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Production and standardization of an on-demand protactinium-233 tracer

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Abstract

Protactinium-233 (^{233}Pa) was generated by neutron activation of thorium and isolated by column chromatography using an octanol-impregnated resin. Absolute activity standardization was performed on ^{233}Pa using three independent methods, the results of which agreed within their associated uncertainties. The standardized ^{233}Pa was used to calibrate a secondary standard ionization chamber and high purity germanium detectors to enable a rapid and traceable method for the production and quantification of this radiotracer.

Keywords Protactinium · Nuclear forensics · Radiochronometry · Standardization · Radionuclide metrology

Introduction

Uranium radiochronometry is of great interest to the nuclear forensics community [1–3]. The ^{235}U/^{231}Pa isotope pair can be used to calculate the separation age of samples containing enriched ^{235}U; a comparison with another radiochronometric pair, ^{234}U/^{230}Th, can provide additional information about the processing history of the material. Accurate dating using the ^{235}U/^{231}Pa nuclear chronometer typically requires access to the short-lived radiotracer ^{233}Pa [$t_{1/2} = 26.98(2)$ d] [4], which is used to quantify the long-lived ^{231}Pa ($t_{1/2} = 32.8$ ky) by methods such as isotope dilution mass spectrometry [5, 6]. The short lived ^{233}Pa is ideal for decay counting primary standardization using coincidence counting and liquid scintillation counting (LSC) methods.

At the present time, access to ^{233}Pa is limited to the handful of laboratories around the world that possess

significant quantities of ^{237}Np ($t_{1/2} = 2.14$ My). As a decay product of ^{237}Np, ^{233}Pa forms continuously in situ, and can be isolated by complex chemical processing of these neptunium sources [5]. However, due to the long half-life of ^{237}Np, significant quantities of ^{233}Pa can only be generated after an interval of months from the previous source reprocessing, limiting its access upon immediate requisition. If the ^{235}U/^{231}Pa dating method is to be applied as a forensic tool in emergency response scenarios, access to ^{233}Pa must be improved significantly.

The deliberate generation of ^{233}Pa by bombarding natural thorium oxide with thermal neutrons was first reported more than 60 years ago [7]; but to our knowledge, this production route is not in use today. Although the reported post-irradiation processing is not appropriate for routine production due to the complex, multi-step chemical treatments and use of hazardous reagents including fluorine and hydrofluoric acid, the production physics of this process is near-ideal. Natural thorium is monoisotopic (100% ^{232}Th), and thus the sole product of its thermal neutron activation is the short-lived radioisotope ^{233}Th ($t_{1/2} = 22$ min), which undergoes beta decay to the desired ^{233}Pa. The moderate cross-section for the ^{232}Th(n, γ)^{233}Th nuclear transformation (σ = 7.4 b) indicates that arbitrary (MBq) quantities of ^{233}Pa can be generated using this production route even in low- and medium-flux nuclear research reactors. A re-investigation of the separation of ^{233}Pa from neutron

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irradiated thorium to identify a methodology that is simple, rapid, and reproducible is therefore in order. The ideal approach would also avoid the use of reagents that require special handling, such as HF-assisted separations described elsewhere [8–10].

As one of the world's leading producers and processors of uranium, Canada is interested in expanding its nuclear forensics capabilities for characterizing samples that are found outside of regulatory control. Towards this goal, the objectives of this work were two-fold: first, to investigate the feasibility of "on-demand" production of ^{233}Pa from thorium at the McMaster Nuclear Reactor, the nation's most powerful research reactor; and second, to conduct standardization measurements at the National Research Council of Canada. The resulting certified reference materials could be used to calibrate secondary radioisotope quantification instrumentation.

Experimental

Neutron irradiation of thorium

Note: As the decay product of ^{233}Pa is the fissile species ^{233}U, neutron irradiation times should be limited to no more than several hours in well-thermalized sites (in the absence of fast neutrons; where E > 1.2 MeV) to ensure that the ^{233}U content of the sample is at a minimum while it is in the reactor core.

