Analytical Protocol Specifications

Analyte List: ^{90}Sr

Analysis Limitations: Perform direct measurement of analyte. Analysis of progeny allowed if radioactive equilibrium is established at laboratory from freshly isolated parent.

Matrix: Raw Cow's Milk (fat content to vary)

Possible Interferences: Fresh beta-emitting, fission-product nuclides if purification steps are inadequate or non-existent.

Concentration Range: 1 to 50 pCi/L

Action Level: 8 pCi/L

Method Validation Level: MARLAP Levels A, C, or D as applicable. See Attachment C for details.

MQOs: A required method uncertainty (u_{MR}) of 0.5 pCi/L at 8 pCi/L and a relative method uncertainty (φ_{MR}) of 6.25% at > 8pCi/L

QC Samples		
Type	**Frequency**	**Evaluation Criteria**
Method blank	1 per batch	See Attachment B
Duplicate	1 per batch	See Attachment B
Matrix Spike*	1 per batch	See Attachment B
Laboratory Control Sample	1 per batch	See Attachment B

Analytical Process Requirements	
Activity	**Special Requirements**
Field Sample Preparation and Preservation	Sample size > 3.5 L; Preserve on ice or with 5 mL of 37% formaldehyde / L sample
Sample Receipt and Inspection	Rad survey samples upon receipt. Return sample receipt acknowledgment letter with date of receipt at lab. Cross index list for Sample ID and assigned Lab ID. Visually inspect containers upon receipt to ensure integrity and normal sample appearance. COC documentation applies.
Laboratory Sample Preparation	Take sufficient aliquant of sample after gamma-ray spectrometry analysis (see separate requirements in the gamma spectroscopy APS). Keep 1 liter as backup until analytical results have been approved by project manager.
Sample Dissolution	None
Chemical Separations	Isolate Sr by cation exchange resin, or precipitation of Sr from soured or dry-ashed milk. Separation from Ca is essential. Rare earth and Ba scavenging steps are necessary to eliminate possible interferences from fresh fission products.
Preparing Sources for Counting	Final source mount to accommodate nuclear instrumentation.
Nuclear Counting	Acceptable counting instrumentation includes: Liquid Scintillation Counter, Gas Proportional Counter or Solid State Beta Detector. Detection. Method must discriminate against potential ^{89}Sr interference by physical means and/or calculation.
Data Reduction and Reporting	See Attachment A
Sample Tracking Requirements	Chain-of-Custody
Other - Chemical Yielding	Gravimetric (must have 99% Ca removal) or ^{85}Sr tracer with > 90% Ca removal.

* Spiking range provided in Attachment B

Attachment A
Data Reduction and Reporting Requirements

Data Reduction

1. Calculation of Sr-90 activity or concentration (pCi/L) can be based on the quantification of Sr-90 and/or Y-90, with proper addressing of decay and ingrowth of Y-90.
2. Calculation of the associated combined standard uncertainty (pCi/L) of the ^{90}Sr concentration.
3. Calculation of the MDC, in terms of pCi/L, shall be sample specific using the detector efficiency and background, counting time, decay and ingrowth factors, Sr yield and sample volume used for the analysis.
4. Calculation of critical level, in terms of pCi/L, shall be sample specific.
5. Calculation of gross, net and background count rate, detector efficiency, chemical yield, decay and ingrowth factors for each sample.
6. Initial review and approval of data reduction equations shall be established during a desk or onsite audit as part of the lab approval/contracting process.
7. No changes in the equations used in data reduction shall be initiated without prior approval of the project manager.

Data Reporting

1. For each sample, the following sample specific parameters shall be reported:
   Batch #, Sample ID, Lab ID, sample collection (reference) date, sample receipt date, estimated (or actual) sample volume received, ^{90}Sr and ^{90}Y separation dates, count date and count time, cross reference to batch QC samples, SOP(s) used, analyst(s), data reviewer(s) and report date.
2. For each sample, the following sample processing parameters or factors shall be reported:
   Gross, net and background count rates, detector efficiency, sample volume processed, ^{90}Sr decay factor, ^{90}Y decay and ingrowth factors, and chemical yield factor.
3. For each sample the following calculated information will be reported:
   critical level, MDC, 90Sr concentration and associated combined standard uncertainty (CSU).
4. Batch quality control results for the laboratory control sample (LCS), method blank, duplicate sample and matrix spike sample shall be reported with each batch of samples:
   Reporting data to include:
   LCS - calculated sample and prepared spike concentration with associated CSUs, and percent difference between sample result and known value
   Blank samples - calculated concentration with associated CSU, sample specific critical level and MDC.
5. Duplicate samples - calculated concentrations with associated CSU for both samples
   Matrix spike - calculated sample and known spike concentration with associated CSUs, and percent difference between sample results.
6. A “Narrative” shall be provided with each batch of samples that describes processes used and any problems encountered or discrepancies noted, including the possible effect on the quality of specific results and actions taken to remedy the problem if recurrent.
7. Reports shall be provided electronically and as a hard copy. An electronic data format will be provided.

