ABACC'S LABORATORY INTERCOMPARISON PROGRAM

Gevaldo L. de Almeida*, Adolfo Esteban**, Osvaldo Cristallini***, Sílvio G. de Almeida****, Roberto Servant*****, Radier M. de Araújo****, Bertha F. Araujo******, Zildete Rocha*******

* Agencia Brasileiro-Argentina de Contabilidade e Controle de Materiais Nucleares - ABACC
Av. Rio Branco, 123 - 5° andar 20040-005 Rio de Janeiro - RJ Brasil

** Comissión Nacional de Energia Atómica - Centro Atómico de Constituyientes
Av. del Libertador, 8250 (1429) Buenos Aires - Argentina

*** Representación de ABACC en Buenos Aires
Av. del Libertador, 8250 (1429) Buenos Aires - Argentina

**** Comissão Nacional de Energia Nuclear CNEN - Serviço de Salvaguardas
Rua General Severiano 90, 22.290-040 Rio de Janeiro - RJ Brasil

***** Comissión Nacional de Energia Atómica - Laboratório de Sede Central
Av. del Libertador, 8250 (1429) Buenos Aires - Argentina

****** Comissão Nacional de Energia Nuclear - Instituto de Pesquisas Energeticas e Nucleares
Travessa R, 400 Cidade Universitária 05508-900 São Paulo - SP Brasil

******* Comissão Nacional de Energia Nuclear - Centro de Desenvolvimento da Tecnologia Nuclear
Rua Prof. Mário Werneck, s/n Cidade Universitária 30161-970 Belo Horizonte - MG Brasil

ABSTRACT

A Laboratory Intercomparison Program involving Brazilian and Argentine laboratories, with the special participation of New Brunswick Laboratory - DOE and IAEA Seibersdorf Safeguards Laboratory, was implanted by ABACC having as main purpose to qualify a network to provide analytical services to this Agency on its role as administrator of the Common System of Accountability and Control of Nuclear Materials. For the 1st. round robin of this Program, 15 laboratories were invited to perform elemental analysis on UO_2 samples, by using any desired method. Thirteen confirmed the participation and 10 reported the results. After an evaluation of the results by using a *Two-Way Variance Analysis* applied to a nested error model, it was found that 5 of them deviate less than 0.1% from the reference value established for the UO_2 uranium contents, being thus situated within the limits adopted for the *target values*, while the remaining ones reach a maximal deviation of 0.44%. The outcome of this evaluation, was sent to the laboratories, providing them with a feedback to improve their performance by applying corrective actions to the detected sources of errors or bias related to the 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, the SCCC, whenever necessary during a safeguards inspection, has to analyze samples of nuclear materials. These analysis are preferentially done by Non-Destructive Assay (NDA) techniques, for they are quicker, cheaper and less intrusive than the Destructive Assay methods.

In many cases although, it's not feasible to use NDA techniques, for the aimed variable cannot be assayed in this way, or the accuracy and precision do not reach the levels required by the accountability. In such cases samples have to be taken and submitted to destructive analysis.

Besides its unique regional features, ABACC do not own any permanent inspector nor analytical network, and for that, uses the existing manpower, facilities and laboratories in both Countries.

Such an approach requires - by credibility reasons - that the inspections activities have to be performed by an unsuspicious party, and hence by inspectors from the *other* Country. This applies also to the Analytical Network used by ABACC, composed by two groups of laboratories in Brazil and Argentina, to which the samples are sent.

Considering that there were no enough basis or justification to select a given laboratory in Brazil and another one in Argentina as Reference Laboratory, ABACC decided rather to use a Laboratory Network, which should be as large as possible. In doing so, it became necessary to apply adequate criteria to evaluate the performance of the laboratories of that network, and for that a Laboratory Intercomparison Program was conceived.

Despite the fact that for ABACC the Intercomparison Program is not a goal in itself, but a mean to obtain a reliable laboratory network to analyze the samples coming from the safeguards inspections, and thus to accomplish its task as administrator of the SCCC, the purpose of this Program is not to exclude the laboratories which eventually present abnormal or *outlier* results, but rather to detect such kind of problems and inform the laboratory, in order that it can promote corrective actions and improve procedures and analytical methods.

