Destructive Analysis of Nuclear Materials at ABACC: Current Status and Future Steps

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Abstract

The Brazilian-Argentine Agency for Accounting and Control of Nuclear Material (ABACC) is a bilateral organization created in 1991 by Argentina and Brazil to verify the peaceful use of nuclear materials and installations in both countries. Among several responsibilities, ABACC has to perform quantitative verification of the declared nuclear material inventories and transactions by independent measurements, performed with systems and techniques that must conform to accepted international standards. In this regard, destructive assay (DA) techniques are of the utmost importance, mainly due to the high-performance levels they can meet in terms of precision and accuracy. ABACC uses DA techniques to detect small biases in the declared nuclear material quantities and to evaluate some of the measurement systems used by facility operators for establishing those declarations. In this paper, we describe how ABACC implements DA in support to its mission: techniques being used, analytical laboratories involved and typical performance levels. We also evaluate the consistency between the values obtained by ABACC and the International Atomic Energy Agency (IAEA) as result of independent collection of samples during joint inspections performed in Argentina and Brazil over the last years. Finally, an update on the status of the ABACC-Cristallini UF6 sampling method in lieu of the conventional method is presented.

1. INTRODUCTION

Destructive analysis (DA) techniques are of fundamental importance for precise and accurate accountancy of nuclear materials in bulk handling facilities at different levels: local (facility operators), national (regulatory authority), regional and international. In conducting safeguards verification activities in Argentina and Brazil, ABACC and the IAEA perform several tasks, including the independent collection of uranium samples for subsequent destructive analysis at highly qualified analytical laboratories. While most of the samples collected by the IAEA are analysed at its own laboratory located in Seibersdorf, Austria [1], ABACC relies on a network of laboratories in Argentina and Brazil [2]. In any case, the level of quality achieved in the results has to be consistent with recognized international standards [3], so that the relevant verification goals can be met. Once a material balance period (typically one year) is closed, with all evaluations properly completed by ABACC and the IAEA, the agencies may interchange their DA results obtained during that period for consistency evaluation and discussion of discrepancies, if any.

Several DA techniques can be used for nuclear material analysis, depending on what needs to determined, the desired precision and accuracy levels, material and human resources available, timing for results obtention etc. In Argentina and Brazil, typical nuclear facilities and material types subject to sampling for DA analysis by ABACC and the IAEA are as follows:

- Commercial Fuel Fabrication Plans: powders, pellets and scraps;
- Commercial Conversion Plants: powders and solutions (pure uranyl nitrate in a process tank); and
- Enrichment Plants: UF_6, both from cylinders and feed and withdrawal process lines.

These uranium samples are analyzed by the Modified Davies & Gray technique [4] for the determination of uranium mass fraction, i.e., mass of U per mass of sample. For isotopic analysis, i.e., the determination of the $^{235}U/^{238}U$ atom or mass ratio, mass spectrometry techniques are used, in particular inductively coupled plasma (ICP-MS) and total evaporation thermal ionization (TE-TIMS) [5].

For quality control of the analytical services provided by the ABACC network of laboratories, traceable uranium reference materials are used for the calibration of the analytical instruments, some of them obtained and distributed by ABACC, in cooperation with international organizations such as the New Brunswick Program Office (NBL) in the USA and the Institute for Reference Materials and Measurements (IRMM) in Europe. ABACC also supports the participation of the laboratories in safeguards measurement evaluation programs promoted by those organizations, as well as in the proficiency test entitled Nuclear Material Round Robin (NMRoRo) organized by the IAEA. Regardless the program under consideration, in general the performance achieved by the referred laboratories has been consistent with internationally recognized target values [3]. Currently, the laboratories are working on the analysis of samples distributed in the scope of the programs promoted by the IAEA and NBL for the biennium 2022/2023.

