LA-UR-17-28113
Approved for public release; distribution is unlimited.

Title: AmO2 Analysis for Analytical Method Testing and Assessment: Analysis Support for AmO2 Production

Author(s): Kuhn, Kevin John; Bland, Galey Jean; Fulwyler, James Brent; Garduno, Katherine; Keller, Russell C.; Klundt, Dylan James; Lujan, Elmer J. W; Mark, Zoe Francoise Elise; Mathew, Kattathu Joseph; Ortega, Laura Claire; Ottenfeld, Chelsea Faith; Porterfield, Donivan R.; Rearick, Michael Sean; Rim, Jung Ho; Schake, Ann Rene; Schappert, Michael Francis; Stanley, Floyd E.; Thomas, Mariam R.; Wylie, Ernest Miller II; Xu, Ning; Tandon, Lav; et al.

Intended for: Report

Issued: 2017-09-08

AmO_2 Analysis for Analytical Method Testing and Assessment:

Analysis Support for AmO_2 Production

Kevin Kuhn, Galey Bland, James Fulwyler, Kathy Garduno, Russell Keller, Dylan Klundt, Elmer Lujan, Zoe Mark, Kattathu Mathew, Laura Ortega, Chelsea Ottenfeld, Donivan Porterfield, Michael Rearick, Jung Rim, Ann Schake, Michael Schappert, Floyd Stanley, Mariam Thomas, Miller Wylie, Ning Xu, and Lav Tandon

INTRODUCTION

Americium oxide samples will be measured for various analytes to support AmO_2 production. The key analytes that are currently requested by the Am production customer at LANL include total Am content, Am isotopics, Pu assay, Pu isotopics, and trace element content including ^{237}Np content. Multiple analytical methods will be utilized depending on the sensitivity, accuracy and precision needs of the Am matrix. Traceability to the National Institute of Standards and Technology (NIST) will be achieved, where applicable, by running NIST traceable quality control materials. This given that there are no suitable AmO_2 reference materials currently available for requested analytes.

The intent of this sample analysis plan is to test and assess method detection limits, accuracy, and precision for analyzing AmO_2 materials. Although the number of test experiments is limited by time, the intent is to demonstrate long-term analytical competence. Analytical methods will be calibrated using NIST traceable standards where suitable reference materials are available. Suitable quality control standards will be identified and processed with test samples as this is a routine practice in actinide analytical chemistry. Analyses will be performed and documented following actinide analytical chemistry quality assurance (QA) and quality controls (QC) protocols and procedures. Results of the analyses will be documented as required by internal QA and QC procedures. Written analytical procedures will be modified as needed following assessment experiments to support the certification of $^{241}AmO_2$ production materials.

Well-characterized AmO_2 materials with demonstrated homogeneity could not be identified and acquired for analytical method test experiments. Instead, an older $^{241}AmO_2$ material previously produced at LANL was located and acquired for use. This material was previously placed in inventory with limited chemistry information and without an assessment of homogeneity. A small mass of $^{243}AmO_2$ material was previously acquired from ORNL.

Test materials will be dissolved and distributed as solutions to eliminate heterogeneity issues and to help establish minimum sample size requirements. A prepared sample solution of parent $^{241}AmO_2$ material will be analyzed to establish baseline values for key analytes.

The small mass of acquired $^{243}AmO_2$ material is suitable for generating a mixed $^{241}Am/^{243}Am$ solution for testing analytical methods. A ^{241}Am-^{243}Am mixture solution will be prepared and used to test and assess existing methods.

An internal technical report will be prepared to formalize the assessment of acquired analytical test data. The report will be submitted for independent review and comment. The final deliverable for this project is an official memo from the project lead and actinide analytical chemistry group leader to the AmO_2 project office announcing the demonstrated suitability of actinide analytical methods to analyze $^{241}AmO_2$ production samples.

