

# Age determination of plutonium using inductively coupled plasma mass spectrometry

U. Nygren,<sup>1,2\*</sup> H. Ramebäck,<sup>1</sup> C. Nilsson<sup>1</sup>

<sup>1</sup>Swedish Defence Research Agency (FOI), Division of NBC Analysis, SE-901 82 Umeå, Sweden

<sup>2</sup>Department of Chemistry, Luleå University of Technology, SE-971 87 Luleå, Sweden

(Received May 4, 2006)

The age of plutonium is defined as the time since the last separation of the plutonium isotopes from their daughter nuclides. In this paper, a method for age determination based on analysis of  $^{241}\text{Pu}/^{241}\text{Am}$  and  $^{240}\text{Pu}/^{236}\text{Pu}$  using ICP-SFMS is described. Separation of Pu and Am was performed using a solid phase extraction procedure including UTEVA, TEVA, TRU and Ln-resins. The procedure provided separation factors adequate for this purpose. Age determinations were performed on two plutonium reference solutions from the Institute for Reference Materials and Measurements, IRMM081 ( $^{239}\text{Pu}$ ) and IRMM083 ( $^{240}\text{Pu}$ ), on sediment from the Marshall Islands (reference material IAEA367) and on soil from the Trinity test site (Trinitite). The measured ages based on the  $^{241}\text{Am}/^{241}\text{Pu}$  ratio corresponded well with the time since the last parent-daughter separations of all the materials. The ages derived from the  $^{236}\text{U}/^{240}\text{Pu}$  ratio were in agreement for the IRMM materials, but for IAEA367 the determination of  $^{236}\text{U}$  was interfered by tailing from  $^{238}\text{U}$ , and for Trinitite the determined age was biased due to formation of  $^{236}\text{U}$  in the detonation of the “Gadget”.

## Introduction

Knowledge of the origin and history of nuclear material is of importance in many different areas, e.g., nuclear forensics (illicit trafficking), environmental studies, emergency preparedness, and in a verification regime for a future fissile material cut-off treaty (FMCT). In the analysis of the origin of plutonium, information on isotopic composition and age of the material is of vital importance.

WALLENUS and colleagues<sup>1–3</sup> have, in a series of publications, exploited different types of mass spectrometers for determining the age and origin of Pu. They applied secondary ion mass spectrometry (SIMS) for the dating of single plutonium particles.<sup>1</sup> Thermal ionization mass spectrometry (TIMS) and quadrupole-based inductively coupled plasma mass spectrometry (ICP-QMS) were used for the age determination of plutonium reference materials and plutonium pellet samples.<sup>2,3</sup> The age determinations using mass spectrometry were primarily based on the  $^{238}\text{Pu}/^{234}\text{U}$ ,  $^{239}\text{Pu}/^{235}\text{U}$  and  $^{240}\text{Pu}/^{236}\text{U}$  ratios, and the results were generally in good agreement with the reported ages. However, some discrepancies were identified, e.g., too low determined ages from the  $^{238}\text{Pu}/^{234}\text{U}$  ratio and too high from the  $^{239}\text{Pu}/^{235}\text{U}$  ratio when analyzing  $\text{PuO}_2$  and mixed oxide fuel (MOX) particles using SIMS. This was due to interference from  $^{238}\text{U}$  in the determination of  $^{238}\text{Pu}$  causing overestimation of the  $^{238}\text{Pu}/^{234}\text{U}$  ratio, and contamination from  $^{235}\text{U}$  causing an underestimated  $^{239}\text{Pu}/^{235}\text{U}$  ratio.

Of the Pu-U pairs, the  $^{240}\text{Pu}/^{236}\text{U}$  ratio is the one expected to be least sensitive to interference from contamination by natural U since the occurrence of  $^{236}\text{U}$

in nature is extremely low.<sup>4</sup> However,  $^{236}\text{U}$  is produced from  $^{235}\text{U}(\text{n},\gamma)^{236}\text{U}$  reactions in nuclear reactors and concentrations of  $^{236}\text{U}$  up to 0.5% (atomic) can be found in spent nuclear fuel.<sup>5</sup> Since in most cases  $^{236}\text{U}$  will be present together with larger amounts of  $^{238}\text{U}$  and  $^{235}\text{U}$ , corrections for abundance sensitivity and hydride formation need to be made when analyzing  $^{236}\text{U}$  using ICP-MS. Due to these interferences and the generally low concentrations of  $^{236}\text{U}$  found in nature, the determination of this nuclide using ICP-MS poses some difficulties. BOULYGA et al.<sup>6,7</sup> have examined the potential of different ICP-MS systems for  $^{236}\text{U}$  determination with application to soil-samples contaminated with fall out from the Chernobyl nuclear power plant accident. In these studies, abundance sensitivity from  $^{238}\text{U}$  on  $m/z=236$  for a sector field (ICP-SFMS; Element) instrument was reported to be  $(5–5.3)\cdot 10^{-6}$  depending on the sample introduction system used.