2. EVALUATION OF HISTORICAL ABACC/IAEA DA PAIRED DATA

In this session, the consistency between independent DA results obtained by ABACC and the IAEA for typical uranium samples collected in Argentina and Brazil during five consecutive years (2016 to 2020) is evaluated based on internationally recognized target uncertainty values (ITV) applicable for safeguards purposes, as well as standard statistical tools. For this, the following methods are used:

a. For each facility, sample type and measurand (U concentration or ^{235}U enrichment), the measurement results obtained by ABACC are evaluated in terms of % RDs with reference to the IAEA values (paired data), as follows:

$$\% \text{ RD} = 100 \times \{(\text{ABACC result} - \text{IAEA result}) / \text{IAEA result}\}.$$

b. Each set of % RD values is tested for statistical outliers. Those are removed, if any.

c. For each set, the mean % difference (same as mean % RD), standard deviation, 95% confidence limit (C.L.) of the mean and statistical significance of between-year standard deviation are reported.

d. The calculation of the 95% C.L. of mean depends upon whether year-to-year variation is significant/marginally significant or not significant as examined through analysis of variance (ANOVA). It is considered significant if the value of the statistical test exceeds 95% of the theoretical F-distribution; it is considered marginally significant if the value is between 90 and 95%, and not significant if the value is less than 90%. If the year-to-year variation is not significant/marginally significant, then the 95% C.L. is calculated as the standard deviation of the mean (standard error) multiplied by the appropriate coverage factor based on the Student's "t" distribution with n-1 degrees of freedom, where n is the total number of data points. If the year-to-year variation is significant, then the 95% C.L. is calculated from variance components for year-to-year and within-year variations and a coverage factor based on the Student's "t" distribution with approximately k-1 degrees of freedom, where k is the total number of years.

e. The mean % RD and the standard deviation are compared with combined uncertainties obtained from the ITV components u(s) and u(r), respectively [3]. For calculating these combined uncertainties, the ITV table 4a for U concentration or 5a for ^{235}U abundance, as well as table 3 for sampling are used, for both ABACC and IAEA results. Results falling within the combined uncertainties indicate consistency with internationally recognized standards for safeguards purposes.

f. ABACC and IAEA results for a certain facility, sample type and quantity determination are considered as statistically consistent or bias-free if the interval defined as the mean % RD ± 95% C.L. includes zero.

A total of fourteen paired data sets were evaluated. The results and conclusions are presented in the following tables.

Table 1: Evaluation summary for uranium mass fraction of UO_2 sintered pellets without burnable poison by Davies & Gray. Samples collected at Fuel Fabrication Plant (FFP-1).

Paired data Set #1	Value	Combined ITV
Number of pairs	20 (no outliers)	
Mean % RD	-0.031	u(s): 0.16
Standard Deviation	0.077	u(r): 0.16
95% C.L. of Mean	0.036	
Year-to-year variation (statistical significance)	88.0%	
Conclusions for Set #1: • The mean % RD (-0.031) and the standard deviation (0.077) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance is not significant.		

Table 2: Evaluation summary for uranium mass fraction of UO_2 sintered pellets without burnable poison by Davies & Gray. Samples collected at Fuel Fabrication Plant (FFP-2).

Paired data Set #2	Value	Combined ITV
Number of pairs	13 (no outliers)	
Mean % RD	0.014	u(s): 0.16
Standard Deviation	0.035	u(r): 0.16
95% C.L. of Mean	0.021	
Year-to-year variation (statistical significance)	58.1%	
Conclusions for Set #2: • The mean % RD (0.014) and the standard deviation (0.035) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance is not significant.		

Table 3: Evaluation summary for uranium mass fraction of UO_2 sintered pellets with burnable poison by Davies & Gray. Samples collected at Fuel Fabrication Plant (FFP-2).

Paired data Set #3	Value	Combined ITV
Number of pairs	5 (no outliers)	
Mean % RD	0.124	0.28
Standard Deviation	0.177	0.40
95% C.L. of Mean	0.220	
Year-to-year variation (statistical significance)	Not determined	
Conclusions for Set #3: • The mean % RD (0.124) and the standard deviation (0.177) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance could not be determined due to the reduced amount of paired data.		

Table 4: Evaluation summary for uranium mass fraction of oxide powders by Davies & Gray. Samples collected at Fuel Fabrication Plant (FFP-1).