Moreover the participants would have the possibility to verify and improve its own performance by detecting those sources of errors statistically significant and estimating its magnitude.

STRUCTURE OF THE LABORATORY INTERCOMPARISON PROGRAM

The Laboratory Intercomparison Program was conceived as a permanent activity with the purpose of verifying the performance of the analytical network used by ABACC, and whenever necessary to notice any participant, about eventual errors and bias, providing them with a feedback for the improvement of methods, techniques and procedures.

After this philosophy, an Intercomparison Group coordinated by ABACC and composed by Brazilian an Argentine researchers was created, having as main tasks to establish a feasible structure for that program, and to propose an adequate approach for its implantation and follow-up, taking into account the existing analytical infrastructure in both Countries.

Within this frame, the Program was divided in two sub-programs: one related to the elemental analysis, and the other one to the isotopic analysis of uranium. It was decided that this last sub-program should be postponed, mainly due to the scarce number of laboratories in Brazil and Argentina which could do isotopic assay, while the first one should be splitted into several periodic round robins.

This Program, was supported by the technical advices and assistance from the New Brunswick Laboratory, as well as by funds, both provided within the Safeguards Agreement between United States Department of Energy (DOE) and ABACC. Besides that, the Program also reckon upon the advices from the IAEA Safeguards Analytical Laboratory at Seibersdorf.

For the 1st. round robin, formal invitation were then sent by ABACC to 15 laboratories in Argentina and Brazil. Thirteen, of them accepted to participate in the Program, but only 10 reported the results. Other internationally recognized laboratories were also contacted in Europe and United States and called to collaborate. These laboratories are presented in the following.

Argentina
* Laboratório de Química Analítica - Sede Central/CNEA
* Laboratorio de Control Químico e Físico - CAC/CNEA
* Depto Ingenieria de Plantas Químicas - CAE/CNEA
* Complejo Fabril de Cordoba - Ciclo Combustible CNEA
* Laboratorio de Química Analítica - CAB/INVAP
Brazil
* Supervisão de Química e Mineralogia CDTN/CNEN
* Laboratorio de Salvaguardas - CNEN
* Laboratorio de Química Quente - IPEN/CNEN
* Lab. de Caracterização Física e Química - IPEN/CNEN
* CentroTecnologico da Marinha em São Paulo - CTMSP
USA
* New Brunswick Laboratory - DOE
Austria
* IAEA Safeguards Analytical Laboratory at Seibersdorf

The chosen material for the 1st. round robin was natural UO2, taking into account that this is a very usual stratum at the nuclear facilities under the ABACC surveillance. Besides that, due to inherent instability of this compound, it would be possible to study the effect of the transit time between sampling and analysis, on the uranium contents, a very important parameter, as it could lead to differences between the operator's declared value and the analysis results.

In order to assure that all laboratories calibrate the instruments on the same basis, it was decided that a reference material should be distributed together with the UO2 samples, eliminating hence any bias arising from the using of different standards.

As reference material, an homogeneous nuclear pure U3O8 was chosen, because it was available, and the laboratories were told to consider it as stechiometrically pure, and to calibrate the instruments under this assumption. Samples of this material were then sent to the internationally recognized laboratories New Brunswick and Seibersdorf where it would be adequately characterized to be used as a secondary standard.

Besides the uranium contents, the laboratories were requested on an optional basis to perform the O/U ratio determination on the UO2 samples.

No suggestion or request to apply any specific technique was made, and hence the laboratories were free to choose any technique, provided that it was used on a routine basis.

Sample and Reference Material Preparation. The material utilized in the 1st. round robin was constituted by 1.5 kg of natural uranium dioxide in the powder form, which was homogenized during 2 hours in a ball mill. Prior to the distribution, this material was analyzed by Instituto de Pesquisas Energeticas e Nucleares - IPEN/CNEN, and the results presented on the Table 1.

In order to assure that the samples were prepared under identical conditions, the fractionation and packaging was performed inside a glove box filled with a dry nitrogen atmosphere.

TABLE 1. Characteristics of the Uranium Dioxide.