PRIMARY OBJECTIVE

Demonstrate the suitability of actinide analytical chemistry methods to support AmO_2 production operations.

OBJECTIVE ACTIVITIES

Test and assess the traceability, precision, and detection limits for actinide analytical methods adapted for the analysis of AmO_2 sample solutions. In instances of suitable method traceability to certified standards, method accuracy for AmO_2 sample analysis will be assessed. The recoveries of Am, Pu, and trace metals from analytical method separations will also be examined.

AMERICIUM PARENT MATERIALS

In order to test and assess analytical methods, two americium materials were acquired as described in **Table 1**. The $^{241}AmO_2$ parent material was previously produced at LANL. The $^{243}AmO_2$ parent was originally procured from the National Isotope Development Center at ORNL and was solubilized by the mass spectrometry team.

Table 1. Americium Parent Materials

Labware ID	Parent Material Name	Description	Material Available
10087	HR-AMP-86S1-TM	$^{241}AmO_2$ powder	2650 mg $^{241}AmO_2$ powder
18553	ORNL NIDC Am243	^{241}Am solution	~7.37 mg ^{243}Am in 110 g solution

Parent ^{241}Am solution will be characterized for Am assay, Am isotope distribution, Pu concentration, Pu isotope distribution, and trace element concentrations. The ^{237}Np content in the ^{241}Am parent material will also be determined. These measurements will set baseline values for parent material composition and will be completed in duplicate.

Parent $^{241}AmO_2$ material was previously analyzed on 2/24/1995 by the predecessor actinide analytical chemistry group. Measurement results from that analysis are presented in **Table 2**. Note that a stoichiometric $^{241}AmO_2$ would produce a theoretical assay value of 88.28 wt%.

Table 2. $^{241}AmO_2$ Parent Material Composition on 2/24/1995

Labware ID	Measurement	Result
10087	^{241}Am Assay	82.21 wt%
10087	Pu Concentration	0.17 wt%

The dissolution and distribution of this parent solution as a sample will be completed. The sample will be submitted with customer sample identifier HR-AMP-86S1-TM P. This sample has been assigned Labware number 22384.

The $^{243}AmO_2$ parent was purchased based on quoted Am isotopic abundance values provided by ORNL. These isotopic abundances were reported without uncertainties or a reference date as shown in **Table 3**.

Table 3. $^{243}AmO_2$ Parent Material Isotopic Composition

Labware ID	Measurement	Result
18553	^{241}Am Abundance	0.012 at%
18553	^{242}Am Abundance	< 0.001 wt%
18553	^{243}Am Abundance	99.987 wt%

$^{241}AmO_2$ Parent Solution HR-AMP-86S1-TM P Preparation

● Assume a ^{241}Am concentration of 79.3 wt% in parent $^{241}AmO_2$ based on decay correction of previously assay measurement ● Prepare a ~252 mg cut of the HR-AMP-86S1-TM parent material ● Dissolve a ~252 mg cut of the HR-AMP-86S1-TM parent material ● Adjust the HR-AMP-86S1-TM AmO_2 parent solution concentration to ~9 mg ^{241}Am per gram solution ● Create parent sample HR-AMP-86S1-TM P with Labware number 22384.

Estimated concentration values for the ^{241}Am parent solution prepared for evaluation are given in **Table 4**. Again, these values are based on the previous analysis by the actinide analytical chemistry group.

