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AGE DETERMINATION OF HIGHLY ENRICHED URANIUM

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Abstract

The present paper describes the individual analytical methodologies (Thermal Ionization Mass Spectrometry, Inductively Coupled Plasma Mass Spectrometry and Alpha Spectrometry) that were developed for uranium age determination and discusses their advantages and drawbacks. With respect to a potential application of the methods (e.g. Fissile Material Cut-off Treaty), the discussion focuses on highly enriched uranium, as this appears to be of highest strategic relevance. The different analytical methodologies were tested using uranium reference materials of different ^{235}U enrichments and of known ages.

1. INTRODUCTION

Obtaining information on the age of nuclear material is of relevance in nuclear forensic science in order to determine the date of the production campaign of the material. This might be helpful to identify the source of the material. Information on the age of highly enriched uranium may also be useful under a strengthened safeguards regime. Furthermore, such information will be of key importance for the verification of a Fissile Material Cut-off Treaty (FMCT). It will allow to distinguish between freshly produced (i.e. enriched or purified) material and material originating from excess weapons material. The same arguments apply basically also for plutonium. Age determination for Pu has been demonstrated earlier for bulk samples as well as for particles [1,2].

The radioactive decay of the actinide isotopes provides a unique chronometer, which is inherent to the material. In highly enriched uranium, the parent/daughter relations ^{234}U/^{230}Th and ^{235}U/^{231}Pa are advantageously used to determine the age of the material. The obtained age refers to the last separation of the daughter nuclide from its parent, i.e. the last purification of the material. Evidently, the accuracy of the measured age depends on the quality of this separation; hence it is based on the assumption of the complete removal of the daughter nuclides during the last separation or purification.

The age determination of uranium is somewhat more difficult than Pu dating, because of the long half-lives of uranium isotopes which lead only to minute amounts of in-growing daughter nuclides. This means that either separation of the Th and the Pa from uranium must be of high chemical recovery and a highly sensitive measurement technique must be applied.

In this work the age determination of highly enriched uranium has been studied using three different techniques: Thermal Ionization Mass Spectrometry (TIMS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Alpha Spectrometry (AS). For TIMS and AS a separation of daughter nuclides was required whereas a direct measurement of the sample was possible by ICP-MS.

2. METHODOLOGY

Age determination of uranium is not a new application. Geologists have determined the ages of rocks, sediments etc. already for tens of years. However, there the time scale is completely different, because geological samples are thousands of years old, whereas uranium, used for nuclear applications, is at the most 60 years old. Because young uranium samples have very high parent/daughter ratios (Fig. 1) due to the long half-lives of uranium isotopes, it makes the age determination of "processed" uranium rather difficult.

Uranium has three candidate parent/daughter relations for the age determination: ^{234}U/^{230}Th, ^{235}U/^{231}Pa and ^{236}U/^{232}Th. The latter relation is valid only for reprocessed U, because the ^{236}U is not naturally occurring isotope. Second limitation for the use of this relation is ^{232}Th, which occurs in nature. This leads to relatively high ^{232}Th blank levels and thus this relation was excluded in the study.

The ^{235}U/^{231}Pa mass ratio is exceedingly high due to the very long half-life of ^{235}U ($T_{1/2} = 7 \times 10^{8}$ a), which of course limits the possibilities of direct measurement. For a direct measurement, an instrument of high dynamic range and high sensitivity is absolute necessity. A U/Pa separation, on the other hand, does not solve the problem, because Pa does not have any other long-lived and/or alpha-active isotope for spiking, and thus the isotope dilution TIMS and AS (ID-TIMS and ID-AS) cannot easily be applied. The best relation for the age determination is thus the ^{234}U/^{230}Th.