PARAMETER	RESULTS	IMPURITIES µg/g
Specific Area *	5.5 ± 0.2	Cd < 0,1
C	0.2135% **	P < 100
S	0.0057% **	Cr = 30
O/U	2.067	Mo < 2
U	87.4 in weight %	Si = 40
H2O	0.60% in weight %	Mn = 5
Average diameter	7.2 µm	Pb < 2
Density	10.2 g/cm^3	Bi < 2
Bulk density	1.9 ± 0.1 g/cm^3	Cu = 15
		Co < 10
		B = 0,3
		Fe = 150
		Ni = 10
		Zn < 10
		Al = 35
		Mg = 20
		Sn = 1,5
		V < 3
		Ba < 1

* BET (m^2/g) ** Relative to the total compound mass.

The U3O8 utilized as reference material, was produced by calcinating an ammonium diuranate (ADU) precipitate, obtained from an homogenized uranium solution taken from a purification process which used solvent extraction (TBP/Kerosene).

As containers for the samples and reference material, penicillin type glass vials provided with a rubber stopper and a metallic seal were utilized, in order to minimize the oxidation and humidity absorption.

Analytical Scheme and Procedures. Every participant was requested to perform a set of analysis of the uranium contents of the sample at three different times: just after receiving of the samples, 30 and 60 days after, according to the analytical scheme presented on Fig.1. For that each laboratory received:

- Three sealed penicillin type flasks labeled as A1, A2 and A3 containing each of them about 15g UO2 sample.
- One sealed penicillin type flask labeled as B1 containing about 15g of U3O8, as reference material.
- Three sealed empty penicillin type flasks labeled as R1, R2 and R3 as weight control recipients.
- One letter of instructions with the analytical scheme.
- A formulary for the emission of the results.
- A formulary for the transfer of nuclear material with the the uranium mass, for nuclear accountability purposes.

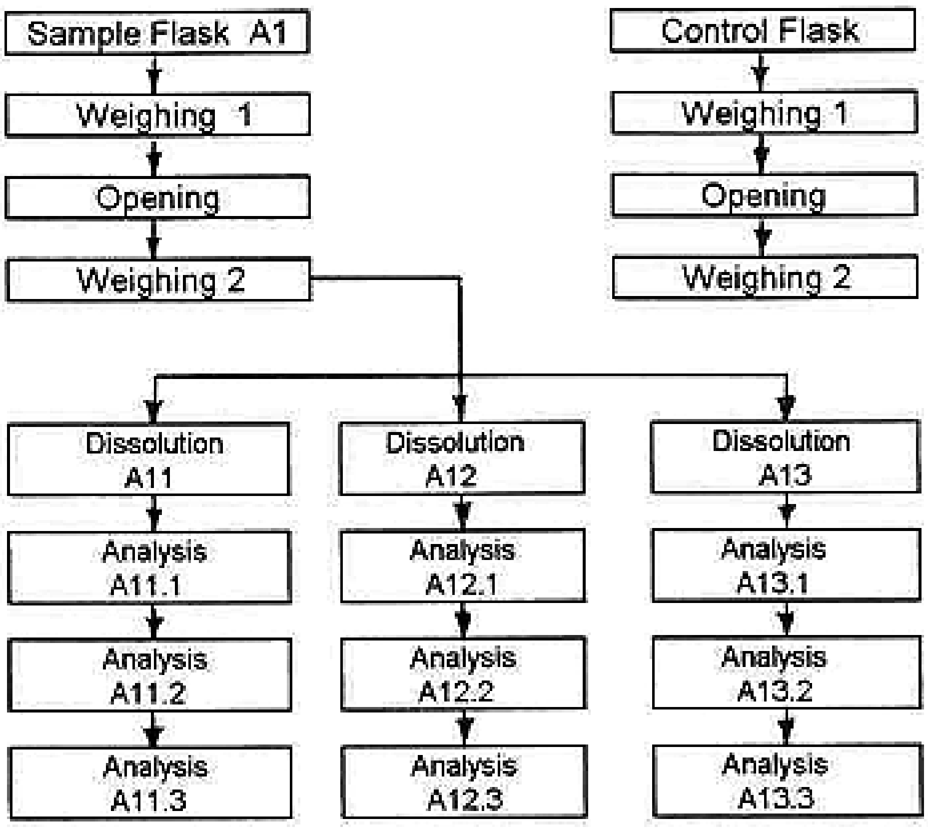

Figure 1. Analytical Scheme stipulated to the laboratories.

