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PROGRESS ON PLUTONIUM ISOTOPIC CRM 946, 947 and 948 RECERTIFICATION

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ABSTRACT

Lawrence Livermore National Laboratory (LLNL) and the New Brunswick Laboratory Program Office (NBL PO) are collaborating on production of purified sub-units of the former NBS 936, 937 and 938 plutonium isotopic reference materials, which will be certified for plutonium isotopic composition and sold as certified reference materials (CRMs) C136A, C137A, and C138A, respectively. These reference materials, employed throughout the United States and international community as standards for isotopic measurement method calibration and quality control, are now over 50 years old, have large certified uncertainties and likely biases in the certified values, and are currently packaged in 0.25 g units that are inconvenient to ship and much larger than typically needed by analytical laboratories. To reduce quantities of in-grown daughter products and potentially also enable their use as Pu radiochronometry reference materials, a two-stage anion exchange purification will be performed to significantly reduce the quantities of U, Am, and Np in the source material. Purification methods were tested on 100 µg sub-units of NBS 947 (C137). The concentrations of Pu, U isotopes, ^{241}Am, and ^{237}Np in the starting material were measured via isotope dilution (ID) multicollector–inductively coupled plasma–mass spectrometry (MC-ICP-MS). Results demonstrate that sub-units were completely purified of ^{241}Am in September 1970, at which time ^{237}Np content was approximately 280 ppm. This is consistent with the known history of NBS 947, however Pu-U chronometers gave model ages in March-April 1972, indicating that U was partially fractionated sometime after purification. Initial concentrations were combined with MC-ICP-MS U, Pu and Am measurements of the purified aliquots and gamma spectrometry with a ^{239}Np tracer to calculate yield and decontamination factors, which were 1.66E+03, 1.14E+05, and 6.29E+02 for U, Am, and Np, respectively. The procedure will be scaled up to purify approximately 245 mg of C137 in a new glovebox at LLNL. After mass spectrometry and gamma spectrometry verify acceptable yield and purification from Am and Np, the purified Pu is to be dissolved in nitric acid and aliquoted into individual units of approximately 1 mg Pu as dry nitrate in FEP Teflon bottles. The purification and production of C137A units and plans for analytical measurements leading to assignment of values and certification will be discussed.

INTRODUCTION

The New Brunswick Laboratory (NBL, now the New Brunswick Laboratory Program Office, NBL PO) collaborated with the National Bureau of Standards (NBS, re-named National Institute of Standards and Technology, NIST) in the 1960s and 1970s to produce and certify three plutonium isotopic reference materials, called NBS 936, 937 and 938. These were respectively re-named CRMs 136, 137 and 138 in the 1980s when NBS formally transferred nuclear reference materials responsibilities and stocks to NBL. The history of these reference materials has been documented elsewhere (Mason & Narayanan 2010). They are still the main U.S. Pu isotopic reference materials relied upon by analytical laboratories and are sold by NBL in their original configuration of approximately 0.25 g Pu as Pu sulfate hexahydrate. The isotopic values and uncertainties from the original certificates issued in 1971, 1971 and 1964, respectively, are decay-corrected and used as reference values, as there have been no measurement campaigns aimed at re-certification until now. Lawrence Livermore National Laboratory (LLNL) and NBL PO are collaborating on production of purified sub-units of these isotopic reference materials to be re-certified by multi-laboratory analysis and distributed as CRMs 136A, 137A and 138A.

From a logistical and safety perspective the need to repackage and distribute the Pu CRMs is clear. Although units this size may be useful for non-destructive analytical techniques such as gamma spectrometry, the amount of Pu far exceeds the needs of most analytical laboratories and may even exceed the allowable activity levels at many facilities. Shipping these units to customers is cumbersome because their activities trigger requirements for Type-B containers that are in short supply. Another concern is possible radiolytic damage to the primary containment after more than 50 years of decay, which leads to high risk of area and personnel contamination when opening the units.

