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# Preparation of samples for the NUSIMEP 5 campaign containing uranium, plutonium and caesium certified for isotopic abundances

L. Benedik, A. Alonso, T. Altzitzoglou, S. Richter, G. Sibbens, A. Stolarz, A. Verbruggen, R. Wellum


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**European Commission**
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

**Contact information**
Roger Wellum or Ljudmila Benedik
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

E-mail: roger.wellum@ec.europa.eu or Ljudmila.Benedik@ec.europa.eu
Tel.: +32 (0)14 571 607
Fax: +32 (0)14 571 863

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



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# 1. Introduction

The NUSIMEP 5 campaign was conceived as a continuation of the previous campaigns in this sequence of the measurement of nuclear traces in environmental test samples.

The samples in N5 were designed to cover more elements than the previous campaigns in which only the isotopic abundances of uranium were required to be measured. The principle of having a chemically complex matrix was followed as the samples then are more realistic and present real challenges for the analytical chemist, which is the situation for actual environmental samples.

For the matrix the same salt solution used in NUSIMEP 4 was used as a basis /1/. All the samples included uranium at the same concentration levels as in NUSIMEP 4. It was decided to add small amounts of plutonium and caesium to some of the samples as both these elements are routinely analysed in environmental samples. Before fixing the main parameters of the samples to be provided in NUSIMEP 5 the inclusion of these two elements was discussed at length both internally at IRMM and at the ESARDA, Destructive Analysis Working Group meetings. Their inclusion was suggested as well by several participants of previous NUSIMEP campaigns.

One constraint accepted at the start was to keep the nuclear and radioactive materials at low enough levels that the samples could be transported as non-radioactive materials and analysed in laboratories that do not have permission to handle nuclear materials. It was therefore decided to prepare 4 solutions with uranium in each at a level similar to previous NUSIMEP campaigns, add Pu to two of the samples and radioactive Cs to the other two.

The participating laboratories were provided with four samples of 1% saline solution in 0.5 M nitric acid. Each sample contained uranium (1 depleted, 1 natural, 2 slightly enriched) at a concentration of 5 $ng \cdot g^{-1}$. Two of them contained very low amounts of Pu isotopes and two of them mixtures of the caesium isotopes $^{134}Cs$ and $^{137}Cs$. The laboratories were requested to measure and report the isotopic amount ratios $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$, $n(^{236}U)/n(^{238}U)$, $n(^{238}Pu)/n(^{239}Pu)$, $n(^{240}Pu)/n(^{239}Pu)$, $n(^{241}Pu)/n(^{239}Pu)$, $n(^{242}Pu)/n(^{239}Pu)$, the activity ratio $^{238}Pu/(^{239}Pu+^{240}Pu)$ and the activity ratio $^{134}Cs$ / $^{137}Cs$. We asked the participating laboratories to perform the measurements using methods of their own choice and to report measured results with uncertainties.

The uranium material was prepared as for previous NUSIMEP campaigns, starting with $UF_6$ for which values of isotopic ratios have been certified at IRMM, hydrolysing and converting to a uranyl nitrate solution, and diluting this before adding to the matrix solution to arrive at the specified 5 $ng \cdot g^{-1}$ concentration. The natural uranium in the salt matrix solution was removed chemically and the trace levels left were then measured by TIMS/IDMS applying a highly enriched $^{233}U$ spike.

Two plutonium certified source materials were available at IRMM with a concentration of 50 $kBq \cdot g^{-1}$. These were diluted to 1 $kBq \cdot g^{-1}$ before adding to the matrix solution of two samples

already mixed with uranium. It was expected that most laboratories would measure the alpha activity ratio $^{238}Pu/(^{239}Pu + ^{240}Pu)$ and therefore the Pu samples were chosen to exhibit realistic alpha ratios. However the calculated alpha ratios from the certified values in 1995 were confirmed by independent measurements at IRMM.

