Development of Pu-241/Am-241 age dating capabilities for analysis of nuclear materials for safeguards

Urska Repinc, Monika Sturm, Andreas Koepf, Andrey Bosko

International Atomic Energy Agency, Department of Safeguards, Office of Safeguards Analytical Services, Seibersdorf, Austria

Abstract

The age of the origin of pure plutonium materials is an important piece of information, as it can be closely examined in the verification of a State's declared nuclear material and activities, and in the detection of undeclared nuclear material and activities. An age dating methodology for the analysis of nuclear material samples containing plutonium, using the Pu-241/Am-241 radio-chronometer is described, and the performance of gamma spectrometry is compared to isotope dilution mass spectrometry using different Am-243 and Pu-242 spike materials, and to thermal ionization mass spectrometry for Pu and Am isotope ratio measurements. Several available reference materials with known production dates were used for analysis and the results were compared to those from external expert laboratories and to the literature.

Introduction

The International Atomic Energy Agency (IAEA) annually performs destructive analysis of approximately 500 uranium and 50 plutonium inspection samples for material balance evaluation as well as for material characterization purposes. The majority of plutonium containing samples are analysed for plutonium isotope ratios and uranium isotope ratios (if samples are mixed U/Pu nitrates) as well as Pu and U assay by applying isotope dilution analysis (IDA) using thermal ionization mass spectrometry (TIMS) instrumentation. Controlled potential coulometry is mainly used for analysis of pure Pu solutions prepared in house to be used as liquid Pu-239 spikes for IDA and as source materials for production of large sized dried spikes (LSD); it is not used for analysis of inspection samples. High resolution gamma spectrometry is used to screen for Pu weight abundance measurements and for determination of Np-237/Pu and Am-241/Pu weight percent ratios. Gamma spectrometry works well for old (aged) Pu materials with higher abundance of Pu-241, but not so well for freshly separated or weapon grade materials. Therefore for freshly separated Pu materials more precise analytical techniques for age dating are needed.

Several expert laboratories (e.g. Los Alamos National Laboratory, European Commission, Joint Research Centre - Karlsruhe and Lawrence Livermore National Laboratory) have been collaborating in a study to determine the age of some widely used isotopic standards. The purpose of this work is to have quality control (QC) standards for chronometric applications in support of nuclear safeguards and nuclear forensics, as no traceable isotopic standards certified for model production dates were available from reference material producers [1]. This was therefore an excellent opportunity for the IAEA to test its own capabilities and to validate age dating methodologies using those and other commercially available reference materials.

The IAEA commitment to develop age dating capabilities was formalized as Expected Outcome #2 of the Safeguards Department D&IS Programme (STR-393) for the biennial period 2020-2021 for SGAS-001, Destructive Analysis (DA) of Nuclear Materials, identified to provide "continued independent information for making safeguards conclusions through new analytical methodologies for destructive analysis". One of the key deliverables was to develop and validate the Pu-241/Am-241 age determination method for nuclear samples containing plutonium, with expected delivery in April 2020. IAEA internal report SG-RP-15605 was issued in October 2020 summarizing the work done [2]. This publication aims to present the age dating methodology that was used in SGAS-NML, and propose approach to be used for routine safeguards sample analysis to the wider international nuclear community.

Calculation of age of Pu materials

The age dating methodology is based on parent/daughter relationship, to determine the time (t) elapsed between the analysis and last purification date, to determine the so called "model" purification age or "model" purification date. This relationship is described by the following equation [3]:

$$t = \frac{1}{\lambda_{\text{parent}} - \lambda_{\text{daughter}}} \ln\left(1 - \frac{N_{\text{daughter}}}{N_{\text{parent}}} \cdot \frac{\lambda_{\text{daughter}} - \lambda_{\text{parent}}}{\lambda_{\text{parent}}}\right)$$