Attachment B
Batch Quality Control Sample Evaluation Criteria

A "batch" of samples is defined as 20 or fewer samples not including the QC samples. The results of the batch QC samples shall be evaluated according to the equations provided below. It should be noted that no action is to be taken when a "not-to-exceed" limit stated below is exceeded for an individual sample. However, if trending of the results indicates multiple results or a trend of results exceeds a limit, stop processing samples and take action to identify and correct the root cause of the problem. Sample processing may resume when corrective actions have been shown to be effective in eliminating the cause of the problem. It is expected that the Laboratory's QA officer and project manager shall provide oversight on the sample processing and track the batch QC results.

Laboratory Control Sample

The ^{90}Sr spike concentration of an LCS shall be between 10 and 20 pCi/L and the spiking uncertainty should be ≤ 5%. The percent deviation (%D) for the LCS analysis is defined as

$$\%D = \frac{SSR - SA}{SA} \times 100\% \qquad 1)$$

where

SSR is the measured result (spiked sample result) and
SA is the spike activity (or concentration) added.

The %D control limit is $\pm 3\ \varphi_{MR} \times 100\%$ or ±19%. For long-term trending, the %D results should be plotted graphically in terms of a quality control chart with the expected mean %D value of zero.

Duplicate Samples

The acceptance criteria for duplicate analysis results depends on the analyte concentration of the sample, which is determined by the average $\bar{x}$ of the two measured results x_1 and x_2.

$$\bar{x} = \frac{x_1 + x_2}{2} \qquad 2)$$

When $\bar{x} < 8$, the control limit for the absolute difference $|\, x_1 - x_2 \,|$ is 4.24 u_{MR}, or 2.1.

When $\bar{x} \geq 8$ pCi/L, the control limit for the *relative percent difference* (RPD), defined as,

$$\mathrm{RPD} = \frac{x_1 + x_2}{\bar{x}} \times 100\% \qquad 3)$$

is 4.24 $\varphi_{\mathrm{MR}} \times 100\%$ or 27 %. For long-term trending, the absolute difference and RPD results should be plotted graphically in terms of a quality control chart with an expected absolute difference and RPD mean values of zero.

Matrix Spikes

The acceptance criteria for matrix spikes uses the "*Z* score," defined below, as the test for matrix spikes. The pre-existing activity (or concentration) must be measured and subtracted from the activity measured after spiking as shown in equations 4) and 5). The ^{90}Sr spike concentration of a matrix spike shall be between 10 and 20 pCi/L and the spiking uncertainty should be ≤ 5%.

$$Z = \frac{SSR - SR - SA}{\varphi_{MR}\sqrt{SSR^2 + \max(SR, UBGR)^2}} \qquad 4)$$

$$Z = \frac{SSR - SR - SA}{0.0625\sqrt{SSR^2 + \max(SR, 8)^2}} \qquad 5)$$

where:

SSR is the spiked sample result,
SR is the unspiked sample result,
SA is the spike concentration added (total activity divided by aliquant mass), and max(SR,8) denotes the maximum of SR and 8 pCi/L.

The control limit for *Z* is set at ± 3. It is assumed that the uncertainty of SA is negligible with respect to the uncertainty of SSR. For long-term trending, the Z results should be plotted graphically in terms of a quality control chart with a Z value of zero as the expected mean value.

Method Blanks When an aliquant of a blank material is analyzed, the target value is zero. However, the measured value may be either positive or negative. The applicable control limit for blank samples shall be within ± 3 u_{MR} or ± 1.5 pCi/L. For long-term trending, the blank results should be plotted graphically in terms of a quality control chart with an expected mean value of zero.

Attachment C
Method Validation Requirements

Prior to processing any milk samples, the laboratory is required to validate its ^{90}Sr in cow's milk radioanalytical method according to the specifications stated in MARLAP Chapter 6. The level of method validation will depend on whether the laboratory has a previously validated method for ^{90}Sr in milk (Level A), will modify a previously validated ^{90}Sr method for a milk matrix (Level C) or must newly develop or adapt a method for ^{90}Sr in cow's milk (Level D). The laboratory shall submit the method validation documentation to the project manager for review and approval prior to the acquisition of a laboratory contract. A summary of the method validation criteria is presented below for the three validation levels.