The property of interest for the Cs is the gamma-emission ratio of the isotopes $^{134}Cs/ ^{137}Cs$. The isotope mixtures of the isotopes were made by weighing together amounts of certified solutions of these isotopes at IRMM and verifying the activity ratios by measuring on a well-characterised Ge detector set-up.

There were several purposes to the solutions prepared for this campaign. It was considered that only a few laboratories would measure the isotope ratios of all three elements, although this was clearly possible (and done at IRMM on a set of the samples for verification purposes). However, which of the elements they would measure and characterise was left up to the individual laboratories. An upper limit of 50 samples was prepared as the response to this particular campaign was not clear at the start of the preparation.

## 2. Selection of materials

The matrix was a solution of salts approximating the composition of seawater but with a 1% salt concentration and acidified to 0.5 M with nitric acid. The material was identical to that used for the matrix preparation in the NUSIMEP 4 campaign and was cleaned of natural uranium in an identical fashion /1/.

The 'bulk' uranium material was, as outlined above, taken from a series of certified $UF_6$ mixtures, hydrolysed and converted to the nitrate form (1000 ppm) and added directly to the matrix solutions.

Plutonium solutions were available at IRMM in a certified form and enriched caesium isotopic materials, $^{134}Cs$ and $^{137}Cs$, were also available as certified solutions. These were mixed together to give the required activity ratios before adding to two of the sample solutions.

## 3. Sample preparation

All lab-ware was pre-cleaned in the IRMM Medium Clean Chemical Laboratory (MCL) and manipulations were carried out in the Ultra Clean Chemical Laboratory (UCCL) class 100 clean working spaces to reduce the risk of contamination with natural uranium. The Pu solutions were handled in a new, unused glove-box to eliminate risk of incorporation of other Pu materials.

The matrix solutions were prepared in the UCCL, outside the IRMM nuclear controlled area; the final solutions of U, Pu and Cs were added to the matrix solutions either in a clean laboratory (MCL) outside the controlled area or on a clean bench within the nuclear controlled area.

The four final solutions consisted of 1 litre of matrix solution, each containing one of the uranium materials. Two of the solutions contained low amounts of Pu and two contained low activity amounts of a Cs isotopic mixture.

## 4. Preparation of matrix

For this campaign the equivalent of 5 L of 1 % saline solution, available from the previous NUSIMEP 4 campaign, was augmented with a second batch of 5 L of the matrix material, stripped of the natural uranium in exactly the same way as the saline solution for NUSIMEP 4 matrix by passing a solution of the salts, acidified to approximately 4 M nitric acid, through an Eichrom U-TEVA column.

For the previous campaign, NUSIMEP 4, the uranium left in the saline solution used for the matrix after this cleansing process was measured by ICP-MS /1/.

The uranium content in the prepared matrix solution was measured for this campaign by IDMS/TIMS. A weighed amount of a highly enriched $^{233}U$ spike (IRMM-058, Table 1) was added to a weighed amount of the matrix solution and after separation of the uranium a series of rhenium filaments was prepared. The $n(^{233}U)/n(^{238}U)$ isotope ratio was measured on a Thermo Electron Triton thermal ionisation mass-spectrometer.

The result of the IDMS measurement was 2.010(37) pg $^{nat}U \cdot g^{-1}$ solution. This value, adopted for calculations of the uranium isotopic composition of the final solutions is comparable to the value determined by ICP-MS for the NUSIMEP 4 campaign (5.47 pg $^{nat}U \cdot g^{-1}$ solution) where the salt concentration was 2% compared to 1% of the NUSIMEP 5 campaign. The uncertainty of the present measurement is lower than that previously obtained for the measurements by ICP-MS where IDMS was not employed.

