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# Validation of Cristallini Sampling Method for $UF_6$ by High Precision Double-Spike Measurements

*Collaboration between  
JRC-G.2, Team METRO  
and SGAS/IAEA*

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## Abstract

The so-called "Cristallini Method" for sampling of UF<sub>6</sub> by adsorption and hydrolysis in alumina pellets inside a fluorothene P-10 tube has been developed by the Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC) several years ago [1]. This method has several advantages compared to the currently used sampling method, for which UF<sub>6</sub> is distilled into a stainless steel tube for transportation, with hydrolysis and isotopic analysis being performed after shipping to the analytical laboratory. Using the Cristallini sampling method the transport is cheaper and relatively safer concerning radiological protection aspects.

In order to be reliable for both scientific and nuclear safeguards applications, the Cristallini sampling method has been subjected to a rigorous validation program. This includes a variety of sampling materials and measurement methods for the isotopic analyses as well as numerous participating laboratories around the world. The involved organizations include laboratories in Argentina, Brazil (collaborating within ABACC), Germany, Belgium (sites of Joint Research Centre, JRC, in Karlsruhe and Geel, respectively), Austria (Safeguards Analytical Services Laboratory of the IAEA) and within the United States, Oak Ridge National Laboratory (ORNL), the NBL-Program office and ASTM.

This technical report describes in particular the application of the "Double Spike" method by thermal ionization mass spectrometry (DS/TIMS) for the validation program of the Cristallini method, performed by staff from the unit JRC-G.2 in Geel/Belgium (formerly IRMM) in collaboration with staff from SGAS/IAEA. The results are in good mutual agreement, but they reveal slight differences for the <sup>235</sup>U/<sup>238</sup>U isotope ratios for samples taken by the Cristallini method compared to samples processed in the traditional manner by distillation and subsequent direct hydrolysis. For test samples prepared by ABACC using the IRMM-020 (0.2% <sup>235</sup>U) and IRMM-022 (0.72% <sup>235</sup>U) certified UF<sub>6</sub> reference materials, significant differences of about 0.01%-0.02% were observed, but for test samples prepared from IRMM-023 (3.3% <sup>235</sup>U) the differences are insignificant. The reason for the observed differences is not yet known, they can be due to fractionation, contamination or memory effects occurred during the sampling or subsequent chemical processing.

The results from JRC-G.2 and SGAS/IAEA using the double spike method play a special role within the validation program due to the high precision of this method. The results are proposed to be included for the intended standardization of the Cristallini sampling method through ASTM, in particular for defining an additional uncertainty component to account for the sampling process and the subsequent sample preparation, which would have to be attributed in the future to all isotopic measurements on samples taken by the Cristallini sampling method.

# 1 Introduction

The ABACC-Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials performs safeguard inspections jointly with the IAEA at enrichment plants in Brazil and Argentina. At enrichment plants in Brazil that use the centrifuge enrichment process, routine and unannounced inspections are performed and UF<sub>6</sub> samples are taken from process lines and cylinders to verify the uranium enrichment conformity with design/operator declarations. ABACC has developed a UF<sub>6</sub> sampling method for uranium enrichment determination (also named ABACC-Cristallini Method [1]) which uses a fluorothene P-10 tube containing alumina pellets that absorb and hydrolyse UF<sub>6</sub> directly during the sampling process, without the need for using liquid nitrogen. The alumina pellets retain up to few hundreds milligrams of U as a solid UO<sub>2</sub>F<sub>2</sub>.

Using the Cristallini method the sampling device is less expensive and the UF<sub>6</sub> sample content kept at the sampling place (archive sample) is lower and less reactive, which applies as well to the residual uranium retained at the analytical laboratory. In addition, since the sample form is solid rather than volatile and chemically less reactive, the transport is cheaper and relatively safer concerning radiological protection aspects.

The Cristallini sampling method has been developed at the CNEA laboratory in Argentina and the results were confirmed by an enrichment facility in Brazil. However, for using this new sampling method for taking nuclear safeguards samples on a worldwide scale, a broader network of collaboration was created. The validation of the Cristallini sampling method was included into the ABACC-DOE collaboration agreement, with NBL, now renamed into the NBL Program office, being the main collaborator. Furthermore, the IAEA has established a jointly executed task with ABACC under the project on destructive analysis of nuclear materials for safeguards with the aim to validate the ABACC-Cristallini Method.

The worldwide joint validation program was started in 2016. This program involves isotope ratio measurements of uranium materials sampled as UF<sub>6</sub> using the two different sampling methods, adsorption on alumina (ABACC-Cristallini method, labelled as "A-C") and the standard direct hydrolysis method (labelled "H"). The goal of the study is to determine if the application of the "A-C" sampling method has any detectable effect on the isotopic composition of the UF<sub>6</sub> material. The test materials used for this program are the UF<sub>6</sub> isotope reference materials IRMM 020 (0.21 % of <sup>235</sup>U), IRMM 022 (0.72 % of <sup>235</sup>U), IRMM 023 (3.3 % of <sup>235</sup>U) and IRMM 029 (4.2 % of <sup>235</sup>U), certified by JRC-G.2 [2]. For each of the four reference materials, every laboratory received two subsamples obtained from the direct hydrolysis and two subsamples taken using the Cristallini method. In this scheme, each laboratory is analysing a total of 16 subsamples contained in P-10 tubes. The P-10 tubes were randomly assigned to the different laboratories to minimize any effect of sampling bias. Each laboratory received a table with the amount of UF<sub>6</sub> loaded within the P-10 tubes. In order to eliminate the risk of cross contamination between reference materials with different <sup>235</sup>U enrichments flowing in the same sampling system, a different manifold was used for each reference material. The P-10 tubes were shipped to the participating laboratories with instructions for the further processing.

In January 2016, also the METRO group of JRC-G.2 was invited by ABACC to participate. However, due to the need for licensing for the import of such nuclear material into Belgium, the time and resources needed for the processing of the samples, it was decided to coordinate with the IAEA laboratories (SGAS) for this project. The IAEA generously agreed to share sample solutions from their preparation with JRC-G.2, which were allowed to be shipped without the need for an import license, due to the much reduced amount of fissile uranium.

It was proposed by JRC-G.2 to utilize the so-called "Double Spike" (DS) method for the isotopic analysis of the samples by TIMS, because this method provides a remarkably

better precision by a factor of about 5-10 compared to other commonly used TIMS methods like the "classical" total evaporation (TE) or "Modified Total Evaporation" (MTE) [3]. This is due to the fact that the certified  $^{233}\text{U}/^{236}\text{U}$  ratio of the double spike, e.g. IRMM-3636a, with a ratio  $^{233}\text{U}/^{236}\text{U}=1.01906(16)$  certified on 01/07/2007 [4], can be used for an internal mass fractionation correction of the measured  $^{235}\text{U}/^{238}\text{U}$  ratio throughout the entire measurement duration of a sample loaded on a filament. Due to the improved precision the double spike technique is already being used widely for scientific applications, in particular in geochemistry and cosmochemistry, for investigating the age and source of natural uranium samples, geochemical or physical processes [5-6], or for determining important half-life values of long-lived isotopes (i.e.  $^{234}\text{U}$  and  $^{230}\text{Th}$ ) for age determinations [7].

Recently, the double spike method has been utilized also as a powerful tool for investigating conversion processes ongoing in nuclear facilities and laboratories, by comparing  $^{235}\text{U}/^{238}\text{U}$  ratios before and after sample processing. This is possible due to the high precision of this method, in particular if samples are measured on the same magazine (also called turret), using the same method parameters, same detector calibration. As explained in detail in [2], the double spike method was used at IRMM to prove the absence of fractionation effects for a non-quantitative distillation of  $\text{UF}_6$  from one "mother" ampoule to a "daughter" ampoule. From both the mother and (several) daughter ampoules  $\text{UF}_6$  material was hydrolysed, each time by again distilling  $\text{UF}_6$  into a separate glass ampoule cooled with liquid nitrogen, followed by opening it to atmosphere and adding water for performing a quantitative hydrolysis. The obtained  $\text{UO}_2\text{F}_2$  materials were subsequently dried and treated with  $\text{HNO}_3$  to prepare a loading solution for DS/TIMS measurements. As a result, the material obtained directly from the mother ampoule was distilled only once, and the materials from the daughter ampoules twice during this program. If there was a fractionation effect during each distillation, the isotopic composition would have been different between the material from the mother and daughter ampoules. But the results for the  $^{235}\text{U}/^{238}\text{U}$  measurements by the double spike method for all mother and daughter materials were in excellent agreement, within a standard deviation of  $<0.002\%$ . This result confirmed the absence of a fractionation effect for distillation of  $\text{UF}_6$ , even in case it is not quantitative. However, this result was not very surprising, because the sublimation of  $\text{UF}_6$  is not expected to cause a mass fractionation, the pressures in the connection line between the ampoules still allow viscous flow, and the subsequent hydrolysis is quantitative. But assumptions like this have to be investigated carefully for working with nuclear materials, and the double spike method has shown to be a powerful tool for this type of work.

As a next step, also the fluorination of solid uranium materials towards  $\text{UF}_6$  gas would have to be examined, which is usually not quantitative and where the risk of fractionation is known to be much higher. Furthermore, the double spike method might also be attractive for quantifying (centrifuge) enrichment processes within enrichment plants in case an improved measurement precision is desired. But usually the performance of quadrupole ICP or  $\text{UF}_6$ -gas source magnetic sector (GSMS) instruments is sufficient for this.  $\text{UF}_6$ -GSMS instruments can perform  $^{235}\text{U}/^{238}\text{U}$  ratio measurements with similar precision as observed for DS/TIMS, but in contrast, the accuracy of  $\text{UF}_6$ -GSMS measurements can be significantly compromised by memory effects stemming from the ion source and accumulated over time within the containers of the inlet system. The double spike method can also be used successfully with MC-ICPMS instruments [7], which have larger fractionation effects but often higher sensitivity compared to TIMS, depending on the sample introduction system.