Table 4. ^{241}Am Test Solution Composition Estimates

Labware ID	Measurement	Result
22384	^{241}Am content	~9 mg ^{241}Am per gram solution
22384	Pu Content	~0.019 mg Pu per gram solution

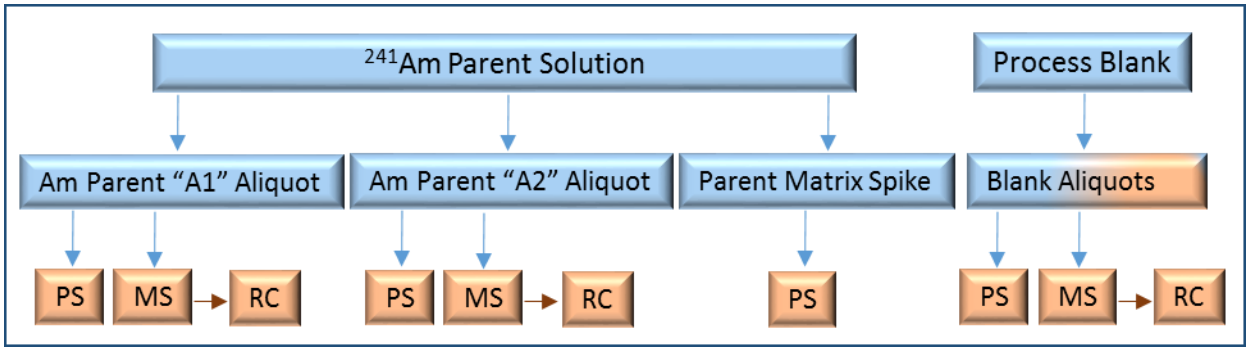
$^{241}AmO_2$ Parent Solution HR-AMP-86S1-TM P Distribution

The distribution of ^{241}Am parent solution HR-AMP-86S1-TM P for analysis is depicted in **Figure 1**. The actual distribution may vary slightly from the depiction to provide flexibility in applying analytical capabilities to the ^{241}Am matrix. Associated instructions for distribution are as follows:

● Distribute two ~1 g aliquots (~9 mg ^{241}Am each) of the HR-AMP-86S1-TM P ^{241}Am parent solution to TIMS (**MS**) ● Dilute and distribute duplicate MS aliquots to radiochemistry (**RC**) for Liquid Scintillation Counting ● Distribute two ~1 g aliquots (~9 mg ^{241}Am each) to ICP-AES (**PS**) ● Distribute two ~112 mg

aliquots (~1 mg ^{241}Am each) to ICP-MS (**PS**) ● Enter aliquots and tasks for HR-AMP-86S1-TM P parent, Labware number 22384

Figure 1. Distribution of ^{241}Am Parent Material Solution



$^{243}AmO_2$ Parent Solution ORNL NIDC AM243 Preparation

● The full 10 mg mass of procured ORNL $^{243}AmO_2$ parent material was previously dissolved and partially consumed by the TIMS team ● Current parent solution consists of approximately 7.39 mg of ^{243}Am in a 110 g solution ● Parent sample solution ORNL NIDC AM243 is available with Labware number 18553.

EXPERIMENTAL TEST & ASSESSMENT PLAN

Parent ^{241}Am and ^{243}Am solutions will be mixed to prepare a ^{241}Am-^{243}Am mixture solution suitable for testing analytical methods. All test experiments will be conducted in duplicate. To the extent possible, solution transfers will be performed gravimetrically. Care should be taken to minimize cross contamination in the gloveboxes and open front hoods. Ideally, experiments should be performed over a period of up to 6 weeks to demonstrate long term statistical control of analytical methods. The experimental requirements represent a test of the overall uncertainty of the analysis, which includes the uncertainties due to sampling (to a limited extent), dissolution (to a limited extent), chemical purification, and analytical method.

^{241}Am-^{243}Am Mixture Solution HR-AMP-86S1-TM A Preparation

A suitable mass of ^{243}Am from a reference material solution [ORNL NIDC Am243] held by the mass spectrometry team will be combined with a suitable mass of the ^{241}Am parent solution [HR-AMP-86S1-TM P] to create a mixture solution with a target ^{243}Am isotopic abundance of ~0.1 wt%. This mixture solution will be characterized and used for replicate analytical method test and assessment tasks. Instructions for preparing the mixture are as follows:

● Dispense a ~19.5 g aliquot (~178 mg ^{241}Am) of the HR-AMP-86S1-TM A ^{241}Am parent solution ● Add a 2.7 g aliquot (~0.18 mg ^{243}Am) of the ORNL NIDC Am243 ^{243}Am solution from MS ● Create test and assessment ^{241}Am/^{243}AmO mixture solution HR-AMP-86S1-TM A with Labware number 22501

The test and assessment mixture derived from Am parent materials is described in **Table 5**.

