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# NWAL Validation report for

# U Assay by Potentiometric Titration (Modified Davies and Gray technique)

# And U and Pu Assay by Isotope Dilution Mass Spectrometry

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March 20221

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# NWAL Validation report for U Assay by Potentiometric Titration (Modified Davies and Gray technique) and U and Pu Assay by Isotope Dilution Mass Spectrometry

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March 2022

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# PREFACE

This document fulfills the requirement to complete the validation process for Uranium Assay by Potentiometric Titration (Davies and Gray method) and Uranium and Plutonium Isotope Dilution by Thermal Ionization Mass Spectrometry as part of the International Atomic Energy Agency's Network of Analytical Laboratories for Nuclear Material Measurements. These methods will be in addition to Uranium and Plutonium isotopic analysis of nuclear materials by Thermal Ionization Mass Spectrometry.

# EXECUTIVE SUMMARY

SRNL Sensing & Metrology, previously Analytical Laboratory, is a member of the IAEA Network of Analytical Laboratories for Nuclear Material Measurement that is qualified to provide Uranium and Plutonium isotopic analysis of nuclear materials by Thermal Ionization Mass Spectrometry. As part of the membership, SRNL participated in the 2019 Nuclear Material Round Robin to maintain the qualification to provide isotopic analysis. SRNL also participated with the additional intent to qualify Uranium Assay by Potentiometric Titration (Davies and Gray method) and Uranium and Plutonium Isotope Dilution by Thermal Ionization Mass Spectrometry as part of the International Atomic Energy Agency's Network of Analytical Laboratories. The proficiency test exercise was conducted by the Office of Safeguards Analytical Services, Department of Safeguards.

SRNL received a Uranium pellet and three vials containing aliquots of a mixed uranium and plutonium dried nitrate. Upon dissolution the pellet was analyzed for Uranium Assay by Potentiometric Titration (Modified Davies and Gray method) and by Isotope Dilution Mass Spectrometry. The mixed U and Pu dried nitrate samples were analyzed for U and Pu assay by Isotope Dilution Mass Spectrometry. The IAEA evaluated the results for the assay methods and consider them satisfactory. This report summarizes results for both Uranium Assay by Potentiometric Titration (Davies and Gray method) and Thermal Ionization Mass Spectrometry Isotope Dilution.

# TABLE OF CONTENTS

# LIST OF TABLES



# LIST OF FIGURES

# LIST OF ABBREVIATIONS

| | |
|---|---|
| CRM | Certified Reference Material |
| IAEA | International Atomic Energy Agency |
| IDMS | Isotope Dilution Mass Spectrometry |
| MNH | Uranium and Plutonium dried nitrate |
| NBL PO | New Brunswick Laboratory Program Office |
| NBS | National Bureau of Standards (precursor to New Brunswick Laboratory) |
| NMRORO | Nuclear Material Round Robin |
| NWAL | Network of Analytical Laboratories |
| SRM | Standard Reference Material |
| SRNL | Savannah River National Laboratory |
| TIMS | Thermal Ionization Mass Spectrometry |
| U DG | Uranium assay by Potentiometric Titration, Modified Davies and Gray method |

## 1.0 Introduction

SRNL Sensing & Metrology, previously Analytical Laboratory, participated in the International Atomic Energy Agency (IAEA) 2019 Nuclear Material Round Robin (NMRORO). The proficiency test exercise was conducted by the Office of Safeguards Analytical Services, Department of Safeguards. The main goal of the 2019 NMRORO was to assess the analytical performance of participating laboratories, including Network of Analytical Laboratories (NWAL) members, NWAL candidates, and nuclear facility operator laboratories in the determination of uranium assay, uranium isotopic ratios in uranium fuel pellet and uranium, plutonium assays and uranium, plutonium isotopic ratios in dried mixed Pu-U nitrate sample. SRNL is currently qualified for U and Pu isotopic analysis. This round robin exercise was used to test the qualified method but was also used as a final test to qualify Uranium Assay by Potentiometric Titration, Modified Davies and Gray technique (U DG) and uranium and plutonium assay by Isotope Dilution Mass Spectrometry (IDMS).

