

Age Determination of Highly Enriched Uranium: Separation and Analysis of ^{231}Pa

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An analytical procedure has been developed for the age determination of highly enriched uranium samples exploiting the mother/daughter pair $^{235}\text{U}/^{231}\text{Pa}$. Protactinium is separated from bulk uranium through highly selective sorption to silica gel and is subsequently quantified using α -spectrometry. The method has been validated using uranium standard reference materials of known ages. It affords decontamination factors exceeding 2.5×10^7 , overall recoveries in the range of 80–85%, and a combined uncertainty below 5%.

In recent years several incidents involving illicit trafficking and smuggling of nuclear material, radioactive sources, and radioactively contaminated materials have raised growing public concern about criminal acts involving nuclear materials.¹ Consequently, research efforts in nuclear forensic science have been intensified in order to develop and improve methods for the identification of the nature and origin of seized materials. Information obtained from the analysis of unknown nuclear materials is of key importance in order to aide authorities that are in charge of developing fast and appropriate response action. For the identification of nuclear materials, various sample characteristics are of relevance, including isotopic composition, the content of chemical impurities, material properties, and the date of production.

Information on the production date, the “age” of nuclear materials, will also be of key importance in other fields of nuclear science, that is, for the verification of a Fissile Materials Cut-Off Treaty (FMCT) in order to distinguish freshly produced materials from “old” excess weapons materials. The age of nuclear materials may also be of relevance under a strengthened safeguards regime to reveal clandestine production of weapons-usable materials, that is, the separation of plutonium or production of highly enriched uranium (HEU).

The dating of plutonium samples was described in detail in refs 2,3 for bulk samples as well as particles. In this work, we will therefore focus on the age determination of highly enriched uranium. The radioactive decay of the uranium isotopes provides a chronometer that is inherent to the material. As shown in Figure



Figure 1. Calculated daughter/parent mass ratios as a function of age (decay time).

1, the mother/daughter pairs $^{234}\text{U}/^{230}\text{Th}$ and $^{235}\text{U}/^{231}\text{Pa}$ can be advantageously used. Because of the relatively long half-lives of ^{234}U (2.46×10^5 years) and ^{235}U (7.04×10^8 years), only minute amounts of daughter nuclides are growing in; therefore, the separation of both Th and Pa from uranium must be of high chemical recovery and must afford large decontamination factors. In general, the age obtained from parent/daughter ratios refers to the last separation of the parent nuclide from its daughters, that is, the last purification of the material. The accuracy of the obtained age therefore depends on the quality of the purification process and assumes that the material has not subsequently been contaminated. Obviously, the availability of two analytical methods relying on both independent parent/daughter pairs will therefore significantly increase the confidence in the experimental results.

Recently, we demonstrated the age determination of highly enriched uranium samples using the parent/daughter relation $^{234}\text{U}/^{230}\text{Th}$.⁴ Following the separation of thorium from bulk uranium using extraction chromatography, thorium concentrations were analyzed using α -spectrometry, thermal ionization mass spectrometry (TIMS), and inductively coupled mass spectrometry (ICPMS). In this work, we will describe a second, independent method for the age determination of HEU using the parent/

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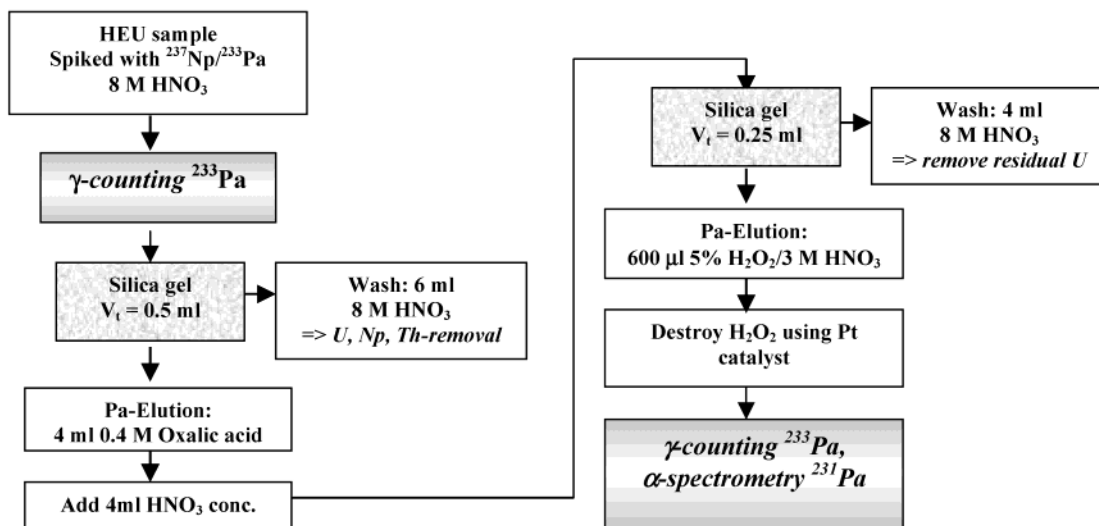