For the Pu-241/Am-241 parent/daughter radiochronometer, λ_{parent} and $\lambda_{daughter}$ are the decay constants of Pu-241 and Am-241, and N_{parent} and $N_{daughter}$ are the amounts of the Pu-241 and Am-241 isotopes present in the sample at the time of analysis. The ingrowth of Am-241 due to the decay of Pu-241, considering relatively short life-time of the Pu-241 (14.325 ± 0.012 y, k=1)[4], provides an excellent radiochronometer of Pu containing materials, although the interpretation of age dating results is not trivial especially when considering analysis of unknown samples. We assume the "model" age of the material represents the actual production date, processing, or purification age of the nuclear material of interest. If the amount of plutonium is sufficiently large, non-destructive analysis can be applied by measuring the activity of Am-241 and Pu-241 directly by gamma spectrometry. If the amount of Pu material is not sufficient and/or a more precise determination is needed, isotope abundances and element assays need to be determined using mass spectrometry techniques. Due to isobaric interferences between Am-241 and Pu-241, trace amounts of Am have to be efficiently separated from Pu that is present in much higher amounts. Pu isotopic abundances have to be precisely measured and element assays need to be determined by IDA. The initial assumption we make when performing age dating analysis is that all Am-241 is completely removed when the Pu was initially produced, and that the sample does not contain any Am-243. For unknown samples this might not always be the case, therefore simultaneous use of "independent chronometers" (like the Pu-239/U-235 parent/daughter relationship) may be used for confirmation.

Experimental

Test samples

Well-characterized reference materials were selected from various available source materials: weapons-grade, fuel and reactor grade materials, and isotopically highly enriched materials as an

exception to typical examples. Those materials have different production ages and are available commercially in sufficient amounts to use them in the future as quality control materials.

The following samples were used in this study, and were given specific internal ID numbers for analysis and reporting:

- 90309-01, NBL CRM 136, Pu sulphate; 12% wt.% Pu-240;
- 90309-02, NBL CRM 137, Pu sulphate; 19% wt.% Pu-240;
- 90309-03, NBL CRM 138, Pu sulphate; 8% wt.% Pu-240;
- 90309-04, NBL CRM 126-A, Pu metal; 93.8 wt.% Pu-239;
- 90309-05, CETAMA MP2 (sample of EQRAIN Pu14), 97 wt.% Pu-239;
- 90309-06, NBL CRM 122, PuO_2 powder; 11.5 wt.% Pu-240;
- 90309-07, IRMM-083, Pu-240 spike solution; 98.97 wt.% Pu-240.

Sample solutions were prepared by dilution with 7M HNO_3, using reference materials listed above. Pu assay in prepared sample solutions ranged from 88 µg Pu/g for IRMM-083, 600 to 700 µg Pu/g for CRM 136/137/138, and 400 µg Pu/g for CRM 122. Slightly higher concentrated solutions were prepared for weapon grade materials CRM 126-A and MP2 because the assay of Am-241 is much lower compared to the other materials.

Sample analytical plan

In addition to the Pu-241/Am-241 chronometer, the Pu-239/U-235 chronometer could also be applied because U assay and isotope analysis of uranium in Pu materials is routinely determined in inspection samples. This chronometer was therefore added to the sample analysis flow chart, as presented in Figure 1. The actual Pu amount in samples used in the age dating validation study was not limited, but based on the amount of material actually consumed for analysis. We assume that for inspection samples the total amount of 4 to 10 mg Pu, delivered in a separate vial for age dating requests, would allow the analyst to prepare approx. 10 mL of stock solution with Pu assay of 400 – 1000 µg/g, without the need to assure quantitative sample transfer. The sample solution would be then aliquoted and those aliquots would subsequently be used for Pu-241/Am-241 and Pu-239/U-235 amount ratios determinations by applying Pu/Am/U IDA and performing U/Pu isotope measurements using total evaporation TIMS.