A possibility to avoid the problem of uranium contamination is to base the dating of Pu material on the ratio  $^{241}\text{Pu}/^{241}\text{Am}$ . This ratio has been used in age determination of plutonium with  $\gamma$ -spectrometry,<sup>8,9</sup> but also for the characterization and dating of Pu found in Chernaya Bay based on measurements by TIMS.<sup>10</sup>

Since  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  are isobars and cannot be separated by the highest resolution available with ICP-SFMS, a thorough chemical separation is required prior to analysis using mass spectrometry. Determination of plutonium isotopes, including  $^{241}\text{Pu}$ , in environmental samples by ICP-MS or TIMS has been reported previously, e.g., in the analysis of the origin of Pu in the environment,<sup>11–14</sup> although in most cases the magnitude of the separation of Pu and Am has not been reported.

\* E-mail: ulrika.nygren@foi.se

Compared to the determination of Pu using ICP-MS, little has been published concerning the determination of  $^{241}\text{Am}$  in environmental samples using ICP-MS. AGARANDE et al.<sup>15</sup> have compared the results of  $^{241}\text{Am}$  analysis in sediment from the vicinity of a French nuclear site using ICP-SFMS and alpha-spectrometry. In that study, a rather time consuming separation procedure (requiring 15 days) based on ion-exchange and solid phase extraction was used, and the magnitude of the achieved separation of Pu and Am was not reported. BOULYGA et al.<sup>16</sup> determined  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{241}\text{Am}$  in mosses by laser ablation ICP-SFMS. Solid phase extraction was used for the separation of Pu and Am, but the achieved separation factor was not reported although the concentrations of  $^{241}\text{Am}$  obtained by LA-ICP-SFMS were higher compared to concentrations obtained by alpha-spectrometric determinations.

The aim of this study was to develop a method for age determination of plutonium material based on chemical separation and the analysis of  $^{241}\text{Pu}/^{241}\text{Am}$  and  $^{240}\text{Pu}/^{236}\text{U}$  using ICP-SFMS. The method has been applied on plutonium reference material solutions and environmental material contaminated with nuclear weapons debris.

## Experimental

### Reagents and standards

The reagents used for sample preparation were nitric acid 65%, hydrochloric acid 37% and  $\text{NaNO}_2$  (all of p.a. grade, Merck, Darmstadt, Germany),  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (98%, A.C.S. reagent grade, Scharlau Chemie S.A., Barcelona, Spain), polyethylene glycol (PEG2000, for synthesis, Merck, Darmstadt, Germany),  $\text{LiBO}_2$  (99.997% Johnson Matthey, Karlsruhe, Germany), Silicagel 60 (Fluka, Buchs, Switzerland) and hydroxyethylidene diphosphonic acid (HEDPA; Briquest ADPA 60A, industrial grade 60%, Albright & Wilson UK Ltd, Oldbury, UK). Graphite crucibles (Alfa, Karlsruhe, Germany) were used for fusion of samples, and filters (Munktell OOM, Grycksbo Pappersbruk AB, Grycksbo, Sweden) were used for separation of flocculated Si. Deionized water from a Milli-Q Element system (Millipore, Molsheim, France) was used for all sample and standard preparations.

For the separation of Am, Pu and U, solid phase extraction based on UTEVA, TEVA, TRU and Ln-resin (all 100–150  $\mu\text{m}$ , Eichrom, Darien IL, USA) was used. The extractants in these resins are trialkyl ( $\text{R}=\text{C}_8$  and  $\text{C}_{10}$ ) methylammonium nitrate (Aliquat336) (TEVA), octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide (CMPO) (TRU), diamyl amylphosphonate (DAAP) (UTEVA) and dialkyl phosphoric acid (HDEHP) (Ln-resin). The separations were performed in disposable plastic 10 ml columns (Poly-

prep, Bio-Rad, Hercules, CA, USA). Standard reference material solutions of  $^{233}\text{U}$  (IRMM 040a, obtained from the Institute of Reference Materials and Measurements, Geel, Belgium),  $^{242}\text{Pu}$  (NIST SRM4334G) and  $^{243}\text{Am}$  (NIST SRM4332D, both obtained from the National Institute of Standards and Technology, Gaithersburg, MD) were used as spike solutions for quantification of the analytes. A standard solution containing U of natural composition (IRMM184) was used for monitoring instrumental dead-time, mass discrimination,  $^{238}\text{U}^1\text{H}^+$ -formation and abundance sensitivity.

The age determinations were performed on two plutonium reference material solutions, IRMM081 ( $^{239}\text{Pu}$ ) and IRMM083 ( $^{240}\text{Pu}$ ), and on one sediment sample from the Enewetak Atoll, Marshall Islands (reference material IAEA367, International Atomic Energy Agency, Vienna, Austria). Age determinations were also performed on "Trinitite", i.e., soil from the test-site in New Mexico where the first nuclear weapons test ever was conducted.