A code was assigned to each laboratory, and the received formularies containing results and comments were translated to the same language by ABACC, assuring hence that nor the laboratory or its Country could be identified during the statistical analysis performed by the Intercomparison Group.

The gross weight of the sample and control flasks should be determined immediately before the analysis, as they were received and again after their opening, making thus possible to detect any material loss from the stopper, in the opening process, while the net weight would make possible to evaluate the stability of the UO2 samples and to perform the necessary corrections for the different elapsed times between sampling and analysis.

Prior to the use of the U3O8 as reference material for the calibration of the analytical instruments, it should be calcinated for 2 hours at 800 °C in the air, a procedure requested as well to the laboratories undertaken to analyze this material in order to furnish a reference value for it.

Uranium Contents of the Reference Material. The uranium contents of the U3O8 used as reference material was established after the determination performed by the New Brunswick Laboratory - US Department of Energy, and by the IAEA Safeguards Analytical Laboratory at Seibersdorf, Austria. By averaging the mean obtained by these laboratories one get the following uranium contents:

[U] =84.693± 0.023 %U

Such a mean represents a purity of 99.873 ± 0.027% by using the atomic weight of 238.0289 as determined by Seibersdorf. This figure was sent to all the participants, in order to correct the results of the analysis of UO2 based on the formerly assumed stechiometric purity of the U3O8.

REPORTED RESULTS

Ten out of 13 laboratories reported the results. Nine laboratories applied the Davies & Gray method, and the remaining one used redox titration with previous reduction with stannous chloride. One laboratory applied additionally controlled potential coulometry, but for evaluation purposes, was considered as 2 individual ones.

An overview of the raw analytical obtained values, after a correction for the purity of the U3O8, performed by themselves using the *Uranium Contents of the Reference Material* supplied by ABACC is shown on the Fig. 2.

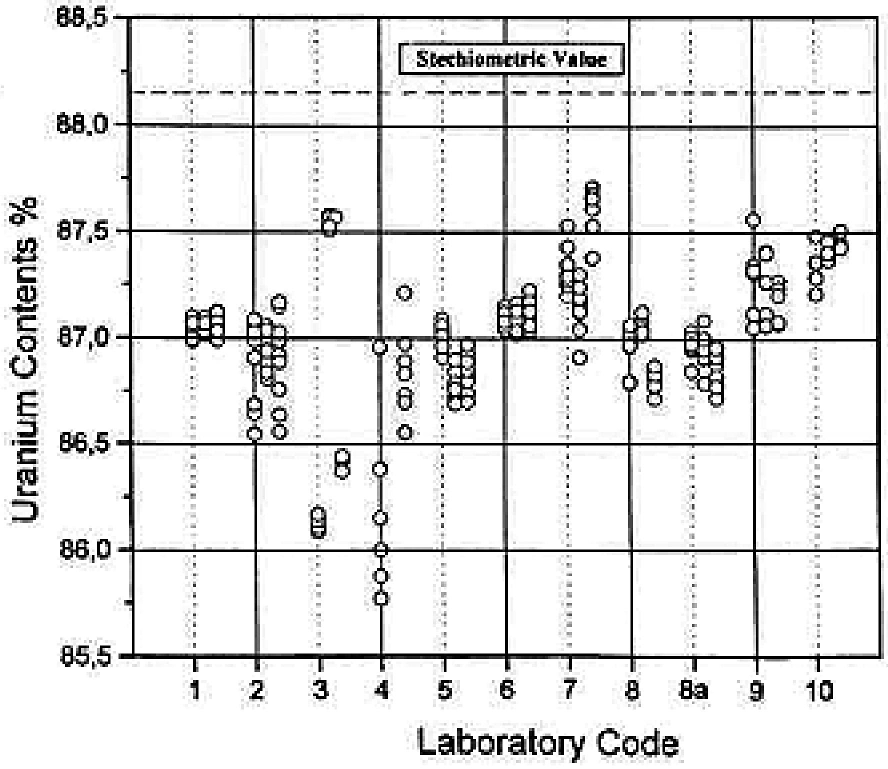

Figure 2. Raw analytical results.

