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NUSIMEP-9: Uranium isotope amount ratios and uranium mass in uranium micro-particles

Nuclear Signatures Inter-laboratory Measurement Evaluation Programme Report to participants

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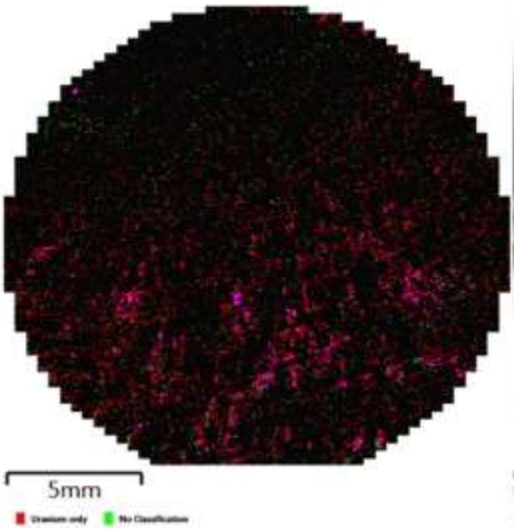
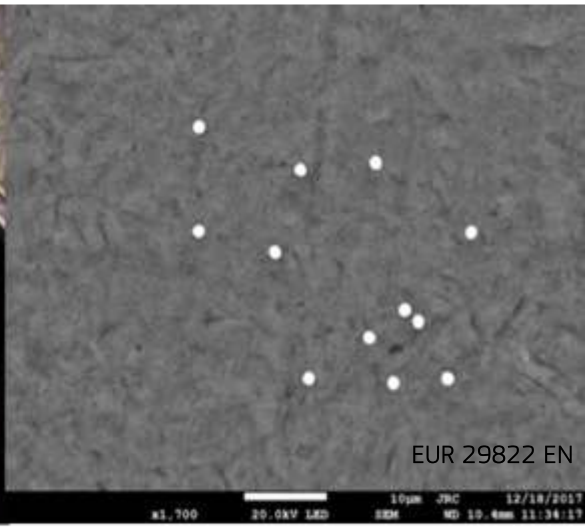
2019





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NUSIMEP-9: Uranium isotope amount ratios and uranium mass in uranium micro-particles

Nuclear Signatures Inter-laboratory Measurement Evaluation Programme

Report to participants

August 2019

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Joint Research Centre

EUROPEAN COMMISSION
DG JOINT RESEARCH CENTRE
Directorate G – Nuclear Safety & Security
Unit G.2 - Standards for Nuclear Safety, Security & Safeguards

Contents

Abstract

The NUSIMEP (Nuclear Signatures Inter-laboratory Measurement Evaluation Programme) is an external quality control programme organised by the European Commission - Joint Research Centre, Directorate G – Nuclear Safety and Security, Unit G.2 for Standards for Nuclear Safety, Security and Safeguards (JRC-Geel, former IRMM), which aims at providing materials for measurements of trace amounts of nuclear materials in environmental matrices.

Measurements of the uranium and plutonium isotopic ratios in small amounts, such as typically found in environmental samples, are required for nuclear safeguards, for the control of environmental contamination and for the detection of nuclear proliferation.

The JRC-Geel, the Forschungszentrum Jülich (Germany) and the IAEA-SGAS (Seibersdorf, Vienna) joined forces to produce and characterise micrometre-sized uranium oxide particles, which can be used for safeguards purposes as Reference Materials (RM).

In this context, JRC-Geel organised a new NUSIMEP proficiency test round, targeting more particularly the IAEA-NWAL network of analytical laboratories. However, NUSIMEP-9 was opened to all laboratories in various scientific fields.

Thirty participants in NUSIMEP-9 received one certified test item, a carbon planchet on which were deposited some thousands U_3O_8 particles of about 1 µm diameter-size of single isotopic composition. They were requested to use their routine analytical procedures and report the $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ isotope amount ratios of ten particles. Participants were also encouraged to measure and report the uranium mass per particle by measuring at least ten particles.

At the end, 25 participants reported results for NUSIMEP-9. These results were evaluated against the certified reference values in accordance with ISO 13528:2015, while guaranteeing full confidentiality with respect to the link between measurement results and the participants' identity.

In general, laboratory's performances in measuring and reporting major and minor uranium isotope amount ratios in the NUSIMEP-9 particles were satisfactory. A few participants undertook to measure and report the uranium mass per particle in NUSIMEP-9 and their overall performance was satisfactory, although with a large scatter of the reported results.

The final evaluation of the participant's performances in the uranium particle analysis of the NUSIMEP-9 test item, the findings and feedback of this proficiency test are presented in this report.

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Summary

1 Introduction

During the past decades, the European Commission Joint Research Centre (EC-JRC) has developed a significant experience in the implementation of nuclear safeguards in support to the International Atomic Energy Agency (IAEA) and more specifically to the Euratom inspectorate. With the implementation of the Additional Protocol (INFCIRC/540), the analysis of so-called environmental samples (such as particles, swipes, etc.) has become one of the most important means of strengthening international nuclear safeguards in order to detect undeclared operations as well as inconsistent or non-conformed data to official declarations [1, 2].

In this context, the IAEA network of analytical laboratories (NWAL) for environmental sampling must apply validated measurement methods for the safeguards analyses since conclusions drawn from their measurements might be used in a court of law and therefore might have political and legal consequences on the international scale. In order to properly assess nuclear treaty compliances and to detect undeclared nuclear activities, new safeguards technologies and methods were developed, such as the determination of isotopic abundances of uranium in microscopic single particles, collected from the swipe samples taken by safeguards inspectors in the different nuclear facilities during nuclear safeguards inspections. Such analytical techniques require the development of new and more complex reference materials (RMs), such as reference materials for particles in nuclear materials to determine, for instance, the origin of the material or its processing history [3]. Such RMs play a key role in analytical quality assurance as they are widely used for the calibration of instruments and measurement systems, for method development and validation, or as quality control samples. They are essential to provide reliable measurement results of high quality in order to draw conclusions on the origin, history, purpose and intended use of the material or sample under investigation. However, to this date, there is no (certified) reference material (CRM) for the uranium isotopic composition in micrometre-sized particles, which would be an essential tool for laboratories carrying out particle analysis while meeting the needs of a quality assurance system and improving their analytical performances [3, 4].

The NUclear Signatures Inter-laboratory Measurement Evaluation Programme (NUSIMEP) was established in 1996 as an external quality control programme organised by the European Commission - Joint Research Centre, Directorate G – Nuclear Safety and Security, Unit G.2 for Standards for Nuclear Safety, Security and Safeguards (JRC-Geel G.2 unit, former IRMM), for nuclear safeguards and environmental laboratories which are involved in the analysis of uranium and plutonium containing materials from the nuclear fuel cycle and nuclear signatures in the environment.

During NUSIMEP Proficiency Testing rounds (PT), participating laboratories receive materials (known as test items) for the measurements of the amounts and of the isotopic abundances of uranium and plutonium present as traces in environmental samples. This gives the opportunity to participating laboratories to demonstrate their measurement capabilities to customers, accreditation bodies and safeguards authorities.

In this context, the JRC-Geel G.2 unit developed uranium particles from certified UF_6 reference materials that were similar to the particles possibly collected on swipe samples by the safeguards inspectors in nuclear facilities. These materials were characterised for uranium isotopic abundances of the particles and were used in the two previous rounds (NUSIMEP-6, 2008 [5] and NUSIMEP-7, 2011 [6]). Both rounds were open to all laboratories carrying out particle analysis in various application fields, but were mainly addressed to the IAEA NWAL. Participating laboratories were asked to use their standard/routine analytical methods and measure the uranium isotopic compositions in a wide size range of hydrolysed UF_6 particles.

NUSIMEP-6 and -7 allowed the assessment of performances of the different analytical techniques used in particle analysis. The consequent feedback collected from the participants allowed the identification of improvements to be implemented and highlighted the need for monodisperse uranium particle reference materials and certified test items with a lower number of particles.

Hence, the JRC-Geel G.2 unit, the Forschungszentrum Jülich (FZJ, Germany) and the IAEA-Safeguards Analytical Service laboratories in Seibersdorf (SGAS, Austria) joined forces to produce and characterise micrometre-sized uranium oxide particles, which can be used as RMs for safeguards purposes [7, 8]. One of these produced uranium microparticle materials (IRMM-2329P) is currently being certified at JRC-Geel G.2 in compliance with the ISO 17034 [6], not only for the uranium isotopic composition, but also for the uranium content and mass per particle. This first CRM in the form of uranium monodisperse particles will be a real breakthrough for the IAEA-NWAL network and the community in the field of particle analysis, since the uranium mass (amount or atom number) per particle will allow laboratories to routinely evaluate and compare their useful yield for uranium during particle measurement in Large Geometry Secondary Ion Mass Spectrometry (LG-SIMS) [9]. It will aslo be beneficial for the analysis with (Fission-Track) Thermal Ionisation Mass Spectrometry (TIMS) and Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) [10, 11].

2 Scope and aim

Several recommendations were made by the IAEA, during the IAEA Technical Meetings on particle analysis in 2017, asking for "future tests using well-characterized materials, to provide a fair assessment of accuracy and precision and encouraging the use of methods to characterize a particle's combined morphology, isotopic, and elemental composition (such as SEM+SIMS/TIMS or LA-ICP-MS)".

The NUSIMEP-9 proficiency testing round on "Uranium isotope amount ratios and uranium mass in uranium micro-particles" was open to all laboratories performing particle analysis in various application fields. In reply to the recommendations set during the recent IAEA Technical Meetings on particles, NUSIMEP-9 targeted mainly laboratories of the IAEA NWAL network, giving these laboratories the opportunity to evaluate the quality of their analytical methods for the analysis of uranium particles.

Participating laboratories in NUSIMEP-9 received one certified test item of monodisperse U_3O_8 particles with an approximate diameter of 1 μm deposited on a carbon planchet of 2.5 cm diameter. These certified test items contain some thousands of micrometre-particles of a single isotopic composition, i.e. with a significantly lower areal density (lower number) of particles than those in the previous NUSIMEP-6 and NUSIMEP-7 test items, following recommendations of the IAEA and participants in the previous NUSIMEP. The uranium particles in NUSIMEP-9 were produced from uranium base solutions by aerosol deposition using a Vibrating Orifice Aerosol Generator (VOAG) [7, 12-13], unlike the two previous NUSIMEP rounds for which the uranium particles had been produced directly from UF_6 materials.

The laboratories participating in NUSIMEP-9 were asked to measure and report the $n(^{235}U)/n(^{238}U)$, $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ isotope amount ratios of ten particles, which belong to the main particle population. In addition, they were asked to report the average value and its associated expanded uncertainty for each of the isotope amount ratios. The average values of the isotope amount ratios were then compared to the reference values for the test item, as defined during the certification of the candidate uranium particle reference material. The measurements of the three isotope amount ratios were obligatory. Participants were encouraged to use their routine methods for the analysis of the measurands per particle, hence a range of mass spectrometric techniques were expected; e.g. Fission-Track TIMS, SIMS, LG-SIMS and (LA)-ICP-MS [3, 9-11].

Additionally, the participating laboratories were strongly encouraged to measure and report the uranium mass per particle by measuring at least ten particles of the main population. Such measurements are usually not carried out in safeguards environmental sampling but are of particular interest for the optimisation of the overall transmission efficiency for LG-SIMS. Uranium mass per particle measurements can also be relevant for TIMS and LA-ICP-MS.

3 Time frame

The NUSIMEP-9 proficiency testing round (PT) was organised according to ISO 17043 [14] and announced for participation beginning of September 2018 (Annex 1). The registration for this PT was open till 19th October 2018. Confirmations of the registration were received from thirty participants from all over the world (Annex 2). Note that some laboratories registered more than once in order to use different instrumental techniques.

Beginning of November 2018, most of the certified test items were sent to the participants within 2 to 5 working days (Annex 3). In addition, participants received an accompanying letter with the instructions for the measurements and their unique participation key (Annex 4), a confirmation of receipt to be returned by participants in order to confirm the good receipt of undamaged samples (Annex 5) and guidelines to guide them through the reporting of the results using the JRC ILC online reporting tool (Annex 6). A unique sample code was attributed to each test item, and linked to the participation key, so as to guarantee both traceability and confidentiality throughout the PT and the results reporting process.

Participants in NUSIMEP-9 were initially invited to report their results for the uranium isotope amount ratios (compulsory) and uranium mass per particle (optional) for February 17th, 2019 the latest. However, this reporting deadline was later extended till March 1st, 2019 (Annex 7).

The NUSIMEP-9 preliminary results (without disclosing the reference values) were first communicated during the 41st ESARDA Symposium in May 2019 in Italy [15].

The characterisation of the NUSIMEP-9 uranium particle certified test item, the homogeneity and short-term stability assessments were carried out as part of the IRMM-2329P certification according to ISO 17034 [16] between November 2017 and September 2018. The certification report is expected to be published before the end of 2019.

4 NUSIMEP-9 uranium particle test item

4.1 Production of the uranium particles

The NUSIMEP-9 uranium particles test items were prepared in the framework of the production and certification of the IRMM-2329P (report in preparation), micrometre-sized monodisperse uranium oxide particles reference material in compliance with ISO 17034 and ISO Guide 35 [17]. The uranium particles were produced from a mixture of mg-size uranium samples in nitrate solution, prepared at JRC-Geel G.2 based on the IRMM-2023 and IRMM-2029 certified solutions [18]. This uranium base solution is later on referred to as IRMM-2329. The IRMM-2329 solution is characterised by a uranium isotopic composition responding to the needs and recommendations of the IAEA, with a ^{235}U enrichment of ca. 3 % and an abundance of ^{236}U in the range of 20-40 ppm. The uranium isotopic composition of the IRMM-2329 was characterised by TIMS/MTE ("modified total evaporation") at JRC-Geel G.2 and then successfully verified at the IAEA-SGAS (Austria) by TIMS/MTE and Multi-Collection-ICP-MS (MC-ICP-MS) (Annex 8).

Upon confirmation of the uranium isotopic composition of IRMM-2329, the solution was sent to the Forschungszentrum Jülich (Germany) for the production of the uranium particles using a special processing set-up with a Vibrating Orifice Aerosol Generator (VOAG, as represented in Figure 1) in order to generate droplets and following a specific procedure to stabilize and homogenize the particles [12, 13]. The produced uranium particles, consisting of U_3O_8 [19], were then deposited onto 25 mm diameter glass-like carbon disks (also known as carbon planchets). More than a hundred units (planchets) of micrometre-sized monodisperse uranium oxide particles were produced and sent back to the JRC-Geel. Scanning Electron Microscopy (SEM) of the uranium particles gave insight on the particle morphology characteristics and confirmed that the particles are of spherical shapes. The main population of particles is of ca. 1.4-1.5 µm diameter-sized particles. Moreover, about 4 % of the particles are "double-particles", i.e. containing twice the uranium amount than the main particle population (resulting from a double-droplet deposition from the VOAG). Each planchet contains at least 15 000 uranium particles.

