2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
***ISBN:* 978-85-99141-04-5**

CHARATERIZATION OF HIGHLY ENRICHED URANIUM IN A NUCLEAR FORENSICS EXERCISE

Marcos R. L. do Nascimento[1], Jorge E. S. Sarkis[2], Antonio L. Quinelato[1] and Nivaldo C. da Silva[1]

[1] Laboratório de Poços de Caldas (LAPOC / CNEN - MG)
Caixa Postal 913
37701-970 Poços de Caldas, MG
pmarcos@cnen.gov.br

[2] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
jesarkis@ipen.br

ABSTRACT

This paper presents the characterization of two metal samples of highly enriched uranium as a contribution of Poços de Caldas Laboratory, LAPOC, a branch of Brazilian National Commission for Nuclear Energy, CNEN, to the Round Robin 3, RR3, coordinated by the Nuclear Forensics International Technical Working Group. A scenario was constructed in which two separate seizures of nuclear material occurred and forensics analysis was requested to help discern whether these incidents were related and whether these incidents exceeded country statutes. Laboratories were instructed to submit assessment reports in 24 hours, one week, and two month timeframes. Besides preliminary evaluations for categorization of the material, our laboratory applied high resolution gamma spectrometry, optical emission spectrometry by inductively coupled plasma, and potentiometric titration for quantitative characterization of the samples. Concerning our technical reports answers for the three main forensics questions formulated by RR3, one of them was inconclusive, considering that LAPOC does not yet have all essential equipments for a fully satisfactory forensics nuclear analysis.

1. INTRODUCTION

In his first speech on nonproliferation as president, Barack Obama addressed the threat of nuclear terrorism as ñthe most immediate and extreme threat to global security.ò He stated that the need to provide greater security for nuclear material and facilities is a global imperative [1]. In this context, nuclear forensics analysis is a powerful tool of investigation that includes the analysis of a sample of nuclear or radioactive material and any associated information to provide evidence for determining the history of the sample material as a support to assess events of illicit trafficking, including the smuggling of nuclear material.

The response to specific nuclear incidents requires a graded approach with three levels of investigations: (1) categorization, (2) characterization, and (3) nuclear forensic interpretation. Categorization is performed to address the threat posed by a specific incident. The goal of categorization is to identify the risk to the safety of first responders, law enforcement personnel, and the public and to determine if there is criminal activity or threat to national security. In this first level a rapid analysis is done, usually performed by high resolution gamma spectrometry, HRGS, in order to determine the type of investigated material (low or

high enriched uranium, plutonium, others radioactive substances). Characterization is performed to determine the nature of the radioactive and associated evidence. Basic characterization provides full elemental analysis of the radioactive material, including major, minor, and traces constituents. For those major constituents of the radioactive material, basic characterization would also include isotopic and phase analysis, if necessary. Nuclear forensic interpretation is the process of correlating the material characteristics with the production history. The goal of nuclear forensic interpretation is to determine the method and time of production. The interpretation may include reactor and process modeling and/or database searches to identify the method of production. The nuclear forensic interpretation is the end product for the International Nuclear forensic Laboratories [2, 3].

By using HRGS, optical emission spectrometry by inductively coupled plasma, ICP-OES, and potentiometer titration, this work contributed to an inter-laboratory comparison exercise (Round Robin Exercise Number 3 ï RR3) organized by the International Technical Working Group for Combating Illicit Trafficking of Nuclear Materials (ITWG). Execution of RR3 spanned from December 2005 to September 2010 with the participation of nine laboratories [4].

Two metal samples of highly enriched uranium (HEU) were selected for the exercise. A scenario was constructed in which two separated seizures of nuclear material occurred and forensic analysis was requested by law enforcement to help discern whether characterization of the seized materials from these two incidences could be used to infer that the incidents were related in any way and whether these incidents exceeded country statutes. The hypothetical country has a statute that prohibits the unauthorized transport of uranium materials in excess of 1 gram and more than 1% enriched in the isotope 235. According to its capacities laboratories used existing nuclear forensic protocols, procedures, and analytic techniques to independently analyze the samples and to identify similarities and differences of the materials´ characteristics. Results obtained by the laboratories were asked to be sent within 24 hours, one week, and 2 months to the ITWG RR3 coordinator. Participating laboratories were requested categorize, characterize and perform nuclear forensics evaluations of the exercise materials and draw conclusions to the questions posed in the scenario. However, considering that the Poços de Caldas laboratory, LAPOC, the techniques of inductively coupled plasma mass spectrometry, ICP-MS, for trace and/or ultra-trace analysis and scanning electron microscopy, SEM, to examine the microstructure of samples, are not yet available, one of the forensic questions formulated by RR3 was inconclusive.

