DEVELOPMENT OF CAPABILITY TO SEPARATE AND MEASURE URANIUM AND PLUTONIUM JOINTLY PRESENT IN LOW-LEVEL ENVIRONMENTAL SAMPLES AT BRAZILIAN AND ARGENTINE LABORATORIES WORKING FOR ABACC

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ABSTRACT

In the framework of the cooperation agreement between the Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC) and the United States Department of Energy/National Nuclear Security Administration (DOE/NNSA), ABACC support laboratories are collaborating with Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), and Lawrence Livermore National Laboratory (LLNL) to develop the capability to measure plutonium, and uranium and plutonium jointly present in environmental samples. Using procedures based on discussions among the DOE experts and participants from Brazilian and Argentinean laboratories, ABACC-support laboratories participated with DOE laboratories in a round-robin exercise to determine the amount and isotopic composition of plutonium, at levels as low as 0.2 ng of Pu, in samples prepared from dried solutions of reference materials. The results from this exercise are presented in this paper along with the difficulties encountered in achieving these results and the appropriate measures being taken to improve laboratory capabilities in Brazil and Argentina. The next planned activity will be training on separation of uranium and plutonium jointly present in environmental samples. This will be followed by another round-robin exercise in which swipe samples spiked with low-level uranium and plutonium will be analyzed for the amount and isotopic composition of both elements. After successful demonstration by ABACC support laboratories of the ability to analyze both uranium and plutonium at levels expected in real environmental samples, this cooperative effort will conclude with an environmental sampling exercise in which samples will be collected from nuclear facilities in Brazil and Argentina.

INTRODUCTION

In April 1994,DOE/NNSA and ABACC signed a Safeguards Cooperation Agreement on research, development, testing, and evaluation of technology, equipment and procedures to improve international safeguards applications. Under this agreement, in November 1996, DOE/NNSA and ABACC initiated a project, Action Sheet 6, to test the ability of participating laboratories to measure uranium concentration and isotopic abundances at levels expected in typical environmental samples. After successfully demonstrating the ability to measure the isotopic composition and quantity of uranium in low-level environmental samples,[1,2,3] a new agreement was signed in July 2005 to continue the development of environmental sample analysis for nuclear safeguards at

ABACC support laboratories. This new project, Action Sheet 15: Development of Environmental Sampling Capability in Support of the Regional Agreement Between Argentina and Brazil, deals with measurement of both U and Pu at levels expected in environmental samples. The project concludes with an exercise in which samples are collected from nuclear facilities in Argentina and Brazil, and analyzed by both ABACC support laboratories and DOE laboratories. Activity 1 under Action Sheet 15 involves analysis of dried solutions of Pu standards for isotopic composition and quantity. After successful demonstration of the capability to make accurate low-level measurements of Pu, ABACC support laboratories will develop and demonstrate the capability to perform the necessary chemistry to separate and purify U and Pu in samples that contain both elements. DOE conducted initial training on U/Pu separation chemistry and purification in March 2005. The results from the initial round-robin exercise of analyzing dried solutions of Pu standards under Activity 1 will be the primary topic of this presentation.

DESCRIPTION OF ACTIVITY 1

In December 2004, ABACC was supplied with New Brunswick Laboratory (NBL) certified reference materials (CRMs) and standards based on NBL CRMs as shown in Table 1.

Table 1. Standards supplied to ABACC.

Standard	Description
CRM 130	^{242}Pu spike
~2% ^{240}Pu	Made from CRM 126
18% ^{240}Pu	Made from CRM 137
CRM 128	1:1 ^{239}Pu:^{242}Pu

In March 2005, prior to initiation of formal activities under Action Sheet 15, DOE provided ABACC with the following list of recommended measurements to be performed by each laboratory using the NBL reference materials and standards listed in Table 1.

1. Use one standard for an instrumental mass bias measurement (NBL CRM 128).
2. Analyze a working standard made from NBL CRM 137 as the "unknown."
3. Use a ^{242}Pu spike to estimate total plutonium in the reference materials made from CRM 126.
4. Measure a plutonium blank in the digested swipe material.

The round-robin test samples for Activity 1 were prepared from the Institute of Reference Materials and Measurements (IRMM) REIMEP-16 solutions by LLNL, and were shipped to ABACC in April 2005. REIMEP is the Regular Interlaboratory Measurement Evaluation Programme conducted by the IRMM. The total Pu and isotopic composition of the samples are given in Tables 2 and 3, respectively. This exercise was designed to test the capability of participating laboratories to precisely and accurately measure plutonium quantity and isotopic abundances at levels expected in typical environmental samples. The analytical performance criteria for this round robin were based on the International Atomic Energy Agency (IAEA) requirements for qualification of laboratories for analysis of environmental samples[4], as shown in Table 4.

