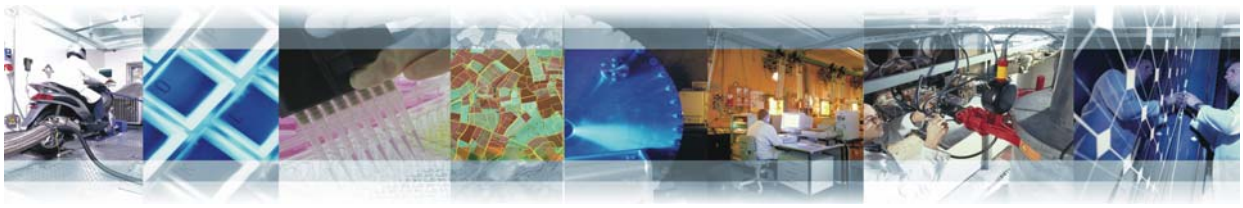

# Certification Report of EQRAIN Plutonium Program N° 10

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

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**Contact information**
André Verbruggen
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

Email: andre.verbruggen@ec.europa.eu

Tel.: +32 (0)14 571 617
Fax: +32 (0)14 571 863

http://www.irmm.jrc.be
http://www.jrc.ec.europa.eu



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# Certification Report of EQRAIN Plutonium Program N° 10

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## *Contents*

## *Introduction*

The EQRAIN Plutonium N°10 (Evaluation de la Qualité des Résultats d'Analyse dans l'Industrie Nucléaire) is an evaluation program set up by CETAMA (la **C**ommission d'**Eta**blissement de **M**ethodes d'**A**nalyses) in order to evaluate the quality of results from nuclear measurement laboratories.
The objective of this programme is to determine the plutonium concentration of a plutonium nitrate solution. Three ampoules were sent to each participant.
At the IM/nuclear group, it was decided to analyse both of the EQRAIN N°10 samples, more specifically sample Pu H53 and Pu H91. The results of this exercise would possibly enable us to identify problems occurring during the handling and measurements by mass-spectrometric Isotope dilution analysis (IDMS) of Pu.
The evaluation of the mass-spectrometry analysis as part of this program could indicate unexplained processes such as the behaviour of the fractionation factor and outlier results not identified during measurements.

## *Isotopic amount ratios*

As the material is originally a MP2 metal, the isotope abundance ratios from the IRMM measurement certificate were used. Recertification of the isotope amount ratios of MP2 was accomplished recently and a certificate was issued valid for 1 January 2007. The values were recalculated for decay to the date of measurement 13 March 2007.

Table 1: Isotopic ratios and abundances

| Isotope amount ratio(s) | |
|---|---|
| $n(^{238}Pu)/n(^{239}Pu)$ | 0.000 030 78(29) |
| $n(^{240}Pu)/n(^{239}Pu)$ | 0.022 432 1(51) |
| $n(^{241}Pu)/n(^{239}Pu)$ | 0.000 235 4(31) |
| $n(^{242}Pu)/n(^{239}Pu)$ | 0.000 075 70(78) |

| amount fraction (·100) | | mass fraction (·100) | |
|---|---|---|---|
| $n(^{238}Pu)/n(Pu)$ | 0.003 010(28) | $m(^{238}Pu)/m(Pu)$ | 0.002 997(28) |
| $n(^{239}Pu)/n(Pu)$ | 97.773 31(58) | $m(^{239}Pu)/m(Pu)$ | 97.764 06(58) |
| $n(^{240}Pu)/n(Pu)$ | 2.193 26(49) | $m(^{240}Pu)/m(Pu)$ | 2.202 24(49) |
| $n(^{241}Pu)/n(Pu)$ | 0.023 02(30) | $m(^{241}Pu)/m(Pu)$ | 0.023 21(30) |
| $n(^{242}Pu)/n(Pu)$ | 0.007 402(76) | $m(^{242}Pu)/m(Pu)$ | 0.007 49(77) |

## *Measurement of isotopic amount concentrations*

The isotope concentrations of the Eqrain N°10 sample were measured by IDMS. From both samples, 3 blends were prepared consisting of 0.15 - 0.20 - 0.25 g sample spiked with 5 g IRMM-049c. Prior to mass-spectrometric measurement the samples were chemically conditioned and purified by anion exchange with nitric acid as medium.
The $n(^{239}Pu)/n(^{242}Pu)$ ratios of the blends were measured on the Finnigan MAT262 thermal ionisation mass spectrometer. A turret was loaded with the 6 blends and 5 standards (IRMM-290 A3, E and G3) and stored with following filename: 27116.