SRNL received a Uranium pellet and three aliquots of a mixed U and Pu dried nitrate sample (MNH). The U pellet was analyzed for uranium assay by U DG and IDMS. The mixed U and Pu MNH sample was analyzed for U and Pu assay by IDMS.

## 2.0 Experimental Procedure

### 2.1 Material Receipt

SRNL received a Uranium pellet and a U and Pu MNH sample on 8 November 2018. The samples were entered in the SRNL Laboratory Information Management System for internal tracking.

**Table 2-1. Identification of Material Received.**

| IAEA Identification Number | Sample Description | Analyte requested |
|---|---|---|
| 80003-01-35 | Pellet | U assay by DG titration and U IDMS |
| 80002-01-075 | MNH | U and Pu isotopic composition |
| 80002-01-076 | MNH | U and Pu IDMS |
| 80002-01-077 | MNH | U and Pu IDMS |

### 2.2 Sample Dissolution and Analysis

#### *2.2.1 Pellet dissolution*

The pellet was dissolved in accordance with ASTM C1347 Standard Practice for Preparation and Dissolution of Uranium Materials for Analysis. See Figure 2-1. All chemicals used were of the highest purity available (e.g., Ultrex™ II, for acids).

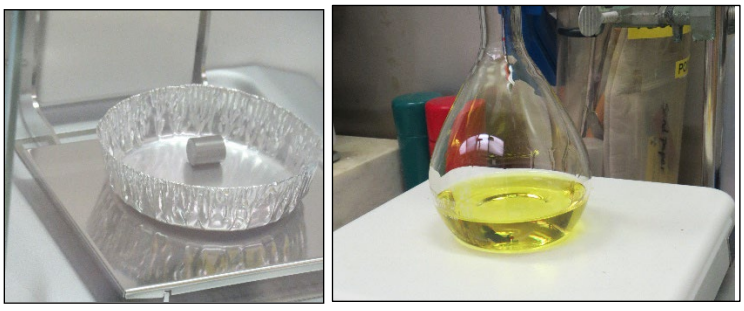

**Figure 2-1. Pellet During Weighing and Dissolution.**

*2.2.2 U assay of Pellet by Potentiometric Titration*

Upon dissolution, six aliquots of approximately 2.5g were taken for U Assay determination by potentiometric titration (U DG). The samples and quality control samples were accurately weighed and dried on a hot plate. Analysis was performed in accordance with ASTM C1267 Standard Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium, commonly referred to as the Modified Davies and Gray technique. Analysis was performed by independent protocol: two different technicians analyzed the samples on two different days, three samples per day. A procedure blank was processed with each set of samples.

*2.2.3 Sample Preparation and Analysis for U Assay of Pellet by U Isotope Dilution Mass Spectrometry*

Four aliquots of approximately 2 g of the pellet solution were delivered to the Thermal Ionization Mass Spectrometry (TIMS) laboratory. The samples were prepped by independent protocol: two different technicians on two different days. Each aliquot was spiked with a New Brunswick Laboratory Program Office Certified Reference Material (NBL PO CRM) 111-A $^{233}$U spike. After the spike and sample were equilibrated, the sample was purified using a EICHROM® UTEVA® ion extraction column assisted by a vacuum box (see Figure 2-2). A procedure blank was processed with each set of samples. The fraction containing the purified uranium was then dried and brought back up in 100 µL of 3 M Ultrex™ II nitric acid. Approximate 500 ng U were plated onto degassed, zone-refined rhenium filaments and then were delivered to the mass spectrometry lab. The samples were then analyzed by the total evaporation method on the Thermo Scientific TRITON™ thermal ionization mass spectrometer.

