Preparation and calibration of a ^{231}Pa reference material

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Abstract

A ^{231}Pa reference material has been characterized for amount of protactinium. This reference material is primarily intended for calibration of ^{233}Pa tracers produced for ^{235}U–^{231}Pa 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 isotopic 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.

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

Introduction

Determining the date of the most recent processing step that resulted in separation of a special nuclear material, such as plutonium or enriched uranium, from its daughter products is one of the most diagnostic attributes than can be derived from nuclear forensic analyses. These dates are referred to as model purification ages and are calculated from the measured atomic ratio of parent–daughter nuclide pairs. The radioactive decay of ^{235}U to ^{231}Pa has been used for determining radiometric ages of relatively young ($< 200,000$ a) uranium-bearing geologic materials since the 1950s [1]. More recently, ^{231}Pa–^{235}U dating has also been utilized to measure model purification ages of uranium materials associated with the nuclear fuel cycle [2–4]. Initially, ^{235}U–^{231}Pa dating was performed using α-counting radioactivity measurement methods but the utility of the 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 more precise measurement results. For this method, the amount of ^{231}Pa in a sample is measured by isotope dilution mass spectrometry (IDMS) using a ^{233}Pa isotopic spike. Regelous et al. [6] demonstrated that ^{231}Pa IDMS measurements can be performed using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) instead of TIMS and noted that the greater ionization efficiency of the MC-ICP-MS method is advantageous when measuring the minute quantity (ng to fg) of ingrown ^{231}Pa that is present in most samples. Despite these advances, the difficulty of preparing and calibrating a ^{233}Pa isotopic IDMS spike has been a significant barrier to routine use of ^{235}U–^{231}Pa dating by the nuclear forensic analytical community.

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 $(2.144 \pm 0.007) \times 10^6$ a [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

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of ^{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, to use ^{233}Pa as an isotopic spike it must be separated from other radionuclides and then calibrated for amount of substance (mol). Once prepared and calibrated, a batch of ^{233}Pa has a useful lifetime of just a few months before there is insufficient material for mass spectrometric analysis.

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 and reverse IDMS by employing efficiency traced liquid scintillation counting (CNET[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% ($k=2$). Although this traceable activity-based calibration was performed using sophisticated counting methods that are not routinely used outside of laboratories specializing in radioactivity measurements, an ion chamber can be calibrated for more routine activity-based ^{233}Pa spike characterization. Varga et al. [4] demonstrated an indirect calibration for ^{233}Pa by using γ-counting methods to measure the molality (mol g^{-1}) of ^{237}Np in a solution that was in secular equilibrium with its ^{233}Pa daughter and adding the unseparated neptunium solution directly to analysis samples. This method avoids a laborious ^{233}Pa spike calibration but will typically have a relatively large uncertainty ($> 2\%$, $k=2$) due to the limits of neptunium assay measurements. More recently, Treinen et al. [13] demonstrated the use of a characterized solution of high-purity ^{231}Pa as a reverse-spike for accurate and reproducible ^{233}Pa calibrations. This calibration was accomplished with less difficulty than rock standards and with uncertainties that are equivalent to, or lower than, those that can be reasonably obtained using activity measurements.

The ^{231}Pa nuclide has a half-life of $(32\,670 \pm 520)$ a [11], which is sufficiently long for a batch of purified ^{231}Pa to be prepared as a calibration reference material with a shelf-life of 20 years or even considerably longer. A ^{231}Pa reference material could be utilized to perform reverse-IDMS

calibrations in parallel with ^{233}Pa IDMS analyses of unknown samples. This would simplify calibration of ^{233}Pa isotopic tracer, increase the reliability of the IDMS measurements, and reduce uncertainties of ^{231}Pa amount measurements made on unknown samples. The preparation and characterization of such 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 the primary characterization value were performed at National Institute of Standards and Technology (NIST), the National Research Council of Canada (NRC), and the National Physical Laboratory in the United Kingdom (NPL).

Experimental

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. Additional aliquots of the S solution were dispensed for analysis of ingrown ^{233}U by IDMS. A subsample of the ^{231}Pa M solution was then diluted to produce the ^{231}Pa reference material (RM) solution which was dispensed to create individual reference material units. In parallel with unit production, subsamples of RM solution were spiked with the S solution. The protactinium isotopic ratios of the mixed ^{233}Pa–^{231}Pa samples were measured to determinate the molality of ^{231}Pa in the RM solution by IDMS. Radioactivity measurements performed on the M and S solutions were used for verification of IDMS measurement results. 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 [13–15] with results summarized here.

