Development of Low-Level Environmental Sampling Capabilities for Uranium at Brazilian and Argentine Laboratories by ABACC

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ABSTRACT

The Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC) with assistance from the U.S. Department of Energy (DOE) began a program to evaluate environmental sampling capabilities at laboratories in Argentina and Brazil in June 1998. The program included staff training conducted in South America and the United States. Several laboratory evaluation exercises were also conducted using standard swipe samples prepared by the International Atomic Energy Agency (IAEA) and a National Institute of Standards & Technology Standard Reference Material 1547, Peach Leaves. The results of these exercises demonstrated that several laboratories were capable of accurately determining the total uranium and uranium isotopic distribution in the peach leaves. To build on these successes, another exercise using standard swipe samples prepared by the IAEA was conducted. A total of 8 sets of 15 swipe samples were prepared and distributed to the six ABACC support laboratories and to two of DOE's Network of Analytical Laboratories (NWAL) that support IAEA's environmental sampling program. Throughout this project, the ABACC laboratories have shown steady progress in contamination control and improvements to the accuracy and precision of their measurements. The results of the latest exercises demonstrate that ABACC now has support laboratories in both Argentina and Brazil that have the capability to measure both the amount and isotopic composition of uranium at levels expected in typical environmental samples (i.e., sub-microgram quantities). This presentation will discuss the final results for the exercise with uranium swipe samples and discuss future activities to develop measurement capabilities for total and isotopic plutonium in environmental samples.

INTRODUCTION

ABACC is using Brazilian and Argentine laboratories to analyze its environmental swipe samples, and is putting a strong effort into preparing its technical staff and inspectors for the implementation of environmental sampling under IAEA's Additional Protocol. To achieve this goal, ABACC and DOE initiated a project under the Safeguards Cooperation Agreement in 1994 (Action Sheet 6: Environmental Sampling). The objective of the project was to assess the capabilities of the analytical laboratories in Argentina and Brazil for analyzing environmental samples collected by ABACC during inspections and to suggest improvements in their sample preparation and measurement procedures.

Because these environmental samples typically contain only trace quantities of nuclear materials, specialized laboratory instrumentation and stringent requirements for sample preparation and contamination control are necessary to obtain reliable results. Initially, technical meetings and workshops were conducted to discuss the requirements for sample collection, analytical methods, and data evaluation. The technical exchanges included experts from ABACC, DOE International Safeguards Division, Oak Ridge National Security Program Office, Oak Ridge National Laboratory (ORNL), and Pacific Northwest National Laboratory (PNNL). Following these technical exchanges, laboratory activities were initiated with Exercise 1, analyses of IAEA-prepared standard swipe samples. Results from this exercise were reported at the Institute of Nuclear Materials Management (INMM) 41st Annual Meeting.[1] Evaluation of data from that exercise showed that the ABACC laboratories made progress in developing the capability to determine both the quantity and isotopic composition of uranium at levels expected in typical environmental samples. However, in most cases, it was evident that uranium contamination was seriously affecting their results. The results highlighted the importance of contamination control in environmental analyses, where the uranium concentration in the sample is often many times less than that found in the ambient environment (i.e., the sample preparation and analysis laboratories).

The next stage in evaluating ABACC environmental sample analysis capabilities involved implementation of stringent contamination-control practices, followed by a quantitative assessment of the uranium blank at each stage of the sample preparation and analysis process. Isotope dilution mass spectrometry (IDMS), using a ^{233}U spike from the New Brunswick Laboratory, was used to measure uranium content. In addition to quantitative blank determinations, ABACC initiated Exercise 2, measuring total and isotopic uranium on National Institute of Standards & Technology (NIST) Standard Reference Material (SRM) 1547, Peach Leaves, which contained an uncertified, but well documented uranium concentration of 0.015 μg/g. This SRM effectively simulates an actual environmental sample and provides a challenging test of low-level analysis capabilities. The results of Exercise 2 demonstrated that several laboratories were capable of accurately determining the total uranium and uranium isotopic distribution in the peach leaves.[2] Based on the demonstrated ability of several ABACC support laboratories to control contamination and measure low-levels of uranium, Exercise 3 was conducted with 15 IAEA-prepared standard swipe samples. Final results from this Exercise 3 are presented in this paper.

