PARTICIPATION OF ABACC LABORATORIES IN MEASUREMENT INTERCOMPARISON PROGRAMS

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Abstract

During 1998, two major sample intercomparison program exercises occurred within the framework of the ABACC-DOE Cooperative Safeguards Program. The first exercise, the second round robin of the ABACC Laboratory Intercomparison Program, included participation by eleven Brazilian and Argentine analytical laboratories, with the DOE New Brunswick Laboratory (NBL) acting as reference laboratory. This Intercomparison Program's main purpose is to qualify and monitor the performance of a network of laboratories to provide ABACC with the necessary means to fulfil its task as administrator of the Common System for Accountability and Control of Nuclear Materials. The second exercise involved the participation of eleven Brazilian and Argentine analytical laboratories in the NBL Safeguards Measurement Evaluation (SME) Program. This exercise had the advantage of direct comparison of performance of ABACC laboratories with that of DOE and NRC laboratories. The analysis plans followed in the two intercomparison programs were designed to enable separate statistical evaluation of several different possible sources of analytical variability and bias. These statistical evaluations were sent to the participants, as feedback to improve their performance by applying the appropriate corrective actions to their methods, techniques and procedures.

INTRODUCTION

The Brazilian-Argentine Agency for Accountability and Control of Nuclear Materials (ABACC), as administrator of the Common System of Accountability and Control for those two countries, has the responsibility to analyze samples of nuclear material taken as necessary during safeguards inspections. These measurements are primarily and preferentially performed by non-destructive assay (NDA) methods, as these methods are quicker, cheaper, and less intrusive than destructive assay methods. In many cases, however, it is not possible to use NDA methods, as the aspect to be quantified cannot be measured in this way, or the accuracy and precision of NDA methods are not of high enough quality to meet accountability requirements. In these cases, samples must be submitted to destructive analysis.

ABACC does not own an analytical laboratory and must depend on the manpower, facilities, and laboratories in both countries. There was not enough justification to select any particular laboratory in Argentina and Brazil as a Reference Laboratory; therefore, ABACC decided instead to use a Laboratory Network, which was selected to be as large as possible. To maintain objectivity, laboratories in one country analyze analytical samples taken from facilities in the other country.

In following this Laboratory Network approach, it became necessary for ABACC to evaluate the performance of the laboratories in the network; for this purpose, a Laboratory Intercomparison Program was designed. The purpose of the program is not to exclude laboratories that occasionally submit abnormal results, but to detect problems where they exist and inform the participating laboratory so that it can institute corrective actions and improve procedures and methods. The participants would also have the opportunity to verify and improve their performance through the identification of statistically significant sources of error and estimation of their magnitude. The ultimate goal, then, is to establish and maintain a reliable Laboratory Network for the analysis of safeguards inspection samples.

To achieve this goal, ABACC coordinated the formation of an Intercomparison Group composed of representatives from Argentine and Brazilian laboratories. The Group's main tasks were to establish a workable structure for the Intercomparison Program and to propose an appropriate approach for its implementation and development, taking into account the existing infrastructure in both countries. Sub-groups were formed to address elemental analysis and isotopic composition of uranium. Isotopic activities have been postponed for the present because of the scarcity of laboratories capable of isotopic measurements, and the fact that this small group of laboratories is further subdivided between laboratories using thermal ionization mass spectrometry and those using gas mass spectrometry.

During 1998, ABACC Network Laboratories participated in two major sample intercomparison activities involving destructive analysis for uranium elemental composition. The first activity was the second round robin of the ABACC Intercomparison Program; the second activity was Argentine and Brazilian laboratory participation in the U.S. Department of Energy's (DOE) New Brunswick Laboratory Safeguards Measurement Evaluation Program. Funding provided within the Cooperative Safeguards Agreement between DOE and ABACC supported both of these activities.

ABACC INTERCOMPARISON PROGRAM – 2ND ROUND ROBIN

The first round robin[1] involved the analysis of a UO_2 powder, a material often encountered in the nuclear fuel cycle. The test material selected for the second round robin was U_3O_8, another material commonly found at nuclear facilities. Fourteen ABACC Network Laboratories were invited to participate; eleven submitted results (two of the laboratories submitted two sets of results, determined by two different methods of analysis, or at two different times, to produce a total of thirteen datasets).

SAMPLE PREPARATION AND ANALYTICAL SCHEME The test material was prepared at IPEN/CNEN in São Paulo. The bulk material, a uniform single batch of U_3O_8, was calcined three times at 800°C; the material was blended between firings to ensure that all the material was evenly calcined. The material was then packaged under dry nitrogen into glass penicillin-type vials, each closed with a rubber stopper and a metallic seal, in order to minimize adsorption of gases and moisture from the air.

