Qualification for Safeguards Purposes of UF_6 Sampling using Alumina – Results of the Evaluation Campaign of ABACC-Cristallini Method

58th INMM

Qualification for Safeguards Purposes of UF_6 Sampling using Alumina – Results of the Evaluation Campaign of ABACC-Cristallini Method

Authors[1]

Esteban, Adolfo[2], Gautier, Eduardo[2], Machado da Silva, Luis[3], Fernández Moreno, Sonia[3], Renha, Geraldo[3], Dias, Fabio[3], Pereira de Oliveira Jr., Olivio[4], Amaraggi, David[5], Mason, Peter[6], Soriano, Michael[6], Croatto, Paul[6],* Zuleger, Evelyn[7], Giaquinto, Joseph[8], *Hexel, Cole[8], Vercouter, Thomas[9], Paredes-Paredes, Eduardo[9], Isnard, Hélène[9], Richter, Stephan[10]

[2] Laboratorios de Control Químico y Físico y de Espectrometría de Masas - Comisión Nacional de Energía Atómica (CNEA). Centro Atómico Constituyentes, Av. Gral. Paz 1499, (B1650KNA) San Martín – Pcia. de Buenos Aires – Argentina.

[3] Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC), Av. Rio Branco 123, Gr 515, 20040-005, Rio de Janeiro, Brazil.

[4] Laboratório de Caracterização de Urânio - Centro Tecnológico da Marinha em São Paulo (CTMSP), Av. Prof. Lineu Prestes 2468, 05508-000, Cidade Universitária, São Paulo, SP, Brazil.

[5]Safeguards Analytical Services, Nuclear Material Laboratory, International Atomic Energy Agency (IAEA), Seibersdorf laboratories, Vienna A-2444, Seibersdorf, Austria.

[6]NBL Program Office - DOE, 9800 South Cass Avenue, Building 350, Argonne, IL, USA.

[7]European Commission, Joint Research Centre (JRC- Karlsruhe), Directorate G - Nuclear Safeguards and Forensics, Analytical Service P.O.Box 2340 D-76125 Karlsruhe, Germany.

[8]Nuclear Analytical Chemistry and Isotopics Laboratory, Chemical Sciences Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN, USA.

[9]Laboratoire de Développement Analytique Nucléaire, Isotopique et Elémentaire (LANIE), Den—Service d'Etudes Analytiques et de Réactivité des Surfaces (SEARS), CEA Saclay, F-91191, Gif-sur-Yvette, France.

[10]European Commission, Joint Research Centre (JRC-Geel), Directorate G - Nuclear Safeguards and Forensics, Geel, Retieseweg 111, B-2440 Geel, Belgium.

Note: The ABACC-Cristallini Method for UF_6 sampling project is being conducted under the SP Tasks BRZ A1765 and ARG A1769, and the cooperation Action Sheet between ABACC and USDOE-NBL.

Summary

The procedure currently used to sample material from process lines in uranium enrichment plants consists of collecting the uranium hexafluoride (UF_6) in gaseous phase by desublimation inside a metal sampling cylinder cooled with liquid nitrogen or in certain facilities in a fluorothene P-10 tube type.

The ABACC-Cristallini method has been proposed to collect the UF_6 (gas) by adsorption in alumina (Al_2O_3) in the form of uranyl fluoride (UO_2F_2) (solid). This method uses a fluorothene P-10 tube type containing alumina pellets that adsorb and hydrolyze UF_6 directly during the sampling. This new method has advantages compared to the usual method with less residual material left at the facility, more simple treatment of the sample and also less constraint related to nuclear material transport regulation.

ABACC invited seven international laboratories to participate in a UF_6 sampling method evaluation campaign. This campaign involved high accuracy measurement of uranium isotopic composition sampled as UF_6 using two different sampling methods: Adsorption on alumina (A-C method) and a standard direct hydrolysis method.

The goal of the campaign was to determine if there is any detectable difference in the isotopic composition of UF_6 materials when sampled by the two methods. Four different IRMM UF_6 Certified Reference Materials were sampled by each of the methods to create four pairs of samples for analysis. Each sample was contained in a P-10 tube, and required sample chemistry preparation steps prior to isotopic analysis.

