J Radioanal Nucl Chem (2010) 286:449–454
DOI 10.1007/s10967-010-0759-2

An inter-calibration campaign using various selected Pu spike isotopic reference materials

R. Jakopič · A. Verbruggen · R. Eykens · F. Kehoe · H. Kühn · Y. Kushigeta · U. Jacobsson · J. Bauwens · S. Richter · R. Wellum · Y. Aregbe

Received: 23 July 2010 / Published online: 19 August 2010

Abstract In nuclear safeguards, precise and accurate isotopic analyses are needed for two major elements from the nuclear fuel cycle: uranium and plutonium. This can be achieved by Isotope Dilution Mass Spectrometry (IDMS), which is one of the most reliable analytical techniques for the determination of plutonium amount content to a high level of accuracy. In order to achieve reliable isotope measurements isotopic reference materials with certified amount of plutonium and isotopic composition are required. At the Institute for Reference Materials and Measurements (IRMM) various plutonium spike reference materials for isotopes ^{239}Pu, ^{240}Pu, ^{242}Pu and ^{244}Pu are available. This enabled the setup of an inter-calibration campaign inter-linking selected plutonium spikes on a metrological basis applying state-of-the-art measurement procedures. The aim of this campaign is threefold: firstly to perform measurements on selected plutonium spike isotopic reference materials for quality control purposes, secondly to verify the amount content and the isotopic composition of the recently produced IRMM-1027m large sized dried (LSD) spikes and thirdly to demonstrate IRMM's measurement capabilities for plutonium analysis via external quality tools. The obtained results using various spike isotopic reference materials will be presented and discussed in this paper. The measurement uncertainties of the IDMS results were calculated according to the guide to the expression of uncertainty in measurement (GUM).

R. Jakopič (✉) · A. Verbruggen · R. Eykens · F. Kehoe · H. Kühn · Y. Kushigeta · U. Jacobsson · J. Bauwens · S. Richter · R. Wellum · Y. Aregbe
Institute for Reference Materials and Measurements, Joint Research Centre, European Commission, Retieseweg 111, 2440 Geel, Belgium
e-mail: rozle.jakopic@ec.europa.eu

Keywords Plutonium · Isotopic reference materials · IDMS · TIMS · Nuclear safeguards

Introduction

By signing the treaty on the non-proliferation of nuclear weapons (NPT) non-nuclear weapon states officially declare to abandon all efforts to develop nuclear weapons and to conclude the safeguards agreements [1]. Nuclear safeguards aims at the verification of the non-diversion of fissile material from its intended and declared peaceful use. A reliable nuclear material accountancy system has to be established by the plant operator and a reliable system of verification is the responsibility of the safeguards authority in charge. Furthermore, the INFCIRC/540 [2], also referred to as the additional protocol (AP), authorizes safeguards authorities to verify the absence of undeclared nuclear activities in all parts of a state's nuclear fuel cycle.

The measurement of amounts of plutonium is recognised as one of the most important tasks in fissile material control. Public opinion is very sensitive to this element, which presents analysts with a difficult task of measuring plutonium at all levels, from large (multi-gram) amounts down to traces in the environment. Reliable, low uncertainty isotopic measurements are needed that provide the basis for a strong verification and detection system to safeguard nuclear materials and activities in line with the NPT and the AP. The fundamental role of reference materials in measurements of amount of material is to establish traceability of a measured value (i.e. the analytical result) to a primary unit of measurement as defined in the SI system. Isotope Dilution Mass Spectrometry (IDMS) is one of the analytical techniques widely used for the

measurements of plutonium content determination. For these reasons plutonium reference materials with certified amount content and isotopic composition with the lowest possible uncertainties are needed for the calibration of mass spectrometers, for validation of a measurement technique and to assess the reproducibility of measurement results in compliance with quality control requirements. IDMS in combination with the correct use of reference materials and quality control tools is an important means for the control of fissile material and verification of environmental samples [3, 4].

