JRC Scientific and Technical Reports

# Preparation and Certification of IRMM-081a and IRMM-086 Spike Isotopic Reference Materials

A. Verbruggen, R. Eykens, F. Kehoe, H. Kühn, S. Richter, Y. Aregbe

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Institute for Reference Materials and Measurements

The mission of the IRMM is to promote a common and reliable European measurement system in support of EU policies.

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Joint Research Centre
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## 1 Abstract

Highly enriched $^{239}$Pu Spike Isotopic Reference Materials (IRMM-086 and IRMM-081a) have been prepared at IRMM.

The certified values[1] for IRMM-086 of 3.752 4(22)·$10^{-6}$ mol $^{239}$Pu per g of solution and for IRMM-081a of 3.745 8(26)·$10^{-7}$ mol $^{239}$Pu per g of solution have been established by mass metrology and subsequently verified by isotope dilution mass spectrometry. The plutonium isotopic composition has been determined by thermal ionisation mass spectrometry and calibration of these measurements by means of synthetic mixtures.

The Isotopic Reference Material is supplied in a sealed glass ampoule containing 5 mL of a 5 M nitric acid solution.

These Isotopic Reference Materials are part of a systematic IRMM programme to supply Spike Isotopic Reference Materials of various isotopes at different concentrations.

## 2 Preparation scheme of the $^{239}$Pu Spike Isotopic Reference Materials

A stock solution was prepared starting from plutonium metal MP2 of French origin (Cetama - CEA). Of the plutonium metal (BC02523), 0.458 59(5) g was dissolved in concentrated nitric acid and a few droplets of conc. hydrofluoric acid. After complete dissolution of the plutonium at a temperature of 80-100°C, the solution was adjusted to 498.74(5) g with water to give a 5 M $HNO_3$ solution.

Using a dispenser, 5 mL aliquots of this solution were distributed in glass ampoules and sealed with a screw cap. A total of 61 ampoules of IRMM-086 (BC02523A) were prepared.

From this batch, 5 ampoules were taken containing 25.999(5) g IRMM-086 and subsequently diluted with 5M nitric acid to a total of 260.33(5) g. This solution was dispensed and transferred into glass screw cap ampoules containing 5 mL of solution IRMM-081a. A total of 47 ampoules of IRMM-081a (BC02523B) were prepared. The certified values for IRMM-081a are derived from those of IRMM-086.

The sequence for the preparation and use of the MP2 stock solution is shown in the flow chart in the figure below.

The stock solution was prepared on 30/10/2000 and mass metrologically controlled. Dispensing of the stock solution into ampoules of IRMM-086 was achieved on 03/02/2006. E-codes refer to the mass metrology certificates when samples from the stock solution where taken. The preparation scheme is shown in Annex 1.

## 3 Certification of IRMM-086 and IRMM-081a

Certified values for the isotope amount ratios, amount contents and uncertainties were calculated according to ISO/GUM recommendations [1] using the GUM Workbench [2] and are based on certified values of the isotope ratios, the weights of the plutonium metal and solutions and of the impurity level of the MP2 metal.

Effective plutonium content was calculated for each individual reference date applying decay corrections on isotope ratios and plutonium content. The sequence of preparation is shown in Figure 3.

---

[1] Note: All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where $u_c$ is the combined standard uncertainty calculated according to the ISO/BIPM guide. They are given in parentheses and include a coverage factor $k = 2$. They apply to the last two digits of the value. The values certified are traceable to the SI.

Certified values for isotope ratios are listed in Table 1 and are valid for 01/01/2007

Table 1: Isotopic composition highly enriched 239Pu Lot BC02523

| Certified amount ratios | |
|---|---|
| $n(^{238}Pu)/n(^{239}Pu)$ | 0.000 030 83(29) |
| $n(^{240}Pu)/n(^{239}Pu)$ | 0.022 432 4(51) |
| $n(^{241}Pu)/n(^{239}Pu)$ | 0.000 237 8(31) |
| $n(^{242}Pu)/n(^{239}Pu)$ | 0.000 075 70(78) |

| amount fraction (·100) | | mass fraction (·100) | |
|---|---|---|---|
| $n(^{238}Pu)/n(Pu)$ | 0.003 015(29) | $m(^{238}Pu)/n(Pu)$ | 0.003 002(28) |
| $n(^{239}Pu)/n(Pu)$ | 97.773 05(58) | $m(^{239}Pu)/n(Pu)$ | 97.763 80(59) |
| $n(^{240}Pu)/n(Pu)$ | 2.193 28(49) | $m(^{240}Pu)/n(Pu)$ | 2.202 27(49) |
| $n(^{241}Pu)/n(Pu)$ | 0.023 25(30) | $m(^{241}Pu)/n(Pu)$ | 0.023 44(31) |
| $n(^{242}Pu)/n(Pu)$ | 0.007 402(76) | $m(^{242}Pu)/n(Pu)$ | 0.007 494(77) |

The molar mass of the uranium is 239.074 790 8(91) $g \cdot mol^{-1}$

The certified values for isotope contents and uncertainty budgets with the major components of uncertainty are listed in Table 2 and Table 3.

Table 2: certified values for IRMM-086 and IRMM-081a

| Quantity | Value | |
|---|---|---|
| IRMM-086 | | |
| Pu isotope amount content ($C_{Pu\text{-}086}$): | 3.838 0(23) | µmol Pu/g |
| Pu mass amount content ($\gamma_{Pu\text{-}086}$): | 917.14(56) | µg Pu/g |
| $^{239}$Pu isotope amount content ($C_{239Pu\text{-}086}$): | 3.752 4(22) | µmol $^{239}$Pu/g |
| $^{239}$Pu mass amount content ($\gamma_{239Pu\text{-}086}$): | 896.62(55) | µg$^{239}$Pu /g |
| IRMM-081a | | |
| Pu isotope amount content($C_{Pu\text{-}081}$): | 0.383 12(26) | µmol Pu/g |
| Pu mass amount content ($\gamma_{Pu\text{-}081}$): | 91.593(63) | µg Pu/g |
| $^{239}$Pu isotope amount content ($C_{239Pu\text{-}081}$): | 0.374 58(26) | µmol $^{239}$Pu/g |
| $^{239}$Pu mass amount content ($\gamma_{239Pu\text{-}081}$): | 89.544(62) | µg $^{239}$Pu /g |

