International Journal of Mass Spectrometry 279 (2009) 87–92

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Isotope ratio measurements of pg-size plutonium samples using TIMS in combination with “multiple ion counting” and filament carburization

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ARTICLE INFO

Article history:
Received 27 August 2008
Received in revised form 8 October 2008
Accepted 10 October 2008
Available online 25 October 2008

Keywords:
TIMS
Multiple ion counting
Filament carburization
Multi-dynamic measurement

ABSTRACT

A sample preparation procedure for isotopic measurements using thermal ionization mass spectrometry (TIMS) was developed which employs the technique of carburization of rhenium filaments. Carburized filaments were prepared in a special vacuum chamber in which the filaments were exposed to benzene vapour as a carbon supply and carburized electrothermally. To find the optimal conditions for the carburization and isotopic measurements using TIMS, the influence of various parameters such as benzene pressure, carburization current and the exposure time were tested. As a result, carburization of the filaments improved the overall efficiency by one order of magnitude.

Additionally, a new “multi-dynamic” measurement technique was developed for Pu isotope ratio measurements using a “multiple ion counting” (MIC) system. This technique was combined with filament carburization and applied to the NBL-137 isotopic standard and samples of the NUSIMEP 5 inter-laboratory comparison campaign, which included certified plutonium materials at the ppt-level. The multi-dynamic measurement technique for plutonium, in combination with filament carburization, has been shown to significantly improve the precision and accuracy for isotopic analysis of environmental samples with low-levels of plutonium.

1. Introduction

Many radioactive elements of natural origin are present in the environment, like uranium, thorium and their decay products, ^{40}K and those produced from the cosmic ray reactions (^{14}C, ^{26}Al, ^{3}H, etc.) while others are man-made and have been produced and released to the environment by human activities. Such element is plutonium which can be found in the environment as a result of nuclear weapon tests, nuclear reactor accidents, discharges from reprocessing power plants, dumping of nuclear waste and accidents with nuclear devices. For assessing different sources of plutonium contamination in the environment, information on the isotopic composition is necessary. Isotope ratios can be referred to as an “isotope fingerprint” providing information on the origin (source) of the material. Pu isotope ratios measured in environmental samples vary according to source of contamination, history and burn-up of nuclear fuel, reactor type, yield, etc. For fallout samples isotope ratios depend on the fissionable material used for the production of the material and the type of weapon test. Determination of the activity and isotope ratios of plutonium isotopes can be applied to various fields such as illicit trafficking of nuclear material, investigation of nuclear accidents, nuclear safeguards, radiation protection, nuclear forensics and low-level environmental monitoring. Methods usually applied for the determination of plutonium isotopes are radio-analytical techniques, such as alpha spectrometry after chemical separation of Pu for determination of ^{238}Pu and $^{239+240}$Pu [1–7] and liquid scintillation counting (LSC) for determination of ^{241}Pu [8–10]. They provide information about the activity concentration (Bq/g) in the sample or ^{238}Pu/$^{239+240}$Pu activity isotope ratio. A major disadvantage of alpha spectrometry for low-activity samples is the usually long counting period, which can take from days to several weeks depending on the sensitivity and precision required. In addition, alpha spectrometry cannot easily resolve the energies of ^{239}Pu and ^{240}Pu (5.15 and 5.16 MeV, respectively), which makes the measurement of the ^{240}Pu/^{239}Pu isotope ratio difficult. Some approaches applying spectrum deconvolution were proposed to improve alpha spectrometry resolution but it did not find wide application for the measurement of ^{240}Pu/^{239}Pu ratio [11,12]. Instead, mass spectrometric techniques such as accelerator mass spectrometry (AMS) [13–15], thermal

