions should be a QC sample and blank. Insert a pin at the last position to automatically stop the carousel. If a second carousel is required, place midrange standards in positions 1 and 2 to check reproducibility of the calibration curve. If this

standard does not agree to within ± 2 chart divisions with the previous run, the complete set of standards must be rerun.

8.2.7. When determinations are completed, place the reagent tubes in distilled water and rinse the system for a minimum of 10 min. Shut off power to the colorimeter and recorder. After rinsing, remove the reagent and wash tubes from the water and pump air until all visible liquid is removed from the system. Shut down the pump by removing the platen. Release the pump tubes from the brackets.

8.2.8. Record chart readings in a Laboratory notebook. The average of the duplicate readings is reported. A very high sample, however, may bias the first peak of a low sample that follows. In this case, both values are recorded and the sample should be reanalyzed.

8.3. Manual procedure.

8.3.1. Set the wavelength control to 600 nm and zero the instrument on a blank. Read the absorbence of standards and samples and record in a Laboratory notebook.

9. Calculations

9.1 Auto analyzer procedure.

9.1.1. The factor to convert from auto analyzer chart reading to concentration can be calculated as follows:

$$F = \frac{S_c \times D}{100} \quad ,$$

where F = factor,
S_c = concentration of highest standard (mg/L), and
D = dilution.

$$C = F \times R \quad ,$$

where C = concentration of sample (mg/L),
F = factor, and
R = chart reading.

9.2 Manual procedure.

9.2.1. Calculate the linear least squares calibration line using the absorbences of the standards. The sample concentration is then calculated by substituting the absorbence as follows:

$$\text{CONC.} = \text{SLOPE} \times \text{ABSORBENCE} + \text{INTERCEPT} \quad .$$

9.3. COD spike recovery should be 40 mg/L $\pm$ 8.0 (allowable) or $\pm$ 4.0 (desirable).

$$R = C_s - C \quad ,$$

where R = amount recovered (mg/L),
C_s = concentration of spiked sample (mg/L), and
C = concentration of unspiked sample (mg/L).

9.4. Percent recovery should be between 80% and 120%.

$$\%R = \frac{R \times 100}{A} \quad ,$$

where $\%R$ = percent recovery,
R = amount recovered (mg/L), and
A = amount added (mg/L).

10. Proper Waste Disposal Practices

10.1. Liquid waste.

10.1.1. Empty contents of reaction vials into a plastic-coated glass bottle that is kept in a secondary containment tray segregated from liquid waste containing cyanide or NH_3-N waste.

10.1.2. Label the bottle with a hazardous waste label indicating Ag, Cr, and Hg in contents.

10.2. Waste pickup.

10.2.1. When the bottle is full, request pickup by Waste Services (CST-17) by using the current Chemical Waste Disposal Request (CWDR). The current Waste Profile Form (WPF) number describing the waste is referenced on the CWDR.

10.2.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

11. Source Materials

11.1. Technicon Industrial Method No. 452-76W (Tarrytown, New York, 1977).

11.2. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Method 508C (American Public Health Association, Washington, DC, 1985).

11.3. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 410.4 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

11.4. A. M. Jirka and M. J. Carter, *Anal. Chem.* **47**, 1397 (1975).

11.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

CHROMIUM VI IN WATER AND WASTE WATER — FLOW INJECTION

Analyte: Hexavalent chromium	**Method No.:** WI260
Matrix: Water and waste water	**Range:** 0.02 - 0.4 mg/L
Procedure: Flow injection colorimetry	**Detection Limit:** 0.02 mg/L
	Accuracy and Precision: 102% ± 7% RSD
Effective Date: 09/16/86 to 09/01/95	**Author:** Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. Chromium VI (Cr^{+6}), in a solution of pH 0.7 to 1.3, is measured directly after reacting with diphenylcarbazide to form a red-violet water-soluble compound that absorbs light at 540 nm.

2. Accuracy and Precision

2.1. The determination of Cr^{+6} in 35 in-house reference samples (0.4 ± 0.04 mg/L) over a period of 6 months had a mean of 0.41 mg/L and a relative standard deviation (RSD) of 7%.

2.2. Twenty samples spiked with chromium at 0.2 mg/L over a period of 6 months had an average recovery of 97% with a standard deviation of ± 0.028 mg/L at the 1σ level. The recoveries ranged from 84% to 108%.

3. Interferences

3.1. Mercury and Mo^{+6} salts also react with color reagent. Up to 200 mg/L of molybdenum or mercury can be tolerated.

3.2. Vanadium also interferes, but concentrations up to 10 times that of chromium will not cause interference.

3.3. Solutions containing reducing agents interfere with spike recovery.

4. Collection and Storage of Samples

4.1. Collect samples for Cr^{+6} in polyethylene bottles, cool to 4°C, and analyze within 24 h.

5. Apparatus

5.1. Automatic sampler: Catalog No. 1100-100, QuikChem Systems, Lachat Instruments, Milwaukee, Wisconsin.

5.2. Sampler/valve controller: Catalog No. 1600-000, QuikChem Systems, Lachat Instruments, Milwaukee, Wisconsin.

5.3. Injection module—dual valve: Catalog No. 1000-600, equipped with sampler timer, QuikChem Systems, Lachat Instruments, Milwaukee, Wisconsin.

5.4. Multidetector chassis: Catalog No. 1300-000, with visible colorimeter, Catalog No. 1301-000, QuikChem Systems, Lachat Instruments, Milwaukee, Wisconsin.

5.5. Proportioning pump: Catalog No. 1200-000, QuikChem Systems, Lachat Instruments, Milwaukee, Wisconsin.

5.6. Chromium VI manifold: Catalog No. 10-124-16-1-A, QuikChem Systems, Lachat Instruments, Milwaukee, Wisconsin.

5.7. Heating bath with circulator: Catalog No. 1000-500, QuikChem Systems, Lachat Instruments, Milwaukee, Wisconsin.

5.8. Gilson dual-pen strip-chart recorder: Model N2, Gilson Medical Electronics, Denver, Colorado.

5.9. Pipettes: class A, volumetric, various sizes.

5.10. Pipettes: 1-mL, Eppendorf.

5.11. Flasks: class A, volumetric, various sizes.

6. Reagents

6.1. Distilled deionized water (DDW). Pass distilled water through an ion exchange column containing a mixture of both acidic cation and basic cation exchange resins.

6.2. Color reagent. In a 500-mL volumetric flask, dissolve 0.20 g of s-diphenylcarbazide in 100 mL of isopropanol (isopropyl alcohol, 99%). Add 350 mL of distilled water and 40 mL of concentrated sulfuric acid. Dilute to volume with distilled water. This solution is stable for 1 month. Keep

CYANIDE IN WASTEWATER — AUTO ANALYZER

Analyte: Cyanide	**Method No.:** WI270
Matrix: Wastewater	**Range:** 5–500 μg/L
Procedure: Automated colorimetry	**Detection Limit:** 10 μg/L
	Accuracy and Precision: 92% $\pm$ 6% RSD
Effective Date: 01/01/85	**Author:** Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment and SOP-1, "Analysis of Cyanide and Sulfide Waste Samples." Refer to Sec. 10 for proper waste disposal practices.

1. Principle of Method

1.1. Metal cyanide complexes are dissociated by ultraviolet irradiation and are separated as HCN from the matrix by acid distillation.

1.2. The HCN is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T. The CNCl reacts with pyridine/barbituric acid to produce a purple complex that can be measured at 570 nm.

2. Accuracy and Precision

2.1. The determination of CN in 30 Environmental Protection Agency (EPA) reference samples (0.538 $\pm$ 0.078 mg/L) over a period of 12 months gave a mean of 0.497 mg/L and a standard deviation of $\pm$0.032 mg/L at the 1-σ level.

2.2. Forty-seven CN samples spiked at 4 mg/L over a period of 12 months had an average recovery of 99% with a relative standard deviation (RSD) of 7.0%. The recoveries ranged from 88 to 115%.

3. Interferences

3.1. Thiocyanates decompose to cyanide, causing a positive interference.

3.2. Sulfides interfere with color development.

4. Collection and Storage of Samples

4.1. Adjust nonacid samples to pH > 12 with 10 N NaOH immediately after collection and analyze as soon as possible. Store samples at 4°C pending analysis. Complete analysis within 14 days.

4.2. Check for oxidizing agents using KI-starch paper (blue is positive). Add ascorbic acid a few crystals at a time until a drop of sample on KI-starch paper produces no color change. Add an additional 0.6 g of ascorbic acid per liter.

4.3. Immediately before CN^- determination, check for sulfide using lead acetate paper (a dark spot, PbS, is positive). Precipitate sulfide with a minimal amount of $Cd(CO_3)_2$ salt until CdS, a yellow precipitate, forms. Recheck until lead acetate paper shows no change. Filter the sample.

5. Apparatus

5.1. Sampler IV: equipped with a 40-slot sample carousel and a 30/h, 4:1 sampling cam. Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.2. Proportioning pump: Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.3. Cyanide manifold: equipped with pump tubes, mixing coils, and 185-nm ultraviolet lamp. Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.4. Colorimeter: equipped with 570-nm filter and 15- by 1.5-mm flow cell. Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.5. Distillation bath: filled with mineral oil and set at 155°C. Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.6. Dual-pen strip-chart recorder: Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.7. Pipettes: class A, volumetric, various sizes.

5.8. Flasks: class A, volumetric, various sizes.

6. Reagents

6.1. Phosphoric acid (reagent-grade, 85%).

6.2. Hypophosphoric acid (reagent-grade, 50%).

6.3. Distillation reagent. Carefully add 250 mL of 85% phosphoric acid and 50 mL of 50% hypophosphoric acid to 700 mL of distilled water in a 1-L volumetric flask. Dilute to volume with distilled water.

6.4. Brij-35 (30% solution). Bran Lubbe or equivalent, Buffalo Groves, Illinois.

6.5. Potassium dihydrogen phosphate (reagent-grade).

6.6. Disodium hydrogen phosphate (reagent-grade).

6.7. Buffer (pH 5.2). Dissolve 13.6 g of potassium dihydrogen phosphate and 0.28 g of disodium hydrogen phosphate in 900 mL of distilled water and dilute to 1 L. Add 0.5 mL of Brij-35 per liter and refrigerate.

6.8. Sodium hydroxide (0.1%). Dissolve 4.0 g of NaOH in 1 L of distilled water.

6.9. Chloramine-T. Add 2.0 g of Chloramine-T to 250 mL of distilled water. Stir until well mixed and filter. Make fresh weekly and refrigerate.

6.10. Pyridine-barbituric acid.

CAUTION: Prepare in a hood. Pyridine is toxic.

Wet 10.0 g of barbituric acid with 50 mL of distilled water. Add 50 mL of pyridine and 10 mL of concentrated hydrochloric acid. Dilute to 500 mL with distilled water. Prepare monthly and refrigerate.

6.11. Sodium hydroxide (10 N). Slowly add 400 g of NaOH to approximately 700 mL of distilled water in a 1000-mL volumetric flask. Stir with a magnetic stirrer until dissolved. Dilute to volume.

6.12. Hydrofluoric acid (concentrated, reagent-grade).

6.13. Hydrofluoric acid (2%). Dilute 2 mL of concentrated hydrofluoric acid to 100 mL in a polyethylene volumetric flask.

6.14. Nitrogen (N_2). Compressed N_2 gas in 15-lb bottle, Los Alamos National Laboratory Gas Facility.

7. Calibration and Standards

7.1. CN stock standard A (100 mg/L).

CAUTION: Cyanide is toxic.

Dissolve 0.250 g of KCN in 0.1% NaOH and dilute to 1 L with 0.1% NaOH. Prepare fresh monthly and keep refrigerated.

7.2. CN stock standard B (5 mg/L). Dilute 5.0 mL of stock standard A to 100 mL with 0.1% NaOH.

7.3. Working standards. Dilute the following volumes of stock standard B to 100 mL with 0.1% NaOH. Prepare fresh daily.

Stock Standard B (mL)	CN (mg/L)
1.0	0.05
2.0	0.1
4.0	0.2
6.0	0.3
8.0	0.4
10.0	0.5

7.4. Set the baseline to zero using the baseline control knob on the colorimeter while pumping distilled water and with all pump tubes in their respective reagents. Set the highest-concentration standard at 100 on the chart paper using the **STD CAL** knob. Lower-concentration standards should read at 80, 60, 40, and 20, respectively. Record chart reading of standards in a Laboratory notebook.

8. Procedure

8.1. Turn on the colorimeter, distillation bath, cooling bath, and recorder, and allow to warm up for 30 min. Distillation bath is preset to 155°C.

8.2. Attach the cyanide manifold in line between the pump and colorimeter. Attach air lines to the segmenter tubes on the pump. Stretch the pump tubes across the brackets. Snap the paten into place. The pump will turn on automatically. Place sample and distillation reagent lines in 2% HF solution and pump about 10 min to clean the distillation coil. Place heating bath lines in the waste receptacle so that

HF does not enter the manifold. Place reagent lines in distilled water and allow the system to wash for 20 min.

8.3. Attach heating bath lines to the pump tubes. Place lines into the proper reagents and allow the pump to run until a steady base line is achieved. Set the base line to zero. Check the system for uniform bubble pattern, leaks, and adequate reagent supply.

8.4. To measure total cyanide, turn on the ultraviolet source in the colorimeter and allow a 2-min warmup before running samples. Turn on the nitrogen immediately before sampling. Free cyanide determinations are completed in the same manner as total cyanide except that the ultraviolet source and nitrogen are not used.

8.5. Load the carousel. Place duplicate aliquots of the six standards in positions 1–12 (highest concentration to lowest). Place duplicate sample aliquots in the carousel in the following order: quality control samples, monthlies, EPA grabs, plating bath, and, rarely, drinking water. The EPA grabs, drinking waters, and environmental waters are run undiluted. The sample load must include at least 10% spikes, 10% duplicates, and 10% quality control samples. To spike a sample, add 1.00 mL of CN stock standard B to 25 mL of sample. Dilute appropriately. The concentration of the spike is 0.2 mg/L. Place blanks at positions 19 and 20 to check baseline drift. Insert a pin at the last position to automatically stop the carousel. If a second carousel is required, place midrange standards in positions 1 and 2 to check reproducibility of the calibration curve. If this standard does not agree to within ± 2 chart divisions with the previous run, the entire set of standards must be rerun.

8.6. When determinations are completed, place the reagent tubes in distilled water and rinse the system for at least 10 min. Shut off power to the heating bath, colorimeter, cooling bath, and recorder. Turn off the N_2 tank. After rinsing, remove the reagent and wash tubes from the solutions and pump air until all visible liquid is removed from the system. Shut down the pump by removing the paten. Release the pump tubes from the brackets.

8.7. Standards or samples containing CN >100 mg/L must be mixed with calcium hypochlorite powder in the hood before discarding. Add one scoop of calcium hypochlorite powder to approximately 100 mL of solution. Stir for one hour. Discard the resulting solution in the hood drain.

8.8. Record chart readings in a Laboratory notebook. The duplicate readings are normally recorded and reported. A very high sample, however, may bias the first peak of a low sample that follows. In this case both values are recorded but only the second peak value is reported.

9. Calculations

9.1. Individual values for standards and samples are entered into the LSQ program in the VAX under the CST LIMS MISCELLANEOUS MENU to obtain the actual values for the samples. A typical terminal session is shown below.

```
CST LIMS MISCELLANEOUS MENU

A.    MEAN
B.    STDDEV (standard deviation)
C.    ALLDATA-SEARCH (ARCHIVE-SEARCH)
D.    QA-HELP
G.    LINREG - Linear Regression
H.    POLY - Polynominal fitting
I.    LSQ - Least Squares fitting
Y.    RETURN TO MAIN LIMS MENU
Z.    EXIT FROM LIMS.  RETURN TO YOUR USER PROMPT.

Enter the LETTER of your choice and <CR>
I

ENTER # OF PTS, MAXDEG (UP TO 2)
12, 2

PLOT TYPE:  LIN=1, LOGX=2, LOGY=3, LOGXY=4
1

FORCE CURVE THROUGH ZERO?  YES=1, NO=0
1

ENTER RESULT-&-STANDARD PAIRS, ONE AT A TIME
 100,   0.5
 100,   0.5
81.0,   0.4
82.3,   0.4
  61,   0.3
  62,   0.3
42.0,   0.2
42.5,   0.2
23.0,   0.1
23.0,   0.1
13.5,   0.05
13.0,   0.05
```

CONSTANT = -0.78261E-11
1 ST POWER = 0.55435E-02
2 ND POWER = 0.48913E-04

EVALUATE SINGLE VALUES? YES=1, NO=0
1

ENTER # PTS TO EVALUATE, THEN SAMPLE RESULT ONE AT A TIME
2
12.0
56.0

MEASURED	ACTUAL VALUE
12.00000	0.05400
56.00000	0.26600

9.2. CN spike recovery should be 0.2 mg/L ± 0.04 (allowable) or ± 0.02 (desirable).

$$R = C_s - C \quad ,$$

where R = amount recovered (mg/L),
C_s = concentration of spiked sample (mg/L), and
C = concentration of unspiked sample (mg/L).

9.3. Percent recovery should be between 85 and 115%.

$$\%R = \frac{R \times 100}{A} \quad ,$$

where %R = percent recovery,
R = amount recovered (mg/L), and
A = amount added (mg/L).

10. Proper Waste Disposal Practices

10.1. Solid waste.

10.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

10.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

10.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

10.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 10.3.

10.2. Liquid waste.

10.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

10.2.2. Label the bottle with a hazardous waste label and a label indicating its use.

10.2.3. Periodically request pickup of the bottle as described in Section 10.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

10.3. Waste pickup.

10.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

10.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

11. Source Materials

11.1. Technicon Industrial Method No. 315-74W with modifications (Tarrytown, New York, 1974).

11.2. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Methods 412A and 412B (American Public Health Association, Washington, DC, 1985).

11.3. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 335.3 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

PHOSPHORUS IN WATER AND WASTEWATER — AUTO ANALYZER

Analyte: Phosphorus	**Method No.:** WI320
Matrix: Water and wastewater	**Range:** 0.04–1.0 mg/L
Procedure: Digestion and automated colorimetry	**Detection Limit:** 0.04 mg/L
	Accuracy and Precision: 114% ± 16% RSD
Effective Date: 06/28/85	**Author:** E. M. Hodge Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. The system is cleaned before the sample is run to remove possible contamination and coating from the tubes.

1.2. Samples are digested so that all phosphorus is in the orthophosphate form.

1.3. The orthophosphate-molybdate-antimony complex that is formed is reduced by ascorbic acid to an intensely blue-colored complex that is proportional to the phosphorus concentration.

1.4. A 660-nm interference filter is used to discriminate the resulting blue color.

1.5. A 37°C heating bath is used to increase the reaction rate.

2. Accuracy and Precision

2.1. The determination of phosphorus in 48 Environmental Protection Agency (EPA) WP481/5 (0.14 ± 0.05 mg/L) reference samples over a period of 12 months had a mean of 0.16 mg/L and a standard deviation of ± 0.022 mg/L at the 1-σ level.

2.2. The relative standard deviation (RSD) of 22 composite determinations over a period of 12 months was 12% at a phosphorus concentration of 0.60 mg/L.

2.3. Twenty-six samples spiked with phosphorus at 0.40 mg/L over a period of 12 months resulted in an average recovery of 95% and an RSD of 10%. The percent recovery ranged from 83% to 110%.

3. Interferences

3.1. As much as 50 mg of FeIII/L and 10 mg of Cu/L can be tolerated.

3.2. Silica causes positive interference. For silica concentrations of 20, 50, and 100 mg/L, the phosphorus results will be high by 0.005, 0.015, and 0.025 mg/L respectively.

3.3. Salt concentrations up to 20% cause an error of less than 1%.

3.4. Because arsenic can be determined by similar methodology, it should be considered when present in high concentrations.

3.5. Nitrite or sulfide interferences may be eliminated by adding an excess of bromine water or a saturated potassium permanganate.

3.6. Distilled deionized water (DDW) must be used to eliminate possible interferences of ammonia and silica.

3.7. All glassware must be washed with hot 1:1 HCl and rinsed with distilled water repeatedly to remove all traces of phosphorus. Avoid commercial detergents.

4. Collection and Storage Samples

4.1. Collect samples in polyethylene bottles and acidify to pH <2 with concentrated sulfuric acid (2.0 mL concentrated H_2SO_4/L) immediately upon collection. Refrigerate pending analysis.

4.2. Complete analysis within 28 days.

5. Apparatus

5.1. Block digester: Model No. BD-40 or equivalent with timer and digestion tubes. Bran Lubbe, Buffalo Groves, Illinois.

5.2. TRAACS 800: Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.3. Linear sampler: Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.4. TRAACS and auto analyzer II operating system (TAOS): Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.5. TRAACS 800 multitest cartridge: Bran Lubbe or equivalent, Buffalo Groves, Illinois.

5.6. Pipettes: class A, volumetric, various sizes.

5.7. Pipettes: 1-mL, Eppendorf.

5.8. Flasks: class A, volumetric, various sizes.

5.9. Bottles: 1-L, clear and amber glass.

5.10. Glass filter: Whatman, GF/C or equivalent.

5.11. Buchner funnel.

5.12. Boiling chips: Hengar or equivalent.

5.13. Centrifuge tubes: 100-mL, disposable.

5.14. Compressed N_2 gas.

6. Reagents

6.1. Distilled deionized water (DDW). Pass distilled water through an ion exchange column containing a mixture of both acidic cation and basic cation exchange resins.

6.2. Sulfuric acid (25%). Add 250 mL of concentrated sulfuric acid to approximately 600 mL of DDW in a 1-L volumetric flask. Cool and dilute to volume.

6.3. Mercuric sulfate solution. Dissolve 8.0 g of red mercuric oxide in 50 mL of 25% sulfuric acid. Dilute to 100 mL with 10% sulfuric acid.

6.4. Digestion solution. Add 200 mL of concentrated sulfuric acid to 700 mL of distilled water. Dissolve 133 g of potassium sulfate in this mixture. Add 25 mL of mercuric sulfate catalyst solution. Dilute to 2 L with DDW.

6.5. Aerosol 22. Sigma Chemical Co. or equivalent, St. Louis, Missouri.

6.6. Ascorbic acid solution. Dissolve 38.5 g of ascorbic acid in 250 mL of DDW. Prepare fresh weekly.

6.7. System wash water solution. Add 3 g of sodium dodecyl sulfate to 1000 mL of DDW.

6.8. Add 80 mL of concentrated sulfuric acid to about 1800 mL of DIH_2O. Dilute to 2 L with DIH_2O.

6.9. Molybdate-antimony solution. Dissolve 11 g of ammonium molybdate and 0.25 g of antimony potassium tartrate in DDW and dilute to 500 mL. Store in an amber bottle. Prepare fresh each month.

6.10. Acid/salt diluent. Dissolve 6.3 g of sodium chloride and 3 g of sodium dodecyl sulfate in 800 mL of DDW. Add 20 mL sulfuric acid and dilute to 1L. Filter through two glass filters in a Buchner funnel. Prepare fresh each week.

7. Calibration and Standards

7.1. Phosphorus stock standard A (1000 mg/L). Dissolve 0.4394 g of potassium dihydrogen phosphate (KH_2PO_4) in approximately 60 mL of distilled water. Dilute to 100 mL with DDW.

7.2. Phosphorus stock standard B (10 mg/L). Dilute 2.0 mL of stock standard A to 200 mL with DDW. Prepare fresh each day.

7.3. Phosphorus stock standard C (1.0 mg/L). Dilute 10 mL of stock standard B to 100 mL with DDW. Prepare fresh each day.

7.4. Working standards. Pipette the following volumes of stock standard B or C into digestion tubes. Add 25 mL of digestion solution and 25 mL of DDW. Prepare fresh each day.

Stock Standard B (mL)	Phosphorus (mg/L)
5.0	1.0
4.0	0.8
2.0	0.4
1.0	0.2

Stock Standard C (mL)	Phosphorus (mg/L)
4.0	0.08
2.0	0.04

8. Digestion Procedure

8.1. Perform at least one day before colorimetric determination.

8.2. Run a set of standards and a DDW blank with each digestion. The sample load must include at least 10% quality control samples, 10% spikes, and 10% digested duplicates. Use standards as described in Step 7.4.

8.3. Add 25 mL of sample and 25 mL of digestion solution to the digestion tubes. To spike a sample, add 1.0 mL of phosphorus stock standard B to 25 mL of sample in a digestion tube. Mix on the vortex mixer. Add three or four Hengar boiling chips.

8.4. With the digestion tube rack in place, preheat the block digester to 200°C by setting the low-temperature control to 0°C and the high-temperature control to 200°C. Turn on the manual switch. When 200°C is attained, set the low-temperature control to 200°C and the high-temperature control to 380°C. Adjust the low-time control to 1-1/2 h and total time to 3 h. Turn on the automatic switch.

NOTE: Place a shield over the hood front to protect personnel from a sudden discharge of hot acid from the digestion tubes.

8.5. As soon as the heat cycle is completed, remove the rack containing the flasks and set aside to cool until no SO_3 fumes are evident. Samples should be dry. Add 50 mL of distilled water to each flask. Mix thoroughly with a vortex mixer. Allow precipitates to settle out. Decant each solution into 100-mL disposable polypropylene centrifuge tubes. Cap and label with sample number and date of digestion. This results in a 1:2 dilution (25 mL to 50 mL).

8.6. Dilute environmental samples that do not require digestion 1:2 with digestion solution.

8.7. Add about 25 mL of distilled water and a few drops of Aerosol 22 to clean the digestion tubes. Mix on the vortex mixer and scrub with a test-tube brush. Rinse with distilled water, 1:1 HCl, and DDW.

9. Actual Run

9.1. Turn on nitrogen gas for air supply.

9.2. Make sure that all accessories are connected, then turn on the computer.

9.3. When the TAOS icon appears, place the mouse arrow on it and click the left mouse button twice.

9.4. When the TAOS logo appears, click once on the **OK** button.

9.5. When the TAOS initial screen appears, click on the desired channel icon along the bottom of the screen to maximize it into a Channel window.

9.6. Click on the button to the right of the Method box to open the Method file window. Then select the desired Method file. Click on **OK** to return to the Channel window.

9.7. Click on the button to the right of the Sample box to open Sample Table files. Then select the desired Sample Table. Click on **OK** to return to the Channel window.

9.8. Click on the button to the right of the Data box to open the Data File window. Then create a new data file by entering an appropriate name for the current run. Click on **OK** to return to the Channel window

9.9. Click on the Action button marked **Standby** to start the run.

9.10. Define the sample table and method. A detailed description of how to define a sample table and method is in the TRAACS and auto analyzer II operating systems.

9.11. Snap the platen into place. The pump will start automatically. Wash all lines with system wash solution. Check for leaks and a uniform bubble pattern.

9.12. Place individual lines into respective reagents with the sample line in the wash receptacle and the saline and acid diluent lines.

9.13. When determinations are completed, place the reagent tubes in system wash and rinse the system for a minimum of 10 min. After rinsing, remove the reagent and wash tubes from the solutions and pump air until all visible liquid is removed from the system. Shut down the pump by removing the paten. Release the pump tubes from the brackets.

9.14. Turn off nitrogen gas supply.

9.15. Sample values can be read in mg/L directly from the printout.

10. Calculations

10.1. Spike recovery of phosphorus should be 0.40 mg/L ± 0.08 (allowable) or ± 0.04 (desirable).

$$R = C_s - C \quad ,$$

where R = amount recovered (mg/L),
C_s = concentration of spiked sample (mg/L), and
C = concentration of unspiked sample (mg/L).

10.2. Percent recovery should be between 85% and 115%.

$$\%R = \frac{R \times 100}{A} \quad ,$$

where $\%R$ = percent recovery,
R = amount recovered (mg/L), and
A = amount added (mg/L).

11. Proper Waste Disposal Practices

11.1. Solid waste.

11.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

11.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

11.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

11.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 11.3.

11.2. Liquid waste.

11.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

11.2.2. Label the bottle with a hazardous waste label and a label indicating its use.

11.2.3. Periodically request pickup of the bottle as described in Section 11.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

11.3. Waste pickup.

11.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

11.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

12. Source Materials

12.1. Technicon Industrial Method No. 329-74 W/B (Tarrytown, New York, 1978).

12.2. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Method 424G (American Public Health Association, Washington, DC, 1985).

12.3. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 365.4 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

Revisions or additions to the procedure are marked (▒▒▒▒▒▒▒▒). Where a section heading is marked, the entire section has been revised.

SILICA IN WATER AND WASTEWATER — FLOW INJECTION

Analyte: Silica	**Method No.:** WI340
Matrix: Water and wastewater	**Range:** 1.0–100 mg/L
Procedure: Flow injection colorimetry using Lachat Quik Chem AE	**Detection Limit:** 1.0 mg/L
	Accuracy and Precision: 117% ± 6% RSD
Effective Date: 02/27/92	**Author:** Kathleen Straw

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. Soluble silica species react with molybdate under acidic conditions to form a yellow silicomolybdate complex.

1.2. This complex is reduced with 1-amino-2-naphthol-4-sulfonic acid (ANSA) and bisulfite to form a heteropoly blue complex that absorbs monochromatic light at 650 nm and 820 nm.

2. Accuracy and Precision

2.1. The determination of SiO_2 in 18 in-house quality control (QC) samples (40.0 ± 4.0 mg/L) over a period of 6 months had a mean of 47 mg/L and a relative standard deviation (RSD) of 6%.

2.2. Eleven samples spiked with 20–40 mg/L of SiO_2 over a period of 6 months had an average recovery of 96% with an RSD of 4%. The recoveries ranged from 90% to 102%.

3. Interferences

3.1. The interference from phosphates is eliminated by the addition of oxalic acid.

3.2. Tannin and large amounts of iron or sulfides interfere. Remove sulfides by boiling an acidified sample. Add ethylenediaminetetraacetic acid, disodium salt (Na_2EDTA) to eliminate the interference from iron.

3.3. Silica contamination may be avoided by storing samples, standards, and reagents in plastic and using American Society for Testing and Materials (ASTM) Type I water.

3.4. High fluoride concentrations can complex silica.

3.5. Oxidizing agents may interfere with color development.

3.6. High silica concentrations may precipitate.

4. Collection and Storage of Samples

4.1. Store samples in plastic bottles at 4°C.

4.2. Analyses must be completed within 28 days.

4.3. Filter all samples except drinking water.

5. Apparatus

5.1. Lachat QuikChem AE Flow Injection Analyzer System (Lachat Instruments, Milwaukee, WI 53218-1239) or equivalent.

5.1.1. Random Access Sampler (A11120).

5.1.2. Proportioning pump (A22100).

5.1.3. Sample-processing module (A24000).

5.1.4. Reaction module for QuikChem method #10-114-27-1-A.

5.1.5. Valve module (33900).

5.1.6. Master computer, IBM 386 SX, 25 MHz, with color monitor and printer.

5.2. Pipettes: class A, volumetric, various sizes.

5.3. Pipettes: 1000-μL Eppendorf, disposable tips.

5.4. Plastic bottles: various sizes.

5.5. Flasks: various sizes, volumetric, Nalgene.

5.6. Plastic test tubes: 12- x 75-mm and 17- x 100-mm.

6. Reagents

NOTE: Use plastic bottles and Nalgene volumetric flasks for preparation and storage of all reagents and standards.

6.1. Oxalic acid solution. Dissolve 50 g of oxalic acid in approximately 450 mL of ASTM Type I water and bring to 500 mL with ASTM Type I water. Store in a plastic bottle.

6.2. Sulfuric acid (concentrated, reagent-grade).

6.3. Ammonium molybdate reagent. Dissolve 20 g of ammonium molybdate in approximately 400 mL of ASTM Type I water. Add 8 mL of concentrated H_2SO_4 and bring to 500 mL with ASTM Type I water. Store in a plastic bottle at 4°C. Prepare fresh each month. Discard reagent if a precipitate or blue color is observed.

6.4. ANSA reagent. Dissolve 2 g of sodium sulfite in approximately 80 mL of ASTM Type I water. Add 0.25 g of 1-amino-2-naphthol-4-sulfonic acid (Kodak #360 or equivalent). Dissolve and dilute to 100 mL with ASTM Type I water.

6.5. Reducing agent. Dissolve 15 g of sodium bisulfite in approximately 250 mL of ASTM Type I water and dilute to 300 mL with ASTM Type I water.

6.6. Mixed reagent. Mix ANSA reagent and reducing agent in a plastic bottle. Add 4 mL of glycerol. Avoid light. Store under refrigeration. Discard reagent when it becomes dark in color or after 6 months. Tubing that carries this reagent clogs easily and needs frequent changing.

6.7. Degas all reagent solutions with He.

7. Calibration and Standards

7.1. SiO_2 stock standard A (1000 mg/L). Dissolve 4.7298 g of sodium metasilicate nonahydrate ($Na_2SiO_2 \bullet 9H_2O$) in approximately 800 mL of ASTM Type I water and dilute to 1 L. Store in a plastic bottle. A commercially prepared standard from Fisher Scientific or HACH may be used.

7.2. Working standards. Pipette the following volumes of stock standard A into 100-mL Nalgene volumetric flasks. Dilute to volume with ASTM Type I water.

Stock Standard A (mL)	SiO_2 (mg/L)
0.5	5
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100

8. Procedure

8.1. Connect sample loop, sampler, waste, reaction module, and carrier lines to valve. Place pump feed lines in reagents. Tighten pump cartridges. Place waste lines in waste container. Insert 820-nm filter in detector.

8.2. Turn all power switches on.

8.3. At prompt from system computer, download SiO_2 High method from menu on master computer.

8.4. Turn on pump and run at speed 35.

8.5. Check for proper flow and look for leaks.

8.6. Check for steady base line.

8.7. Initiating a run. Select SAMPLES from MAIN MENU. Select TRAY DEFINITION and SUBMIT. Select EDIT and IDENTIFICATION. Enter QC and sample identification for the run including 10% QCs, duplicates, and spikes. Follow last entry with "..." to end. Select SUBMIT and SUBMIT CURRENT TRAY. Printer switch should be on CHART RECORDER.

8.8. Calibration. Fill large plastic tubes with standards and smaller tubes with samples. Load sampler cartridges. Check for shape of peaks on monitor. At completion of standard peaks and approval of the calibration, the tray is processed

automatically. (See software manual for procedure to manually approve the calibration.)

8.9. Results. Select RESULTS/APPROVAL from MAIN MENU. Select CALIBRATION TRAY and CALIBRATION GRAPHS and STATS to view the calibration. Select SAMPLE TRAY and REPORTS for report of tray. Switch to MASTER PRINTER. Print report.

8.10. Rinse reagent feed lines and place in ASTM Type I water. Pump to flush system at least 10 min. Remove lines from water and then pump lines dry. Turn all power off. Loosen pump cartridges then remove reagent lines and sample loop.

8.11. System notes.

8.11.1. Timing - automatic.
Pump speed 35.
Cycle period 65 s.
Inject to start of peak period 30 s.
Inject to end of peak period 92 s.

8.11.2. Carrier is helium - degassed H_2O.

8.11.3. Manifold tubing is 0.8-mm (0.032-in.) i.d.

8.11.4. Reagent lines are 0.03-in. i.d.

9. Calculations

9.1. Samples are spiked by adding 1.0 mL of standard A to a 50-mL volumetric flask and bringing to volume with sample. Spike concentration of SiO_2 added is 20 mg/L.

$$R = C_s - C \quad ,$$

where R = amount recovered (mg/L),
C_s = concentration of spiked sample (mg/L), and
C = concentration of unspiked sample (mg/L).

9.2. Percent recovery should be between 85% and 115%. If recovery is outside acceptable limits, check open and blind QC results and duplicate precision. If these are within specifications, report value with comment "spike recovery outside

acceptable limits." Check duplicates, QCs, check standards, and blanks and report the result if these are okay for the run. Troubleshoot if spikes are consistently out.

$$\%R = \frac{R \times 100}{A},$$

where %R = percent recovery,
R = amount recovered (mg/L), and
A = amount added (mg/L).

10. Proper Waste Disposal Practices

10.1. No hazardous waste is generated by this procedure.

11. Source Materials

11.1. QuikChem Method No. ~~10-114-27-1-A~~ (Lachat Instruments, Milwaukee, Wisconsin, 1991).

11.2. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Method 425C (American Public Health Association, Washington, DC, 1985).

11.3. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 370.1 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

HARDNESS OF WATER AND WASTE WATER—CALCULATION

Analyte: Calcium and magnesium	**Method No.:** WI428
Matrix: Water and waste water	**Range:** 1-2000 mg/L
Procedure: Calculation	**Detection Limit:** 0.1 mg/L
Effective Date: 11/04/91 to 09/01/95	**Author:** Harold P. Patterson

SAFETY NOTE: Before beginning this procedure, read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. Calcium and magnesium are determined in solution by atomic absorbtion (AA), inductively coupled plasma mass spectrometry (ICPES), or ion chromatography (IC). Total hardness is the sum of the calcium and magnesium contributions both expressed as $CaCO_3$ in mg/L.

2. Accuracy and Precision

2.1. Determined by analytical method of choice.

3. Interferences

3.1. Determined by analytical method of choice.

4. Collection and Storage

4.1. Determined by analytical method of choice.

5. Calibration and Standards

5.1. Determined by analytical method of choice.

6. Calculation

6.1. The concentrations of calcium and magnesium in a sample are determined analytically and these concentrations are added together to determine hardness.

$$H = C + M \quad ,$$

where H = hardness of water as $CaCO_3$ (mg/L),
C = concentration of Ca in the sample (mg/L), and
M = concentration of Mg in the sample (mg/L).

6.2. Example.

$$\text{Hardness as } CaCO_3 \text{ mg/L} = 2.497 \text{ mg Ca/L} + 4.118 \text{ mg Mg/L}$$

7. Source Materials

7.1. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Waste Water*, 16th ed., Method 314 (American Public Health Association, Washington, DC, 1985), p. 209.7.

FLUORIDE IN WATER AND WASTEWATER—FLOW INJECTION

Analyte: Fluoride	**Method No.:** WI460
Matrix: Water and wastewater	**Range:** 0.1–5.0 mg/L
Procedure: Flow injection with ion-selective electrode on Lachat QuikChem AE	**Detection Limit:** 0.10 mg/L **Accuracy and Precision:** 100% ± 3% RSD
Effective Date: 04/21/92	**Author:** Kathleen Straw

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. A buffer is added to both standards and samples to adjust ionic strength to a uniformly high value and to complex interfering metals.

1.2. Fluoride is determined potentiometrically using a combination fluoride electrode and the Lachat QuikChem Flow Injection Analyzer. The fluoride electrode consists of lanthanum fluoride crystal across which a potential is developed by fluoride ions. The reference cell is a $Ag/AgCl/Cl^-$ cell. The reference junction is of the annular liquid-junction type and encloses the fluoride-sensitive crystal.

2. Accuracy and Precision

2.1. The determination of fluoride in 25 Environmental Protection Agency (EPA) quality control (QC) samples (1.00 ± 0.05 mg/L) over a period of 16 months had a mean of 1.0 mg/L and a relative standard deviation (RSD) of 3%.

2.2. Thirty samples spiked with 1.0 mg/L of F^- over a period of 16 months resulted in an average recovery of 102% and an RSD of 5%. The percent recovery ranged from 86% to 110%.

3. Interferences

3.1. At high pH, hydroxide interferes with electrode response when $[OH] > 0.1\ [F^-]$.

3.2. At pH <5 the hydrogen ion complexes the fluoride ion.

3.3. The polyvalent cations Si^{+4}, Al^{+3}, and Fe^{+3} interfere by forming complexes with fluoride. CDTA (1,2-cyclohexylenediaminetetraacetic acid) is added to preferentially complex these cations and eliminate this interference when these concentrations do not exceed 3.0 mg of Al^{+3} or 20 mg of Fe^{+3}/L.

4. Collection and Storage of Samples

4.1. Collect samples in polyethylene bottles. No additional preservation is necessary.

4.2. Complete analysis within 28 days.

5. Apparatus

5.1. Lachat QuikChem AE Flow Injection Analyzer System (Lachat Instruments, Milwaukee, WI 53218-1239) or equivalent.

5.1.1. Random access sampler (A11120).

5.1.2. Reagent pump (A22100).

5.1.3. Sample processing module (A24001).

5.1.4. Reaction module for QuikChem method #10-109-12-2-A.

5.1.5. Fluoride ion-selective electrode (ISE) detector (24914).

5.1.6. ISE for fluoride (13304).

5.1.7. ISE flow cell (50948).

5.1.8. IBM PS/2 Model #30-286 computer with IBM color monitor (#8512-001).

5.2. Pipettes: class A, volumetric, various sizes.

5.3. Flasks: class A, volumetric, various sizes, Nalgene.

5.4. Pipette: 1000-μL, Eppendorf, disposable tips.

5.5. Bottles: 1-L, polyethylene, clear, opaque.

5.6. Beakers: 50-mL, disposable, polyethylene.

6. Reagents

NOTE: Prepare and store all reagents in polyethylene to avoid contamination from borosilicate glass. Use distilled deionized water. Degas all reagents with helium for 1 min.

6.1. Sodium hydroxide (5 N). Dissolve 200 g of NaOH in distilled water. Cool and dilute to 1 L.

6.2. Stock #1 fluoride standard (100 mg/L). Dissolve 0.221 g of anhydrous sodium fluoride (NaF) in distilled water and dilute to 1 L or dilute 10.0 mL of Banco 1000-mg F^-/L standard to 100 mL with distilled H_2O. Store in a chemical-resistant polyethylene bottle. Or use a fluoride standard solution (100 $\pm$ 1 mg/L as F), such as catalog no. 232-49, Hach Co., Loveland, Colorado.

6.3. Total ionic strength adjustment buffer (TISAB). Add 57 mL of glacial acetic acid, 30 g of NaOH, 58.0 g of NaCl, and 4.0 g of CDTA to 500 mL of distilled deionized water in a 1-L beaker. Stir to partially dissolve. Adjust pH to 5.0–5.5 range using 5 N NaOH (approximately 25 mL). Transfer solution to a 1-L volumetric flask, add 0.5 mL of stock standard (100 mg/L), dilute to volume, and mix. Store in polyethylene.

6.4. Carrier solution (1.0 mg/L of F). Add 10 mL of stock standard (100 mg/L) to 1-L volumetric flask. Bring to volume and mix well.

6.5. Electrode conditioning solution. Mix together in 1-L container 500 mL of TISAB buffer and 500 mL of carrier solution.

7. Calibration and Standards

7.1. Working stock standard #2 (5.0 mg of F^-/L). In a 1-L volumetric flask, dilute 50.0 mL of stock standard A to volume with distilled deionized water and mix.

7.2. Calibration standards. Add the following volumes of standard B to 250-mL polyethylene flasks; make up to volume with distilled deionized water and mix:

Stock Standard #2 (mL)		Conc. (mg F^-/L)
250.0	No dilution	5.00
100.0	or 5.0 mL std #1	2.00
50.0		1.00
25.0		0.50
10.0		0.20
5.0		0.10

8. Procedure

8.1. Preparation of fluoride electrode.

NOTE: This procedure applies only to new electrodes or electrodes that have been stored dry.

8.1.1. Assembly: Remove the protective boot from the end of the electrode and put a couple of milliliters of filling solution (Orion no. 90-00-01) into the electrode through the fill hole in the body. Tilt and shake the electrode to wet the green O-ring at the top of the electrode. Unscrew the electrode cap about three turns then push the body into the cap and allow the solution to drain out of the electrode. Retighten the electrode cap then fill the electrode with filling solution to the level of the fill hole. Suspend the electrode in a beaker containing electrode conditioning solution and allow to equilibrate for at least 2 h, or preferably overnight.

8.1.2. Prepare the following to check the electrode:

Test solution 1. 10.0 mg of F^-/L.
To a 100-mL container, add 5.0 mL of standard A, 50.0 mL of TISAB buffer, and 45.0 mL of water. Shake or stir to mix thoroughly.

Test solution 2. 1.00 mg of F^-/L.
To a 100-mL container, add 0.50 mL of standard A, 50.0 mL of TISAB buffer, and 49.5 mL of water. Shake or stir to mix thoroughly.

Test solution 3. 0.00 mg of F^-/L.
To a 100-mL container, add 50.0 mL of TISAB and 50.0 mL of distilled deionized water. Shake or stir to mix thoroughly.

8.1.3. Determine the slope of the electrode.

Attach the conditioned electrode to a digital volt meter using an appropriate patch cord. Set the meter to read DCmV. (Beckman pH meter set to mV). Place the electrode tip in test solution 2. When the meter reading is stable for at least 5 s, record the reading in mV. This is reading A. Rinse the electrode briefly and place it in test solution 1. When the meter reading is stable for at least 5 s, record the reading in mV. This is reading B. Rinse the electrode and place in test solution 3. This is reading C. Calculate the differences (in mV) between reading A and reading B (A - B) and between reading C and reading A (C - A). If both differences are larger than 45 mV, the electrode passes the test and should perform well. If the electrode fails, polish the sensing surface with fluoride toothpaste, rinse thoroughly, and soak overnight in electrode conditioning solution before retesting.

8.2. Connect the electrode cable to the fluoride detector head. Connect the ground. Fill the electrode with filling solution to level of opening. Finger-tighten the electrode into the flow cell.

8.3. Connect the sample loop, sampler, waste, reaction module, and carrier lines to the valve. Place the pump feed lines in the reagents. Tighten the pump cartridges.

8.4. Turn all power switches on.

8.5. At the prompt from the system computer, download FNEW method (Channel #2) from the menu on the master computer.

8.6. Turn on the pump and run at speed 35.

8.7. Check for proper flow and look for leaks.

8.8. Check for steady base line approximately midscale.

8.9. Initiating a run.

Select SAMPLES from MAIN MENU. Select TRAY DEFINITION and SUBMIT. Select EDIT and IDENTIFICATION. Enter QC and sample identification for the run including 10% QCs, duplicates, and spikes. Follow last entry with "..." to end. Select SUBMIT and SUBMIT CURRENT TRAY. Printer switch should be on CHART RECORDER.

8.10. Calibration.

Check for shape of peaks on monitor. At completion of standard peaks and approval of the calibration, the tray is processed automatically. (See software manual for procedure to manually approve the calibration.)

8.11. Results.

Select RESULTS/APPROVAL from MAIN MENU. Select CALIBRATION TRAY and CALIBRATION GRAPHS and STATS to view the calibration. Select SAMPLE TRAY and REPORTS for report of tray. Switch to MASTER PRINTER. Print the report.

8.12. Rinse the reagent feed lines and place them in distilled deionized water. Pump to flush the system at least 10 min. Remove the lines from the water and pump the lines dry. Turn all power off. Loosen the pump cartridges and remove the reagent lines and sample loop. Remove the electrode, disconnect the ISE cable, and store the electrode in the flask containing conditioning solution.

8.13. System settings.

Parameter, evaluation, signal processing:

Pump speed: 35

System unit signal processing scheme, direct voltage, ADC setting no. 1.

Parameter, presentation, data window:

Top scale response:	1.50
Bottom scale response:	1.00

Parameter, timing, mode:

MANUAL timing:	Y

Parameter, timing, periods:

Cycle period:	60.00 s
Transition to LOAD:	18.00 s
Transition to INJECT:	30.00 s
Leading base-line start:	7.00 s
Leading base-line width:	2.00 s

Peak start:	14.00 s
Peak width:	15.00 s
Trailing base-line start:	67.00 s
Trailing base-line width:	2.00 s

NOTE: As in the EPA Method 340.2, the sample is automatically mixed on the manifold with an equal volume of buffer. The standard curve is nonlinear and therefore point-to-point segmentation is used in the data reduction. To increase baseline stability and decrease the response time of the electrode, the carrier contains 1 mg of F/L. This results in inverted peaks for standards 0.50, 0.20, and 0.10. The characteristics of the fluoride electrode change as the electrode ages. A 60-s cycle is typical for a new electrode. As the electrode ages, the response time lengthens to compensate for this. The time required for the electrode response to return to base line between injections of the high standards is the minimum cycle time that should be used. If the recovered concentrations for the check standards are consistently high, the cycle period needs to be increased. The output of the electrode in the carrier stream (base-line voltage) changes with the age of the electrode. After several months of operation, the data window will need to be changed so that the trace for the base line is at the center of the screen.

9. Calculations

9.1. Samples are spiked by adding 0.50 mL of standard A to a 50-mL volumetric flask and bringing to volume with sample. Spike concentration of F^- added is 1.0 mg/L.

$$R = C_s - C \quad ,$$

where R = amount recovered (mg/L),
C_s = concentration of spiked sample (mg/L), and
C = concentration of unspiked sample (mg/L).

9.2. Percent recovery should be between 85% and 115%.

$$\%R = \frac{R \times 100}{A} \quad ,$$

where $\%R$ = percent recovery,
R = amount recovered (mg/L), and
A = amount added (mg/L).

10. Proper Waste Disposal Practices

10.1. No hazardous waste is generated by this procedure.

11. Source Materials

11.1. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Method 413B (American Public Health Association, Washington, DC, 1985).

11.2. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 340.2 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

11.3 QuikChem Method 10-109-12-2-A (Lachat Instruments, Milwaukee, Wisconsin, 1992).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

SULFITE IN WATER AND WASTEWATER — TITRIMETRY

Analyte: Sulfite	**Method No.:** WI529
Matrix: Water and wastewater	**Spike Range:** 1–500 mg/L
Procedure: Titrimetry	**Accuracy and Precision:** See Step 2.1.
Effective Date: 11/30/90	**Author:** Harold P. Patterson

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. An acidified sample containing a starch indicator is titrated with a standard potassium iodide-iodate titrant to a faint, permanent, blue end point which occurs when the sulfite has been completely exhausted.

2. Accuracy and Precision

2.1. No in-house quality control sample is available at this time.

3. Interferences

3.1. The accuracy of the method is affected if the temperature of the sample is above 50°C.

3.2. Contact with air may cause oxidation of the sulfite. This effect may be minimized by not filtering the sample and by keeping the burette tip below the surface of the sample.

3.3. Other oxidizing substances such as organic compounds, ferrous iron, and sulfide can cause a positive interference. Sulfide can be removed by adding zinc acetate and then analyzing the supernate after the precipitate has settled.

3.4. Nitrite gives a negative interference by oxidizing the sulfite when the sample is acidified. This interference can be eliminated by the addition of sulfamic acid.

3.5. Copper and other heavy metals can cause a negative interference by acting as a catalyst to oxidize the sulfite. This can be overcome by addition of ethylenediaminetetraacetic acid (EDTA) to complex the metals.

4. Collection and Storage of Samples

4.1. Minimize contact with air. If the temperature of the sample is greater than 50°C it must be cooled. Add 1 mL of EDTA solution to polyethylene bottles before sample collection. Analyze for sulfite as soon as possible after taking the sample, preferably at the collection site.

5. Apparatus

5.1. Burette: 25-mL, Brinkman digital or equivalent. VWR Scientific, Los Alamos, NM.

5.2. Flask: 125-mL, Erlenmeyer. VWR Scientific, Los Alamos, NM.

5.3. Flask: 1-L, class A, volumetric. VWR Scientific, Los Alamos, NM.

5.4. Pipettes: class A, various sizes. VWR Scientific, Los Alamos, NM.

6. Reagents

6.1. Sulfuric acid (50%). Carefully and slowly add 50 mL of concentrated H_2SO_4 to 50 mL of distilled water.

6.2. Starch solutions (0.5%). Preserved with salicylic acid. Banco chemicals or equivalent, VWR Scientific, Los Alamos, NM.

6.3. Potassium iodide-iodate titrant (0.0125 N). Dissolve 445.8 mg of anhydrous potassium iodate (dried for 2 h at 120°C), 4.25 g of potassium iodide, and 310 mg of sodium bicarbonate in water in a 1-L volumetric flask and dilute to volume. The titrant is equivalent to 500 μg of SO_3/mL.

6.4. Sulfamic acid (crystalline).

6.5. EDTA reagents. Dissolve 2.5 g of EDTA disodium salt in 100 mL of distilled water.

6.6. Spike solution. Add 0.5 g of Na_2SO_3 (anhydrous) to a 1-L volumetric flask and dilute to volume with distilled water.

6.7. Zinc acetate.

7. Procedure

7.1. Pipette a 50-mL sample into a 250-mL Erlenmeyer flask. Add 50 mL of distilled water.

7.2. Add 1 mL of 50% H_2SO_4 solution to the flask.

7.3. Add 0.1 g of sulfamic acid crystals.

7.4. Add 1 mL of starch solution.

7.5. Titrate with potassium iodide-iodate titrant until a faint but permanent blue color develops. Slowly swirl the flask to prevent mixing with air. View the color change against a white background. Run duplicate samples.

7.6. Run a 50-mL distilled water blank using the above titration procedure (Steps 7.1 to 7.5).

7.7. Run a 50-mL aliquot of the spike solution using the above titration procedure (Steps 7.1 to 7.5). Check the titer of this solution each time you use it for spiking because it changes slowly with time. Spiking samples will determine if there are any interferences.

7.8. Add 50 mL of the spike solution to 50 mL of sample and run using the above titration procedure (Steps 7.1 to 7.5).

7.9. If sulfide is present, it can be removed by pretreating 100 mL of solution with 0.5 g of zinc acetate and analyzing the supernate after the precipitate has settled. Sulfide is not normally found in our plant discharge.

8. Calculations

8.1. Use the following equation to calculate SO_3 concentration:

$$\text{mg/L } SO_3 = \frac{(A - B) \times N \times 40{,}000}{V} ,$$

where A = potassium iodide-iodate titrant used for sample (mL),
B = potassium iodide-iodate titrant used for blank (mL),
N = normality of potassium iodide-iodate titrant,

40,000 = constant used to convert to equivalence of sulfite/L, and
V = volume of sample (mL).

8.2. Calculate the spike recovery using the following equation:

$$\% \text{ Recovery} = \frac{S - B}{S_a} \times 100 \quad ,$$

where S = SO_3 of sample (mg/L),
B = SO_3 in blank (mg/L), and
S_a = SO_3 added to sample (mg/L).

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

9.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. Label the bottle with a hazardous waste label and a label indicating its use.

9.2.3. Periodically request pickup of the bottle as described in Section 9.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

9.3. Waste pickup.

9.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Material

10.1. American Public Health Association , American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 17th ed., Method 4500-SO_3^{-2} B (American Public Health Association, Washington, DC, 1989).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TOTAL CATIONS IN WATER AND WASTEWATER — ION EXCHANGE AND POTENTIOMETRIC TITRATION

Analyte: Total cations	**Method No.:** WI530
Matrix: Water and wastewater	**Detection Limit:** 0.1 meq/L
Procedure: Ion exchange and potentiometric titration	**Precision:** $\pm 1.1\%$
Effective Date: 05/01/86	**Author:** Harold P. Patterson

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The accuracy of the chemical analysis of wastewater samples can be checked by determining the total cations present in the sample by ion exchange. A serious discrepancy between the total cations, milliequivalents per liter (meq/L), and the total cation concentration found by summing the analyzed constituents in meq/L can uncover a gross error in the analyses.

1.2. This ion-exchange method is based on replacement of cations in the original sample with hydrogen ions furnished by a strong acidic cation exchange resin. The acid produced by passing a nonacidic wastewater sample through an ion-exchange column packed with a strongly acidic cation exchange resin is titrated with standard sodium hydroxide solution. The total alkalinity of the original sample must be measured to complete the calculation.

2. Detection Limit

2.1. A detection limit of 0.1 meq/L can be expected using a 10-mL sample aliquot.

3. Accuracy and Precision

3.1. No standard material is presently available to determine accuracy.

3.2. A monthly composite sample was analyzed six times over a 4-month period, giving an average value of 8.48 meq/L with a standard deviation of 0.1 meq/L at the 1-σ level.

4. Interference

4.1. Complexing agents such as ethylenediaminetetraacetic acid (EDTA) can interfere.

5. Collection and Storage of Samples

5.1. Use nonacid samples and analyze as soon as possible.

6. Apparatus

6.1. Pipettes: class A, various sizes.

6.2. Beakers: various sizes.

6.3. Ion-exchange columns: 10- x 100-mm glass column with 50-mL reservoir at the top. Made at the Los Alamos National Laboratory glass shop.

6.4. Column supports.

6.5. pH paper: in the range of 3.0–5.5.

6.6. Burette: 10-mL with 0.05-mL divisions.

6.7. Magnetic stirrer.

6.8. Stirring bars: Teflon.

6.9. Glass wool.

6.10. pH meter: Beckman or equivalent, Model pHI 70, VWR Scientific, Los Alamos, New Mexico.

6.11. Stirring rod: 10- x 180-mm.

6.12. Pyrex baking dish: 8- x 10-in.

6.13. Buchner funnel: 500-mL, with filter flask and vacuum tubing.

6.14. Filter paper: Whatman No. 54 or equivalent, to fit Buchner funnel.

6.15. Heat lamps.

6.16. Volumetric flasks: 1-L.

7. Reagents

7.1. Ion-exchange resin. Bio-Rad AG 50W-X8 or equivalent, 50–100 mesh hydrogen-form.

7.2. Hydrochloric acid (concentrated, reagent-grade).

7.3. Potassium acid phthalate solution (National Bureau of Standards [NBS] potassium biphthalate). Dry approximately 20 g of NBS potassium acid phthalate at 120°C for 2 h. Cool in a desiccator. Weigh 10.0 ± 0.5 g (to the nearest mg). Transfer solution to a 1-L volumetric flask and dilute to volume.