Table 5. Americium Test and Assessment Solution Derived from Parents

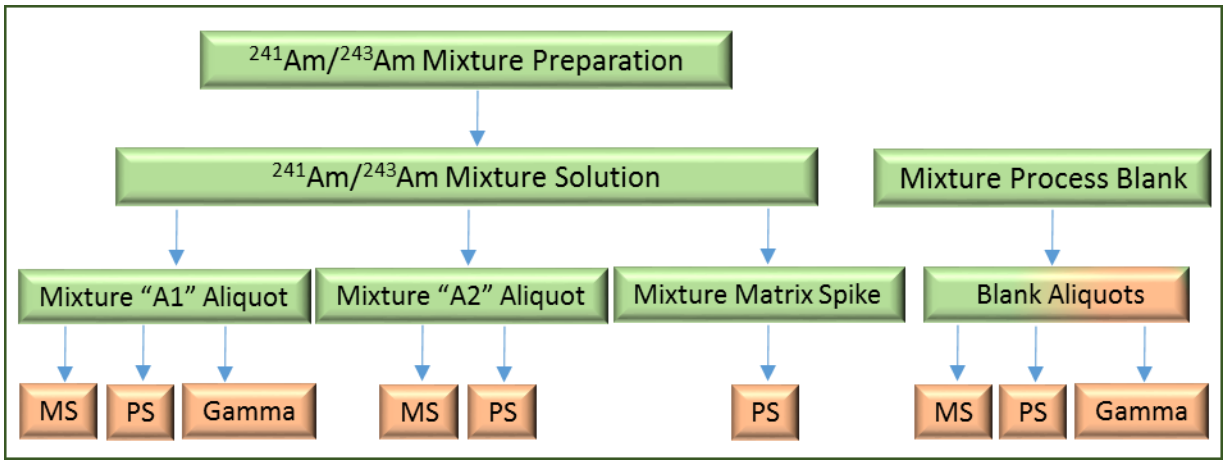
Labware ID	Test Solution Name	Description	Material Available
22501	HR-AMP-86S1-TM A	^{241}Am-^{243}Am mixture solution	~8 mg Am per gram solution

Estimated concentration values for the ^{241}Am-^{243}Am mixture solution prepared for method test and assessment are given in **Table 6**. Again, these values are based on the 1995 analysis of the ^{241}Am parent by the analytical chemistry group.

Table 6. ^{241}Am-^{243}Am Mixture Test Solution Composition Estimates

Labware ID	Measurement	Result
22501	Am content	~8 mg total Am per gram solution
22501	^{241}Am Abundance	~99.90 wt%
22501	^{243}Am Abundance	~0.10 wt%

Figure 2. Initial Distribution of Am Mixture Solution HR-AMP-86S1-TM A



^{241}Am-^{243}Am Mixture Solution HR-AMP-86S1-TM A Distribution 1

The initial distribution of test and assessment Am mixture solution HR-AMP-86S1-TM A for analysis is described in **Figure 2**. The actual distribution may vary slightly from the depiction to provide flexibility in applying analytical capabilities to the Am mixture matrix. Associated instructions for distribution are as follows:

- Distribute one ~1 g aliquot (~8 mg Am) of the HR-AMP-86S1-TM A ^{241}Am/^{243}Am mixture solution to NDA Gamma Spec (**GAMMA**)
- Distribute two ~1 g aliquots (~8 mg Am each) of the ^{241}Am/^{243}Am mixture solution to TIMS (**MS**)
- Distribute two ~1 g aliquots (~8 mg Am each) of the ^{241}Am/^{243}Am mixture solution to ICP-AES (**PS**)
- Distribute two ~112 mg aliquots (~1 mg Am each) of the