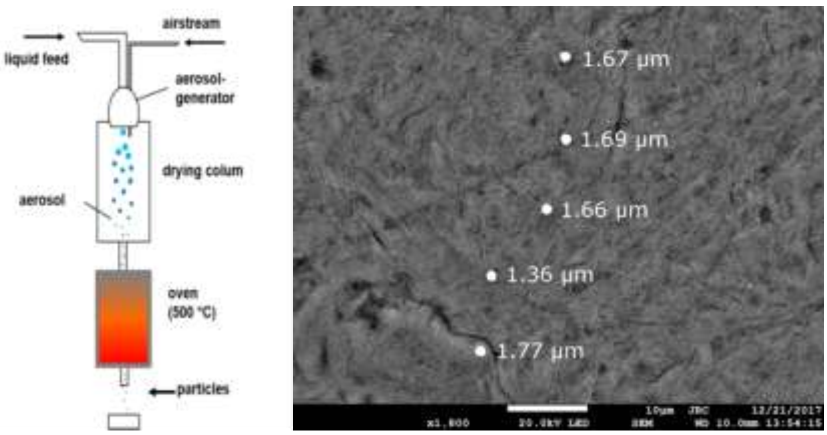

Figure 1. Left: Scheme of the particle production set-up (VOAG), as designed and used in FZJ (Germany) and Right: Scanning Electron Microscope image of the uranium micro-particles in NUSIMEP-9 (JRC-Geel)

4.2 Characterisation and verification of uranium isotopic composition and uranium mass (amount) per particle

In order to guarantee the integrity of the uranium isotopic ratios from the IRMM-2329 solution to the produced uranium particles, so-called "process control measurements" (i.e. verification measurements) were carried out at the IAEA-SGAS, in compliance with ISO 17025 [20]. For this purpose, several planchets were leached using Suprapur® nitric acid and the dissolved particles from the uranyl nitrate leachates were measured by MC-ICP-MS at the IAEA-SGAS. The measurement results from these leachates were then directly compared to the uranium isotopic composition in the IRMM-2329 solution measured by MC-ICP-MS during the same measurement sequence. Thereby, systematic uncertainty contributions arising from the mass bias correction, tailing, hydrate corrections and detector inter-calibrations could be avoided.

The results of the process control measurements by MC-ICP-MS clearly demonstrated that the isotopic composition of the original uranium solution was not altered during the entire particle production process (Annex 8). Finally, for the certification of IRMM-2329P, none of the techniques (LG-SIMS, FT-TIMS or LA-MC-ICP-MS) commonly employed in particle analysis was used. The certification of this particle reference material is therefore independent on the characteristics of these typically applied particle analysis techniques.

In addition to the determination of the uranium isotopic composition of the particles, the uranium amount content (mass of uranium) per particle was determined at JRC-G.2 by Isotope Dilution TIMS (ID-TIMS) in 10 selected particles picked up by an optical microscope equipped with micromanipulators and deposited onto a carburized single rhenium filament; followed by spiking with IRMM-058 (^{233}U spike, 2 pg/µL). Verification measurements of the uranium mass per particle using MC-ICP-MS were carried out at IAEA-SGAS and confirmed the uranium mass per particle value that had been previously determined by ID-TIMS at JRC-G.2.

4.3 Homogeneity

The between-sample homogeneity of the uranium particle test items was evaluated according to ISO 17034 and ISO Guide 35 [16, 17], during the certification of the IRMM-2329P to ensure that the reference values of the test items (uranium isotope amount ratios and the uranium amount per particle) are applicable to all produced units of the material, within the stated uncertainties.

During the characterisation and process control measurements, the isotopic composition of the uranium particles was verified to be in good agreement with the certified uranium composition of the IRMM-2329 solution. Therefore no between-sample homogeneity study for the uranium isotopic composition of the particles was deemed necessary.

On the other hand, the homogeneity of the uranium amount content (mass) per particle in the candidate test items was assessed during the characterisation and certification of the IRMM-2329P, using a set of six units, which were selected by a random stratified sampling scheme. For each unit, five aliquots were prepared by transferring for each aliquot 10 particles from each unit onto a carburised Re filament using micromanipulators installed under an optical microscope.

After transfer, 3 µL of a ^{233}U spike (IRMM-058) was added volumetrically using a calibrated pipette for ID-TIMS measurements of the ^{238}U, ^{235}U and ^{233}U using the ion counter detector on a Triton. The degree of homogeneity between the uranium from the spike and from the particles was assessed by observation of the $n(^{233}\text{U})/n(^{238}\text{U})$ ratio during the course of the measurement. During each measurement sequence, a procedural blank (consisting of the 3 µL of IRMM-058 spike and HNO_3 only), and four quality control samples prepared from IRMM-023 micro-particles were analysed. These measurements were performed in a randomized manner to detect possible trends in the analytical and production sequences.

The total amount of uranium present on the filament was calculated using the IDMS equation (Equation 1) and the associated uncertainty was calculated in accordance with ISO Guide 98-3:2008 (GUM) [21] using GUM Workbench:

$$n_x = n_y \times \frac{(R_y - R_b)}{(R_b - R_x)} \times \frac{\sum R_x}{\sum R_y} \qquad \text{Equation 1}$$

In which R_y, R_x and R_b are the $n(^{233}\text{U})/n(^{238}\text{U})$ isotope amount ratios of the spike, sample and blend respectively. The isotope amount ratio of the spike (IRMM-058) was taken from its certificate, the isotope amount ratio of the sample was taken from the certified value of the IRMM-2329P particles and the isotope amount ratio of the blend was measured by TIMS. ΣR_x and ΣR_y are the sum of isotope amount ratios of the sample and spike respectively and n_y is the amount of uranium added to the blend, which was calculated based on the certified isotope amount content of the spike (IRMM-058), the transferred volume of the spike and the density of the spike, calculated in accordance to Sakurai and Tachimori [22]. Finally, the uranium amount per particle was calculated after subtracting the amount of uranium measured in the procedural blank analysed per each sequence and by dividing by the number of transferred particles (i.e. ten for all prepared aliquots).

Finally the evaluation of between-sample homogeneity contribution was carried out using a one-way analysis of variance (ANOVA), according to ISO Guide 35 and the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [23]. In order to determine the between-sample variation (s_s true standard deviation) and the u^*_{bb}, which represents the maximum heterogeneity that could be hidden by the intrinsic variability of the method and thus depends on the mean squares within bottles and the degrees of freedom of the mean squares within bottles, a one-way ANOVA was performed. The u^*_{bb} can be understood as the "detection limit" of the homogeneity study. Consequently, the uncertainty of homogeneity, noted u_{hom}, can be estimated either as s_s or as u^*_{bb} in case of $s_s < u^*_{bb}$. In the case of the amount content of uranium in IRMM-2329P the value of s_s was larger than u^*_{bb}, so s_s was adopted as uncertainty contribution to account for potential inhomogeneity of the uranium amount in the particle reference material. This approach is similar to tests determining whether an proficiency test (PT) material is sufficiently homogeneous for its purpose as described in the ISO 13528 [24] where the unit heterogeneity s_s is compared with the standard deviation for proficiency assessment (σ_{pt}) with the condition for homogeneity that $s_s \leq 0.3 \cdot \sigma_{pt}$. The relative σ_{pt} for the uranium mass per particle in NUSIMEP-9 has been set to 20 % (k =2) based on the determination results for this measurand value during the certification of IRMM-2329P.

4.4 Stability

Stability testing is necessary to establish the conditions for storage (long-term stability) as well as the conditions for dispatch of the materials to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C can be reached and stability under these conditions must be demonstrated, if the samples are to be transported without any additional cooling.

As demonstrated in previous NUSIMEP PT rounds [5, 6], the uranium isotopic composition is inherently independent on temperature that can be expected during transport and storage. Therefore, no short-term stability study was performed for the uranium isotope amount ratios in the particles.

Stability studies for the uranium amount per particle of IRMM-2329P were carried out using an isochronous design fully described in the certification report of IRMM-2329P (in preparation). In this approach, two units of IRMM-2329P were selected using a randomly stratified scheme. For the short-term stability study, one unit was stored at 4 °C and the other at 60 °C for 7, 14 and 21 days. Finally, the 18 aliquots (18 filaments) were measured during the same analytical sequence by ID-TIMS.

The method to assess whether a PT material is sufficiently stable for its purpose is described in ISO 13528 [24]. These tests compare the general average of the measurand obtained during the homogeneity assessment noted $\bar{y}_1$ (here, the uranium amount content per particle as determined during the characterisation of the uranium amount in IRMM-2329P) with the average of this measurand obtained in the frame of the stability assessment, after 3 weeks, noted $\bar{y}_2$. The absolute difference of these averages is then compared to the standard deviation for proficiency assessment σ_{pt} using the assessment criterion for the stability check, as defined in ISO 13528, $|\bar{y}_1 - \bar{y}_2| \leq 0.3 \cdot \sigma_{pt}$.

Table 1. Homogeneity and stability checks of the uranium mass in the NUSIMEP-9 test items according to ISO 13528

Homogeneity		**Stability**	
σ_{pt}	3.02 fmol (20 %)	$\bar{y}_1$	15.05 fmol
0.3 σ_{pt}	0.91 fmol	$\bar{y}_2$	15.30 fmol
s_s (1)	0.83 fmol (5.5 %)	$\lvert\bar{y}_1 - \bar{y}_2\rvert$	0.25 fmol
$s_s \leq 0.3\ \sigma_{pt}$	YES - Homogeneous	$\lvert\bar{y}_1 - \bar{y}_2\rvert \leq 0.3\ \sigma_{pt}$	YES - Stable

(1) the standard deviation for between-sample homogeneity s_s, taken from the certification report of IRMM-2329P

4.5 Assignment of NUSIMEP-9 reference values

The NUSIMEP-9 reference values x_{pt} for the uranium isotope amount ratios $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ and the uranium mass per particle (in pg), together with their respective associated expanded uncertainties $U(x_{pt})$ (k =2) are given in Table 2 and in the certification report of IRMM-2329P, since the NUSIMEP-9 reference values (x_{pt}) are the certified values (x_{CRM}) of the IRMM-2329P reference material.

Table 2. NUSIMEP-9 reference values and their respective expanded uncertainties ($k = 2$) for the uranium isotope amount ratios and the uranium mass per particle

	Reference values, x_{pt}	$U(x_{pt})$ (k=2) (1)	$U(x_{pt})_{,rel}$ (k=2) (1)	σ_{pt} (2)
$n(^{234}U)/n(^{238}U)$ [mol·mol^{-1}]	0.00034083	0.00000019	0.056 %	2.5 %
$n(^{235}U)/n(^{238}U)$ [mol·mol^{-1}]	0.033902	0.000012	0.036 %	0.5 %
$n(^{236}U)/n(^{238}U)$ [mol·mol^{-1}]	0.00003021	0.00000012	0.40 %	50 %
Uranium mass per particle [pg]	3.58	0.67	19 %	20 %

(1) Expanded uncertainties corresponding to a confidence interval of 95 % according to the GUM [21]

(2) Standard deviations for proficiency assessment criteria (as defined in Section 5)

5 Laboratories' performance evaluation: scoring of results

The individual laboratory performances for the three uranium isotope amount ratios and the uranium mass per particle in NUSIMEP-9 were expressed in compliance with ISO 13528 by means of z and ζ (zeta) scores (see Equation 2 and Equation 3).

$$z = \frac{x_i - x_{pt}}{\sigma_{pt}}$$ Equation 2

$$\zeta = \frac{x_i - x_{pt}}{\sqrt{u(x_i)^2 + u(x_{pt})^2}}$$ Equation 3

Where

x_i is the measurement result reported by a participant

x_{pt} is the certified reference value (assigned value as given in Table 2)

$u(x_{pt})$ is the standard uncertainty of the reference value (derived from Table 2)

$u(x_i)$ is the standard uncertainty reported by a participant

σ_{pt} is the standard deviation for proficiency assessment (Table 2)

The z score for NUSIMEP-9 indicates whether a laboratory is able to perform the measurement in accordance with what can be considered as good practice for IAEA NWALs. The respective standard deviations for proficiency assessment used for the evaluation in NUSIMEP-9 of the measurements of the uranium isotope amount ratios and mass per particle are given in Table 2 and in the following sections.

The ζ score gives an indication of whether the uncertainty reported by a laboratory is consistent with the laboratory deviation from the reference value. An unsatisfactory ζ score may then depict an underestimation of the uncertainty reported by the laboratory or a large deviation to the reference value.

For the ζ scores, the standard uncertainty of the laboratory ($u(x_i)$) was calculated as the reported uncertainty divided by the coverage factor (k) provided by participants.

Although in the evaluation of NUSIMEP-9 scores (z and ζ) were used, the evaluation of the laboratory performance results based on the ζ score might be of more relevance to participants than the z score based on the proficiency assessment criteria. Indeed, standard deviations for proficiency assessment criteria σ_{pt} in NUSIMEP-9 were based on the ones from NUSIMEP-7, i.e. for smaller sized uranium particles and with similar isotope amount ratios but for test items with double deposition. These test items contained particles with two different isotopic compositions and were produced by aerosol deposition. Therefore the NUSIMEP-7 test items were closer to a real-life swipe sample, whereas NUSIMEP-9 test item is more of a quality control sample type.

The z and ζ scores can be interpreted according to ISO 13528 [24] as:

- satisfactory performance (green) for |score| ≤ 2,
- questionable performance (yellow) for 2 < |score| ≤ 3,
- unsatisfactory performance (red) for |score| > 3.

However, the IUPAC International Harmonised Protocol [23] suggests that participants may apply their own scoring settings and recalculate the scores if the purpose of their measurements is different.

In NUSIMEP-9, the standard deviations for proficiency assessment (σ_{pt}) of the determination of the three uranium isotope amount ratios are based on the performance assessment criteria used in NUSIMEP-7 to evaluate the measurements of the uranium isotope amount ratios, thereby reflecting IAEA safeguards requirements for the analysis of these measurands in environmental samples. The standard deviations for performance assessment criteria are therefore: $0.005 \cdot x_{pt}$ (0.5 %) for $n(^{235}U)/n(^{238}U)$, $0.025 \cdot x_{pt}$ (2.5 %) for $n(^{234}U)/n(^{238}U)$ and $0.5 \cdot x_{pt}$ (50 %) for $n(^{236}U)/n(^{238}U)$.

The individual laboratory performances for the analysis of uranium mass per particle were also evaluated by means of of z and ζ scores, with a standard deviation for proficiency assessment (σ_{pt}) for this measurand set as $0.2 \cdot x_{pt}$ (20 %) (i.e. of 0.716 pg). Since there is no existing knowledge or previous experience in the measurement of such measurand, there was no pre-defined value for the assessment criterion for the uranium mass per particle in NUSIMEP-9. Therefore, it was determined here based on the results obtained for the certification of the uranium mass per particle in IRMM-2329P.

6 NUSIMEP-9 Reported results

6.1 Participants in NUSIMEP-9

Twenty-eight participants (individual laboratories) registered to the NUSIMEP-9 round; two of them registered twice to report results obtained by two different techniques, yielding a possible reporting of 30 individual lab results.

At the end of the 1st reporting period (February 17th, 2019), not all laboratories reported their results and the deadline for reporting was extended till March 1st, 2019. At this date, 23 results were reported for the uranium isotopic amount ratios and 5 results for the uranium mass per particle.

Two participants could not report in time, since they experienced some technical/instrumentation issues. These two laboratories were then granted an additional two-month time to complete the analysis, and managed to report their results in time to be included in the NUSIMEP-9 report. Another participant could not report any results due to some technical/instrumentation issues. Furthermore, two participants informed that they would not report because they were unable to analyse the sample using their routine and validated analytical method as the uranium concentration of the test item was lower than expected. Finally, another participant could not measure the samples using gamma-ray spectrometry as planned, due to the low concentration, while another participant withdrew from reporting.