To reduce radioactivity and aid in the re-certification effort, the Pu is to be chemically purified from ingrown daughters prior to redistributing into smaller units. Ingrown ^{241}Am, particularly in CRMs 137 and 136, creates a gamma dose and contributes significantly to the overall alpha activity of the material. There are several motivations for re-certification of isotopic values. The relative abundances of ^{241}Pu and ^{238}Pu have decreased significantly due to decay since certification. Additionally, there have been substantial advances in mass spectrometry technology and techniques in the decades since the original certification measurements were made. With higher-precision isotopic measurements now prevalent, concerns about measurement biases are at a finer scale than previously resolvable, thus analytical laboratories require higher-precision isotopic standards for quality control purposes. Based on recent measurements described below, we expect that the re-certification effort will reduce the relative uncertainties of Pu isotopic abundances by a factor of 3 to 4. There is also a desire within the nuclear forensic community for radiochronometry reference materials, and while NBL PO has no imminent plans to certify model age or parent-daughter isotope ratios, the purified and re-certified Pu isotopic CRMs may be appropriate as working reference materials for radiochronometry.

Over the years, the NBL investigated the magnitude of possible biases in the Pu isotopic ratios of C136, C137 and C138, and more recently the NBL PO requested analytical data from LLNL and the International Atomic Energy Agency (IAEA) to support their evaluation. Table 1 summarizes results of extensive measurements made by the three labs, which overall indicate that the new certified values for 240/239 Pu isotopic ratios may be expected to decrease by -0.02% for C136 and C137 and to increase by 0.04% for C138. These anticipated shifts are well within the stated uncertainties of the certified values, so there is no evidence of significant bias in the certificates. Given the remarkable agreement between results from different methods and laboratories, combined with the use of a gravimetrically prepared and independently measured plutonium calibration standard (C128), the NBL PO expects that the relative uncertainty in 240/239 for CRM 137A after re-certification measurement campaigns can be reduced to approximately 0.03%. The NBL PO additionally plans to re-issue the original C136, C137 and C138 certificates with updated values and uncertainties based on these measurements, along with comparative measurements from other units of the CRMs.

Table 1: Summary of 240/239 isotopic measurements undertaken to investigate whether any certificate biases exist for CRMs 136, 137, or 138.

Laboratory, Year	CRM	n	% RD from Certificate	Certified Uncertainty	Analytical method*
LLNL, 2019	C126A	30	0.0032 %	± 0.026 %	MC-ICP-MS
IAEA,	C126A	27	0.006 %	± 0.026 %	TIMS
NBL, 2003	C136	22	-0.018 %	± 0.12 %	TIMS
NBL, 1999-2001	C136	11	- 0.021 %	± 0.12 %	TIMS Frac Correction
NBL, 1999-2001	C136	39	- 0.020 %	± 0.12 %	TIMS Total Evaporation
IAEA	C137	18	-0.021 %	± 0.12 %	TIMS
NBL, 2003	C137	25	-0.022 %	± 0.12 %	TIMS
NBL, 1999-2001	C137	14	- 0.029 %	± 0.12 %	TIMS Frac Correction
NBL, 1999-2001	C137	47	- 0.019 %	± 0.12 %	TIMS Total Evaporation
LLNL, 2019	C138	54	0.034 %	± 0.12 %	MC-ICP-MS

* MC-ICP-MS = multicollector inductively coupled mass spectrometry
TIMS = thermal ionization mass spectrometry

TEST SCALE SUB-UNIT CHARACTERIZATION

Several 100 µg aliquots of NBL C137 Pu sulfate tetrahydrate were prepared in 20 mL glass vials at some time in the past and were expected to have similar chemical composition and concentrations of contaminants as the bulk 245 mg C137 Pu sulfate tetrahydrate units. Thus, one of these units was characterized to assess the levels of actinide impurities, and several were used to test Pu purification chemistry. For preliminary characterization, the residue was dissolved in 4 M HNO_3/0.01 M HF and transferred quantitatively to a pre-weighed 30 mL Savillex Teflon vial with a total solution mass of approximately 18 g. A gravimetric aliquot was removed from this solution for characterization.