### Sample pre-treatment

*Lithium borate fusion:* The sediment reference material was dissolved using lithium borate fusion. Approximately 0.2 g (Trinitite) or 4 g (IAEA367) was weighed and mixed in a graphite crucible with  $\text{LiBO}_2$  at a flux to sample ratio of 3:1. Approximately 0.2 ml of a spike solution containing about  $100\text{ pg}\cdot\text{g}^{-1}$   $^{233}\text{U}$ ,  $^{243}\text{Am}$  and  $^{242}\text{Pu}$  were added to the sample (this amount was also weighed to the accuracy of 0.1 mg, which also was the accuracy used for all sample and spike weighing in this work). Samples were then fused at  $1050\text{ }^\circ\text{C}$  in a furnace for 10–15 minutes and transferred (after cooling) to a glass beaker containing 1.4M  $\text{HNO}_3$ . The volume of 1.4M  $\text{HNO}_3$  used was approximately 100 times the sample weight. The melt was dissolved under heating ( $\geq 100\text{ }^\circ\text{C}$ ) and stirring, and the solution was allowed to evaporate to half of the initial volume. In order to prevent precipitation of silicic acids during the following separation procedure, PEG2000 was added to a concentration of 0.002M to flocculate the dissolved Si. The samples were left at room temperature overnight and then the precipitate was removed by filtering. This resulted in a  $\text{HNO}_3$  concentration of approximately 2.8M which was suitable for the following solid phase extraction procedure.

It was also found that the analysis of IRMM081 required a lithium-borate fusion in order to achieve similar chemical behaviour of the Pu in IRMM081 and the added  $^{242}\text{Pu}$  spike. If fusion was not conducted, the Pu from IRMM081 was lost to a higher degree than the  $^{242}\text{Pu}$  spike in the following solid phase extraction separation. The reason for this is not known at present, but one explanation might be that some of the Pu in IRMM081 is in polymeric form. The IRMM has since

June 2005 withdrawn this material due to instability and varying concentrations. In order to achieve an amorphous melt in the fusion of this material, silicaGel was added to  $\text{LiBO}_2$  in a ratio of 1:5. Of this mixture, 1 gram was used for the fusion of 0.2 ml IRMM081 sample (containing  $10.21 \text{ ng } ^{239}\text{Pu}\cdot\text{g}^{-1}$ ) and 0.2 ml spike solution. The fusion procedure was performed in the same way as described above, with the exceptions that 20 ml 1.4M  $\text{HNO}_3$  and 0.08 g PEG2000 were used.

Material not pre-treated by fusion, i.e., IRMM083, was added to a sample solution of 5 ml 3M  $\text{HNO}_3$  together with 0.2 ml spike solution as described above. Aliquots of 0.2 ml IRMM083 diluted to  $13.48 \text{ ng } ^{240}\text{Pu}\cdot\text{g}^{-1}$  were used for the analysis.

*Solid phase extraction separation:* The separations of Pu, U and Am were performed using solid-phase extraction. A redox procedure, first described by MOORE and HUDGENS<sup>17</sup> was used to adjust Pu to Pu(IV) while keeping Am as trivalent. First, Pu was reduced to the trivalent state by adding  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to a concentration of  $15 \text{ mg}\cdot\text{ml}^{-1}$  and heating at  $90^\circ\text{C}$  for 5 minutes. After cooling to approximately  $40^\circ\text{C}$ ,  $\text{NaNO}_2$  was added at a concentration of  $18 \text{ mg}\cdot\text{ml}^{-1}$  to oxidize Pu(III) to Pu(IV).

UTEVA (1 ml), TEVA (1 ml) and TRU resin (2 ml) were added to 10 ml plastic columns and the resins were conditioned with 5 ml 3M  $\text{HNO}_3$ . The columns were mounted in series starting with TEVA followed by UTEVA and TRU. The sample was loaded on the resins and the beaker was rinsed with 3 ml 3M  $\text{HNO}_3$ , which was added to the columns. Under these conditions, Pu(IV) is retained on the TEVA resin, U(VI) on UTEVA while Am(III) is retained on TRU.<sup>18</sup> The columns were then separated from each other and the TEVA column was rinsed with 20 ml 3M  $\text{HNO}_3$  to remove uranium. Plutonium was then eluted using 5 ml 0.1% HEDPA.<sup>19</sup> The UTEVA column was rinsed using 5 ml 5M HCl and 5 ml 3M  $\text{HNO}_3$  after which U was eluted using 5 ml 0.1% HEDPA. The TRU-column was mounted on top of a column containing 0.5 ml Ln-resin that had been pre-conditioned with 1 ml 0.01M  $\text{HNO}_3$ . 20 ml 0.01M  $\text{HNO}_3$  was then added to the columns to transfer americium from TRU to the Ln-resin. Americium was eluted from the Ln-resin using 3 ml 0.5M  $\text{HNO}_3$ .