Material preparation

An initial clean up step was performed on approximately 20 mg of ^{231}Pa stored at LLNL. This procedure, described in [16], is a precipitation of a hydrous protactinium oxide ($Pa_2O_5 \cdot xH_2O$) from a HF acid solution and repeated rinses of the precipitate. After this step, the protactinium was

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[1] The acronym CNET refers to the ^{3}H efficiency-traced liquid scintillation counting methodology developed by Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) and the National Institute of Standards and Technology (NIST). This method is also referred to as the CIEMAT/NIST method.

Fig. 1 ^{231}Pa reference material production and characterization process. The "M Solution" is the concentrated ^{231}Pa master solution purified for this project. The "RM Solution" is a stock solution prepared for production of reference material units and the "S Solution" is the ^{233}Pa spike prepared for primary calibration of the RM solution. Heavier arrows in the figure indicate material transfers and analyses performed for the primary calibration for the molality of ^{231}Pa in the RM solution. Lighter arrows indicate material transfer and analyses for verification measurements
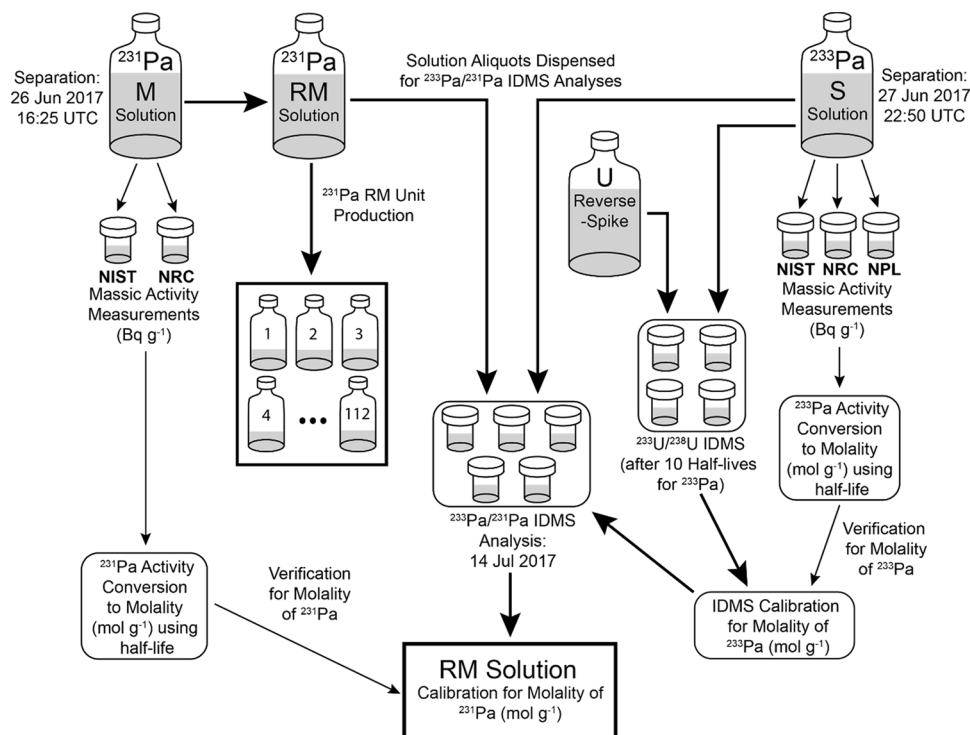
again dissolved in HF (Seastar Chemicals Inc., Vancouver, Canada)[2] and a subsample containing 2 mg protactinium was dried first in perchloric acid and then dried two times in concentrated HNO$_3$ (Seastar Chemicals Inc., Vancouver, Canada). An additional separation was then performed on this sample using a silica gel column chemistry technique described in Treinen et al. [17]. A subsample of this purified material (approximately 125 µg of ^{231}Pa) was prepared as the M solution by diluting the ^{231}Pa in a mixed solution of 2 mol L^{-1} HNO$_3$ and 0.1 mol L^{-1} HF. Aliquots of the M solution (5 mL) were transferred to Savillex perfluoroalkoxy (PFA) Teflon vials (Minneapolis, MN, USA) and shipped to NPL, NRC, and NIST for massic activity measurements. MC-ICP-MS mass scans of the purified M solution showed a $n(227)/n(^{231}$Pa$)$ ratio of approximately 1×10^{-7}, indicating low levels of ^{231}Pa decay products (^{227}Ac and ^{227}Th). Another mass spectrometric analysis of the ^{231}Pa master solution, performed 6 months after purification, indicated a $n(227)/n(^{231}$Pa$)$ ratio that was 0.9% higher than expected from ingrowth alone. Based on these data, it is estimated that approximately 85% of the 227 amu contaminant, present immediately after purification, was unsupported ^{227}Th