Paired data Set #4	Value	Combined ITV
Number of pairs	27 (no outliers)	
Mean % RD	-0.006	u(s): 0.14
Standard Deviation	0.173	u(r): 0.32
95% C.L. of Mean	0.068	
Year-to-year variation (statistical significance)	85.9%	
Conclusions for Set #4: • The mean % RD (-0.006) and the standard deviation (0.173) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance is not significant.		

Table 5: Evaluation summary for uranium mass fraction of oxide powders by Davies & Gray. Samples collected at Fuel Fabrication Plant (FFP-2).

Paired data Set #5	Value	Combined ITV
Number of pairs	14 (no outliers)	
Mean % RD	-0.041	u(s): 0.14
Standard Deviation	0.190	u(r): 0.32
95% C.L. of Mean	0.110	
Year-to-year variation (statistical significance)	72.9%	
Conclusions for Set #5: • The mean % RD (-0.041) and the standard deviation (0.190) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance is not significant.		

Table 6: Evaluation summary for uranium mass fraction of pure uranyl nitrate solution (approx. 400 g-U/L) by Davies & Gray. Samples collected at a Conversion Plant.

Paired data Set #6	Value	Combined ITV
Number of pairs	11 (no outlier)	
Mean % RD	-0.103	u(s): 0.14
Standard Deviation	0.745	u(r): 0.20
95% C.L. of Mean	0.501	
Year-to-year variation (statistical significance)	0.2%	
Conclusions for Set #6: • The mean % RD (-0.103) is within the combined systematic u(s) ITV component. However, the standard deviation (0.745) is out of the combined random u(r) ITV component. • Year-to-year variance is not significant.		

Table 7: Evaluation summary for ^{235}U enrichment of natural and low enriched (< 1wt% ^{235}U) UO_2 sintered pellets without burnable poison by TIMS. Samples collected at Fuel Fabrication Plant (FFP-1).

Paired data Set #7	Value	Combined ITV
Number of pairs	30 (one outlier)	
Mean % RD	-0.038	u(s): 0.29
Standard Deviation	0.308	u(r): 0.29
95% C.L. of Mean	0.117	
Year-to-year variation (statistical significance)	19.3%	

Conclusions for Set #7:

- The mean % RD (-0.038) is within the combined systematic u(s) ITV component. However, the standard deviation (0.308) is marginally higher than the random u(r) ITV component.
- Year-to-year variance is not significant.

Table 8: Evaluation summary for ^{235}U enrichment of low enriched (< 1wt% ^{235}U) oxide powders by TIMS. Samples collected at Fuel Fabrication Plant (FFP-1).

Paired data Set #8	Value	Combined ITV
Number of pairs	12 (one outlier)	
Mean % RD	0.301	u(s): 0.28
Standard Deviation	0.391	u(r): 0.29
95% C.L. of Mean	0.263	
Year-to-year variation (statistical significance)	36.5%	

Conclusions for Set #8:

- The mean % RD (0.301) is marginally higher than the combined systematic u(s) ITV component and standard deviation (0.391) is higher than the random u(r) component established in the ITVs.
- There is a significant bias between ABACC and IAEA results.
- Year-to-year variance is not significant.

Table 9: Evaluation summary for ^{235}U enrichment of low enriched (> 1wt% ^{235}U) oxide powders by TIMS. Samples collected at Fuel Fabrication Plant (FFP-1).

Paired data Set #9	Value	Combined ITV
Number of pairs	12 (no outliers)	
Mean % RD	-0.064	u(s): 0.14
Standard Deviation	0.116	u(r): 0.16
95% C.L. of Mean	0.073	
Year-to-year variation (statistical significance)	66.9%	
Conclusions for Set #9: • The mean % RD (-0.064) and the standard deviation (0.116) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance is not significant.		

Table 10: Evaluation summary for ^{235}U enrichment of low enriched (> 1wt% ^{235}U) UO_2 sintered pellets by TIMS. Samples collected at Fuel Fabrication Plant (FFP-2).