*Sample preparation for  $\gamma$ -spectrometric determination of Pu-ratios:* An aliquot of 4 g of Trinitite was dissolved using  $\text{LiBO}_2$  and Si was removed by flocculation with PEG2000 (as described above). The sample was then loaded on 4 ml TEVA resin and the resin was rinsed using 40 ml 3M  $\text{HNO}_3$ . The resin was transferred to a 5 ml vial for  $\gamma$ -spectrometric measurement.

### Instrumentation

Mass spectrometric measurements were performed using an Element2 ICP-SFMS instrument (Thermo-Finnigan, Bremen, Germany). The instrument was equipped with a semi-demountable Fassel quartz torch and a CD-2 guard electrode. Sample introduction was performed using a conical nebulizer and a cyclonic spray chamber ("Twister" – both from GlassExpansion, Melbourne, Australia). Self-aspiration, resulting in a sample flow rate of approximately  $0.2 \text{ ml}\cdot\text{min}^{-1}$ , was used throughout the investigation. The guard electrode was ground and the automatic, soft-ware induced dead time correction inactivated. Torch position, lens parameters and nebulizer gas flow rates were optimized daily to obtain a maximum sensitivity for  $^{238}\text{U}^+$ . All measurements were performed using low resolution ( $m/\Delta m=300$ ). Instrument and data acquisition settings are shown in Table 1.

Gamma-spectrometric measurements were performed using a coaxial high-purity germanium (HPGe), low-energy photon detector (EG&G Ortec, USA).

### Data acquisition and evaluation

Instrumental dead-time, mass discrimination,  $^{238}\text{U}^1\text{H}^+$  formation and abundance sensitivity were monitored using solutions containing uranium of natural composition (IRMM184) in 0.1% HEDPA. Dead-time and mass discrimination were calculated according to APPELBLAD and BAXTER<sup>20</sup> and the results from the sample determinations were correspondingly corrected. The determinations of  $^{239}\text{Pu}$  and  $^{236}\text{U}$  were also corrected for possible contribution from  $\text{UH}^+$  formation and abundance sensitivity of  $^{238}\text{U}$  and  $^{235}\text{U}$ . The determination of  $^{241}\text{Pu}$  was also corrected for abundance sensitivity from  $^{239}\text{Pu}$  when necessary. Throughout this study, the "raw data" or "channel data" that can be obtained from the instrument software were used, and the evaluations of these data were performed manually. This was done due to the discovery of a post-acquisition introduced bias in the software evaluations.<sup>21</sup> The uncertainties of the results were calculated according to ISO/GUM<sup>22</sup> using the software GUM Workbench® (Metrodata GmbH, D-79639 Grenzach-Whylen, Germany). All reported uncertainties are expanded uncertainties with a coverage factor of two ( $k=2$ ).

The age determination based on  $\gamma$ -spectrometric analysis of  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  were evaluated using the soft-ware PC/FRAM (EG&G Ortec, USA). The determination of  $^{240}\text{Pu}/^{239}\text{Pu}$  in Trinitite using  $\gamma$ -spectrometry was based on the 51.6 keV and 45.2 keV  $\gamma$ -emissions for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , respectively. The 38.6 keV  $\gamma$ -emission for  $^{239}\text{Pu}$  was used to establish a relative efficiency function for the energy region.

Table 1. Instrument and data acquisition settings for the ICP-SFMS determinations

Instrument settings	
Argon flow rates	
Cooling gas	14 l·min <sup>-1</sup>
Auxiliary gas	1 l·min <sup>-1</sup>
Nebulizer gas	~0.95 l·min <sup>-1</sup>
RF power	1300W
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.8 mm orifice diameter
Data acquisition settings	
Resolution ( $m/\Delta m$ )	300
Detection mode	Pulse counting
Data acquisition mode	E-scan
Quantitative determination of U, Am and Pu	
Isotopes	<sup>232</sup> Th <sup>+</sup> , <sup>233</sup> U <sup>+</sup> , <sup>235</sup> U <sup>+</sup> , <sup>236</sup> U <sup>+</sup> , <sup>238</sup> U <sup>+</sup> , <sup>239</sup> Pu <sup>+</sup> , <sup>240</sup> Pu <sup>+</sup> , <sup>241</sup> Pu <sup>+</sup> / <sup>241</sup> Am <sup>+</sup> , <sup>242</sup> Pu <sup>+</sup> , <sup>243</sup> Am <sup>+</sup>
Sample time	10 ms (except for <sup>232</sup> Th <sup>+</sup> and <sup>238</sup> U <sup>+</sup> where 2 ms was used)
Mass window	5%
Samples per peak	100
Number of scans	500
Settling time	1 ms (default minimum)
Magnet mass	232.038 u
Monitoring of dead-time, mass discrimination and abundance sensitivity/UH <sup>+</sup> formation	
Isotopes and polyatomic ions	<sup>234</sup> U <sup>+</sup> , <sup>235</sup> U <sup>+</sup> , <sup>236</sup> U <sup>+</sup> , <sup>237</sup> U <sup>+</sup> , <sup>238</sup> U <sup>+</sup> , <sup>238</sup> U <sup>1</sup> H <sup>+</sup> and <sup>238</sup> U <sup>1</sup> H <sub>2</sub> <sup>+</sup>
Sample time	2 ms for <sup>238</sup> U <sup>+</sup> , 5 ms for <sup>235</sup> U <sup>+</sup> and 10 ms for all others
Mass window	5%
Samples per peak	100
Number of scans	900
Settling time	1 ms (default minimum)
Magnet mass	234.040 u

