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## Determination of the age of highly enriched uranium

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**Abstract** This paper describes the analytical methods (thermal ionization mass spectrometry, inductively coupled plasma mass spectrometry, and alpha spectrometry) that have been developed for determination of the age of uranium and discusses their advantages and limitations. With regard to potential application of the methods (e.g. Fissile Material Cut-off Treaty), the discussion focuses on highly enriched uranium, because this seems to be of highest strategic relevance.

The different analytical methods were tested and validated by use of uranium reference materials of different  $^{235}\text{U}$  isotope abundance and of known ages. The results show that thermal ionization mass spectrometry and alpha spectrometry are both very accurate and precise techniques for this application. Inductively coupled plasma mass spectrometry, on the other hand, although less precise, because of the different approach to the analytical problem, is still sufficiently accurate to be used as a rapid screening method.

**Keywords** Age determination · Uranium · Mass spectrometry · Alpha spectrometry · Fissile Material Cut-off Treaty

### Introduction

All isotopes of uranium are subject to radioactive decay. The isotopes common in weapons-grade or reactor-grade material are relatively long lived. Low enriched uranium is generally used for power reactors whereas highly enriched uranium is required for weapons purposes.

The age of nuclear material is of relevance in nuclear forensic science, to determine the date of production of the material. This has great importance when identifying

the source of the material. Information about the age of highly enriched uranium (HEU) might also be useful under a strengthened safeguards regime to reveal possible clandestine operations. Such information will, furthermore, be of key importance for verification of a Fissile Material Cut-off Treaty (FMCT). FMCT is an agreement (still under discussion) which would stop production of HEU and plutonium for nuclear weapons. Age determination will thus enable the analyst to distinguish between freshly produced (i.e. enriched or purified) material and material originating from excess weapons material, thus being "old". The same arguments apply basically to plutonium also. Reliability and accuracy of Pu age determination have been demonstrated earlier for bulk samples and for particles [1, 2].

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

Determination of the age of uranium is somewhat more difficult than Pu dating, because of the considerably longer half-lives of uranium isotopes which lead to minute amounts only of in-growing daughter nuclides. This means that both 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 three different techniques used to determine of the age of highly enriched uranium – thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP–MS), and alpha spectrometry (AS) – have been studied. For TIMS and AS separation of daughter nuclides was required whereas a direct measurement of the parent/daughter ratio was possible by ICP–MS.

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## Methodology

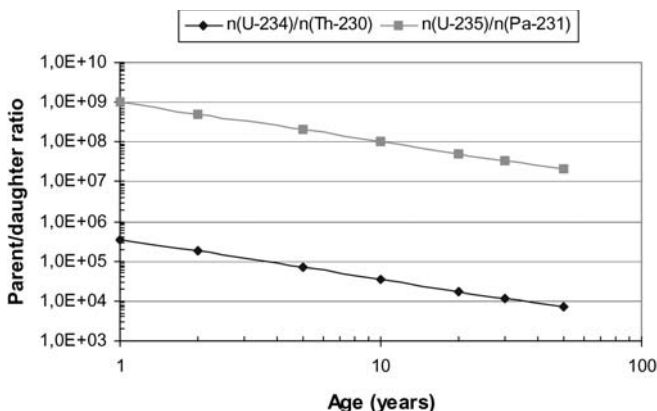
Age determination of uranium as such is not a new application – geologists have been determining the ages of rocks, sediments, etc., for tens of years. The time scale is, however, completely different, because geological samples are thousands or millions of years old whereas uranium used for nuclear applications is at most 60 years old. This makes determination of the age of “processed” uranium rather difficult, because young uranium samples have very high parent/daughter ratios, because of the long half-lives of uranium isotopes (Table 1).