Table 3: Uncertainty budget for certified amount contents

| Quantity | Description | Value | | % |
|---|---|---|---|---|
| IRMM-086 | | | | |
| $m_{Sol-MP2}$ | mass primary solution | 498.740(60) | g | 7.1 |
| $m_{Pu}$ | mass MP2 Pu metal | 0.458 590(60) | g | 8.4 |
| $\eta_{MP2final}$ | Pu metal purity + decay | 0.999 06(40) | g/g | 84.6 |
| IRMM-081a | | | | |
| $m_{Sol-MP2}$ | mass primary solution | 498.740(60) | g | 2.8 |
| $m_{Pu}$ | mass MP2 Pu metal | 0.458 590(60) | g | 3.3 |
| $\eta_{MP2final081a}$ | Pu metal purity + decay | 0.998 83(40) | g | 67.4 |
| $m_{Sol-before086}/m_{Sol-after086}$ | evaporation primary solution | 497.57/497.80(58) | g | 5.6 |
| $m_{Sol-before081a}$ | Sample from IRMM-086 | 25.999 0(58) | g | 13.4 |
| $m_{Sol-081a}$ | Final solution IRMM-081a | 260.330(58) | g | 13.3 |

The half-lifes used in the decay calculations are in Table 4.

Table 4: half-lifes of Pu isotopes

| | |
|---|---|
| $^{238}$Pu : | 8.77 (03) · $10^1$ $a^2$ |
| $^{239}$Pu : | 2.411 (03) · $10^4$ $a^2$ |
| $^{240}$Pu : | 6.563 (07) · $10^3$ $a^2$ |
| $^{241}$Pu : | 1.429 (06) · $10^1$ $a^3$ |
| $^{242}$Pu : | 3.735 (11) · $10^5$ $a^2$ |

## 4 Verification of IRMM-086 and IRMM-081a

The isotopic composition of the plutonium metal MP2 used for the spike isotopic reference material IRMM-086 has been verified by measuring isotope abundance ratios on 6 filament loadings, of 200 nanogram according to the method described previously. The ratio $n(^{239}Pu)/n(^{240}Pu)$ was measured on static Faraday multicollector, the ratios $n(^{238}Pu)/n(^{239}Pu)$, $n(^{241}Pu)/n(^{239}Pu)$ and $n(^{242}Pu)/n(^{239}Pu)$ were measured separately on a secondary electron multiplier which was calibrated against the Faraday multicollector using the $^{240}$Pu isotope.

Samples were measured for the isotopic composition using the total evaporation technique on the MAT262. By using the total evaporation technique [3] the measurement is continued until the sample is exhausted. This is done in order to minimize mass fractionation effects.

[2] IAEA, Decay data of the Transactinium Nuclides, Technical Reports Series No. 261, 1986

[3] P. De Bièvre, A. Verbruggen, 'A new measurement of the $^{241}$Pu half-life by isotope mass spectrometry', Metrologia, 199, 36, 25-31

The measurements were made on the MAT262 TIMS, turret T26629.

The measured ratios compared to the calculated values from the certificates are listed in Table. The certified ratios for Pu are taken from the recertification of MP2 at IRMM (2007) as in the IRMM certificate in Annex 4.

Table 5: Isotopic amount ratios of plutonium in the batch solution. Values from the certificate are compared with values calculated from measurement of isotopic ratios in a sample of IRMM-081a valid for 01 January 2007. Expanded Uncertainties are given in brackets (coverage factor *k*=2).

| | Measured value | Certified value |
|---|---|---|
| $n(^{238}Pu)/n(^{239}Pu)$ | 0.000 030 51(10) | 0.000 030 83(29) |
| $n(^{240}Pu)/n(^{239}Pu)$ | 0.022 435 8(76) | 0.022 432 4(51) |
| $n(^{241}Pu)/n(^{239}Pu)$ | 0.000 241 7(10) | 0.000 237 8(31) |
| $n(^{242}Pu)/n(^{239}Pu)$ | 0.000 075 37(30) | 0.000 075 70(78) |

The verification of the plutonium isotope amount content for Isotopic Reference Material IRMM-081a and therefore for IRMM-086 has been achieved by selection of 3 ampoules from the batch. From each ampoule, two weighed fractions were transferred to a recipient and spiked with a weighed fraction of IRMM-049c. Weighings were carried out using a syringe which was weighed before and after the transfer of aliquots into the recipient. The certificate for mass metrology is shown in Annex.

The series of 6 spiked solutions described above were heated to dryness, then chemically conditioned Pu fractions separated by the standard ion-exchange method (*Work Instructions: 042 'Spiking, isotopic exchange and preliminary separation for mixtures of uranium and plutonium'; 035 'Separation of Pu for TIMS measurements of isotopic ratios for IDMS or for isotopic abundances'*).

A magazine was loaded with one filament for each blend; the remaining positions were filled by IRMM-290 standards. The plutonium was measured on the MAT 262 (*Work Instruction: 113 'Pu isotopic measurements in total evaporation using the MAT 261'*).

The results of these IDMS measurements are given in Table 6 and shown in Figure 1 compared with the Pu amount contents as calculated from the masses of the dissolved metals and solutions, taking into account the certified chemical purities of the starting materials and making corrections for isotopic decay. There was good agreement between the isotopic amounts by IDMS and those calculated from the weights of the starting materials and the final solution.

Table 6: Amount content of $^{239}Pu$. Values from the certificate and metrological weighing are compared with values calculated from measurement of samples. Expanded Uncertainties are given in brackets (coverage factor *k*=2).

| | Certified value | Measured value |
|---|---|---|
| C(Pu) $mol \cdot g^{-1}$ | $3.745\ 9(26) \cdot 10^{-7}$ | $3.750\ 8(56) \cdot 10^{-7}$ |

