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Preparation of simulated urine samples containing certified uranium for the NUSIMEP 4 campaign

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NUSIMEP

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1. Introduction

Uranium is an analyte of high importance in the fields of safeguards, fissile material accountancy and control and also in nuclear non-proliferation. The NUSIMEP 4 campaign was conceived as a continuation of the previous campaigns devoted to measurements of uranium isotopic ratios in various matrices. NUSIMEP 2 was designed to test the measurement of uranium isotope ratios in a simple (dried nitrate) matrix and for NUSIMEP 3 a saline solution as a more challenging matrix was employed. In the present campaign a simulated urine was chosen as the matrix. The analysis of the uranium isotopic content in this medium is important for detecting and measuring exposure to uranium, in particular to measure the exposure to depleted uranium in war zones where munitions with depleted uranium metal were used.

Again, as for NUSIMEP 2 and NUSIMEP 3, the intention is to prepare samples for testing the measurement of the uranium isotopic ratios or abundances and not the concentration. The last parameter is not generally considered to be of so much interest as the element is ubiquitous in nature and natural levels in urine vary considerably within a given population.

For producing the uranium mixtures and certifying the uranium isotopic abundances the previous methodology used for NUSIMEP 2 and 3 was followed. A matrix was prepared with certifiably low amounts of (natural) uranium; the uranium bulk material was prepared by mixing certified UF_6 and converting it into the nitrate form. The $n(^{235}U)/n(^{238}U)$ was certified by measurement on the MAT 511 gas-source mass-spectrometer and the minor isotope ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ were measured and certified by Thermal Ionisation Mass Spectrometry, TIMS using the certified $n(^{235}U)/n(^{238}U)$ values for calibration of the internal mass-fractionation.

As part of a larger campaign for measurement of uranium isotopic ratios, eight uranium isotopic mixtures were made as UF_6 and certified by this method. These materials will be used for CCQM and NUSIMEP campaigns.

Two of the uranium isotopic mixtures were selected for this campaign, one depleted and one slightly enriched.

2. Sample preparation

2.1. Selection of materials

Collection and certification (and keeping over a long time period) of natural urine was not deemed to be a workable route. Instead it was decided to make a ‘simulated’ urine matrix using the same saline as for NUSIMEP 3 with addition of urea to provide organic material. The saline solution had to be stripped of natural uranium before use in the preparation of the matrix for NUSIMEP 4.

The ‘bulk’ uranium material was, as outlined above, taken from a series of UF_6 mixtures, and after hydrolysing and converting to the nitrate was dissolved in 1 M nitric acid, thereby creating a solution with1000 ppm (1 mg $U \cdot g^{-1}$ solution) concentration of uranium. An aliquot of this solution was added directly to the matrix solution.

It was also decided to have a higher concentration of uranium in the simulated urine samples than would be expected in ‘real’ urine where typical concentrations of up to 50 ppt (50 pg $U \cdot g^{-1}$ urine) are found. We have no experience of the stability of uranium in such weak solutions and prefer to keep the concentration higher. A concentration of 5 ppb (5 ng $U \cdot g^{-1}$ solution) was chosen following NUSIMEP 3 where such concentrations were found to present measurement difficulties for participants (even though for routine measurements of uranium enrichment in urine considerably lower uranium concentration can be expected).

2.2. Preparation of simulated urine

It was decided to prepare a simulated urine consisting of urea at the concentration of about 17 $g \cdot l^{-1}$ (normal concentration of urea in urine is lower but to simplify the organic composition only urea was used as an organic component) and a saline solution at a similar concentration i.e. about 17 g of salts$\cdot l^{-1}$ in 0.5 M nitric acid.

The urea used for the urine preparation was from Merck (catalogue no.1.08488), chosen out of 4 products of different suppliers considered for this campaign. The decision was taken based on analytical certificates. The saline solution was a prepared mixture of inorganic salts (Aquarium Systems, Instant Ocean®), nitrate and phosphate free. Deionised water produced by Milli-Q system (Millipore, USA) was used for dissolving the salts and the urine acidity was adjusted with J.T Baker ultra-pure nitric acid.