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doi:10.1016/j.ijms.2008.10.014

ionization mass spectrometry (TIMS) [16–18] and inductively coupled plasma mass spectrometry (ICP-MS) [19–25] have been used as ultrasensitive mass spectrometric techniques for the determination of the $^{240}Pu/^{239}Pu$ and the other isotope ratios. AMS is characterized by low measurement background but is not widely used due to the necessity for a tandem accelerator. ICP-MS is widely used due to simple sample preparation, high sample throughput, sensitivity, good accuracy and precision. However, uranium hydride formation ($^{238}UH^+$) and peak tailing from the ^{238}U ion beam limit the use for the determination of plutonium at very low concentration levels. To measure smallest amounts of plutonium with high precision and accuracy, a sophisticated detection system would be desirable. A multiple ion counting detection (MIC) system in combination with e.g., thermal ionization mass spectrometry (TIMS) holds the potential to meet this requirement. The main disadvantage of the TIMS source to the ICP-MS source is the low ionization efficiency of the sample for ion production which plays an important role at low-level amounts of plutonium, particularly for measurements of isotopes having low abundance, such as ^{241}Pu and ^{242}Pu. Due to isobaric interference of ^{238}U, TIMS is generally not used for the determination of the $^{238}Pu/^{239}Pu$ isotope ratio.

Different approaches are described in the literature in order to enhance the overall efficiency (atoms detected to atoms loaded) of the sample in thermal ionization mass spectrometry. One of them is a cavity ion source [26–28] where higher overall efficiencies of the sample were obtained due to a higher temperature and a larger ratio of surface area to volume and confined geometry (shape and size). This was achieved by replacing the conventional flat ribbon filament with a high efficiency cavity source. The resin bead technique uses a boat-shaped filament (V-shaped) [29–31] where a strip of rhenium is folded to form a boat shape to hold a larger amount of sample. Due to the addition of carbon from the resin, higher overall efficiency can be achieved. Other approaches such as applying different additives like collodion, aquadac and graphite as a carbon source and coatings like platinum, gold and silver have also been tested [32].

Within this study, carburization of the rhenium filaments using pure benzene gas as a carbon provider was tested at IRMM for two reasons. Firstly, the carburization procedure using benzene in the gas form is expected to produce a more reproducible and more homogenous distribution of carbon on or within the filaments rather than the application of carbon in a form of a solution or a suspension. Secondly, a virtual zero background could be expected by avoiding the addition of any chemicals such as graphite and aquadac which might always contain traces of ^{238}U.

Rhenium filaments are exposed to benzene vapour at high temperature within a special carburization vacuum chamber; thereby carbon is dissolved into the rhenium filament. A metal–carbon solid solution is formed with enhanced electron work function (Φ) compared to pure rhenium. When the sample is heated within the TIMS ion source, carbon diffuses to the surface of the filament and interacts with plutonium to form various carbides. Carbon also serves as a reducing agent, which promotes the production of plutonium ions at the expense of undesirable oxide species. This helps to keep the cations in a reduced ionic state allowing for a higher proportion + 1 charged ion to be produced during filament heating. This results in substantially more stable and more intense ion beams for a given amount of material [33].

2. Experimental

2.1. Radiochemical separation of Pu

Samples (NUSIMEP 5 and NBL-137) were transferred into the conical Teflon vessels and evaporated to near dryness. Then 1 mL of 3 M HNO_3 was added to dissolve and oxidize plutonium. Plutonium was then reduced to Pu(III) by addition of 50 μL 1.25 M $FeCl_2$ and 100 μL 1 M $NH_2OH{\cdot}HCl$. After 5 min, 100 μL 1 M $NaNO_2$ was added to oxidize plutonium to Pu(IV). The sample solution was loaded onto the preconditioned TEVA column in 3 M HNO_3. After washing the Teflon vessel and the column twice with 1.2 mL of 3 M HNO_3, plutonium was eluted from the column with 4.5 mL 9 M HCl–0.1 M NH_4I solution. The Pu effluent was evaporated to dryness and treated with 65% HNO_3 and 30% H_2O_2 to destroy the iodine and traces of organic constituents. The dry residue was then dissolved in 0.5 M HNO_3 and loaded onto carburized Re filaments for TIMS measurement.