Uranium has three candidate parent/daughter relationships for the age determination –  $^{234}\text{U}/^{230}\text{Th}$ ,  $^{235}\text{U}/^{231}\text{Pa}$ , and  $^{236}\text{U}/^{232}\text{Th}$ . The latter relationship is valid only for irradiated and reprocessed U, because the  $^{236}\text{U}$  is not a naturally occurring isotope. The second limitation on the use of this relationship is that  $^{232}\text{Th}$  occurs in nature, which leads to non-negligible  $^{232}\text{Th}$  blank levels in the chemical reagents and solvents. This relationship was not, therefore, considered in this study.

The  $^{235}\text{U}/^{231}\text{Pa}$  ratio is exceedingly high, i.e.  $10^7$ – $10^9$  (Fig. 1), because of the very long half-life of  $^{235}\text{U}$ ; this limits the possibility of direct measurement, for which an instrument of high dynamic range and high sensitivity is thus an absolute necessity. We could, on the other hand, also calculate the age on the basis of the indirectly determined parent/daughter ratio, i.e. by adding appropriate spikes, perform chemical separation, and measure the amount of parent nuclide ( $^{235}\text{U}$ ) and daughter nuclide ( $^{231}\text{Pa}$ ). This, however, is found to be difficult, because

**Table 1** Half-lives of uranium and its daughter nuclides [3]

Nuclide	$T_{1/2}$ (a)
$^{234}\text{U}$	$2.46 \times 10^5$
$^{235}\text{U}$	$7.04 \times 10^8$
$^{236}\text{U}$	$2.34 \times 10^7$
$^{230}\text{Th}$	$7.55 \times 10^4$
$^{231}\text{Pa}$	$3.28 \times 10^4$
$^{232}\text{Th}$	$1.41 \times 10^{10}$



**Fig. 1** Calculated parent/daughter ratios of uranium as a function of “age” (decay time)

there is no long-lived Pa isotope available that could serve as spike (neither for alpha spectrometry nor for mass spectrometry). The best relationship for determination of the age of uranium is, therefore,  $^{234}\text{U}/^{230}\text{Th}$ .

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

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

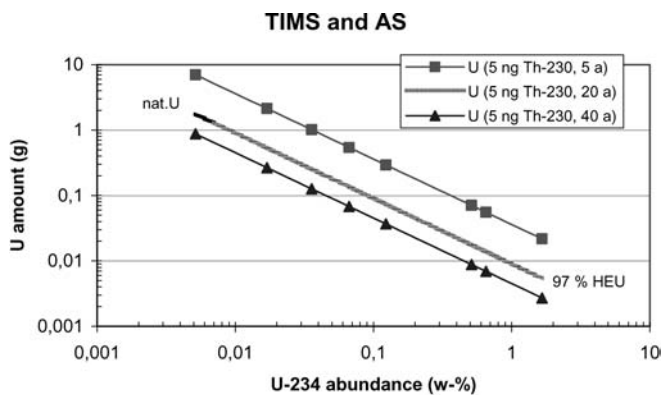
where time or “age”  $t$  can be obtained from.

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

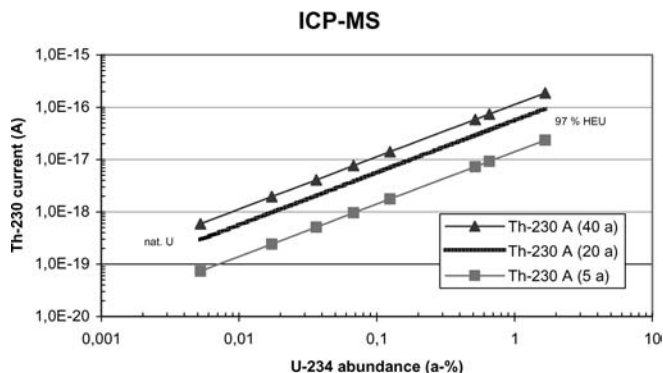
where  $R$  is the measured  $^{230}\text{Th}/^{234}\text{U}$ -atom ratio and  $\beta$  is a factor combining the  $^{234}\text{U}$  and  $^{230}\text{Th}$  decay constants,  $= (\lambda_{U-234} - \lambda_{Th-230})$  and

$$K \text{ is the activity ratio} = \frac{\lambda_{U-234}}{(\lambda_{Th-230} - \lambda_{U-234})} \quad (3)$$