[1] *Dr. Osvaldo Cristallini (In Memoriam), widely renowned Argentine radio-chemist, has developed the "ABACC-Cristallini" method for UF_6 sampling.*

Qualification for Safeguards Purposes of UF_6 Sampling using Alumina – Results of the Evaluation Campaign of ABACC-Cristallini Method

This paper presents the results obtained from seven laboratories which will be used for the technical certification process that ABACC is pursuing for qualification of the UF_6 sampling ABACC–Cristallini method for uranium isotopic determination.
The results will also be the basis of the validation process to confirm that the new method can be used for routine safeguards application and process control at the enrichment plants.

1. Introduction

The ABACC-Cristallini Method for sampling UF_6 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) [1-3]. This method has several advantages compared to the currently used sampling method, for which UF_6 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 ABACC-Cristallini sampling method based on ASTM Standards [4-6], manipulation of the samples at laboratory is much easier (no need for cooling with liquid nitrogen), the transport is cheaper and relatively safer concerning radiological protection aspects since the sample is transported as solid (UO_2F_2). The use of Polychlorotrifluoretylene (PCTFE) translucent tube has the potential to avoid unnecessary long sampling time because it allows seeing the color change of the pellets during sampling (white to yellow).
In order to establish the reliability of the method for nuclear safeguards applications and ^{235}U enrichment determination, the ABACC-Cristallini sampling method has been subjected to a rigorous validation program. This included using four UF_6 Certified Reference Materials (CRM) as a source of uranium hexafluoride, and sampling each of the four CRMs by two methods. The samples were distributed to participating laboratories, and then measured by the labs using their mass spectrometric methods for uranium isotopic composition, particularly $^{235}U/^{238}U$.
The primary evaluation objective of the validation exercise was to determine if the ABACC-Cristallini and direct hydrolysis sampling methods give 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, Austria, Belgium, Brazil, France, Germany and USA[2, 4-10].

2. Samples and Measurements

The worldwide joint validation program was started in October 2015. This program involves isotope ratio measurements of uranium materials sampled as UF_6 using two different sampling methods: adsorption on alumina (ABACC-Cristallini method) and the standard direct hydrolysis method. The goal of this study is to determine if the application of the ABACC-Cristallini sampling method has any detectable effect on the isotopic composition of the UF_6 material when measured by high accuracy mass spectrometry. The test materials used for this program are the UF_6 isotope reference materials IRMM CRM 020 (0.21% of ^{235}U), IRMM CRM 022 (0.72% of ^{235}U), IRMM CRM 023(3.3% of ^{235}U) and IRMM CRM 029 (4.2% of ^{235}U), certified by JRC-Geel [7]. For each of the four reference materials, each participating laboratory received two subsamples obtained from the direct hydrolysis and two subsamples taken using the ABACC-Cristallini method. During production of the subsamples from the JRC CRM's, a

[2] URENCO (NL) had received the samples for the analyisis of the A-C Method. The preliminary results are being evaluated.

different sampling manifold was used for each CRM in order to eliminate the risk of cross contamination.
A detailed procedure for recovery of uranium adsorbed in the alumina pellets was suggested to participating laboratories.
The Table 1 lists the IRMM UF_6 n(^{235}U)/n(^{238}U) certified values with their expanded Uc (k=2) and relative uncertainties (% rel Uc). Additionally, the table includes a column indicating the International Atomic Energy Agency's International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials [8] for the enrichment of each material. The ITV-2010 values provide a 'state of the practice' target uncertainty for laboratories in this case performing safeguards isotopic enrichment measurements.

CRM	n(^{235}U)/n(^{238}U)	Uc (k=2)	% rel Uc	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 UF_6 n(235U)/n(238U) certified values with their expanded uncertainties

The relative uncertainties on the n(^{235}U)/n(^{238}U) ratios for the IRMM UF_6 reference materials are some of the smallest available.