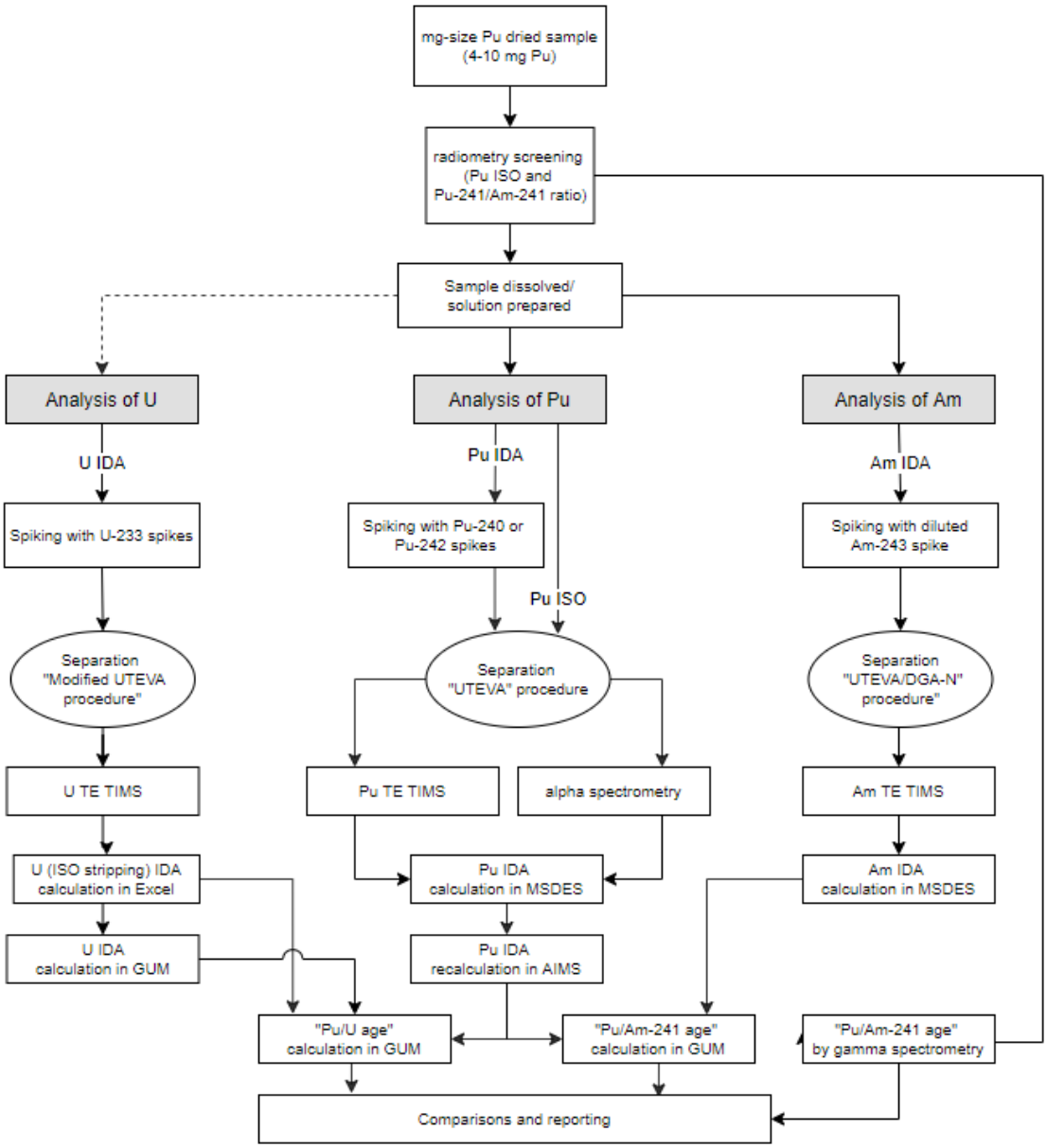

Figure 1. Sample processing flow chart for age dating analysis; with Pu/U age analysis added as an option to use independent chronometers for increased reliability of results (MSDES is an in-house TIMS data evaluation software tool and TIMS results reporting application, and AIMS is an in-house laboratory information management system).

Non-destructive analysis using high resolution gamma spectrometry

Non-destructive high-resolution gamma spectrometry analysis, which is routinely applied by the IAEA for characterizing plutonium containing materials, was used to measure Pu stock solutions prepared from reference materials listed above. During the measurement double-bagged sample vials are automatically positioned above the shielded low-energy high-purity germanium detector (LEGe)

using the sample changer and counted for a predefined time required to achieve desirable counting statistics. Depending on Am-241 activity level, either a 1.1 mm or 1.6 mm thick cadmium filter was placed on top of the detector in order to suppress the high intensity 59.5 keV gamma line of Am-241. The acquired spectra were analysed using the Multi-Group Analysis isotopic code (MGA v10.0) for plutonium isotopic composition and Am-241 content. MGA uses information from the gamma and X-ray peaks located in the 59 - 208 keV energy range, with most of the data obtained from the analysis of a highly overlapping 94 - 104 keV region. The region from 94 to 104 keV contained peaks from all of the isotopes of interest, except for Pu-242, the content of which was determined using a correlation technique. Am-241/Pu-241 weight ratio could be determined with high precision, therefore a separation date for plutonium samples with production ages of approximately 10 to 30 years can be estimated with a rather low combined uncertainty of 0.1 to 0.2 years.

