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Age determination of single plutonium particles after chemical separation

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ABSTRACT

Age determination of single plutonium particles was demonstrated using five particles of the standard reference material, NBS 947 (Plutonium Isotopic Standard, National Bureau of Standards, Washington, D.C. 20234, August 19, 1982, currently distributed as NBL CRM-137) and the radioactive decay of ^{241}Pu into ^{241}Am . The elemental ratio of Am/Pu in Pu particles found on a carbon planchet was measured by wavelength dispersive X-ray spectrometry (WDX) coupled to a scanning electron microscope (SEM). After the WDX measurement, each plutonium particle, with an average size of a few μm , was picked up and relocated to a silicon wafer inside the SEM chamber using a micromanipulator. The silicon wafer was then transferred to a quartz tube for dissolution in an acid solution prior to chemical separation. After the Pu was chemically separated from Am and U, the isotopic ratios of Pu ($^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$) were measured with a thermal ionization mass spectrometer (TIMS) for the calculation of Pu age. The age of particles determined in this study was in good agreement with the expected age (35.9 a) of NBS 947 within the measurement uncertainty.

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1. Introduction

Age determination of nuclear materials collected on environmental samples from nuclear facilities is useful to detect undeclared activities. This particle analysis procedure has recently been developed in the Clean Laboratory Unit of the Safeguards Analytical Laboratory of the International Atomic Energy Agency (IAEA) [1,2]. Some methods of age determination of Pu particles have been investigated in the past using secondary ion mass spectrometry (SIMS) and the parent–daughter mass ratios, $^{238}\text{Pu}/^{234}\text{U}$, $^{239}\text{Pu}/^{235}\text{U}$ and $^{240}\text{Pu}/^{236}\text{U}$ [3,4]. Other studies were performed with nanogram quantities of a plutonium reference material in solution [5,6]. In one of these two studies [5], the isotopic compositions of Pu and U in standard solutions were measured with thermal ionization mass spectrometry (TIMS) after chemical separation and the isotope ratio of $^{241}\text{Pu}/^{241}\text{Am}$ was determined by high resolution γ -spectrometry without chemical separation. Another study of Pu age determination of a reference solution was performed with standard solutions and sediment reference material by inductively coupled plasma mass spectrometry (ICP-MS) and γ -spectrometry [6]. These methods have however the disadvantage that the contribution of the U isotopes in the original material will have an affect on the final results. A study of the determination of the time since the last purification of weapons

grade plutonium by performing γ -ray measurements of Pu and Am nuclides has also been reported [7].

Although the methods of Pu age determination have been studied before, the chemical separation of Pu, Am and U was not performed in single particles and the amount of Pu used was in the nanogram range in the reference solutions.

In this study, the measurement was focused on μm -sized individual Pu particles containing picogram quantities. The Pu particles were first located on a carbon planchet using the back-scattered electron image, and the Am/Pu elemental ratio was measured with wavelength dispersive X-ray spectrometry (WDX) in the scanning electron microscope (SEM). WDX allows the measurement of the Am/Pu ratio at these low levels, which is not possible by γ -ray spectrometry. After the WDX measurement, each μm -sized plutonium particle was picked up and relocated to a silicon wafer inside the SEM chamber using a micro manipulator. The silicon wafer was then transferred to a quartz tube for dissolution of the particle in an acid solution prior to chemical separation. After the Pu was chemically separated from Am and U, the isotopic ratios of Pu ($^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$) were measured with a thermal ionization mass spectrometer (TIMS) for the calculation of age. Initial tests were carried out with the standard reference material NBS 947 [8], which was produced in December 1971. The age of NBS 947 Pu particles obtained in this study was consistent with the expected value. The Am fraction was also measured with TIMS following chemical separation from Pu to confirm if ^{243}Am exists in the sample, to allow a correction of the elemental Am/Pu ratio obtained with

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WDX. The influence of decay of ^{241}Am to ^{237}Np on the age-dating result was also considered.

This new method could enhance the capability of the IAEA to detect undeclared nuclear activities in facilities covered by comprehensive safeguards agreements.

2. Experimental

2.1. Instruments

The instruments used in this study were: SEM (Philips XL30 with LaB_6 crystal as electron source), equipped with energy dispersive X-ray spectrometer (EDX: EDAX International, with 10 mm^2 of $\text{Si}(\text{Li})$ detector area and super ultra thin window), and WDX (Oxford Co. Ltd). A micro-manipulator (MM3A-EM, Kleindiek Nanotechnik GmbH) was installed in the SEM sample chamber for relocation of the particles from the sample planchet to Si wafers.