2.2. Carburization technique

A set of rhenium filaments was placed into a filament bake out device (Thermo Finnigan) and evacuated. After a sufficient vacuum pressure was established (7×10^{-7} mbar), the filaments were subjected to a heating routine for degassing and cleaning (30 min, 1750 °C). After degassing the filaments were placed into a carburization vacuum chamber, which allowed the inlet of a pure vapour of benzene at a controlled vapour pressure. After the chamber was evacuated the benzene was introduced into the chamber through a valve and the filament current was adjusted to a predetermined level to heat the filament for a defined period of time. In order to find the optimal conditions, carburization experiments were performed at various filament currents (2.5–4.0 A) and benzene pressures (1×10^{-5} to 1×10^{-3} mbar) so that the filaments would contain different amounts of dissolved carbon.

2.3. Triton TIMS

The determination of plutonium ratios in extremely small quantities of analyte ($< 10^{-10}$ g) requires the measurement of low intensity ion beams, usually $< 10^{-16}$ A. For such signal levels an ion counting detection system is ideal. The isotope ratios can be measured by switching the peaks of interest into a single ion counter. However, the precision of a peak-jumping suffers from variations in signal intensity between each peak measurement. Multiple collector mass spectrometers, which are capable of the simultaneous determination of a number of isotopes, have been available for several years [34]. The multi collector array has generally consisted of Faraday collectors plus a single, fixed ion counting device. More recently continuous dynode electron multipliers (CDEM) have been manufactured to match the width of Faraday detectors and thus fit into the multi-collector array. They can be readily installed to replace individual Faraday cups in a multi detector mass spectrometer or bundled together and located along the detector plane with a set of Faraday cups. On the IRMM Triton mass spectrometer, nine Faraday cups, one conventional discrete dynode electron multiplier, and seven CDEMs were installed. The width of the CDEMs is identical to the standard Faraday cups, and thus the ion counters can be aligned with single unit mass spacing for the measurement of high mass elements such as U and Pu. Six of the small ion counters were bundled together and positioned on the low mass side of the L4 Faraday cup, see Fig. 1. One additional ion counter was positioned on the high mass side of the L4 Faraday cup [35]. The advantage of multiple ion counting is the simultaneous collection of several isotopes of a given element. It overcomes many of the problems such as transient signal variation in sample emission and ionization, which would significantly reduce the attainable precision of a single collector measurement. For a given sample, a multiple ion counting measurement makes use of a greater number of ions counted for each isotope compared to a peak-jumping measurement using

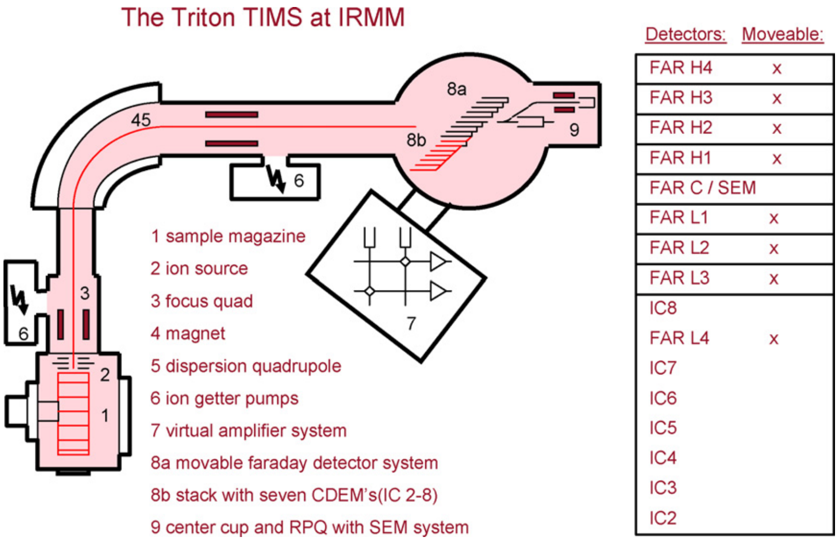

Fig. 1. The configuration of the Triton TIMS at IRMM.

only a single ion counting detector and therefore provides improved counting statistics by a factor of two or more. Multiple ion counting is thus advantageous for the cases where the sample size is restricted. In addition, multiple ion counting eliminates the need for drift correction algorithms that are required in single collector measurements and thus eliminate a potential source of systematic error [34,35].