Each participant was supplied with three vials of the test material and three sintered UO_2 pellets. The participants were asked to perform a set of analyses of the uranium concentration of the U_3O_8 sample at three different times: just after receiving the samples, and at 15 and 30 days after receipt. The UO_2 pellets, which were certified for uranium concentration by the Institute for Reference Materials and Measurements (IRMM) in Geel, Belgium, were used to calibrate the measurement system immediately before each set of analyses.

For each analytical period, the U_3O_8 sample was split into three weighed portions and dissolved. Three aliquants from each of the three dissolutions were analyzed. This produced 27 results over the three analytical periods. This analysis scheme allowed for the estimation of four separate types of errors: analytical uncertainty, dissolution and treatment error, between-sample variation, and calibration and other systematic errors.

ABACC asked the U.S. DOE's New Brunswick Laboratory to supply a reference value for the test material, which was used to estimate the significance of the ABACC laboratories' overall bias. As a Reference Material Laboratory, NBL used its own Certified Reference Material (CRM 112-A, Uranium Metal Assay Standard) to calibrate its measurement system. To ensure that this did not introduce a bias between NBL's and ABACC laboratories' results, NBL also analyzed several IRMM certified UO_2 pellets. Statistical evaluation indicated no significant difference between NBL's mean of the UO_2 pellet results and the IRMM certified value.

Attempts to dissolve the U_3O_8 resulted in a small amount of insoluble residue. The solution was filtered, and the filter paper was ashed, dissolved, and added to the rest of the dissolved sample. After this treatment, no insoluble residue remained. NBL then followed an analytical scheme similar to that followed by the ABACC laboratories, except that the three days of analysis were performed in a shorter timeframe, and two analysts were used, to produce a total of 54 results. The NBL reference value, with its 95% confidence limit, has the following value:

$$RV = 84.688 \pm 0.036 \text{ \%U.}$$

REPORTED RESULTS, PRECISION AND ACCURACY ABACC supplied to each reporting laboratory the value for the uranium concentration of the IRMM UO_2 pellet, which was then used by the individual laboratories to calibrate their analytical systems or bias-correct their results. Ten laboratories used versions of the Davies and Gray titration, one laboratory used a redox titration with reduction by stannous chloride, and one laboratory used both controlled potential coulometry and Davies and Gray titration. The individual determined values are displayed in Figure 1; the horizontal line is at the reference value. The results are grouped in clusters, with each cluster representing a set of individual results produced by a specific laboratory on a specific day. Laboratories 9 and 11 each produced two sets of results.

