

Comparison of ABACC-Cristallini and Direct Hydrolysis Uranium Hexafluoride (UF₆) Sampling Methods on Isotopic Composition

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1. Introduction

The ABACC-Cristallini (A-C) Method for sampling UF₆ 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) (1-4). This method has several advantages compared to the currently used sampling method, for which UF₆ is cryogenically transferred into a stainless steel vessel for transportation, with hydrolysis and isotopic analysis being performed after shipping to the analytical laboratory. Using the A-C sampling method, manipulation of the samples at a laboratory is much simpler and transport of the samples is easier since sample is transported as solid (UO₂F₂) and not as a gas (UF₆).

In order to establish the reliability of the method for nuclear safeguards applications and ²³⁵U enrichment determination, the A-C sampling method was subjected to a rigorous method validation program. This included using four UF₆ Certified Reference Materials (CRM) as a source of uranium hexafluoride, and sampling each of the four CRMs by the two methods. The samples were distributed to participating laboratories, then measured by the labs using their mass spectrometric methods for uranium isotopic composition, particularly ²³⁵U/²³⁸U.

The primary evaluation objective of the validation exercise was to determine if the A-C and direct hydrolysis sampling methods yield uranium isotopic measurements in agreement with each other. Additionally, the two sampling methods measurement results were compared with the certified values for the CRMs to ensure sample integrity.

Seven laboratories around the world participated in the validation program. The involved organizations include laboratories in Argentina, Brazil, Germany, Belgium, France, Austria and the USA¹. The participating laboratories included:

- Laboratorio de Espectrometría de Masas – Gerencia Química – Comisión Nacional de Energía Atómica (CNEA); Buenos Aires, Argentina
- Laboratório de Caracterização de Urânio - Centro Tecnológico da Marinha em São Paulo (CTMSP), Brazil
- Nuclear Analytical Chemistry and Isotopics Laboratory, Oak Ridge National Laboratory (ORNL), Oak Ridge, USA

¹ After the exercise began, URENCO (NL) requested and received samples for the analysis of the A-C Method. Their results are currently being evaluated.

- Safeguards Analytical Services, Nuclear Material Laboratory (IAEA), Seibersdorf, Austria
- Joint Research Centre, Directorate G – Karlsruhe (JRC-Karlsruhe); Germany
- Joint Research Centre, Directorate G-Geel (JRC-Geel); Belgium
- Laboratoire de Development Analytique Nucleaire, Isotopique et Elementaire (LANIE), France

The validation program was coordinated jointly by ABACC and the NBL Program Office.

2. Samples and Measurements

The worldwide joint validation program was started in October 2015. The CNEA laboratory in Buenos Aires, Argentina produced sets of samples contained in P-10 tubes, by the two sampling methods, for each of the four UF₆ CRMs. During production of the samples, a different, cleaned manifold was used between each CRM to eliminate the risk of cross-contamination. Each participating laboratory received two subsamples obtained from the direct hydrolysis and two subsamples taken using the A-C method, for each of the four CRM's.

Each laboratory was asked to follow a recovery protocol for sample dissolution and preparation prior to isotopic composition determination.

Table 1 lists the IRMM UF₆ ²³⁵U/²³⁸U ratio certified values with their absolute and relative uncertainties (5). Additionally, the table includes a column indicating the requirements of the International Atomic Energy Agency's "International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials" (6) for the enrichment of each material. The ITV-2010 values provide a 'state of the practice' target uncertainty for laboratories performing safeguards isotopic enrichment measurements in determining ²³⁵U enrichment.

CRM	n(U235)/n(U238)	Uc	% rel U	ITV-2010
IRMM-020	0.00209570	0.00000060	0.029	0.70%
IRMM-022	0.0072562	0.0000012	0.017	0.28%
IRMM-023	0.0338810	0.0000060	0.018	0.14%
IRMM-029	0.044052	0.000014	0.032	0.14%

Table 1: IRMM UF₆ CRM ²³⁵U/²³⁸U ratio certified values with absolute and relative uncertainties.