Each laboratory performed isotopic analyses of duplicate samples for each of the reference materials sampled by both the ABACC-Cristallini and direct hydrolysis. The Laboratory G submitted results for one of the CRM´s. The Table 2 summarizes the methods each laboratory employed and which reference materials were used for instrument calibration and quality control. With the exception of the Laboratory F, 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. With the exception of the Laboratory F, all individual results were compared using a two-sample t-test. 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 Laboratory F, in collaboration with the Laboratory C, performed a double-spike measurement technique which is capable of much greater accuracy and precision in determining isotopic composition.

Lab	Isotopic Measurement Method	RM's for Calibration/Quality Control(QC) (QC in parentheses)
A	Conventional TIMS	NBL U005A, C125A (NBL U500)
B	TE TIMS	NBL U030A (U005A,112A,U020A, C125A)
C	TE/MTE TIMS	IRMM 184 (IRMM 183,185,185,187)
C	TIMS double spike	IRMM 3636a (IRMM 3050, IRMM 184)
D	MTE TIMS	IRMM 187 & 184 (IRMM 075-2, 075-4)
E	MTE TIMS	NBL U010 (IRMM 183,184, 185, 186)
F	TIMS double spike	IRMM 3636a (IRMM 3050, IRMM 184)
G	MC-ICP-MS	IRMM 183 (IRMM 183)

Table 2: 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.

3.1 Laboratory A

The Laboratory A used the conventional Thermal Ionization Mass Spectrometry (TIMS) method for measurement of the materials. NBL U005A was used for calibration for IRMM-020 and IRMM-022 samples and NBL C125A for IRMM-023 and IRMM-029. The lab reported individual turret data, including calibration, NBL U500 for QC and samples. 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 n(U235)/n(U238) ratio for the IRMM-022 sample. The difference between the ABACC-Cristallini and hydrolysis results for this material was about 0.11% relative.

3.2 Laboratory B

The Laboratory B employed the total evaporation TIMS for 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.

3.3 Laboratory C

The Laboratory C used the Total Evaporation (TE) [10] method for n(U235)/n(U238) determination and the Modified Total Evaporation (MTE) [11] for n(U234)/n(U238), n(U235)/n(U238) and n(U236)/n(U238) measurements of the materials.

No statistically significant difference between the sampling methods was detected except in the n(U235)/n(U238) 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 Laboratory C were nearly identical to the Laboratory F 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%).

3.4 Laboratory D

The Laboratory D 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 marginal statistically significant difference between the sampling methods was detected in the n(U235)/n(U238) ratio for the IRMM-023 sample. This difference was about 0.01% relative. Statistically significant differences between the sampling methods were detected in all ratios for the IRMM-029 sample. These differences were about 0.02% relative.

3.5 Laboratory E

The Laboratory E 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 n(U234)/n(U238) ratio and n(U235)/n(U238) ratio. A marginal statistically significant difference between the sampling methods was detected in the n(U236)/n(U238) ratio for the IRMM-022 sample. This difference was about 0.42% relative.

3.6 Laboratory F

In January 2016, the Laboratory F was invited by ABACC to participate. It was proposed by Laboratory F 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 technical JRC report [9] describes in particular the application of the "Double Spike" method by thermal ionization mass spectrometry (DS/TIMS) for the validation program of the ABACC-Cristallini method, performed by staff from the Laboratory F in collaboration with staff from the Laboratory C. The results are in good mutual agreement, but they reveal slight differences for the n(U235)/n(U238) isotope ratios for samples taken by the ABACC-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% 235U) and IRMM-022 (0.72% 235U) certified UF_6 reference materials, significant differences of about 0.01%-0.02% were observed, but for test samples prepared from IRMM-023 (3.3% 235U) the differences are insignificant. The reason for the observed differences is not yet known and unlikely to be linked to any cause investigated so far (fractionation, contamination or memory effects occurred during the sampling or subsequent chemical processing).

3.7 Laboratory G

The Laboratory G reported on the analysis for one of the UF_6 CRM's (IRMM-020) for the inter-comparison exercise for the ABACC-Cristallini 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.

The Table 3 below summarizes the results of the two-sample t test for each laboratory, with the exception of the Laboratory F results. For Laboratories F and C using the TIMS double spike method performed on the same sample set, the average relative differences for IRMM 020 and IRMM 022 are listed. The uncertainties are based on the measurements from both Laboratories F and C, with correlations due to the use of the same double spike reference material for calibration taken into account.