### Calculation of the age of the Pu-material

The determination of the age of Pu-material was based on the mother/daughter relationship between <sup>241</sup>Pu/<sup>241</sup>Am or <sup>240</sup>Pu/<sup>236</sup>U. This relationship is described by:

$$t = \frac{1}{\lambda_1 - \lambda_2} \cdot \ln \left[ 1 - \left( \frac{\lambda_2}{\lambda_1} - 1 \right) \frac{N_2}{N_1} \right] \quad (1)$$

In this equation,  $t$  is the age of the material,  $\lambda_1$  and  $\lambda_2$  are the decay constants of Pu and the respective daughter nuclide and  $N_1$  and  $N_2$  are the amounts of the mother and daughter nuclide at the time of analysis. The half-lives used in the calculations were obtained from the Evaluated Nuclear Structure Data File (ENSDF).<sup>23</sup>

### Results and discussion

The obtained ages based on ICP-SFMS determined <sup>241</sup>Am/<sup>241</sup>Pu and <sup>236</sup>U/<sup>240</sup>Pu ratios are shown in Table 2. Determinations were performed on three sub-samples of each material, plus one  $\gamma$ -spectrometric analysis of IRMM081 and IRMM083. No  $\gamma$ -spectrometric dating could be performed on IAEA367 and the Trinitite due to low concentrations of the analytes in these materials. The table also specifies the reference ages of the

materials. These are based on the date of purification for the IRMM materials,<sup>24</sup> and the date of the detonation of “the Gadget” for the Trinitite.<sup>25</sup> For IAEA367, the time period when the US conducted testing of thermonuclear weapons at the Enewetak Atoll was used as reference date (see the discussion below).<sup>25,26</sup>

As can be seen from the table, the ages determined by the <sup>241</sup>Am/<sup>241</sup>Pu ratio correspond well (as indicated by the expanded standard uncertainties,  $k=2$ ) with the reference ages as well as with the  $\gamma$ -spectrometric determinations. A condition for age determination based on this kind of mother/daughter nuclide ratio is that there is no amount of daughter nuclide present at  $t=0$ , or that this initial amount is known. In the case of IRMM081, it was known that the material contained <sup>241</sup>Am at a concentration of 250  $\mu\text{g}\cdot\text{g}^{-1}$  directly after purification.<sup>24</sup> Calculations based on this concentration and the concentration of <sup>241</sup>Pu at the time of separation using Eq. (1) results in an off-set in the age of 2.4 years for which the determined age in Table 2 has been corrected. It should be noted that the purification process used for IRMM081 at the reference time  $t=0$  was electrolysis, while anion-exchange of Pu(IV) was used for IRMM083.<sup>24</sup> Hence, it seems as if Am, at least to some extent, has not been separated from Pu in the electrolysis process while the use of anion-exchange has resulted in a more thorough separation. A small bias in

the age determination based on TIMS analysis of the  $^{241}\text{Am}/^{241}\text{Pu}$  ratio in NBS Pu-reference material was also reported by WALLENIUS and MAYER.<sup>2</sup> This was also explained by incomplete Pu-Am separation in the purification of the Pu material.

The ages determined by the  $^{236}\text{U}/^{240}\text{Pu}$  ratio are in agreement with the reference values for the two Pu reference material solutions. For the materials containing nuclear weapons debris, two problems arose in the measurement of  $^{236}\text{U}$ . In the IAEA367 sediment,  $^{236}\text{U}$  could not be significantly quantified due to abundance sensitivity from primarily  $^{238}\text{U}$ . The magnitude of the abundance sensitivity, defined as the net intensity on  $m/z=236$  divided by the net intensity of  $^{238}\text{U}$ , was  $(1.94\pm 0.26)\cdot 10^{-6}$  in this study. When analyzing the Trinitite, abundance sensitivity was small compared to the intensity from  $^{236}\text{U}^+$  but the determined ages are much higher than the reference ages. An explanation to these high results is production of  $^{236}\text{U}$  via  $(n,\gamma)$  reactions of  $^{235}\text{U}$  in the detonation of the nuclear weapon.