Level A method validation pertains to a previously validated method for ^{90}Sr in milk. No additional testing is required if the method previously has been successfully validated and the available method validation documentation has been reviewed and approved by the project manager. Documentation of method validation should conform to the specifications provided below.

Level C method validation is to be conducted when a validated ^{90}Sr method for a non-milk matrix is modified for applicability for the milk matrix, e.g., when the EPA 905 ^{90}Sr in water method is modified for use with a milk matrix. A method validation plan should be developed and documented. Validation Level C requires the preparation and analysis of five replicate cowmilk samples (internal performance testing samples) spiked at three different concentrations. For this project the three levels of 1, 10, 20 pCi/L (or within ± 15% of the values) should be used in the validation process. Each sample result for the lowest level (below the action level) must be within $\pm 2.9\ u_{MR}$ or ± 1.45 pCi/L of the spiked concentration value. Each sample result from the two higher spiked levels (above the action level) must be within $\pm 2.9\ \varphi_{MR} \times 100\%$ or ± 18% of the spiked concentration value. Documentation of method validation should conform to the specifications provided below.

Level D method validation is to be conducted when a new method is specifically developed or adapted from the literature for the project's ^{90}Sr in milk application. Validation Level D requires the preparation and analysis of seven replicate cow's milk samples (internal performance testing samples) spiked at three different concentrations. For this project the three levels of 1, 10, 20 pCi/L (or within ± 15% of the values) should be used in the validation process. Each sample result for the lowest level (below the action level) must be within ± 3.0 u_{MR} or ± 1.5 pCi/L of the spiked concentration value. Each sample result from the two higher spiked levels (above the action level) must be within $\pm 3.0\ \varphi_{MR} \times 100\%$ or ± 19% of the spiked concentration value. Documentation of method validation should conform to the specifications provided below.

Method Validation Documentation

Documentation to be submitted to the project manager includes: Method Validation Plan, Method Number, Analyst(s) analyzing the samples, spiked concentration values, experimental results and comparison to the acceptable performance criteria for the validation level.

EXAMPLE METHOD VALIDATION REVIEW FORM

Laboratory: **XYZ Laboratory** *Proposed Method:* **W34 Radiochemistry with Gas Proportional Counting**

Nuclide: **Sr-90** *Matrix*: **Milk** *Action Level*: **8 pCi/L**

Method Validation Level: **MARLAP Level C**

Required Method Uncertainty, u_{MR}: **0.5 pCi/L** at or below the Action Level

Required Relative Method Uncertainty, φ_{MR}: **6.25 %** (at or) above the Action Level

Acceptance Criteria:

Test Level 1: known value ± [**2.9** × (φ_{MR} × known value)] = **25.00** ± **4.53** pCi/L (± **18.1**%)

Test Level 2: known value ± [**2.9** × u_{MR}] = **8.00** ± **1.45** pCi/L

Test Level 3: known value ± **[2.9** × u_{MR}] = **3.00** ± **1.45 pCi** / **L**

Data Evaluation

Trial #	Test Level 1 Acceptable Range 20.5 – 29.5 pCi/L Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N	Test Level 2 Acceptable Range 6.55 – 9.45 pCi/L Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N	Test Level 3 Acceptable Range 1.50 – 4.50 pCi/L Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N
1	29.1 ± 1.7	+4.1	Y	8.23 ± 0.48	+0.23	Y	3.81 ± 0.29	+0.81	Y
2	24.1 ± 1.2	-0.9	Y	9.37 ± 0.53	+1.37	Y	2.23 ± 0.16	-0.77	Y
3	21.7 ± 1.3	-3.3	Y	7.80 ± 0.45	-0.20	Y	2.76 ± 0.22	-0.24	Y
4	26.6 ± 1.6	+1.6	Y	8.34 ± 0.51	+0.34	Y	3.41 ± 0.25	+0.41	Y
5	25.2 ± 1.4	+0.2	Y	7.25 ± 0.44	-0.75	Y	3.00 ± 0.23	0.00	Y

*** 1σ -- Combined Standard Uncertainty, k=1 (one standard deviation)*
Rounding of acceptable range limited by uncertainty of reported result

Laboratory XYZ Method Validation Data for Radiochemistry
Gamma Spectrometric Analysis of ^{241}Am in Ground Water

Introduction

Laboratory XYZ wishes to validate a method to determine ^{241}Am in ground water. The APS specifies MQOs for required method uncertainty, u_{MR}, as 0.98 pCi/L at the Action Level of 15 pCi/L. Therefore, the required relative method uncertainty, $\varphi_{MR} = u_{MR}/AL$ at and above the action level concentration, or 0.065 (i.e., 6.5%).