The isotopic composition of Pu was measured with a ThermoElectron Triton instrument using ion counting detection with a secondary electron multiplier and peak jumping measurement scheme. The final purified fraction of Pu was loaded from solution on a rhenium single-filament along with graphite powder. The temperature used for the measurements was $1440\text{ }^\circ\text{C}$ and 3–5 blocks (10 scans per block) of measurements were performed for each sample. The mass dependent bias was corrected by measuring 120 pg of NBL 128 standard ($^{239}\text{Pu}/^{242}\text{Pu}=0.99937$ as certified on 1st October, 1985). The bias correction factor (BCF) calculated from the repeated results of 11 measurements and the formula reported by Bayne in 1996 [9] was 0.0001 amu^{-1} . The method for Pu analysis was described in detail in a previous paper [10].

2.2. Materials

The standard reference material NBS 947 (plutonium sulphate tetrahydrate) [8] was used in this study. For the chemical separation, supra pure grade nitric acid, hydrogen peroxide, hydroiodic acid and boric acid, and analytical grade hydrochloric acid and hydrofluoric acid (MERCK KGaA) were used. The hydrobromic acid used for the final Pu purification for TIMS measurements was super pure grade from SEARSTAR CHEMICALS Inc. Water ($18.2\text{ M}\Omega$) was prepared by deionizing with mixed resin (Milli-Q Element).

2.3. Sample preparation for SEM, EDX and WDX measurements

The Pu particles were transferred on to a carbon planchet directly from the vial of standard material. The planchet was put on a sample

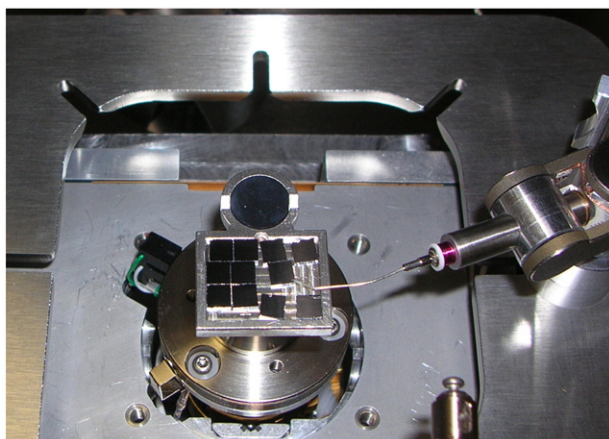


Fig. 1. Sample stage (carbon planchet and Si wafers) and micromanipulator mounted in the SEM sample changer.

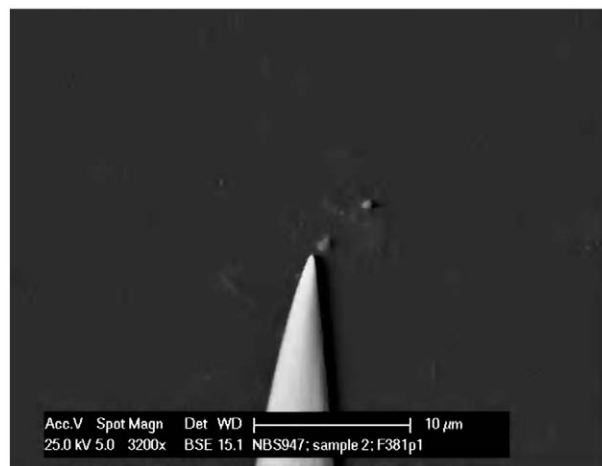


Fig. 2. Approach to a Pu particle (NBS 947) with a tungsten needle of the micro manipulator.

stage together with Si wafers and placed in the sample chamber of the SEM (Fig. 1). After locating the Pu particles using the back-scattered electron image and the EDAX Particle/Phase Analysis software, the elemental Am/Pu ratio of each particle was calculated from the intensities of $\text{M}\alpha$ X-rays measured with WDX. Each particle was then picked up using the micro manipulator and relocated onto a Si wafer (Fig. 2). The Si wafer with the particle was removed from the SEM chamber and transferred into a quartz vial for subsequent chemical separation.

