Protactinium-231 (^{231}Pa) Measurement for Isotope Chronometry in Nuclear Forensics

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Abstract: One of the key nuclear forensic signatures of the processing history of an unknown nuclear material is the material's age i.e., the time since the material was last chemically processed. Agreement between the results from two different chronometric pairs increases the confidence in the age dating analysis. The ^{231}Pa/^{235}U chronometric system has been found to be a useful complementary system to the more commonly applied ^{230}Th/^{234}U system. The Australian Nuclear Science and Technology Organisation's (ANSTO) Nuclear Forensic Research Facility (NFRF) is currently developing the capability to measure ^{231}Pa ($t_{1/2}$ = 32,760 years) and then apply these measurements to age dating for nuclear forensic investigations. This paper will focus on the procedure developed for ^{233}Pa production by neutron irradiation of Th and the radiochemical separation of ^{233}Pa from Th. The work completed to date and work planned will be described.

1. Introduction

Uranium series disequilibria measurements have been used for radiometric dating for many decades, mainly for elucidating geological and environmental processes. Recently, such measurements have been applied to the dating of nuclear materials (i.e., determination of the time since the material was last processed) for nuclear forensic applications. While ^{230}Th/^{234}U is the most widely employed uranium chronometric system, the ^{235}U decay scheme also yields a highly valuable chronometric relationship, ^{231}Pa/^{235}U. Although this latter approach has been shown to represent a viable complementary chronometric system to ^{230}Th/^{234}U, in particular for highly enriched uranium materials (^{235}U > 20%), it has largely remained underutilised in most investigations. The reason for this is the challenging chemistry required to separate Pa and the need to produce an artificial spike isotope, ^{233}Pa, for accurate mass spectrometry measurements. ANSTO is well placed to develop a ^{231}Pa measurement capability as the ^{233}Pa spike required for ^{231}Pa measurement by isotope dilution mass spectrometry can be produced by neutron irradiation of Th in our 20 MW Open Pool Australian Lightwater (OPAL) research reactor. The scheme for ^{233}Pa production is as follows:

$$^{232}\mathrm{Th}\ (n,\gamma)\ ^{233}\mathrm{Th} \xrightarrow[]{\beta\ \textit{decay,}\ \textit{22.3 mins}} {}^{233}\mathrm{Pa} \xrightarrow[]{\beta\ \textit{decay,}\ \textit{26.97 days}} {}^{233}\mathrm{U}\ (t\ ½\ 159{,}200\ \mathit{yrs})$$

An advantage of this means for ^{233}Pa spike production over milking ^{233}Pa from the alpha decay of ^{237}Np is that once calibrated no further ^{233}Pa grows in from residual Np. The procedure developed in this work for separation of Pa from Th avoids the use of highly hazardous perchloric acid [1].

Various methods for Pa measurement have been described such as alpha (for ^{231}Pa) and gamma (for ^{233}Pa) spectrometry [2], thermal ionisation mass spectrometry (TIMS) [3], multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and recently accelerator mass spectrometry (AMS) [4]. As we do not currently have access to a TIMS or a MC-ICP-MS for radioactive samples, the use of a quadrupole inductively coupled plasma mass spectrometer (ICP-qMS) was investigated for its potential for ^{231}Pa/^{233}Pa measurement.

2. Work to date

2.1. Target irradiation and measurement

The Th target for ^{233}Pa production was prepared based on the procedure described in Bourdon et al., 1999. [5]. The thermal neutron flux at the LE2 pneumatic irradiation position within the OPAL reactor was approximately 7.5 x 10^{12} $n.cm^{-2}.s^{-1}$. Appropriate software [6] was used to calculate the activity of ^{233}Pa generated corresponding to various initial masses of ^{232}Th, irradiation times and cooling times (time elapsed once the irradiated Th is removed from the reactor). Initial parameters selected were a starting mass of 100 µg of Th, 9 hours irradiation and a 4 day cooling time (to give a ^{233}Pa activity of approximately 120 kBq*)* but the irradiation time was later increased to 20 hours (to produce an activity of around 200 kBq).