The Institute for Reference Materials and Measurements (IRMM) is one of the few institutes worldwide that produces and certifies plutonium reference materials. They are part of a systematic IRMM programme to supply reference materials of various isotopes, in particular uranium and plutonium, at different concentrations. The production and certification of nuclear reference materials involves parameters such as stability, homogeneity, etc., that need to be looked at in regular time intervals. Particularly for plutonium, due to radioactive decay, the certified values have to be regularly corrected: a process which leads to an increase in measurement uncertainty depending on the spike isotope composition. Moreover, the Pu spike solutions also have a possibility of being unstable over time, probably due to radiolysis.

An inter-calibration campaign using state-of-the art measurement procedures has therefore been carried out at IRMM linking the plutonium spike reference materials available at the institute. The following nuclear isotopic reference materials were used in the campaign: IRMM-049c (^{242}Pu), IRMM-049b (^{242}Pu), IRMM-046b (^{242}Pu and ^{233}U), IRMM-083 (^{240}Pu) and IRMM-081a (^{239}Pu) and one external certified plutonium inter-laboratory comparison test sample EQRAIN-11 (^{239}Pu) from CEA/CETAMA. All the uncertainties for the IDMS measurements were estimated according to the guide to the expression of uncertainty in measurement (GUM) [5].

Experimental

Selection of Pu spikes

Different series of IDMS measurements on Triton Thermal Ionization Mass Spectrometer (TIMS) were performed in order to establish or to confirm the inter-relation between different Pu spikes available at IRMM. The Pu spikes for this inter-calibration campaign were selected according to following criteria: availability, certified isotope, year of certification and suspected to be candidate for re-certification:

- IRMM-1027m LSD spikes: certified amount in each vial of about 2 mg plutonium, ($n(^{239}\text{Pu})/n(\text{Pu}) = 0.978$) and about 50 mg uranium ($n(^{235}\text{U})/n(\text{U}) = 0.195$) as nitrate covered with organic polymer CAB (cellulose acetate butyrate).
- IRMM-049c: ^{242}Pu spike solution, about 100 μg Pu/g solution, 0.36665(49) μmol ^{242}Pu/g, $n(^{242}\text{Pu})/n(\text{Pu}) = 0.941$.
- IRMM-049b: ^{242}Pu spike solution, about 100 μg Pu/g solution, 0.41738(28) μmol ^{242}Pu/g, $n(^{242}\text{Pu})/n(\text{Pu}) = 0.999$.
- IRMM-046b: ^{233}U and ^{242}Pu spike solution, about 1 mg U/g solution and about 100 μg Pu/g solution, 0.46571(70) μmol ^{242}Pu/g, $n(^{242}\text{Pu})/n(\text{Pu}) = 0.943$.
- IRMM-083: ^{240}Pu spike solution, about 1000 μg Pu/g solution, 4.4064(22) μmol ^{240}Pu/g, $n(^{240}\text{Pu})/n(\text{Pu}) = 0.990$.
- IRMM-081a: ^{239}Pu spike solution, about 100 μg Pu/g solution, 0.37480(23) μmol ^{239}Pu/g, $n(^{239}\text{Pu})/n(\text{Pu}) = 0.978$.
- EQRAIN-11: CETAMA inter-laboratory comparison for ^{239}Pu amount content.

Preparation of blend solutions

Blend solutions were prepared by metrological weighing (substitution weighing). Four different series were prepared in order to interlink IRMM-1027m LSD spikes with IRMM-049c, IRMM-049b, IRMM-046b and IRMM-083 spikes from IRMM. Additional four series were prepared to interlink IRMM-049c, IRMM-049b, IRMM-046b and IRMM-083 spikes with IRMM-081a and Eqrain-11. The Pu inter-calibration scheme is shown in Fig. 1.

Chemical treatment (separation) of Pu

The blend solutions were evaporated to near dryness and the residue dissolved in 2 M HNO_3. Plutonium oxidation state was adjusted to Pu(IV) prior to separation on the column. A redox cycle was done in which Pu was first reduced to Pu(III) by addition of 1.25 M $FeCl_2$ and 1 M $NH_2OH{\bullet}HCl$ and then oxidised to Pu(IV) by addition of 1 M $NaNO_2$. Finally, concentrated HNO_3 was added to obtain Pu(IV) in 8 M HNO_3.