The laboratory has performed gamma spectrometric analysis of groundwater samples previously, but has not had their gamma detector calibrated to 59 keV where the ^{241}Am gamma is located. Detector calibration is completed using a ^{241}Am source (NIST traceable) and a count time of 150 minutes for a 4 L sample.

The software method for gamma-ray analysis uses the region of interest (ROI) routine rather than a peak search algorithm. Each sample is counted for a period of 100 minutes, as are the blanks.

Aliquants from the NIST-traceable source are taken and appropriately diluted to 20, 10, and 5 pCi/L. Three of each of these solutions are made using laboratory demineralized water and nitric acid and placed in separate, new Marinelli beakers. These samples are analyzed according to Procedure XYZ 15-10 “Americium Analysis By Gamma Spectrometry” (a new procedure and detector calibration are newly created for this analysis).

A sample of ground water is spiked with the ^{241}Am standard and analyzed along with a set of blank samples. The blank samples are made from demineralized water and nitric acid to the same concentration of the samples and also placed in new Marinelli beakers.

Analysis results for the gamma spectrometric results of the samples’ matrix spikes and blanks are shown below.

Data:

Method Validation Study

Nominal Concentrations	20 pCi/L		10 pCi/L		5 pCi/L	
Trial Number	pCi/L	$\pm 1\ \sigma$	pCi/L	$\pm 1\ \sigma$	pCi/L	$\pm 1\ \sigma$
1	24.8	1.1	14.8	1.6	9.5	1.6
2	22.5	1.5	13.9	1.3	8.6	1.8
3	21.8	1.3	14.3	1.4	9.3	1.6

Based on the information above, complete the Method Validation Data Review Form on the following page.

Procedure XYZ 15-10: Analysis of Liquid Samples for ^{241}Am by Gamma Spectrometry

Introduction

Analysis for ^{241}Am in groundwater samples can be performed by utilizing its gamma ray emission line at 59 keV. Sample count time is 25,000 seconds for a 4-L Marinelli beaker, to achieve a minimum detectable concentration (MDC) of 1.5 pCi/L. Water samples shall have been preserved by adding sufficient concentrated nitric acid to a 4-L Marinelli beaker so that the pH of the sample is less than 2.0. Sample acidification is important so that americium does not precipitate out during the long count times required to achieve the required MDC.

References

1. Procedure XYZ 1-1 QA Program for Gamma Spectrometric Analysis.
2. USNRC Regulatory Guide 4.15.
3. MARLAP. 2004. Multi-Agency Radiological Laboratory Analytical Protocols Manual. Volumes 1–3. Washington, DC: EPA 402-B-04-001A-C, NUREG 1576, NTIS PB2004-105421.

Precautions

1. New Marinelli beakers shall be used for each new sample.
2. Only Detectors 1 and 2 can achieve the stated MDC for ^{241}Am in 25,000 seconds. Detectors 4, 5, and 6 require at least 35,000 seconds. All count times must be adjusted to accommodate these detectors.
3. A daily background shall be performed prior to the start of each batch of samples. Daily background counts are 15,000 seconds per detector.
4. Acidification of groundwater samples generally requires 15 mL of concentrated nitric acid to a 4 liter sample. The solution pH must be verified to be < 2.0 before commencing the gamma spectrometric analysis.

Procedure

1. Transfer approximately 2 L of sample to the 4-L Marinelli beaker.
2. Add 15 mL of concentrated nitric acid.
3. Transfer enough sample to bring the Marinelli beaker to the mark designated “4 L.”
4. Using a stirring rod and pH paper, verify that the pH of the solution is less than 2.0. If pH is ≥ 2.0 add an additional 10 mL of concentrated nitric acid, stir well and allow to stand overnight and repeat the pH measurement.
5. Place the lid snugly on the Marinelli beaker, “burp” the container, and seal the lid interface with electrical tape.
6. Wipe the outside of the Marinelli beaker with a clean, dry cloth.
7. Place the Marinelli beaker on the detector can, close the cave, and put up the “in use” flag.
8. Enter the preset count time according to the detector selected (see Precautions).
9. When the count is finished verify the following parameters on the gamma-ray printout sheets:
    a. Detector
    b. Count time for the detector used to achieve an MDC of 1.5 pCi/L
    c. Sample size
    d. The Sample date
    e. The count date
    f. MDC for ^{241}Am is ≤ 1.5 pCi/L if no gamma ray peak is identified.
10. Log the values for each sample in the client folder on the LABDATA system. Values that are below the MDC should be logged as “zero.”