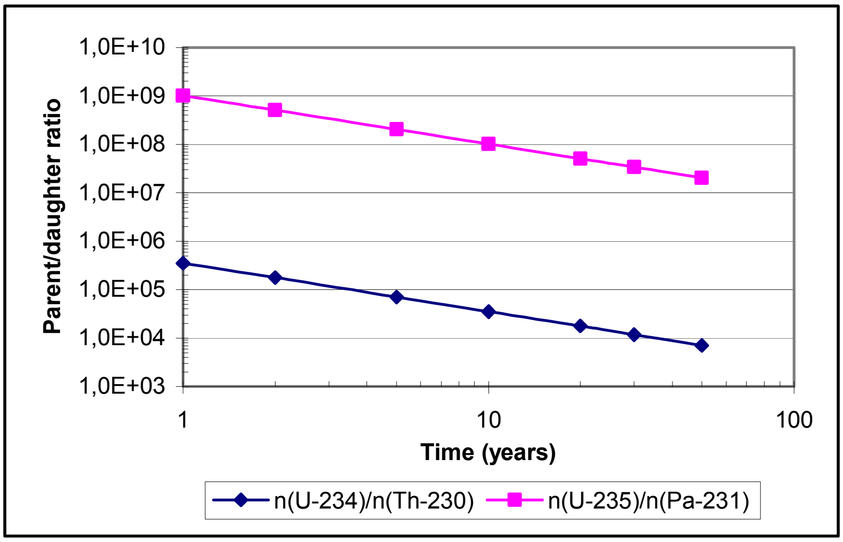

Fig.1. Parent/daughter ratios of uranium.

The age of uranium material is calculated from the equation of basic radioactive decay, $N = N_0 \times e^{-\lambda t}$. An example for age calculation from the ^{234}U/^{230}Th ratio is shown below.

$$\frac{N_{U-234}}{N_{Th-230}} = \frac{N_{0U-234} \times e^{-\lambda_{U-234} t}}{(N_{0U-234} - N_{U-234}) \times e^{-\lambda_{Th-230} t}} \tag{1}$$

where time or "age" t can be solved from.

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

where

R is the measured **^{230}Th/^{234}U**-atom ratio

β is a factor composed of the ^{234}U and ^{230}Th decay contants = $(\lambda_{U-234} - \lambda_{Th-230})$

K is the activity ratio = $\frac{\lambda_{U-234}}{(\lambda_{Th-230} - \lambda_{U-234})}$.

3. MATERIALS

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 are 50 %, 80 % and 85 % enriched in ^{235}U, respectively. The standards consist of U_3O_8 powders and their preparation dates are rather well known [3].

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.

TEVA ion chromatography resin (50-100μ, Eichrom Ind.) was used as purchased without further purification. The resin was packed in plastic columns (Bio-Rad), making up bed volumes of approx. 0.4 ml.

4. U/Th SEPARATION

Prior to TIMS and AS measurements, Th and U had to be separated. The experimental procedure used in this work for the separation of Th from bulk U is shown in Fig. 2. It is based on already existing procedure [4], but which was modified to some extent to be adapted better for this application. After conditioning the TEVA column with approx. 8 bed volumes of 2 M HNO_3, sample solutions typically containing 10 mg U_3O_8 dissolved in 2 M HNO_3 and spiked with ^{228}Th (ID-AS) or ^{232}Th (ID-TIMS) were added onto the column. Typical sample volumes were 2.0 ml and average flow rates approx. 0.2 ml/min.

The column was washed with 10 ml 2 M HNO_3 to remove U followed by elution of Th using 6 M HCl. Approx. 90% of the Th could typically be recovered in 1 ml 6 M HCl. The Th fraction was evaporated to near dryness, redissolved in conc. HNO_3, evaporated again and redissolved in 2 M HNO_3. This solution could be used directly for Th quantification by TIMS. The preparation of planchets for α-spectroscopy from this solution was not successful due to the formation of crusts after sample evaporation, yielding α-spectra of poor resolution. The TEVA resin was found to release significant amounts of presumably organic materials when treated with 6 M HCl and these residues could not be destroyed even by repeated evaporation with HNO_3. Therefore a second purification step had to be performed for the analysis of Th by ID-AS. The Th fraction, redissolved in 2 M HNO_3, was added onto a second TEVA column. The column was washed with 10 ml 2 M HNO_3 to remove any residual U followed by elution of Th with 1 ml 0.02 M HF/0.02 M HNO_3, typically recovering 90% of the Th. Aliquots of 0.5 ml of this solution could be directly used for the preparation of planchets yielding α-spectra of highly improved resolution.