Table 2. Pu Quantity in dried solutions for Activity 1**.**

Sample ID	Total Pu, ng	1-sd uncertainty
PuXC-1	1.013	0.027
PuXC-2	0.854	0.023
PuXC-3	0.554	0.015
PuXC-4	0.252	0.007
Blank	0.00001	0.00005

Table 3. Plutonium data for ABACC dried solutions for Activity 1.

Sample ID	$^{240}Pu/^{239}Pu$		$^{241}Pu/^{239}Pu$		$^{242}Pu/^{239}Pu$	
	Atom ratio	1-sd uncertainty	Atom ratio	1-sd uncertainty	Atom ratio	1-sd uncertainty
PuXC-1	0.65765	0.00059	0.002244	0.000075	0.000421	0.000011
PuXC-2	0.42756	0.00236	0.001599	0.000054	0.000291	0.000006
PuXC-3	0.24613	0.00018	0.001080	0.000057	0.000188	0.000006
PuXC-4	0.11104	0.00015	0.000702	0.000026	0.000111	0.000004

Table 4. Analytical performance criteria (for 10 ng of U or 0.1 ng of Pu).

Measured values	Typical accuracy
U amount	≤ 10 %
Pu amount	≤ 10 %
$^{235}U/^{238}U$	≤ 1 %
$^{234}U/^{238}U$	≤ 10 %
$^{236}U/^{238}U$	≤ 10 %
$^{240}Pu/^{239}Pu$	≤ 10 %
Fission and activation products by high resolution gamma spectrometry	≤ 10 %

Laboratories participating in the exercise are listed below:

ABACC Support Laboratories

- *Instituto de Radioproteção e Dosimetria* of the National Nuclear Energy Commission of Brazil in Rio de Janeiro, Brazil (IRD-CNEN)
- *The Laboratorio de Analises Quimicas* of the Dioxitek, Planta Córdoba, Córdoba, Argentina, and Laboratorio Ambiental of the Autoridad Regulatoria Nuclear (ARN), Buenos Aires, Argentina
- *Laboratório de Caracterização Quimica* and *Departamento de Radioproteção Ambiental* of the Instituto de Pesquisas Energéticas e Nucleares (IPEN) in São Paulo, SP, Brazil (IPEN-CNEN/SP)
- *Laboratorio de Analises Quimicas* of the National Atomic Energy Commission of Argentina in Buenos Aires, Argentina (CNEA)

DOE Laboratories

- *Pacific Northwest National Laboratory* (PNNL)
- *Lawrence Livermore National Laboratory* (LLNL)

Laboratories were asked to report data in the formats given in Tables 2 and 3, and to provide the additional information presented in Table 5.

Table 5. Information on Pu swipe samples analysis

	PNNL	LLNL	IRD	IPEN (B)	IPEN (C)	Dioxitek (D)	Dioxitek (E)	CNEA - UAQ
(1) Was the plutonium purified before analysis of mass 241Pu/239Pu?	NO	YES	YES	NO	NO	NO	NO	NO
(2) Was Total Pu (nanograms) measured by isotope dilution using 242Pu spike?	NO	NO	YES	NO	NO	NO	NO	YES
(3) If the answer to (2) is "Yes", please report the 242Pu/239Pu for the spiked sample.	NA	NA	1.444012043 1.536466496 2.033776968 4.195457997	NA	NA	NA	NA	1.142 1.304 1.987 2.419
(4) If the answer to (2) is "Yes", were any corrections made for the spike isotopic composition?	NA	NA	YES	NA	NA	NA	NA	NO
(5) Was the 242Pu/239Pu reported as Primary Data measured on an un-spiked aliquot?	NO	YES	YES	YES	YES	YES	YES	YES
(6) Were any corrections made for laboratory blank ?	NO	NO	NO	NO	NO	NO	NO	NO
(7) If the anwer to (2) is "No", please describe the method used to determine Total Pu.	All samples were spiked with Pu-244. we did not run a spike and unspiked splits of the samples.	Isotope dilution mass spec analysis using Pu-244 spike.	NA	The Pu content was determined using external calibration method with CRM126. Mass discrimination calculated by using 239Pu/242Pu measured in the CRM 128.	The Pu content was determined using external calibration method with CRM126. Mass discrimination calculated by using 239Pu/242Pu measured in the CRM 128.	Fully quantitative calibration with 6 standards of Pu 242, and calibration concentrations defined by isotope.	Fully quantitative calibration with 6 standards of Pu 242, and calibration concentrations defined by isotope.	NA
Instrumentation	ICP-MS PQ2	Multi-Collector ICP-MS GV IsoProbe	Quadrupole ICP-MS with ultrasonic nebulizer from Perkin-Elmer (Elan 6000)	High resolution ICP-MS ELEMENT 1	High resolution ICP-MS ELEMENT 1	ICP-MS, Plasma Quad3 Thermo Elemental	ICP-MS, Plasma Quad3 Thermo Elemental	TIMS Finnigan MAT 262
Comments		240Pu/239Pu ratios were measured using simultaneous multicollection technique with channeltron multipliers.						The blank was measured but the number of counts was too low to confirm a ratio. Uranigan was found in the samples.