($T_{1/2} = 18.62 \pm 0.09$ days [18]) and the remainder was ^{227}Ac ($T_{1/2} = 21.782 \pm 0.003$ a [19]). 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, particularly measurements performed within several months of purification.

The RM solution was prepared from the M solution as a stock material for production of the reference material units. A 4 g subsample of the M solution was transferred to a pre-cleaned and weighed 1 L fluorinated ethylene propylene (FEP) Teflon bottle, diluted with 650 mL of a mixed 2 mol L^{-1} HNO$_3$ and 0.1 mol L^{-1} HF solution, and homogenized by hand shaking (gravimetrically determined dilution factor is 187.279 ± 0.047, $k = 2$). Five (5) subsamples of the ^{231}Pa RM solution were prepared for IDMS analysis by transferring carefully weighed aliquots (0.5–1.0 g) to new pre-cleaned Savillex vials. The potential for weighing bias due to evaporation during dispensing was minimized for these subsamples (and all subsequent spike or sample aliquots for IDMS analyses) by transferring the solution using disposable low-density polyethylene pycnometers (Canus Inc., Ottawa, Canada) with capillary tips. Masses of the subsamples were determined by the difference between the pycnometer mass when filled with solution and after dispensing. At least 3 replicates weighings were performed for all mass measurements. The balance used for this work was a calibrated 5-place XPE 105 electronic balance (Metter-Toledo, Columbus, OH, USA) that was regularly checked for accuracy and linearity using a calibrated weight set.

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[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.

Following preparation of the IDMS analysis samples, the RM solution was dispensed using a Hamilton MICRO-LAB 600 dispenser (Reno, NV, USA) outfitted with a new 5 mL dispensing syringe. Intake and dispensing tubing was thoroughly flushed by rinsing with a dilute HNO_3 and HF mixed solution followed by deionized water. Prior to dispensing the RM solution, approximately 30 mL of mixed 2 mol L^{-1} HNO_3 and 0.1 mol L^{-1} HF solution was run through the apparatus (6 dispensing cycles). The uptake tubing was then transferred to the RM solution stock bottle and 30 mL of the solution was dispensed before filling the first reference material unit. A total of 112 ^{231}Pa reference material units were prepared with each unit comprised of 5 mL of solution in a pre-cleaned and pre-weighed 30 mL FEP bottle that was previously labelled with a number corresponding to the order in which the bottle was filled. Each unit was tightly capped after receiving the solution and all units were then carefully reweighed. The reference material units were filled in a single effort lasting approximately 1 h. The mean mass of dispensed solution was 5.2978 g with an expanded uncertainty of 0.0022 g ($k = 2$). Individual unit bottles were packaged by wrapping the top of the bottle and cap with polytetrafluoroethylene (PTFE) Teflon tape which, in turn, was wrapped with vinyl tape to prevent loosening of the cap or unravelling of the PTFE 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 batch of ^{233}Pa IDMS spike was prepared by separation from a high-purity ^{237}Np solution (65 mg of ^{237}Np in HCl). This separation was performed using an AG MP-1 M anion exchange resin followed by a silica gel separation, as described in [17]. The purification procedure was completed at 22:50 UTC on 27 June 2017. A 1 mol L^{-1} HNO_3 solution is used in the silica gel separation procedure as a rinse prior to eluting the protactinium. MC-ICP-MS mass scans of this rinse solution indicated a $n(^{233}$Pa$)/n(^{238}$U$)$ ratio of approximately 0.011 whereas ^{238}U was not observed in the separated ^{233}Pa; thus demonstrating the protactinium was quantitatively separated from uranium, including ingrown ^{233}U. Mass scans of the separated protactinium also indicated a $n(^{233}$Pa$)/n(^{237}$Np$)$ atom ratio of > 3 which corresponds to an activity ratio greater than 1.0×10^8. The total integrated quantity of ^{233}Pa that could grow in from this proportion of ^{237}Np, over the course of project activities (300 days), is inconsequential ($< 0.01\%$ relative to the amount of ^{233}Pa present after purification). The purified ^{233}Pa was dissolved in a mixed 2 mol L^{-1} HNO_3 and 0.1 mol L^{-1} HF solution to produce the ^{233}Pa S solution with an estimated massic activity of ≈ 30 kBq g^{-1} at the time of preparation. On 28 June 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 vials which were capped, weighed, and stored for later measurement of ^{233}U.