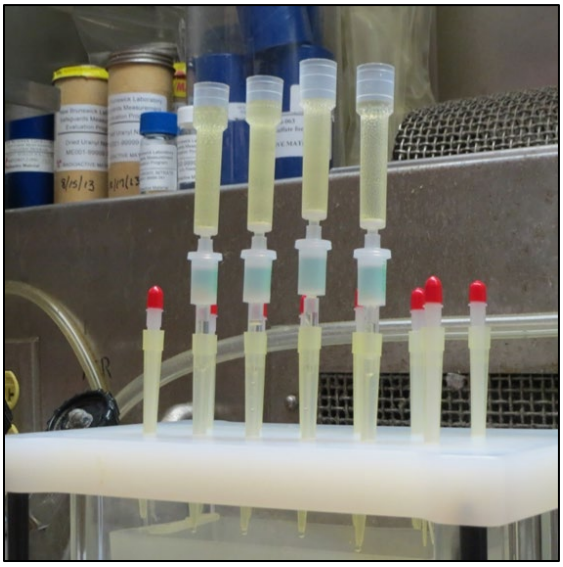

**Figure 2-2. EICHROM® Extraction Resin Columns on a Vacuum Box for Purification of IDMS Samples.**

*2.2.4 Dissolution of Mixed U-Pu Dried Nitrate Sample.*

The mixed U-Pu dried nitrate sample (MNH) was dissolved by adding 1 mL of 3 M Ultrex™ II nitric acid to each vial. The solution was swirled in the vial to mix it and check for any remaining "stickiness" on the bottom and sides of the vial. Then, an additional 3 mL of 3 M Ultrex™ II nitric acid was added to the vial. Though the MNH appeared to dissolve immediately, the solution was allowed to sit for at least 24 hours to ensure complete dissolution. See Figure 2-3.

**Figure 2-3. Dissolution of the Mixed U-Pu Dried Nitrate Sample.**

*2.2.5 Sample Preparation and Analysis for U and Pu Assay of Dried MNH by U and Pu Isotope Dilution Mass Spectrometry*

The U and Pu fractions were prepared separately for the assay samples, to minimize interference. This was possible because there was ample sample. Both the U and Pu samples were prepared under the independent analysis protocol; two different technicians prepared a sample from each vial on two different days. All chemicals used were of the highest purity available (e.g., Ultrex™ II, for acids).

To prepare the Pu samples, each technician prepared two aliquots of the sample and spiked them with $^{244}$Pu (NBS SRM 996). The valence was adjusted with ferrous sulfamate and then sodium nitrite. The samples were then purified on EICHROM® TEVA® resin, using a two-column procedure to ensure that all the U was removed from the Pu fraction. For the two-column procedure, the first fraction was purified on a single column (similar to Figure 2-2), then the Pu fraction was adjusted to return to the correct valence and acid form, and was run through a second, clean TEVA® resin column. The final Pu fraction was dried and brought back up in 100 µL of nitric acid. Approximately 250 ng of Pu was then plated onto a degassed, zone-refined rhenium filament in preparation for TIMS analysis.

The uranium samples were also prepared using the two-column method. Each batch of samples contained two aliquots of the sample and were spiked with $^{233}$U (NBL PO CRM 111-A). The samples were then loaded onto a single EICHROM® UTEVA® column (as shown in Figure 2-2). The purified uranium fraction was then adjusted to return it to the correct valence and acid form, and was then further purified on a second, clean UTEVA® column. The final U fraction was dried and brought back up in 200 µL of nitric acid. Approximately 500 ng U was then plated onto a degassed, zone-refined rhenium filament in preparation for TIMS analysis.

The U and Pu IDMS samples were analyzed on the Thermo Scientific TRITON™ thermal ionization mass spectrometer using the total evaporation method in accordance with ASTM C1672. Each wheel was analyzed with Quality Control (QC) samples (see section 2.3).

## 2.3 Quality Assurance

*2.3.1 U Assay by Potentiometric Titration*

Quality Control (QC) Samples are prepared from a Uranium metal CRM (either NBL PO CRM 115 or NBL PO CRM 112-A) in accordance with ASTM C1347 Standard Practice for Preparation and

Dissolution of Uranium Materials for Analysis. As per SRNL internal procedures a QC sample was analyzed before and after analysis each day. The results of the QC samples must be within the 95% confidence interval to be acceptable. All QC samples were acceptable. In addition, a procedural blank was analyzed with each batch. Procedural blanks indicated no correction was needed.