For the measurements described in this report, the double spike isotope reference material IRMM-3636a was used for TIMS measurements. IRMM-3636a has a uranium concentration of about 0.1 mg/g, it is a 10-fold dilution of the original double spike material IRMM-3636 with a concentration of about 1.0 mg/g. IRMM-3636 was prepared gravimetrically using highly ( $>99.96\%$ ) enriched  $^{233}\text{U}$  and  $^{236}\text{U}$  starting materials [4]. The  $^{233}\text{U}/^{236}\text{U}$  ratio was adjusted to about 1:1 and certified with an extended relative

uncertainty of 0.016% (coverage factor  $k=2$ ). The isotopic composition is shown in Table 1. By mixing the  $^{233}\text{U}/^{236}\text{U}$  double spike solution with the sample on the filament and applying internal mass fractionation correction, the  $^{235}\text{U}/^{238}\text{U}$  ratio of a given sample can be determined with high precision and accuracy [4].

In the past double spike reference materials similar to IRMM-3636 have already been prepared at various laboratories. However, the unique characteristics of IRMM-3636 are the high isotopic enrichment of the starting materials, leading to quite low abundances of the  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  isotopes in the double spike, and the specific preparation technique. The double spike mixture at JRC-G.2 was made gravimetrically with the basic principle of dissolving weighable amounts of highly enriched oxides into solutions and mixing the solutions in the desired proportions gravimetrically. Prior to mixing, the  $^{233}\text{U}$  and  $^{236}\text{U}$  starting materials were purified using the same reagents and procedures, which involved anion exchange in nitric acid medium, cation exchange in  $\text{HNO}_3/\text{THF}$  and precipitation as peroxide. The purified  $^{233}\text{U}$  and  $^{236}\text{U}$  starting materials were calcined under (as much as possible) identical conditions of temperature and humidity in order to form  $\text{U}_3\text{O}_8$  and to ensure that both enriched materials have the same stoichiometry. The purified and calcined  $^{233}\text{U}$  and  $^{236}\text{U}$  oxides were dissolved into  $\text{HNO}_3$  solution gravimetrically and the solutions were then mixed gravimetrically to obtain the double spike solution. The isotopic composition was calculated based on the weights of the  $^{233}\text{U}$  and  $^{236}\text{U}$  starting materials and their isotopic compositions, which were measured by TIMS. Due to their high enrichments, the uncertainties of the TIMS measurements for the starting materials did not contribute significantly to the calculation of the  $^{233}\text{U}/^{236}\text{U}$  isotope ratio of the double spike.

Isotope Ratio	Certified Value Uncertainty with coverage factor $k=2$ , 1 July 2007
$^{233}\text{U}/^{236}\text{U}$	1.01906(16)
$^{234}\text{U}/^{236}\text{U}$	0.000366 06(48)
$^{235}\text{U}/^{236}\text{U}$	0.000045 480(74)
$^{238}\text{U}/^{236}\text{U}$	0.000234 81(38)

Table 1: The isotopic composition of the double spike reference material IRMM-3636(a)

As the final stage, a careful mass spectrometric verification measurement of the  $^{233}\text{U}/^{236}\text{U}$  ratio was performed using a Triton TIMS at JRC-G.2. For this purpose the double spike "sample" was mixed with an approximate amount ratio of 1:1 with the synthetic isotope reference material IRMM-3050. IRMM-3050 is the original synthetic mixture of highly enriched  $^{235}\text{U}$  and  $^{238}\text{U}$  spikes, part of which was mixed with a  $^{233}\text{U}$  spike to obtain the IRMM-074 series [8]. For the verification measurement the known  $^{235}\text{U}/^{238}\text{U}$  ratio of 1.000259(81) in IRMM-3050 was used for internal mass fractionation correction to measure  $^{233}\text{U}/^{236}\text{U}$  of the "sample" IRMM-3636. The very low uncertainty of the  $^{235}\text{U}/^{238}\text{U}$  ratio for IRMM-074 is due to the fact that the purified oxides were mixed and dissolved together to form a master solution; whereas for the mixed spike, IRMM-3636, solutions of  $^{233}\text{U}$  and  $^{236}\text{U}$  were mixed, reflected in a higher uncertainty for the double spike. For the verification measurement of IRMM-3636 a multi-dynamic procedure was applied in order to minimize any influence and uncertainty contributions arising from the Faraday amplifier gains and cup efficiencies. This was achieved by measuring the  $^{235}\text{U}/^{238}\text{U}$  ratio of IRMM-3050 using the same pair of Faraday cups as the  $^{233}\text{U}/^{236}\text{U}$  ratio of IRMM-3636. The result for the mass spectrometric verification measurement of IRMM-3636 was given by a ratio of  $^{233}\text{U}/^{236}\text{U}=1.019090(86)$ . The relative expanded uncertainty of 0.0086% (coverage factor  $k=2$ ) is only slightly higher than the relative uncertainty of 0.0081% for the IRMM-3050 synthetic reference material. This mass spectrometric result is in excellent agreement with the calculated

ratio from the gravimetric mixing,  $^{233}\text{U}/^{236}\text{U}=1.01906(16)$ , the relative difference 0.003(12)% being insignificant. Note that IRMM-3050 is an internally used reference material and not available from JRC-G.2. for other laboratories.

The double spike technique is frequently used in geochemistry, where also reliable standard materials for the precise and accurate measurements of  $^{238}\text{U}/^{235}\text{U}$  isotope ratios in natural sample materials have gained an increasingly important role. Recent findings do not only show variability for the  $^{238}\text{U}/^{235}\text{U}$  isotope ratios in nature of up to 0.13% but also emphasize that accurate  $^{238}\text{U}/^{235}\text{U}$  isotope ratios are needed for reliable and consistent Pb-Pb dating of geological samples. Therefore, in 2010, the commonly used 'consensus value' of 137.88 for the  $^{238}\text{U}/^{235}\text{U}$  isotope ratio of the NBS SRM 960 (NBL CRM 112a) standard has been re-measured in a collaborative effort by several geochemistry laboratories and JRC-G.2 [9]. The new data have been acquired using new isotopic reference materials, for example IRMM-3636a, but also other double spike materials, combined with variety of instrumentation types and new measurement methods. The result was a new average value of 137.837(15) for the  $^{238}\text{U}/^{235}\text{U}$  isotope ratio of NBS SRM 960. This new consensus value is about 0.031% lower than the old consensus value. Moreover, it is traceable to the SI and an uncertainty statement is provided according to the Guide to the Expression of Uncertainty in Measurements (GUM). As an alternative to NBS SRM 960, the (close to) natural reference material IRMM-184 has been re-measured as well by several laboratories using the double spike IRMM-3636, resulting in a  $^{238}\text{U}/^{235}\text{U}$  value of 137.683(20), which is in agreement with the certified value of 137.697(41). But NBL CRM 112A still remains the primary choice as quality control and even as a reference material for external normalization for high precision  $^{238}\text{U}/^{235}\text{U}$  measurements. This popularity is due to its widespread availability, e.g. in nuclear laboratories as well as in the scientific area, and due to the very low  $^{236}\text{U}$  relative abundance, which is below the detection limit of  $6 \times 10^{-10}$  of the MTE method [3], compared to IRMM-184 ( $1.2 \times 10^{-7}$ ) and IRMM-3050 ( $3.8 \times 10^{-5}$ ).

Based on the experience with the double spike method, JRC-G.2 proposed to ABACC and IAEA to use this method as a tool for the investigation of the Cristallini sampling process with the best possible precision and accuracy for the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio. For the so-called "minor" ratios  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  the MTE method was selected as the best choice at SGAS/IAEA.

## 2 Experimental

Isotope ratio measurements using the DS/TIMS method were performed at JRC-G.2 and SGAS/IAEA using TRITON TIMS instruments following an agreed loading plan. Table 2 shows the main characteristics of the 16 samples obtained in P-10 tubes from ABACC. The sample preparation was performed in the uranium chemical preparation laboratory at SGAS/IAEA. All loading solutions were adjusted to have an approximate U-concentration of 2.0 mg U/ mL for both the MTE and the double spike method.

For the double spike method the mass fractionation corrections are performed internally using the certified  $^{233}\text{U}/^{236}\text{U}$  ratio, therefore no additional reference materials have to be measured for this correction, like for the MTE method. However, quality control samples (QCS) were included into the measurement sequences. At JRC-G.2., IRMM-3050 and IRMM-184 were used, at SGAS only IRMM-184 was used. In addition to the sequences for the Cristallini validation project, several additional quality control sequences were measured at JRC-G.2, which included the reference materials IRMM-3050, IRMM-184, NBL CRM 112A and IRMM-022.

The sample turret loading schemes for the sequences measured at JRC-G.2 and SGAS/IAEA are shown below in Tables 3-5. The turret holds 21 positions, 4 were allocated for QCS, 16 positions were allocated for samples taken either using the direct hydrolysis method ("H") or the ABACC-Cristallini method "A-C". The turret schemes are defined in a way that "H" and "A-C" samples are evenly spread over the entire

measurement sequence, but not always in the same order. Positon 21 was allocated to a test sample of the double spike IRMM-3636a to be measured by total evaporation in order to check for possible cross-contamination, in particular with  $^{235}\text{U}$  and  $^{238}\text{U}$  from the samples and QCS, during the loading procedure.

For the filament loading, first the double spike, usually a 1 $\mu\text{L}$ -drop of IRMM-3636a containing 100ng of uranium, was loaded on the filament, followed by loading 2-3 1 $\mu\text{L}$ -drops of the sample containing 4-6 $\mu\text{g}$  of uranium using a different pipette tip. This is done to avoid as much as possible, that the double spike, which contains only small and well known amounts of  $^{235}\text{U}$  and  $^{238}\text{U}$ , could become cross-contaminated from the samples. The sample/spike ratio was about 40-60. The sample heating pattern was designed in a way similar to the MTE method in order to achieve a total sample consumption within a consistent time period of 2-3 hours for each filament. The use of the MTE heating script [3] allows a cross-check of results calculated by internal normalization for the double spike method with the data calculated in MTE-mode (but with inferior precision) from the samples and QCS materials. Furthermore, the  $^{233}\text{U}/^{236}\text{U}$  ratio corrected for the  $^{236}\text{U}$  from the sample can be checked for consistency of the correction between all different sample and QCS measurements. The target for the sum intensity of all isotopes  $^{233}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$  and  $^{238}\text{U}$  is about 20 V on a Faraday cup connected to an amplifier with a  $10^{11}\Omega$  resistor, this equivalent to a sum ion current of about  $2 \times 10^{-10}$  A. Amplifiers with  $10^{12}\Omega$  resistors were used for more precise detection of the  $^{233}\text{U}$  and  $^{236}\text{U}$  ion beams, for depleted materials they were used for  $^{235}\text{U}$  and  $^{236}\text{U}$ .