Final Conditions

1. All samples shall be disposed of in the containers marked “Acid Waste.”
2. Each detector shall be inspected for cleanliness following each sample counting period.

EXAMPLE METHOD VALIDATION REVIEW FORM

Laboratory: _________________ *Proposed Method:* **XYZ 15-10 Americium Analysis by Gamma Spectrometry**

Nuclide: _________________ *Matrix*: _________________ *Action Level*: ____________ pCi/L

Method Validation Level: MARLAP Level __

Required Method Uncertainty, u_{MR}: _____________ ____ / __ at or below the Action Level

Required Relative Method Uncertainty, φ_{MR}: ________ ___ (at or) above the Action Level

Acceptance Criteria:

Test Level 1: known value ± [______ × (φ_{MR} × known value)] = _______ ± _______ pCi / L (± ____ %)

Test Level 2: known value ± [______ × u_{MR}] = known value ±_______ _____ / __

Test Level 3: known value ± [______ × u_{MR}] = known value ±_______ _____ / __

Data Evaluation

	Test Level 1 **Acceptable Range _____ – _____ pCi/L**			**Test Level 2** **Acceptable Range _____ – _____ pCi/L**			**Test Level 3** **Acceptable Range _____ – _____ pCi/L**		
Trial #	**Measured ± 1σ** pCi/L**	**Δ pCi/L**	**Accepted Y/N**	**Measured ± 1σ** pCi/L**	**Δ pCi/L**	**Accepted Y/N**	**Measured ± 1σ** pCi/L**	**Δ pCi/L**	**Accepted Y/N**
1	±			±			±		
2	±			±			±		
3	±			±			±		

*** 1σ -- Combined Standard Uncertainty, k=1 (one standard deviation)*
Rounding of acceptable range limited by uncertainty of reported result

Laboratory XYZ Method Validation Data for Radiochemistry Alpha Spectrometric Analysis of ^{241}Am in Ground Water

Introduction:

Looking for a more sensitive in ground water method for ^{241}Am than gamma spectrometry, Laboratory XYZ decides to use alpha spectrometry to determine ^{241}Am in ground water. Again, the APS specifies MQOs for required method uncertainty, u_{MR}, as 0.98 pCi/L at the Action Level of 15 pCi/L. Therefore, the required relative method uncertainty at and above the action level concentration, $\varphi_{MR} = u_{MR}/AL$, or 0.065 (i.e., 6.5%).

The laboratory has never analyzed ^{241}Am in water by radiochemistry on a routine basis. For this project, the laboratory downloads, from a commercial web site, a widely used radiochemical method for ^{241}Am in water. The method is reviewed for project applicability and for laboratory instrumentation and equipment availability. The radiochemist at the laboratory decides to use the cerium floride microprecipitation rather than electrodeposition for the last purification step and final sample mounting for counting by the alpha spectrometer.

Because this is a new method obtained from a nationally known method source that has not previously been used or validated by the laboratory. The method has been modified and a method validation plan is established to test the method to meet Method Validation Level D.

Internal test samples are prepared by adding sufficient amounts of a NIST-traceable ^{241}Am standard solution to separate eight liter deionized water solutions (in high-density polyethylene containers) to obtain 20, 15, and 5 pCi/L concentrations. Prior to spiking, the solutions are made acidic by adding concentrated HCl (5 mL/L of sample). Seven 1 L samples are taken from each container and analyzed according to Procedure W04 (attached). An ^{243}Am radiotracer is used with each sample to determine the ^{241}Am chemical yield for the sample processed. Seven 1 L analytical blanks are prepared from acidified demineralized water (HCl) and are included as a fourth concentration level.

Analytical results for the alpha spectrometric measurements of the test samples and blanks are shown below.