*2.3.2 U and Pu assay by Isotope Dilution Mass Spectrometry*

The IDMS samples were spiked with certified reference materials of a unique (compared to the sample) isotopic composition. The spike is used as an internal standard to calculate the U and Pu assay of the sample. For Pu IDMS, both the IAEA samples and the IDMS quality control samples were spiked with $^{244}$Pu, using standard reference material (SRM) 996 from the National Bureau of Standards (NBS – the precursor to the National Institute of Standards and NBL PO). The IAEA samples and the U IDMS QC samples were spiked with $^{233}$U, NBL PO CRM 111-A.

Multiple QC samples were analyzed with each batch of U and Pu IDMS samples. The total evaporation method typically requires limited correction for mass bias due to fractionation of the isotopes during the thermal heating of the sample. To determine if mass bias correction is required for the sample run, five comparator isotopic QC samples were inserted randomly through the sample sequence, and the results were used to calculate a mass discrimination factor. For the SRNL TIMS instrument, U total evaporation analysis typically requires a small correction, while Pu total evaporation analysis typically requires no correction. Two to three different isotopic QC samples were loaded onto the sample wheel to verify that the corrected analyses met QC requirements within two-sigma of the method uncertainty. For both the comparator and isotopic QC samples, SRNL uses the U-series isotopic NBL PO CRM (e.g., NBL PO CRM U500, U030-A, U-010, U050 etc.). These QCs verify the instrument and method functionality.

Finally, for each shift in which U or Pu IDMS are prepared, duplicate U or Pu IDMS QC samples were prepared side-by-side with the IAEA samples. For U IDMS, the IDMS QC samples are the same as the ones used for U assay by potentiometric titration. The Pu IDMS sample is a well-characterized working reference material that is prepared in-house and is characterized by Pu coulometry and verified by Pu IDMS. This is the same QC material used for coulometry analysis. Both U and Pu IDMS QC results are compared to U D&G and Pu coulometry QC results on a regular basis. The results of the IDMS QC analysis must be within the 95% confidence interval to be acceptable. Otherwise, the IDMS samples that were prepared with the QC samples are rejected and must be prepared again.

## 3.0 Results and Discussion

For each method of analysis, results from each day of analysis were summarized and submitted as a replicate value. All results were summarized and submitted to IAEA in the reporting template provided by IAEA. See Tables 3-1 and 3-2.

**Table 3-1. Values Reported for U Pellet.**

| Measurand | Method | Unit | Replicate | Vial ID | Measurand Value | Expanded Uncert. (95% CL) | Coverage Factor |
|---|---|---|---|---|---|---|---|
| U-ASSAY | U D&G | [g/g]x 100% | 1 | 80003-01-35 | 88.1786 | 0.256 | 2.00 |
| U-ASSAY | U D&G | [g/g]x 100% | 2 | 80003-01-35 | 88.1656 | 0.256 | 2.00 |
| U-ASSAY | U IDMS | [g/g]x 100% | 1 | 80003-01-35 | 87.9847 | 0.484 | 2.00 |
| U-ASSAY | U IDMS | [g/g]x 100% | 2 | 80003-01-35 | 88.1611 | 0.485 | 2.00 |

**Table 3-2. Values Reported for Mixed Uranium-Plutonium Dried Nitrate.**

| Measurand | Method | Unit | Replicate | Vial ID | Reference Date (YYYY-MM-DD) | Measurand Value | Expanded Uncert. (95% CL) | Coverage Factor |
|---|---|---|---|---|---|---|---|---|
| U-ASSAY | U IDMS | [g/g]x 100% | 1 | 80002-01-76 | 2018/10/31 | 0.970360 | 0.00534 | 2.00 |
| U-ASSAY | U IDMS | [g/g]x 100% | 2 | 80002-01-77 | 2018/10/31 | 0.970980 | 0.00534 | 2.00 |
| U-ASSAY | PU IDMS | [g/g]x 100% | 1 | 80002-01-76 | 2018/10/31 | 0.232020 | 0.00174 | 2.00 |
| U-ASSAY | PU IDMS | [g/g]x 100% | 2 | 80002-01-77 | 2018/10/31 | 0.232280 | 0.00174 | 2.00 |