7.4. NaOH (1 N). Use DILUT-IT solution and prepare according to product instructions. VWR Scientific, Los Alamos, New Mexico.

7.5. NaOH (0.02 N). Prepare a 0.02 N NaOH solution from the 1 N NaOH DILUTE-IT solution by diluting 20 mL of the 1 N NaOH to 1 L in a volumetric flask. Standardize against the potassium acid phthalate solution.

7.5.1. Standardization of 0.02 N NaOH. Pipette 15 mL of the potassium acid phthalate solution from Step 7.3 into a 100-mL beaker. Add 20 mL of distilled H_2O. Titrate with 0.02 N NaOH solution to a pH of 8.7.

7.5.2. Calculate the normality of the sodium hydroxide.

$$N = \frac{A \times B}{204.2 \times C} ,$$

where N = normality of sodium hydroxide,
A = potassium acid phthalate weighed into 1-L flask in Step 7.3 (g),
B = volume of potassium acid phthalate used (mL), and
C = volume of sodium hydroxide used (mL).

7.6. pH buffer solutions (pH 4, 7, and 10). VWR Scientific, Los Alamos, New Mexico.

7.7. Potassium dihydrogen phosphate (NBS standard). Dry KH_2PO_4 in a desiccator. Weigh out 54.436 g and transfer to a 1-L volumetric flask. Add 180.2 mL of 1 N NaOH and dilute to volume with distilled water.

7.8. Washed sea sand. VWR Scientific, Los Alamos, New Mexico.

7.8.1. Add sand to the 400-mL mark of a 2-L beaker.

7.8.2. Place the beaker in a hood and add concentrated HCl to the 600-mL mark. Mix the HCl well into the sand with a large glass stirring rod. Let stand overnight.

7.8.3. While still in the hood, pour off excess HCl into another large waste beaker. Add 400 mL of distilled water and slurry with a large glass stirring rod to dilute the HCl. Let the sand settle and pour the solution off into the waste beaker. Wash with two additional 400-mL portions of distilled H_2O. Pour the waste beaker of HCl directly into a laboratory sink while running water for dilution.

7.8.4. Mount a 500-mL Buchner funnel containing a No. 54 filter paper on a 1-L filter flask. Transfer the beaker containing the sand to the 500-mL Buchner funnel.

7.8.5. Turn on the vacuum to suction off the liquid. Add 400 mL of distilled H_2O to wash the HCl from the sand. Wash with two additional 400-mL portions of distilled H_2O. Draw off as much liquid as possible with the vacuum.

7.8.6. Transfer the sand to a large Pyrex baking dish and place under heat lamps until completely dry.

7.8.7. Transfer the sand to a 600-mL beaker and cover to keep clean.

8. Calibration and Standards

8.1. Check the normality of the 0.02 N NaOH used for titration against the NBS potassium acid phthalate as in Steps 7.5.1 and 7.5.2.

9. Procedure

9.1. Prepare as many ion-exchange columns as needed by placing a small piece of glass wool in the bottom of each column to hold back the resin slurry.

9.1.1. Add a water slurry of AG 50W-X8, 50–100 mesh hydrogen-form resin so that the resin fills the column to no less than 1/2 in. from the reservoir. Release any air bubbles that form in the resin by stirring with a stirring rod. Add distilled water to the reservoir and allow the resin to settle.

9.1.2. Add approximately 1/2 in. of washed sea sand to hold the resin in place. Release any air bubbles that form between the resin and sand interface by gentle agitation with a stirring rod.

9.1.3. Wash the column with 50 mL of distilled water. Discard washes. Place a clean 150-mL beaker with a Teflon stirrer under the column.

9.2. Place 5 mL of a nonacidic sample of TA-50 raw weekly composite (RWC) and 5 mL of TA-50 final weekly composite (FWC) sample into two separate columns. Collect the column effluents in the 150-mL beaker.

9.3. Place a 20-mL aliquot of nonacidic TA-257 RWC into another column. Collect the effluent in the 150-mL beaker.

9.4. Wash all columns with approximately 100 mL of distilled water and collect this wash in the 150-mL beaker.

9.5. Check the pH of the solution that discharges from the column using pH paper. Add an additional 5 to 10 mL of distilled water wash when no pH color change is indicated (pH 4 to 6). Allow the column to drain completely and remove the beaker containing the sample.

9.6. Titrate to a 4.5 pH end point using a standardized 0.02 N NaOH solution with a 10-mL burette graduated in 0.05-mL increments. The titration end point should be determined with a pH meter.

9.7. Column regeneration.

9.7.1. The column can be used again after the ion-exchange resin has been regenerated. Pass 50 mL of 3 N HNO_3 through the column.

9.7.2. Wash the column with sufficient distilled water to remove the excess 3 N HNO_3. Verify that excess 3 N HNO_3 was removed by checking the effluent with pH paper (pH of 4 to 6). The column can now be used for another sample.

10. Operation of Equipment

10.1. Calibrate the pH meter with standard pH buffers 4 and 7 or 7 and 10 depending on the expected pH range of the sample. Recalibrate after 4 h or after ambient temperature changes greater than 10°F.

10.2. Standardization of pH meter.

10.2.1. Pour 40 mL of pH 7 buffer into a 50-mL beaker. Add a stirring bar. Rinse the electrode with water and wipe with a Kimwipe. Immerse electrodes well below the surface of the solution and turn on the magnetic stirrer.

10.2.2. Clear the memory of the pH meter by pressing the **CLR** button. Be sure **ATC** and **AUTO** mode are activated.

10.2.3. Press the button corresponding to the first point of the two-point calibration curve. Let the instrument cycle until **AUTO** stops blinking on the instrument display and a prompt arrow appears. The value should be 7.00 ± 0.1.

10.2.4. Remove the electrodes and rinse with distilled water. Wipe off excess water with a Kimwipe. Do this between all readings.

10.2.5. Pour 40 mL of the second pH buffer into a beaker and add a stirring bar. Turn on the stirring motor. Immerse electrodes well below the surface of the solution.

10.2.6. Press the second button of the two-point calibration curve. Let the instrument cycle as before. The pH value obtained should be within ±0.1 pH units of the certified value. The instrument is now calibrated.

10.2.7. Check the calibration by reading a pH 7 buffer. Press the pH button and let the instrument cycle. The reading should be 7.00 ± 0.1. Restandardize the instrument if the value obtained is different from 7.00 ±0.1.

10.3. Check the quality control standard.

10.3.1. Dilute 5 mL of the solution prepared in Step 7.7 to 1 L with distilled water.

10.3.2. The pH of this solution equals 6.87 ± 0.06. The pH value should be in the range of 6.81–6.93. Restandardize the pH meter if the pH is out of range.

10.4. Make all sample readings with electrodes well below the surface of the water and while the sample is being stirred. Read in pH mode without auto for samples.

11. Calculations

11.1. Calculate the milliequivalents of total cations in the sample using the following equation:

$$E = \frac{A \times B \times 1000}{C} + \frac{D}{50},$$

where E = total cations (meq/L),
A = volume of standard NaOH used (mL),
B = normality of standard NaOH,
C = volume of sample used (mL), and
D = total alkalinity (mg/L).

11.2. Use the following table to convert from mg/L to meq/L.

Analyte in (mg/L)	Divide Analyte by the Atomic Wt.
Na	23
Ca	20
Mg	12
K	39
NH_3-N	14
Total Alkalinity	50
Cl	35.5
F	19
SO_4	48
NO_3-N	14

11.3. The total analyzed anions in meq/L should balance the total cations (E) in meq/L. The difference between the two should be less than 10%. The total analyzed cations should agree with the determined (E) value. Correct any serious discrepancies by repeating those cation or anion analyses that appear to be in error.

12. Proper Waste Disposal Practices

12.1. Solid waste.

12.1.1. If solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is competed on a case-by-case basis.

12.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

12.1.3. If CST-17 determines that the hazardous of radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

12.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 12.3.

12.2. Liquid waste.

12.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

12.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace-metal waste.

12.2.3. Periodically request pickup of the bottle as describe in Section 12.3. Keep the bottle in the secondary containment tray unit pickup by CST-17.

12.3. Waste pickup.

12.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced ont the CWDR.

12.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

13. Source Material

13.1. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater* ,16th ed., Method 404C and 402 (American Public Health Association, Washington, DC, 1985).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

FLASH POINT — PENSKY-MARTENS CLOSED-CUP TESTER

Analyte: Flammable organics	**Method No.:** WI630
Matrix: Fuels, oils, solid suspensions, and other liquids	**Range:** Room temperature to 230°F
	Accuracy: 100.7% for 1-Hexanol
Procedure: The temperature in °F at which the vapor above a fluid substance flashes on application of a flame is determined in a Pensky-Martens apparatus.	**Precision:** ±2.4% RSD
Effective Date: 05/01/86	**Author:** Harold P. Patterson

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The sample is heated slowly in a closed cup with constant stirring. A small flame is directed into the vapor phase above the cup at 2°F intervals. The flash point is the lowest temperature at which the vapor ignites when the flame is applied (see Source Material 10.1).

2. Accuracy and Precision

2.1. The flash point of 1-Hexanol was determined 29 times over a period of 6 months. The mean was 146.1°F and the standard deviation was ±3.5°F at the 1-σ level. The flash point value for 1-Hexanol in Langes Handbook of Chemistry, 8th Ed., is 145°F.

3. Interferences

3.1. A halo or enlarged flame must be distinguished from the actual flame that flashes in the cup.

4. Collection and Storage of Samples

4.1. Collect at least 250 mL of sample.

4.2. Collect samples in glass bottles.

5. Apparatus

5.1. Pensky-Martens closed-cup flash point tester: VWR Scientific, Los Alamos, New Mexico.

5.2. Electric stirring motor.

5.3. Thermometer: for flash point apparatus, to measure to 230°F.

5.4. Rubber tubing: 1/4-in.-i.d., for burner.

5.5. Safety matches.

5.6. Rubber gloves.

5.7. Safety fire extinguisher: KIDDE, multipurpose, dry chemical.

6. Calibration Standards

6.1. 1-Hexanol. Chemically pure with a closed-cup flash point of 145°F.

7. Procedure

7.1. Perform the test in a draft-free compartment. This can be accomplished by surrounding the apparatus with a plastic safety shield in a well-ventilated hood.

7.2. Thoroughly dry the cup and stirrer before testing.

7.3. For safety, wear rubber gloves when handling samples and opening bottles. Transfer samples in a well-ventilated hood. Fill the cup with the sample to be tested to the filling mark indicated on the cup. Place the cup in the heater.

7.4. Place the lid on the cup and secure it in place.

7.5. Attach the stirrer to the apparatus.

7.6. Insert the thermometer.

7.7. Light the test flame and adjust to a height of approximately 1/8 in.

7.8. Turn on the stirrer at the lower speed.

7.9. Stop the stirrer after 1 min. Introduce the flame into the vapor space of the test chamber by twisting the spring-loaded knob of the flame mechanism. Hold the knob for 1 s and then release it to let the spring mechanism return to its original position.

CAUTION: Never have the stirrer on while introducing flame into the test chamber.

There should be a distinctive flash within the chamber itself. It may be necessary to turn off the room lights to see the flash. Do not confuse the true flash point with the bluish halo that sometimes forms around the test flame at application. If the sample flashes at room temperature, record the flash point as less than room temperature in °F.

7.10. If the sample does not flash at room temperature, turn on the sample heater at the **ON-OFF** switch in the multiple outlet bar. The heating apparatus should be set at **45** on the dial and taped in place to prevent accidental overheating of the sample. This gives a heating rate of about 6°F/min.

7.11. Apply the flame to the test chamber at 2°F intervals, after stopping the stirrer. Record the temperature in °F when the first flash is observed.

7.12. If the sample does not flash at a low temperature, continue heating to a maximum of 160°F. If the sample still doesn't flash at 160°F record the flash point as greater than 160°F.

7.13. Be sure to shut off the sample heater at the multiple outlet bar to cool down the sample after the flash point has been observed or 160°F has been reached, whichever occurs first, to prevent overheating the sample and causing a possible fire in the sample cup.

7.14. Dispose of the sample in the properly marked waste container and place towels used for cleaning in the designated container.

7.15. Include 10% duplicates with each sample set.

7.16. Run 1-Hexanol as the standard. A corrected flash point of 145°F $\pm$ 4°F should be obtained for the standard (see Source Materials 10.1 and 10.2).

8. Calculations

8.1. Call Air Quality (ESH-17) (7-7049) for the ambient barometric pressure in mm Hg.

8.2. The observed flash point is corrected to a barometric pressure of 760 mm Hg.

$$F_c = F + [0.06\ (760 - P)] \quad ,$$

where F_c = corrected flash point (°F),
F = observed flash point (°F), and
P = ambient barometric pressure (mm Hg).

8.3. Report the observed flash point. Report the corrected flash point only if requested.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

9.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. Label the bottle with a hazardous waste label and a label indicating its use.

9.2.3. Periodically request pickup of the bottle as described in Section 9.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

9.3. Waste pickup.

9.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordamce with Laboratory policy.

10. Source Materials

10.1. *ASTM Methods Manual*, "Standard Test Methods for Pensky-Martens Closed Tester," ASTM Designation: D93-80 (American Society of Testing Materials, 1980).

10.2. *Langes Handbook of Chemistry*, 8th ed. (McGraw-Hill Book Company, New York, New York, 1952), p. 41.

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

HEAT CAPACITY OF COMBUSTIBLE MATERIALS

Analyte: Flammable organics	**Method No.:** WI640
Matrix: Fuels, oils, organic liquids	**Range:** 10 - 25,000 Btu/lb
Procedure: The amount of heat generated when a combustible material burns in an oxygen atmosphere is measured in Btu/lb of sample.	**Accuracy and Precision:** 100% ± 0.4% **Detection Limit:** 1 ± 1 Btu/lb
Effective Date: 11/04/86 to 09/01/95	**Author:** Harold P. Patterson

SAFTEY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. Combustible materials to be tested are burned under controlled conditions in an oxygen atmosphere in a Parr oxygen bomb. The amount of heat generated in the bomb is collected and measured in an adiabatic calorimeter. The amount of heat generated is calculated in units of Btu/lb of sample. The instrument used is a Parr 1241 adiabatic oxygen bomb calorimeter.

2. Accuracy and Precision

2.1. Pure benzoic acid tablets provided by the Parr Instument Co. are used as quality control standards. Over a 3-y period these samples gave a mean value of 11,377 ± 45 Btu/lb at the 1σ level. The true value of the benzoic acid is 11,372 Btu/lb.

2.2. A limit of detection was determined to be 1 ± 1 Btu/lb based on a 1-g sample, the ability to read to 0.005°F, and a minimum detectable parameter of 0.1 mL alkali, 0.01% sulfur, and 5 cm of fuse wire.

3. Interference

3.1. The calorimeter must be adjusted initially so that there is uniform cycling of hot and cold water additions and there is no difference observed between the bucket and jacket temperature. A tight seal must be maintained on the sample bomb during the operation.

3.2. Occasionally a bomb will misfire resulting in zero combustion or the evidence of poor combustion (carbon or soot) will be seen. See the Parr Instruction Manual for the 1241 adiabatic oxygen bomb calorimeter (Source Material 10.1, pp. 16-17) for cause and corrections.

4. Sample Handling

4.1. Quickly weigh volatile samples and transfer them to the sample bomb. If samples are extremely volatile it may be necessary to weigh the sample in a gelatin capsule.

4.2. Samples high in sulfur or containing over 20 mg of chlorine can corrode the sample bomb. Use smaller samples in these cases.

5. Apparatus

5.1. Parr 1241 adiabatic oxygen bomb calorimeter: equipped with a bucket and jacket thermometer, thermistor probes, and a remote firing switch. Parr Instrument Co., VWR Scientific, Los Alamos, New Mexico.

5.2. Thermometer vibrator.

5.3. Parr 1541 water heater: Parr Instrument Co., VWR Scientific, Los Alamos, New Mexico.

5.4. Parr 1551 water cooler: Parr Instrument Co., VWR Scientific, Los Alamos, New Mexico.

5.5. Parr 1108 oxygen bomb: Parr Instrument Co., VWR Scientific, Los Alamos, New Mexico.

5.6. Parr 45C10 nickel-chrome alloy fuse wire: Parr Instrument Co., VWR Scientific, Los Alamos, New Mexico.

5.7. Sample cups: stainless steel.

5.8. Parr 1825 filling connector for O_2 cylinder and bomb: Parr Instrument Co., VWR Scientific, Los Alamos, New Mexico.

5.9. Bomb head support stand.

5.10. Thermometer reading lens.

5.11. Balance: capable of weighing 2000 ± 0.5 g.

5.12. Analytical balance.

INORGANIC TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

Analyte: Trace metals	**Method No.:** WI650
Matrix: Sludges, soils, and RCRA wastes	
Procedure: Acid leach to extract metals	
Effective Date: 04/01/87	**Authors:** Mary Carol Williams Daniel J. Gerth

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure and Source Materials 11.3 and 11.4 for proper waste disposal practices.

1. Principle of Method

1.1. The toxicity characteristic leaching procedure (TCLP) is designed to determine the mobility of contaminants present in liquid, solid, and multiphasic wastes.

1.2. For liquid wastes (i.e., those containing <0.5% solid material), the waste, after filtration through a 0.6- to 0.8-μm glass-fiber filter, is defined as the TCLP extract.

1.3. For solid wastes or wastes containing significant amounts of solid material, the particle size of the waste is reduced (if necessary), and the liquid phase, if any, is separated from the solid phase and stored at 4°C for later analysis. The solid phase is extracted with 20 times its weight of extraction fluid. The choice of extraction fluid employed depends on the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6- to 0.8-μm glass-fiber filter.

1.4. If a total analysis of the waste demonstrates that individual contaminants are not present or that they are present at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

1.5. If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste and the liquid extract are combined and analyzed. If incompatible, the liquids are analyzed separately, and the results are mathematically combined to yield a volume-weighted average concentration.

1.6. The maximum concentrations of contaminants for characteristics of toxicity are as follows:

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (mg/L)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0

2. Accuracy and Precision

2.1. A well-characterized matrix is not available to measure either accuracy or precision. Spike recovery is variable depending on the absorptive characteristics of the matrix.

3. Interferences

3.1. Chloride interferes, causing low recoveries for Cr, As, Se, and Ag.

3.2. Samples can be extremely complex and can have a multitude of unidentified, continuously variable interferences.

4. Handling and Storage of Samples

4.1. Preservatives must NOT be added to samples.

4.2. Sludges from TA-50 or TA-57 must be handled in a glove box. The handler must wear an anti-C laboratory coat, safety glasses, and rubber gloves. Weighing and dissolution must be completed in a glove box.

4.3. TCLP extracts should be preserved with nitric acid at a pH <2, prepared for analysis, and analyzed as soon as possible following extraction.

5. Apparatus

5.1. Glove box: with balance, for use with radioactive samples, if necessary.

5.2. Extraction vessel: 2-L bottle, borosilicate glass or plastic.

5.3. Magnetic stirring bar: Teflon-coated.

5.4. Magnetic stirrer: heavy duty.

5.5. Agitation apparatus: capable of rotating the extraction vessel end over end at 30 $\pm$ 2 rpm, from Associated Design and Manufacturing Company, Alexandria, Virginia, or equivalent to meet United States Environmental Protection Agency (EPA) requirements as described in "Test Methods for Evaluating Solid Wastes" (40 CFR 261).

5.6. Pressure filter holder: Fisher Model 09-753-25K or equivalent to meet EPA requirements as described in "Test Methods for Evaluating Solid Wastes" (40 CFR 261).

5.7. Filter media: 0.7-μm, Whatman GFF, Whatman Laboratory Products, Clifton, New Jersey, or equivalent to meet EPA requirements as described in "Test Methods for Evaluating Solid Wastes" (40 CFR 261).

5.8. Polyethylene bottle: 250-mL.

5.9. pH meter: calibrated in accordance with manufacturer's specifications.

5.10. Hot plate.

5.11. Laboratory balance: any balance accurate to $\pm$0.01 g.

6. Reagents

6.1. American Society for Testing and Materials (ASTM) Type I water.

6.2. Hydrochloric acid, 1.0 N: prepare from American Chemical Society (ACS) reagent-grade (87 mL/L).

6.3. Nitric acid, 1.0 N: prepare from ACS reagent-grade (60 mL/L).

6.4. Sodium hydroxide, 10 N.

6.5. Acetic acid: glacial, ACS reagent-grade.

6.6. Extraction fluid no. 1: prepare by adding 11.4 mL of glacial acetic acid to 1975 mL of ASTM Type I water. Add 12.9 mL of 10 N NaOH. When correctly prepared, the pH of this fluid is 4.93 ± 0.05.

6.7. Extraction fluid number 2: prepare by adding 11.4 mL of glacial acetic acid to 1989 mL of ASTM Type I water. When correctly prepared, the pH of this fluid is 2.88 ± 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked before use to ensure that these fluids were accurately prepared.

6.8. Metal standards, 1000-mg/L stock solutions. See individual metal procedures.

6.9. Nitric acid: concentrated, reagent-grade.

6.10. Nitric acid, 1%: dilute 10 mL of concentrated nitric acid to 1000 mL with ASTM Type I water.

6.11. Spike solution: use 1000-mg/L metal standards in the nitrate or oxide form. Add 10 mL of Ag; 5 mL each of As, Cr, Pb, and Se; 1 mL of Cd; and 100 mL of Ba. Add standard solutions to approximately 100 mL 1% HNO_3. Dilute to 1000 mL with 1% HNO_3. Do not use HCl solutions, which will precipitate silver.

Element	Spike solution concentration (mg/L)	Spiked sample concentration (mg/L)
As	5	0.1
Cd	1	0.02
Cr	5	0.1
Pb	5	0.1
Se	5	0.1
Ag	5	0.1
Ba	100	10.0

7. Procedure

7.1. The preliminary TCLP evaluations are performed on representative samples of waste (aliquot size of 100 g) that will not actually undergo TCLP extraction. These evaluations include preliminary determination of the percent solids of the waste; determination of whether the waste contains insignificant solids and is therefore its own extract after filtration; determination of whether the solid portion of the waste requires particle-size reduction; and determination of which extraction fluid is to be used.

NOTE: If 100-g sample is not available, adjust reagent volumes accordingly in order to maintain the same sample-to-reagent ratio as above.

7.2. Preliminary determination of percent solids. Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid can be forced by applied pressure, as described below.

7.2.1. If the waste will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solids), proceed to Step 7.5.

7.2.2. If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This separation involves the filtration device described in Steps 5.6–5.7 and is outlined in Steps 7.2.3–7.2.10.

7.2.3. Weigh the filter and the container that will receive the filtrate.

7.2.4. Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.2.5. Weigh out a representative subsample of the waste (100-g minimum) and record the weight.

7.2.6. Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged before filtration. Centrifugation is to be used only as an aid to filtration. If centrifugation is used, the liquid should be decanted and filtered and the solid portion of the waste filtered through the same filtration system.

7.2.7. Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). If filtration of the waste at 4°C reduces the amount of expressed liquid below what would be expressed at room temperature,

allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (> 1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.2.5 to determine the weight of the waste sample that will be filtered.

7.2.8. Gradually apply gentle pressure (1–10 psi) until pressurizing gas moves through the filter. If this point is not reached under 10 psi and if no additional liquid has passed through the filter in any 2-min interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10-psi, if the pressurizing gas has not moved through the filter and if no additional liquid has passed through the filter in any 2-min interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter or when liquid flow has ceased at 50 psi (i.e., filtration does not produce any additional filtrate within any 2-min period), filtration is stopped.

NOTE: Instantaneous application of high pressure can degrade the glass-fiber filter and may cause premature plugging.

7.2.9. The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. But even after applying pressure filtration, as outlined in Step 7.2.8, this material may not filter. If this is the case, the material in the filtration device is defined as a solid. The original filter is **NOT** to be replaced with a fresh filter under any circumstances. Only one filter is to be used.

7.2.10. Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.2.3) from the total weight of the filtrate-filled container. The weight of the solid phase of the waste sample is determined by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Step 7.2.5.

7.2.11. Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\%S = \frac{W_S \times 100}{W_T} ,$$

where $\%S$ = percent solids,
W_S = weight of solid, and
W_T = total weight of waste.

7.3. Determination of whether waste is liquid or has insignificant amounts of solid material. If the sample obviously has a significant amount of solid material, the solid phase must be extracted. Proceed to Step 7.4 to determine if the waste requires particle-size reduction, and reduce particle size if necessary. Determine whether the waste is liquid or has insignificant amounts of solid material, which need not undergo extraction, as follows:

7.3.1. Remove the solid phase and filter from the filtration apparatus.

7.3.2. Dry the filter and solid phase at 100 ± 20°C until two successive weighings yield the same value within ±1%. Record the final weight.

NOTE: Caution should be taken to ensure that the solid will not flash upon heating. The drying oven should be vented to a hood or appropriate device.

7.3.3. Calculate the percent dry solids as follows:

$$\%D_s = \frac{(W_{wf} - W_f) \times 100}{W_i} ,$$

where: $\%D_s$ = percent dry solids,
W_{wf} = weight of dry waste and filter,
W_f = tared weight of filter, and
W_i = initial weight of sample.

7.3.4. If the percent dry solids is <0.5%, the waste after filtration is defined as the TCLP extract. If the percent dry solids is ≥0.5% and TCLP is to be performed, return to the beginning of this section (Step 7.1) with a new representative waste sample, so that it can be determined if particle-size reduction is necessary (Step 7.4) and so that the appropriate extraction fluid may be determined (Step 7.5) on a fresh portion of the solid phase of the waste.

7.4. Determination of whether the wastes require particle-size reduction (particle size is reduced during this step). Using the solid portion of the waste, evaluate the solid for particle size. If the solid has a surface area per gram ≥ 3.1 cm^2 or is < 1 cm in its smallest dimension (i.e., is capable of passing through a 9.5-mm [0.375-in.] standard sieve), particle-size reduction is not required (proceed to Step 7.5). If the surface area is smaller or the particle size larger than described above, the solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above.

7.5. Determination of appropriate extraction fluid. If the solid content is $\geq 0.5\%$ of the waste and if TCLP extraction is to be done (Section 8), determine the appropriate fluid (Steps 6.6–6.7) to use as follows.

7.5.1. Weigh out a small subsample of the solid phase of the waste, reduce the particle size (if necessary) to approximately 1-cm-diam or less, and transfer 5.0 g of the solid phase of the waste to a 250-mL (or larger) beaker or Erlenmeyer flask.

7.5.2. Add 96.5 mL of reagent water (ASTM Type I) to the beaker, cover with a watch glass, and stir vigorously for 5 min with a magnetic stirrer. Measure and record the pH. If the pH is < 5.0, extraction fluid No. 2 is used. Proceed to Section 8.

7.5.3. If the pH from Step 7.5.2 is > 5.0, add 3.5 mL of 1.0 N HCl, slurry briefly, cover with a watch glass, heat to 50°C, and hold at 50°C for 10 min.

7.5.4. Let the solution cool to room temperature and record the pH. If the pH is < 5.0, use extraction fluid No. 1. If the pH is > 5.0, use extraction fluid No. 2. Proceed to Section 8.

7.6. The sample of waste used in this step must **NOT** be used any further. Use a new sample of the waste for extractions in Steps 8 and 9.

8. Extraction Procedure

8.1. Although a sample of at least 100 g (solid and liquid phases) is required, a larger sample may be more appropriate, depending on the solids content of the waste sample (percent solids, see Step 7.2) and whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid. Enough solids should be generated for extraction so that the volume of TCLP extract will be sufficient to support all the determinations required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all the determinations

required, it is recommended that more than one extraction be performed and that the extracts from each extraction be combined and then aliquoted for analysis.

8.2. If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Step 7.2), weigh out a representative subsample of the waste (100-g minimum) and proceed to Step 8.11.

8.3. If the sample is liquid or multiphasic, liquid/solid separation is required. This separation involves filtration and is outlined in Steps 8.4 to 8.10 below.

8.4. Weigh the container that will receive the filtrate.

8.5. Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure it. Acid-wash the filter.

8.6. Weigh out a representative subsample of the waste (100-g minimum) and record the weight. If the waste was shown to contain <0.5% dry solids (Step 7.3), the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all the determinations required of the TCLP extract. For wastes containing >0.5% dry solids (Steps 7.2 or 7.3), use the percent solids information obtained in Step 7.2 to determine the optimum sample size (100-g minimum) for filtration. Enough solids should be generated after filtration to support the determinations to be performed on the TCLP extract.

8.7. Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged before filtration. Centrifugation is to be used only as an aid to filtration. If centrifugation is used, the liquid should be decanted and filtered and the solid portion of the waste filtered through the same filtration system.

8.8. Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder. If filtration of the waste at 4°C reduces the amount of expressed liquid below what would be expressed at room temperature, allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 8.6, to determine the weight of the waste sample that will be filtered.

8.9. Gradually apply gentle pressure (1–10 psi) until pressurizing gas moves through the filter. If this point is not reached below 10 psi and if no additional liquid has

passed through the filter in any 2-min interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase, if the pressurizing gas has not moved through the filter and if no additional liquid has passed through the filter in any 2-min interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter or when the liquid flow has ceased at 50 psi (i.e., filtration does not produce any additional filtrate within a 2-min period), filtration is stopped.

NOTE: Instantaneous application of high pressure can degrade the glass-fiber filter and may cause premature plugging.

8.10. The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Step 8.15) or stored at 4°C until time of analysis.

NOTE: Some wastes (such as oily wastes and some paint wastes) will obviously contain some material that appears to be a liquid. But even after applying vacuum or pressure filtration, as outlined in Step 8.9, this material may not filter. If this is the case, the material in the filtration device is defined as a solid and is carried through the extraction as a solid. The original filter is not to be replaced with a fresh filter under any circumstances. Only one filter is to be used.

8.11. If the waste contains $<0.5\%$ dry solids (see Step 7.3), proceed to Step 8.15. If the waste contains $>0.5\%$ dry solids (see Step 7.2 or 7.3) and if particle-size reduction of the solid was needed in Step 7.4, proceed to Step 8.12. If particle-size reduction was not required in Step 7.4, quantitatively transfer the solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase, and proceed to Step 8.13.

8.12. The solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Step 7.4. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase.

NOTE: The waste should be sieved only through a Teflon-coated sieve, to avoid possible contamination of the sample. Surface area requirements are meant for filamentous (e.g., paper or cloth) and similar waste materials. Actual measurement of surface area is not recommended.

8.13. Determine the amount of extraction fluid to add to the extractor vessel as follows:

Weight of extraction fluid = 0.5 × % solids × weight of waste filtered.

Slowly add this amount of appropriate extraction fluid (see Step 7.5) to the extractor vessel. Close the extractor bottle tightly (Teflon tape can be used to ensure a tight seal), secure it in the rotary extractor device, and rotate it at 30 ± 2 rpm for 18 ± 2 h. Ambient temperature (i.e., temperature of room in which extraction is to take place) must be maintained at 22 ± 3°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., lime or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be opened periodically (e.g., after 15 min, 30 min, and 1 h) and vented into a hood.

8.14. Following the extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a new glass-fiber filter, as outlined in Step 8.9. For final filtration of the TCLP extract, the filter may be changed, if necessary, to facilitate filtration. Filter(s) must be acid-washed if the mobility of metals is being evaluated.

8.15. The TCLP extract is prepared as follows:

8.15.1. If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 8.14 is defined as the TCLP extract. Proceed to Step 8.16.

8.15.2. If compatible (i.e., multiple phases will not result on combination), the filtered liquid resulting from Step 8.14 is combined with the initial liquid phase of the waste obtained in Step 8.9. This combined liquid is defined as the TCLP extract. Proceed to Step 8.16.

8.15.3. If the initial liquid phase of the waste obtained from Step 8.9 is not or may not be compatible with the filtered liquid resulting from Step 8.14, these liquids are not combined. These liquids, collectively defined as the TCLP extract, are analyzed separately and the results are combined mathematically. Proceed to Step 8.16.

8.16. Following collection of the TCLP extract, record the pH of the extract. The extract should be immediately aliquoted for analysis and properly preserved (metals aliquots must be acidified with concentrated nitric acid to pH <2). The TCLP extract must be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals other than mercury must be acid digested.

8.17. The contaminant concentrations in the TCLP extract are compared with the thresholds identified in the appropriate regulations. Refer to Source Material 11.1 for quality assurance requirements.

9. Calculations

9.1. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm 0.5\%$), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final analyte concentration} = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2} ,$$

where V_1 = the volume of the first phase (L),
C_1 = the concentration of the contaminant of concern in the first phase (mg/L),
V_2 = the volume of the second phase (L), and
C_2 = the concentration of the contaminant of concern in the second phase (mg/L).

Chromium concentrations must be interpreted differently. A waste containing chromium will be determined to be toxic if (1) the waste extract has an initial pH of <7 and contains more than 5 mg/L of hexavalent chromium in the resulting extract, or (2) the waste extract has an initial pH >7 and a final pH >7 and contains more than 5 mg/L of hexavalent chromium in the extract, or (3) the waste extract has an initial pH >7 and a final pH <7 and contains more than 5 mg/L of total chromium, unless the chromium is trivalent. To determine whether the chromium is trivalent, the sample must be processed according to an alkaline digestion method (Method 3060) and analyzed for hexavalent chromium (Methods 7195, 7196, or 7197). (Refer to SW-846 Manual, Source Material 11.1.)

9.2. Calculation for standard additions:

$$C = \frac{D \times R_u \times C_s}{R_u - R_s} ,$$

where C = concentration of unknown,
D = dilution of both standard and unknown (must be the same for each),
R_u = instrument reading of unknown,

C_s = concentration of standard added, and
R_s = instrument reading of unknown plus standard.

10. Proper Waste Disposal Practices

10.1. Soil-water slurry.

10.1.1. The TCLP waste consists of approximately 1500 mL of a slurry that remains after filtering the sample for TCLP analysis.

10.1.2. If, after analysis, the sample is found to be below the levels of concern for the TCLP analytes, dispose of the liquid portion of the sample in a sink approved for the disposal of inorganic acids and bases. Dispose of the solid portion of the sample as ordinary laboratory trash.

10.1.2.1. Concern levels:

Cd, Se,	>	1 ppm
Ag, As, Cr, Pb	>	5 ppm
Ba	>	100 ppm

10.1.3. If, after analysis, the sample is found to be above the level of concern for any of the TCLP analytes, accumulate the slurry in a coated glass bottle in a secondary containment tray.

10.1.3.1. Label the bottle with a hazardous waste label indicating its use for the TCLP waste samples.

10.1.3.2. When the bottle is full, keep it in the secondary containment tray pending pickup by Waste Services (CST-17).

10.2. Waste pickup.

10.2.1. When the waste bottle is full, request CST-17 to pick it up by using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form (WPF) number describing the waste is referenced on the CWDR.

10.2.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

11. Source Materials

11.1. *Test Methods for Evaluating Solid Waste, SW-846* (Office of Solid Waste and Emergency Response, Washington, D.C., 1982).

11.2. *Federal Register*, Vol. 51, No. 216, pp. 40643-40652.

11.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

11.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

OIL AND GREASE (TOTAL RECOVERABLE)

Analyte: Nonvolatile hydrocarbons	**Method No.:** WI660
Matrix: Water and wastewater	**Detection Limit:** 0.5 mg/L
Procedure: Extraction	**Accuracy and Precision:** 100% ± 9.3%
Effective Date: 09/02/87	**Author:** Harold P. Patterson

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The sample is acidified to a low pH (<2) and serially extracted with fluorocarbon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue is weighed.

1.2. This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, and industrial and domestic wastes. It is applies to the determination of relatively nonvolatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

1.3. The method does not apply to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through No. 2 fuel oils are completely or partially lost in the solvent removal operation.

1.4. Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Recoveries of these materials will be low.

2. Detection Limit

2.1. The method covers the range from 0.5 to 1000 mg/L of extractable material.

3. Accuracy and Precision

3.1. The accuracy and precision for this method was determined using a blind quality control sample. Thirteen determinations were made over a 6-month period with a mean recovery of 100% ± 9.3%.

4. Interference

4.1. The definition of oil and grease is based on the procedure used. The nature of the oil and/or grease and the presence of extractable nonoily matter will influence the material measured and the interpretation of results.

5. Collection and Storage of Samples

5.1. Collect a 1-L sample in a glass bottle. If analysis is to be delayed for more than a few hours, preserve the sample by the adding 5 mL of 50% HCl at the time of collection and refrigerate at 4°C.

5.2. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

6. Apparatus

6.1. Separatory funnel: 2000-mL with Teflon stopcock.

6.2. Vacuum source.

6.3. Boiling flask: 125-mL.

6.4. Filter paper: No. 40, 11-cm-diam.

6.5. Constant-temperature bath and shaker: Yamato or equivalent, supplied by VWR Scientific, Los Alamos, New Mexico.

6.6. Vacuum tubing: 1/8-in.-i.d.

6.7. Drying desiccator.

6.8. Graduated cylinder: 1-L.

6.9. Reflux condensor.

7. Reagents

7.1. Hydrochloric acid (50%). Mix an equal volume of distilled water with concentrated hydrochloric acid.

7.2. Fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane).

7.3. Anhydrous sodium sulfate.

8. Procedure

8.1. With a wax pencil, mark the meniscus of the sample on the sample bottle as received. Save the bottle for later measurement of sample volume.

8.2. If the sample was not acidified at the time of collection, add 5 mL of hydrochloric acid to the sample bottle. Mix the sample and check the pH by touching pH-sensitive paper to the cap to ensure that the pH is 2 or lower. Add more acid if necessary.

8.3. Pour the sample into the 2000-mL separatory funnel.

8.4. Tare a boiling flask (predried in an oven at 103°C and stored in a desiccator).

8.5. Add 30 mL of fluorocarbon-113 to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 min. Allow the layers to separate. Filter the solvent layer into the flask through a funnel containing solvent-moistened filter paper.

NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g of sodium sulfate into the filter paper cone and slowly draining the emulsion through the salt. Additional 1-g portions can be added to the cone as required.

8.6. Repeat Step 8.5 twice, using additional portions of fresh solvent. Combine all solvent in the boiling flask.

8.7. Rinse the tip of the separatory funnel, the filter paper, and the funnel with a total of 10 mL of solvent and collect the rinsings in the flask.

8.8. Place the boiling flask in the constant-temperature bath, adjusted to 70°C. Secure the flask. Place the shaker-bath in a well-ventilated hood. Connect the flask to a reflux condensor. Collect the refluxed freon in a clean flask and save for reuse. Oil and residues will remain in the flask.

8.9. When all the fluorocarbon has evaporated from the flask, eliminate the remaining solvent vapor by removing the flask from the bath and inserting a vacuum tube about midcenter of the flask to sweep out the flask with air for 15 s. Wipe the outside of flask well to remove excess moisture and fingerprints.

8.10. Cool the boiling flask in a desiccator for 30 min and weigh.

8.11. Run a reagent blank with the above method to make a correction if necessary.

8.12. Add water to the sample bottle saved from Step 8.1 and fill to the line marked with the wax pencil. Pour this water into a graduated cylinder to measure the sample volume.

9. Calculation

9.1. Calculate the total recoverable oil and grease as follows.

$$C = \frac{R - B}{V} ,$$

where C = total oil and grease (mg/L),
R = residue, gross weight of extraction flask minus the tare weight (mg),
B = blank determination, residue of equivalent volume of extraction solvent (mg), and
V = volume of sample (mL).

10. Proper Waste Disposal Practices

10.1. Solid waste.

10.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

10.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

10.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

10.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 10.3.

10.2. Liquid waste.

10.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

10.2.2. Label the bottle with a hazardous waste label and a label indicating its use.

10.2.3. Periodically request pickup of the bottle as described in Section 10.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

10.3. Waste pickup.

10.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

10.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

11. Source Material

11.1. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 413.1 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

SPECIFIC GRAVITY OF WATER AND WASTEWATER

Analyte: Dissolved solids in solution	**Method No.:** WI670
Matrix: Water and wastewater	**Accuracy:** ± 1%
Procedure: Specific gravity	
Effective Date: 10/01/87	**Author:** Harold P. Patterson

SAFETY NOTE: No chemicals are used in this procedure. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 7 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The specific gravity of a substance is the ratio of the weight of any volume of that substance to the weight of an equal volume of some other substance taken as the standard (usually water) at a stated temperature.

1.2. The specific gravity is measured directly with a hydrometer at 60°F.

2. Accuracy

2.1. The estimated accuracy from direct reading of the hydrometer is ±1%.

3. Interference

3.1. The measurement will be inaccurate if the sample temperature is not at 60°F.

4. Collection and Storage of Samples

4.1. Samples should be stored in an airtight container to prevent evaporation.

5. Apparatus

5.1. Thermometer: in degrees Fahrenheit with a 0–100°F range.

5.2. Hydrometers: to cover range of 0.70 to 2.00. VWR Scientific, Los Alamos, New Mexico.

5.3. Hydrometer cylinder: 300-mL. VWR Scientific, Los Alamos, New Mexico.

5.4. Constant-temperature water bath: Yamato or equivalent, VWR Scientific, Los Alamos, New Mexico.

6. Procedure

6.1. Adjust the temperature of the solution to be tested to 60°F. This can be done by swirling the sample in its closed container under cold running tap water or heating in a constant-temperature water bath at 60°F.

6.2. Select a hydrometer that is within the range of the specific gravity of the solution.

6.3. Fill the hydrometer cylinder with approximately 200 mL of the solution to be tested.

6.4. Carefully insert the hydrometer into the cylinder, being careful not to drop and break the hydrometer by hitting the bottom of the cylinder.

6.5. Be sure the hydrometer is floating away from the bottom and sides of the cylinder.

6.6. Read the specific gravity directly from the hydrometer at the meniscus of the liquid.

7. Proper Waste Disposal Practices

7.1. Solid waste.

7.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

7.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

7.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

7.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 7.3.

7.2. Liquid waste.

7.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and

keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

7.2.2. Label the bottle with a hazardous waste label and a label indicating its use.

7.2.3. Periodically request pickup of the bottle as described in Section 7.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

7.3. Waste pickup.

7.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

7.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

8. Source Material

8.1. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Method 213E (American Public Health Association, Washington, DC, 1985).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRACE METAL DIGESTION — DRINKING WATER, SURFACE WATER, AND NPDES EFFLUENTS

Analyte: Trace metals	**Method No.:** WI680
Matrix: Water, aqueous waste, leachates, and National Pollutant Discharge Elimination System (NPDES) effluents	
Procedure: Nitric acid digestion	
Effective Date: 03/01/85 to 09/01/95	**Author:** Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equiment.

1. Principle of Method

1.1. Principle.

1.1.1. Organic and inorganic metal complexes are decomposed by hot nitric acid and converted to soluble nitrate salts.

1.2. Definitions.

1.2.1. Dissolved elements — those elements that will pass through a 0.45-μm membrane filter.

1.2.2. Suspended elements — those elements that are retained by a 0.45-μm membrane filter.

1.2.3. Total elements — concentration determined on an unfiltered sample following vigorous digestion (Step 6.3) or the sum of the dissolved plus suspended concentrations (Step 6.1 plus 6.2).

1.2.4. Total recoverable elements — concentration determined on an unfiltered sample following treatment with hot, dilute, mineral acid.

2. Interferences

2.1. Volatile metals or metal complexes (Se, As) may be lost during prolonged heating.

2.2. For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus that come into contact with the sample are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (1) contributing contaminants through leaching or surface desorption and (2) by depleting concentrations through absorption.

3. Sample Handling and Preservation

3.1. The digestion and analysis of all metals must be completed within six months of collection.

3.2. The collection and treatment of the sample prior to analysis requires special attention. Laboratory glassware, including the sample bottle (whether polyethylene, polyproplyene, or FEP-fluorocarbon), should be thoroughly washed with detergent and tap water and rinsed in the following order with 1:1 nitric acid/tap water, 1:1 hydrochloric acid/tap water, and finally, distilled deionized water (DDW).

3.3. Chromic acid may be useful for removing organic deposits from glassware. The glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. (A commercial product, NO-CHROMIX, is available from Godax Laboratories, 6 Varick St., New York, NY.)

3.4. If an active analytical quality control program using spiked samples and reagent blanks verifies that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

3.5. Before collecting the sample, decide what type of data are desired (dissolved, suspended, or total) so that the appropriate preservation and pretreatment steps may be taken. Any filtration or acid preservation must be performed at the time the sample is collected or as soon as possible thereafter.

3.5.1. Dissolved elements. Filter the sample through a 0.45-μm membrane filter as soon as practical after collection.

NOTE: The use of glass or plastic filtering apparatus is recommended to avoid possible contamination.

Use the first 50-100 mL of filtered sample to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 HNO_3 to a pH of 2 or less. Normally, 3 mL of 1:1 acid per liter should be sufficient to preserve the sample.

PREPARATION OF AQUEOUS SAMPLES FOR SPECTROCHEMICAL ANALYSIS— FAAS AND ICPOES

Analyte: Total suspended and dissolved metals	**Method No.:** WI681 (EPA 200.0, 200.8 and SW846 3010)
Matrix: Water and wastewater	
Procedure: Open beaker digestion with HNO_3 and HCl	
Effective Date: 08/01/93	**Authors:** Richard Robinson Richard Foust

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 8. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure for proper waste disposal practices.

1. Principle of Method

The sample is digested with nitric acid and evaporated to low volume. It is then refluxed with hydrochloric acid, cooled, and brought to final volume with American Society for Testing and Materials (ASTM) Type I water. The resulting solution is divided into two parts, one for flame atomic absorption spectrometry (FAAS) analysis and the other for inductively coupled plasma–optical emission spectrometry (ICPOES) analysis.

2. Applicability

2.1. This method is used for the preparation of samples for the determination of total, dissolved, and suspended metals in aqueous samples. It is based on United States Environmental Protection Agency (EPA) Methods 200.0 and 200.8 and SW 846 Method 3010, and it is approved for National Pollution Discharge Elimination System (NPDES) samples.

2.2. Samples prepared by this method may be analyzed by FAAS or ICPOES, using the methods listed in Table I (found at the end of this procedure). The metals for which the method is applicable are listed in Table I.

3. Definitions

3.1. Laboratory control standard (LCS). An aliquot of laboratory reagent water to which known quantities of the method analytes are added in the laboratory.

3.2. Matrix spike. A matrix spike analysis is performed by adding a predetermined quantity of stock solutions of certain analytes to a sample matrix before sample digestion and analysis. The concentration of the spike should be at the regulatory standard level or the practical quantitation limit for the method. No spike of the analyte is necessary when the concentration of the analyte in the sample is greater than 0.1%.

3.3. Laboratory process blank. An aliquot of reagent water that is treated exactly as a sample, including exposure to all glassware, equipment, reagents, and acids that are used with other samples.

3.4. Quality control sample (QCS). A solution of target analytes of known concentration used to fortify an aliquot of LCS matrix. The QCS is obtained from a source outside the laboratory and is used to check laboratory performance.

3.5. Sample duplicate. Duplicate samples are two separate samples taken from the same source (i.e., sample containers) and processed and analyzed independently.

3.6. Dissolved metal concentration. The concentration of metal in an aqueous sample that will pass through a 0.45-μm membrane filter assembly, before sample acidification.

3.7. Suspended metal concentration. The concentration of metal(s) in an aqueous sample that will not pass through a 0.45-μm membrane filter assembly, before sample acidification.

3.8. Total metal concentration. The concentration of metal(s) in an unfiltered aqueous sample, as determined after vigorous acid digestion, or the sum of the concentrations of dissolved and suspended metal(s).

4. Quality Control

4.1. Four laboratory control samples are processed and analyzed with each batch of 20 samples.

4.1.1. A laboratory process blank is carried throughout the entire digestion and is analyzed with each batch of 20 samples.

4.1.2. A laboratory control standard is processed and analyzed with each batch of 20 samples.

4.1.3. A sample duplicate is processed and analyzed with each batch of 20 samples.

4.1.4. A matrix spike is processed and analyzed with each batch of 20 samples.

5. Collection, Preservation, and Storage of Samples

5.1. For the determination of total metals, acidify the sample with 1:1 high-purity HNO_3 to pH < 2.0 at the time of collection.

5.1.1. Store the sample in precleaned linear polyethylene or Teflon bottles.

5.1.2. Do not filter the sample before processing.

5.1.3. Complete the analysis within 6 months.

5.2. For the determination of dissolved metals, filter the sample through a 0.45-μm membrane filter as soon as practical after collection.

5.2.1. Use the first 50–100 mL of the sample to rinse the filter flask. Discard this portion and collect the required volume of filtrate.

5.2.2. Acidify the filtrate with 1:1 high-purity HNO_3 to pH < 2.0.

5.2.3. Store the sample in precleaned linear polyethylene or Teflon bottles.

5.2.4. Complete the analysis within 6 months.

6. Interferences

6.1. Contamination and loss are prime considerations when preparing samples for trace-metal analysis. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination in the laboratory environment. A clean laboratory work area designated for trace-element sample handling must be used.

6.2. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching or (2) depleting element concentrations through adsorption processes.

7. Apparatus

7.1. Clean all reusable labware (glass, quartz, polyethylene, Teflon, etc.) thoroughly before use. Test disposable labware for contamination before use.

7.2. Labware should be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with water, and soaked 4 h in a mixture of dilute nitric and hydrochloric acids, followed by rinsing with ASTM Type I water and oven drying.

NOTE: Do not use chromic acid for cleaning glassware.

7.3. Balance: analytical, capable of accurately weighing to $\pm$ 0.1 mg.

7.4. Beakers: Griffin, borosilicate glass or Teflon, 100- or 150-mL.

7.5. Centrifuge tubes: clear polypropylene, 50-mL, with flat-top cap.

7.6. Filter unit: Nalgene sterilization filter unit, 0.45-μm, 115-mL, or equivalent.

7.7. Graduated cylinders.

7.8. Hot plate: Thermolyne 2200 or equivalent, capable of maintaining temperature to $\pm$ 5°C.

7.9. Micropipettes: Rainin or equivalent, various sizes.

7.10. Volumetric flasks: assorted sizes.

7.11. Wash bottle: one-piece stem, polyethylene, with screw closure, 500-mL.

7.12. Watch glasses: borosilicate glass or Teflon, 2- and 3-in.

8. Reagents

8.1. ASTM Type I water.

8.2. Nitric acid (concentrated, high-purity). SeaStar, Baker Ultrex, or equivalent.

8.3. Hydrochloric acid (concentrated, high-purity). SeaStar, Baker Ultrex, or equivalent.

8.4. Hydrochloric acid (1:1). Dilute 500 mL of high-purity HCl to 1.0 L with ASTM Type I water.

9. Calibration and Standards

9.1. Micropipettes are calibrated quarterly at 10%, 50% and 100% of maximum volume. Results of calibration should be recorded in a laboratory notebook.

9.2. The analytical balance is calibrated regularly. An instrument accuracy check is performed annually by Standards and Calibration (ESH-9).

10. Procedure

10.1. Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of high-purity concentrated HNO_3. Cover the beaker with a watch glass.

10.2. Place the beaker on a hot plate and cautiously evaporate to a low volume (approximately 5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry.

10.3. Cool the beaker and add another 3-mL portion of high-purity concentrated HNO_3. Cover the beaker and return it to the hot plate, allowing the sample to reflux for 1 h.

10.4. Remove the watch glass after 1 h and examine the digestate for reaction completeness. Digestion is complete if the sample is light in color or the appearance does not change with continued refluxing. If the digestion is not complete, repeat step 10.3 as necessary.

10.5. When the digestion is complete, remove the watch glass and allow the sample to evaporate to 5–15 mL. Do not allow any portion of the beaker bottom to go dry. If this occurs, the sample must be redigested.

10.6. Cool the beaker and add 10 mL of 1:1 HCl. Return the beaker to the warm hot plate for 15 min to dissolve any precipitate or residue.

10.7. Rinse the beaker walls and watch glass with ASTM Type I water and, when necessary, filter the sample with the Nalgene filter apparatus to remove any undissolved material.

10.8. Rinse the filter several times with 10–15 mL portions of ASTM Type I water and bring the final volume to 100 mL with ASTM Type I water.

10.9. Swirl the solution until it is homogeneous.

10.10. Label two centrifuge tubes with the sample number and pour approximately equal 50-mL volumes into the centrifuge tubes. One tube will be for FAAS analysis and the other will be for ICPOES analysis.

10.11. The sample is now ready for spectrochemical analysis.

11. Calculations

11.1. There are no calculations for samples run directly by FAAS or by ICPOES.

11.2. Samples that are diluted by the instrument operator must be corrected by applying the correct dilution factor before the results are reported.

12. Proper Waste Disposal Practices

12.1. Solid waste.

12.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

12.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

12.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

12.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 12.3.

12.2. Liquid waste.

12.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

12.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace-metal waste.

12.2.3. Periodically request pickup of the bottle as described in Section 12.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

12.3. Waste pickup.

12.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

12.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

13. Source Material

13.1. "Test Methods for Evaluation of Solid Waste: Laboratory Manual of Physical and Chemical Methods," EPA Report No. SW-846 (November 1986).

13.2. U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (rev. March 1983).

13.3. U.S. Environmental Protection Agency, "Methods for the Determination of Metals in Environmental Samples," EPA-600 4-91/010 (June 1991).

13.4. Wagner, R. E. and Yogis, G. A. *Guide to Environmental Analytical Methods*, Genium Publishing Corp., Schenectady, N. Y. (1992).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TABLE I. EPA METHODS BY WHICH SAMPLES PREPARED WITH THIS PROCEDURE MAY BE ANALYZED.

	FAAS Methods		ICPOES Methods	
Analyte	EPA 200 Series	SW-846 7000 Series	EPA 200 Series	SW-846 6000 Series
Aluminum	202.1	7020	200.7	6010
Arsenic	—	—	200.7	6010
Barium	208.1	7080	200.7	6010
Beryllium	210.1	7090	200.7	6010
Cadmium	213.1	7130	200.7	6010
Calcium	215.1	7140	200.7	6010
Chromium	218.1	7190	200.7	6010
Cobalt	219.1	7200	200.7	6010
Copper	220.1	7210	200.7	6010
Iron	236.1	7380	200.7	6010
Lead	239.1	7420	200.7	6010
Magnesium	242.1	7450	200.7	6010
Manganese	243.1	7460	200.7	6010
Molybdenum	246.1	7480	200.7	6010
Nickel	249.1	7520	200.7	6010
Potassium	258.1	7610	200.7	6010
Selenium	—	—	200.7	6010
Sodium	273.1	7770	200.7	6010
Thallium	279.1	7840	200.7	6010
Vanadium	286.1	7910	200.7	6010
Zinc	289.1	7950	200.7	6010

PREPARATION OF AQUEOUS SAMPLES FOR SPECTROCHEMICAL ANALYSIS– GFAAS AND ICPMS

Analyte: Total, suspended, and dissolved metals	**Method No.:** WI685 (EPA 200.0, 200.8 and SW846 3020)
Matrix: Water and wastewater	
Procedure: Open beaker digestion with HNO_3	
Effective Date: 08/01/93	**Authors:** Richard Robinson Richard Foust

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 8. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure for proper waste disposal practices.

1. Principle of Method

The sample is digested with nitric acid and evaporated to low volume. It is then cooled and brought to final volume with American Society for Testing and Materials (ASTM) Type I water. The resulting solution is divided into two parts, one for graphite furnace atomic absorption spectromety (GFAAS) analysis and the other for inductively coupled plasma–mass spectrometry (ICPMS) analysis.

2. Applicability

2.1. This method is used for the preparation of samples for the determination of total, dissolved, and suspended metals in aqueous samples. It is based on United States Environmental Protection Agency (EPA) Methods 200.0 and 200.8 and SW 846 Method 3020, and it is approved for National Pollution Discharge Elimination System (NPDES) samples.

2.2. Samples prepared by this method may be analyzed by GFAAS or ICPMS, using the methods listed in Table I (found at the end of this procedure). The metals for which the method is applicable are listed in Table I.

3. Definitions

3.1. Laboratory control standard (LCS). An aliquot of laboratory reagent water to which known quantities of the method analytes are added in the laboratory.

3.2. Matrix spike. A matrix spike analysis is performed by adding a predetermined quantity of stock solutions of certain analytes to a sample matrix prior to sample digestion and analysis. The concentration of the spike should be at the regulatory standard level or the practical quantitation limit for the method. No spike of the analyte is necessary when the concentration of the analyte in the sample is greater than 0.1%.

3.3. Laboratory process blank. An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, reagents, and acids that are used with other samples.

3.4. Quality control sample (QCS). A solution of target analytes of known concentration used to fortify an aliquot of LCS matrix. The QCS is obtained from a source outside to the laboratory and is used to check laboratory performance.

3.5. Sample duplicate. Duplicate samples are two separate samples taken from the same source (i.e., sample containers) and processed and analyzed independently.