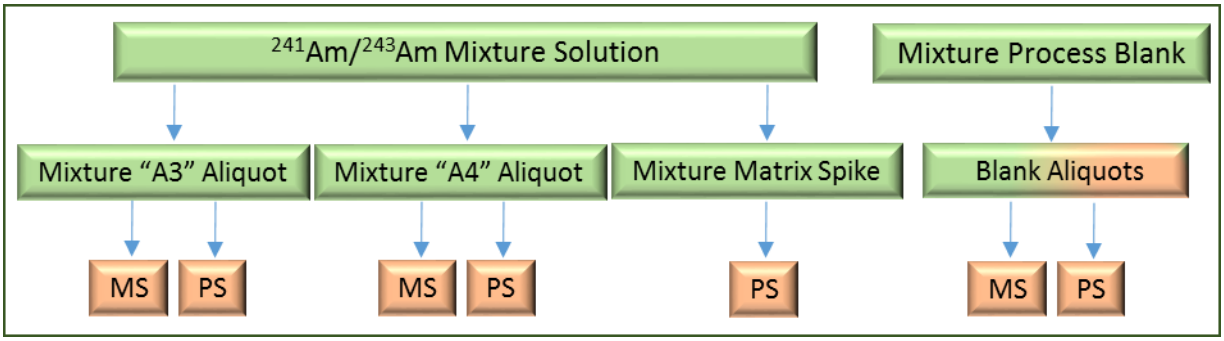
^{241}Am/^{243}Am mixture solution to ICP-MS (**PS**) ● Enter aliquots and tasks under test and assess mixture sample HR-AMP-86S1-TM A, Labware number 22501

^{241}Am-^{243}Am Mixture Solution HR-AMP-86S1-TM A Distribution 2

The second distribution of test and assessment Am mixture solution HR-AMP-86S1-TM A for analysis is described in **Figure 3**. Again, the actual distribution may vary slightly from the depiction to provide flexibility in applying analytical capabilities to the Am mixture matrix. Associated instructions for distribution are as follows:

● Distribute two ~1 g aliquots (~8 mg Am each) of the HR-AMP-86S1-TM A ^{241}Am/^{243}Am mixture solution to TIMS (**MS**) ● Distribute two ~1 g aliquots (~8 mg Am each) of the ^{241}Am/^{243}Am mixture solution to ICP-AES (**PS**) ● Distribute two ~112 mg aliquots (~1 mg Am each) of the ^{241}Am/^{243}Am mixture solution to ICP-MS (**PS**) ● Enter aliquots and tasks under test and assess mixture sample HR-AMP-86S1-TM A, Labware number 22501