RESULTS AND DISCUSSION

The data from this round robin were normalized to the "true" values given in Tables 2 and 3, and plotted in Figs. 1- 4. For $^{240}Pu/^{239}Pu$, all of the laboratories demonstrated the capability to make this measurement near the level of the IAEA performance criterion for this ratio ($\leq$ 10 % for 0.1 ng of Pu), as shown in Fig. 1. Only two laboratories (LLNL and IRD) separated and purified the samples. As shown in Fig. 2, there is a significant ^{241}Am contribution to the signal at mass 241 for the laboratories that did not perform the separation. The data plotted in Fig. 2 demonstrate that americium separation is required for an accurate determination of plutonium isotopic values in environmental samples. The amount of ^{242}Pu present in these samples is very small, and, as shown in Fig. 3, even the better-performing laboratories experienced difficulties in accurately measuring ^{242}Pu for the smaller samples (Pu XC-3 and Pu XC-4, which contain a total of 0.1 pg and 0.04 pg ^{242}Pu, respectively). The determination of total plutonium, plotted in Fig. 4, was made using both

isotope dilution and calibration curves, depending on the laboratory. Not all laboratories meet the IAEA goal for accuracy (10%), even at the upper end of the expected concentration range, but one of the ABACC laboratories did get very good results. This shows that it is necessary to improve procedures, materials and process understanding in some of the laboratories. One important observation on the results is the cross contamination with uranium observed in some laboratories due to the nature of other work performed in these laboratories.

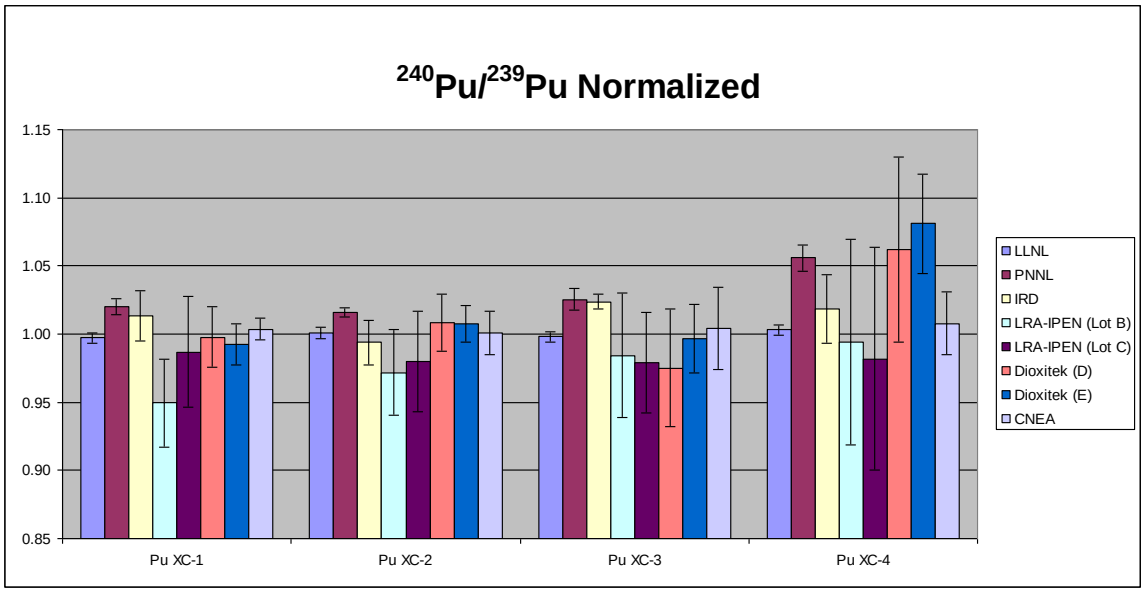


Figure 1. $^{240}Pu/^{239}Pu$ from the laboratories participating in the round robin.