**Table 1: Isotopic ratios of spike IRMM-058 used for IDMS of the uranium in the matrix solution for NUSIMEP 5**

| | |
|---|---|
| $n(^{234}U)/n(^{233}U)$ : | 0.000 352 4(14) |
| $n(^{235}U)/n(^{233}U)$ : | 0.000 004 124(29) |
| $n(^{236}U)/n(^{233}U)$ : | 0.000 000 043 4(14) |
| $n(^{238}U)/n(^{233}U)$ : | 0.000 010 43(21) |

### *4.1. Production and certification of 'bulk' uranium*

As for previous NUSIMEP campaigns uranium isotopic mixtures were prepared in the gas phase by mixing selected, certified uranium material in the form of $UF_6$. The uranium isotopic ratio $n(^{235}U)/n(^{238}U)$ was then certified by gas-source mass spectrometry, measuring each material relative to two certified $UF_6$ reference materials. Samples of each $UF_6$ material were hydrolysed and converted into uranyl nitrate. Finally, the samples were dissolved in 0.5 M $HNO_3$ to obtain a uranium solution with a concentration of 1 mg $U \cdot g^{-1}$ solution (1000 ppm).

The materials used for NUSIMEP 5 were taken from the internal IRMM catalogue of $UF_6$ reference materials. For NUSIMEP 5D the certified reference material, IRMM-186, was used.

The measurement of the minor isotopes by TIMS has been described previously /2/. The certified $n(^{235}U)/n(^{238}U)$ ratio from the gas mass-spectrometry is used to calibrate the mass-fractionation factor for measurements on a thermal ionisation mass-spectrometer of the minor isotopes. The $n(^{234}U)/n(^{238}U)$ ratio was measured with both masses in Faraday cups in parallel. The $n(^{236}U)/n(^{238}U)$ ratio was measured with mass 236 by the secondary electron ion (SEM) counter and the 238 mass on the Faraday cup. The response of the SEM was calibrated by measuring a suitable peak (mass 234 or 235) on both Faraday and SEM. The method has been previously described in detail and forms the basis of the measurement of minor isotope abundances of uranium at IRMM.

The four uranium materials covered the range from depleted to slightly enriched (~3%) in $^{235}U$.

### *4.2. Preparation and certification of plutonium isotopic mixtures*

Two plutonium certified source materials (EUROMET 2 and EUROMET 3) were available at IRMM with a concentration of 50 $kBq \cdot g^{-1}$ and an alpha activity ratio $^{238}Pu/(^{239}Pu+^{240}Pu)$ of approximately 2. Samples of these solutions were purified from in-grown $^{241}Am$ and other decay products and the resulting solutions were diluted to about 1 $kBq \cdot g^{-1}$ before adding to the matrix solution. Each sample for the participants contained approximately 1 Bq Pu alpha activity. It was expected that most laboratories would measure the alpha activity ratio $^{238}Pu/(^{239}Pu + ^{240}Pu)$ and therefore the Pu samples were chosen to exhibit realistic and different alpha ratios. However, all the Pu isotopes were certified by mass-spectrometry and the calculated alpha ratios were confirmed by independent measurements at IRMM.

The alpha activity ratios of the two materials were certified by more than one method in 1994 and 1996 as part of the EUROMET project 325. The identity and validity of the solutions were confirmed for NUSIMEP 5 by measuring the alpha spectrum of an aliquot of each of the EUROMET solutions after separation of Pu from decay products. Details of the measurements and certification of the two Pu materials are given in /3/.

The activity ratios of the plutonium in the NUSIMEP 5 samples A and B were certified by correcting the certified values from 1995 for decay to the reference date of 01/01/2006 for NUSIMEP 5.

The molar isotopic ratios for the plutonium were based on certification measurements by TIMS in 1995, which at that time were done to provide an independent confirmation of the Pu alpha activity ratios. The certified values of the isotopic abundances done in 1995 were corrected for decay up to 01/01/2006.