The isotopic measurements were carried out in static Faraday multi-collector mode using the total evaporation technique as described in [1, 2] and in working instruction WI-0115 of the IRMM IM-Unit quality system.

The fractionation factor derived from the measurements of the series of IRMM-290 samples was applied in the IDMS GUM workbenches [3, 4] as follows:

$$K_{applied} = K_{meas} * K_{base}$$

where $K_{base}$ = 1 with a relative standard uncertainty = 0.015%

$K_{base}$ is included to eliminate inadvertently arriving at a K factor with negligible uncertainty: always a risk with a small series of measurements.
The overview of measurement results for the samples is shown in Table 2. The K factor, calculated by the ratio of the observed values and certified values for $n(^{242}Pu)/n(^{239}Pu)$ for this part of the campaign is shown in Table 3. Mean values per magazine were calculated as well as the overall value of $K_{meas}$ = 0.999 71 ± 0.000 23 (SE for n=6).

For the calculation of the isotopic concentrations of the samples of Eqrain N°10, the values of Table 1, 2 and 3 are the input values of the GUM workbench. In the calculation using GUM workbench, a term $\delta_i$ is added to each individual isotope dilution calculation. This term expresses a possible effect in the measurement which contributes to the uncertainty – if present. Each δ has a value of zero and a standard uncertainty that can be adjusted if necessary. Each δ has the same uncertainty, $u(\delta)$.
The value of $u(\delta)$ is assigned after inspection of the absolute difference between individual isotope dilution results and their mean value as given in each case by:

$$\varepsilon i = | c_{Pui} - c_{Pumean}|$$

In this measurement campaign the uncertainty contribution from each εi to the final uncertainty of $C_{Pu}$ was 1.7%. This is negligible contribution to the overall uncertainty and shows that the assumption that an extra effect is present in the IDMS measurements is not warranted.

Table 4 shows the result of the IRMM measurements.
Table 5 shows the components of uncertainty for samples H53 and H91 of Eqrain N°10.
All data used can be found in S:\Im UNIT\Secure Data\Project Data\EQRAIN10
All values for plutonium isotope ratios and concentrations are corrected for decay to 13 March 2007.

Table 2: Measurements of blends

| | ID | filename | $n(^{242}Pu)/n(^{239}Pu)$ |
|---|---|---|---|
| 1 | FIL 03 H53 015 | 27308.CSV | 0.696 644 |
| 2 | FIL 05 H53 020 | 2730806.CSV | 0.533 245 |
| 3 | FIL 07 H53 030 | 2730808.CSV | 0.425 158 |
| 4 | FIL 09 H91 015 | 2730810.CSV | 0.684 964 |
| 5 | FIL 11 H91 020 | 2730812.CSV | 0.484 927 |
| 6 | FIL 13 H91 025 | 2730814.CSV | 0.427 092 |

Table 3: Calculated fraction factor for $n(^{239}Pu)/n(^{242}Pu)$ ratio

| Date | ID | Reference Mat | $K[n(^{242}Pu)/n(^{239}Pu)]$ |
|---|---|---|---|
| 13/05/04 | FIL 04 E3 TE | IRMM-290 E3 | 0.999 94 |
| 13/05/04 | FIL 06 G3 TE | IRMM-290 G3 | 0.999 65 |
| 13/05/04 | FIL 08 A3 TE | IRMM-290 A3 | 1.000 04 |
| 13/05/04 | FIL 10 E3 TE | IRMM-290 E3 | 0.998 86 |
| 13/05/04 | FIL 12 G3 TE | IRMM-290 G3 | 1.000 09 |
| | | average | 0.999 71 |
| | | SE | 0.000 23 |

