ABACC LABORATORIES QUALITY ASSURANCE THROUGH SECONDARY STANDARDS EXCHANGE PROGRAM

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ABSTRACT

In September 1999, the Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC), with assistance from the New Brunswick Laboratory (NBL) of the U.S. Department of Energy, started a new cooperative activity with, among other objectives, the production and characterization of a traceable uranium secondary standard and the performance of the Third Round Robin for ABACC's laboratory network. Brazil and Argentina have fabricated UO_2 pellets for use as a secondary standard. Samples from the two batches were sent to NBL for the determination of the reference values for both uranium concentration (%U) and isotopic composition for each batch.

ABACC and NBL then organized the Third ABACC Round Robin for Brazilian and Argentine laboratories that are part of the ABACC network. The laboratories comprising the network can be used to analyze real samples collected during the ABACC inspections.

The Brazilian and Argentine pellets were distributed to all the laboratories together with the protocol to be followed for the uranium concentration analysis, the forms for reporting the measurement results, and natural UO_2 pellets (CETAMA OU1) to be used as reference material. For the laboratories with capability of measuring isotopics, NBL reference material CRM 125-A was provided.

Several laboratories from each country provided results. As soon as the measurement results were sent to the organizers, they were statistically evaluated by NBL. During a meeting held at ABACC headquarters with the participation of NBL representatives, the ABACC technical support officer, and representatives of all the participant laboratories, the results were discussed and compared with the reference values. All the laboratories had the occasion, in an open discussion, to explain and show the difficulties and problems they faced during the exercise. ABACC had the opportunity not only to judge the quality of the measurements these laboratories performed, but also to determine possible improvements in their measurement processes.

INTRODUCTION

ABACC uses Brazilian and Argentine laboratories to analyze its destructive samples collected during the inspections. The laboratories in the ABACC network perform inventory verification measurements. To improve the quality of these analyses, ABACC and NBL have established a cooperative effort to maintain a quality control and quality assurance program through the preparation and characterization of a secondary standard, implementation of a sample exchange program, and the evaluation of laboratory exchange data. These activities are performed under the DOE/ABACC Safeguards Cooperation Agreement started in November 1996 and the corresponding Action Sheet 11: Laboratory Quality Assurance Through Standards and Sample Exchange Programs.

The scope of this Action Sheet is the production and characterization of a traceable secondary standard to unify the traceability of ABACC analytical results to a single source, and the

continuation of laboratory Intercomparison programs to monitor the performance of ABACC's analytical network.

This Intercomparison program among laboratories has been conceived as a permanent activity and the Third ABACC/NBL Round Robin took place in 2002. The results are presented in this paper. Results of the nine participant laboratories for uranium concentration and three participant laboratories for isotopic composition were statistically evaluated by NBL using analysis of variance (ANOVA) and other statistical techniques. The NBL characterization of the samples is presented as well.

REFERENCE VALUES OF ABACC UO_2 PELLETS

Separate batches of pellets (500 each) were fabricated in Brazil and Argentina for use in the Intercomparison program. In 2001, New Brunswick Laboratory received thirty of these UO2 pellets (15 pellets from each batch) for analysis. Both assay (%U) and isotopic composition were measured for samples from each batch. Each pellet contained about 1 gram of material. The estimated assay of the pellets was 88.1%U. Each batch of pellets was assigned an NBL number and then was given a separate unit number, 01 through 15. Randomly selected pellets from each batch were sampled and analyzed for uranium concentration, isotopic composition, and impurities content, according to a sampling and analysis plan.

Eight pellets from each of the two batches were dissolved for analysis. During the dissolution of the two batches of samples, the pellets from Brazil left a carbonaceous residue in the bottom of the dissolution beakers. The residue was readily dissolved with added heat and refluxing. No special handling or treatment was necessary to complete the dissolution of the samples.

The uranium elemental concentration determinations were performed according to the NBL Modified Titrimetric Method, a potentiometric titration to a fixed endpoint using a standard pH meter in millivolt mode. The isotopic analyses were performed using the NBL Finnigan TRITON thermal ionization mass spectrometer. The impurity determinations were made using the NBL inductively coupled plasma atomic emission spectrometer (ICP-AES). The results of the NBL characterization are summarized in Tables 1 and 2 below.