3.6. Dissolved metal concentration. The concentration of metal in an aqueous sample that will pass through a 0.45-μm membrane filter assembly, before sample acidification.

3.7. Suspended metal concentration. The concentration of metal(s) in an aqueous sample that will not pass through a 0.45-μm membrane filter assembly, before sample acidification.

3.8. Total metal concentration. The concentration of metal(s) in an unfiltered aqueous sample, as determined after vigorous acid digestion, or the sum of the concentrations of dissolved and suspended metal(s).

4. Quality Control

4.1. Four laboratory control samples are processed and analyzed with each batch of 20 samples.

4.1.1. A laboratory process blank is carried throughout the entire digestion and analyzed with each batch of 20 samples.

4.1.2. A laboratory control standard is processed and analyzed with each batch of 20 samples.

4.1.3. A sample duplicate is processed and analyzed with each batch of 20 samples.

4.1.4. A matrix spike is processed and analyzed with each batch of 20 samples.

5. Collection, Preservation, and Storage of Samples

5.1. For the determination of total metals, acidify the sample with 1:1 high-purity HNO_3 to pH < 2.0 at the time of collection.

5.1.1. Store the sample in precleaned linear polyethylene or Teflon bottles.

5.1.2. Do not filter the sample before processing.

5.1.3. Complete the analysis within 6 months.

5.2. For the determination of dissolved metals, filter the sample through a 0.45-μm membrane filter as soon as practical after collection.

5.2.1. Use the first 50–100 mL of the sample to rinse the filter flask. Discard this portion and collect the required volume of filtrate.

5.2.2. Acidify the filtrate with 1:1 high-purity HNO_3 to pH < 2.0.

5.2.3. Store the sample in precleaned linear polyethylene or Teflon bottles.

5.2.4. Complete the analysis within 6 months.

6. Interferences

6.1. Contamination and loss are prime considerations when preparing samples for trace-metal analysis. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination in the laboratory environment. A clean laboratory work area designated for trace-element sample handling must be used.

6.2. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching or (2) depleting element concentrations through adsorption processes.

7. Apparatus

7.1. Clean all reusable labware (glass, quartz, polyethylene, Teflon, etc.) thoroughly before use. Test disposable labware for contamination before use.

7.2. Labware should be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with water, and soaked 4 h in a mixture of dilute nitric and hydrochloric acids, followed by rinsing with ASTM Type I water and oven drying.

NOTE: Do not use chromic acid for cleaning glassware.

7.3. Balance: analytical, capable of accurately weighing to $\pm$ 0.1 mg.

7.4. Beakers: Griffin, borosilicate glass or Teflon, 100- or 150-mL.

7.5. Centrifuge tubes: clear polypropylene, 50-mL, with flat-top cap.

7.6. Filter unit: Nalgene sterilization filter unit, 0.45-μm, 115-mL, or equivalent.

7.7. Graduated cylinders.

7.8. Hot plate: Thermolyne 2200 or equivalent, capable of maintaining temperature to $\pm$ 5°C.

7.9. Micropipettes: Rainin or equivalent, various sizes.

7.10. Volumetric flasks: assorted sizes.

7.11. Wash bottle: one-piece stem, polyethylene, with screw closure, 500-mL.

7.12. Watch glass: borosilicate glass or Teflon, 2.5- and 3-in.

8. Reagents

8.1. ASTM Type I water.

8.2. Nitric acid (concentrated, high-purity). SeaStar, Baker Ultrex, or equivalent.

9. Calibration and Standards

9.1. Micropipettes are calibrated quarterly at 10%, 50%, and 100% of maximum volume. Results of calibration should be recorded in a laboratory notebook.

9.2. The analytical balance is calibrated regularly. An instrument accuracy check is performed annually by Standards and Calibration (ESH-9).

10. Procedure

10.1. Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of high-purity concentrated HNO_3. Cover the beaker with a watch glass.

10.2. Place the beaker on a hot plate and cautiously evaporate the sample to a low volume (approximately 5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry.

10.3. Cool the beaker and add another 3-mL portion of high-purity concentrated HNO_3. Cover the beaker and return it to the hot plate, allowing the sample to reflux for 1 h.

10.4. Remove the watch glass after 1 h and examine the digestate for reaction completeness. Digestion is complete if the sample is light in color or the appearance does not change with continued refluxing. If the digestion is not complete, repeat step 10.3 as necessary.

10.5. When the digestion is complete, remove the watch glass and allow the sample to evaporate to 5–15 mL. Do not allow any portion of the beaker bottom to go dry. If this occurs, the sample must be redigested.

10.6. Cool the beaker and add 10 mL of ASTM Type I water. Return the beaker to the warm hot plate for 15 min to dissolve any precipitate or residue.

10.7. Rinse the beaker walls and watch glass with ASTM Type I water and, if necessary, filter the sample with the Nalgene filter apparatus to remove any undissolved material.

10.8. Rinse the filter several times with 10–15 mL portions of ASTM Type I water and bring the final volume to 100 mL with ASTM Type I water. Record the final sample volume in the log book.

10.9. Swirl the solution until it is homogeneous.

10.10. Label two centrifuge tubes with the sample number and pour approximately equal 50-mL volumes into the centrifuge tubes. One tube will be for GFAAS analysis and the other will be for ICPMS analysis.

10.11. The diluted digestate contains approximately 3–5% (v/v) HNO_3 and is now ready for spectrochemical analysis. Withdraw aliquots of appropriate volume and add any required matrix modifier or reagent before analysis.

11. Calculations

11.1. There are no calculations for samples run directly by GFAAS or by ICPMS.

11.2. Samples that are diluted by the instrument operator must be corrected by applying the correct dilution factor before the results are reported.

12. Proper Waste Disposal Practices

12.1 Solid waste.

12.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

12.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

12.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

12.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 12.3.

12.2. Liquid waste.

12.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

12.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace-metal waste.

12.2.3. Periodically request pickup of the bottle as described in Section 12.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

12.3. Waste pickup.

12.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request Form (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

12.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

13. Source Material

13.1. "Test Methods for Evaluation of Solid Waste: Laboratory Manual of Physical and Chemical Methods," EPA Report No. SW-846 (November 1986).

13.2. U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (rev. March 1983).

13.3. U.S. Environmental Protection Agency, "Methods for the Determination of Metals in Environmental Samples," EPA-600 4-91/010 (June 1991).

13.4. Wagner, R. E. and Yogis, G. A. *Guide to Environmental Analytical Methods*, Genium Publishing Corp., Schenectady, N. Y. (1992).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TABLE I. EPA METHODS BY WHICH SAMPLES PREPARED WITH THIS PROCEDURE MAY BE ANALYZED.

	FAAS Methods		ICPMS Methods	
Analyte	EPA 200 Series	SW-846 7000 Series	EPA 200 Series	SW-846 6000 Series
Beryllium	210.2, 200.9	7091	200.8	6020
Cadmium	213.2, 200.9	7131	200.8	6020
Chromium	218.2, 200.9	7191	200.8	6020
Cobalt	219.2, 200.9	7201	200.8	6020
Lead	239.2, 200.9	7221	200.8	—
Molybdenum	246.2	7481	200.8	6020
Thallium	279.2, 200.9	7841	200.8	6020
Vanadium	286.2	7911	200.8	—

PREPARATION OF SEDIMENT, SLUDGE, AND SOIL SAMPLES FOR SPECTROCHEMICAL ANALYSIS—FAAS AND ICPOES

Analyte: Total metals	**Method No.:** WI690 (EPA 200.0, 200.8 and SW846 3050)
Matrix: Sediments, sludges, and soils	
Procedure: Open-beaker digestion with HNO_3 and HCl and 30% H_2O_2	
Effective Date: 08/01/93	**Authors:** Richard Robinson Richard Foust

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 8. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure for proper waste disposal practices.

1. Principle of Method

A sample of sediment, sludge, or soil is digested with nitric acid and hydrogen peroxide, then heated with hydrochloric acid and reduced to a small volume. The sample is cooled and brought to final volume with American Society for Testing and Materials (ASTM) Type I water. The resulting solution can be analyzed spectrochemically for various metals.

2. Applicability

2.1. This method is for preparation of samples for the determination of total metals in sediments, soils, sludges, oils, miscellaneous solids, and miscellaneous liquids. It is based on United States Environmental Protection Agency (EPA) Methods 200.0 and 200.8 and SW-846 Method 3050, and it is approved for National Pollution Discharge Emission Study (NPDES) samples.

2.2. Samples prepared by this method may be analyzed by flame atomic absorption spectrometry (FAAS) or inductively coupled plasma–optical emission spectrometry (ICPOES), using the methods listed in Table I. The metals for which the method is applicable are listed in Table I.

2.3. Miscellaneous liquids and solids and oils prepared by this method may be analyzed by inductively coupled plasma–mass spectrometry (ICPMS) or graphite furnace atomic absorption spectrometry (GFAAS).

3. Definitions

3.1. Laboratory control standard (LCS). An aliquot of laboratory reagent water to which known quantities of the method analytes are added in the laboratory.

3.2. Matrix spike. A matrix spike analysis is performed by adding a predetermined quantity of stock solutions of certain analytes to a sample matrix prior to sample digestion and analysis. The concentration of the spike should be at the regulatory standard level or the practical quantitation limit for the method. No spike of the analyte is necessary when the concentration of the analyte in the sample is greater than 0.1%.

3.3. Laboratory process blank. An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, reagents, and acids that are used with other samples.

3.4. Quality control sample (QCS). A solution of target analytes of known concentration used to fortify an aliquot of LCS matrix. The QCS is obtained from a source outside the laboratory and is used to check laboratory performance.

3.5. Sample duplicate. Duplicate samples are two separate samples taken from the same source (i.e., sample containers) and processed and analyzed independently.

3.6. Dissolved metal concentration. The concentration of metal in an aqueous sample that will pass through a 0.45-μm membrane filter assembly, before sample acidification.

3.7. Suspended metal concentration. The concentration of metal(s) in an aqueous sample that will not pass through a 0.45-μm membrane filter assembly, before sample acidification.

3.8. Total metal concentration. The concentration of metal(s) in an unfiltered aqueous sample, as determined after vigorous acid digestion, or the sum of the concentration of dissolved and suspended metal(s).

4. Quality Control

4.1. Four laboratory control samples are processed and analyzed with each batch of 20 samples.

4.1.1. A laboratory process blank is carried throughout the entire digestion and analyzed with each batch of 20 samples.

4.1.2. A laboratory control standard is processed and analyzed with each batch of 20 samples.

4.1.3. A sample duplicate is processed and analyzed with each batch of 20 samples.

4.1.4. A matrix spike is processed and analyzed with each batch of 20 samples.

5. Collection, Preservation, and Storage of Samples

5.1. Prewash all sample containers with detergents, acids, and ASTM Type I water. Plastic, glass, and Teflon containers may be used for storing solid samples.

5.2. Solid samples must be at least 200 g in mass.

5.3. Store solid samples at 4°C until analyzed.

6. Interferences

6.1. Contamination and loss are prime considerations when preparing samples for trace-metal analysis. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment. A clean laboratory work area designated for trace-element sample handling must be used.

6.2. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching or (2) depleting element concentrations through adsorption processes.

6.3. Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether this method is applicable to a given waste.

7. Apparatus

7.1. Clean all reusable labware (glass, quartz, polyethylene, Teflon, etc.) thoroughly before use. Test disposable labware for contamination before use.

7.2. Labware should be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with water and soaked 4 h in a mixture of dilute nitric and hydrochloric acids, followed by rinsing with ASTM Type I water and oven drying.

NOTE: Do not use chromic acid for cleaning glassware.

7.3. Balance: analytical, capable of accurately weighing to ± 0.1 mg.

7.4. Beakers: Griffin, borosilicate glass or Teflon, 100- or 150-mL.

7.5. Balls, shaker: Tungsten carbide, 1/4- or 3/8-in.

7.6. Centrifuge tubes: clear polypropylene, 50-mL, with flat-top cap.

7.7. Filter unit: Nalgene sterilization filter unit, 0.45-μ, 115-mL, or equivalent.

7.8. Graduated cylinders.

7.9. Hot plate: Thermolyne 2200 or equivalent, capable of maintaining temperature to ± 5°C.

7.10. Micropipettes: Rainin or equivalent, various sizes.

7.11. Shaker: Eberbach, reciprocating, No. 6000 or equivalent.

7.12. Volumetric flasks: assorted sizes.

7.13. Wash bottle: one-piece stem, polyethylene, with screw closure, 500-mL.

7.14. Watch glass: borosilicate glass or Teflon, 2 1/2- and 3-in.

8. Reagents

8.1. ASTM Type I water.

8.2. Hydrochloric acid (concentrated, high-purity). SeaStar, Baker Ultrex, or equivalent.

8.3. Nitric acid (concentrated, high-purity). SeaStar, Baker Ultrex, or equivalent.

8.4. Hydrogen peroxide (American Chemical Society reagent-grade, 30%).

9. Calibration and Standards

9.1. Micropipettes are calibrated quarterly at 10%, 50%, and 100% of maximum volume. Results of calibration should be recorded in a Laboratory notebook.

9.2. The analytical balance is calibrated regularly. An instrument accuracy check is performed annually by Standards and Calibration (ESH-9).

10. Procedure

10.1. Place 5–10 g of sample into a preweighed 125-mL Griffin beaker, then record the weight. Dry the sample at 105°C overnight or until constant weight is reached. Record the dry weight and calculate and record the percent solids.

10.2. Transfer all of the dried sample to a plastic centrifuge tube, add one tungsten carbide shaker ball, and place on a shaker for 1 h at high speed.

10.3. Transfer 0.8 g $\pm$ 0.1 g of the sample into a preweighed 125-mL Griffin beaker and record the weight (to the nearest 0.001 g) in the initial weight column of the digestion logbook.

10.4. Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass.

10.5. Place the beaker on a hot plate, heat the sample to 95°C, and reflux for 10 to 15 min.

10.6. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux the sample for an additional 30 min.

10.7. Repeat Step 10.6.

10.8. Remove the watch glass and cautiously evaporate the sample to a low volume (approximately 5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry.

10.9. Cool the beaker and add 2 mL of ASTM Type I water. Cautiously add 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until the effervescence subsides and allow the beaker to cool.

10.10. Continue to add 30% H_2O_2 in 1- to 2-mL aliquots, with warming, until the effervescence is minimal. Repeat this process until a total of 10 mL of 30% H_2O_2 has been added to the sample.

10.11. Add 5 mL of high-purity concentrated HCl and 10 mL of ASTM Type I water. Return the covered beaker to the hot plate and heat for an additional 15 min,

making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry.

10.12. Rinse the beaker walls and watch glass with ASTM Type I water and, when necessary, filter the sample with the Nalgene filter apparatus to remove any undissolved material.

10.13. Rinse the filter several times with 10–15 mL portions of ASTM Type I water and bring the final volume to 100 mL with ASTM Type I water. Record the final sample volume in the logbook.

10.14. Swirl the solution until it is homogeneous.

10.15. Label two centrifuge tubes with the sample number and pour approximately equal 50-mL volumes into the centrifuge tubes. One tube will be for FAAS analysis and the other will be for ICPOES analysis.

10.16 The diluted digestate contains approximately 3–5% (v/v) HCl and 3-5% (v/v) HNO_3 and is now ready for spectrochemical analysis. Withdraw aliquots of appropriate volume and add any required matrix modifier or reagent before analysis.

11. Calculations

11.1. Samples diluted by the instrument operator must be corrected by applying the correct dilution factor before the results are calculated and reported.

11.2. The corrected metal concentration, A, is used to calculate metal concentration as follows:

$$\text{Metal Concentration, } \mu g/g = \frac{(A - B)}{C},$$

where A = metal concentration reported from spectrometer, after dilution correction (μg/mL),
B = volume of diluted digestate (mL), and
C = mass of sample used (g).

11.3. Samples digested without drying must be corrected for percent moisture as follows:

$$\text{Metal Concentration, } \mu g/g = U \times \frac{W}{C} ,$$

where U = metal concentration reported as wet weight (μg/g),
W = wet weight of the sample (g), and
C = dry weight of sample (g).

12. Proper Waste Disposal Practices

12.1. Solid waste.

12.1.1. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

12.1.2. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

12.1.3. If CST-17 determines that the hazardous or radioactive components of the solid waste are below the level of concern, dispose of the waste as ordinary laboratory trash.

12.1.4. If CST-17 determines that the solid waste is hazardous or radioactive, request pickup of the contaminated waste as described in Section 12.3.

12.2. Liquid waste.

12.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a glass jar in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

12.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace-metal waste.

12.2.3. Periodically request pickup of the bottle as described in Section 12.3. Keep the bottle in the secondary containment tray until pickup by CST-17.

12.3. Waste pickup.

12.3.1. Request pickup of solid or liquid waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

12.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

13. Source Material

13.1. "Test Methods for Evaluation of Solid Waste: Laboratory Manual of Physical and Chemical Methods," EPA Report No. SW-846 (November 1986).

13.2. U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (rev. March 1983).

13.3. U.S. Environmental Protection Agency, "Methods for the Determination of Metals in Environmental Samples," EPA-600 4-91/010 (June 1991).

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TABLE I. EPA METHODS BY WHICH SAMPLES PREPARED WITH THIS PROCEDURE MAY BE ANALYZED.

	FAAS Methods		ICPOES Methods	
Analyte	EPA 200 Series	SW-846 7000 Series	EPA 200 Series	SW-846 6000 Series
Aluminum	202.1	7020	200.7	6010
Arsenic	—	—	200.7	6010
Barium	208.1	7080	200.7	6010
Beryllium	210.1	7090	200.7	6010
Cadmium	213.1	7130	200.7	6010
Calcium	215.1	7140	200.7	6010
Chromium	218.1	7190	200.7	6010
Cobalt	219.1	7200	200.7	6010
Copper	220.1	7210	200.7	6010
Iron	236.1	7380	200.7	6010
Lead	239.1	7420	200.7	6010
Magnesium	242.1	7450	200.7	6010
Manganese	243.1	7460	200.7	6010
Molybdenum	246.1	7480	200.7	6010
Nickel	249.1	7520	200.7	6010
Potassium	258.1	7610	200.7	6010
Selenium	—	—	200.7	6010
Sodium	273.1	7770	200.7	6010
Thallium	279.1	7840	200.7	6010
Vanadium	286.1	7910	200.7	6010
Zinc	289.1	7950	200.7	6010

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Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance

Los Alamos
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The page numbering convention used in this manual consists of the specific procedure number (shown at left in list below) followed by the page number for that procedure. Thus, QCI110-2 is page two of procedure QCI110. The right column in the list below gives each procedure's status or effective date.

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QCO122 High Explosives on Soil—QC Sample Preparation 03/95

QCO130 Organic Compounds on Tubes and Badges—QC Sample Preparation . . . 12/94

QCO140 Pesticides on Soil—QC Sample Preparation 10/94

QCO150 Pesticides in Water—QC Sample Preparation 10/94

QCO160 Polychlorinated Biphenyls on Florisil Tubes—
QC Sample Preparation . . . . . In Progress

QCO170 Polychlorinated Biphenyls in Oil—QC Sample Preparation 10/94

QCO180 Polychlorinated Biphenyls in Water—QC Sample Preparation 10/94

QCO190 Polychlorinated Biphenyls on Soil—QC Sample Preparation 10/94

QCO200 Polychlorinated Biphenyls on Swipes—QC Sample Preparation 10/94

QCO210 Semivolatile Organic Compounds on Soil—QC Sample Preparation 12/94

QCO220 Semivolatile Organic Compounds in Water—QC Sample Preparation . . . 12/94

QCO225 Total Petroleum Hydrocarbons on Soil—QC Sample Preparation 07/93

QCO230 Volatile Organic Compounds on Charcoal Tubes—
QC Sample Preparation . . . . . In Progress

QCO240 Volatile Organic Compounds in Oil—QC Sample Preparation . . . In Progress

QCO250 Volatile Organic Compounds on Soil—QC Sample Preparation 12/94

QCO260 Volatile Organic Compounds in Water—QC Sample Preparation 12/94

Quality Control Analytical Procedures - Radiochemistry

QCR100 Americium-241 in Urine—QC Sample Preparation 03/95

QCR105 Americium-241 on Soil—QC Sample Preparation 06/95

QCR110 Cesium-137 on Soil—QC Sample Preparation 06/95

QCR120 Cesium-137 on Vegetation Ash—QC Sample Preparation 06/95

QCR130 Cesium-137 in Water—QC Sample Preparation 06/95

QCR138 Gross Alpha and Gross Beta on Filter Media—QC Sample Preparation . 03/95

QCR140 Gross Alpha and Gross Beta on Soil—QC Sample Preparation 08/95

QCR150 Gross Alpha and Gross Beta in Water—QC Sample Preparation 09/95

QCR153 Gross Gamma on Soil—QC Sample Preparation . . . . . Retired

QCR155 Gross Gamma in Water—QC Sample Preparation . . . . . Retired

QCR160 Plutonium and Americium on Soil—QC Sample Preparation 07/95

QCR165 Radionuclides on Fecal Material—QC Sample Preparation 06/95

QCR170 Radionuclides on Vegetation Ash—QC Sample Preparation 07/95

QCR180 Plutonium and Americium in Water—QC Sample Preparation 09/95

QCR190 Plutonium-238 in Urine—QC Sample Preparation 03/95

QCR200 Plutonium-239 in Urine—QC Sample Preparation 03/95

QCR210 Radionuclides on Filter Media—QC Sample Preparation 08/95

QCR220 Radium-226 in Water—QC Sample Preparation 08/95

QCR230 Strontium-90 on Soil—QC Sample Preparation 09/95

QCR240 Strontium-90 in Water—QC Sample Preparation 01/95

QCR250 Tritium and Percent Moisture on Soil—QC Sample Preparation 11/95

QCR260 Tritium in Urine—QC Sample Preparation 03/95

QCR270 Tritium in Water—QC Sample Preparation 09/95

QCR280 Uranium in Soil—QC Sample Preparation . . . . . Retired

QCR290 Uranium-235 in Urine—QC Sample Preparation . . . . . Retired

QCR300 Uranium-238 in Urine—QC Sample Preparation . . . . . Retired

Miscellaneous Procedures

General Procedure for Cleaning Laboratory Equipment . . . . . In Progress

QCM200 Preparation of a Vegetation Ash Matrix 09/94

Quality Control Analytical Procedures - Intercomparison Studies

QCS100 EPA Air Filter Performance Evaluation Study 07/95

QCS110 DOE Beryllium Intercomparison Study Procedure 04/95

QCS120 EPA Drinking Water Study 09/95

QCS130 EPA Gamma in Water Performance Evaluation Study 07/95

QCS140 EPA Gross Alpha and Beta in Water Intercomparison Study 06/95

QCS150	EPA Blind A and B Performance Evaluation Study	08/95
QCS160	NPDES Study	In Progress
QCS170	NIOSH PAT Program	08/95
QCS180	EPA Plutonium in Water Performance Evaluation Study	09/95
QCS190	EML Quality Assessment Program	In Progress
QCS200	EPA Radionuclides in Milk Intercomparison Study	07/95
QCS210	EPA Radium in Water Performance Evaluation Study	Retired
QCS220	EPA Strontium in Water Performance Evaluation Study	07/95
QCS230	EPA Tritium in Water Performance Evaluation Study	07/95
QCS240	EPA Uranium-Radium in Water Intercomparison Study	06/95
QCS250	EPA Water Pollution Study	In Progress

BERYLLIUM AND LEAD FOR VEGETATION ASH — QC SAMPLE PREPARATION

Analyte: Beryllium, lead	**Method No.:** QCI100
Matrix: Soil	**Spike Range:** Be 10–20 μg/g Pb 20–100 μg/g
Procedure: Inductively coupled plasma–mass spectrometry (ICPMS)	**Accuracy and Precision:** Be 100% ± 4.0%RSD Pb 100% ± 6.4%RSD
Effective Date: 03/22/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the standards listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Vegetation ashes were tested for use as a suitable matrix for quality control (QC) samples for the analysis of Be and Pb. No vegetation ash samples were acceptable because of generally high Be and low Pb recovery from the spiked ash samples. Although it is desirable to match the matrix of the QC sample to that of the samples to be analyzed, it has not yet been possible to match the matrix for this determination.

1.2. A soil with a certified Pb concentration in the desired spike range and a low noncertified Be concentration was chosen from our library of reference materials. This material is overspiked with Be and used as a QC sample for the analysis of Be and Pb in vegetation ash.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. Propagated error for beryllium.

2.1.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 4.0% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.2. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.3. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 ,$$

where SD_T = RSD (% error),
R^2_M = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
R^2_{M3} = relative variance of balance.

2.2. Propagated error for lead.

2.2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the balance. An RSD of 6.4% has been calculated for the calibration and weighing process based on the following function.

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = calibration error, and
M2 = weighing error.

2.2.2. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} \quad ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.2.3. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_M = relative variance of standard, and
R^2_{M2} = relative variance of balance.

2.3. Analysis by ICPMS of QC samples prepared during 1989 and 1990 using this procedure (N = 2) gave a mean recovery of 115% ± 2% for Be and 82% ± 4% for Pb at the 1-σ level. The data are published in Source Materials 10.1 and 10.2.

3. Collection and Storage of Samples

3.1. QC soil samples for the determination of Be and Pb are stored in Teflon beakers at room temperature pending analysis.

4. Apparatus

4.1. Beakers: 250-mL, Teflon.

4.2. Autopipette: 100-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Balance: 200-g minimum capacity, 0.1-mg accuracy.

4.5. Spatula.

4.6. Aluminum foil.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. No reagents are required.

6. Calibration and Standards

6.1. The soil selected as a matrix for Be and Pb QCs should have a certified Pb concentration (28.2 $\pm$ 1.8 μg/g) in the desired range and a noncertified Be concentration (1.5 μg/g) of less than 5 μg/g, such as National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1646.

6.2. Obtain a standard such as the 1000-μg/mL Be solution from Spex Industries, Inc. (3880 Park Avenue, Edison, NJ 08820) and dilute to 100 μg/mL to overspike the certified soil.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. With each set of certified soil QC samples overspiked with Be, submit 0.25 g of the same certified soil not overspiked with Be to determine the Be concentration in the certified soil matrix. This will later be subtracted by the analyst from the Be concentration of the overspiked QC sample.

7.2. Place a Teflon beaker on the balance. Tare the balance.

7.3. Accurately weigh 0.25 g of the selected soil into the beaker. Record the weight of the soil on the beaker for reference by the analyst.

7.4. Spike an aliquot of 100-μg/mL Be standard solution on the soil so that the concentration of the Be overspike, minus the Be concentration present in the reference material, falls into the desired spike range.

7.5. Accurately weigh an additional 0.25 g of the reference material to be used to determine the amount of Be present in the reference material and mark it as the nonspiked sample.

7.6. Because a paper label does not adhere well to a Teflon beaker, write the QC sample number on the beaker. Destroy the paper label associated with the sample number used.

7.7. Cover the beaker with aluminum foil and store at room temperature pending analysis.

7.8. The concentration of Pb in the QC sample is the certified Pb concentration listed for the reference material.

7.9. The concentration of Be in the QC sample is the concentration of the overspike only. The analyst determines the Be concentration in the unspiked certified soil and subtracts that concentration from the total Be concentration in the overspiked QC sample to obtain the concentration of the Be overspike.

7.10. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the certified concentration and uncertainty of Pb in the reference material as the concentration of Pb in the QC sample (μg/g).

8.2. Record the concentration of Be in the QC sample as the concentration of the Be overspike only, not as the sum of the Be overspike and the noncertified Be concentration in the soil matrix material (μg/g). The total Be concentration equals the Be concentration in the sample overspike plus the Be concentration of the certified soil.

8.3. Calculate spike concentration as in the following example.

8.3.1. If 0.2505 g of NIST SRM 1646 with a certified Pb concentration of 28.2 $\pm$ 1.8 μg/g and a noncertified Be concentration of 1.5 μg/g is overspiked with 30 μL of a 100-μg/mL Be standard, the concentration of Pb in the QC sample will be 28.2 μg/g and the concentration of the Be overspike in the QC sample will be 12 μg/g. Multiply the result by the RSD calculated in Steps 2.1 and 2.2 to obtain the uncertainty.

$$\frac{(100\ \mu g/mL)\ (1\ mL/1000\ \mu L)\ (30\ \mu L)}{0.2505\ g} = 12\ \mu g/g$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, complete the appropriate paperwork on a case-by-case basis.

9.1.2.1. Complete a Waste Profile Form (WPF) describing the solid waste and send it to Waste Services (CST-17) for review.

9.1.2.2. If the CST-17 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If the CST-17 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a coated glass bottle in a secondary containment tray. Keep it segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace metal waste.

9.2.3. Open the bottle only for the period of time necessary to add waste.

9.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by the CST-17.

9.2.5. Label a new bottle for further use.

9.3. Waste pickup.

9.3.1. Request pickup by CST-17 of liquid waste containing trace metals using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 1646, Estuarine Sediment" (National Institute of Standards and Technology, Washington, DC, June 1982).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

MERCURY ON TUBES — QC SAMPLE PREPARATION

Analyte: Hg	**Method No.:** QCI115
Matrix: Sorbent tube	**Spike Range:** 0.05–0.5 μg/tube
Procedure: Cold vapor atomic absorption (CVAA)	**Accuracy and Precision:** 100% $\pm$ 3.2% RSD
Effective Date: 02/25/93	**Authors:** Michael N. Jasperson Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.2 for proper waste disposal practices.

1. Principle of Method

1.1. A tube containing a sorbent material is spiked with a Hg standard.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with use of the microsyringe, balance, and volumetric flask. A relative standard deviation (RSD) of 3.2% at the 1-σ level has been calculated for the error of the standard and for the pipetting, dilution, and spiking process based on the following function:

$$D = \frac{M1 \times M2 \times M4}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = pipetting error,
M3 = dilution error, and
M4 = spiking error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of autopipette,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe, and
100 = factor to convert to percentage.

2.2. Analysis by cold vapor atomic absorption (CVAA) of QC samples prepared during 1993 using this procedure (n=5) gave a mean recovery of 111% ± 12% at the 1-σ level.

3. Collection and Storage of Samples

3.1. Samples are prepared on-demand and stored at room temperature.

4. Apparatus

4.1. Volumetric flasks: 5- and 25-mL.

4.2. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Graduated cylinder: 25-mL.

4.5. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.6. Spatula.

4.7. Weighing dish: small, polyethylene.

4.8. Sorbent tube: Hopcalite or equivalent.

4.9. Labels printed with QC sample numbers.

5. Reagents

5.1. Nitric acid (16 M, ultrapure) suitable for trace metal analysis.

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testing and Materials (ASTM) Types I, II, or III and free of interferences with the analytical method.

5.3. Potassium dichromate (analytical reagent-grade).

6. Calibration and Standards

6.1. Spectroscopy-grade Hg standard solution, 10-μg/mL concentration preferred. More concentrated standards (such as those supplied by Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820) may be diluted to a Hg concentration of 10 μg/mL.

6.2. Prepare a stabilizing solution for the Hg with a $Cr_2O_7^{=}$ concentration of 50 mg/mL.

6.2.1. Tare a small polyethylene weighing dish on the balance.

6.2.2. Accurately weigh 341 $\pm$ 2 mg of analytical-grade $K_2Cr_2O_7$ into the weighing dish.

6.2.3. Use reagent water to quantitatively rinse the $K_2Cr_2O_7$ into a 5-mL volumetric flask and to dilute the solution to volume. Mix by inversion.

6.2.4. Calculate the $Cr_2O_7^{=}$ concentration of the stabilizing solution as in the example in Step 8.1.

6.3. Prepare a 10-μg/mL Hg standard solution from a 1000-μg/mL standard solution.

6.3.1. Place 15 mL of reagent water into a 25-mL volumetric flask.

6.3.2. Add 2.5 mL of ultrapure nitric acid to the water in the flask to produce a final acid concentration of 10% by volume.

6.3.3. Add 50 μL of the stabilizing solution with a $Cr_2O_7^=$ concentration of 50 mg/mL to the acidified water to produce a $Cr_2O_7^=$ concentration of 0.01% by weight.

CAUTION: The nitric acid and $Cr_2O_7^=$ stabilizing solution must be added to the water before the mercury spike to prevent the immediate loss of Hg.

6.3.4. Add 250 μL of a 1000-μg/mL Hg standard solution to the water in the flask.

6.3.5. Dilute to volume with reagent water. Mix by inversion.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed.

7.2. Use the same size sorbent tube as that of the field samples submitted.

7.3. Break off the tip of the entrance end of the sorbent tube. The entrance end is the end with the glass wool plug over the sorbent material bed and an air space between the end of the tube and the sorbent material bed.

7.4. Using a syringe, spike a volume of the Hg standard onto the sorbent material bed to reach the desired spike range. Spike the standard beginning in the middle of the sorbent material bed and drawing the syringe needle toward the glass wool plug at the top of the bed as the spiking is completed. The entire volume of the spike solution should be on the sorbent material bed and not on the walls of the sample tube.

7.5. Cap both ends of the sample tube with the plastic tube caps and wrap Teflon tape around the broken end.

7.6. Label the tube with a QC sample number.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the $Cr_2O_7^{=}$ concentration of the stabilizing solution using the following atomic weights and example.

8.1.1. Atomic weights: K = 39.1, Cr = 52.0, and O = 16.0.

8.1.2. If 341.0 mg of $K_2Cr_2O_7$ is dissolved in 5 mL of reagent water, the $Cr_2O_7^{=}$ concentration in the stabilizing solution is 50 mg/mL.

$$\frac{\left(\frac{216.0 \text{ g } Cr_2O_7^{=}}{294.2 \text{ g } K_2Cr_2O_7}\right)(341.0 \text{ mg } K_2Cr_2O_7)}{5 \text{ mL}} = 50 \text{ mg } Cr_2O_7^{=}/\text{mL} \quad .$$

8.2. Calculate Hg spike concentrations as in the following example.

8.2.1. If 15 μL of a 10-μg/mL Hg standard is spiked into a sorbent tube, the Hg concentration in the sample is 0.15 μg/tube. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(10 \ \mu\text{g/mL})\ (1 \text{ mL}/1000 \ \mu\text{L})\ (15 \ \mu\text{L})}{\text{tube}} = 0.15 \ \mu\text{g/tube} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not normally generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, complete the appropriate paperwork on a case-by-case basis.

9.1.2.1. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

9.1.2.2. If CST-17 determines that the solid waste is contaminated below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.2.3. If CST-17 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a coated glass bottle in a secondary containment tray. Keep it segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. Open the bottle only for the period of time necessary to add waste.

9.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.5. Label a new bottle for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. C. Feldman, "Preservation of Dilute Mercury Solutions," *Anal. Chem.* **46**, 99-102 (1974).

10.2. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp.45-47.

OIL AND GREASE IN WATER — QC SAMPLE PREPARATION

Analyte: Oil and grease	**Method No.:** QCI120
Matrix: Water	**Spike Range:** 20–100 mg/L
Procedure: Gravimetry	**Accuracy and Precision:** 100% ± 0.8% RSD
Effective Date: 02/02/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Reagent water is spiked with vegetable oil to prepare a quality control (QC) sample for oil and grease in water.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the balance. Since the analyst takes the sample to dryness, it is not necessary to dilute the sample to exactly one liter, and the assumption is made that L = 1. A relative standard deviation (RSD) of 0.8% at the 1-σ level has been calculated for the weighing process based on the following function:

$$D = \frac{M1}{L} ,$$

where D = calculated result,
M1 = weighing error, and
L = 1.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . .(variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} / L} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of balance, and
L = 1.

2.2. Analysis by gravimetry of QC samples prepared from 1990 through 1994 using this procedure gave the following recoveries. The data are published in Source Materials 10.1 through 10.3.

TABLE I. SPIKE RECOVERY DATA FOR OIL/GREASE IN WATER

	Mean ± std dev (%)	Number of Samples
1990	91 ± 8	13
1991	95 ± 4	8
1992	94 ± 12	14
1993	94 ± 8	11
1994	92 ± 8	5

3. Collection and Storage of Samples

3.1. QC samples are prepared in 1-L jars with Teflon-lined lids and are refrigerated pending analysis.

4. Apparatus

4.1. Glass jars: 1-L, with Teflon-lined screw-cap lids.

4.2. Weighing dish: small, polyethylene.

4.3. Sample dropper: glass or polyethylene.

4.4 Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.5. Labels printed with QC sample numbers.

5. Reagents

5.1. Freon. Used to transfer the oil into the water.

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testing and Materials (ASTM) Type I, II, and III and free of interferences with the analytical method.

6. Calibration and Standards

6.1. Spike QC samples with a pure vegetable oil, such as one used in cooking.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 1-L oil-and-grease-in-water QC sample in a glass jar.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include 3 mL of Freon in 1 L of reagent water in a jar with a Teflon-lined lid to be used as a blank.

7.3. Place a small polyethylene weighing dish on the balance. Tare the balance.

7.4. Using a sample dropper, add vegetable oil to the weighing dish to reach the desired spike range and record the weight.

7.5. Fill a 1-L glass jar nearly full of reagent water. The analyst will use the entire sample, assuming the volume to be 1 L.

7.6. Using a clean sample dropper and less than 3 mL of Freon, quantitatively transfer the oil from the weighing dish into the water in the 1-L jar.

7.7. Place the Teflon-lined lid on the jar and label it with a QC sample number.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter the information into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of oil and grease in the water as mg/L.

8.2. Calculate the spike concentration as in the following example.

8.2.1. If 50 mg of vegetable oil is quantitatively transferred into 1 L of reagent water, the oil and grease concentration in the water is 50 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

9. Proper Waste Disposal Practices

9.1. The hazardous components of an oil-and-grease sample are organic compounds. Dispose of waste as waste contaminated with organic compounds.

9.2. Solid waste.

9.2.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples contaminated with organic compounds) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.2.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.2.5. Place a new plastic bag into the waste can for continued use.

9.2.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.2.7. Send a reference to the current Waste Profile Form (WPF) describing the waste along with the sealed bag.

9.2.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.2.9. The larger container has a sealing cover. Open the can only for the period of time necessary to add waste.

9.2.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.3. Liquid waste.

9.3.1. Accumulate liquid waste containing organic compounds (such as rinses from syringes, out-of-date stock solutions, excess QC samples, and incorrectly spiked samples) in a covered metal can in a secondary containment tray and keep segregated from PCB-contaminated liquid waste.

9.3.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.3.3. Open the can only for the period of time necessary to add waste.

9.3.4. When the can is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.3.5. Label a new can for further use.

9.4. Waste pickup.

9.4.1. Request CST-17 to pick up a full container or can of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.4.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. B. Brooks, W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, N. L. Koski, E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1179-72 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN BULK MATERIALS — QC SAMPLE PREPARATION

Analytes: Ag, As, Ba, Cd, Cr, Hg, Ni, Pb, Se, Tl, Zn	**Method No.:** QCI135
Matrix: Oil	**Spike Range:** 0.2–20 μg/g, dependent on the analytical method (see Table I)
Procedure: Analysis by ICPMS, ICPAES, ETVAA, or CVAA	**Accuracy and Precision:** 100% ± 2.0% RSD
Effective Date: 02/08/93	**Authors:** Michael N. Jasperson Nancy Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.1 for proper waste disposal practices.

1. Principle of Method

1.1. Obtain or prepare single-element or multielement standards in oil.

1.2. The concentration of the working standards should be approximately 100 μg/g.

1.2.1. As, Se, and Hg standards may be obtained as single-element standards because of their relative instability at low concentrations in oil.

1.3. Spike an aliquot of each standard into a vial to reach the desired spike range. Dilute as necessary with base oil.

1.3.1. As, Se, and Hg quality control (QC) samples may be prepared separately because of their relative instability at low concentrations in oil.

1.4. The methods of analysis are inductively coupled plasma-mass spectrometry (ICPMS), inductively coupled plasma-atomic emission spectroscopy (ICPAES), electrothermal vaporization atomic absorption (ETVAA) spectroscopy, or cold vapor atomic absorption (CVAA) spectrometry.

1.5. The QC spike range depends on the analytical method. Refer to Table I for the spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN OIL				
Analyte	ICPMS (μg/g)	ICPAES (μg/g)	ETVAA (μg/g)	CVAA (μg/g)
Ag	0.2 - 12.5	1.0 - 20.0		
As	0.2 - 12.5		0.2 - 12.5	
Ba	0.2 - 12.5	1.0 - 20.0		
Cd	0.2 - 12.5	1.0 - 20.0		
Cr	0.2 - 12.5	1.0 - 20.0		
Hg				1.0 - 5.0
Ni	0.2 - 12.5.	1.0 - 20.0		
Pb	0.2 - 12.5	1.0 - 20.0		
Se	0.2 - 12.5		0.2 - 12.5	
Tl	0.2 - 12.5	1.0 - 20.0		
Zn	0.2 - 12.5	1.0 - 20.0		

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with the use of the analytical balance. A relative standard deviation (RSD) of 2% at the 1-σ level has been calculated for the error of the standard and for the weighing and dilution process based on the following function:

$$D = \frac{M1 \times M2 \times M4}{M3 \times M5} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error, see 6.2.1,
M3 = weighing error, see 6.2.6,
M4 = weighing error, see 7.3.1, and
M5 = weighing error, see 7.3.4.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate RSD deviation using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.1.3. All variables contributing to the error associated with the preparation of these QC samples were considered. The largest errors were used in the error propagation calculations.

2.2. Results of analysis by ICPMS, ICPAES, ETVAA, and CVAA of QC samples prepared between 1993 and 1994 using these procedures are summarized in Table II below.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN BULK MATERIAL

Analyte	1993 Mean ± std dev (%)			N[a]	1994 Mean ± std dev (%)			N[a]
Ag	104	±	2	4	86	±	20	10
As	68	±	34	3	88	±	22	10
Ba	103	±	11	4	106	±	8	10
Cd	100	±	3	4	94	±	7	10
Cr	104	±	3	4	107	±	10	10
Hg	82	±	2	4	92	±	6	10
Ni	99	±	3	2	121	±	20	7
Pb	103	±	6	4	126	±	38	8
Se	81	±	30	4	92	±	23	10
Tl	18	±	4	2		—		—
Zn		—		—		—		—

N[a] = number of samples.

3. Collection and Storage of Samples

3.1. The QC samples are prepared as close as possible to the time of analysis because all elements are unstable at low concentrations.

4. Apparatus

4.1. Glass vials: 5-mL, with Teflon-lined lids.

4.2. Pasteur pipettes: polyethylene, disposable.

4.3. Bottles: 60-mL, high-density polyethylene.

4.4. Bottles: 60-mL, amber high-density polyethylene.

4.5. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. Conostan 75 Base Oil or equivalent: Conostan, Inc., P.O. Box 1267, Ponca City, OK 74603.

5.2. Conostan stabilizer or equivalent: Conostan, Inc., P.O. Box 1267, Ponca City, OK 74603.

6. Calibration and Standards

6.1. Obtain single-element or multielement standards in oil with a concentration of approximately 100 μg/g.

6.2. Alternatively, prepare 100-μg/g metals-in-oil standards from 5000-μg/g metals-in-oil standards.

6.2.1. Add 500 mg of a 5000-μg/g metals-in-oil standard to a clean, tared, 60-mL high-density polyethylene bottle.

6.2.2. Record the mass added. **DO NOT** tare the balance.

6.2.3. Repeat Step 6.2.1 for each of the remaining 5000-μg/g standards desired in the dilution.

6.2.4. Add 150–200 mg of commercial stabilizer solution to achieve 0.6–0.8% by weight of stabilizer after dilution.

6.2.5. Record the mass added. **DO NOT** tare the balance.

6.2.6. Add the manufacturer's 75 Base Oil to bring the total mass to 25.0 g.

6.2.7. Cap and mix the standard by inversion.

6.2.8. Label the bottle with information identifying the standard.

6.2.9. Prepare the silver standard in an amber polyethylene bottle or an uncolored polyethylene bottle completely wrapped in aluminum foil to protect the silver from photodegradation.

6.3. Check the concentration of the 100-μg/g As, Se, and Hg standards periodically. Discard and replace a standard when degradation is noted.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed as close to the time of analysis as possible because all of the metals are relatively unstable at the low concentrations made for QCs. Periodically omit one or more of the metal analytes from the QC sample as a blank for that metal.

7.2. Determine which analytical method will be used. Select the spike range for the method from Table I.

7.3. Preparation of QC samples containing all metals except mercury.

7.3.1. Add standards gravimetrically. Weigh an aliquot of a 100-μg/g single-element or multielement standard into a 5-mL glass vial with Teflon-lined lid to reach the desired spike range determined from Table I.

7.3.2. Record the standard used and mass added. **DO NOT** tare the balance.

7.3.3. Repeat Steps 7.3.1 and 7.3.2 for each desired standard.

7.3.4. Add the manufacturer's 75 Base Oil to bring the total mass of the QC sample to 3 g.

7.3.5. Cap the vial and mix by inversion.

7.4. Preparation of a mercury QC sample.

7.4.1. Weigh an aliquot of the 100-μg/g Hg standard into a 5-mL glass vial with Teflon-lined lid to reach the desired spike range determined from Table I.

7.4.2. Record the mass added. **DO NOT** tare the balance.

7.4.3. Add 18–24 mg of commercial stabilizer solution to achieve 0.6–0.8% by weight of stabilizer after dilution.

7.4.4. Record the mass added. **DO NOT** tare the balance.

7.4.5. Add the manufacturer's 75 Base Oil to bring the total mass to 3 g.

7.4.6. Cap the vial and mix by inversion.

7.5. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of each metal in the QC sample as μg/g.

8.2. Calculate spike concentrations for each metal in the QC sample as in the following example.

8.2.1. If 0.2672 g of 100-μg/g As standard is diluted to 3.0027 g with 75 Base Oil, the concentration of As in the sample is 8.9 μg/g. Multiply the result by the RSD calculated in Step 2.1. to obtain the uncertainty.

$$\frac{(0.2672\ \text{g})\ (100\ \mu\text{g/g})}{3.0027\ \text{g}} = 8.9\ \mu\text{g/g} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, and empty vials) that has been contaminated with organic compounds in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Liquid waste containing trace metals in oil is accumulated in a polyethylene bottle in a secondary containment tray and kept segregated from any other accumulated waste.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal-in-oil waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste.

9.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals in oil by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS ON FILTER MEDIA — QC SAMPLE PREPARATION

Analyte: Metals	**Method No.:** QCI140
Matrix: Filters	**Spike Range:** 0.01–4000 μg/filter, depending on analyte and analytical method
Procedure: ICPMS, ICPAES, ETVAA, or FAA	**Accuracy and Precision:** 100% ± 3.6% RSD
Effective Date: 01/01/84	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. One or more standard solutions of single metals are spiked onto filter papers, preferably of the same type used to collect the samples.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. The methods of analysis for these filters are inductively coupled plasma–mass spectrometry (ICPMS), inductively coupled plasma–atomic emission spectrometry (ICPAES), flame atomic absorption (FAA) spectroscopy, or electrothermal vaporization atomic absorption (ETVAA) spectroscopy.

1.4. The QC spike range depends on the metal of interest and the method of analysis. Refer to Table I below for spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS ON FILTER MEDIA				
Analyte	FAA (μg/filter)	ETVAA (μg/filter)	ICPAES (μg/filter)	ICPMS (μg/filter)
Ag	2.5–10			0.2–1.0
Al	10–30		40–4000	
As		0.1–1.0	15–300	
Au				0.2–1.0
Ba			10–100	
Be	1–10		10–100	
Bi				0.05–0.5
Ca	10–30		100–500	
Cd		0.01–0.1	4–400	
Co			2–50	
Cr	5–20		10–100	
Cu	5–20		6–600	0.05–2
Fe	5–20		10–100	
Li	2–10		10–100	
Mn	5–20			
Mo			10–100	
Ni	5–20		10–100	0.2–1.0
Pb	5–20	0.2–1.0	10–100	0.05–0.2
Sb			20–300	
Se			20–300	
Sn		0.2–1.0		
Sr				1–5
Ta	5–15			1–5

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS ON FILTER MEDIA (cont)

Analyte	FAA (μg/filter)	ETVAA (μg/filter)	ICPAES (μg/filter)	ICPMS (μg/filter)
Th				0.05–0.5
Tl		0.1–0.6	10–100	0.01–0.05
U				1–5
Zn			2–30	0.2–1.0

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with use of the pipette. A relative standard deviation (RSD) of 3.6% at the 1-σ level has been calculated for the error of the standard and for the spiking process based on the following function:

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = standard error, and
M2 = spiking error.

2.1.1. Calculate relative variance using the following equation:

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} \quad ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation:

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
100 = factor to convert to percentage.

2.1.3. If two pipettes ($P_1 + P_2$) are used to add the analyte to the filter paper, use the following equation to calculate the pipetting error:

$$R_{M2} = \frac{\sqrt{\sigma_1^2 + \sigma_2^2}}{P_1 + P_2} ,$$

where σ_1 = standard deviation of first pipette,
σ_2 = standard deviation of second pipette,
P_1 = mean of first pipette, and
P_2 = mean of second pipette.

Square R_{M2} and substitute this value in the equation in Step 2.1.2 to calculate the percent RSD for the use of two pipettes.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by ICPMS, ICPAES, ETVAA, and FAA are summarized in Table II below. Recovery data are published in Source Material 10.1.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS ON FILTER MEDIA

Analyte	1992 Mean ± std dev (%)			N	1993 Mean ± std dev (%)			N	1994 Mean ± std dev (%)			N
Ag	89.3	±	8.5	4	104.7	±	8.6	10	78.9	±	24.4	12
Al		—			107.3	±	9.6	5	115.2	±	23.9	8
As	81.6	±	3.0	3	77.3	±	8.2	4	99.5	±	9.4	16
Ba	98.1	±	4.9	8	101.7	±	3.7	10	107.5	±	14.2	5
Be	101.6	±	8.9	278	104.4	±	9.3	314	101.9	±	9.7	19
Bi	113.3	±	4.7	2	—					—		4
Ca	98.8	±	1.7	2	121.1	±	20.4	2	105.5	±	11.3	5
Cd	100.7	±	6.5	39	102.7	±	9.5	47	96.8	±	10.1	41
Co		—			—				103.8	±	11.0	7
Cr	113.6	±	18.2	30	103.8	±	6.5	35	99.7	±	16.7	28
Cu	123.8	±	20.5	7	108.9	±	16.8	8	107.0	±	12.4	4
Fe	67.8	±	80.9	2	111.7	±	14.6	6	109.7	±	16.9	6
Li		—			106.0	±	17.8	2	99.6	±	6.7	5
Mg	101.7	±	2.4	2	106.2	±	13.1	4	101.0	±	11.4	5
Mn		—			123.1	±	27.7	8	99.4	±	9.3	6
Mo		—			52.2	±	11.7	2	109.1	±	31.7	5
Ni	98.6	±	6.6	21	110.4	±	9.5	14	106.6	±	10.6	13
Pb	103.3	±	7.4	169	106.7	±	11.4	195	100.1	±	14.6	11
Sb		—			120.2	±	2.7	2	109.0	±	3.4	3
Se	131.3	±	7.9	2	97.7	±	19.7	3	104.4	±	9.7	2
Sn	99.3	±	0.9	2	30.6	±	0.8	2	69.1	±	50.1	6
Sr	89.0	±	1.4	2	116.3	±	23.0	2	105.8	±	13.0	5
Ta	2.1	±	2.4	2	—					—		2
Ti		—			79.4	±	18.8	4	99.2	±	14.2	5
Tl	96.3	±	12.0	7	114.7	±	18.7	9	95.1	±	4.7	7
U	105.1	±	10.5	54	111.4	±	6.1	7	102.6	±	1.2	4
V	115.5	±	3.5	2	93.3	±	9.4	2	96.2	±	6.6	5
Zn	103.0	±	7.2	17	99.8	±	10.5	18	101.9	±	16.6	20

N = Number of samples.

3. Collection and Storage of Samples

3.1. QC samples are dried after spiking and stored in plastic filter containers at room temperature pending analysis.

4. Apparatus

4.1. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.2. Spatula.

4.3. Platinum crucibles: approximately 50-mL capacity, with platinum covers. Each crucible should have a unique identifying number stamped or etched into it.

4.4. Desiccator.

4.5. Beaker: 50-mL, glass.

4.6. Flasks: 100- and 500-mL, volumetric, class A, glass.

4.7. Pipette: 10-mL, volumetric, class A, glass.

4.8. Graduated cylinder: 25-mL.

4.9. Filter paper: usually 1.25-in.-diam, cellulose acetate or paper filters, such as Whatman No. 41 or 42.

4.10. Autopipette: 100-μL, Rainin or equivalent.

4.11. Pipette tips: disposable.

4.12. Microsyringes: 10- and 25-μL capacity, gas-tight.

4.13. Filter containers: plastic.

4.14. Filter support: clean polyethylene bottle caps or beakers or similar support, slightly smaller in diameter than the filters to be spiked.

4.15. Heat lamp.

5. Reagents

5.1. Hydrochloric acid (ultrapure, suitable for trace-metal analysis).

5.2. Nitric acid (ultrapure, suitable for trace-metal analysis).

5.3 Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testing and Materials (ASTM) Type I, II, and III and free of interferences with analytical method.

6. Calibration and Standards

6.1. Use spectroscopy-grade metal standards (100–10,000 μg/mL) such as those from Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820.

6.2. If a more dilute standard is needed to reach the desired spike range, dilute a concentrated standard, taking care to match the type and concentration of acid in the dilution to those in the concentrated standard.

6.3. Solutions of the analyte of interest in the concentration range 100–10,000 μg/mL may be prepared from analytical-grade compounds for use as standards if suitable standard solutions are not readily available.

6.4. Prepare a standard for the determination of total uranium and $^{235}U/^{238}U$ isotopic ratios through ICPMS by dissolving a certified natural U_3O_8 standard, such as National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 950b, in 7.8 M HNO_3. The uranium concentration of the standard should be 1 mg/mL. The $^{235}U/^{238}U$ isotopic ratio of natural uranium is 0.0072.

6.4.1. Use ultrapure HNO_3 and reagent water to prepare the uranium standard solutions. Prepare 7.8 M HNO_3 by diluting 25 mL of concentrated HNO_3 to 50 mL with reagent water. Prepare 1.6 M HNO_3 by diluting 1 mL of concentrated HNO_3 to 10 mL with reagent water. Prepare 1% HNO_3 by diluting 5 mL of concentrated HNO_3 to 500 mL with reagent water.

6.4.2. Weigh 1 g of certified natural U_3O_8 into a platinum crucible. Cover the crucible with the platinum lid.

6.4.3. Heat the U_3O_8 in a muffle furnace at 900°C for 1 h.

6.4.4. Cool the U_3O_8 in a desiccator overnight.

6.4.5. Accurately weigh 590 $\pm$ 1 mg of the U_3O_8 into a 50-mL beaker.

6.4.6. With gentle heating, dissolve the U_3O_8 in 20 mL of 7.8 M ultrapure HNO_3.

6.4.7. Evaporate the solution to near dryness.

6.4.8. Redissolve the residue in 10 mL of 1.6 M HNO_3.

6.4.9. Quantitatively transfer the uranium solution into a 500-mL volumetric flask with 1% HNO_3 and dilute the solution to volume with 1% HNO_3.

6.4.10. Calculate the concentration of the resultant natural uranium standard as in the example in Step 8.1.

6.5. Make a uranium standard with a concentration of 100 μg/mL by diluting the 1 mg/mL uranium standard. Use reagent water and ultrapure HNO_3.

6.5.1. Place approximately 70 mL of reagent water into a 100-mL volumetric flask.

6.5.2. Add 1 mL of concentrated HNO_3 to the flask to achieve a final acid concentration of 1%.

6.5.3. Add 10 mL of the 1 mg/mL natural uranium standard to the volumetric flask using a volumetric pipette.

6.5.4. Dilute the solution to volume with reagent water.

6.5.5. Calculate the concentration of the resultant natural uranium standard. The $^{235}U/^{238}U$ isotopic ratio in the standard is 0.0072.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically include a nonspiked filter to be used as a blank.

7.2. Select a standard solution containing the analyte of interest in a concentration such that a minimum amount of the standard will be needed to reach the desired spike range.

7.3. An autopipette may be used for spike volumes within the acceptable range of the autopipette. Microsyringes should be used for smaller spike volumes.

7.4. The volume of standard solution added to the filter at one time should never be large enough to allow contact of the solution with the filter support, which could cause loss of solution to the support. To add larger volumes of standard, it may be necessary to add the standard in more than one aliquot, allowing the filter to dry after each addition.

7.5. Place a filter paper on a bottle cap, beaker, or similar support so such that most of the filter is within the rim of the support.

7.6. Spike the standard solution onto the filter to reach the desired spike range.

7.7. If more than one analyte will be spiked on the filter, dry the filter after addition of each standard solution.

7.8. Dry the filters under a heat lamp or allow them to air dry.

7.9. Place the dried filters in plastic filter containers segregating the different analyte combinations and concentrations.

7.10. Label each container with a QC sample number.

7.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter the information into the CVS and CVD databases on the VAX.

7.12. National Institute for Occupational Safety and Health (NIOSH) Proficiency Analytical Testing (PAT) intercomparison samples.