Method Validation Study Data for Validation of Method Uncertainty:

Test Concentrations	20 pCi/L	15 pCi/L Action Level	5 pCi/L	0 pCi/L Blank
Trial Number	**Measured pCi/L ± 1s CSU**			
1	20.6 ±1.2	15.83 ± 0.97	5.22 ± 0.44	0.021 ± 0.013
2	19.1 ±1.1	15.77 ± 0.97	4.57 ± 0.38	-0.015 ± 0.015
3	20.4 ±1.2	14.25 ± 0.87	5.82 ± 0.49	0.031 ± 0.022
4	20.9 ±1.2	13.73 ± 0.84	4.46 ± 0.38	0.010 ± 0.013
5	19.8 ±1.1	14.78 ± 0.90	4.77 ± 0.40	0.013 ± 0.013
6	19.5 ±1.1	15.31 ± 0.94	5.38 ± 0.45	-0.024 ± 0.013
7	20.6 ±1.2	16.4 ±1.0	6.32 ± 0.53	0.006 ± 0.013

Laboratory XYZ Method W04
Radiochemical Analysis of ^{241}Am in Water by Alpha Spectrometry
Abbreviated Method with Major Detail

1. Scope
1.1 This procedure describes a method for separation and quantification of americium in water.

2. Summary of Method
2.1 A calcium phosphate precipitation technique is used to concentrate and remove actinides from water samples. Americium is separated by extraction chromatography from other actinides prior to measurement by alpha spectrometry. Sequential extraction chromatography uses a CMPO-TBP resin column to remove actinides (Ac, Th, Pa, U, Np, Pu) and lanthanides (La, Ce, etc.) from the sample. Americium and the lanthanides are eluted from the column. If excessive lanthanides are in the sample, an Aliphatic Quaternary Amine resin column is used to separate americium from the lanthanides. A ^{243}Am radiotracer is used to monitor chemical yield and correct results for losses during preparation.

3. Interferences
3.1 Actinides with unresolvable alpha energies such as ^{241}Am and ^{238}Pu must be chemically separated to enable ^{241}Am quantification. This method separates these radionuclides effectively.
3.2 Very high levels of phosphate in the sample may cause a chemical interference. Adjusting the amount of phosphate added to coprecipitate the actinides may be necessary in these cases.

4. Apparatus - see detailed procedure W04

5. Reagents - see detailed procedure W04

6. Procedure
6.1. *Water Sample Preparation:*
6.1.1. If required, filter a 1L sample through a 0.45 micron filter.
6.1.2. Add 5 mL of concentrated HCl (sp gr 1.19) per L of sample (0.5 mL per 100 mL) to acidify each sample.
6.1.3. Add appropriate tracers and/or analyze standards per lab protocol.
6.1.4. *Calcium phosphate precipitation option:*
6.1.4.1 Add 0.5 mL of 1.25M $Ca(NO_3)_2$ to each beaker.
6.1.4.2 Allow the samples to heat until boiling.
6.1.4.3 Once the samples boil, add 2-3 drops of phenolphthalein indicator and 200 µL of 3.2M $(NH_4)_2HPO_4$ solution.
6.1.4.4 Add enough concentrated NH_4OH with a squeeze bottle to reach the phenolphthalein end point and form $Ca_3(PO_4)_2$ precipitate.
6.1.4.5 Separate the precipitate from solution by decanting the supernatant
6.1.4.6 Transfer the precipitate to a centrifuge tube and centrifuge the precipitate for approximately 10 minutes at 2000 rpm.
6.1.4.7 Decant supernatant and discard to waste.
6.1.4.8 Wash the precipitate with an amount of water approximately twice the volume of the precipitate. Mix well on a vortex mixer. Centrifuge for 5-10 minutes. Discard the supernatant.

6.1.4.9 Dissolve precipitate in approximately 5 mL concentrated nitric acid. Transfer solution to a 100 mL beaker. Rinse centrifuge tube with 2-3 mL of concentrated nitric acid and transfer to beaker. Evaporate solution to dryness.

6.2. *Am/La Separations using extraction chromatographic resins:*

6.2.1 *Redissolve calcium phosphate precipitate:*

6.2.1.1 Dissolve each precipitate with 10 mL of 3M HNO_3-1M $Al(NO_3)_3$.

6.2.1.2 Add approximately 200 mg of ascorbic acid to each solution, swirling to mix.

6.2.2 *Am Separation Using a CMPO-TBP Extraction Resin*:

6.2.2.1 For each sample dissolved, place a CMPO-TBP Resin column in the column rack.

6.2.2.2 Pipet 5 mL of 2M HNO_3 into each column to condition resin and allow to drain.

6.2.2.3 Transfer each solution from step 6.2.1.2 into the appropriate CMPO-TBP Resin column by pouring and/or using a plastic transfer pipet.

6.2.2.4 Allow the load solution to drain through column.

6.2.2.5 Pipet 5 mL of 2M HNO_3 into the sample beaker and transfer this rinse to the appropriate column using the same plastic transfer pipet. Allow to drain.