A uranium (U) reverse-spike was prepared for high-precision IDMS measurements of ^{233}U in the decayed ^{233}Pa calibration samples. The starting material for the reverse-spike was CRM 112-A uranium metal assay and isotopic standard [20]. For initial preparation of the uranium solution, a 0.25 g piece CRM 112-A metal was twice cleaned in 8 mol L^{-1} HNO_3 to remove any uranium oxide prior to weighing. The metal was then dried, weighed, and dissolved in 70 mL of a mixed 2 mol L^{-1} HNO_3 and 0.05 mol L^{-1} HF solution to produce a relatively concentrated master solution. A 2-stage serial dilution of this uranium master solution was performed to create the U reverse-spike with a molality of (111.80 ± 0.14) pmol g^{-1} ($k = 2$).

Characterization measurements

The 4 calibration aliquots of the S solution were stored for period of 298 days, after which the samples were reweighed to correct for any change to the solution mass due to evaporation. Individual samples were then split, mixed with the U reverse-spike solution, and measured on the LLNL Nu-plasma HR MC-ICP-MS (Nu Instruments Ltd, Wrexham, UK). 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% of ^{233}Pa initially present in the S solution had decayed to ^{233}U but less than 0.0003% of the ingrown ^{233}U had decayed to ^{229}Th. Accordingly, with only a small correction for remaining ^{233}Pa, uranium IDMS on these subsamples provides a quantitative value for the amount of ^{233}Pa originally present in the purified solution.

The molality of ^{231}Pa in the RM solution was measured by IDMS using the ^{233}Pa S solution as an isotopic spike. IDMS aliquots of the RM solution were mixed with aliquots of the S solution and a final purification of the mixed solutions was performed using the silica gel method. The $n(^{233}$Pa$)/n(^{231}$Pa$)$ isotopic ratio measurements for the IDMS analyses were performed, in duplicate, approximately 7 h after purification. These measurements were made on the LLNL Nu-plasma MC-ICP-MS; details of the analysis procedure are provided in Table 1. The protactinium IDMS analyses were performed 17 days after purification of the ^{233}Pa S solution, so 35% of the ^{233}Pa in the spike had decayed, requiring a substantial decay correction.

Verification measurements

Massic radioactivity analyses for ^{233}Pa in the S solution and ^{231}Pa in the M solutions were incorporated into the reference material production project as metrologically independent

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

Parameter	Pa IDMS analyses	U IDMS analyses
Instrument	Nu-plasma HR multi-collector inductively-coupled plasma mass spectrometer	
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 [22]	CRM U010
Quality control CRM	U005-A [23] and CRMs 129-A [24]	CRM U005-A and CRM 112-A
Corrections applied	Detector baseline, instrument background, detector gains, mass bias	

Revised uranium isotopic ratio values cited in [21] were used for CRMs U010 and U005-A

verification measurements for the molality of these nuclides. A primary [233]Pa massic activity measurement for the S solution was made by NIST using a live-timed $4\pi\beta$-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 [13]. NRC also performed a primary calibration of S solution using an LTAC method and performed additional activity measurements using a CNET ^{3}H efficiency-traced liquid scintillation counting method and a Triple-to-Double Coincidence Ratio (TDCR) method [14]. Finally, the S solution massic activity was measured by NPL using a $4\pi\beta$-γ coincidence counting method (Keightley, personal communication, 7 February 2018).

Massic activity calibrations for [231]Pa in the M solution were performed by NRC using two LSC activity measurements methods, CNET and TDCR [14]. Activity measurements of the M solution at NIST included the CNET method and α spectrometry [15]. The NIST measurements were performed in July of 2017, shortly after the samples were received, and additional CNET measurements were made in November of 2017. [233]Pa was added to α spectrometry samples as a yield monitor for electrodeposition of the [231]Pa sources and the detectors were calibrated for energy and efficiency using U, Am, and Pu electrodeposited sources. NPL did not report any measurements for the [231]Pa.