On the Fig.2, the results from each laboratory are grouped in clusters. Every cluster represents thus the set of single results reported by a specific laboratory. Within a given cluster, every group of points belonging to each of the 3 vertical lines corresponds to the analysis performed at the stipulated times - immediately, 30 and 60 days after receiving the sample.

DATA TREATMENT

To evaluate the performance of the laboratories, two basic criteria were used: the *precision* and the *accuracy* of the results.

While the analysis of the intrinsic data dispersion for the same laboratory furnishes a figure associated with the overall precision of the measurements, the accuracy can only be obtained by comparison with a *reference value*.

The actual uranium contents of the distributed UO2 samples was unknown, and hence, to evaluate the above mentioned accuracy, a *reference value* had to be established, after a weight correction as described on the next section. The *reference value* for the UO2 samples was obtained in two steps. First, a *grand mean* was obtained by averaging the mean of all the 11 laboratories.

This *grand mean* GM, for all the 11 participants and its 95% confidence limits is presented in the following:

GM = 87.021 ± 0.177 %U

The deviation of the mean obtained by each laboratory from the grand mean are shown on Fig. 3.

The second step was the determination of a depurated mean, as *reference value* computed after the results from some selected laboratories, using two criteria.

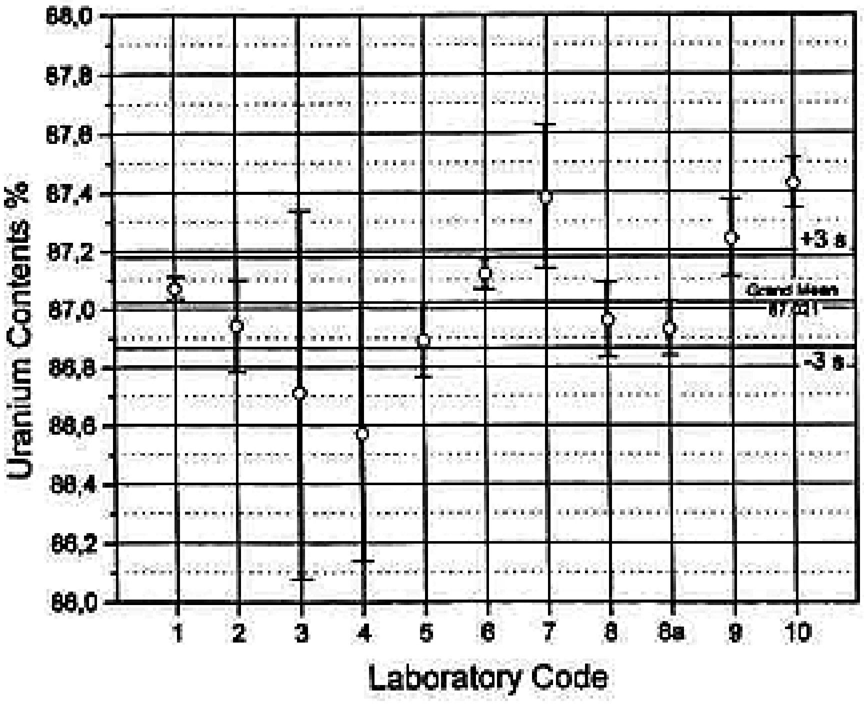

Figure 3. Individual and *grand mean*.

As the 1st. selection criterion, those laboratories which mean deviates from the grand mean by more than ±3s were considered as *outliers*, and excluded from the computing of the depurated mean. The value of s is computed by performing a variance pooling engulfing the variances of the individual means of all laboratories [2].

The 2nd. utilized criterion was the precision achieved by the laboratories, which excluded the laboratories 3, 4 and 7. Indeed, although one cannot state that there are statistically significant differences between their results and the *grand mean*, i.e., they couldn't be excluded after the 1st. criterion, those results were discarded due to the high related standard deviation.

After the application of these criteria, 5 laboratories were excluded, and the results from the 6 remaining ones, again submitted to the same criterion using the depurated mean, and all the six passed.