7.12.1. Prepare filters using the metals designated by NIOSH as being included in the current set of intercomparison samples. Follow Steps 7.5 through 7.11 above. Refer to Table III for spike ranges.

TABLE III. SPIKE RANGES FOR NIOSH PAT FILTERS

Cr	5–100 μg/filter
Pb	15–100 μg/filter
Cd	5–25 μg/filter
Zn	50–200 μg/filter

7.12.2. Obtain a NIOSH-PAT filter sample from a previous intercomparison round and assign it a QC sample number as an additional QC sample.

7.12.3. Record the sample identification, concentration, and uncertainty supplied by NIOSH for the filter in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.12.4. Place the four QC samples into plastic filter containers or clean cellophane envelopes, label with QC sample numbers, and distribute with the NIOSH-PAT intercomparison samples.

8. Calculations

8.1. Calculate the concentration of the uranium standard solution using the following atomic weights and example.

8.1.1. The atomic weight of U is 238.029, and the atomic weight of O is 16. The molecular weight of U_3O_8 recorded on the bottle label for the NIST SRM U_3O_8 may also be used.

8.1.2. The purity of the NIST U_3O_8 is recorded on the certificate for the SRM used.

8.1.3. If 589.6 mg of 99.968% pure U_3O_8 that has been heated in the muffle furnace is dissolved in acid and diluted to 500 mL, the uranium concentration in the standard will be 1.0 g/L.

$$\frac{\left(\frac{714.087 \text{ g U}}{842.0822 \text{ g } U_3O_8}\right)(0.99968)\ (0.5896 \text{ g})}{(500 \text{ mL})\ (1 \text{ L}/1000 \text{ mL})} = 1.0 \text{ g/L} \quad .$$

8.1.4. The $^{235}U/^{238}U$ isotopic ratio in natural uranium is 0.0072 ± 0.0007.

8.2. Record sample concentrations as mg/filter, μg/filter, or ng/filter.

8.3. Calculate the spike concentration for each metal in the QC sample as in the following example.

8.3.1. If 30 μL of a 100-μg/mL beryllium standard is spiked onto a cellulose acetate filter, the concentration of Be in the QC sample is 3 μg/filter. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(100\ \mu\text{g/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (30\ \mu\text{L})}{\text{filter}} = 3\ \mu\text{g/filter} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form (WPF) describing the solid waste is completed and sent to Waste Services (CST-17) for review.

9.1.2.2. If the CST-17 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If the CST-17 determines that the solid waste is contaminated above the level of concern, pickup of the contaminated waste is requested as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Liquid waste containing hazardous contaminants (such as solutions of trace metals) is accumulated in a coated glass bottle in a secondary containment tray and kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal

Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 950b, Uranium Oxide (U_3O_8)" (National Institute of Standards and Technology, Washington, DC, March 1978).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN NITRIC ACID — QC SAMPLE PREPARATION

Analyte: Metals	**Method No.:** QCI170
Matrix: Water, soil	**Accuracy and Precision:** 100% ± 4.3% RSD
Procedure: ICPMS, ICPAES, FAA, ETVAA, CVAA, or CALC, depending on metal and concentration range	**Spike Range:** 1 μg/L–200 mg/L
Effective Date: 04/01/88	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified water is spiked with standard solutions of metals.

1.2. An acidified water quality control (QC) sample represents the solution resulting from the extraction of the metals from a soil matrix and is analyzed from that point using the same analytical procedure applied to the unknown samples.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed using the same analytical procedure or applicable sections of the procedure.

1.4. Methods of analysis depend on the metal and its concentration. They include inductively coupled plasma–mass spectrometry (ICPMS), inductively coupled plasma–atomic emission spectrometry (ICPAES), flame atomic absorption (FAA) spectroscopy, electrothermal vaporization atomic absorption (ETVAA) spectroscopy, cold vapor atomic absorption (CVAA) spectroscopy, and calculation (CALC) .

1.5. The QC spike range depends on the metal of interest and the method of analysis. Refer to Table I below for spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN NITRIC ACID

Analyte	ETVAA/ICPMS (mg/L)	FAA/ICPAES (mg/L)	CVAA (mg/L)
Al	0.05–0.2	1–200	
Ag	0.01–0.10	0.2–2.0	
As	0.01–0.10	0.1–5.0	
B	0.02–0.20	0.5–30	
Ba	0.01–0.10	0.1–10	
Be	0.01–0.10	0.05–2	
Ca		1–200	
Cd	0.01–0.10	0.1–5	
Co	0.01–0.10	0.1–5	
Cr	0.01–0.10	0.1–5	
Cu	0.01–0.10	0.1–5	
Fe	0.02–0.50	1.0–6	
Hg			0.001–0.010
K	0.02–0.50	1.0–20	
Li	0.01–0.10	0.1–5	
Mg	0.02–0.50	1.0–20	
Mn	0.01–0.10	0.1–5	
Mo	0.01–0.10	0.1–5	
Na	0.02–0.50	1.0–20	
Ni	0.01–0.10	0.1–5	
Pb	0.01–0.10	1.0–20	
Sb	0.01–0.10	0.2–5	
Se	0.005–0.10	0.2–5	
Sn	0.01–0.10	0.2–2	

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN NITRIC ACID (cont)			
Analyte	ETVAA/ICPMS (mg/L)	FAA/ICPAES (mg/L)	CVAA (mg/L)
Sr	0.01–0.10	0.1–5	
Ti	0.01–0.10	1.0–20	
Tl	0.01–0.10	5.0–20	
U	0.01–0.10		
V	0.02–0.10	0.2–20	
Zn	0.01–0.1	0.2–2	

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and the error associated with the use of the pipette and the volumetric flask. A relative standard deviation (RSD) of 4.3% at the 1-σ level has been calculated for the spiking and dilution process based on the following functions.

2.1.1. One dilution of the standard.

2.1.1.1. Use the following function for standards requiring a single dilution:

$$U = \frac{M1 \times M2}{M3},$$

where U = uncertainty,
M1 = standard error,
M2 = spiking error, and
M3 = dilution error.

2.1.1.2. Calculate relative variance for each variable using the following equation:

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.1.3. Calculate percent RSD using the following equation:

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.1.2. Two dilutions of the standard.

2.1.2.1. Use the following function for standards requiring a second dilution:

$$U = \frac{M1 \times M2}{M3} \times \frac{M4}{M5} ,$$

where U = uncertainty of standard,
M1 = standard error,
M2 = first spiking error,
M3 = first dilution error,
M4 = second spiking error, and
M5 = second dilution error.

2.1.2.2. Calculate relative variance for each variable using the following equation:

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2.3. Calculate RSD using the following equation:

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5}} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of first pipette,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of second pipette,
R^2_{M5} = relative variance of second volumetric flask, and
100 = factor to convert to percentage.

2.2. All variables contributing to the error associated with the preparation of these QC samples were considered. The largest errors were used in the error propagation calculations.

2.3 Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by ICPMS, ICPAES, FAA, ETVAA, or CVAA are summarized in Table II. The data are published in Source Material 10.1.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN NITRIC ACID

Analyte	1992 Mean ± std dev (%)			N	1993 Mean ± std dev (%)			N	1994 Mean ± std dev (%)			N
Ag	99.3	±	14.5	355	97.9	±	20.0	375	77.2	±	29.1	218
Al	97.8	±	8.5	248	98.2	±	13.6	194	101.8	±	11.4	163
As	99.2	±	11.8	316	100.7	±	10.8	540	101.2	±	15.8	213
Au		—				—			89.3	±	10.0	4
B	103.5	±	6.4	59	90.6	±	12.1	72	89.5	±	14.8	71
Ba	101.3	±	9.1	349	101.8	±	12.5	434	98.4	±	6.3	248
Be	100.5	±	8.6	355	98.9	±	10.8	461	97.2	±	7.3	235
Ca	100.5	±	7.3	172	101.6	±	9.4	137	101.3	±	10.1	128
Cd	99.6	±	14.8	379	100.2	±	12.0	459	94.2	±	12.3	267
Co	100.7	±	7.8	235	95.2	±	9.3	191	97.4	±	7.9	190
Cr	99.9	±	11.5	394	97.4	±	11.3	482	99.0	±	11.0	285
Cu	99.7	±	10.2	273	102.4	±	8.9	221	98.5	±	8.3	197
Fe	98.8	±	8.8	258	101.4	±	11.1	167	101.3	±	11.4	179
Hg	97.2	±	11.8	332	98.9	±	10.9	427	97.8	±	8.0	237
K	98.0	±	9.0	175	95.3	±	12.0	118	91.7	±	14.3	127
Li	92.3	±	15.3	105	96.4	±	7.1	87	94.2	±	9.0	49
Mg	98.4	±	10.3	213	100.3	±	12.7	135	101.9	±	12.2	138
Mn	98.5	±	7.6	194	99.5	±	10.4	188	97.1	±	8.2	173
Mo	102.2	±	11.7	163	105.0	±	13.2	109	103.9	±	8.6	114
Na	101.7	±	4.9	192	100.5	±	11.8	120	94.4	±	12.6	131
Ni	101.3	±	8.3	341	100.3	±	9.4	385	98.4	±	9.4	247
Pb	99.7	±	13.1	439	102.0	±	13.3	518	97.4	±	13.9	290
Sb	97.9	±	14.6	225	95.5	±	13.9	232	92.4	±	16.0	197
Se	97.3	±	10.9	347	99.3	±	8.4	542	99.9	±	15.7	222
Sn		—			97.0	±	7.2	35	105.3	±	12.9	24
Sr	101.1	±	12.1	122	103.9	±	7.7	104	100.8	±	8.9	99
Th		—			107.3	±	10.3	8	115.4			1
Ti	103.0	±	1.7	4	113.4	±	4.9	2		—		
Tl	98.1	±	12.3	281	100.6	±	12.4	256	96.7	±	16.4	176
U	100.5	±	13.6	287	102.7	±	13.2	138	105.9	±	14.0	117
V	99.0	±	7.4	198	100.2	±	8.9	221	98.2	±	7.8	171
Zn	97.5	±	15.9	252	100.0	±	9.6	252	98.0	±	8.6	203
HARD		—			105.5	±	3.9	3	98.9	±	8.9	9

N = number of samples.

3. Collection and Storage of Samples

3.1. Mercury standard samples must be stored in glass containers with $Cr_2O_7^{=}$ added as a stabilizer. Refer to Method No. QCI200 for the preparation and storage of Hg standard samples.

3.2. If the QC sample contains Ag, it must be protected from light to prevent reduction and subsequent loss of Ag. Store the sample at room temperature in an amber high-density polyethylene bottle or in an uncolored high-density polyethylene bottle completely wrapped in aluminum foil.

3.3. If any of the metal standard solutions contains HCl, it may not be added to a solution containing Ag because the Ag will be lost as insoluble AgCl.

3.4. QC samples are prepared in a volumetric flask and are aliquoted into high-density polyethylene bottles for storage at room temperature pending analysis.

4. Apparatus

4.1. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.2. Spatula.

4.3. Platinum crucible: approximately 50-mL capacity, with platinum cover. The crucible should have a unique identifying number stamped or etched into it.

4.4. Desiccator.

4.5. Beaker: 50-mL, glass.

4.6. Volumetric flasks: 10-, 50-, 100-, and 500-mL, class A, glass.

4.7. Graduated cylinders: 10- and 25-mL.

4.8. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.9. Pipette tips: disposable.

4.10. Volumetric pipettes: 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, and 10-mL, class A, glass.

4.11 Bottles: 125- and 250-mL, high-density polyethylene.

4.12. Aluminum foil.

4.13. Bottles: 125- and 250-mL, amber, high-density polyethylene.

4.14. Labels printed with QC sample numbers.

5. Reagents

5.1. Nitric acid (16 M, ultrapure, suitable for trace-metal analysis).

5.2. Water (18-MΩ/cm or greater resistivity, specified in American Society for Testing and Materials [ASTM] document D1193-91 as ASTM Type I water and referred to as reagent water in this procedure).

5.3. Potassium dichromate (reagent-grade).

6. Calibration and Standards

6.1. Spectroscopy-grade metal standards (100–10,000 μg/mL) from Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820, or equivalent.

6.2. If a more dilute standard is needed to reach the desired spike range, dilute a concentrated standard, taking care to match the kind and concentration of acid in the dilution to those in the concentrated standard.

6.3. Prepare a standard for the determination of Cr in the +6 oxidation state by dissolving reagent-grade $K_2Cr_2O_7$ in reagent water. The Cr^{+6} concentration of the standard should be 1000 μg/mL.

6.3.1. Tare a 50-mL volumetric flask on the balance.

6.3.2. Accurately weigh 141.5 $\pm$ 0.2 mg of analytical-grade $K_2Cr_2O_7$ into the flask.

6.3.3. Dissolve the salt and dilute the standard to volume with reagent water.

6.3.4. Calculate the Cr^{+6} concentration of the standard as in the example in Step 8.1.

6.4. Prepare a standard for the determination of total uranium and $^{235}U/^{238}U$ isotopic ratios through ICPMS by dissolving a certified natural U_3O_8 standard, such as National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 950b, in 7.8 M HNO_3. The uranium concentration of the standard should be 1 mg/mL. The $^{235}U/^{238}U$ isotopic ratio of natural uranium is 0.0072.

6.4.1. Use ultrapure HNO_3 and reagent water to prepare the uranium standard solutions. Prepare 7.8 M HNO_3 by diluting 25 mL of concentrated HNO_3 to 50 mL with reagent water. Prepare 1.6 M HNO_3 by diluting 1 mL of concentrated HNO_3 to 10 mL with reagent water. Prepare 1% HNO_3 by diluting 5 mL of concentrated HNO_3 to 500 mL with reagent water.

6.4.2. Weigh 1 g of a certified natural U_3O_8 into a platinum crucible. Cover the crucible with the platinum lid.

6.4.3. Heat the U_3O_8 in a muffle furnace at 900°C for 1 h.

6.4.4. Cool the U_3O_8 in a desiccator overnight.

6.4.5. Accurately weigh 590 $\pm$ 1 mg of the U_3O_8 into a 50-mL beaker.

6.4.6. With gentle heating, dissolve the U_3O_8 in 20 mL of 7.8 M ultrapure HNO_3.

6.4.7. Evaporate the solution to near dryness.

6.4.8. Redissolve the residue in 10 mL of 1.6 M HNO_3.

6.4.9. Quantitatively transfer the uranium solution into a 500-mL volumetric flask with 1% HNO_3 and dilute the solution to volume with 1% HNO_3.

6.4.10. Calculate the concentration of the resultant natural uranium standard as in the example in Step 8.2.

6.5. Prepare a uranium standard with a concentration of 100 μg/mL by diluting the 1-mg/mL uranium standard. Use reagent water and ultrapure HNO_3.

6.5.1. Place approximately 70 mL of reagent water into a 100-mL volumetric flask.

6.5.2. Add 1 mL of concentrated HNO_3 to the flask to achieve a final acid concentration of 1%.

6.5.3. Add 10 mL of the 1-mg/mL natural uranium standard to the volumetric flask using a volumetric pipette.

6.5.4. Dilute the solution to volume with reagent water.

6.5.5. Calculate the concentration of the resultant natural uranium standard. The $^{235}U/^{238}U$ isotopic ratio in the standard is 0.0072.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically omit one or more metals from the acidified standard as a blank QC for those metals.

7.2. This procedure describes the preparation of five 100-mL aliquots of multielement standard, five 100-mL aliquots of silver standard, and two 250-mL aliquots of natural uranium standard. QC samples may be prepared in larger or smaller quantities than described in this procedure, adjusting apparatus size as necessary.

7.3. For a multielement QC sample, a 100-mL minimum volume is needed for analysis by ICPMS or ETVAA, and a 200-mL minimum volume is needed for analysis by ICPAES or FAA.

7.3.1. Place approximately 400 mL of reagent water in a 500-mL volumetric flask.

7.3.2. Add 15 mL of 16 M ultrapure HNO_3 to the water to produce a final acid concentration of 3% by volume.

7.3.3. Use a new disposable pipette tip to spike each metal standard solution into the QC sample to avoid contamination of the standards. Spike an aliquot of each metal standard solution into the acidified water in the flask to reach the desired spike range for that metal.

NOTE: If any of the metal standard solutions used to prepare the QC sample contains HCl, do not include Ag in the sample because it will be lost as insoluble AgCl. Prepare a separate QC sample for Ag.

7.3.4. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.3.5. Divide the QC sample evenly among five 125-mL high-density polyethylene bottles. If Ag has been included in the sample, use amber 125-mL high-density polyethylene bottles or uncolored bottles completely wrapped in aluminum foil.

7.3.6. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 500-mL volumetric flask.

7.4. Preparing a separate Ag QC sample.

7.4.1. Place approximately 400 mL of reagent water into a 500-mL volumetric flask.

7.4.2. Add 15 mL of 16 M ultrapure HNO_3 to produce a final acid concentration of 3% by volume.

7.4.3. Spike an aliquot of Ag standard solution into the acidified water in the flask to reach the desired spike range.

7.4.4. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.4.5. Divide the QC sample evenly between five amber 125-mL high-density polyethylene bottles or five uncolored 125-mL high-density polyethylene bottles. The uncolored bottles must be completely wrapped in aluminum foil to prevent loss of Ag.

7.4.6. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 500-mL volumetric flask.

7.5. For the determination of total uranium and $^{235}U/^{238}U$ isotopic ratios through ICPMS, prepare a QC sample from the natural uranium standard made from a certified natural U_3O_8 material.

7.5.1. Place approximately 400 mL of reagent water into a 500-mL volumetric flask.

7.5.2. Add 15 mL of ultrapure nitric acid to produce a final acid concentration of 3% by volume.

7.5.3. Spike an aliquot of 100-μg/mL natural uranium standard into the acidified water in the flask to reach the desired spike range for total uranium.

7.5.4. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.5.5. Divide the QC sample evenly between two 250-mL high-density polyethylene bottles.

7.5.6. Label each bottle with a QC number and store at room temperature pending analysis. The same QC number may be used for both aliquots of a QC sample from the same 500-mL volumetric flask.

7.6 Calculate the hardness expressed as $CaCO_3$ concentration in the QC sample using the Ca and Mg concentrations. See Step 8.5.

8. Calculations

8.1. Calculate the concentration of the Cr^{+6} standard solution using the following atomic weights and example.

8.1.1. Atomic weight of K = 39.1.
Atomic weight of Cr = 52.0.
Atomic weight of O = 16.0.

8.1.2. If 141.5 mg of $K_2Cr_2O_7$ is dissolved in 50 mL of reagent water, the Cr^{+6} concentration in the standard is 1000 μg/mL.

$$\frac{\left(\frac{104\ \text{g}\ Cr^{+6}}{294.2\ \text{g}\ K_2Cr_2O_7}\right)(141.5\ \text{mg}\ K_2Cr_2O_7)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{50\ \text{mL}} = 1000\ \mu\text{g}\ \frac{Cr^{+6}}{\text{mL}} \quad .$$

8.2. Calculate the concentration of the uranium standard solution using the following atomic weights and example.

8.2.1. Atomic weight of U = 238.029.
Atomic weight of O = 16.
The molecular weight of U_3O_8 recorded on the bottle label for NIST SRM U_3O_8 may also be used.

8.2.2. The purity of the NIST U_3O_8 is recorded on the certificate for the SRM used.

8.2.3. If 589.6 mg of 99.968% pure U_3O_8, which has been heated in the muffle furnace, is dissolved in acid and diluted to 500 mL, the uranium concentration in the standard will be 1.0 g/L.

$$\frac{\left(\frac{714.087\ \text{g U}}{842.0822\ \text{g}\ U_3O_8}\right)(0.99968)\ (0.5896\ \text{g})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 1.0\ \text{g/L} \quad .$$

8.2.4. The $^{235}U/^{238}U$ isotopic ratio in natural uranium is 0.0072 ± 0.0007.

8.3. Record the concentration of each metal in the QC sample as μg/L or mg/L.

8.4. Calculate spike concentrations for each metal in the QC sample as in the following example:

8.4.1. If 250 μL of a 100-μg/mL Se standard is used to spike 400 mL of acidified water and the solution is diluted to 500 mL, the concentration of Se in the sample is 50 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(100\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(250\ \mu L)}{(500\ mL)\ (1\ L/1000\ mL)} = 50\ \mu g/L \quad .$$

8.4.2. If 450 μL of 1000-μg/mL Ag standard is used to spike 400 mL of acidified water and the solution is diluted to 500 mL, the concentration of Ag in the sample is 900 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1000\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(450\ \mu L)}{(500\ mL)\ (1\ L/1000\ mL)} = 900\,\mu g/L \quad .$$

8.4.3. If 400 μL of 100-μg/mL natural uranium standard is used to spike 400 mL of acidified water and the solution is diluted to 500 mL, the concentration of U in the sample is 80 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(100\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(400\mu L)}{(500\ mL)\ (1\ L/1000\ mL)} = 80\ \mu g/L \quad .$$

8.4.4 The $^{235}U/^{238}U$ isotopic ratio in natural uranium is 0.0072 $\pm$ 0.0007.

8.5. Calculate the hardness expressed as $CaCO_3$ concentration in the QC samples using the following equation and example:

$$\text{Hardness} = (\text{Ca concentration})\ (2.5) + (\text{mg concentration})\ (4.12) \quad ,$$

where the constants are derived as follows:

$$\frac{CaCO_3 \text{ Molecular Weight}}{\text{Ca Atomic Weight}} = \frac{100}{40} = 2.5 \quad .$$

$$\frac{CaCO_3 \text{ Molecular Weight}}{\text{mg Atomic Weight}} = \frac{100}{24.3} = 4.12 \quad .$$

8.5.1. If the concentration of Ca in the QC sample is 45 mg/L and the concentration of mg in the QC sample is 32 mg/L, the hardness expressed as $CaCO_3$ concentration in the QC sample is 244.3 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$(45 \text{ mg/L})\ (2.5) + (32 \text{ mg/L})\ (4.12) = 244.3 \text{ mg/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form (WPF) describing the solid waste is completed and sent to Waste Services (CST-17) for review.

9.1.2.2. If CST-17 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If CST-17 determines that the solid waste is contaminated above the level of concern, pickup of the contaminated waste is requested as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Liquid waste containing hazardous contaminants (such as solutions of trace metals) is accumulated in a coated glass bottle in a secondary containment

tray and is kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 950b, Uranium Oxide (U_3O_8)" (National Institute of Standards and Technology, Washington, DC, March 1978).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN HYDROCHLORIC ACID — QC SAMPLE PREPARATION

Analyte: Metals	**Method No.:** QCI180
Matrix: Water, soil	**Spike Range:** Dependent on element and analytical method (see Step 1.5)
Procedure: ICPAES, FAA, or ETVAA, depending on metal and concentration range	**Accuracy and Precision:** 100% ± 5% RSD
Effective Date: 01/17/91	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.2 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified water is spiked with standard solutions of metals. Tin and titanium are more stable in hydrochloric acid than in nitric acid.

1.2. The acidified water quality control (QC) sample represents the solution resulting from the extraction of the metals from a soil matrix.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed from the extraction step in the same analytical procedure used for unknown samples.

1.4. The method of analysis depends on the metal and its concentration. The methods include inductively coupled plasma–atomic emission spectrometry (ICPAES), flame atomic absorption (FAA) spectroscopy, and electrothermal vaporization atomic absorption (ETVAA) spectroscopy. QC samples of trace elements in hydrochloric acid are not run by inductively coupled plasma–mass spectrometry (ICPMS) because the hydrochloric acid interferes.

1.5. The QC spike range depends on the metal of interest and on the method of analysis. Refer to Table I below for spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN HYDROCHLORIC ACID

Element	ICPAES (mg/L)	FAA (mg/L)	ETVAA (mg/L)
Sn	2–30	0.1–1	0.010–0.060
Ti	0.1–2	2–5	0.005–0.050

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with the use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 5.0% at the 1-σ level has been calculated for standard preparation and for the spiking and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance for each variable using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.1.3. All variables contributing to the error associated with the preparation of these QC samples were considered. The largest errors were used in the error propagation calculations.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by ICPAES, FAA, and ETVAA are summarized in Table II below. The data are published in Source Material 10.1.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN HCL

Analyte	1992 Mean ± std dev (%)	N	1993 Mean ± std dev (%)	N	1994 Mean ± std dev (%)	N
Sn	102.1 ± 4.3	(6)	101.5 ± 11.5	(6)	—	
Ti	102.0 ± 7.2	(3)	—		—	

N = number of samples.

3. Collection and Storage of Samples

3.1. QC samples are prepared in a volumetric flask and are aliquoted into high-density polyethylene bottles for storage at room temperature pending analysis.

4. Apparatus

4.1. Flasks: 200-mL, glass, class A volumetric.

4.2. Graduated cylinder: 100-mL.

4.3. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Pipettes: 2-, 3-, 4-, 5-, and 6-mL, glass, class A volumetric.

4.6. Bottles: 125-mL, high-density polyethylene.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. Hydrochloric acid (12 M, ultrapure, suitable for trace-metal analysis).

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean water conforming to American Society for Testing and Materials (ASTM) Types I, II, III and free of interferences with the analytical method.

6. Calibration and Standards

6.1. Spectroscopy-grade metal standards (100–10,000 μg/mL) from Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820, or equivalent.

6.2. If a more dilute standard is needed to reach the desired spike range, dilute a concentrated standard, taking care to match the type and concentration of acid in the dilution to those in the concentrated standard.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically omit one or more metals from the acidified sample as a blank QC for those metals.

7.2. This procedure describes the preparation of two 100-mL aliquots of a QC sample. QC samples may be prepared in larger or smaller quantities than described in this procedure, adjusting apparatus size and reagent volume as necessary.

7.3. Place approximately 100 mL of reagent water into a 200-mL volumetric flask.

7.4. Add 40 mL of ultrapure hydrochloric acid to the water in the flask.

7.5. Use a new disposable pipette tip to spike each metal standard solution into the QC sample to avoid contamination of the standards. Spike an aliquot of each metal standard solution into the acidified water in the flask to reach the desired spike range for that metal.

7.6. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.7. Divide the QC sample evenly between two 125-mL high-density polyethylene bottles.

7.8. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for both aliquots of a QC sample from the same 200-mL volumetric flask.

8. Calculations

8.1. Record the concentration of each metal in the QC sample as μg/L or mg/L.

8.2. Calculate the spike concentration for each metal in the QC sample as in the following example.

8.2.1. If 3.0 mL of a 1000-μg/mL Sn standard is used to spike 180 mL of acidified water and the solution is diluted to 200 mL, the concentration of Sn in the sample is 15 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1000\ \mu g/mL)\ (3.0\ mL)\ (1\ mg/1000\mu g)}{(200\ mL)\ (1\ L/1000\ mL)} = 15\ mg/L \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form (WPF) describing the solid waste is completed and sent to Waste Services (CST-17) for review.

9.1.2.2. If CST-17 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If CST-17 determines that the solid waste is contaminated above the level of concern, pickup of the contaminated waste is requested as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Liquid waste containing hazardous contaminant (such as solutions of trace metals) is accumulated in a coated glass bottle in a secondary containment tray and kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91, (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN WATER — QC SAMPLE PREPARATION

Analytes: Boron, bromide, calcium, chloride, fluoride, lithium, magnesium, phosphorus, potassium, silicon, sodium, sulfate	**Method No.:** QCI190
Matrix: Water	**Spike Range:** Dependent on the element (see Table I)
Procedure: FIA, ACOLOR, ISE, or IC	**Accuracy and Precision:** 100% ± 3% RSD
Effective Date: 10/01/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.2 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare individual standard solutions of bromide, chloride, fluoride, and sulfate salts in reagent water.

1.2. Obtain commercially prepared single-element solutions of boron, calcium, lithium, magnesium, phosphorus, potassium, silicon, and sodium.

1.3. Spike the chosen volume of each standard separately or in various combinations into reagent water or distilled water as specified in Sec. 7.

1.4. Methods of analysis depend on the analyte and its concentration. They include flow injection analysis (FIA), ion-selective electrode (ISE), ion chromatography (IC), and colorimetry (ACOLOR).

1.5. The quality control (QC) spike range depends on the analyte of interest and the analytical method. Refer to Table I for spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN WATER

Analyte	Spike range (mg/L)	Analysis method
Chloride (Cl)	5.0–50	FIA/IC
Bromide (Br)	5.0–50	FIA/IC
Fluoride (F)	0.1–2.0	ISE
Sulfate (SO_4)	5.0–30	FIA/IC
Phosphorus (P)	0.04–1.0	ACOLOR
Boron (B)	0.1–6.0	FIA
Silicon (Si)	3–50	FIA
Silica (SiO_2)	5–100	FIA
Sodium (Na)	5–30	IC
Potassium (K)	3–20	IC
Calcium (Ca)	5–30	IC
Magnesium (Mg)	3–20	IC
Lithium (Li)	1–10	IC

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with the use of the pipette and volumetric flask. A relative standard deviation (RSD) of 3% at the 1-σ level has been calculated for the error of the standard and for the spiking and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2),
$\overline{X}$ = mean value of each variable (M), and
100 = factor to convert to percent.

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
R^2_{M3} = relative variance of volumetric flask.

2.1.3. If a second pipette is used to obtain the desired analyte concentration, use the following equation.

$$R_{M2} = \frac{\sqrt{\sigma_1^2 + \sigma_2^2}}{P_1 + P_2} ,$$

where σ_1 = standard deviation of first pipette error,
σ_2 = standard deviation of second pipette error,
P_1 = mean of first pipette, and
P_2 = mean of second pipette.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by FIA, ISE, ACOLOR, and IC are summarized in Table II below. The data are published in Source Material 10.1.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN WATER

Analyte	1992 Mean ± std dev (%)	N[a]	1993 Mean ± std dev (%)	N[a]	1994 Mean ± std dev (%)	N[a]
B	101 ± 2	(7)	95 ± 7	(4)		
Br			93 ± 5	(6)	93 ± 3	(13)
Ca	112 ± 4	(2)				
Cl	98 ± 8	(7)	102 ± 8	(8)	93	(1)
F	86 ± 16	(2)	99 ± 7	(2)		
K	108 ± 2	(2)				
Li	98	(1)				
Mg	105 ± 3	(2)	114	(1)		
Na	110 ± 1	(2)	200	(1)		
P	106 ± 36	(18)	104 ± 14	(4)	154 ± 60	(2)
Si					103 ± 7	(10)
SO_4	97 ± 14	(8)	95 ± 5	(5)	95	(1)

N[a] = number of samples.

3. Collection and Storage of Samples

3.1. QC samples for boron, fluoride, and silicon are prepared in polypropylene flasks to avoid interactions with borosilicate glass. All other samples may be made in glass flasks.

3.2. Spiked QC samples are aliquoted and stored in high-density polyethylene bottles at room temperature pending analysis.

4. Apparatus

4.1. Flasks: 50-, 250-, and 500-mL, class A volumetric, glass.

4.2. Flasks: 50-, 100-, and 500-mL, volumetric, polypropylene, Nalgene or equivalent.

4.3. Spatula.

4.4. Pipettes: 1- and 2-mL, class A volumetric, glass.

4.5. Auto-pipette: 100-μL and 1000-μL, Rainin or equivalent.

4.5. Auto-pipette: 100-μL and 1000-μL, Rainin or equivalent.

4.6. Pipette tips: disposable.

4.7. Bottles: 60-, 125-, and 250-mL, high-density polyethylene.

4.8. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.9. Labels printed with QC sample numbers.

5. Reagents

5.1. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testing and Materials (ASTM) Type I, II, or III and free of interferences with the analytical method.

5.2. Distilled water. Used to dilute silicon QC samples. Deionized water is not used because deionization may result in high levels of silicon when the resin begins to degrade, even though the resistivity of the water remains acceptable.

5.3. Potassium bromide (anhydrous, reagent-grade).

5.4. Sodium chloride (reagent-grade).

5.5. Sodium fluoride (reagent-grade).

5.6. Sodium sulfate (anhydrous, reagent-grade).

6. Calibration and Standards

6.1. Spectroscopy-grade metal standards (1000–10,000 μg/mL). Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820, or equivalent.

6.2. If a more dilute standard is needed to reach the desired spike range, dilute a concentrated standard, taking care to match the kind and concentration of acid in the dilution to those in the concentrated standard. Use distilled water to make dilutions of a silicon standard.

6.3. Standard solutions for bromide, chloride, fluoride, and sulfate are made from salts.

6.4. Thoroughly rinse all glassware before preparing standards. The presence of nitric acid may oxidize bromide ion to bromine; it will also interfere with analysis by ion

chromatography by giving a broad nitrate ion peak, which may obscure the differentiation and quantitation of other anions present.

6.5. Prepare a standard solution of bromide ion at approximately 20 mg/mL using solid anhydrous potassium bromide.

6.5.1. Accurately weigh 1.5 ± 0.03 g of solid anhydrous potassium bromide into a 50-mL volumetric flask.

6.5.2. Add approximately 30 mL of reagent water and swirl the flask to dissolve the salt.

6.5.3. Dilute the solution to volume with reagent water and mix by inversion.

6.5.4. Transfer the solution to a 60-mL high-density polyethylene bottle and label the bottle with information identifying the standard.

6.5.5. Record information on standard preparation in the QC Laboratory notebook.

6.6. Prepare a standard solution of chloride ion at approximately 20 mg/mL using sodium chloride.

6.6.1. Dry 2 ± 0.1 g of solid sodium chloride at approximately 140°C for 30 min before using it to prepare the standard chloride solution.

6.6.2. Accurately weigh 1.65 ± 0.04 g of dried sodium chloride into a 50-mL volumetric flask.

6.6.3. Add approximately 30 mL of reagent water and swirl the flask to dissolve the salt.

6.6.4. Dilute the solution to volume with reagent water and mix by inversion.

6.6.5. Transfer the solution to a 60-mL high-density polyethylene bottle and label the bottle with information identifying the standard.

6.6.6. Record information on standard preparation in the QC Laboratory notebook.

6.7. Prepare a standard solution of fluoride ion at approximately 1000 μg/mL using solid sodium fluoride.

6.7.1. Make the fluoride standard in a polypropylene (Nalgene) volumetric flask to avoid reaction of the fluoride with borosilicate glass.

6.7.2. Accurately weigh 0.11 ± 0.005 g of solid anhydrous sodium fluoride into a 50-mL polypropylene volumetric flask.

6.7.3. Add approximately 30 mL of reagent water and swirl the flask to dissolve the salt.

6.7.4. Dilute the solution to volume with reagent water and mix by inversion.

6.7.5. Transfer the solution to a 60-mL high-density polyethylene bottle and label the bottle with information identifying the standard.

6.7.6. Record information on standard preparation in the QC Laboratory notebook.

6.8. Prepare a standard solution of sulfate ion at approximately 20 mg/mL using solid anhydrous sodium sulfate.

6.8.1. Accurately weigh 1.48 ± 0.03 g of solid anhydrous sodium sulfate into a 50-mL volumetric flask.

6.8.2. Add approximately 30 mL of reagent water and swirl the flask to dissolve the salt.

6.8.3. Dilute the solution to volume with reagent water and mix by inversion.

6.8.4. Transfer the solution to a 60-mL high-density polyethylene bottle and label the bottle with information identifying the standard.

6.8.5. Record information on standard preparation in the QC Laboratory notebook.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically omit one or more analytes from the QC sample as a blank QC for those analytes.

7.2. QC samples may be prepared in larger or smaller quantities than described in this procedure, adjusting apparatus size as necessary.

7.3. This step describes the preparation of three approximately 150-mL aliquots of a standard containing bromide, chloride, fluoride, and sulfate anions.

7.3.1. Prepare QC samples containing fluoride in polypropylene (Nalgene) volumetric flasks to avoid loss of fluoride ion due to reaction with borosilicate glass.

7.3.2. Place approximately 400 mL of reagent water into a 500-mL polypropylene volumetric flask.

7.3.3. Spike aliquots of bromide, chloride, fluoride, and sulfate standards made from salts of the anions into the water to reach the desired spike range listed in Table I.

7.3.4. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.3.5. Divide the QC sample evenly among three 250-mL high-density polyethylene bottles.

7.3.6. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 500-mL volumetric flask.

7.4. This step describes the preparation of four 25-mL aliquots of boron standard.

7.4.1. Prepare QC samples containing boron in polypropylene (Nalgene) volumetric flasks to prevent contamination by leaching of borosilicate glass surfaces.

7.4.2. Place approximately 80 mL of reagent water into a 100-mL polypropylene volumetric flask.

7.4.3. Add an aliquot of boron standard solution to the water to reach the desired spike range listed in Table I.

7.4.4. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.4.5. Divide the QC sample evenly among four 60-mL high-density polyethylene bottles.

7.4.6. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 100-mL volumetric flask.

7.5. This step describes the preparation of five 100-mL aliquots of silicon standard.

7.5.1. Prepare QC samples containing silicon in polypropylene (Nalgene) volumetric flasks to prevent contamination by leaching of borosilicate glass surfaces.

7.5.2. Use distilled water to prepare silicon QC samples. Degrading ion-exchange resin used to make deionized water may contaminate the sample with silicon.

7.5.3. Place approximately 400 mL of distilled water into a 500-mL polypropylene volumetric flask.

7.5.4. Add an aliquot of silicon standard to the water to reach the desired spike range for silicon listed in Table I.

7.5.5. Dilute the QC sample to volume with distilled water. Mix by inversion.

7.5.6. Divide the QC sample evenly among five 125-mL high-density polyethylene bottles.

7.5.7. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all five aliquots of a QC sample from the same 500-mL volumetric flask.

7.6. This step describes the preparation of five 100-mL aliquots of phosphorus standard.

7.6.1. Place approximately 400 mL of reagent water into a 500-mL volumetric flask.

7.6.2. Add an aliquot of phosphorus standard solution to the water to reach the desired spike range listed in Table I.

7.6.3. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.6.4. Divide the QC sample evenly among five 125-mL high-density polyethylene bottles.

7.6.5. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 500-mL volumetric flask.

7.7. This step describes the preparation of five 50-mL aliquots of a standard containing calcium, magnesium, potassium, sodium, and lithium.

7.7.1. Place approximately 200 mL of reagent water into a 250-mL volumetric flask.

7.7.2. Add aliquots of the Ca, Mg, K, Na, and Li standard solutions to the water to reach the desired spike range listed in Table I.

7.7.3. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.7.4. Divide the QC sample evenly among five 60-mL high-density polyethylene bottles.

7.7.5. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 250-mL volumetric flask.

7.8. For each QC sample prepared, record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX. Record the concentration of the silicon QC sample in terms of both Si and SiO_2.

8. Calculations

8.1. Calculate the concentration of a bromide standard solution made from anhydrous potassium bromide using the following atomic weights and example.

8.1.1. Atomic weight of K = 39.1.
Atomic weight of Br = 79.9.

8.1.2. If 1.5000 g of KBr is dissolved in 50 mL of reagent water, the bromide concentration in the standard is 20 mg/mL.

$$\frac{\left(\frac{79.9 \text{ g Br}}{119.0 \text{ g KBr}}\right)(1.5000 \text{ g})(1000 \text{ mg/g})}{50 \text{ mL}} = 20 \text{ mg/mL} \quad .$$

8.2. Calculate the concentration of a chloride standard solution made from dried sodium chloride using the following atomic weights and example.

8.2.1. Atomic weight of Na = 23.0.
Atomic weight of Cl = 35.5.

8.2.2. If 1.6500 g of NaCl is dissolved in 50 mL of reagent water, the chloride concentration in the standard is 20 mg/L.

$$\frac{\left(\frac{35.5 \text{ g Cl}}{58.5 \text{ g NaCl}}\right)(1.6500 \text{ g})(1000 \text{ mg/g})}{50 \text{ mL}} = 20 \text{ mg/L} \quad .$$

8.3. Calculate the concentration of a fluoride standard solution made from sodium fluoride using the following atomic weights and example.

8.3.1. Atomic weight of Na = 23.0.
Atomic weight of F = 19.0.

8.3.2. If 0.1110 g of NaF is dissolved in 50 mL of reagent water, the fluoride concentration in the standard is 1004 μg/mL.

$$\frac{\left(\frac{19.0 \text{ g F}}{42.0 \text{ g NaF}}\right)(0.1110 \text{ g})(1{,}000{,}000 \ \mu\text{g/g})}{50 \text{ mL}} = 1004 \ \mu\text{g/mL} \quad .$$

8.4. Calculate the concentration of a sulfate standard solution made from anhydrous sodium sulfate using the following atomic weights and example.

8.4.1. Atomic weight of Na = 23.0.
Atomic weight of S = 32.1.
Atomic weight of O = 16.0.

8.4.2. If 1.4750 g of Na_2SO_4 is dissolved in 50 mL of reagent water, the sulfate concentration in the standard is 20 mg/mL.

$$\frac{\left(\frac{96.1 \text{ g } SO_4}{142.1 \text{ g } Na_2SO_4}\right)(1.4750 \text{ g})(1000 \text{ mg/g})}{50 \text{ mL}} = 20 \text{ mg/mL} \quad .$$

8.5. Record the concentration of each analyte in a QC sample as μg/L or mg/L.

8.6. Calculate spike concentrations for each analyte in the QC sample as in the following examples.

8.6.1. If 750 μL of a 20-mg/mL Br standard is spiked into 400 mL of reagent water and the solution is diluted to 500 mL, the concentration of Br in the QC sample is 30 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(20\ \text{mg/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (750\ \mu\text{L})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 30\ \text{mg/L} \quad .$$

8.6.2. If 300 μL of a 1000-μg/mL boron standard is spiked into 80 mL of reagent water and the solution is diluted to 100 mL, the concentration of boron in the QC sample is 3 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1000\ \mu\text{g/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(300\mu\text{L})\left(\frac{1\ \text{mg}}{1000\ \mu\text{g}}\right)}{(100\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 3\ \text{mg/L} \quad .$$

8.6.3. If 900 μL of a 10,000-μg/mL Si standard is spiked into 400 mL of distilled water and the solution is diluted to 500 mL, the concentration of Si in the QC sample is 18 mg/L. The concentration of a Si QC sample is recorded in terms of both Si and SiO_2.

$$\frac{(10{,}000\ \mu\text{g/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(900\ \mu\text{L})\left(\frac{1\ \text{mg}}{1000\ \mu\text{g}}\right)}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 18\ \text{mg/L} \quad .$$

The concentration of the QC sample in terms of SiO_2 is calculated from the concentration in terms of Si.

A QC sample with a concentration of 18 mg/L Si has a concentration of 38 mg/L SiO_2.

$$(18 \text{ mg Si/L}) \left(\frac{60.1 \text{ g } SiO_2}{28.1 \text{ g Si}} \right) = 38 \text{ mg } SiO_2\text{/L} \quad .$$

Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.6.4. If 250 μL of a 1000-μg/mL P standard is spiked into 400 mL of reagent water and the solution is diluted to 500 mL, the concentration of P in the QC sample is 500 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1000 \ \mu\text{g/mL}) \left(\frac{\text{mL}}{1000 \ \mu\text{L}} \right) (250 \ \mu\text{L})}{(500 \text{ mL}) \ (1 \text{ L}/1000 \text{ mL})} = 500 \ \mu\text{g/L} \quad .$$

8.6.5. If 150 μL of a 10,000-μg/mL Mg standard is spiked into 200 mL of reagent water and the solution is diluted to 250 mL, the concentration of Mg in the QC sample is 6 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(10{,}000 \ \mu\text{g/mL}) \left(\frac{1 \text{ mL}}{1000 \ \mu\text{L}} \right) (150 \ \mu\text{L}) \left(\frac{1 \text{ mg}}{1000 \ \mu\text{g}} \right)}{(250 \text{ mL}) \ (1 \text{ L}/1000 \text{ mL})} = 6 \text{ mg/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form (WPF) describing the solid waste is completed and sent to Waste Services (CST-17) for review.

9.1.2.2. If CST-17 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If CST-17 determines that the solid waste is contaminated above the level of concern, pickup of the contaminated waste is requested as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Liquid waste containing hazardous contaminants (such as solutions of trace metals) is accumulated in a coated glass bottle in a secondary containment tray and kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste to it.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. ASTM, *1992 Annual Book of ASTM Standards*, vol. 11.01, specification D1193-91, Standard Specification for Reagent Water, pp.45-47.

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS FOR WATER AND SOIL (MERCURY BY TCLP) — QC SAMPLE PREPARATION

Analyte: Hg	**Method No.:** QCI200
Matrix: Water	**Spike Range:** 1–4 μg/L
Procedure: Toxicity characteristic leaching procedure (TCLP) followed by cold vapor atomic absorption (CVAA) spectroscopy	**Accuracy and Precision:** 100% ± 5.9% RSD
Effective Date: 09/29/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified water containing $Cr_2O_7^{=}$ as a stabilizer is spiked with a Hg standard.

1.2. The acidified water quality control (QC) sample may represent the solution resulting from the extraction of Hg from a soil matrix.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure or those sections of the procedure that are applicable.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask and of the pipette. A relative standard deviation (RSD) of 5.9% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared from 1991 through 1994 using this procedure and analyzed by cold vapor atomic absorption spectroscopy gave the recoveries found in Table I. The data are published in Source Materials 10.2 and 10.3.

TABLE I. MERCURY SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

	Spike range µg/L	Mean ± std dev (%)	Number of samples
1991	1.0–2.9	92 ± 19	30
	3.0–4.0	96 ± 11	33
1992	1.0–2.9	94 ± 17	73
	3.0–4.0	96 ± 16	56
1993	1.0–2.9	100 ± 20	102
	3.0–10.0	96 ± 5	85
1994	1.0–2.9	92 ± 11	31
	3.0–10.0	98 ± 7	200

3. Collection and Storage of Samples

3.1. Low-level Hg solutions must be stabilized to maintain their certified concentration longer than a few hours. Studies of the preservation of dilute Hg solutions (see Source Material 10.1) show that a dilute Hg solution will maintain its concentration for as long as five months if it is preserved with 0.01% $Cr_2O_7^{=}$ and 5% HNO_3 and stored in a glass container.

3.2. QC samples are stored in glass bottles at room temperature pending analysis.

3.3. If QC samples for Hg are not used within five months of the date they were made, they are discarded.

4. Apparatus

4.1. Volumetric flasks: 5-, 25-, and 250-mL.

4.2. Autopipette: 100- and 1000-µL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Graduated cylinder: 25-mL.

4.5. Bottles: 4-oz, glass, with Teflon-lined screw caps.

4.6. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.7. Spatula.

4.8. Weighing dish: small, polyethylene.

4.9. Labels printed with QC sample numbers.

5. Reagents

5.1. Nitric acid (16 M, ultrapure) suitable for trace metal analysis.

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testing and Materials (ASTM) Types I, II, or III and free of interferences with the analytical method.

5.3. Potassium dichromate (analytical reagent-grade).

6. Calibration and Standards

6.1. Spectroscopy-grade Hg standard solution, 10-μg/mL concentration preferred. More concentrated standards (such as those supplied by Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820) may be diluted to a Hg concentration of 10 μg/mL.

6.2. A spectroscopy-grade 10-μg/mL Hg standard solution is spiked into acidified water containing $K_2Cr_2O_7$ as a stabilizer for the Hg.

7. Procedure

7.1. Prepare a stabilizing solution for the Hg with a $Cr_2O_7^{=}$ concentration of 50 mg/mL.

7.1.1. Tare a small polyethylene weighing dish on the balance.

7.1.2. Accurately weigh 341 $\pm$ 2 mg of analytical-grade $K_2Cr_2O_7$ into the weighing dish.

7.1.3. Use reagent water to quantitatively rinse the $K_2Cr_2O_7$ into a 5-mL volumetric flask and to dilute the solution to volume. Mix by inversion.

7.1.4. Calculate the $Cr_2O_7^{=}$ concentration of the stabilizing solution as in the example in Step 8.1.

7.2. Prepare a 10-μg/mL Hg standard solution from a 1000-μg/mL standard solution.

7.2.1. Place 15 mL of reagent water into a 25-mL volumetric flask.

7.2.2. Add 2.5 mL of ultrapure nitric acid to the water in the flask to produce a final acid concentration of 10% by volume.

7.2.3. Add 50 μL of the stabilizing solution with a $Cr_2O_7^=$ concentration of 50 mg/mL to the acidified water to produce a $Cr_2O_7^=$ concentration of 0.01% by weight.

CAUTION: The nitric acid and $Cr_2O_7^=$ stabilizing solution must be added to the water before the mercury spike to prevent the immediate loss of Hg.

7.2.4. Add 250 μL of a 1000-μg/mL Hg standard solution to the water in the flask.

7.2.5. Dilute to volume with reagent water. Mix by inversion.

7.3. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically include a sample of 5% HNO_3 and 0.01% $Cr_2O_7^=$ as a blank.

7.4. This procedure describes the preparation of two approximately 100-mL aliquots of a QC sample. QC solutions may be prepared in larger or smaller quantities than described in this procedure. Adjust apparatus size as necessary.

7.5. Place approximately 200 mL of reagent water into a 250-mL volumetric flask.

7.6. Add 12.5 mL of ultrapure nitric acid to the water to produce a final acid concentration of 5% by volume.

7.7. Add 500 μL of the stabilizing solution with a $Cr_2O_7^=$ concentration of 50 mg/mL to the acidified water to produce a $Cr_2O_7^=$ concentration of 0.01% by weight.

NOTE: The nitric acid and $Cr_2O_7^=$ stabilizing solution must be added to the water before the mercury spike to prevent the immediate loss of Hg.

7.8. Spike an aliquot of the 10-μg/mL Hg standard into the acidified water to reach the desired spike range.

7.9. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.10. Divide the QC sample evenly between two 4-oz glass bottles.

7.11. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for both aliquots of a QC sample from the same 250-mL volumetric flask.

7.12. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the $Cr_2O_7^=$ concentration of the stabilizing solution using the following atomic weights and example.

8.1.1. Atomic weights: K = 39.1, Cr = 52.0, and O = 16.0.

8.1.2. If 341.0 mg of $K_2Cr_2O_7$ is dissolved in 5 mL of reagent water, the $Cr_2O_7^=$ concentration in the stabilizing solution is 50 mg/mL.

$$\frac{\left(\frac{216.0 \text{ g } Cr_2O_7^=}{294.2 \text{ g } K_2Cr_2O_7}\right)(341.0 \text{ mg } K_2Cr_2O_7)}{5 \text{ mL}} = 50 \text{ mg } Cr_2O_7^=/\text{mL} \quad .$$

8.2. Calculate Hg spike concentrations as in the following example.

8.2.1. If 50 μL of a 10-μg/mL Hg standard is diluted to 250 mL in acidified water containing $Cr_2O_7^=$ stabilizing solution, the Hg concentration in the sample is 2 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(10 \ \mu\text{g/mL})\ (1 \text{ mL}/1000 \ \mu\text{L})\ (50 \ \mu\text{L})}{(250 \text{ mL})\ (1 \text{ L}/1000 \text{ mL})} = 2 \ \mu\text{g/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not normally generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, complete the appropriate paperwork on a case-by-case basis.

9.1.2.1. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

9.1.2.2. If CST-17 determines that the solid waste is contaminated below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.2.3. If CST-17 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a coated glass bottle in a secondary containment tray. Keep it segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace metal waste.

9.2.3. Open the bottle only for the period of time necessary to add waste.

9.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.5. Label a new bottle for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal

Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. C. Feldman, "Preservation of Dilute Mercury Solutions," *Anal. Chem.* **46**, 99-102 (1974).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. B. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, N. L. Koski, E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. SPEX Industries, Inc., "Certificate of Analysis for Metals" (SPEX Industries, Inc., Edison, NJ 08820, October 1990).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.6. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp.45-47.

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN WATER (CN) — QC SAMPLE PREPARATION

Analyte: CN	**Method No.:** QCI210
Matrix: Water	**Spike Range:** 0.1–0.5 mg/L
Procedure: Automated colorimetry	**Accuracy and Precision:** 100% ± 12% RSD
Effective Date: 02/02/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Slightly alkaline blank water is spiked with a commercially prepared cyanide spiking solution.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask and of the pipette. A relative standard deviation (RSD) of 12% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared from 1991 through 1994 using this procedure and analyzed by automated colorimetry gave the following recoveries at the 1-σ level. The data are published in Source Materials 10.2 and 10.3.

TABLE I. SPIKE RECOVERY DATA FOR CN

Year	Mean ± std dev	Number of Samples
1991	82 ± 7	23
1992	74 ± 12	40
1993	83 ± 16	48
1994	73 ± 30	40

3. Collection and Storage of Samples

3.1. QC samples are prepared in a volumetric flask and are aliquoted into high-density polyethylene bottles and refrigerated pending analysis.

CAUTION: QC samples must be prepared in an alkaline matrix because cyanide in an acid matrix will release hydrogen cyanide gas, which is extremely hazardous.

4. Apparatus

4.1. Flasks: 250-mL, volumetric, glass, class A.

4.2. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Pipette: 2-mL, volumetric, class A.

4.5. Bottles: 60-mL, high-density polyethylene.

4.6. Labels printed with QC sample numbers.

4.7. Glass vials: with Teflon-lined caps.

5. Reagents

5.1. Sodium hydroxide (50% or approximately 10 M).

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean water conforming to American Society for Testing and Materials (ASTM) Types I, II, or III and free of interferences with the analytical method.

6. Calibration and Standards

6.1. A commercially prepared cyanide solution is used as a stock solution. National Institute of Standards and Technology (NIST) or Environmental Protection Agency (EPA) traceability is desirable for the stock solution.

6.2. If the manufacturer certifies the concentration of the standard after dilution according to specified instructions, the concentration of the original stock solution must be back-calculated before it is used, taking any dilution instructions into consideration.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically include an unspiked water sample made alkaline with 0.02 M NaOH as a blank.

7.2. This procedure describes the preparation of five 50-mL aliquots of QC samples. QC samples may be prepared in larger or smaller quantities than described in this procedure. Adjust apparatus size as necessary.

7.3. Back-calculate the concentration of the undiluted cyanide stock solution. See Step 8.1.

7.4. Place approximately 200 mL of reagent water in a 250-mL volumetric flask.

7.5. Add 500 μL of 50% NaOH to the water to produce a final NaOH concentration of 0.02 M.

CAUTION: Cyanide compounds must not be added to an acidic solution because hydrogen cyanide gas is released and is very hazardous. Work with cyanide solutions in an approved fume hood.

7.6. Spike an aliquot of undiluted cyanide stock solution into the water in the flask to reach the desired spike range.

7.7. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.8. Divide the QC sample evenly among five 60-mL high-density polyethylene bottles.

7.9. Label each bottle with a QC sample number and refrigerate pending analysis. Use the same QC number for all five aliquots of the QC sample.

7.10. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.11. Store the unused portion of the cyanide stock solution in a glass vial with a Teflon-lined cap and refrigerate.

8. Calculations

8.1. Back-calculate the concentration of the undiluted cyanide stock solution as in the following example.

8.1.1. If the concentration of the cyanide stock solution is 0.50 mg/L after dilution of a 10-mL aliquot to 1 L according to instructions, the concentration of the undiluted cyanide sample is calculated as follows:

$$(0.50 \text{ mg/L})\ (1 \text{ L}/10 \text{ mL}) = 0.05 \text{ mg/mL} \quad .$$

8.1.2 The concentration of 0.05 mg/mL is then used to determine the aliquot used to spike the alkaline water sample.

8.2. Record the concentration of CN in the QC sample as mg/L.

8.3. Calculate CN concentrations as in the following example.

8.3.1. If 2 mL of a 0.05-mg/mL CN standard is used to spike 250 mL of alkaline water, the concentration of CN in the sample will be 0.40 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(0.05 \text{ mg/mL})\ (2 \text{ mL})}{(250 \text{ mL})\ (1 \text{ L}/1000 \text{ mL})} = 0.40 \text{ mg/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not normally generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, complete the appropriate paperwork on a case-by-case basis.

9.1.2.1. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

9.1.2.2. If CST-17 determines that the solid waste is contaminated below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.2.3. If CST-17 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Step 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste contaminated with cyanide in a glass bottle in a secondary containment tray and keep it in a basic solution segregated from any other liquid waste.

9.2.2. Label the bottle with a hazardous waste label and a label indicating the presence of cyanide. If the bottle is too small to accommodate the hazardous waste label, apply the label to the secondary container.

9.2.3. Open the bottle only for the period of time necessary to add waste to it and keep it in a functioning fume hood whenever it is open.

9.2.4. When the waste is ready for disposal, keep the bottle in the secondary containment tray pending pickup by CST-17.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a bottle of cyanide-contaminated waste by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. US Environmental Protection Agency, "Instructions for Cyanide Quality Control Sample" (US Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, February 1990).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual,* Los Alamos National Laboratory Manual, Chapter 1(most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN WATER (NO_2-N) — QC SAMPLE PREPARATION

Analyte: NO_2-N	**Method No.:** QCI220
Matrix: Water	**Spike Range:** 0.1–1.0 mg/L
Procedure: Flow Injection Colorimetry	**Accuracy and Precision:** 100% ± 5.8% RSD
Effective Date: 10/22/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Sodium nitrite is weighed into a volumetric flask.