Results

The massic activity values for [231]Pa in the M solution and for [233]Pa in the S solution that were reported by the radioactivity measurement laboratories are summarized in Table 2. Also shown in the table are values for molality of [233]Pa in the S solution and molality of [231]Pa in the RM solution that were calculated from the activity data. Fitzgerald et al. [15] noted

that both CNET 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. 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.

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.

The molality of [233]Pa in the S solution was a key variable for the protactinium IDMS measurements made to determine the molality of [231]Pa in the 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 [231]Pa in the 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

Table 2 Measured massic activity and calculated molality of ^{233}Pa in the S solution, measured massic activity of ^{231}Pa in the M solutions, and calculated molality of ^{231}Pa in the RM solution

Analysis laboratory	Analysis method	S solution ^{233}Pa massic activity (Bq g^{-1})	S solution molality of ^{233}Pa (pmol g^{-1})
NIST	LTAC*	26,320 ± 170	0.1470 ± 0.0010
NIST	HPGe γ spectrometry	26,120 ± 570	0.1459 ± 0.0032
NRC	LTAC*	26,190 ± 370	0.1463 ± 0.0021
NRC	Coincidence counting	26,340 ± 450	0.1471 ± 0.0025
NRC	TDCR	26,310 ± 220	0.1469 ± 0.0012
NRC	CNET 1	26,040 ± 230	0.1454 ± 0.0013
NRC	CNET 2	26,130 ± 250	0.1459 ± 0.0014
NPL	Coincidence counting*	26,340 ± 180	0.1471 ± 0.0010
Analysis laboratory	Analysis method	M solution ^{231}Pa massic activity (Bq g^{-1})	RM solution molality of ^{231}Pa (pmol g^{-1})
NIST	α Spectrometry*	2096 ± 68	27.6 ± 1.0
NIST	CNET Corrected	2154 ± 67	28.41 ± 0.73
NIST	CNET	2175 ± 67	28.7 ± 1.0
NRC	CNET*	2193 ± 66	28.92 ± 0.98
NRC	TDCR	2266 ± 41	29.88 ± 0.72

Molality of ^{233}Pa was converted from massic activity using the evaluated ^{233}Pa half-life [12] of (26.98 ± 0.2) days ($k = 1$). The molality of ^{231}Pa in the RM solution was calculated from the M solution massic activity using the dilution factor of 187.279 ± 0.047 ($k = 2$) and the evaluated ^{231}Pa half-life [11] of (32 670 ± 260) a ($k = 1$). 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 [13] for ^{233}Pa and [15] for ^{231}Pa. All massic activity values for NRC are from [14] and the cited ^{233}Pa activity value from NPL is from Keightley (personal communication, 7 February 2018). CNET 1 and 2 refer to analyses performed on liquid scintillation counters from different manufacturers

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

Fig. 2 Measurement data for molality of ^{233}Pa in the 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
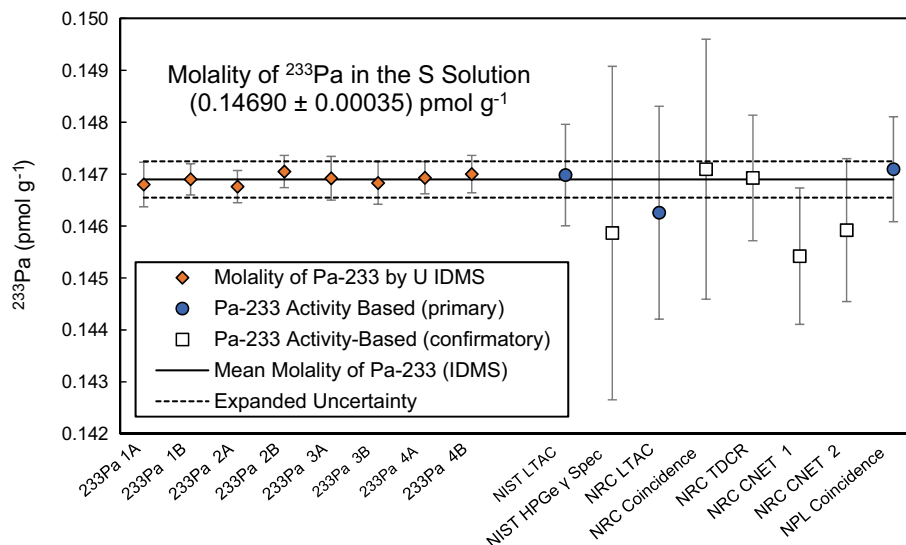
the LSC-based measurement methods range from 3 to 8% higher than the IDMS value.