The separation of Pu was accomplished by passing the sample solution through a preconditioned anion-exchange column (Bio-Rad AG1-X4, 100-200 mesh). The column was washed with 8 M HNO_3 and finally, Pu was eluted with 0.35 M HNO_3 and evaporated to near dryness. This separation (purification) procedure was repeated 3 times for plutonium in order to avoid interferences with uranium in mass spectrometric measurements. The purified Pu

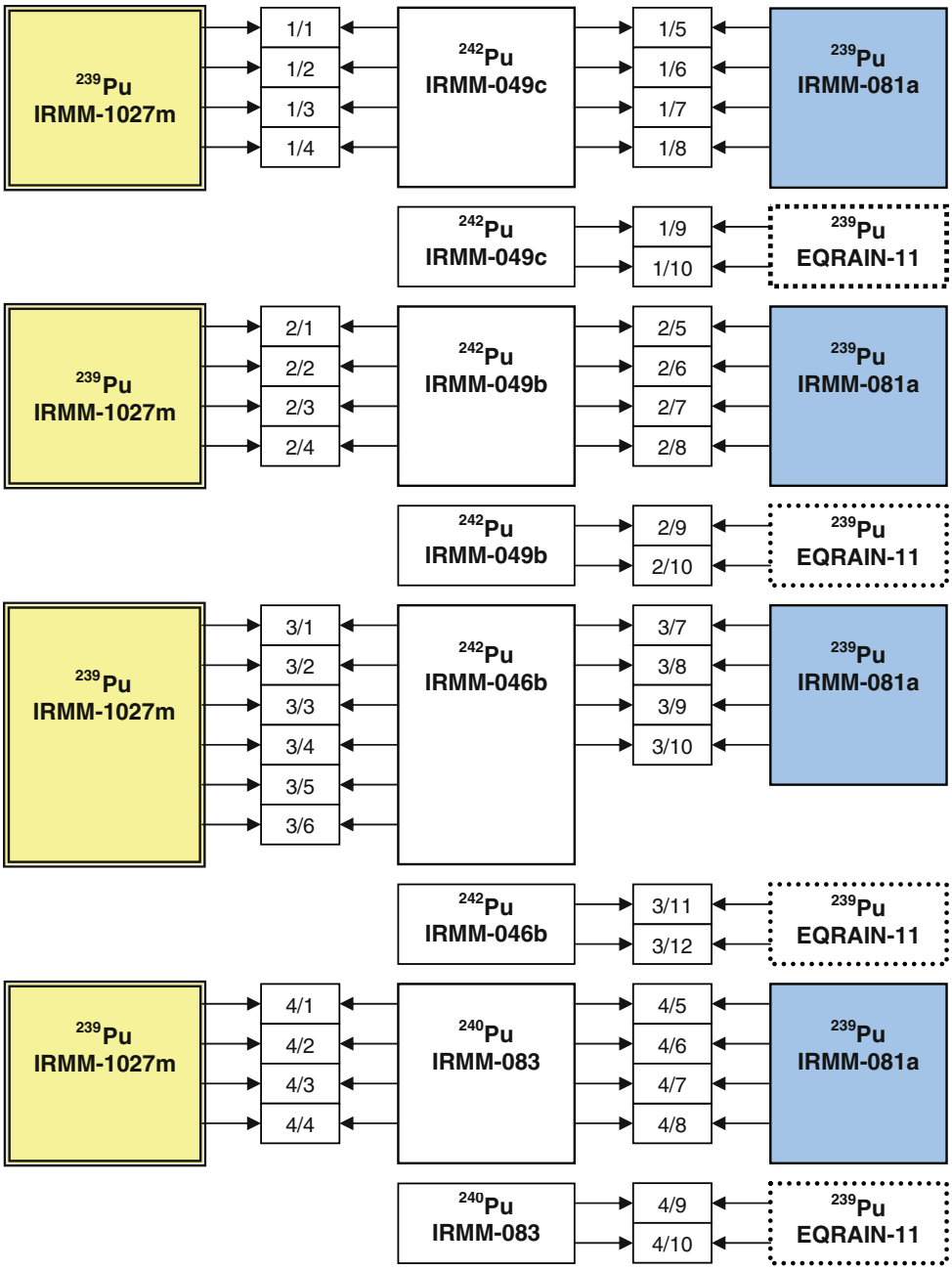

Fig. 1 Inter-calibration scheme of IRMM Pu spike reference materials and Eqrain-11

fraction was evaporated, dissolved in 1 M HNO_3 and loaded onto Re filaments for mass-spectrometry measurements. The flowchart of IDMS is shown in Fig. 2.