In a typical experiment, thorium (IV) nitrate pentahydrate (152.6 mg, 99.9%, Strem Chemicals) was heated at 120 °C for 3 h to generate thorium (IV) nitrate dihydrate as discrete white pellets (138.9 mg). The dihydrate was weighed into a polyethylene vial and heat-sealed; the vial was then placed within a larger polyethylene vial that was subsequently heat-sealed. The double-encapsulated target was irradiated for 6 h in site 9C (ϕ_{th} = 9.0–10 × 10^{12} n/cm^2/s) of the McMaster Nuclear Reactor (MNR) at a nominal operating power of 3 MW. The activated thorium was stored underwater for a minimum of 4 h after end of irradiation to allow decay of ^{233}Th and grow-in of ^{233}Pa. The ^{233}Pa activity (∼ 86.2 MBq) was estimated using an AtomLab 400 Dose Calibrator.

Isolation of ^{233}Pa

The ^{233}Pa was separated from the thorium nitrate target material using methods loosely adapted from recent work by Jerome et al. with protactinium-231 [11]. Octanol-impregnated solid support (TK400 resin, 100–150 μm) was used as received from TrisKem. Acids utilized in the conditioning and elution tests such as concentrated hydrochloric acid (12 M, > 99.999% trace metals) and

sulfuric acid (18 M, 95–98%) were obtained from Sigma-Aldrich and diluted with ultra-pure water (> 18 MΩ cm) as required. While several elution chemistries were tested, two main methods were selected for the final production.

Method A: elution in sulfuric acid

TK400 resin (2.00 g) was slurried in water and poured into a glass chromatography column (o.d. = 10 mm). An irradiated target (5–10 MBq, 40–60 mg) was dissolved in 6 M HCl (500 uL). The resulting clear pale yellow solution was loaded onto the resin column, and was washed with 6 M HCl (25 mL) to remove thorium and uranium. The ^{233}Pa was eluted in 2.5 M H$_2$SO$_4$ (3 × 6 mL) with an efficiency of greater than 95%.

Method B: elution in hydrochloric acid

TK400 resin (2.00 g) was poured into a glass chromatography column (o.d. = 10 mm) and conditioned with 10 M HCl (10 mL). An irradiated target (30–85 MBq, 40–60 mg)) was dissolved in 10 M HCl (1 mL) and loaded onto the resin column. The resin was washed with 10 M HCl (20 mL) to remove the thorium and uranium; greater than 95% of the ^{233}Pa was subsequently eluted in 1.0 M HCl (10 mL), collecting in 1 mL fractions to maximize the activity concentration. Typically, 70–95% of the ^{233}Pa was recovered in only three fractions (3 × 1 mL).

The identity and radionuclidic purity of the resulting ^{233}Pa solutions were verified using an Ortec GMX N-type High Purity Germanium (HPGe) coaxial radiation detector (30% efficiency, 70 mm endcap). Gamma spectra were acquired using GammaVision for Windows Version 5.31 and analyzed using the Aptec MCA Application Version 7.04 (Canberra Co., 2002) software package. The efficiency of the detector was determined over the energy range 0.10–1.4 MeV using a mixed $^{152/154/155}$Eu multi-gamma standard disc source (Canberra). Small quantities (< 5 MBq) of ^{233}Pa were initially quantified on the HPGe detector based on its efficiency curve. For larger activities and routine quantification, an aliquot of ^{233}Pa was quantified using the HPGe detector efficiency curve, then measured in an AtomLab 400 ion chamber Dose Calibrator on the ^{60}Co setting to determine an approximate, uncalibrated, dial value (36.6). At the conclusion of this work, a certified reference calibration source was measured in the AtomLab 400 at MNR, yielding a calibrated dial value of 33.7 ± 0.3 at the 95% confidence level,[1] which will facilitate the rapid

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[1] The uncertainty associated with this instrument in this energy range is approximately 10%, which is likely greater than any minor geometry-induced errors accounting for < 1% deposition of ^{233}Pa on the walls of the glass ampoule.

and accurate determination of future ^{233}Pa production batches. The uncertainty on this value only reflects the uncertainty of the calibrant.

