Results of the REIMEP-17 and NUSIMEP-8 Inter-laboratory Comparison

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ABSTRACT

Confidence in measurement results is established via reference materials, reference measurements and inter-laboratory comparisons. The Institute for Reference Materials and Measurements of the Joint Research Centre of the European Commission (EC-JRC-IRMM) has a long time experience in the development of nuclear isotopic reference materials and in the organisation of inter-laboratory comparisons (ILCs) in compliance with the respective international ISO guides.

The Regular European Inter-laboratory measurement Evaluation Programme (REIMEP) was established at IRMM in 1982 for carrying out external quality control of the measurements for the elements characteristic of the nuclear fuel cycle, while the Nuclear Signatures Inter-laboratory Measurement Evaluation Programme (NUSIMEP) aims to provide test samples for the measurement of trace amounts of nuclear material in environmental matrices. Participants in REIMEP/NUSIMEP can benchmark their measurement results against independent and traceable reference values, assessing their measurement capabilities in line with international or national quality goals.

The REIMEP-17 and NUSIMEP-8 certified test samples were prepared from dissolution of mixed oxide fuel in nitric acid and addition of natural uranium. In REIMEP-17 laboratories received two test samples with undisclosed values of the U, Pu amount content and U and Pu isotope amount ratios. The certified test sample REIMEP-17A had a concentration typical for undiluted input solution whereas REIMEP-17B was a diluted fraction thereof. The NUSIMEP-8 certified test sample was prepared by further gravimetrical dilution of REIMEP-17B. Measurement of the $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$ ratios were obligatory while the measurement of other ratios were optional.

Laboratories were asked to apply their routine analytical procedures and report the results with associated measurement uncertainty. The participant results have been evaluated against the independent certified reference value by means of z and zeta scores in compliance with ISO 13528:2005. In general, the REIMEP-17 results were satisfactory and in compliance with the International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials (ITV2010). The NUSIMEP-8 results were overall satisfactory and met the International Atomic Energy Agency Measurement Quality Goals (IAEA-SGAS-QC) for the analysis of bulk environmental samples.

INTRODUCTION

Reliable measurements of nuclear materials are required in context of verification measures of states declarations of their nuclear activities in line with the Treaty on the Non-proliferation of Nuclear Weapons (NPT) [1] and the Euratom Treaty. Measurements of amount content and isotope ratios, in particular of uranium and plutonium in samples taken from proliferation-sensitive stages of the nuclear fuel cycle such as enrichment and reprocessing are of major importance. As a part of the Additional Protocol (INFCIRC/540) [2], environmental sampling has become an important tool to detect the (unavoidable) traces in the environment originating from technological activities. In environmental sampling, swipe samples for bulk and particle analysis are collected around and inside a nuclear facility. Laboratories carrying out measurements of nuclear material and environmental samples are subject to a rigorous quality management system and are required to demonstrate their measurement capabilities on a regular and timely basis to legal and safeguards authorities. This also includes participation in inter-laboratory comparisons (ILCs).
For that reason, the EC-JRC-IRMM and EC-JRC-ITU (Institute for Transuranium Elements) jointly organised REIMEP-17 on "Plutonium and uranium amount content, and isotope amount ratios in synthetic input solution" for Euratom and IAEA safeguards laboratories, nuclear plant operators and nuclear material laboratories. Two sample solutions were prepared with different uranium and plutonium amount contents. REIMEP-17A was supplied in 3 mol•L^{-1} nitric solution with a U, Pu concentration typical for undiluted input solutions. The other solution REIMEP-17B was a diluted fraction thereof and was supplied in 8 mol•L^{-1} nitric solution. Participants were asked to report the U and Pu amount content, the $n(^{238}\text{Pu})/n(^{239}\text{Pu})$, $n(^{240}\text{Pu})/n(^{239}\text{Pu})$, $n(^{241}\text{Pu})/n(^{239}\text{Pu})$, $n(^{242}\text{Pu})/n(^{239}\text{Pu})$, and the $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$, $n(^{236}\text{U})/n(^{238}\text{U})$ amount ratios with associated measurement uncertainties. In parallel to REIMEP-17 also low-level samples suitable for NUSIMEP inter-laboratory comparison were provided in support to environmental laboratories and in particular to the IAEA Network of analytical laboratories (NWAL) for environmental sampling. The NUSIMEP-8 was prepared in 1 mol•L^{-1} nitric solution by gravimetrical dilution of REIMEP-17B. Only measurement of the major isotope ratios $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ were obligatory due to the low amount of nuclear material in the samples; measurement of other isotope ratios were optional. The preparation and shipment of the certified test samples to the participants were carried out by EC-JRC-ITU. The reference values were established by isotope dilution mass spectrometry (IDMS) and thermal ionisation mass spectrometry (TIMS) at EC-JRC-IRMM.