Isotope measurements by TIMS

IDMS was applied for the determination of the plutonium amount content in the samples. Using a spike reference material, the plutonium content in an unknown sample (C_x) can be determined through a measurement of the isotope ratio in a blend (sample + spike) following the equation below:

$$c_x = c_y \frac{m_y}{m_x} \frac{R_y - R_b}{R_b - R_x} \frac{\sum(R_i)_x}{\sum(R_i)_y},$$

where c_y is the element content of the spike used in the determination, m_x and m_y are the masses of sample and spike, respectively, R_x, R_y and R_b are the isotope amount ratios of the sample, spike and the blend, respectively, and $\Sigma(R_i)_x$ and $\Sigma(R_i)_y$ are the sums of all isotope ratios in the sample and spike, respectively.

Thermal Ionization Mass Spectrometry (TIMS) was used to measure the plutonium isotope ratios. The IRMM Triton TIMS (Thermo Fisher Scientific) is equipped with

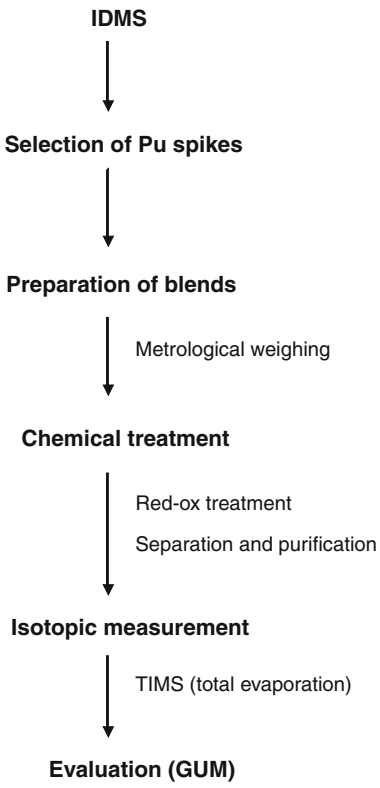

Fig. 2 The flowchart of the IDMS

nine Faraday cups, one conventional discrete dynode electron multiplier (SEM), and seven continuous dynode electron multipliers (CDEMs). The isotopic measurements were performed in total evaporation (TE) mode, which is a frequently used technique in order to minimize the influence of mass fractionation effects in the ion source. In total evaporation mode the filament current is regulated to achieve a steady count rate intensity during the measurement. This is continued until the sample is completely consumed. The isotopic reference material (IRMM-290/A3) was measured with the same technique as the samples on the same sample magazine to measure the mass fractionation [6, 7].

Results and discussion

Measurements against IRMM-1027m

IRMM-1027m LSD spikes are large-sized dried spikes, containing about 50 mg of uranium with ^{235}U mole fraction of 19.5% and about 1.8 mg of plutonium with ^{239}Pu mole fraction of 97.8% which are certified for the Pu amount content and for the isotope abundances. They are prepared from accurately weighed high purity metals. The values of the uranium and plutonium isotopic contents of the final certified spike solution are directly traceable to the SI via the masses of the starting materials and have low uncertainties. LSD spikes are produced by IRMM in support to EURATOM safeguards and used to measure the uranium and plutonium content of dissolved fuel solutions using IDMS at the 'On Site Laboratory (OSL)' at Sellafield (UK) and the 'Laboratoire sur Site (LSS)', La Hague (France), the sites of the two large European reprocessing plants [8, 9]. In the last 10 years LSD spikes have become a fundamental part of the fissile material control of irradiated nuclear fuel.

The Pu amount content of IRMM-049c, IRMM-049b, IRMM-046b and IRMM-083 spike reference solutions was verified against the IRMM-1027m prepared from primary reference materials.

The verification measurements were performed by IDMS on the Triton TIMS. The results are shown in Fig. 3.

