

**UPDATE ON THE HIGH PRECISION TITRATION METHOD FOR URANIUM ASSAY
SUPPORTED BY NBL PROGRAM OFFICE**

Kayron Rogers¹, Robert Watters², Michael Holland², Anna Tourville², Ben Roach¹, Cole Hexel¹, Joseph Giaquinto¹, Peter Mason²

1. Oak Ridge National Laboratory, Oak Ridge, TN, USA
2. NBL Program Office, Oak Ridge, TN, USA

ABSTRACT

The NBL Program Office (NBL PO) has coordinated with Oak Ridge National Laboratory (ORNL) to implement the High Precision Titration (HPT) method for uranium assay measurements. The measurement method has been successfully developed and qualified, therefore ORNL has progressed to performing analyses critical to the mission of the NBL PO. The HPT method is vital to producing the next generation of certified reference materials for uranium assay, and provides the highest accuracy and precision of currently-known uranium assay methods. The method has been extensively studied for systematic sources of error, and is considered one of the NBL PO's critically-evaluated methods suitable for direct certification of uranium assay. The work described here focused on establishing the use of the latest version of NIST's SRM 136 potassium dichromate series (SRM 136f) which NBL had not fully validated prior to the labs closure. This work also focused on investigating small differences reported between SRM 136e and 136f. The NBL PO evaluated the history of all of its primary uranium reference materials, including CRM 112-A natural uranium metal, and worked with NIST in investigating the small differences in the two dichromate SRM's. ORNL performed comparative experiments on SRM 136e and 136f using CRM 112-A. The results of the experiment will be presented here, along with NBL PO's plans to re-evaluate the CRM 112-A certified uncertainty to comply with JCGM 100, "Guide to the expression of uncertainty in measurement."

INTRODUCTION

The Nuclear Analytical Chemistry (NAC) section at Oak Ridge National Laboratory (ORNL) began establishment of the High Precision Titrimetric (HPT) method in 2018 with funding and direction provided by the NBL Program Office (NBL PO)^{1,2}. HPT is a metrologically valid procedure which produces uranium assay measurements with uncertainties at or below 0.012%, thereby acting as an excellent method for the certification and/or verification of reference materials. HPT was historically used in this capacity for several uranium reference materials at NBL; and thus with NBL closure the NBL PO sought to establish and maintain the capability at ORNL. Accordingly, a dedicated HPT laboratory was set up at ORNL and NBL PO personnel conducted a week-long training in September 2019. A suite of HPT analytical procedures was developed based upon the training and previous procedures from NBL. In 2020, an analyst became qualified to perform the HPT method with uranium metal samples by demonstrating proficiency in the titration of certified reference material (CRM)

112-A. The NBL PO and ORNL have discussed the possibility of including the HPT method in 17025 accreditation.

The HPT method was developed at NBL in the 70s as a scaled-up modification of the Davies and Gray titration³. By increasing the sample size of uranium to 2.5 – 3.5 g from 20 - 250 mg, HPT imparts uranium assay values with improved precision and accuracy (<0.01%) due to more accurate weighing and reduced perturbances from interferences. The fundamental chemistry of the analysis is the reduction of U(VI) to U(IV), followed by potentiometric titration of U(IV) to U(VI) with potassium dichromate. The use of the National Institute of Standards and Technology (NIST) standard reference material (SRM) 136 series potassium dichromate, along with a calibrated measurement system (i.e. analytical balance, environmental monitoring and mV meter), provides metrological traceability of the uranium assay value. Historically at NBL, NIST SRM 136c and 136e have been used as the oxidant in the certification and/or verification of uranium certified reference materials, one example being CRM 112-A uranium metal assay and isotopic standard.