A total of 25 individual laboratory results were submitted from 23 different laboratories, since two laboratories reported two measurement results each using two different analytical techniques (Table 3). Twelve of the participating laboratories had already taken part in the previous campaigns organised by JRC-G.2 on particle analysis, NUSIMEP-6 and NUSIMEP-7. Fourteen laboratories belong to the IAEA NWAL network. All five Non-Proliferation-Treaty designated nuclear weapon states/countries reported results (Figure 2).

Table 3. Number of participants in NUSIMEP-9 per country

Country	Number of participants
Australia	1
Canada	1
China	1
Czech Republic	1
France	2
Republic of Korea	1
Russian Federation	1
Sweden	1
United Kingdom	1
United Nations	1
United States	12

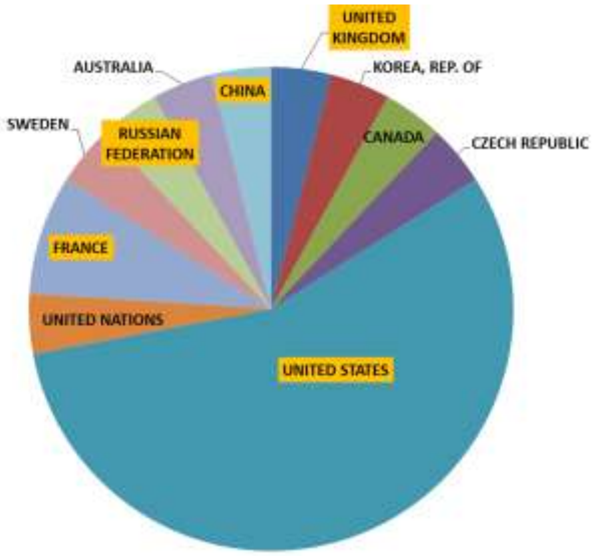

Figure 2. Percent participation in NUSIMEP-9 of the different countries; weapon states highlighting in yellow

6.2 General observations

Participants in NUSIMEP-9 received, for each registration, one certified test item consisting of a carbon planchet of 2.5 cm diameter loaded with some thousands monodisperse U_3O_8 particles of the micrometre-sized diameter of a single isotopic composition.

The laboratories participating in NUSIMEP-9 were asked to measure (compulsory) using their routine methods for particle analysis; and report the $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ isotope amount ratios of ten particles, which belong to the main particle population. Therefore, ten individual measurement results per isotope amount ratios had to be reported, without stating the measurement uncertainty. In addition, they had to report the average value of these ten measurement results and its associated uncertainty for each of the isotope amount ratios, stating the coverage factor (k) used to report the uncertainty.

By this mean, the average values of each isotope amount ratios could be directly compared to the reference values for the certified test item (Table 2), assessed during the certification of the candidate uranium particle reference material, IRMM-2329P.

Moreover, and for the first time in a proficiency testing round on particle analysis, participating laboratories were strongly encouraged to measure and report the uranium mass per particle in picogramme (pg, 10^{-12} g) by measuring at least ten particles of the main population. Since this kind of measurements is not commonly carried out for particle analysis in safeguards environmental sampling, laboratories were free to use the analytical technique and procedure of their choice. In this case, participants were asked to report the average value of the measurements of 10 different particles of the main population and the associated uncertainty stating the coverage factor (k) used.

Participants were also asked to complete a questionnaire to collect feedback, particularly in order to get an overview of the different laboratory expertise in the particle analysis field, their capabilities, to gain insights on the way the participants analysed the samples (Annex 9).

Finally, all the 25 participants' results were reported for the three uranium isotope amount ratios and 5 participants reported as well the uranium mass per particle.

6.3 Measurement results

The participants' measurement results were evaluated against the certified reference values (Table 2) as defined during the certification process of the candidate uranium particle reference material in compliance with ISO 17043 and ISO 13528 [14, 24].

The participants' results are presented in Figure 3, Figure 4 and Figure 5 for the uranium isotope amount ratios and in Figure 6 for the uranium mass per particle. All the results and the respective uncertainties with the coverage factors *k* are displayed as reported by the participants.

The Annex 10 to Annex 13 present the laboratories' reported values for the uranium isotope amount ratios and for the uranium mass per particle, with the analytical techniques and z and ζ (zeta) scores.

Moreover, full confidentiality is guaranteed with respect to the link between measurement results and the participants' identity, participants being represented by their respective lab code.

6.3.1 The uranium isotope amount ratios

In general, NUSIMEP-9 participants performed well in reporting the three uranium isotope amount ratios (in $mol{\cdot}mol^{-1}$) as measured in the Low-Enriched Uranium (LEU) particles and averaged for 10 measured particles.

Participants reported most of the major $n(^{235}U)/n(^{238}U)$ ratios with deviations from the reference value of less than 0.2 % (Figure 3, Annex 10). Most of the $n(^{235}U)/n(^{238}U)$ ratios being within ±1 % deviation from the NUSIMEP-9 reference value, with a proficiency assessment criterion, corresponding here to $0.005{\cdot}x_{pt}$.

Most of the $n(^{234}U)/n(^{238}U)$ ratios were reported within 1.4 % of the reference value (Figure 4, Annex 11) and within the limits based on the proficiency assessment criterion corresponding here to $0.025{\cdot}x_{pt}$.

Most of the minor $n(^{236}U)/n(^{238}U)$ amount ratios were reported with deviations of less than 5 % from the reference value (Figure 5, Annex 12). All laboratories, except for one, reported values well within the limits set for the proficiency assessment criterion for the $n(^{236}U)/n(^{238}U)$, corresponding here to $0.5{\cdot}x_{pt}$. Also, it is interesting to note that a majority of them showed positive deviations, i.e. reported higher ratio values than the reference value.

As can be seen in the Figure 3 to Figure 5, most of the participants reported satisfactory results for the uranium isotope amount ratios (red dashed lines in the Figures) in the NUSIMEP-9 test item.

These observations can be explained by the fact that the NUSIMEP-9 test items are more of a quality control sample type than the previous NUSIMEP-7 test items, with a bigger particle size (1.5 µm diameter size compared to 0.7 µm diameter size for NUSIMEP-7 test item). Moreover, the abundance of ^{236}U in the NUSIMEP-9 test items was similar to the NUSIMEP-7 test items with double deposition (ca. 30 ppm).

Therefore, the standard deviation for the NUSIMEP-9 proficiency assessment of 50 % for the $n(^{236}U)/n(^{238}U)$ isotope amount ratio appears far too large for this measurand in the NUSIMEP-9 PT round, compared to the robust standard deviation (s^* of 3.3 %.) for all the reported laboratory results for this measurand as calculated with the Algorithm A of ISO 13528

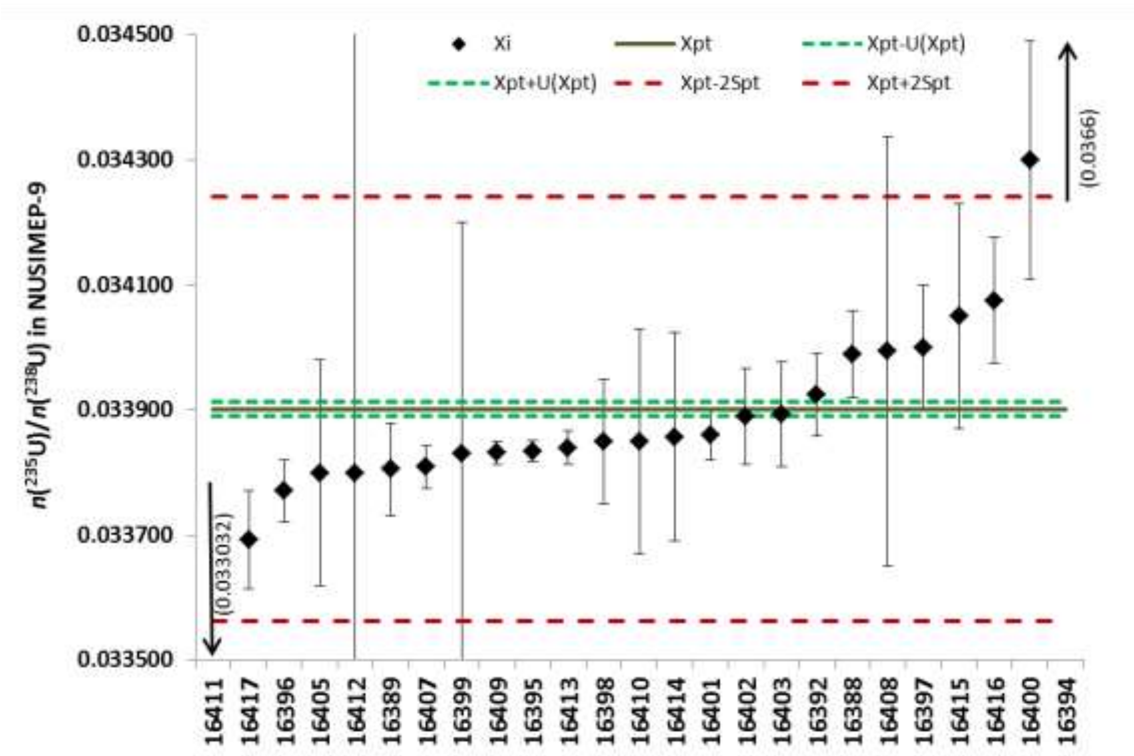

Figure 3. The $n(^{235}U)/n(^{238}U)$ isotope amount ratios as reported by participants (x_i, $U(x_i)$) and compared to the reference value of $x_{pt} \pm U(x_{pt})$ = 0.033902 ± 0.000012 (k =2) mol·mol^{-1} (green line and dashed green lines; dashed red lines corresponding to $x_{pt} \pm 2\,\sigma_{pt}$)

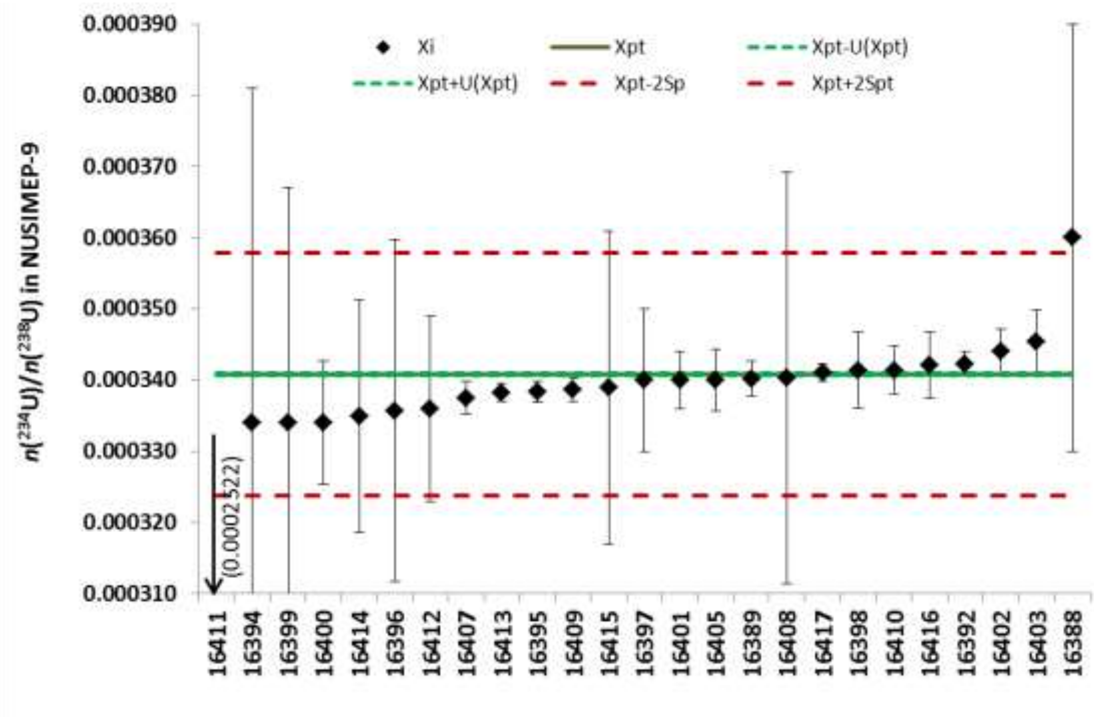

Figure 4. The $n(^{234}U)/n(^{238}U)$ isotope amount ratios as reported by participants (x_i, $U(x_i)$) and compared to the reference value of $x_{pt} \pm U(x_{pt})$ = 0.00034083 ±0.00000019, (k =2) mol·mol^{-1} (green line and dashed green lines; dashed red lines corresponding to $x_{pt} \pm 2\,\sigma_{pt}$)

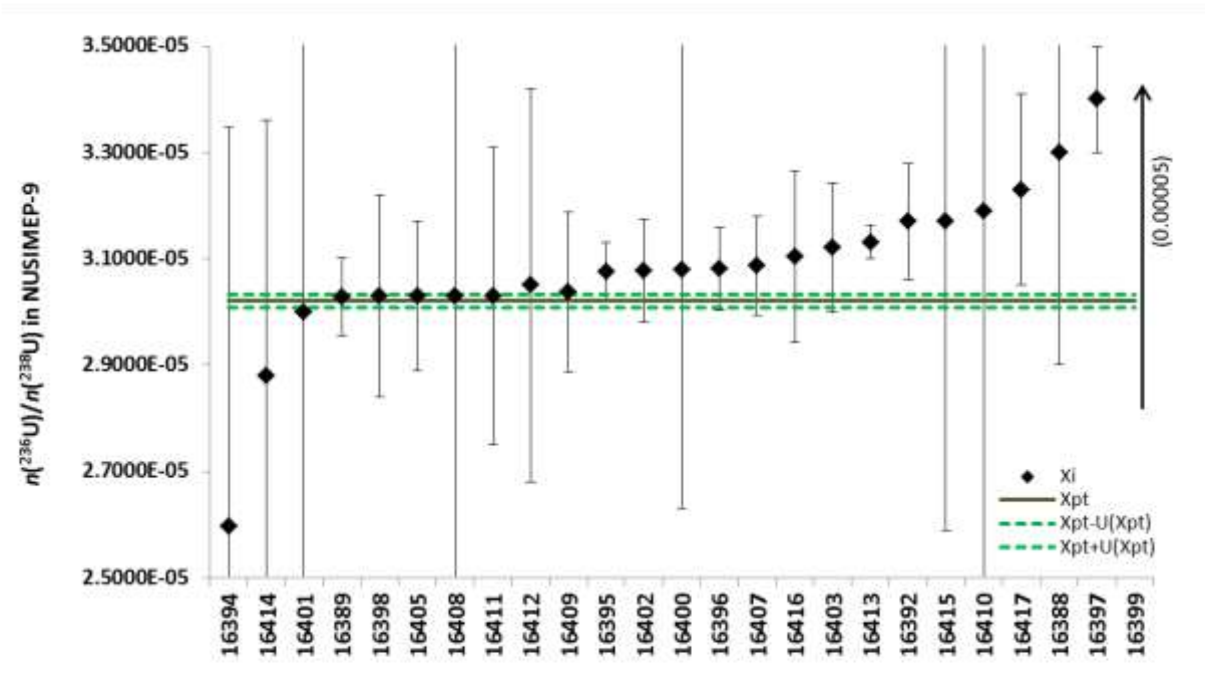

Figure 5. The $n(^{236}U)/n(^{238}U)$ isotope amount ratios as reported by participants (x_i, $U(x_i)$) and compared to the reference value of $x_{pt} \pm U(x_{pt})$ = 0.00003021 ±0.00000012, (k =2) mol·mol^{-1} (green line and dashed green lines; dashed red lines corresponding to $x_{pt} \pm 2\,\sigma_{pt}$)