The measurement results using IRMM-049c, IRMM-049b, and IRMM-083 agreed well with the IRMM-1027m values for plutonium amount content calculated from the amounts of dissolved metal and solution (mass metrology). The ratios, certified *vs.* measured, for IRMM-049c, IRMM-049b and IRMM-083 were 1.0001, 0.9991 and 1.0004, respectively. The certified value in Fig. 3 is shown with a solid line and the mean (average) of the measured values with a dotted line with the respective expanded uncertainties ($k = 2$).

The results for IRMM-046b showed a difference of about 0.14% from its certified value. This spike material has already been suspected to be due for re-certification. This small deviation could be due to instability of the spike solution; however, more tests need to be done to confirm that. This observation could also be explained with the fact that the certification of IRMM-046b reference materials was originally done in 1995 applying different measurement equipments and standards which resulted in higher measurement uncertainties. Since that time, mass spectrometric measurements and equipment have improved,

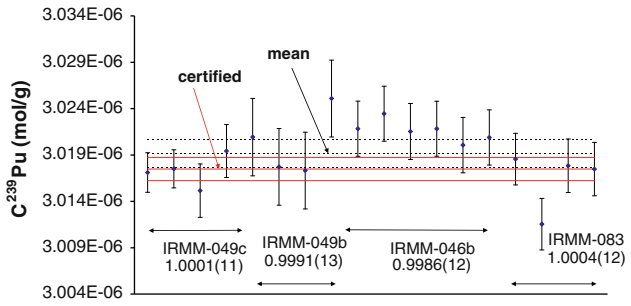

Fig. 3 Amount concentration of ^{239}Pu in IRMM-1027m (from the weights of metals and solution) compared with the measured values by IDMS (with expanded uncertainties, $k = 2$)

leading to results with better precision and accuracy and thus much smaller uncertainties could be achieved.

As a result of this inter-calibration campaign it was confirmed that IRMM-1027m LSD spikes can be used to re-certify the Pu amount content and isotope abundances in IRMM-046b. The results for the IRMM-1027m measured against IRMM-046b using this new provisional certified value are shown in Fig. 4. In the scope of this inter-calibration study and with the results from IRMM-1027m and Eqrain-11 a re-certified value for the Pu content of IRMM-046b will be derived.

Measurements against IRMM-081a

Results of the verification measurements of IRMM-049b and IRMM-083 against IRMM-081a are shown in Figs. 5 and 6. Agreement between the certified and the measured values could be confirmed. Similar conclusions can be drawn for IRMM-049c.

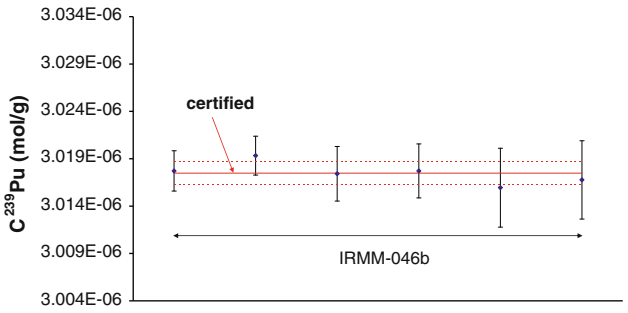

Fig. 4 Amount concentration of ^{239}Pu in IRMM-1027m (from the weights of metals and solution) compared with the measured values by IDMS (with expanded uncertainties, $k = 2$) using the new provisional values of re-certified IRMM-046b

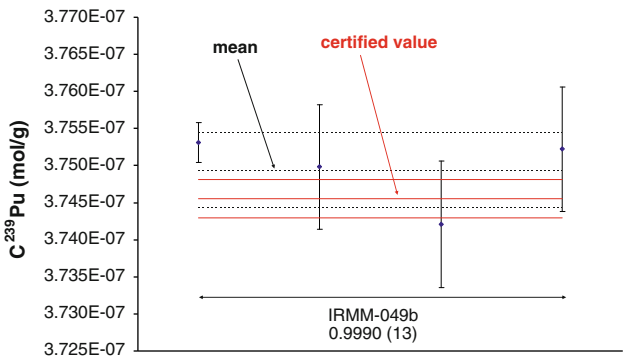

Fig. 5 Amount concentration of ^{239}Pu in IRMM-081a (certified value) compared with the measured values by IDMS with IRMM-049b (with expanded uncertainties, $k = 2$)