2.4. Chemical separation

Chemical separation of Pu and Am was performed in an ISO Class 5 area of the IAEA Clean Laboratory. The particle on a Si wafer was soaked in 1 ml of $16\text{ mol L}^{-1}\text{ HNO}_3$ in a quartz vial and heated to dryness. The Si wafer was then rinsed with 1 ml of $16\text{ mol L}^{-1}\text{ HNO}_3$ and the Si wafer was removed. The washed solution was heated again with a few drops of 30%-hydrogen peroxide. The residue was then fumed with a few drops of $16\text{ mol L}^{-1}\text{ HNO}_3$ three times. The residue was dissolved into 2 ml of $8\text{ mol L}^{-1}\text{ HNO}_3$ and chemical separation performed. The sample solution was loaded on 2 ml of anion exchange resin bed, AG MP-M1 (50–100 mesh, BIO-RAD Inc), conditioned with 20 ml of $8\text{ mol L}^{-1}\text{ HNO}_3$. This column was stacked over the TRU resin (Eichrom Technologies, LLC) column conditioned with 20 ml of $8\text{ mol L}^{-1}\text{ HNO}_3$ so that the effluent from the AG MP-M1 column drips onto the TRU resin bed. After the separation of Am, U and other nuclides with 15 ml of $8\text{ mol L}^{-1}\text{ HNO}_3$, these two columns were handled separately. The AG MP-M1 column was washed with $10\text{ mol L}^{-1}\text{ HCl}$ and Pu was eluted with a freshly prepared solution of 15 ml of $0.1\text{ mol L}^{-1}\text{ HI}-9\text{ mol L}^{-1}\text{ HCl}$. The resulting fraction was dried and converted to the chloride form by fuming with a few drops of $10\text{ mol L}^{-1}\text{ HCl}$ several times. After the Pu ions were adjusted to Pu(IV) by adding H_2O_2 , the residue was dissolved in 2 ml of $10\text{ mol L}^{-1}\text{ HCl}$ solution and the solution was loaded on to the column filled with AG MP-M1 conditioned with 20 ml of $10\text{ mol L}^{-1}\text{ HCl}$. After rinsing the resin with $\text{HCl}-\text{H}_2\text{O}_2$, the Pu was eluted with 15 ml of 44–49 wt.% HBr. The solution was heated to dryness and then converted to the nitrate form by fuming with a few drops of $16\text{ mol L}^{-1}\text{ HNO}_3$ for several times. The Eichrom TRU resin column was rinsed with 20 ml of $8\text{ mol L}^{-1}\text{ HNO}_3$ and Am was eluted with 15 ml of $0.1\text{ mol L}^{-1}\text{ HCl}$. The Am eluate was then heated to dryness and converted to a chloride form. This Am fraction was then dissolved in 2 ml of $10\text{ mol L}^{-1}\text{ HCl}$ and loaded on 1 ml of AG MP-M1 resin conditioned with 10 ml of $10\text{ mol L}^{-1}\text{ HCl}$. The Am was eluted with 10 ml of $10\text{ mol L}^{-1}\text{ HCl}$ and the eluant was heated to dryness and converted to nitrate form by fuming with 16 mol L^{-1}

HNO₃. For real environmental samples, an additional reagent, e.g., hydrofluoric acid may be required to dissolve Pu oxide particles completely. The method for Pu analysis was described in detail in a previous paper [10].

3. Results and discussion

3.1. Calculation of age

The Pu particle age at time t was calculated with the following equations.

$${}^{241}\text{Pu}_t = {}^{241}\text{Pu}_0 \times e^{-\lambda t} \quad (1)$$

$${}^{241}\text{Am}_t = {}^{241}\text{Pu}_0 - {}^{241}\text{Pu}_t = {}^{241}\text{Pu}_0 \times (1 - e^{-\lambda t}) \quad (2)$$

$$\frac{{}^{241}\text{Pu}_t}{{}^{241}\text{Am}_t} = \frac{e^{-\lambda t}}{1 - e^{-\lambda t}} \quad (3)$$

$$t = \frac{1}{\lambda} \ln \left[\frac{{}^{241}\text{Am}_t}{{}^{241}\text{Pu}_t} + 1 \right] \quad (4)$$

where λ is the decay constant of ²⁴¹Pu and ²⁴¹Pu₀ is the amount of ²⁴¹Pu at time 0. The initial amount of ²⁴¹Am is assumed to be zero and it is assumed that no fractionation has occurred between the mother-daughter radionuclides. The half lives of Pu nuclides used in this study were from the IAEA handbook of nuclear data for safeguards (2007) [11], namely, 14.29 a for ²⁴¹Pu. Another commonly used value, 14.35 a, [12] would produce different results from the present study. The decay of ²⁴¹Am to ²³⁷Np was considered for the correction of the results (see Section 3.4. below).

3.2. Elemental ratio of Am/Pu measured with WDX

The elemental ratio of Pu/Am and the ²⁴¹Pu isotope abundance are needed to calculate t using the equation above. The Pu/Am ratio of NBS 947 particles (produced in December, 1971) measured with WDX is shown in Table 1. The dimension of particles analyzed in this study ranged from 2 to 5.7 μm. The results of the PuMα/AmMα ratio measured with WDX were from 0.0386 to 0.0484 with a counting statistics dominated uncertainty (relative standard deviation) of 1.5 to 6.5%.