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 5.3 g of solution dispensed to each unit. The 0.35% relative expanded uncertainty for the molality of ^{231}Pa in the RM solution is much greater than the relative difference in solution masses. As a result, the variability in the mass of RM solution dispensed to individual reference material units corresponds to trivial differences in the calculated amount of ^{231}Pa in each unit and this variability does not significantly increase the uncertainty for the

Table 3 IDMS sample data and measurement results for the molality of ^{233}Pa in the S solution

Sample ID	^{233}Pa S solution* aliquots (g)	U reverse-spike aliquots (g)	Measured isotope ratio $n(^{238}U)/n(^{233}U)$	Molality of ^{233}Pa (pmol 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

The quantity measured by IDMS was the molality of ^{233}U in the decayed S solution (pmol ^{233}U g^{-1}). Corrections for solution evaporation and undecayed ^{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

*Correction factors for ^{233}Pa sample aliquots were applied to compensate for relatively small evaporative losses (from 0.3 to 1.0%) that occurred over the interval between dispensing and aliquoting for IDMS (298 d). These factors were calculated as the quotient of the solution mass at the time of initial dispensing and the solution mass immediately prior to aliquoting for IDMS analyses

Fig. 3 Molality of ^{231}Pa in the 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 ($k = 2$) interval for this mean value (dashed lines) are included in the figure
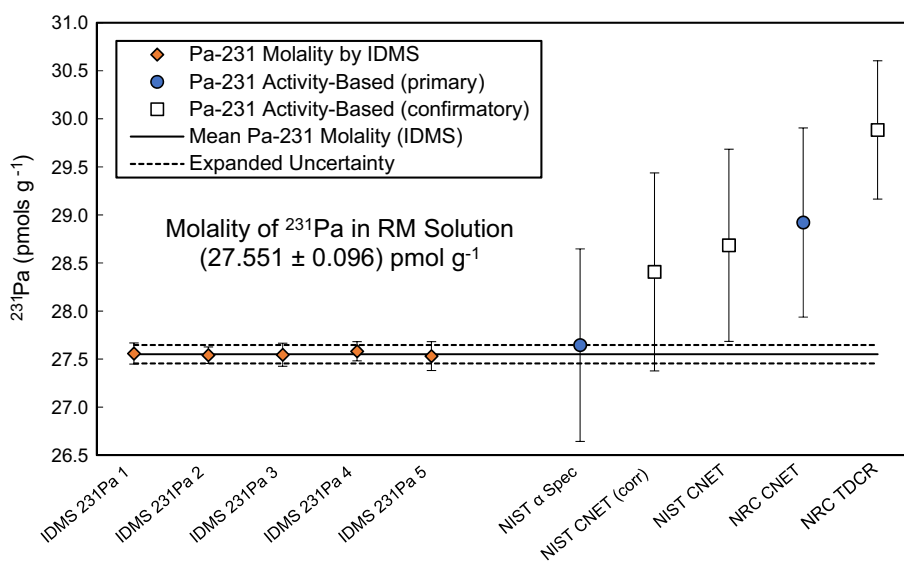
amount ^{231}Pa. Accordingly, a single value and uncertainty for amount ^{231}Pa can be applied to every unit in the production run. This value, of (145.96 ± 0.51) pmol ($k = 2$), was calculated using the mean buoyancy-corrected mass of solution aliquots dispensed to the units and uncertainty components 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 [25, 26] and includes all significant sources of uncertainty. A detailed uncertainty budget for the calculated amount of ^{231}Pa is provided in Table 5.

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 [27], the production project was planned and executed to satisfy the quality requirements for CRMs as outlined in international guidance documents [28, 29]. General requirements for a high-quality analytical reference material include stability, homogeneity, and metrological traceability. Additionally, characterized attribute values should have GUM-compliant

Table 4 IDMS sample data and measurement results for the molality of ^{231}Pa in the RM solution

Sample ID	^{231}Pa RM solution aliquots (g)	^{233}Pa spike aliquots (g)	Measured isotope ratio* $n(^{233}\text{Pa})/n(^{231}\text{Pa})$	Molality of ^{231}Pa (pmol 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

For IDMS calculations, the molality of ^{233}Pa in the S solution was decay corrected to the time of final purification for 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

