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LLNL-JRNL-789377

Preparation and Calibration of a ^{231}Pa Reference Material

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31-May-2019

Journal of Radioanalytical and Nuclear Chemistry

Title Page

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Lawrence Livermore IM release number: LLNL-JRNL-789377

Preparation and calibration of a Protactinium-231 reference material

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Abstract

A ^{231}Pa reference material has been characterized for amount of Pa. This reference material is primarily intended for calibration of ^{233}Pa tracers produced for ^{231}Pa - ^{235}U model age measurements associated with nuclear forensics and nuclear safeguards. Primary measurements for characterization were made by isotope dilution mass spectrometry of a purified ^{231}Pa solution using a ^{233}Pa spike. The spike was calibrated by allowing multiple aliquots of the ^{233}Pa spike solution to decay to ^{233}U and then measuring the ingrown ^{233}U by isotope dilution mass spectrometry using a certified uranium assay and isotopic standard as a reverse-spike. The new ^{231}Pa reference material will simplify calibration of the ^{233}Pa isotope dilution spikes, provide metrological traceability, and potentially reduce the overall measurement uncertainty of model ages.

Key Words

Isotope dilution mass spectrometry, Nuclear forensics, ^{231}Pa, ^{233}Pa, Radiochronometry, Reference material

Introduction

The ^{231}Pa - ^{235}U disequilibria method for determining radiometric ages of uranium bearing materials has been used extensively for dating formation ages of relatively young (< 200,000 years) geologic materials [1]. More recently, the method has been adapted for measuring model purification ages of nuclear materials [2-4]. ^{231}Pa - ^{235}U dating was initially performed using α-counting radioactivity measurement methods but the utility of activity-based measurements was hindered by the limited resolution of the technique. Pickett et al. [5] developed a ^{231}Pa - ^{235}U dating method that uses thermal ionization mass spectrometry (TIMS) to achieve faster and higher-precision measurement results. For this method, the molality of ^{231}Pa is measure by isotope dilution mass spectrometry (IDMS) using a ^{233}Pa isotopic spike. Regelous et al. [6] demonstrated ^{231}Pa IDMS measurements using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) which has the advantage greater ionization efficiency for the analyte than TIMS and comparable isotopic ratio measurement precision.

A significant barrier to routine use of the ^{231}Pa - ^{235}U dating method by the analytical community is the difficulty of preparing and calibrating a ^{233}Pa isotopic spike. The two principal methods for obtaining starting material for a ^{233}Pa IDMS spike are separation from ^{237}Np [5, 7] and thermal neutron irradiation of ^{232}Th [7-10]. The ^{237}Np nuclide has a half-life of $(2.144 \pm 0.007)\ 10^6$ years [11] decaying by α particle emission directly to ^{233}Pa with a half-life of only (26.98 ± 0.02) days [12]. ^{233}Pa approaches 99% of the secular equilibrium concentration with ^{237}Np after about 180 days, which approximates the frequency with which a ^{233}Pa spike can be "milked" from a ^{237}Np "cow". Irradiation of the ^{232}Th can produce ^{233}Pa on-demand but requires access to a sufficiently intense thermal neutron flux and appropriate handling facilities for the irradiated material.

Regardless of production method, ^{233}Pa must be separated and calibrated for amount of material to be used as an isotopic spike and has a useful lifetime a just a few months. Calibration of ^{233}Pa has traditionally been performed by reverse-IDMS using geological materials containing uranium that is assumed to be in secular equilibrium with its decay products. This calibration method requires a difficult dissolution of a silicate rock material, is fundamentally dependent on a known or precisely measured uranium concentration, and results in a complicated traceability chain for the measurements. Naperstkow et al. [10] avoided the use of rock standards for reverse IDMS by

employing efficiency traced liquid scintillation (CIEMAT/NIST[1]), 4πβ-γ coincidence, and 4πβ-γ anticoincidence radioactivity measurement methods to calibrate a ^{233}Pa solution with resulting uncertainties between 0.8 % and 1 % ($k = 2$). This activity-based calibration is robust and traceable but requires sophisticated counting methods that are not routinely used outside of laboratories that specialize in radioactivity measurements. Varga et al. [4] demonstrated an indirect calibration for ^{233}Pa by using γ-counting methods to calibrate the amount of ^{237}Np in a solution that was in secular equilibrium with its ^{233}Pa daughter and adding the unseparated Np solution directly to analysis samples. Although this method avoided a laborious ^{233}Pa spike calibration and bias due to potential loss of ^{233}Pa during separation from Np, the indirect ^{233}Pa calibration had a relative uncertainty of greater than 2% ($k = 2$). Treinen et al. [13] recently demonstrated that accurate and reproducible ^{233}Pa calibrations can be achieve with less difficulty and equivalent or lower uncertainties than calibrations using rock standards or activity measurements by using a "known" high-purity ^{231}Pa material as a reverse-spike.

The ^{231}Pa nuclide has a moderately long half-life of (32670 ± 520) years [11]. Accordingly, a batch of purified ^{231}Pa can be standardizing for amount of material (mol) and be used as a calibration reference material with a shelf life of 20 years or more. A ^{231}Pa reference material that can be analyzed in parallel with unknown samples would simplify calibration of ^{233}Pa isotopic tracers, increase the reliability of these measurements, and decrease uncertainties of ^{231}Pa amount measurements by IDMS. The preparation and characterization of a ^{231}Pa reference material specifically for calibration of ^{233}Pa isotopic spikes is described here. This new reference material was produced as part of an ongoing United States Department of Homeland Security program to enhance analytical capabilities for nuclear forensics. Production of the ^{231}Pa reference material and characterization measurements were performed at Lawrence Livermore National Laboratory (LLNL). Activity measurements for verification of characterization analysis results were performed at National Institute of Standards and Technology (NIST), the National Research Council Canada (NRC), and the National Physical Laboratory in the United Kingdom (NPL).

Experimental

[1] The acronym CIEMAT/NIST refers to the two laboratories that collaborated in developing the protocol for this liquid scintillation tracing methodology; viz., the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) and the National Institute of Standards and Technology (NIST).

