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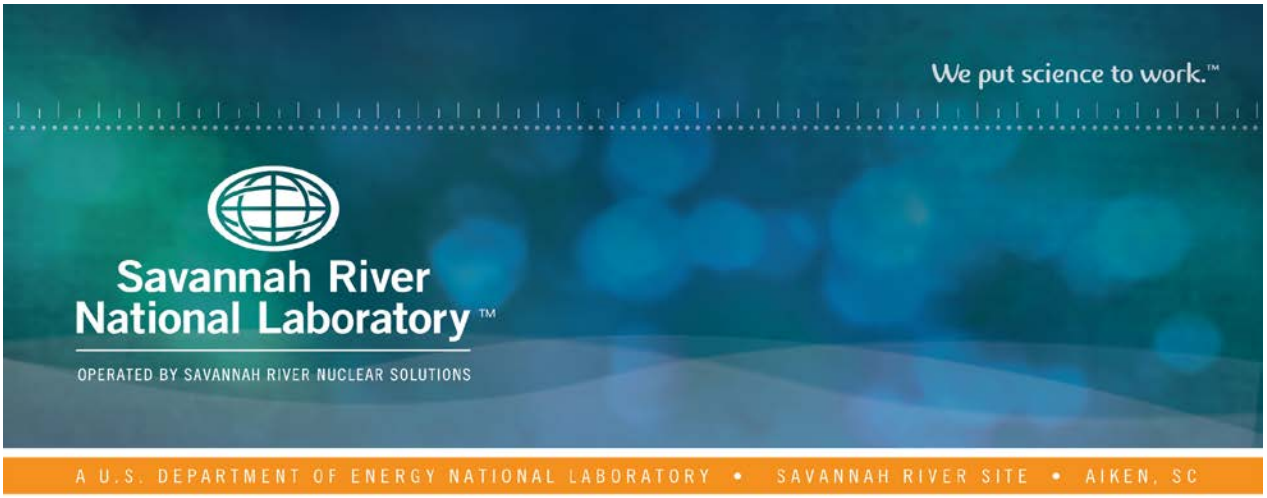

Validation of Modified Controlled-potential coulometric assay of Plutonium

Maria E. Morales-Arteaga

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REVIEWS AND APPROVALS

AUTHORS:

_____

Maria E. Morales-Arteaga, Analytical Laboratories Date

TECHNICAL REVIEW:

_____

Rebecca Thomas, Analytical Laboratories Date

APPROVAL:

_____

David Best, Manager Date
F/H Area Laboratory Services

_____

W. L. Melton, III, Manager Date
F/H Area Laboratory Services

EXECUTIVE SUMMARY

The test method for the Controlled-potential coulometric assay of plutonium used in SRNL F/H laboratories was modified in accordance to ISO 12183- Nuclear fuel technology — Controlled-potential coulometric assay of plutonium. The modifications will expand the possible drying and pre-treatment techniques which in turn will expand the type of samples that could be analyzed.

The modifications included allowing drying samples as nitrates, following JAEA's method. In addition, hydrogen peroxide treatment for valance adjustment in accordance with ISO 12183-2016. An average % recovery of 100.17% was obtained for the test samples. For the control samples, an average percent recovery of 99.999% was obtained.

It was demonstrated that a comparable per cent recovery is achievable. It is important to emphasize that attention to detail and proper worker techniques are crucial for successful results.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CRM	Certified Reference Material
CPC	Controlled-potential coulometry
IAEA	International Atomic Energy Agency
ISO	International Standards Organization
JAEA	Japan Atomic Energy Agency
JCGM	Joint Committee for Guides in Metrology
LSD	Large Size Dried
MOX	Mixed Oxide
NBL	New Brunswick Laboratory
QA	quality assurance
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 Introduction

The International Atomic Energy Agency (IAEA) has requested the analysis of twenty (20) dried plutonium nitrate samples by coulometry at Savannah River National Laboratory (SRNL) with iron correction. The samples were prepared by the Japan Atomic Energy Agency (JAEA) in support of their production of standards to be used for safeguards purposes at the Japan Nuclear Fuel Limited. The analysis will support the Mixed Oxide (MOX)-Pu4 characterization. This is a Pu standard material (called MOX-Pu4), which will be the starting material of Large Size Dried (LSD) spike preparation. The samples will be shipped with additional quality assurance (QA) samples prepared from New Brunswick Laboratory (NBL) Certified Reference Material (CRM) 126.