Sample ID	Reference Material	$^{235}\text{U}$ Enrichment	Sampling method*	Tube number	Declared U mass, mg
80203-01-N	IRMM-020	0.2%	H	5	105
80203-02-N	IRMM-020	0.2%	A-C	10	136
80203-03-N	IRMM-020	0.2%	A-C	22	115
80203-04-N	IRMM-020	0.2%	H	23	130
80203-05-N	IRMM-022	0.72%	A-C	40	112
80203-06-N	IRMM-022	0.72%	H	61	102
80203-07-N	IRMM-022	0.72%	H	65	124
80203-08-N	IRMM-022	0.72%	A-C	68	124
80203-09-N	IRMM-023	3.3%	H	69	94
80203-10-N	IRMM-023	3.3%	A-C	74	111
80203-11-N	IRMM-023	3.3%	H	77	118
80203-12-N	IRMM-023	3.3%	A-C	90	132
80203-13-N	IRMM-029	4.2%	A-C	112	137
80203-14-N	IRMM-029	4.2%	A-C	116	136
80203-15-N	IRMM-029	4.2%	H	117	138
80203-16-N	IRMM-029	4.2%	H	135	159

Table 2: Samples received at SGAS/IAEA in P-10 tubes from ABACC. H=standard hydrolysis method (shaded in grey), A-C=ABACC-Cristallini method. N in the 1<sup>st</sup> column denotes the sample set. For MTE measurements at SGAS/IAEA sets 18 and 19 were used, for double spike measurements at SGAS/IAEA set 20 was assigned, and for double spike measurements at JRC-G.2 sets 21-24 were provided by the IAEA.

Position	Sample	Position	Sample	Position	Sample
1	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	8	4µg (=2µL) 80203-01-N + 100ng (=1µL) IRMM-3636a	15	4µg (=2µL) 80203-03-N + 100ng (=1µL) IRMM-3636a
2	4µg (=2µL) 80203-01-N + 100ng (=1µL) IRMM-3636a	9	4µg (=2µL) 80203-02-N + 100ng (=1µL) IRMM-3636a	16	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a
3	4µg (=2µL) 80203-01-N + 100ng (=1µL) IRMM-3636a	10	4µg (=2µL) 80203-02-N + 100ng (=1µL) IRMM-3636a	17	4µg (=2µL) 80203-04-N + 100ng (=1µL) IRMM-3636a
4	4µg (=2µL) 80203-02-N + 100ng (=1µL) IRMM-3636a	11	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	18	4µg (=2µL) 80203-04-N + 100ng (=1µL) IRMM-3636a
5	4µg (=2µL) 80203-02-N + 100ng (=1µL) IRMM-3636a	12	4µg (=2µL) 80203-04-N + 100ng (=1µL) IRMM-3636a	19	4µg (=2µL) 80203-03-N + 100ng (=1µL) IRMM-3636a
6	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	13	4µg (=2µL) 80203-04-N + 100ng (=1µL) IRMM-3636a	20	4µg (=2µL) 80203-03-N + 100ng (=1µL) IRMM-3636a
7	4µg (=2µL) 80203-01-N + 100ng (=1µL) IRMM-3636a	14	4µg (=2µL) 80203-03-N + 100ng (=1µL) IRMM-3636a	21	300ng (=1µL) IRMM-3636a

Table 3: Turret loading scheme for samples 80203-01-N – 80203-04-N (IRMM-020, enrichment 0.2% <sup>235</sup>U), labelled as turret 11 at SGAS/IAEA and turret 15 as JRC-G.2. The "H" samples are shaded in grey. QCS: quality control samples, at JRC-G.2, IRMM-3050 and IRMM-184 were used, at SGAS/IAEA only IRMM-184 was used. N denotes the sample set. For double spike measurements at SGAS/IAEA set 20 was assigned, and for double spike measurements at JRC-G.2 sets 22-23 were used.

Position	Sample	Position	Sample	Position	Sample
1	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	8	4µg (=2µL) 80203-06-N + 100ng (=1µL) IRMM-3636a	15	4µg (=2µL) 80203-08-N + 100ng (=1µL) IRMM-3636a
2	4µg (=2µL) 80203-06-N + 100ng (=1µL) IRMM-3636a	9	4µg (=2µL) 80203-05-N + 100ng (=1µL) IRMM-3636a	16	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a
3	4µg (=2µL) 80203-06-N + 100ng (=1µL) IRMM-3636a	10	4µg (=2µL) 80203-05-N + 100ng (=1µL) IRMM-3636a	17	4µg (=2µL) 80203-07-N + 100ng (=1µL) IRMM-3636a
4	4µg (=2µL) 80203-05-N + 100ng (=1µL) IRMM-3636a	11	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	18	4µg (=2µL) 80203-07-N + 100ng (=1µL) IRMM-3636a
5	4µg (=2µL) 80203-05-N + 100ng (=1µL) IRMM-3636a	12	4µg (=2µL) 80203-07-N + 100ng (=1µL) IRMM-3636a	19	4µg (=2µL) 80203-08-N + 100ng (=1µL) IRMM-3636a
6	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	13	4µg (=2µL) 80203-07-N + 100ng (=1µL) IRMM-3636a	20	4µg (=2µL) 80203-08-N + 100ng (=1µL) IRMM-3636a
7	4µg (=2µL) 80203-06-N + 100ng (=1µL) IRMM-3636a	14	4µg (=2µL) 80203-08-N + 100ng (=1µL) IRMM-3636a	21	300ng (=1µL) IRMM-3636a

Table 4: Turret loading scheme for samples 80203-04-N – 80203-08-N (IRMM-022, enrichment 0.72% <sup>235</sup>U), labelled as turret 12 at SGAS/IAEA and turret 16 as JRC-G.2. The "H" samples are shaded in grey. QCS: quality control sample, at JRC-G.2, IRMM-3050 was used, at SGAS/IAEA IRMM-184 was used. N denotes the sample set. For double spike measurements at SGAS/IAEA set 20 was assigned, and for double spike measurements at JRC-G.2 set 22 was used.

Position	Sample	Position	Sample	Position	Sample
1	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	8	4µg (=2µL) 80203-09-N + 100ng (=1µL) IRMM-3636a	15	4µg (=2µL) 80203-12-N + 100ng (=1µL) IRMM-3636a
2	4µg (=2µL) 80203-09-N + 100ng (=1µL) IRMM-3636a	9	4µg (=2µL) 80203-10-N + 100ng (=1µL) IRMM-3636a	16	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a
3	4µg (=2µL) 80203-09-N + 100ng (=1µL) IRMM-3636a	10	4µg (=2µL) 80203-10-N + 100ng (=1µL) IRMM-3636a	17	4µg (=2µL) 80203-11-N + 100ng (=1µL) IRMM-3636a
4	4µg (=2µL) 80203-10-N + 100ng (=1µL) IRMM-3636a	11	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	18	4µg (=2µL) 80203-11-N + 100ng (=1µL) IRMM-3636a
5	4µg (=2µL) 80203-10-N + 100ng (=1µL) IRMM-3636a	12	4µg (=2µL) 80203-11-N + 100ng (=1µL) IRMM-3636a	19	4µg (=2µL) 80203-12-N + 100ng (=1µL) IRMM-3636a
6	QCS (4µg,=2µL) + 100ng (=1µL) IRMM-3636a	13	4µg (=2µL) 80203-11-N + 100ng (=1µL) IRMM-3636a	20	4µg (=2µL) 80203-12-N + 100ng (=1µL) IRMM-3636a
7	4µg (=2µL) 80203-09-N + 100ng (=1µL) IRMM-3636a	14	4µg (=2µL) 80203-12-N + 100ng (=1µL) IRMM-3636a	21	300ng (=1µL) IRMM-3636a

Table 5: Turret loading scheme for samples 80203-09-N – 80203-12-N (IRMM-023, enrichment 3.3%  $^{235}\text{U}$ ), labelled as turret 13 at SGAS/IAEA and turret 17 as JRC-G.2. The "H" samples are shaded in grey. QCS: quality control sample, at JRC-G.2, IRMM-3050 was used, at SGAS/IAEA IRMM-184 was used. N denotes the sample set. For double spike measurements at SGAS/IAEA set 20 was assigned, and for double spike measurements at JRC-G.2 set 22 was used.

For the materials with sample ID 80203-13-N – 80203-16-N (IRMM-029, enrichment 4.2%  $^{235}\text{U}$ ), one sequence was measured at SGAS/IAEA, but the results were not acceptable for this project. The reason was that the sample of IRMM-029 contains  $^{236}\text{U}$  with an abundance of about 1%, preventing a reliable correction of the  $^{233}\text{U}/^{236}\text{U}$  ratio of the double spike for  $^{236}\text{U}$ , which is needed for the internal correction. If much more double spike was added, the tailing contribution from  $^{236}\text{U}$  towards  $^{235}\text{U}$  would become a difficult matter to correct for. Thus, the data are not used and no measurements of IRMM-029 samples were performed at JRC-G.2.

### 3 Results

Within this section the results for double spike measurements of all "H" and "A-C" samples 80203-01-N – 80203-12-N are presented, see Tables 6 and 7 below.