Standardization of ^{233}Pa

The most concentrated fraction from Method B (approximately 25 MBq in 1 mL) was sent to the National Research Council (NRC) of Canada in Ottawa, Ontario for standardization. Upon receipt, the bulk ^{233}Pa was diluted to 30 mL and pycnometers were used to dispense the solution to produce aliquots contained in silanized glass ampoules. Thin film (VYNS[2]) sources and a set of ten quenched LSC vials were produced using a pycnometer. The thin film sources were made by depositing 10–50 mg drops of the solution onto a VYNS film with the addition of a single drop of a surfactant (Catanac SN) and left to dry in a 40 °C air stream. The quenched LSC set was prepared with 15 mL of cocktail (Ultima Gold). Roughly 10–50 mg drops of the ^{233}Pa solution were deposited in each vial. Increasing amounts of nitromethane (0–100 μL) were added to act as the quenching agent. No additional reagents were added.

4πβ-γ coincidence counting

NRC implements a 4πβ-γ coincidence and anti-coincidence [12] counting method for the standardization of radionuclides consisting of a β-emission followed immediately by a γ. The NRC 4πβ-γ primary detection system consists of a pressurized proportional gas chamber (PPC), in which the VYNS sources are inserted. The PPC is filled with P10 counting gas to a pressure of 10 atm and registers the β-emissions. The PPC is sandwiched between two NaI crystals coupled to PMTs, that act together to form a γ-channel. The analog signals are counted with scalars and analyzed for coincidence/anti-coincidence as described in [12]. An electronic threshold was utilized to vary the β efficiency. The PPC β inefficiency was traced by centering the γ gate on the 311.904(5) keV transition of the ^{233}Pa decay scheme.

Liquid scintillation counting

Primary standard LSC techniques require a model of the physical and chemical processes involved in light emission and of the statistics of photon emission and detection [13]. The CIEMAT/NIST [14] efficiency tracing method was used to determine the absolute activity of the ^{233}Pa standard. This method requires the input of an experimental counting efficiency of a tracer nuclide which in this analysis was determined using a NIST traceable ^{3}H standard.

The ^{233}Pa efficiencies were calculated for the CIEMAT/NIST method using the MICELLE2 code [15]. Two commercial counters, a Wallac 1410 and a Hidex-300SL-METRO, were utilized for the LSC measurements.

Results and discussion

Increasing regulation of thorium—a substance that is subject to international safeguards restrictions—has resulted in decreased availability of thorium-containing compounds from standard chemical suppliers. Consequently, thorium (IV) nitrate hydrate Th(NO$_3$)$_4$·5H$_2$O was procured for this project despite its low thermal stability and resultant unsuitability as an irradiation target. Fortunately, the thermal behavior of this compound has been well characterized: loss of water of hydration occurs in two discrete steps, and is followed upon further heating by step-wise denitration, ultimately yielding thorium (IV) oxide [16, 17]. Unfortunately, as the thermal stability of this thorium series increases, the complexes' solubility in aqueous media decreases. The desire for a highly water soluble target material to facilitate post-irradiation processing must therefore be balanced against the need for a thermally stable thorium complex that meets regulatory requirements for neutron irradiation materials.

Two irradiation targets were investigated in detail: thorium (IV) dinitro oxide Th(O)(NO$_3$)$_2$, and thorium (IV) nitrate dihydrate Th(NO$_3$)$_4$·2H$_2$O, both of which were prepared by heating thorium (IV) nitrate pentahydrate as described in [16, 17]. As gamma heating and neutron recoil can cause localized temperature increases within a target, all neutron irradiations were conducted using a large-volume sample irradiation tube with sufficient headspace to avoid pressurization in the event of target outgassing.