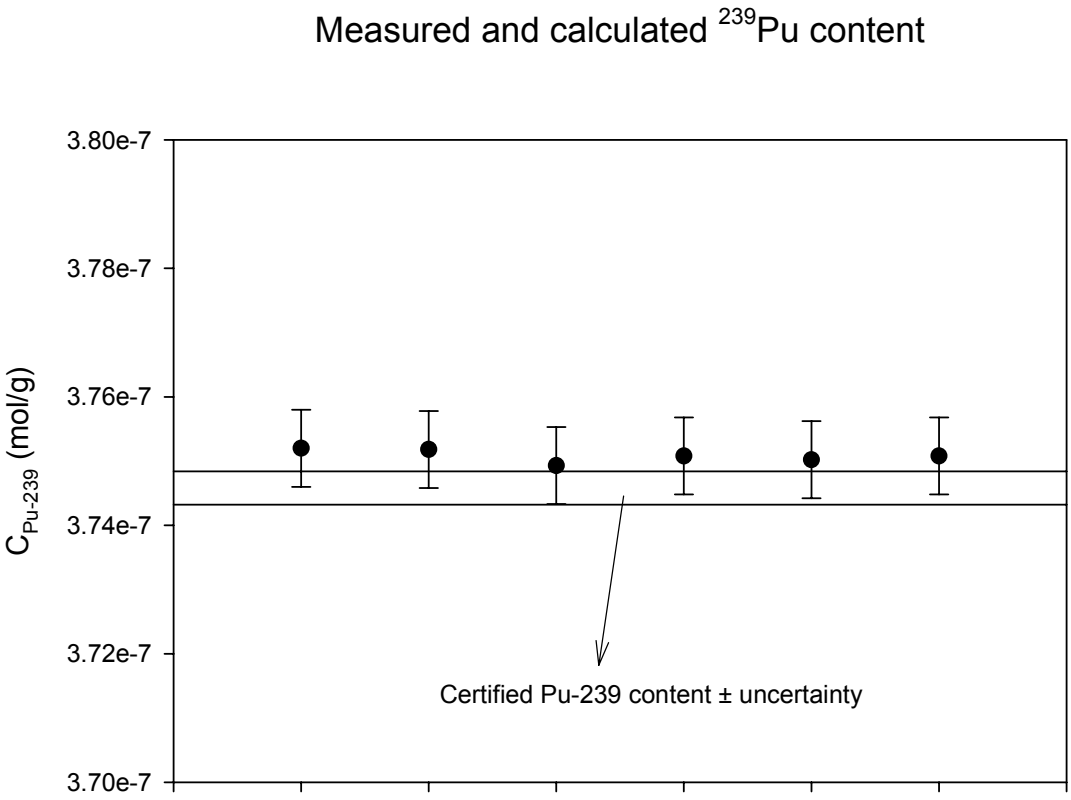



Figure 1: 'Metrological' concentration of plutonium in IRMM-081a (from the weights of metals and solution) compared with the measured values by IDMS.

## 5 Conclusion

Two $^{239}$Pu Spike Isotopic Reference Materials have been prepared and certified for $^{239}$Pu isotope amount content. The certification of the spike is based on the metrological data, the certificate of the base material and the verification measurements. The final certification values are established by mass-metrology of the metals and the solutions. The agreement was satisfactory.

The materials prepared are commercially available from IRMM, Geel as reference material IRMM-081a and IRMM-086

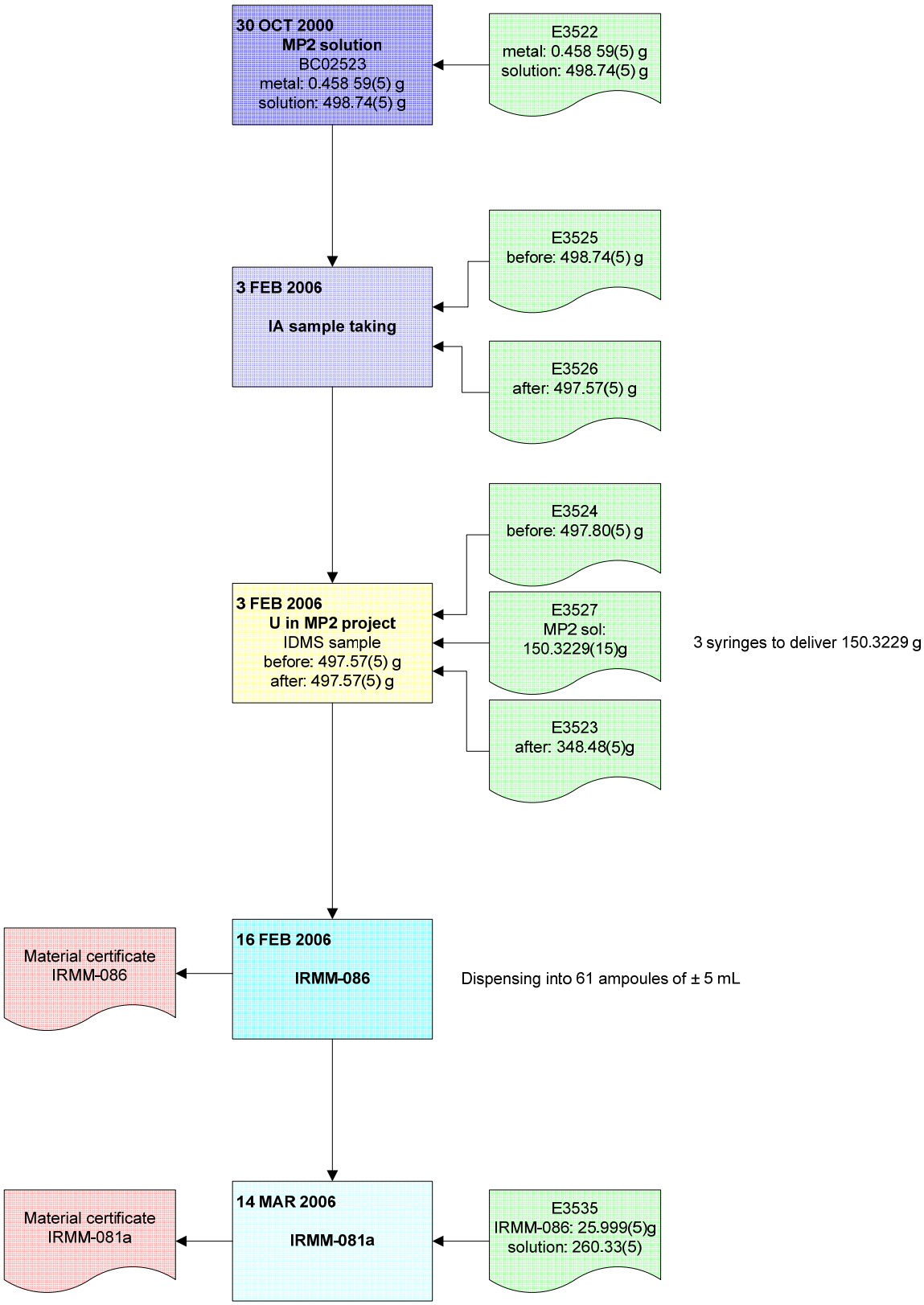
## 6 References

[1] International Organisaton for Standardisation, Guide to the Expression of Uncertainty in Measurements, ©ISO, ISBN 92-67-10188-9, Geneva, Switserland 1993