JRC-G.2 sample ID	$^{235}\text{U}/^{238}\text{U}$ using DS Method	Uc (k=2) without Uc of DS	Uc (k=2) including Uc of DS ( $\pm 0.016\%$ )
80203-01-23 (H)	0.00209568	0.00000025	0.00000041
80203-02-23 (A-C)	0.00209608	0.00000010	0.00000034
80203-03-23 (A-C)	0.00209602	0.00000005	0.00000033
80203-04-23 (H)	0.00209566	0.00000010	0.00000035
Average H	0.00209567	0.00000014	0.00000036
Average A-C	0.00209605	0.00000012	0.00000036
Rel. diff. A-C vs H	0.0185%		
Uc of rel. diff. (k=2)	0.0088%		
80203-05-22 (A-C)	0.00725599	0.00000017	0.00000115
80203-06-22 (H)	0.00725539	0.00000019	0.00000116
80203-07-22 (H)	0.00725558	0.00000011	0.00000114
80203-08-22 (A-C)	0.00725603	0.00000009	0.00000114
Average H	0.00725549	0.00000031	0.00000120
Average A-C	0.00725601	0.00000024	0.00000119
Rel. diff. A-C vs H	0.0072%		
Uc of rel. diff. (k=2)	0.0054%		
80203-09-22 (H)	0.03387848	0.00000054	0.00000535
80203-10-22 (A-C)	0.03387877	0.00000034	0.00000533
80203-11-22 (H)	0.03387976	0.00000066	0.00000536
80203-12-22 (A-C)	0.03388079	0.00000032	0.00000533
Average H	0.03387903	0.00000098	0.00000551
Average A-C	0.03387964	0.00000132	0.00000558
Rel. diff. A-C vs H	0.0018%		
Uc of rel. diff. (k=2)	0.0049%		

Table 6: Results for double spike measurements of all "H" and "A-C" samples 80203-01-N – 80203-12-N from JRC-G.2, which are samples of IRMM-020, IRMM-022 and IRMM-023, with enrichments 0.2%, 0.72% and 3.3%  $^{235}\text{U}$ . The "H" samples are shaded in grey.

SGAS/IAEA sample ID	$^{235}\text{U}/^{238}\text{U}$ using DS Method	Uc (k=2) without Uc of DS	Uc (k=2) including Uc of DS ( $\pm 0.016\%$ )
80203-01-20 (H)	0.00209565	0.00000005	0.00000033
80203-02-20 (A-C)	0.00209602	0.00000010	0.00000034
80203-03-20 (A-C)	0.00209607	0.00000003	0.00000033
80203-04-20 (H)	0.00209577	0.00000002	0.00000033
Average H	0.00209571	0.00000014	0.00000036
Average A-C	0.00209605	0.00000015	0.00000037
Rel. diff. A-C vs H	0.0161%		
Uc of rel. diff. (k=2)	0.0097%		
80203-05-20 (A-C)	0.00725580	0.00000017	0.00000115
80203-06-20 (H)	0.00725507	0.00000012	0.00000115
80203-07-20 (H)	0.00725527	0.00000013	0.00000115
80203-08-20 (A-C)	0.00725576	0.00000010	0.00000114
Average H	0.00725517	0.00000027	0.00000119
Average A-C	0.00725578	0.00000029	0.00000120
Rel. diff. A-C vs H	0.0084%		
Uc of rel. diff. (k=2)	0.0055%		
80203-09-20 (H)	0.03387911	0.00000033	0.00000533
80203-10-20 (A-C)	0.03387999	0.00000046	0.00000534
80203-11-20 (H)	0.03388001	0.00000066	0.00000536
80203-12-20 (A-C)	0.03388161	0.00000087	0.00000539
Average H	0.03387956	0.00000102	0.00000552
Average A-C	0.03388080	0.00000164	0.00000566
Rel. diff. A-C vs H	0.0037%		
Uc of rel. diff. (k=2)	0.0057%		

Table 7: Results for double spike measurements of all "H" and "A-C" samples 80203-01-20 – 80203-12-20 from SGAS/IAEA, which are samples of IRMM-020, IRMM-022 and IRMM-023, with enrichments 0.2%, 0.72% and 3.3%  $^{235}\text{U}$ . The "H" samples are shaded in grey.

The uncertainties of the averages are based on consistency checks [10] for all samples with same sampling method (either "H" or "A-C") and same enrichment, achieving overlap of all individual measurements with their average. All ratios were measured with at least four replicate filaments, and the averages calculated from those. The uncertainties for the averages are presented both without the uncertainty from the certified double spike and also including the uncertainty from the certified double spike, which is the dominating source of uncertainty in this case. All measured ratios obtained

for these test samples prepared from well-known reference materials agree well with the respective certified values, as shown in Fig. 1a,b,c below.

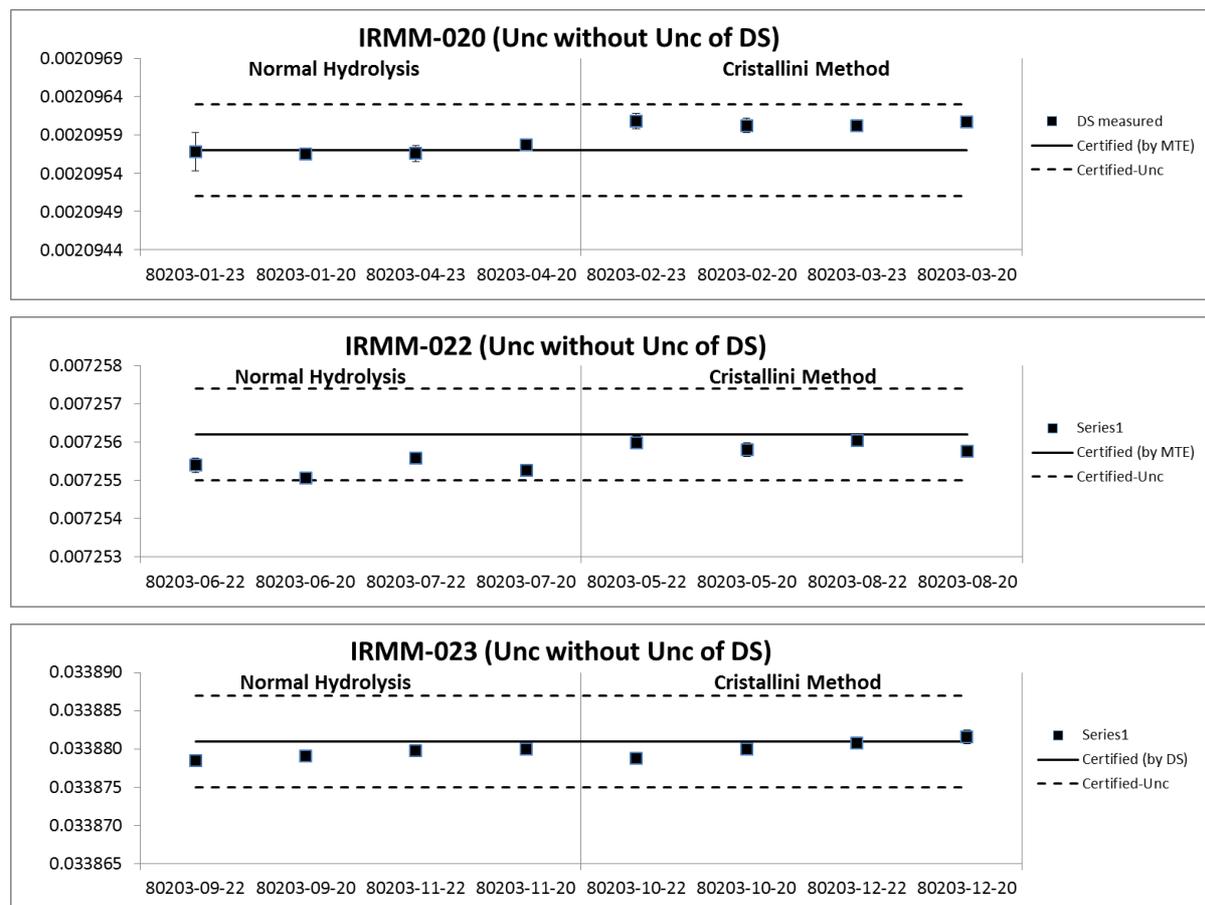
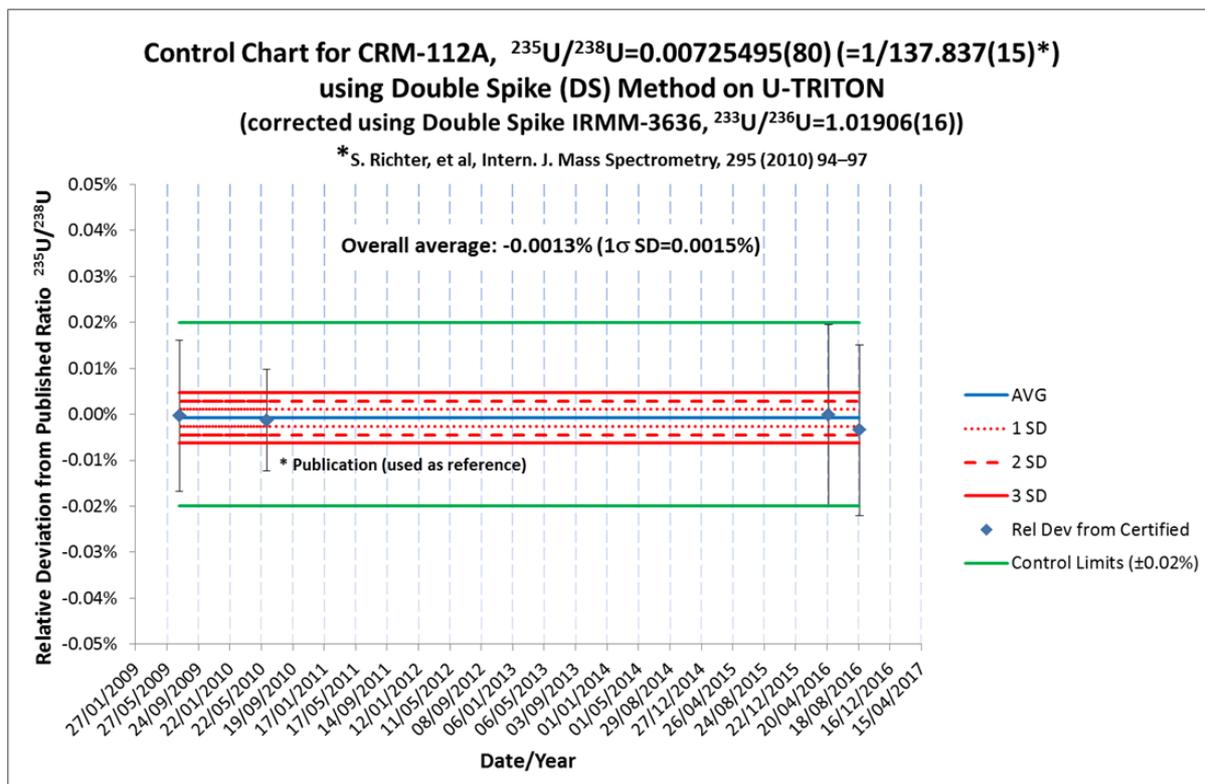
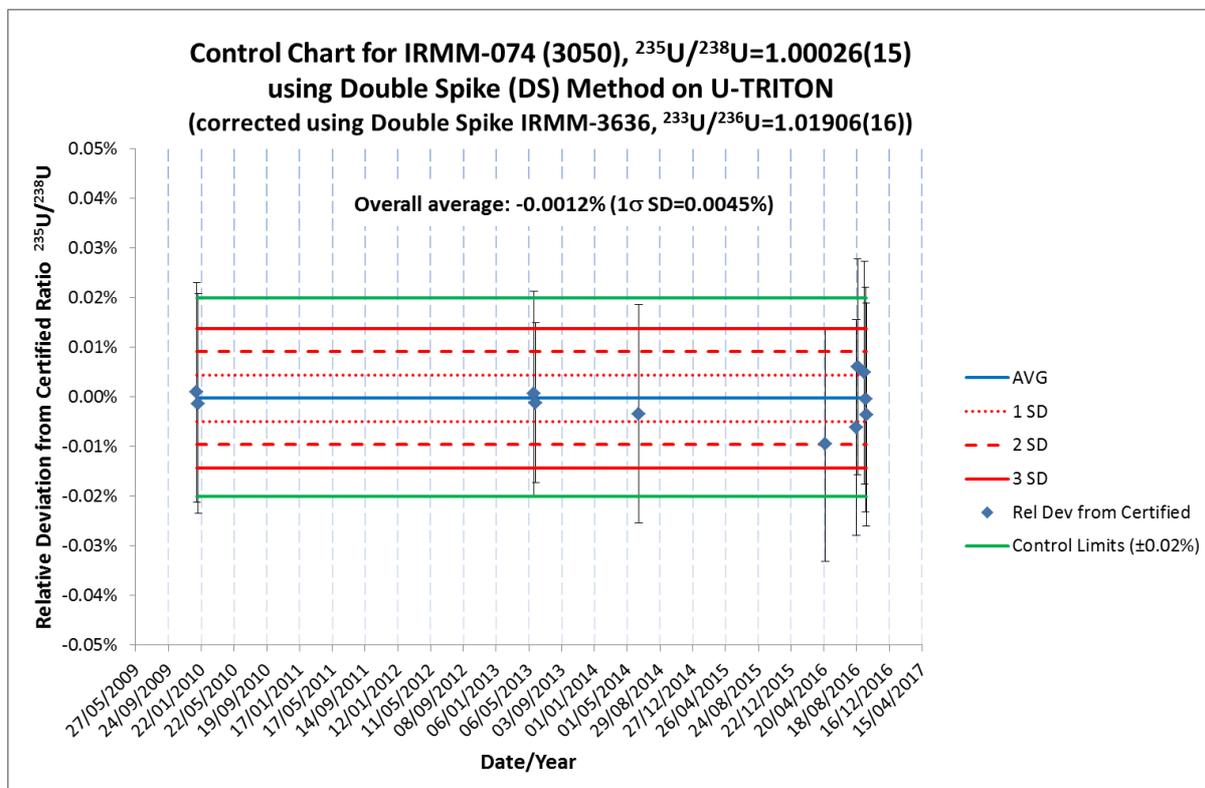


