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UNCERTAINTY EVALUATION IN 2008 IAEA PROFICIENCY TEST USING PHOSPHOGYPSUM

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ABSTRACT

LAPOC participated in the 2008 IAEA ALMERA (*Analytical Laboratories for the Measurement of Environmental Radioactivity*) Proficiency Test (PT) for phosphogypsum, which is a NORM (Naturally Occurring Radioactive Material) derived from phosphate industry, an abundant solid waste of low cost. Its reutilization would avoid environmental impact in large areas where the product is stored. Research involving possible uses for phosphogypsum is ever more important, from economic, technological, and environmental points of view. This paper describes results from this Proficiency Test (measured radionuclides: ^{234}U, ^{238}U, ^{226}Ra, ^{230}Th, and ^{210}Pb), as well as a short description of the nuclear analytical techniques emphasizing sources of uncertainty, such as Alpha Spectrometry (Alpha Analyst, Canberra, surface barrier detectors) and Gamma Spectrometry (Canberra, Hyper Pure Germanium Detector with 45 % efficiency). Corrections for decay, reference date, and recovery were applied. As an example, results obtained for ^{210}Pb through the use of a specific uncertainty calculation software are presented below. Each parameter whose uncertainty is quantified was carefully described, with appropriate numerical value and unit, to determine its partial contribution to the combined total uncertainty. Results from PTs provide independent information on performance of a Laboratory and have an important role in method validation; especially because it allows the assessment of the method performance over an entire range of concentrations and matrices. PTs are an important tool to demonstrate equivalence of measurements, if not their metrological comparability, and to promote education and improvement of Laboratory practice.
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1. INTRODUCTION

The most used process for phosphate fertilizer production is the phosphatic rock attack with concentrated sulfuric acid and water. In this case, the main products from chemical reactions

are phosphoric acid, simple superphosphate (SSP), and triple superphosphate (TSP). Wastes from processing are PG (dihydrate calcium sulfate) and hydrofluoric acid [1].

Research involving possible uses for PG is ever more important, from economic, technological, and environmental points of view. This is an abundant waste, of low cost. Its reutilization would avoid environmental impact in large areas where the product is stored. It is a solid waste containing radioactive material, classified as NORM (Naturally Occurring Radioactive Material).

Even though PG is composed mainly from dihydrate calcium sulfate, it can present elevated levels of impurity from the matrix rock. These rocks transfer insoluble or acid soluble impurities to PG, such as heavy metals (Cd and Zn), metalloids (As and Se), fluorides, and natural series radionuclides [2]. As a consequence, PG disposal in piles may result in environmental impact as leaching and superficial drainage of toxic elements, sulfates, and radium (^{226}Ra and ^{228}Ra in soluble form) can result in contamination of water bodies, as well as direct gamma irradiation from piles (harmful to workers), release of aerosol caused by eolic erosion of the pile, and ^{222}Rn gas inhalation (also harmful to workers) [3, 4].

The rate of PG generation is of approximately 4.8 tons for each ton of produced phosphoric acid. Worldwide annual production can be estimated in 150 million tons. From this total, around 12 million tons come from Brazil [5], and most of it from Minas Gerais State, Uberaba region. Thus PG reutilization would contribute to preserve natural gypsum reserves, guaranteeing preservation of natural resources; a fundamental principle of sustainable development.

Most radionuclides contained in NORM materials belong to decay chains that start with ^{235}U, ^{238}U, and ^{232}Th. However, during the past years, many industries increased the proportion of NORM materials in final products or wastes, generating TENORMs (Technologically Enhanced Naturally Occurring Radioactive Materials). Such activities include general and sand mining and milling operations, fossil fuel burning, incrustation and sludge from petroleum extraction, metal refinement, uranium mining and milling, as well as manufacturing of phosphate fertilizers [6].

The Brazilian Nuclear Energy Commission Laboratory (CNEN-LAPOC) participated in the first PT for phosphogypsum analysis, organized by the International Atomic Energy Agency (IAEA). Results obtained were reported in May 2009, within the proposed deadline. Future statistics provided by IAEA will serve to establish whether LAPOC's performance is adequate for analyzing this waste material.

Participation and data from Proficiency Tests (PT) provide independent information on performance of a Laboratory and have an important role in method validation; especially because it allows the assessment of method performance over an entire range of concentrations and matrices. PTs are an important tool to demonstrate equivalence of measurements, if not their metrological comparability, and to promote education and improvement of Lab practices.