Savannah River Site (SRS) has used controlled-potential coulometric assay for select key accountability measurements, external exchange program measurements, and secondary standards characterization. The method is in full compliance with ASTM C1108–12, Standard Test Method for Plutonium by Controlled-Potential Coulometry, and ISO 12183-2016, Controlled-Potential Coulometric Assay of Plutonium.

The procedure used at SRNL Analytical Laboratories for controlled-potential coulometric assay was modified to allow drying samples as nitrates, following JAEA's method. In addition, hydrogen peroxide treatment for valance adjustment in accordance with ISO 12183-2016 was incorporated. This report summarizes the validation, and qualification of the modified method. These coulometric measurements are performed in full compliance with ISO 12183 and uncertainty calculations comply with JCGM 100.

2.0 Experimental Procedure

SRNL Plutonium standards were dried as nitrates in penicillin vials (supplied by JAEA), following procedure supplied by JAEA to replicate the dried nitrate samples supplied by JAEA. Once dried as nitrates, the samples were transferred quantitatively, using 8 M Nitric acid, into coulometry cells. These samples were then treated with hydrogen peroxide 30 % for valance adjustment. Samples were covered with a watch glass to prevent loss of solution from slow effervescence cause by the H_2O_2 reaction. After a color change to blue, indicating the presence of Pu^{+3}, the samples were heated on a hot plate to achieve a change to Pu^{+4}, as evidenced by a second color change to green. The condensate on the watch glass was rinsed into the test sample, sulphuric acid added, and the solution fumed to dryness under heat lamps. From this point forward the routine SRNL CPC method was followed to analyze the samples.

2.1 Initial batch

An initial batch of 10 samples, including control samples, was prepared and analyzed. The results from the initial test were not satisfactory. None of the results had a percent recovery over 99.9 %. The average percent recovery was 99.76%. Results are summarized in Table 2-1. These results indicated more testing and the modification of the technique was required.

Table 2-1. Summary of results for initial batch.

Sample ID	Analysis Date	mg Pu found	mg Pu , Iron Corrected	% Recovery
200736719	6/30/2017	6.2745	6.2676	99.7851
200736720	6/30/2017	6.2682	6.2613	99.6848
200736721	7/1/2017	6.2761	6.2692	99.81054
200733672-T1	7/8/2017	0.8748	0.8747	99.9886
200733674-T1	8/7/2017	0.8747	0.8743	99.6149
200734920-T1	8/7/2017	0.8738	0.8734	99.6918
200734922-T1	8/7/2017	0.8744	0.874	99.8458
200735650-T1	8/7/2017	0.8727	0.8723	99.7484
200735652-T1	8/7/2017	0.8738	0.8734	99.7260
			average	99.7662
			Standard dev.	0.11
200736722 (control)	07/01/2017	6.2856	6.2787	99.9620

2.2 Second batch

For the second batch of sample testing the reasons for a lower recovery were adresed. Several reasons could lead to a lower recovery, among them loss of sample during drying process, innefective valence change, and incomplete transfer of sample form the penicilin vial.

To adress the possible loss of sample during drying process, the samples were dried at a lower temperature and the temperature was increase in slowly.

Then we adresed the reason involved with processing samples. First, we confirmed that the valence change was being effective. A test was performed by adding 8 M nitric acid to a dried Plutonium sulfate sample in a coulometry cell. The hydrogen peroxide valance adjustment was performed and the samples were analyzed. The test confirmed that the results were comparable, therefore we can conclude that the valence adjustment procedure is effective. The average percent recovery was 99.986 % with a standard deviation of 0.05. Another indication of innefective or incomplete valence change is the increase of grams of plutonium calculated upon consecutive analysis of the same sample. To test this one sample was consequiteively analyzed with results being comparable, no statistical differnce was observed with a per cent relative differnce of 0.02 %. This %RD is comparable to results obtained when re-analizing routine samples.