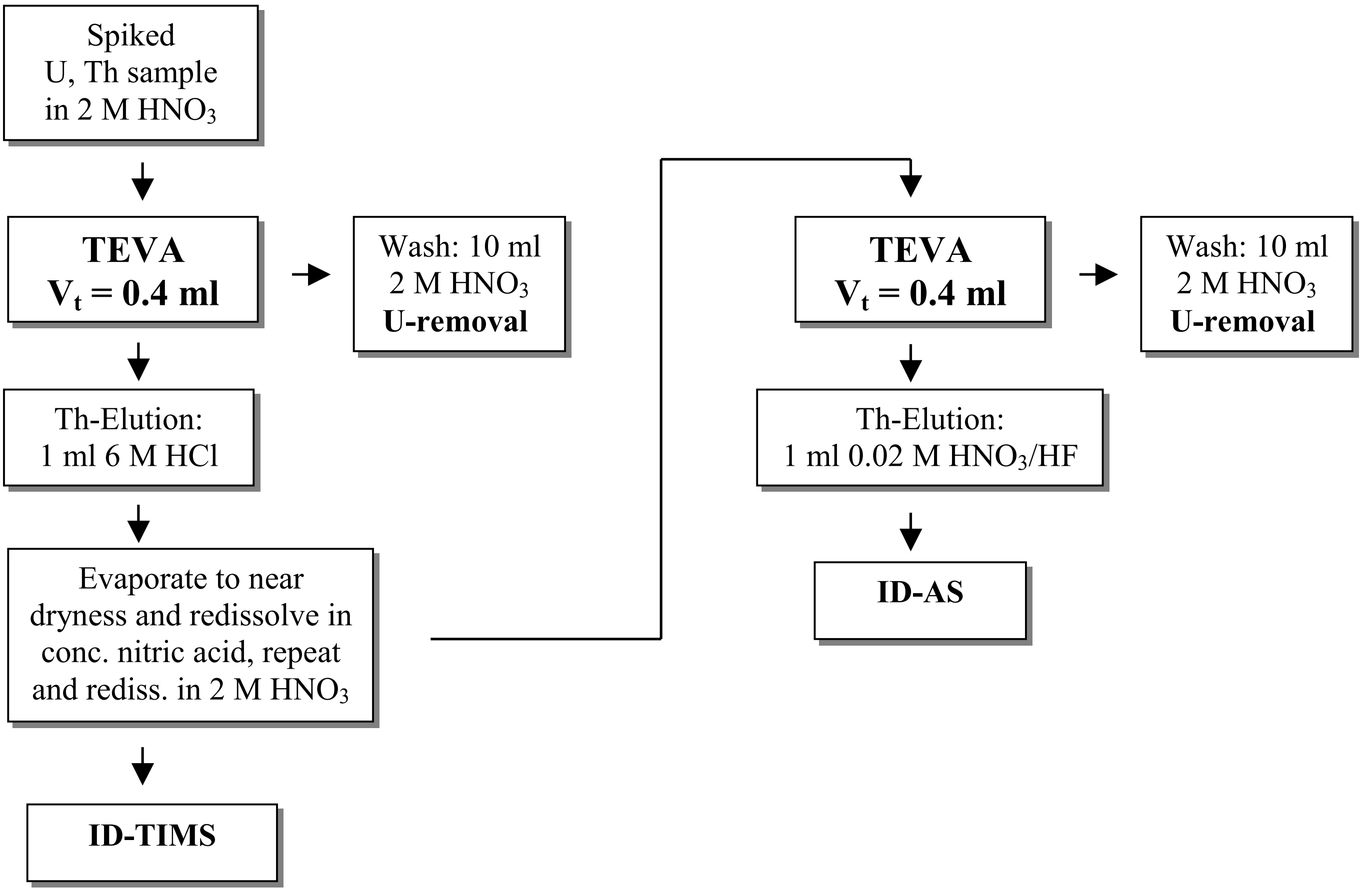

Fig. 2: Experimental procedure used for U/Th separation.