Figure 2. Experimental procedure used for the separation of protactinium from highly enriched uranium.

daughter relation $^{235}\text{U}/^{231}\text{Pa}$. In the literature, the use of $^{235}\text{U}/^{231}\text{Pa}$ for the determination of uranium materials has so far been reported for many geochronological studies, with sample ages generally on a time scale of 10^3 to 10^5 years.⁵ In the case of HEU samples, typically 10–50 years old, however, the in-growing amounts of ^{231}Pa will be ~ 2 –4 orders of magnitude lower, therefore requiring separation procedures with even higher decontamination factors and recovery. We will describe the separation of ^{231}Pa from bulk uranium by highly selective sorption of protactinium to silica gel followed by α -spectrometric quantification. The method was tested and validated using uranium reference materials of different uranium enrichments and of known ages. The obtained ages will be compared with the results obtained previously using the parent/daughter pair $^{234}\text{U}/^{230}\text{Th}$.

EXPERIMENTAL SECTION

Nitric acid and hydrochloric acid solutions were prepared from suprapur grade reagents (Merck). Water was obtained from a Milli-Q water purification system. All other chemicals were reagent grade and were used as received.

Uranium isotopic standard reference materials U-500, U-800 and U-850 from New Brunswick Laboratory, NBL (materials were produced and formerly sold by National Bureau of Standards, NBS) were used in the study. They were 50, 80, and 85% enriched in ^{235}U , respectively. The standards consist of U_3O_8 powders, the preparation dates of which are rather well-known and hereafter referred to as “assumed ages”.⁶ Sample solutions were prepared by dissolving weighed amounts of U_3O_8 in concentrated nitric acid, followed by adjustment of the acidity to 8 M HNO_3 . The concentration of uranium was analyzed by isotope dilution thermal ionization mass spectrometry (ID-TIMS).

Silica gel (63–200- μm particle size) was washed, dried, and packed in plastic columns with a diameter of ~ 3 mm, making up bed volumes of 0.25 mL and 0.5 mL. The columns were conditioned with several bed volumes of 8 M HNO_3 prior to use. Average flow rates were 0.1 mL/min.

Samples for α -spectrometry (total volume 700–800 μL) were prepared by successively adding aliquots of 100 μL onto a stainless steel planchette and evaporating the sample solution after each

addition using a heat lamp. After evaporation of the last aliquot, the planchette was heated to ~ 700 $^\circ\text{C}$ for 2 min. Samples were counted using a Soloist α -spectrometry system (EG&G Ortec) with variable counting times until 10 000 counts was reached in the region of interest of the peak of ^{231}Pa . The efficiency of the α -detector was calibrated using a mixed plutonium standard (ST 946, PTB Braunschweig).

Analytical Approach. As illustrated in Figure 1, typical HEU samples produced during the last 50 years contain parts-per-billion amounts of ^{231}Pa relative to ^{235}U . Samples sizes are generally in the milligram range; therefore, suitable experimental procedures need to afford the separation and quantification of picogram amounts of protactinium. Methods for the separation of protactinium from a variety of sample matrixes have been described in detail in the literature, including precipitation, solvent extraction, ion-exchange, extraction chromatography, and sorption to silica gel.⁷ The use of silica gel seemed to be most promising for our purposes, since sorption to silica gel affords the separation of protactinium from virtually any kind of metal and does not generate large amounts of waste.

For the quantification of ^{231}Pa in the required concentration range, the use of mass spectrometric methods, that is, ICPMS, was considered. However, the strong tendency of protactinium to hydrolysis and sorption in dilute acids leads to considerable memory effects in the mass spectrometer, making the reliable quantification of trace amounts of protactinium by ICPMS very difficult. The quantification of picogram amounts of ^{231}Pa was, therefore, performed using α -spectrometry. Since no other α -emitting isotope of protactinium is available, a solution of ^{237}Np that is in radiochemical equilibrium with its daughter ^{233}Pa was used as the tracer, and the recovery of Pa was monitored through measurement of the γ -emission of ^{233}Pa at 311 keV.