A summary of the target preparation procedure follows: a 100 µL aliquot of 1000 µg/mL Th standard solution (Astral Scientific, $Th(NO_3)_4$ solution, 3% (abs) HNO_3) was placed into a Teflon beaker. The aliquot was dried to a small drop on a hot plate. The drop was then deposited onto a cleaned and weighed 2 cm^2 piece of Al foil and dried completely using a heat lamp. On completion of drying, the foil was allowed to cool, re-weighed, then carefully folded and loaded into a clean high density polyethylene (HDPE) 'snap-cap' capsule (Posthumus plastics). The capsule had been thoroughly cleaned to ensure no residual organics or other contaminants were present and was handled using gloves only. The target was then included in a 'can assembly' for loading into the reactor.

Once the irradiated target had cooled for 4 days, the ^{233}Pa content in the target was measured using gamma-ray spectrometry (HPGe detector; Ortec GEM35-70 (P-type, 35% relative efficiency) connected to an Ortec DSPec-50 digital spectrometer). The detector was calibrated for energy and efficiency by measuring a series of calibrated point sources at a distance of ~23cm from the detector end-cap. The absolute efficiency of the detector (in this geometry) was calculated to produce a calibration curve using 'Hyperlab' software. Hyperlab corrected the activity of each calibration source at the time of its measurement and then used the relative gamma abundances of each peak (it has an extensive nuclear data library built-in) to produce the points on the curve, which was then fitted using a 6th order polynomial.

The irradiated Th target was measured for 1 hour at approximately the same source-detector distance. For this initial measurement, the irradiated HDPE capsule containing the Al foil was placed into another, slightly larger, capsule and placed directly on the detector sample holder. Hyperlab uses all of the significant peaks it finds (see Table 2) and calculates a weighted average to produce the final activity. No correction was performed for the difference in geometry between the reference efficiency curve and the sample, resulting in a slightly lower reported activity. For comparison, the activity of one of the target dissolutions was also measured. An aliquot of the target dissolution was dried and measured on a Canberra Type GC 5019 (HPGE 50% relative efficiency) detector and compared to a point source calibration, similar to the measurement procedure described above. The measured (decay corrected) activity was 3.5 % greater than that obtained on the solid target.

The gamma-ray spectrum of the irradiated target is shown in Figure 1 and a list of the significant gamma-ray peaks for ^{233}Pa is given in Table 1. Five targets have been irradiated to date; the measured activity of ^{233}Pa produced using a 9 hour irradiation ranged from 105 to 125 kBq (corresponding to ~0.15 ng ^{233}Pa; specific activity of ^{233}Pa = 7.687x10^{14} Bq/g). Other isotopes detected were ~1 kBq ^{72}Ga (t ½ = 14.1 h, from Al foil), ~0.8 kBq ^{51}Cr (t ½ = 27.70 d, from plastic capsule), traces of ^{214}Pb and ^{214}Bi from the lead shielding and ^{65}Zn (t ½ = 244.06 d). No other impurities able to be measured using gamma spectrometry were present.