DESCRIPTION OF THE EXERCISE

Exercise 3 was designed to test the ability of participating laboratories to precisely and accurately measure uranium quantity and isotopic abundances at levels commensurate with environmental samples. Each laboratory received 5 sets of swipes prepared in triplicate (15 swipes total) with uranium spikes and total quantities given in Table 1. One of the sets (3 swipes) was blank swipe material. One of the three blank swipes was identified for the participating laboratories. As can be seen in Table 1, two sets of swipes were prepared with small differences in uranium isotopes (approximately 3% ^{235}U) and two sets were spiked with different quantities of a uranium standard at approximately 20% ^{235}U.

Table 1. Uranium Composition for Swipe Samples

Sample	ASSAY ng U/swipe	U-234 (atom %)	U-235 (atom %)	U-236 (atom %)	U-238 (atom %)
LEU makeup	176.85±0.35	0.0276	3.0169	0.0006	96.9549
NBL U030a	175.59±0.34	0.02778	3.0404	0.0006	96.9312
NBL U200 (1)	119.48±0.24	0.1247	20.0129	0.2115	79.6509
NBL U200 (2)	85.99±0.11	0.1247	20.0129	0.2115	79.6509
Swipe blank	0.535±0.03				

The exercise participants were:

ABACC Laboratories

- *Instituto de Radioproteção e Dosimetria* of the National Nuclear Energy Commission of Brazil in Rio de Janeiro, Brazil (IRD-CNEN)
- *Laboratorio de Mediciones Ambientales* of the Argentinean Nuclear Regulatory Authority (ARN) in Buenos Aires, Argentina
- *Laboratorio de Analises Quimicas* of the Dioxitek, Planta Córdoba, Córdoba, Argentina
- *Laboratório de Caracterização de* UF_6 of the São Paulo Navy Technological Center in Sao Paulo, SP, Brazil (CTM-SP)
- *Laboratório de Caracterização Quimica* of the Instituto de Pesquisas Energéticas e Nucleares (IPEN) in São Paulo, SP, Brazil (IPEN-CNEN/SP-1)
- *Departamento de Radioproteção Ambiental* of the IPEN in São Paulo, SP, Brazil (IPEN-CNEN/SP-2).

US Department of Energy Laboratories

- Oak Ridge National Laboratory
- Pacific Northwest National Laboratory

Several South American laboratories did not have the mass spectrometer system required to complete the analyze on these samples. Therefore, several laboratories teamed with other laboratories that had the required analytical instrumentation. For example, ARN in Buenos Aries digested a set of samples and sent them to Dioxitek for analysis by inductively coupled plasma-mass spectrometry (ICP-MS).

Because most of the laboratories supporting ABACC employ ICP-MS , it was decided that PNNL would also use ICP-MS, while ORNL would employ the method traditionally used for analysis of environmental samples: thermal ionization mass spectrometry (TIMS). Each laboratory was instructed to report the following data:

- Total uranium (ng U/swipe) + uncertainty*
- Atom % ^{234}U + uncertainty*
- Atom % ^{235}U + uncertainty*
- Atom % ^{236}U + uncertainty*
- Atom % ^{238}U + uncertainty*

*Uncertainty: Report total uncertainty (random + systematic) at 95% confidence level