6.3.2 The uranium mass per particle

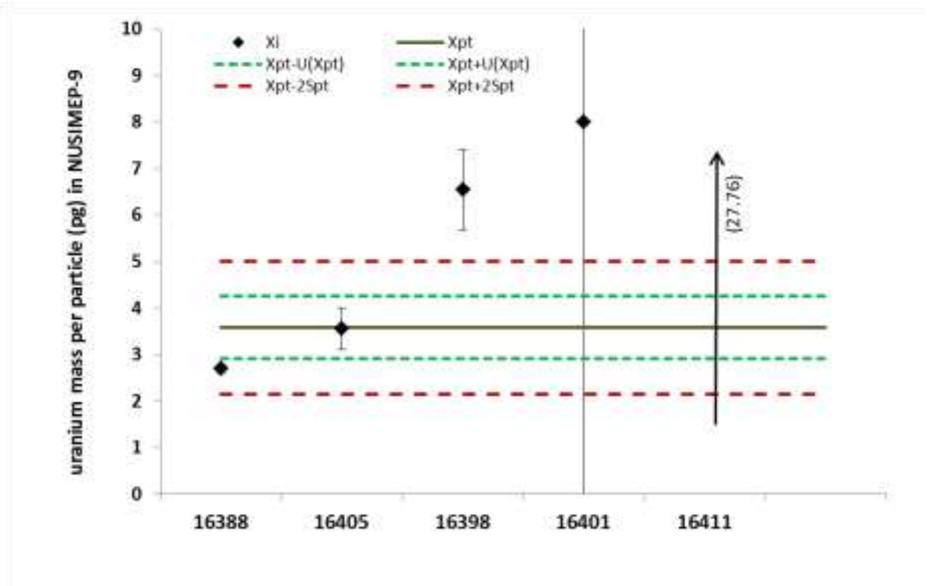

Figure 6. The uranium mass per particle (in pg) as reported by participants (x_i, $U(x_i)$) and compared to the reference value of $x_{pt} \pm U(x_{pt})$ = 3.58 ±0.67 pg, (k =2) (green line and dashed green lines; dashed red lines corresponding to $x_{pt} \pm 2\,\sigma_{pt}$)

Participants in NUSIMEP-9 could report the uranium mass per particle (in pg), although this was not compulsory and was likely to be challenging for most of the participating laboratories, since not commonly measured in routine analyses of environmental samples. Nevertheless, five laboratories reported this measurand (Figure 6, Annex 13). The spread among these five reported values is quite large, with one participant reporting a uranium mass per particle largely overestimated, but also one with a reported value with only -0.6 % deviation from the reference value for the uranium mass per particle.

6.4 Evaluation of the laboratories' performances

Overall, the participants' performances in reporting the three uranium isotope amount ratios as measured in NUSIMEP-9 test items were satisfactory (Table 4). Independently of the chosen technique (FT-TIMS, LG-SIMS, Nano-SIMS, SIMS or various ICP-MS), participants managed to successfully measure the major and minor uranium isotope amount ratios, while reporting as well uncertainties in the range of those expected for such measurements and that are of the same order as the expanded uncertainty on the reference value.

Moreover, it is interesting to note that participants' performances are even more satisfactory for the minor isotope ratios than for the major $n(^{235}U)/n(^{238}U)$ isotope amount ratio, for which more variability between laboratory results is observed (Table 4).

Participants' performances for the determination of the uranium mass per particle are acceptable (Table 4), especially considering the challenge that this measurement represents for the laboratories, since it is not part of the regular laboratory procedure and analysis. Several mass spectrometry techniques have been used to determine the mass of uranium per particle, although a preliminary analysis using SEM may have been used in some cases.

Table 4. Overview of scores for participants' reported results for $n(^{235}U)/n(^{238}U)$, $n(^{234}U)/n(^{238}U)$, $n(^{236}U)/n(^{238}U)$ and uranium mass per particle with S(satisfactory), Q(questionable) and U (unsatisfactory)

		z score			**ζ score**			**z and ζ scores**
	n[(1)]	**S**	**Q**	**U**	**S**	**Q**	**U**	**S**
$n(^{235}U)/n(^{238}U)$	25	88 %	4 %	8 %	56 %	16 %	28 %	52 %
$n(^{234}U)/n(^{238}U)$	25	92 %	4 %	4 %	84 %	12 %	4 %	80 %
$n(^{236}U)/n(^{238}U)$	25	100 %	0 %	0 %	88 %	4 %	8 %	88 %
Uranium mass per particle	5	40 %	0 %	60 %	40 %	20 %	40 %	20 %

(1) n is the number of reported results for this measurand

7 Further information extracted from the questionnaire

In addition to the reporting of results, participants in NUSIMEP-9 were asked to answer several questions (see Annex 9) related to the analytical and measurement protocols applied for the analysis of the uranium particles in the test item. Some of the participants' replies to the questionnaire are discussed in Sections 7.1 to 7.5.

7.1 A representative study

Among the 23 participants in NUSIMEP-9, more than half of the laboratories are IAEA NWALs.

A majority of the participants indicated that their main missions are to do research and development and carry out measurements in the field of nuclear forensics or/and for fissile material control or safeguards, while also performing analyses in environmental sciences (Figure 7).

As mentioned previously, most of the participating laboratories have already participated in previous NUSIMEP proficiency testing rounds and participate as well in other exercises as the IAEA round robins (e.g. with analysis of trace elements in Uranium Ore Concentrates), in the Table Exercises (CMX) organised by the International Technical Working Group in Nuclear Forensics (ITWG) or in customer specific Quality Control programmes.

Most of the participants, declared to have experience in performing analysis of the uranium isotopic composition of micro-particles (Table 5), since it also includes the IAEA NWALs. Therefore, all the labs, except for one, treated the NUSIMEP-9 test item applying their routine analytical procedure for this sample type.

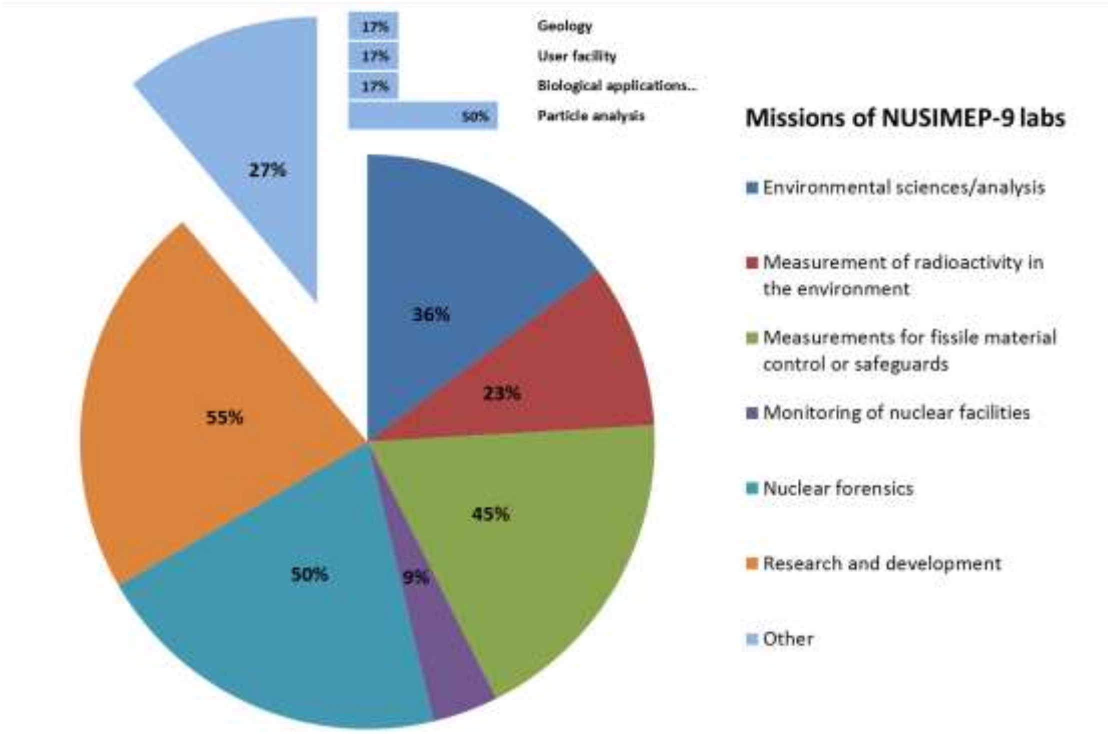

Figure 7. Missions of the participating laboratories in NUSIMEP-9

Table 5. Laboratories' experience in measurements of uranium isotopic composition in particles and number of this type of measurements carried out by the experienced laboratories per year

Not experienced	9 % [1]		
Less experienced	18 %		
Experienced	73%	0-50 measurements/year	44 % [2]
		50-100 measurements/year	19 %
		>100 measurements/year	25 %

[1] Percentage of laboratories among the total NUSIMEP-9 participants

[2] Percentage of laboratories among the NUSIMEP-9 participants who replied to this question

Consequently, this confirms that NUSIMEP-9 has targeted the appropriate community of laboratories in the field of particle analysis and was designed for assessing the current laboratories' capabilities in this field.

7.2 Method of analysis

The participants in NUSIMEP-9 reported results for the uranium isotope amount ratios using a wide range of techniques, but the main applied technique was based on the principle of Secondary Ion Mass Spectrometry, with LG-SIMS being broadly used (43 % of the participants), then nanoSIMS and traditional SIMS (each used by 13 % of the laboratories). The second technique applied was FT-TIMS, being used by 22 % of the participants. A few participants used techniques based on ICP-MS or a combination of techniques.

The participant's results for the uranium isotope amount ratios and uranium mass per particle with respect to the analytical techniques used are given in Annex 10, Annex 11, Annex 12 and Annex 13.

In Annex 10, it can be seen that almost 50 % of the reported results using the LG-SIMS technique are significantly lower than the reference value for the $n(^{235}U)/n(^{238}U)$ ratio. Apart from this observation, the laboratories' performances in analysing these measurands were found to be quite independent from the technique applied.

7.3 Quality system and use of standard reference materials

Three participants declared being authorised (they have a mandate) for the analysis of uranium isotope amount ratios in micro-particles, five laboratories declared being accredited ISO 17025 for this kind of analysis and two laboratories are certified ISO 9001.

All participants routinely use (certified) reference materials, mostly for mass bias correction and instrument calibration. The reference materials used by the participants for the analysis of the NUSIMEP-9 test item are given in Annex 14, as well as the methods used to correct for mass bias during the measurements (since (C)RMs are often used for such corrections).

7.4 Determination of measurement uncertainty

All of the participants in NUSIMEP-9 reported measurement uncertainties for the average result of each of the three uranium isotope amount ratios and the uranium mass per particle, giving as well the coverage factor (k varying here from k = 1, 1.96 or extended value, 2, 2.1 and 2.26).

However, a bit less than half of the NUSIMEP-9 participants stated that they calculated these uncertainties according to the ISO/IEC Guide 98-3:2008 (GUM) [21], the other half indicated that they evaluated their measurement uncertainties by, for instance, using similar approaches to the GUM, pooling the variances of replicates or by using the standard deviation from the mean of the number of measurements.

The major contributors to the final reported uncertainties, independently of the analytical technique used, were mainly linked to: counting/measurement statistics, mass fractionation or mass bias, hydride correction and dead time correction.

7.5 Determination of uranium mass

Most of the laboratories do not perform routinely such kind of measurements, although it is of particular interest to monitor the sensitivity, in particular ionization efficiency, of particle measurement techniques. Therefore, most of the laboratories do not have yet the capabilities or validated methods available to carry out such analysis.

Consequently, the few laboratories, which carried out the challenging analysis and measurements of the uranium mass per particle, had to develop or adapt an analytical method to determine the uranium mass in the particles of the test item. For this, they used a variety of methods; performing the analysis mostly with SIMS or ICP-MS after external calibration of the instruments and using available (C)RMs for mass bias corrections (see Table 6). One lab reported to have performed a particle transfer, prior to the analysis, using micro-manipulation. All the laboratories stated to have reported the final uncertainty on the uranium mass per particle according to the ISO/IEC Guide 98-3:2008 (GUM) [21] and provided the associated coverage factor (k). The major contribution to the uncertainty came from the counting/measurement statistics and also the determination of the exact particle diameter when using SEM.

Table 6. List of the (C)RMs used by laboratories for the analysis of the uranium mass per particle in NUSIMEP-9

Lab codes	(C)RMs used
16388	NIST U030 for mass bias, IRMM040a for mass measurement
16398	no CRMs, use of UO_2 particles produced by ICSM
16401	UO_2 material gained during CMX-5
16405	No CRMs. Microspheres from U020a batch reported by Ranebo et al were used for calibration.
16411	CRM 010

8 Feedback and Outlook on future NUSIMEP proficiency testing rounds

Some participants reported that the number of particles per planchet/disk and their dispersion on the carbon planchet were appropriate for individual particle analysis using SIMS or FT-TIMS.

A few participants reported to have observed some uranium halo (of a few micrometres) around the particles. This observation shall be further investigated during the stability post-monitoring of the uranium particles in the context of the IRMM-2329P certification.

Some participants reported as well the presence of some silica debris. These supposedly come from some steps during the particle production process.

Finally, a large number of participants expressed their surprise at the lack of possibility to report uncertainty on the individual measurement results for the isotope amount ratios. Indeed, unlike the reporting during NUSIMEP-7, the new online reporting tool interface (JRC MILC) does not provide anymore the possibility to report uncertainty on the individual results but solely on the average. This change was largely motivated by the shared use of the JRC ILC online reporting tool with communities from non-nuclear fields (Food and Feed, Environmental, etc) for which only the average of the measurement results and its uncertainty are usually reported to customers.

All laboratories expressed interest in participating in future NUSIMEP proficiency testing rounds on micro-particle analysis. A majority of the participants would like to participate in future proficiency testing rounds involving the analysis of micro-particles of uranium with mixtures of single and multi-isotopic compositions. A large number of candidates (ca. 59 %) would like to have test items with mono- or poly-disperse particles of plutonium or mixed U/Pu in a wide range of ratios (e.g. from 1:1 to 1:100). Less than half of the laboratories expressed interest in analysing mixed U/Th particles in the context of a future NUSIMEP proficiency testing round. Finally, only a couple of laboratories expressed interest in participating in a proficiency testing round on mixed U/Ln particles.

Most of the participants would prefer to continue to receive test items of particles distributed on a glass-like carbon disk (with planchets of 25 mm diameter or even smaller), which appears to be an appropriate substrate for a wide range of techniques. Half of the participants expressed interest in receiving as well cotton swipe test items. A few laboratories mentioned that they would be interested in analysing particles distributed on silicon disks/wafers.