Lab	IRMM 020	IRMM 022	IRMM 023	IRMM 029
A	No	Marginal	No	No
B	No	No	No	No
C	No	No	No	~0.015%
D	No	No	Marginal	0.02%
E	No	No	No	No
F (and C)	0.0173(66)%	0.0078(39)%	No	NA
G	No	-	-	-

Table 3: Indication and magnitude of statistical significance between ABACC-Cristallini and direct hydrolysis samples measured for n(U235)/n(U238) ratio for four UF_6 certified reference materials.

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, without adjusting for correlations.

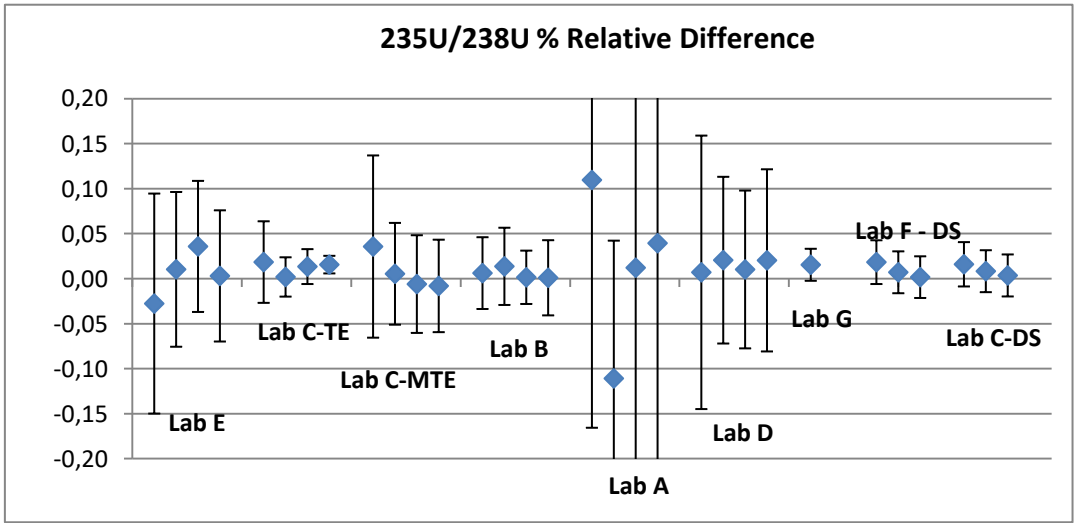

Figure 1: Relative Differences n(U235)/n(U238) ABACC-Cristallini and Hydrolysis methods for each UF_6 CRM

The figure 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 (LAB C –TE for IRMM 029) of the 31 data sets.

The results for the relative differences (between the ratios from the two sampling methods) using the double spike method performed by Laboratories F and C agree well with each other but they are different from zero. This is not visible in Figure 1, because the error bars/uncertainties of differences were calculated without adjusting for correlations.

Combined laboratory n(U235)/n(U238) ratio plot averages for each of the UF_6 reference materials and sampling methods are shown below. Six laboratories reported expanded uncertainties for each sample. The Laboratory A error bars reflect a two standard deviation indication of precision. Error bars are the lab-reported uncertainties.