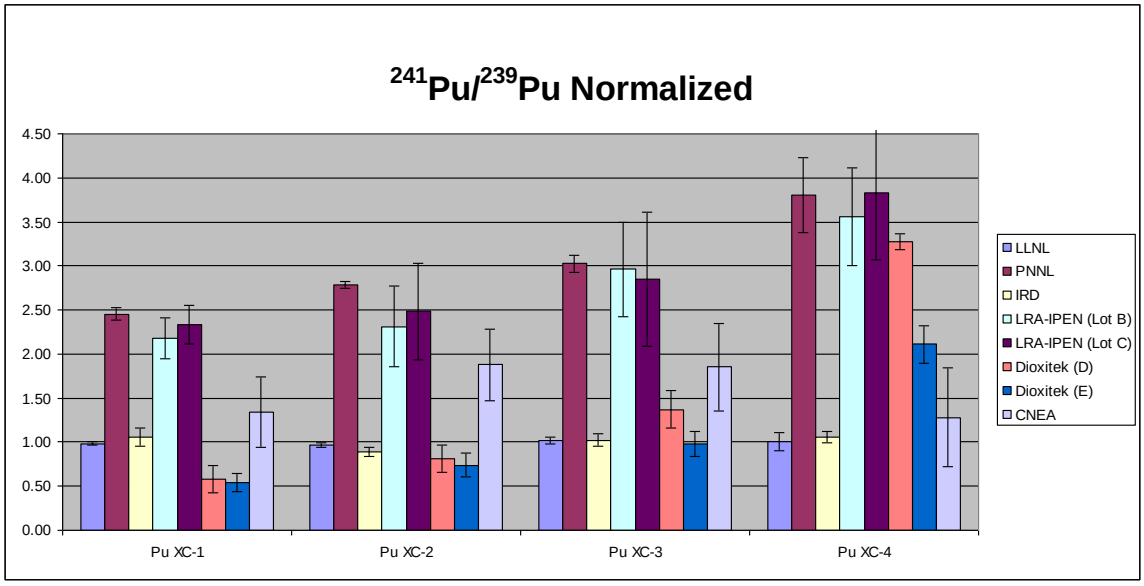


Figure 2. $^{241}Pu/^{239}Pu$ from the laboratories participating in the round robin.