Fig 1a,b,c: Isotope ratios measured using double spike method, in comparison with the respective certified values. The uncertainties for the averages are presented without the uncertainty from the used certified double spike.

Also the results of all QCS measurements using the double spike method agree well with their respective certified values, and/or published consensus values [9] in case of IRMM-184 and NBL CRM 112A. The long term QCS control charts for IRMM-3050, NBL CRM 112A and IRMM-184 at JRC-G.2 and the newly established QCS control chart for IRMM-184 at SGAS/IAEA are shown in Figures 2 a,b,c,d. The QCS control charts confirm the long-term precision of about 0.0015% to 0.0045% and the accuracy at a level of about 0.0025% that is achievable using the double spike method.

For the Cristallini validation program all "H" and "A-C" samples were only to be compared to each other, thus they were measured on the same turret and within the same sequence under as much as possible similar measurement conditions. But if double spike results of the same sample material are measured on different sample turrets, or different instruments, or even in different laboratories, and have to be compared, slight differences in instrument performance, Faraday cup efficiencies, gain calibrations, etc might lead to different results and cause additional uncertainties. One approach would be to normalize all double spike results to well established double spike data for suitable QCS materials. One suitable candidate material would be NBL CRM 112A, which is used for this purpose already frequently in geochemistry laboratories, being available in many of these laboratories and also safeguards laboratories, having no <sup>236</sup>U to be corrected for, and for which a consensus value has been established recently [8]. For the current

validation program this was not yet considered, and other materials were chosen for which more QCS data were already available, like IRMM-3050 at JRC-G.2. The use of IRMM-3050 has the advantage, that the  $^{235}\text{U}/^{238}\text{U}$  ratio was obtained through gravimetric preparation which provides an independent check for the accuracy of the DS results. However, the disadvantage of IRMM-3050 is the risk of cross-contamination during sample loading in combination with natural or even depleted sample materials.



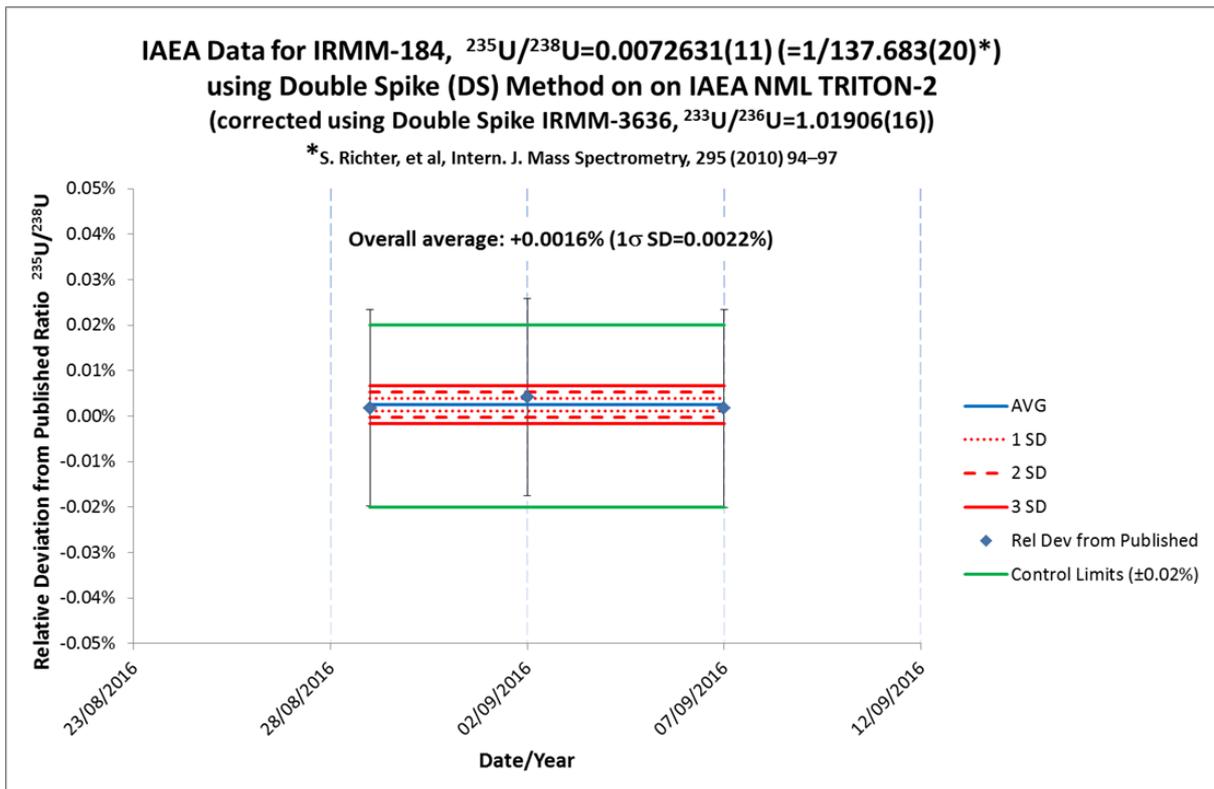
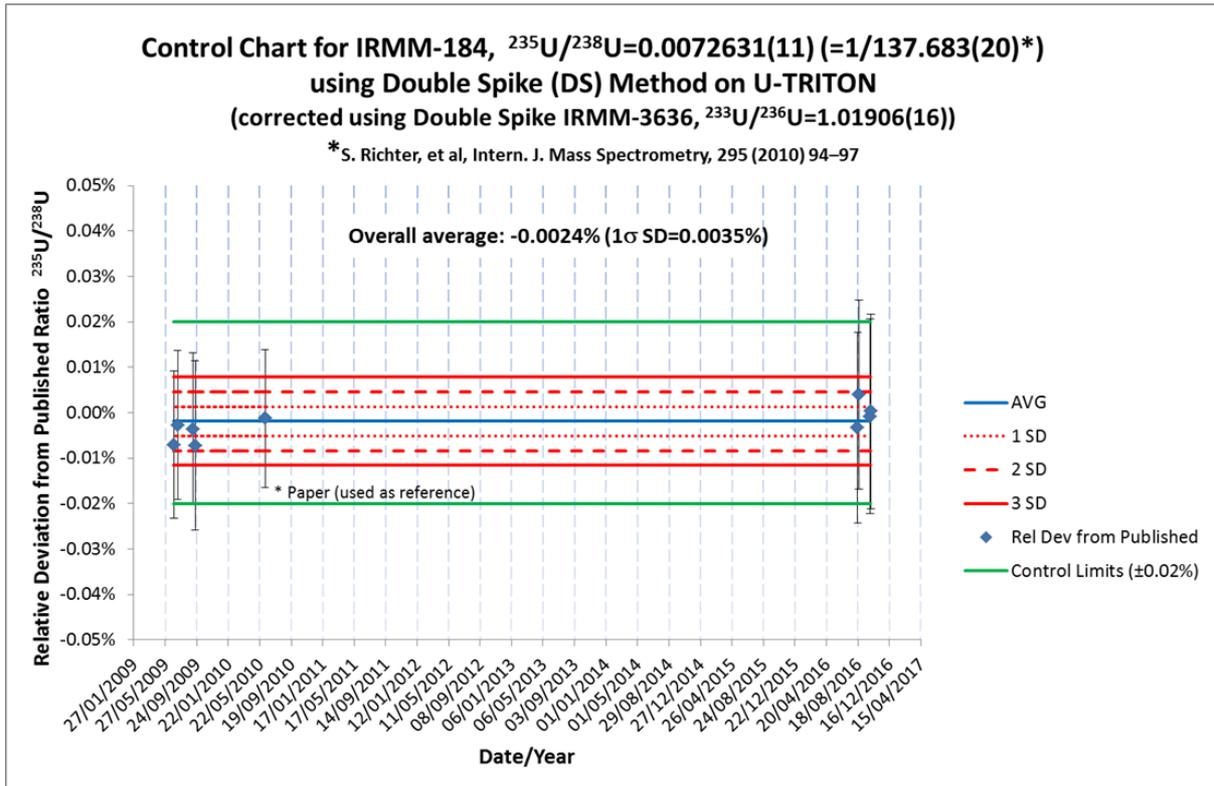