CRM 112-A was originally issued as a standard in 1972 by the National Bureau of Standards (NBS) as SRM 960⁴. The certificate of analysis for NBS SRM 960 stated a uranium assay value of 99.975 ± 0.017 weight percent. The method of analysis used to determine this certified attribute value was constant current coulometric titration of the uranyl ion U^{+6} with electrogenerated titanous ions, corrected for Fe and V⁵. In 1981, NBS 960 was transferred to NBL for storage and distribution. Six years later in 1987, the standard was renamed CRM 112-A and a new certificate of analysis was issued with uranium assay of 99.975 ± 0.006 weight percent. Subsequently, the standard material was repackaged and verified for uranium assay in 1998 and again in 2010. While generating data from the 2010 verification of CRM 112-A and as part of the effort to qualify SRM 136f for NBL use, NBL began to observe small differences in titrations performed with SRM 136e and 136f. These observations, which came after SRM 136f was issued in 2008, were based upon independent data sets for the two 136 issues, but not for a simultaneous sequence.

The study described in this paper served several purposes: to further exercise proficiency of the method at ORNL while also executing a continuation of a study concerning SRM 136e and 136f initiated at NBL and with detailed discussions with NIST. Furthermore, these measurements were used to establish the suitability of SRM 136f for future use. Analysis of this data by NBL PO will be used as independent verification of the certified U assay value of CRM 112-A and to calculate an uncertainty in compliance with JCGM 100, “Guide to the expression of uncertainty in measurement” to ensure compliance with ISO 17034^{6,7}.

EXPERIMENTAL

HPT Titration

In HPT analysis, a sample of uranium metal is pickled with nitric acid, dried with acetone and then weighed accurately up to seven significant digits. Based upon the weight of the uranium metal, solid potassium dichromate is accurately weighed at an amount approximately 5 mg less than the stoichiometric equivalent for the reaction. The weights for uranium and potassium dichromate are corrected for buoyancy. The uranium sample is dissolved in phosphoric acid and reduced to U(IV) with ferrous sulfate. Any excess Fe(II) is oxidized to Fe(III) with the addition of nitric acid, catalyzed

by molybdate. NO_2^- formed in this reaction is reduced to N_2 with sulfamic acid. Before the titration, the solution is diluted with 100 mL of water and vanadyl sulfate is added to sharpen the endpoint. A saturated calomel electrode and platinum working electrode is inserted into the solution. The pre-weighed potassium dichromate is added to the solution and then the potentiometric endpoint is reached, by weight, with a standard, gravimetrically-prepared potassium dichromate solution.

Reagents and Equipment

A Mettler Toledo XPR26 six-place analytical balance was used for weighing of the uranium metal and solid potassium dichromate while a Mettler Toledo AT201 five-place balance was used for weighing the wash bottle with titrant solution. A combination traceable meter purchased from Fisher Scientific was used to measure barometric pressure, temperature, and relative humidity used for air density calculations. The mV meter was an OHAUS ST3100 equipped with an OHAUS STREF2 saturated calomel electrode as the reference and a 99.95% platinum coiled wire working electrode, connected to the meter via BNC cable soldered to copper alligator clip. An Oakton pH simulator verified the mV reading from the mV meter. CRM 112-A was cut from original 26 grams rods into 2.5 – 3.5 gram pieces; a McMaster-Carr threaded rod cutter was used for the cutting. SRM 136e and 136f, solid potassium dichromate were acquired unopened from NIST, and dried simultaneously according to certificate drying instructions. A solution of each SRM 136e and 136f was gravimetrically prepared with each preparation being verified with standard Davies and Gray titration. The chemicals used in this study are listed in Table 1.

Table 1. Make and Lot of Chemicals

Chemical	Make/Grade	Lot
Acetone	Fisher/Optima	114485
Nitric Acid	Fisher/Trace Metal	1117100
Phosphoric Acid	Acros Organics/ACS Reagent	B0538660A
Hydrofluoric Acid	Fisher/Optima	5213102
Sulfuric Acid	JT Baker/ACS	000021909
Ferrous Sulfate Heptahydrate	Fisher/Certified ACS	175908
Ammonium Molybdate	Fisher Chemical/Certified ACS	165885
Sulfamic Acid	MP/ACS	7647K
Vanadyl Sulfate Hydrate	Aldrich/ $\geq 99.99\%$ Trace Metal Basis	MKBT1390V