Table 1: Content of simulated urine

	saline components [$g \cdot l^{-1}$]	Organic components [$g \cdot l^{-1}$]
Na	5.40	
K	0.20	
Mg	0.65	
Ca	0.20	
Cl	9.60	
SO_4	1.35	
Si	Negligible	
Urea		17.0
TOTAL	17.4	17.0

All steps of the urine preparation were performed in the clean (MCL) and ultra clean chemical laboratories (UCCL) at IRMM. The lab-ware was cleaned following the requirements of trace elements analyses (leaching with acid baths followed by de-acidifying in Milli-Q water). An air survey of working spaces in the laboratories was performed to estimate the potential contamination with natural uranium. Prior to preparation of the matrix solution each component was analysed for its natural uranium content. As the result of these analyses the saline solution was found to contain U at the concentration of about 1 $ng \cdot g^{-1}$ (ppb) level and therefore had to be purified from uranium to be used as the basis of the matrix for this campaign. The level of uranium concentration (a few ppt) in urea was considered to be too low to have significant influence on uranium isotopic ratio in final mixtures and urea was used for synthetic urine preparation without purification treatment.

The saline purification was performed by adjusting the solution to 3 M in nitric acid and passing it through U-TEVA columns (100 - 150 µm mesh resin) from *Eichrom Technologies, USA.* A large volume of saline solution had to be purified as the solution was needed for NUSIMEP 4 as well as for the CCQM–P48 Pilot Study, for production of the reference urine materials and for forthcoming NUSIMEP campaigns. To speed up the purification process a set of parallel columns was built. In designing the set-up care was taken that the saline solution should have no contact with the air during the whole cleaning process. Moreover, to completely eliminate contamination by natural uranium present in the air, the purification process was performed in the UCCL, class 10 at IRMM.

The solution in 3 M nitric acid was found to be sufficient to ensure nearly 100 % (> 99.5 %) uranium retention as proved by subsequent measurements of the uranium concentration performed by ICP-MS, although it is reported by Eichrom [1] that the highest retention coefficient is achieved from solutions greater than 5 M nitric acid.

After purification, the saline solution was diluted with Milli-Q water and adjusted to 0.5 M in nitric acid and the urea then added to complete the simulated urine matrix solution. The final acidity was checked by titration with TRIS (Tris(hydroxymethyl)-aminomethane).

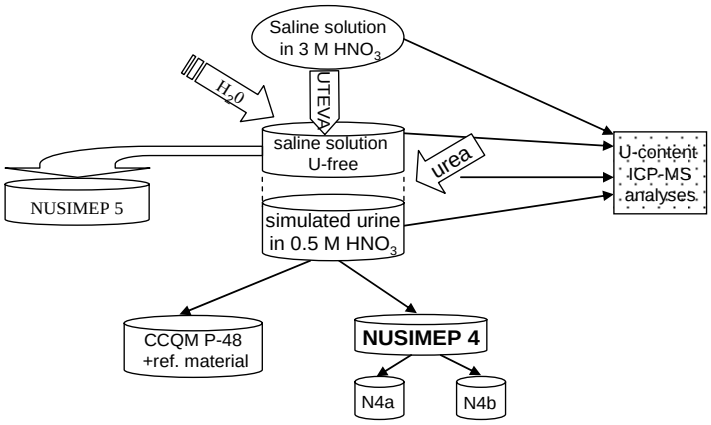

Fig.1. Flow chart of NUSIMEP 4 sample preparation

Both the purified saline solution and the final simulated urine were analysed for uranium traces. The uranium concentration in saline solution dropped down to the ppt level (232 pg·g^{-1} of salts) which resulted in a uranium concentration in the final urine on the level of 5.47 pg·g^{-1} solution.