2. MATERIAL AND METHODS

2.1. Material Provided

Two metal samples of HEU were provided by the ITWG RR3 organization, with specific codification for each performing laboratory, but nominally were designated as A and B for all laboratories.

2.2. Isotopic and Chemical Analysis

The drawing scheme shown in Figure 1, summarize the methods and procedures performed by LAPOC for HEU samples analysis.

Uranium isotopic analysis (^{234}U, ^{235}U, ^{238}U) were done by HRGS, using a Canberra Model ISOCS, in situ object counting system, spectrometer with HPGe low energy detector (efficiency 20%), operating in lab mode. The system encompasses a low background shield. Efficiency calibration was performed using Monte Carlo simulation by using a template provided by the system. The spectra of the samples were taken at around 12 cm distance from the detector.

Minor and trace elements were detected by ICP-OES, using a Varian model Liberty sequential spectrometer. The procedure embodied the sample solubilization with HNO_3/HCl, following its dryness and HNO_3 6M redissolution, extraction of uranium into a tributylphosphate/isoctane (1:1) organic fase, and finally, determination of elements in aqueous fase.

Total uranium was determined by ferrous reduction in phosphoric acid followed by dichromate potentiometer titration.

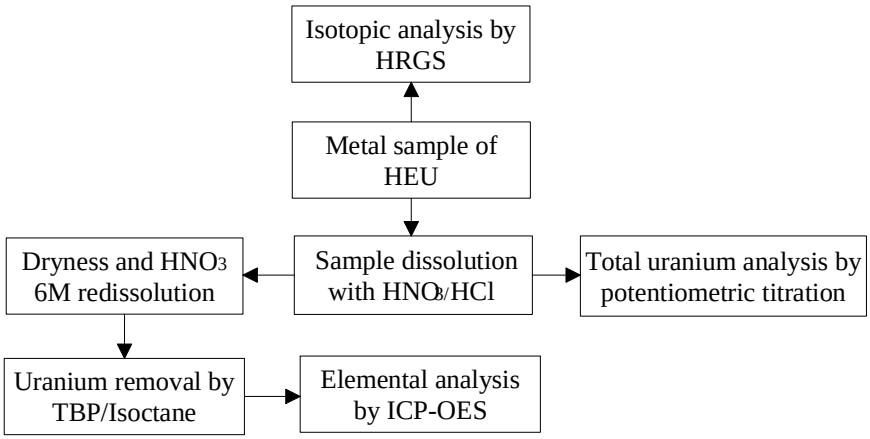

Figure 1. Drawing scheme of methods applied for HEU samples analysis.

3. RESULTS AND DISCUSSION

3.1. 24 Hours Evaluations

The first evaluations over the received samples, which comprise visual inspection, photography, physical parameters, dose rate, and enrichment level of nuclear material category, were submitted to the RR3 coordinator through the first report within the determined 24-hour deadline. These data are summarized on Table 1. The category of the nuclear material was initially done in a semi-quantitative way, through scanning by HRGS, of which the ^{235}U content exceeded the country statute.

Table 1. Visual inspection, physical, radiological, and enrichment level data

Parameter	Sample A	Sample B
Color	dark grayish-brown	dark grayish-brown
Form	isosceles trapezoid	isosceles trapezoid
Weight (g)	4.6888 ± 0.0002	5.7926 ± 0.0002
Density (g/cm^3)	17.03	17.69
Dose rate (μS/h)	0.68	0.76
Enrichment level (^{235}U %)	over 90	over 90

3.2. One Week and Two Month Evaluations

Measured uranium isotopic abundances for the exercises samples are displayed in Table 2. ^{238}U cannot be directly measured by HRGS once it has no significant gamma energy line. To overcome that constraint, this uranium isotope was determined by high energy line at 1001 keV provided by its daughter ^{234m}Pa. The later is a short-lived daughter of ^{234}Th, which is an immediate daughter of ^{238}U. In short period of time ^{234}Th reaches secular equilibrium with ^{238}U, due to its half-live of 24.1 days. For ^{234} U determination it was used the 120.9 keV gamma line whereas ^{235}U it was analyzed by line 185.7 keV. In both cases the calibrations take into account the self absorption effect.

The results comparison of all participants laboratories [4], showed that the abundance measured for ^{235}U ranged from 92.5% to 93.0% for sample A and 90.4 to 91.8% for sample B.