Initial irradiation experiments employed short activation times (< 2 h) and focused on the more thermally stable mixed oxide/nitrate complex. While separation of ^{233}Pa was achieved for this novel irradiation target using both solvent extraction [18] and ion exchange chromatography [19] strategies, process optimization focused exclusively on the TK400 resin approach [11] due to its simplicity and high recovery yields. Both hydrochloric and sulfuric acid were found to be effective in eluting ^{233}Pa from this resin; however, the radioisotope is recovered in smaller volumes using dilute hydrochloric acid. The resulting ^{233}Pa solutions were subjected to neutron activation analysis to quantify any residual thorium. The thorium content of the post-processing ^{233}Pa was below the limit of detection[3] which is consistent

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[2] Poly-vinyl chloride poly-vinyl acetate.

[3] A precise value for the limit of detection is strongly dependent on the sample matrix (approximately 1–10 μg). For example, the presence of hydrochloric acid significantly increases the limit of detection due to the formation of ^{38}Cl, whereas it is much lower in nitric or sulfuric matrices.

with the observation in reference 11 that thorium washes through TK400 during sample loading, and protactinium is selectively retained until dilute acid is introduced. Furthermore, no other gamma emitting radionuclidic impurities were detected (e.g. ^{233}U, fission products) as well-thermalized irradiation sites were used for the thorium activation. Having successfully completed several neutron activations with no indication of heating within the oxide/nitrate irradiation target, a brief trial irradiation and processing of the more thermally sensitive thorium (IV) nitrate dihydrate was undertaken. No pressurization of the target vial or thermal degradation of the target material was detected. No difference in quality of the post-processing ^{233}Pa was observed compared to the mixed oxide/nitrate target. However, the fraction of the pre-processing activity recovered was 10–30% higher, at approximately 95% of the total activity. The higher yields associated with the hydrated target material are likely due to its greater solubility in aqueous media. Complete dissolution of the mixed oxide/nitrate irradiation target prior to column loading was difficult to achieve. An additional advantage of thorium (IV) nitrate dihydrate is its rapid (3 h) preparation time from a commercially available complex. As a result of these experiments, thorium (IV) nitrate dihydrate was identified as the preferred target material for the production of ^{233}Pa.

Having identified a preferred target material, irradiation site, and post-irradiation separation process, the scale of the ^{233}Pa production was gradually increased to approximately 85 MBq by increasing the irradiation time to 6 h. No pressurization of the target vial was observed, indicating that this process can be scaled up further, if necessary, by increasing the mass of target material.

A batch of the ^{233}Pa prepared by the optimized procedure described here (Method B) was used for the standardization measurements using three complementary approaches. The anti-coincidence result defined the absolute activity determination with the other primary methods acting as validation measurements. The thin film sources had a very high measured efficiency between 60 and 90% indicating the high quality of the produced counting artifact. The uncertainty budgets for the coincidence and anti-coincidence primary methods are given in Table 1. The uncertainty is dominated by the uncertainty of the extrapolation. The massic activity for the ^{233}Pa was 0.784 ± 0.008 MBq/g (k = 2) on November 21, 2017 at 12:00 EST.

The calculated efficiency range for the LSC quenched set was very high, above 95%. An ionization quenching parameter kB value of 0.0075 cm MeV^{-1} was used in the modelling. Variation of the kB value between 0.005 and 0.012 cm MeV^{-1} had a small effect (0.24%) on the calculated activities but nevertheless knowledge of kB was one of the main contributers to the total uncertainty of the massic activity determined by this method (see Table 1 for a complete uncertainty budget). Furthermore, LSC counting indicated no other alpha or beta-emitting radionuclidic impurities were present in the sample post-processing.