TABLE I- Uranium Concentration Determinations

NBL NUMBER	ABACC ID NUMBER	Mean %U	95%C.I.
01NU0051	ABACC-ARG	88.132	0.015
01NU0052	ABACC-BRA	88.071	0.020

TABLE II – Isotopic and Atomic Weight Determinations

NBL ID No	ABACC ID No	Mean Wt $\%^{234}U$	Mean Wt $\%^{235}U$	Mean Wt $\%^{236}U$	Mean Wt $\%^{238}U$	Atomic Weight
01NU0051	ABACC-ARG	0.0054	0.7128	0.0001	99.2816	238.028853
01NU0052	ABACC-BRA	0.0053	0.7117	0.0001	99.2829	238.028892
	COMBINED	0.0053	0.7123± 0.0012	0.0001	99.2822	238.0289±0.001

There is a statistically significant (> 95% significance) difference in the atomic weights of the samples; however, this difference is of no practical significance.

The assay analysis indicates that the two batches are close to the same value, but slightly different. One batch has a uranium concentration of 88.132%U±0.015 and the other has a uranium concentration of 88.071%U±0.020, presumably due to slight differences in processing. Uncertainties are quoted as 95% confidence intervals. This difference in the assay values of 0.061% is statistically significant. Given that the 2000 International Target Values[1] (ITVs) for random and systematic errors are 0.1%, the difference of 0.061% is significant if these pellets are used as samples in a measurement evaluation program. The isotopic analyses also show the two batches are slightly different in isotopic composition. Given the capability of the ABACC measurement processes, the difference is not significant and combined values are used.

For uranium concentration measurements, some ABACC laboratories have performed much better than the International Target Values in the past. Thus the assay differences provided an opportunity to test the abilities of the participant laboratories to detect the assay difference between the batches.

PROCEDURES FOR THE ABACC SAFEGUARDS MEASUREMENTS EVALUATION ROUND ROBIN#3

For this third round of the ABACC Intercomparison Program, nine laboratories participated by analyzing the pellets for uranium assay and three of these laboratories also analyzed the isotopic content.

The participant laboratories were:

- Laboratório de Control Quimico y Fisico, Unidad de Combustibles Nucleares, Centro Atomico Constituyentes, CNEA/Argentina;
- Unidad de Actividad Quimica, Centro Atomico Constituyentes, CNEA/Argentina;
- Laboratório Quimica Analitica, Unidad de Actividad Materiales y Combustibles Nucleares, Centro Atomico Ezeiza, CNEA/Argentina;
- Grupo de Metodologias Nucleares de Analisis, Unidad de Actividad Quimica, Centro Atomico Constituyentes, CNEA/Argentina;
- Planta de Fabricacion de Polvos de Uranio, Unidad de Actividad Combustibles Nucleares, Centro Atomico Constituyentes, CNEA/Argentina;
- Serviço de Química e Mineralogia, Centro de Desenvolvimento de Tecnologia Nuclear, CNEN/Brazil;
- Laboratório de Caracterização de Urânio e Laboratório de Espectrometria de Massas, Centro Tecnológico da Marinha em São Paulo – CTMSP/Brazil;
- Serviço de Analises Quimicas e Ensaios de Materiais, Divisão de Quimica e Materiais Nucleares, Instituto de Engenharia Nuclear, CNEN/Brazil;
- Laboratório de Salvaguardas, Coordenadoria de Salvaguardas, Diretoria de Radioproteção e Segurança Nuclear, CNEN/Brazil;
- Laboratório de Caracterização Química, Instituto de Pesquisas Energéticas e Nucleares , CNEN/Brazil.

For uranium concentration measurements, each laboratory was sent a total of nine pellets; three French CETAMA OU1 standard 0.4-gram UO2 pellets for use as reference material (for

uranium concentration measurements only), three 1-gram UO2 pellets manufactured by Argentina; and three 1-gram UO2 pellets manufactured by Brazil. It was important to track and report the country of manufacture for each of the 1-gram pellets analyzed.

For the laboratories with the capability of measuring enrichment, three pellets of NBL CRM 125-A uranium dioxide pellets were sent for use as an isotopic reference standard.