2.3. Production 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. The UF_6 mixtures were homogenised by heating above the triple point and cooling. This was repeated 3 times. Samples of the prepared materials were distilled into small stainless-steel vials, hydrolysed with nitric acid, dried and heated at 300 °C to convert into the UO_3 form and to remove traces of fluoride. The weighed samples of the uranium oxide were converted into uranyl nitrate by dissolving in 8 M nitric acid and evaporating to dryness. To assure complete conversion into the nitrate form the dissolution-evaporation was repeated twice with sub-boiled 1 M HNO_3. The resulting nitrates were dissolved in 3 % HNO_3 to obtain 1 mg U·g^{-1} (1000 ppm) solutions. Aliquots of these solutions were added to the simulated urine solution to produce N4-a and N4-b. The uranium solutions were also used for subsequent measurements of the minor isotopic abundances by TIMS.

2.4. Mixing ‘bulk’ and matrix material

To prepare the solutions to be analysed by campaign participants the simulated urine was mixed with the solutions of the uranium isotopic mixtures described above.

Portions of 2 l of the urine were decanted from the common batch into 2 cleaned containers. 10.5 µl of the corresponding solution of uranium isotopic mixture was pipetted into each container to prepare the two NUSIMEP 4 solutions, labelled ‘N4-a’ and ‘N4-b’ with 5 $ng \cdot g^{-1}$ (ppb) total uranium concentration.

2.5. Sample containers

Before dispensing, the N4-a and N4-b solutions were stored for about 3 weeks. After bottling into the final containers they were stored overnight in an upside-down position to check that the bottles were leak-tight. The neck was wrapped with Parafilm inside and outside the screw cap. No container showed a leak in this test.

For bottling and transporting the sample solutions to the participants, screw cap polypropylene, plasma cleaned Wheaton (Wheaton Science Products, USA) sampling containers were used.

From the experience of the previous NUSIMEP campaigns it was known that leaking during transport can be a problem so several sealing improvements were investigated: replacing the original cap insert (waxed card) with one made of Teflon, wrapping the neck with Parafilm before screwing the cap and wrapping the neck and then the cap with Parafilm. Containers with a few millilitres of nitric acid were sealed in plastic bags together with a piece of paper and the discolouring of the paper by acid fumes was observed. The best results were achieved for the containers with neck and cap wrapped with Parafilm.

Possible contamination originating from the screw cap materials of the containers was controlled as well. A few ml of 0.5 M HNO_3 were added to a number of containers which were then stored in the normal and in an upside-down position for several weeks. This method of storing allowed us to compare possible contamination by uranium extracted from the lid by fumes as well as by liquid acid. The uranium concentration in the solutions was then measured by ICP-MS. No significant elution of uranium was registered.

3. Measurements and certification of uranium

3.1. Natural uranium in the matrix components

Inductively coupled plasma source mass spectrometry (ICP-MS) was used to measure the content of natural uranium in all urine components prior to mixing with the uranium isotopic mixtures as well as to check possible leaching of uranium from the sample containers.

3.1.1. Sample preparation for the measurements

The urea and urine samples were mineralised prior to the ICP-MS analyses. Approximately 0.2 g of urea dissolved in 10 ml of H_2O, or 10 ml of urine with addition of concentrated nitric acid and H_2O_2 were digested in a microwave digestion unit (MLS 1200 Mega High Performance Microwave Digestion Unit) following a preset heating programme. The digested samples were transferred to conical PTFE vessels, evaporated to dryness and the residues dissolved in 10 ml of 2 % HNO_3.

Air survey and saline solution samples were evaporated to dryness with the addition of small amounts of diluted nitric acid and HF to assure mineralization of possible organic deposits. The dry residues were as above dissolved in 10 ml of 2 % HNO_3.

The uranium separation on U-Teva columns was applied only for measurements of uranium content in the saline solution.