2.4. Multi-dynamic measurements

For the MIC system the multi-dynamic measurement technique provides improvements in accuracy and precision by applying an internal calibration for the CDEM detectors during the measurement and thereby eliminating the drift caused by the steady degradation of CDEM detectors. Similar approach was already used for uranium isotopic measurements [34]. When all isotopes of interest are detected simultaneously in several steps of a multi-dynamic mass cycle, the isotope ratio can be calculated in a way that the calibration factors of all ion counters are eliminated for so called minor ratios, e.g., for the ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu ratios in case of plutonium. In contrast, the so called major ratio ^{240}Pu/^{239}Pu is measured in a peak-jumping mode using IC3 in steps 1/2, using IC4 in steps 2/3 and using IC5 in steps 3/4, see Table 1, and is therefore also independent on the efficiencies of the CDEMs. A correction factor, the so-called K-factor, for the ^{240}Pu/^{239}Pu ratio has to be determined externally using the known ^{240}Pu/^{239}Pu isotope ratio of the NBL-137 isotopic standard in order to correct the major ratio for mass fractionation, to be measured using the same technique on the same sample magazine. Table 1 shows the mass cycle for plutonium isotopes in a multi-dynamic measurement.

Table 1
The multi-dynamic mass cycle for plutonium isotopic measurement.

Step	Channel					
	IC2	IC3	IC4	IC5	IC6	IC7
1	239	240	241	242		
2		239	240	241	242	
3			239	240	241	242
4				239	240	241

3. Results and discussion

3.1. Carburization tests

Various benzene pressures and carburization currents were tested in order to find the optimal conditions for the isotopic measurement which would give the highest overall efficiency and stable ion currents to perform an isotopic measurement. Applying a benzene pressure of 1×10^{-3} mbar gave the best results. Lower benzene pressures resulted in lower overall efficiencies and very unstable ion current signals. The overall efficiency was best obtained when the rhenium filaments were carburized at filament currents of 3.5 A or 4 A. Lowering the carburization current also gave lower overall efficiency. Even though the plutonium isotope ratios obtained with the filaments carburized at filament currents of 3.5 A or 4 A agreed well with the certified values, the best results in terms of overall efficiency and the stability of an ion current signal were obtained at filament current of 3.5 A and benzene pressure 1×10^{-3} mbar. An average overall efficiency of about 3.1% was obtained; which is a ten fold improvement compared to non-carburized filaments and peak-jumping technique. The summary of the overall efficiencies at 1×10^{-3} mbar benzene pressure and different carburization times and currents is shown in Fig. 2. For each set of conditions the number of replicates was more than eight and the uncertainties were at the level of about 30%. However, this was sufficient to draw the conclusion for optimizing the carburization conditions.

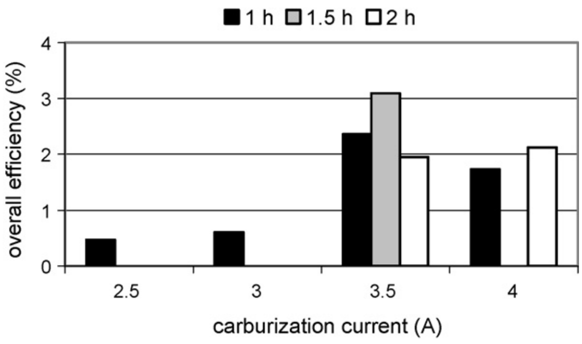

Fig. 2. Overall efficiency at different carburization currents and periods for benzene pressure of 1×10^{-3} mbar.

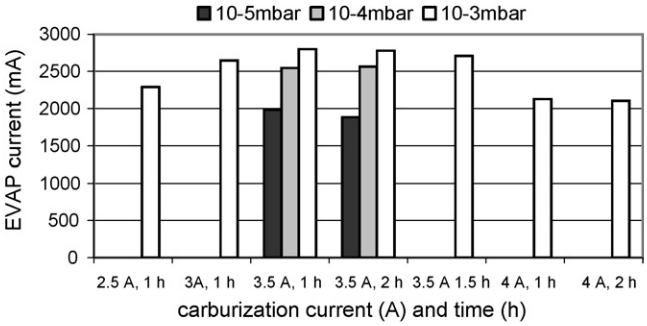

Fig. 3. The dependence of the evaporation (EVAP) filament current on benzene pressure and carburization current and time.