The outcome of the NUSIMEP-9 proficiency testing round will be discussed in more detail during the IAEA technical meeting on particle analysis of environmental samples in nuclear safeguards that will be held in November (19-22) 2019 in Vienna (Austria).

9 Conclusions

NUSIMEP-9 took place almost seven years after the last proficiency testing round of this kind (NUSIMEP-7 [6]). However, unlike the previous NUSIMEP campaigns, the uranium particles of the NUSIMEP-9 test item were produced in FZJ using the Vibrating Orifice Aerosol Generator resulting in monodisperse particles. For that reason, the produced U_3O_8 particles were larger than the ones produced in the past by means of aerosol deposition (1.5 µm diameter size for NUSIMEP-9 compared to 0.7 µm diameter size for NUSIMEP-7) and have a ^{236}U abundance of ca. 30 ppm, i.e. similar to the second enrichment of the NUSIMEP-7 double deposition test items.

During the last seven years, laboratories involved in the analysis of particles, in particular in the context of safeguards analyses of environmental samples have further developed validated and accurate methods and techniques to perform measurements of this kind, notably using LG-SIMS. Therefore, NUSIMEP-9 was a good way to assess the technical levels and capabilities of the laboratories and advances in the field of particle analysis, especially with respect to ISO 17025 [20].

In general, laboratory's performances in measuring and reporting major and minor uranium isotope amount ratios in the NUSIMEP-9 particles were satisfactory (with 52 %, 80 % and 88% satisfactory performances for the $n(^{235}U)/n(^{238}U)$, $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ ratios respectively). This confirms that, independently of the technique used (LG SIMS, ICP-MS, FT-TIMS), the uranium test items for NUSIMEP-9 were fit-for-purpose.

However, these excellent laboratory's performances (the satisfying z scores) of most of the NUSIMEP-9 participants may indicate that the proficiency assessment criteria applied in NUSIMEP-9 are not appropriate. Indeed, the proficiency assessment criteria applied in this project were based on the NUSIMEP-7 "real-life" particles that were produced by simulating ambient conditions in a facility and not for better quality samples as in NUSIMEP-9.

For the future, it is recommended to define specific proficiency assessment criteria appropriate for specific PT items/materials.

Additionally, NUSIMEP-9 offered for the first time to the participants the possibility to determine the uranium mass per particle using their technique of choice. A few participants undertook this challenging analysis and despite the large spread in participants' results, the overall performance is satisfactory, with one expert lab even confirming the reference value for the uranium mass per particle in NUSIMEP-9.

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List of abbreviations and definitions

Abbreviations

AMS	Accelerator Mass Spectrometry
ANOVA	Analysis of Variance
CMX	Collaborative Materials Exercise
CRM	Certified Reference Material
EC	European Commission
ESARDA	European Safeguards Research and Development Association
FZJ	Forschungszentrum Jülich
(FT-)TIMS	(Fission Track) Thermal Ionisation Mass Spectrometry
GUM	Guide to the Expression of Uncertainty in Measurement
HPS	Health and Physics Sector
(HR)-ICP-MS	(High-resolution) Inductively Coupled Plasma Mass Spectrometry
IAEA	International Atomic Energy Agency
ID	Isotope Dilution
ILC	Inter-Laboratory Comparison
ISO	International Organization for Standardization
ITWG	International Technical Working Group in Nuclear Forensics
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint research Centre
LEU	Low enriched Uranium
(LA)-ICP-MS	(Laser Ablation) Inductively Coupled Plasma Mass Spectrometry
(LG)-SIMS	(Large Geometry) Secondary Ion Mass Spectrometry
(MC)-ICP-MS	(Multi-Collector) Inductively Coupled Plasma Mass Spectrometry
MTE	Modified Total Evaporation
NBL	New Brunswick Laboratory
NPT	Treaty on the Non-Proliferation of Nuclear Weapons
NUSIMEP	Nuclear Signatures Interlaboratory Measurement Evaluation Programme
NWAL	Network of Analytical Laboratories
PT	Proficiency Test
RM	Reference Material
SEM(-EDX)	Scanning electron Microscopy (Energy Dispersive X-ray Spectroscopy)
SGAS	Safeguards Analytical Services
UOC	Uranium Ore Concentrate
VOAG	Vibrating Orifice Aerosol Generator

Notations

k	Coverage factor
s^*	Robust standard deviation (a standard deviation calculated by a robust algorithm)
s_s	between-sample standard deviation

$U(x_{pt})$	Expanded uncertainty of the test item reference value
U_{hom}	Uncertainty of (between-sample) homogeneity
u^{*}_{bb}	Minimum uncertainty contribution to homogeneity
$U(x_i)$	Expanded uncertainty as reported by the participating laboratory
x_i	Value(s) reported by the participating laboratory
x_{pt}	Reference value(s) of the test item
$\overline{y}_1$	Average of measurand values (here uranium mass per particle) from homogeneity study
$\overline{y}_2$	Average of measurand values (here uranium mass per particle) from stability study

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Annexes

Annex 1. NUSIMEP-9 Announcement letter

EUROPEAN COMMISSION
DG JOINT RESEARCH CENTRE
Directorate G – Nuclear Safety & Security
Unit G.2 - Standards for Nuclear Safety, Security & Safeguards

Geel, 7 September 2018
Ares(2018)4595317

The Nuclear Signatures Inter-laboratory Measurement Evaluation Programme

NUSIMEP-9: Uranium isotope amount ratios and uranium mass in uranium micro-particles

NUSIMEP is an external quality control programme organised by the European Commission - Joint Research Centre Directorate G – Nuclear Safety & Security, Unit G.2 - Standards for Nuclear Safety, Security & Safeguards (JRC-GEEL, former IRMM) with the goal of providing materials for measurements of trace amounts of nuclear materials in environmental matrices.

Measurements of the uranium and plutonium isotopic ratios in small amounts, such as typically found in environmental samples, are required for nuclear safeguards, for the control of environmental contamination and for the detection of nuclear proliferation. The two last NUSIMEP campaigns of measurements of isotopic ratios in micrometre-sized uranium particles were NUSIMEP-6 and NUSIMEP-7, in which the participants measured the uranium isotope amount ratios in hydrolysed UF_6 particles with a wide range of particle sizes.

We would like to announce the forthcoming NUSIMEP-9 inter-laboratory comparison: "Uranium isotope amount ratios and uranium mass in uranium microparticles" and invite laboratories to participate.

Participating laboratories in NUSIMEP-9 will receive one certified test item of U_3O_8 particles with an approximate diameter of 1 µm deposited on a carbon planchet of 2.5 cm diameter. The certified test item contains some thousand microparticles of a single isotopic composition.

The participating laboratories will be asked to measure and report the $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ isotope amount ratios (compulsory) of ten particles, which belong to the main particle population. The participants are asked to use their routine analytical procedures.

Additionally, the participating laboratories are strongly encouraged to measure and report the uranium mass per particle by measuring at least ten particles (optional).

The participants' measurement results will be evaluated against the certified reference values in accordance to ISO 17043 and ISO 13528. Full confidentiality is guaranteed with respect to the link between measurement results and the participants' identity.

Retieseweg 111, B-2440 Geel - Belgium.
Telephone: +32-(0)14- 571-681.
Fax: +32-(0)14-571-862.
E-mail: JRC-NUSIMEP@ec.europa.eu

1

The participation fee is € 600 (including sample dispatch), which has to be paid upon receipt of the certified test item. Due to the nature of this comparison only a limited number of items (units) are available. Test items will be allocated to participants in order of registration until the stock of NUSIMEP-9 items is exhausted.

The NUSIMEP-9 test items will be shipped from the EC-JRC-GEEL to the participants. We ask each participant to provide the following information:

1) Contact person (full name, e-mail address and telephone number)

5) Delivery address (not a PO box, but a real address)

Please register electronically for this inter-laboratory comparison using the following link:

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=2061

Once you have submitted your registration electronically, please follow the procedure indicated: a) print your registration form; b) sign it; and c) fax or email it to us. Your received fax/email is the confirmation of your participation.

The **deadline for registration** is **19 October 2018**.

Samples will be sent to participants in October-November 2018.

The deadline for submission of results is 17 February 2019.

Please do not hesitate to contact us in case you need more information.

Yours sincerely,

Célia Venchiarutti
NUSIMEP-9 Co-ordinator

Stephan Richter
NUSIMEP-9 Co-ordinator

Annex 2. NUSIMEP-9 Example of confirmation of registration

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

JRC Geel

Registration for participation in

NUSIMEP-9

Person details

Title
First Name
Surname
Gender
Telephone
Extension
Fax
E-mail

Organisation details

Organisation
Organisation Department
Organisation Address
Zip code
City
Country
Telephone
Extension
Fax
E-mail

Please could you check your registration details as inserted into our database, on your approval please sign and return this registration form immediately to JRC Geel. Only on receipt of the signed registration form is your registration definitive.

In case more than one registration form is received from your laboratory, different registration names will count as multiple registrations.

Celia VENCHIARUTTI Fax: +32-14-571 863
JRC Geel, Retieseweg 111, B-2440 Geel, Belgium

Signature/Company stamp:

Date:

Annex 3. Email announcing shipment of test items to participants in NUSIMEP-9

Ref. Ares(2018)5489830 - 25/10/2018

EUROPEAN COMMISSION
DG JOINT RESEARCH CENTRE
Directorate G – Nuclear Safety & Security
Unit G.2 - Standards for Nuclear Safety, Security & Safeguards

NUSIMEP

Dear «title» «surname»,

You were registered successfully for NUSIMEP-9, the "Nuclear Signatures Inter-laboratory Measurement Evaluation Programme: Uranium isotope amount ratios and uranium mass in uranium microparticles" and we are pleased to inform you that your NUSIMEP-9 certified test item has been sent to you and should be delivered to your laboratory at the address provided during your registration.

If you wish to track this shipment, you can check the delivery on the website of DHL (http://www.dhl.be) using the following tracking number: «DHL»

The samples consist of a carbon planchet (vitreous carbon disk) loaded with uranium particles of the micron diameter size, with undisclosed isotope amount ratio values $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ and an undisclosed uranium mass per particle.
We remind you that measurement of the isotope amount ratios $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ are obligatory. We strongly encourage you to carry out the analysis of the uranium mass per particle, but remind you that this measurement is optional.

Measurements are to be performed according to your routine analytical procedures, if applicable.
Your measurement results will be evaluated against the certified reference values. Full confidentiality is guaranteed with respect to the link between results and the participants' identity.

To login to the result reporting page you need a participant key given in the accompanying letter that will be enclosed with the test item and your email address (as provided in the registration form). Please read the accompanying letter carefully and do keep your unique participant key («partKey») that is given in this accompanying letter. This is your password to login and report your results.
We are also sending you guidelines to guide you through the online reporting of your results.

Please be aware of the reporting deadline, which is **17 February 2019**.

Upon receipt of the test item, you will have to complete and return to us your duly completed form "Confirmation of receipt". Upon receipt of this confirmation, we will send you and your organisation the invoice for the participation fee.

We wish you success with your measurements and do not hesitate to contact us if you have any questions or problems.

Kind regards,

Célia Venchiarutti
NUSIMEP-9 Co-ordinator

Stephan Richter
NUSIMEP-9 Co-ordinator

Retieseweg 111, B-2440 Geel - Belgium
Telephone: +32-(0)14-571-681
Fax: +32-(0)14-571-862
E-mail: JRC-NUSIMEP@ec.europa.eu

Annex 4. NUSIMEP-9 Accompanying letter

Ref. Ares(2018)5489479 - 25/10/2018

EUROPEAN COMMISSION
DG JOINT RESEARCH CENTRE
Directorate G – Nuclear Safety & Security
Unit G.2 - Standards for Nuclear Safety, Security & Safeguards

NUSIMEP

Geel, 25 October 2018

«title» «firstname» «surname»
«organisation»
«department»
«address1»
«address2»
«address3»
«address4»
«zip» «town»
«country»

The Nuclear Signatures Inter-laboratory Measurement Evaluation Programme
NUSIMEP-9: Uranium isotope amount ratios and uranium mass in uranium microparticles

Dear «title» «surname»,

Thank you very much for your participation in NUSIMEP-9.

Together with this letter we are sending to you the NUSIMEP-9 certified test item for particle analysis (carbon planchet loaded with uranium micro-particles of single isotopic composition) as specified in the NUSIMEP-9 announcement:

https://ec.europa.eu/jrc/en/interlaboratory-comparisons/NUSIMEP

Please check whether the test item remained undamaged during transport. Then sign the "Confirmation of receipt" form and return it to us by email or fax (+32 14 571 862).

Participants are reminded that they are responsible for "the sample disposal and costs involved".

The particles are separated by at least a few micrometres on average, although small agglomerates may also be present on the carbon planchet. It is recommended to store the planchet in its protective case and in a dry environment. Special caution as to the correct side on which the particles are deposited when placing the planchet back into its case

Participants in NUSIMEP-9 are asked to apply the same measurement procedures as used in routine sample analysis of this kind, if applicable.

The uranium isotope amount ratios have to be measured and reported for ten different particles belonging to the main particle population. Also, the averages and their associated uncertainties have to be reported. Measurement of the isotope amount ratios $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ is obligatory.

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1

We remind you that in addition to the uranium isotope amount ratios, participants have the possibility to measure and report the uranium mass per particle (optional). For the analysis of the uranium mass per particle, at least ten particles should be analysed; only the mean value will need to be reported.

If your laboratory has an established method for the quantification of the uranium mass per particle, we would strongly encourage you to perform the analysis according to your established method. If your laboratory does not have an established method for the determination of the uranium mass per particle, we would like to refer you to the following publications, describing various methods to quantify the uranium mass per particle:

- Ranebo *et al.*, J Anal Atom Spectrom 24 (2009) 277-287. doi: 10.1039/b810474c
- Kraiem *et al.*, Anal Chim Acta 748 (2012) 27-44. doi: 10.1016/l.aca.2012.08.030

To report your results, please go to the reporting webpage at:

https://web.jrc.ec.europa.eu/ilcReportingWeb

To login to this webpage, you will need the following personal password key:

«partKey»

The result reporting page will be active from **1st December 2018** on till the **17 February 2019 midnight (24:00 GMT)**.

Enclosed with this letter, we are sending you Guidelines to guide you through the reporting procedure. As you will notice, you will have to complete the online questionnaire in order to submit your results using the online reporting tool.

Do not forget to submit and confirm always when required. Check your results carefully for any errors before submission, since this is your definitive confirmation.

Directly after submitting your results and filling out the questionnaire online, you will be prompted to print the completed report (pdf document). Please do so, sign the paper version and return it by e-mail (JRC-NUSIMEP@ec.europa.eu) or fax (+32 14 571 862).

The deadline for submission of results is 17 February 2019.

Please keep in mind that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies and analysts alike.

Please do not hesitate to contact us in case you need more information.

Yours sincerely,

Stephan Richter

Célia Venchiarutti
NUSIMEP-9 Co-ordinator

Stephan Richter
NUSIMEP-9 Co-ordinator

Annex 5. NUSIMEP-9 form for confirmation of receipt

Ref. Ares(2018)5308900 - 16/10/2018

EUROPEAN COMMISSION
DG JOINT RESEARCH CENTRE
Directorate G – Nuclear Safety & Security
Unit G.2 - Standards for Nuclear Safety, Security & Safeguards

NUSIMEP

Geel, 16 October 2018
ARES REF

«title» «firstname» «surname»
«organisation»
«department»
«address1»
«address2»
«address3»
«address4»
«zip» «town»
«country»

NUSIMEP-9

Confirmation of receipt of the test item A

Please return this form as soon as possible upon receipt of your sample(s).
This confirms that the sample package arrived.
In case the package is damaged, please state this on this form and contact us immediately.