The agreement between the three different primary methods was excellent and is summarized graphically in Fig. 1. Further validation can also be derived from an international comparison between NRC (publication in preparation), NIST [20] and NPL on the massic activity of ^{233}Pa material prepared by LLNL; which was derived from a legacy ^{237}Np source. In this case the solution solvent was 2 M HNO$_3$ and 0.1 M HF. Nevertheless, the agreement between these groups was reported to be excellent providing further confidence in the results contained in this study.[4]

Single isotopic radioactive certified reference material is typically disseminated through the shipment of a liquid artifact contained in glass ampoules. Due to the adhesive nature of protactinium on glass, the ampoules were silanized before filling. Multiple ampoules were prepared at the time of standardization and then subsequently opened at later dates and re-measured. When opened, gravimetric dilutions were performed prior to measurement. The dilution factors were also determined radiometrically through measurement in calibrated ion chambers [21]. The massic activity could be recovered if the radiometric dilution factors were used but significant losses were being observed otherwise. This was an indication of the adsorption of the ^{233}Pa onto the glass despite its pretreatment prior to filling. The addition of HF lessened the loss but it was still significant. (See Fig. 2).

As a result of the evidence of sticking of the ^{233}Pa to the silanized glass, an unopened the ampoule retains its traceability and function as a calibrant but is not a suitable tracer for the calibration of an atom counting ^{231}Pa standard or for any other radiochemistry analysis. Monte Carlo calculations indicate that in the highly unlikely event that ^{233}Pa leaches out of the solution entirely and deposits on the inner layer of the glass ampoule, the calibration factor would change by 0.7%. This is within the 95% confidence limit that is set for the standardized activity and the major contributor to the ionization chamber calibration factor. However, all experimental evidence to date indicates that less than 1% of the ^{233}Pa plates out. Thus, these MC calculations represent a worst-case scenario that is unlikely to occur.

Measurements over the period of several months indicated that the total activity could be recovered, accounting for isotope decay. Therefore for this exercise we are confident that the calibrant returned to MNR for calibration of their ionization chamber could be used and act suitably as a

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[4] Richard Essex, NIST (2018) Private Communication.

Table 1 Uncertainty components for the primary methods used in the determination of the massic activity of the MNR produced ^{233}Pa

Uncertainty	Anti-coincidence $u_i(\%)$	Coincidence $u_i(\%)$	CIEMAT/NIST $u_i(\%)$	Evaluation
Counting statistics	0.03	0.02	0.25	A
Weighted uncertainty on the mean of 13 dried point sources on VYNS films				
Weighted uncertainty the mean of 10 LSC vials each counted 5 times on two independent counters				
Background	0.05	0.05	0.10	A
Standard deviation of 10 background measurements or 10 LSC blanks				
Live time	0.05			B
Previous sensitivity tests				
Dead time		0.03		B
Previous sensitivity tests				
Resolving time		0.01		B
Previous sensitivity tests				
Extrapolation	0.55	0.45		A
Average standard deviation of 13 fits				
Quenching parameter			0.24	B
Standard deviation of calculated activity for model kb = 0.005–0.012 with zero slope fits				
^{3}H tracer			0.12	B
Propagated error on tritium tracer.				
Weighing	0.03	0.03	0.03	B
Calibration of the microbalance				
^{233}Pa half-life	0.04	0.05	0.04	B
Uncertainty of the decay correction between measurement and reference times				
^{233}Pa decay data			0.09	B
β-branching ratios varied as input to the MICELLE2 efficiency calculation code				
Dilution	0.01	0.01	0.01	B
Propagated uncertainty on dilution factors				
Impurities				
None detected				
Combined standard uncertainty $u_c(\%)$	0.55	0.45	0.39	

traceable calibrant. Nevertheless, work will continue to stabilize the isotope in solution resulting in a proper and indefinite standard. Several approaches to stabilizing the ^{233}Pa in solution to eliminate deposition are currently being evaluated, and will be presented in a future publication.