The results were evaluated against the reference values by means of z and zeta scores in compliance with ISO 13528:2005 [3]. The International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials (ITV2010) [4] and the IAEA Measurement Quality Goals for the analysis of bulk environmental samples (IAEA-SGAS-QG) [5], were used as criterion for evaluation of participants' performance.

RESULTS

Individual laboratory performance was expressed in terms of z and zeta scores in accordance with ISO 13528 [3].

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \quad \text{and} \quad zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

Where x_{lab} is the measurement result reported by a participant, X_{ref} is the certified reference value (assigned), u_{ref} is the standard uncertainty of the reference value, u_{lab} is the standard uncertainty reported by a participant and $\hat{\sigma}$ is the standard deviation for proficiency assessment.

Both scores can be interpreted as satisfactory (S) result for $|score| \leq 2$, questionable (Q) result for $2 < |score| \leq 3$ and unsatisfactory (U) result for $|score| > 3$.

The z score in REIMEP-17 and NUSIMEP-8 indicates whether a laboratory is able to perform the measurement in accordance with the ITV2010 [4] and the IAEA-SGAS-QG [5], respectively. The zeta score provides an indication whether the estimate of uncertainty is consistent with the laboratory's deviation from the reference value. It is calculated only for those results that were accompanied by an uncertainty statement. An unsatisfactory zeta score may be caused by an underestimated uncertainty or by a large deviation from the reference value. For all satisfactory zeta scores it is also evaluated whether the relative standard uncertainty reported by a participant ($u_{lab;rel}$) is within the ITV2010 and the IAEA-SGAS-QG, respectively. If this was the case, then YES was issued otherwise NO. The scores per measurand under investigation in REIMEP-17A are summarised in Table 1. Due to withdrawals, delays in the shipment of the samples, and problems with the transport containers, the number of participating laboratories in REIMEP-17 shrank from originally sixteen registered institutes to nine participants.

Table 1: Overview of the scores in REIMEP-17A: Satisfactory (S), Questionable (Q), Unsatisfactory (U); n is the number of results for which a score was given

REIMEP-17A	ITV-2010[(3)]	z score				zeta score				acceptable uncertainty for $\|zeta\| \leq 2$
		S	Q	U	n	S	Q	U	n	YES
U content[(1)]	0.18%	22%	44%	33%	9	56%	11%	33%	9	40%
Pu content[(1)]	0.18%	22%	56%	22%	9	44%	33%	22%	9	0%
U content[(2)]	0.28%	78%	11%	11%	9	-	-	-	-	80%
Pu content[(2)]	0.28%	78%	22%	-	9	-	-	-	-	75%
$n(^{234}U)/n(^{238}U)$	/	-	-	-	-	56%	22%	22%	9	-
$n(^{235}U)/n(^{238}U)$	0.28%	78%	11%	11%		89%	11%	-	9	75%
$n(^{236}U)/n(^{238}U)$	/	-	-	-	-	50%	17%	13%	6	-
$n(^{238}Pu)/n(^{239}Pu)$	1.8%	78%	11%	11%	9	78%	11%	11%	9	57%
$n(^{240}Pu)/n(^{239}Pu)$	0.11%	100%	-	-	9	89%	11%	-	9	88%
$n(^{241}Pu)/n(^{239}Pu)$	0.28%	89%	11%	-	9	100%	-	-	9	78%
$n(^{242}Pu)/n(^{239}Pu)$	0.36%	100%	-	-	9	78%	11%	11%	9	71%

(1) Using large size spikes (such as LSD) for glove box conditions

(2) Using small size spikes for glove box conditions or using large size spikes (such as LSD) for hot cell conditions

(3) Relative combined standard uncertainty

The ITVs are different depending on analytical approaches and techniques applied. In the case of isotope dilution mass spectrometry (IDMS), ITVs also depend on the type of spike used and whether the analysis is carried out under glove box or hot cell conditions. Since this information is not known to the REIMEP-17 organisers, the results for the uranium and plutonium content in REIMEP-17 were evaluated according to both ITV criteria. It can be concluded that the participants in REIMEP-17 performed reasonably well and in compliance with the respective ITV2010. In particular, the measurement performance for the uranium and plutonium isotope amount ratios was satisfactory in REIMEP-17A and in REIMEP-17B. This confirms that the ITV2010 are achievable target values under state-of-practice conditions. As it can be seen from Table 1 there is room for improvement in reporting uncertainties because for some of the measurands less than 50% of the REIMEP-17 participants with $\|zeta\| \leq 2$ reported acceptable uncertainties. As there are no ITVs defined for the minor uranium isotope amount ratios, there were no z scores issued for $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$.