The final solutions of the two mixtures were diluted to 1 $kBq \cdot g^{-1}$ concentrations and 50 µL of these solutions were added to the 1 L containers with samples A and B, yielding approximately 1 Bq per 20 mL sample for the participants.

A series of measurements of the concentration of Pu at the same levels as used in this campaign in the same matrix solution was carried out to demonstrate that the concentration of the Pu did not change, e.g. by precipitation or plating out on the walls of the containing vessel,

over a time period of several months. Up to 6 months, no difference in the concentration was found within the accuracy of the measurements of the small samples. This work will be published separately.

### *4.3. Preparation and certification of caesium isotopic mixtures*

Certified solutions of $^{134}Cs$ and $^{137}Cs$ were available at IRMM. These were mixed by weighing to produce two solutions with activity ratios of approximately 6:1 and 14:1 ($^{137}Cs/^{134}Cs$). The activity ratios were certified based on the certificates of the original solutions and the mass-metrology of the mixes. These ratios were confirmed by careful measurements on sources made from each of the mixes. Further details of the preparation and certifications can be found in /4/.

The final solutions of the two mixtures were diluted to 1 $kBq \cdot g^{-1}$ concentrations and 50 µL of these solutions were added to the 1 L containers with samples C and D, yielding approximately 1 Bq per 20 mL sample for the participants.

## 5. Mixing bulk and matrix material: verification of NUSIMEP 5 samples

The recipients for the final N5 samples were four 1 L bottles, cleaned as described previously /1/ and labelled NUSIMEP 5A, 5B, 5C, 5D.

### *5.1. Sample containers*

In the previous NUSIMEP campaigns, screw-capped polypropylene bottles were used for the samples sent to the participants. Some problems were found with leakages from a small number of the bottles during transport and therefore for NUSIMEP 5 plastic long-necked transfer pipettes were used as sample ampoules. These could be heat-sealed in such a way that no leakage was possible, even under severe transport conditions. Two 10 mL ampoules were used for each NUSIMEP 5 sample. This also allowed some flexibility for participants in using the two ampoules combined or separately.

The ampoules were cleaned before use by prolonged soaking in 1 M $HNO_3$ and rinsing in sub-boiled water in the MCL. One complete sample set was transferred into the ampoules, sealed and labelled before moving on to the next sample set. One hundred ampoules were filled from each set, enough for a maximum of 50 samples.

Solutions were transported as non-radioactive and labelled as “environmental test samples: saline solutions”. No reports of sample losses or leakages were received.

### *5.2. Verification measurements*

The uranium isotope composition, the plutonium alpha ratio $^{238}Pu/(^{239}Pu+^{240}Pu)$ and the $^{134}Cs/^{137}Cs$ activity ratio were measured on a set of the NUSIMEP 5 samples at IRMM. This was to verify the samples and also to add the IRMM measured results to the list of measurements

performed by participants. These measured results will be added to the database of supplied results together with those from the participants.

The plutonium activity ratios for the two solutions were also verified on the solution containing Pu before it was diluted and added to the matrix solutions /3/.

The certified values for all three elements however, were calculated solely from the values of the concentrated source materials, with small corrections for the uranium isotopic compositions from the natural uranium in the matrix material.

The certified values were sent to participants on acceptance of their measured results.

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*Authors: L. Benedik, A. Alonso, T. Altzitzoglou, S. Richter, G. Sibbens, A. Stolarz, A. Verbruggen, R. Wellum*
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**Abstract**

Four solutions with different isotopic composition were prepared as samples for the NUSIMEP-5 comparison exercise. Each contained uranium (5 ppb), two in addition Pu and two Cs in low amounts in a 1 % saline solution.

The uranium isotopic abundances were certified at IRMM on 4 individual $UF_6$ materials. Both the activity and isotopic ratios of the plutonium were also certified at IRMM. Certified $^{134}Cs$ and $^{137}Cs$ materials were mixed.

The certified values for all the parameters that were requested to be measured are appended.

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