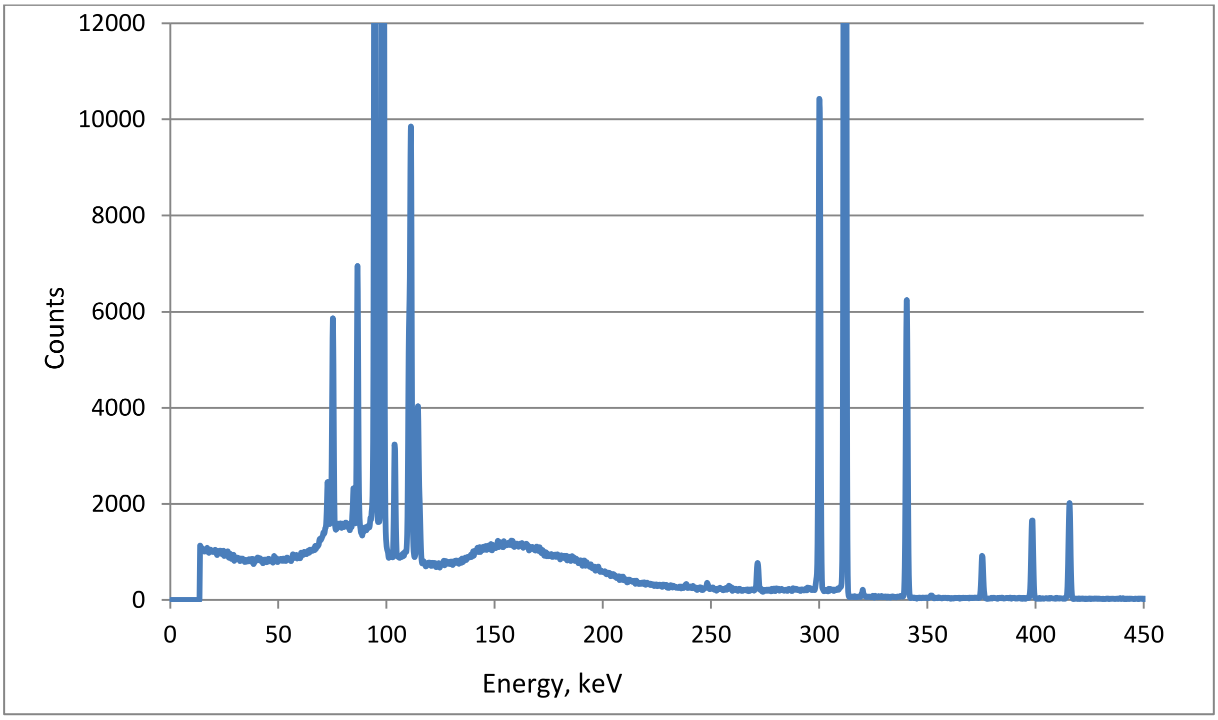

FIG. 1. *Gamma-ray spectrum of* ^{233}*Pa*

Table I. List of gamma-ray energies of ^{233}Pa [7]. The 'found peaks' were used to calculate the total activity of ^{233}Pa in the irradiated target

Energy (keV)	Line Intensity (Relative)	Found Peak (keV)
40.35	0.039	
51.5	0.0008	
57.9	0.0009	
75.3	1.39	75.27
86.7	1.97	86.57
92	0.004	
103.83	0.87	103.83
248.5	0.059	248.31
258.2	0.0039	258.58
271.48	0.328	271.56
298.5	0.035	298.86
300.12	6.62	298.86
311.89	**38.6**	311.92
340.47	4.47	340.48
375.45	0.679	375.39
398.46	1.39	398.44
415.79	1.745	415.69

2.2. Separation of Pa from Th

The procedure developed here is based on the one described by Bourdon et al., 1999 and Koornneef et al., 2010 [5, 8]. The irradiated Al foil target was dissolved in 10 mL of 9 M HCl. This solution was loaded onto an anion exchange column (2 mL Bio-Rad pre-filled poly-prep AG1-X8 resin, 100-200 mesh) that had been conditioned with 6 mL of 9 M HCl. Once loaded with the dissolved target solution, the column was washed with ~3 column volumes (cv) of 9 M HCl to remove Th and Al. Protactinium remains on the column in 9 M HCl while thorium does not; protactinium (V) (and uranium (VI)) forms anionic chloride complexes (see below) while thorium (IV) does not. Protactinium was eluted from the column with 9 M HCl + 0.1 M HF (~3 cv).

Protactinium yields during chemical separations were monitored using a gamma counter (2480 Wizard2, Wallac/Perkin Elmer with a NaI detector). Aliquots of the various fractions were adjusted to a fixed volume (1 mL) to eliminate geometry factors. The instrument was normalised for ^{233}Pa using the 311.9 keV peak (using the irradiated target prior to dissolution). A handheld radiation monitor was used as a quick check of ^{233}Pa content in the wash solutions, Pa fraction and the column during the separations. Once the target was dissolved in 9 M HCl, separation of Pa from Th was carried out soon after as even in strong aqueous HCl solutions Pa shows a strong tendency to hydrolyse. After extended periods of time colloidal dispersions may form, particles of which show a tendency to adhere to the walls of the vial, be it glass or polyethylene [9].