RESULTS AND DISCUSSION

CRM 112-A Analysis with 136e and 136f

A study was planned to assess the previously mentioned differences found between SRM 136e and 136f. The high precision titration method was performed using CRM 112-A and controlling all variables while alternating titrations with SRM 136e and 136f. The experiment was performed on two separate days, once in November 2020 and again in April 2021. Each issue of 136 was used to titrate 10 samples on the first analysis day and 9 samples on the second analysis day, resulting in a total of 19 titrations for each 136e and 136f. The identities of the 136e and 136f samples were blinded to the analyst, by repackaging into bottles marked “A” and “B” by a second chemist.

In the first set of titrations in November, a problem resulted in an unstable endpoint for four of the titrations, which were therefore considered outliers. This was attributed to volume reduction of phosphoric acid during the uranium dissolution step without allowing time for the acid to be reconstituted with water, which happens through atmospheric absorption. This prevented some pre-titration reactions from going to completion. Nevertheless, a second set of titrations was performed in April to provide confidence in the results and evaluate day-to-day reproducibility.

Figure 1 plots the data for the titrations and includes the mean and standard deviations for the uranium assay result of CRM 112-A for the total of all titrations for SRM 136e versus 136f. The mean value for uranium assay of CRM 112-A using SRM 136f as the titrant was 0.999749 g U/g metal (n=17); and was 0.999786 g U/g metal (n=16, one sample was overtitrated) for SRM 136e, with the Certified value being 0.99975. The relative standard deviation for each set of total titrations rounded to 0.003% for both sets, which is well within the capability of the HPT method.

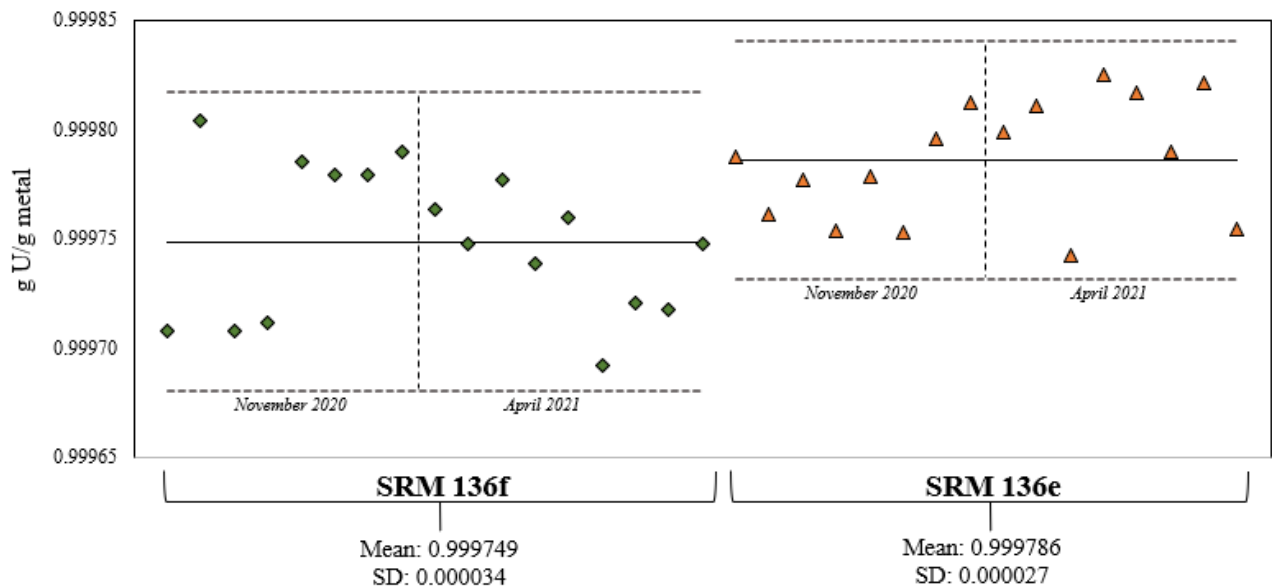


Figure 1. Uranium assay results from the comparison of SRM136e and 136e using the HPT method. The solid black line represents the mean uranium assay value for CRM 112-A of all titrations for each dichromate, while the horizontal dotted grey line represents two standard deviations calculated for all titrations. The vertical dotted line delineates between the two days of titrations.