1.2. Immediately before use, the weighed salt is dissolved in reagent water and the solution is used to spike reagent water for use as a quality control (QC) sample.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with use of the pipette, balance, and volumetric flask. A relative standard deviation (RSD) of 5.8% at the 1-σ level has been calculated for the error of the standard and for the spiking, weighing, and dilution process based on the following function:

$$D = \frac{M1 \times M2 \times M4}{M3 \times M5} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,
M4 = pipette error, and
M5 = second dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2}$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2 + R_{M5}^2} \times 100$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of pipette,
R^2_{M5} = relative variance of second volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared from 1991 through 1994 using this procedure and analyzed by flow injection colorimetry gave the following recoveries at the 1-σ level. The data are published in Source Materials 10.1. and 10.2.

TABLE I. SPIKE RECOVERY DATA FOR NO_2-N IN WATER		
Year	Mean ± std dev	Number of Samples
1991	99 ± 29	5
1992	99 ± 15	5
1993	95 ± 17	5
1994	108 ± 14	14

3. Collection and Storage of Samples

3.1. Aliquots of crystalline sodium nitrite to be diluted and used to prepare QC samples are stored at room temperature pending analysis.

3.2. A water solution of sodium nitrite cannot be stored as a QC sample because nitrite in solution is readily oxidized to nitrate by the oxygen in the air.

4. Apparatus

4.1. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.2. Flasks: 10- and 100-mL, volumetric.

4.3. Spatula.

4.4. Autopipette: 100-μL, Rainin or equivalent.

4.5. Pipette tips: disposable.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. Sodium nitrite (analytical reagent-grade, crystalline).

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testing and Materials (ASTM) Type I, II, or III and free of interferences with the analytical method.

6. Calibration and Standards

6.1. Dissolve 10–100 mg of analytical-grade crystalline sodium nitrite in 10 mL of reagent water immediately before use.

6.2. Spike 50 μL of the sodium nitrite solution into 100 mL of reagent water to prepare the QC sample.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 100-mL QC sample.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3. Accurately weigh between 10 and 100 mg of sodium nitrite into a 10-mL volumetric flask.

7.4. Stopper the flask and label it with a QC sample number. Store the sample at room temperature pending final dilution by the analyst.

7.5. The sodium nitrite should be dissolved and diluted as close to time of analysis as possible to prevent loss of the QC sample through oxidation of nitrite to nitrate.

7.6. Place a label on the flask with instructions to the analyst for completion of the QC sample as described below.

7.6.1. Dissolve the sodium nitrite in reagent water in the 10-mL volumetric flask. Dilute the solution to volume with reagent water. Mix by inversion.

7.6.2. Place approximately 90 mL of reagent water in a 100-mL volumetric flask.

7.6.3. Spike 50 μL of the sodium nitrite solution from the 10-mL flask into the water in the 100-mL flask.

7.6.4 Dilute the QC sample in the 100-mL flask to volume with reagent water. Mix by inversion.

7.6.5. Analyze the QC sample immediately after preparation, using the same QC sample number that is on the 10-mL volumetric flask.

7.7. Calculate the concentration of the QC sample as the concentration after final dilution in the 100-mL flask by the analyst.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of NO_2-N in the QC sample as mg/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. Atomic weights: Na = 23, N = 14, and O = 16. The ratio of the atomic weight of N in $NaNO_2$ to the molecular weight of $NaNO_2$ is 14:69.

8.2.2. If 55.8 mg of sodium nitrite is dissolved in 10 mL of reagent water, the NO_2-N concentration in the resulting stock solution will be 1.13 mg/mL.

$$\frac{(55.8 \text{ mg } NaNO_2)\ (14 \text{ mg N}/69 \text{ mg } NaNO_2)}{10 \text{ mL}} = 1.13 \text{ mg N/mL} \quad .$$

8.2.3. If 50 μL of the $NaNO_2$ stock solution with a NO_2-N concentration of 1.13 mg/mL is used to spike 100 mL of reagent water, the final concentration of NO_2-N in the QC sample will be 0.57 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1.13 \text{ mg N/mL})\ (1 \text{ mL}/1000\ \mu\text{L})\ (50\ \mu\text{L})}{(100 \text{ mL})\ (1 \text{ L}/1000 \text{ mL})} = 0.57 \text{ mg/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not normally generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, complete the appropriate paperwork on a case-by-case basis.

9.1.2.1. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Services (CST-17) for review.

9.1.2.2. If CST-17 determines that the solid waste is contaminated below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.2.3. If CST-17 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a coated glass bottle in a secondary containment tray and keep it segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace metal waste.

9.2.3. Open the bottle only for the period of time necessary to add waste.

9.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.5. Label a new bottle for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992, " Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

HIGH EXPLOSIVES ON SOIL—QC SAMPLE PREPARATION

Analyte: High-Explosives Compounds	**Method No.:** QCO122
Matrix: Soil	**Spike Range:** 0.2–10 μg/g
Procedure: High-performance liquid chromatography	**Accuracy and Precision:** 100% ± 10% RSD
Effective Date: 05/25/94	**Authors:** Michael N. Jasperson Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals used in this procedure. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.1 for proper waste disposal practices.

1. Principle of Method

1.1. Obtain working standards containing high-explosives compounds chosen primarily from the list in Table I with each analyte at a concentration of approximately 1.0 mg/mL.

TABLE I. HIGH-EXPLOSIVES COMPOUNDS

Compound	Chemical Abstract Service (CAS) Number
2-Amino-4,6-Dinitrotoluene	35572782
4-Amino-2,6-Dinitrotoluene	1946510
1,3-Dinitrobenzene	99650
2,4-Dinitrotoluene	121142
2,6- Dinitrotoluene	606202
HMX	2691410
Nitrobenzene	98953
4-Nitroethylbenzene	100129
2-Nitrotoluene	88722
3-Nitrotoluene	99081
4-Nitrotoluene	99990
RDX	121824

TABLE I. HIGH-EXPLOSIVES COMPOUNDS (cont)	
Compound	CAS Number
TETRYL	479458
TNT	118967
1,3,5-Trinitrobenzene	99354

1.2 Spike the high-explosives standard directly onto a soil sample.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the error of the standard and on the error associated with use of the microsyringe and balance. A relative standard deviation (RSD) of 10% has been calculated for the error of the standard and for the spiking and weighing process based on the following:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of microsyringe,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analyses by high-performance liquid chromatography (HPLC) of QC samples prepared during 1994 using this procedure are tabulated below.

TABLE II. SPIKE RECOVERY DATA FOR HIGH EXPLOSIVES ON SOIL

Analyte	CAS #	1994 Mean ± std dev (%)			N
2-Amino-4,6-Dinitrotoluene	35572782	—			
4-Amino-2,6-Dinitrotoluene	1946510	—			
1,3-Dinitrobenzene	99650	86.7	±	9.3	12
2,4-Dinitrotoluene	121142	81.5	±	7.0	12
2,6- Dinitrotoluene	606202	78.7	±	10.0	11
HMX	2691410	94.2	±	9.5	12
Nitrobenzene	98953	19.4	±	7.1	9
4-Nitroethylbenzene	100129	—			
2-Nitrotoluene	88722	26.8	±	14.1	9
3-Nitrotoluene	99081	39.9	±	18.2	10
4-Nitrotoluene	99990	48.9	±	19.0	9
RDX	121824	119.0	±	18.2	12
TETRYL	479458	36.0	±	20.3	8
TNT	118967	91.0	±	14.1	12
1,3,5-Trinitrobenzene	99354	56.2	±	29.3	12

N = number of samples.

3. Collection and Storage of Samples

3.1. The blank soil matrix and the spiked samples should be stored in amber glass bottles fitted with Teflon-lined lids. Avoid using plastic containers and lids because phthalates may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for the analysis of high-explosives compounds on soil is 14 days.

4. Apparatus

4.1. Syringes: gas-tight, 10-, 25-, 50-, 100-, 250-, 500-, and 1000-μL.

4.2. Bottles: 1-oz, amber glass with Teflon-lined lids.

4.3. Vials: 1.5-mL, amber glass.

4.4. Caps: Teflon-lined to fit vials.

4.5. Teflon tape.

4.6. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.7. Pipettes: Pasteur, disposable glass.

4.8. Pipette bulb: rubber, to fit Pasteur pipette.

4.9. Labels printed with QC sample numbers.

5. Reagents

5.1. Soil. A clean, dry 10-g aliquot is required for each sample. A suitable soil does not contain the analyte of interest and presents few interferences to the analytical method.

5.2. Blank soil heated to nominally 100°C for 5 h and stored in glass is used as a sample matrix.

6. Calibration and Standards

6.1. High-explosives standards in a 1:1 mixture of acetonitrile and methanol are available in concentrations of 0.1 mg/mL and 1.0 mg/mL from Accustandard.

6.2. After opening the heat-sealed ampules containing high-explosives standards, transfer the contents into amber vials with screw caps lined with Teflon. Wrap the caps with Teflon tape. Remove the original label and affix it to the vial or transfer the standards information to a label on the new vial.

6.3. Store stock standards in a refrigerator.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.1.1. Sample size and container type may be varied to meet analytical requirements. Avoid the use of plastic containers for QC samples to be analyzed for organic constituents. This procedure describes the preparation of a high-explosives-on-soil QC sample using 10 g of blank soil and a 1-oz amber glass bottle.

7.1.2. Accurately weigh 10 g of blank soil into a 1-oz amber glass bottle with a Teflon-lined lid. Record the mass of soil on the bottle with a felt-tipped pen for reference by the analyst.

7.1.3. Remove a vial of standard containing the desired analytes from the refrigerator and allow it to reach room temperature.

7.1.4. Spike a volume of the standard directly onto the soil to reach the desired spike range. Avoid wetting the bottle walls.

7.1.5. Cap the bottle and label it with a QC sample number.

7.1.6. Return the vial containing the high-explosives standard to the refrigerator.

7.1.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.1.8. Store the QC samples in the refrigerator pending analysis.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use only with high explosives.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

8. Calculations

8.1. Calculate the concentration of each analyte in the QC sample using the following example.

8.1.1. If 50 μL of a high-explosives standard containing 1.0 mg/mL of TNT is spiked onto 10.0 g of soil, the TNT concentration in the QC sample is 5.0 μg/g.

$$\frac{(1.0\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(50\ \mu\text{L})}{10.0\ \text{g}} = 5.0\ \mu\text{g/g}\ .$$

8.1.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.2. Record the analyte concentrations in the QC sample in μg/g.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) contaminated with organic compounds in a covered metal can lined with a plastic bag and keep it segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the sealed bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) in a covered metal can in a secondary containment tray.

9.2.1.1. Keep liquid waste containing organic compounds segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the time necessary to add vials.

9.2.2.4. When the jar is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full container of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF number that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

ORGANIC COMPOUNDS ON TUBES AND BADGES -- QC SAMPLE PREPARATION

Analyte: Organic compounds	**Method No.:** QCO130
Matrix: Charcoal tubes and organic vapor monitor badges	**Spike Range:** Charcoal tube: 30–300 μg/tube Organic vapor monitor: 30–100 μg/sample NIOSH-PAT study: 0.2–2 mg/tube
Procedure: Gas chromatography with mass spectrometry (GCMS)	**Accuracy and Precision:** 100% $\pm$ 8.2% RSD
Effective Date: 03/05/84	**Author:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.10 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution of organic compounds of interest selected primarily from Table I (found at the end of this procedure) in a solvent compatible with the analytical extraction method.

1.2. The solvent most commonly used is carbon disulfide. Methylene chloride is also used frequently. If possible, the solvent should have a shorter chromatographic retention time than the organic compounds of interest in the solution.

1.3. Spike the stock directly into a charcoal tube or onto the filter paper inside an organic vapor monitor (OVM) badge.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the error of the standard and on the error associated with use of the microsyringe, balance, and volumetric flask. A relative standard deviation (RSD) of 8.2% has been calculated for the error of the standard and for spiking, weighing, and dilution, based on the following:

$$D = \frac{M1 \times M2 \times M4}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error, and
M4 = spiking error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 \times R_{M3}^2 \times R_{M4}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe, and
100 = factor to convert to percentage.

2.2. Analyses by GCMS of QC samples prepared between 1984 and 1989 using this procedure are found in Table II below. The data for these and more recent analyses are published in Source Materials 10.1 through 10.9.

TABLE II. SPIKE RECOVERY DATA FOR CHARCOAL TUBE AND BADGE

Compound	Year	Mean ± std dev (%)	(N)
Benzene	1984	106 ± 2	4
	1985	133 ± 1	3
	1986	86 ± 3	3
	1987	61 ± 8	3
	1988	83 ± 6	4
	1989	118 ± 4	3
Carbon tetrachloride	1984	98 ± 9	4
	1985	103 ± 4	3
	1986	97 ± 2	5
	1987	110 ± 11	7
	1988	100 ± 6	8
	1989	90 ± 12	12
Cellosolve acetate	1986	95 ± 5	3
	1987	102 ± 4	3
	1988	102 ± 2	4
Chloroform	1984	116 ± 9	8
	1985	101 ± 4	3
	1986	95 ± 3	3
	1987	88 ± 5	4
	1988	99 ± 12	4
	1989	109 ± 2	4
1,2-Dichloroethane	1984	91 ± 12	4
	1985	99 ± 3	6
	1986	130 ± 40	2
	1987	95 ± 5	7
	1988	99 ± 2	7
	1989	94 ± 6	11
p-Dioxane	1985	94 ± 4	6
	1986	101 ± 5	3
	1988	100 ± 1	4
Methyl chloroform	1984	106 ± 7	8
Methyl ethyl ketone	1984	93 ± 8	3
Trichloroethane	1989	89 ± 4	4

TABLE II. SPIKE RECOVERY DATA FOR CHARCOAL TUBE AND BADGE (cont)

Compound	Year	Mean ± std dev (%)	(N)
Trichloroethylene	1984	90 ± 8	4
	1985	102 ± 4	3
	1986	106 ± 7	2
	1987	94 ± 6	3
	1988	100 ± 1	4
	1989	90 ± 2	4
Toluene	1984	101 ± 1	3
	1985	105 ± 2	3
	1986	94 ± 6	3
	1987	98 ± 6	8
	1988	86 ± 1	4
	1989	96 ± 3	3
o-Xylene	1984	101 ± 1	3
	1985	103 ± 6	9
	1986	95 ± 5	6
	1987	101 ± 13	7
	1988	89 ± 4	8
	1989	96 ± 4	4

3. Collection and Storage of Samples

3.1. Charcoal tubes are received heat-sealed at both ends with plastic caps to seal the ends after the tubes are opened. OVM badges are received in sealed cans. The OVM badges include a closure cap with center and side ports, a charcoal sorbent disc, and a spacer plate above the disc.

3.2. Spiked tubes and badges are stored in a freezer pending analysis.

4. Apparatus

4.1. Volumetric flasks: 1- and 2-mL, class A, glass.

4.2. Pipettes: Pasteur, disposable, glass.

4.3. Pipette bulb: rubber, to fit Pasteur pipette.

4.4. Syringes: gas-tight, 10-, 25-, 50-, and 100-μL.

4.5. Microspatulas.

4.6. Sorbent sample tubes: charcoal, 100-mg primary bed, 50-mg backup bed.

4.7. Sorbent sample tubes: charcoal, 400-mg primary bed, 200-mg backup bed.

4.8. Organic vapor monitors: 3M OVM #3500 or equivalent from 3M, St. Paul, MN 55144-1000.

4.9. Paper filters: 25- to 28-mm-diameter, Whatman #2, #41, #42, or equivalent.

4.10. Teflon tape.

4.11. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.12. Laboratory oven: capable of sustaining 100–150°C.

4.13. Labels printed with QC sample numbers.

5. Reagents

5.1. Carbon disulfide (reagent-grade).

5.2. Methylene chloride (reagent-grade).

5.3. 1,2-Dichloroethane (reagent-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade analytes, chosen primarily from the list of target compounds in Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19381). Add solid analytes first, then liquid analytes after the addition of solvent.

6.2. Solvent choice for the stock solution matrix depends on the analytes included in the solution and on the analytical extraction method. If possible, the solvent should have a shorter chromatographic retention time than the analyte of interest.

6.2.1. Carbon disulfide is the solvent most commonly used.

6.2.2. A stock solution containing carbon disulfide, methylene chloride, or acrylonitrile as an analyte should use 1,2-dichloroethane as a solvent because methylene chloride, acrylonitrile, and carbon disulfide co-elute.

6.2.3. A stock solution containing ethanol as an analyte should use methylene chloride as a solvent because ethanol forms a colloidal suspension in carbon disulfide.

6.2.4. A stock solution containing 1,1,1-trichloroethane as an analyte should use carbon disulfide or methylene chloride as a solvent because 1,1,1-trichloroethane and 1,2-dichloroethane co-elute.

6.3. The stock solution may be prepared in a 1.0- or 2.0-mL volumetric flask. A solution containing multiple analytes is more conveniently prepared in a 2.0-mL volumetric flask.

6.3.1. The usual concentration range of a stock solution is between 5 and 20 mg/mL. A more concentrated stock solution may be required to prepare a QC sample with a higher spike range. The concentration of the stock solution should be such that a spike volume equal to or less than 15 μL onto a small charcoal tube or OVM badge and equal to or less than 30 μL onto a large charcoal tube will bring all analytes into the desired spike range.

6.3.2. Charcoal-tube QC samples prepared to accompany National Institute for Occupational Safety and Health Proficiency Analytical Testing (NIOSH PAT) intercomparison samples are spiked in the range 0.2–2 mg/tube. A stock solution with analytes in the concentration range of 15–150 mg/mL will reach the desired spike range on a small charcoal tube QC sample when a spike volume of 15 μL or less is used.

6.3.3. Add a solid analyte to a clean, tared 1.0- or 2.0-mL volumetric flask to reach the desired stock concentration range. Record the mass of the analyte added and tare the balance. Repeat for each solid analyte. See Step 8.1.

6.3.4. Add the solvent chosen for the stock solution matrix to the volumetric flask until it reaches approximately halfway to the graduation mark. Stopper the flask.

6.3.5. Swirl the flask to dissolve the solid analytes.

6.3.6. Calculate the volumes of the liquid analytes needed to reach the desired stock concentration range. See Steps 8.2 through 8.3.

6.3.7. Place the stoppered flask on the analytical balance and tare the balance.

6.3.8. Using a syringe, add a liquid analyte just above the surface of the solvent to reach the desired stock concentration range. Restopper the flask and record the mass and volume of the analyte added. Tare the balance. Repeat for each liquid analyte added.

6.3.9. Dilute the solution to volume with the solvent chosen in Step 6.3.4.

6.3.10. Mix by gently inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

6.3.11. Wrap Teflon tape around the stopper of the volumetric flask.

6.3.12. Label the flask with information identifying the stock solution and its expiration date.

6.3.13. The stock solution is stable for approximately 2 weeks when stored at -20°C.

6.4. For QC samples containing multiple analytes, more than one stock solution may be prepared using different analytes. The combination of analytes in the QC sample may be varied by spiking with more than one stock solution.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with semivolatile compounds and a second group of syringes for use only with volatile compounds.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into the waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. The spike range for volatile organic compounds on charcoal tubes or on OVM badges varies with the analyte spiked.

7.3.1. For most analytes, the spike range is 30–100 μg/tube or 30–100 μg/badge.

7.3.2. For analytes with a shorter retention time than carbon disulfide during gas chromatography, the spike range is 100–300 μg/tube or 100–300 μg/badge. Acetone, methanol, ethanol, 2-propanol, and Freon are included in this category.

7.3.3. The spike range for analytes in QC samples prepared to accompany NIOSH PAT samples is 0.2–2 mg/tube.

7.4. Preparation of QC samples for volatile organic compounds on charcoal tubes.

7.4.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.4.2. Use the same size charcoal tube for the QC samples as was used to collect the samples to be analyzed.

7.4.3. The total spike volume onto small charcoal tubes should be equal to or less than 15 μL and onto large charcoal tubes should be equal to or less than 30 μL to avoid saturation of the primary charcoal bed.

7.4.4. Remove the stock solution from the freezer and allow it to come to room temperature. Do not allow the stock solution to sit at room temperature for longer than 1 h before spiking the QC sample.

7.4.5. Break off the tip of the entrance end of the charcoal tube. The entrance end is the end with the glass wool plug over the primary charcoal bed and an air space between the end of the tube and the charcoal bed.

7.4.6. Using a syringe, spike a volume of stock solution onto the primary charcoal bed to reach the desired spike range. Spike the solution beginning in the middle of the primary charcoal bed and drawing the syringe needle toward the glass wool plug at the top of bed as the spiking

is completed. The entire volume of spike solution should be on the charcoal bed and not on the walls of the sample tube.

7.4.7. Cap both ends of the sample tube with the plastic tube caps and wrap Teflon tape around the broken end.

7.4.8. Label the tube with a QC sample number.

7.4.9. Return the stock solution to the freezer.

7.4.10. Store the QC samples in a freezer pending analysis.

7.4.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.5. Preparation of QC samples for volatile organic compounds on OVM badges.

7.5.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.5.2. The total spike volume onto an OVM badge should be equal to or less than 15 μL.

7.5.3. Remove the stock solution from the freezer and allow it to come to room temperature. Do not allow the stock solution to sit at room temperature for longer than 1 h before spiking the QC sample.

7.5.4. Remove the OVM badge from the can in which it was received.

7.5.5. Remove and discard the plastic ring and white film from the badge.

7.5.6. Place a 25- to 28-mm paper filter onto the spacer plate above the charcoal disc. Snap the closure cap onto the badge. Close the side port.

7.5.7. Using a syringe, spike a volume of the stock onto the filter paper through the center port to reach the desired spike range. Close the center port.

7.5.8. Return the badge to the can in which it was received and label the can with a QC number.

7.5.9. The badge should be kept in the refrigerator for at least 16–24 h before analysis to achieve complete transfer of the organic compounds from the filter paper onto the charcoal sorbent or in a freezer for longer periods of time pending analysis.

7.5.10. Return the stock solution to the freezer.

7.5.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Solid analytes used in the stock solution are measured directly by mass.

8.2. Calculate the volume of neat liquid analyte to add to the stock solution as in the following example.

8.2.1. Read the density of the neat liquid analyte from Table I. The density of chloroform is 1.492 mg/μL.

8.2.2. The desired spike range for 1 mL of stock is 5–20 mg of neat analyte.

8.2.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 1 mL of stock solution.

$$\frac{5\ \text{mg}}{1.492\ \text{mg}/\mu\text{L}} \text{ to } \frac{20\ \text{mg}}{1.492\ \text{mg}/\mu\text{L}} = 3.4 \text{ to } 13.4\ \mu\text{L} \quad .$$

For chloroform, 3.4–13.4 μL of the neat analyte should be diluted to 1 mL to reach the desired concentration range of 5–20 mg/mL in the stock solution.

8.3. Calculate the concentration of each neat analyte in the stock solution as in the following example.

8.3.1. If 5 μL of chloroform, weighing 7.5 mg, is diluted to 1 mL of stock solution, the concentration of chloroform in the stock solution is 7.5 mg/mL.

$$\frac{7.5\ \text{mg}}{1\ \text{mL}} = 7.5\ \text{mg/mL} \quad .$$

8.4. Calculate the concentration of each analyte on a charcoal-tube QC sample as in the following example.

8.4.1. If 6 μL of a stock solution containing 7.5 mg/mL of chloroform is spiked onto a charcoal tube, the concentration of chloroform in the QC sample is 45 μg/sample. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(7.5\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(6\ \mu\text{L})}{\text{sample}} = 45\ \mu\text{g/sample}$$

8.5. Calculate the concentration of each analyte on an OVM badge QC sample as in the following example.

8.5.1. If 9 μL of a stock solution containing 7.5 mg/mL of chloroform is spiked onto an OVM badge, the concentration of chloroform in the QC sample is 67.5 μg/sample. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(7.5\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(9\ \mu\text{L})}{\text{sample}} = 67.5\ \mu\text{g/sample}$$

8.6. Record the analyte concentration on a charcoal-tube QC sample or an OVM badge as μg/sample or mg/sample.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste contaminated with organic compounds (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full and keep the can in the secondary containment tray pending pickup by CST-17.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4 Cap the jar when full and keep the jar in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag, can, or jar of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

10.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

10.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

10.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

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10.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.7. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.8. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.9. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.10. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked ( ). Where a section heading is marked, the entire section has been revised.

TABLE I. ORGANIC COMPOUNDS

Compound	CAS Number	Density of liquids (mg/μL)
acetone	67641	0.791
benzene	71432	0.874
bromobenzene	108861	1.491
bromochloromethane	74975	1.991
bromodichloromethane	75274	1.980
bromoform	75252	2.894
bromomethane	74839	0.838
2-butanone (MEK)	78933	0.805
n-butylbenzene	104518	0.860
sec-butylbenzene	135988	0.863
tert-butylbenzene	98066	0.867
carbon disulfide	75150	1.266
carbon tetrachloride	56235	1.594
chlorobenzene	108907	1.107
chlorodibromomethane	124481	2.451
chloroethane	75003	0.891
chloroform	67663	1.492
1-chlorohexane	544105	0.879
2-chlorotoluene	95498	1.083
4-chlorotoluene	106434	1.070
1,2-dibromo-3-chloropropane	96128	2.093
1,2-dibromoethane	106934	2.180
dibromomethane	74953	2.477
1,2-dichlorobenzene	95501	1.306
1,3-dichlorobenzene	541731	1.288
1,4-dichlorobenzene	106467	1.241
1,1-dichloroethane	75343	1.176
1,2-dichloroethane	107062	1.256
1,1-dichloroethene	75354	1.213
cis-1,2-dichloroethene	156592	1.284
trans-1,2-dichloroethene	156605	1.257
1,2-dichloropropane	78875	1.156
1,3-dichloropropane	142289	1.190
2,2-dichloropropane	594207	1.082
1,1-dichloropropene	563586	1.169
cis-1,3-dichloropropene	10061015	1.224

TABLE I. ORGANIC COMPOUNDS (cont)

Compound	CAS Number	Density of liquids (mg/μL)
trans-1,3-dichloropropene	10061026	1.224
ethylbenzene	100414	0.867
hexachlorobutadiene	87683	1.665
2-hexanone	591786	0.812
isopropylbenzene	98828	0.864
4-isopropyltoluene	99876	0.860
methylene chloride	75092	1.325
4-methyl-2-pentanone (MIK)	108101	0.800
naphthalene	91203	solid
n-propylbenzene	103651	0.862
styrene	100425	0.909
1,1,1,2-tetrachloroethane	630206	1.598
1,1,2,2,-tetrachloroethane	79345	1.586
tetrachloroethene	127184	1.623
toluene	108883	0.867
1,2,3-trichlorobenzene	87616	solid
1,2,4-trichlorobenzene	120821	1.454
1,1,1-trichloroethane	71556	1.338
1,1,2-trichloroethane	79005	1.435
trichloroethene	79016	1.464
trichlorofluoromethane	75694	1.494
1,2,3-trichloropropane	96184	1.387
1,2,4-trimethylbenzene	95636	0.889
1,3,5-trimethylbenzene	108678	0.864
vinyl acetate	108054	0.934
o-xylene	95476	0.870
mixed xylenes (total)	1330207	0.860

SEMIVOLATILE ORGANIC COMPOUNDS ON SOIL – QC SAMPLE PREPARATION

Analyte: Semivolatile organic compounds	**Method No.** QCO210
Matrix: Soil	**Spike Range:** 0.67–6.67 mg/kg
Procedure: Gas chromatography and mass spectrometry (GCMS)	**Accuracy and Precision:** 100% ± 5.2% RSD
Effective Date: 01/22/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare stock solutions in acetone of 4–10 semivolatile compounds chosen primarily from the list in Table I, found at the end of this procedure.

1.2. Spike the stocks onto 30 g of blank soil.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask, microsyringe, and balance. A relative standard deviation (RSD) of 5.2% at the 1-σ level has been calculated for the error of the standard and for spiking, weighing, and dilution based on the following:

$$D = \frac{M1 \times M2 \times M4}{M3 \times M5},$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,
M4 = spiking error, and
M5 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2 + R_{M5}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe,
R^2_{M5} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analysis by GCMS of QC samples prepared between 1990 and 1991 using this procedure are summarized in Table II below. The data are published in Source Materials 10.1 and 10.2.

TABLE II. SPIKE RECOVERY DATA FOR SEMIVOLATILE ORGANIC COMPOUNDS ON SOIL

	1990			1991		
Compound	Mean	± std dev	(n)	Mean	± std dev	(n)
Acenaphthene		—		62		(1)
Acenaphthylene		—			—	
Aniline	10	± 4	(3)		—	
Anthracene	80	± 28	(12)	85	± 10	(8)

TABLE II. SPIKE RECOVERY DATA FOR SEMIVOLATILE ORGANIC COMPOUNDS ON SOIL (cont.)

Compound	1990 Mean	± std dev	(n)	1991 Mean	± std dev	(n)
Azobenzene	—			—		
Benzo[a]anthracene	—			—		
Benzo[b]fluoranthene	98		(2)	78	± 9	(3)
Benzo[k]fluoranthene	—			—		
Benzoic acid	50	± 37	(8)	20	± 7	(3)
Benzo[g,h,i]perylene	—			—		
Benzo[a]pyrene	—			60		(1)
Benzyl alcohol	62	± 16	(4)	73	± 37	(8)
Bis(2-chloroethoxy)methane	—			—		
Bis(2-chloroethyl)ether	67	± 9	(5)	79	± 12	(4)
Bis(2-chloroisopropyl)ether	—			—		
Bis(2-ethylhexyl)phthalate	—			—		
4-Bromophenyl phenylether	—			—		
Butyl benzyl phthalate	—			—		
4-Chloroaniline	—			—		
4-Chloro-3-methylphenol	—			76	± 16	(5)
2-Chloronaphthalene	—			58	± 12	(6)
2-Chlorophenol	—			58	± 10	(3)
4-Chlorophenyl phenyl ether	—			—		
Chrysene	—			135	± 60	(4)
Di-n-butyl phthalate	—			67	± 4	(6)
Di-n-octyl phthalate	—			124	± 91	(3)
Dibenzo[a,h]anthracene	—			—		
Dibenzofuran	—			—		
1,2-Dichlorobenzene	—			94		±110
1,3-Dichlorobenzene	—			—		
1,4-Dichlorobenzene	9			(1) 57		± 90
2,4-Dichlorophenol	66		(2)	62	± 14	(6)
Diethyl phthalate	111	± 33	(12)	69		(1)
2,4-Dimethylphenol	35		(2)	58	± 12	(5)
Dimethyl phthalate	78		(2)	—		
4,6-Dinitro-2-methylphenol	—			—		
2,4-Dinitrophenol	—			—		
2,4-Dinitrotoluene	—			88		(1)
2,6-Dinitrotoluene	—			68		(1)
Fluoranthene	—			93	± 12	(8)

TABLE II. SPIKE RECOVERY DATA FOR SEMIVOLATILE ORGANIC COMPOUNDS ON SOIL (cont.)

Compound	1990 Mean	± std dev	(n)	1991 Mean	± std dev	(n)
Fluorene		—			—	
Hexachlorobenzene	54		(1)		—	
Hexachlorobutadiene	59	± 18	(12)	66	± 18	(8)
Hexachlorocyclopentadiene	36		(1)	64		(2)
Hexachloroethane	9		(1)	51	± 27	(4)
Indeno[1,2,3-cd]pyrene		—			—	
Isophorone	64	± 18	(11)		—	
2-Methylnaphthalene		—			—	
2-Methylphenol		—			—	
4-Methylphenol		—			—	
Naphthalene	55	± 20	(3)	55	± 5	(3)
2-Nitroaniline		—			—	
3-Nitroaniline		—		23	± 11	(3)
4-Nitroaniline	39	± 23	(3)	31	± 13	(4)
Nitrobenzene	59		(2)		—	
2-Nitrophenol		—			—	
4-Nitrophenol	77	± 32	(5)	75	± 15	(11)
N-Nitrosodiphenylamine		—		77		(1)
N-Nitrosodi-n-propylamine		—			—	
Pentachlorophenol		—			—	
Phenanthrene	89		(2)		—	
Phenol	64	± 9	(6)		—	
Pyrene		—			—	
1,2,4-Trichlorobenzene		—			—	
2,4,5-Trichlorophenol	74	± 11	(3)		—	
2,4,6-Trichlorophenol		—			—	

3. Collection and Storage of Samples

3.1. The blank soil matrix and the spiked samples should be stored in glass bottles fitted with Teflon-lined lids. Avoid using plastic containers and lids because phthalates, which are semivolatile compounds, may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for the analysis of semivolatile compounds in soil is 14 days.

4. Apparatus

4.1. Volumetric flask: 5-mL, class A, glass.

4.2. Syringes: gas-tight, 25-, 50-, 100-, and 250-μL.

4.3. Spatulas.

4.4. Pipettes: Pasteur, glass.

4.5. Pipette bulb: rubber, to fit Pasteur pipette.

4.6. Vials: 1.5-mL, glass.

4.7. Caps: open-top, to fit vials.

4.8. Septa: Teflon/silicone discs to fit open-top caps.

4.9. Teflon tape.

4.10. Bottles: 2-oz, glass, with Teflon-lined caps.

4.11. Analytical balance: 200-g minimum capacity, 0.1-mg accuracy.

4.12. Laboratory oven: capable of sustaining 100–150°C.

4.13. Labels printed with QC sample numbers.

5. Reagents

5.1. Soil. A clean, dry 30-g aliquot is required for each sample. A suitable soil does not contain the analyte of interest and presents few interferences to the analytical method.

5.2. Blank soil, heated to nominally 100°C for 5 h and stored in glass, is used as a sample matrix.

5.3. Acetone (analytical-grade).

5.4. Methanol (analytical-grade).

5.5. Methylene chloride (analytical-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade semivolatile analytes chosen primarily from Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19387). Use both acid and base/neutral semivolatile analytes because the two fractions are extracted separately before being recombined for analysis. Add solid analytes first, then liquid analytes after the addition of solvent.

6.1.1. Add 8–12 mg of a solid semivolatile analyte to a clean, tared 5.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.2. Add approximately 2 mL of acetone to the flask, stopper the flask, and swirl it to see if all analytes will dissolve. If not, methylene chloride and/or methanol may be added to effect total dissolution. For example, chrysene requires methylene chloride and methanol and gentle heating to effect total dissolution.

6.1.3. Place the stoppered flask on the analytical balance and tare the balance.

6.1.4. Calculate the volumes of liquid analytes needed to reach a weight spike range of 8–12 mg in 5 mL of stock solution. See Step 8.2.

6.1.5. Using a syringe, add a liquid analyte just above the surface of the acetone. Stopper the flask and record the mass and volume of the analyte added. Tare the balance. Repeat for each liquid analyte.

6.1.6. Dilute the solution to volume with acetone. Mix by inversion.

6.1.7. Discard the solution in the neck of the flask to minimize concentration changes due to loss of analytes from the surface of the solution.

6.1.8. The concentration of analytes in the stock solution will be 1.5–2.5 mg/mL.

6.1.9. Transfer the stock solution to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.10. Label the vials with information identifying the standard and with the expiration date.

6.1.11. The standard solution in acetone is stable for approximately 3 months stored at -20°C.

6.2. Prepare additional stock solution using different analytes selected primarily from Table I. The number of analytes in the QC sample may be increased by using more than one stock solution to spike the sample.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with semivolatile compounds.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into a waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for approximately 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Sample size and container type may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes the preparation of a semivolatiles-on-soil QC sample using 30 g of soil and a 2-oz glass bottle.

7.3.2. Remove a vial of semivolatile stock solution from the freezer and allow it to come to room temperature. Do not let the vial sit at room temperature for longer than 2 h before spiking the QC sample.

7.3.3. Some analytes may crystallize out of solution in the freezer. Visually inspect the stock solution. If any precipitate is present, gently warm the solution on a hot plate and swirl it to redissolve the precipitate. Avoid

excessive or prolonged heating, which would cause analytes to be lost from the solution.

7.3.4. Accurately weigh 30 g of blank soil into a 2-oz glass bottle. Record the mass of soil on the bottle with a felt-tipped pen for reference by the analyst.

7.3.5. Using a gas-tight syringe, spike a volume of the standard onto the surface of the soil to reach the desired spike range. Blank QC samples may be prepared by spiking acetone onto the soil. The analyst will use the entire sample.

7.3.6. Cap the vial with a Teflon-lined lid and label it with a QC number.

7.3.7. Return the stock solution to the freezer.

7.3.8. Refrigerate the QC sample pending analysis. The maximum holding time for semivolatile organic compounds on soil is 14 days.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Use 8–12 mg of a solid analyte in 5.0 mL of stock solution.

8.2. Calculate the volume of neat liquid analyte needed to prepare a stock solution in the range of 8–12 mg/5 mL.

8.2.1. Read the density of the neat liquid analyte from Table I. The density of nitrobenzene is 1.196 mg/μL.

8.2.2. The desired weight spike range for 5 mL of stock solution is 8–12 mg of neat analyte.

8.2.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 5 mL of stock solution.

$$\frac{8\ \text{mg}}{1.196\ \text{mg}/\mu\text{L}} \text{ to } \frac{12\ \text{mg}}{1.196\ \text{mg}/\mu\text{L}} = 6.7 \text{ to } 10.0\ \mu\text{L} \quad .$$

For nitrobenzene, between 6.7 and 10 μL of the neat analyte should be diluted to 5 mL to reach the desired concentration range of 1.5–2.5 mg/mL in the stock solution.

8.3. Calculate the concentration of each analyte in the stock solution as in the following examples.

8.3.1. If 9.6 mg of solid anthracene is dissolved in 5.0 mL of stock solution, the concentration of anthracene in the stock solution is 1.92 mg/mL.

$$\frac{9.6\ \text{mg}}{5.0\ \text{mL}} = 1.92\ \text{mg/mL} \quad .$$

8.3.2. If 9 μL of liquid nitrobenzene, weighing 10.8 mg, is diluted in 5 mL of stock solution, the concentration of nitrobenzene in the stock solution is 2.16 mg/mL.

$$\frac{10.8\ \text{mg}}{5\ \text{mL}} = 2.16\ \text{mg/mL} \quad .$$

8.4. Calculate the concentration of each analyte in the QC sample as in the following example.

8.4.1. If 60 μL of a stock standard solution containing 1.92 mg/mL of anthracene and 2.16 mg/mL of nitrobenzene is spiked onto 30.0018 g of blank soil, the concentration of anthracene in the QC sample will be 3.84 mg/kg. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1.92\ \text{mg/mL})\ (60\ \mu\text{L})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)}{30.0018\ \text{g}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)} = 3.84\ \text{mg/kg} \quad .$$

The concentration of nitrobenzene in the QC sample will be 4.32 mg/kg. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(2.16\ \text{mg/mL})\ (60\ \mu\text{L})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)}{30.0018\ \text{g}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)} = 4.32\ \text{mg/kg} \quad .$$

8.5. Record the analyte concentrations in the QC sample in mg/kg or μg/g.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste contaminated with organic compounds (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4. Cap the jar when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag, can, or jar of waste contaminated with organic compounds by using the current Chemical Waste Disposal

Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked ( ). Where a section heading is marked, the entire section has been revised.

TABLE I. SEMIVOLATILE ORGANIC COMPOUNDS

Analyte	CAS No.	Category	Density of liquid, (mg/μL)
acenaphthene	83329	Base/Neutral	solid
acenaphthylene	208968	Base/Neutral	0.899
aniline	62533	Base/Neutral	1.022
anthracene	120127	Base/Neutral	solid
azobenzene	103333	Base/Neutral	1.090
benz[a]anthracene	56553	Base/Neutral	solid
m-benzidine	92875	Base/Neutral	solid
benzo[b]fluoranthene	205992	Base/Neutral	solid
benzo[k]fluoranthene	207089	Base/Neutral	solid
benzoic acid	65850	Acid	solid
benzo[g,h,i]perylene	191242	Base/Neutral	solid
benzo[a]pyrene	50328	Base/Neutral	solid
benzyl alcohol	100516	Base/Neutral	1.045
bis(2-chloroethoxy)methane	111911	Base/Neutral	solid
bis(2-chloroethyl)ether	111444	Base/Neutral	1.220
bis(2-chloroisopropyl)ether	108601	Base/Neutral	solid
bis(2-ethylhexyl) phthalate	117817	Base/Neutral	0.981
4-bromophenyl phenyl ether	101553	Base/Neutral	1.423
butyl benzyl phthalate	85687	Base/Neutral	0.966
4-chloroaniline	106478	Base/Neutral	solid
4-chloro-3-methylphenol	59507	Acid	solid
2-chloronaphthalene	91587	Base/Neutral	solid
2-chlorophenol	95578	Acid	1.241
4-chlorophenyl phenyl ether	7005723	Base/Neutral	solid
chrysene	218019	Base/Neutral	solid
di-n-butyl phthalate	84742	Base/Neutral	1.043
di-n-octyl phthalate	117840	Base/Neutral	0.981
dibenz[a,h]anthracene	53703	Base/Neutral	solid
dibenzofuran	132649	Base/Neutral	solid
1,2-dichlorobenzene	95501	Base/Neutral	1.306
1,3-dichlorobenzene	541731	Base/Neutral	1.288
1,4-dichlorobenzene	106467	Base/Neutral	1.241
3,3´dichlorobenzidine	91941	Base/Neutral	solid
2,4-dichlorophenol	120832	Acid	solid

TABLE I. SEMIVOLATILE ORGANIC COMPOUNDS (cont)

Analyte	CAS No.	Category	Density of liquid, (mg/μL)
diethyl phthalate	84662	Base/Neutral	1.118
2,4-dimethylphenol	105679	Acid	1.027
dimethyl phthalate	131113	Base/Neutral	1.190
4,6-dinitro-2-methylphenol	534521	Acid	solid
2,4-dinitrophenol	51285	Acid	solid
2,4-dinitrotoluene	121142	Base/Neutral	solid
2,6-dinitrotoluene	606202	Base/Neutral	solid
fluoranthene	206440	Base/Neutral	solid
fluorene	86737	Base/Neutral	solid
hexachlorobenzene	118741	Base/Neutral	solid
hexachlorobutadiene	87683	Base/Neutral	1.665
hexachlorocyclopentadiene	77474	Base/Neutral	1.702
hexachloroethane	67721	Base/Neutral	2.091
indeno[1,2,3-cd]pyrene	193395	Base/Neutral	solid
isophorone	78591	Base/Neutral	0.923
2-methylnaphthalene	91576	Base/Neutral	1.000
2-methylphenol	95487	Acid	1.048
4-methylphenol	106445	Acid	1.034
naphthalene	91203	Base/Neutral	solid
2-nitroaniline	88744	Base/Neutral	solid
3-nitroaniline	99092	Base/Neutral	solid
4-nitroaniline	100016	Base/Neutral	solid
nitrobenzene	98953	Base/Neutral	1.196
2-nitrophenol	88755	Acid	solid
4-nitrophenol	100027	Acid	solid
N-nitrosodimethylamine	62759	Base/Neutral	1.006
N-nitrosodiphenylamine	86306	Base/Neutral	solid
N-nitrosodi-n-propylamine	621647	Base/Neutral	solid
pentachlorophenol	87865	Acid	1.978
phenanthrene	85018	Base/Neutral	solid
phenol	108952	Acid	solid
pyrene	129000	Base/Neutral	solid
1,2,4-trichlorobenzene	120821	Base/Neutral	1.454
2,4,5-trichlorophenol	95954	Acid	solid
2,4,6-trichlorophenol	88062	Acid	solid

SEMIVOLATILE ORGANIC COMPOUNDS IN WATER – QC SAMPLE PREPARATION

Analyte: Semivolatile organic compounds	**Method No.:** QCO220
Matrix: Water	**Spike Range:** 20–200 μg/L
Procedure: Gas chromatography and mass spectrometry (GCMS)	**Accuracy and Precision:** 100% ± 5.2% RSD
Effective Date: 01/01/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare stock solutions of 4–10 semivolatile compounds in acetone selected primarily from the list in Table I, found at the end of this procedure.

1.2. Spike the stocks into 1 L of distilled water.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with use of the microsyringe, balance, and volumetric flask. Since the analyst uses the entire sample, it is not necessary to dilute the sample to exactly 1 L, and the assumption is made that M5=1. A relative standard deviation (RSD) of 5.2% at the 1-σ level has been calculated for the error of the standard and for spiking, weighing, and dilution based on the following:

$$D = \frac{M1 \times M2 \times M4}{M3 \times M5} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,

M4 = pipette error, and
M5 = second dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation. Since the analyst uses the entire sample, it is not necessary to dilute the sample to exactly 1 L, and the assumption is made that $R^2_{M5}=0$.

$$\%S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe,
R^2_{M5} = relative variance of second volumetric flask, and
100 = factor to convert to percentage.

2.2. Analyses by GCMS of QC samples prepared between 1990 and 1991 using this procedure are summarized in Table II below. The data are published in Source Materials 10.1 and 10.2.

TABLE II. SPIKE RECOVERY DATA FOR SEMIVOLATILE ORGANIC COMPOUNDS IN WATER

	1990		1991	
Compound	Mean ± std dev	(n)	Mean ± std dev	(n)
Acenaphthene	—		84 ± 18	(4)
Acenaphthylene	—		—	
Aniline	84 ± 19	(4)	88	(1)
Anthracene	58 ± 15	(5)	—	

TABLE II. SPIKE RECOVERY DATA FOR SEMIVOLATILE ORGANIC COMPOUNDS IN WATER (cont)

Compound	1990 Mean ± std dev	(n)	1991 Mean ± std dev	(n)
Azobenzene	—		—	
Benzo[a]anthracene	—		—	
Benzo[b]fluoranthene	—		85	(2)
Benzo[k]fluoranthene	—		—	
Benzoic acid	54 ± 35	(9)	57 ± 43	(4)
Benzo[g,h,i]perylene	—		—	
Benzo[a]pyrene	—		40	(2)
Benzyl alcohol	53 ± 29	(4)	79 ± 22	(6)
Bis(2-chloroethoxy)methane	—		—	
Bis(2-chloroethyl)ether	63 ± 7	(4)	60 ± 19	(4)
Bis(2-chloroisopropyl)ether	—		—	
Bis(2-ethylhexyl)phthalate	—		—	
4-Bromophenyl phenyl ether	—		—	
Butyl benzyl phthalate	—		—	
4-Chloroaniline	—		—	
4-Chloro-3-methylphenol	—		67 ± 29	(4)
2-Chloronaphthalene	—		60	(2)
2-Chlorophenol	—		60 ± 15	(4)
4-Chlorophenyl phenyl ether	—		—	
Chrysene	—		16	(1)
Di-n-butyl phthalate	—		29	(2)
Di-n-octyl phthalate	—		66 ± 15	(4)
Dibenzo[a,h]anthracene	—		—	
Dibenzofuran	—		—	
1,2-Dichlorobenzene	—		—	
1,3-Dichlorobenzene	—		—	
1,4-Dichlorobenzene	—		31	(2)
2,4-Dichlorophenol	58	(2)	67	(2)

TABLE II. SPIKE RECOVERY DATA FOR SEMIVOLATILE ORGANIC COMPOUNDS IN WATER (cont)

Compound	1990 Mean ± std dev	(n)	1991 Mean ± std dev	(n)
Diethyl phthalate	46 ± 56	(4)	15	(2)
2,4-Dimethylphenol	—		70 ± 15	(6)
Dimethyl phthalate	—		—	
4,6-Dinitro-2-methylphenol	—		—	
2,4-Dinitrophenol	—		—	
2,4-Dinitrotoluene	—		—	
2,6-Dinitrotoluene	—		42 ± 25	(4)
Fluoranthene	—		78 ± 19	(6)
Fluorene	—		—	
Hexachlorobenzene	64 ± 6	(3)	—	
Hexachlorobutadiene	47 ± 6	(5)	50 ± 6	(4)
Hexachlorocyclopentadiene	48	(2)	46 ± 12	(4)
Hexachloroethane	48	(2)	—	
Indeno[1,2,3-cd]pyrene	—		—	
Isophorone	69 ± 13	(5)	—	
2-Methylnaphthalene	—		—	
2-Methylphenol	—		—	
4-Methylphenol	—		—	
Naphthalene	—		58	(2)
2-Nitroaniline	—		—	
3-Nitroaniline	—		70	(2)
4-Nitroaniline	—		80 ± 17	(4)
Nitrobenzene	—		—	
2-Nitrophenol	—		—	
4-Nitrophenol	85 ± 23	(6)	62 ± 20	(8)
N-Nitrosodiphenylamine	—		42 ± 27	(4)
N-Nitrosodi-n-propylamine	—		—	
Pentachlorophenol	92 ± 27	(6)	—	
Phenanthrene	64	(2)	—	
Phenol	49 ± 14	(4)	66	(2)
Pyrene	—		—	

TABLE II. SPIKE RECOVERY DATA FOR SEMIVOLATILE ORGANIC COMPOUNDS IN WATER (cont)

Compound	1990 Mean ± std dev	(n)	1991 Mean ± std dev	(n)
1,2,4-Trichlorobenzene	—		—	
2,4,5-Trichlorophenol	74 ± 17	(10)	—	
2,4,6-Trichlorophenol	—		—	

3. Collection and Storage of Samples

3.1. Distilled water is used as the blank matrix. Use water that has not been run through plastic tubing or stored in plastic holding vessels because phthalates, which are semivolatile organic compounds, may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for semivolatiles in water is 7 days.

4. Apparatus

4.1. Volumetric flasks: 5-mL, class A, glass.

4.2. Syringes: gas-tight, 25-, 50-, 100-, and 250-μL.

4.3. Spatulas.

4.4. Pipettes: Pasteur, glass.

4.5. Pipette bulb: rubber, to fit Pasteur pipette.

4.6. Vials: 1.5-mL, glass.

4.7. Caps: open-top, to fit vials.

4.8. Septa: Teflon/silicone discs to fit open-top caps.

4.9. Teflon tape.

4.10. Bottles: 1-L wide-mouth glass jars, amber, precleaned, with Teflon-lined lids.

4.11. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.12. Laboratory oven: capable of sustaining 100–150°C.

4.13. Labels: printed with QC sample numbers.

5. Reagents

5.1. Acetone (analytical-grade).

5.2. Methanol (analytical-grade).

5.3. Methylene chloride (analytical-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade semivolatile analytes chosen primarily from Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19381). Use both acid and base/neutral semivolatile analytes because the two fractions are extracted separately before being recombined for analysis. Add solid analytes first, then liquid analytes after the addition of solvent.

6.1.1. Add 8–12 mg of a solid semivolatile analyte to a clean, tared 5.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.2. Add approximately 2 mL of acetone to the flask, stopper the flask, and swirl it to see if all analytes will dissolve. If not, methylene chloride and/or methanol may be added to effect total dissolution. For example, chrysene requires methylene chloride and methanol and gentle heating to effect total dissolution.

6.1.3. Place the stoppered flask on the analytical balance and tare the balance.

6.1.4. Calculate the volumes of liquid analytes needed to reach a weight spike range of 8–12 mg in 5 mL of stock solution. See Step 8.2.

6.1.5. Using a syringe, add a liquid analyte just above the surface of the acetone. Stopper the flask and record the mass and volume of analyte added. Tare the balance. Repeat for each liquid analyte added.

6.1.6. Dilute the solution to volume with acetone. Mix by inversion.

6.1.7. Discard the solution in the neck of the flask to minimize concentration changes due to loss of analytes from the surface of the solution.

6.1.8. The concentration of analytes in the stock solution will be 1.5–2.5 mg/mL.

6.1.9. Transfer the stock solution to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.10. Label the vials with information identifying the standard and with the expiration date.

6.1.11. The stock solution in acetone is stable for approximately three months stored at -20°C.

6.2. Prepare additional stock solutions using different analytes selected primarily from Table I. The number of analytes in the QC sample may be increased by using more than one solution to spike the sample.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with semivolatile compounds.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into a waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for approximately 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Samples size and container type may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes

the preparation of a 1-L semivolatiles-in-water QC sample in an amber glass jar.

7.3.2. Remove a vial of semivolatile stock solution from the freezer and allow it to come to room temperature. Do not let the vial sit at room temperature for longer than 2 h before spiking the QC sample.

7.3.3. Some analytes may crystallize out of solution in the freezer. Visually inspect the stock solution. If any precipitate is present, gently warm the solution on a hotplate and swirl it to redissolve the precipitate. Avoid excessive or prolonged heating that would cause analytes to be lost from the solution.

7.3.4. Fill a precleaned 1-L amber bottle to the neck with distilled water. Use only distilled water that has not been stored in plastic or run through plastic tubing.

7.3.5. Using a syringe, spike a volume of the solution below the surface of the water to reach the desired spike range. Blank QC samples may be prepared by spiking acetone into the water. The analyst will use the entire sample assuming a 1-L volume.

7.3.6. Cap the bottle and label it with a QC sample number.

7.3.7. Return the stock solution to the freezer.

7.3.8. Refrigerate the QC sample pending analysis. The maximum holding time for semivolatile organic compounds in water is 7 days.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Use 8–12 mg of a solid analyte in 5.0 mL of stock solution.

8.2. Calculate the volume of a neat liquid analyte needed to prepare a stock solution in the range of 8–12 mg/5 mL.

8.2.1. Read the density of the neat liquid analyte from Table I. The density of nitrobenzene is 1.196 mg/μL.

8.2.2. The desired weight spike range for 5 mL of stock solution is 8–12 mg of neat analyte.

8.2.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 5 mL of stock solution.

$$\frac{8\ \text{mg}}{1.196\ \text{mg}/\mu\text{L}} \text{ to } \frac{12\ \text{mg}}{1.196\ \text{mg}/\mu\text{L}} = 6.7 \text{ to } 10.0\ \mu\text{L} \quad .$$

For nitrobenzene, between 6.7 and 10 μL of the neat analyte should be diluted to 5 mL to reach the desired concentration range of 1.5–2.5 mg/mL in the stock solution.

8.3. Calculate the concentration of each analyte in the stock solution as in the following examples.

8.3.1. If 9.6 mg of solid anthracene is dissolved in 5.0 mL of stock solution, the concentration of anthracene in the stock solution is 1.92 mg/mL.

$$\frac{9.6\ \text{mg}}{5.0\ \text{mL}} = 1.92\ \text{mg/mL} \quad .$$

8.3.2. If 9 μL of liquid nitrobenzene, weighing 10.8 mg, is diluted in 5 mL of stock solution, the concentration of nitrobenzene in the stock solution is 2.16 mg/mL.

$$\frac{10.8\ \text{mg}}{5\ \text{mL}} = 2.16\ \text{mg/mL} \quad .$$

8.4. Calculate the concentration of each analyte in the QC sample as in the following example.

8.4.1. If 60 μL of a stock standard solution containing 1.92 mg/mL of anthracene and 2.16 mg/mL of nitrobenzene is spiked into 1 L of distilled water, the concentration of anthracene in the QC sample will be 115 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1.92\ \text{mg/mL})\ (60\ \mu\text{L})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{1\ \text{L}} = 115\ \mu\text{g/L} \quad .$$

The concentration of nitrobenzene in the QC sample will be 130 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(2.16\ \text{mg/mL})\ (60\ \mu\text{L})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{1\ \text{L}} = 130\ \mu\text{g/L} \quad .$$

8.5. Record the analyte concentrations in the QC sample in μg/L.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste contaminated with organic compounds (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4. Cap the jar when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag, can, or jar of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report, LA-12436-MS (1992).

10.3. M. S. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked ( ). Where a section heading is marked, the entire section has been revised.