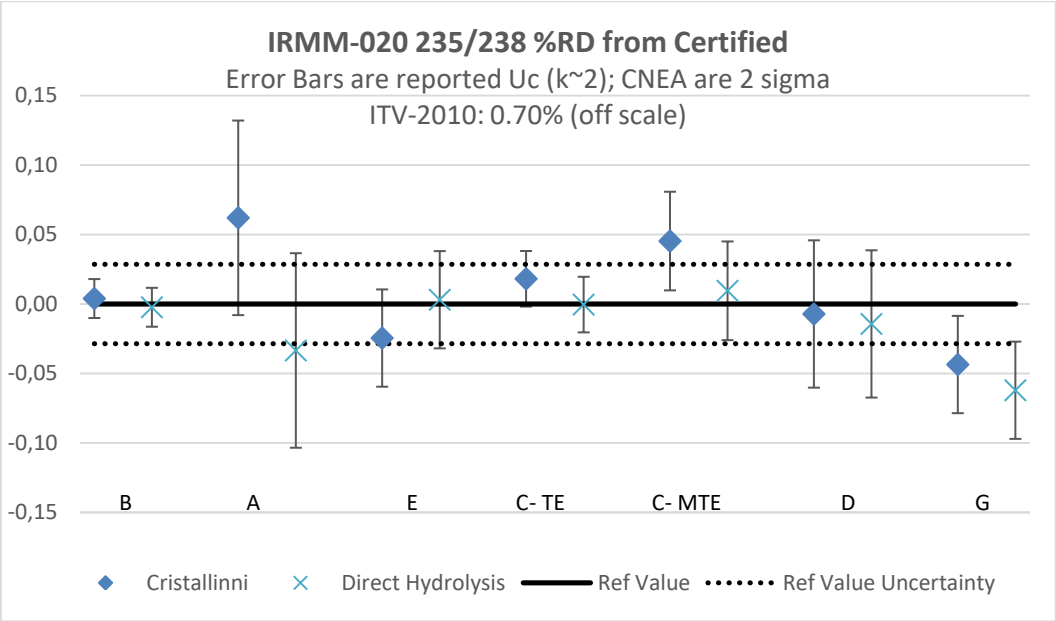

Figure 2: IRMM-020 n(U235)/n(U238) %RD from Certified Isotopic Ratio

IRMM 020 results indicate good agreement between the ABACC-Cristallini and hydrolysis samples and with the certified value of the CRM. Additionally, all results are well within the ITV-2010 target values for n(U235)/n(U238) determination for a material of this enrichment.

The results presented here shows that any difference for the n(U235)/n(U238) ratio between the ABACC-Cristallini and direct hydrolysis methods is very small. Only the Laboratories F and C double spike measurements definitively demonstrated a small difference for two of the three samples they analyzed.