Isotope amount ratio measurements by MC-TIMS

The IAEA has three Thermo Fisher Triton multi-collector thermal ionisation mass spectrometers (MC-TIMS) for nuclear material analysis. The total evaporation (TE) method is used to perform measurements of U, Pu and Am isotope amount ratios, as well as to measure isotope amount ratios of those elements in sample-spike mixtures (or spikes), when employing the IDA technique. Americium isotope ratio measurements were not done previously, but implemented at the time age dating project started, to be able to measure Am aliquots using existing TIMS instrumentation.

Plutonium isotope amount ratio measurements were performed using TE TIMS method, with 10 V summed plutonium signal. For Am isotope amount ratio measurements a 3V (or 6 V) summed americium signal was used. Non-zone-refined rhenium (Re) filaments and tungsten (W) filaments are used in a double filament assembly. The Re filaments were degassed prior loading. Sample aliquots are loaded onto W filaments by drop loading with a pipette, usually loading is 50 - 100 ng Pu and 25 - 100 ng of Am. Typically a volume of 1 µL, but up to 5 µL can be loaded on the filament (for Am required amount might not be so easy to obtain, requiring up to 5 µL of the Am fraction to be loaded onto a filament). The same method, settings, parameters, and Faraday cups are used for the measurement of inspection samples and standards/CRMs that are used as measurement controls.

Plutonium isotope dilution analysis (Pu IDA)

At least six aliquots were taken from each of the prepared stock solutions for isotopic composition (two aliquots) and Pu assay determination by IDA (four to six aliquots). For Pu IDA quad spike QS-92 containing high abundances of Pu-242/Pu-244 (and U-233/U-236) isotopes or KRI RM2-662 Pu-242 spikes were used, for several sample solutions both spikes were used to provide higher confidence in the obtained results. The IDMS equation as defined in ASTM C1672-07 [5] was used, taking Pu-239 as the base isotope, while both Pu-242 (and Pu-244) as spike isotope, with exception for the IRMM-083 material where Pu-240 has been taken as base isotope. All Pu aliquots were separated using TRISKEM UTEVA extraction column separation, using 6 M HNO_3 for loading, additional volumes of 6 M HNO_3 to remove the Am fraction, and 0.2 M hydroxylamine hydrochloride/0.02 M ascorbic acid/2 M HNO_3 for selective elution of Pu. After the separation the purified Pu fraction was diluted to 100 µg Pu/mL with 3 M HNO_3 and measured by TE TIMS.

Americium isotope dilution analysis (Am IDA)

At least four aliquots were taken from each of the prepared stock solutions for Am assay determination by IDA, and as assumption was taken that sample does not contain any other Am isotopes but Am-241, no measurements were done for isotopic composition determination. As the Am-241/Pu-241 amount ratio results were available from gamma spectrometry screening, and the Pu assay results from IDA, the amount of Am in those sample aliquots could be calculated.

The Am amount in those aliquots was very low for materials with low abundance of Pu-241 (~0.9 µg for CRM 126-A, ~0.5 µg for MP2, 0.15 µg for IRMM-083 and 3 µg for CRM 138), while significantly higher Am amounts were present in the higher Pu-241 abundant materials (15 µg for CRM 136 and 17 µg for CRM 137). Two spike materials were used for Am IDA, both prepared by gravimetric dilution from original spike ampoules. NPL Am-243 is a very high abundant (monoisotopic) spike obtained from the United Kingdom. IRMM-0243, a high abundant Am-243 spike, was obtained from the European Commission. The NPL Am-243 diluted spike, for which certified values were obtained by gamma spectrometry, was analysed with the IRMM-0243 original spike solution, using reverse IDA, and the Pu-241 as the spike isotope. It was possible to use both the gravimetrically diluted IRMM-0243 spike solutions and the NPL Am-243 diluted spike for Am IDA. For NPL Am-243 a bias correction of -0.25% was applied to Am assay to assure traceability to the reference material IRMM--0243. Characteristics of the spikes used in the study for Pu and Am IDA are presented in Table 1.