Figure 1
ABACC Round Robin
All Data

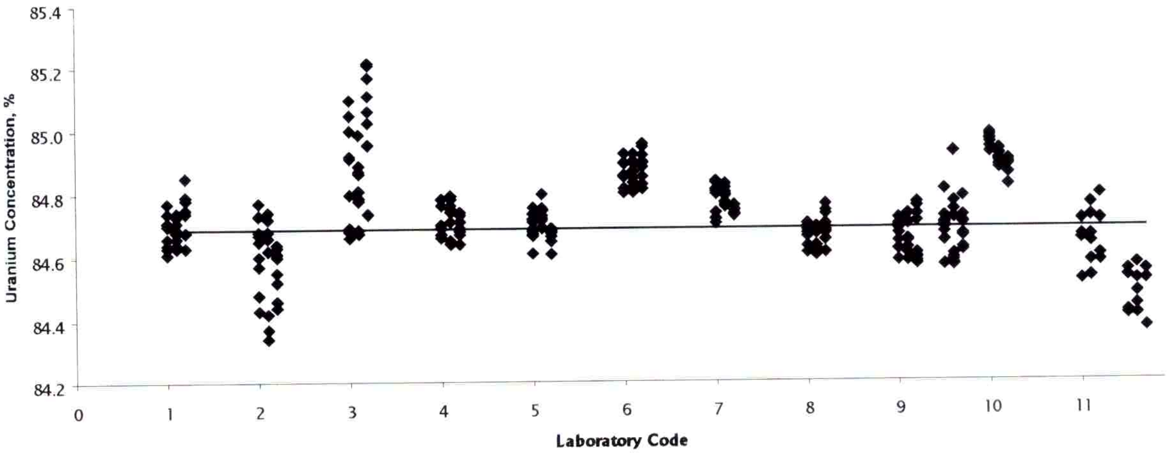
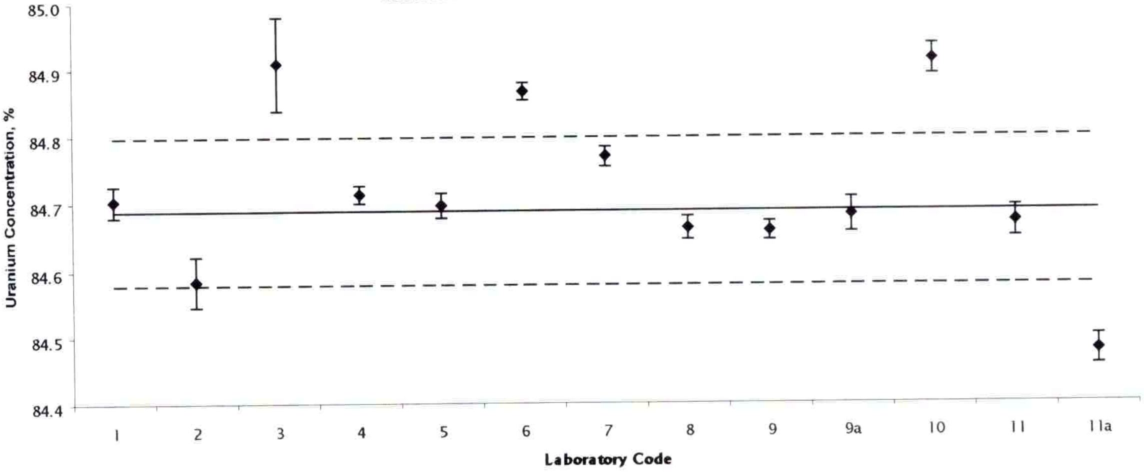


Figure 2 displays the individual laboratory means and standard deviations plotted *versus* the NBL reference value bracketed by its 3 **?** limits.

Figure 2
ABACC Round Robin
Individual Means and Standard Deviations



The ABACC grand mean for all thirteen sets of results was 84.713 ± 0.075 %U. This grand mean was compared with the NBL reference value of 84.688 ± 0.036 %U. Results show that there is no statistically significant difference between the NBL value and the ABACC grand mean, indicating no statistically significant bias in the ABACC overall results.

VARIANCE ANALYSIS OF THE INDIVIDUAL RESULTS The data were first examined to determine if the variation due to time of analysis was significant. The second analytical period, scheduled for 15 days after the first, actually ranged from 14-27 days. The third analytical period, scheduled for 30 days after the first, ranged from 30-51 days. The time effect was determined to be not statistically significant, which indicated that the packaging preserved the integrity of the sample. Several laboratories indicated that they were not able to completely dissolve the material.

The individual results produced by following the analytical scheme may exhibit variability produced by four types of errors:

- Measurement errors (SI)
- Treatment and dissolution errors (SB)
- Errors caused by variation between samples (SA)
- Calibration and other systematic errors.

All the measurements performed on aliquants taken from the same dissolution constitute a *group* with an average group variance of SI^2, while a collection of all measurements performed on the same sample constitute a *class*, with an average group variance of SA^2. Thus, there are three classes and nine groups for each laboratory. The parameter SB is the error between groups due solely to handling and dissolution, i.e. after excluding measurement errors. The results for each laboratory were evaluated using a *Two-Way Variance Analysis*[2], applied to a nested error model; the results are shown in the following table.

Table 1: Summary of Two-Way Variance Analysis for Individual Laboratories ABACC Round Robin

Laboratory Number	Mean %U	95% C.I.	Difference From R.V. %U	Statistical Significance of Difference	Measurement Error SI	Treatment Error SB	Sample Variation SA^2
1	84.70	0.10	0.02	0.60	0.054	0.007	0.037
2	84.58	0.16	-0.12	-2.74	0.086	0.102	SA^2 ■ 0
3	84.91	0.30	0.26	3.12	0.072	0.141	0.087
4	84.71	0.06	0.03	1.59	0.044	0.030	SA^2 ■ 0
5	84.70	0.08	0.01	0.39	0.031	0.017	0.029
6	84.87	0.05	0.21	13.02	0.049	SB^2 ■ 0	0.015
7	84.77	0.06	0.10	5.20	0.015	0.033	0.016
8	84.66	0.07	-0.03	-1.48	0.028	0.028	0.023
9	84.66	0.06	-0.04	-2.12	0.055	0.026	SA^2 ■ 0
9a	84.68	0.11	-0.01	-0.27	0.060	0.020	SA^2 ■ 0
10	84.91	0.10	0.27	9.49	0.022	SB^2 ■ 0	0.039
11	84.67	0.10	-0.02	-0.74	0.057	0.061	SA^2 ■ 0
11a	84.48	0.10	-0.25	-9.02	0.040	0.064	SA^2 ■ 0