RESULTS AND DISCUSSION

Last year the results from three of the six ABACC laboratories and two DOE laboratories were reported and discussed at the 43rd INMM meeting[3]. During recent months, results from the remaining three ABACC laboratories have been completed and are summarized in Table 2 along with the data from the other laboratories that participated in this exercise. Generally, the uranium isotopic results compare favorably with the certificate or expected values provided by the IAEA Safeguards Analytical Laboratory. All ABACC laboratory results were performed in clean, controlled facilities employing ICP-MS. For comparison purposes, the DOE laboratories used both ICP-MS (PNNL) and TIMS (ORNL). As can be seen in the comparison, the ICP-MS and TIMS isotopic results are in very close agreement for ^{235}U and ^{238}U. In fact, the results for the minor uranium isotopes, ^{234}U and ^{236}U, from three of the ABACC laboratories (IRD, Dioxitex and CNEN/SP-2) compare extremely well with the expected results. The other three ABACC laboratories experienced problems with background or lack of sensitivity for the minor isotopes in the low concentration samples. For samples with larger amounts of uranium, this problem became less discernable. One of the ABACC laboratories experienced a contamination problem indicated by a blank concentration approximately twenty times higher than the other five ABACC laboratories.

Four of the six ABACC laboratories and both DOE laboratories reported low isotopic ^{235}U results for the low enriched uranium makeup samples. It should be pointed out that this standard was prepared by mixing a certified reference material with natural uranium; the isotopic values were calculated from the mixing ratio. The other isotopic results in Table 2 are in close agreement with the expected or certified values for all the participating laboratories.

The results from the swipes prepared with New Brunswick Laboratory CRM U030a and CRM U200 for all ABACC laboratories are summarized in Table 3. There were 12 data sets from the six ABACC laboratories for CRM U200 and six data sets for CRM U030a. The ^{235}U isotopic comparisons with the certified values are 20.1460 versus a certified value of 20.0129 atom percent, and 3.0343 versus a certified value of 3.0404 atom percent for the two NBL CRM U200 and U030a, respectively. These data compare favorably with the certified values, especially considering the relatively small sample size and the fact that the data were obtained by ICP-MS.

The *Instituto de Radioproteção e Dosimetria (IRD)* performed extremely well for both isotopic measurements and uranium assay. The IRD uranium assay measurements were within 0.3% of the expected values. The DOE laboratory employing TIMS (ORNL) also demonstrated very good quantitative recovery on all samples. The other laboratories demonstrated erratic uranium recovery to varying degrees; however, the recovery did not affect the quality of the isotopic measurements as can be seen by comparing the laboratory data with the expected values in Table 2. Poor recovery is often caused by lack of chemical equilibrium for the spike isotope. Data from one sample from the PNNL laboratory performing ICP-MS showed evidence of contamination, and was not included in the averages in Table 2. PNNL also had a systematic bias associated with the total uranium content of the swipe samples. Their values were 71.8% of the certified value. This discrepancy was traced to the ^{233}U spike that was found to be 139.3% high. Blanks for all but one of the participating laboratories were less than 1-ng/swipe. This is very encouraging because it demonstrates that all of the laboratories participating in this exercise have developed effective contamination control programs, which is an absolute requirement for making precise and accurate low-level uranium measurements on environmental samples.

Table 2. Comparison of uranium results .

LEU Makeup

U Isotopic (At. %)	Calculated Value	IAEA (SAL)	IRD	ARN/ DIOXITEK	DIOXITEK	CTM-SP	IPEN-CNEN/SP-1	IPEN-CNEN/SP-2	PNNL	ORNL
234	0.0276	0.0285	0.02726 ±0.00079	0.0261 ±0.0008	0.0264 ±0.0003	*	0.029 ±0.0059	0.0261 ±0.0026	0.0268 ±0.0003	0.0276 ±0.0014
235	3.0169	3.0190	2.9823 ±0.035	2.9843 ±0.013	2.9925 ±0.0058	2..994 ±0.038	3.059 ±0.051	3.0258 ±0.1353	2.9519 ±0.0035	2.9871 ±0.0743
236	0.0006	0.0020	0.0006 ±0.0002	0.0006 ±0.0001	0.0006 ±0.0001	*	0.0029 ±0.0039	0.00068 ±0.0039	0.0011 ±0.0001	0.0009 ±0.0003
238	96.9549	96.9504	96.9898 ±0.035	96.9869 ±0.0216	96.9806 ±0.0058	97.006	96.922 ±1.05	96.9474 ±0.2133	96.6869 ±0.13	96.9845 ±0.0184
ng/swipe.	176.85 ±0.35	-	177.21 ±1.8	144.4 ±4.6	163 ±2	151 ±7	241 ±3	165.9 ±1.2	128.1	166 ±7.5
MS type		TIMS	ICP	ICP	ICP	ICP	ICP	ICP	ICP	TIMS