The relative uncertainties on the ²³⁵U/²³⁸U ratios for the IRMM UF₆ reference materials are some of the smallest available and were determined by state-of-the-art methods and measurements at a reference laboratory.

Each laboratory was asked to perform isotopic analyses of duplicate samples for each of the reference materials sampled by both A-C and direct hydrolysis methods. The JRC-Geel laboratory, using samples provided by the IAEA, performed a double-spike isotopic measurement method on three of CRM's (see below). The LANIE laboratory submitted results for one of the CRM's. Table 2 below summarizes the methods each laboratory employed and which reference materials were used for instrument calibration

and quality control. With the exception of the JRC-Geel laboratory, all submitted results for sample pairs (A-C & hydrolysis for each CRM) were compared using a two-sample t-test. For each facility, for each material, the sample mean and sample standard deviation of the measurements for each sampling method were calculated. The two-sample t-test statistic assuming unequal variances was calculated for each data set. This statistic is:

$$t = \frac{|m_A - m_D|}{\sqrt{\left(\frac{s_A}{\sqrt{n_A}}\right)^2 + \left(\frac{s_D}{\sqrt{n_D}}\right)^2}},$$

where m is the sample mean, s is the simple sample standard deviation, and n is the number of observations, for both alumina (A) and direct hydrolysis (D) sets of data. The t statistic is distributed as a two-sided student's "t" distribution with $n_A + n_D - 2$ degrees of freedom. Large values of the statistic indicate a statistically significant difference between the sampling methods results. A significant difference between the results is indicated when the alpha value is less than 5%. A marginal significance is detected when the alpha value is between 5% and 10%.

The JRC-Geel laboratory, in collaboration with the IAEA Nuclear Measurements Laboratory, performed a double-spike measurement technique which is capable of much greater accuracy and precision in determining isotopic composition. The JRC-Geel results are taken directly from their report (7).

Lab	Isotopic Measurement Method	RM's for Calibration/QC (QC in parentheses)
CNEA	Conventional TIMS	NBL U005A, C125A (NBL U500)
CTMSP	TE TIMS	NBL U030A (U005A,112A,U020A, C125A)
IAEA	TE/MTE TIMS	IRMM 184 (IRMM 183, 185, 186 ,187)
IAEA	TIMS double spike	IRMM 3636a (IRMM 3050, IRMM 184)
JRC-Karlsruhe	MTE TIMS	IRMM 187 & 184 (IRMM 075-2, 075-4)
ORNL	MTE TIMS	NBL U010 (IRMM 183,184, 185, 186)
JRC-Geel	TIMS double spike	IRMM 3636a (IRMM 3050, IRMM 184)
LANIE	MC-ICP-MS	IRMM 183 (IRMM 183)

Table 3: Summary of the methods each laboratory employed and which reference materials were used for instrument calibration and quality control. TIMS: thermal ionization mass spectrometry; TE: total evaporation; MTE: modified total evaporation; MC-ICP-MS: multi-collector inductively coupled mass spectrometry

3. Individual Laboratory Results

This section will briefly describe the method each laboratory used and any statistically significant difference detected between results for each sampling methods. Tables and plots of the combined results for each CRM and sampling method are presented further below.

A two-sample t-test was used to statistically compare the two methods isotopic results for each reference material. A marginally significant difference is detected by the t statistic when its

alpha value is less than 10% and greater than 5%. A statistically significant difference is detected by the t statistic when its alpha value is less than 5%.

a. CNEA Laboratory Results:

The CNEA Laboratory used the conventional Thermal Ionization Mass Spectrometry (TIMS) method for measurement of the materials. NBL U005A, C125A were used for calibration of the mass spectrometer, the former for IRMM-020 and IRMM-022 samples, and the latter for IRMM-023 and IRMM-029. The lab reported individual turret data. The conventional method of mass spectrometric analysis is not capable of the precision of the total evaporation and modified total evaporation methods, and thus the reported results show a larger standard deviation than the other labs.