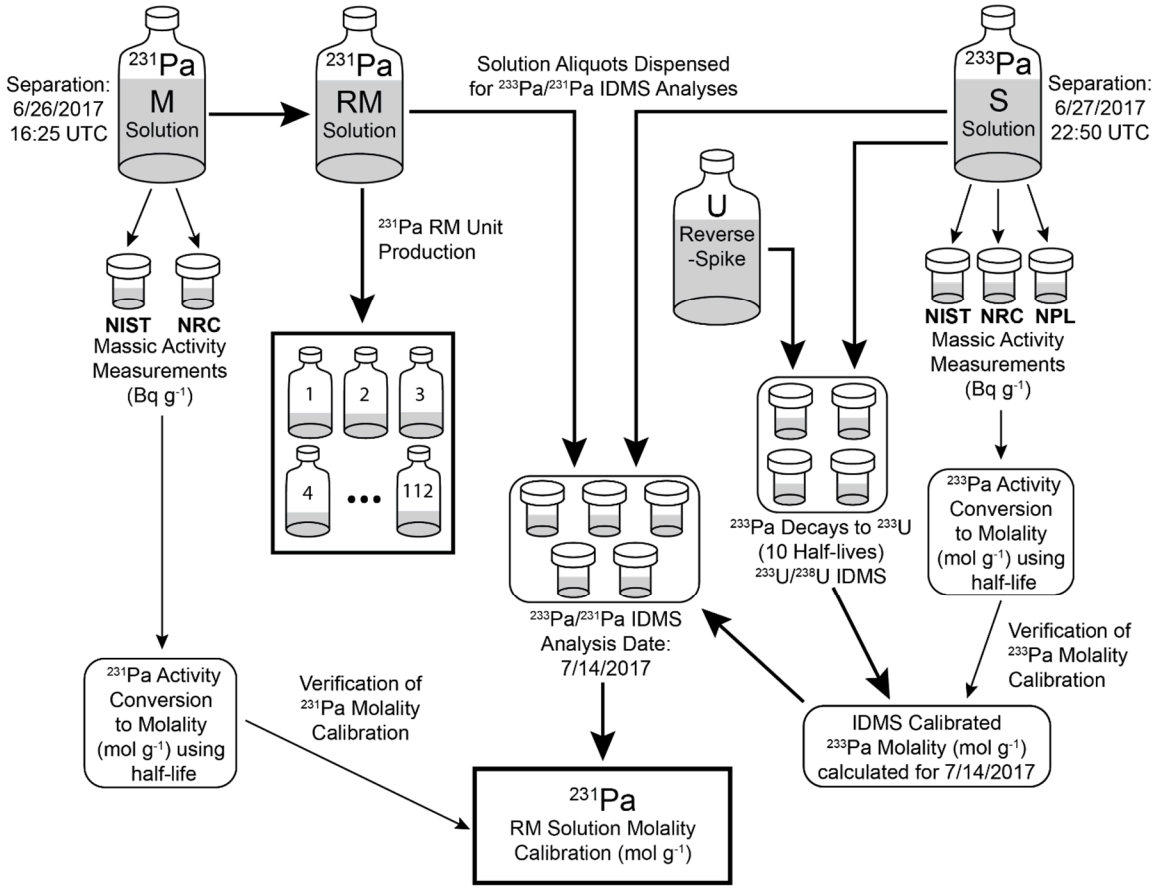

Fig. 1 Schematic of the ^{231}Pa reference material production and characterization process. The heavier arrows indicate material transfer and analyses performed for the primary calibration of the ^{231}Pa molality of the RM solution. Lighter arrows indicate material transfer and analyses for verification measurements.

Figure 1 is a schematic of the process for preparation and characterization of the ^{231}Pa reference material. A purified ^{231}Pa master (M) solution and a freshly separated ^{233}Pa spike (S) solution were prepared on consecutive days. Carefully weighed aliquots were taken from both M and S solutions and shipped to NIST, NPL, and NRC for activity measurements. A subsample of the ^{231}Pa M solution was diluted to produce the ^{231}Pa reference material (RM) solution which was aliquoted to produce individual reference material units. Aliquots of the ^{233}Pa S solution were added to subsamples of ^{231}Pa RM solution and were dispensed directly to Teflon vials for future analysis of ingrown ^{233}U by IDMS. The isotopic ratios of the mixed ^{233}Pa - ^{231}Pa samples were measured for IDMS determination of the ^{231}Pa in the RM solution molality. Radioactivity measurements were performed on the ^{231}Pa M and ^{233}Pa S solutions to verify the IDMS measurement results. The

preparation of the protactinium solutions, production of the reference material units, and characterization analyses are described in further detail below. Activity measurements performed for verification of the characterization analyses are described elsewhere [14-16] with results summarized here.

Material Preparation

LLNL staff retrieved approximately 2 mg of concentrated ^{231}Pa stored at the laboratory and performed an oxide precipitation as an initial clean up step. On 26 June 2017, 125 µg of the ^{231}Pa was subsampled and prepared as a ^{231}Pa M solution by separation from ingrown daughter products using a silica gel column chemistry technique described in Treinen et al. [13]. Immediately after separation, the purified ^{231}Pa was diluted in a solution of 2 mol L^{-1} HNO_3 (Seastar Chemicals Inc., Vancouver, Canada)[2] and 0.1 mol L^{-1} HF (Seastar Chemicals Inc., Vancouver, Canada) and sample aliquots from the M solution were and shipped to NPL, NRC, and NIST. MC-ICP-MS mass scans of the purified solution showed a $n(227)/n(^{231}Pa)$ ratio of approximately $1x10^{-7}$, indicating low levels of ^{231}Pa decay products (^{227}Ac and ^{227}Th). Another mass spectrometric analysis of the ^{231}Pa master solution was performed six months after purification. This analysis indicated a $n(227)/n(^{231}Pa)$ ratio higher than expected from ingrowth alone. Based on this data, it is estimated that approximately 85% of the 227 amu contaminant, present immediately after purification, was unsupported ^{227}Th ($T_{1/2}$ = 18.62 ± 0.09 days [17]) and the remainder was ^{227}Ac ($T_{1/2}$ = 21.782 ± 0.003 years [18]). This excess material is not detrimental to use of the ^{231}Pa as an IDMS calibration standard, but it does represent a potentially significant source of bias for radioactivity measurements of the solution performed within several months of purification.

On 13 July 2017, a subsampled of ^{231}Pa M solution was diluted to create the ^{231}Pa RM solution for preparation of the ^{231}Pa reference material units. Approximately 4 g of the ^{231}Pa M solution was transferred to a pre-cleaned and weighed 1 L FEP Teflon bottle and diluted with a mixed solution of 2 mol L^{-1} HNO_3 and 0.1 mol L^{-1} HF to an estimated molality of roughly 28 pmols g^{-1} (gravimetrically determined dilution factor of 187.279 ± 0.047, k = 2). The diluted solution (~750

[2] Certain commercial equipment, instruments, software, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

ml) was then mixed by hand shaking. Five (5) samples of the ^{231}Pa RM solution were prepared for IDMS analysis by transferring 0.5 g to 1.0 g portions of the solution to new pre-clean Savillex vials (Savillex Inc., Minneapolis, MN, USA). To minimize the potential for bias due to evaporation, these aliquots (and all subsequent spike or sample aliquots for IDMS analyses) were weighed by difference using disposable low-density polyethylene (LDPE) pycnometers with capillary tips. Multiple replicates weighings (3 to 4) of the pycnometers were made before and after dispensing solution using a calibrated 5-place XPE 105 electronic balance (Metter-Toledo, Columbus, OH, USA) that was checked use using calibrated weights.