Protactinium binds strongly to the column and it was found that an increased number of washes (~ 6-7 cv) could be used to remove as much Th as possible with no Pa breakthrough. In this way a separation/decontamination factor of Pa from Th of greater than $2x10^4$ for this first column could be achieved. The chemical yield of ^{233}Pa was approximately 100%. Any residual ^{232}Th in the spike may interfere with ^{233}Pa or ^{231}Pa measurements using mass spectrometry so further separations were carried out until the Pa/Th ratio was greater than 10. For further separations all traces of HF must be removed from the eluant to render the Pa adsorbable by the ion exchange resin. There are several reported means of removing HF: repeated evaporation of HCl/HF solution to dryness and addition of HCl [10]; addition of boric acid to complex fluoride ions (e.g [5] [3]) where avoiding drying down may prevent Pa loss by hydrolysis; and addition of perchloric acid and evaporation at 180 °C to fume off all the fluoride ions [1]. Alternatively, Regelous et al.[11] chose to increase the concentration of HF as Pa is strongly adsorbed onto anionic exchange resin in strong (>2 M) HF as fluoride complexes (see Fig. 2).

Barnett et al. [12] demonstrated that treating a mixed HCl/HF elutriant with boric acid successfully rendered Pa resorbable by anion exchange resin. Boric acid forms a very stable fluroborate ion, releasing the Pa from the fluoride ion and rendering the Pa resorbable as a chloride complex. Figure 2 shows the distribution coefficients of Pa(V) as functions of the HCl and HF concentration taken from Kim et al.[13]. Barnett et al.[12] suggested optimum treatment of the 9 M HCl/0.1 M HF eluent was to dilute the HF to <0.03 M with 9 M HCl and add 0.1 M boric acid (H_3BO_3). It was found in the current work that it was necessary to add excess H_3BO_3 (>0.1 M), take the solution to near dryness and then make up to ~10-15 mL with 9 M HCl to obtain chemical recoveries of ^{233}Pa of >90%.

The chemistry of Pa during the separations has been described in the literature; anionic complexes of Pa present in > 8 M HCl are $PaCl_8^{3-}$, $PaOHCl_7^{3-}$ and $PaOCl_6^{3-}$ [14] . According to Kim, et al. (1973), in HF solutions of low acidity, Pa forms oxo and hydroxo fluoride complexes of positive and neutral charge. Above 0.001 M hydrogen and fluoride ion concentration, mainly PaF_7^{2-} ions exist, whereas at high fluoride concentration PaF_8^{3-} ions are present and at high acidity the $HPaF_7^-$ species is possible. In 9 M HCl/0.1M HF the complexes most likely to be present are $HPaF_7^-$ and PaF_7^{2-} [14].