In Fig. 3, the dependence of the evaporation filament current for the isotopic measurement in the TIMS instrument on the benzene pressure and on the current during carburization and carburization time is shown. Higher benzene pressure required higher evaporation filament currents during the isotopic measurement. This can be explained with the fact that higher pressures used during the carburization resulted in higher amount of carbon dissolved into the filament. To release the dissolved carbon back onto the surface, where physical and chemical processes take place (e.g., formation of Pu carbides) higher temperatures are needed [33]. The formation of different carbides and other species during heating of the sample was observed by Kraiem et al. [32] for uranium by using various carbon additives such as collodion or graphite. Similar reactions, in particular the formation of Pu carbides, can be expected for plutonium, as already proposed by Kelley and Robertson [33]. On the other hand, longer benzene exposure times did not much affect the evaporation currents required for measurements. They were about the same for filaments carburized for 1 h or 2 h. This suggested that after a certain amount of time, the filaments were “saturated” with carbon and longer exposure to benzene did not affect the filament condition anymore.

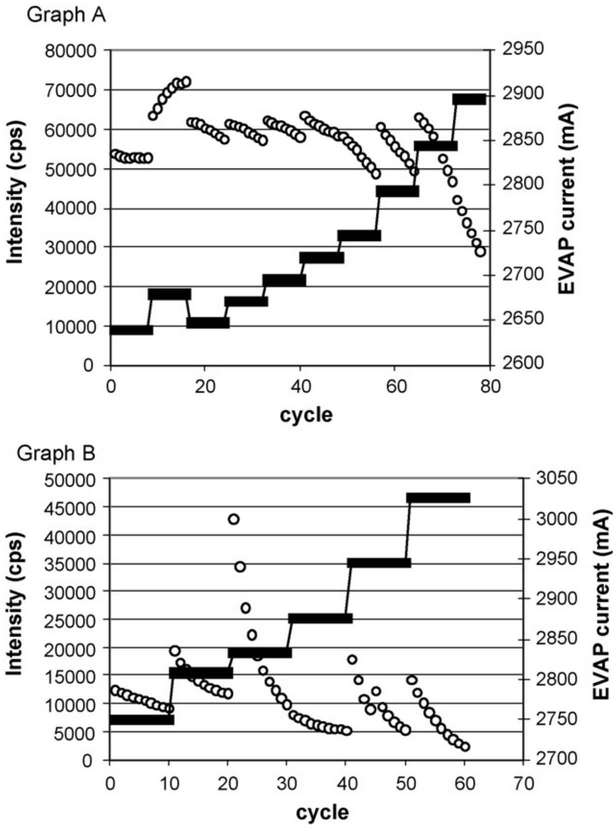

Fig. 4. ^{239}Pu count rate intensities (circles) and evaporation filament currents (squares) during the measurement of NBL-137. The filaments were carburized at: 3.5 A, 1×10^{-3} mbar for 1.5 h (Graph A) and 3.5 A, 1×10^{-5} mbar for 1 h (Graph B).

Table 2
The comparison of the relative standard deviation (RSD) for NBL-137 obtained with peak-jumping (PJ) with carburized filaments (3.5 A, 1.5 h and 1×10^{-3} mbar) and with static with non-carburized filaments.

Isotope ratio	RSD (%)	
	PJ (carburized)	Static (non-carburized)
^{240}Pu/^{239}Pu	0.02	1.4
^{241}Pu/^{239}Pu	0.19	1.2
^{242}Pu/^{239}Pu	0.17	2.3

In Fig. 4 two graphs obtained during an isotopic measurement of NBL-137 standard are presented. Graph A shows the results obtained when the filaments were carburized at 3.5 A and benzene pressure of 1×10^{-3} mbar for 1.5 h. The ^{239}Pu ion signal during the measurement was more stable with higher ^{239}Pu intensity; which allowed up to 12 blocks of an isotopic measurement with the ^{239}Pu intensity on average of about 50,000–60,000 cps (cps = counts per second). This is a big improvement compared to the low benzene pressure of 1×10^{-5} mbar used for the filament carburization for the experiments in graph B. As it can be seen from the graph B, the ^{239}Pu ion current stability and intensity were much lower.