6.2.2.6 Pipet 5 mL of 2 M HNO_3- 0.1 M $NaNO_2$ directly into each column, rinsing each column reservoir while adding the 2 M HNO_3- 0.1 M $NaNO_2$.
Note: Sodium nitrite is used to oxidize Pu+3 to Pu+4 and enable the Pu/Am separation

6.2.2.7 Add 5 mL of 0.5M HNO_3 to each column and allow to drain.
Note: 0.5M HNO_3 is used to lower the nitrate concentration prior to conversion to the chloride system.

6.2.2.8 Discard the load and rinse solutions to waste.

6.2.2.9 Ensure that clean, labeled beakers or vials are below each column.

6.2.2.10 Add 3 mL of 9M HCl to each column to convert to chloride system. Collect eluate.

6.2.2.11. Add 20 mL of 4M HCl to elute americium. Collect eluate in same beaker. Set beakers aside for Am/La separation option 6.2.3

6.2.3 *Option: Separation of americium from lanthanides using Aliphatic Quaternary Amine Resin as required by significant lanthanides causing americium alpha spectral degradation:*

6.2.3.1 For each sample dissolved, place a Aliphatic Quaternary Amine column in the column rack.

6.2.3.2 - 6.2.3.14 steps - see detailed procedure.

6.2.3.15 Dissolve sample in 10 mL of 4M HCl

6.3 *Sample preparation for counting;*

6.3.1 Add 0.2 mL of cerium carrier to each beaker from step 6.2.3.15.

6.3.2 Add 1.0 mL of concentrated HF to each beaker. Swirl to mix. Let the solutions sit for at least 30 minutes before filtering.

6.3.3 Set up a 0.1 micron 25 mm filter, glassy side down on a Gelman filter apparatus, 50 mL polysulfide funnel and 100 mL polypropylene Erlenmeyer flask.

6.3.4 Add 3-5 mL of 80% ethanol to each filter, applying vacuum and ensuring there are no leaks along the sides. Add 2-3 mL of water to each filter.

6.3.5 Filter the sample and rinse 50 mL centrifuge tube with 5 mL water, transferring this rinse to the filter apparatus.

6.3.6 Wash each filter with 3-5 mL of ethanol.

6.3.7 Remove filters, place in plastic Petri dishes, and dry under (UV) lamps for a few minutes.

6.3.8 Mount filters on stainless planchets, using double-sided tape or glue stick and count by alpha spectrometry.

7. Alpha Spectrometry Counting

7.1 Setup and perform an energy and efficiency calibration of the alpha spectrometry system according to the detailed Procedure W04.

7.2 Place the mounted sample on the appropriate calibrated shelf of the alpha spectrometer vacuum chamber.

7.3 Close the vacuum chamber door and initiate vacuum pump to slowly evacuate the chamber according to the detailed procedure W04.

7.4 Apply bias between the sample planchet and detector.

7.5 Apply detector bias and begin counting for a time period to meet MQO requirements.

8. Calculations

8.1 Calculate ^{241} Am sample concentration and associated uncertainty, critical level and MDC according to the equations in the detailed procedure W04.

9. Notes

9.1 *Bias* - A mean chemical yield of 95% has been reported for americium. Since results are corrected based on spike recovery, no significant bias should exist for the method.

References - See detailed procedure.

METHOD VALIDATION REVIEW FORM

Laboratory: _________________ *Proposed Method:* ___________________________

Nuclide: _________________ *Matrix*: _________________ *Action Level*: ____________ pCi/L

Method Validation Level: MARLAP Level ___

Required Method Uncertainty, u_{MR}: _____________ ____ / __ at or below the Action Level

Required Relative Method Uncertainty, φ_{MR}: ________ ___ (at or) above the Action Level

Acceptance Criteria:

Test Level 1: known value ± [____× (φ_{MR} × known value)] = _______ ± _______ pCi / L (± ___ %)

Test Level 2: known value ± [______ × u_{MR}] = known value ±_______ _____ / __

Test Level 3: known value ± [______ × u_{MR}] = known value ±_______ _____ / __

Data Evaluation

	Test Level 1 **Acceptable Range _____ – _____ pCi/L**			**Test Level 2** **Acceptable Range _____ – _____ pCi/L**			**Test Level 3** **Acceptable Range _____ – _____ pCi/L**		
Trial #	**Measured ± 1σ** pCi/L**	**Δ pCi/L**	**Accepted Y/N**	**Measured ± 1σ** pCi/L**	**Δ pCi/L**	**Accepted Y/N**	**Measured ± 1σ** pCi/L**	**Δ pCi/L**	**Accepted Y/N**
1	±			±			±		
2	±			±			±		
3	±			±			±		
4	±			±			±		
5	±			±			±		
6	±			±			±		
7	±			±			±		