2. MATERIALS AND METHODS

2.1 Experimental Procedure

LAPOC Laboratory followed an experimental procedure in order to determine activity concentrations for natural radionuclides in a PG sample. After sampling at the collection site (Figure 1), each sample was weighted (for humid mass determination) and dried for 24 hours at 80°C (for dry mass determination), sieved, and placed in an acrylic cylindrical geometry container.

Measurement of ^{210}Pb was accomplished through a Gamma Spectrometry System (HPGe detector with beryllium window of 0.5 mm thickness). The detector shielding was composed of a lead wall (105 mm thickness), copper wall (2 mm), and lucite wall (4 mm). The activity concentration for ^{210}Pb was calculated through a specific energy photopeak of 46.5 KeV, employing a self-absorption correction factor.

^{226}Ra was measured through a Gas Proportional Counting System (Tennelec S5XLB). In addition, the result for radium was also verified by Gamma Spectrometry, using ^{214}Pb and ^{214}Bi photopeaks. Both results were compatible, but by choice only the result obtained through proportional counting was reported.

^{234}U, ^{238}U, and ^{230}Th measurements were done through Alpha Spectrometry (Alpha Analyst) with recoveries always superior to 90%.

Figure 1: Aerial View of Phosphogypsum Piles from Uberaba, MG, Brazil (collection site). GPS Coordinates: 19°59'21"S 47°52'55"W. [7].

2.2 Nuclear Analytical Techniques

Gamma Spectrometry can be employed to determine a wide variety of radionuclides in different matrices. The potential of this nuclear technique allows the study of gamma emitting nuclides in energies that can vary from 30 keV to 2000 keV. An advantage is its capacity to

determine different nuclides simultaneously in the same sample, without the need for chemical separation. Detection is normally accomplished in Germanium detectors connected to multi-channel analyzers and adequate software to identify energies corresponding to different gamma emitting nuclides. Radioactive decay corrections are necessary, mainly for those short-lived radionuclides.

The greatest contribution of Alpha Spectrometry for determination of uranium and thorium isotopes is to determine alpha emitters with low detection limits, which is the ideal for workers occupationally exposed. The detection of such isotopes at low levels requires a pre-concentration step and long counting times, with low background equipment. In this study, Alpha Spectrometry measurements showed a typical recovery of approximately 80 to 95% (^{232}U and ^{229}Th tracers were added to monitor recovery). Uranium and thorium were separated by chromatography resins from Eichrom Technologies in order to allow their quantification. Formed salts were dissolved with 2 mol L^{-1} hydrochloric acid. Detection limit was determined for each radionuclide electrodeposited in a silver planchet. Equipment quality assurance was verified through regular calibrations of the Alpha Spectrometry system (using certified standard mixed alpha source from Analytics Inc., Model SRS 63997-121). Main identified sources of uncertainty were sample preparation, volume (sample and tracers), chromatographic extraction procedures, and spectrum analysis.

A Gas Proportional Counter from Canberra Tennelec Series 5 Extra Low Background (SS5XLB) equipped with a sample changer was employed for ^{226}Ra determination. Proper alpha self absorption corrections were applied as needed, using calibration curves prepared with ^{241}Am standard solution. The calibration depends on layer thickness, composition of the source, and sample distribution on the plate. Characteristic efficiencies determined through ^{90}Sr + ^{90}Y and ^{241}Am, were 0.46 and 0.26, respectively. The simultaneous count mode sets the system high voltage to the beta plateau voltage. At this voltage, the proportional counter is sensitive to all ionizing radiation and the separation of alpha and beta particles is accomplished using pulse height. P-10 was used as a counting gas (90% Argon and 10% CH_4) with a flow adjusted to a pressure slightly above atmospheric pressure. Planchets of 2 inches were used to spontaneously deposit the standards. For this particular system an optimum alpha plateau was achieved at a 480 V operating voltage, while the beta plateau was found at 1395 V. Standard sources for efficiency determination were prepared exactly as the samples. These standard solutions and the samples were evaporated on a stainless steel planchet and counted. A Gamma Spectrometry System was employed to determine ^{133}Ba, which was necessary in order to evaluate the recovery of radium isotopes.