In Table 2 the comparison of the repeatability in terms of the relative standard deviation for peak-jumping using carburized filaments and static mode using non-carburized filaments is shown. Both peak-jumping and static measurements were performed in ion counting mode using the same heating profile. The improvement in the repeatability for measurements with carburized filaments is obvious. This improvement is only due to the use of carburized filaments, because the ionization efficiency does not depend on the way the ion beams were detected, whether it was done in peak-jumping mode or in static mode. Due to higher count rates and consequently better counting statistics as a result of higher overall efficiency, a much better reproducibility was obtained for the measurements using carburized filaments, an improvement by a factor of 6–10 or even more was achieved.

3.2. Verification measurements for NUSIMEP 5 campaign samples using carburized filaments

The Nuclear Signatures Inter-laboratory Measurement Evaluation Programme (NUSIMEP 5) [36] was established to support the growing need to measure the isotopic abundance of elements characteristic for the nuclear fuel cycle in trace amounts in the environment. In the NUSIMEP 5 campaign, a 1% saline solution was used as matrix and participants were required to measure uranium, plutonium and caesium isotopes. In this study NUSIMEP 5-A and NUSIMEP 5-B samples were analyzed, which contained small amounts (pg) of plutonium. The results of this study are presented in Figs. 5–7 as measurements #20, #21 and #22, all the other measurements are the results submitted by participating laboratories. The straight lines in Figs. 5–7 mark the range of certified reference value and the dotted lines (acceptance level) mark the range from the reference value chosen in the campaign as the criterion of good result [36].

Since for the NBL-137 standard the best results were obtained with the filaments carburized at 3.5 A and a benzene pressure of 1×10^{-3} mbar for 1.5 h, the same carburization conditions were applied for measurements of the NUSIMEP 5-A and 5-B samples,

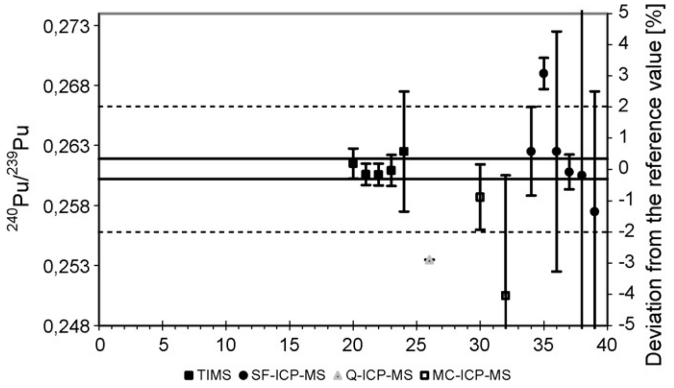

Fig. 5. Measurements of ^{240}Pu/^{239}Pu for the NUSIMEP5-A campaign sample. Measurement #20 was performed in static mode [36], without carburized filaments and without the multi-dynamic technique. Measurements #21, 22 were performed within this work using carburized filaments in combination with the multi-dynamic technique. Uncertainties were calculated according to the GUM [37].

using the multi-dynamic technique. The isotopic ratio ^{240}Pu/^{239}Pu is the easiest of the Pu isotope ratios to measure by mass spectrometry techniques. The results in Fig. 5 show, that laboratories did not have problems measuring this ratio. The ^{241}Pu/^{239}Pu results in Fig. 6 show that only few laboratories submitted results within the acceptance level. The improvement in accuracy and precision for TIMS measurements at IRMM is clearly shown in Figs. 6 and 7. Earlier measurements with the static total evaporation technique where non-carburized filaments were used are shown as #20. New measurement results with significantly improved overall efficiency and much smaller uncertainties using the multi-dynamic technique in combination with carburized filaments are shown as #21 and #22, representing two sample magazines of measurements. Although the ^{242}Pu/^{239}Pu ratio (Fig. 7) was in the same order of magnitude as the ^{241}Pu/^{239}Pu, many laboratories had difficulties in measuring this ratio successfully, probably due to interferences at mass 242, which have been corrected successfully for measurements done at IRMM. Interferences at mass 241 in NBL-137 isotopic standard were not observed. The correction for a small interference at mass 242 in samples NUSIMEP 5-A and B was done by subtracting an observed deviation for the ^{242}Pu/^{239}Pu ratio obtained in the NBL-137 isotopic standard. This was justified because the same chemistry and the same sample loading were applied to samples and standard and therefore similar impurities and interferences can be assumed. On the contrary, at mass 241 no interferences were observed in the NBL-137 isotopic standard and no corrections had to be applied to the NUSIMEP 5-A and NUSIMEP 5-B sample measurements.