Immediately following preparation of the analysis samples, the remaining ^{231}Pa RM solution was dispensed to produce 112 units of the ^{231}Pa reference material. Each unit is comprised of 5 mL of solution in a pre-cleaned and pre-weighed 30-mL FEP Teflon bottle that was labelled with a number corresponding to the fill order. The solution was dispensed using a Hamilton MICROLAB 600 dispenser (Reno, NV, USA) that was outfitted with a new 5 mL dispensing syringe. Teflon intake and dispensing tubing was thoroughly flushed by rinsing with a dilute HNO_3 – HF mixed solution followed by deionized water. Immediately prior to dispensing the ^{231}Pa Stock solution, approximately 30 mL of 2 mol L^{-1} HNO_3 - 0.1 mol L^{-1} HF solution was run through the apparatus (5 or 6 dispensing cycles). The uptake tubing was then transferred to the Stock bottle and 30 mL of the solution was dispensed before filling the first reference material unit. Each filled unit was tightly capped immediately after receiving the stock solution and all units were then carefully reweighed. The reference material units were filled in single effort lasting approximately 1 hour. The mean mass of dispensed solution was 5.2978 g with an expanded uncertainty of (k = 2) of 0.0022 g. Individual unit bottles were packaged by wrapping the top of the bottle and cap with Teflon tape which, in turn, was wrapped with vinyl tape to prevent loosening of the cap or unravelling of the Teflon tape. Each bottle was placed in an individual aluminized Mylar pouch along with acid-resistant absorbent pads and the pouch was then heat sealed.

A single batch of ^{233}Pa was prepared for calibration measurements and for use as an IDMS spike. A stock of a high-purity ^{237}Np cow solution was milked for ingrown ^{233}Pa daughter product. The LLNL Np cow consists of 65 mg of Np in an HCl solution. The separation of ^{233}Pa from the Np cow was performed using an AG MP-1M anion exchange resin method detailed in Treinen et al. [13]. This purification was completed at 22:50 UTC on 27 June 2017. A MC-ICP-MS mass scan

of the separated ^{233}Pa showed a ^{233}Pa to ^{237}Np atom ratio of >3 which corresponds to an activity ratio greater than 1.0 x 10^8. The total integrated quantity of ^{233}Pa that can grow in from this proportion of ^{237}Np over the course of project activities (300 days) is also inconsequential (< 0.1 ppm relative to the starting amount of ^{233}Pa present after purification). The purified ^{233}Pa was dissolved in a volume of 2 mol L^{-1} HNO_3 and 0.1 mol L^{-1} HF to produce a ^{233}Pa S solution with an estimated massic activity of ≈ 30 kBq g^{-1} at the time of preparation. On June 28, 2017 aliquots of the S solution were transferred to Savillex Teflon vials and shipped to NIST, NRC, and NPL for activity calibrations. Another 4 aliquots of the ^{233}Pa solution were transferred to Savillex vials which were capped, weighed, and stored for later calibration by measurement of ingrown ^{233}U.

A solution made from a uranium metal assay and isotopic standard, CRM 112-A [19], was prepared as a uranium (U) reverse-spike for high-precision IDMS measurements of ^{233}U in the decayed ^{233}Pa calibration samples. The uranium solution was initially prepared in October of 2017 when a 0.25-g piece of the uranium metal was twice cleaned in 8 mol L^{-1} HNO_3 to remove any uranium oxide prior to weighing. This metal was then dissolved in a 2 mol L^{-1} HNO_3 - 0.05 mol L^{-1} HF solution to produce a relatively concentrated solution. A 2-stage serial dilution of this solution was performed to create the U reverse-spike, with a molality of (111.80 ± 0.14) pmols g^{-1} ($k = 2$).

Characterization Measurements

The 4 calibration aliquots of the ^{233}Pa S solution were stored for 298 days (decay period > 10 half-lives), until April of 2018, when the samples were reweighed to correct for any solution mass loss due to evaporation. The individual samples were then split, spiked with the U reverse-spike solution, and measured on the LLNL Nu-plasma MC-ICP-MS. Mass spectrometry analysis conditions for these measurements are described in Table 1. The $n(^{233}U)/n(^{238}U)$ isotopic ratios of the spiked samples were measured on 4 May 2018, by which time greater than 99.9% ^{233}Pa had decayed to ^{233}U but less than 0.0003% of the ingrown ^{233}U had decayed to ^{229}Th. Accordingly, uranium IDMS on these subsamples can provide a quantitative value for the amount of ^{233}Pa originally present in the purified solution.

The ^{231}Pa molality of the RM solution was measured by IDMS using the ^{233}Pa S solution as an isotopic spike. The previously prepared ^{231}Pa IDMS aliquots were mixed with aliquots of the ^{233}Pa S solution on 13 July 2017. A final purification of the IDMS mixes was performed using the silica gel method at 18:20 UTC on 14 July 2017 and the mass spectrometry analyses were performed, in duplicate, the same day. The $n(^{233}\text{Pa})/n(^{231}\text{Pa})$ isotopic ratio measurements were made on the LLNL Nu-plasma MC-ICP-MS with details of the analysis conditions provided in Table 1. To minimize decay corrections and maximize the measurable amount of ^{233}Pa, the IDMS mixes were made and the mass spectrometry analyses were performed within a few weeks of ^{233}Pa S solution preparation. Calculation of the ^{231}Pa molality for the RM solution, however, could not be performed until 10 months later when the ^{233}Pa S solution calibration was completed.

Table 1 Summarized MC-ICP-MS measurement conditions for protactinium and uranium isotopic ratio analyses of IDMS samples for the ^{231}Pa RM solution and the ^{233}Pa S solution. Revised U isotopic ratio values cited in [20] were used for CRMs U010 and U005-A.