The amount of uranium needed for analysis depends on the  $^{234}\text{U}$  isotope abundance and consequently on the  $^{235}\text{U}$  enrichment, because the higher the  $^{235}\text{U}$  enrichment, the higher the abundance of  $^{234}\text{U}$ . For TIMS and AS analyses 5 to 10 ng of  $^{230}\text{Th}$  is needed. Figure 2 shows that only a few milligrams of “old” HEU is sufficient ( $\sim 1\%$   $^{234}\text{U}$ ) to obtain 5–10 ng  $^{230}\text{Th}$ , whereas for natural U (0.0055%  $^{234}\text{U}$ ), more than 1 g of material is required. For direct  $^{234}\text{U}/^{230}\text{Th}$  ratio measurement by ICP–MS the situation is different. The measurement range is limited at the upper end by the saturation of the amplifiers of the Faraday detectors ( $>10^{-10}$  A) and at the lower end by the background and noise of the ion counter ( $\sim 10^{-19}$  A). For our ICP–MS instrument the maximum U concentration was considered to be  $1 \mu\text{g g}^{-1}$ . An ion current of  $10^{-18}$  A of  $^{230}\text{Th}$  is, on the other hand, a feasible limit of quantification. From Fig. 3 we can see that for young U samples the required  $^{234}\text{U}$  abundance is approximately 0.1% (corresponding to HEU of  $\sim 15\%$   $^{235}\text{U}$ ) whereas for older samples we can go down to 1%  $^{235}\text{U}$ -enriched U samples ( $^{234}\text{U} \sim 0.01\%$ ).



**Fig. 2** Amounts of uranium needed for TIMS and AS analysis



**Fig. 3** Required  $^{234}\text{U}$  abundance in U samples for direct  $^{234}\text{U}/^{230}\text{Th}$  ratio determination by ICP-MS

## Experimental

### Materials

The uranium isotopic standard reference materials used in the study were U-500, U-800, and U-850 from New Brunswick Laboratory (NBL; materials were produced and formerly sold by National Bureau of Standards, NBS). They are 50%, 80%, and 85% enriched in  $^{235}\text{U}$ , respectively. The standards consist of  $\text{U}_3\text{O}_8$  powder; the preparation dates are rather well known and hereafter referred to as “assumed ages” [4].

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 (50–100  $\mu\text{m}$ , Eichrom) 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.

### Separations

Before TIMS and AS measurement 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. 4. It is based on the selective ex-

traction of Th(IV) from nitric acid media, by use of the extraction chromatographic resin TEVA, developed by Horwitz et al. [5]. After conditioning the TEVA column with approx. 4 mL  $2\text{ mol L}^{-1}\text{ HNO}_3$ , sample solutions typically containing 10 mg  $\text{U}_3\text{O}_8$  dissolved in  $2\text{ mol L}^{-1}\text{ HNO}_3$  and spiked with  $^{228}\text{Th}$  (ID-AS) or  $^{232}\text{Th}$  (ID-TIMS) were applied to the column. Typical sample volumes were 2.0 mL and average flow rates approx.  $0.2\text{ mL min}^{-1}$ .

The column was washed with 10 mL  $2\text{ mol L}^{-1}\text{ HNO}_3$  to remove U followed by elution of Th by use of  $6\text{ mol L}^{-1}\text{ HCl}$ . Approx. >95% of the Th could typically be recovered in 1 mL  $6\text{ mol L}^{-1}\text{ HCl}$ . The Th fraction was evaporated to near dryness, redissolved in conc.  $\text{HNO}_3$ , evaporated again, and redissolved in  $2\text{ mol L}^{-1}\text{ HNO}_3$ . This solution could be directly used for the quantification of Th by TIMS.