Second, we performed tests to ensure a quantititive tranfer of the sample by increasing the amount of acid used to quantitatively transfer the samples. This was achieved by performing one extra rinse of the penicillin vial. Also, the amount of sulfuric acid used to rinse the watch glass after valence change was increased.

The average per cent recovery was 99.97%. Results for the second test are summarized in Table 2-2.

Table 2-2. Summary of results for second batch.

Sample ID	Analysis Date	mg Pu found	mg Pu , Iron Corrected	% Recovery
200738183-T1	7/17/17	10.8578	10.8401	99.96035
200738183-T3	7/20/17	10.8573	10.8396	99.95574
200738183-T4	7/20/17	10.857	10.8393	99.95297
200740883	8/24/2017	10.8631	10.8453	100.0083
200740884	8/25/2017	10.8603	10.8425	99.98248
200740885	8/26/2017	10.8666	10.8488	100.0406
200740886	8/27/2017	10.8539	10.8361	99.92346
			Average	99.9748
			Standard dev.	0.04

2.3 Quality Assurance

At least one control sample was prepared with each test batch. The control samples were not dried as nitrate. The samples were weigh directly into a coulometry cell, sulfuric acid added, and samples were dried under heat lamps as plutonium sulfate.

The average percent recovery was 99.999%. Results are summarized in Table 2-3.

Table 2-3. Summary of results for control samples.

Sample ID	Analysis Date	mg Pu found	mg Pu , Iron Corrected	% Recovery
200736722	7/1/2017	6.2856	6.2787	99.96179
200734920-3	7/26/2017	0.8767	0.8763	100.0228
200734922-3	7/26/2017	0.8753	0.8749	99.94859
200738586	8/9/2017	10.8578	10.84	99.95943
200740890	8/25/2017	10.8857	10.8679	100.2167
200740891	8/26/2017	10.8611	10.8433	99.98986
200740892	8/27/2017	10.8652	10.8474	100.0277
200740893	8/28/2017	10.8579	10.8401	99.96035
200740894	9/1/2017	10.8521	10.8343	99.90686
			average	99.999
			Standard dev.	0.09

3.0 Results and Discussion

From the results presented above we can conclude that the changes implemented to increase the recovery of samples had a positive effect. It is possible to achieve a recovery comprable to the recovery obtained with the previous methodology.

It is suspected that the principal component of the variability observed in the first batch of test samples is a result of the drying process implemented. To adress this, the samples were dried at a lower temperature and the temperature was increase in slowly. However, this drying process will not be part of the analysis process for the JAEA samples. Samples were received as a nitrate and will be qualitatively transferred, treated with hydrogen peroxide for valence change, dried as plutonium sulfate, and analyzed.

Based on the results, it is recommended to continue with the analysis of samples for JAEA using the modified sample preparartion method.

4.0 Conclusions

The test method for the Controlled-potential Coulometric assay of plutonium used in SRNL F/H laboratories was modified in accordance to ISO 12183- Nuclear fuel technology — Controlled-Potential Coulometric Assay of Plutonium. The modifications will expand the possible sample preparation and pre-treatment techniques to be used in sample preparation. This, accordingly, will expand the type of samples that could be analyzed and the customers we can serve.

It was demonstrated that a comparable percent recovery is achievable. It is important to emphasize that attention to detail and proper worker techniques are crucial for successful results.

5.0 Recommendations, Path Forward or Future Work

It will be advantageous to improve the process of drying samples as nitrates in penicillin vials. This will facilitate exchange of samples with other facilities. IAEA has already demonstrated an interest on exchanging samples. It is recommended that for this purpose we procure more penicillin vials. Also, it is recommended to obtain guidance form JAEA regarding the process.

6.0 References

6.1 International Standard ISO 12183-2016, Nuclear fuel technology — Controlled-potential coulometric assay of plutonium.
6.2 ASTM C1108-12, Standard Test Method for Plutonium by Controlled-Potential Coulometry
6.3 L3.05-10065, COULOMETRY PU AND NP, Revision: 8
6.4 AHA LAB-2428, Controlled-potential coulometric measurement of plutonium and neptunium.
6.5 JCGM 100:2008, Guide to the expression of uncertainty in measurement.