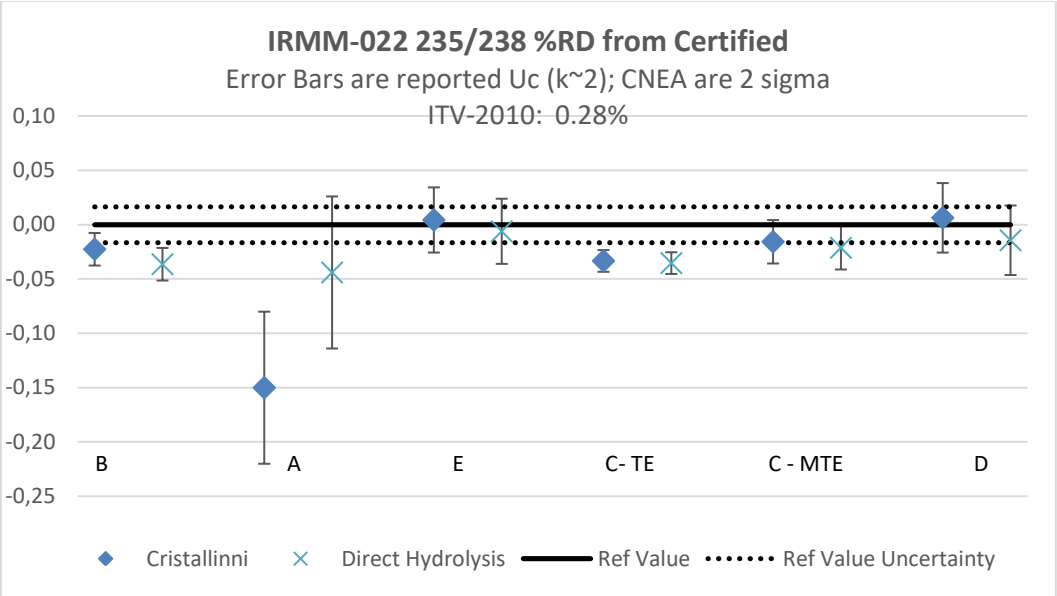

Figure 3: IRMM-022 n(U235)/n(U238) %RD from Certified Isotopic Ratio

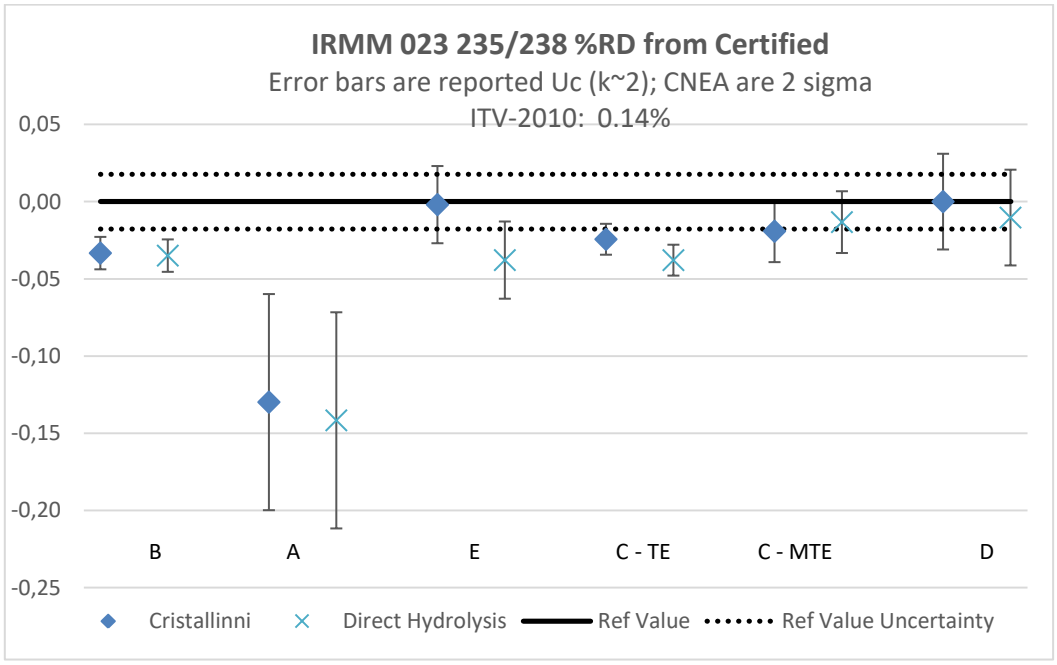

Figure 4: IRMM-023 n(U235)/n(U238) %RD from Certified Isotopic Ratio

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 n(U235)/n(U238) ratio to be approximately 0.010% on average higher than the direct hydrolysis samples. No general trend could be seen in the n(U234)/n(U238) or n(U236)/n(U238) ratios.