No statistically significant difference between the sampling methods was detected for any of the samples. A marginal significant difference was detected for the $^{235}\text{U}/^{238}\text{U}$ ratio for the IRMM-022 sample. The difference between the A-C and hydrolysis results for this material was about 0.11% relative.

b. CTMSP Laboratory Results:

The CTMSP Laboratory employed their total evaporation TIMS method for isotopic measurement of the materials. NBL U030A was used for calibration and NBL U005A, U112A, U020A and U125A were used for QC.

No statistically significant difference between the sampling methods was detected for any of the IRMM samples.

c. Joint Research Center-Karlsruhe (JRC-Karlsruhe) Results:

The JRC-Karlsruhe used the Thermal Ionization Mass Spectrometry (TIMS) - Modified Total Evaporation (MTE) for the measurement of the materials. IRMM-187 was used for mass fractionation correction for IRMM-020 and IRMM-029 and IRMM 184 was used for IRMM-022 and IRMM-023. IRMM-075/2 was used for QC and background correction verification for IRMM-020 and IRMM-029 and IRMM-075/4 was used for IRMM-022 and IRMM-023.

No statistically significant difference between the sampling methods was detected in the IRMM-020 and IRMM-022 samples. A marginally statistically significant difference between the sampling methods was detected in the $^{235}\text{U}/^{238}\text{U}$ ratio for the IRMM-023 sample. This difference was very small, approximately 0.01% relative. Statistically significant differences between the sampling methods were detected in all ratios for the IRMM-029 sample. These differences were also quite small, approximately 0.02% relative.

d. IAEA Safeguards Analytical Services(IAEA) Results:

The IAEA SGAS used three methods. The Total Evaporation (TE) method for $^{235}\text{U}/^{238}\text{U}$ determination and the Modified Total Evaporation (MTE) for $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ measurements of the materials. IRMM-184 was used for mass fractionation

correction and IRMM-183, 185, 186 and 187 were used for QC. The IAEA lab also performed double-spike TIMS analyses, identical to the method used by JRC-Geel. The method is explained further in section f below.

For the TE and MTE analyses, no statistically significant difference between the sampling methods was detected, except in the $^{235}\text{U}/^{238}\text{U}$ ratio for the IRMM-029 sample. The difference between the sampling methods for this CRM was very small, approximately 0.015% relative.

For the double spike analyses, the IAEA results were nearly identical to the JRC-Geel results detailed below, indicating very small, significant differences between IRMM-020 (0.016%) and IRMM 022 (0.008%) samples, but not significant for IRMM 023 (0.005%).

e. Oak Ridge National Laboratory (ORNL) Results:

The ORNL used the Thermal Ionization Mass Spectrometry (TIMS) - Modified Total Evaporation (MTE) for the measurement of the materials. NBL-U010 was used for mass fractionation correction for IRMM-020, -022, -023, and -029. IRMM 183, 184, 185 and 186 were used for QC for IRMM-020, -023, -023, and -029 respectively.

No statistically significant difference between the sampling methods was detected in the IRMM-020, -023 and -029 samples or in the -022 sample for $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ ratios. A marginally statistically significant difference between the sampling methods was detected in the $^{236}\text{U}/^{238}\text{U}$ ratio for the IRMM-022 sample. This difference was about 0.42% relative.

f. JRC-G.2 Geel Laboratory (JRC-Geel) results:

JRC-G.2 proposed 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).

A JRC (7) 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 A-C method, performed by staff from the unit JRC-G.2 in Geel/Belgium (formerly IRMM) in collaboration with staff from the IAEA Safeguards Analytical Services Laboratory (SGAS/IAEA). The results 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 A-C 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% ^{235}U) and IRMM-022 (0.72% ^{235}U) certified UF_6 reference materials, significant differences of 0.019% and 0.0072% were observed, but for test samples prepared from IRMM-023 (3.3% ^{235}U) the difference of 0.0018% was insignificant. The reason for the observed, slight differences is not yet known. They can be due to fractionation, contamination or memory effects which occurred during the sampling or subsequent chemical processing.

g. CEA-LANIE:

CEA-LANIE reported on the analysis for one of the UFCRM's (IRMM-020) for the inter-comparison exercise for the A-C method. The measurements were performed on an MC-ICPMS instrument. The CRM used to perform mass bias correction and QC for this sample was the IRMM 183. The numbers for both sampling methods were so close that there is not even the slightest statistical significance in the differences between the two sampling results.