*** 1σ -- Combined Standard Uncertainty, k=1 (one standard deviation)*
Rounding of acceptable range limited by uncertainty of reported result

AMERICIUM 241
EXERCISE SOLUTIONS

EXAMPLE METHOD VALIDATION REVIEW FORM

Laboratory: **XYZ Laboratory** *Proposed Method:* **XYZ 15-10 Americium Analysis by Gamma Spectrometry**

Nuclide: **Am-241** *Matrix*: **Ground Water** *Action Level*: **10** **pCi/L**

Method Validation Level: **MARLAP Level B**

Required Method Uncertainty, u_{MR}: **0.975 pCi/L** at or below the Action Level

Required Relative Method Uncertainty, φ_{MR}: **6.5 %** (at or) above the Action Level

Acceptance Criteria:

Test Level 1: known value ± [**2.8** × φ_{MR} × known value)] = **20.0** ± **3.8** **pCi** / **L** (± **18.2** %)

Test Level 2: known value ± [**2.8** × u_{MR}] = **10.00** ± **1.88** **pCi** / **L**

Test Level 3: known value ± [**2.8** × u_{MR}] = **5.00** ± **1.88** **pCi** / **L**

Data Evaluation

Trial #	Test Level 1 Acceptable Range 16.2 – 23.8 pCi/L Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N	Test Level 2 Acceptable Range 8.12 – 11.88 pCi/L Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N	Test Level 3 Acceptable Range 2.99 – 7.01 pCi/L Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N
1	24.8 ± 1.1	+4.8	N	14.8 ± 1.6	+4.8	N	9.5 ± 1.6	+4.5	N
2	22.5 ± 1.5	+2.5	Y	13.9 ± 1.3	+3.9	N	8.6 ± 1.8	+3.6	N
3	21.8 ± 1.3	+1.8	Y	14.25 ± 0.87	+4.25	N	9.3 ± 1.6	+4.3	N

*** 1σ -- Combined Standard Uncertainty, k=1 (one standard deviation)*

Rounding of acceptable range limited by uncertainty of reported result

EXAMPLE METHOD VALIDATION REVIEW FORM

Laboratory: **XYZ Laboratory** *Proposed Method:* **Laboratory XYZ Alpha Spectrometry Method W04**

Nuclide: **Am-241** *Matrix*: **Ground Water** *Action Level*: **10 pCi/L**

Method Validation Level: **MARLAP Level D**

Required Method Uncertainty, u_{MR}: **0.975 pCi/L** at or below the Action Level

Required Relative Method Uncertainty, φ_{MR}: **6.5 %** (at or) above the Action Level

Acceptance Criteria:

Test Level 1: known value ± [**2.9** × (φ_{MR} × known value)] = **20.00** ± **3.90** pCi/L (± **19.5**%)

Test Level 2: known value ± [**2.9** × u_{MR}] = **15.00** ± **2.93** **pCi** / **L**

Test Level 3: known value ± [**2.9** × u_{MR}] = **5.00** ± **2.93** **pCi** / **L**

Data Evaluation

Trial #	Test Level 1 Acceptable Range 16.1 – 23.9 pCi/L			Test Level 2 Acceptable Range 12.08 – 17.93 pCi/L			Test Level 3 Acceptable Range 2.08 - 7.93 pCi/L		
	Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N	Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N	Measured ± 1σ** pCi/L	Δ pCi/L	Accepted Y/N
1	20.6 ± 1.2	0.6	Y	15.83 ± 0.97	0.83	Y	5.22 ± 0.44	0.22	Y
2	19.1 ± 1.1	0.9	Y	15.77 ± 0.97	0.77	Y	4.57 ± 0.38	-0.43	Y
3	20.4 ± 1.2	0.4	Y	14.25 ± 0.87	-0.75	Y	5.82 ± 0.49	0.82	Y
4	20.9 ± 1.2	0.9	Y	13.73 ± 0.84	-1.27	Y	4.46 ± 0.38	-0.54	Y
5	19.8 ± 1.1	0.2	Y	14.78 ± 0.90	-0.22	Y	4.77 ± 0.40	-0.23	Y
6	19.5 ± 1.1	0.5	Y	15.31 ± 0.94	0.31	Y	5.38 ± 0.45	0.38	Y
7	20.6 ± 1.2	0.6	Y	16.4 ± 1.0	1.4	Y	6.32 ± 0.53	1.32	Y

*** 1σ -- Combined Standard Uncertainty, k=1 (one standard deviation)*

Rounding of acceptable range limited by uncertainty of reported result

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