A critical parameter in developing this method was a thorough separation of  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  since these nuclides would otherwise mutually interfere during the measurements. The performance of the separation was evaluated by monitoring the amounts of  $^{243}\text{Am}$  in the Pu fraction and  $^{242}\text{Pu}$  in the Am fraction. The resulting separation factors, defined as the added amount divided by the amount found in respective fraction were  $\geq 3560$  for  $^{242}\text{Pu}$  in the Am-fractions and  $\geq 696$  for  $^{243}\text{Am}$  in the Pu-fraction. Considering that the expected ratios of  $^{241}\text{Pu}/^{241}\text{Am}$  will vary from 20 to 0.06 for ages from 1 to 60 years, these separation factors are more than adequate. The chemical yields for the separation were  $(61\pm 8)\%$  for Am,  $(73\pm 5)\%$  for Pu and  $(64\pm 10)\%$  for U.

In the analysis, the ratios of the Pu-isotopes were also determined. The ratios obtained for the IRMM Pu reference materials were compared with the certified ratios for these materials and the values were in agreement with each other at the 95% confidence level. The ratios obtained for IAEA367 and the Trinitite are shown in Table 3. The obtained ratios for both  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{241}\text{Pu}/^{239}\text{Pu}$  in IAEA367 are higher than the average values of global fall-out, i.e.,  $0.1808\pm 0.0057$  for  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $0.00264\pm 0.00020$  for  $^{241}\text{Pu}/^{239}\text{Pu}$  ( $k=1$ ).<sup>12</sup> Different constructions of nuclear weapons were tested at Enewetak, both fission and thermonuclear (fusion) weapons. The first thermonuclear device ever tested, “Mike”, detonated at the Enewetak Atoll on October 31, 1952 with a yield of 10.4 Mton. The  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{241}\text{Pu}/^{239}\text{Pu}$  ratios in the debris from this test have been reported to be  $0.363\pm 0.004$  and  $0.0030\pm 0.0004$  (decay corrected to November 17, 2005 and  $k=1$ ).<sup>27</sup> A relatively high  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio is characteristic of thermonuclear weapons due to high neutron fluencies, thus creating  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  from neutron capture by  $^{238}\text{U}$  present in the uranium blanket.<sup>28</sup> Hence, the ratio of 0.30 found in this study indicates significant contribution of debris from thermonuclear devices. Further “successful” thermonuclear tests yielding more than 1 Mton were conducted at Enewetak in 1954 (“Nectar” 1.69 Mton), 1956 (“Apache” 1.85 Mton) and 1958 (“Koa” 1.37 Mton, “Oak” 8.9 Mton and “Pine” 2 Mton).<sup>25,29</sup> This limits the actual reference date for the age determination to the range 1952 to 1958, as indicated in Table 2. The results displayed in Table 2 are centered around 1955.

Table 2. Results of the age determinations

Sample	Date of analysis	Determined age, years, based on:		Reference age, years
		$^{241}\text{Am}/^{241}\text{Pu}$	$^{236}\text{U}/^{240}\text{Pu}$	
IRMM083:1	Dec 13, 2005	$12.2 \pm 0.3$	$12.5 \pm 0.4$	12.5
IRMM083:2		$12.3 \pm 0.3$	$12.2 \pm 0.4$	
IRMM083:3		$12.3 \pm 0.3$	$12.4 \pm 0.4$	
<i>IRMM083:γ</i>		<i><math>12.1 \pm 1.4</math></i>		
IRMM081:1	Oct 27, 2005	$30.7 \pm 0.8$	$26.9 \pm 3.0$	30.4
IRMM081:2		$30.7 \pm 0.7$	$31.4 \pm 2.9$	
IRMM081:3		$29.8 \pm 0.7$	$31.1 \pm 3.0$	
<i>IRMM081:γ</i>		<i><math>29.3 \pm 0.4</math></i>		
IAEA367:1	Nov 17, 2005	$51.8 \pm 2.7$	n.d.	47.3–53.1
IAEA367:2		$50.8 \pm 2.7$	n.d.	
IAEA367:3		$49.5 \pm 2.8$	n.d.	
Trinitite:1	Oct 27, 2005	$58.4 \pm 1.4$	$176 \pm 4$	60.3
Trinitite:2		$59.4 \pm 1.4$	$204 \pm 5$	
Trinitite:3		$58.8 \pm 1.3$	$201 \pm 5$	

The results from the  $\gamma$ -spectrometric measurements are included as well (numbers in italics). The determined age of IRMM081 has been corrected for an off-set age of 2.4 years due to residual of  $^{241}\text{Am}$  after purification of the plutonium material.