3.3. Pu isotope ratios and abundance of ²⁴³Am measured with TIMS

The Pu isotopic ratios of NBS 947 particles measured by TIMS after chemical separation are shown in Table 2. The results of age calculation using the equations above are shown in Table 3. The Am isotope ratio in the Am fraction after the chemical separation from Pu was also measured with TIMS to confirm the absence of ²⁴³Am without adding any spike. ²⁴³Am could not be detected in this material, thus no correction was required and the entire Am X-ray intensity was attributed to ²⁴¹Am.

Table 1
The Am/Pu ratio of NBS 947 particles calculated with WDX measurements

Particle	Dimension (μm) ^a	AmMα/PuMα	RSD (%) ^b
A	2–3	0.0450	2.2
B	2–3	0.0425	2.2
C	2–3	0.0386	2.8
D	5–6	0.0384	1.5
E	1–2	0.0484	6.5

^a Dimensions show an approximate value since the shape of the particles were irregular.

^b Relative standard deviation obtained from the counting statistics of WDX measurement for Am and Pu.

Table 2
Isotopic ratios of Pu of NBS 947 particles after chemical separation measured with TIMS

Particle	²⁴⁰ Pu/ ²³⁹ Pu	SD ^a	²⁴¹ Pu/ ²³⁹ Pu	SD ^a	²⁴² Pu/ ²³⁹ Pu	SD ^a
A	0.2428	0.0035	0.0108	0.0012	0.0154	0.0011
B	0.2285	0.0053	0.0105	0.0011	0.0155	0.0002
C	0.2406	0.0030	0.0108	0.0002	0.0158	0.0007
D	0.2409	0.0026	0.0110	0.0007	0.0155	0.0004
E	0.2499	0.0031	0.0105	0.0003	0.0177	0.0023
Certified value ^b	0.2409	0.0003 ^c	0.01058	0.00005 ^c	0.01561	0.00005 ^c

^a Standard deviation from repetition of 3–5 measurements (E: differences between two measurements).

^b The certified values are corrected the date (October 2007), when the chemical separation was performed. The half life of Pu nuclides were used the value from the IAEA Handbook of Nuclear Data for Safeguards (2007) (<http://www-nds.iaea.org/sgnucdat/>) [11].

^c Uncertainty of certified value [8].

3.4. Influence of ²⁴¹Am decay on the results

²⁴¹Am decays into ²³⁷Np with a half life of 432.6 a [11]. In this decay system of ²⁴¹Pu–²⁴¹Am, the half life of the daughter nuclide is longer than that of the parent nuclide, and the radioactive equilibrium does not exist. The influence of the decay of ²⁴¹Am on the ratio of ²⁴¹Pu/²⁴¹Am was calculated as 5.9% for the sample age of 35.9 a. This correction was applied to the age calculation.

3.5. Uncertainty component

The dominant uncertainty component was found to be counting statistics in the measurement of the Am/Pu element ratio by WDX as well as the Pu isotope abundances measured by TIMS. The uncertainty of the WDX measurements of Pu/Am ranged from 1.5 to 6.5 % relative and that of the TIMS measurements of Pu isotope ratios and Pu isotope abundance ranged from 0.2 to 18 % relative and 0.2 to 0.5 % relative, respectively. The combined standard uncertainty (with coverage factor, k=1) calculated for the Pu age using the Am/Pu element ratio as measured by WDX combined with the ²⁴¹Pu isotopic abundance as measured by TIMS gives 1.6 – 8.6 % (following the GUM [13] model). The accuracy (bias) in the age of the obtained results ranged from 1 – 8 % (Table 3).

4. Conclusions

The procedure for age determination of Pu in single particles was demonstrated for particles of a standard reference material (NBS 947), using SEM, WDX and TIMS. The calculated age from 5 particles is in good agreement with the expected age within 1–8% relative. The comparison of the results for Pu standard NBS 947 with the expected age shows the accuracy of this method with uncertainty of <8.6% relative. In this study, the abundance of ²³⁸Pu was neither determined nor involved in the age calculation. According to the certificate, the predicted abundance of ²³⁸Pu is 0.23% (Oct. 2007), and the influence of this value on the age calculation is negligible compared with the total

Table 3
Age of NBS 947 particles calculated with the results of Am/Pu ratio (WDX) and Pu isotopic ratios (TIMS)

Particle	Age (year)	Difference from certificate		Total Uc ^a
		Year	%	
A	38.8	+2.9	8	2.3
B	38.2	+2.3	7	2.4
C	36.2	+0.3	1	2.9
D	35.6	–0.3	1	1.6
E	37.4	+1.5	4	8.6
Age in certificate ^b (referred to November 2007)		35.9		

^a Total uncertainty.

^b Cited from the certificate of NBS 947, produced 3 December 1971 [8].

uncertainty. However the determination of the ^{238}Pu abundance is necessary to apply to the age calculation of real samples. The application of this method is expected to be useful in the detection of undeclared nuclear activities for safeguards purposes.

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