Paired data Set #10	Value	Combined ITV
Number of pairs	18 (one outlier)	
Mean % RD	-0.049	u(s): 0.16
Standard Deviation	0.072	u(r): 0.16
95% C.L. of Mean	0.037	
Year-to-year variation (statistical significance)	50.3%	
Conclusions for Set #10: • The mean % RD (-0.049) and the standard deviation (0.072) are within the respective combined systematic u(s) and random u(r) ITV components. • There is a significant bias between ABACC and IAEA results. • Year-to-year variance is not significant.		

Table 11: Evaluation summary for ^{235}U enrichment of low enriched (> 1wt% ^{235}U) oxide powders by TIMS. Samples collected at Fuel Fabrication Plant (FFP-2).

Paired data Set #11	Value	Combined ITV
Number of pairs	13 (no outlier)	
Mean % RD	-0.027	u(s): 0.14
Standard Deviation	0.049	u(r): 0.16
95% C.L. of Mean	0.029	
Year-to-year variation (statistical significance)	65.5%	
Conclusions for Set #11: • The mean % RD (-0.027) and the standard deviation (0.049) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance is not significant.		

Table 12: Evaluation summary for ^{235}U enrichment of low enriched (> 1wt% ^{235}U) UF$_6$ by TIMS.

Paired data Set #12	Value	Combined ITV
Number of pairs	11 (one outlier)	
Mean % RD	-0.059	u(s): 0.14
Standard Deviation	0.192	u(r): 0.20
95% C.L. of Mean	0.137	
Year-to-year variation (statistical significance)	67.1%	
Conclusions for Set #12: • The mean % RD (-0.059) and the standard deviation (0.192) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance is not significant.		

Table 13: Evaluation summary for ^{235}U enrichment of natural UF$_6$ by TIMS.

Paired data Set #13	Value	Combined ITV
Number of pairs	9 (one outlier)	
Mean % RD	0.126	u(s): 0.28
Standard Deviation	0.188	u(r): 0.32
95% C.L. of Mean	0.157	
Year-to-year variation (statistical significance)	38.0%	
Conclusions for Set #13: • The mean % RD (0.126) and the standard deviation (0.188) are within the respective combined systematic u(s) and random u(r) ITV components. • Year-to-year variance is not significant.		

Table 14: Evaluation summary for ^{235}U enrichment of depleted UF$_6$ by TIMS.

Paired data Set #14	Value	Combined ITV
Number of pairs	13 (two outliers)	
Mean % RD	0.484	u(s): 1.44
Standard Deviation	0.552	u(r): 1.44
95% C.L. of Mean	0.371	
Year-to-year variation (statistical significance)	73.2%	
Conclusions for Set #14: • The mean % RD (0.484) and the standard deviation (0.552) are within the respective combined systematic u(s) and random u(r) ITV components. • There is a significant bias between ABACC and IAEA results. • Year-to-year variance is not significant.		

3. UF_6 SAMPLING USING THE ABACC-Cristallini METHOD: CURRENT STATUS

Collection of samples of uranium hexafluoride (UF_6) for subsequent destructive analysis to determine enrichment and other parameters is a common practice in gaseous centrifuge enrichment plants (GCEP). The standard method for this sampling is to collect a liquid sample during a cylinder homogenization operation or a gaseous sample from process feed, tail and product headers using a cryogenic collection method. Both of these methods typically collect a few grams of material, much more than is needed for the isotopic analysis. Also, the transportation of solid UF_6 over international borders has become more complicated. The ABACC-Cristallini method [6] has been developed as an improvement on the standard gaseous collection by collecting the UF_6 as an inert salt on an alumina substrate using a passive vacuum instead of the cryogenic method. By controlling the amount of alumina substrate previously inserted into the sample vessel, one can approximately determine the amount of sample to be collected, typically 100 - 300 mgU. One application is the collection of samples during safeguards inspections in GCEPs for isotopic analysis only. In 2019 the method was published by ASTM International as C1880-19 “Standard Practice for Sampling Gaseous Uranium Hexafluoride Using Alumina Pellets”, after being submitted to a comprehensive assessment of the results obtained from sampling and isotopic analysis exercises that had been conducted at laboratory scale. One of the important outcomes from the exercises was to demonstrate that the uncertainty associated with the method is negligible in comparison with the uncertainties associated with the most frequently used isotopic analysis methods, i.e., TIMS and ICP-MS.