Each participating laboratory sent the analytical results to ABACC and NBL. NBL then evaluated the data and sent data evaluation reports to each laboratory and to ABACC.

RESULTS

The results (precision and bias) obtained by the ABACC laboratories for uranium concentration and uranium enrichment are shown in Tables III and IV, respectively. The methods used for the measurements are also presented. To ensure the anonymity of participating laboratories for this paper, the ordering of the laboratories is different than in the preceding list. Numbers were assigned randomly. Laboratories 3, 4, and 8 performed both enrichment and assay measurements.

Two different methods were used to determine uranium concentration. All except one laboratory used some variant of dichromate titration. Laboratory 8 used inductively coupled plasma-optical emission spectrometry (ICP-OES). For uranium enrichment measurements, two laboratories used thermal ionization mass spectrometry (TIMS), and one laboratory used inductively coupled plasma mass spectrometry (ICP-MS).

The ITV2000 values for titration of uranium oxides are 0.1% and the bias also 0.1%. For uranium enrichment the ITV2000 for TIMS-NU is 0.2% for precision and 0.2% for bias. For ICP-MS and ICP-OES (methods used by Laboratory 8) there are no International Target Values.

TABLE III
U Concentration
ABACC Pellets-RR3

Lab	Method	Precision	Bias
1	Titration	0.064%	0.004%
2	Titration	0.111%	-0.224%
3	Titration	0.062%	-0.043%
4	Titration	0.169%	0.423%
5	Titration	0.022%	-0.032%
6	Titration	3.082%	-3.818%
7	Titration	0.056%	0.013%
8	ICP-OES	0.652%	-0.002%
9	Titration	0.055%	-0.061%

TABLE IV
U Enrichment
ABACC Pellets-RR3

Lab	Isotopics	Precision	Bias
1			
2			
3	TIMS	0.134%	-0.218
4	TIMS	0.267%	0.540
5			
6			
7			
8	ICP-MS	0.299%	-0.060
9			

The results for uranium concentration are presented graphically in Figures 1 and 2, and the results of the uranium enrichment measurements are shown in Figure 3. The range of the y-axis in Figure 1 is large to show the results from Laboratory 6. Figure 2 is the same set of data but with the y-axis scale adjusted so that the performance of other laboratories may be seen clearly. The statistic plotted on the y-axis is the percent relative difference (%RD). In order to normalize the data for evaluation, the percent relative difference from the reference value is defined as

% RD = [(observed value - reference value)/reference value](100%),

A corresponding %RD was calculated for each reported measurement value.