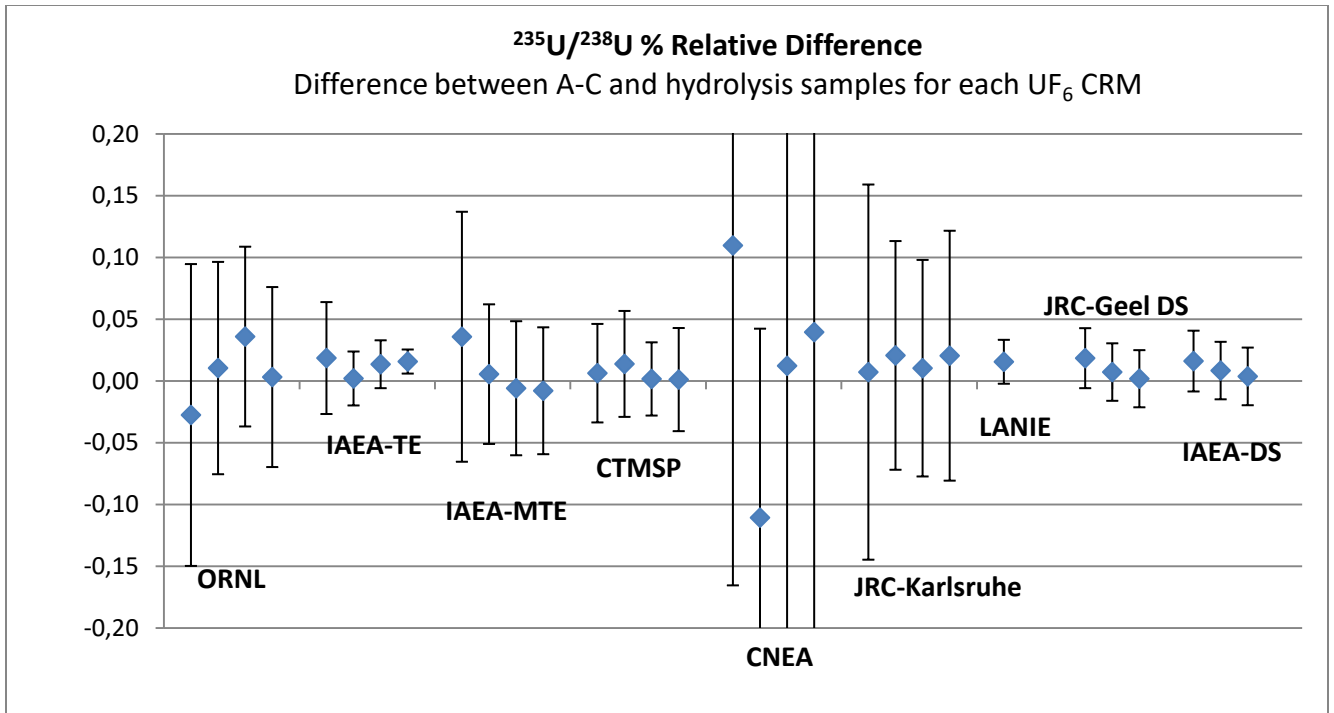
Table 3 below summarizes the results of the two-sample t test for each laboratory, with the exception of the JRC-Geel and IAEA double spike results. For the IAEA and JRC-Geel double spike analyses, the relative difference for IRMM 020 and IRMM 022 are listed based on disagreement between the uncertainties determined for the measurements performed on each sample set. The relative difference for IRMM 023 using the double spike method was not significant (within uncertainties of the method).