## 4.0 Conclusions

The IAEA submitted a report in which the IAEA 2019 Nuclear Material Round Robin is described and includes the evaluation of the results submitted by the participating laboratories. The report also includes recommendations of participants of the 2019 NMRORO Technical Meeting that took place in Vienna, 18-20 June 2019.

See Tables 4-1 and 4-2 for a summary of the evaluation of results, extracted from the IAEA report.

**Table 4-1. IAEA Laboratory Summary Evaluation for Uranium Pellet.**

| Lab Code | Test Item | Method | Result, [g/g]x100% | ū (Result), [g/g]x100% | z-score | zeta-score |
|---|---|---|---|---|---|---|
| AI | U-ASSAY | U D&G | 88.172 | 0.091 | 0.60 | 1.03 |
| AJ | U-ASSAY | U IDMS | 88.07 | 0.17 | -0.03 | -0.02 |

**Table 4-2. IAEA Laboratory Summary Evaluation for Mixed Uranium-Plutonium Dried Nitrate**

| Lab Code | Test Item | Method | Result, [g/g]x100% | ū (Result), [g/g]x100% | z-score | zeta-score |
|---|---|---|---|---|---|---|
| AJ | U-ASSAY | U IDMS | 0.9707 | 0.0019 | -0.96 | -0.75 |
| AJ | PU-ASSAY | PU IDMS | 0.23215 | 0.00062 | 0.14 | 0.12 |

The tables contain the result, which is the mean of all values reported, and the pooled standard uncertainty, ū. The proficiency assessment performed by IAEA used z-score and zeta-scores. The z-score is considered an indicator of fitness for purpose of laboratory produced results, whereas zeta-scores can only be interpreted as a test of whether the participant's uncertainty is consistent with the observed deviation. The z-score quantifies the distance between the average measurement result and the assigned value in units of the proficiency test standard deviation. The zeta-score quantifies the distance between the average measurement result and the assigned value in units of the combined standard uncertainty of the average reported value and the uncertainty of the assigned value. Any score that exceeds 3 in absolute value, i.e., $z_i \geq |3|$, indicates that there is likely a significant bias in the average measurement result and is defined as "unacceptable" in ISO 13528:2015. For all SRNL analyses, both z-score and zeta-score, values were less than 2, indicating results were acceptable.

## 5.0 Recommendations, Path Forward or Future Work

The U Assay by Potentiometric Titration (Modified Davies and Gray technique) method is currently an ISO/IEC 17025:2017 accredited method. For mass spectrometry the U and Pu isotopic analysis by conventional TIMS (in accordance with ASTM C1625) is currently an ISO-IEC 17025:2017 accredited method. The ISO-IEC 17025:2017 accreditation also covers the quality control program for both U Assay by Potentiometric Titration and TIMS methods. Although not accredited methods, IDMS analyses and isotopic analyses by total evaporation are compliant with ISO/IEC 17025:2017. In the future it is the intent of the laboratory to continue participation in available proficiency testing programs, namely NBL PO SME program and IAEA NWAL NMRORO. Upon approval and acceptance of these methods as part of SRNL NWAL, they will be available to the IAEA, if requested.

## 6.0 References


- ASTM International C1267 Standard Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium. West Conshohocken, PA.
- ASTM International C1347 Standard Practice for Preparation and Dissolution of Uranium Materials for Analysis. West Conshohocken, PA.
- ASTM International C1625 Standard Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry. West Conshohocken, PA.
- ASTM International. C1672 Standard Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer. West Conshohocken, PA.
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