TABLE I. SEMIVOLATILE ORGANIC COMPOUNDS

Analyte	CAS No.	Category	Density of liquid, (mg/μL)
acenaphthene	83329	Base/Neutral	solid
acenaphthylene	208968	Base/Neutral	0.899
aniline	62533	Base/Neutral	1.022
anthracene	120127	Base/Neutral	solid
azobenzene	103333	Base/Neutral	1.090
benz[a]anthracene	56553	Base/Neutral	solid
m-benzidine	92875	Base/Neutral	solid
benzo[b]fluoranthene	205992	Base/Neutral	solid
benzo[k]fluoranthene	207089	Base/Neutral	solid
benzoic acid	65850	Acid	solid
benzo[g,h,i]perylene	191242	Base/Neutral	solid
benzo[a]pyrene	50328	Base/Neutral	solid
benzyl alcohol	100516	Base/Neutral	1.045
bis(2-chloroethoxy)methane	111911	Base/Neutral	solid
bis(2-chloroethyl)ether	111444	Base/Neutral	1.220
bis(2-chloroisopropyl)ether	108601	Base/Neutral	solid
bis(2-ethylhexyl) phthalate	117817	Base/Neutral	0.981
4-bromophenyl phenyl ether	101553	Base/Neutral	1.423
butyl benzyl phthalate	85687	Base/Neutral	0.966
4-chloroaniline	106478	Base/Neutral	solid
4-chloro-3-methylphenol	59507	Acid	solid
2-chloronaphthalene	91587	Base/Neutral	solid
2-chlorophenol	95578	Acid	1.241
4-chlorophenyl phenyl ether	7005723	Base/Neutral	solid
chrysene	218019	Base/Neutral	solid
di-n-butyl phthalate	84742	Base/Neutral	1.043
di-n-octyl phthalate	117840	Base/Neutral	0.981
dibenz[a,h]anthracene	53703	Base/Neutral	solid
dibenzofuran	132649	Base/Neutral	solid
1,2-dichlorobenzene	95501	Base/Neutral	1.306
1,3-dichlorobenzene	541731	Base/Neutral	1.288
1,4-dichlorobenzene	106467	Base/Neutral	1.241
3,3´-dichlorobenzidine	91941	Base/Neutral	solid
2,4-dichlorophenol	120832	Acid	solid

TABLE I. SEMIVOLATILE ORGANIC COMPOUNDS (cont)

Analyte	CAS No.	Category	Density of liquid, mg/μL
diethyl phthalate	84662	Base/Neutral	1.118
2,4-dimethylphenol	105679	Acid	1.027
dimethylphthalate	131113	Base/Neutral	1.190
4,6-dinitro-2-methylphenol	534521	Acid	solid
2,4-dinitrophenol	51285	Acid	solid
2,4-dinitrotoluene	121142	Base/Neutral	solid
2,6-dinitrotoluene	606202	Base/Neutral	solid
fluoranthene	206440	Base/Neutral	solid
fluorene	86737	Base/Neutral	solid
hexachlorobenzene	118741	Base/Neutral	solid
hexachlorobutadiene	87683	Base/Neutral	1.665
hexachlorocyclopentadiene	77474	Base/Neutral	1.702
hexachloroethane	67721	Base/Neutral	2.091
indeno[1,2,3-cd]pyrene	193395	Base/Neutral	solid
isophorone	78591	Base/Neutral	0.923
2-methylnaphthalene	91576	Base/Neutral	1.000
2-methylphenol	95487	Acid	1.048
4-methylphenol	106445	Acid	1.034
naphthalene	91203	Base/Neutral	solid
2-nitroaniline	88744	Base/Neutral	solid
3-nitroaniline	99092	Base/Neutral	solid
4-nitroaniline	100016	Base/Neutral	solid
nitrobenzene	98953	Base/Neutral	1.196
2-nitrophenol	88755	Acid	solid
4-nitrophenol	100027	Acid	solid
N-nitrosodimethylamine	62759	Base/Neutral	1.006
N-nitrosodiphenylamine	86306	Base/Neutral	solid
N-nitrosodi-n-propylamine	621647	Base/Neutral	solid
pentachlorophenol	87865	Acid	1.978
phenanthrene	85018	Base/Neutral	solid
phenol	108952	Acid	solid
pyrene	129000	Base/Neutral	solid
1,2,4-trichlorobenzene	120821	Base/Neutral	1.454
2,4,5-trichlorophenol	95954	Acid	solid
2,4,6-trichlorophenol	88062	Acid	solid

VOLATILE ORGANIC COMPOUNDS ON SOIL – QC SAMPLE PREPARATION

Analyte: Volatile organic compounds	**Method No.:** QCO250
Matrix: Ottawa sand	**Spike Range:** 100–200 μg/kg
Procedure: Analysis by purge-and-trap extraction, gas chromatography and mass spectrometry (PTGC)	**Accuracy and Precision:** 100% $\pm$ 2.0% RSD
Effective Date: 03/19/91	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution in methanol of three to six volatile organic compounds chosen primarily from the list in Table I, found at the end of this procedure.

1.2. Spike the stock solution into methanol.

1.3. The methanol stock dilution is spiked onto the soil matrix immediately before analysis.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the error of the standard and on the error associated with the use of the microsyringe, balance, and volumetric flask. A relative standard deviation (RSD) of 2.0% at the 1-σ level has been calculated for the error of the standard and for spiking, weighing, and dilution based on the following:

$$D1 = \frac{M1 \times M2}{M3} ,$$

$$D2 = \frac{\left(\frac{D1 \times M5}{(D1 \times M5) + M4}\right) \times M6}{M7} ,$$

$$D3 = \frac{(M3 \times M4)^2}{((M1 \times M2 \times M5) + (M3 \times M4))^2} ,$$

where D1 = first dilution calculated result,
D2 = final calculated result,
D3 = factor for percent RSD formula in Sec. 2.1.2,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,
M4 = first pipetting error,
M5 = second pipetting error,
M6 = third pipetting error, and
M7 = weighing error.

2.1.1. Calculate relative variance using the following equation:

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation:

$$S_{D_T} = \sqrt{R^2_{M7} + R^2_{M6} + ((R^2_{M1} + R^2_{M2} + R^2_{M3} + R_{M4} + R_{M5}) \times D3)} \times$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,

R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second microsyringe,
R^2_{M6} = relative variance of third microsyringe,
R^2_{M7} = relative variance of balance,
D3 = factor above Sec. 2.1, and
100 = factor to convert to percentage.

2.2. Analytical results from samples prepared between 1990 and 1991 using this procedure and analyzed by purge-and-trap extraction, gas chromatography and mass spectrometry, are summarized in Table II below. The data for these and more recent analyses are published in Source Materials 10.1 through 10.4.

TABLE II. RECOVERY DATA FOR VOLATILE ORGANIC COMPOUNDS ON SOIL

Compound	1990 Mean	± std dev	(n)	1991 Mean	± std dev	(n)
Acetone		—		44	± 17	(27)
Benzene	64	± 30	(4)	34		(1)
Bromobenzene		—		92	± 18	(14)
Bromochloromethane	52		(1)		—	
Bromodichloromethane		—		103	± 25	(11)
Bromoform		—		95	± 26	(9)
Bromomethane		—			—	
2-Butanone (MEK)	110	± 72	(12)	52	± 22	(13)
n-Butylbenzene	24		(1)		—	
sec-Butylbenzene		—			—	
tert-Butylbenzene		—			—	
Carbon disulfide	34	± 14	(3)	37		(1)
Carbon tetrachloride	59	± 34	(5)	102	± 48	(11)
Chlorobenzene	53	± 23	(9)	85	± 18	(15)
Chlorodibromomethane	57	± 29	(5)	97	± 22	(17)
Chloroethane		—			—	
Chloroform		—		79	± 28	(8)
2-Chlorotoluene		—		88	± 36	(6)
4-Chlorotoluene		—			—	
1,2-Dibromo-3-chloropropane		—			—	
1,2-Dibromoethane	29		(2)		—	
Dibromomethane		—		82	± 23	(8)
1,2-Dichlorobenzene		—		94	± 11	(11)

TABLE II. RECOVERY DATA FOR VOLATILE ORGANIC COMPOUNDS ON SOIL (cont)

Compound	1990 Mean	± std dev	(n)	1991 Mean	± std dev	(n)
1,3-Dichlorobenzene		–			–	
1,4-Dichlorobenzene	9		(1)	57	± 9	(4)
1,1-Dichloroethane	56	± 21	(8)	26	± 16	(3)
1,2-Dichloroethane	66	± 25	(10)	97	± 42	(14)
1,1-Dichloroethene		–			–	
cis-1,2-Dichloroethene		–			–	
trans-1,2-Dichloroethene		–			–	
1,2-Dichloropropane	77		(1)	73	± 38	(7)
1,3-Dichloropropane		–			–	
2,2-Dichloropropane		–			–	
1,1-Dichloropropene		–			–	
cis-1,3-Dichloropropene	36	± 22	(5)		–	
trans-1,3-Dichloropropene	93	± 51	(5)		–	
Ethylbenzene	51	± 24	(11)	76	± 31	(9)
2-Hexanone	138	± 67	(8)	69	± 22	(9)
Isopropylbenzene		–			–	
p-Isopropyltoluene		–			–	
Methylene chloride		–		83	± 53	(27)
4-Methyl-2-pentanone (MIK)		–		94	± 20	(14)
n-Propylbenzene	32		(1)	67	± 22	(5)
Styrene	36		(2)	84	± 22	(14)
1,1,1,2-Tetrachloroethane	57		(1)	85	± 18	(5)
1,1,2,2-Tetrachloroethane		–		104	± 16	(11)
Tetrachloroethene	46	± 24	(12)	75	± 28	(15)
Toluene	53	± 28	(11)	71	± 24	(15)
1,1,1-Trichloroethane	48	± 29	(3)	98	± 45	(15)
1,1,2-Trichloroethane	67	± 32	(10)	86	± 21	(24)
Trichloroethene	42	± 28	(5)	71	± 26	(9)
Trichlorofluoromethane		–			–	
1,2,3-Trichloropropane		–		89	± 15	(5)
1,2,4-Trimethylbenzene		39	(1)	84	± 17	(8)
1,3,5-Trimethylbenzene		–			–	
Vinyl acetate	48	± 43	(5)	68		(2)
Mixed xylenes (total)	35		(1)	80	± 19	(5)

3. Collection and Storage of Samples

3.1. Ottawa sand is used as a blank soil matrix.

3.2. The QC spiking solution is refrigerated pending use. The maximum holding time for the analysis of volatile organics on soil is 14 days.

4. Apparatus

4.1. Volumetric flasks: 5-mL, class A, glass.

4.2. Syringes: gas-tight, 10-, 25-, 50-, 100-, and 2500-μL.

4.3. Microspatula.

4.4. Pipettes: Pasteur, disposable, glass.

4.5. Pipette bulb: rubber, to fit Pasteur pipette.

4.6. Vials: 1.5-mL, glass, amber.

4.7. Caps: open-top, to fit vials.

4.8. Septa: Teflon/silicone discs to fit open-top caps.

4.9. Teflon tape.

4.10. Autosampler vials with Teflon-lined septa and crimp-tops: 11- x 30-mm vials and 11-mm silicone cap liner with Teflon face.

4.11. Portable crimper for sealing caps on autosampler vials.

4.12. Decapper for removing caps from autosampler vials.

4.13. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.14. Laboratory oven: capable of sustaining 100–150°C.

4.15. Labels printed with QC sample numbers.

5. Reagents

5.1. Methanol (reagent-grade).

5.2. Ottawa sand: a clean, dry 5.0-g aliquot is required for each sample.

5.2.1. Standard quality Ottawa sand, graded to 20–30 mesh and used for preparing cement tensile-strength samples, meets American Society for Testing and Materials (ASTM) C190 specifications.

5.2.2. Ottawa sand heated to nominally 500°C for a minimum of 2 h is used as a sample matrix.

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade volatile analytes chosen primarily from Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19381). Add solid analytes first, then liquid analytes after the addition of solvent.

6.1.1. Add 8–12 mg of a solid volatile analyte to a clean, tared 5.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.2. Add approximately 3 mL of methanol to the flask, stopper the flask, and swirl it to dissolve the analytes.

6.1.3. Place the stoppered flask on the analytical balance and tare the balance.

6.1.4. Calculate the volumes of liquid analytes needed to reach a weight spike range of 8–12 mg in 5 mL of stock solution. See Step 8.1.

6.1.5. Using a gas-tight syringe, add a liquid analyte just above the surface of the methanol. Stopper the flask and record the mass and volume of the analyte added. Tare the balance. Repeat for each liquid analyte added.

6.1.6. Dilute the solution to volume with methanol.

6.1.7. Mix by **gently** inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

6.1.8. Discard the solution in the neck of the flask to minimize concentration changes due to loss of volatile analytes from the surface of the solution.

6.1.9. The concentration of analytes in the stock solution will be between 1.5–2.5 mg/mL.

6.1.10. Transfer the stock solution to 1.5-mL amber vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.11. Label the vials with information identifying the standard and with the expiration date.

6.1.12. The stock solution is stable for approximately 3 months when stored at -20°C.

6.2. Prepare additional stock solutions using different analytes chosen primarily from Table I. The number of analytes in the QC samples may be increased by using more than one stock solution to prepare the QC spiking solution.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with volatile analytes.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into a waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Sample size and container type may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes the preparation of a volatiles-on-soil QC sample using 5 g of Ottawa sand.

7.3.2. Remove one or more vials of volatile stock standard from the freezer and allow them to reach room temperature. Do not allow the vials to sit at

room temperature for longer than 2 h before preparing the QC spiking solution.

7.3.3. Some analytes may crystallize out of solution in the freezer. Visually inspect the stock solution. If any precipitate is present, gently warm the solution on a hot plate and swirl it to redissolve the precipitate. Avoid excessive or prolonged heating, which would cause analytes to be lost from the solution.

7.3.4. Using a gas-tight syringe, add 1500 μL of methanol to an autosampler vial to be used as a matrix for the QC spiking solution.

7.3.5. Seal the vial with a septum and crimp the top.

7.3.6. Spike a volume of stock standard, through the septum and below the surface of the methanol, to reach a concentration range of 75–150 μg/1.5 mL for each analyte in the QC spiking solution.

7.3.7. More than one stock standard may be spiked into the methanol to increase the number of analytes in the QC sample.

7.3.8. Replace the punctured septum and cap from the autosampler vial with a new septum and cap.

7.3.9. Label the vial with a QC sample number.

7.3.10. Include directions for the analyst to spike 10 μL of the QC spiking solution onto 5.0 g of preheated Ottawa sand just before analysis.

7.3.11. Return the stock standard to the freezer.

7.4. Refrigerate the QC spiking solution pending use. The maximum holding time for a volatile QC spiking solution for soil is 14 days.

7.5. The analyst will spike 10 μL of the QC spiking solution onto an accurately weighed 5.0-g aliquot of preheated Ottawa sand just before analysis.

7.6. Calculate the analyte concentrations in the QC sample in μg/kg based on a 10-μL aliquot of the QC spiking solution on 5.0000 g of preheated Ottawa sand.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the volume of neat liquid analyte needed to prepare a stock solution in the range of 8–12 mg/5 mL.

8.1.1. Read the density of the neat liquid analyte from Table I. The density of toluene is 0.867 mg/μL.

8.1.2. The desired weight spike range for 5 mL of stock solution is 8–12 mg of neat analyte.

8.1.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 5 mL of stock solution.

$$\frac{8\ \text{mg}}{0.867\ \text{mg}/\mu\text{L}} \text{ to } \frac{12\ \text{mg}}{0.867\ \text{mg}/\mu\text{L}} = 9.2 \text{ to } 13.8\ \mu\text{L} \quad .$$

For toluene, between 9.2 and 13.8 μL of the neat analyte should be diluted to 5 mL to reach the desired concentration range of 1.5–2.5 mg/mL in the stock solution.

8.2. Calculate the concentration of each analyte in the stock solution as in the following example.

8.2.1. If 12 μL of toluene, weighing 10.4 mg, is diluted in 5 mL of stock solution, the concentration of toluene in the stock solution is 2.08 mg/mL.

$$\frac{10.4\ \text{mg}}{5\ \text{mL}} = 2.08\ \text{mg/mL} \quad .$$

8.3. Calculate the concentration of each analyte in the QC spiking solution as in the following example.

8.3.1. The final volume of the QC spiking solution is the total of 1500 μL of methanol plus the volumes of all the QC spiking solutions added to the methanol.

8.3.2. If 60 μL of a stock solution containing 2.08 mg/mL of toluene and 50 μL of a second QC stock solution are both added to 1500 μL of methanol in

an autosampler vial, the concentration of toluene in the QC spiking solution is 0.0775 $\mu g/\mu L$.

$$\frac{(2.08\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(60\ \mu\text{L})\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{1500\ \mu\text{L} + 60\ \mu\text{L} + 50\ \mu\text{L}} = 0.0775\ \frac{\mu\text{g}}{\mu\text{L}}$$

8.4. Calculate the concentration of each analyte in the QC sample as in the following example.

8.4.1. When the analyst spikes 10 μL of the QC spiking solution containing 0.0775 $\mu g/\mu L$ toluene onto 5.0000 g of preheated Ottawa sand, the concentration of toluene in the resulting QC sample will be 155 $\mu g/kg$. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(0.0775\ \mu\text{g}/\mu\text{L})\ (10\ \mu\text{L})}{(5.0000\ \text{g})\ (\text{kg}/1000\ \text{g})} = 155\ \mu\text{g/kg} \quad .$$

8.5. Record the analyte concentrations in the QC sample in $\mu g/kg$ based on the analyst spiking a 10-μL aliquot of the QC spiking solution on 5.0000 g of preheated Ottawa sand.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste contaminated with organic compounds (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4 Cap the jar when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag, can, or jar of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

[redacted] M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked ([redacted]). Where a section heading is marked, the entire section has been revised.

TABLE I. VOLATILE ORGANIC COMPOUNDS

Compound	CAS Number	Density of liquids (mg/μL)
acetone	67641	0.791
benzene	71432	0.874
bromobenzene	108861	1.491
bromochloromethane	74975	1.991
bromodichloromethane	75274	1.980
bromoform	75252	2.894
bromomethane	74839	0.838
2-butanone (MEK)	78933	0.805
n-butylbenzene	104518	0.860
sec-butylbenzene	135988	0.863
tert-butylbenzene	98066	0.867
carbon disulfide	75150	1.266
carbon tetrachloride	56235	1.594
chlorobenzene	108907	1.107
chlorodibromomethane	124481	2.451
chloroethane	75003	0.891
chloroform	67663	1.492
chloromethane	74873	gas
2-chlorotoluene	95498	1.083
4-chlorotoluene	106434	1.070
1,2-dibromo-3-chloropropane	96128	2.093
1,2-dibromoethane	106934	2.180
dibromomethane	74953	2.477
1,2-dichlorobenzene	95501	1.306
1,3-dichlorobenzene	541731	1.288
1,4-dichlorobenzene	106467	1.241
dichlorodifluoromethane	75718	gas
1,1-dichloroethane	75343	1.176
1,2-dichloroethane	107062	1.256
1,1-dichloroethene	75354	1.213
cis-1,2-dichloroethene	156592	1.284
trans-1,2-dichloroethene	156605	1.257
1,2-dichloropropane	78875	1.156
1,3-dichloropropane	142289	1.190
2,2-dichloropropane	594207	1.082
1,1-dichloropropene	563586	1.169

TABLE I. VOLATILE ORGANIC COMPOUNDS (cont)

Compound	CAS Number	Density of liquids (mg/μL)
cis-1,3-dichloropropene	10061015	1.224
trans-1,3-dichloropropene	10061026	1.224
ethylbenzene	100414	0.867
2-hexanone	591786	0.812
isopropylbenzene	98828	0.864
4-isopropyltoluene	99876	0.860
methylene chloride	75092	1.325
methyl iodide	74884	2.280
4-methyl-2-pentanone (MIK)	108101	0.800
n-propylbenzene	103651	0.862
styrene	100425	0.909
1,1,1,2-tetrachloroethane	630206	1.598
1,1,2,2,-tetrachloroethane	79345	1.586
tetrachloroethene	127184	1.623
toluene	108883	0.867
1,1,1-trichloroethane	71556	1.338
1,1,2-trichloroethane	79005	1.435
trichloroethene	79016	1.464
trichlorofluoromethane	75694	1.494
1,2,3-trichloropropane	96184	1.387
1,1,2-trichlorotrifluoroethane	76131	1.575
1,2,4-trimethylbenzene	95636	0.889
1,3,5-trimethylbenzene	108678	0.864
vinyl chloride	75014	0.9121
mixed xylenes (total)	1330207	0.860

VOLATILE ORGANIC COMPOUNDS IN WATER—QC SAMPLE PREPARATION

Analyte: Volatile organic compounds	**Method No.:** QCO260
Matrix: Water	**Range:** 30–150 μg/L
Procedure: Analysis by purge-and-trap extraction, gas chromatography and mass spectrometry (PTGC)	**Accuracy and Precision:** 100% ± 5.3% RSD
Effective Date: 04/25/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution in methanol of three to six volatile organic compounds chosen primarily from the list in Table I, found at the end of this procedure.

1.2. Prepare a 1:20 dilution in methanol of the stock solution.

1.3. Spike the diluted standard into distilled water.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the error of the standard and on the error associated with the use of the microsyringe, balance, and volumetric flask. A relative standard deviation (RSD) of 5.3% at the 1-σ level has been calculated for standard preparation and for weighing, spiking, and dilution based on the following:

$$D = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5 \times M7} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,

M3 = first dilution error,
M4 = first pipette error,
M5 = second dilution error,
M6 = second pipette error, and
M7 = third dilution error.

2.1.1. Calculate relative variance for each variable using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2 + R_{M5}^2 + R_{M6}^2 + R_{M7}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe,
R^2_{M7} = relative variance of third volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1990 and 1991 using this procedure and analyzed by purge-and-trap extraction, gas chromatography, and mass spectrometry are summarized in Table II below. The data for these and more recent analyses are published in Source Materials 10.1 through 10.4.

TABLE II. SPIKE RECOVERY DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER

Compound	1990 Mean	± std dev	(n)	1991 Mean	± std dev	(n)
Acetone		—		95	± 8	(17)
Benzene	94	± 30	(13)	88		(1)
Bromobenzene		—		98	± 6	(9)
Bromochloromethane	110		(10)		—	
Bromodichloromethane		—		131		(2)
Bromoform	61		(1)	102	± 8	(8)
Bromomethane		—			—	
2-Butanone (MEK)	90	± 58	(19)	56	± 20	(3)
n-Butylbenzene		—			—	
sec-Butylbenzene		—			—	
tert-Butylbenzene		—			—	
Carbon disulfide	98	± 62	(14)	75	± 27	(4)
Carbon tetrachloride	76	± 12	(8)	89	± 22	(3)
Chlorobenzene	85	± 18	(20)	85	± 5	(10)
Chlorodibromomethane	82	± 22	(10)	95	± 15	(9)
Chloroethane		—			—	
Chloroform		—		100	± 13	(3)
2-Chlorotoluene		—		78	± 12	(4)
4-Chlorotoluene		—			—	
1,2-Dibromo-3-chloropropane		—			—	
1,2-Dibromoethane	108		(1)		—	
Dibromomethane		—		106	± 11	(3)
1,2-Dichlorobenzene		—		74		(2)
1,3-Dichlorobenzene		—			—	
1,4-Dichlorobenzene	64		(2)		—	
1,1-Dichloroethane	104	± 27	(22)	85	± 10	(4)
1,2-Dichloroethane	102	± 14	(16)	120	± 36	(9)
1,1-Dichloroethene		—			—	
cis-1,2-Dichloroethene		—			—	
trans-1,2-Dichloroethene		—			—	
1,2-Dichloropropane	96	± 20	(3)	86	± 13	(10)
1,3-Dichloropropane		—			—	
2,2-Dichloropropane		—			—	
1,1-Dichloropropene		—			—	
cis-1,3-Dichloropropene	52	± 10	(13)		—	

TABLE II. SPIKE RECOVERY DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER (cont)

Compound	1990 Mean	± std dev	(n)	1991 Mean	± std dev	(n)
trans-1,3-Dichloropropene	169	± 35	(13)		—	
Ethylbenzene	78	± 18	(22)	75	± 10	(10)
2-Hexanone	94	± 43	(23)	72	± 32	(8)
Isopropylbenzene		—			—	
p-Isopropyltoluene		—			—	
Methylene chloride		—		80	± 23	(14)
4-Methyl-2-pentanone (MIK)		—		84	± 12	(5)
n-Propylbenzene		—		53	± 16	(4)
Styrene	77		(2)	67	± 19	(5)
1,1,1,2-Tetrachloroethane	97		(2)	87	± 5	(4)
1,1,2,2-Tetrachloroethane		—			—	
Tetrachloroethene	77	± 19	(19)	74	± 7	(9)
Toluene	80	± 19	(20)	75	± 4	(9)
1,1,1-Trichloroethane	85	± 24	(11)	86	± 16	(6)
1,1,2-Trichloroethane	94	± 10	(19)	95	± 8	(17)
Trichloroethene	76	± 9	(7)	82	± 5	(4)
Trichlorofluoromethane		—			—	
1,2,3-Trichloropropane		—		106	± 5	(4)
1,2,4-Trimethylbenzene		—		48	± 27	(3)
1,3,5-Trimethylbenzene		—			—	
Vinyl acetate	56	± 40	(8)		—	
Mixed xylenes	326		(1)	63	± 16	(4)

3. Collection and Storage of Samples

3.1. Distilled water purged with nitrogen gas is used as the blank matrix for spiking. Use water that has not been stored in plastic holding vessels or run through plastic tubing because phthalates may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for volatile organic compounds in water is 7 days. Preservation with HCl increases the holding time to 14 days.

4. Apparatus

4.1. Volumetric flasks: 5- and 50-mL, class A, glass.

4.2. Autopipette: 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Syringes: gas-tight, 10-, 25-, 50-, 100-, and 500-μL.

4.5. Microspatula.

4.6. Pipettes: Pasteur, disposable, glass.

4.7. Pipette bulb: rubber, to fit Pasteur pipette.

4.8. Vials: 1.5-mL, glass, amber.

4.9. Caps: open-top, to fit vials.

4.10. Septa: Teflon/silicone discs to fit open-top caps.

4.11. Teflon tape.

4.12. Vials: 40-mL, glass, zero headspace, with open-top screw caps with Teflon/silicone septa, precleaned.

4.13. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.14. Laboratory oven: capable of sustaining 100–150°C.

4.15. Bottle: gas-washing, with fritted dispersion disc, 500-mL minimum capacity.

4.16. Tubing and adapters: Teflon, to connect gas-washing bottle to nitrogen gas cylinder.

4.17. Labels printed with QC sample numbers.

5. Reagents

5.1. Methanol (analytical-grade).

5.2. Hydrochloric acid (concentrated, reagent-grade).

5.3. Nitrogen gas (high-purity) in a compressed gas cylinder.

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade volatile analytes chosen primarily from Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19381). Add solid analytes first, then liquid analytes after the addition of solvent.

6.1.1. Add 8–12 mg of a solid volatile analyte to a clean, tared 5.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each analyte.

6.1.2. Add approximately 3 mL of methanol to the flask, stopper the flask, and swirl it to dissolve the analytes.

6.1.3. Place the stoppered flask on the analytical balance and tare the balance.

6.1.4. Calculate the volumes of liquid analytes needed to reach a weight spike range of 8–12 mg in 5 mL of stock solution. See Step 8.1.

6.1.5. Using a syringe, add a liquid analyte just above the surface of the methanol. Stopper the flask and record the mass and volume of the analyte added. Tare the balance. Repeat for each liquid analyte added.

6.1.6. Dilute the solution to volume with methanol.

6.1.7. Mix by **gently** inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

6.1.8. Discard the solution in the neck of the flask to minimize concentration changes due to loss of volatile analytes from the surface of the solution.

6.1.9. The concentration of analytes in the stock solution will be 1.5–2.5 mg/mL.

6.1.10. Transfer the stock solution to 1.5-mL amber vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.11. Label the vials with information identifying the standard and its expiration date.

6.1.12. The stock solution is stable for approximately 3 months when stored at -20°C.

6.2. Prepare additional stock solutions using different analytes chosen primarily from Table I. The number of analytes in the QC samples may be increased by combining the stocks in a 1:20 dilution.

6.3. Prepare a 1:20 dilution of the stock solution.

6.3.1. Add approximately 4 mL of methanol to a clean 5-mL volumetric flask.

6.3.2. Using a syringe, add 250 μL of a stock solution just above the surface of the methanol. Repeat for each stock solution to be combined in the 1:20 dilution.

6.3.3. Dilute the solution to volume with methanol.

6.3.4. Mix by **gently** inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

6.3.5. Discard the solution in the neck of the flask to minimize concentration changes due to the loss of volatile analytes from the surface of the solution.

6.3.6. The concentration of analytes in the dilution will be 0.075–0.125 mg/mL.

6.3.7. Transfer the dilution to 1.5-mL amber vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the cap.

6.3.8. Label the vials with information identifying the standard and its expiration date.

6.3.9. The standard dilution is stable for approximately 3 months when stored at -20°C.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with volatile analytes.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into a waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Sample size and container size may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes the preparation of a 50-mL volatiles-in-water QC sample transferred to a 40-mL zero headspace glass vial. To prepare a blank QC sample, omit the spike of the volatiles standard (Step 7.3.6.).

7.3.2. Remove a vial of a 1:20 dilution of volatile stock standards from the freezer and allow it to reach room temperature. Do not let the vial sit at room temperature for longer than 2 h before spiking the QC sample.

7.3.3. Some analytes may crystallize out of solution in the freezer. Visually inspect the stock solution. If any precipitate is present, gently warm the solution on a hot plate and swirl it to redissolve the precipitate. Avoid excessive or prolonged heating, which would cause analytes to be lost from the solution.

7.3.4. Put 100–200 mL of distilled water into a gas-washing bottle fitted with a fritted gas-dispersion disc and connected to a nitrogen purge-gas tank. Use only distilled water that has not been stored in plastic or run through plastic tubing. Purge the water with nitrogen gas for at least 15 min to remove any volatile compounds dissolved in the water.

7.3.5. Add approximately 45 mL of the purged water to the 50-mL volumetric flask. Add 0.5 mL of concentrated HCl to the water as a preservative for the QC sample.

7.3.6. Spike a volume of a 1:20 dilution of a standard below the surface of the water to reach the desired spike range. Spike near the bottom of the flask using a syringe.

7.3.7. Dilute the solution to volume with purged water.

7.3.8. Mix by **gently** inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

7.3.9. Discard the solution in the neck of the flask to minimize concentration changes due to the loss of volatile analytes from the surface of the solution.

7.3.10. Pour the sample into a 40-mL, glass, zero-headspace vial leaving no headspace. Discard the excess sample.

7.3.11. Label the vial with a QC sample number.

7.3.12. Return the 1:20 dilution of the standard to the freezer.

7.3.13. Refrigerate the QC sample pending analysis. The maximum holding time for volatile organic compounds in water preserved with HCl is 14 days.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the volume of neat liquid analyte needed to prepare a stock solution in the range of 8–12 mg/5 mL.

8.1.1. Read the density of the neat liquid analyte from Table I. The density of toluene is 0.867 mg/μL.

8.1.2. The desired weight spike range for 5 mL of stock solution is 8–12 mg of neat analyte.

8.1.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 5 mL of stock solution.

$$\frac{8\ \text{mg}}{0.867\ \text{mg}/\mu\text{L}} \text{ to } \frac{12\ \text{mg}}{0.867\ \text{mg}/\mu\text{L}} = 9.2 \text{ to } 13.8\ \mu\text{L} \quad .$$

For toluene, between 9.2 and 13.8 μL of the neat analyte should be diluted to 5 mL to reach the desired concentration range of 1.5–2.5 mg/mL in the stock solution.

8.2. Calculate the concentration of each analyte in the stock solution as in the following example.

8.2.1. If 12 μL of toluene, weighing 10.4 mg, is diluted in 5 mL of stock solution, the concentration of toluene in the stock solution is 2.08 mg/mL.

$$\frac{10.4\ \text{mg}}{5\ \text{mL}} = 2.08\ \text{mg/mL} \quad .$$

8.3. Calculate the concentration of each analyte in the 1:20 dilution of the stock solution as in the following example.

8.3.1. If 250 μL of a stock solution containing 2.08 mg/mL of toluene is diluted to 5 mL with methanol, the concentration of toluene in the 1:20 stock dilution is 0.104 μg/μL.

$$\frac{(2.08\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(250\ \mu\text{L})}{(5\ \text{mL})\left(\frac{1000\ \mu\text{L}}{1\ \text{mL}}\right)} = 0.104\ \mu\text{g}/\mu\text{L} \quad .$$

8.4. Calculate the concentration of each analyte in the QC water sample as in the following example.

8.4.1. If 30 μL of a 1:20 stock dilution containing 0.104 μg/μL of toluene is spiked into 50 mL of distilled water, the concentration of toluene in the sample is 62 μg/L. Multiply the result by the RSD calculated in Step 2.1. to obtain the uncertainty.

$$\frac{(0.104\ \mu g/\mu L)\ (30\ \mu L)}{(50\ mL)\left(\frac{1\ L}{1000\ mL}\right)} = 62\ \mu g/L \quad .$$

8.5. Record the analyte concentration in the QC sample in μg/L.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste contaminated with organic compounds (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4 Cap the jar when full and keep it in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag, can, or jar of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.4. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry : 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TABLE I. VOLATILE ORGANIC COMPOUNDS

Compound	CAS Number	Density of liquids (mg/μL)
Acetone	67641	0.791
Benzene	71432	0.874
Bromobenzene	108861	1.491
Bromochloromethane	74975	1.991
Bromodichloromethane	75274	1.980
Bromoform	75252	2.894
Bromomethane	74839	0.838
2-Butanone (MEK)	78933	0.805
n-Butylbenzene	104518	0.860
sec-Butylbenzene	135988	0.863
tert-Butylbenzene	98066	0.867
Carbon disulfide	75150	1.266
Carbon tetrachloride	56235	1.594
Chlorobenzene	108907	1.107
Chlorodibromomethane	124481	2.451
Chloroethane	75003	0.891
Chloroform	67663	1.492
Chloromethane	74873	gas
2-Chlorotoluene	95498	1.083
4-Chlorotoluene	106434	1.070
1,2-Dibromo-3-chloropropane	96128	2.093
1,2-Dibromoethane	106934	2.180
Dibromomethane	74953	2.477
1,2-Dichlorobenzene	95501	1.306
1,3-Dichlorobenzene	541731	1.288
1,4-Dichlorobenzene	106467	1.241
Dichlorodifluoromethane	75718	gas
1,1-Dichloroethane	75343	1.176
1,2-Dichloroethane	107062	1.256
1,1-Dichloroethene	75354	1.213
cis-1,2-Dichloroethene	156592	1.284
trans-1,2-Dichloroethene	156605	1.257
1,2-Dichloropropane	78875	1.156
1,3-Dichloropropane	142289	1.190
2,2-Dichloropropane	594207	1.082

TABLE I. VOLATILE ORGANIC COMPOUNDS (cont)

Compound	CAS Number	Density of liquids (mg/μL)
1,1-Dichloropropene	563586	1.169
cis-1,3-Dichloropropene	10061015	1.224
trans-1,3-Dichloropropene	10061026	1.224
Ethylbenzene	100414	0.867
2-Hexanone	591786	0.812
Isopropylbenzene	98828	0.864
4-Isopropyltoluene	99876	0.860
Methylene chloride	75092	1.325
Methyl iodide	74884	2.280
4-Methyl-2-pentanone (MIK)	108101	0.800
n-Propylbenzene	103651	0.862
Styrene	100425	0.909
1,1,1,2-Tetrachloroethane	630206	1.598
1,1,2,2,-Tetrachloroethane	79345	1.586
Tetrachloroethene	127184	1.623
Toluene	108883	0.867
1,1,1-Trichloroethane	71556	1.338
1,1,2-Trichloroethane	79005	1.435
Trichloroethene	79016	1.464
Trichlorofluoromethane	75694	1.494
1,2,3-Trichloropropane	96184	1.387
1,1,2-Trichlorotrifluoroethane	76131	1.575
1,2,4-Trimethylbenzene	95636	0.889
1,3,5-Trimethylbenzene	108678	0.864
Vinyl chloride	75014	0.9121
mixed Xylenes (total)	1330207	0.860

AMERICIUM-241 IN URINE — QC SAMPLE PREPARATION

Analyte: Americium-241	**Method No.:** QCR100
Matrix: Urine	**Spike Range:** 0.0–1.0 pCi/sample
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 4% RSD
Effective Date: 01/01/75	**Authors:** Margaret A. Gautier William D. Moss Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.6 to 10.8 for proper waste disposal practices.

1. Principle of Method

1.1. A pool of blank urine is prepared.

1.2. The blank urine is aliquoted and spiked with a known standard.

1.3. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the graduated cylinder and the pipette. A relative standard deviation (RSD) of 4.0% at the 1-σ level has been calculated for the calibration, spiking, and aliquoting process based on the following:

$$D = \frac{M1 \times M2}{M3 + M2} ,$$

where D = calculated result,
M1 = calibration error,

M2 = spiking error, and
M3 = aliquoting error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{\frac{\left[R_{M1}^2 (M3 + M2)^2 + M3^2 (R_{M2}^2 + R_{M3}^2)\right]}{(M3 + M2)^2}} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
M3 = volume of cylinder,
M2 = volume of pipette,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of cylinder, and
100 = factor to convert to percentage.

2.2 Analysis by radiochemistry and alpha spectrometry of QC samples prepared between 1992 and 1994 using this procedure gave a mean recovery of 100% ± 11% RSD. The data are published in Source Material 10.1 and are summarized in Table I below.

TABLE I. AMERICIUM-241 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR AMERICIUM-243 RECOVERY

Year	Spike level pCi/sample	Mean ± RSD (%)			Number of Samples
1992	0.24	123	±	-	1
	0.48	106	±	6	2

TABLE I. AMERICIUM-241 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR AMERICIUM-243 RECOVERY (cont)

Year	Spike level pCi/sample	Mean	±	RSD (%)	Number of Samples
1993	0.22	97	±	-	1
	0.45	93	±	10	3
	0.54	85	±	7	3
	0.90	87	±	9	2
1994	0.23	108	±	9	3
	0.46	99	±	4	3
	0.55	103	±	-	1
	0.91	98	±	5	2

3. Collection and Storage of Samples

3.1. Urine is collected as needed from group personnel who have no known contact with radiation work. It is used to form a pool of blank urine.

3.2. Spiked QC samples are refrigerated at a nominal temperature of 4°C pending analysis.

4. Apparatus

4.1. Beakers: 4- or 5-L, polyethylene.

4.2. Graduated cylinders: 500-mL.

4.3. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Specimen containers: 16-oz jars with screw caps.

4.6. Labels printed with QC sample numbers.

4.7. Heat lamp.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless-steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: The phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon, Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick, manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. QC samples are spiked with an ^{241}Am standard prepared in 4 N HNO_3. The solution is counted on a zinc sulfide scintillation system calibrated with National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.2. The ^{241}Am standard should be at a concentration of approximately 1.0 pCi/mL.

6.3. The ^{241}Am standard was calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NIST SRM 4322. Recalibrate the standard solution yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.4. Direct plating procedure.

6.4.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs, which have been cleaned with acetone. Evaporate the solution to dryness under a heat lamp.

6.4.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.4.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.4.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.4.5. Place a piece of Mylar film over all the layers.

6.4.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.4.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.4.8. The count room data are corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates, then assign the value to the standard.

7. Procedure

7.1. Working with bodily fluids is discussed in detail in SOP-4, "Handling Human Biological Fluids and Tissues," found in Appendix III of the Environmental Chemistry Safety Manual.

NOTE: Wear safety glasses, gloves, and a lab coat. Each day prepare a 1:100 dilution of household bleach in water in a spray bottle. Use this solution to thoroughly clean the work area after sample preparation is completed. Rinse gloves in a 1:100 dilution of household bleach in water and discard them. Wash hands with soap and water.

7.2. Prepare a pool from blank urine sufficient in volume to allow 400 mL for each QC sample to be prepared.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Include blank QCs prepared from the same urine pool as the spiked samples.

7.4. Record QC standard information, sample spike amount, concentration, and uncertainty in the QC Laboratory notebook.

7.5. Label bottles with QC sample numbers.

7.6. Aliquot 400 mL of blank urine into each sample bottle.

7.7. Spike the blank urine with aliquots of standard as determined in Step 7.3.

7.8. Screw caps on bottles and refrigerate at a nominal temperature of 4°C pending analysis.

7.9. Enter the spike concentrations of each QC into the CVS and CVD databases on the VAX. This procedure is done annually because the same concentration levels are used throughout the year.

8. Calculations

8.1. Record spike concentrations as pCi/sample of urine.

8.2. Calculate the spike concentration for a 500-μL aliquot of ^{241}Am standard using the following equation:

$$\text{pCi/sample per spike amount} = 1.0\ \text{pCi/mL} \times 0.500\ \text{mL} = 0.50\ \text{pCi/sample} \quad .$$

8.3. Spike concentrations calculated in Step 8.2 are tabulated below.

Spike amount (μL)	Concentration (pCi/sample)	Uncertainty ($\pm$4.0%)
250	0.25	0.01
500	0.50	0.02
600	0.60	0.02
900	0.90	0.04

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Radiochemically contaminated waste.

9.2.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.1.5. Put a new plastic bag into the waste can for continued use.

9.2.1.6. Place the sealed bag into a cardboard box lined with a plastic bag labeled to indicate its use for radioactively contaminated waste.

9.2.1.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.1.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.1.9. Line a new box with a plastic bag and label it for continued use.

9.2.1.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.1.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.2.2. Biohazardous waste.

9.2.2.1. If urine-contaminated solid waste is disinfected, dispose of it in the same manner as any other waste. Refer to Source Material 10.8.

9.2.2.2. If urine sample containers are rinsed well with a 10% solution of bleach, dispose of the rinse solution down the drain. Refer to Source Material 10.5.

9.2.2.3. If the excess urine is diluted with bleach to make a 5% (v/v) solution, dispose of this solution down the drain. Refer to Source Material 10.5.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of radioactively contaminated solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. *EML Procedures Manual*, 25th ed., H. L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, New York, August 1982).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4322, Americium-241 Alpha-Particle Solution Standard" (National Institute of Standards and Technology, Washington, DC, November 1986).

10.4. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard," (National Institute of Standards and Technology, Washington, DC, April 1982).

10.5. M. Phillips, "Handling Human Biological Fluids and Tissues," SOP-4, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Los Alamos National Laboratory document (November 1993).

10.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.8. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

AMERICIUM-241 ON SOIL — QC SAMPLE PREPARATION

Analyte: Americium-241	**Method No.:** QCR105
Matrix: Sand	**Spike Range:** 1–10 pCi/g
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.1% RSD
Effective Date: 06/11/92	**Authors:** Michael N. Jasperson Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is spiked with an ^{241}Am standard. The sand is used in place of soil as the quality control (QC) matrix for ^{241}Am analysis by gamma-ray spectrometry.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. Because the method of analysis is nondestructive, the QC samples can be reused.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 3.1% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,

M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analysis by gamma-ray spectrometry of QC samples prepared between 1992 and 1994 using this procedure gave the following recoveries at the 1-σ level. The data are published in Source Material 10.1.

TABLE I. AM-241 SPIKE RECOVERY DATA

	Mean ± std dev (%)	Number of Samples
1992	112 ± 7	7
1993	77 ± 53	4
1994	88 ± 30	116

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Bottles: 500-mL, high-density polyethylene.

4.2. Balance: 200-g minimum capacity, 0.1-g accuracy.

4.3. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Heat lamp.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. Sand. A clean and dry 100-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. QC samples are spiked with an ^{241}Am standard prepared in 4 N HNO_3 at a concentration of approximately 2400 pCi/mL.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentrations.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{241}Am standard should be calibrated against a National Institute of Standards and Technology (NIST) - certified ^{241}Am Standard Reference Material (SRM) solution. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.5. Direct plating procedure.

6.5.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs and evaporate to dryness under a heat lamp.

6.5.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.5.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.5.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.5.5. Place a piece of Mylar film over all the layers.

6.5.6 Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.5.7. Submit the samples to the count room for alpha scintillation counting and request a 60,0000-s (overnight) per sample count.

6.5.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of 100-g sample aliquot in a 500-mL high-density polyethylene bottle.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3. Accurately weigh 100 g of sand into a 500-mL high-density polyethylene bottle. Record the weight of the sand on the bottle for reference by the analyst.

7.4. Spike an aliquot of ^{241}Am standard onto the sand to reach an ^{241}Am concentration in the desired spike range. Be careful to wet only the sand and not the container walls.

7.5. Dry the spiked sand under a heat lamp. Periodically mix the sample by shaking it until all large clumps are broken up.

7.6. Cap the bottle and label it with a QC sample number.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{241}Am on the sand as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 300 μL of a 2400-pCi/mL ^{241}Am standard is used to spike 100.0 g of sand, the ^{241}Am concentration in the sand will be 7.2 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(2400\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (300\ \mu\text{L})}{100.0\ \text{g}} = 7.20\ \text{pCi/g} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid waste that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples)

in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) number describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

CESIUM-137 ON SOIL — QC SAMPLE PREPARATION

Analyte: Cesium-137	**Method No.:** QCR110
Matrix: Sand	**Spike Range:** 5–60 pCi/g
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 04/12/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is spiked with a ^{137}Cs standard. The sand is used in place of soil as the quality control (QC) matrix for ^{137}Cs analysis by gamma-ray spectrometry.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. Because the method of analysis is nondestructive, the QC samples can be reused provided the ^{137}Cs concentration is decayed periodically.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2 Analysis by gamma-ray spectrometry of QC samples prepared between 1992 and 1994 using this procedure gave a mean recovery of 117% ± 17% at the 1-σ level. The data are published in Source Material 10.2 and are summarized below.

TABLE I. CESIUM-137 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

	Spike range (pCi/g)	Mean ± RSD (%)	Number of Samples
1992	0–15	112 ± 17	13
	15–30	122 ± 12	8
	30–45	121 ± 19	4
	45–70	120 ± 22	2

TABLE I. CESIUM-137 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION (cont)					
	Spike range (pCi/g)	Mean ± RSD (%)			Number of Samples
1993	0–15	119	±	13	8
	15–30	109	±	18	12
	30–45	113	±	13	9
	45–70	111	±	12	6
1994	0–15	116	±	15	50
	15–30	120	±	21	71
	30–45	120	±	20	41
	45–70	116	±	18	25

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Bottles: 500-mL, high-density polyethylene.

4.2. Balance: 200-g minimum capacity, 0.1-g accuracy.

4.3. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Heat lamp.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. Sand. A clean and dry 100-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{137}Cs standard prepared in 1 M HCl at a concentration of approximately 6000 pCi/mL.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentrations.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{137}Cs standard should be calibrated against a National Institute of Standards and Technology (NIST) - certified ^{137}Cs Standard Reference Material (SRM) solution such as NIST SRM 4233-B. The standard solution should be recalibrated yearly using gamma spectroscopy. Record all data in the QC Laboratory notebook.

6.5. Decay the ^{137}Cs standards each year.

6.5.1. The half-life of ^{137}Cs is 30 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at desired time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$ or the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 100-g sample in a 500-mL high-density polyethylene bottle.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 100-g aliquot of the unspiked sand as a blank.

7.3. Accurately weigh 100 g of sand into a 500-mL high-density polyethylene bottle. Record the weight of the sand on the bottle for reference by the analyst.

7.4. Spike an aliquot of ^{137}Cs standard onto the sand to reach a ^{137}Cs concentration in the desired spike range. Be careful to wet only the sand and not the container walls.

7.5. Dry the spiked sand under a heat lamp. Periodically mix the sample by shaking it until all large clumps are broken up.

7.6. Cap the bottle and label it with a QC sample number.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{137}Cs on the sand as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 500 μL of a 6000-pCi/mL ^{137}Cs standard is used to spike 100.0 g of sand, the ^{137}Cs concentration in the sand will be 30 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(6000\ \text{pCi/mL})\ (500\ \mu\text{L})\ (1\ \text{mL}/1000\ \mu\text{L})}{100.0\ \text{g}} = 30\ \text{pCi/g} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid waste that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) number describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste Pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4233-B, Cesium-137 Burn-Up Standard" (National Institute of Standards and Technology, Washington, DC, November 1979).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

CESIUM-137 ON VEGETATION ASH — QC SAMPLE PREPARATION

Analyte: Cesium-137	**Method No.:** QCR120
Matrix: Vegetation ash	**Spike Range:** 5–60 pCi/g
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 04/19/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 and 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Blank vegetation ash is spiked with a ^{137}Cs standard.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. Because the method of analysis is nondestructive, the QC sample can be reused provided the ^{137}Cs concentration is decayed periodically.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2 Analysis by gamma ray spectrometry of QC samples prepared between 1992 and 1994 using this procedure gave a mean recovery of 105% ± 16% at the 1-σ level. The data are published in Source Material 10.3 and are summarized below.

TABLE I. CESIUM-137 ON VEGETATION ASH SPIKE RECOVERY DATA

Year	Mean ± RSD (%)	Number of Samples
1992	130 ± 23	2
1993	92 ± 14	7
1994	92 ± 12	5

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Bottles: 500-mL, high-density polyethylene.

4.2. Balance: 200-g minimum capacity, 0.1-g accuracy.

4.3. Spatula.

4.4. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.5. Pipette tips: disposable.

4.6. Heat lamps.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. Blank vegetation ash is used as the sample matrix. A 100-g aliquot is required for each sample.

5.2. A suitable vegetation ash does not contain the analyte of interest and presents few interferences to the analytical method. Commercially available dry pet or farm stock foods may be ashed to provide a suitable matrix. Preparation of a vegetation ash matrix is described in Method No. QCM200.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{137}Cs standard prepared in 1 M HCl at a concentration of approximately 6000 pCi/mL.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentrations.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{137}Cs standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{137}Cs Standard Reference Material (SRM) solution such as NIST SRM 4233-B. The standard solution should be recalibrated yearly using gamma spectroscopy. Record all data in the QC Laboratory notebook.

6.5. Decay the ^{137}Cs standards each year.

6.5.1. The half-life of ^{137}Cs is 30 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} \quad ,$$

where A_t = the activity at desired time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$ or the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 100-g sample in a 500-mL high-density polyethylene bottle.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 100-g aliquot of the unspiked vegetation ash as a blank.

7.3. Accurately weigh 100 g of blank vegetation ash into a 500-mL high-density polyethylene bottle. Record the weight of ash on the bottle for reference by the analyst.

7.4. Pipette an aliquot of ^{137}Cs standard onto the ash to reach a ^{137}Cs concentration in the desired spike range. Be careful to wet only the ash and not the container walls.

7.5. Dry the spiked sample under a heat lamp, periodically mixing it by shaking, until completely dry and homogeneous.

7.6. Cap the bottle and label it with a QC sample number.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{137}Cs in the vegetation ash sample as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 750 μL of a 6000-pCi/mL ^{137}Cs standard is spiked on 100.0 g of blank vegetation ash, the concentration of ^{137}Cs in the ash will be 45 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(6000\ \text{pCi/mL})\ (750\ \mu\text{L})\ (1\ \text{mL}/1000\ \mu\text{L})}{100.0\ \text{g}} = 45\ \text{pCi/g} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.6. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4233-B, Cesium-137 Burn-Up Standard" (National Institute of Standards and Technology, Washington, DC, November 1979).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

CESIUM-137 IN WATER — QC SAMPLE PREPARATION

Analyte: Cesium-137	**Method No.:** QCR130
Matrix: Water	**Spike Range:** 500–2000 pCi/L
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 04/17/90	**Author:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Water is spiked with a ^{137}Cs standard.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. Because the method of analysis is nondestructive, the QC sample can be reused provided the ^{137}Cs concentration is decayed periodically.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analysis by gamma-ray spectrometry of QC samples prepared between 1992 and 1994 using this procedure gave a mean recovery of 104% ± 22% at the 1-σ level. The data are published in Source Material 10.1 and are summarized below.

TABLE I. CESIUM-137 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

	Spike range (pCi/L)	Mean ± std dev (%)	Number of Samples
1992	500–1000	106 ± 32	10
	1000–2000	90 ± 26	3

TABLE I. CESIUM-137 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION (cont)			
	Spike range (pCi/L)	Mean ± std dev (%)	Number of Samples
1993	0–500	107 ± 16	23
	500–1000	102 ± 21	10
	1000–2000	93 ± 26	10
1994	0–500	131 ± 21	11
	500–1000	91 ± 13	4
	1000–2000	111 ± 20	8

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flask: 500-mL, glass, class A.

4.2. Bottles: 500-mL, high-density polyethylene.

4.3. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Labels printed with QC sample numbers.

5. Reagents

5.1. Nitric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. QC samples are spiked with a ^{137}Cs standard prepared in 1 M HCl at a concentration of approximately 6000 pCi/mL.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentrations.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{137}Cs standards should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{137}Cs Standard Reference Material (SRM) solution such as NIST SRM 4233-B. The standard solution should be recalibrated yearly using gamma spectroscopy. Record all data in the QC Laboratory notebook.

6.5. Decay the ^{137}Cs standards each year.

6.5.1. The half-life of ^{137}Cs is 30 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} \quad ,$$

where A_t = the activity at desired time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$ or the decay constant where $T_{1/2}$ is the half-life.

7. Procedure

7.1 Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 500-mL sample in a glass volumetric flask.

7.2 Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 500-mL aliquot of the unspiked acidified water as a blank.

7.3. Measure approximately 400 mL of distilled water into a 500-mL volumetric flask.

7.4. Add 1.25 mL of concentrated HNO_3 to the water in the flask to reach a pH of approximately 1.

7.5. Spike an aliquot of ^{137}Cs standard into the flask to reach a ^{137}Cs concentration in the desired spike range.

7.6. Fill the volumetric flask to volume with distilled water and mix by inverting.

7.7. Transfer the solution to a 500-mL high-density polyethylene bottle and label it with a QC sample number.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{137}Cs in the solution as nCi/L or pCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 100 μL of a 6000-pCi/mL ^{137}Cs standard is used to spike 500 mL of acidified water, the concentration of ^{137}Cs in the acidified water will be 1200 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(6000\ \text{pCi/mL})\ (100\ \mu\text{L})\ (1\ \text{mL}/1000\ \mu\text{L})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 1200\ \text{pCi/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4233-B, Cesium-137 Burn-Up Standard" (National Institute of Standards and Technology, Washington, DC, November 1979).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

GROSS ALPHA AND GROSS BETA ON FILTER MEDIA—QC SAMPLE PREPARATION

Analyte: Gross alpha and gross beta	**Method No.:** QCR138
Matrix: Filters	**Spike Range:** 10–100 pCi/filter
Procedure: Proportional counting	**Accuracy and Precision:** Gross alpha 100% ± 14.5% RSD Gross beta 100% ± 3.2% RSD
Effective Date: 07/28/92	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.1 and 10.2 for proper waste disposal practices.

1. Principle of Method

1.1. Hydrophobic filters are spiked with ^{241}Am and ^{90}Sr standards.

1.2. Hydrophobic filter material must be used to prevent penetration of ^{241}Am standard solution below the surface of the filter with subsequent loss of alpha radiation due to shielding by the filter material.

1.3. Gross beta is contributed equally by ^{90}Sr and by the ^{90}Y radioactive decay product that are in equilibrium in the ^{90}Sr standard solution.

1.4. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure or those parts of the procedure that are applicable.

1.5. Because the method of analysis is nondestructive, the QC samples can be reused, providing the gross beta concentration is decayed periodically.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with use of the pipette. A relative standard deviation

(RSD) of 14.5% for gross alpha and 3.2% for gross beta at the 1-σ level has been calculated for the error of the standard and for the spiking process based on the following function:

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = standard error, and
M2 = spiking error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} \quad ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by proportional counting gave a mean recovery of 92 ± 13% for gross alpha and 102 ± 12 % for gross beta at the 1-σ level. The data are summarized in Table I below.

TABLE I. SPIKE RECOVERY FOR GROSS ALPHA AND GROSS BETA ON FILTERS

	Gross Alpha				Gross Beta			
	Mean ± std dev (%)			Number of Samples	Mean ± std dev (%)			Number of Samples
1992	86	±	11	16	94	±	3	16
1993	86	±	10	163	93	±	6	160
1994	103	±	9	100	116	±	4	100

3. Collection and Storage of Samples

3.1. QC samples are dried after spiking and are sealed in stainless-steel planchets.

3.2. The samples are stored in planchets at room temperature pending analysis.

4. Apparatus

4.1. Filter paper: 1.875-in.-diam, Microsorban or equivalent hydrophobic material.

4.2. Planchets: stainless-steel, nominal 2-in.-diam, 0.25-in. deep.

4.3. Glue stick or equivalent adhesive.

4.4. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.5. Pipette tips: disposable.

4.6. Heat lamp.

4.7. Labels printed with QC sample numbers.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless-steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: The phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 0.0005-in.-thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.2. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.3. Gross alpha.

6.3.1. QC samples are spiked with an ^{241}Am standard prepared in 4 N HNO_3 at a concentration of approximately 470 pCi/mL. The solution is counted on a zinc sulfide scintillation system calibrated with National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.3.2. The ^{241}Am standard should be calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NIST SRM 4322. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.3.3. Direct plating procedure.

6.3.3.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs, which have been cleaned with acetone. Evaporate the solution to dryness under a heat lamp.

6.3.3.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.3.3.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.3.3.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.3.3.5. Place a piece of Mylar film over all the layers.

6.3.3.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.3.3.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.3.3.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.4. Gross beta.

6.4.1. QC samples are spiked with a ^{90}Sr standard in 2 M HCl at a concentration of approximately 850 pCi/mL.

6.4.2. The ^{90}Sr standard should be calibrated against a NIST or an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.4.3. Decay the ^{90}Sr standards each year.

6.4.3.1. The half-life of ^{90}Sr is 28.5 years.

6.4.3.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at desired time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms,

γ = (ln 2)/$T_{1/2}$ or the decay constant, and
$T_{1/2}$ = the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically omit the ^{241}Am or the ^{90}Sr spike from the filter as a blank QC for gross alpha or for gross beta.

7.2. Place a 1.875-in.-diam hydrophobic filter paper into a 2-in. stainless-steel planchet.

NOTE: Hydrophobic filter material must be used to prevent penetration of ^{241}Am standard solution below the surface of the filter with subsequent loss of alpha radiation due to shielding by the filter material.

7.3. Spike an aliquot of ^{241}Am standard onto the filter to reach the desired spike range for gross alpha, distributing the solution over the entire filter surface.