The masses of Pu, U and ^{241}Am were determined via MC-ICP-MS with a NuPlasma-HR using standard isotope dilution methodology with in-house ^{244}Pu, ^{233}U, and ^{243}Am spikes, respectively. As no isotope dilution spike was available for Np, the mass of ^{237}Np was determined using a method documented elsewhere (Williams et al. 2019) which employs ^{239}Np as an isotopic tracer and gamma spectrometry to determine the yield from purification chemistry. Table 2 summarizes the concentrations of the progeny relative to Pu. The Pu and U isotopic compositions were also measured via MC-ICP-MS, and the ^{237}Np-^{241}Am-^{241}Pu, ^{236}U-^{240}Pu, and ^{235}U-^{239}Pu radiochronometers were assessed. The model date given by the ^{241}Am-^{241}Pu chronometer indicates complete purification from Am in September 1970. This is consistent with the historical record which shows that a 169 g batch of the source material was purified by anion exchange and converted to the sulfate form between September 1 and November 4, 1970 (Mason & Narayanan 2010). The Np measurement indicates that at the time of complete ^{241}Am removal the material still contained approximately 280 ppm ^{237}Np. Both U-Pu chronometers indicate that the sample was purified from uranium in March-April 1972. It is unknown whether the apparent open-system behavior of the uranium daughters is specific to these 100 µg aliquots or would also be observed in the larger units, however, characterization of progeny concentrations in the 0.25 g units prior to purification and aliquoting is outside our project scope.

Table 2: Relative concentrations of contaminants measured in a 100 μg sub-unit of C137.

Contaminant	g contaminant per g Pu
U	3.00E-03
^{241}Am	4.35E-02
^{237}Np	2.64E-03

TEST SCALE PURIFICATION CHEMISTRY

Anion exchange chromatography was selected as the purification method as it is straightforward and known to be effective at removing Am from Pu, Am being the primary radiological contaminant. To improve purification from U daughters we opted for Eichrom AG-1-X4 anion exchange resin rather than the AG-1-X8 resin that we normally use, and to perform two cycles of anion exchange chemistry. Anion exchange resin was cleaned and converted to nitrate form. Seastar ultrapure acids were used, and the process uranium blank was shown to be negligible. Several variations of the anion exchange procedure were tested with sub-unit aliquots ranging from 45 to 100 μg Pu and evaluated for Pu yield and decontamination from Am, Np, and U using a combination of gamma spectrometric and MC-ICP-MS measurements (Parsons-Davis et al. 2020). Different Pu valence state adjustment reagents were tested with a ^{239}Np radiotracer to see if there were significant differences in Np elution behavior, and we found that 6-7% Np eluted in the HCl/HI Pu elution fraction whether H_2O_2 or $NaNO_2$ was used. As complete purification from Np is not the primary concern of this project, we did not pursue alternative chemistry schemes that may have improved the separation. The use of H_2O_2 was initially favored as it has demonstrated improved yields for Pu anion exchange at the g scale (Henderson 2021) and kg scale (Marsh & Gallegos 1987). However, in the test scale chemistry we obtained inconsistent results and very poor Pu yield using overnight H_2O_2 treatment. Therefore, the procedure adopted will use $NaNO_2$ and H_2O_2 would be used in recovery efforts if too much Pu is lost to the colloidal phase. In the 100 μg tests the initial dissolution of the sulfate with nitric acid appeared to produce primarily Pu(IV) as expected. At 79.5 ± 0.5 % the test-scale yield of the adopted procedure was not optimal but acceptable for the planned production effort, and the decontamination factors were 1.66E+03, 1.14E+05, and 6.29E+02 for U, Am, and Np, respectively. Figure 1 shows a schematic of the purification procedure in the context of the planned C137A production.