3.1.2. Measurements by Inductively-Couple-Plasma Mass Spectrometry (ICP-MS)

The uranium contents in urea and in the cleaned saline were measured using a Elan 6000 quadrupole ICP-MS (Perkin-Elmer Sciex); the uranium content in the final urine matrix by a single-detector double-focussing magnetic sector Element 2 (Thermo Finnigan). The uranium content in the air survey samples and in solutions used to check the leaching effect in the sample containers were also measured with the Elan 6000. More details about these measurements are published [2].

3.2. 'Bulk' uranium certification by TIMS measurements

The measurement by TIMS has been described previously [3,4]. The measured value of the $n(^{235}U)/n(^{238}U)$ ratio compared to the value certified from the gas mass-spectrometry is used to calculate the mass-fractionation factor for each individual measured filament. 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 multiplier (SEM) ion 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 [3,4] and forms the basis of the measurement of minor isotope abundances of uranium at IRMM.

3.3 TIMS verification measurements of isotopic ratios in samples N4-a and N4-b

The uranium isotopic ratios in the simulated urine mixtures were measured by thermal ionisation mass-spectrometry.

Uranium was separated from the analysed solutions of mixture N4-a and N4-b by absorbing it on U-TEVA resins.

To study if the matrix pre-treatment prior to the recovery of the uranium on the resin has an influence on the measurement of the isotopic ratios, samples solutions were treated in 3 different ways before passing through U-TEVA resin. N4-a and N4-b sample solutions were mineralised a) by microwave digestion as described above for the measurement of uranium in the matrix, b) by evaporation with a mixture of conc. HNO_3 and H_2O_2, and c) not mineralised at all.

All solutions were adjusted to 3 M HNO_3 and passed through U-TEVA columns to absorb the uranium. The columns were washed with 20 column free volumes (cfv) of 6 M HCl. Uranium was then eluted from the columns with 10 cfv of 0.01 M HCl. The effluents were evaporated to dryness with the addition of a small amount of 6 M HNO_3, the dry residues were re-dissolved in 0.2 ml H_2O_2 and again evaporated to dryness to remove the organic traces. The dry residues were then dissolved in 20.0 µl 6 M HNO_3 and divided into two parts: half of the solution was used for TIMS measurements and half was transferred into 10 ml of 2 % HNO_3 for future ICP-MS measurements.

No influence of the treatment methods could be seen in the TIMS measurements of the uranium isotopic ratios in the samples. The mean value of the measurements is given in the table 2 (the certified values of these ratios are given below in Annex 1)

Table 2: Values of uranium isotopic ratios in samples N4-a and N4-b verified by TIMS

	$n(^{234}U)/n(^{238}U)$	$n(^{235}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Sample N4-a	$5.04(13)\ 10^{-5}$	$7.037(103)\ 10^{-3}$	
Sample N4-b	$1.592(171)\ 10^{-4}$	$1.722\ 4(86)\ 10^{-2}$	$2.46(1.58)\ 10^{-5}$

4. Certification of NUSIMEP 4 samples

4.1 Basics of calculation of the final isotopic ratios

The final uranium isotopic ratios of the two NUSIMEP 4 samples were certified based on the certificates of the bulk uranium material, prepared initially as UF_6 with corrections for the measured content of the natural uranium in the matrix materials.

Of the possible contributions to the final uranium isotopic ratios, only the contribution from the natural uranium remaining after purification in the saline solution used to prepare the simulated urine samples needed to be taken into account. The possible contributions from lab-ware and from other sources were demonstrated to be negligible. A comprehensive study was made to check and eliminate such possible sources of uranium. Feasible sources were considered to be reagents, lab-ware and air-borne contamination. Use of cleaned glass-ware (quartz) and plastic-ware, highest (certified) quality ultra-pure reagents, Milli-Q water as well as carrying out all preparatory work in ultra clean chemical environment (UCCL class 10) kept all these contributions of natural uranium effectively to zero levels.

The certified values of the uranium isotopic ratios are given in Annex 1 and an uncertainty budget is shown in Annex 2 in which the relative contributions to the final certified isotopic ratios can be seen.

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