7.4. The gross beta count is contributed equally by ^{90}Sr and by the ^{90}Y radioactive decay product, which are in equilibrium in the ^{90}Sr standard solution.

7.4.1. The concentration of the ^{90}Sr standard solution is expressed in terms of ^{90}Sr, although half the gross beta count is contributed by ^{90}Sr and the other half by ^{90}Y.

7.4.2. Divide the spike range in half and use the concentration of the ^{90}Sr standard solution to determine the amount of standard solution to use to reach the desired spike range of 5–50 pCi/filter.

7.4.3. Spike the determined amount of ^{90}Sr standard onto the filter, distributing the solution over the entire filter surface.

7.4.4. The gross beta count will be within the spike range of 10–100 pCi/filter because ^{90}Y in the standard solution contributes a gross beta count equal to that contributed by the ^{90}Sr. The beta concentration in the QC sample based on the amount of ^{90}Sr added must be multiplied by 2 to determine the total gross beta concentration. See Step 8.2.

7.5. Dry the filter in the planchet under a heat lamp, being careful not to melt the filter.

7.6. Cut a piece of Mylar film to cover the top and sides of the planchet.

7.7. Use a glue stick to apply adhesive to the outside edges of the planchet.

7.8. Stretch the Mylar film over the top of the planchet and stick it firmly to the outside edges.

7.9. Trim away the excess Mylar film.

7.10. Label the planchet with a QC sample number.

7.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter the information into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the gross alpha concentration using the following example.

8.1.1. If 75 μL of a 470-pCi/mL ^{241}Am standard is spiked onto a filter, the gross alpha concentration in the QC sample is 35.2 pCi/filter. Multiply the result by RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(470\ \text{pCi/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(75\ \mu\text{L})}{\text{filter}} = 35.2\ \text{pCi/filter} \quad .$$

8.2. Calculate the gross beta concentration using the following example.

8.2.1. If 30 μL of a 850-pCi/mL ^{90}Sr standard is spiked onto a filter, the beta concentration contributed by ^{90}Sr in the QC sample is 25.5 pCi/filter.

$$\frac{(850\ \text{pCi/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(30\ \mu\text{L})}{\text{filter}} = 25.5\ \text{pCi/filter} \quad .$$

8.2.2. Multiply the beta concentration contributed by ^{90}Sr by 2 to determine the total gross beta concentration contributed by ^{90}Sr and ^{90}Y together.

$$(25.5\ \text{pCi/filter})\ (2) = 51\ \text{pCi/filter} \quad .$$

8.2.3. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.3. Record the gross alpha and gross beta concentrations of the filter in pCi/filter.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.2. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4322, Americium-241 Alpha-Particle Solution Standard" (National Institute of Standards and Technology, Washington, DC, November 1986).

10.4. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard," (National Institute of Standards and Technology, Washington, DC, April 1982).

GROSS ALPHA AND GROSS BETA ON SOIL — QC SAMPLE PREPARATION

Analyte: Gross alpha and gross beta	**Method No.:** QCR140
Matrix: Sand	**Spike Range:** 2.5–10 pCi/g
Procedure: Proportional counting	**Accuracy and Precision:** Gross alpha 100% ± 4.5% RSD Gross beta 100% ± 3.2% RSD
Effective Date: 06/01/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand spiked with ^{241}Am and ^{90}Sr standards is used in place of soil as the quality control (QC) matrix for gross alpha and gross beta analysis by proportional counting.

1.2. Gross beta is contributed equally by ^{90}Sr and the ^{90}Y radioactive decay products that are in equilibrium in the ^{90}Sr standard solution.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 4.5% at the 1-σ level for gross alpha and 3.2% at the 1-σ level for gross beta has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by proportional counting are tabulated below. The data are published in Source Material 10.1.

TABLE I. SPIKE RECOVERY FOR GROSS ALPHA AND GROSS BETA ON SOIL

	Gross Alpha		Gross Beta	
	Mean ± std dev (%)	N	Mean ± std dev (%)	N
1992	123 ± 55	27	115 ± 24	27
1993	119 ± 28	8	120 ± 29	8
1994	73 ± 20	14	92 ± 14	12

N = Number of samples.

3. Collection and Storage of Samples

3.1. Store QC samples in glass beakers covered with plastic wrap at room temperature pending analysis.

4. Apparatus

4.1. Beakers: 100-mL, glass.

4.2. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Balance: 200-g minimum capacity, 0.1-mg accuracy.

4.5. Spatula.

4.6. Plastic wrap.

4.7. Heat lamp.

4.8. Labels printed with QC sample numbers.

4.9. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.10. Discs: stainless-steel, 2.22-cm-diam.

4.11. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.12. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.13. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Sand. A clean, dry 2-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. When certified primary standards are available, dilute them to make standards at the desired concentration.

6.2. Calibrate standard solutions that are not made from certified primary standards against an appropriate certified standard.

6.3. Gross alpha.

6.3.1. Spike QC samples with an ^{241}Am standard prepared in 4 N HNO_3 at a concentration of approximately 180 pCi/mL. Count the solution on a zinc sulfide scintillation system calibrated with National Bureau of Standards (NBS) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.3.2. Calibrate the ^{241}Am standard against a National Institute of Standards (NIST)-certified ^{241}Am alpha-particle solution standard, such as NBS SRM

4322. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.3.3. Direct plating procedure.

6.3.3.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.3.3.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures the package is tightly sealed when assembled.

6.3.3.3. Place the stainless-steel disc containing the sample on the filter paper, making sure to center the disc.

6.3.3.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.3.3.5. Place a piece of Mylar film over all the layers.

6.3.3.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.3.3.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) count for each sample.

6.3.3.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.4. Gross beta.

6.4.1. Spike QC samples with a ^{90}Sr standard in 2 M HCl at a concentration of approximately 180 pCi/mL.

6.4.2. Calibrate the ^{90}Sr standard against an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.4.3. Decay the ^{90}Sr standards each year.

6.4.3.1. The half-life of ^{90}Sr is 28.5 years.

6.4.3.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 2-g sample aliquot in a 100-mL glass beaker.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 2-g aliquot of the deep-well sand for use as a blank, omitting the ^{241}Am, the ^{90}Sr, or both.

7.3. Accurately weigh a 2-g aliquot of clean, dry sand into a 100-mL beaker. Record the weight of the sand on the beaker with a felt-tipped pen for reference by the analyst.

7.4. Spike an aliquot of ^{241}Am standard onto the sand in the beaker to reach the desired spike range for gross alpha.

7.5. The gross beta count is contributed equally by ^{90}Sr and the ^{90}Y radioactive decay products, which are in equilibrium in the ^{90}Sr standard solution.

7.5.1. The concentration of the ^{90}Sr standard solution is expressed in terms of ^{90}Sr although half the gross beta count is contributed by ^{90}Sr and the other half by ^{90}Y.

7.5.2. Divide the spike range in half and use the concentration of the ^{90}Sr standard solution to determine the amount of standard solution to use to reach the desired spike range of 1.25–5.0 pCi/g.

7.5.3. Spike the determined amount of ^{90}Sr standard onto the sand in the beaker.

7.5.4. The gross beta count will be within the spike range of 2.5–10.0 pCi/g because ^{90}Y in the standard solution contributes a gross beta count equal to that contributed by the ^{90}Sr. The beta concentration in the QC sample based on the amount of ^{90}Sr added must be multiplied by 2 to determine the total gross beta concentration.

7.6. Label the beaker with a QC sample number.

7.7. Air dry the QC sample or dry it under a heat lamp to remove excess moisture.

7.8. Cover the beaker with plastic wrap and store the sample at room temperature pending analysis.

7.9. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Determine background contributions to gross alpha and gross beta counts and add them to the spiked alpha and beta concentrations.

8.2. Record the gross alpha and gross beta concentrations on the sand as pCi/g.

8.3. Calculate the gross alpha spike concentration as in the following example.

8.3.1. If 50 μL of a 180-pCi/mL ^{241}Am standard is spiked onto 2.0000 g of sand, the gross alpha concentration in the sand is 4.5 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(180\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (50\ \mu\text{L})}{2.0000\ \text{g}} = 4.5\ \text{pCi/g} \quad .$$

8.3.2. Add the alpha background to the alpha concentration from the ^{241}Am spike to obtain the total gross alpha concentration in the QC sample.

$$4.5\ \text{pCi/g} + 4.9\ \text{pCi/g} = 9.4\ \text{pCi/g} \quad .$$

8.4. Calculate the gross beta concentration as in the following example.

8.4.1. If 35 μL of a 174-pCi/mL ^{90}Sr standard is spiked onto 2.000 g of sand, the beta concentration contributed by ^{90}Sr in the sample is 3.0 pCi/g.

$$\frac{(174\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (35\ \mu\text{L})}{2.0000\ \text{g}} = 3.0\ \text{pCi/g} \quad .$$

8.4.2. Multiply the beta concentration contributed by ^{90}Sr by 2 to determine the combined gross beta concentration contributed by ^{90}Sr and ^{90}Y.

$$(3.0\ \text{pCi/g})\ (2) = 6.0\ \text{pCi/g} \quad .$$

8.4.3. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4.4. Add the beta background to the beta concentration contributed by the combined ^{90}Sr and ^{90}Y to obtain the total gross beta concentration in the QC sample.

$$6.0\ \text{pCi/g} + 2.4\ \text{pCi/g} = 8.4\ \text{pCi/g} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

10.5. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

GROSS ALPHA AND GROSS BETA IN WATER — QC SAMPLE PREPARATION

Analyte: Gross alpha and gross beta	**Method No.:** QCR150
Matrix: Water	**Spike Range:** 5–20 pCi/L
Procedure: Proportional counting	**Accuracy and Precision:** Gross alpha 100% ± 3.4% RSD Gross beta 100% ± 3.2% RSD
Effective Date: 06/01/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. A quality control (QC) sample for the determination of gross alpha and gross beta in water is prepared by spiking 0.5 M HCl with ^{241}Am and ^{90}Sr standards.

1.2. Gross beta is contributed equally by ^{90}Sr and by the ^{90}Y radioactive decay products that are in equilibrium in the ^{90}Sr standard solution.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask and of the pipette. A relative standard deviation (RSD) of 3.4% at the 1-σ level for gross alpha and 3.2% at the 1-σ level for gross beta has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by proportional counting are summarized in Table I below. The data are published in Source Material 10.1.

TABLE I. SPIKE RECOVERY FOR GROSS ALPHA AND GROSS BETA IN WATER

	Gross Alpha		Gross Beta	
	Mean ± std dev (%)	N	Mean ± std dev (%)	N
1992	140 ± 29	25	110 ± 32	23
1993	115 ± 40	24	105 ± 20	28
1994	96 ± 22	32	99 ± 21	45

N = Number of samples.

3. Collection and Storage of Samples

3.1. QC samples are prepared in an acid medium in a volumetric flask and stored in the flask at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 1-L, glass, class A.

4.2. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Labels printed with QC sample numbers.

4.5. Heat lamp.

4.6. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.7. Discs: stainless-steel, 2.22-cm-diam.

4.8. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.9. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.10. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Numours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Hydrochloric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. When they are available, dilute certified primary standards to make standards at the desired concentration.

6.2. Calibrate standard solutions that are not made from certified primary standards against an appropriate certified standard.

6.3. Gross alpha.

6.3.1. Spike QC samples with an ^{241}Am standard prepared in 4 N HNO_3 at a concentration of approximately 18 pCi/mL. Count the solution on a zinc sulfide scintillation system calibrated with National Bureau of Standards (NBS) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.3.2. Calibrate the ^{241}Am standard against a National Institute of Standards and Technology (NIST)-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.3.3. Direct plating procedure.

6.3.3.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.3.3.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures the package is tightly sealed when assembled.

6.3.3.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.3.3.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.3.3.5. Place a piece of Mylar film over all the layers.

6.3.3.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.3.3.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) count for each sample.

6.3.3.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.4. Gross beta.

6.4.1. Spike QC samples with a ^{90}Sr standard in 2 M HCl at a concentration of approximately 170 pCi/mL.

6.4.2. Calibrate the ^{90}Sr standard against an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.4.3. Decay the ^{90}Sr standards each year.

6.4.3.1. The half-life of ^{90}Sr is 28.5 years.

6.4.3.2. The following equation describes the rate of radioactive decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 1-L sample aliquot in a volumetric flask.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically omit the ^{241}Am, the ^{90}Sr, or both from the QC sample for use as a blank.

7.3. Add approximately 800 mL of distilled water to a 1-L volumetric flask.

7.4. Add 43 mL of 12 M HCl to the water in the flask to produce a final acid concentration of 0.5 M.

7.5. Spike an aliquot of ^{241}Am standard into the water in the flask to reach the desired spike range for gross alpha.

7.6. The gross beta count is contributed equally by ^{90}Sr and by the ^{90}Y radioactive decay products that are in equilibrium in the ^{90}Sr standard solution.

7.6.1. The concentration of the ^{90}Sr standard solution is expressed in terms of ^{90}Sr although half the gross beta count is contributed by ^{90}Sr and the other half by ^{90}Y.

7.6.2. Divide the spike range in half and use the concentration of the ^{90}Sr standard solution to determine the amount of standard solution to use to reach the desired spike range of 2.5–10.0 pCi/L.

7.6.3. Spike the determined amount of ^{90}Sr standard into the water in the flask.

7.6.4. The gross beta count will be within the spike range of 5–20 pCi/L because ^{90}Y in the standard solution contributes a gross beta count equal to that contributed by the ^{90}Sr. The beta concentration in the QC sample based on the amount of ^{90}Sr added must be multiplied by 2 to determine the total gross beta concentration.

7.7. Dilute the QC sample to volume with distilled water. Mix by inversion. Label the flask with a QC sample number and store at room temperature pending analysis.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of gross alpha and gross beta in the QC sample as pCi/L.

8.2. Calculate the gross alpha spike concentration as in the following example.

8.2.1. If 300 μL of a 17.73-pCi/mL ^{241}Am standard is used to prepare a 1-L QC sample, the gross alpha concentration in the sample is 5.3 pCi/L.

$$\frac{(17.73\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (300\ \mu\text{L})}{1\ \text{L}} = 5.3\ \text{pCi/L} \quad .$$

8.2.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.3. Calculate the gross beta spike concentration as in the following example.

8.3.1. If 25 μL of a 174-pCi/mL ^{90}Sr standard is used to prepare a 1-L QC sample, the beta concentration contributed by ^{90}Sr in the sample is 4.4 pCi/L.

$$\frac{(174\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (25\mu\text{L})}{1\ \text{L}} = 4.4\ \text{pCi/L} \quad .$$

8.3.2. Multiply the beta concentration contributed by ^{90}Sr by 2 to determine the total gross beta concentration contributed by ^{90}Sr and ^{90}Y.

$$(4.4\ \text{pCi/L})\ (2) = 8.8\ \text{pCi/L} \quad .$$

8.3.3. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the

transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

10.5. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

PLUTONIUM AND AMERICIUM ON SOIL — QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, and Americium-241	**Method No.:** QCR160
Matrix: Soil	**Spike Range:** 0.1–1 pCi/g
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** ^{238}Pu 100% ± 3.4% RSD ^{239}Pu 100% ± 3.1% RSD ^{241}Am 100% ± 4.5% RSD
Effective Date: 04/12/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is spiked with ^{238}Pu, ^{239}Pu, and ^{241}Am standards.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the pipette and of the balance. Relative standard deviations (RSDs) of 3.4% for ^{238}Pu, 3.1% for ^{239}Pu, and 4.5% for ^{241}Am at the 1-σ level have been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,

M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by radiochemistry and alpha spectrometry are summarized in Table I below. The data are published in Source Material 10.1.

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM ON SOIL

	Radionuclide	Mean ± std dev (%)	Number of Samples
1992	^{238}Pu	103 ± 19	75
	^{239}Pu	98 ± 12	59
	^{241}Am	108 ± 19	41
1993	^{238}Pu	100 ± 8	97
	^{239}Pu	105 ± 12	91
	^{241}Am	98 ± 8	49
1994	^{238}Pu	97 ± 15	204
	^{239}Pu	98 ± 14	201
	^{241}Am	100 ± 9	67

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Bottles: 500-mL, high-density polyethylene.

4.2. Balance: 200-g capacity, 0.1-mg accuracy.

4.3. Autopipette: 100-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Spatula.

4.6. Heat lamp.

4.7. Labels printed with QC sample numbers.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless-steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Sand. A clean and dry 10-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. QC samples are spiked with ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3 and with an ^{241}Am standard prepared in 4 N HNO_3. The plutonium standards are heated at 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state.

6.2. The radionuclide standards should have concentrations of approximately 180 pCi/mL.

6.3. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.4. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.5. The ^{238}Pu standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{238}Pu alpha-particle solution standard, such as National Bureau of Standards (NBS) Standard Reference Material (SRM) 4323.

The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. The ^{239}Pu standard should be calibrated against a NIST-certified ^{239}Pu alpha-particle solution standard, such as NBS SRM 4331. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. The ^{241}Am standard should be calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.8. All solutions are counted on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22

to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 10-g sample aliquot in a 500-mL high-density polyethylene bottle.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically analyze a 10-g aliquot of the unspiked sand as a blank.

7.3. Accurately weigh 10 g of clean, dry sand into a 500-mL high-density polyethylene bottle. Record the weight of sand on the polyethylene bottle with a felt-tipped pen for reference by the analyst.

7.4. Spike aliquots of the Pu and Am standard solutions onto the sand to reach the desired spike range.

7.5. Air-dry the samples or dry under a heat lamp until excess liquid is gone.

7.6. Cap the sample bottles and label with a QC sample number. The entire contents of the bottle must be analyzed.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, and ^{241}Am on the sand as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 20 μL of a 175-pCi/mL ^{238}Pu standard is used to spike 10.0000 g of sand, the ^{238}Pu concentration in the sand is 0.35 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(175\ \frac{\text{pCi}}{\text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(20\ \mu\text{L})}{10.0000\ \text{g}} = 0.35\ \text{pCi/g} \quad .$$

8.3. Spike concentrations for ^{239}Pu and ^{241}Am are calculated like spike concentrations for ^{238}Pu using the equation in Step 8.2.1.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid waste that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.5. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.6. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4331, Plutonium-239 Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, March 1975).

10.7. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

RADIONUCLIDES ON FECAL MATERIAL—QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, and Americium-241	**Method No.:** QCR165
Matrix: Fecal material	**Spike Range:** 1–10 pCi/sample
Procedure: Analysis by radiochemistry and alpha spectrometry	**Accuracy and Precision:** Pu^{238} 100% ± 3.6% RSD Pu^{239} 100% ± 4.0% RSD Am^{241} 100% ± 4.5% RSD
Effective Date: 12/02/91	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.1 through 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Blank fecal material is spiked with ^{238}Pu, ^{239}Pu, and ^{241}Am standards.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC sample preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the pipette. A relative standard deviation (RSD) of 3.6% for ^{238}Pu, 4.0% for ^{239}Pu, and 4.5% for ^{241}Am at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = calibration error, and
M2 = spiking error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
100 = factor to convert to percent.

2.2. Analytical results from QC samples prepared from 1992 through 1994 using this procedure and analyzed by radiochemistry and alpha spectrometry are summarized in Table I below. The data are published in Source Material 10.4.

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM IN FECAL MATERIAL

	Mean ± std dev (%)	N
^{238}Pu	96 ± 12	14
^{239}Pu	101 ± 19	13
^{241}Am	102 ± 23	9

N = number of samples.

3. Collection and Storage of Samples

3.1. Fecal material from animals, such as dogs, which are omnivorous and have a high fat content in their diet, provides a suitable blank sample matrix.

3.2. Spiked samples are stored in a freezer pending analysis.

4. Apparatus

4.1. Plastic bags: 12-oz with press-together locking seal.

4.2. Balance: 200-g minimum capacity, 0.1-mg accuracy.

4.3. Spatula.

4.4. Autopipette: 100-μL, Rainin or equivalent.

4.5. Labels printed with QC sample numbers.

4.6. Heat lamp.

4.7. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.8. Discs: stainless-steel, 2.22-cm-diam.

4.9. Alpha phosphor on Mylar: The phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.10. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon, Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.11. Mylar film: 1.5-in.-wide rolls, 0.0005-in.-thick, manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. A 100-g aliquot of fecal material is required for each sample.

6. Calibration and Standards

6.1. QC samples are spiked with ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3 and with an ^{241}Am standard prepared in 4 N HNO_3. The plutonium standards are heated at 80°C for 2 h to convert Pu in the polymeric form to the ionic +4 state.

6.2. The radionuclide standards should have concentrations of approximately 180 pCi/mL.

6.3. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.4. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.5. The ^{238}Pu standard should be calibrated against a National Bureau of Standards (NBS)-certified ^{238}Pu alpha-particle solution standard, such as NBS Standard Reference Material (SRM) 4323. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. The ^{239}Pu standard should be calibrated against a NBS-certified ^{239}Pu alpha-particle solution standard, such as NBS SRM 4331. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. The ^{241}Am standard should be calibrated against a NBS-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.8. All solutions are counted on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs and evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper. Be sure the disc is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 100-g fecal QC sample in a plastic bag.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically analyze an aliquot of unspiked fecal material as a blank.

7.3. Weigh 100.0 g of blank fecal material into a 12-oz plastic bag with a press-together seal.

7.4. Spike aliquots of the Pu and Am standard solutions onto the feces to reach the desired spike range.

7.5. Press together the seal on the plastic bag.

7.6. Place the plastic bag containing the spiked feces into a second 12-oz plastic bag.

7.7. Seal the outer plastic bag.

7.8. Label the outer bag with a QC sample number.

7.9. Store the sample in a freezer pending analysis.

7.10. The analyst will remove the inner plastic bag and ash the bag and the fecal sample it contains.

7.11. Record the QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, and ^{241}Am on the feces as pCi/sample.

8.2. Calculate spike concentrations using the following example.

8.2.1. If 15 μL of a 182.9 pCi/mL ^{239}Pu standard is spiked onto 100.1910 g of fecal material in a plastic bag, the ^{239}Pu concentration in the sample will be 2.74 pCi/sample. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(182.9\ \frac{\text{pCi}}{\text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(15\ \mu\text{L})}{\text{sample}} = 2.74\ \text{pCi/sample} \quad .$$

8.3. Calculate spike concentrations for ^{238}Pu and ^{241}Am just as spike concentrations for ^{239}Pu using the example in Step 8.2.1.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid waste that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) number describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Request form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17).

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual,* Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.2. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual,* Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual,* Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.5. National Bureau of Standards, "Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

10.6. National Bureau of Standards, "Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

10.7. National Bureau of Standards, "Standard Reference Material 4331, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, March 1975).

10.8. National Bureau of Standards, "Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

RADIONUCLIDES ON VEGETATION ASH — QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, Americium-241, and Strontium-90	**Method No:** QCR170
Matrix: Vegetation ash	**Spike Range:** 1–10 pCi/g
Procedure: Radiochemistry and alpha spectrometry or gas-flow proportional counting	**Accuracy and Precision:** ^{238}Pu 100% ± 3.5% RSD ^{239}Pu 100% ± 3.2% RSD ^{241}Am 100% ± 4.5% RSD ^{90}Sr 100% ± 3.2% RSD
Effective Date: 06/15/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Blank vegetation ash is spiked with ^{238}Pu, ^{239}Pu, ^{241}Am, and ^{90}Sr standards.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. Relative standard deviations (RSDs) of 3.5% for ^{238}Pu, 3.2% for ^{239}Pu, 4.5% for ^{241}Am, and 3.2% for ^{90}Sr at the 1-σ level have been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} \quad ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by gas-flow proportional counting or radiochemistry and alpha spectrometry are summarized in Table I below. The data are published in Source Material 10.1.

TABLE I. SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION			
	Spike range, (pCi/g)	Mean ± std dev (%)	Number of Samples
^{238}Pu			
1992	1.0–5.0	108 ± 7	3
1993	1.0–5.0	99 ± 6	9
	5.0–10.0	98 ± 0.6	2
1994	1.0–5.0	105 ± 9	3
	5.0–10.0	100 ± 4	5
^{239}Pu			
1992	1.0–5.0	105 ± 5	3
1993	1.0–5.0	99 ± 4	9
	5.0–10.0	103 ± 6	3
1994	1.0–5.0	104 ± 4	5
	5.0–10.0	99 ± 6	5
^{241}Am			
1992	1.0–5.0	87.9	1
1994	1.0–10.0	95 ± 6	3
^{90}Sr			
1992	1.0–5.0	108 ± 20	2
1993	1.0–5.0	109 ± 9	6
	5.0–10.0	94 ± 9	6
1994	1.0–5.0	101 ± 14	4
	5.0–10.0	93 ± 16	7

3. Collection and Storage of Samples

3.1. Spiked QC samples are covered with plastic wrap and stored at room temperature pending analysis.

4. Apparatus

4.1. Beakers: 600-mL, glass.

4.2. Balance: 300-g capacity, 0.1-mg accuracy.

4.3. Autopipette: 100-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Plastic wrap.

4.6. Labels printed with QC sample numbers.

4.7. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.8. Discs: stainless-steel, 2.22-cm-diam.

4.9 Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.10. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.11. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Vegetation ash. A 1-g aliquot is required for each sample.

5.2. A suitable vegetation ash does not contain the analyte of interest and presents few interferences to the analytical method. Commercially available dry pet or farm stock foods may be ashed to provide a suitable vegetation ash. Preparation of a vegetation ash matrix is described in Method No.QCM200. Previously analyzed vegetation ash samples that did not contain Pu, Am, or Sr may also be used as a QC matrix.

6. Calibration and Standards

6.1. QC samples are spiked with either ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3, an ^{241}Am standard prepared in 4 N HNO_3, or a ^{90}Sr standard prepared in 2 M HCl. The plutonium standards are heated at 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state.

6.2. The radionuclide standards should have concentrations of approximately 180 pCi/mL.

6.3. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.4. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.5. The ^{238}Pu standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{238}Pu alpha-particle solution standard, such as National Bureau of Standards (NBS) Standard Reference Material (SRM) 4323. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. The ^{239}Pu standard should be calibrated against a NIST-certified ^{239}Pu alpha-particle solution standard, such as NBS SRM 4331. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. The ^{241}Am standard should be calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook

6.8. The Pu and Am solutions are counted on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.10. The ^{90}Sr standard should be calibrated against a NIST or an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.11. Decay the ^{90}Sr standards each year.

6.11.1. The half-life of ^{90}Sr is 28.5 years.

6.11.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 1-g sample in a 600-mL glass beaker.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically analyze a 1-g aliquot of the unspiked vegetation ash as a blank.

7.3. Accurately weigh 1 g of vegetation ash into a 600-mL beaker. Record the weight of the ash on the beaker with a felt-tipped pen for reference by the analyst.

7.4. Spike aliquots of the Pu, Am, or Sr standard solutions onto the vegetation ash to reach the desired spike range.

7.5. Cover the beaker with plastic wrap and label it with a QC sample number. The entire contents of the beaker must be analyzed.

7.6. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, ^{241}Am, and ^{90}Sr on the vegetation ash as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 15 μL of a 175-pCi/mL ^{238}Pu standard is used to spike 1.0000 g of vegetation ash, the ^{238}Pu concentration in the ash is 2.6 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(175\ \frac{\text{pCi}}{\text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(15\ \mu\text{L})}{1.0000\ \text{g}} = 2.6\ \text{pCi/g} \quad .$$

8.3. Spike concentrations for ^{239}Pu, ^{241}Am, and ^{90}Sr are calculated like spike concentrations for ^{238}Pu using the equation in Step 8.2.1.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid water that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) number describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the

transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992, " Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. National Bureau of Standards, "Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.5. National Bureau of Standards, "Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.6. National Bureau of Standards, "Standard Reference Material 4331, Plutonium-239 Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, March 1975).

10.7. National Bureau of Standards, "Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

Revisions or additions to the procedure are marked ( ). Where a section heading is marked, the entire section has been revised.

PLUTONIUM AND AMERICIUM IN WATER — QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, and Americium-241	**Method No.:** QCR180
Matrix: Water	**Spike Range:** 0.1–5 pCi/L
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** ^{238}Pu 100% ± 5.1% RSD ^{239}Pu 100% ± 1.7% RSD ^{241}Am 100% ± 1.9% RSD
Effective Date: 08/02/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.6 and 10.7 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified blank water is spiked with ^{238}Pu, ^{239}Pu, and ^{241}Am standards.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the volumetric flask and of the pipette. Relative standard deviations (RSDs) of 5.1% for ^{238}Pu, 1.7% for ^{239}Pu, and 1.9% for ^{241}Am at the 1-σ level have been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,

M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by radiochemistry and alpha spectrometry are summarized in Table I below. The data are published in Source Material 10.1.

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM IN WATER

	Radionuclide	Mean ± std dev (%)	Number of Samples
1992	^{238}Pu	104 ± 10	21
	^{239}Pu	108 ± 22	20
	^{241}Am	98 ± 18	12
1993	^{238}Pu	104 ± 13	22
	^{239}Pu	106 ± 14	30
	^{241}Am	93 ± 10	13

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM IN WATER (cont)

	Radionuclide	Mean ± std dev (%)	Number of Samples
1994	^{238}Pu	100 ± 8	42
	^{239}Pu	104 ± 14	43
	^{241}Am	94 ± 10	18

3. Collection and Storage of Samples

3.1. QC samples are prepared in an acid medium in a volumetric flask and are stored in the flask at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 500-mL, glass, class A.

4.2. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Pipette: 2-mL, class A volumetric.

4.5. Labels printed with QC sample numbers.

4.6. Heat lamp.

4.7. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.8. Discs: stainless-steel, 2.22-cm-diam.

4.9. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.10. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.11. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Hydrochloric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. QC samples are spiked with ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3 and with an ^{241}Am standard prepared in 4 N HNO_3. The plutonium standards are heated at a nominal temperature of 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state.

6.2. The concentration of the ^{238}Pu, ^{239}Pu, and ^{241}Am standards should be between approximately 2 and 6 pCi/mL.

6.3. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.4. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.5. The ^{238}Pu standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{238}Pu alpha-particle solution standard, such as National Bureau of Standards (NBS) Standard Reference Material (SRM) 4323. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. The ^{239}Pu standard should be calibrated against a NIST-certified ^{239}Pu alpha-particle solution standard, such as NBS SRM 4331. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. The ^{241}Am standard should be calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.8. All solutions are counted on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs and evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.10. Alternatively, an Environmental Protection Agency (EPA) Plutonium in Water crosscheck sample may be used as a QC sample. After dilution and distribution of a crosscheck study, the remainder of the stock solution is transferred to a glass container for storage to prevent the loss of the radionuclides to the walls of the EPA polyethylene container.

6.10.1. EPA records the concentration of the standard after dilution according to EPA instructions.

6.10.2. The concentration of the original stock solution must be back-calculated before it is used, taking the EPA dilution instructions into consideration.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 500-mL sample aliquot in a volumetric flask.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include an unspiked water sample acidified to 3 N with HCl as a blank.

7.3. Place approximately 300 mL of distilled water into a 500-mL volumetric flask.

7.4. Add 125 mL of 12 M HCl to produce a final acid concentration of 3 M.

7.5. Spike aliquots of the Pu and Am standard solutions into the water to reach the desired spike range.

7.6. Dilute the QC sample to volume using distilled water. Mix by inversion. Label the flask with a QC sample number and store at room temperature pending analysis.

7.7. EPA crosscheck standard.

7.7.1. The EPA standard contains only plutonium.

7.7.2. Back-calculate the concentration of the original stock before an aliquot is taken. See Step 8.3.

7.7.3. EPA recommends mixing the standard for 10 to 15 min before an aliquot is taken.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, and ^{241}Am in the water as pCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 300 μL of a 2-pCi/mL ^{238}Pu standard is used to spike 450 mL of acidified water and the solution is diluted to 500 mL, the ^{238}Pu

concentration in the acidified water is 1.2 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(2\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (300\ \mu\text{L})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 1.2\ \text{pCi/L} \quad .$$

8.2.2. Spike concentrations for ^{239}Pu and ^{241}Am are calculated like spike concentrations for ^{238}Pu using the equation in Step 8.2.1.

8.3. If an EPA crosscheck Plutonium in Water sample will be used to make a QC standard for plutonium in water, the undiluted concentration of the crosscheck sample must first be calculated.

8.3.1. If the concentration of the EPA sample is 10.6 ± 1.1 pCi/L after dilution of a 500-mL aliquot to 4 L, the concentration of the undiluted sample is calculated as follows:

$$(10.6\ \text{pCi/L})\ (4\ \text{L}/500\ \text{mL})\ (1000\ \text{mL/L}) = 84.8\ \text{pCi/L} \quad .$$

The concentration of 84.8 pCi/L is then used to determine the aliquot used to spike the acidified water sample.

8.3.2. If 4 mL of the 84.8-pCi/L EPA sample is spiked into 400 mL of acidified water and is diluted to 500 mL with distilled water, the plutonium concentration is 0.68 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(84.8\ \text{pCi/L})\ (1\ \text{L}/1000\ \text{mL})\ (4\ \text{mL})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 0.68\ \text{pCi/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.3. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.4. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4331, Plutonium-239 Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, March 1975).

10.5. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

10.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

PLUTONIUM-238 IN URINE — QC SAMPLE PREPARATION

Analyte: Plutonium-238	**Method No.:** QCR190
Matrix: Urine	**Spike Range:** 0.0–0.40 pCi/sample
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 3.7% RSD
Effective Date: 01/01/75	**Authors:** Margaret A. Gautier William D. Moss Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.6 to 10.8 for proper waste disposal.

1. Principle of Method

1.1. A pool of blank urine is prepared.

1.2. The blank urine is aliquoted and spiked with a known standard.

1.3. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with the use of the graduated cylinder and the pipette. A relative standard deviation (RSD) of 3.7% at the 1-σ level has been calculated for the calibration, spiking, and aliquoting process based on the following:

$$D = \frac{M1 \times M2}{M3 + M2} ,$$

where D = calculated result,

M1 = calibration error,
M2 = spiking error, and
M3 = aliquoting error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{\frac{\left[R^2_{M1}\,(M3 + M2)^2 + M3^2\,(R^2_{M2} + R^2_{M3})\right]}{(M3 + M2)^2}} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
M3 = volume of cylinder,
M2 = volume of pipette,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of cylinder, and
100 = factor to convert to percentage.

2.2. Analysis by radiochemistry and alpha spectrometry of QC samples prepared between 1992 and 1994 using this procedure gave a mean recovery of 95% ± 14% RSD. The data are published in Source Material 10.1 and are summarized in Table I below.

TABLE I. PLUTONIUM-238 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR PLUTONIUM-242 RECOVERY

Year	Spike level (pCi/sample)	Mean	±	RSD (%)	Number of Samples
1992	0.07	100	±	12	24
	0.14	89	±	10	27
	0.25	86	±	9	25
	0.50	85	±	8	25
1993	0.06	105	±	24	30
	0.12	107	±	13	28
	0.20	103	±	11	31
	0.40	102	±	6	25
1994	0.07	90	±	14	27
	0.13	91	±	10	31
	0.22	92	±	10	28
	0.44	96	±	10	12

3. Collection and Storage of Samples

3.1. Urine is collected as needed from group personnel who have no known contact with radiation work. It is used to form a pool of blank urine.

3.2. Spiked QC samples are refrigerated at a nominal temperature of 4°C pending analysis.

4. Apparatus

4.1. Beakers: 4- or 5-L, polyethylene.

4.2. Graduated cylinders: 500-mL.

4.3. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Specimen containers: 16-oz jars with screw caps.

4.6. Labels printed with QC sample numbers.

4.7. Heat lamp.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless-steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: The phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon, Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick, manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{238}Pu standard prepared in 2 N HNO_3 and heated at a nominal temperature of 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state. The solution is counted on a zinc sulfide scintillation system calibrated with National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.2. The ^{238}Pu standard should be at a concentration of approximately 0.8 pCi/mL.

6.3. The ^{238}Pu standard was calibrated against a NIST-certified ^{238}Pu alpha-particle solution standard, such as SRM 4323. Recalibrate the standard solution yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.4. Direct plating procedure.

6.4.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs, which have been cleaned with acetone. Evaporate the solution to dryness under a heat lamp.

6.4.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.4.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.4.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.4.5. Place a piece of Mylar film over all the layers.

6.4.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.4.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.4.8. The count room data are corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Working with bodily fluids is discussed in detail in SOP-4, "Handling Human Biological Fluids and Tissues," found in Appendix III of the Environmental Chemistry Safety Manual.

NOTE: Wear safety glasses, gloves, and a lab coat. Each day prepare a 1:100 dilution of household bleach in water in a spray bottle. Use this solution to thoroughly clean the work area after sample preparation is completed. Rinse gloves in a 1:100 dilution of household bleach in water and discard them. Wash hands with soap and water.

7.2. Prepare a pool from blank urine sufficient in volume to allow 400 mL for each QC sample to be prepared.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Include blank QCs prepared from the same urine pool as the spiked samples.

7.4. Record QC standard information, sample spike amount, concentration, and uncertainty in the QC Laboratory notebook.

7.5. Label bottles with QC sample numbers.

7.6. Aliquot 400 mL of blank urine into each sample bottle.

7.7. Spike the blank urine with aliquots of standard as determined in Step 7.3.

7.8. Screw caps on bottles and refrigerate at a nominal temperature of 4°C pending analysis.

7.9. Enter the spike concentrations of each QC into the CVS and CVD databases on the VAX. This procedure is done annually because the same concentration levels are used throughout the year.

8. Calculations

8.1. Record spike concentrations as pCi/sample of urine.

8.2. Calculate the spike concentration for a 150-μL aliquot of ^{238}Pu standard using the following equation.

$$\text{pCi/sample per spike amount} = 0.8\ \text{pCi/mL} \times 0.150\ \text{mL} = 0.12\ \text{pCi/sample} \quad .$$

8.3. Spike concentrations calculated in Step 8.2 are tabulated below.

Spike amount (μL)	Concentration (pCi/sample)	Uncertainty ($\pm$ 3.7%)
75	0.06	0.002
150	0.12	0.004
250	0.20	0.007
500	0.40	0.015

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Radiochemically contaminated waste.

9.2.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.1.5. Put a new plastic bag into the waste can for continued use.

9.2.1.6. Place the sealed bag into a cardboard box lined with a plastic bag labeled to indicate its use for radioactively contaminated waste.

9.2.1.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.1.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.1.9. Line a new box with a plastic bag and label it for continued use.

9.2.1.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.1.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.2.2. Biohazardous waste.

9.2.2.1. If urine-contaminated solid waste is disinfected, dispose of it in the same manner as any other waste. Refer to Source Material 10.8.

9.2.2.2. If urine sample containers are rinsed well with a 10% solution of bleach, dispose of the rinse solution down the drain. Refer to Source Material 10.5.

9.2.2.3. If the excess urine is diluted with bleach to make a 5% (v/v) solution, dispose of this solution down the drain. Refer to Source Material 10.5.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of radioactively contaminated solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. *EML Procedures Manual*, 25th ed., H. L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, New York, August 1982).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4323, Plutonium-238 Alpha-Particle Solution Standard" (National Institute of Standards and Technology, Washington, DC, November 1986).

10.4. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Institute of Standards and Technology, Washington, DC, April 1982).

10.5. M. Phillips, "Handling Human Biological Fluids and Tissues," SOP-4, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Los Alamos National Laboratory document (November 1993).

10.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.8. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

PLUTONIUM-239 IN URINE — QC SAMPLE PREPARATION

Analyte: Plutonium-239	**Method No.:** QCR200
Matrix: Urine	**Spike Range:** 0.0–0.46 pCi/sample
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 01/01/75	**Authors:** Margaret A. Gautier William D. Moss Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.6 to 10.8 for proper waste disposal.

1. Principle of Method

1.1. A pool of blank urine is prepared.

1.2. The blank urine is aliquoted and spiked with a known standard.

1.3. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the graduated cylinder and the pipette. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and aliquoting process based on the following:

$$D = \frac{M1 \times M2}{M3 + M2} ,$$

where D = calculated result,
M1 = calibration error,

M2 = spiking error, and
M3 = aliquoting error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{\frac{\left[R^2_{M1}\,(M3 + M2)^2 + M3^2\,(R^2_{M2} + R^2_{M3})\right]}{(M3 + M2)^2}} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
M3 = volume of cylinder,
M2 = volume of pipette,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of cylinder, and
100 = factor to convert to percentage.

2.2 Analysis by radiochemistry and alpha spectrometry of QC samples prepared between 1992 and 1994 using this procedure gave a mean recovery of 100% ± 12% RSD. The data are published in Source Material 10.1 and are summarized in Table I below.

TABLE I. PLUTONIUM-239 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR PLUTONIUM-242 RECOVERY

Year	Spike level (pCi/sample)	Mean ± RSD (%)			Number of Samples
1992	0.06	94	±	14	21
	0.15	96	±	12	25
	0.22	100	±	7	25
	0.44	100	±	8	26

TABLE I. PLUTONIUM-239 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR PLUTONIUM-242 RECOVERY (cont)

Year	Spike level (pCi/sample)	Mean	±	RSD (%)	Number of Samples
1993	0.06	99	±	12	26
	0.14	104	±	12	30
	0.21	106	±	10	30
	0.43	104	±	8	28
1994	0.06	96	±	18	27
	0.14	104	±	12	28
	0.22	100	±	10	30
	0.43	102	±	10	27

3. Collection and Storage of Samples

3.1. Urine is collected as needed from group personnel who have no known contact with radiation work. It is used to form a pool of blank urine.

3.2. Spiked QC samples are refrigerated at a nominal temperature of 4°C pending analysis.

4. Apparatus

4.1. Beakers: 4- or 5-L, polyethylene.

4.2. Graduated cylinders: 500-mL.

4.3. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Specimen containers: 16-oz jars with screw caps.

4.6. Labels printed with QC sample numbers.

4.7. Heat lamp.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless-steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: The phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon, Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick, manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{239}Pu standard prepared in 2 N HNO_3 and heated at a nominal temperature of 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state. The solution is counted on a zinc sulfide scintillation system calibrated with National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.2. The ^{239}Pu standard should be at a concentration of approximately 1.5 pCi/mL.

6.3. The ^{239}Pu standard was calibrated against a NIST-certified ^{239}Pu alpha-particle solution standard, such as SRM 4331. Recalibrate the standard solution yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.4. Direct plating procedure.

6.4.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs, which have been cleaned with acetone. Evaporate the solution to dryness under a heat lamp.

6.4.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.4.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.4.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.4.5. Place a piece of Mylar film over all the layers.

6.4.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.4.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.4.8. The count room data are corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Working with bodily fluids is discussed in detail in SOP-4, "Handling Human Biological Fluids and Tissues," found in Appendix III of the Environmental Chemistry Safety Manual.

NOTE: Wear safety glasses, gloves, and a lab coat. Each day prepare a 1:100 dilution of household bleach in water in a spray bottle. Use this solution to thoroughly clean the work area after sample preparation is completed. Rinse gloves in a 1:100 dilution of household bleach in water and discard them. Wash hands with soap and water.

7.2. Prepare a pool from blank urine sufficient in volume to allow 400 mL for each QC sample to be prepared.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Include blank QCs prepared from the same urine pool as the spiked samples.

7.4. Record QC standard information, sample spike amount, concentration, and uncertainty in the QC Laboratory notebook.

7.5. Label bottles with QC sample numbers.

7.6. Aliquot 400 mL of blank urine into each sample bottle.

7.7. Spike the blank urine with aliquots of standard as determined in Step 7.3.

7.8. Screw caps on bottles and refrigerate at a nominal temperature of 4°C pending analysis.

7.9. Enter the spike concentrations of each QC into the CVS and CVD databases on the VAX. This procedure is done annually because the same concentration levels are used throughout the year.

8. Calculations

8.1. Record spike concentrations as pCi/sample of urine.

8.2. Calculate the spike concentration for a 300-μL aliquot of ^{239}Pu standard using the following equation:

$$\text{pCi/sample per spike amount} = 1.52\ \text{pCi/mL} \times 0.300\ \text{mL} = 0.46\ \text{pCi/sample} \quad .$$

8.3. Spike concentrations calculated in Step 8.2 are tabulated below.

Spike amount (μL)	Concentration (pCi/sample)	Uncertainty ($\pm$ 3.3%)
40	0.06	0.002
100	0.15	0.005
150	0.23	0.008
300	0.46	0.015

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Radiochemically contaminated waste.

9.2.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.1.5. Put a new plastic bag into the waste can for continued use.

9.2.1.6. Place the sealed bag into a cardboard box lined with a plastic bag labeled to indicate its use for radioactively contaminated waste.

9.2.1.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.1.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.1.9. Line a new box with a plastic bag and label it for continued use.

9.2.1.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.1.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.2.2. Biohazardous waste.

9.2.2.1. If urine-contaminated solid waste is disinfected, dispose of it in the same manner as any other waste. Refer to Source Material 10.8.

9.2.2.2. If urine sample containers are rinsed well with a 10% solution of bleach, dispose of the rinse solution down the drain. Refer to Source Material 10.5.

9.2.2.3. If the excess urine is diluted with bleach to make a 5% (v/v) solution, dispose of this solution down the drain. Refer to Source Material 10.5.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of radioactively contaminated solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. *EML Procedures Manual*, 25th ed., H. L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, New York, August 1982).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4331, Plutonium-239 Alpha-Particle Solution Standard" (National Institute of Standards and Technology, Washington, DC, March 1975).

10.4. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Institute of Standards and Technology, Washington, DC, April 1982).

10.5. M. Phillips, "Handling Human Biological Fluids and Tissues," SOP-4, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Los Alamos National Laboratory document (November 1993).

10.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.8. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

RADIONUCLIDES ON FILTER MEDIA — QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, and Americium-241	**Method No.:** QCR210
Matrix: Filters	**Spike Range:** 0.45–2.25 pCi/filter
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** ^{238}Pu 100% ± 4.3% RSD ^{239}Pu 100% ± 1.9% RSD ^{241}Am 100% ± 1.9% RSD
Effective Date: 01/21/85	**Authors:** Margaret A. Gautier Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.7 and 10.8 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is placed on a Microsorban filter and is spiked with ^{238}Pu, ^{239}Pu, and ^{241}Am standards. The standards are spiked onto sand because the filters are hydrophobic.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the pipette. A relative standard deviation (RSD) of 4.3% for ^{238}Pu, 1.9% for ^{239}Pu, and 1.9% for ^{241}Am at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = calibration error, and
M2 = spiking error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
100 = factor to convert to percentage.

2.2 Analytical results from QC samples prepared between 1992 and 1994 using this procedure and analyzed by radiochemistry and alpha spectrometry are tabulated below. The data are published in Source Material 10.1.

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM ON FILTERS

	Radionuclide	Mean ± std dev (%)	Number of Samples
1992	^{238}Pu	100 ± 6	11
	^{239}Pu	100 ± 8	11
	^{241}Am	86 ± 7	11
1993	^{238}Pu	104 ± 7	23
	^{239}Pu	106 ± 7	23
	^{241}Am	88 ± 7	16

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM ON FILTERS (cont)			
	Radionuclide	Mean ± std dev (%)	Number of Samples
1994	^{238}Pu	98 ± 3	10
	^{239}Pu	100 ± 8	10
	^{241}Am	86 ± 7	17

3. Collection and Storage of Samples

3.1. Microsorban filters are obtained from the sample submitter.

3.2. QC samples are prepared in a platinum crucible with a platinum cover and are kept at room temperature pending analysis.

4. Apparatus

4.1. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.2. Pipette tips: disposable.

4.3. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.4. Spatula.

4.5. Platinum crucibles: approximately 50-mL capacity with platinum covers. Each crucible should have a unique identifying number stamped or etched into it.

4.6. Heat lamp.

4.7. Microsorban filters: 8-cm-diam polyethylene filter obtained from the sample submitter.

4.8. Labels printed with QC sample numbers.

4.9. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.10. Discs: stainless-steel, 2.22-cm-diam.

4.11. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide, William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.12. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.13. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Sand. A clean, dry 0.1-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. Spike QC samples with ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3 and with an ^{241}Am standard prepared in 4 N HNO_3. Heat the plutonium standards at a nominal temperature of 80°C for 2 h to convert Pu in the polymeric form to the ionic +4 state. Count all solutions on a zinc sulfide scintillation system calibrated with National Bureau of Standards (NBS) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard.

6.2. The ^{239}Pu standard should be at a concentration of approximately 2 pCi/mL. The ^{238}Pu and ^{241}Am standards should be at a concentration of approximately 17 pCi/mL.

6.3. When they are available, dilute certified primary standards to make standards at the desired concentration.

6.4. Calibrate standard solutions that are not made from certified primary standards against an appropriate certified standard.

6.5. Calibrate the ^{238}Pu standard against a National Institute of Standards and Technology (NIST)-certified ^{238}Pu alpha-particle solution standard, such as NBS SRM 4323. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. Calibrate the ^{239}Pu standard against a NIST-certified ^{239}Pu alpha-particle solution standard such as NBS SRM 4331. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. Calibrate the ^{241}Am standard against a NIST-certified ^{241}Am alpha-particle solution standard such as NBS SRM 4322. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.8. Count all solutions on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on to each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures the package is tightly sealed when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) count for each sample.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically submit an unspiked filter as a blank.

7.2. Cut a Microsorban filter in half and fold it so that it fits into a 50-mL platinum crucible.

7.3. Place the crucible with the filter on the balance and tare the balance.

7.4. Weigh 0.1 g of clean, dry sand onto the filter. Because the filter is hydrophobic, the sand is used to absorb the Pu and Am standard solutions.

7.5. Spike aliquots of the Pu and Am standard solutions onto the sand to reach the desired spike range.

7.6. Dry the spiked sand and filter under a heat lamp.

7.7. A paper label should not be affixed to the platinum crucible because it will be destroyed during the ashing procedure.

7.8. Assign a QC sample number to the QC sample and note the unique identifying number that is etched or stamped onto the platinum crucible body. Make a list of the QC sample numbers and the corresponding crucible number.

7.9. When the sample is dry, cover the crucible with a platinum cover and keep it at room temperature pending analysis.

7.10. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, and ^{241}Am on the filter as pCi/filter.

8.2. Calculate the spike concentrations as in the following example.

8.2.1. The weight of the sand placed on top of the filter does not enter into the calculation.

8.2.2. If 80 μL of a 16.42-pCi/mL ^{238}Pu standard is spiked onto sand on the Microsorban filter, the ^{238}Pu concentration in the filter will be 1.3 pCi/filter. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(16.42\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (80\ \mu\text{L})}{\text{filter}} = 1.3\ \text{pCi/filter} \quad .$$

8.3. Spike concentrations for ^{239}Pu and ^{241}Am are calculated in the same way as spike concentrations for ^{238}Pu, using the equation in Step 8.2.2.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. *EML Procedures Manual*, 25th ed., H.L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, New York, August 1982).

10.3. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

10.4. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

10.5. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4331, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, March 1975).

10.6. National Bureau of Standards, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

10.7. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.8. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

RADIUM-226 IN WATER — QC SAMPLE PREPARATION

Analyte: Radium-226	**Method No.:** QCR220
Matrix: Water	**Spike Range:** 0.5–5.0 pCi/L
Procedure: Proportional counting or radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 2.1% RSD
Effective Date: 02/05/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.3 and 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. A quality control (QC) sample for the determination of ^{226}Ra in water is prepared by spiking 0.12 M HCl with a ^{226}Ra standard.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 2.1% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,

M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1991 and 1994 using this procedure and analyzed by proportional counting or by radiochemistry and alpha spectrometry are tabulated below. The data are published in Source Materials 10.1 and 10.2.

TABLE I. SPIKE RECOVERY FOR RADIUM-226 IN WATER

	Mean ± std dev	Number of Samples
1991	82 ± 19	8
1992	93 ± 17	4
1993	98 ± 19	4
1994	112 ± 15	8

3. Collection and Storage of Samples

3.1. QC samples are stored in volumetric flasks at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 1-L.

4.2. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Labels printed with QC sample numbers.

5. Reagents

5.1. Hydrochloric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. QC samples are spiked with a ^{226}Ra standard in 0.1 M HNO_3 at a concentration of approximately 10 pCi/mL.

6.2. A certified ^{226}Ra standard, such as National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4958 (gamma-ray standard), is diluted to produce a standard with a ^{226}Ra concentration of approximately 10 pCi/mL.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 1-L sample aliquot in a volumetric flask.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include 1 L of 0.12 M HCl as a blank.

7.3. Add approximately 900 mL of distilled water to a 1-L volumetric flask.

7.4. Add 10 mL of 12 M HCl to the water in the flask to produce 0.12 M acid.

7.5. Add an aliquot of ^{226}Ra standard to the water in the flask to reach the desired spike range.

7.6. Dilute the QC sample to volume with distilled water. Mix by inversion. Label the flask with a QC sample number and store at room temperature pending analysis.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{226}Ra in the QC sample as pCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 220 μL of a 10-pCi/mL ^{226}Ra standard is used to prepare a 1-L QC sample, the ^{226}Ra concentration in the sample will be 2.2 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(10\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (220\ \mu\text{L})}{1\ \text{L}} = 2.2\ \text{pCi/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid waste that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992, " Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. National Institute of Standards and Technology, "Certificate of Analysis for Radium-226" (National Institute of Standards and Technology, Washington, DC, March 1968).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

STRONTIUM-90 ON SOIL — QC SAMPLE PREPARATION

Analyte: Strontium-90	**Method No.:** QCR230
Matrix: Sand	**Spike Range:** 2–45 pCi/g
Procedure: Proportional counting or radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 3.0% RSD
Effective Date: 04/07/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.3 and 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is spiked with a ^{90}Sr standard. The sand is used in place of soil as the quality control (QC) matrix for ^{90}Sr analysis.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 3.0% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analytical results from samples prepared between 1992 and 1994 using this procedure and analyzed by proportional counting or radiochemistry and alpha spectrometry are tabulated below. The data are published in Source Material 10.1.

TABLE I. SPIKE RECOVERY FOR STRONTIUM-90 IN SOIL

	Mean ± std dev (%)	Number of Samples
1992	99 ± 9	58
1993	92 ± 11	52
1994	91 ± 26	144

3. Collection and Storage of Samples

3.1. Pending analysis, QC samples are stored at room temperature in Teflon beakers covered with aluminum foil.

4. Apparatus

4.1. Beakers: 250-mL, Teflon.

4.2. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Balance: 200-g capacity, 0.1-mg accuracy.

4.5. Spatula.

4.6. Aluminum foil.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. Sand. A clean and dry 2-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. When they are available, certified primary standards should be diluted to make a standard at the desired concentration.

6.2. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.3. QC samples are spiked with a ^{90}Sr standard prepared in 2 M HCl at a concentration of approximately 870 pCi/mL.

6.4 The ^{90}Sr standard should be calibrated against an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.5. Decay the ^{90}Sr standards each year.

6.5.1. The half-life of ^{90}Sr is 28.5 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at desired time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 2-g sample in a 250-mL Teflon beaker.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 2-g aliquot of the unspiked sand as a blank.

7.3. Accurately weigh a 2-g aliquot of clean, dry sand into a 250-mL Teflon beaker. Record the weight of the sand on the beaker with a felt-tipped pen for reference by the analyst.

7.4. Spike an aliquot of ^{90}Sr standard onto the sand to reach the desired spike range.

7.5. Because a paper label does not adhere well to a Teflon beaker, write the QC number assigned to the sample on the beaker with a pen and destroy the paper label associated with the sample number used. Cover the top of the beaker with aluminum foil and store it at room temperature pending analysis.

7.6. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{90}Sr on the sand as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 15 μL of a 871-pCi/mL ^{90}Sr standard is used to spike 2.0000 g of sand, the ^{90}Sr concentration in the sand will be 6.5 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(871\ \frac{\text{pCi}}{\text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(15\ \mu\text{L})}{2.0000\ \text{g}} = 6.5\ \text{pCi/g}\ .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid water that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. US Environmental Protection Agency, "Calibration Certificate for Strontium-90" (Environmental Monitoring Systems Laboratory, Quality Assurance Division, Las Vegas, Nevada, June 1987).

10.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, in Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised

STRONTIUM-90 IN WATER — QC SAMPLE PREPARATION

Analyte: Strontium-90	**Method No.:** QCR240
Matrix: Water	**Spike Range:** 8–400 pCi/L
Procedure: Proportional counting	**Accuracy and Precision:** 100% ± 3.2 % RSD
Effective Date: 11/28/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 and 10.5 for proper waste disposal.

1. Principle of Method

1.1. A quality control (QC) sample for the determination of ^{90}Sr in water is prepared by spiking 0.08 M HCl with a ^{90}Sr standard.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and the volumetric flask. A relative standard deviation (RSD) of 3.2% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2 Analytical results from samples prepared between 1990 and 1994 using this procedure and analyzed by proportional counting are summarized in Table I below. The data are published in Source Materials 10.1 through 10.3.