*A correction factor (0.99936 ± 0.00059) was applied to measured $n(^{233}\text{Pa})/n(^{231}\text{Pa})$ 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 $n(^{233}\text{Pa})/n(^{231}\text{Pa})$ ratio of a mixed solution and the $n(^{233}\text{U})/n(^{231}\text{Pa})$ ratio of the same solution after the decay of ^{233}Pa

Table 5 ^{231}Pa reference material uncertainty budget for amount of ^{231}Pa contained in each unit

Uncertainty component	Description	Assessment type	$U_i\,\%$
$b_{^{231}\text{Pa}}$	Measurement repeatability; standard uncertainty of 5 independent measurements for ^{231}Pa molality of RM solution.	A	0.032
$b_{^{233}\text{Pa}}$	Measurement repeatability; standard uncertainty of 8 independent measurements for ^{233}Pa molality of S solution.	A	0.023
b_{C112-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 uranium and protactinium 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 protactinium and uranium in MC-ICP-MS, blank corrections, background corrections, and collector efficiencies.	B	0.086
R_{U010}	CRM U010; standard uncertainty of $n(^{235}\text{U})/n(^{238}\text{U})$ ratio for CRM used to calibrate the mass spectrometer.	B	0.051
Remainder	Remainder correction; estimated uncertainty for ^{233}U 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%	

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 calculated using the GUM Workbench software (Metrodata GmbH, Weil am Rhein, Germany)

uncertainties [24] 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 [30]. 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) [31]. Furthermore, the authors have observed that protactinium in a 2 mol L^{-1} HNO_3 and 0.1 mol L^{-1} HF mixed solution shows no apparent change in molality of protactinium 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 ensure that the ^{231}Pa reference material will remain fit-for-purpose over the long-term, the units are characterized for amount of ^{231}Pa and each unit is contained in a weighed Teflon bottle (bottle mass values to be provided with units). With these values, a user can utilize the 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 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 d, it can be stated, with a high degree of confidence, that the characterized reference material units are monoisotopic and therefore isotopically homogeneous.

To minimize the potential for temporal changes to the molality of ^{231}Pa in the RM solution, preparation of the solution, 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 h). Variability that could be caused by differential protactinium contamination was minimized by performing preparation and production work in a class 10 000 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 [27] for amount of ^{231}Pa was maintained for the two main stages of the calibration process. First, the molality of ^{233}Pa in the spike solution was measured by a primary IDMS analysis method [32, 33] 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 verified 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 value for the molality of ^{233}Pa in the 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 ^{233}Pa in the S solution was utilized for IDMS analyses of ^{231}Pa in the RM solution. All masses for the ^{231}Pa IDMS sample preparation were also measured on a calibrated balance that was verified using calibrated check weights. An isotopic standard for protactinium is not feasible, so mass spectrometric measurements were calibrated using the CRM U010 isotopic reference material. Although the MC-ICP-MS mass fractionation behavior of uranium and protactinium are likely to differ, these differences tend to be small for neighboring elements [34] and an estimated uncertainty component for potential bias in the mass spectrometry results was included in the 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 calibrated balance.