The *reference value* RV, and its 95% confidence limit for the UO2 has the following value:

$$RV = 86.985 \pm 0.094 \ \%U$$

Weight Change Correction. The laboratories reported the results of the single analysis as weight percent of uranium. Since these values can be affected by weight changes caused by humidity absorption and oxidation, it becomes necessary to correct the effect of the elapsed time - since the sampling and packaging until the opening of the flasks - on the weight. This was determined by taking the net weight change of the samples, as reported by the laboratories.

As shown on Fig. 4 there is a slight but clear weight increase against the time. Such an effect, although taken into account to correct the analysis results, is nevertheless statistically irrelevant when compared with the dispersion obtained among the laboratories.

Actually this effect could be detected only due to the unexpected delay to export the samples and logistic problems specific of each laboratory, since one can observe that within 60 days, as previously planned, the intrinsic dispersion would make very difficult to infer any trend.

The net weight change although tangible, is very small, ranging between + 0.013 and + 0.052%. Nevertheless, the results presented by the laboratories were corrected by using the Uranium Correction Factor **ft** calculated after the following expressions:

$$\%Uc = \%Um \cdot ft \qquad (1)$$

$$ft = 1 + \Delta p \qquad (2)$$

$$\Delta p = (A - B - Ra + Rb) \ / \ (B - T) \qquad (3)$$

where:

%Uc = corrected %U

%Um = measured %U

A = Gross weight of the sample flask at the opening moment prior to the analysis.

B = Gross weight of the sample flask at the sampling moment.

T = Tare of the sample flask at the sampling moment.

Ra = Weight of the open control flask prior to the analysis.

Rb = Weight of the open control flask at the sampling moment.

The values presented on the evaluation tables and graphs of the variance analysis on next section are the corrected ones. The ft values are situated in the range 1.000128 - 1.000525.

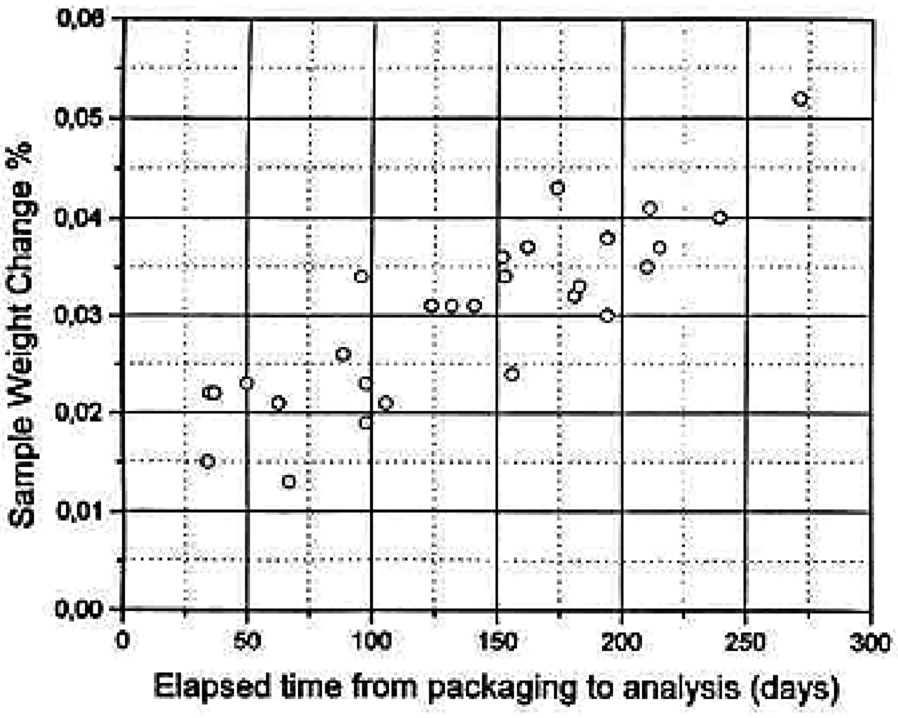

Figure 4. Effect of the elapsed time between sampling and analysis on the sample weight.

Variance Analysis of the Individual Results. The individual results arising from the adopted analytical scheme are subjected to 4 types of errors:

- Measurement errors - SI
- Treatment and dissolution errors - SB
- Errors caused by fluctuation between samples - SA
- Calibration and other systematic errors

All the measurements performed on the same dissolution constitutes a *group* with an average group variance SI^2, while a collection of all measurements done on the same sample constitutes a *class*, with an average group variance SA^2. Hence, there are 3 classes and 9 groups for each laboratory.