The participant results for the Pu amount content in REIMEP-17A are displayed in Figure 1.

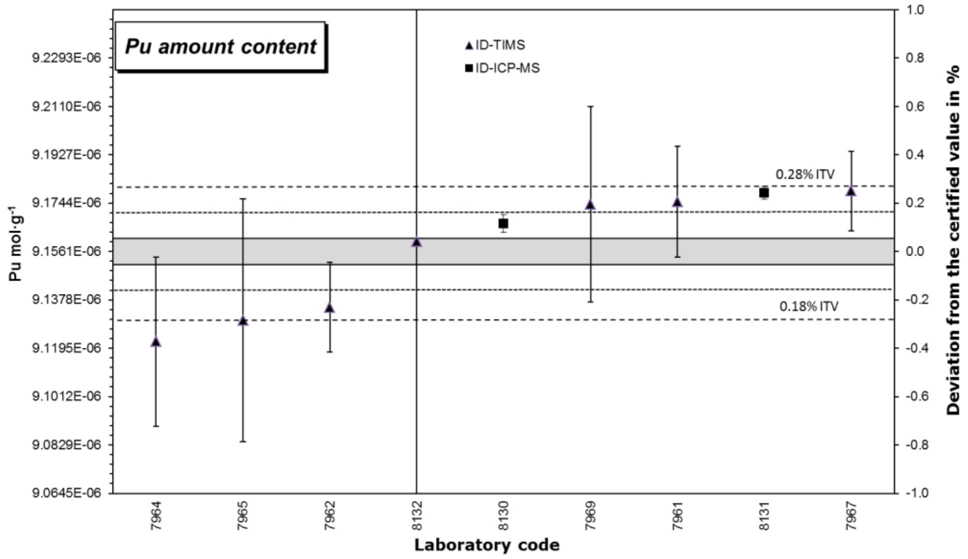

Fig 1: The participant results of the Pu amount content in REIMEP-17A with reported measurement uncertainties. The grey band represents the reference value ± expanded uncertainty, *k*=2. The dotted lines represent the ITVs.

Table 2 summarises the scores per measurand under investigation in NUSIMEP-8. As there are no IAEA-SGAS-QG [5] defined for the $n(^{238}Pu)/n(^{239}Pu)$, there were no z scores issued for this amount ratio. The total number of participants in NUSIMEP-8 (with and without a score) is nineteen.

It has to be kept in mind that according to the International Union of Pure and Applied Chemistry (IUPAC) International Harmonized Protocol [6] participants can apply their own scoring settings and recalculate the scores if the purpose of their measurements is different.

Table 2: Overview of the scores in NUSIMEP-8: Satisfactory (S), Questionable (Q), Unsatisfactory (U); n is the number of results for which a score was given

NUSIMEP-8	IAEA-SGAS-QG[(1)]	z score				zeta score				acceptable uncertainty for $\|zeta\| \leq 2$
		S	Q	U	n	S	Q	U	n	YES
$n(^{234}U)/n(^{238}U)$	10%	75%	13%	13%	16	69%	6%	25%	16	82%
$n(^{235}U)/n(^{238}U)$	1%	41%	6%	53%	17	47%	12%	41%	17	50%
$n(^{236}U)/n(^{238}U)$	10%	18%	18%	64%	11	82%	9%	9%	11	56%
$n(^{238}Pu)/n(^{239}Pu)$	/	-	-	-	-	63%	13%	25%	8	-
$n(^{240}Pu)/n(^{239}Pu)$	10%	100%	-	-	15	87%	-	13%	15	100%
$n(^{241}Pu)/n(^{239}Pu)$	10%	82%	-	18%	11	64%	-	36%	11	71%
$n(^{242}Pu)/n(^{239}Pu)$	10%	85%	8%	8%	13	69%	-	31%	13	100%

(1) Relative combined standard uncertainty

The majority of participants in NUSIMEP-8 performed well and in compliance with the respective IAEA-SG-QG, in particular for the plutonium amount ratios and $n(^{234}U)/n(^{238}U)$ amount ratio. However, for measurements of the $n(^{235}U)/n(^{238}U)$ amount ratio only less than half of the participants achieved satisfactory scores. This was partly due to the fact that the IAEA-SG-QG is more stringent for that specific ratio. In the case of $n(^{236}U)/n(^{238}U)$, the relative expanded uncertainty of the reference value is larger than the respective IAEA-SGAS-QG. This means that the uncertainty of the $n(^{236}U)/n(^{238}U)$ reference value is too large for the purpose of this ILC, which can easily be seen in Table 2 by the increase of satisfactory zeta scores compared to the high number of unsatisfactory z scores. For the other isotope amount ratios 63% - 87% of the participants achieved satisfactory zeta scores, with even 100% of acceptable uncertainty results for $n(^{240}Pu)/n(^{239}Pu)$ and $n(^{242}Pu)/n(^{239}Pu)$.