The preparation of planchets for  $\alpha$ -spectroscopy from this solution was not successful, because of the formation of crusts after sample evaporation, yielding  $\alpha$ -spectra of poor resolution. The TEVA resin used was found to release significant amounts of, presumably, organic materials when treated with  $6\text{ mol L}^{-1}\text{ HCl}$  and these residues could not be destroyed even by repeated evaporation with  $\text{HNO}_3$ . It was, therefore, necessary to perform a second purification step for analysis of Th by ID-AS. The Th fraction, redissolved in  $2\text{ mol L}^{-1}\text{ HNO}_3$ , was applied to a second TEVA column. The column was washed with 10 mL  $2\text{ mol L}^{-1}\text{ HNO}_3$  to remove any residual U followed by elution of Th with 1 mL  $0.02\text{ mol L}^{-1}\text{ HF}/0.02\text{ mol L}^{-1}\text{ HNO}_3$ , typically recovering >95% Th. This solution (0.5 mL aliquots) could be used directly to prepare planchets yielding  $\alpha$ -spectra of highly improved resolution.

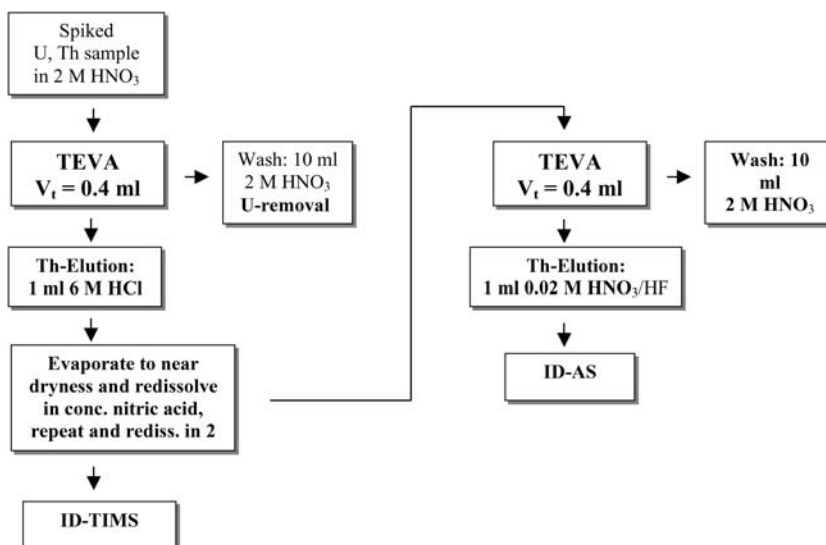
Recoveries after individual separation steps were monitored by measuring the gamma-activity of  $^{231}\text{Th}$  at 84.2 and 81.2 keV. Recovery from the overall separation procedure was typically >90% with a decontamination factor for uranium in the thorium fraction exceeding  $10^6$ .

### Instrumentation

#### Thermal ionization mass spectrometry (TIMS)

Two different TIMS instruments were used to perform the isotope ratio measurements to determine the  $n(^{234}\text{U})/n(^{230}\text{Th})$  ratio indirectly. First,  $n(^{234}\text{U})$  was measured by IDMS, using  $^{233}\text{U}$  as a spike. A routine measurement procedure was applied using a Finnigan MAT 261 instrument. The procedure includes a double-filament assembly and multi-collection by means of Faraday collectors, using the total-evaporation method [6]. Secondly, the  $n(^{230}\text{Th})$  was also measured by IDMS, using  $^{232}\text{Th}$  as a spike. Because Th frac-