Fig 2a,b,c,d: QCS control charts for IRMM-3050, NBL CRM 112A and IRMM-184 at JRC-G.2 and for newly established QCS control chart for IRMM-184 at SGAS/IAEA.

Since all sample measurements were measured using the same double spike IRMM-3636a, its uncertainty is not relevant if ratios are compared against each other. In Tables 6 and 7 also the averages for all "H" samples and all "A-C" samples, respectively,

with the same enrichment measured on the same sample turret are calculated. These averages usually include results for 8 filaments (except for outliers with technical reasons) arising from 2 sub-samples measured by 4 replicate filaments on the same turret, e.g. 80203-01 and 80203-04 for all "H" measurements on turrets 11 (SGAS/IAEA) and 15 (JRC-G.2), see Table 3.

The uncertainties of the averages are calculated using a so-called consistency check, described in [10]. For this calculation, the uncertainties of all individual measurements (without the uncertainty from the certified double spike) are taken into account and the standard error of the mean (i.e. the average). For each individual measurement, the difference to the average is calculated with the combined uncertainty arising from both of them. In case the difference for any of the individual measurements is significant (i.e. larger than its own uncertainty), an additional uncertainty component is added to all of the individual measurements, in order to account for an unknown common effect. Subsequently the uncertainty of the average is re-calculated, taking into account the augmented uncertainties of all individual measurements and the standard error of the mean (i.e. the average). This goes slightly beyond the recommendation presented in [10] and might be considered an overestimation of the uncertainty for the average, but this approach was chosen to ensure that the uncertainty of the average is not at the lower limit given by the narrowest overlap of the individual results with the average.

After calculating the averages for all "H" and for all "A-C" measurements, the relative difference of the "A-C" average from the "H" average is derived, and the uncertainty for this relative difference based on the uncertainties of the averages. From the results in Tables 6 and 7, also shown in Fig. 3, it is obvious, that for the samples prepared from IRMM-020 and IRMM-022 with  $^{235}\text{U}$  enrichments of 0.2% and 0.72%, respectively, significant deviations were obtained between the ratios from sampling with the Cristallini method ("A-C") and the ratios from sampling with direct hydrolysis ("H").

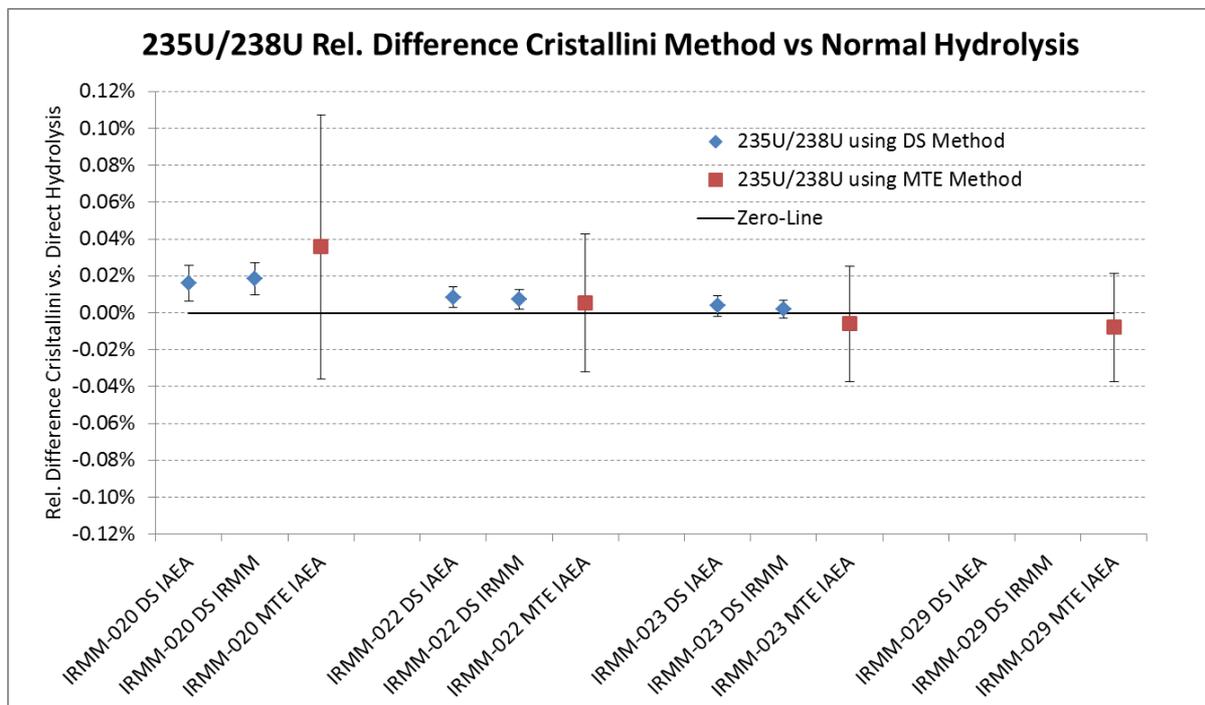


Fig. 3: Relative differences of isotope ratio measurements between Cristallini sampling and normal hydrolysis sampling.

The deviations are at the magnitude of about 0.017% for the 0.2% enriched materials, and about 0.008% for the 0.72% enriched materials. For the 3.3% enriched materials

the difference also has a positive sign but is below 0.005%, and not significant. The relative differences agree very well between the two laboratories performing the double spike measurements, SGAS/IAEA and JRC-G.2.

In Fig.3. also data derived from MTE measurements performed at SGAS/IAEA are shown for comparison. For the uncertainty of the relative difference between MTE measurements, all the common sources of uncertainty have been removed, e.g. the uncertainty of the  $^{235}\text{U}/^{238}\text{U}$  ratio of the reference material to correct for mass fractionation for MTE (IRMM-184,  $\pm 0.03\%$ ), because this uncertainty affects all measurements in the same way. To account for differences in the MTE running conditions due to different chemical preparation procedures, an additional relative uncertainty of 0.02% for comparative MTE measurements has been added in compliance with the MTE standard document ASTM-1832, section 14.6.3.1.

It is obvious from Fig.3, that the uncertainties for the relative differences for the double spike measurements from both JRC-G.2 and SGAS/IAEA are much smaller compared to those for the MTE method. This is due to the much better repeatability of double spike measurements compared to MTE and TE measurements, and confirms the usefulness of the double spike method for this validation program. It is also interesting to note, that the differences between "A-C" and "H" data obtained by MTE, without being significant, seem to follow the same trend with the  $^{235}\text{U}$  enrichment as recognized for the double spike method.

The differences between "A-C" and "H" obtained from double spike measurements are much smaller than typical uncertainties encountered for safeguards measurements. The differences might be due to the Cristallini sampling method itself or caused somewhere in the subsequent chemical preparation. A mass fractionation effect upon the adsorption of  $\text{UF}_6$  gas into the alumina pellets, similar to what has been observed during adsorption of uranium into Mn-oxyhydroxides [5], was also considered as a possibility, but the observed trend with the enrichment and the absence of a significant relative difference for the 3.3% enriched materials do rather not support this assumption.

As a result from the double spike measurements performed at SGAS/IAEA and JRC-G.2 which are in good mutual agreement, it can be suggested, that an additional uncertainty component of about 0.02% should be introduced to all  $^{235}\text{U}/^{238}\text{U}$  isotope measurements for samples taken using the Cristallini sampling method. As a consequence, a typical uncertainty of 0.040% for TE/MTE safeguards measurements would thereby increase towards about 0.045%, which is not much of a change. This would still be far below the ITVs (International Target Values [11]), which are 0.7% for DU and 0.28% for NU (not shown in Fig.3, they would be out of scale). It would allow all additional uncertainties due to the special sampling method and subsequent chemical processing to be accounted for in the mass spectrometric analysis. This uncertainty component is proposed to be stated within the ASTM standard document for the Cristallini sampling process, which is foreseen if the validation program is successful.