NBL U030a

U Isotopic (At. %)	Certified Value	IAEA (SAL)	IRD	ARN/ DIOXITEK	DIOXITEK	CTM-SP	IPEN-CNEN/SP-1	IPEN-CNEN/SP-2	PNNL	ORNL
234	0.02778	0.0285	0.02748 ±0.0012	0.0280 ±0.0006	0.0280 ±0.0006	*	0.026 ±0.0049	0.0261 ±0.0045	0.0276 ±0.0003	0.0273 ±0.0010
235	3.0404	3.0412	3.0099 ±0.043	3.0097 ±0.0086	3.0246 ±0.0086	3.022 ±0.030	3.076 ±0.074	3.0636 ±0.0804	3.0313 ±0.0030	3.0088 ±0.108
236	0.0006	0.0020	0.0007 ±0.0002	0.0007 ±0.0001	0.0006 ±0.0001	*	*	0.0014 ±0.0039	0.0008 ±0.0010	0.0010 ±0.0004
238	96.9312	96.9283	96.9617 ±0.044	96.9619 ±0.0108	96.9465 ±0.0088	96.978	96.937 ±1.3	96.9094 ±0.2132	96.9404 ±0.170	96.9162 ±0.1771
ng/swipe.	175.59 ±0.34	-	176.10 ±2.1	135.5 ±1.7	157 ±2	160 ±8	240 ±2	160.4 ±0.6	119	170 ±11
MS type		TIMS	ICP	ICP	ICP	ICP	ICP	ICP	ICP	TIMS

NBL U200 (1)

U Isotopic (At. %)	Certified Value	IAEA (SAL)	IRD	ARN/ DIOXITEK	DIOXITEK	CTM-SP	IPEN-CNEN/SP-1	IPEN-CNEN/SP-2	PNNL	ORNL
234	0.1247	0.1248	0.1228 ±0.0028	0.1320 ±0.0021	0.134 ±0.0027	0.147 ±0.021	0.122 ±0.014	0.1215 ±0.0058	0.1223 ±0.0007	0.1222 ±0.0055
235	20.0129	20.0182	19.6822 ±0.12	20.6120 ±0.061	20.769 ±0.060	20.0419 ±0.060	20.094 ±0.25	19.9979 ±0.2843	19.8227 ±0.0865	20.7842 ±0.667
236	0.2115	0.2112	0.2063 ±0.0033	0.2203 ±0.0026	0.224 ±0.0037	0.232 ±0.02	0.212 ±0.013	0.2107 ±0.0048	0.2046 ±0.0050	0.2104 ±0.0068
238	79.6509	79.6458	79.9887 ±0.12	79.0350 ±0.3506	78.881 ±0.057	79.572 ±0.27	79.572 ±0.91	79.6700 ±0.8599	79.8504 ±0.216	79.8832 ±0.1987
ng/swipe.	119.48 ±0.24	-	118.78 ±1.4	104.3 ±1.1	105 ±1	93 ±5	133 ±2	117.3 ±0.6	82	114 ±7.4
MS type		TIMS	ICP	ICP	ICP	ICP	ICP	ICP	ICP	TIMS

Table 2. Comparison of uranium results (continued).

