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

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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 $^{230}\text{Th}/^{234}\text{U}$ is the most widely employed uranium chronometric system, the ^{235}U decay scheme also yields a highly valuable chronometric relationship, i.e., $^{231}\text{Pa}/^{235}\text{U}$. Although this latter approach has been shown to represent a viable complementary chronometric system to $^{230}\text{Th}/^{234}\text{U}$, in particular for highly enriched uranium materials ($^{235}\text{U} > 20\%$), it has largely remained underutilised in most investigations. The reason for this is the challenging chemistry required to separate protactinium and the need to produce an artificial spike isotope ^{233}Pa for accurate mass spectrometry measurements.

The Australian Nuclear Science and Technology Organisation (ANSTO) is currently developing the capability to measure ^{231}Pa ($t_{1/2} = 32,760$ years) and then apply these measurements to various fields of research. The main area of application will be nuclear forensic investigations. This paper will describe the procedure developed at ANSTO to produce the ^{233}Pa spike for ^{231}Pa measurement by mass spectrometry. A brief outline of the chemistry of Pa will be presented and radiochemical procedures for separation of Pa from Th and U will also be described.

ANSTO is well placed to develop a ^{231}Pa measurement capability; the ^{233}Pa spike required for ^{231}Pa measurement by isotope dilution mass spectrometry can be produced by neutron irradiation of Th in our OPAL research reactor.

Appropriate target preparation and irradiation conditions were determined: ^{232}Th (100 μg in dilute nitric) was deposited on Al foil and irradiated for 9 hours at a neutron flux of approx. $7.5 \times 10^{12} \text{ n.cm}^{-2}\text{s}^{-1}$ and allowed to cool for 4 days. The ^{233}Pa activity in the cooled target was approx. 100 kBq (corresponding to approx. 0.14 ng ^{233}Pa ; specific activity of $^{233}\text{Pa} = 7.687 \times 10^{14} \text{ Bq/g}$) measured using gamma spectrometry.

A procedure was developed to isolate Pa from Th via anion exchange chromatography. The irradiated Al foil target was dissolved in 9 M HCl and this solution was loaded onto a ~4 mL anion exchange (AG1-X8 resin) column preconditioned with ~12 mL 9 M HCl. Once loaded, the column was washed with ~3 column volumes (CV) of 9 M HCl to remove Th and Al. Pa was eluted using 9M HCl/0.1M HF. The Pa fraction required further purification; residual ^{232}Th in the spike may interfere with ^{233}Pa or ^{231}Pa measurements using mass spectrometry. Treating the mixed HCl/HF 'Pa fraction' with boric acid successfully rendered Pa resorbable by anion exchange resin. A handheld radiation monitor was used as a quick check of ^{233}Pa content in the wash solutions, Pa fraction and on the column. More precise measurements employed a gamma counter using the 311.9 keV peak. Gamma counter results for each column separation were used to determine the recovery of Pa during the separation/purification procedures.

Pa possesses a very high tendency to undergo hydrolysis. When conducting ion exchange separations with Pa, it is essential to handle Pa in the monomeric form as hydrolysed polymeric compounds may lead to masking effects so that separation is incomplete. At trace levels of Pa, the formation of hydrolysis products can be avoided by the presence of the fluoride anion.

Pa was similarly separated from U solutions using anion exchange column chromatography.

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