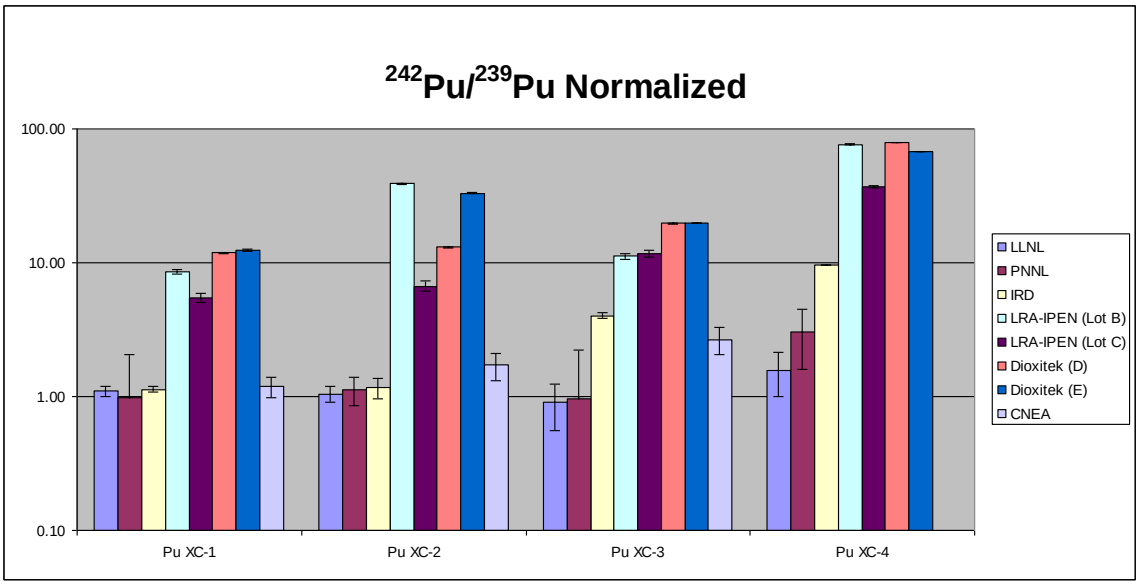
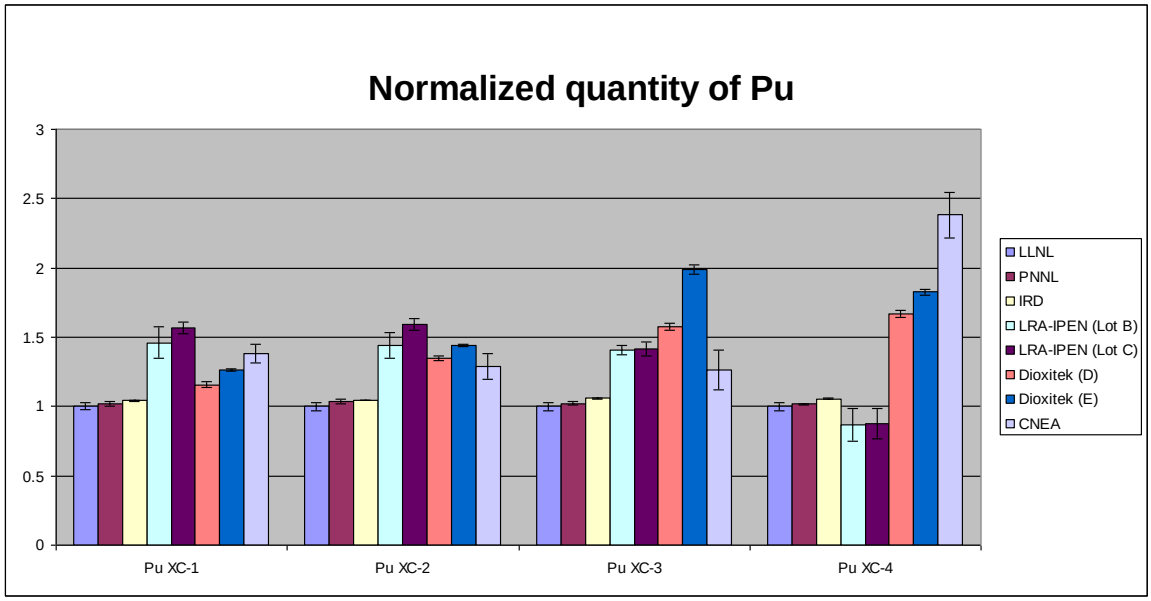


Figure 3. $^{242}Pu/^{239}Pu$ from the laboratories participating in the round robin.



Normalized to LLNL measured value.

Figure 4. Quantity of Pu from the laboratories participating in the round robin.

FUTURE ACTIVITIES

Activity 2 of Action Sheet 15 requires the measurement of both U and Pu on cotton swipe samples that will be prepared with characteristics close to those listed in Table 6. This will require U/Pu separation and purification, and because of the difficulty associated with this activity, the standards used to prepare the swipe samples will also be supplied as dried solutions.

After successful demonstration by ABACC's support laboratories of their capability to analyze both uranium and plutonium at levels expected in real environmental samples, this cooperative effort will

conclude with Activity 3, an environmental sampling exercise in which samples will be collected near nuclear facilities in Brazil and Argentina and analyzed for U and Pu isotopic composition and quantity, and gamma-emitting radionuclides.

Table 6. Activity 2 round robin sample characteristics**.**

ng Pu	U/Pu	+/-	% Variation from nominal value
*	10,000	1000	10
*	1000	200	20
*	100	50	50
*	20	-	-

*Note: Samples will be prepared with 0.1 to 0.5 ng Pu

CONCLUSIONS

This initial round-robin exercise demonstrated that ABACC support laboratories have the potential to analyze low-level environmental samples for plutonium. One of the laboratories obtained results very near the expected values for both isotopic and quantitative measurements of plutonium. Many of the laboratories uncovered significant procedural problems, such as the necessity for separating americium prior to determination of plutonium. In addition, contamination problems were observed at several laboratories. A new round robin is planned that will require analyzing swipe samples with U and Pu.

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