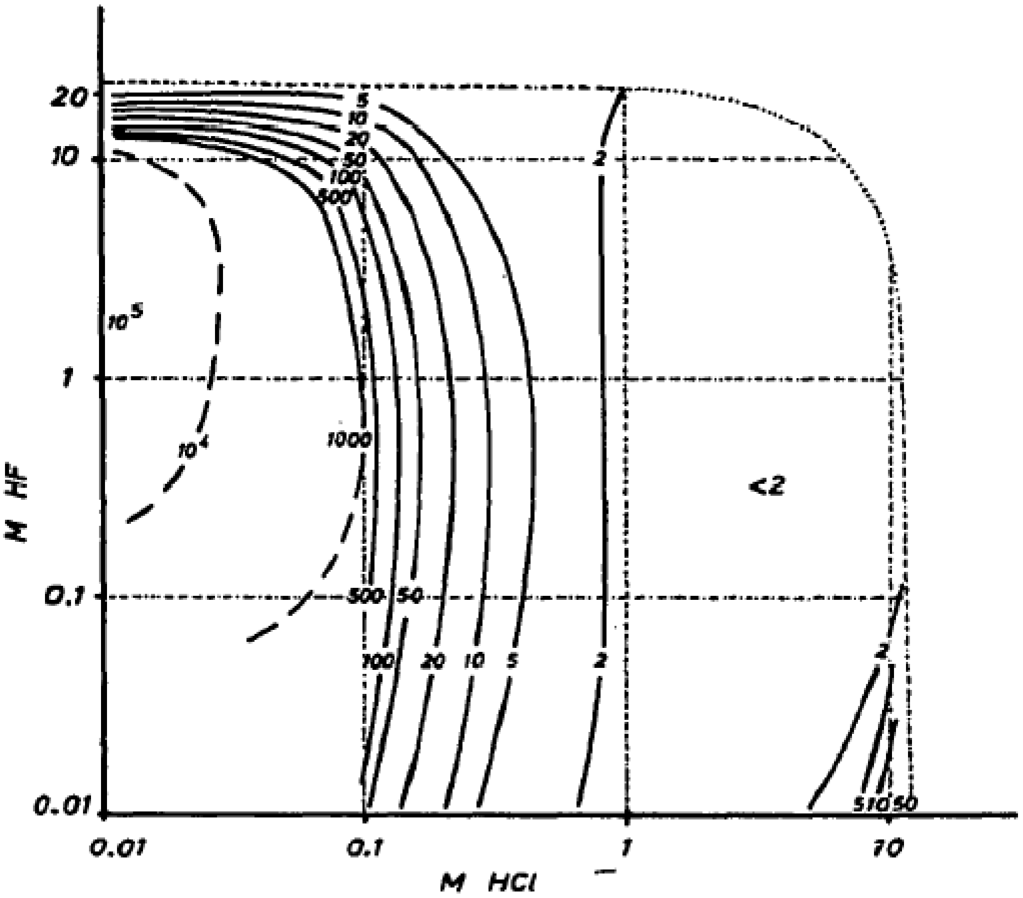

FIG. 2. *Distribution coefficients of Pa(V) as functions of the hydrochloric and hydrofluoric acid concentration, from Kim et al. [13]*

For ICP-MS analysis, the 9 M HCl/0.1 M HF eluants were evaporated to near dryness and made up in 2% HNO_3/0.4% HF; fluoride ions strongly complex Pa and prevent its hydrolysis. As ^{233}Pa decays to ^{233}U with a short half-life (26.97 days), measurements were carried out within a few days of separation.

3. Planned Work

3.1 Measurement of Pa using ICP-qMS

Recently, quadrupole ICP-MS has been used for ^{230}Th/^{234}U dating of ancient carbonates [15] and its potential for ^{231}Pa/^{235}U dating for nuclear forensics is currently being investigated here. Mass spectrometric measurements were carried out using a Bruker 820 ICP-MS housed in a laboratory designed to handle radioactive materials and equipped with a low-flow (100 µL min^{-1}) PFA micro-concentric nebulizer (flow rate controlled using peristaltic pump) connected to a Peltier-cooled PFA Scott-type spray chamber. Prior to the analysis of samples the instrument was tuned using a 1 ng g^{-1} multielement solution (Varian High-Purity Standards). Ion optics were optimised for maximum U sensitivity; sensitivity was approximately 3.0x10^5 cps for 1 ng g^{-1} ^{233}U.

The limit of detection (based on the three times the standard deviation of the blank method) for ^{233}Pa was ~ 0.5 pg/g. Preliminary test work using a previously dated HEU sample from a Nuclear Forensics International Technical Working Group (ITWG) interlaboratory comparison exercise [16] as an unknown, NBS U100 to calibrate the ^{233}Pa spike solution [1], and NBS U500 for instrumental mass bias correction, gave good agreement for the ^{231}Pa/^{235}U age of the material (i.e., result determined here overlapped with previously determined age within the uncertainty of ~7%, k=2).

3.2 Separation and Measurement of Th and Pa

The planned U/Th/Pa separation scheme for uranium samples is given in Figure 3. This procedure allows for the measurement of U isotopics, ^{230}Th and ^{231}Pa, to enable the application of both the ^{230}Th/^{234}U and ^{231}Pa/^{235}U isotope chronometers in a single sample dissolution.