The molality of ^{233}Pa in the S solution, as measured by IDMS, was independently verified by activity-based analyses performed at NIST, NRC, and NPL, providing a high level of confidence in the calibration of this material. Values for molality of ^{231}Pa in the RM solution calculated from LSC-based massic activity measurement on the M solution are, however, higher than those measured by IDMS. Observations from mass spectrometry on the ^{231}Pa M 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 ^{227}Ac daughter products. The presence of 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 total activity (i.e.
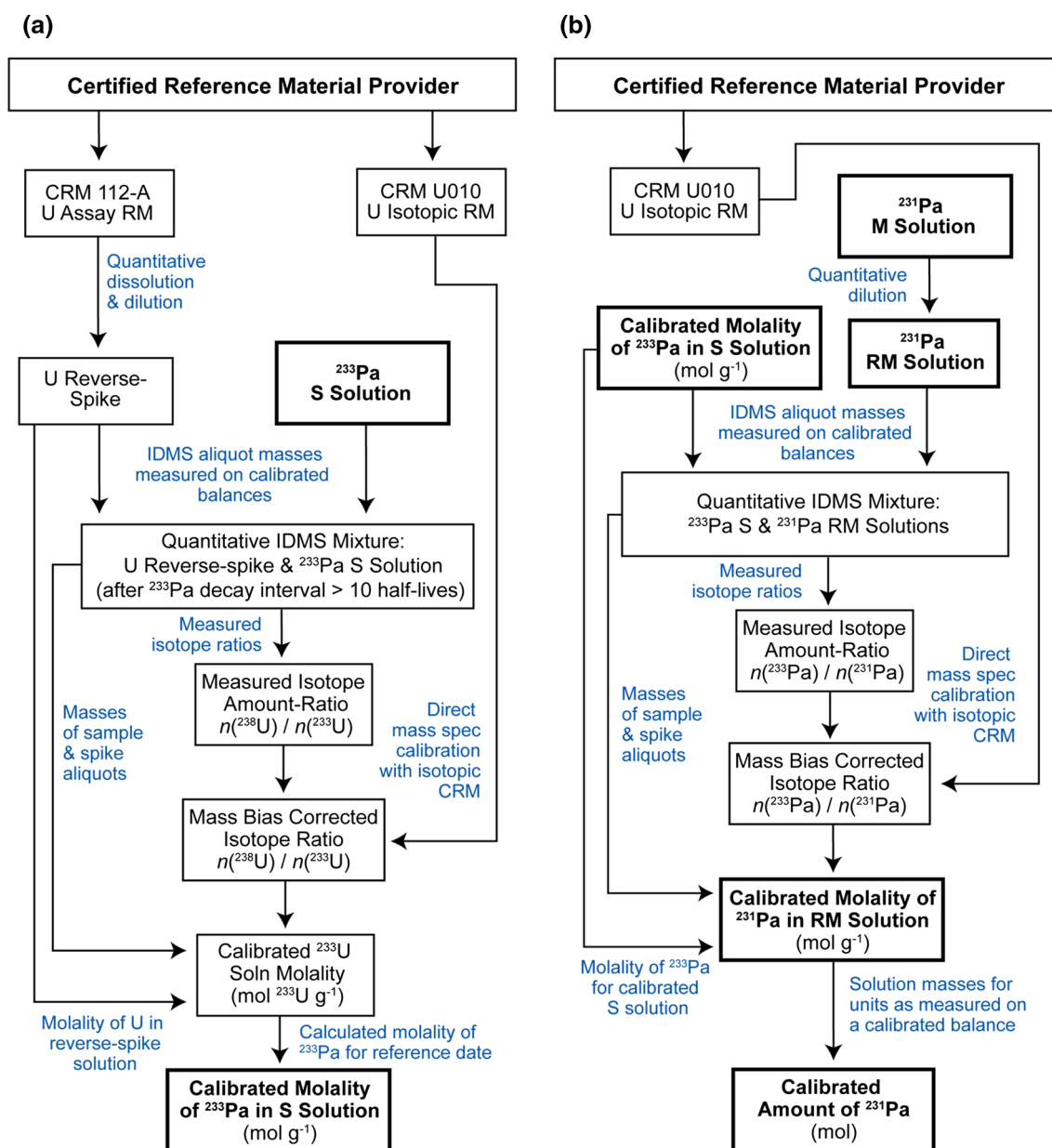
(a)

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(b)

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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 (**a**) and the [231]Pa reference material (**b**)

LSC based methods CNET 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 the 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 activity 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 decay were measured, so these results were not affected by the presence of small proportions of unsupported decay-chain products. The calculated value for the [231]Pa molality of the RM 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 ^{233}Pa in the S solution prepared for calibration of ^{231}Pa in the RM solution was precisely measured using a primary analysis method (i.e. IDMS) and independently verified by massic activity measurements at 3 metrology laboratories. This uniquely well characterized ^{233}Pa material enabled high-precision primary measurements of the molality of ^{231}Pa in the RM solution used to prepare units of the ^{231}Pa reference material. The molality of ^{231}Pa was independently verified by α spectrometry massic activity measurements performed at NIST. Individual units were carefully prepared from the RM solution resulting in a metrologically traceable reference material that is suitable for calibration of ^{233}Pa spikes that are produced by analytical laboratories on an as-needed basis. The relative expanded uncertainty for amount of ^{231}Pa in each reference material unit is 0.35% which should allow for reliable ^{233}Pa spike calibrations and similarly well constrained measurements of ^{231}Pa for determination of ^{235}U–^{231}Pa model ages.

Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

Human and animal rights This article does not contain any studies with human or animal subjects performed by the any of the authors.

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