**Fig. 4** Experimental procedure used for U/Th separation



**Table 2** Operating conditions of the NU Instruments MC-ICP-MS

Nebulizer	MicroMist	Aridus
Spray chamber	NU Instruments	
RF power (W)	1350	
RF generator frequency (MHz)	27.1	
Outer gas flow rate (L min <sup>-1</sup> )	16.5	
Intermediate gas flow rate (L min <sup>-1</sup> )	1.3	
Nebulizer gas flow rate (L min <sup>-1</sup> )	0.9	1.0
Sample flow rate (μL min <sup>-1</sup> )	400	60
Sweep gas flow rate (L min <sup>-1</sup> )		3.5
Spray chamber temperature (°C)		70
Desolvator temperature (°C)		160
Sampling cone	Nickel with a 1.2-mm orifice	
Skimmer cone	Nickel with a 0.9-mm orifice	
Mass resolution (m/Δm)		350
Integration time (s/cycle)		5
Cycles/run		10
Runs		3
Replicates		3

tions were present at very low concentrations, a more sensitive detection method, namely ion counting, was required. This was done by means of a Micromass Sector 54 instrument, which has five movable Faradays, three movable Channeltrons, and a fixed Daly and a Faraday in array [7]. The Channeltrons and the Daly are operated in pulse-counting mode.  $n(^{230}\text{Th})/n(^{232}\text{Th})$  ratio measurements were made by using of peak-jumping by Daly. The acquisition time was 5s/isotope and a maximum of nine blocks (10 cycles/block) was measured. Finally  $n(^{234}\text{U})/n(^{230}\text{Th})$  was calculated and the age of the material was derived by use of Eq. (2).

#### Inductively coupled plasma mass spectrometry (ICP-MS)

$n(^{234}\text{U})/n(^{230}\text{Th})$  and  $n(^{235}\text{U})/n(^{231}\text{Pa})$  ratios were measured by use of a double-focusing, multi-collector ICP-MS (Nu Plasma) manufactured by Nu Instruments. The instrument contains 12 fixed Faraday cups and a secondary electron multiplier (SEM, operated in pulse-counting mode), in an array. The ratios were determined by measuring the  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  ion currents using the SEM, while the ion currents of the respective U isotopes were measured using the Faraday cups. This enabled direct ratio determinations and no U/Th/Pa separation or spiking was required. The operating conditions of the instrument are given in Table 2.

#### Alpha spectrometry (AS)

Samples for alpha spectrometry were prepared by pipetting sample solution (500 μL) on to stainless steel planchettes (Tracerlab). Planchettes were dried on a hotplate at 80 °C, then heated to approximately 700 °C for 5 min, and left to cool before measurement. Samples were counted for 60,000 s using a TC 256 alpha spectrometer (Tennelec). Detection efficiencies were calibrated by use of a certified mixed nuclide standard (AMR43, Amersham).

## Results and discussion

Results from age determination by use of the three different techniques are compiled in Tables 3, 4, 5, and 6. They are all corrected to the same date, i.e. 1.1.2002. Uncertainties are expressed according to ISO/BIPM as combined

**Table 3** Ages obtained from  $^{234}\text{U}/^{230}\text{Th}$  ratios determined by ID-TIMS

Sample	Assumed age (a)	Determined age (a)	Bias (%)
U-500-I	39.13	38.82±0.42 (1.07%)	-0.78
U-500-II		38.80±0.44 (1.13%)	-0.83
U-800-I	43.29	42.59±0.57 (1.33%)	-1.62
U-800-II		42.80±0.55 (1.28%)	-1.14
U-850-I	44.00	43.51±0.56 (1.28%)	-1.11
U-850-II		43.04±1.10 (2.55%)	-2.18