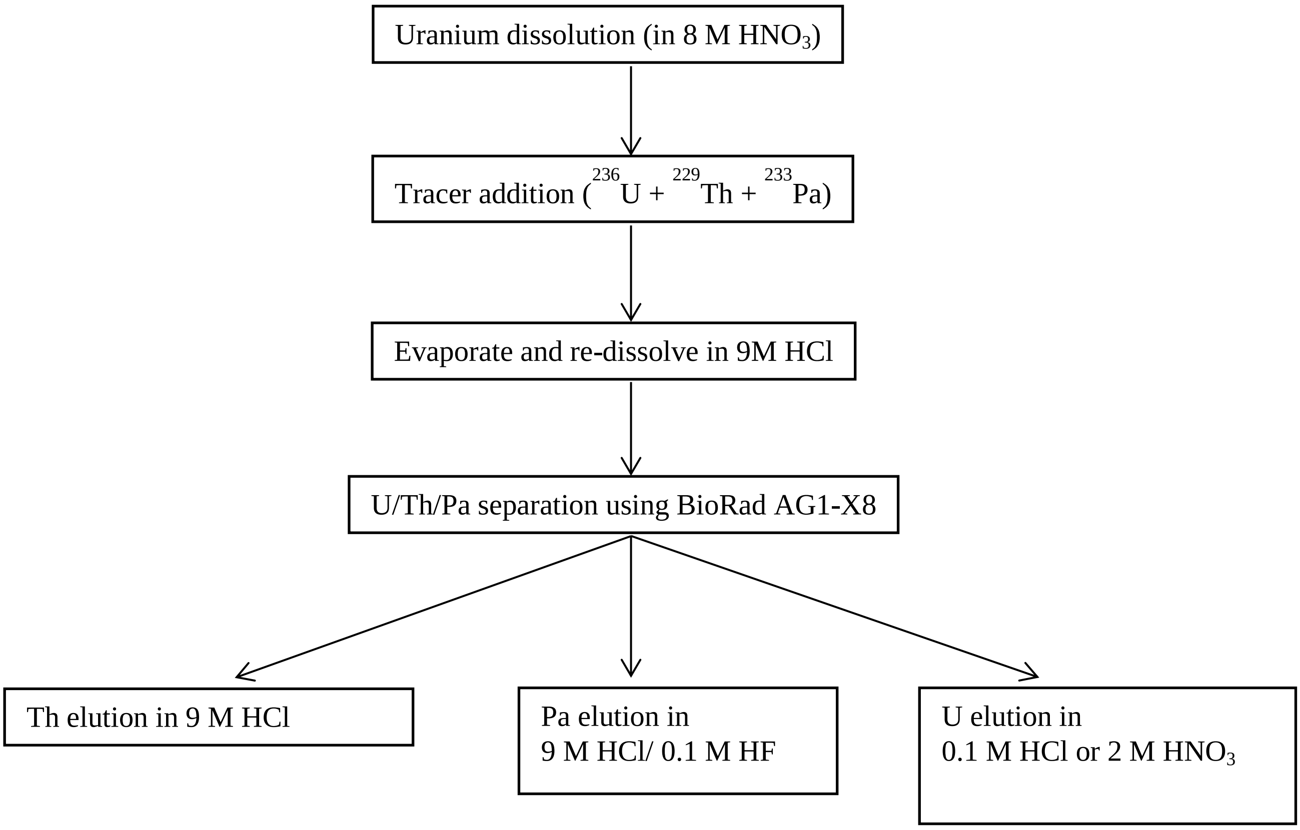

FIG. 3. *Summary of radiochemical separation scheme for U, Th and Pa for uranium materials.*

Validation of the separation and measurement procedure is planned using previously measured NBS uranium standards [1, 17].

3.3 MC-ICP-MS and AMS

ANSTO is currently in the process of purchasing a MC-ICP-MS instrument in collaboration with the University of Wollongong, Australia. The potential of MC-ICP-MS for Pa measurement has been demonstrated previously and was recently used for the first time for nuclear forensics [1]. We will also develop a procedure using MC-ICP-MS measurement here. In addition, ANSTO’s Centre for Accelerator Science (CAS) has recently taken delivery of a 1MV accelerator system custom designed with the capability to perform high efficiency, high precision accelerator mass spectrometry (AMS) across the full mass range. High mass resolution analyzers, at low and high energy, coupled to a novel fast isotope switching system, will enable high quality analysis of actinide radioisotopes. This instrument will be investigated for its potential for measurement of very low (femtogram) Pa concentrations.

4. Conclusions

Procedures for the production and radiochemical separation of ^{233}Pa have been developed at ANSTO to allow ^{231}Pa measurement for ^{231}Pa/^{235}U isotope chronometry for nuclear forensic investigations. Future work will focus on mass spectrometric measurements of a range of U-bearing samples using quadrupole ICP-MS, MC-ICP-MS and AMS.

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6. References

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