Two of the 351 original data points were statistical outliers, and were excluded from further statistical analysis. This evaluation included a series of outlier tests, the application of the Snedcar F-test, to estimate the statistical significance of the dissolution and sample errors, the Bartlett's chi-square test to evaluate the consistency of the measurement and dissolution errors, as well as the Student-T test to determine the significance of the difference between each individual mean and the reference value. The tests showed that dissolution and sample treatment were the major source of errors. The results from seven of the participants indicated excess difference due to dissolution, significant at the 95% level calculated using two degrees of freedom; one of these was classified as significant at the 99% level.

Each laboratory received a set of the results of all the participants, as shown in Table 1, and an individual evaluation of its own performance, with related comments.

NBL SAFEGUARDS MEASUREMENT EVALUATION PROGRAM

Using funding supplied by the Cooperative Safeguards Agreement between DOE and ABACC, the Network Laboratories also analyzed materials from the NBL Safeguards Measurement Evaluation (SME) Program in 1998. The materials selected for analysis were ampulated uranyl nitrate solutions, the most direct test of analytical uncertainty, as no preparation is required (except aliquanting). The solutions were prepared from NBL Certified Reference Material 112-A, Uranium Metal Assay Standard. The uranium concentration reference values were calculated from titrations of the ampulated solutions. To further verify the reference values determined by titration, these reference values were compared to the prepared values, which were calculated from the certified value of the reference material, and the metal and dilution weights. These calculated concentrations were not significantly different from the reference values determined by titration.

Each laboratory was supplied with two ampules, differing slightly from each other in uranium concentration. There was only one analytical period, with a simpler design than that used in the ABACC Round Robin. The participants were asked to take four aliquants from each ampule, and analyze two from each ampule on each of two days, producing eight results. This scheme allowed for the estimation of overall precision and bias, and short-term variability.

REPORTED RESULTS, PRECISION AND ACCURACY NBL received 95 datapoints from eleven participating laboratories. The individual determined values are displayed in Figure 3; the horizontal line represents the reference values. The results are grouped in clusters, with each cluster representing a set of individual results produced by a specific laboratory on a specific day. It should be noted that there is no relationship between the ABACC Round Robin laboratory codes and the SME Program codes.

Figure 3
NBL SME Program
All Data

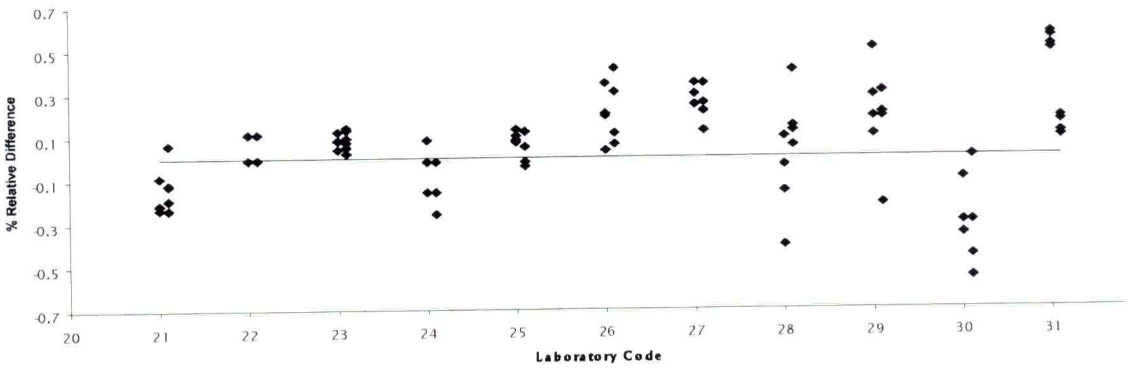
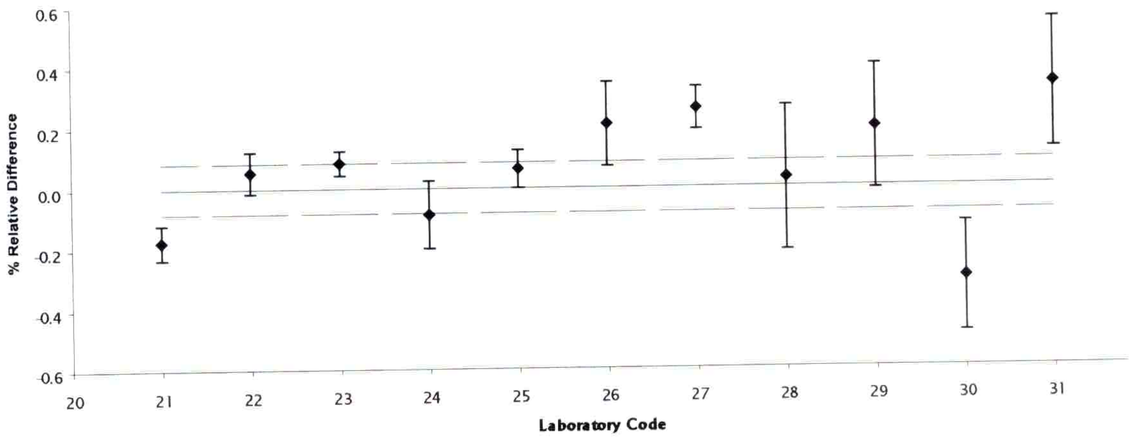