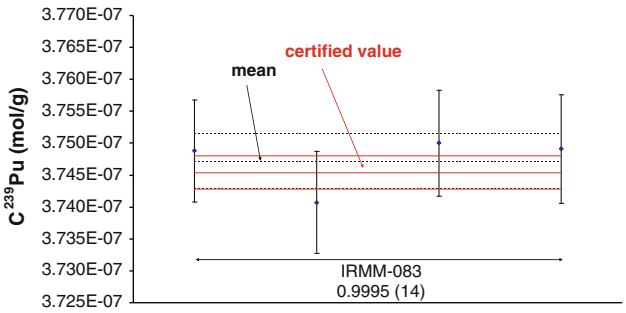

Fig. 6 Amount concentration of ^{239}Pu in IRMM-081a (certified value) compared with the measured values by IDMS with IRMM-083 (with expanded uncertainties, $k = 2$)

Measurements against EQRAIN-11

One main activity of CETAMA (Commission d'ETAblissement des Méthodes d'Analyse du CEA) is the inter-laboratory comparisons programme, called EQRAIN, organised at regular intervals for the analysis of uranium and plutonium (http://www-cetama.cea.fr). The certified test sample in EQRAIN-11 is a plutonium nitrate solution with undisclosed value for isotope amount content. IRMM successfully linked the participation in EQRAIN-11 to this inter-calibration campaign by determining the plutonium isotope amount content of the EQRAIN-11 certified test sample applying IDMS using IRMM-049c, IRMM-049b, IRMM-083 and the provisionally re-certified IRMM-046b obtained from IRMM-1027m. The results reported by IRMM were in excellent agreement with the reference value provided by CETAMA to participants after result reporting. EQRAIN-11 is still ongoing and therefore the plutonium amount content is not disclosed in this paper. Figure 7 shows instead the measurement results normalised to the EQRAIN-11 reference value.

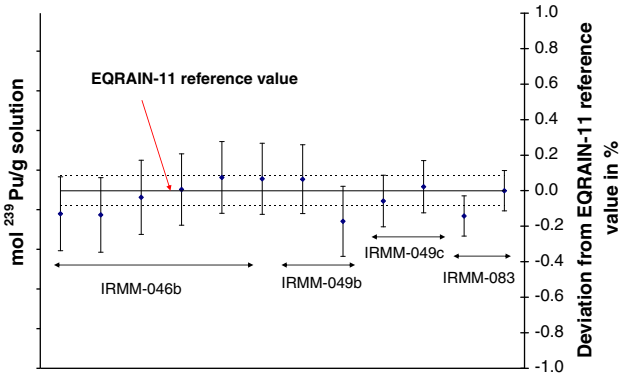

Fig. 7 Normalised amount concentration of ^{239}Pu in EQRAIN-11 compared with the measured values by IDMS (with expanded uncertainties, $k = 2$)

Conclusion

IRMM carried out an inter-calibration campaign on a selection of certified plutonium spike reference materials against an IRMM "primary reference material" and an external certified test sample. All three envisaged aims of this campaign, namely verification measurements, quality control of Pu reference materials and demonstration of measurement capability, were met. As a result of this study the amount content and the isotopic composition of the gravimetrically produced and certified IRMM-1027m large sized dried (LSD) spikes was verified and at the same time the compatibility of IRMM-049c, IRMM-049b, IRMM-083 and IRMM-081a was confirmed. Furthermore 12 IDMS re-certification measurements of IRMM-046b were performed in the scope of interlinking the various Pu reference materials. An external certified inter-laboratory test sample was also successfully interlinked to this comparability study. In general it can also be concluded that there is a strong indication that the IRMM plutonium spike solutions are homogeneous even years after production. However, to confirm that additional samples need to be analysed in the future. This inter-calibration campaign using state-of-the art measurement procedures demonstrates IRMM's measurement capability, confirms the traceability of the values of the plutonium isotopic contents to the SI and underpins the confidence in the use of isotopic plutonium reference materials for safeguards verification and environmental measurements. It also underlines IRMM's leading role as a provider of isotopic plutonium reference materials. In the next stage new plutonium isotope reference materials will be linked to this compatibility study.

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