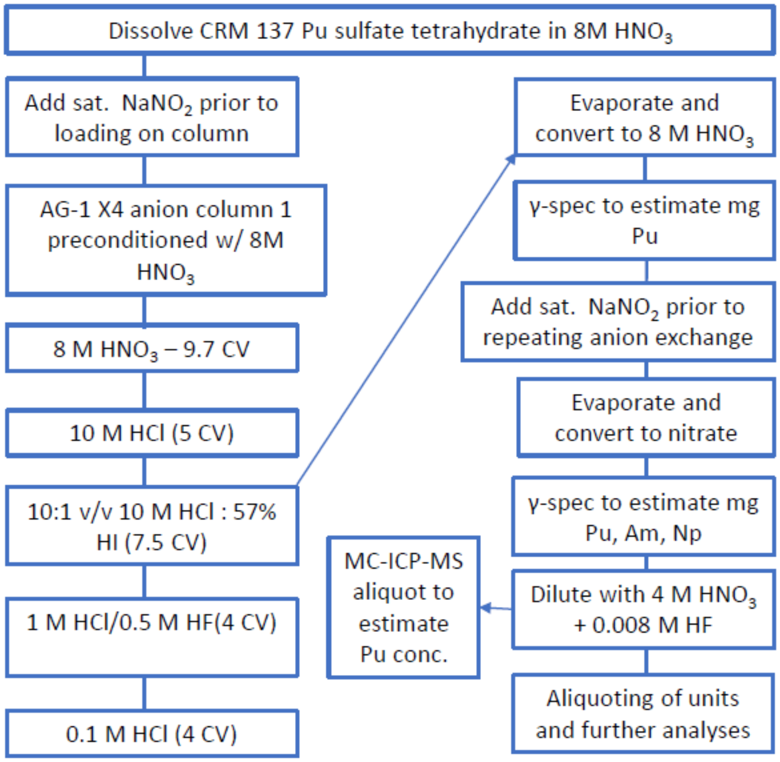

Figure 1: Schematic showing the planned chemical processing of C137 by anion exchange prior to aliquoting as 1 mg units of C137A.

PRODUCTION OF C137A

The production of C137A via purification and aliquoting of CC137 according to Figure 1 is planned to occur in a new glovebox in Building 151 at LLNL, which is a radiological facility. A detailed work plan was collaboratively prepared by LLNL and NBL PO, and execution of the work is imminent at the time of this manuscript. A single unit each of C136, 137, and 138 was shipped from Los Alamos National Laboratory to the Superblock, a Category 2 nuclear facility at LLNL for storage until each production run. The processing of the material in B151 was carefully planned with extra scrutiny as the activities of the C137 unit represent a significant fraction of the facility limits. The procedure has already been tested with blank solutions to verify that the planned process is mechanically sound. Glass columns with a 10 mL bed volume were custom made by Ace glassware, and 240 mL Savillex jars will be used to collect eluted solutions. For the evaporation and distillation of HCl/HI fraction, concentrated nitric acid is added prior to connecting the jar to a gentle flow of N_2 gas and a set of Savillex impingers to trap and neutralize acid fumes. After two cycles of anion exchange chemistry the Pu will be converted to nitrate form and diluted in 4 M HNO_3/0.008 M HF. The Pu concentration will be measured by isotope dilution MC-ICP-MS, then a Hamilton 600 auto dispenser will be used to aliquot 1 mg Pu into each of 110 30 mL FEP bottles. The solution will be dried slowly, then each bottle packaged appropriately for distribution as C137A.