Parameter	Pa IDMS Analyses	U IDMS Analyses
Instrument	Nu-Plasma HR MC-ICP-MS (Charlestown, MA, USA)	
Collectors	^{231}Pa L2 Faraday cup ^{233}Pa axial Faraday cup	^{233}U L3 Faraday cup ^{238}U H1 Faraday cup
Introduction System	Cetac Aridus II (Omaha, NE, USA)	
Nebulizer	Cetac PFA Nebulizer	
Nebulizer Gas Flow	0.9 L/min	0.9 L/min
Solution Uptake	100 µL/min	100 µL/min
Mass Bias CRM	CRM U010 [20]	CRM U010
Quality Control CRM	CRMs 129-A [21] & U005-A [22]	CRM U005-A & CRM 112-A
Corrections Applied	detector baseline, instrument background, detector gains, mass bias	

Verification Measurements

Radioactivity analyses of the ^{233}Pa S and ^{231}Pa M solutions were incorporated into the reference material production project as metrologically independent verification measurements for the molality of these nuclides. A primary ^{233}Pa massic activity measurement for the ^{233}Pa S solution was made by NIST using a live-timed 4πβ-γ anti-coincidence counting method (LTAC) and confirmatory measurements were made by γ-spectrometry on efficiency-calibrated HPGe detectors. Details of the methods and data reduction for these analyses are provided in [14]. NRC also performed a primary calibration of ^{233}Pa S solution using an LTAC method and performed

additional activity measurements using an ^{3}H efficiency traced liquid scintillation counting method (CIEMAT/NIST) and a Triple-to-Double Coincidence Ratio (TDCR) method [15]. Finally, the ^{233}Pa spike solution massic activity was measured by NPL using a 4πβ-γ coincidence counting method [Keightley, person communication, 7 February 2018].

Massic activity calibrations for the ^{231}Pa M solution performed by NRC included two gross LSC activity measurements methods, CIEMAT/NIST and TDCR [15]. Activity measurements of the ^{231}Pa M solution at NIST included the CIEMAT/NIST method and α spectrometry [16]. The NIST measurements were performed in July of 2017, shortly after the samples were received, and additional CIEMAT/NIST measurements were made in November of 2017. Nuclide-specific α spectrometry measurements for ^{231}Pa were made using ^{233}Pa as a yield tracer and detectors were calibrated for energy and efficiency using U, Am, and Pu electrodeposited sources.

Results

The massic activity values reported by the NMIs for the ^{231}Pa M solution and ^{233}Pa S solution are summarized in Table 2. Also shown in the table are molality values for the ^{233}Pa S solution and the ^{231}Pa RM solution that were calculated from the activity data using evaluated half-lives (and the dilution factor for ^{231}Pa RM solution). Fitzgerald et al. [16] noted that both CIEMAT/NIST and preliminary γ-spectrometry measurements of the ^{231}Pa master solution showed radioactivity in the samples declining for several weeks after receipt and then increasing again due to ingrowth of ^{231}Pa daughter products. This pattern indicates the presence of an unsupported radioactive contaminant. Activity corrections were applied to the NIST and NRC counting data for ingrowth of ^{231}Pa decay chain products and an attempt was made by NIST to perform an empirical correction for the contaminant radioactivity. This correction, however, is not likely to be sufficient due the lack of quantitative data about the amount or proportion of nuclide(s) comprising the contaminating material. NRC did not attempt to apply a correction for contaminating nuclides in the ^{231}Pa M solution.

Table 2 Measured massic activities for the ^{233}Pa S solution and ^{231}Pa M solutions and calculated molality values for the ^{233}Pa S and the ^{231}Pa RM solution are listed. ^{233}Pa molality was converted from massic activity using an evaluated half-life for the nuclide [12]. The molality ^{231}Pa RM solution was calculated from the M solution massic activity using the dilution factor (187.279 ±

0.047, $k = 2$) and the evaluated half-life for ^{231}Pa [11]. All values are decay corrected to a reference time of 27 June 2017 22:50 UTC. Uncertainties are expanded uncertainties ($U = k\ u_c$) with a coverage factor (k) of 2. NIST massic activity values are from [14] for ^{233}Pa and [16] for ^{231}Pa. All massic activity values for NRC are from [15] and the cited ^{233}Pa activity value from NPL is from [Keightley, person communication, 7 February 2018]. CIEMAT/NIST 1 and 2 refer to analyses by NRC performed on liquid scintillation counters from different manufacturers.

Analysis Laboratory	Analysis Method	*^{233}Pa S Solution* Massic Activity (Bq g^{-1})	*^{233}Pa S Solution* Molality (pmol ^{233}Pa g^{-1})
NIST	LTAC*	26320 ± 170	0.1470 ± 0.0010
	HPGe γ spectrometry	26120 ± 570	0.1459 ± 0.0032
NRC	LTAC*	26190 ± 370	0.1463 ± 0.0021
	Coincidence Counting	26340 ± 450	0.1471 ± 0.0025
	TDCR	26310 ± 220	0.1469 ± 0.0012
	CIEMAT/NIST 1	26040 ± 230	0.1454 ± 0.0013
	CIEMAT/NIST 2	26130 ± 250	0.1459 ± 0.0014
NPL	Coincidence Counting*	26340 ± 180	0.1471 ± 0.0010
Analysis Laboratory	Analysis Method	*^{231}Pa M Solution* Massic Activity (Bq g^{-1})	*^{231}Pa RM Solution* Molality (pmol ^{233}Pa g^{-1})
NIST	α Spectrometry*	2096 ± 68	27.6 ± 1.0
	Corrected CIEMAT/NIST	2154 ± 67	28.41 ± 0.73
	CIEMAT/NIST	2175 ± 67	28.7 ± 1.0
NRC	CIEMAT/NIST*	2193 ± 66	28.92 ± 0.98
	TDCR	2266 ± 41	29.88 ± 0.72

* Primary or highest confidence activity measurements, as designated by the analysis laboratories.

The results for the IDMS calibration of the ^{233}Pa S solution are summarized in Fig. 2 and details are provided Table 3. The 8 replicate measurement results agree within uncertainties and have an observed variability of only 0.07% relative standard deviation. The mean measured ^{233}Pa molality for a reference date of 27 June 2017 22:50 UTC is 0.14690 pmol g^{-1} with an expanded uncertainty of 0.00035 pmol g^{-1} (0.24 % relative, $k = 2$). This value is consistent with ^{233}Pa molality values derived from primary and confirmatory massic activities calibrations performed at the radioactivity laboratories.