The experimental procedure developed in this work for the separation of Pa from bulk U is shown in Figure 2. Following the γ -measurement of a weighed aliquot of the spiked solution, the

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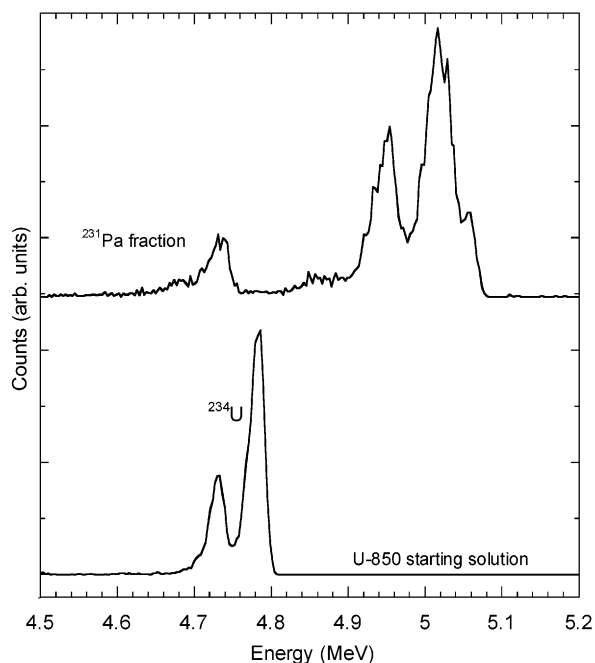


Figure 3. α -Spectra of U-850 sample solution and separated ^{231}Pa fraction.

sample solution was added onto a silica gel column of 0.5 mL volume. Bulk uranium; neptunium, introduced through the spiking process; thorium; and other impurities were washed through the column using 6 mL of 8 M HNO_3 . Protactinium was then eluted using 0.4 M oxalic acid with a recovery of typically 90–95% in 4 mL of eluent. This first separation step was found to afford decontamination factors exceeding 10^5 ; however, because of the large mass ratio of uranium over protactinium in the starting solution (approximately 10^7 – 10^8), the protactinium fraction still contained residual uranium, making a second separation step necessary. Here, the use of 0.4 M oxalic acid as eluent has the advantage that the protactinium eluate can be directly added onto a second silica gel column ($V_i = 0.25$ mL) after it has been acidified by addition of 4 mL of concentrated nitric acid. Protactinium was sorbed onto silica gel from the resulting 0.2 M oxalic acid/7.2 M HNO_3 solution, while residual uranium was washed through the column. After a further washing step using 4 mL of 8 M HNO_3 , protactinium was eluted from the column using 600 μL of 5% H_2O_2 /3 M HNO_3 with a recovery of $\sim 95\%$ for the second separation step. Hydrogen peroxide in the eluate was decomposed by addition of platinum foil. After the decomposition was completed (typically after several hours), the solution was transferred into another vial, the platinum foil was washed with 100 μL of 0.02 M HNO_3 /0.02 M HF , the solutions were combined, and the protactinium recovery was quantified by γ -spectrometry. Overall recoveries of the two-column separation procedure typically varied from 80 to 85%. The final protactinium fraction was then evaporated on a stainless steel planchette of a geometry that closely resembles the geometry of the nuclide standard used for the calibration of the α -spectrometer.

RESULTS AND DISCUSSION

The effectiveness of the separation procedure is illustrated in Figure 3, showing the α -spectra of a typical sample solution (U-

Table 1. Half Lives and Main α -Emissions of ^{231}Pa and ^{234}U ⁸

nuclide	energy (MeV)	emission probability (%)	half-life (y)
^{231}Pa	5.014	25.4	3.28×10^4
	4.951	22.9	
	5.030	20.0	
	5.059	11.0	
	4.735	8.5	
^{234}U	4.775	71.4	2.46×10^5
	4.723	28.4	

850) and the extracted protactinium fraction. The lower spectrum corresponds to 1.5 μg of U_3O_8 and was counted for 6×10^4 s. The protactinium fraction shown in the upper spectrum, counted for 1×10^6 s, corresponds to ~ 150 μg of ^{231}Pa extracted from 10.2 mg of U_3O_8 . The spectrum of the unspiked starting solution in the energy range from 4.5 to 5.2 MeV is characterized by the α -emissions of ^{234}U at 4.72 and 4.78 MeV. The α -spectrum of the Pa fraction is essentially free of uranium, corresponding to a decontamination factor for the protactinium fraction exceeding 2.5×10^7 . The main decay energies of ^{234}U and ^{231}Pa are summarized in Table 1.