Conclusions

Neutron irradiation of natural thorium represents a convenient and facile route to MBq quantities of the important forensic radiotracer ^{233}Pa. Standardization of this material enabled the production of certified ^{233}Pa sources for instrument calibration, so that this radioisotope can be quantified rapidly and traceably in the future. Canada's nuclear forensics capabilities have been enhanced significantly by this work, as our laboratories can now provide certified ^{233}Pa calibrants within days of a request. Further experimental work is ongoing to fully eliminate the deposition behavior of ^{233}Pa on glass surfaces, and will ultimately enable the production and distribution of certified ^{233}Pa radiotracer solutions.
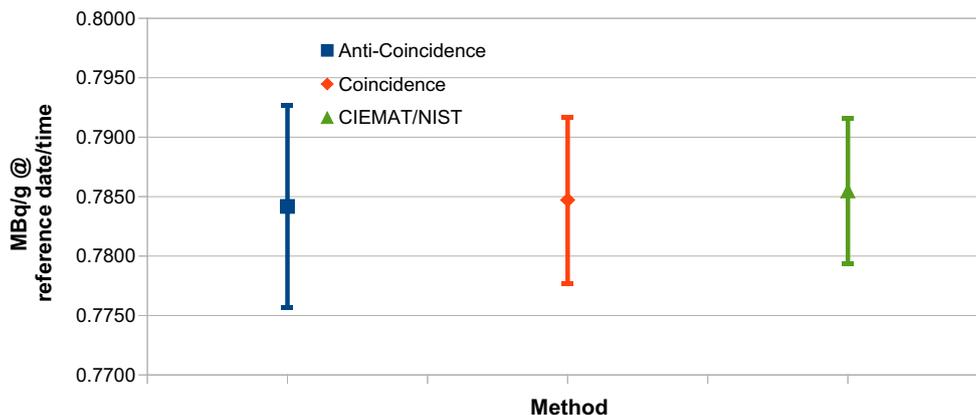
Fig. 1 Activity concentration for the ^{233}Pa tracer as a function of primary method used. All uncertainty bars are expanded uncertainties at 95% confidence level (k = 2)

Fig. 2 Radioactive losses of ^{233}Pa due to storage in 1 M HCl in salinized glass as a function of time of containment. The * corresponds to a solution of 1 M HCl and 0.1 M HF. All uncertainty bars are expanded uncertainties at 95% confidence level (k = 2)
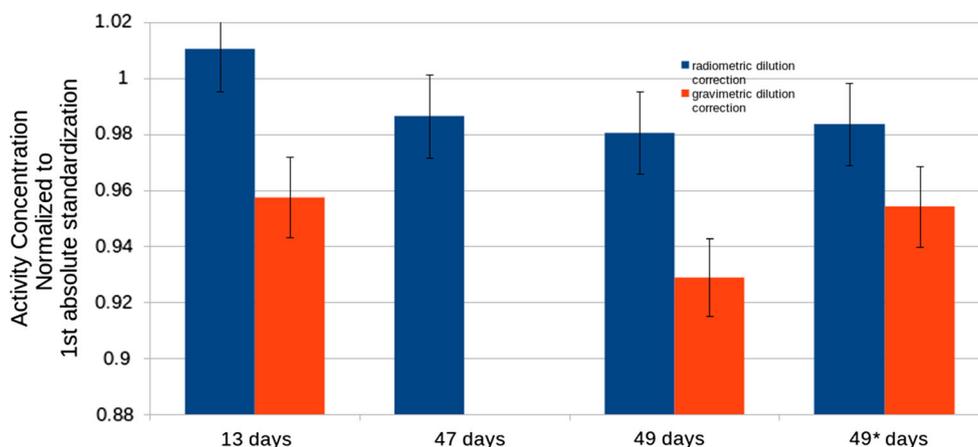
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