Figure 3. Second Distribution of Am Mixture Solution HR-AMP-86S1-TM A

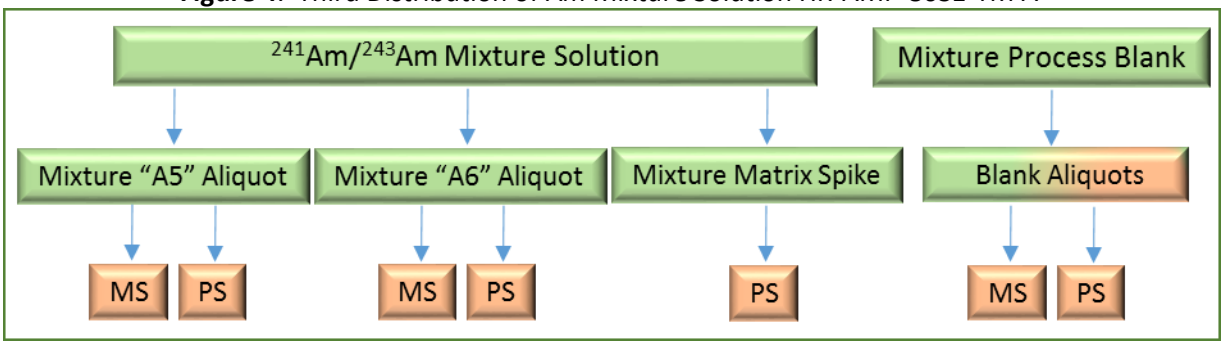


^{241}Am-^{243}Am Mixture Solution HR-AMP-86S1-TM A Distribution 3

The third and final distribution of test and assessment Am mixture solution HR-AMP-86S1-TM A for analysis is described in **Figure 4**. Associated instructions for distribution are as follows:

● Distribute two ~1 g aliquots (~8 mg Am each) of the HR-AMP-86S1-TM A ^{241}Am/^{243}Am mixture solution to TIMS (**MS**) ● Distribute two ~1 g aliquots (~8 mg Am each) of the ^{241}Am/^{243}Am mixture solution to ICP-AES (**PS**) ● Distribute two ~112 mg aliquots (~1 mg Am each) of the ^{241}Am/^{243}Am mixture solution to ICP-MS (**PS**) ● Enter aliquots and tasks under test and assess mixture sample HR-AMP-86S1-TM A, Labware number 22501

Figure 4. Third Distribution of Am Mixture Solution HR-AMP-86S1-TM A



ANALYTICAL TEST & ASSESSMENT METHODS

Gamma Spectrometry or Alternate Radiochemical Techniques (NDA)

The following radiochemistry methods may be tested and assessed…

- Am, Np, and Pu Concentration by Gamma Spectrometry
- Liquid Scintillation Counting (LSC) and/or Alpha Spectrometry

Calibration/standardization must be performed using NIST traceable standards. Appropriate NIST traceable solutions obtained from Eckert and Ziegler or NIST reference material solutions are to be used to as QCs and run with each batch along with appropriate blanks/backgrounds matching the time frame of each experiment.

Sample preparation and measurement experiments have to be performed over a 6 week period. Protocols and software for concentration determination of the analytes have to be documented. Success criterion for these experiments include determination of MDL based on blanks/backgrounds. Accuracy, precision and uncertainty for analytes will be based on the analysis of mixture solutions on specific detection systems and counting geometries.

Mass Spectrometry

The following thermal ionization mass spectrometry methods will be tested and assessed…

- Am Assay by ID TIMS
- ^{241}Am and ^{243}Am Isotopic Abundances by TIMS
- Pu Concentration by ID TIMS
- ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu Isotopic Abundances by TIMS

Appropriate NIST traceable solutions obtained from NIST or equivalent solutions are to be used as quality controls and run with each batch along with appropriate process blanks for each of the analytes mentioned above. For Am isotope and assay determination NIST traceable standards are preferred for the experiments. For Pu, the mass spectrometer accuracy is evaluated using NIST Standard Reference Materials (SRMs) which are run with every batch of samples. These data sets have formed the basis for

control charts and are used to assure the method is meeting performance criteria and to determine historical method performance.

Sample preparation and measurement experiments have to be performed over a 6 week period. Ion exchange chromatographic methods to separate out isobaric interference have to be documented. Accuracy, precision and overall uncertainty for the analytes mentioned based on TIMS analyses have to be documented. Instruments have to be tracked for these experiments. Success criterion for these experiments include determination of MDL for minor isotopes of Am and Pu.