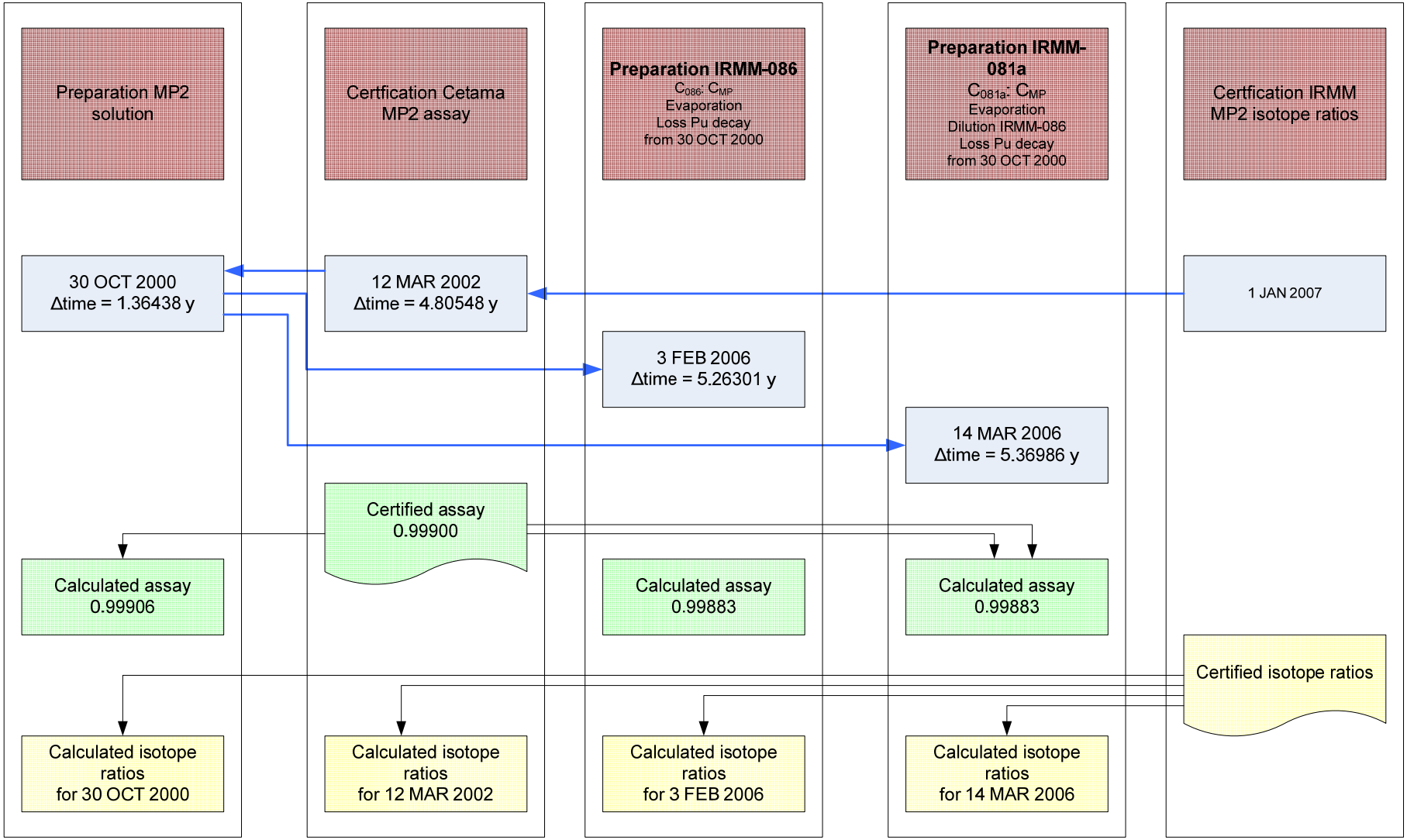
[2] GUM Workbench, Metrodata GmbH, www.metrodata.de

[3] Richter S., S. A. Goldberg (2003), Improved Techniques for High Accuracy Isotope Ratio Measurements of Nuclear Materials using Thermal Ionization Mass Spectrometry, International Journal of Mass Spectrometry, 229 (2003) 181-197.

## *Annex 1: preparation scheme of MP2 solutions*



## *Annex 2: Logical decay flowchart*



## *Annex 3: certificate of plutonium metal: Cetama MP2*

CETAMA

COMMISSARIAT A L'ENERGIE ATOMIQUE

COMMISSION D'ETABLISSEMENT DES METHODES D'ANALYSE

cea

REFERENCE MATERIAL CERTIFICATE

PLUTONIUM METAL

"MP2"

**Sample n° Axxx Mass : 0.xxxxxx ± 0.000012 g**
**(For the values x see page 4)**

The reference material to which this certificate relates is intended for the calibration of chemical composition measurement. The overall chemical content of plutonium is certified. The confidence interval associated with the certified value for a single sample, takes into account uncertainties associated to with analysis and heteregenity of metal. This content, expressed as a percentage of mass, was the following on 12 march 2002 for a single sample with a probability level of 0.95.

**99.90 ± 0.04 %**

THE TRUE MASS OF THE SAMPLE A ± **12 µg**, RELATED TO A VACUUM, IS THAT INDICATED IN THIS CERTIFICATE AND ON THE AMPOULE.

*The possibility of surface oxidation makes it impossible to envisage weighing at the time of use*

Isotopique composition is certified on 12 march 2001 : see certificate IRMM page3

The preparation, analysis and certification of the plutonium to which this certificate relates was carried out by different units of the CEA group under the supervision of the Committee for Establishing Analysis Methods (CETAMA).

Le responsable MR

CETAMA
CEA VALRHO Marcoule
B. P. 17171
30207 BAGNOLS SUR CEZE CEDEX FRANCE
Téléphone (33) 4.66.79.69.88 - Télécopie (33) 4.66.79.69.89

CETAMA certifié ISO 9001:2000 par AFAQ



Version : 06/2001

On 12/03/200, the metal contained around:

- by weight, 489 $mg.kg^{-1}$ of uranium,
- by weight, 438 $mg.kg^{-1}$ of américium..

## UTILISATION

The sample, which consists of a piece of metal, is supplied in a double glass ampoule filled with pure nitrogen at a pressure of around 0.1 Pascal.