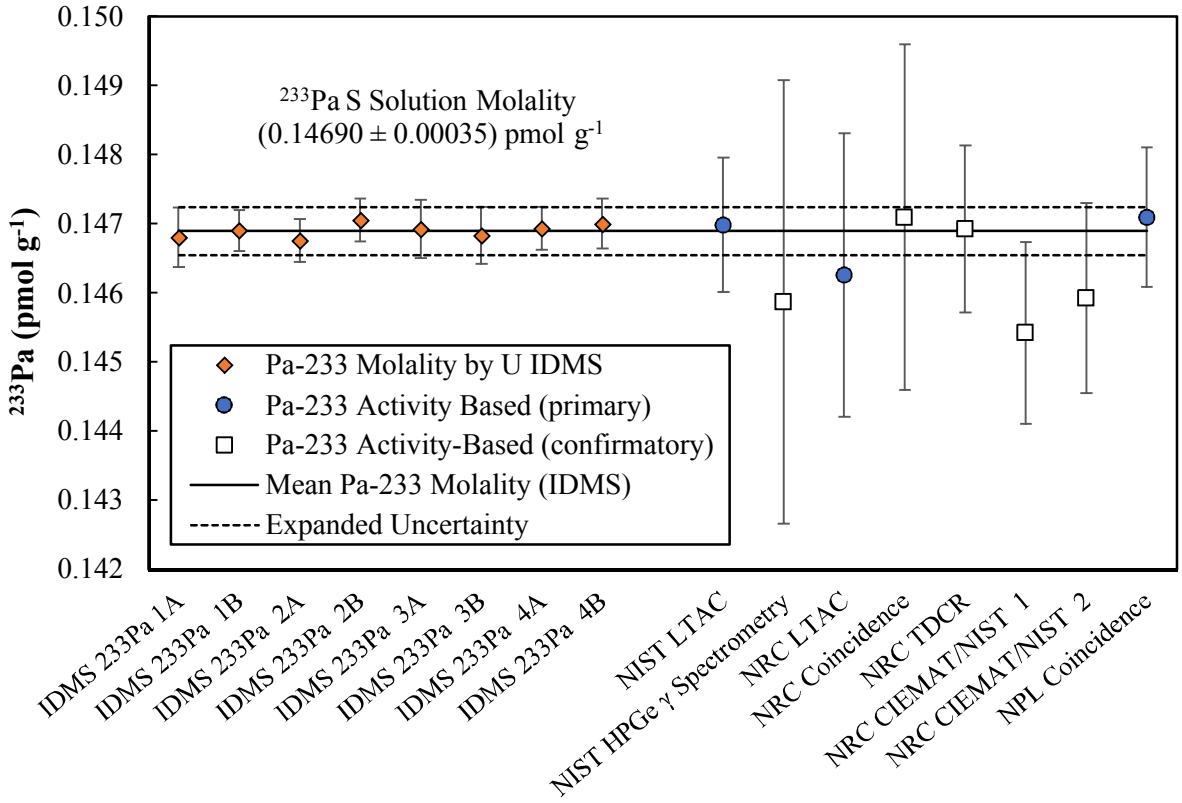

Fig. 2 Measurement data for molality of the ^{233}Pa S solution. All values are for a reference time of 27 June 2017 22:50 UTC. Error bars for data points are expanded uncertainties ($U = k\,u_c$) with a coverage (k) factor of 2. A mean value for the IDMS data (solid line) and an expanded uncertainty interval for the mean value (dashed lines) are included in the figure.

Table 3 IDMS sample data and measurement results or the ^{233}Pa S solution. The quantity measured by IDMS was the molality of ^{233}U in the decayed ^{233}Pa S solution (pmol ^{233}U g^{-1}). Corrections for solution evaporation and remaining ^{233}Pa were applied to the IDMS data to yield molality of ^{233}Pa at the reference time of 27 June 2017 22:50 UTC. Uncertainties are expanded uncertainties ($U = k\,u_c$) with a coverage factor (k) of 2. All mass values are corrected for air buoyancy.

Sample ID	^{233}Pa Spike* Aliquots (g)	U Reverse-Spike Aliquots (g)	Measured Isotope Ratio $n(^{238}U)/n(^{233}U)$	Molality (pmol ^{233}Pa g^{-1})
^{233}Pa 1A	2.0640 ± 0.0010	0.3613 ± 0.0010	132.21 ± 0.30	0.14680 ± 0.00057
^{233}Pa 1B	2.0586 ± 0.0010	0.7128 ± 0.0010	261.35 ± 0.59	0.14690 ± 0.00048
^{233}Pa 2A	1.7827 ± 0.0010	0.5993 ± 0.0010	254.01 ± 0.58	0.14676 ± 0.00049
^{233}Pa 2B	2.3084 ± 0.0010	0.6633 ± 0.0010	216.67 ± 0.49	0.14705 ± 0.00049
^{233}Pa 3A	1.6769 ± 0.0010	0.3569 ± 0.0010	160.64 ± 0.37	0.14692 ± 0.00057
^{233}Pa 3B	2.5439 ± 0.0010	0.4086 ± 0.0010	121.31 ± 0.28	0.14683 ± 0.00055
^{233}Pa 4A	1.9842 ± 0.0010	0.6033 ± 0.0010	229.45 ± 0.51	0.14693 ± 0.00049
^{233}Pa 4B	2.2204 ± 0.0010	0.4804 ± 0.0010	163.19 ± 0.37	0.14700 ± 0.00052

* Evaporation Correction Factors for ^{233}Pa sample aliquots were applied to compensate for evaporative loss over the 298-day interval between dispensing and aliquoting for IDMS. These factors were calculated as the quotient of the solution mass at the time of initial dispensing and the mass of solution immediately prior to aliquoting for IDMS analyses.

The molality of the ^{233}Pa S solution was a key variable for the protactinium IDMS measurements made to determine the molality of the ^{231}Pa RM solution. The ^{231}Pa IDMS results are shown in Fig. 3 with details provided in Table 4. These results are also highly repeatable and have an observed variability of only 0.07% relative standard deviation. The mean molality of the ^{231}Pa RM solution is 27.55 pmol g^{-1} with an expanded uncertainty of 0.12 pmol g^{-1} (0.35% relative, k = 2). The activity-based molality value calculated from alpha spectrometry measurements (Table 2) is essentially indistinguishable from the IDMS data. Activity-based molality values calculated from the LSC-based measurement methods range from 3% to 8% higher than the IDMS value.