Lab	IRMM 020	IRMM 022	IRMM 023	IRMM 029
CNEA	No	Marginal	No	No
CTMSP	No	No	No	No
IAEA	No	No	No	~0.015%
JRC-Karlsruhe	No	No	Marginal	0.02%
ORNL	No	No	No	No
JRC-Geel DS	0.019%	0.0072%	No	-
IAEA DS	0.016%	0.0084%	No	-
CEA-LANIE	No	-	-	-

Table 3: Indication and magnitude of statistical significance between A-C and direct hydrolysis samples measured for $^{235}\text{U}/^{238}\text{U}$ ratio for four UF_6 certified reference materials. "DS" for the IAEA and JRC-Geel results denotes the use of the double-spike method.

4. Summary Analysis

Figure 1 below charts each laboratory's results for the relative differences (%) between the sampling methods for each IRMM CRM, using the average for each laboratory/sample. The error bars for the differences are the square root of the sum of variance of each analysis.



The figure clearly demonstrates the good agreement in results between the two sampling methods. The zero value is included within the interval defined by the error bars of the measurements for all but one of the 31 data sets.

Combined laboratory $^{235}\text{U}/^{238}\text{U}$ ratio plot averages for each of the UF_6 reference materials and sampling methods are shown in Figure 2 below. Six laboratories reported expanded uncertainties for each sample. The CNEA laboratory error bars reflect a two standard deviation indication of precision. Error bars are the lab-reported uncertainties.

IRMM 020:

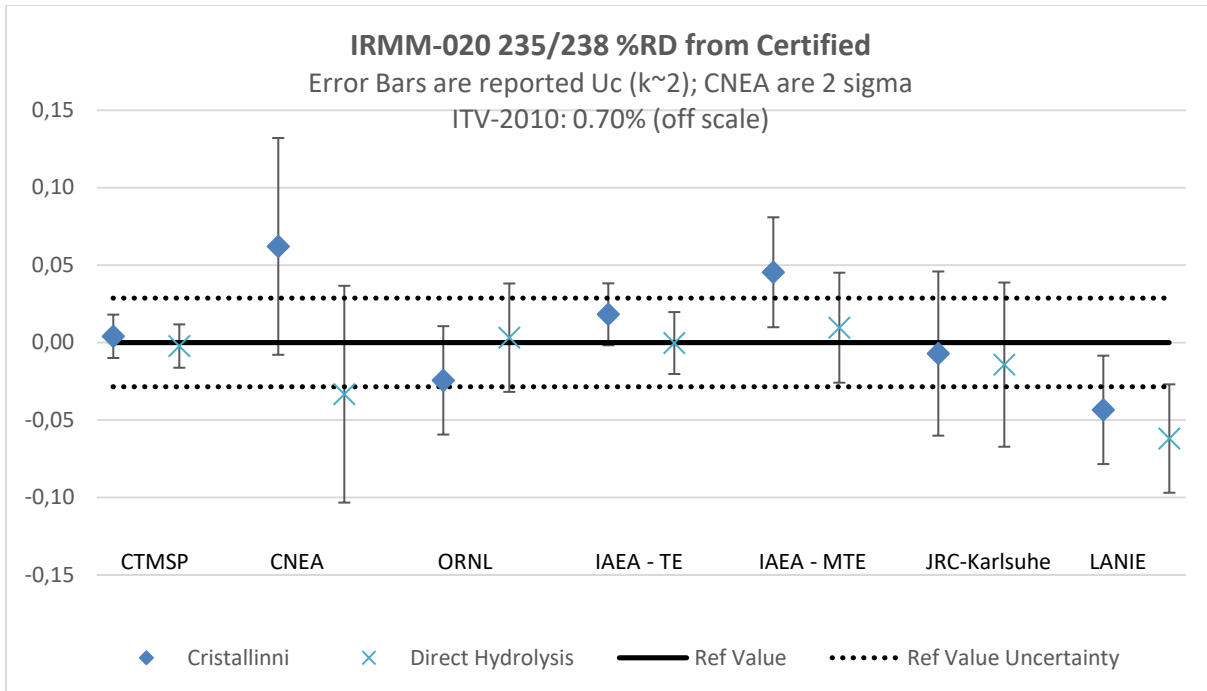
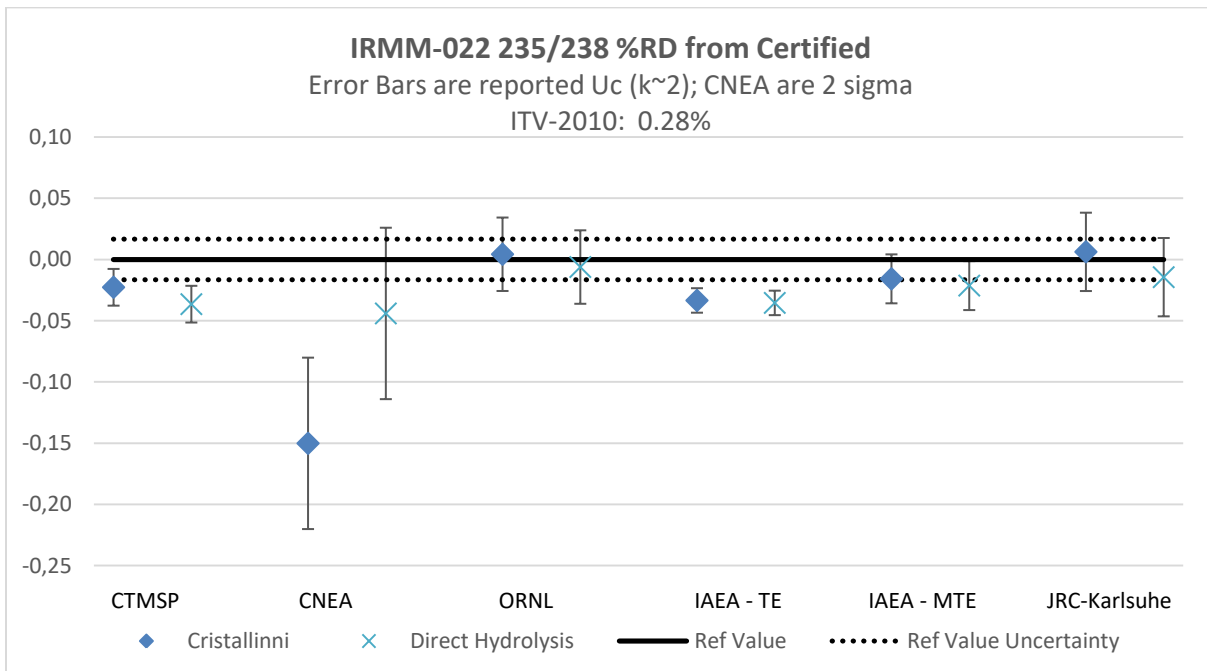