SAMPLE CODE(S) ....-................

REMARKS ....

....

....

DATE OF PACKAGE ARIVAL ....

SIGNATURE ....

Please return this form to:

Célia Venchiarutti (NUSIMEP-9 Co-ordinator)

E-mail: JRC-NUSIMEP@ec.europa.eu

Fax: +32 14 571 862

European Commission
Joint Research Centre - JRC
Directorate G – Nuclear Safety & Security
Unit G.2 - Standards for Nuclear Safety, Security & Safeguards
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Fax: +32-(0)14-571-862.
E-mail: JRC-NUSIMEP@ec.europa.eu

Annex 6. NUSIMEP-9 Guidelines

Ref. Ares(2018)5489269 - 25/10/2018

EUROPEAN COMMISSION
DG JOINT RESEARCH CENTRE
Directorate G – Nuclear Safety & Security
Unit G.2 - Standards for Nuclear Safety, Security & Safeguards

NUSIMEP

NUSIMEP-9: Uranium isotope amount ratios and uranium mass in uranium microparticles

Participant's guidelines for the reporting of results via the online reporting tool

Retieseweg 111, B-2440 Geel - Belgium
Telephone: +32-(0)14- 571-881
Fax: +32-(0)14-571-862
E-mail: JRC-NUSIMEP@ec.europa.eu
https://ec.europa.eu/jrc/en/interlaboratory-comparisons/NUSIMEP

Sample mailing content list

The sample shipment contains the following pieces:

- One certified test item for analysis, in the form of a carbon planchet (vitreous carbon disks) containing uranium micro-particles. Please see the accompanying letter for more information regarding the analysis;

- An accompanying letter to the sample, including the participation key. The **participation key is a unique code and is required as password** to access the online reporting webpage and enter your results (see following section);

- A form of "confirmation of receipt", please return it to the NUSIMEP-9 co-ordinator upon receipt of the sample, duly completed and signed.

Reporting of results

The online reporting tool to submit the measurement results can be found at:

https://web.jrc.ec.europa.eu/ilcReportingWeb

Figure 1 Login to online reporting tool with your unique participant key

To log in, please provide as password your participation key (given in the accompanying letter) and use the email address that you gave in your registration form.

Once logged in, you are automatically redirected to the main menu of the ILC reporting tool, from where you can enter your results, fill in the questionnaire and preview the results and questionnaire.

Figure 2 Result submission page

1. Result submission

There are three options to submit your measurement results:

- Per measurand ("*Report by measurand*"),
- All results at once ("*Report for ALL measurands at once*"),
- Via Microsoft Excel ("*Report values through Excel*").

When selecting the "*Report by measurand*" option, the following page appears, where the sample/measurand needs to be selected using the drop-down menu at the top of the page. Please note that the entered data should be saved before changing the measurand.

Figure 3: Submission of results by measurand

- For each sample/measurand, a table appears with the following columns:

Sample: the selected measurand for which to enter the data together with the type of measurand (*Isotopic ratio* for the uranium isotope amount ratios and *Concentration* for the uranium mass per particle).

Measurement: the description of the measurement results, either *Measurement#xx* (for each of the ten single particle measurements) or *Average*, which should represent the mean value based on all measurements performed for the given sample/measurand.

Note that the average/mean isotope amount ratio has to be entered twice: as mean together with the measurement results for the ten particles and as *Isotope ratios average*. Only this latter will be used for the data evaluation.

Reference Date: not applicable for NUSIMEP-9.

Result: the results can be entered in three ways, which can be chosen using the select tool. Please note that all numerical values need to be entered using a **dot (".") as decimal separator** and no thousands separator is to be used.

- "="; as a given value with uncertainty and coverage factor;
- ">"; as a lower limit, no uncertainty/coverage factor can be entered;
- "<"; as an upper limit, no uncertainty/coverage factor can be entered.

Unit: the unit corresponding to the reported value. For the isotope amount ratios, this is always "*Ratio*", for the uranium mass per particle, this is always "*pg*" (picogram, 10^{-12} g).

Uncert. Value: the absolute expanded uncertainty of the entered result (only in case of given values, i.e. "=" in the select tool), either as ratio (for the isotope ratios) or in picogram (for the uranium mass per particle).

Coverage factor k: the coverage factor at which the expanded uncertainty value (previous field) is reported (only in case of given values, i.e. "=" in the select tool).

Technique: the technique which was used to obtain the measurement results. Please select one from the drop-down list. If the used technique is not in the list, select "*Other*" and specify the applied technique. The technique only needs to be provided for the average of the results. The other fields can be left empty.

To save your results, please press the "*Save page results*" button at the bottom of the page to save the page as displayed. **Save the results before changing to a different measurand**.

- By selecting the "*Report for ALL measurands at once*" from the main menu, the results for all samples and all measurands can be entered on a single page, in a similar way as described previously. Note that measurands marked with an asterix are mandatory.
- The measurement results can also be submitted using a pre-defined Excel worksheet using the "*Report values through Excel*" option. After selecting this option, please download and save the provided Excel file to a known location before opening. The measurement results should be entered into the white fields, where the measurand can be found in column C, the sample in column D and the measurement replicate in column E. Please enter all data as **numeric values, not as scientific values** (i.e. 0.01 instead of 1E-2), as this will lead to an error message. Please note that it is strongly recommended to **not change the technique using Excel**. Also note that column M "*Recovery%*" does not need to be filled in.

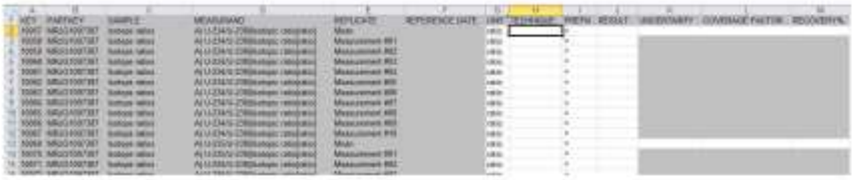


Figure 4: Preview of Excel sheet used to enter the results.

After entering the data and saving the file, the saved file can be uploaded using the JRC reporting tool; first select the file via the "*Browse*" button, then upload the file via the "*Upload*" button. Once loaded, you will be redirected automatically to the reporting tool, in which you can verify your results and provide the measurement technique. Please save the data before returning to the main page.

Managing your results in the result input grid

You can delete the reported **Uncert. Value** and the selected **Technique** using the *eraser* at the end of each row (next to "Technique").

At the bottom of the screen, you can either:

1) *Clear* the entire reported results.

2) *Save* your results (this will temporarily keep them available).

3) *Validate and save* your results, this will create a draft pdf document, which you can then see in the ILC Reporting page by clicking on "Preview reported values" (please see Section 3 below).

4) Once you saved your results by either option 2) or 3), use the *Back to main page* button to go back to the ILC reporting page.

Note that as long as the results are not submitted (see section 4), the values can still be changed.

2. QUESTIONNAIRE

Before the results can be submitted, the questionnaire needs to be filled in. Please open the questionnaire using the "*Fill in questionnaire*" option from the main menu. The questionnaire can be saved in-between using the "*Save questionnaire*" button located at the bottom of the page. Questions marked with an asterix (*) are mandatory.

Attention! As for the *result reporting interface*, there is no reminder message set for the questionnaire when you click on the *Clear* button (all data/inputs will be deleted from the questionnaire)! So do save your data regularly before clicking on *Clear Questionnaire*!

3. PREVIEW OF REPORTED RESULTS

To preview the entered results before submission, press the "*Preview reported values*" option from the main menu, which opens a pdf file with the entered results.

Please be aware that closing the window automatically closes the reporting tool, please **use the return button of your browser to return to the ILC reporting tool**. Similar to the reported results, the questionnaire can be previewed using the "*Preview reported questionnaire*" button.

4. SUBMISSION OF RESULTS

Note that you cannot submit your results alone, but must fill and submit the questionnaire as well.

After verification of your results and the questionnaire, you can submit your results by pressing the "*Submit my results*" button in the main menu. Please ensure the "*I confirm I reported my results and answered the questionnaire*" checkbox is activated. **Once submitted, the results/questionnaire cannot be changed anymore!**

After submission, you will be redirected automatically to a confirmation page from which you can download a pdf file containing your submitted results. Please **send the duly signed pdf document via email or fax** to the ILC co-ordinator.

Further assistance

We hope these guidelines will be of help. However, if you have any further questions, please do not hesitate to contact us via our functional mailbox:

JRC-NUSIMEP@ec.europa.eu

Yours sincerely,

Célia Venchiarutti
NUSIMEP-9 Co-ordinator

Stephan Richter
NUSIMEP-9 Co-ordinator

Annex 7. Letter for extension of reporting of results

EUROPEAN COMMISSION
DG JOINT RESEARCH CENTRE
Directorate G – Nuclear Safety & Security
Unit G.2 - Standards for Nuclear Safety, Security & Safeguards

NUSIMEP

Geel, 8 February 2019

Ares(2019)753695

The Nuclear Signatures Inter-laboratory Measurement Evaluation Programme

NUSIMEP-9: Uranium isotope amount ratios and uranium mass in uranium micro-particles

Subject: Deadline extension for submission of results

Dear NUSIMEP-9 participants,

Due to the issue with our online reporting tool, we decided to extend the deadline for the reporting of NUSIMEP-9 results to: **1st March 2019**.

This is the definite deadline for submission of results and there will be no further extension.

To guide you through the reporting of your results, please follow the guidelines that were enclosed with your certified test item(s).

Do not forget to fill in the associated questionnaire. Your results cannot be submitted without the completed questionnaire.

After online submission of your results, we remind you that the final pdf (with results and questionnaire) has to be sent to the ILC coordinator using the following email address: JRC-NUSIMEP@ec.europa.eu.

Please do not hesitate to contact us if you need more information or assistance.

Yours sincerely,

Célia Venchiarutti

NUSIMEP-9 Co-ordinator

Stephan Richter

NUSIMEP-9 Co-ordinator

Retieseweg 111, B-2440 Geel - Belgium.
Telephone: +32-(0)14- 571-681.
Fax: +32-(0)14-571-862.
E-mail: JRC-NUSIMEP@ec.europa.eu

1

Annex 8. Certified uranium amount isotope ratios in IRMM-2329P

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Directorate G - Nuclear Safety and Security
Unit G.2 - Standards for Nuclear Safety, Security and Safeguards (SN3S)

Certificate of Reference Measurement #3867

Customer	
Company/Institute	JRC
Division	Unit G.2
Address	Retieseweg 11
	2440 Geel
	Belgium
Requestor	JRC-G.2

Sample Information	
Sample type	Uranium nitrate solution for particle production
Sample reference	IRMM-2329
Date of receipt of sample(s)	04/04/2017
JRC sample identification	27004
Condition of sample	Uranium nitrate solution, 2mg U / mL

Measurement Results

Analyte	Result	Unit	Method
$n(^{234}U)/n(^{238}U)$	0.00034083(19)	mol / mol	TIMS/MTE
$n(^{235}U)/n(^{238}U)$	0.033902(12)	mol / mol	TIMS/MTE
$n(^{236}U)/n(^{238}U)$	0.00003021(12)	mol / mol	TIMS/MTE

Derived Quantities

Molar Mass	237.950844(34)

Amount fraction (×100)		Mass fraction (×100)	
$n(^{234}U)/n(U)$	0.032953(18)	$m(^{234}U)/m(U)$	0.032412(18)
$n(^{235}U)/n(U)$	3.2778(11)	$m(^{235}U)/m(U)$	3.2378(11)
$n(^{236}U)/n(U)$	0.002921(12)	$m(^{236}U)/m(U)$	0.002897(12)
$n(^{238}U)/n(U)$	96.6863(11)	$m(^{238}U)/m(U)$	96.7269(11)

This report may only be reproduced in full and with the written consent of the requestor.
Results relate only to samples analysed. No feedback within 4 weeks constitutes acceptance of the report.
Potential sample rests may be destroyed after this period.

Page 1 of 2 F-D-00377v4

Uncertainties:
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[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 traceability to SI is established through IRMM-074. Uncertainties include an extrapolated contribution for homogeneity, as described in[2].

Analytical measurement procedure:

- Sample preparation has been accomplished by J. Truyens
- Mass spectrometric measurements have been accomplished by S. Richter
- Analytical method/technique used : TIMS/MTE
- The atomic masses, used in the calculations, are[3]:
- The half-lives used in the calculations are: N/A
- The mass spectrometer was calibrated using IRMM-074
- Quality control samples used were IRMM-075/1 and IRMM-075/2

Date of analysis (dd/mm/yyyy)	27/04/2017
Date of internal analysis report (dd/mm/yyyy)	14/06/2017
Certification date normalised to (reference date)	27/04/2017 at 12:00 h

Backup Files and Raw Data
Folder: "G:\JRC.G.2\Nuclear Safeguards\Nuclear\Particles\Certification U Particle RM IRMM-2329-2330\TIMS MTE Measurements of Base Solutions IRMM-2329-2330"
Data Files: "T170424 MTE IRMM-2329-SEM-2330-SEM-FAR.xls" "Calculation homogeneity extrapolation-2 - applied for IRMM-2329-2330.xls" "IRMM-2329.SMU"

Annexes
Copy of Internal Analysis Report (2 pages)

JRC G.2 Unit Head: Prof. Dr. W. Mondelaers

Signature and date:

22/06/17

References:

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

2 Mialle, S., Richter, S., Hennessy, C., Truyens, J., Jacobsson, U., et al, "Certification of uranium hexafluoride reference materials for isotopic composition", 8th International Conference on Isotopes, Chicago, Aug. 24-29, 2014. J Radioanal Nucl Chem, Vol 305, 2015, pp. 255–266.

3 G. Audi and A.H. Wapstra, The 2003 atomic mass evaluation, Nuclear Physics A 729(2003) 337-676

Annex 9. NUSIMEP-9 Questionnaire

Milc questionnaire

Comparison for NUSIMEP-9

Thank you very much for filling in this questionnaire! Your inputs/feedbacks are very valuable to us. All the mandatory fields (*) of this questionnaire have to be filled in. You can only submit your results reporting form once this questionnaire is complete. All answers will be treated confidentially (non-disclosure of the identity of the laboratories).