The parameter SB is the error between groups, which is related exclusively to the dissolutions, i.e., after excluding the measurement errors.

The results of each laboratory, after the correction for weight changes were evaluated utilizing the *Two-Way Variance Analysis* [1], applied to a nested error model, and the outcome is resumed on Table 2.

Each laboratory received a set of results of all participants, as shown on Table 2, and an individual evaluation of its own performance, with the related comments.

This evaluation included the application of the Snedcar F-test, to judge the stastitical significance of the dissolution and sample errors, the Bartlett's Chi-Square-test to judge the consistency of the measurement and dissolution errors, as well as the t-Student to determine the significance of the deviation between each individual mean and the reference value.

The outcome of those tests had shown that treatment and dissolution were the major source of errors. Indeed, the results from 5 laboratories indicated differences between groups, although only 2 of them could be classified as highly significant.

The errors caused by fluctuation between classes (samples) appears in second place, but they should rather be attributed to measurement and calibration bias, since the distributed samples were homogeneous, and their uranium contents had been properly corrected for the time effect.

TABLE 2. Summary of the *Two-Way Variance Analysis* for Individual Laboratories.

Laboratory Number	Individual Mean (%U)	95% Confidence Limit	Difference to Ref. Value %U	Statistical significance of difference	Measurement Error **SI**	Treatment Error **SB**	SB²=Average Group Variance **SA**
1	87.07	0.04	+ 0.08	2.19	0.041	$SB^2 < 0$	0.008
2	86.94	0.16	- 0.05	0.94	0.151	0.067	$SA^2 < 0$
3	86.71	1.86	- 0.28	0.64	0.031	$SB^2 < 0$	0.750
4	86.57	3.55	- 0.42	1.48	0.314	0.141	0.372
5	86.89	0.30	- 0.09	1.21	0.074	$SB^2 < 0$	0.117
6	87.12	0.06	+ 0.14	3.52	0.047	0.026	0.007
7	87.38	0.65	+ 0.40	2.57	0.066	0.110	0.252
8	86.96	0.31	- 0.02	0.30	0.069	$SB^2 < 0$	0.121
8a	86.93	0.16	- 0.05	1.03	0.060	0.057	0.050
9	87.24	0.21	+ 0.25	4.17	0.055	0.141	$SA^2 < 0$
10	87.43	≈ 0.11	+ 0.44	9.84	-	-	-

CONCLUSION

Ten out of 13 laboratories which accepted the ABACC invitation to participate in the Laboratory Intercomparison Program, reported the results.

When all these results were compared with a *reference value* for UO_2 - obtained by averaging the individual mean of all the laboratories, excluding those which deviate more than 3s from the grand mean - it was observed that 5 of them deviate less than ± 0.1% U from it, being thus situated within the limits adopted for the *target values* [3], while the remaining ones lie between this value and ± 0.44%.

The variance analysis of the single laboratories had shown that treatment and dissolution were the major source of errors, followed by calibration and measurement bias. It's expected that this information will propitiate an useful feedback for the application of corrective actions by each laboratory to improve its analytical procedures.

Despite the large time intervals - exceeding 250 days - from sampling to analysis, it was verified that its effect on the sample weight, was below 0.05%, showing the adequacy of the utilized sample vials.

Despite the effort of some laboratories which informed the results of the O/U ratio assigned as optional, the general evaluation of the results couldn't be performed due to the scarce amount of results received.

The experience acquired during this 1st. round robin of the Laboratory Intercomparison Program, and the related data evaluation was very profitable and useful to improve the future steps of this program, which will be soon continued with the 2nd. round robin.

For that, it's the ABACC intention to increase as much as possible the number of participants, for this will enlarge its analytical network, providing concomitantly a higher statistically representative basis to evaluate the individual results.

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REFERENCES

[1] Aigner, H., Hhun,A., Deron,S., **Results of the Analyses of the Intercomparison Samples of Natural Dioxide SR-1**, IAEA/RL/69, August 1980.

[2] Mandel J., **Statistical Analysis of Experimental Data** John Willey, 1994.

[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.