**Table 4** Ages obtained from  $^{234}\text{U}/^{230}\text{Th}$  ratios determined directly by ICP-MS

Sample	Assumed age (a)	Determined age (a)	Bias (%)	Nebulizer
U-500	39.13	36.87±0.30 (0.81%)	-5.75	Aridus
		36.90±0.72 (1.94%)	-5.68	MicroMist
		36.21±0.61 (1.68%)	-7.44	MicroMist
U-800	43.29	39.30±0.40 (1.01%)	-9.21	Aridus
		41.42±0.38 (0.91%)	-4.31	Aridus
		39.80±0.33 (0.83%)	-8.06	Aridus
		40.05±1.07 (2.66%)	-7.48	MicroMist
		39.54±0.80 (2.01%)	-8.66	MicroMist
U-850	44.00	42.99±0.13 (0.30%)	-2.29	Aridus
		41.22±0.82 (1.98%)	-6.31	MicroMist
		41.02±0.22 (0.53%)	-6.77	MicroMist

**Table 5** Ages obtained from  $^{234}\text{U}/^{230}\text{Th}$  ratios determined directly by ICP-MS, after correction for ionization efficiency

Sample	Assumed age (a)	Determined age (a)	Bias (%)
U-500	39.13	39.77±0.41 (1.04%)	1.63
U-800	43.29	43.40±0.90 (2.07%)	0.25
U-850	44.00	45.26±1.15 (2.55%)	2.87

**Table 6** Ages obtained from  $^{234}\text{U}/^{230}\text{Th}$  ratios determined by ID-AS

Sample	Assumed age (a)	Determined age (a)	Bias (%)	Rel. Diff. (α-TIMS)
U-500	39.13	38.13±1.37 (3.60%)	-2.54	-1.74
		38.61±1.40 (3.62%)	-1.32	-0.51
U-800	43.29	42.81±1.80 (4.21%)	-1.11	0.27
		42.37±1.29 (3.14%)	-2.13	-0.75
U-850	44.00	43.51±1.41 (3.24%)	-1.11	0.53

uncertainty  $U=u_c \times k$  using a coverage factor of 2 (i.e. 95% coverage). They were calculated by use of commercially available software, GUM Workbench [8].

### Isotope dilution thermal ionization mass spectrometry (ID-TIMS)

From each reference material two subsamples were individually spiked, separated, and measured. The results are shown in Table 3. The experimentally determined ages are in good agreement with the assumed ages, even if they seem to be slightly negatively biased. The rather large combined uncertainties of the ages (1.0–2.5%) are mainly because of the standard deviation of the  $^{230}\text{Th}/^{232}\text{Th}$  ratio measurements. This could be reduced in the future by reducing the random uncertainty (Type A) contribution (i.e. increasing the number of filaments measured). Despite this a combined uncertainty below 1% seems hardly achievable, because Type B uncertainty contributions would then dominate.

### Inductively coupled plasma mass spectrometry (ICP-MS)

The ages obtained from direct measurements of the  $n(^{234}\text{U})/n(^{230}\text{Th})$  ratio by ICP-MS are shown in Table 4. The results are consistently negatively biased ranging from –2% to –9%. The variation is neither sample- nor nebulizer-dependent. The within-run standard deviations of the individual measurements are very good, despite the low counting rate of  $^{230}\text{Th}$ , i.e. ~50 cps using the MicroMist and ~300 cps using the Aridus nebulizer.

The negatively biased results might be because of different ionization efficiencies of U and Th (ionization potentials are 6.19 and 6.31 eV, respectively [9]); they might also arise from the large excess of uranium in the sample. Several synthetic U/Th mixtures were prepared gravimetrically from certified standards of high-purity U and Th. The mixtures were prepared independently, to exclude possible dilution errors. The U concentrations were kept constant at  $500 \text{ ng g}^{-1}$  whereas U/Th ratios were varied over several orders of magnitude, to check and quantify possible systematic effects (Fig. 5). These tests showed that the Th ionization yield is inferior to that of uranium. This was quite unexpected, because it is generally assumed that a plasma ion source would ionize all elements up to 7 eV with >98% efficiency [10].