Table 4: Measured Isotope concentration of Eqrain N°10 samples (Uc *k*=2)

| Solution Reference | Pu mass content ($g \cdot kg^{-1}$) measured | Pu mass content ($g \cdot kg^{-1}$) certified |
|---|---|---|
| H53 | 4.161 2(70) | 4.162(4) |
| H91 | 4.256 9(64) | 4.261(4) |

Table 5: Components of uncertainty for IDMS of sample H53

| Quantity | Value | Standard Uncertainty | Index |
|---|---|---|---|
| $\Delta t_{MP2}$ | 0.20260 a | $1.56 \cdot 10^{-3}$ a | 0.0 % |
| $R_{238/239}$ | $30.833 \cdot 10^{-6}$ mol/mol | $146 \cdot 10^{-9}$ mol/mol | 0.0 % |
| $R_{240/239}$ | 0.02243240 mol/mol | $2.54 \cdot 10^{-6}$ mol/mol | 0.0 % |
| $R_{241/239}$ | $237.77 \cdot 10^{-6}$ mol/mol | $1.55 \cdot 10^{-6}$ mol/mol | 0.0 % |
| $R_{242/239}$ | $75.704 \cdot 10^{-6}$ mol/mol | $389 \cdot 10^{-9}$ mol/mol | 0.0 % |
| $\tau_{238}$ | 87.700 a | 0.300 a | 0.0 % |
| $\tau_{239}$ | 24110.0 a | 30.0 a | 0.0 % |
| $\tau_{240}$ | 6563.00 a | 7.00 a | 0.0 % |
| $\tau_{241}$ | 14.2900 a | 0.0600 a | 0.0 % |
| $\tau_{242}$ | $373.50 \cdot 10^{3}$ a | 1100 a | 0.0 % |
| $c_{y.IRMM049c}$ | $366.650 \cdot 10^{-9}$ g/mol | $245 \cdot 10^{-12}$ g/mol | 62.6 % |
| $R_{239/242Pu.IRMM049c}$ | $2.2120 \cdot 10^{-3}$ mol/mol | $17.0 \cdot 10^{-6}$ mol/mol | 0.0 % |
| $\Delta t_{spike}$ | 10.8695 a | 0.0111 a | 0.0 % |
| $R_{b1}$ | 1.435450 | $144 \cdot 10^{-6}$ | 0.2 % |
| $R_{b2}$ | 1.875310 | $188 \cdot 10^{-6}$ | 0.2 % |
| $R_{b3}$ | 2.352070 | $235 \cdot 10^{-6}$ | 0.2 % |
| $m_{x1}$ | 0.154320 g | $28.9 \cdot 10^{-6}$ g | 0.5 % |
| $m_{x2}$ | 0.201620 g | $28.9 \cdot 10^{-6}$ g | 0.3 % |
| $m_{x3}$ | 0.254390 g | $28.9 \cdot 10^{-6}$ g | 0.2 % |
| $m_{y1}$ | 4.996700 g | $289 \cdot 10^{-6}$ g | 0.0 % |
| $m_{y2}$ | 4.999000 g | $289 \cdot 10^{-6}$ g | 0.0 % |
| $m_{y3}$ | 5.016400 g | $289 \cdot 10^{-6}$ g | 0.0 % |
| $K_{meas}$ | 1.000285 | $228 \cdot 10^{-6}$ | 7.3 % |
| $K_{base}$ | 1.000000 | $150 \cdot 10^{-6}$ | 3.2 % |
| $\delta_1$ | 0.0 | $10.0 \cdot 10^{-9}$ | 8.4 % |
| $\delta_2$ | 0.0 | $10.0 \cdot 10^{-9}$ | 8.4 % |
| $\delta_3$ | 0.0 | $10.0 \cdot 10^{-9}$ | 8.4 % |
| $\gamma_{Pu}$ | $4.16119 \cdot 10^{-3}$ g/g | $3.51 \cdot 10^{-6}$ g/g | |