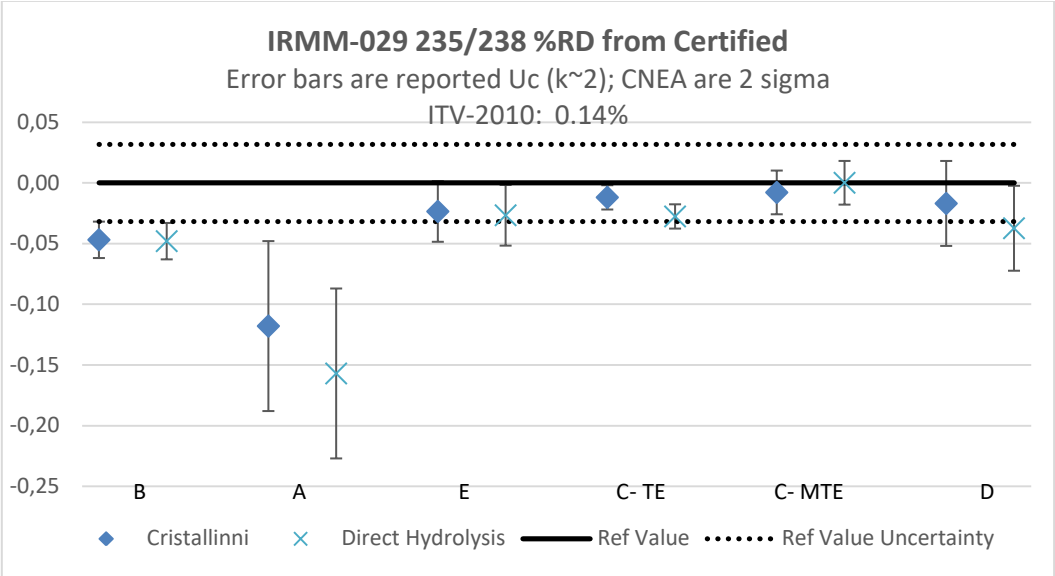

Figure 5: IRMM-029 n(U235)/n(U238) %RD from Certified Isotopic Ratio

The Table 4 lists the average %RD between ABACC-Cristallini and direct hydrolysis n(U235)/n(U238) results for each sample and laboratory.

Lab	IRMM 20 ITV 0.70%	IRMM 22 ITV 0.28%	IRMM 23 ITV 0.14%	IRMM 29 ITV 0.14%
A	0.110	-0.111	0.012	0.040
B	0.006	0.014	0.002	0.001
C TE	0.019	0.002	0.014	0.016
C MTE	0.036	0.0055	-0.006	-0.008
C DS	0.016	0.0084	0.0037	-
D	0.007	0.021	0.010	0.020
E	-0.028	0.010	0.036	0.003
F	0.017	0.008	<0.005	NA
G	0.020	-	-	-

Table 4: Relative percent difference between ABACC-Cristallini and direct hydrolysis samples for measured n(U235)/n(U238) ratio.

Of the 31 sample pair differences measured, only four of them indicated ABACC-Cristallini n(U235)/n(U238) ratios that were lower than the direct hydrolysis result. The majority of the differences ranged between 0.01% - 0.02%.

5. Conclusions

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

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 is yet unknown (unlikely to be related to sampling method, small biases inherent to the mass spectrometric instrumentation due to alumina or other impurities).

Nevertheless, as Laboratories F and C 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 0.7% to 0.14%.

In conclusion, for the purposes of nuclear safeguards and process control, the ABACC-Cristallini UF_6 sampling method provides comparable results to the direct hydrolysis method for sampling UF_6 for uranium isotopic determinations.

6. References

1. A. Esteban, O. Cristallini and J. Perrotta, "UF_6 Sampling Method Using Alumina", 29th ESARDA Annual Meeting, France (2007).
2. E. Galdoz, A. Esteban, O. Cristallini, J. Perrotta, "UF_6 Sampling Method Using Alumina", 49th INMM Annual Meeting, USA (2008).
3. O. Cristallini, A. Esteban, E. Gautier, L. Machado da Silva, S. Fernández Moreno, G. Renha, A. Bonino, O. Pereira Jr and F. Dias, "Qualification for Safeguards of the ABACC-Cristallini method - Comparison of isotopic results from UF_6 samples obtained using two methods", Workshop on Separation Phenomena in Liquids and Gases (SPLG), Argentina (2015).
4. ASTM C-1689-08 Standard Practice for Sub-sampling of Uranium Hexafluoride
5. ASTM C 1346-08 (Reapproved 2014) Standard Practice for Dissolution of UF_6 from P-10 tubes.
6. ASTM C1703 − 08 (Reapproved 2013) Standard Practice for Sampling of Gaseous Uranium Hexafluoride.
7. S. Mialle, S. Richter, C. Hennessy, J. Truyens, U. Jacobsson and Y. Aregbe, "Certification of uranium hexafluoride reference materials for isotopic composition", J. Radioanal Nucl. Chem. 305 (2015) 255-266.
8. International Atomic Energy Agency, STR-368, "International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials", (2010).
9. S. Richter, J. Hiess, and U. Jacobsson, "Validation of Cristallini Sampling Method for UF_6 by High Precision Double-Spike Measurements", Collaboration between JRC-G.2, Team METRO and SGAS/IAEA, JRC Technical Reports (2016).
10. ASTM C1672 - 17 Standard Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer.
11. ASTM C1832 - 16 Standard Test Method for Determination of Uranium Isotopic Composition by the Modified Total Evaporation (MTE) Method Using a Thermal Ionization Mass Spectrometer.