The shape of the curve shown in Fig. 5 suggests several superimposing effects. Slight non-linearity is already apparent for U/Th ratios between 1 and 100, which were measured using two Faraday cups. This might be because of a matrix effect with growing uranium excess. For ratios from 1000 to 500,000 non-linearity of the ion-counter or incomplete dead time correction might cause further bias. This needs to be studied in more detail to find a comprehensive and quantitative explanation for these observations.

Our preliminary results were, however, corrected for the observed bias, using an empirical factor which we obtained from measurement the synthetic mixtures at a U/Th ratio of 10,000, which corresponds to the  $^{234}\text{U}/^{230}\text{Th}$  ratio in the samples (Table 5).

The  $^{235}\text{U}/^{231}\text{Pa}$  ratio was also measured but, because the counting rate of  $^{231}\text{Pa}$  (~4 cps with MicroMist) was too

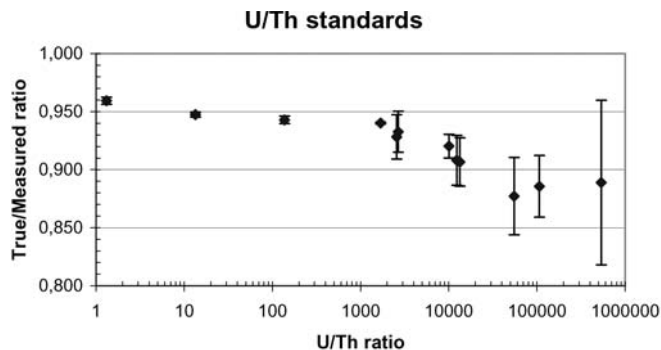


Fig. 5 Dependence of ionization efficiency on U/Th ratio

low, the ages obtained were highly positively biased and it was not possible to detect differences between the samples.

### Isotope dilution alpha spectrometry (ID-AS)

Typical alpha-spectra used for determination of the age of highly enriched uranium are shown in Fig. 6 for the reference material U-800 before and after U/Th separation. All spectra were counted for 60,000 s, the spectrum of the starting solution corresponds to  $1.5 \mu\text{g}$  of  $\text{U}_3\text{O}_8$  whereas the thorium fractions were extracted from approx.  $4.2 \text{ mg}$   $\text{U}_3\text{O}_8$ . The spectrum of the starting solution is characterized by the alpha-emissions of  $^{235}\text{U}$  at 4.40 MeV and  $^{234}\text{U}$  at 4.72 and 4.78 MeV. The alpha-spectrum of the Th frac-

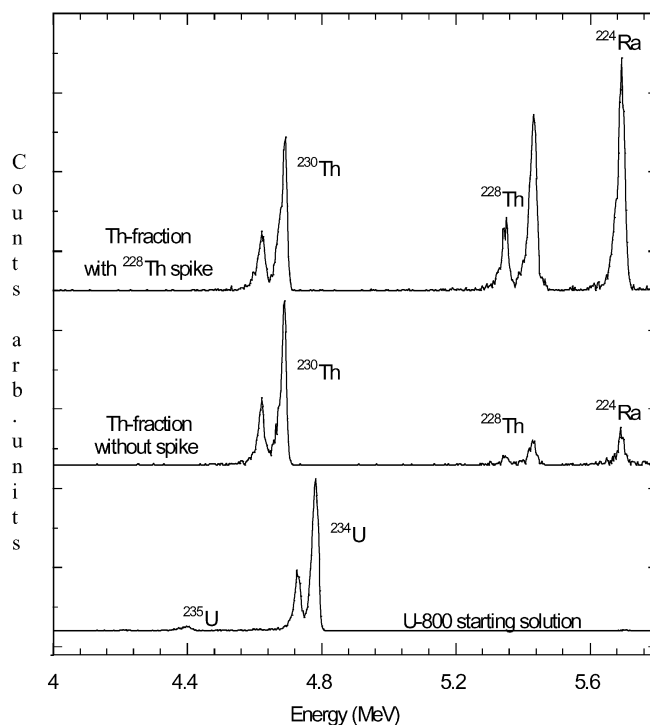
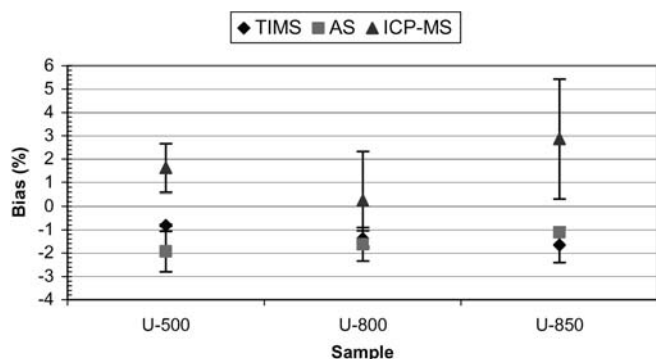