Submission Form

1. **Laboratory**

1.1. What is the mission of your laboratory? *

- ☐ a) Environmental sciences
- ☐ b) Measurement of radioactivity in the environment
- ☐ c) Measurements for fissile material control or safeguards
- ☐ d) Monitoring of nuclear facilities
- ☐ e) Nuclear forensics
- ☐ f) Research and development
- ☐ g) Other

1.1.1. If 'Other', please specify *

1.2. Is your laboratory a member of the IAEA Network of Analytical Laboratories (NWAL)? *

- ○ a) Yes
- ○ b) No

- Page 1 of 14 -

1.3. Is your laboratory working according to a quality management system? *

- a) ISO 17025
- b) ISO 9001
- c) Other
- d) No

1.3.1. If 'Other', please specify *

1.4. Is this your first participation in a NUSIMEP exercise? *

- a) Yes
- b) No

1.4.1. If No, in which NUSIMEP exercises have you already participated? *

1.5. Does your laboratory participate in other inter-laboratory comparisons (ILC's)? *

- a) Yes
- b) No

1.5.1. If 'Yes', please specify which ILC's *

2. Uranium isotope amount ratios in microparticles

2.1. Is your laboratory certified, accredited or authorised for the analysis of uranium isotope amount ratios in microparticles? *

- ☐ a) Certified (ISO 9001)
- ☐ b) Accredited (ISO 17025)
- ☐ c) Authorised (mandated)
- ☐ d) Not applicable

2.2. How does your laboratory rate itself for these types of measurements? *

- ○ a) Experienced
- ○ b) Less experienced
- ○ c) Not experienced

2.3. How many measurements of this type does your laboratory routinely perform per year? *

- ○ a) 0-10
- ○ b) 11-50
- ○ c) 51-100
- ○ d) >100
- ○ e) Not applicable

2.4. Was the NUSIMEP-9 sample treated according to the same analytical procedure routinely used for this sample type? *

- ○ a) Yes
- ○ b) No
- ○ c) Not applicable

2.4.1. If 'No', please describe why it was not performed according to your routine analytical procedure *

2.5. Which (C)RMs were used during the analysis? *

2.6. How did you select (scan) the particle(s) for your measurements? *

- ☐ a) SEM/EDX
- ☐ b) FT
- ☐ c) SIMS (APM)
- ☐ d) Other
- ☐ e) Not applicable

2.6.1. If 'Other', please specify *

2.6.2. Please give a brief description on the particle selection

2.7. Was a particle transfer performed? *

- ○ a) Yes
- ○ b) No

2.7.1. If 'Yes', please describe the particle transfer *

2.8. Was a chemical treatment applied? *

- ○ a) Yes
- ○ b) No

2.8.1. If 'Yes', please describe the chemical treatment *

2.9. Are your reported uncertainties for the isotope amount ratios calculated according to ISO/IEC Guide 98-3:2008 (GUM)? *

- a) Yes
- b) No

2.9.1. If 'No', how was the uncertainty estimated? *

2.9.2. Please list the major uncertainty contributions to the reported isotope amount ratios *

2.10. Did you apply a correction for mass fractionation/mass bias to your measurement results?

- a) Yes
- b) No

2.10.1. If 'Yes', how was the mass fractionation corrected for? *

2.11. Could you specify your measurement conditions/parameters?

3. **Total uranium mass per particle (from question 3.2, mandatory only if you reported the U mass par particle)**

3.1. Which (C)RMs did you use during the analysis?

3.2. How did you select (scan) the particle(s) for your measurements?

- ☐ a) Scanning electron microscopy (SEM)
- ☐ b) Fission track (FT)
- ☐ c) Optical microscopy
- ☐ d) SIMS (APM)
- ☐ e) Other
- ☐ f) Not applicable

3.2.1. If 'Other', please specify *

3.2.2. Please give a brief description of your particle selection procedure

3.3. Was a particle transfer performed?

- ○ a) Yes
- ○ b) No

3.3.1. If 'Yes', please give a brief description on your particle transfer procedure *

3.4. Please describe your analytical procedure

3.5. How was your measurement calibrated?

- a) Isotope dilution
- b) Standard addition
- c) External calibration
- d) Other

3.5.1. If 'Other', please specify *

3.5.2. If 'Isotope dilution', did you verify the equilibrium between the spike and the particle(s)? *

- a) Yes
- b) No

3.5.2.1. If 'Yes', please describe your verification procedure *

3.5.2.2. If 'No', please state your confidence in the thorough mixing of the spike with the sample

3.6. If applicable, what type of instrument was used for mass spectrometric measurements?

- a) ICP-MS
- b) TIMS
- c) SIMS

○ d) Other

3.6.1. If 'Other', please specify *

3.7. If applicable, which uranium isotopes were analysed?

3.8. Did you apply any correction factors (e.g. recovery)?

○ a) Yes

○ b) No

3.8.1. If 'Yes', please descibe which corrections were applied *

3.9. How many particles were analysed simultaneously?

3.10. How many replicate analyses were performed on the sample?

3.11. Did you encounter any debris and/or particles with double the amount of uranium compared to the main particle population?

☐ a) Debris

☐ b) Particles with double the mass of uranium

☐ c) No

3.11.1. If applicable, how did you handle the analysis of such particles?

3.12. If applicable, please give the used molar masses and reference (literature) used for the calculation of the uranium mass

See table **Molar masses** at bottom

3.13. Is your reported uncertainty for the uranium mass per particle calculated according to ISO/IEC Guide 98-3:2008 (GUM)?

- a) Yes
- b) No

3.13.1. If 'No', how was the uncertainty estimated? *

3.13.2. Please list the major uncertainty contributions to the reported uranium mass per particle

3.14. Did you report the U mass per particle? *

- a) Yes
- b) No

3.14.1. If 'No', what prevented you from performing this analysis? *

3.14.2. If 'Yes', does your laboratory routinetly perform this analysis? *

- a) Yes
- b) No

3.14.2.1. If 'Yes', was the NUSIMEP-9 sample treated according to the same analytical procedure routinely used for this kind of sample type? *

- a) Yes
- b) No

3.14.2.1.1. If 'No', please described why it was not performed according to your routine analytical procedure: *

4. **Further remarks**

4.1. Would you be interested in participating in future NUSIMEP ILC's on the analysis of microparticles? *

- a) Yes
- b) no

4.1.1. If 'Yes', what type(s) of particles would you be interested in? *

- a) U only
- b) Pu only
- c) mixed U/Pu
- d) mixed U/Th
- e) mixed U/Ln
- f) monodisperse/polydisperse
- g) single/multi-isotopic compositions

☐ h) other

4.1.1.1. If you are interested in mixed particles, which ratios would you be interested in?

4.1.2. If 'Yes', what type of substrates would you be interested in (e.g. carbon disk, cotton swipe)?

4.1.3. If 'Yes', would you be open to receiving smaller substrates?

○ a) Yes

○ b) No

4.2. Does your laboratory have other tools/methods to analyse individual micrometre-sized uranium particles?

☐ a) Morphological studies (e.g. SEM)

☐ b) Structural analysis (e.g. μ-Raman, μ-XRD)

☐ c) Impurity analysis (e.g. FIB-MS, SEM/EDX)

☐ d) Geolocalisation (e.g. $\delta 18O$, REE determinations)

☐ e) Age dating (e.g. Th-230/U-234 chronometer)

☐ f) Other

4.2.1. If applicable, did you perform any such measurements on the NUSIMEP-9 sample(s)?

○ a) Yes

○ b) No

4.2.1.1. If 'Yes', could you please indicate which type of measurement and the obtained result?

4.2.2. If 'Other', please specify

4.3. Would you like to see additional property values being tested in future NUSIMEP ILC's?

- a) Yes
- b) No

4.3.1. If 'Yes', which values would you be interested in? *

4.4. Do you have any other feedback/comments on NUSIMEP-9?

4.5. What is your opinion of this NUSIMEP-9 ILC? *

Molar masses

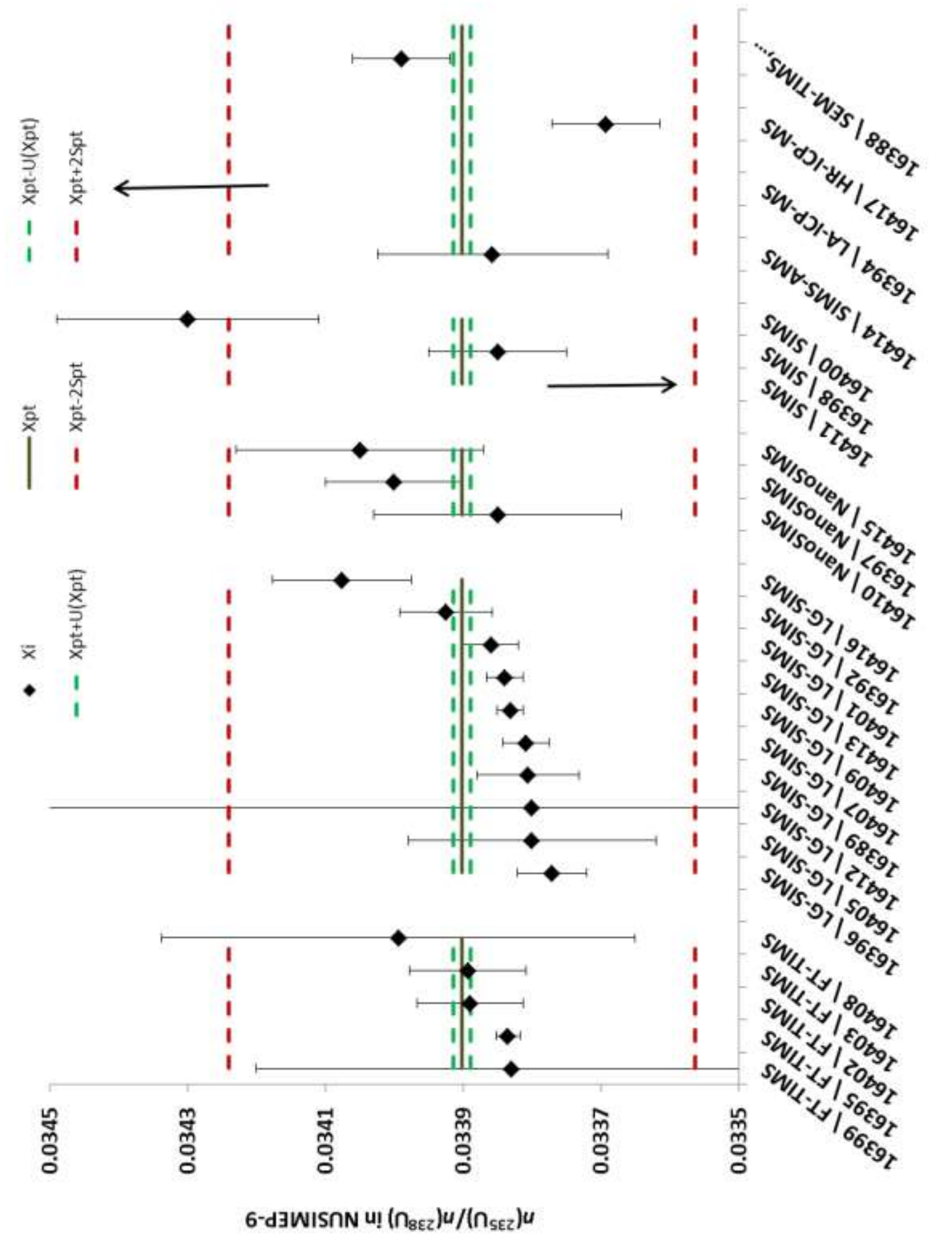
Please give the molar masses and references (literature) used for the calculation of the uranium mass per particle

Questions/Response table	*Molar mass [g/mol]*	*Expanded uncertainty [g/mol]*	*Coverage factor (k)*	*Reference*
U-233				
U-234				
U-235				
U-236				
U-238				

Annex 10. NUSIMEP-9 Participants' results for the $n(^{235}U)/n(^{238}U)$ per analytical techniques

Table 7: NUSIMEP-9 participants' reported results for $n(^{235}U)/n(^{238}U)$ (x_i and $U(x_i)$ expanded uncertainty with k coverage factor as given by participants) and evaluation of laboratory performances by means of z and ζ scores

Lab Code	x_i	$U(x_i)$	k	Analytical technique used	z score	ζ score
16388	0.03399	0.00007	1	SEM-TIMS, SIMS, SEM-ICP-MS	0.52	1.25
16389	0.033806	0.00007405	2	LG-SIMS	-0.57	-2.55
16392	0.033925	6.68879E-05	1	LG-SIMS	0.13	0.34
16394	0.0366	0.00199	1	LA-ICP-MS	15.92	1.36
16395	0.033835	0.000017	1	FT-TIMS	-0.40	-3.61
16396	0.033771	0.00005	2.26	LG-SIMS	-0.77	-5.61
16397	0.0340	0.0001	2	NanoSIMS	0.58	1.94
16398	0.03385	0.0001	1	SIMS	-0.31	-0.52
16399	0.03383	0.00037	1	FT-TIMS	-0.42	-0.19
16400	0.0343	0.00019	2	SIMS	2.35	4.18
16401	0.03386	0.00004	2	LG-SIMS	-0.25	-1.97
16402	0.03389	0.00007685	2	FT-TIMS	-0.07	-0.31
16403	0.033894	0.00008401	2	FT-TIMS	-0.05	-0.20
16405	0.03380	0.00018	2.10	LG-SIMS	-0.60	-1.19
16407	0.033809	0.000034	1	LG-SIMS	-0.55	-2.67
16408	0.033994	0.0003435	2	FT-TIMS	0.54	0.54
16409	0.033832	1.84664E-05	2	LG-SIMS	-0.41	-5.90
16410	0.03385	0.00018	2	NanoSIMS	-0.31	-0.58
16411	0.033032	0.000086	1.96	SIMS	-5.13	-19.54
16412	0.0338	0.0013	2	LG-SIMS	-0.60	-0.16
16413	0.03384	0.0000272	1	LG-SIMS	-0.37	-2.20
16414	0.033857	0.0001668	2	SIMS-AMS	-0.26	-0.53
16415	0.03405	0.00018	2	NanoSIMS	0.87	1.64
16416	0.034076	0.000100962	1.962363	LG-SIMS	1.02	3.34
16417	0.033693	0.000078	2	HR-ICP-MS	-1.23	-5.26