Figure 1. Uranium concentration, wide scale

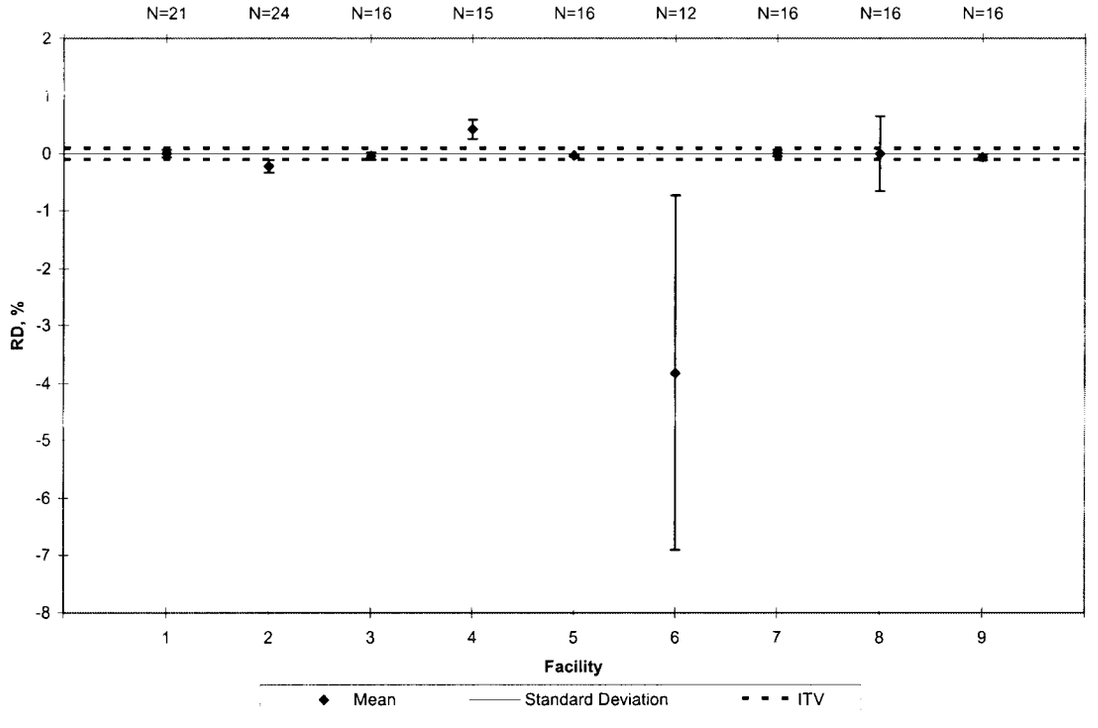


Figure 2. Uranium concentration, narrow scale

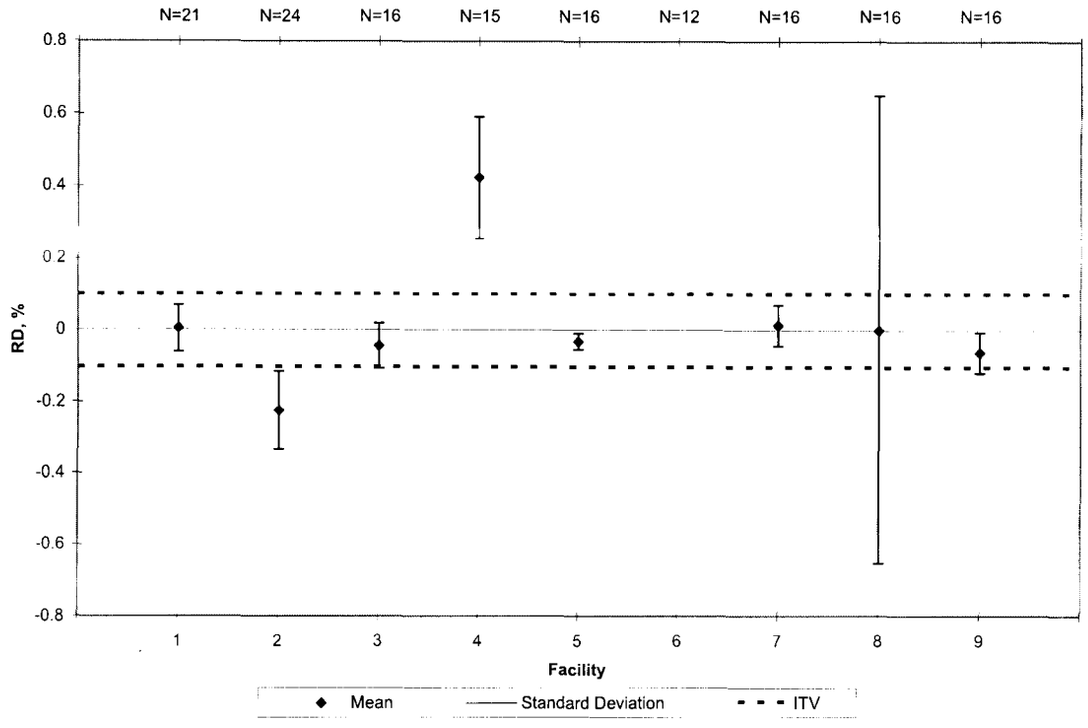
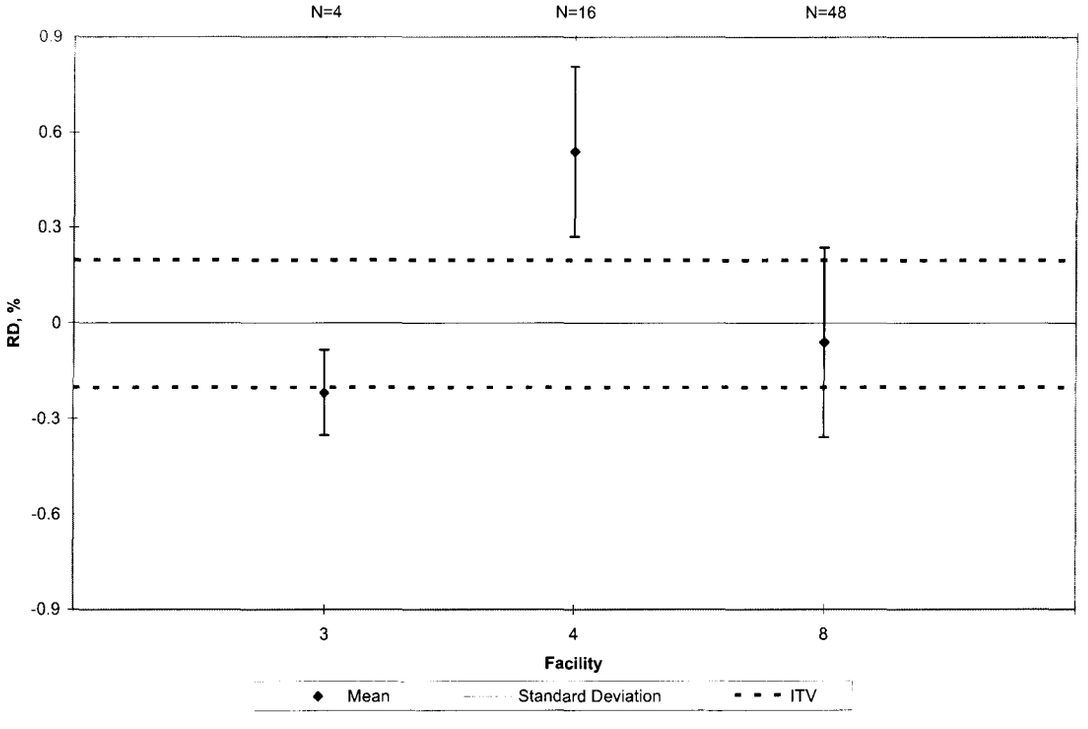