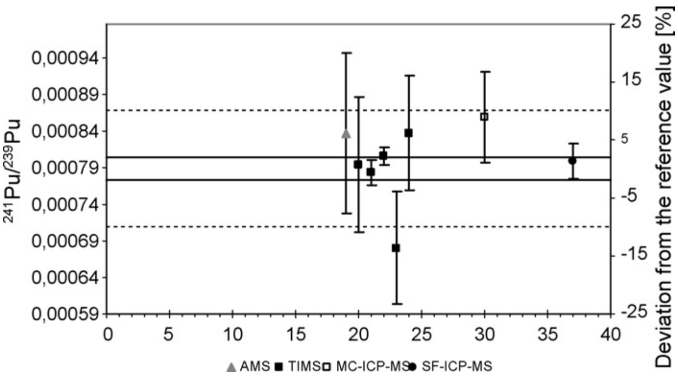

Fig. 6. Measurements of ^{241}Pu/^{239}Pu for the NUSIMEP5-A campaign sample. Measurement #20 was performed in static mode [36], without carburized filaments and without the multi-dynamic technique. Measurements #21, 22 were performed within this work using carburized filaments in combination with the multi-dynamic technique. Uncertainties were calculated according to the GUM [37].

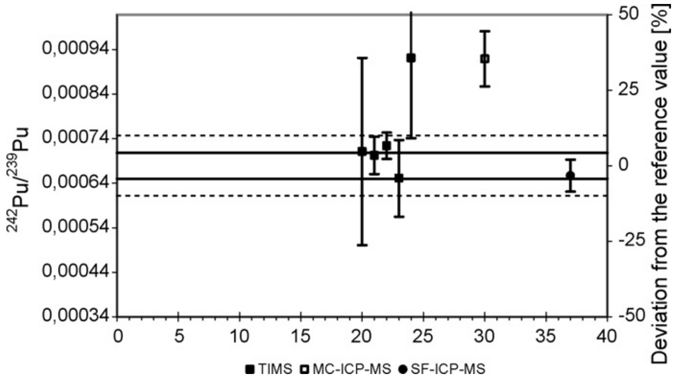

Fig. 7. Measurements of ^{242}Pu/^{239}Pu for the NUSIMEP5-A campaign sample. Measurement #20 was performed in static mode [36], without carburized filaments and without the multi-dynamic technique. Measurements #21, 22 were performed within this work using carburized filaments in combination with the multi-dynamic technique. Uncertainties were calculated according to the GUM [37].

4. Conclusions

The multi-dynamic measurement technique combined with the “multiple ion counting” (MIC) system of the Triton TIMS was successfully applied for the measurement of pg-size plutonium samples. Moreover, a sample preparation approach involving the carburization of the TIMS sample filaments using benzene gas was introduced and optimized and resulted in an improvement of about one order of magnitude of the overall efficiency for low-level plutonium samples. This new method for low-level Pu measurements was tested on the NBL-137 isotopic standard and applied to the NUSIMEP 5-A and NUSIMEP 5-B inter-laboratory comparison samples. As a result of the enhanced overall efficiency, more stable ion beams and higher count rate intensity signals were obtained, thus improving the precision and the accuracy of Pu isotope ratio measurement on the environmental level samples, especially for the minor ratios ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu. This constitutes a significant improvement to IRMM’s capabilities for nuclear safeguards support in “environmental sampling”. This achievement is of scientific importance because the minor ratios provide an important source of additional information on the production processes of nuclear material. Together with the major ratio, ^{240}Pu/^{239}Pu, they can be used as a “fingerprint” to characterize different sources of plutonium in the environment.

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