Table 6: Components of uncertainty for IDMS of sample H91

| Quantity | Value | Standard Uncertainty | Index |
|---|---|---|---|
| $\Delta t_{MP2}$ | 0.20260 a | $1.56 \cdot 10^{-3}$ a | 0.0 % |
| $R_{238/239}$ | $30.833 \cdot 10^{-6}$ mol/mol | $146 \cdot 10^{-9}$ mol/mol | 0.0 % |
| $R_{240/239}$ | 0.02243240 mol/mol | $2.54 \cdot 10^{-6}$ mol/mol | 0.0 % |
| $R_{241/239}$ | $237.77 \cdot 10^{-6}$ mol/mol | $1.55 \cdot 10^{-6}$ mol/mol | 0.0 % |
| $R_{242/239}$ | $75.704 \cdot 10^{-6}$ mol/mol | $389 \cdot 10^{-9}$ mol/mol | 0.0 % |
| $\tau_{238}$ | 87.700 a | 0.300 a | 0.0 % |
| $\tau_{239}$ | 24110.0 a | 30.0 a | 0.0 % |

| Quantity | Value | Standard Uncertainty | Index |
|---|---|---|---|
| $\tau_{240}$ | 6563.00 a | 7.00 a | 0.0 % |
| $\tau_{241}$ | 14.2900 a | 0.0600 a | 0.0 % |
| $\tau_{242}$ | $373.50 \cdot 10^{3}$ a | 1100 a | 0.0 % |
| $c_{y.IRMM049c}$ | $366.650 \cdot 10^{-9}$ g/mol | $245 \cdot 10^{-12}$ g/mol | 78.0 % |
| $R_{239/242Pu.IRMM049c}$ | $2.2120 \cdot 10^{-3}$ mol/mol | $17.0 \cdot 10^{-6}$ mol/mol | 0.0 % |
| $\Delta t_{spike}$ | 10.8695 a | 0.0111 a | 0.0 % |
| $R_{b1}$ | 1.459930 | $146 \cdot 10^{-6}$ | 0.2 % |
| $R_{b2}$ | 2.062160 | $206 \cdot 10^{-6}$ | 0.2 % |
| $R_{b3}$ | 2.341420 | $234 \cdot 10^{-6}$ | 0.2 % |
| $m_{x1}$ | 0.153500 g | $28.9 \cdot 10^{-6}$ g | 0.7 % |
| $m_{x2}$ | 0.217300 g | $28.9 \cdot 10^{-6}$ g | 0.3 % |
| $m_{x3}$ | 0.245800 g | $28.9 \cdot 10^{-6}$ g | 0.3 % |
| $m_{y1}$ | 4.995200 g | $289 \cdot 10^{-6}$ g | 0.0 % |
| $m_{y2}$ | 5.008400 g | $289 \cdot 10^{-6}$ g | 0.0 % |
| $m_{y3}$ | 4.988100 g | $289 \cdot 10^{-6}$ g | 0.0 % |
| $K_{meas}$ | 1.000285 | $228 \cdot 10^{-6}$ | 9.1 % |
| $K_{base}$ | 1.000000 | $150 \cdot 10^{-6}$ | 3.9 % |
| $\delta_1$ | 0.0 | $6.00 \cdot 10^{-9}$ | 2.3 % |
| $\delta_2$ | 0.0 | $6.00 \cdot 10^{-9}$ | 2.3 % |
| $\delta_3$ | 0.0 | $6.00 \cdot 10^{-9}$ | 2.3 % |
| $\gamma_{Pu}$ | $4.25693 \cdot 10^{-3}$ g/g | $3.22 \cdot 10^{-6}$ g/g | |

## *Conclusions*

The measurement of the samples provided through the Eqrain N°10 program has proven to be very useful. A number of conclusions could be drawn:
Analysis of the components of uncertainty on the ratio of measured values of IDMS on the MAT262 gave very satisfactory result. The major contributor to the total uncertainty is the uncertainty of the spike isotopic reference material used (62.6% and 78.0%); the influence of the fractionation is ca 10-15%. The variation within the IDMS sub-samples can contribute up to 25 % of the total uncertainty.
The results of the independent measurements of the samples show that we can have high confidence in our capacity to provide reliable results. We have found acceptable agreement with the certified value demonstrating the reliability of our procedures, methodology and competence of the people.

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[1] R. Fiedler, Int. J. of Mass Spectr., 146,147 (1995) 91-97.
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[3] International Organisaton for Standardisation, Guide to the Expression of Uncertainty in Measurements, ©ISO, ISBN 92-67-10188-9, Geneva, Switserland 1993
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