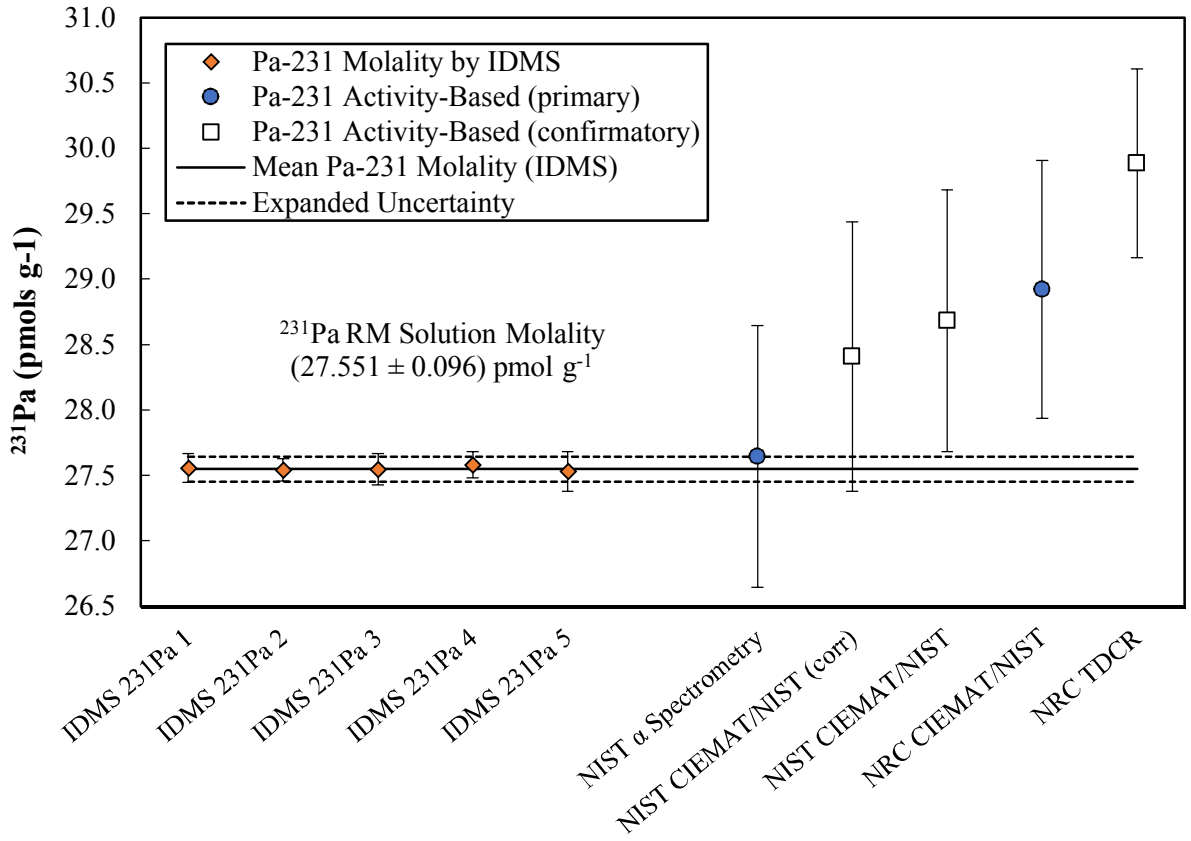

Fig. 3 Molality data for the ^{231}Pa RM solution. All values are for a reference time of 27 June 2017 22:50 UTC. Error bars for data points are expanded uncertainties ($U = k\,u_c$) with a coverage factor (k) of 2. A mean value for the IDMS data (solid line) and an expanded uncertainty interval for this mean value (dashed lines) are included in the figure.

Table 4 IDMS sample data and measurement results for the ^{231}Pa RM solution. For IDMS calculations the molality the ^{233}Pa S solution was decay corrected to the time of final purification of the protactinium IDMS mixes, 14 July 2017 18:20 UTC. Uncertainties are expanded uncertainties ($U = k\ u_c$) with a coverage factor (k) of 2. All mass values are corrected for air buoyancy.

Sample ID	^{231}Pa RM Solution Aliquots (g)	^{233}Pa Spike Aliquots (g)	Measured Isotope Ratio* $n(^{233}Pa)/n(^{231}Pa)$	Molality (pmol ^{231}Pa g^{-1})
^{231}Pa 1	0.6318 ± 0.0010	3.0843 ± 0.0010	0.016894 ± 0.000046	27.56 ± 0.13
^{231}Pa 2	1.0531 ± 0.0010	3.5580 ± 0.0010	0.011701 ± 0.000048	27.54 ± 0.11
^{231}Pa 3	0.7848 ± 0.0010	3.4152 ± 0.0010	0.015067 ± 0.000047	27.55 ± 0.14
^{231}Pa 4	0.5688 ± 0.0010	3.4580 ± 0.0010	0.021023 ± 0.000044	27.58 ± 0.12
^{231}Pa 5	0.8931 ± 0.0010	3.1462 ± 0.0010	0.012203 ± 0.000055	27.53 ± 0.16

* A correction factor (0.99936 ± 0.00059) was applied to measured $n(^{233}Pa)/n(^{231}Pa)$ ratios to account for mass spectrometer efficiency differences between ^{233}Pa and ^{233}U. The correction factor was calculated based on the relative proportion of ^{233}U that grew in over the interval between purification and the mass spectrometer measurements and an observed transmission efficiency difference between uranium and protactinium (-8.7%). This transmission difference was empirically determined based on the bias between the measured $n(^{233}Pa)/n(^{231}Pa)$ ratio of a mixed solution and the $n(^{233}U)/n(^{231}Pa)$ ratio of the same solution after the decay ^{233}Pa.

The measured masses of RM solution dispensed to the ^{231}Pa reference material units have a maximum difference of only 3.1 mg (excluding a single outlier unit) which is only 0.06% of the approximately 5.3 g mass of solution dispensed to the units. The 0.35% relative expanded uncertainty for the molality of ^{231}Pa RM solution is much greater than the range of solution masses. As a result, the difference in amount ^{231}Pa dispensed to individual reference material units is smaller than the last significant figure of the calculated amount value for each unit. Accordingly, a single ^{231}Pa amount value is applicable to every unit in the production run. This value, of (145.96 ± 0.51) pmol (k = 2), was calculated using the mean buoyancy-corrected mass of solution aliquots dispensed to the units and uncertainty components for the range of observed masses and for a correction applied to compensate for solution evaporation during dispensing. The uncertainty for the ^{231}Pa amount value for the reference material units was estimated in accordance with

international guidance for measurement uncertainty [24, 25] and includes all significant sources of uncertainty. A detailed uncertainty budget for the calculated amount of ^{231}Pa is provided in Table 5.

Table 5 ^{231}Pa reference material uncertainty budget for amount of ^{231}Pa contained in each unit. Assessment Type A denotes evaluation by statistical methods and Type B denotes evaluation by other methods. u_i% is the percent relative standard uncertainty for the indicated uncertainty component. The uncertainty model presented in this table was prepared using the GUM Workbench software (Metrodata GmbH, Weil am Rhein, Germany).