Table 3. Obtained isotope amount ratios from analysis of IAEA367 and Trinitite

Sample	Determined Pu-ratios $^{240}\text{Pu}/^{239}\text{Pu}$	$^{241}\text{Pu}/^{239}\text{Pu}$
IAEA367:1	$0.299 \pm 0.004$	$(2.65 \pm 0.35) \cdot 10^{-3}$
IAEA367:2	$0.295 \pm 0.004$	$(2.75 \pm 0.36) \cdot 10^{-3}$
IAEA367:3	$0.296 \pm 0.004$	$(2.97 \pm 0.40) \cdot 10^{-3}$
Trinitite:1	$0.02493 \pm 0.00009$	$(2.93 \pm 0.18) \cdot 10^{-5}$
Trinitite:2	$0.02487 \pm 0.00009$	$(2.77 \pm 0.18) \cdot 10^{-5}$
Trinitite:3	$0.02486 \pm 0.00009$	$(2.86 \pm 0.16) \cdot 10^{-5}$
<i>Trinitite: <math>\gamma</math></i>	<i><math>0.0249 \pm 0.0047</math></i>	

The result of the  $\gamma$ -spectrometric measurement of  $^{240}\text{Pu}/^{239}\text{Pu}$  in the Trinitite is included as well (in italics).

The Pu ratios found in the Trinitite are also shown in Table 3. PAREKH et al.<sup>30</sup> have recently published a study of the radioactive content of Trinitite, where the  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{241}\text{Pu}$  (via  $^{241}\text{Am}$ ) were quantified using  $\gamma$ -spectrometry.<sup>30</sup> The isotope amount ratios calculated from the results of that study are  $0.0129 \pm 0.0030$  for  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $(3.33 \pm 0.14) \cdot 10^{-5}$  for  $^{241}\text{Pu}/^{239}\text{Pu}$  (decay corrected to 05-11-17 and  $k=1$ ). Although the uncertainties in these results are high, the ratio of  $^{240}\text{Pu}/^{239}\text{Pu}$  is significantly different from the ratios obtained by ICP-SFMS determinations presented in Table 3. In order to verify the ICP-SFMS results, a  $\gamma$ -spectrometric analysis was also performed on the Trinitite. It was found necessary to do a Pu-separation on the sample prior to analysis to reduce interference from, e.g.,  $^{152}\text{Eu}$  (see details in the Experimental Section). The resulting  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio was in agreement with the mass spectrometric results (Table 3). In a study conducted by the U.S. EPA on the levels of Pu around the Trinity site,<sup>31</sup> the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of a "high" plutonium concentration sample was  $0.0254 \pm 0.0007$  (calculated from Table 3 in Reference 31,  $k=1$ ) which is also in agreement with the results found in this study.

### Conclusions

It is shown in this paper that an accurate and precise age determination of Pu can be obtained with the presented method. The separation procedure developed yielded a more than adequate separation of Pu and Am, and the chemical yields of U, Pu and Am were satisfactory. Of the two ratios used, the  $^{241}\text{Pu}/^{241}\text{Am}$  ratio provided reliable results with the exception the analysis of IRMM081 where initial  $^{241}\text{Am}$  was present. After correction for this, the resulting ages were in agreement with the reported age of the material. For the samples containing nuclear weapons debris, the age determination based on the  $^{240}\text{Pu}/^{236}\text{U}$  was limited due to formation of  $^{236}\text{U}$  in the detonation of the weapon.

The determination of  $^{236}\text{U}$  was also hampered due to abundance sensitivity from relatively large quantities of naturally-occurring U in the sample. The results show the importance of basing age determinations of Pu on more than one ratio in order to avoid interferences from, e.g., amounts of the daughter nuclide present at  $t=0$ .

\*

The authors would like to thank Douglas C. BAXTER for valuable comment of the manuscript and Annika TOVEDAL for assisting in the age determination using  $\gamma$ -spectrometry. Martin GOLIATH is acknowledged for valuable discussions concerning the formation of heavy isotopes in nuclear weapon detonations.