TABLE I. SPIKE RECOVERY FOR STRONTIUM-90 IN WATER

	Mean ± std dev (%)	Number of Samples
1990	92 ± 10	6
1991	92 ± 9	5
1992	96 ± 11	7
1993	98 ± 12	19
1994	96 ± 8	14

3. Collection and Storage of Samples

3.1. QC samples are stored in volumetric flasks at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 500-mL, class A, glass.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Labels printed with QC sample numbers.

5. Reagents

5.1. Hydrochloric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. When they are available, certified primary standards should be diluted to make a standard at the desired concentration.

6.2. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.3. QC samples are spiked with a ^{90}Sr standard in 2 M HCl at a concentration of approximately 870 pCi/mL.

6.4. The ^{90}Sr standard should be calibrated against an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.5. Decay the ^{90}Sr standards each year.

6.5.1. The half-life of ^{90}Sr is 28.5 years.

6.5.2. The following equation describes the rate of radioactive decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at t = 0,
e = the base of natural logarithms,
λ = the decay constant = (ln 2)/$T_{1/2}$, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Samples size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 500-mL sample in a volumetric flask.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include 500 mL of 0.08 M HCl as a blank.

7.3. Add approximately 400 mL of distilled water to a 500-mL volumetric flask.

7.4. Add 3.5 mL of 12 M HCl to the water in the flask to produce 0.08 M acid.

7.5. Add an aliquot of ^{90}Sr standard to the water in the flask to reach the desired spike range.

7.6. Dilute the QC sample to volume with distilled water. Mix by inversion. Label the flask with a QC sample number and store the flask at room temperature pending analysis.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{90}Sr in the QC sample as pCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 150 μL of a 870-pCi/mL ^{90}Sr standard is used to make a 500-mL QC sample, the ^{90}Sr concentration in the sample will be 261 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(870\ \frac{pCi}{mL}\right)\left(\frac{1\ mL}{1000\ \mu L}\right)(150\ \mu L)}{(500\ mL)\left(\frac{1\ L}{1000\ mL}\right)} = 261\ pCi/L \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box .

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3 M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRITIUM AND PERCENT MOISTURE ON SOIL — QC SAMPLE PREPARATION

Analyte: Tritium and percent moisture	**Method No.:** QCR250
Matrix: Sand	**Spike Range:** Tritium 80–400,000 pCi/L or 2–10,000 pCi/sample Percent moisture 2–5% H_2O
Procedure: Liquid scintillation counting and gravimetry	**Accuracy and Precision:** Tritium 100% ± 2.6% RSD Percent moisture 100% ± 9% RSD
Effective Date: 04/07/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 and 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is aliquoted and spiked with a tritiated water standard.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. Propagated error for tritium.

2.1.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 2.6% at the 1-σ level has been calculated for the calibration and spiking process based on the following function:

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = calibration error, and
M2 = spiking error.

2.1.2. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} \quad ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.3. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
100 = factor to convert to percentage.

2.2. Propagated error for percent moisture.

2.2.1. The propagated error on QC preparation is based on the error associated with use of the analytical balance. An RSD of 9.0% has been calculated for the weighing process based on the following function:

$$D = \frac{M3}{M1 + M2} \quad ,$$

where D = calculated result,
M3 = weighing error of water,

M1 = weighing error of first soil aliquot, and
M2 = weighing error of second soil aliquot.

2.2.2. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.2.3. Calculate percent RSD using the following equation.

$$S_{D_T} = \frac{\sqrt{(R^2_{M3} + R^2_{M2})M2^2 + (R^2_{M3} + R^2_{M1})M1^2 + 2R^2_{M3}\ M1\ M2}}{(M1 + M2)} \times 1$$

where S_{D_T} = RSD (% error),
R^2_{M3} = relative variance of weight of water,
R^2_{M2} = relative variance of weight of second soil aliquot,
M2 = weight of second soil aliquot,
R^2_{M1} = relative variance of weight of first soil aliquot,
M1 = weight of first soil aliquot, and
100 = factor to convert to percentage.

2.3. Analysis by liquid scintillation counting of QC samples prepared from 1992 through 1994 using this procedure gave the following recoveries for tritium. Analysis by gravimetry of QC samples for percent moisture gave the following recoveries. The data are published in Source Material 10.1.

TABLE I. ^3H AND PERCENT MOISTURE SPIKE RECOVERY DATA

Year	^3H	N	H_2O	N
1992	101 ± 20%	60	84 ± 12%	10
1993	86 ± 15%	56	99 ± 15%	85
1994	84 ± 9%	104	91 ± 22%	148

N = Number of samples.

3. Collection and Storage of Samples

3.1. QC samples are covered with plastic wrap and frozen pending analysis.

3.2. Data obtained in 1994 indicate that the QC samples are stable for at least five months if kept frozen until time of analysis.

4. Apparatus

4.1. Beakers: 1-L.

4.2. Pipettes: 10-, 15-, 20-, and 25-mL, class A volumetric.

4.3. Desiccator.

4.4. Drying oven: capable of reaching at least 110°C.

4.5. Spatula.

4.6. Plastic wrap.

4.7. Labels printed with QC sample numbers.

4.8. Balance: 1-kg minimum capacity, 0.1-g accuracy.

4.9. Jars: 1-L with Teflon-lined caps.

5. Reagents

5.1. Sand. A clean and dry 500-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

6. Calibration and Standards

6.1. QC samples are spiked with tritium standards that contain ^3H in the concentration range 80 to 400,000 pCi/L.

6.2. A 25-mL aliquot of a ^3H standard in the concentration range 80 to 400,000 pCi/L spiked onto 500.0 g of clean, dry sand will produce a QC sample containing ^3H in the concentration range 2 to 10,000 pCi/sample and a total moisture content of approximately 5% by weight. The volume of water spiked onto the sand may vary between 10 and 25 mL but must be at least 10 mL.

6.3. Decay the ^3H standards semiannually.

6.3.1. The half-life of ^3H is 12.35 years.

6.3.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at desired time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$ or the decay constant, where $T_{1/2}$ is the half-life.

6.4. The ^3H standard was calibrated against a National Institute of Standards and Technology (NIST)-certified ^3H Standard Reference Material (SRM), such as NIST SRM 4927B, a solution of tritiated water. Recalibrate the standard solution yearly by liquid scintillation counting.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. An aliquot of distilled water added to a soil sample may be included as a blank for ^3H analysis.

7.2. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of 500 g of sample in a 1-L glass jar.

7.3. Dry approximately 600 g of soil in a 1-L beaker at 105–110°C overnight.

7.4. Cool the soil in a desiccator.

7.5. Place a 1-L jar on a balance with a capacity of at least 1000 g. Tare the balance.

7.6. Add 300 g of soil to the jar. Record the weight and tare the balance.

7.7. Pipette 10 to 25 mL of tritium standard onto the center of the soil. Record the weight and tare the balance.

7.8. Add 200 g of soil to the jar to cover the wet soil, to bring the total soil weight to 500 ± 1 g and to achieve 2 to 5% H_2O. Record the final soil weight on the jar with a felt-tipped pen for reference by the analyst.

7.9. Label the jar with a QC sample number.

7.10. Cover the jar with plastic wrap, cap with Teflon-lined lid, and freeze pending analysis.

7.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the weight percent of extractable (unbound) water (H_2O^-) using the total sample weight (e.g., 500 g of soil plus 25 g of added H_2O).

8.2. Record the concentration of tritium as pCi/L. The tritium is measured as pCi/L and not as pCi/g because the determination measures the tritium concentration in the water in the sample and not the tritium concentration on the soil. Tritium concentration can be related to sample weight through the percent of H_2O^- in the sample.

8.3. Calculate the spike concentrations as in the following example.

8.3.1. If 25 mL of a 200,000-pCi/L tritium standard is used to spike 500.0 g of soil, the concentration of tritium in the sample is 200,000 pCi/L (5000 pCi/25 mL). Multiply the result by the RSD calculated in Step 2.1.1 to obtain the uncertainty.

$$(200{,}000\ \text{pCi/L})\ (1\ \text{L}/1000\ \text{mL})\ (25\ \text{mL}) = 5{,}000\ \text{pCi/sample} \quad .$$

8.3.2. The percent moisture is approximately 5% H_2O. Multiply the result by the RSD calculated in Step 2.2.1 to obtain the uncertainty.

$$\frac{(25\ \text{mL}\ H_2O)\ (1\ \text{g/mL}) \times 100}{500.0\ \text{g soil} + 25.0\ \text{g}\ H_2O} = 4.8\%\ H_2O \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) number describing the waste in the box .

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory LA-12790-MS (1994).

10.2. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4927-B, Hydrogen-3" (National Institute of Standards and Technology, Washington, DC, January 1979).

10.3. M. P. Unterweger, B. M. Coursey, F. J. Schima, and W. B. Mann, "Preparation and Calibration of the 1978 National Bureau of Standards Tritiated-water Standards," *International Journal of Applied Radiation and Isotopes* **31**, 611-614 (1980).

10.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*," Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRITIUM IN URINE — QC SAMPLE PREPARATION

Analyte: Tritium	**Method No.:** QCR260
Matrix: Urine	**Spike Range:** 0.0–10.0 μCi/L
Procedure: Liquid scintillation counting	**Accuracy and Precision:** 100% ± 3.7% RSD
Effective Date: 01/01/75	**Authors:** Margaret A. Gautier William D. Moss Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.5 to 10.7 for proper waste disposal.

1. Principle of Method

1.1. A pool of blank urine is prepared.

1.2. The blank urine is aliquoted and spiked with a known standard.

1.3. Quality control (QC) samples are submitted for analysis with each routine analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six preparations of the standard and on the error associated with the use of the graduated cylinder and the pipette. A relative standard deviation (RSD) of 3.7% at the 1-σ level has been calculated for the calibration, spiking, and aliquoting process based on the following:

$$D = \frac{M1 \times M2}{M3 + M2} ,$$

where D = calculated result,
M1 = calibration error,

M2 = spiking error, and
M3 = aliquoting error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate the percent RSD using the following equation.

$$S_{D_T} = \sqrt{\frac{\left[R_{M1}^2 (M3 + M2)^2 + M3^2 (R_{M2}^2 + R_{M3}^2)\right]}{(M3 + M2)^2}} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
M3 = volume of cylinder,
M2 = volume of pipette,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of cylinder, and
100 = factor to convert to percentage.

2.2 Analysis by liquid scintillation counting of QC samples prepared between 1992 and 1994 using this procedure gave a mean recovery of 99% ± 7% RSD. The data are published in Source Material 10.1 and are summarized in Table I below.

TABLE I. TRITIUM SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

Year	Spike Level (μCi/L)	Mean	±	RSD (%)	Number of Samples
1992	0.40	108	±	9	24
	0.67	107	±	6	24
	4.09	105	±	7	24
	8.17	104	±	6	24
	0.39	100	±	19	28
	0.66	94	±	5	24

TABLE I. TRITIUM SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION (cont)

Year	Spike Level (μCi/L)	Mean	±	RSD (%)	Number of Samples
	3.97	94	±	7	28
	7.95	94	±	6	22
1993	0.39	91	±	8	18
	0.65	91	±	8	21
	3.87	92	±	5	17
	7.75	92	±	5	16
	0.38	98	±	9	22
	0.64	98	±	6	22
	3.77	99	±	6	24
	7.55	98	±	6	22
1994	0.37	102	±	7	22
	0.62	99	±	5	20
	3.67	100	±	3	20
	7.33	101	±	4	18
	0.36	102	±	8	11
	0.60	99	±	14	11
	3.57	102	±	2	12
	7.13	102	±	2	12

3. Collection and Storage of Samples

3.1. Urine is collected as needed from group personnel who have no known contact with radiation work. It is used to form a pool of blank urine.

3.2. Spiked QC samples are refrigerated at a nominal temperature of 4°C pending analysis.

4. Apparatus

4.1. Beakers: 4- or 5-L, polyethylene.

4.2. Graduated cylinders: 50-mL.

4.3. Autopipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Specimen containers: 120-mL with screw caps, sterile inner surface, catalog no. C8845-3, Baxter Health Care Corp., Tempe, AZ 85282, or equivalent.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. QC samples are spiked with tritium standards. The standards should be at a concentration of approximately 40 and 750 μCi/L.

6.2. Decay the tritium standard in January and July.

6.2.1. The half-life of tritium is 12.43 years.

6.2.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at $t = 0$,
e = the base of natural logarithms,
λ = the decay constant = $(\ln 2)/T_{1/2}$, where $T_{1/2}$ is the half-life.

6.3. The ^3H standard was calibrated against a National Institute of Standards and Technology (NIST)-certified ^3H solution of tritiated water, such as NIST Standard Reference Material (SRM) 4927B. Recalibrate the standard solution yearly by liquid scintillation counting. Record all data in the QC Laboratory notebook.

7. Procedure

7.1. Working with bodily fluids is discussed in detail in SOP-4, "Handling Human Biological Fluids and Tissues," found in Appendix III of the Environmental Chemistry Safety Manual.

NOTE: Wear safety glasses, gloves, and a lab coat. Each day prepare a 1:100 dilution of household bleach in water in a spray bottle. Use this solution to thoroughly clean the work area after sample preparation is completed. Rinse gloves in a 1:100 dilution of household bleach in water and discard them. Wash hands with soap and water.

7.2. Prepare a pool of blank urine sufficient in volume to allow 50 mL for each QC sample to be prepared.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Include blank QCs prepared from the same urine pool as the spiked samples. Tritium QC samples may be divided into two aliquots because only a 200-μL sample size is required by the analyst.

7.4. Record QC standard information, sample spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook.

7.5. Label bottles with QC sample numbers.

7.6. Aliquot 50 mL of blank urine into each sample bottle.

7.7. Spike the blank urine with aliquots of standard as determined in Step 7.3.

7.8. Screw caps on bottles and refrigerate at a nominal temperature of 4°C pending analysis.

7.9. Enter the spike concentration of each QC into the CVS and CVD databases on the VAX. This procedure is done annually because the same concentration levels are used throughout the year.

8. Calculations

8.1. Calculate spike concentration for a 300-μL aliquot of ^{3}H standard and report concentration as μCi/L using the following equation.

$$\frac{(750\ \mu\text{Ci/L})\ (1\ \text{L}/1{,}000{,}000\ \mu\text{L})\ (300\ \mu\text{L})}{50\ \text{mL}\ (1\ \text{L}/1000\ \text{mL})} = 4.50\ \mu\text{Ci/L} \quad .$$

8.2. Spike concentrations calculated in Step 8.1 are tabulated below.

Concentration of standard (μCi/L)	Spike amount (μL)	QC concentration (pCi/sample)	Uncertainty ($\pm$3.7%)
—	0	0.00	0.00
40	600	0.48	0.02
40	1000	0.80	0.03
750	300	4.50	0.17
750	600	9.00	0.33

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Radiochemically contaminated waste.

9.2.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.1.5. Put a new plastic bag into the waste can for continued use.

9.2.1.6. Place the sealed bag into a cardboard box lined with a plastic bag labeled to indicate its use for radioactively contaminated waste.

9.2.1.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.1.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.1.9. Line a new box with a plastic bag and label it for continued use.

9.2.1.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.1.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.2.2. Biohazardous waste

9.2.2.1. If urine-contaminated solid waste is disinfected, dispose of it in the same manner as any other waste. Refer to Source Material 10.7.

9.2.2.2. If urine sample containers are rinsed well with a 10% solution of bleach, dispose of the rinse solution down the drain. Refer to Source Material 10.4.

9.2.2.3. If the excess urine is diluted with bleach to make a 5% (v/v) solution, dispose of this solution down the drain. Refer to Source Material 10.4.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of radioactively contaminated solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. M. P. Unterweger, B. M. Coursey, F. J. Schima, and W. B. Mann, "Preparation and Calibration of the 1978 National Bureau of Standards Tritiated-water Standards," *International Journal of Applied Radiation and Isotopes* **31**, 611-614 (1980).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4927-B, Hydrogen-3" (National Institute of Standards and Technology, Washington, DC, January 1979).

10.4. M. Phillips, "Handling Human Biological Fluids and Tissues," SOP-4, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Los Alamos National Laboratory document (November 1993).

10.5. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.6. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.7. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRITIUM IN WATER — QC SAMPLE PREPARATION

Analyte: Tritium	**Method No.:** QCR270
Matrix: Water	**Spike Range:** 10–20 nCi/L
Procedure: Liquid scintillation counting	**Accuracy and Precision:** 100% ± 3.7% RSD
Effective Date: 03/29/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 and 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. A quality control (QC) sample for the determination of tritium in water is prepared by diluting a tritium standard with distilled water.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 3.7% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,

M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\bar{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\bar{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analysis by liquid scintillation counting of QC samples from 1992 through 1994 using this procedure gave the following recoveries. The data are published in Source Material 10.1.

TABLE I. TRITIUM IN WATER SPIKE RECOVERY DATA

Year	Mean ± std dev (%)	Number of Samples
1992	101 ± 15	157
1993	98 ± 11	138
1994	95 ± 9	50

3. Collection and Storage of Samples

3.1. QC samples are transferred to glass scintillation vials and are stored at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 25-mL, Class A.

4.2. Autopipette: 100-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Graduated cylinder: 10-mL.

4.5. Scintillation vials: glass.

4.6. Parafilm.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. When a certified primary standard is available, dilute it to make a standard at the desired concentration.

6.2. Calibrate standard solutions that are not made from certified primary standards against an appropriate certified standard.

6.3. Prepare QC samples by diluting a tritium standard to 10 mL with distilled water. The standard should be at a concentration of approximately 20 nCi/mL.

6.4. Calibrate the ^{3}H standard against a National Institute of Standards and Technology (NIST)-certified ^{3}H Standard Reference Material (SRM), such as NIST SRM 4927B, a solution of tritiated water. Recalibrate the standard solution annually by liquid scintillation counting and decay the ^{3}H concentration midway through the calibration period.

6.5. Decay the ^{3}H standards semiannually.

6.5.1. The half-life of ^3H is 12.35 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_0 = the activity at $t = 0$,
e = the base of natural logarithms, and
λ = (ln 2)/T1/2, the decay constant, where T1/2 is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. A 10-mL aliquot of distilled water may be included as a blank.

7.2. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of two ~10-mL aliquots in scintillation vials.

7.3. Preparation of QC blanks.

7.3.1. Prepare and seal QC blank samples before any tritium solutions are opened to avoid contamination of the blanks by tritiated water vapor.

7.3.2. Using a graduated cylinder, measure 10 mL of distilled water into a glass scintillation vial.

7.3.3. Cap the vial and wrap the cap with Parafilm.

7.3.4. Label the vial with a QC sample number.

7.3.5. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

7.4. Preparation of QC spiked samples.

7.4.1. Pour ~20 mL of distilled water into a 25-mL volumetric flask.

7.4.2. Pipette an aliquot of the tritium standard solution into the flask to reach the desired spike range.

7.4.3. Dilute the standard to volume with distilled water. Mix by inverting.

7.4.4. Divide the QC sample evenly between two glass scintillation vials.

7.4.5. Cap the vials and wrap the caps with Parafilm.

7.4.6. Label the vials with a QC sample number. The same QC sample number may be used for both aliquots from the same flask.

7.4.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^3H in the water as pCi/L or nCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 20 μL of a 20-nCi/mL tritium standard is used to spike 25 mL of distilled water, the concentration of tritium in the sample is 16 nCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(20\ \frac{\text{nCi}}{\text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(20\ \mu\text{L})}{(25.0\ \text{mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)} = 16\ \text{nCi/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) number describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the

transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, N.L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4927-B, Hydrogen-3" (National Institute of Standards and Technology, Washington, DC, January 1979).

10.3. M. P. Unterweger, B. M. Coursey, F. J. Schima, and W. B. Mann, "Preparation and Calibration of the 1978 National Bureau of Standards Tritiated-water Standards," *International Journal of Applied Radiation and Isotopes* **31**, 611-614 (1980).

10.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

URANIUM IN SOIL — QC SAMPLE PREPARATION

Analyte: Uranium	**Method No.:** QCR280
Matrix: Soil	**Spike Range:** 10-500 μg/g
Procedure: Delayed neutron activation	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 08/09/89 to 01/01/93	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the standards listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.5 and 10.6 for proper waste disposal practices.

1. Principle of Method

1.1. Two soils with certified uranium contents are combined in varying proportions to make quality control (QC) samples with uranium concentrations in the desired spike range.

1.2. No soils tested had a sufficiently low and consistent uranium background to allow use as a blank sample or as a soil sample matrix.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standards and on the error associated with use of the analytical balance. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration and spiking process based on the following function:

$$D = \frac{M1\ M3 + M2\ M4}{M3 + M4} ,$$

where D = calculated result,
M1 = calibration error of standard one,

M2	=	calibration error of standard two,
M3	=	weighing error of standard one, and
M4	=	weighing error of standard two.

2.2. Calculate relative variance using the following equation:

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where	R^2_M	=	relative variance,
	M	=	M1. . .(variable),
	σ^2	=	variance (std dev^2), and
	$\overline{X}$	=	mean value of each variable (M).

2.3. Calculate percent RSD using the following equation:

$$S_{D_T} = \sqrt{A + B} \times 100 ,$$

where

$$A = \frac{(R^2_{M3} + R^2_{M4})\,(M2 - M1)^2\, M3^2\, M4^2}{(M3 + M4)^2\,(M2\,M4 + M1\,M3)^2} ,$$

$$B = \frac{R^2_{M2}\, M2^2\, M4^2 + R^2_{M1}\, M1^2\, M3^2}{(M2\,M4 + M1\,M3)^2} ,$$

SD_T	=	RSD (% error),
R^2_{M3}	=	relative variance of standard weight one,
R^2_{M4}	=	relative variance of standard weight two,
M2	=	calibration error of standard two,
M1	=	calibration error of standard one,
M3	=	weighing error of standard one,
M4	=	weighing error of standard two,
R^2_{M2}	=	relative variance of standard two,
R^2_{M1}	=	relative variance of standard one, and
100	=	factor to convert to percentage.

2.4. Analysis by delayed neutron activation of QC samples prepared during 1989 and 1990 using this procedure gave a mean recovery of 94% ± 2% RSD. The data are published in Source Materials 10.1 and 10.2 and are summarized Table I below.

EPA AIR FILTER PERFORMANCE EVALUATION STUDY

Analyte: Alpha, beta ^{90}Sr, and ^{137}Cs	**Method No.:** QCS100
Matrix: Air Filter	
Procedure: Proportional counting for alpha and beta; gamma spectroscopy for ^{137}Cs: radiochemical alpha spectrometry for ^{90}Sr	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits air filter performance evaluation samples for alpha, beta, ^{90}Sr, and ^{137}Cs analysis.

1.2. One blank filter is included in the set.

2. Collection and Storage of Samples

2.1. No dilution or aliquoting is required.

2.2. Samples are sealed with chain-of-custody tape and stored at room temperature pending analysis.

3. Apparatus

3.1. Chain-of-custody tape.

3.2. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. Samples are received in individual filter cases.

5.2. Seal each case with chain-of-custody tape.

5.3. Label the cases with a QC sample number. The same QC sample number may be used for replicate samples.

5.4. Store the samples at room temperature pending analysis.

5.5. Distribute a copy of the EPA reporting sheet with the samples.

5.6. Record on the copy of the EPA reporting sheet distributed to the analyst that ^{137}Cs by gamma spectroscopy MUST be completed before the filters are digested for the other analyses.

5.7. Submit one QC sample (NEVER A BLANK), where available, matching the matrix of the performance evaluation sample.

5.8. Establish an in-house due date for the study, allowing sufficient time to record and report the data to EPA to meet their stated deadline.

5.9. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analyses requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.10. Deliver the samples and all paperwork to the Sample Management team for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Report the data to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. No waste is generated by this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6 M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

DOE BERYLLIUM INTERCOMPARISON STUDY PROCEDURE

Analyte: Beryllium	**Method No.:** QCS110
Matrix: Filters	
Procedure: Inductively coupled plasma–atomic emission spectroscopy	
Effective Date: 01/01/87	**Authors:** Rebecca Eaton Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. Filter media intercomparison samples for beryllium analysis are prepared and distributed by Oak Ridge National Laboratory.

2. Collection and Storage of Samples

2.1. No dilution or aliquoting is necessary.

2.2. Samples are labeled, sealed with chain-of-custody tape, and stored at room temperature pending analysis.

3. Apparatus

3.1. Chain-of-custody tape.

3.2. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. Samples are received in individual filter cases.

5.2. Seal each case with chain-of-custody tape.

5.3. Label each case with a QC sample number.

5.4. Store the samples at room temperature pending analysis.

5.5. Distribute a copy of the reporting sheet and procedure information request sheet with the samples.

5.6. Submit QC samples, prepared as described in Method No. QCI140, Trace Elements on Filter Media—QC Sample Preparation, along with the intercomparison samples.

5.7. Establish an in-house deadline for the Quality Assurance and Data Management (QADM) team that allows sufficient time to record and mail the sample intercomparison data by the stated deadline.

5.8. Record the intercomparison study identity, agency, sample numbers, sample descriptions, analyses requested, date received, in-house deadline, and matrix in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and in the CVD database on the VAX.

5.9. Deliver all study samples, QC samples, and all paperwork to the Sample Management team for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the intercomparison study report sheet, making sure the reported units match those requested by the study.

6.2. Send the completed report form to the sample submitter by the required deadline.

6.3. Record in the External Quality Assurance Samples notebook the results and the date the report was sent.

7. Intercomparison Certified Values

7.1. When the certified study sample values are received from Oak Ridge National Laboratory, enter the values on the samples data sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, symbol (if appropriate), certified values and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the QADM files and send a copy of the report to the team leader of the team or group who performed the analyses.

8. Proper Waste Disposal Practices

8.1. No waste is generated by this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.2. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.5. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised.

EPA DRINKING WATER STUDY

Analytes: Inorganic and organic compounds	**Method No.:** QCS120
Matrix: Water	
Procedure: ACOLR, CALC, CVAA, ETVAA, FIA, GE, GRAB, IC, ICPAES, ICPMS, ISE, TITR, GCEC, and GCMS	
Effective Date: 01/01/84	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits drinking water samples for inorganic and organic analyses.

1.2. The study set consists of several ampules containing solutions that are diluted to prepare water samples for analysis.

1.3. Some analytes or analyses may be omitted.

1.4. Methods of analysis depend on the analyte. They include automated colorimetry (ACOLR), calculation (CALC), cold vapor atomic absorption spectroscopy (CVAA), electrothermal vaporation atomic absorption (ETVAA), flow-injection analysis (FIA), glass electrode (GE), gravimetry (evaporation) (GRAB), ion chromatography (IC), inductively coupled plasma–atomic emission spectrometry (ICPAES), inductively coupled plasma–mass spectrometry (ICPMS), ion-selective electrodes (ISE), titration (TITR), gas chromatography with electron capture (GCEC), and gas chromatography–mass spectrometry (GCMS).

2. Collection and Storage of Samples

2.1. No dilution or aliquoting is necessary.

2.2. Samples are labeled and stored at room temperature pending analysis.

3. Apparatus

3.1. Labels printed with study sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. Samples are received in individual ampules.

5.2. Label each ampule with a study sample number and store them at room temperature pending analysis. The analyst will dilute the samples according to EPA instructions prior to analysis.

5.3. Label the reporting sheet and the dilution instruction sheets with the study sample numbers to which they pertain.

5.4. Include a quality control (QC) sample (NEVER A BLANK) for each analysis.

5.4.1. Commercially available EPA-certified samples may be used as QC samples.

5.4.2. Alternatively, QC samples may be prepared as described in the following QC sample preparation procedures:

QCI170 Trace Elements in Nitric Acid,
QCI190 Trace Elements in Water,
QCI200 Trace Elements for Water and Soil (Mercury by TCLP),
QCI210 Trace Elements in Water (CN),
QCI215 Trace Elements in Water (Minerals and Nutrients),
QCI220 Trace Elements in Water (NO_2-N),
QCO220 Semivolatile Organic Compounds in Water, or
QCO260 Volatile Organic Compounds in Water.

5.4.3 Label each QC sample with a QC sample number. Label the instruction sheets for QC sample preparation with the QC samples number(s) to which they pertain.

5.5. Divide the study samples, QC samples, and corresponding paperwork into one set for inorganic analysis and one set for organic analysis.

5.6. A table indicating the analyses to be performed on each study sample and the associated QC samples may be created to provide guidance to the analyst.

5.7. Distribute a copy of the reporting sheets, preparation instructions for the study samples, other study information sheets, and preparation instructions for the QC samples with each study set.

5.8. Establish an in-house due date for the analyses, allowing sufficient time to record and report data to meet the EPA stated deadline.

5.9. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, matrix, and analyses requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA Drinking Water report sheets, making sure the reported units match those requested by the study.

6.2. Send the original and one copy of the completed report forms to EPA by the required deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Intercomparison Certified Values

7.1. When the certified study sample values are received from EPA, enter the values on the samples data sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, symbol (if appropriate), certified values and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group which performed the analyses.

8. Proper Waste Disposal Practices

8.1. No waste is generated by this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

9.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

9.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

9.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.7. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.8. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.9. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

EPA GAMMA IN WATER PERFORMANCE EVALUATION STUDY

Analyte: ^{60}Co, ^{65}Zn, ^{106}Ru, ^{134}Cs, ^{137}Cs, and ^{133}Ba	**Method No.:** QCS130
Matrix: Water	
Procedure: Gamma spectrometry	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.7 and 9.8 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for ^{60}Cs, ^{65}Zn, ^{106}Ru, ^{134}Cs, ^{137}Cs, and ^{133}Ba analysis. Samples are diluted according to supplied instructions.

2. Collection and Storage of Samples

2.1. Performance evaluation samples are distributed in triplicate as 500-mL aliquots in 500-mL polyethylene bottles sealed with chain-of-custody tape.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 100-, 250-, 500-, and 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Bottles: 500-mL, high-density polyethylene.

3.5. Long glass stirring rod.

3.6. Teflon-coated magnetic stirring bar.

3.7. Magnetic stirring plate.

3.8. Chain-of-custody tape.

3.9. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. Hydrochloric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of a 2-L aliquot.

5.1.2. If EPA instructions call for dilution of a 500-mL sample aliquot to 4 L, the same dilution is achieved by diluting a 250-mL sample aliquot to 2 L.

5.2. Prepare 2 L of 0.5 M hydrochloric acid.

5.2.1. Put approximately 1900 mL of distilled water into a 2000-mL graduated cylinder.

5.2.2. Add 85.5 mL of 12 M HCl to the water, using a 100-mL graduated cylinder.

5.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.4. Mix the acid with a long stirring rod.

5.3. Transfer a 250-mL aliquot of the performance evaluation sample to a 2-L volumetric flask, using a 250-mL graduated cylinder.

5.4. Dilute the sample to volume with 0.5 M HCl.

5.5. Mix by inversion.

5.6. Pour the 2-L sample aliquot into a 5-L beaker and set it on a stirring plate.

5.7. Place a Teflon-coated stirring bar in the beaker and stir the solution slowly for 20-30 min.

5.8. Using a graduated cylinder, measure 500-mL aliquots into each of three 500-mL high-density polyethylene bottles.

5.9. Dispose of excess sample as radioactively contaminated liquid waste.

5.10. Cap the bottles and seal with chain-of-custody tape.

5.11. Label each bottle with a QC sample number and store the samples at room temperature pending analysis. The same QC sample number may be used for replicate aliquots.

5.12. Write the sample collection date on the label for reference by the analyst.

5.13. Include one QC sample (NEVER A BLANK) prepared as described in Method No. QCR130, Cesium-137 in Water—QC Sample Preparation.

5.14. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.15. Establish an in-house due date for the analysis, allowing sufficient time to record and report the data to EPA to meet their stated deadline.

5.16. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analyses requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.17. Deliver the samples and all paperwork to the Sample Management team for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Report the data to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results, and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of liquid radioactively contaminated waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactive contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

9.7. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.8. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

EPA GROSS ALPHA AND BETA IN WATER PERFORMANCE EVALUATION STUDY

Analyte: Gross alpha/beta	**Method No.:** QCS140
Matrix: Water	
Procedure: Proportional counting	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for gross alpha and gross beta analysis.

2. Collection and Storage of Samples

2.1. The sample is NOT diluted.

2.2. Sample is stored at room temperature pending analysis.

3. Apparatus

3.1. Chain-of-custody tape.

3.2. Label printed with sample number.

4. Reagents

4.1. None required.

5. Procedure

5.1. Sample is received in a plastic collapsible bottle.

5.2. Seal the bottle with chain-of-custody tape.

5.3. Label the bottle with a QC sample number. The same sample number may be used for replicate analyses.

5.4. Store the sample at room temperature pending analysis.

5.5 Distribute a copy of the EPA instructions and reporting sheet with the sample.

5.6 Include at least one QC sample (NEVER A BLANK), following Method No. QCR150, Gross Alpha and Gross Beta in Water—QC Sample Preparation.

5.7. Establish an in-house deadline for the analysis, allowing sufficient time to record and report data to meet EPA stated deadline.

5.8. Record the performance evaluation study identity, agency, sample numbers, sample description, date-received, in-house deadline, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance notebook, and the CVD database on the VAX.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Report data to EPA by the EPA stated deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter them in the External Quality Assurance Samples notebook on the appropriate sheet.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the analyst who performed the analyses.

8. Proper Waste Disposal Practices

8.1. No waste is generated by this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Health and Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

EPA BLIND A AND B PERFORMANCE EVALUATION STUDY

Analyte: Sample A: gross alpha, ^{226}Ra, and U
Sample B: gross beta, ^{90}Sr, ^{134}Cs, ^{137}Cs, and ^{60}Co

Method No.: QCS150

Matrix: Water

Procedure: Proportional counting (PC) for gross alpha and gross beta; gamma spectroscopy (G) for ^{134}Cs, ^{137}Cs, and ^{60}Co; radiochemical alpha spectrometry (RAS) for ^{90}Sr; inductively coupled plasma–mass spectrometry (ICPMS) and kinetic phosphoresence analysis (KPA) for U

Effective Date: 01/01/84

Authors: Carolyn J. Macdonell
Nancy L. Koski
Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.10 and 9.11 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits two water performance evaluation samples. Sample A includes analyses for gross alpha, ^{226}Ra, ^{228}Ra, and U. Sample B includes analyses for gross beta, ^{89}Sr, ^{90}Sr, ^{134}Cs, ^{137}Cs, and ^{60}Co. Samples are diluted according to supplied instructions.

1.2. Analysis is not performed for ^{226}Ra, ^{228}Ra, or ^{89}Sr.

2. Collection and Storage of Samples

2.1. Triplicate 900-mL aliquots for gross alpha and gross beta analyses are distributed in 1000-mL beakers. The beakers are covered with plastic wrap and sealed with chain-of-custody tape.

2.2. Triplicate 500-mL aliquots for ^{90}Sr analysis are distributed in 600-mL beakers. The beakers are covered with plastic wrap and sealed with chain-of-custody tape.

2.3. Triplicate 100-mL aliquots for U analysis by ICPMS are distributed in 125-mL polyethylene bottles. The bottles are sealed with chain-of-custody tape.

2.4. Triplicate 10-mL aliquots for U analysis by KPA are distributed in 25-mL glass bottles. The bottles are sealed with chain-of-custody tape.

2.5. Triplicate 500-mL aliquots for ^{134}Cs, ^{137}Cs, and ^{60}Co analyses are distributed in 500-mL high-density polyethylene bottles. ^{134}Cs, ^{137}Cs, and ^{60}Co are analyzed on each aliquot. The bottles are sealed with chain-of-custody tape.

2.6. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 25-, 250-, 500-, 1000-, 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Beakers: 600- and 1000-mL, glass.

3.5. Bottles: 125- and 500-mL, high-density polyethylene.

3.6. Bottles: 25-mL, glass.

3.7. Long glass stirring rod.

3.8. Teflon-coated magnetic stirring bars.

3.9. Magnetic stirring plate.

3.10. Plastic wrap.

3.11. Chain-of-custody tape.

3.12. Labels printed with study sample numbers.

4. Reagents

4.1. Nitric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of three 2-L aliquots.

5.1.2. If EPA instructions call for dilution of a 250-mL sample aliquot to 4 L the same dilution is achieved by diluting a 125-mL sample aliquot to 2 L.

5.2. Preparation of the 2-L aliquots of sample A.

5.2.1. Add a Teflon-coated stirring bar to the 1-quart container of concentrated sample A and stir the solution for approximately 10 min to redissolve any precipitates and ensure homogeneity of the sample.

5.2.2. Prepare 2 L of 0.1 M HNO_3.

5.2.2.1. Put approximately 1950 mL of distilled water into a 2000-mL graduated cylinder.

5.2.2.2. Add 12.8 mL of 16 M HNO_3 to the water, using a 25-mL graduated cylinder.

5.2.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.2.4. Mix the acid with a long glass stirring rod.

5.2.3. Transfer a 125-mL aliquot of performance evaluation sample A into a 2-L volumetric flask using a 250-mL graduated cylinder.

5.2.4. Dilute the sample to volume with 0.1 M HNO_3.

5.2.5. Mix by inversion.

5.2.6. Pour the 2-L sample aliquot into a 5-L beaker.

5.2.7. Repeat Steps 5.2.2 through 5.2.5.

5.2.8. Combine the second 2-L sample aliquot with the first and set the beaker on a stirring plate.

5.2.9. Place a Teflon-coated stirring bar in the beaker and stir the solution slowly for approximately 10 min.

5.2.10. Using a graduated cylinder, measure 900-mL aliquots into each of three 1000-mL beakers for gross alpha analysis.

5.2.11. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.2.12. Repeat Steps 5.2.2 through 5.2.5.

5.2.13. Combine the additional 2-L sample with the sample remaining in the 5-L beaker.

5.2.14. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 10 min.

5.2.15. Using a graduated cylinder, measure 100-mL aliquots into each of three 125-mL polyethylene bottles for U analysis by ICPMS.

5.2.16. Using a graduated cylinder, measure 10-mL aliquots into each of three 25-mL glass bottles for U analysis by KPA.

5.2.17. Seal each bottle with chain-of-custody tape.

5.2.18. Dispose of the excess sample as radioactively contaminated liquid waste.

5.3. Preparation of the 2-L aliquots of sample B.

5.3.1. Add a Teflon-coated stirring bar to the 1-quart container of concentrated sample B and stir the solution for approximately 10 min to redissolve any precipitates and ensure homogeneity of the sample.

5.3.2. Prepare 2 L of 0.1 M HNO_3.

5.3.2.1. Put approximately 1950 mL of distilled water into a 2000-mL graduated cylinder.

5.3.2.2. Add 12.8 mL of 16 M HNO_3 to the water, using a 25-mL graduated cylinder.

5.3.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.3.2.4. Mix the acid with a long glass stirring rod.

5.3.3. Transfer a 125-mL aliquot of performance evaluation sample B into a 2-L volumetric flask using a 250-mL graduated cylinder.

5.3.4. Dilute the sample to volume with 0.1 M HNO_3.

5.3.5. Mix by inversion.

5.3.6. Pour the 2-L sample aliquot into a 5-L beaker.

5.3.7. Repeat Steps 5.3.2 through 5.3.5.

5.3.8. Combine the second 2-L sample aliquot with the first and set the beaker on a stirring plate.

5.3.9. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 10 min.

5.3.10. Using a graduated cylinder, measure 900-mL aliquots into each of three 1000-mL beakers for gross beta analysis.

5.3.11. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.3.12. Repeat Steps 5.3.2 through 5.3.5.

5.3.13. Combine the additional 2 L of sample with the sample remaining in the 5-L beaker.

5.3.14. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 10 min.

5.3.15. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers for ^{90}Sr analysis.

5.3.16. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.3.17. Using a graduated cylinder, measure 500-mL aliquots into each of three 500-mL high-density polyethylene bottles for ^{134}Cs, ^{137}Cs, and ^{60}Co analyses.

5.3.18. Seal each bottle with chain-of-custody tape.

5.3.19. Dispose of excess sample as radioactively contaminated liquid waste.

5.4. Label each beaker and bottle with a study sample number and store the samples at room temperature pending analysis. The same study sample number may be used for replicate aliquots.

5.5. Include QC samples (NEVER A BLANK) prepared as described in the following methods: QCR150, Gross Alpha and Gross Beta in Water—QC Sample Preparation; QCR130, Cesium-137 in Water—QC Sample Preparation; QCR240, Strontium-90 in Water—QC Sample Preparation; and QCI170, Trace Elements in Nitric Acid—QC Sample Preparation, for natural uranium analysis by ICPMS, and a QC sample for the analysis of uranium in water by KPA.

5.6. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.7. Establish an in-house due date for the analyses, allowing sufficient time to record and report data to EPA to meet their stated deadline.

5.8. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analyses requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.9. Deliver the samples and all paperwork to the Sample Management team for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Report the data to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of liquid radioactively contaminated waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactive contaminated waste.

8.2.3. Open the can only for the period of time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

9.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

9.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

9.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.7. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.8. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.9. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

9.10. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.11. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

NIOSH PAT PROGRAM

Analyte: Metals and organic compounds	**Method No.:** QCS170
Matrix: Air filters and sorbent tubes	
Procedure: Inductively coupled plasma–atomic emission spectroscopy (ICPAES) and gas chromatography with mass spectrometry (GCMS)	
Effective Date: 01/01/84	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The National Institute for Occupational Safety and Health (NIOSH) Proficiency Analytical Testing (PAT) Program submits air filters and sorbent tubes for analyses.

1.2. The air filters are impregnated with trace levels of metals. One blank filter is included in the set.

1.3. The sorbent tubes contain up to three different organic chemicals. One blank tube is included in the set.

1.4. Trace metals are measured by inductively coupled plasma–atomic emission spectroscopy (ICPAES). Organic analytes are measured by gas chromatography with mass spectrometry (GCMS).

2. Collection and Storage of Samples

2.1. No dilution or aliquoting is necessary.

2.2. Samples are labeled, and the cases containing the air filters are sealed with chain-of-custody tape. Filter samples are stored at room temperature pending analysis. Tube samples are stored in a freezer pending analysis.

3. Apparatus

3.1. Chain-of-custody tape.

3.2. Labels printed with study sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. Samples are received in individual filter cases or sorbent tubes.

5.2. Seal each filter case with chain-of-custody tape.

5.3. Label each filter case and sorbent tube with a study sample number. Store the filter samples at room temperature and the sorbent tubes in the freezer pending analysis.

5.4. Include quality control (QC) samples (NEVER A BLANK) prepared as described in the following methods: QCI140, Trace Elements on Filter-Media—QC Sample Preparation, and QCO130, Organic Compounds Tubes and Badges—QC Sample Preparation. Match the analytes in the QC samples to those in the NIOSH PAT samples.

5.5. Include one air filter and one sorbent tube from a previous NIOSH PAT round for use as a QC. Remove the PAT labels and label each with a QC sample number. Seal the filter case with chain-of-custody tape.

5.6. A table indicating the analyses to be performed on each study sample and the associated QC samples may be created to provide guidance to the analyst.

5.7. Distribute a copy of the reporting sheet and other study information sheets with the sample set for inorganic analysis and with the sample set for organic analysis.

5.8. Establish an in-house due date for the analyses, allowing sufficient time to record and report the data to meet the NIOSH PAT stated deadline.

5.9. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, matrix, and analyses requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

6. Reporting of Results

6.1. When the analyses are completed, fill out the NIOSH PAT report sheet. Make sure that the units of the reported results match those requested by the study.

6.2. Report the data by the required deadline.

6.3. Record in the External Quality Assurance Samples notebook the results and the date the report was sent.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from the NIOSH PAT Program, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. No waste is generated by this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

9.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

9.3. M. A. Gautier, E. S. Gladney, W. K. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

9.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.7. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.8. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.9. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

EPA PLUTONIUM IN WATER PERFORMANCE EVALUATION STUDY

Analyte: Plutonium	**Method No.:** QCS180
Matrix: Water	
Procedure: Radiochemical alpha spectrometry	
Effective Date: 01/01/84	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.10 and 9.11 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for ^{239}Pu analysis. Samples are diluted according to supplied instructions.

2. Collection and Storage of Samples

2.1. Performance evaluation samples are distributed in triplicate 300-mL and 500-mL aliquots for radiochemical analysis, using biological, bioassay, and environmental analytical procedures.

2.2. Samples are sealed with chain-of-custody tape and stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 25-, 250-, 500-, and 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Beakers: 400- and 600-mL, glass.

3.5. Long glass stirring rod.

3.6. Teflon-coated magnetic stirring bar.

3.7. Magnetic stirring plate.

3.8. Plastic wrap.

3.9. Chain-of-custody tape.

3.10. Labels printed with study sample numbers.

4. Reagents

4.1. Hydrochloric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of two 2-L aliquots.

5.1.2. If EPA instructions call for dilution of a 500-mL sample aliquot to 4 L, the same dilution is achieved by diluting a 250-mL sample aliquot to 2 L.

5.2. Prepare 2 L of 3 M hydrochloric acid (HCl).

5.2.1. Put approximately 1400 mL of distilled water into a 2000-mL graduated cylinder.

5.2.2. Add 513 mL of 12 M HCl to the water using a 500-mL and a 25-mL graduated cylinder.

5.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.4. Mix the acid with a long stirring rod.

5.3. Transfer a 250-mL aliquot of the performance evaluation sample into a 2-L volumetric flask using a 250-mL graduated cylinder.

5.4. Dilute the sample to volume with 3 M HCl.

5.5. Mix by inversion.

5.6. Pour the 2-L sample aliquot into a 5-L beaker.

5.7. Repeat Steps 5.2 through 5.5.

5.8. Combine the second 2-L sample aliquot with the first and set the beaker on a stirring plate.

5.9. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 10 min.

5.10. Using a graduated cylinder, measure 300-mL aliquots into each of three 400-mL beakers for analysis using the biological analytical procedure for Pu (Method No. RT500).

5.11. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers for analysis using the environmental analytical procedure for Pu (Method No. ER160).

5.12. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers for analysis using the bioassay analytical procedure for Pu (Method No. R170).

5.13. Dispose of excess sample as radioactively contaminated liquid waste.

5.14. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.15. Label each beaker with a study sample number and store the samples at room temperature pending analysis. The same study sample number may be used for replicate aliquots.

5.16. Include three quality control (QC) samples (NEVER A BLANK) prepared as described Method No. QCR180, Plutonium and Americium in Water—QC Sample Preparation.

5.17. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.18. Establish an in-house due date for the analysis, allowing sufficient time to record and report the data to EPA to meet their stated deadline.

5.19. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Report data to EPA by the required EPA deadline.

6.3. In the External Quality Assurance Samples notebook, record the results and the date the report was sent to EPA.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) number describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal Record (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

9.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

9.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

9.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.7. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.8. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.9. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

9.10. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.11. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

EPA RADIONUCLIDES IN MILK PERFORMANCE EVALUATION STUDY

Analyte: ^{90}Sr	**Method No.:** QCS200
Matrix: Biological	
Procedure: Radiochemical alpha spectrometry	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.7 and 9.8 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits performance evaluation samples for ^{131}I, ^{137}Cs, ^{40}K, ^{90}Sr, and ^{89}Sr analysis. Samples are diluted according to supplied instructions.

1.2. Analysis is not performed for ^{131}I, ^{137}Cs, ^{40}K and ^{89}Sr.

2. Collection and Storage of Samples

2.1. Performance evaluation samples are distributed in triplicate as 500-mL aliquots in 600-mL beakers covered with plastic wrap and sealed with chain-of-custody tape.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Graduated cylinder: 500-mL.

3.2. Beakers: 600-mL, glass.

3.3. Plastic wrap.

3.4. Chain-of-custody tape.

3.5. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers.

5.2. Reserve excess sample until analysis is completed then dispose of it as radioactively contaminated liquid waste.

5.3. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.4. Label each beaker with a QC sample number and store the samples at room temperature pending analysis. The same QC sample number may be used for replicate aliquots.

5.5. Include one QC sample (NEVER A BLANK) prepared as described in Method No. QCR170, Radionuclides on Vegetation Ash—QC Sample Preparation.

5.6. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.7. Establish an in-house due date for the analysis, allowing sufficient time to record and report the data to EPA to meet their stated deadline.

5.8. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.9. Deliver the samples and all paperwork to the Sample Management team for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA result sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Report the data to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactive contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

9.7. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.8. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

EPA STRONTIUM IN WATER PERFORMANCE EVALUATION STUDY

Analyte: ^{90}Sr	**Method No.:** QCS220
Matrix: Water	
Procedure: Radiochemical alpha spectrometry	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.7 and 9.8 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for ^{89}Sr and ^{90}Sr analysis. Samples are diluted according to supplied instruction.

1.2. Analysis is not performed for ^{89}Sr.

2. Collection and Storage of Samples

2.1. Performance evaluation samples are distributed in triplicate as 500-mL aliquots in 600-mL beakers covered with plastic wrap and sealed with chain-of-custody tape.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 100-, 250-, 500-, and 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Beakers: 600-mL, glass.

3.5. Long glass stirring rod.

3.6. Teflon-coated magnetic stirring bar.

3.7. Magnetic stirring plate.

3.8. Plastic wrap.

3.9. Chain-of-custody tape.

3.10. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. Hydrochloric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of one 2-L aliquot.

5.1.2. If EPA instructions call for dilution of a 500-mL sample aliquot to 4 L, the same dilution is achieved by diluting a 250-mL sample aliquot to 2 L.

5.2. Prepare 2 L of 0.5 M HCl.

5.2.1. Put approximately 1900 mL of distilled water into a 2000-mL graduated cylinder.

5.2.2. Add 85.5 mL of 12 M HCl to the water, using a 100-mL graduated cylinder.

5.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.4. Mix the acid with a long stirring rod.

5.3. Transfer a 250-mL aliquot of the performance evaluation sample into a 2-L volumetric flask, using a 250-mL graduated cylinder.

5.4. Dilute the sample to volume with 0.5 M HCl.

5.5. Mix by inversion.

5.6. Pour the 2-L sample aliquot into a 5-L beaker and set it on a stirring plate.

5.7. Place a Teflon-coated stirring bar in the beaker and stir the solution slowly for 20–30 min.

5.8. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers.

5.9. Dispose of excess sample as radioactively contaminated liquid waste.

5.10. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.11. Label each beaker with a QC sample number and store the samples at room temperature pending analysis. The same QC sample number may be used for replicate aliquots.

5.12. Include one QC sample (NEVER A BLANK) prepared as described in Method No. QCR240, Strontium-90 in Water—QC Sample Preparation.

5.13. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.14. Establish an in-house due date for the analysis, allowing sufficient time to record and report the data to EPA to meet their stated deadline.

5.15. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.16. Deliver the samples and all paperwork to the Sample Management team for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Report the data to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactive contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

9.7. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.8. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

EPA TRITIUM IN WATER PERFORMANCE EVALUATION STUDY

Analyte: Tritium	**Method No.:** QCS230
Matrix: Water	
Procedure: Liquid scintillation counting	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for tritium analysis.

2. Collection and Storage of Samples

2.1. No dilution or aliquoting is required.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Chain-of-custody tape.

3.2. Labels printed with sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. The tritium sample is received in a small bottle. A blank is received in a second bottle.

5.2. Seal the bottles with chain-of-custody tape.

5.3. Label the bottles with sample numbers. The same sample number may be used for replicate aliquots taken from the bottle by the analyst.

5.4. Store the samples at room temperature pending analysis.

5.5. Submit at least one QC sample (NEVER A BLANK) prepared as described in Method No. QCR270, Tritium in Water—QC Sample Preparation.

5.6. Distribute a copy of the EPA reporting sheet with the samples.

5.7. Establish an in-house due date for the study, allowing sufficient time to record and report the data to EPA to meet their stated deadline.

5.8. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.9. Deliver the samples and all paperwork to the Sample Management team for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Report the data to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook on the appropriate sheet.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the group in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. No radioactively contaminated waste or hazardous waste is generated using this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1993).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

EPA URANIUM-RADIUM IN WATER PERFORMANCE EVALUATION STUDY

Analyte: Uranium-Radium **Method No.:** QCS240

Matrix: Water

Procedure: RAS and KPA for radiochemistry analysis; ICPMS for inorganic chemistry analysis

Effective Date: 01/01/85

Authors: Carolyn J. Macdonell
Nancy L. Koski
Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.7 and 9.8 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for natural U, ^{226}Ra, and ^{228}Ra analyses. Samples are diluted according to supplied instructions.

1.2. Analysis is not performed for ^{228}Ra.

2. Collection and Storage of Samples

2.1. Triplicate 900-mL aliquots for ^{226}Ra analysis are distributed in 1000-mL beakers. The beakers are covered with plastic wrap and sealed with leakproof tape and chain-of-custody tape.

2.2. Triplicate 10-mL aliquots for natural U are distributed in 25-mL glass bottles for analysis by kinetic phosphorometric analysis (KPA). The bottles are sealed with leakproof tape and chain-of-custody tape.

2.3. Triplicate 500-mL aliquots for natural U are distributed in 500-mL high-density polyethylene bottles for analysis by radiochemical alpha spectrometry (RAS). The bottles are sealed with leakproof tape and chain-of-custody tape.

2.4. Triplicate 200-mL aliquots for natural U are distributed in 200-mL high-density polyethylene bottles for analysis by inductively coupled plasma–mass spectrometry (ICPMS). The bottles are sealed with leakproof tape and chain-of-custody tape.

2.5. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 10-, 25-, 100-, 250-, 500-, and 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Beakers: 1000-mL, glass.

3.5. Bottles: 250- and 500-mL, high-density polyethylene.

3.6. Bottles: 25-mL, glass.

3.7. Long glass stirring rod.

3.8. Teflon-coated magnetic stirring bar.

3.9. Magnetic stirring plate.

3.10. Plastic wrap.

3.11. Chain-of-custody tape.

3.12. Leakproof tape.

3.13. Labels printed with sample numbers.

4. Reagents

4.1. Hydrochloric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of three diluted 2-L aliquots. Sample volume preparation may be varied depending on analyses performed.

5.1.2. If EPA instructions call for dilution of a 250-mL sample aliquot to 4 L, the same dilution ratio is achieved by diluting a 125-mL sample aliquot to 2 L.

5.2. Preparation of the 2-L aliquot.

5.2.1. Prepare 2 L of 0.5 M hydrochloric acid.

5.2.1.1. Put approximately 1900 mL of distilled water into a 2000-mL graduated cylinder.

5.2.1.2. Add 85.5 mL of 12 M HCl to the water, using a 100-mL graduated cylinder.

5.2.1.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.1.4. Mix the acid with a long stirring rod.

5.2.2. Transfer a 125-mL aliquot of the performance evaluation sample into a 2-L volumetric flask using a 100-mL and 25-mL graduated cylinder.

5.2.3. Dilute the sample to volume with 0.5 M HCl.

5.2.4. Mix by inversion.

5.2.5. Pour the 2-L sample aliquot into a 5-L beaker.

5.2.6. Repeat steps 5.2.1 to 5.2.4.

5.2.7. Combine the second 2-L diluted sample aliquot with the first and set the beaker on a stirring plate.

5.2.8. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for 20 to 30 min.

5.2.9. Using a graduated cylinder, measure 900-mL aliquots into each of three 1000-mL beakers for ^{226}Ra analysis.

5.2.10. Cover each beaker with plastic wrap and seal with leakproof tape and chain-of-custody tape.

5.2.11. Repeat steps 5.2.1. to 5.2.4.

5.2.12. Combine the additional 2-L diluted sample with the sample remaining in the 5-L beaker.

5.2.13. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 20 to 30 min.

5.2.14. Using a graduated cylinder, measure 10-mL aliquots into each of three 25-mL glass bottles for natural U analysis by KPA.

5.2.15. Using a graduated cylinder, measure 200-mL aliquots into each of three 250-mL high-density polyethylene bottles for natural U analysis by ICPMS.

5.2.16. Using a graduated cylinder, measure 500-mL aliquots into each of three 500-mL high-density polyethylene bottles for natural U analysis by RAS.

5.2.17. Dispose of the excess sample as radioactively contaminated liquid waste.

5.2.18. Cap the bottles and seal them with leakproof tape and chain-of-custody tape.

5.2.19. Label each bottle with a sample number and store the samples at room temperature pending analysis. The same sample number may be used for replicate aliquots.

5.2.20. Include at least one each quality control sample (NEVER A BLANK) for the analysis of uranium in water by RAS, for the analysis of uranium in water by KPA, for the analysis of uranium in water by ICPMS, and for the analysis of ^{226}Ra in water by RAS.

5.3. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.4. Establish an in-house deadline for the analyses, allowing sufficient time to record and report data to meet the EPA stated deadline.

5.5. Record the performance evaluation study identity, agency, sample numbers, sample description, date received, in-house deadline, dilution and aliquoting information,

matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.1.1. The specific activity of natural uranium is 0.68 pCi/ug. If uranium analytical results are expressed in ug/L, multiply the result by 0.68 to convert to pCi/L for the EPA report.

6.1.2. A uranium analytical value of 25.2 ug/L converts to 17.1 pCi/L.

$$(25.2\ \mu g/L)\ (0.68\ pCi/\mu g) = 17.1\ pCi/L \quad .$$

6.2. Report data to EPA by the EPA stated deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter them on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management team files and send a copy of the report to the analyst who performed the analyses.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactive contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) number describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the

transportation of radioactive contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Health and Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

9.7. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.8. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

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