Statistical Evaluation of Bias

A simple *t* test was conducted to evaluate if the difference between the two sets of measurement results was significant, revealing that the difference was significant at the 95% confidence level. In practicality, however, the relative uncertainty for SRM 136e stated on the certificate is 0.010% compared to 0.0044% for SRM 136f, which means that this “difference” can be accounted for within the provided uncertainty from NIST and is only observed due to the precision and accuracy of the

HPT method. It is also of note that the SRM 136f material was of much higher purity than 136e, which also contributes to the significantly smaller uncertainty assigned to SRM 136f. The certified value for SRM 136e and 136f are 99.984 % and 99.9954 %, respectively.

CONCLUSIONS

It is very promising that the uranium assay value for CRM 112-A titrated with SRM 136f exactly matched the uranium assay value from the 1970's measured with the coulometric titration. The agreement between the two independent analytical methods, decades apart, adds further confidence in the uranium assay value of C112A. The data produced using SRM 136f will act as a validation of the certificate assay of CRM 112-A. Furthermore, the data set will be used to reevaluate the uncertainty according to the JCGM 100, "Guide to the expression of uncertainty in measurement" but is expected to remain close to the current value of ± 0.00006 g U/g metal.

The NAC section is focused on maintaining the lab space, qualification of the method and furthering use of the method by developing proficiency with other uranium compounds such as U_3O_8 and UO_2 . Ultimately, ORNL seeks to become accredited to ISO 17025 for the HPT method.

ACKNOWLEDGEMENTS

The NBL Program Office, P. Mason, Director, funded these efforts as part of their measurement quality mission. The NBL PO resides within the NNSA's NA12 Office of Stockpile Production Integration.

REFERENCES

1. Rogers, K.; Roach, B.; Parikh, J.; Wightman, H.; Ilgner, R.; Chattin, M.; Hexel, C.; Giaquinto, J. *New Capability at ORNL: High Precision Uranium Titration*; ORNL/TM-2021/1915; Oak Ridge National Laboratory: Oak Ridge, TN, 2021.
2. Rogers, K.; Roach, B.; Giaquinto, J.; Ilgner, R.; Hesse, H.; Chattin, M.; Hexel, C.; Voeks, A.; Hui, N.; Stiffin, A.; Mason, P. Establishing a High Precision Titrimetric Laboratory at Oak Ridge National Laboratory to Support the NBL Program Office's Mission. In *Annual Meeting Proceedings of the 60th INMM Annual Meeting*, Palm Desert, California, July 14–18, 2019.
3. Eberle, A.R.; Lerner, M.W. *Application of the New Brunswick Laboratory Titrimetric Method (Ferrous Ion Reduction) to the Precise Assay of Uranium Metal*; NBL-258; U.S. Atomic Energy Commission, New Brunswick, NJ, 1971.
4. U.S. Department of Energy, NBL Program Office. *A History of the United States Primary Uranium Reference Material – Origin, Production, Certification of Uranium Metal SRM 960/CRM 112-A*; NBL-RM-2010-CRM-112A. 2010.
<https://www.energy.gov/nnsa/downloads/crm-112a-production-and-certification-history> (accessed 2021-07-30).
5. Marinenko, G.; Koch, W. F.; Etz, E. S.; High Precision Coulometric Titration of Uranium. *Journal of Research of the National Bureau of Standards*. **1982**, 88 (2), 117–124.
6. Joint Committee for Guides in Metrology. *Evaluation of measurement data – Guide to the expression of uncertainty in measurement*; JCGM 100:2008.

7. International Organization for Standardization. *General Requirements for the Competence of Reference Material Producers*; ISO 17034:2016.