Table 1. Spike materials used for Pu IDA and Am IDA and its characteristics

Analysis	Material	Characteristics
Pu IDA	KRI RM2-662-2004	94.91 µg Pu/g 99.324 at% Pu-242
	QS-92_A, quad spike	0.9741 mg U/g 50.444 at% U-236, 49.334 at% U-233 6.367 µg Pu/g 72.510 at% Pu-242 26.522 at% Pu-244
Am IDA	IRMM-0243, diluted spike	0.1468 µg Am/g 88.007 at% Am-243, 11.981 at% Am-241
	NPL Am-243, diluted spike	0.17919 µg Am/g 99.999 at% Am-243

The spiked aliquots were separated with a tandem column separation procedure using TRISKEM UTEVA plus DGA-N (N,N,N',N'-tetra-n-octyldiglycolamide) extraction columns, with each column filled with ~ 0.5 mL of resin. DGA extraction resins are highly effective at extracting trivalent actinides and lanthanides from nitric acid [6]. A similar separation procedure was used by Wang *et al* [7], to remove U and Pu and other impurities. The sample solution was loaded on a UTEVA + DGA-N tandem in 7 M HNO3/1 M $NaNO_2$ (to adjust the oxidation state of Pu to 4+), adding additional 7 M HNO_3/0.1M $NaNO_2$, removing UTEVA (retaining U/Pu, wasting UTEVA), washing the DGA column with an addition of 7 M HNO_3/0.1 M $NaNO_2$, followed by washing the DGA-N

column with 0.5 M HNO_3/0.05 M oxalate to remove traces of Pu, then reducing the HNO_3 concentration by adding 0.05M HNO_3 followed by stripping the Am fraction using 0.5 M HCl. Alpha spectrometry was used to quantify the presence of Pu-239+240 in the Am-241 fraction collected after separation. This information was used to calculate the decontamination factor for Am. The UTEVA + DGA-N separation procedure was applied on several aliquots of CRM 126-A (high abundant Pu-239+240 wt% material), each containing ~100 µg Pu. The activity ratio for (Pu-239+240)/Am-241 at the time of analysis was 22.42. After separation on UTEVA + DGA-N, the Am fraction was evaporated till dryness and dissolved in a small volume of 3 M HNO_3, then a 10 µL subsample was taken for the alpha spectrometry measurement to be measured for presence of plutonium with comparing alpha peaks from Am-241 (5.443 MeV and 5.486 MeV) to Pu-239+240 alpha peaks (summed peak at ~5.15 MeV). Based on activity measurements, the decontamination factor for six UTEVA + DGA-N separation tests varied from 1096 to 1938. The tandem column separation procedure was effective enough for Am measurements using TIMS to the levels that are realistically achievable using single column separation, as still some minor amounts of Pu-239 would usually be detected (usually in the ratio range of 10^{-6} for Pu-239/Am-241). At the same time, we observed that Am spike material IRMM-0243, that has been measured directly by TIMS, without separation applied, also contains Pu-239 in significantly higher amounts (Pu-239/Am-241 ratio ~0.00245).

For the use of NPL Am-243 diluted spike, decay correction was not needed (while for IRMM-0243 decay correction has to be done), therefore the monoisotopic spike was found to be very valuable, especially for samples with very low Am-241 content, as even the smallest amount of Am-241 in the spike significantly changed the isotopic ratios of the sample-spike mixture. The highest spike/sample amount ratio (therefore measured Am-243/241 ratios) were achieved for samples containing low amounts of Am-241 (Am-243/241 of ~0.2 for CRM 126-A, 0.38 for MP2, 0.2-0.5 for IRMM-083), while for other samples measured ratios were rather low (Am-243/241 of 0.005-0.006 for CRM 136, 137, ~0.03 for CRM 138, ~0.04 for CRM 122). To be able to estimate the measurement uncertainty for different Am-243/241 ratio measurements, 4 different IRMM-0243 and NPL spike mixtures were prepared covering ratio measurements from 0.0028 to 0.015, as well as to be used as associated QC materials for TE TIMS, while IRMM-0243 is used as standard.

For the IDA model age calculations, we applied the following approach:

- Pu decay correction was done to correct the Pu results from the Pu analysis date to the Am analysis date. For the Pu-241 isotope abundances the standard deviation of the measured Pu-241/239 ratios was taken as a most realistic estimate of uncertainty, as these results are often very dependent on the quality of the UTEVA separation;
- The NPL Am-243 spike was prepared by dilution. Since the source material had a rather large uncertainty of 0.85% (k=2), the average Am assay results for the samples were assigned an uncertainty of approximately 1% (k=2), although the variability of results might be much lower than that value;
- IRMM-0243 spike was decay corrected to the exact Am IDA analysis date;
- a generous uncertainty of 0.1% (k=2) was assigned to the Am-243/241 ratio measurements for sample-spike mixtures TE TIMS measurements;

- the assumption was taken that samples do not contain Am-243, and Am-241 abundance was taken as 100% wt. and assumed uncertainty of 0.1% relative (k=2) was assigned to this value, as it is very unlikely that sample would contain any Am-243;
- from the GUM uncertainty budget for age determination we could identify that the major uncertainty sources are the Am assay of the spike and the weight percent abundance of Pu-241.