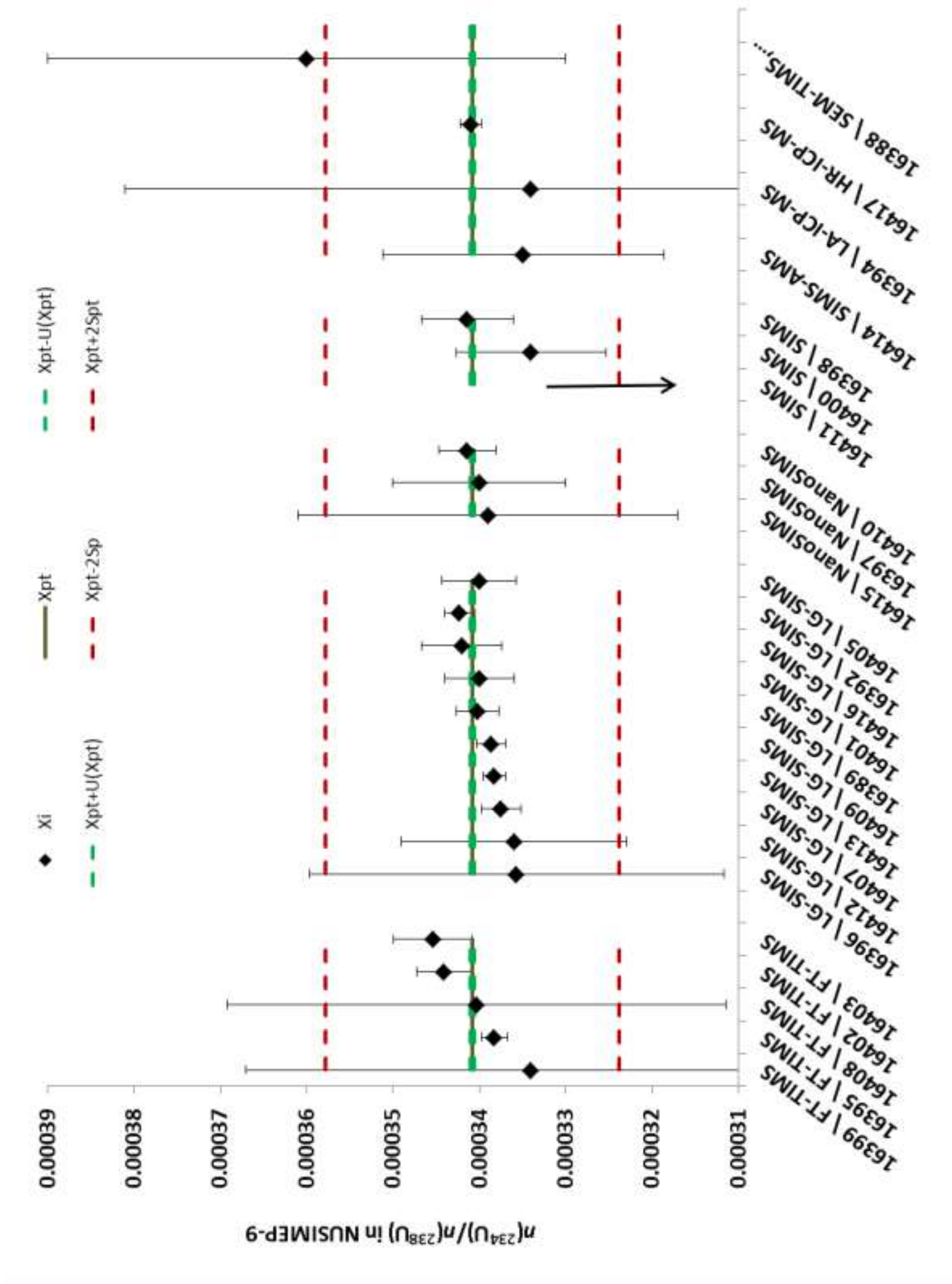
$x_{pt} \pm U(x_{pt})$ = 0.033902 ± 0.000012 $(k = 2)$ mol·mol^{-1} (green line and dashed green lines)

$x_{pt} \pm 2\,\sigma_{pt}$ (with σ_{pt} as $0.005 \cdot x_{pt}$, dashed red lines)

Annex 11. NUSIMEP-9 Participants' results for the $n(^{234}U)/n(^{238}U)$ per analytical techniques

Table 8: NUSIMEP-9 participants' reported results for $n(^{234}U)/n(^{238}U)$ (x_i and $U(x_i)$ expanded uncertainty with *k* coverage factor as given by participants) and evaluation of laboratory performances by means of z and ζ scores

Lab Code	x_i	$U(x_i)$	*k*	Analytical technique used	z score	ζ score
16388	0.00036	0.00003	1	SEM-TIMS, SIMS, SEM-ICP-MS	2.25	0.64
16389	0.00034	0.000002478	2	LG-SIMS	-0.08	-0.53
16392	0.000342	1.70401E-06	1	LG-SIMS	0.17	0.85
16394	0.000334	0.000047	1	LA-ICP-MS	-0.80	-0.15
16395	0.000338	0.000001495	1	FT-TIMS	-0.30	-1.71
16396	0.000336	0.000024	2.26	LG-SIMS	-0.60	-0.48
16397	0.00034	0.00001	2	NanoSIMS	-0.10	-0.17
16398	0.000341	0.0000053	1	SIMS	0.07	0.11
16399	0.000334	0.000033	1	FT-TIMS	-0.80	-0.21
16400	0.000334	0.0000087	2	SIMS	-0.80	-1.57
16401	0.00034	0.000004	2	LG-SIMS	-0.10	-0.41
16402	0.000344	0.000003121	2	FT-TIMS	0.38	2.09
16403	0.000345	0.000004529	2	FT-TIMS	0.53	2.00
16405	0.00034	0.0000043	2.11	LG-SIMS	-0.10	-0.41
16407	0.000338	0.0000023	1	LG-SIMS	-0.39	-1.45
16408	0.00034	0.0000289	2	FT-TIMS	-0.06	-0.04
16409	0.000339	1.65997E-06	2	LG-SIMS	-0.26	-2.61
16410	0.000341	0.0000033	2	NanoSIMS	0.07	0.34
16411	0.000252	0.0000026	1.96	SIMS	-10.40	-66.64
16412	0.000336	0.000013	2	LG-SIMS	-0.57	-0.74
16413	0.000338	0.000001271	1	LG-SIMS	-0.30	-2.02
16414	0.000335	0.0000163	2	SIMS-AMS	-0.70	-0.73
16415	0.000339	0.000022	2	NanoSIMS	-0.21	-0.17
16416	0.000342	4.62636E-06	1.962363	LG-SIMS	0.14	0.51
16417	0.000341	0.0000012	2	HR-ICP-MS	0.02	0.28

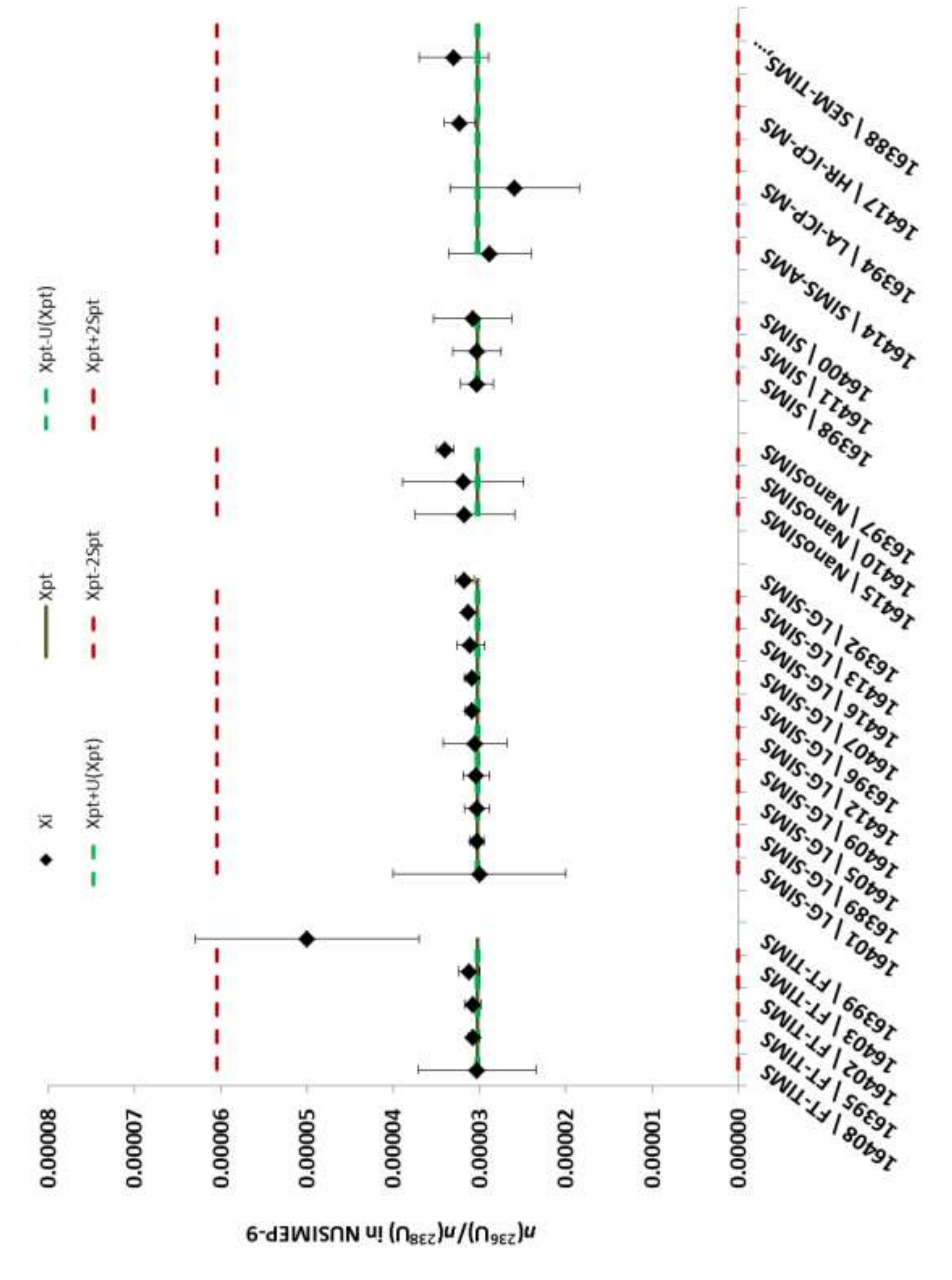


$x_{pt} \pm U(x_{pt})$ = 0.00034083 ±0.00000019 (k =2) mol·mol^{-1} (green line and dashed green lines)
$x_{pt} \pm 2\,\sigma_{pt}$ (with σ_{pt} as $0.025 \cdot x_{pt}$, dashed red lines)

Annex 12. NUSIMEP-9 Participants' results for the $n(^{236}U)/n(^{238}U)$ per analytical techniques

Table 9: NUSIMEP-9 participants' reported results for $n(^{236}U)/n(^{238}U)$ (x_i and $U(x_i)$ expanded uncertainty with k coverage factor as given by participants) and evaluation of laboratory performances by means of z and ζ scores

Lab Code	x_i	$U(x_i)$	k	Analytical technique used	z score	ζ score
16388	0.000033	0.000004	1	SEM-TIMS, SIMS, SEM-ICP-MS	0.18	0.70
16389	0.000030289	0.000000739	2	LG-SIMS	0.01	0.21
16392	0.0000317	1.09288E-06	1	LG-SIMS	0.10	1.36
16394	0.00002597	0.0000075	1	LA-ICP-MS	-0.28	-0.57
16395	3.07593E-05	5.433E-07	1	FT-TIMS	0.04	1.00
16396	0.000030815	0.00000078	2.26	LG-SIMS	0.04	1.73
16397	0.000034	0.000001	2	NanoSIMS	0.25	7.53
16398	0.0000303	0.0000019	1	SIMS	0.01	0.05
16399	0.00005	0.000013	1	FT-TIMS	1.31	1.52
16400	0.0000308	0.0000045	2	SIMS	0.04	0.26
16401	0.00003	0.00001	2	LG-SIMS	-0.01	-0.04
16402	0.000030774	0.000000975	2	FT-TIMS	0.04	1.15
16403	0.000031211	0.000001221	2	FT-TIMS	0.07	1.63
16405	0.0000303	0.0000014	2.26	LG-SIMS	0.01	0.14
16407	0.00003087	0.00000093	1	LG-SIMS	0.04	0.71
16408	0.0000303	0.0000068	2	FT-TIMS	0.01	0.03
16409	3.03718E-05	1.5012E-06	2	LG-SIMS	0.01	0.21
16410	0.0000319	0.0000070	2	NanoSIMS	0.11	0.48
16411	0.0000303	0.0000028	1.96	SIMS	0.01	0.06
16412	0.0000305	0.0000037	2	LG-SIMS	0.02	0.16
16413	3.13127E-05	3.168E-07	1	LG-SIMS	0.07	3.42
16414	0.0000288	0.0000048	2	SIMS-AMS	-0.09	-0.59
16415	0.0000317	0.0000058	2	NanoSIMS	0.10	0.51
16416	3.10366E-05	1.61511E-06	1.962363	LG-SIMS	0.05	1.00
16417	0.0000323	0.0000018	2	HR-ICP-MS	0.14	2.32



$x_{pt} \pm U(x_{pt})$ = = 0.00003021 ±0.00000012 $(k = 2)$ mol·mol^{-1} (green line and dashed green lines)
$x_{pt} \pm 2\ \sigma_{pt}$ (with σ_{pt} as $0.5{\bullet}x_{pt}$, dashed red lines)

Annex 13. NUSIMEP-9 Participants' results for the uranium mass per particle

Table 10: NUSIMEP-9 participants' reported results for the uranium mass per particle (x_i and $U(x_i)$ expanded uncertainty with *k* coverage factor as given by participants) and evaluation of laboratory performances by means of z and ζ scores

Lab Code	x_i	$U(x_i)$	k	Analytical technique used	z score	ζ score
16388	2.7	0.1	1	SEM-ICP-MS	-1.23	-2.52
16398	6.54	0.86	1	SIMS	4.13	3.21
16401	8	8	2	SEM-EDX	6.17	1.10
16405	3.56	0.45	2.37	LG-SIMS	-0.03	-0.05
16411	27.76	0.85	1.96	SEM	33.77	44.12

Annex 14. List of standard reference materials used by participants during the analysis of the uranium isotope amount ratios in NUSIMEP-9

Lab codes	(C)RMs used during the analysis	Correction for the mass bias/mass fractionation
16388	U020A, U100, U200	The certified reference material is used for correction of the mass fractionation.
16389	CRM-129a	by reference to CRM-129a U235/U238 ratio
16392	NBS U010, NBS U030a, NBS U050, IRMM 023	Mass bias measured on U010 for 235/238, assumed linear law for other isotopes, add an uncertainty term that reflected the deviation from linear mass bias for 234 and 236 (and 235) over all other standards as function of isotopic ratio
16394	CRM-125A	The mass bias was corrected using CRM-125A at the experimental conditions as close as possible to the NUSIMEP sample analysis.
16395	SRM U005a and U030a	A Mass Bias correction of 1.6 ± 0.5 ‰ was applied to all ratios for each analyses using an exponential correction.
16396	NBS U010	per amu value applied, measured using U010 235/238 ratio
16397	CRM129-A, U200	Measurement of CRM ratio was used as correction factor
16398	NBS U010, NBS U100, NBS U500	mass bias was measured on NBS U100 particles and was applied on each analysed NU9 particle
16399	NBS U100 and NBS U010	
16400	CRM U010	Two CRM U010 particles (on an Si planchet) were measured shortly before the measurement of NUSIMEP particles (deposited on a Si daughter planchet). The correction factor was equal to the ratio of certified value and the measured value
16401	NIST SRM U-020, NIST SRM U-100	According to Cameca particle measurement instructions
16402	CRM-129A	by reference to CRM-129A 235U/238U ratio
16403	CRM-129A	by reference to CRM-129A 235U/238U ratio
16405	U900	linear correction per amu determined from U900 particle measurements
16407	U030	exponential mass bias correction based on replicate of U030 measurements; average 235/238U=0.031700259 (n=4)
16408	U010, U030	correction factor derived from 5/8 ratio measurements of CRMs, distributed to 4/8 and 6/8 using a exponential equation.
16410	CRM U500	Bias correction factor was applied to the sample by comparing the measured U500 value to the certificate.
16411	CRM 010	CRM
16412	U030	U030 standard
16413	SRM U005a	A Mass Bias correction of 0.4± 1.0 ‰ was applied to all ratios for each analysis using an exponential correction.
16414	CRM U010, CRM U030A	Measuring U CRMS 010, 030A
16415	CRM U010	Linear function Rcor=Rraw(1+mbDm)
16417	NBL U010 as the mass bias, IRMM 183,184,185 analyzed three time each throughout the sequence	Ratios were corrected by direct comparison with NBL U010 (M/C), and verified by exponential model after being corrected for method blanks, hydride formation, and SEM/IC yield.

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