5. TECHNIQUES

5.1. Thermal Ionization Mass Spectrometry (TIMS)

Two different TIMS instruments were used for performing the isotope ratio measurements to determine the $n(^{234}U)/n(^{230}Th)$ ratio indirectly. First, $n(^{234}U)$ was measured by IDMS using ^{233}U as a spike. A routine measurement procedure was applied using a Finnigan MAT 261 instrument. The procedure includes double filament assembly and multi-collection by Faraday collectors using the total evaporation method [5]. Secondly, the $n(^{230}Th)$ was measured also by IDMS using ^{232}Th as a spike. Because Th-fractions had very low concentrations, a more sensitive detection method, namely ion counting, was required. This was done by Micromass Sector 54 instrument, which has six Faradays, three Channeltrons and a Daly in array [6]. The Channeltrons and the Daly are operated in pulse counting mode. $n(^{230}Th)/n(^{232}Th)$ ratio measurements were done using peak-jumping by Daly. The acquisition time was 5s/isotope and max. 9 blocks (10 cycles/block) were measured. Finally, the $n(^{234}U)/n(^{230}Th)$ was calculated and the age of the material was derived according to Eq.2.

5.2. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

$n(^{234}U)/n(^{230}Th)$ and $n(^{235}U)/n(^{231}Pa)$ ratios were measured using double-focusing, multi-collector ICP-MS from NU Instruments. The instrument contains 12 Faraday cups and a secondary electron multiplier (SEM, operated in pulse counting mode) in array. The ratios were measured using SEM for the ^{230}Th and ^{231}Pa, and Faradays for the U-isotopes. This enabled direct ratio determinations and no U/Th/Pa separation was required.

5.3. Alpha Spectrometry (AS)

Samples for alpha spectrometry were prepared by pipetting aliquots of 500 µl of sample solution onto stainless steel planchettes (Tracerlab). Planchettes were dried on a heat plate at 80 ºC, followed by heating to approximately 700 ºC for 5 min, and allowed to cool down before measurement. Samples were analyzed using a Tennelec TC 256 alpha spectrometer. Detection efficiencies were calibrated using a certified mixed nuclide standard (AMR43, Amersham). Typical counting times varied from 20000 s to 60000 s.

6. RESULTS AND DISCUSSION

Age determination results of three different techniques are compiled in Tables I-III. Uncertainties are expressed according to ISO/BIPM as combined uncertainty $U = u_c \times k$ using a coverage factor of 2 (i.e. 95 % coverage).

6.1. Isotope Dilution Thermal Ionization Mass Spectrometry (ID-TIMS)

The results of the age determination by ID-TIMS are presented in Table I. They are in good agreement with the assumed ages, even if the ages show to be slightly negatively biased. This can be due to the possible ^{232}Th contamination, and in future more care has to be taken in the blank determination.

The rather large combined uncertainties of the ages (1.0-2.5 %) are mainly caused by the standard deviation of the ^{230}Th/^{232}Th ratio measurements. This could be decreased in future by reducing the random uncertainty (Type A) contribution (i.e. increasing the number of measured filaments). However, combined uncertainty below 1 % appears unrealistic, because then the uncertainty contributions of systematic nature (Type B), e.g. the spikes, dominate.

Table I. Age determination from the ^{234}U/^{230}Th ratio by ID-TIMS.

Sample	Assumed age (a)	Determined age (a)	Bias (%)
U-500-I	38.46	38.14 ± 0.41 (1.07 %)	-0.83
U-500-II	„	38.12 ± 0.43 (1.13 %)	-0.88
U-800-I	42.67	41.79 ± 0.56 (1.34 %)	-2.06
U-800-II	„	42.00 ± 0.53 (1.26 %)	-1.57
U-850-I	43.38	42.61 ± 0.55 (1.29 %)	-1.78
U-850-II	„	42.15 ± 1.07 (2.54%)	-2.84

6.2. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The ages obtained from direct measurements of the n(^{234}U)/n(^{230}Th) and n(^{235}U)/n(^{231}Pa) ratios by ICP-MS are seen in Table II. The results show to be very inaccurate, which cannot be explained even by the large measurement uncertainties. A reason for this is not quite understood yet, because the instrument is new and only few tests were possible to do until now. An explanation could be the differences of ionisation potentials of U, Th and Pa (6.19, 6.31 and 5.89 eV respectively) [7]. This would result lower ages from the ^{234}U/^{230}Th ratio than from the ^{235}U/^{231}Pa ratio, which is actually here the case. However, it is well known that plasma ion source should ionize all elements till 7 eV > 98 % efficiency [8], thus slightly different ionization potentials should not affect the results, at least not to such a great extent.