The ampoule must be opened with care inside a glove box. All the sample must be transferred to the dissolver.

Cover with 0.1 $mol.l^{-1}$ hydrochloric acid. The ampoule must be thoroughly washed with the same acid to recover any particles of metal which may have become separated. In 2 ml fractions, add the necessary quantity of 12 $mol.l^{-1}$ hydrochloric acid of guaranteed purity to obtain a 4 $mol.l^{-1}$ hydrochloric acid solution. Allow dissolving to proceed without heating for 10 to 15 minutes, then heat to boiling point. If there are still particles of plutonium at the bottom of the dissolver after heating for two hours, add 2 ml of 12 $mol.l^{-1}$ hydrochloric acid and 2 drops of 1 $mol.l^{-1}$ hydrofluoric acid and continue heating for another two hours. Repeat the operation if necessary until the material is totally dissolved.
If plutonium fluoride precipitates out, add a few drops of aluminium nitrate (approximately one $mol.l^{-1}$)..
Allow to cool and adjust to the required volume.

## ADDITIONAL INFORMATION

The certified plutonium content has been deduced from analysis of impurities carried out by five laboratories and checked by chemical assay of the plutonium in two different laboratories using three different methods of analysis.
Spark Source Mass Spectrometry has given a full analysis of the impurities and, where concentration levels allowed, inductively-coupled plasma atomic emission spectrometry has been used to establish the concentrations of some of them.
The uranium was determined by laser spectrofluorimetry and the americium by gamma spectrometry.Carbon was determined by coulometry, after transformation into gaseous form by combustion in oxygen.
The gases were analysed by chromatography in the aqueous phase:

- for nitrogen and oxygen after extraction by high temperature stream under an inert gas,
- for hydrogen after diffusion in a vacuum.

## *Annex 4: certificate of plutonium metal: isotopic abundances IRMM*

EUROPEAN COMMISSION
DIRECTORATE GENERAL JRC
JOINT RESEARCH CENTRE
IRMM
Institute for Reference Materials and Measurements

**CERTIFICATE of a reference measurement**

*IM/MeaC/07/116*

*11 April 2007*

SUBJECT : Recertification of CEA CETAMA MP2

1. Applicant: A. Verbruggen

2. Sample Identification:
   - CEA/CETAMA/MP2
   - Chemical form: Pu metal provided by CEA/CETAMA

3. Measurands:
   - Isotopic composition

| isotope amount ratio(s) | |
|---|---|
| $n(^{238}Pu)/\ n(^{239}Pu)$ | 0.000 030 83(29) |
| $n(^{240}Pu)/\ n(^{239}Pu)$ | 0.022 432 4(51) |
| $n(^{241}Pu)/\ n(^{239}Pu)$ | 0.000 237 8(31) |
| $n(^{242}Pu)/\ n(^{239}Pu)$ | 0.000 075 70(78) |

| amount fraction (·100) | | mass fraction (·100) | |
|---|---|---|---|
| $n(^{238}Pu)/n(Pu)$ | 0.003 015(29) | $m(^{238}Pu)/m(Pu)$ | 0.003 002(28) |
| $n(^{239}Pu)/n(Pu)$ | 97.773 05(58) | $m(^{239}Pu)/m(Pu)$ | 97.763 80(59) |
| $n(^{240}Pu)/n(Pu)$ | 2.193 28(49) | $m(^{240}Pu)/m(Pu)$ | 2.202 27(49) |
| $n(^{241}Pu)/n(Pu)$ | 0.023 25(30) | $m(^{241}Pu)/m(Pu)$ | 0.023 44(31) |
| $n(^{242}Pu)/n(Pu)$ | 0.007 402(76) | $m(^{242}Pu)/m(Pu)$ | 0.007 494(77) |

molar mass: 239.074 790 8(91) $g \cdot mol^{-1}$

4. Date of sample receipt : n.a.
   Date of completion of measurement : 7 November 2006

5. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where $u_c$ is the combined standard uncertainty estimated following the ISO/BIPM guide[1]. They are given in parentheses and include a coverage factor $k$=2. They apply to the last two digits of the value. The values certified are traceable to the SI. The primary certified values are the isotope amount ratio ; other values are derived from them. Reproducing the derived values may result in difference due to rounding errors.

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switserland, 1993

Uncertainty budget :

| Quantity | Value | Standard Uncertainty | Index |
|---|---|---|---|
| Atomic mass $^{239}Pu$ | 239.05215760 g/mol | $5.1 \cdot 10^{-6}$ g/mol | 59.6 % |
| Measurement ratio 240/239 | 0.02243535 mol/mol | $3.81 \cdot 10^{-6}$ mol/mol | 14.9 % |
| Measurement ratio 241/239 | $240 \cdot 10^{-6}$ mol/mol | $450 \cdot 10^{-9}$ mol/mol | 0.9 % |
| Measurement ratio 242/239 | $75 \cdot 10^{-6}$ mol/mol | $175 \cdot 10^{-9}$ mol/mol | 0.4 % |
| $variability_{241/239}$ | 0.0 mol/mol | $2.65 \cdot 10^{-6}$ mol/mol | 21.0 % |
| $variability_{242/239}$ | 0.0 mol/mol | $650 \cdot 10^{-9}$ mol/mol | 3.0 % |
| $M_{Pu}$ | 239.07478500 g/mol | $6.46 \cdot 10^{-6}$ g/mol | |

6. The traceability to SI is established through standards from IRMM-290.

7. Analytical measurement procedure
   - Mass spectrometric measurments were performed by H Kühn an F Kehoe for the $[n(^{238}Pu)/n(^{239}Pu)]$, $[n(^{240}Pu)/n(^{239}Pu)]$, $[n(^{241}Pu)/n(^{239}Pu)]$ and $[n(^{242}Pu)/n(^{239}Pu)]$ using the MAT262 TIMS, sample solutions were prepared for TIMS analysis by F Kehoe. A. Verbruggen was responsible for preparation and issuance of the certificate.
   - The atomic masses, used in the calculation are from G. Audi and A.H. Wapstra.[2]
   - Reference numbers of the measurement data: measurements number T26629, T26A03, T26B07, logged in S:\D04-IM\Secure Data\Project Data\MP2 (based on 081a and LSD1027i)\MP2 IA Summary MAT262 measurements.
   - Full details of the preparation and the certification procedure can be found in certification report EUR*****.