From each reference material, a number of subsamples were individually spiked, separated, and measured. The age of uranium material was calculated from the equation of basic radioactive decay, $N = N_0 \times e^{-\lambda t}$. An example for age calculation from the $^{235}\text{U}/^{231}\text{Pa}$ ratio is shown below.

$$\frac{N_{\text{U}-235}}{N_{\text{Pa}-231}} = \frac{N_{0,\text{U}-235} \times e^{-\lambda_{\text{U}-235}t}}{(N_{0,\text{U}-235} - N_{\text{U}-235}) \times e^{-\lambda_{\text{Pa}-231}t}} \quad (1)$$

Time or “age” t can be solved from

$$t = \frac{\ln\left(1 - \frac{R}{K}\right)}{\beta} \quad (2)$$

where R is the measured $^{231}\text{Pa}/^{235}\text{U}$ atom ratio; β is a factor composed of the ^{235}U and ^{231}Pa decay constants ($\lambda_{\text{U}-235} - \lambda_{\text{Pa}-231}$); and K is the activity ratio, $\lambda_{\text{U}-235}/(\lambda_{\text{Pa}-231} - \lambda_{\text{U}-235})$.

The results of the age determination of U-500, U-800, and U-850 via $^{235}\text{U}/^{231}\text{Pa}$ by isotope dilution α -spectrometry (ID-AS) are summarized in Table 2. Uncertainties are expressed according to ISO/BIPM as combined uncertainty $U = u_c \times k$ using a coverage factor of 2.2 (that is, 95% coverage). They were calculated using a commercially available software, the GUM Workbench.⁹

The data show good agreement with the assumed ages and an average bias of -1.7 , -4.4 , and -2.7% for U-500, U-800, and U-850, respectively. In comparison with the ages determined in an earlier work using the ratio $^{234}\text{U}/^{230}\text{Th}$,⁴ the uncertainty of the measurement as well as the bias was found to be somewhat higher. This may be caused by the fact that an α -emitting tracer for protactinium (other than ^{231}Pa) is not available, and the recovery of the separation procedure can be monitored only up

(8) *Nuclides 2000*, version 1.00, European Communities, 1999.

(9) GUM (Guide for the Expression of Uncertainty in Measurements) Workbench, version 2.3, Metrodata GmbH: Grenzach-Wyhlen, Germany, 2001.

Table 2. Results of the Age Determination of HEU by ID-AS from the $^{235}\text{U}/^{231}\text{Pa}$ Ratio^a

sample	assumed age (y)	determined age (y)	bias (%)	method	reference
U-500	39.3	38.7 ± 1.8	-1.7	ID-AS ^b	this work
	38.8	38.1 ± 1.4	-1.8	ID-AS	4
	38.5	38.1 ± 0.4	-1.0	ID-TIMS ^c	4
	39.1	39.8 ± 0.4	+1.6	ICPMS	4
U-800	43.5	41.6 ± 2.0	-4.4	ID-AS	this work
	43.0	42.3 ± 1.5	-1.6	ID-AS	4
	42.7	41.9 ± 1.3	-1.9	ID-TIMS	4
	43.3	43.4 ± 0.9	+0.3	ICPMS ^d	4
U-850	44.2	43.0 ± 2.1	-2.7	ID-AS	this work
	43.8	43.3 ± 1.4	-1.1	ID-AS	4
	43.4	42.4 ± 0.8	-2.3	ID-TIMS	4
	44.0	45.3 ± 1.2	+2.9	ICPMS	4

^a Values determined via $^{234}\text{U}/^{230}\text{Th}$ shown for comparison (from ref 4); ^b Isotope dilution α -spectrometry. ^c Isotope dilution thermal ionization mass spectrometry. ^d Inductively coupled mass spectrometry.

to the preparation of the α -target. The possibility of the occurrence of minor losses of protactinium during the evaporation of the sample solution onto the α -target has to be taken into account and may lead to a slightly negative bias.

CONCLUSIONS

An experimental method for the age determination of highly enriched uranium exploiting the mother/daughter pair $^{235}\text{U}/^{231}\text{Pa}$ has been developed and successfully validated on standard reference materials. The separation of parts-per-billion amounts of protactinium from uranium samples is achieved by highly selective sorption to silica gel. Protactinium is subsequently quantified by α -spectrometry within a combined uncertainty below 5%. The method exhibits a combined uncertainty and bias slightly larger than an alternative method described earlier using the mother/daughter pair $^{234}\text{U}/^{230}\text{Th}$,⁴ but it has been found valuable in validating the experimental results by means of a second, independent analysis. The availability of two methods relying on two independent mother/daughter pairs provides strong measurement assurance to the analytical results.

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