2.3 Uncertainty Determination

The GUM software (Guide to Uncertainty of Measurement), Version 2.3, was employed to determine the combined and expanded uncertainty for each measurement. Evaluation of measurement uncertainty according to GUM is a useful and accepted tool to evaluate results of a measurement, provided that input uncertainty components are correctly evaluated. It allows the comprehension of what and how things were carried out, combining prior knowledge and observations in a consistent and well-defined way. Finally, it does not require measuring with smallest achievable uncertainty, but with the most realistic one.

3. RESULTS AND DISCUSSION

Experimental results for IAEA-2008-04 Almera Proficiency Test of natural radionuclides are summarized on Table 1, with their respective combined and expanded uncertainty. Table 2 presents photopeak energies employed for Gamma Spectrometry determination of ^{210}Pb and ^{226}Ra.

Participation in PTs have been used at LAPOC as an effective tool for monitoring radioanalytical measurement performance and also to identify presence of variances in measurement results that are related to instrument performance and technical procedures.

The GUM software was employed in this PT to determine the expanded uncertainty for each measurement, and main uncertainty sources were identified for each radioanalytical method. This software analyzes the uncertainty of any measurement, test or analysis, including calibrations, physical testing and chemical analyses. Statistical and mathematical analysis and calculations follow the rules of the "ISO Guide to the Expression of Uncertainty in Measurement" and a requirement document of the "European Cooperation for Accreditation" [9, 10, 11]. The complete result of the examination is presented as a value with associated expanded uncertainty, and automatically or manually selected coverage factor.

For a measurement result, the combined standard uncertainty is the estimated standard deviation equal to the positive square root of the total variance obtained by combining all variance and covariance components, however evaluated, using the law of propagation of uncertainty. The final stage is to multiply the combined standard uncertainty by the chosen coverage factor in order to obtain an expanded uncertainty. In cases where the distributions concerned are normal, a coverage factor of 2 gives an interval containing approximately 95 % of the distribution of values.

Most sources of uncertainty in radioanalytical measurements [12], as the sources in this Intercomparison Exercise, were classified as normal probability distribution. A rectangular probability function was chosen when calculated uncertainty was associated with volume. The uncertainty of the detector efficiency was estimated from a series of repeated observations by calculating the standard deviation of the mean.

Table 1. Summary of Results for phosphogypsum 2009 PT

Phosphogypsum (results in dry mass) (humidity = 2.1%)	Activity (Bq kg^{-1})	Combined Uncertainty (Bq kg^{-1})	Expanded Uncertainty (Bq kg^{-1})	IAEA Results / Combined Uncertainty (Bq kg^{-1})
^{234}Uranium	118.1	20.7	41	120 ± 4.5
^{238}Uranium	106.9	18.8	38	120 ± 5.5
^{230}Thorium	219.1	17	34	211 ± 4.5
^{226}Radium	800.1	75.4	150	780 ± 31
^{210}Lead	613.5	30.8	62	680 ± 29

Table 2. Energy photopeaks for determination of specific activities

Radionuclide	Energy Photopeak
^{210}Pb	46.5 keV
^{226}Ra	^{214}Pb (351.9 keV and 295.2 keV)
	^{214}Bi (609.3 keV and 1120.6 keV)

Following reference [8], Uranium detection limit by Alpha Spectrometry was determined to be 0.000035 mg kg^{-1} or $8.54x10^{-4}$ Bq Kg^{-1}. A conversion factor of 0.0244 was used to convert mg kg^{-1} to Bq g^{-1} for U. Thorium detection limit was determined to be 0.000035 mg kg^{-1} or $4.435x10^{-4}$ Bq Kg^{-1}. A conversion factor of 0.0041 was used to convert mg kg^{-1} to Bq g^{-1} for Th. Finally, radium detection limit was calculated as twice the standard deviation of Alpha Background (0.1820 Bq g^{-1}).

Tables 3 to 7 present uncertainty budgets for all radionuclides quantified in phosphogypsum, with their respective parameter variables. Associated standard uncertainty is shown, as well as type of distribution, sensitivity coefficient and contribution of each variable to the combined uncertainty.