Table 2. Uranium isotopic analysis by HRGS (weight percent)

Sample	^{234}U	^{235}U	^{238}U
A	0.890 ± 0.052	92.75 ± 2.64	6.35 ± 0.26
B	0.831 ± 0.048	91.67 ± 2.60	7.50 ± 0.30

Table 3 provides the elemental analysis results of samples A and B, done by LAPOC, as well as the average result of each element from all participant laboratories. On the average of results per element from all laboratories, 1 or 2 results that were widely dispersed in relation to the others, were eliminated by a statistical exclusion rule. LAPOC only presented results for six elements in view of the limitations of the employed method (uranium extraction with tributylphosphate / isoctane and elements determination in aqueous phase by ICP-OES) and also the non-availability of a suitable alternative technique as ICP-MS. A few more qualified

laboratories succeeded in determining a larger number of elements, using various analytical techniques, with a total of 20 determined elements, as presented in the RR3 report [4].

Table 3. Minor and trace elements measurements (mg/kg)

Component	Sample A (1)	Sample A Average (2)	Sample B (1)	Sample B Average (2)
Al	14 ± 5	16 ± 4	10 ± 3	16 ± 6
Cr	10 ± 2	12 ± 2	10 ± 2	12 ± 2
Cu	8 ± 2	10 ± 3	8 ± 2	10 ± 2
Fe	100 ± 4	95 ± 14	150 ± 4	112 ± 25
Mn	5 ± 1	6 ± 2	6 ± 1	6 ± 2
Ni	38 ± 3	49 ± 8	30 ± 4	39 ± 5

(1) LAPOC results; (2) Average of all participants laboratories

The total uranium analysis in HEU samples, using potentiometric titration is shown on table 4. After chemical assay, the concentrations were recalculated according to uranium isotopic composition. Comparing these results to those obtained by the sum of the isotopes ^{234}U, ^{235}U and ^{238}U determined by HRGS, the results are consistent when taking into account the range of uncertainty in both methods.

Table 4. Uranium total by potentiometric titration

Sample	Total U (%)
A	99,8 ± 0.4
B	99.5 ± 0.3

Concerning the three main forensic questions formulated by RR3 - (1) if the enriched uranium proportions exceed the country statute, (2) if the characteristics of the samples and source were related to the seizures, and (3) if could exist more material at large, our assessment and conclusions are summarized below:

(1) Conclusive positive (linked): both samples are highly uranium enriched. The enrichments are higher than 90% and the mass are in excess of 1g.
(2) Conclusive similar: qualitative (Table1) and quantitative characteristics (Tables 2, 3 and 4) denote that the two seized materials are reasonably from the same source, and that the two seizures are related.
(3) Inconclusive: considering the overall situation, further detailed investigations by law enforcement, should be made necessary in order to verify if more material could be found at large.

4. CONCLUSIONS

The high resolution gamma spectrometry method showed to be suitable for the characterization of highly enriched uranium on the proposed exercise of illicit trafficking of nuclear material. Although other techniques applied by LAPOC were not sufficient in allowing the forensic issues to be more conclusive, the results shown in previous tables were consistent in relation to the average of other participating laboratories.

With the lessons learned from this exercise and assuming the acquisition of new techniques such as inductively coupled plasma mass spectrometry and scanning electron microscopy, LAPOC will undoubtedly be consolidated as a nuclear forensics laboratory.

ACKNOWLEDGMENTS

The authors would like to thank FAPEMIG and CNEN for financial support to this work as well as Dr Rich Hanlen, RR3 coordinator, for all the help provided during the achievement of this project and the Department of Energy / USA for financial aid at the final RR3 meeting in Dijon, France. Thanks are due to Danila Dias for carefully checking the manuscript.

REFERENCES

1. M. Krupa, ñCombating the nuclear terrorist threat: a comprehensive approach to nuclear security,ò *Journal of Nuclear Material Management*, **Vol. 38**, pp.30-35 (2010).
2. International Atomic Energy Agency, IAEA. Nuclear Forensics Support. ñReference document for responding to illicit events involving nuclear or other radioactive materialsò. Rev. 5, January 2005.
3. C. T. Nguyen and J. Zsigrai, ñBasic characterization of highly enriched uranium by gamma spectrometryò, *Nucl. Instr. Meth.* **B246**, pp. 417-424 (2006).
4. R. Hanlen, Coordinator, ñRound Robin 3 Exercise Reportò, Nuclear Forensics International Technical Working Group, Pacific Northwest National Laboratory, Richland, USA, 2011.