Table II. Age determination results from the direct ^{234}U/^{230}Th and ^{235}U/^{231}Pa ratio measurements by ICP-MS.

Sample	Assumed age (a)	Determined age (a) ^{234}U/^{230}Th	Bias	Determined age (a) ^{235}U/^{231}Pa	Bias
U-500	38.83	25.00 ± 7.14 (28.6 %)	-35.6 %	44.09 ± 2.16 (4.90 %)	13.5 %
U-800	43.04	29.05 ± 5.14 (17.7 %)	-32.5 %	48.76 ± 5.64 (11.6 %)	13.3 %
U-850	43.75	34.35 ± 0.31 (0.90 %)	-21.5 %	50.14 ± 8.38 (16.7 %)	14.6 %

6.3. Isotope Dilution Alpha Spectrometry (ID-AS)

The results of the age determination for the U-500 and U-800 by ID-AS are summarized in Table III. These data are based on only a single separation experiment for each of the reference materials and need to be further validated. The preliminary data show very good agreement with the assumed ages, indicating that ID-AS can be used as a second independent method in addition to ID-TIMS for the age determination of highly enriched uranium.

Table III. Age determination results from the ^{234}U/^{230}Th ratio by ID-AS.

Sample	Assumed age (a)	Determined age (a)	Bias (%)
U-500	38.75	37.80 ± 1.09 (2.88 %)	-2.45
U-800	42.96	42.47 ± 1.23 (2.90 %)	-1.14

7. CONCLUSIONS

In this work the age determination of HEU has been demonstrated by three different techniques. It shows that more laborious techniques, ID-TIMS and ID-AS, give more accurate results than the direct determination by ICP-MS, and they are in good agreement with the assumed ages. The results are slightly negatively biased, however being mostly within the measurement uncertainties. The rather poor preliminary results obtained by ICP-MS show that more studies are needed in this area to explain the highly negatively biased results from the ^{234}U/^{230}Th ratio, and in as a consequence of this, to improve the method.

The applicability of the developed method to young uranium materials could not be tested, because young highly enriched uranium reference materials are not available, at least commercially. However, in theory the ID-TIMS should also be suitable for younger HEU samples. This is because ^{232}Th is used not only as a spike but also as a carrier and thus even smaller amounts (~20 times less) of ^{230}Th in the sample should be possible to get recovered. Of course, the precision will suffer, because the measured ^{230}Th/^{232}Th ratio gets lower. This could be compensated using bigger sample amounts, but it is not recommended, not only to avoid the handling of big amounts of HEU but also because it will affect the efficiency of the U/Th separation.

Acknowledgement

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REFERENCES

[1] Wallenius, M., Mayer, K., "Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry", Fresenius' J. Anal. Chem. Vol. 366, No. 3, 2000, 234-238.
[2] Wallenius, M., Tamborini, G., Koch, L., "The age of plutonium particles", Radiochim. Acta 89, 2001, 55-58.
[3] Private communication, Margaret Tolbert, DOE, USA.
[4] Horwitz, E.P., Dietz, M.L., Chiarizia, R., Diamond, H., Maxwell III, S.L., Nelson, M.R., "Separation and preconcentration of actinides by extraction chromatography using a supported liquid anion exchanger: application to the characterization of high-level nuclear waste solutions", Anal. Chim. Acta 310, 1995, 63-78.
[5] Romkowski, M., Franzini, S., Koch, L., "Mass-spectrometric analysis of sub-nanocurie samples of uranium and plutonium", Proceedings of the 8th Annual ESADRA Symposium, 12-14 May 1987, 111-113.
[6] Wallenius, M., Kühn, H., Mayer, K., Koch, L., "First performance tests of a multi-micro-channeltron thermal ionisation mass spectrometer", Advances in Mass Spectrometry, Vol.14 (CD-ROM), 1997.
[7] Lide, D.R. (Editor-in-Chief), CRC Handbook of Chemistry and Physics, 81st Edition.
[8] Platzer, I.T., "Modern isotope ratio mass spectrometry", Chemical Analysis, Vol. 145, John Wiley & Sons, 1997.