Table 3. Uncertainty Budget: ^{234}U

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C (Peak area)	4230.0	65.1	normal	0.028	1.8 mBq/g	0.8 %
Efc (Efficiency)	0.17910	$2.80 \cdot 10^{-3}$	normal	-660	-1.8 mBq/g	0.8 %
M (Mass)	0.9798000 g	$11.3 \cdot 10^{-6}$ g	rectangular	-120	$-1.4 \cdot 10^{-3}$ mBq/g	0.0 %
Y (Yield)	1.020	0.173	normal	NA	-21 mBq/g	98.4 %
T (Counting time)	$200.04 \cdot 10^{3}$ Seconds					
	A (^{234}U Activity)		118.1 mBq/g	20.7 mBq/g		

Table 4. Uncertainty Budget: ^{238}U

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C (Peak area)	3827.1	62.0	normal	0.028	1.7 mBq/g	0.9 %
Efc (Efficiency)	0.17910	$2.80 \cdot 10^{-3}$	normal	-600	-1.7 mBq/g	0.8 %
M (Mass)	0.9798000 g	$11.3 \cdot 10^{-6}$ g	rectangular	-110	$-1.2 \cdot 10^{-3}$ mBq/g	0.0 %
Y (Yield)	1.020	0.173	normal	NA	-19 mBq/g	98.4 %
T (Counting time)	$200.04 \cdot 10^{3}$ Seconds					
	A (^{238}U Activity)	106.9 mBq/g		18.8 mBq/g		

Table 5. Uncertainty Budget: ^{230}Th

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C (Peak area)	7028.0	83.6	normal	0.031	2.6 mBq/g	2.3 %
Efc (Efficiency)	0.17260	$2.70 \cdot 10^{-3}$	normal	-1300	-3.4 mBq/g	4.0 %
M (Mass)	0.9810000 g	$11.3 \cdot 10^{-6}$ g	rectangular	-220	$-2.5 \cdot 10^{-3}$ mBq/g	0.0 %
Y (Yield)	0.9470	0.0709	normal	NA	-16 mBq/g	93.6 %
T (Counting time)	$200.04 \cdot 10^{3}$ seconds					
	A (^{230Th} activity)	219.1 mBq/g		17.0 mBq/g		

Table 6. Uncertainty Budget: ^{226}Ra

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C (Sample Counting)	37.570 cpm	0.775 cpm	normal	21	17 Bq/kg	4.9 %
Cbg (Background Counting)	0.2900 cpm	0.0600 cpm	normal	-21	-1.3 Bq/kg	0.0 %
M (Mass)	$983.990 \cdot 10^{-6}$ kg	$215 \cdot 10^{-9}$ kg	rectangular	$-810 \cdot 10^{3}$	-0.17 Bq/kg	0.0 %
Y (Chemical Yield)	0.8336	0.0760	normal	NA	-74 Bq/kg	95.1 %
Nabs (Self Absorption Coefficient)	0.2184					
F (Constant Related to Self Absorption)	3.3494					
λ (Radon Decay Constant)	0.181 1/days					
T (Time between radium precipitation and Counting)	30.0 days					
	A (^{226}Ra activity)	800.1 Bq/kg		75.4 Bq/kg		

Table 7. Uncertainty Budget: ^{210}Pb

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C (Peak area)	8490	406	normal	0.075	30 Bq/kg	97.5 %
Cbg (Background Peak area)	300.0					
Efc (Efficiency)	0.135000	$680 \cdot 10^{-6}$	normal	-4500	-3.1 Bq/kg	1.0 %
M (Mass)	0.032270000 kg	$225 \cdot 10^{-9}$ kg	rectangular	-19000	$-4.3 \cdot 10^{-3}$ Bq/kg	0.0 %
Y (Yield)	0.041					
T (Counting time)	85350.0 Seconds					
AbsA (Sample Self absorption)	1.39040	$6.66 \cdot 10^{-3}$	normal	440	2.9 Bq/kg	0.9 %
AbsS (Standard Self absorption)	1.21750	$4.83 \cdot 10^{-3}$	normal	-500	-2.4 Bq/kg	0.6 %
	A (^{210}Pb activity)	613.5 Bq/kg		30.8 Bq/kg		

4. CONCLUSIONS

According to real radionuclide activity concentration values available from IAEA, and presented on Table 1, all radionuclide measurements performed during the IAEA-2008-04 ALMERA Proficiency Test (PT) discussed in this study were within the acceptable range, for both trueness and precision criteria.

Proficiency Tests can verify accuracy, precision, and variations within radioanalytical techniques. As this matures, the overall rate of analytical errors tends to decrease as participants become more aware, as personnel, methods, and procedures change.

Ultimately, a measurement uncertainty can be used to decide whether there is a difference between results from different Laboratories or results from the same Laboratory at different occasions (time trends, etc.). It is also useful to express an uncertainty value when comparing results to allowable values, such as tolerance limits and allowable (legal) concentrations.

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