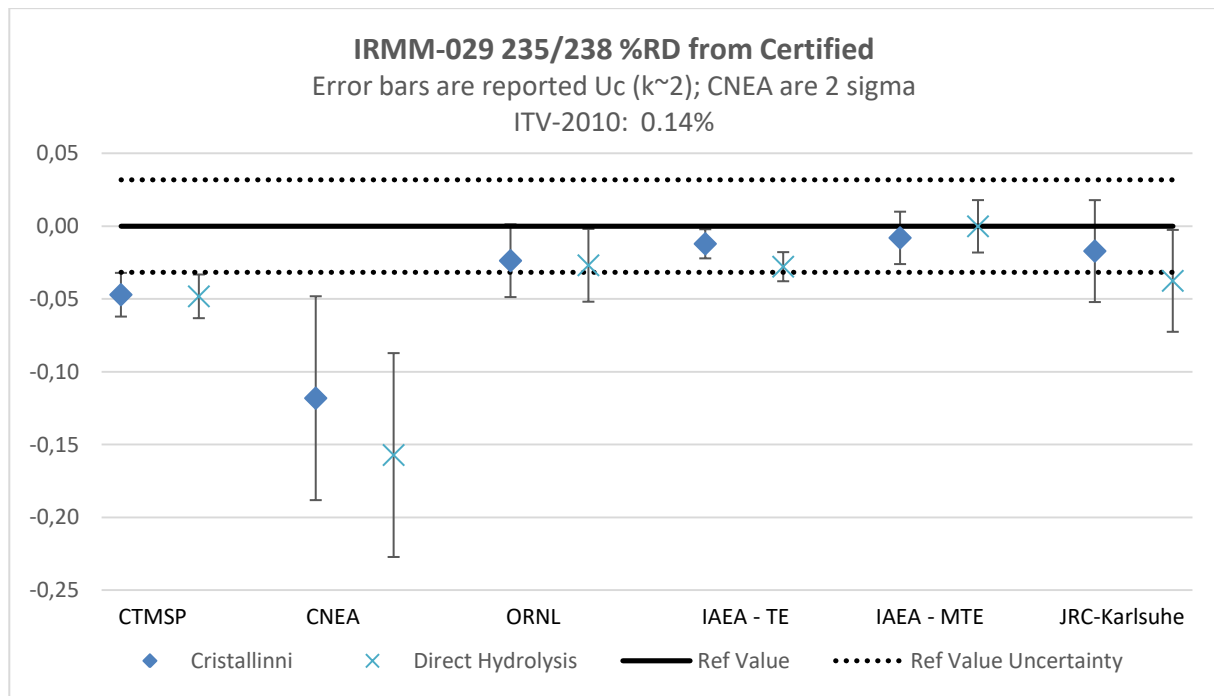
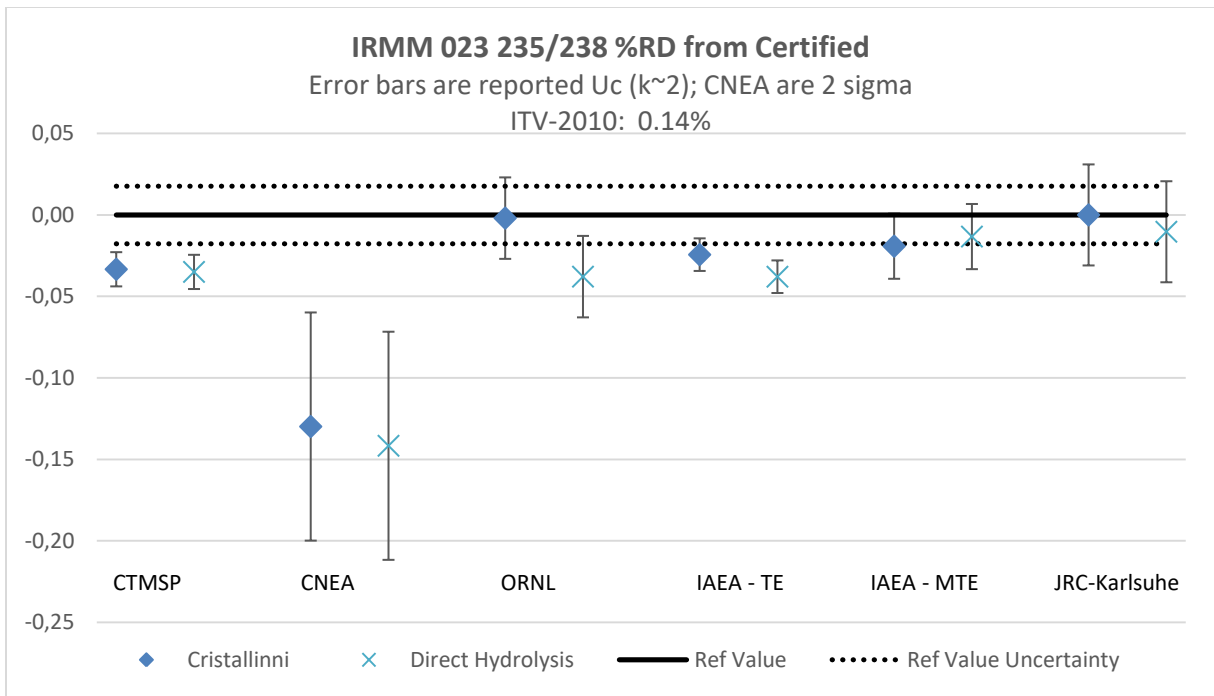
Figure 2: IRMM-020 n(U235)/n(U238) %RD from the Certified Isotopic Ratio