Figure 3. Uranium enrichment



On each figure, the mean is shown as a diamond at the center of error bars. Also, dashed lines are plotted corresponding to the ITVs for titration (uranium concentration) or TIMS (uranium enrichment). Note that these ITVs are not applicable to ICP-OES and ICP-MS. If the mean is within the pair of dashed lines, the bias of the measurement is within the ITV for systematic error. If the magnitude of the error bar (mean value to end of error bar) is smaller than the ITV (0 to positive dashed ITV line), the precision is within the ITV for random error. For example, for uranium concentration, Laboratory 5 is within the ITVs for both bias and precision, while Laboratory 2 is outside the ITV for systematic error and almost within for random error.

DISCUSSION

At a meeting at ABACC Headquarters in May 2003, participating laboratories presented their results and explained any difficulties encountered. Participating laboratories identified probable causes of higher-than-expected uncertainties. Just as importantly, procedural steps taken to ensure high-quality results were also presented by the laboratories. Significant errors were introduced at some laboratories from impure reagents, lack of temperature control, and electronic instrument malfunctions.

Several laboratories obtained excellent results for uranium concentration measurements by titration. Laboratories 1, 3, 5, 7, and 9 were well within the ITVs. In addition, determination of uranium concentration by ICP-OES was unbiased and had random errors that were small for this type of measurement.

For uranium enrichment, Laboratory 3 was essentially within the ITV for systematic error and within the ITV for random error. Laboratory 4 was close to the ITV for random error, but had a bias that had been recognized previously on other analyses. Laboratory 8 used ICP-MS, and met the (TIMS) ITV for systematic error. The precision was 1.5 times the (TIMS) ITV for random error, and is considered to be an excellent result for this method. The need for an ICP-MS ITV was discussed.

FUTURE PLANS

ABACC network laboratories will continue to participate in future sample exchanges of uranium materials. Improvements are expected in the performance of laboratories as the significant sources of uncertainty are controlled or eliminated.

This work is supported by the U.S. Department of Energy, Office of International Safeguards (NA-243) and ABACC.

REFERENCES

[1] Deron, S. et al, "International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Materials", Journal of Nuclear Materials Management XXX, No. 2 (2002).