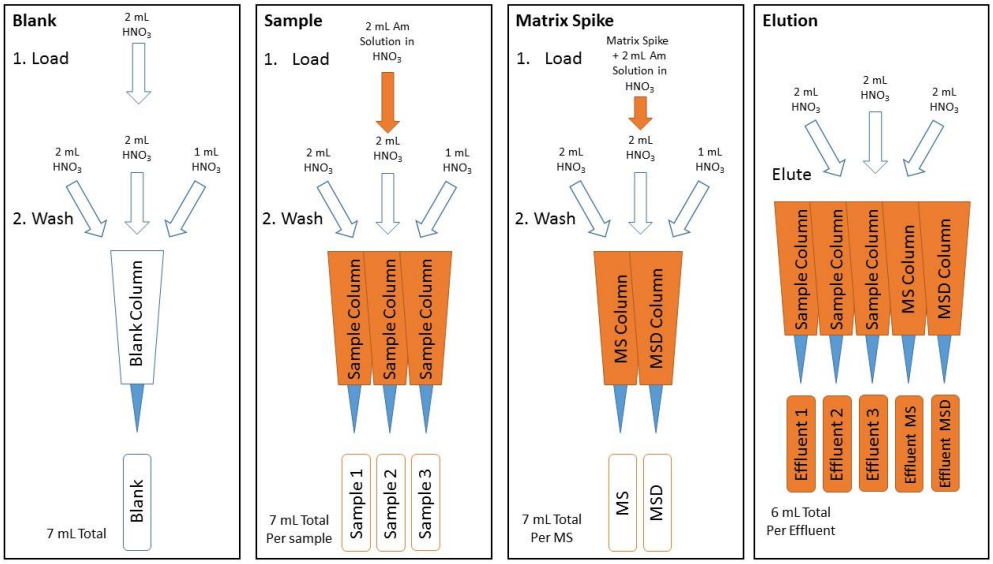
<u>Plasma Spectrometry</u>

The following plasma spectrometry will be tested and assessed…

- ❑ ^{237}Np Concentration by ICP-MS
- ❑ Trace Element Concentration by ICP-AES
- ❑ Trace Element Concentration by ICP-MS

Inductively coupled plasma instruments are calibrated using NIST traceable standards which are run with every batch of samples. The experimental plan is covered in the document: *Determination of trace impurities in americium oxide: method validation plan*, Miller Wylie, Ning Xu, Michael Rearick, & Kattathu Mathew (dated: xxx, Memo or LA-UR-17-24882). A schematic of the experimental plan is shown in **Figure 5**.

Figure 5. Schematic for the proposed separation experiments.



Appropriate traceable solutions obtained from NIST or equivalent solutions are to be used to as quality controls and run with each batch along with appropriate process blanks for each of the analytes mentioned above.

Sample preparation and measurement experiments have to be performed over a 6 week period. Ion exchange chromatographic methods to separate out spectroscopic interferences will have to be documented. Accuracy, precision and overall uncertainty for the analytes mentioned above based on the analysis of baseline spiked solutions using AES and MS have to be documented. Instruments have to be tracked for these experiments. Success criterion for these experiments include determination of MDL for major and minor trace elements including ^{237}Np.

MEASUREMENT DATA EVALUATION

Examine the combined results from three replicate measurements of $^{241}Am/^{243}Am$ mixture solution samples to estimate recoveries, method precision and total uncertainty and minimum detection limits. Consider measurement traceability and the evaluation of method accuracy. Utilize NIST traceable quality control data as necessary for this purpose. Prepare documentation such that it will pass a NBL data and record evaluation process.

CONCLUSION

Completion of results from the experiments described above will be documented in the form of a memo to assure/confirm that the AAC group has re-established the capability to analyze production $^{241}AmO_2$ materials for specification conformance. Results will also provide a defined degree of confidence in the repeatability of analytical AmO_2 sample measurements and estimates for minimum detection limits, precision, and accuracy for analytical techniques listed above as applied to similar sample matrices. Work instructions supporting this task are to be updated following completion of these experiments.

MILESTONES

Presentation at the program review: **August 29-30, 2017**

Memo to customer: **Friday, September 8, 2017**

Analytical Method Suitability to Support $^{241}AmO_2$ Production