8. These samples will be stored for a minimum period of six months from the date of this certificate

André Verbruggen
Group leader Nuclear Chemistry

Stephan Richter
Group leader Nuclear Mass Spectrometry

Copies
P Taylor, IM unit head
Y Aregbe, Action leader Nuclear Safeguards
F Kehoe
H Kühn

[2] G. Audi and A.H. Wapstra, The 2003 atomic mass evaluation, Nucl Phys A729 (2003) 337-676

## *Annex 5: Mass Metrology certificate*

JOINT RESEARCH CENTRE
EUROPEAN COMMISSION

**Certificate of weighing**

Institute for Reference Materials and Measurements

E. 3543 **Issued date**: 6 July2006 **Page** 1 of 1

**Applicant:** Mr Verbruggen **Group: IM-Nuclear**

**Project:** IRMM-081a

**Description:** IDMS of U and Pu of the mothersolution.

**Date of receipt of request:** 1 June 2006 **Weighing date**: 12 June 2006

---

The reported results applies only to the objects / samples described in this certificate

| Identification number | Mass IRMM-081a in g | Mass IRMM-049c in g |
|---|---|---|
| IRMM-081a/ 7-1 | 2.5058 (5) | 2.5135 (5) |
| IRMM-081a/ 7-2 | 2.4997 (5) | 2.5387 (5) |
| IRMM-081a/17-1 | 2.4915 (5) | 2.5748 (5) |
| IRMM-081a/17-2 | 2.5070 (5) | 2.5015 (5) |
| IRMM-081a/42-1 | 2.4944 (5) | 2.5130 (5) |
| IRMM-081a/42-2 | 2.5074 (5) | 2.5006 (5) |

### Observations:

The measurements and uncertainty estimates, were performed according to working instruction WI-0185, "Mass determination by substitution weighing"on balance AT 201. The reported weighing result is valid when the air density is 1.20 ±0.03 $kgm^{-3}$ and the object density is 1000 ±100 $kgm^{-3}$.

### Traceability:

The certified mass values are traceable to the International Kilogram Prototype via regular calibrations of the IRMM principal kilogram. The set of working mass standards M3 was used as reference in the mass determination.

### Uncertainty:

All reported uncertainties are expanded uncertainties $U = k \cdot u_c$ where $u_c$ is the combined standard uncertainty calculated according to the ISO/BIPM Guide to the expression of Uncertainty in Measurement. The coverage factor $k = 2$ corresponds to a coverage probability of about 95%. $U$ applies to the last digit of the value of the measurement result and is given in parentheses ().

### Annexes:

Signature
Mass Metrology Service

Retieseweg, B-2440 Geel, Belgium; Tel.: +32-(0)14-571 211 • Fax: +32-(0)14-571 978• http://www.irmm.jrc.be
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The mission of IRMM is to promote a common and reliable European measurement system in support of EU policies.

***Annex 6: Certificate IRMM-081a***

**IRMM**

Institute for Reference Materials and Measurements

## CERTIFICATE
## ISOTOPIC REFERENCE MATERIAL IRMM-081a

**3.745 8(26) · $10^{-7}$ mol ($^{239}$Pu) · $g^{-1}$ (solution)**

The Spike Isotopic Reference Material is supplied with an isotope amount content of $^{239}$Pu certified as above.

The amount of the other plutonium isotopes present is related to the $^{239}$Pu content through the following certified amount ratios:

| | |
|---|---|
| $n(^{238}Pu)/n(^{239}Pu)$ : | 0.000 031 03(29) |
| $n(^{240}Pu)/n(^{239}Pu)$ : | 0.022 433 8(51) |
| $n(^{241}Pu)/n(^{239}Pu)$ : | 0.000 247 2(34) |
| $n(^{242}Pu)/n(^{239}Pu)$ : | 0.000 075 70(78) |

This corresponds to an isotopic composition with the following abundances :

| amount fraction (·100) | | Mass fraction (·100) | |
|---|---|---|---|
| $n(^{238}Pu)/n(Pu)$ | 0.003 034(29) | $m(^{238}Pu)/m(Pu)$ | 0.003 021(29) |
| $n(^{239}Pu)/n(Pu)$ | 97.772 00(60) | $m(^{239}Pu)/m(Pu)$ | 97.762 74(61) |
| $n(^{240}Pu)/n(Pu)$ | 2.193 40(49) | $m(^{240}Pu)/m(Pu)$ | 2.202 38(49) |
| $n(^{241}Pu)/n(Pu)$ | 0.024 17(34) | $m(^{241}Pu)/m(Pu)$ | 0.024 37(34) |
| $n(^{242}Pu)/n(Pu)$ | 0.007 402(76) | $m(^{242}Pu)/m(Pu)$ | 0.007 494(77) |

The molar mass of the plutonium in this sample is 239.074 810 1(95) $g \cdot mol^{-1}$

From the certified values, the following amount and mass contents are derived:

| | |
|---|---|
| 3.831 2(26) · $10^{-7}$ | mol (Pu) · $g^{-1}$ (solution) |
| 8.954 4(62) · $10^{-5}$ | g ($^{239}$Pu) · $g^{-1}$ (solution) |
| 9.159 3(63) · $10^{-5}$ | g (Pu) · $g^{-1}$ (solution) |

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NOTES

1. This Spike Isotopic Reference Material is traceable to the SI in the shortest possible way. The values of the Pu isotope ratios were measured at IRMM and are traceable to the SI via the values of the isotope ratios of the isotopic reference material IRMM-290. The Pu content of this spike is traceable to the SI via reference material CETAMA MP2. Measurements calibrated by this Isotopic Reference Material have therefore the potential of being traceable to the SI.

2. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where $u_c$ is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They are given in parentheses and include a coverage factor $k$=2. They apply to the last two digits of the value. The values certified are traceable to the SI.

3. This Reference Material was prepared by metrological dilution of IRMM-086 which was prepared by metrological weighing of Pu metal (CETAMA MP2) according to the guidelines in its accompanying Reference Material Certificate of Analysis and dissolution in $HNO_3$. Subsequently the diluted solution was dispensed into individual units.

4. The Spike Isotopic Reference Material IRMM-081a comes in a glass ampoule with screw cap containing about 2.2 µmol plutonium in 5 mL of a chemically stable 5M $HNO_3$ solution.