Figure 4 displays the individual laboratory mean percent relative differences and standard deviations plotted versus the NBL reference value bracketed by 3 **?** limits.
The ABACC grand mean percent relative difference is +0.057 ± 0.126 %RD. This result indicates that there is no statistically significant difference between the NBL reference values and the ABACC grand mean.

Figure 4
NBL SME Program
Individual Mean % Differences and Standard Deviations



VARIANCE ANALYSIS OF THE INDIVIDUAL RESULTS NBL performed a series of outlier tests as well as a standard *One-Way Variance Analysis* on each individual set of data and the pooled results. There was one laboratory-declared outlier, which was excluded from further statistical analysis. The outlier tests did not find any additional outlying points; however, suspect data were rejected for one possibly defective ampule, analyzed by one laboratory. The results are shown in the following table.

Table 2: Summary of One-Way Variance Analysis for Individual Laboratories
SME Program

Laboratory	%RD	95% C.I.	n	Statistical Significance of %RD
21	-0.18	0.05	8	-8.61
22	0.05	0.11	4	1.53
23	0.08	0.03	10	6.69
24	-0.09	0.09	8	-2.23
25	0.06	0.05	8	2.82
26	0.21	0.11	8	4.27
27	0.26	0.04	16	14.70
28	0.03	0.20	8	0.30
29	0.19	0.17	8	2.65
30	-0.30	0.15	8	-4.77
31	0.33	0.96	8	4.37

The results showed one laboratory (31) had significant short-term variation. The bias was significant at the 99.9% level for three laboratories, and at the 99% level for two additional laboratories, as calculated from the 95% C.L.s, using n-1 degrees of freedom for all laboratories except for the one with significant short-term variation.

ABACC participants received individual results for each data set submitted to NBL. Additionally, NBL recently published and distributed the SME Program annual report, including graphs of comparative results.

CONCLUSION

Eleven of fourteen invited laboratories participated in both the 2nd Round Robin Laboratory Intercomparison Program, and in the NBL SME Program.

For the ABACC Round Robin, eight dataset means fell within the currently adopted target limits[3] of ± 0.1% U, while the remaining five dataset means were within ± 0.27 %U. This is an improvement from the previous Round Robin. As in the previous Round Robin, the variance analysis of the single participants' results showed that the treatment and dissolution were the major source of errors, followed by the calibration and measurement bias. These results should aid the participants by providing useful feedback and suggesting appropriate corrective actions.

For the NBL SME Program, even though the overall grand mean for %RD showed no statistically significant bias, many individual laboratories did show a statistically significant bias. Five of the laboratory means fell within the currently adopted target limits of ± 0.1% U, while the remaining six laboratory means were within ± 0.33 %U.

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[1] Gevaldo L. de Almeida *et. al.*, "ABACC'S Laboratory Intercomparison Program," Proceedings of the VI Congresso Geral de Energia Nuclear, Rio de Janeiro, Brazil, Oct. 1996.

[2] H. Aigner, H. Huhn, and S. Deron, "Results of the Analyses of the Intercomparison Samples of Natural Dioxide SR-1," IAEA/RL/69, August 1980.

[3] Deron *et al.*, "1993 International Target Values for Uncertainty Components in Fissile Isotope and Element Accountancy for the Effective Safeguarding of Nuclear Materials," IAEA STR-294, October 1993.