NBL U200(2)

U Isotopic (At. %)	Certified Value	IAEA (SAL)	IRD	ARN/ DIOXITEK	DIOXITEK	CTM-SP	IPEN-CNEN/SP-1	IPEN-CNEN/SP-2	PNNL	ORNL
234	0.1247	0.1248	0.1234 ±0.0043	0.1305 ±0.0024	0.131 ±0.0031	0.156 ±0.02	0.121 ±0.015	0.1230 ±0.0074	0.1228 ±0.0006	0.1224 ±0.0050
235	20.0129	20.0182	19.7279 ±0.133	20.3957 ±0.056	20.4570 ±0.0281	19.828 ±0.20	20.088 ±0.41	20.0586 ±0.4367	19.8006 ±0.0422	19.6627 ±0.665
236	0.2115	0.2112	0.2050 ±0.0040	0.2259 ±0.0024	0.224 ±0.0028	0.250 ±0.020	0.215 ±0.019	0.2087 ±0.0143	0.2048 ±0.0006	0.2083 ±0.0059
238	79.6509	79.6458	79.9437 ±0.0136	79.2477 ±0.1206	79.187 ±0.0265	79.766 ±0.25	79.575 ±1.25	79.6101 ±0.1751	79.8720 ±0.136	80.0065 ±0.2916
ng/swipe.	85.99 ±0.11	-	85.82 ±1.2	80.6 ±1.1	77.8 ±0.9	66 ±3	98.2 ±1.1	99.4 ±0.4	61.8	86 ±4.6
MS type		TIMS	ICP	ICP	ICP	ICP	ICP	ICP	ICP	TIMS

Blank data.

U Isotopic (At. %)	IAEA (SAL)	IRD	ARN/ DIOXITEK	DIOXITEK	CTM-SP	IPEN-CNEN/SP-1	IPEN-CNEN/SP-2	PNNL	ORNL
234	-	-	-	-	-	-	-	0.318	0.025
235	-	-	-	-	9.07 ±1	-	-	1.034	0.992
236	-	-	-	-	-	-	-	0.251	0.035
238	-	-	-	-	90.97 ±1	-	-	98.397	98.957
ng/swipe.	0.54±0.03	0.64±0.03	0.38±0.04	0.30±0.02	0.9±0.1	19.9±0.1	0.06 ±0.0005	0.7	0.83±0.44
MS type	TIMS	ICP	ICP	ICP	ICP	ICP	ICP	ICP	TIMS

Table 3. Summary of ABACC data.

CRM U030a	^{234}U	^{235}U	^{236}U	^{238}U
Certified value	0.02778±0.00006	3.0404±0.0016	0.0006±0.000005	96.9312±0.0016
ABACC average	0.0271±0.0010	3.0343±0.0284	0.00085±0.0004	96.9491±0.0240

CRM U200	^{234}U	^{235}U	^{236}U	^{238}U
Certified value	0.1247±0.0003	20.0129±0.020	0.2115±0.0006	79.6509±0.021
ABACC average	0.1304±0.0111	20.1460±0.344	0.2195±0.01288	79.5040±0.3470

CONCLUSIONS

ABACC's support laboratories have shown significant progress in developing environmental sample analysis capability with each of the evaluation exercises that began in 1998. This exercise has demonstrated that laboratories in both Argentina and Brazil have the capability of measuring both the amount and isotopic composition of uranium at the levels expected in typical environmental samples (i.e., sub-microgram quantities). A major factor in developing this capability is the fact that the laboratories have shown steady progress in contamination control and improvements in measurement capability.[1, 2, 3]

FUTURE PLANS

ABACC's support laboratories have successfully demonstrated an ability to analyze uranium in environmental samples. The next stages in the continued development of environmental sampling capabilities at ABACC laboratories are to:

- Supply Pu spike standards to appropriate laboratories that support ABACC
- Conduct an exercise with swipe samples prepared with plutonium standards (modeled on the uranium exercises)
- Conduct an environmental sampling exercise at nuclear facilities in South America

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