Estimated ages of the materials obtained by gamma spectrometry and destructive analysis using the Pu-241/Am-241 age dating methodology by applying a combination of Pu IDA and Am IDA, are presented in Table 2 together with uncertainty at k=2.

Table 2. Determined model age of selected reference materials in comparison to literature data [1,8]

Sample	Method	Analysis date	Estimated age and uncertainty (years)		Model age and uncertainty (days)	Production date and uncertainty (days)
90309-01 (CRM136)	gamma spec	2018-08-29	47.87	0.29%	1970-10-15 ± 50	1970-03-30 ± 60
	IDA, NLP spike	2019-01-07	48.591	0.44%	1970-06-05 ± 78	
90309-02 (CRM137)	gamma spec	2018-08-29	46.707	0.28%	1971-12-14 ± 49	1970-09-15 ± 60
	IDA, IRMM spike	2018-11-30	48.11	0.26%	1970-10-21 ± 46	
	IDA, NLP spike	2018-12-13	48.06	0.44%	1970-11-22 ± 77	
90309-03 (CRM138)	gamma spec	2018-08-29	53.496	0.56%	1965-03-01 ± 110	1963-09-15 ± 180
	IDA, NLP spike	2019-01-07	55.965	0.41%	1963-01-20 ± 84	
90309-04 (CRM 126-A)	gamma spec	2018-08-30	19.575	2.23%	1999-02-01 ± 159	2001-07-15 ± 180
	IDA, NLP spike	2019-01-08	17.753	0.78%	2001-04-08 ± 51	
90309-05 (MP2)	gamma spec	2018-02-14	34.019	0.84%	1984-02-07 ± 104	
	IDA, NLP spike	2019-01-08	35.439	0.56%	1983-08-01 ± 72	
90309-06 (CRM122)	gamma spec	2018-09-28	38.644	0.30%	1980-02-05 ± 42	
	IDA, NLP spike	2019-01-08	39.602	0.52%	1979-06-03 ± 75	
90309-07 (IRMM-083)	gamma spec	2018-11-01	24.988	0.67%	1993-11-05 ± 61	1993-06-13 ± 60
	IDA, IRMM spike	2019-01-28	25.596	0.37%	1993-06-24 ± 35	
	IDA, NLP spike	2019-01-28	25.55	0.67%	1993-07-11 ± 63	

In general gamma spectrometry provided very reliable results for a Pu age determination when the amount of Pu is sufficient and the Am-241 can be reliably measured. Gamma spectrometry results for IRMM-083 are a perfect example, as this is a highly enriched Pu-240 material with a very low Am-241 content. The results were obtained with 90-h counting time, and agree well with the model age determined by gamma spectrometry reported by Nygren *et al* (1993-11-06 ± 511 days), that reported reference production date for this material to be 1993-06-13 [8]. For weapon grade materials with low Pu-241 abundances, like CRM 126-A and MP2, the Am-241 activity is low, and therefore gamma spectrometry cannot provide reliable results, especially if material has been recently separated.

For samples 90309-02 and 90309-07 two results obtained by IDA are presented, as they were obtained by the use of different Am spikes (NPL-243 and IRMM-0243). The obtained IAEA-NML results were compared with the consensus values for the model purification dates and their corresponding uncertainties, as those were published recently [1]. For MP2 Pu metal the production date was not

found in literature, the same is true for CRM 122, although it could be identified from the literature that MP2 source material could be produced before 1985 [9].

Conclusions

A destructive analysis method for Am IDA determination using TIMS was developed for the purpose of Pu age determination. The IRMM-0243 spike was used for both direct age determinations and for validation of the valuable monoisotopic spike material NPL Am-243, the latter being especially useful for analysis of materials with very low Am-241. The proposed Pu-241/Am-241 age dating methodology using the radio-chronometer was also validated using several Pu reference materials and proved to be fit for purpose. The IAEA is therefore capable to make age determinations from Pu-bearing samples, with specific emphasis on weapon grade materials with recent production dates.

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