Fig. 6 Alpha spectra of spiked and unspiked Th-fractions and U-solution



**Fig. 7** Comparison of the results obtained from the different techniques

tion separated from an unspiked U-800 sample (middle spectrum) in the energy range from 4.0–5.9 MeV gives the bands of  $^{230}\text{Th}$  at 4.62 and 4.69 MeV,  $^{228}\text{Th}$  at 5.34 and 5.42 MeV, and  $^{224}\text{Ra}$  at 5.69 MeV. The peak area of  $^{228}\text{Th}$  has to be corrected for the contribution from emissions of  $^{224}\text{Ra}$  at 5.45 MeV with an emission probability of 4.9%. The activity of  $^{228}\text{Th}$ , originating from the decay of  $^{232}\text{U}$ , was determined for each reference material by analyzing unspiked samples. The activity ratios  $^{228}\text{Th}/^{230}\text{Th}$  found were  $0.1342 \pm 0.0089$  for U-500,  $0.1552 \pm 0.0026$  for U-800 and  $0.3518 \pm 0.0018$  for U-850. The upper spectrum in Fig. 6 shows a typical alpha-spectrum obtained from the Th fraction extracted from a U-800 sample spiked with  $^{228}\text{Th}$ .

The results obtained from determination of the age of U-500, U-800, and U-850 by ID-AS are summarized in Table 6. The data show that agreement was very good, not only for with the assumed ages, but also with ID-TIMS results, indicating that ID-AS can be used as a second independent method, in addition to ID-TIMS, for determination of the age of HEU. The results from all three techniques are compiled in Fig. 7.

## Conclusions

In this work a method for determination of the age of HEU has been developed and checked against certified

reference materials of known age. It was demonstrated that three different measurement techniques can be applied for this purpose. The more laborious techniques, ID-TIMS and ID-AS, give more accurate results than direct determination by ICP-MS, and they are in good agreement with the assumed ages. The results are slightly negatively biased, however, although mostly within the measurement uncertainties. In application of this methodology for verification of a fissile material cut-off treaty (i.e. distinguishing between old and freshly produced HEU) this small bias would not affect the conclusion.

The rather poor preliminary results obtained by ICP-MS could be explained partly by differences between ionization efficiencies for U and Th. When the results were corrected with an experimentally determined correction factor we obtained results which were closer to the assumed ages. Thus direct  $^{234}\text{U}/^{230}\text{Th}$  ratio measurement can be used as a “screening” method for HEU age determination, to obtain the first estimate of the age.

**Acknowledgement** The authors would like to thank Rudolf Fiedler, Adrian Nicholl, Roger Molinet, and Ramon Carlos Marquez for their valuable contributions to this work. Furthermore, the co-operation of NBL by providing essential information on the age of the uranium reference materials is highly appreciated.

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