Currently, both ABACC and the IAEA are focusing on performing industrial scale testing, i.e., taking samples in GCEPs. In Brazil, a field trial was conducted in 2021 at a commercial GCEP. For this, a special authorization was granted by the Operator (Industrias Nucleares do Brasil – INB) and the State Regulatory Authority (Brazilian Nuclear Energy Commission – CNEN) [7]. During the testing, samples of natural, depleted and enriched uranium were collected using both the standard gaseous sampling practice and the ABACC-Cristallini method. The sample vessel was a metallic stainless-steel P-10 tube for the ABACC-Cristallini samples and a type A croft bottle for the standard gaseous sampling. The isotopic analysis at different laboratories was concluded and the results obtained are currently under review.

In order to have the ABACC-Cristallini method approved for routine use during safeguards inspections, ABACC is working on the following tasks:

- To review and publish the results of the joint field trial conducted at the Brazilian Commercial GCEP in 2021. The goal is to demonstrate that the method is safe, robust and reliable for use during routine safeguards inspections;
- To explore the possibility to use non-metallic P-10 tubes made with polychlorotrifluoroethylene (PCTFE). This type of vessel was successfully used during the qualification exercises at laboratory scale and would represent significant practical benefits and economic savings in comparison with the metallic vessels;
- To consolidate an internationally recognized target value for the sampling uncertainty associated with the method. The initial discussions that took place during the Consultants Group Meeting on International Target Values 2020 for Measurement Uncertainties in Safeguarding Nuclear Materials leaded by the IAEA and carried out in June 2021 indicated that the estimated sampling uncertainty associated with the

ABACC-Cristallini method is significantly lower than the current estimate for the traditional gaseous sampling of low enriched UF_6 (0.1% rel.).

4. CONCLUSIONS

In general, the evaluation of paired ABACC/IAEA DA data for samples collected simultaneously from the same item and under the same conditions during joint inspections conducted between 2016 and 2020 in Argentina and Brazil indicates good consistency with the current ITVs. From the evaluated data, the following outcomes can be highlighted:

- Uranium mass fraction determination in highly concentrated nitrate solution by the Davies & Gray method is subject to uncertainties of random nature higher than the corresponding combined ITV. One possible reason is that the sampling uncertainty stated in the ITV, which is a single value for any condition (concentration level, tank volume, sampling method, etc), is not adequate for the conditions under evaluation. Another possible reason may be associated with the procedure for manipulation of the liquid sample in the laboratory.
- ^{235}U enrichment determination in low enriched (< 1wt% ^{235}U) pellets and powders by TIMS presented uncertainties marginally higher that the corresponding combined ITVs. One possible reason is that the blending of NU with LEU powders performed as part of the process to produce the referred powders and pellets has a relevant impact on the sampling uncertainty, not observable in the cases where blending is not conducted (powders and pellets enriched above 1wt% ^{235}U). The current ITVs do not make such a differentiation.

In both cases, further investigation on the causes of the observed uncertainties is recommended.

Statistically significant biases between ABACC and IAEA results were observed in some cases, all involving ^{235}U enrichment determination by TIMS: low enriched (< 1wt% ^{235}U) oxide powders, low enriched (> 1wt% ^{235}U) UO_2 sintered pellets and depleted UF_6. However, they are always within the corresponding systematic components of the ITV. Although not significant for safeguards evaluation purposes, these biases should be investigated and corrective actions implemented, if possible.

On the ABACC-Cristallini method for UF_6 sampling, ABACC considers it is ready for use during actual safeguards inspections in Argentina and Brazil. The expectation is that all necessary validations be completed in 2022 and the authorizations for routine use during safeguards inspections be granted by facility operators and State authorities in early 2023.

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