### References

1. M. WALLENUS, G. TAMBORINI, L. KOCH, *Radiochim. Acta*, 89 (2001) 55.
2. M. WALLENUS, K. MAYER, *Fresenius J. Anal. Chem.*, 366 (2000) 234.
3. M. WALLENUS, *Origin Determination of Reactor Produced Plutonium by Mass Spectrometric Techniques: Application to Nuclear Forensics Science and Safeguards*, Academic Dissertation, University of Helsinki, Helsinki, Finland, 2001, ISBN 951-45-9707-9.
4. S. RICHTER, A. ALONSO, W. DE BOLLE, R. WELLM, P. D. P. TAYLOR, *Intern. J. Mass Spectrom.*, 193 (1999) 9.
5. D. L. DONOHUE, *J. Alloys Comp.*, 271 (1998) 11.
6. S. F. BOULYGA, J. L. MATUSEVICH, V. P. MIRONOV, V. P. KUDRJASHOV, L. HALICZ, I. SEGAL, J. A. MCLEAN, A. MONTASER, J. S. BECKER, *J. Anal. At. Spectrom.*, 17 (2002) 958.
7. S. F. BOULYGA, J. S. BECKER, *J. Anal. At. Spectrom.*, 17 (2002) 1143.
8. R. P. KEEGAN, R. J. GEHRKE, *Appl. Radiation Isotopes*, 59 (2003) 137.
9. D. WEST, A. C. SHERWOOD, *Annal. Nucl. Energy*, 8 (1981) 441.
10. J. N. SMITH, K. M. ELLIS, K. NEAS, S. DAHLE, D. MATISHOV, *Deep-Sea Res. II*, 42 (1995) 1471.
11. L. W. COOPER, J. M. KELLEY, L. A. BOND, K. A. ORLANDINI, J. M. GREBMEIER, *Marine Chem.*, 69 (2000) 253.
12. J. M. KELLEY, L. A. BOND, T. M. BEASLEY, *Sci. Total Environ.*, 237/238 (1999) 483.
13. M. E. KETTERER, K. M. HAFNER, J. W. MIETELSKI, *J. Environ. Radioact.*, 73 (2004) 183.
14. M. E. KETTERER, K. M. HAFER, C. L. LINK, D. KOLWAITE, J. WILSON, J. W. MIETELSKI, *J. Anal. At. Spectrom.*, 19 (2004) 241.
15. M. AGARANDE, S. BENZOUAIR, P. BOUISSET, D. CALMET, *Appl. Radiation Isotopes*, 55 (2001) 161.
16. S. F. BOULYGA, D. DESIDERI, M. A. MELI, C. TESTA, J. S. BECKER, *Intern. J. Mass Spectrom.*, 226 (2003) 329.
17. F. L. MOORE, J. E. HUDGENS Jr., *Anal. Chem.*, 29 (1957) 1767.
18. E. P. HORWITZ, M. L. DIETZ, R. CHIARIZIA, H. DIAMOND, S. L. MAXWELL III, M. R. NELSON, *Anal. Chim. Acta*, 310 (1995) 63.
19. U. NYGREN, I. RODUSHKIN, C. NILSSON, D. C. BAXTER, *J. Anal. At. Spectrom.*, 18 (2003) 1426.
20. P. K. APPELBLAD, D. C. BAXTER, *J. Anal. At. Spectrom.*, 15 (2000) 557.

21. A. SJÖGREN, P. K. APPELBLAD, A. TOVEDAL, H. RAMEBÄCK, *J. Anal. At. Spectrom.*, 20 (2005) 320.
22. *Guide to the Expression of Uncertainty in Measurement*, International Organisation for Standardisation, ISO-GUM, Geneva, Switzerland, 1995, ISBN 92-67-10188-9.
23. *Evaluated Nuclear Structure Data File (ENSDF)*, National Nuclear Data Center (NNDC), Brookhaven National Laboratory, 2005.
24. M. BERGLUND, Institute for Reference Material and Measurement, Geel, Belgium, personal communication.
25. *United States Nuclear Tests; July 1945 through September 1992*, DOE/NV-209-REV 15, United States Department of Energy, Nevada Operations Office, Las Vegas, Nevada, December 2000.
26. S. BALLESTRA, J. J. LOPEZ, J. GASTAUD, D. VAS, V. NOSHKIN, *Report on the Intercomparison Run IAEA-376, Radionuclides in Pacific Ocean Sediment*, IAEA/AL/046, International Atomic Energy Agency, Monaco, 1991.
27. H. DIAMOND, P. R. FIELDS, C. S. STEVENS, M. H. STUDIER, S. M. FRIED, M. G. INGRAM, D. C. HESS, G. L. PYLE, J. F. MECH, W. M. MANNING, A. GHIORSO, S. G. THOMPSON, G. H. HIGGINS, G. T. SEABORG, C. I. BROWNE, H. L. SMITH, R. W. SPENCE, *Phys. Rev.*, 119 (1960) 2000.
28. L. E. DE GEER, *Sci. Global Secur.*, 2 (1991) 351.
29. M. C. CARTER, A. A. MOGHISSI, *Health Phys.*, 33 (1977) 55.
30. P. P. PAREKH, T. M. SEMKOV, M. A. TORRES, D. K. HAINES, J. M. COOPER, P. M. ROSENBERG, M. E. KITTO, *J. Environ. Radioact.*, 85 (2006) 103.
31. R. L. DOUGLAS, *Levels and Distribution of Environmental Plutonium Around the Trinity Site*, ORP/LV-78-3, U. S. Environmental Protection Agency, Office of Radiation Programs, Las Vegas Facility, Las Vegas, Nevada, October, 1978.