For the minor ratios  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  no meaningful results can be obtained by the double spike method, due to the isobaric interferences for  $^{234}\text{U}$  and  $^{236}\text{U}$  from the double spike material itself. The sample/spike ratio is also chosen in a way that the measured  $^{236}\text{U}$  ion beam intensity is dominated by the double spike itself and not by the sample, but as a consequence no meaningful  $^{236}\text{U}/^{238}\text{U}$  ratios for the sample can be derived. The minor ratios  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  have been analysed by the MTE method at SGAS/IAEA (results not shown in this report), but no significant differences were observed between "H" and "A-C" materials. Thus, the same additional uncertainty component of about 0.02% for using the Cristallini sampling method could be introduced also to the minor ratios  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$ , although this would make no difference typical safeguards measurements, at least not for the MTE measurements for this validation program at SGAS/IAEA.

## 4 Conclusions

High precision double spike isotope ratio measurements for test samples taken using the ABACC-Cristallini method were performed in comparison with measurements for samples taken in the traditional manner by distillation and subsequent direct hydrolysis. The results obtained at SGAS/IAEA and JRC-G.2 are in good mutual agreement, but they reveal slight differences for the  $^{235}\text{U}/^{238}\text{U}$  isotope ratios for samples taken by the Cristallini method compared to samples processed by the classical direct hydrolysis sampling method. For test samples prepared by ABACC using the IRMM-020 (0.2%  $^{235}\text{U}$ ) and IRMM-022 (0.7%  $^{235}\text{U}$ ) certified  $\text{UF}_6$  reference materials, significant differences of about 0.01%-0.02% were observed, but for test samples prepared from IRMM-023 (3.3%  $^{235}\text{U}$ ) the differences were below 0.005% and insignificant. The slight trend of the differences with the  $^{235}\text{U}$  enrichment was already indicated by MTE measurements performed (only) at SGAS/IAEA (although differences were not significant). The reason for the observed differences between the sampling methods is not yet known, they can be due to mass fractionation, contamination, memory or other still unknown effects occurred during the sampling or subsequent chemical processing.

The results from JRC-G.2 and SGAS/IAEA using the double spike method are characterized by their high precision. But the observed differences should not prevent the Cristallini sampling method from being implemented and further-on used for its intended purpose, as a new sampling method for nuclear safeguards measurements, in most cases mainly for confirming the declared enrichment of uranium materials within the nuclear fuel cycle. The benefits of the Cristallini sampling method are significant, a reduction of the sample amounts to be transported and to be kept at the facilities, and an improvement of the safety and cost of nuclear transports. But the slight differences observed at JRC-G.2 and SGAS/IAEA using the double spike method should not be neglected but rather included for the intended standardization of the Cristallini sampling method through ASTM, in particular by defining an additional uncertainty component to account especially for the Cristallini sampling process and the subsequent sample preparation. This uncertainty component should be attributed in the future to all isotopic measurements on samples taken by the Cristallini sampling method.

According to ABACC where the sampling was performed exclusively, a different sampling manifold was used for each reference material with a different  $^{235}\text{U}$  enrichment in order to eliminate the risk of cross contamination between materials flowing into the same sampling system. The results coming from other participating laboratories have to be carefully evaluated, where the measurements might have been performed using different instrumentation and methods, and on different sample sets obtained from ABACC. The double spike and MTE measurements performed at SGAS/IAEA and JRC-G.2 were all performed on the same sample set, and show very good mutual agreement, which also confirms the reliability of the applied mass spectrometric measurements and methods.

It would be interesting to observe if similar slight deviations are obtained for other sample sets analysed at other laboratories, e.g. at JRC-G.II.6 (Unit for Nuclear Safeguards and Forensics) in Karlsruhe, Germany. As mentioned already during the discussions about the planning of the validation program, JRC-G.2 would be glad to offer support to all other participating laboratories for obtaining the IRMM-3636a double spike reference material and for the implementation of the double spike method. This support already worked out successfully at the SGAS laboratory at the IAEA. Also for additional interested laboratories this kind of support would have to be organized within the frame of EU support programme to the IAEA.

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## List of abbreviations and definitions

ABACC	in Portuguese: "Agência Brasileiro-Argentina de Contabilidade e Controle de Materiais Nucleares" , in English: "Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials"
ASTM	American Society for Testing and Materials, United States
CNEA	Comisión Nacional de Energía Atómica – Centro Atómico Constituyentes, Buenos Aires, Argentina.
DOE	Department of Energy, United States
DS	Double Spike, Double Spike method
IAEA	International Atomic Energy Agency, United Nations
IRMM	Institute for Reference Materials and Measurements (formerly). The nuclear activities of IRMM are continued at JRC - Unit G.2, named "Standards for Nuclear Safety, Security and Safeguards" (SN3S)
ITV	International Target Value
JRC	Joint Research Centre, European Commission
ORNL	Oak Ridge National Laboratories, Department of Energy, United States
MTE	Modified Total Evaporation method, used in TIMS (see below)
NBL	New Brunswick Laboratory (formerly), now renamed as "NBL Program Office"
SGAS	Safeguards Analytical Services (IAEA), located in Seibersdorf, Austria
TE	Total evaporation method, used in TIMS (see below)
TIMS	Thermal Ionization Mass Spectrometry

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Fig 2a,b,c,d: QCS control charts for IRMM-3050, NBL CRM 112A and IRMM-184 at JRC-G.2 and for newly established QCS control chart for IRMM-184 at SGAS/IAEA.

Fig. 3: Relative differences of isotope ratio measurements between Cristallini sampling and normal hydrolysis sampling.

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Table 1: The isotopic composition of the double spike reference material IRMM-3636(a)

Table 2: Samples received at SGAS/IAEA in P-10 tubes from ABACC. H=standard hydrolysis method, A-C=ABACC-Cristallini method. N in the 1<sup>st</sup> column denotes the sample set. For MTE measurements at SGAS/IAEA sets 18 and 19 were used, for double spike measurements at SGAS/IAEA set 20 was assigned, and for double spike measurements at JRC-G.2 sets 21-23 were provided by the IAEA. Set 24 remains in the safe at JRC-G.2. in case more measurements have to be done.

Table 3: Turret loading scheme for samples 80203-01-N – 80203-04-N (IRMM-020, enrichment 0.2% <sup>235</sup>U), labelled as turret 11 at SGAS/IAEA and turret 15 as JRC-G.2. QCS: quality control sample, at JRC-G.2., IRMM-3050 and IRMM-184 were used, at SGAS/IAEA IRMM-184 was used. N denotes the sample set. For double spike measurements at SGAS/IAEA set 20 was assigned, and for double spike measurements at JRC-G.2 sets 22-23 were used.

Table 4: Turret loading scheme for samples 80203-04-N – 80203-08-N (IRMM-022, enrichment 0.72% <sup>235</sup>U), labelled as turret 12 at SGAS/IAEA and turret 16 as JRC-G.2. QCS: quality control sample, at JRC-G.2., IRMM-3050 was used, at SGAS/IAEA IRMM-184 was used. N denotes the sample set. For double spike measurements at SGAS/IAEA set 20 was assigned, and for double spike measurements at JRC-G.2 set 22 was used.

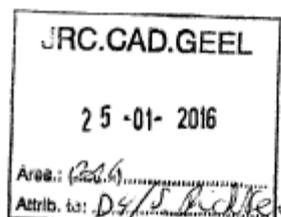
Table 5: Turret loading scheme for samples 80203-09-N – 80203-12-N (IRMM-023, enrichment 3.3% <sup>235</sup>U), labelled as turret 13 at SGAS/IAEA and turret 17 as JRC-G.2. QCS: quality control sample, at JRC-G.2, IRMM-3050 was used, at SGAS/IAEA IRMM-184 was used. N denotes the sample set. For double spike measurements at SGAS/IAEA set 20 was assigned, and for double spike measurements at JRC-G.2 set 22 was used.

Table 6: Results for double spike measurements of all "H" and "A-C" samples 80203-01-N – 80203-12-N from JRC-G.2, which are samples of IRMM-020, IRMM-022 and IRMM-023, with enrichments 0.2%, 0.72% and 3.3% <sup>235</sup>U.

Table 7: Results for double spike measurements of all "H" and "A-C" samples 80203-01-20 – 80203-12-20 from SGAS/IAEA, which are samples of IRMM-020, IRMM-022 and IRMM-023, with enrichments 0.2%, 0.72% and 3.3% <sup>235</sup>U.

## Annexes

1. Letter from S. G. Solmesky, Secretary of ABACC, to S. Richter, JRC-G.2 (formerly IRMM)



ABACC

Ref. Ares(2016)388947 - 25/01/2016  
AGÊNCIA BRASILEIRO-ARGENTINA  
DE CONTABILIDADE E CONTROLE  
DE MATERIAIS NUCLEARES  
AGENCIA BRASILEÑO-ARGENTINA  
DE CONTABILIDAD Y CONTROL DE  
MATERIALES NUCLEARES

MO-0026.00/2016

Rio de Janeiro, January 13<sup>th</sup> 2016

Dr. Stephan RICHTER  
Scientific Officer for Nuclear Mass Spectrometry  
European Commission  
Directorate-General Joint Research Centre  
Institute for Reference Materials and Measurements  
Unit "Standards for Nuclear Safety, Security and Safeguards" (SN3S)  
Retieseweg 111  
B-2440 Geel, BELGIUM

Ref. Qualification of ABACC-Cristallini Method for UF6 Sampling

Dear Dr Stephan Richter,

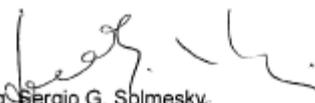
ABACC would like to invite your laboratory to participate in a UF6 sampling method evaluation campaign. This campaign will involve high accuracy measurement of uranium isotopes sampled as UF6 using two different sampling methods: Adsorption on alumina (ABACC-Cristallini or A-C method) and a standard direct hydrolysis method.

The goal of the campaign is to determine if there is any detectable difference in the isotopic composition of UF6 materials when sampled by the two methods. Four different IRMM UF6 Certified Reference Materials were sampled by each of the methods to create four pairs of samples for analysis. Each sample is contained in a P-10 tube, and will require dissolution and sample preparation prior to isotopic analysis.