IRMM 020 results indicate good agreement between the A-C and hydrolysis samples and with the certified value of the CRM. Additionally, all results are well within the ITV-2010 target values for $^{235}\text{U}/^{238}\text{U}$ determination for a material of this enrichment.

IRMM 022:



IRMM 023:



The results presented here show that any difference for the $^{235}\text{U}/^{238}\text{U}$ ratio between the ABACC-Cristallini and direct hydrolysis methods is very small. Only the JRC-Geel and IAEA double-spike analyses demonstrated a statistically significant difference for two of the three samples they analyzed.

It is interesting to note that the differences between the two sampling methods, while not statistically significant in almost all cases, does show a general trend for the ABACC-Cristallini samples' $^{235}\text{U}/^{238}\text{U}$ ratio to be approximately 0.010% on average higher than the direct hydrolysis samples. No general trend could be seen in the $^{234}\text{U}/^{238}\text{U}$ or $^{236}\text{U}/^{238}\text{U}$ ratios.

Table 4 below lists the average %RD between A-C and direct hydrolysis sample $^{235}\text{U}/^{238}\text{U}$ results for each CRM and laboratory.

Lab	IRMM 020 (ITV: 0.70%)	IRMM 022 (ITV: 0.28%)	IRMM 023 (ITV: 0.14%)	IRMM 029 (ITV: 0.14%)
CNEA	0.110	-0.111	0.012	0.040
CTMSP	0.006	0.014	0.002	0.001
IAEA TE	0.019	0.002	0.014	0.016
IAEA MTE	0.036	0.0055	-0.006	-0.008
JRC-Karlsruhe	0.007	0.021	0.010	0.020
ORNL	-0.028	0.010	0.036	0.003
JRC-Geel DS	0.019	0.0072	0.0018	-
IAEA DS	0.016	0.0084	0.0037	-
LANIE	0.020	-	-	-

Table 4: Relative percent difference between A-C and direct hydrolysis samples for measured $^{235}\text{U}/^{238}\text{U}$ ratio.

Of the 31 sample pair differences measured, only four of them indicated ABACC-Cristallini $^{235}\text{U}/^{238}\text{U}$ ratios that were lower than the direct hydrolysis results. The majority of the differences ranged between 0.01% - 0.02%. Only the JRC-Geel and IAEA double spike measurements, capable of very small uncertainties, were performed with sufficient accuracy to conclude that there is a significant, though very small, difference between the methods for two of the three samples JRC-Geel examined. In all cases, these potential differences are very small.

5. Conclusions

For the purposes of nuclear material accountancy (e.g., safeguards) and process control, the A-C UF_6 sampling method provides comparable results to the direct hydrolysis method for sampling UF_6 for uranium isotopic determinations.

There are some indications that there may be a very small difference in the $^{235}\text{U}/^{238}\text{U}$ ratio between the two sampling methods. This difference is indicated in two of the three samples measured by JRC-Geel and the IAEA using the double-spike method, with magnitudes of about <0.02% and <0.008%, with no significant difference detected for the third sample. The remaining laboratory data do not provide conclusive evidence of a difference. .

Of the 31 individual laboratory data sets for each material, 27 had the ABACC-Cristallini method results average higher than the direct hydrolysis results. The probability of this happening by sheer chance is approximately < 0.04%. The possible sources of the difference may be a slight memory effect/contamination in sampling, a chemical/physical nature related to the sampling method, small biases inherent to the mass spectrometric instrumentation due to alumina or other impurities, or other unknown causes. As JRC-Geel suggest in their analysis report, it may

be good practice to include a contribution to the total uncertainty for future measurements of samples taken by the ABACC-Cristallini method. The additional contribution, on the order of 0.01-0.02%, will have little effect on the majority of measurements performed. And as a practical matter, these differences are dwarfed when compared to the ITV-2010 values for DU and LEU which range from 0.70% to 0.14%.

In conclusion, for the purposes of nuclear safeguards and process control, the ABACC-Cristallini UF₆ sampling method provides comparable results to the direct hydrolysis method for sampling UF₆ for uranium isotopic determinations.

Acknowledgements:

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