5. Due to radioactive decay, the Pu element concentration decreases by 0.0042 % · $a^{-1}$.

   The half lives, used in the calculations, are

   $^{238}Pu$ : 8.77 (03) · $10^1$ a [1]
   $^{239}Pu$ : 2.411 (03) · $10^4$ a [1]
   $^{240}Pu$ : 6.563 (07) · $10^3$ a [1]
   $^{241}Pu$ : 1.429 (06) · $10^1$ a [2]
   $^{242}Pu$ : 3.735 (11) · $10^5$ a [1]
   $^{244}Pu$ : 8.00 (09) · $10^7$ a [1]

6. The atomic masses, used in the calculations, are[3]

| | | |
|---|---|---|
| $^{238}Pu$: | 238.049 559 9(40) | g·mol$^{-1}$ |
| $^{239}Pu$: | 239.052 163 4(40) | g·mol$^{-1}$ |
| $^{240}Pu$: | 240.053 813 5(40) | g·mol$^{-1}$ |
| $^{241}Pu$: | 241.056 851 5(40) | g·mol$^{-1}$ |
| $^{242}Pu$: | 242.058 742 6(40) | g·mol$^{-1}$ |
| $^{244}Pu$: | 244.064 204(5) | g·mol$^{-1}$ |

[1] IAEA, Decay data of the Transactinium Nuclides, Technical Reports Series No. 261, 1986
[2] P. De Bièvre, A. Verbruggen, 'A new measurement of the $^{241}Pu$ half-life by isotope mass spectrometry', Metrologia, 199, **36**, 25-31
[3] G. Audi and A.H. Wapstra, The 2003 atomic mass evaluation, Nucl Phys A729(2003) 337-676.

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7. Values for isotope abundance ratios, isotopic compositions and for concentrations are valid for March 14, 2006.

8. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

9. Using this Spike Isotopic Reference Material, the Pu content in an unknown sample can be determined by Isotope Dilution, through a measurement of the isotope amount ratio $R(B) = n(^{239}Pu)/n(^{240}Pu)$ in a blend. It should be computed with the aid of the following equation which enables an easy quantification of the uncertainty sources in the procedure :

$$c\left(^{240}Pu,X\right) = \frac{R(Y)-R(B)}{R(B)-R(X)} \cdot R(X) \cdot \frac{m(Y)}{m(X)} \cdot c\left(^{239}Pu,Y\right)$$

$$c(Pu,X) = \frac{R(Y)-R(B)}{R(B)-R(X)} \cdot \frac{\sum Ri(X)}{\sum Ri(Y))} \cdot \frac{m(Y)}{m(X)} \cdot c(Pu,Y)$$

where:

| | | |
|---|---|---|
| $R(X)$ | = | amount ratio $n(^{239}Pu)/n(^{240}Pu)$ in the unknown sample material X |
| $R(Y)$ | = | amount ratio $n(^{239}Pu)/n(^{240}Pu)$ in the spike material Y |
| $m(X)$ | = | mass of the unknown sample used in the measurement |
| $m(Y)$ | = | mass of the sample of spike solution used in the measurement |
| $c(Pu,X)$ | = | amount content of Pu · $g^{-1}$ sample material |
| $c(Pu,Y)$ | = | amount content of Pu · $g^{-1}$ spike solution |
| $c\left(^{240}Pu,Y\right)$ | = | amount content of $^{240}$Pu · $g^{-1}$ spike solution |
| $c\left(^{239}Pu,X\right)$ | = | amount content of $^{239}$Pu · $g^{-1}$ sample material |
| $\sum Ri(X)$ | = | sum of all amount ratios in sample material X |
| $\sum Ri(Y)$ | = | sum of all amount ratios in spike material Y. |

The isotopic measurements by Thermal Ionisation Mass Spectrometry were performed by S Richter and H Kühn. Isotopic measurements were calibrated against synthetic plutonium isotope mixtures prepared by J Broothaerts. Chemical preparation of the samples for isotopic measurements was performed F Kehoe.

Metrological weighings needed for the preparation and certification were performed by R Eykens. The ampoulation of this Spike Isotopic Reference Material was accomplished by R Eykens and F Kehoe.

The overall co-ordination leading to the establishment, certification and issuance of this Spike Isotopic Reference Material was carried out by A Verbruggen.

B-2440 GEEL
August 2007

Y Aregbe
IRMM Safeguards Coordinator

P Taylor
Head
Isotope Measurements Unit

08/2007

***Annex 7: Certificate IRMM-086***

**IRMM**
Institute for Reference Materials and Measurements

## CERTIFICATE
## ISOTOPIC REFERENCE MATERIAL IRMM-086

**$3.752\ 4(22) \cdot 10^{-6}$ mol ($^{239}$Pu) · g$^{-1}$ (solution)**

The Spike Isotopic Reference Material is supplied with an isotope amount content of $^{239}$Pu certified as above.

The amount of the other plutonium isotopes present is related to the $^{239}$Pu content through the following certified amount ratios:

| | |
|---|---|
| $n(^{238}Pu)/n(^{239}Pu)$ : | 0.000 031 05(29) |
| $n(^{240}Pu)/n(^{239}Pu)$ : | 0.022 434 0(51) |
| $n(^{241}Pu)/n(^{239}Pu)$ : | 0.000 248 5(34) |
| $n(^{242}Pu)/n(^{239}Pu)$ : | 0.000 075 70(78) |

This corresponds to an isotopic composition with the following abundances :

| | amount fraction (·100) | | Mass fraction (·100) |
|---|---|---|---|
| $n(^{238}Pu)/n(Pu)$ | 0.003 036(29) | $m(^{238}Pu)/m(Pu)$ | 0.003 023(29) |
| $n(^{239}Pu)/n(Pu)$ | 97.771 86(60) | $m(^{239}Pu)/m(Pu)$ | 97.762 60(61) |
| $n(^{240}Pu)/n(Pu)$ | 2.193 41(49) | $m(^{240}Pu)/m(Pu)$ | 2.202 39(49) |
| $n(^{241}Pu)/n(Pu)$ | 0.024 29(34) | $m(^{241}Pu)/m(Pu)$ | 0.024 49(34) |
| $n(^{242}Pu)/n(Pu)$ | 0.007 402(76) | $m(^{242}Pu)/m(Pu)$ | 0.007 494(77) |

The molar mass of the plutonium in this sample is 239.074 812 8(96) g·mol$^{-1}$

From the certified values, the following amount and mass contents are derived:

| | |
|---|---|
| $3.838\ 0(23) \cdot 10^{-6}$ | mol (Pu) · g$^{-1}$ (solution) |
| $8.966\ 2(55) \cdot 10^{-4}$ | g ($^{239}$Pu) · g$^{-1}$ (solution) |
| $9.171\ 4(56) \cdot 10^{-4}$ | g (Pu) · g$^{-1}$ (solution) |

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NOTES

1. This Spike Isotopic Reference Material is traceable to the SI in the shortest possible way. The values of the Pu isotope ratios were measured at IRMM and are traceable to the SI via the values of the isotope ratios of the isotopic reference material IRMM-290. The Pu content of this spike is traceable to the SI via reference material CETAMA MP2. Measurements calibrated by this Isotopic Reference Material have therefore the potential of being traceable to the SI.

2. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where $u_c$ is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They are given in parentheses and include a coverage factor $k$=2. They apply to the last two digits of the value. The values certified are traceable to the SI.

3. This Reference Material was prepared by metrological weighing of Pu metal (CETAMA MP2) according to the guidelines in its accompanying Reference Material Certificate of Analysis and dissolution in $HNO_3$. Subsequently the solution was dispensed into individual units.

4. The Spike Isotopic Reference Material IRMM-086 comes in a glass ampoule with screw cap containing about 22 µmol plutonium in 5 mL of a chemically stable 5M $HNO_3$ solution.

5. Due to radioactive decay, the Pu element concentration decreases by 0.0042 % · $a^{-1}$.

   The half lives, used in the calculations, are

   $^{238}Pu$ : 8.77 (03) · $10^1$ a [1]
   $^{239}Pu$ : 2.411 (03) · $10^4$ a [1]
   $^{240}Pu$ : 6.563 (07) · $10^3$ a [1]
   $^{241}Pu$ : 1.429 (06) · $10^1$ a [2]
   $^{242}Pu$ : 3.735 (11) · $10^5$ a [1]
   $^{244}Pu$ : 8.00 (09) · $10^7$ a [1]

6. The atomic masses, used in the calculations, are[3]

| | | |
|---|---|---|
| $^{238}Pu$: | 238.049 559 9(40) | g·mol$^{-1}$ |
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| $^{240}Pu$: | 240.053 813 5(40) | g·mol$^{-1}$ |
| $^{241}Pu$: | 241.056 851 5(40) | g·mol$^{-1}$ |
| $^{242}Pu$: | 242.058 742 6(40) | g·mol$^{-1}$ |
| $^{244}Pu$: | 244.064 204(5) | g·mol$^{-1}$ |

[1] IAEA, Decay data of the Transactinium Nuclides, Technical Reports Series No. 261, 1986
[2] P. De Bièvre, A. Verbruggen, 'A new measurement of the $^{241}Pu$ half-life by isotope mass spectrometry', Metrologia, 199, **36**, 25-31
[3] G. Audi and A.H. Wapstra, The 2003 atomic mass evaluation , Nucl Phys A729(2003) 337-676.

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7. Values for isotope abundance ratios, isotopic compositions and for concentrations are valid for February 3, 2006.

8. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

9. Using this Spike Isotopic Reference Material, the Pu content in an unknown sample can be determined by Isotope Dilution, through a measurement of the isotope amount ratio $R(B) = n(^{239}Pu)/n(^{240}Pu)$ in a blend. It should be computed with the aid of the following equation which enables an easy quantification of the uncertainty sources in the procedure :

$$c\left(^{240}Pu,X\right)=\frac{R(Y)-R(B)}{R(B)-R(X)}\cdot R(X)\cdot\frac{m(Y)}{m(X)}\cdot c\left(^{239}Pu,Y\right)$$

$$c\left(Pu,X\right)=\frac{R(Y)-R(B)}{R(B)-R(X)}\cdot\frac{\sum Ri(X)}{\sum Ri(Y))}\cdot\frac{m(Y)}{m(X)}\cdot c\left(Pu,Y\right)$$

where:

| | | |
|---|---|---|
| $R(X)$ | = | amount ratio $n(^{239}Pu)/n(^{240}Pu)$ in the unknown sample material X |
| $R(Y)$ | = | amount ratio $n(^{239}Pu)/n(^{240}Pu)$ in the spike material Y |
| $m(X)$ | = | mass of the unknown sample used in the measurement |
| $m(Y)$ | = | mass of the sample of spike solution used in the measurement |
| $c(Pu,X)$ | = | amount content of Pu · $g^{-1}$ sample material |
| $c(Pu,Y)$ | = | amount content of Pu · $g^{-1}$ spike solution |
| $c\left(^{240}Pu,Y\right)$ | = | amount content of $^{240}$Pu · $g^{-1}$ spike solution |
| $c\left(^{239}Pu,X\right)$ | = | amount content of $^{239}$Pu · $g^{-1}$ sample material |
| $\sum Ri(X)$ | = | sum of all amount ratios in sample material X |
| $\sum Ri(Y)$ | = | sum of all amount ratios in spike material Y. |

The isotopic measurements by Thermal Ionisation Mass Spectrometry were performed by S Richter and H Kühn. Isotopic measurements were calibrated against synthetic plutonium isotope mixtures prepared by J Broothaerts. Chemical preparation of the samples for isotopic measurements was performed F Kehoe.

Metrological weighings needed for the preparation and certification were performed by R Eykens. The ampoulation of this Spike Isotopic Reference Material was accomplished by R Eykens and F Kehoe.

The overall co-ordination leading to the establishment, certification and issuance of this Spike Isotopic Reference Material was carried out by A Verbruggen.

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August 2007

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European Commission

**EUR 22944 EN – Joint Research Centre – Institute for Reference Materials and Measurements**

Title: Preparation and Certification of IRMM-081a and IRMM-086 Spike Isotopic Reference Materials

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Abstract

Highly enriched $^{239}$Pu Spike Isotopic Reference Materials (IRMM-086 and IRMM-081a) have been prepared at IRMM

The certified values for IRMM-086 of 3.752 4(22)·$10^{-6}$ mol $^{239}$Pu per g of solution and for IRMM-081a of 3.745 8(26)·$10^{-7}$ mol $^{239}$Pu per g of solution have been established by mass metrology and subsequently verified by isotope dilution mass spectrometry. The plutonium isotopic composition has been determined by thermal ionisation mass spectrometry and calibration of these measurements by means of synthetic mixtures.

The Isotopic Reference Material is supplied in a sealed glass ampoule containing 5 mL g of a 5 M nitric acid solution.

These Isotopic Reference Materials are part of a systematic IRMM programme to supply Spike Isotopic Reference Materials of various isotopes at different concentrations.

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