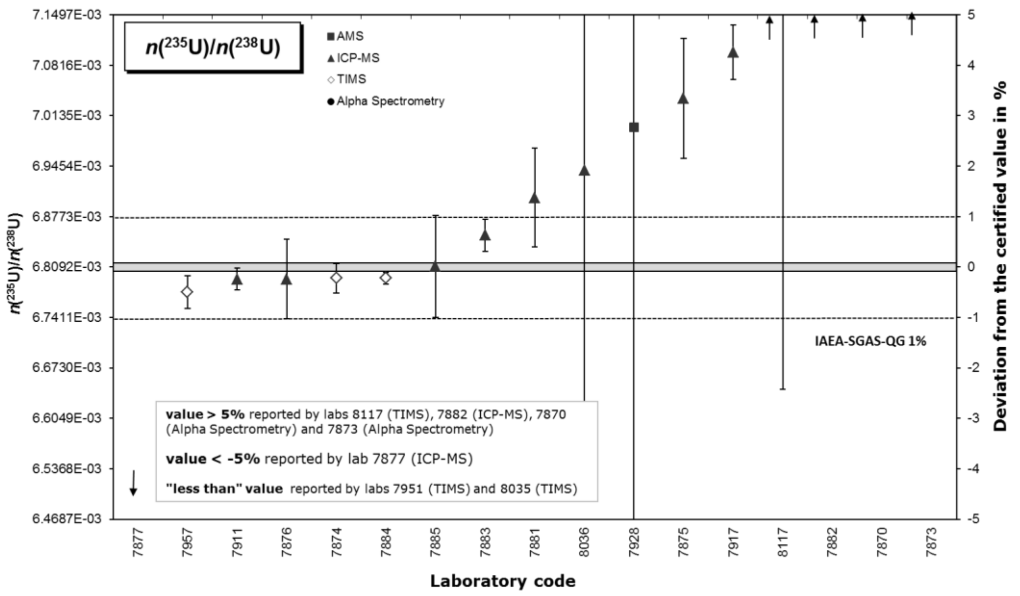

Fig 2: The participant results of the $n(^{235}U)/n(^{238}U)$ amount ratio in NUSIMEP-8 with reported measurement uncertainties. The grey band represents the reference value ± expanded uncertainty, k=2. The dotted lines represent the IAEA-SGAS-QG.

CONCLUSIONS

It can be concluded that the participants in REIMEP-17 performed well for the measurements of uranium and plutonium amount content in compliance with the respective ITV2010. In particular, the measurement performance for the plutonium isotope amount ratios was very good for both REIMEP-17 samples. This confirms the measurement capabilities of laboratories in the field of nuclear material analysis and at the same time serves as a confirmation that the stringent ITV2010 are achievable target values under state-of-practice conditions. Some larger spread of results was observed for the $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ amount ratios. Some differences in the uncertainty estimates provided by the participants were observed even using the same instrumental technique. The participants in NUSIMEP-8 performed very well for the measurements of the plutonium amount ratios and the $n(^{234}U)/n(^{238}U)$ amount ratio. On the other hand, it was surprising that less than 50% of the participants could meet the IAEA-SGAS-QG for the $n(^{235}U)/n(^{238}U)$ uranium ratio. It has to be taken into account that the IAEA-SGAS-QG for this ratio is 10 times more stringent than for all the other amount ratios. A larger spread of results for the $n(^{236}U)/n(^{238}U)$ amount ratio was to be expected due to the fact that ^{236}U is the least abundant isotope in the NUSIMEP-8 sample.

Participation in REIMEP-17 and NUSIMEP-8 of laboratories dedicated to nuclear material and environmental sample analysis but also of institutes with other missions was extremely useful and of mutual benefit to the participants and to the ILC organisers.

REFERENCES

[1] The structure and content of agreements between the agency and states required in connection with the Treat on non-proliferation of nuclear weapons, INFCIRC 153 (corrected), Vienna, June 1972

[2] Model protocol additional to the agreement(s) between state(s) and the International Atomic Energy Agency for the application of safeguards, INFCIRC 540 (corrected), Vienna, September 1997

[3] ISO 13528:2005: Statistical methods for use in proficiency testing by inter-laboratory comparison

[4] International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials, IAEA-STR-368, Vienna, November 2010

[5] Procedure Qualification Procedure for the Network of Analytical Laboratories for Environmental Sampling IAEA Department of Safeguards SG-SGAS-9006

[6] M. Thompson, M.L.R. Ellison, R. Wood (2006), Pure Appl. Chem. 78:145-196