Uncertainty Component	Description	Assessment Type	u_i%
b_{231Pa}	Measurement repeatability; standard uncertainty of 5 independent measurements for ^{231}Pa molality of RM solution.	A	0.032
b_{233Pa}	Measurement repeatability; standard uncertainty of 8 independent measurements for ^{233}Pa molality of S solution.	A	0.023
$b_{C112\text{-}A}$	IDMS tracer; standard uncertainty for uranium molality of diluted CRM 112-A solution used as U reverse-spike.	B	0.090
Decay	Decay correction; uncertainties associated with the ^{233}Pa half-life and the interval between initial ^{233}Pa purification and IDMS measurements.	B	0.035
Efficiency	Transmission efficiency; uncertainty of correction factor to compensate for differing mass spectrometer transmission efficiencies between U and Pa during IDMS measurements.	B	0.030
M_{IDMS}	Aliquot mass; uncertainty component associated with mass measurements of solution aliquots for IDMS.	B	0.085
M_{unit}	Unit mass; uncertainty component encompassing the maximum difference in the mass of dispensed solution aliquots and potential evaporative loss during dispensing.	B	0.027
MassSpec	Mass spectrometry; estimated uncertainty associated with mass spectrometry including potential differences in mass fractionation of Pa and U in MC-ICP-MS, blank corrections, background corrections, and collector efficiencies.	B	0.086
R_{U010}	CRM U010; standard uncertainty of $n(^{235}U)/n(^{238}U)$ ratio for CRM used to calibrate the mass spectrometer.	B	0.051
Remainder	Remainder correction; estimated uncertainty for ^{233}U molality measurements resulting from the proportion of ^{233}Pa remaining in IDMS samples after 10 half-lives.	B	0.008
Relative combined standard uncertainty		0.173 %	
Relative expanded uncertainty (k = 2)		0.35 %	

Discussion

The goal of this project was to produce a ^{231}Pa reference material characterized for amount of ^{231}Pa. Although this material is not being provided as a Certified Reference Material (CRM) per the definition in [26], the production project was planned and executed to satisfy the quality requirements for CRMs as outlined in international guidance documents [27, 28]. General requirements for a high-quality analytical reference material include stability, homogeneity, and metrological traceability. Additionally, characterized attribute values should have GUM-compliant uncertainties [23] and independent verification of the attribute values should be performed, when possible.

Stability of the ^{231}Pa reference material units is an important consideration. Protactinium typically occurs in solution as the pentavalent cation, Pa(V), and has long been known to form colloids that adsorb onto container walls [29]. This tendency could result in highly variable characteristics for a production run of a protactinium reference material. To mitigate the potential for this source of variability, the ^{231}Pa RM solution was prepared as a mixture of 2 mol L^{-1} HNO_3 and 0.1 mol L^{-1} HF. Sub μg g^{-1} concentrations of Pa(V) are reasonably stable in HNO_3 solutions of greater than 1.0 mol L^{-1} and Pa(V) is highly soluble in HF solutions, even in relatively dilute solutions (e.g. 3.9 g L^{-1} in 0.05 mol L^{-1} HF) [30]. Furthermore, the authors have observed that protactinium in a 2 mol L^{-1} HNO_3 - 0.1 mol L^{-1} HF solution shows no apparent change in molality for durations of greater than 1 year. Although it is anticipated that the ^{231}Pa will remain in solution, it is also expected that the solution in the reference material units will change in molality due to evaporative losses of the aqueous solution from the container. To assure that the reference material will remain fit-for-purpose over the long-term, the ^{231}Pa reference material units are characterized for amount of ^{231}Pa and each unit container is weighed Teflon bottles (bottle mass values to be provided with units). With these values, a user can utilize the ^{231}Pa RM solution as received, dilute the solution in the unit container with an appropriate acid solution, or perform a quantitative transfer of the ^{231}Pa.

It is difficult to envision a mechanism that would produce unit-to-unit heterogeneity in the ^{231}Pa reference material production run. The separated protactinium used to prepare the ^{231}Pa RM solution was essentially monoisotopic and mass spectrometric analysis of the material did not indicate the presence of significant quantities of parent elements for protactinium nuclides, such

as uranium or neptunium. Considering the purity of the starting material and the fact that ^{231}Pa is the only isotope of protactinium with a half-life greater than 27 days, it can be stated, with a high degree of confidence, that the characterized reference material units are monoisotopic and therefore isotopically homogeneous. To assure that potential temporal changes to the molality of ^{231}Pa RM solutions would be minimized, the creation the RM solution, the preparation of the IDMS characterization samples, and production of the reference material units were performed during a single work day with all 112 units dispensed over a relatively short period (1 hour). Variability that could be caused by differential protactinium contamination was minimized by performing preparation and production work in a class 10000 clean facility, using only new precleaned labware for all stages of the project, and using high-purity reagents for preparation, production, and analysis (double distilled acids, 18.2 MΩ cm water). Finally, variability in the amount of material transferred to the units was constrained by use of a high-precision automated dispenser and verified by carefully weighing of all unit bottles before and after dispensing.

Metrological traceability [26] for the amount of ^{231}Pa in the reference material was maintained for the two main stages of the calibration process. First, the molality of the ^{233}Pa spike solution was measured by a primary IDMS analysis method [31, 32] which took advantage of the relatively rapid decay of ^{233}Pa to the long-lived ^{233}U nuclide (Fig. 4a). This allowed for a certified uranium assay and isotopic reference material (CRM 112-A) to be used as an isotopic spike. All masses for the analyses were measured on a calibrated balance that was checked against calibrated weight sets during project activities. Mass spectrometric measurements were corrected for instrumental bias using replicate measurement of an appropriate uranium isotopic reference material (CRM U010). A molality value for the ^{233}Pa S solution, at the time of the ^{231}Pa IDMS analyses, was calculated by using the evaluated half-life for ^{233}Pa to perform the appropriate decay correction from the time of purification. For the second stage of the calibration process (Fig. 4b), the traceable molality of the ^{233}Pa S solution was utilized for IDMS analyses of the ^{231}Pa RM solution. All masses for the ^{231}Pa IDMS sample preparation were also measured on a checked and calibrated balance. An isotopic standard for Pa is not feasible, so mass spectrometric measurements were calibrated using the certified CRM U010 isotopic reference material. Although the MC-ICP-MS mass fractionation behavior of uranium and protactinium are likely to differ [33], these differences tend to be small for neighboring elements and an uncertainty component for potential bias in the mass spectrometry results was included in the uncertainty budget for the attribute value. Finally,

the average mass for the ^{231}Pa RM solution distributed to each unit was determined from multiple replicate weighings of each sample unit on a checked and calibrated balance.