Amidst the dispensing of C137A units, three analytical aliquots will be dispensed into pre-weighed bottles and diluted for analyses. Initial “t=0” measurements of Pu isotopic composition, Pu assay, ^{241}Am assay, ^{234,235,236}U assay, and ^{237}Np assay will be made for aliquots of all 3 solutions shortly after purification. Pu isotopic composition aliquots will be diluted for aspiration into the NuPlasma HR MC-ICP-MS and instrumental mass bias correction for all Pu isotope ratios will be made using the standard-sample-standard bracketing technique and the CRM 128 Pu standard. Alpha counting sources will be electrodeposited and counted with Ortec Ultra-AS detectors to measure the relative ^{238}Pu abundance. The ^{244}Pu spike to be used for isotope dilution measurements was prepared as described in Essex et al. 2019. Americium will be isolated from aliquots via 2 cycles of anion exchange in 9 M HCl, and ^{241}Am will be measured by IDMS using a very-high purity ^{243}Am provided by NPL (UK) to the US nuclear forensic community. The U isotopes 234, 235, and 236 will be measured by IDMS using a high-purity U-233 spike prepared in-house and calibrated with natural-U standard solutions of NBS 960 (CRM 112A). Uranium will be isolated from the spiked aliquots via LaF_3 precipitation to remove bulk Pu, with further Pu removed by Eichrom TEVA resin column chromatography followed by U purification with UTEVA resin. Np will be measured according to R.W. Williams et al., 2019. Aliquots of Pu will be spiked with ^{239}Nptracer and then three HNO_3-MeOH-HAmHCl columns will be run sequentially, ensuring that Np is purified sufficiently from Pu to avoid excessive instrument contamination and to eliminate interferences (tailing) during mass spectrometry.

Production and informational measurements of C137A are expected to occur in the early Fall 2021 and will be followed by measurements to support the certification of C137A as a Pu isotopic standard. Production of C136A and C138A and their associated measurements are expected to occur in 2022.

RECERTIFICATION PLANS

The certification of the plutonium isotopes will be performed using the NBL PO mode of certification involving value assignment using one or more critically evaluated methods at two or more collaborating laboratories (e.g. TIMS, MC-ICP-MS). Several laboratories have prepared measurement plans in collaboration with the NBL PO. All analyses must use C128 Plutonium 239:242 Equal Atom CRM as the primary calibrant for isotopic determinations. Target uncertainty for the purified C136A, C137A and C138A isotope ratios are summarized in Table 3 and should be achievable using C128 as calibrant in modern mass spectrometers, as demonstrated in the Certification of CRM 126A Plutonium Metal.

Table 3: Target uncertainties for new certified values of Pu isotopes in C136A, C137A and C138A.

Pu isotope ratio	Target relative uncertainty
240/239	<0.04%
238/239	~0.3%
241/239	<0.1%
242/239	<0.1%

The NBL PO has not established target uncertainties for potential certification of U, Am and Np content, U isotopic composition, and related separation date. It is possible none, some or all these isotopes will be certified at a later date depending on degree of purification and availability of methods with suitable traceability and critical evaluation. In any case, the NBL PO plans on initial issuance of Certificates for C136A, C137A and C138A which include informational values for the three. The revised Certificate of Analysis for C136, C137 and C138 will not carry new information regarding the U, Np and Am contents.

CONCLUSIONS

LLNL and NBL PO are collaborating on production of purified sub-units of the former NBS 936, 937 and 938 plutonium isotopic reference materials to be re-certified as new CRMs that will better serve the needs of the modern nuclear analytical community. Production of C137A units is set to occur in Fall 2021 and will be followed by isotopic measurement campaigns at multiple laboratories that will contribute to new certification of Pu isotopic ratios. Small sub-units of C137 were characterized and used for small-scale test chemistry. A full unit of C137 will be purified by two cycles of anion exchange in a new glovebox at LLNL and used to prepare 110 1 mg units of C137A. Informational values for Pu isotopic composition, Pu assay, ^{241}Am assay, ^{234,235,236}U assay, and ^{237}Np assay will be provided from measurements performed at LLNL shortly after purification. Production of C136A and C138A are expected to occur in 2022.

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