A total of seven laboratories have been invited to participate in the campaign. Please, find attached some remarks about the qualification program and suggested sample preparation and measurement schemes. If you agree to participate, please respond with the name and contact information for a shipping and a technical contact.

Thank you for your consideration and we hope your laboratory will be willing to participate. Questions or comments are welcome, and please respond with your willingness to participate to: Sonia Fernández Moreno (sfmoreno@abacc.org.br) and Luis Carlos Machado (machado@abacc.org.br).

Sincerely yours,

  
Eng. Sergio G. Solmesky  
Secretary

2. Letter from Y. Kuno (Director, Office of SGAS/IAEA) to S. Richter, JRC-G. 2 (formerly IRMM)



Atoms for Peace

الوكالة الدولية للطاقة الذرية  
国际原子能机构  
International Atomic Energy Agency  
Agence Internationale de l'énergie atomique  
Международное агентство по атомной энергии  
Organismo Internacional de Energía Atómica

Vienna International Centre, PO Box 100, 1400 Vienna, Austria  
Phone: (+43 1) 2600 • Fax: (+43 1) 26007  
Email: Official.Mail@iaea.org • Internet: <http://www.iaea.org>

Mr Stephan Richter

European Commission  
Directorate-General Joint Research Centre  
Institute for Reference Materials and  
Measurements  
Retieseweg 111  
B-2440 GEEL  
BELGIUM

In reply please refer to: G5.0  
Dial directly to extension: (+431) 2600-28565

2016-08-11

Subject: Consultant under EC B 1752, "Training on Mass Spectrometry and Other Analytical Techniques

Dear Dr. Richter,

I would like to acknowledge your visit (consultancy assignment) to SGAS for technical support in the area of mass spectrometry (Task EC B 1752) for performing linearity studies on the two NEPTUNE™ multi-collector inductively coupled plasma mass spectrometers (MC-ICP-MS). The visit was very successful, as recognized by the joint publication "Linearity testing and dead-time determination for MC-ICP-MS ion counters using the IRMM-072 series of uranium isotope reference materials " by S Richter, S. Konegger-Kappel, S. Bulyha, G. Stadelmann, A. Koepf and H. Siegmund, within the Journal for Analytical Atomic Spectrometry, 2016, 31, 1647-1657.

I am furthermore grateful for your support regarding routine analyses of safeguards samples by thermal ionization mass spectrometry using the modified total evaporation technique, which is used by SGAS following the new ASTM standard document, C1832-16.

The IAEA would very much appreciate your continued support in mass spectrometric techniques in the future, in particular for analyses being performed using the "Double Spike" method, which will enable very accurate determination of the uranium isotopic composition in UF<sub>6</sub> samples in support of validation of the "Cristallini" sampling method.

Yours sincerely,

Yusuke Kuno  
Director  
Office of Safeguards Analytical Services  
Department of Safeguards

3. Certificate of Reference Measurement for validation of Cristallini sampling method, sample ID 80203-01 to 80203-12. (3 pages).



EUROPEAN COMMISSION  
JOINT RESEARCH CENTRE

Directorate G – Nuclear Safety and Security  
Unit G.2 - Standards for Nuclear Safety, Security and Safeguards (SN35)

## Certificate of Reference Measurement #3677

Customer	
Company	International Atomic Energy Agency (IAEA)
Division	Department of Safeguards
Address	Office of Safeguards Analytical Services
	Friedensstrasse
	A-2444 Seibersdorf, Austria
Requestor	S. Balsley

Sample Information	
Sample type(s)	Uranium samples for Cristallini Validation Project IAEA sample IDs 80203-01 – 80203-16
Date of receipt of sample(s)	10/08/2016
Customer sample(s) identification	See Request for Analysis #3677 (attached), sample ID 25505
Condition of sample(s)	Uranium in nitric acid solution

Measurement Results				
Sub-sample ID	Analyte	Result (± expanded uncertainty <sup>1,2</sup> ) in mol / mol	Result (± expanded uncertainty <sup>1,2</sup> ) in mol / mol	Method <sup>4</sup>
Date:	06/10/2016			
80203-01 (H <sup>5</sup> )	$n(^{236}\text{U})/n(^{235}\text{U})$	0.00209568(25)	0.00209568(41)	TIMS/DS
80203-02 (A-C <sup>6</sup> )	$n(^{236}\text{U})/n(^{235}\text{U})$	0.00209608(10)	0.00209608(34)	TIMS/DS
80203-03 (A-C)	$n(^{235}\text{U})/n(^{235}\text{U})$	0.00209602(05)	0.00209602(33)	TIMS/DS
80203-04 (H)	$n(^{235}\text{U})/n(^{235}\text{U})$	0.00209566(10)	0.00209566(35)	TIMS/DS
Average <sup>7</sup> H	$n(^{235}\text{U})/n(^{235}\text{U})$	0.00209567(14)	0.00209567(36)	TIMS/DS
Average <sup>7</sup> A-C	$n(^{235}\text{U})/n(^{235}\text{U})$	0.00209605(12)	0.00209605(36)	TIMS/DS
Rel. Diff.A-C vs. H		+0.0185(88)%	Not applicable <sup>8</sup>	TIMS/DS
Date:	16/09/2016			
80203-05 (A-C)	$n(^{236}\text{U})/n(^{235}\text{U})$	0.00725599(17)	0.00725599(115)	TIMS/DS
80203-06 (H)	$n(^{236}\text{U})/n(^{235}\text{U})$	0.00725539(19)	0.00725539(116)	TIMS/DS
80203-07 (H)	$n(^{236}\text{U})/n(^{235}\text{U})$	0.00725558(11)	0.00725558(114)	TIMS/DS
80203-08 (A-C)	$n(^{236}\text{U})/n(^{235}\text{U})$	0.00725603(09)	0.00725603(114)	TIMS/DS
Average H	$n(^{236}\text{U})/n(^{235}\text{U})$	0.00725549(31)	0.00725549(120)	TIMS/DS

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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.

Average A-C	$n(^{236}\text{U})/n(^{235}\text{U})$	0.00725601(24)	0.00725601(119)	TIMS/DS
Rel. Diff.A-C vs. H		+0.0072(54)%	Not applicable <sup>a</sup>	TIMS/DS
Date:	20/09/2016			
80203-09 (H)	$n(^{235}\text{U})/n(^{236}\text{U})$	0.03387848(54)	0.03387848(536)	TIMS/DS
80203-10 (A-C)	$n(^{235}\text{U})/n(^{236}\text{U})$	0.03387877(34)	0.03387877(533)	TIMS/DS
80203-11 (H)	$n(^{235}\text{U})/n(^{236}\text{U})$	0.03387976(66)	0.03387976(536)	TIMS/DS
80203-12 (A-C)	$n(^{235}\text{U})/n(^{236}\text{U})$	0.03388079(32)	0.03388079(533)	TIMS/DS
Average H	$n(^{235}\text{U})/n(^{236}\text{U})$	0.03387903(98)	0.03387903(551)	TIMS/DS
Average A-C	$n(^{235}\text{U})/n(^{236}\text{U})$	0.03387964(132)	0.03387964(568)	TIMS/DS
Rel. Diff.A-C vs. H		+0.0018(49)%	Not applicable <sup>a</sup>	TIMS/DS

Notes:	
1	Uncertainties are given as expanded (k=2) uncertainties according to the ISO Guide to the Expression of Uncertainty (GUM), corresponding to an approximate 95% confidence interval)
2	Expanded Uncertainties (k=2) are given in this column <u>without</u> the Uncertainty Contribution of the Double Spike IRMM-3636a
3	Expanded Uncertainties (k=2) are given in this column <u>including</u> the Uncertainty Contribution of the Double Spike IRMM-3636a ( $n(^{235}\text{U})/n(^{236}\text{U})=1.01906(16)$ , certified on 01/07/2007).
4	TIMS/DS: TIMS-Double Spike Method, acc. to Richter et al., Intern. J of Mass Spectrom., 269 (2008) 145–148
5	Sample prepared from UF <sub>6</sub> material by direct Hydrolysis
6	Sample prepared from UF <sub>6</sub> material by the Cristallini sampling process using alumina pellets
7	The Uncertainties of the averages are based on consistency checks (acc. to R Kessel et al, in Accred. qual Assur), achieving overlap of all individual measurements with their average
8	The Uncertainty Contribution of the Double Spike IRMM-3636a cancels out for the relative difference between average (H) and average (A-C)

Date of analysis (dd/mm/yyyy)	20/09-06/10/2016
Date of internal analysis report (dd/mm/yyyy)	12/10/2016
Certification date normalised to (reference date)	12/10/2016 at 12:00 h

Backup Files and Raw Data
Files names for raw data stored at JRC G.2:
Results of mass spectrometric measurements for this request are stored as follows. For samples 80203-01 - 80203-16 (IRMM-020): "G:\JRC.G.2\Nuclear Safeguards\Nuclear\Cristallini Method - Copy\Measurement DATA\IRMM Turret 15 - IRMM-020" The relevant data file is: "T161006 Turret 15 Cristallini DS IRMM F-D-00447 Revision 3.xls "
For samples 80203-04 - 80203-08 (IRMM-022): " G:\JRC.G.2\Nuclear Safeguards\Nuclear\Cristallini Method - Copy\Measurement DATA\IRMM Turret 16 - IRMM-022" The relevant data file is: "T160916 Turret 16 Cristallini DS IRMM F-D-00447 Revision 3.xls "
For samples 80203-09 - 80203-12 (IRMM-023): "G:\JRC.G.2\Nuclear Safeguards\Nuclear\Cristallini Method - Copy\Measurement DATA\IRMM Turret 17 - IRMM-023" The relevant data file is: "T160920 Turret 17 Cristallini DS IRMM F-D-00447 Revision 3.xls "

Ratiesweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. <http://irmm.jrc.ec.europa.eu>

## Annexes

1. Copy of External Analysis Request (1 page, letter by Y. Kuno, Director Office of Safeguards Analytical Services at IAEA)
2. Copy of (internal) Request for Analysis (1 page)
3. Copy of Internal Test Report (2 pages)
4. Copy of External Test Report (3 pages)

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

Signature and date:



18/10/2016

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