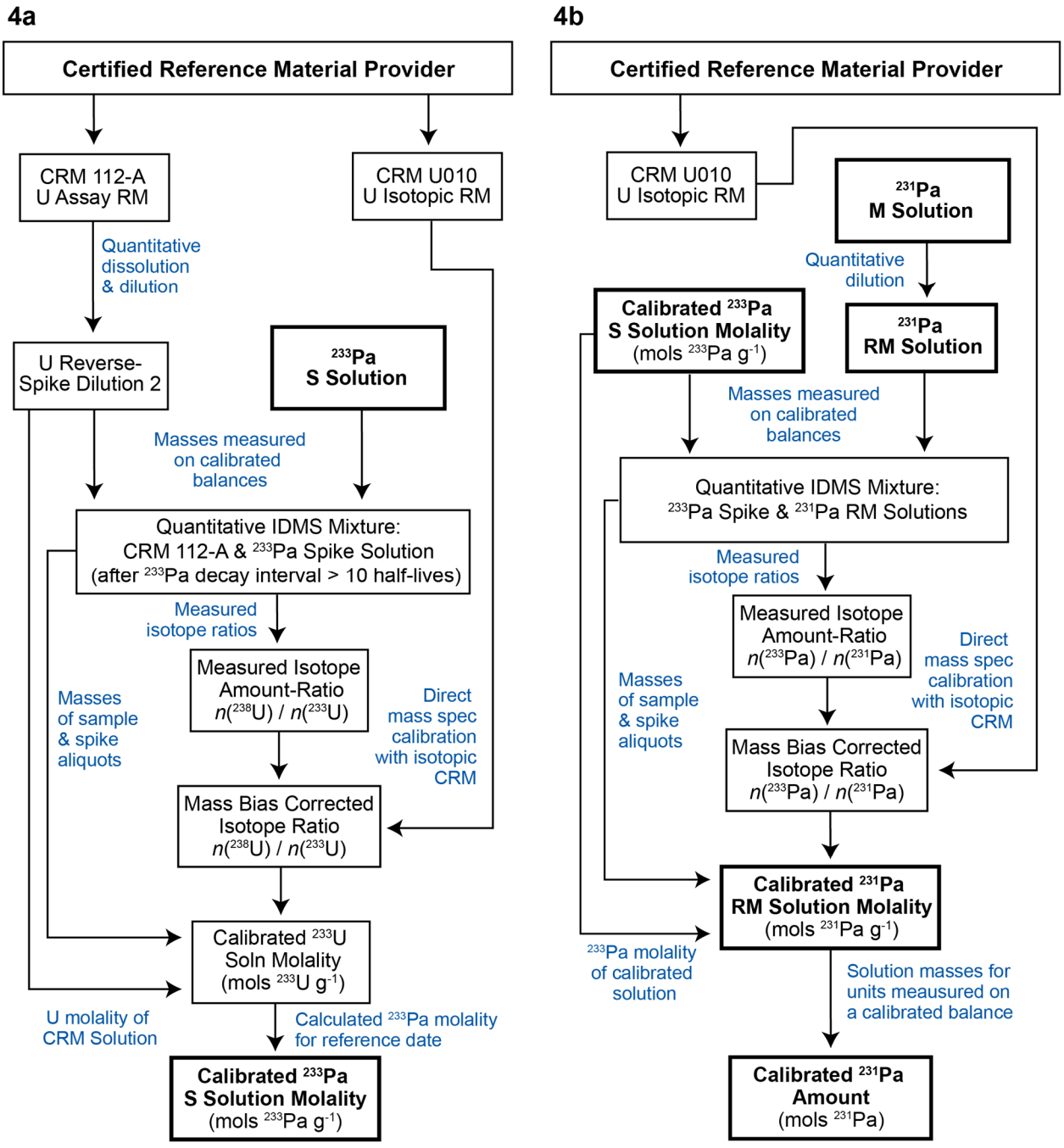

Fig. 4 Schematic of the traceability chain for amount of ^{231}Pa. The diagram indicates the direct relationship between measurements necessary for calibration of the ^{233}Pa S solution (4a) and the ^{231}Pa reference material (4b).

The molality value for the ^{233}Pa S solution, as measured by IDMS, was independently verified by activity-based analyses by NIST, NRC, and NPL, providing a high level of confidence in the calibration of this material. Several massic activity measurements of ^{231}Pa M solution by NIST and NRC, however, are consistent higher molality values in the ^{231}Pa RM solution than the IDMS measured value. Observations from mass spectrometry on the ^{231}Pa solution and the activity measurements themselves provide an explanation for this discrepancy. Mass spectrometric scans of the ^{231}Pa Master solution following the final purification procedure (prior to shipment for activity measurements) showed a small, but measurable, proportion of nuclides at 227 amu, probably ^{227}Th and/or ^{227}At daughter products. The presence of these unsupported radioactive contaminants was also observed in LSC and γ spectrometry measurements made at NIST shortly after the samples were received. Calibration methods that measure gross activity (i.e. LSC based methods CIEMAT/NIST and TDCR) must be corrected for radioactive contaminants and for ingrowth of decay chain products from the time of purification. Due to limited data available to radioactivity laboratories, developing a correction for the unsupported daughter products was not performed or could only be poorly constrained. As expected, this contamination resulted in elevated massic activities values from the LSC-based measurement methods used at NIST and NRC. The α spectrometry measurements performed at NIST had the advantage that only alpha particle energies characteristic of ^{231}Pa were measured, so these results were not affected by the presence of small proportions of unsupported daughter products. The calculated value for the ^{231}Pa molality of the Stock solution based on the α spectrometry measurements is essentially identical to the IDMS results, providing independent verification of the characterized value.

Conclusion

The molality of the ^{233}Pa S solution prepared for calibration of the ^{231}Pa RM solution was precisely measured using a primary analysis method (i.e. IDMS) and independently verified by activity measurements at 3 metrology laboratories. This uniquely well characterized ^{233}Pa material enabled high-precision primary measurements of the reference material solution used to prepare units of the ^{231}Pa reference material which were verified by independent α spectrometry measurements at NIST. Individual reference material units were carefully prepared from the ^{231}Pa RM solution resulting in a metrologically traceable reference material that is suitable for calibration of ^{233}Pa spikes produced by analytical laboratories on an as needed basis. The relative expanded

uncertainty of the reference material is 0.35% which should allow for reliable ^{233}Pa spike calibrations with an expanded uncertainty of 0.5% or better and similarly well constrained measurements of ^{231}Pa amount for determination of ^{231}Pa-^{235}U radiochronometric model ages.

Acknowledgement

Funding for project at LLNL and at NIST was provided by the United Stated Department of Homeland Security. Analyses performed at NRC and NPL were internally funded.

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