2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-05-2

AVAILABILITY OF Po-210 PRESENT IN PHOSPHOGYPSUM USED IN AGRICULTURE: PRECISION AND ACCURACY OF THE METHODOLOGY

Guilherme H. Groppo, Barbara P. Mazzilli and Cátia H. R. Saueia

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
g.groppo@ipen.br, mazzilli@ipen.br, chsaueia@ipen.br

ABSTRACT

Phosphogypsum (PG) is a NORM residue of the phosphate fertilizer industry, and is stored in stacks at a rate of 5.5 x 10^6 tons annually. In Brazil, PG has been used for many years as a soil conditioner. The Brazilian regulatory agency has established a limit of 1000 Bq kg^{-1} for Ra-226 and Ra-228 and below this limit its use in agriculture is exempted of regulatory control. This study aims to determine the availability of the radionuclide Po-210 in the use of PG in agriculture as a soil conditioner. The Po-210 was purified and concentrated using a Sr-Spec resin. The final activity concentration was determined by spontaneous deposition of Po-210 in a silver disk and measurement by alpha spectrometry. The accuracy and precision of the methodology was checked by using a standard reference material provided by International Atomic Energy Agency, IAEA 385 – Irish Sea Sediment, and a Po-210 standard solution provided by Instituto de Radioproteção e Dosimetria (IRD). The precision and accuracy achieved varied from 2.2% to 7.6% and from 1.5% to 17.5%, respectively.

1. INTRODUCTION

The Brazilian phosphate fertilizer industry occupies the 6th position in the world ranking. Industrial fertilizer main source is the phosphate rock, and the most common process is based on the attack of phosphate rock with sulfuric acid [1]. However, during the chemical process, there is a generation of a byproduct, called phosphogypsum, which can be classified as Technologically Enhanced Naturally Occurring Radioactive Material (TENORM). About 5 tons of phosphogypsum is produced for every ton of phosphoric acid manufactured and is stored in Brazil at a rate of 5.5 10^6 tons annually [2].

The main problem associated with this material concerns the relatively high levels of natural radionuclides of uranium and thorium series and other contaminants which could have an impact on the environment. There is a concern related to the possible contamination of groundwater under phosphogypsum stacks, and to radon exhalation which may pose a health risk to people working and living close to a stack [3]. One possibility of reducing the environmental impact of the PG stacks is to re-use it in agriculture.

In Brazil, phosphogypsum has been used for many years as a soil conditioner. The Brazilian regulatory agency has established a limit of 1000 Bq kg^{-1} for Ra-226 and Ra-228 and below this limit its use in agriculture is exempted of regulatory control [4].

This study is part of a research project sponsored by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP - 2010-10587-0) entitled “Availability of metals and radionuclides in tropical soils amended with phosphogypsum” and aims to determine the availability of the radionuclide Po-210 in the use of PG in agriculture as a soil conditioner. The methodology chosen for the Po-210 determination is based on the purification and concentration using a Sr-Spec resin [5]. The final activity concentration was determined by spontaneous deposition of Po-210 in a silver disk and measurement by alpha spectrometry. The accuracy and precision of the methodology was checked by using a standard reference material provided by International Atomic Energy Agency: IAEA-385 – Irish Sea Sediment and a Po-210 standard solution provided by Instituto de Radioproteção e Dosimetria (IRD).

2. MATERIALS AND METHODS

The precision and accuracy of the experimental procedure were performed by using a standard reference material provided by International Atomic Energy Agency: IAEA 385 – Irish Sea Sediment, with activity of 32.9 Bq kg^{-1}. The analysis was performed in six samples. The following procedure was adopted for the preparation of the sample: 0.5 g of the reference material IAEA-385 was weighed and digested on a microwave MARS (Microwave Accelerated Reaction System) (Figure 1) after adding 15 mL of 65% HNO_3. For the total digestion, the temperature necessary was 200ºC for about 25 minutes. After the dissolution of the sample, 300 μL of Po-209 radioactive tracer (activity concentration of 1.7251 Bq g^{-1}) was added for the determination of the chemical yield.

Figure 1: Digestion of the samples in the microwave.

The precision and accuracy of the experimental procedure were also performed by using a Po-210 standard solution provided by Instituto de Radioproteção e Dosimetria (IRD), with activity of 1.43±0.21 Bq kg^{-1}. The analysis was performed in duplicate. A volume of 300 μL of Po-209 radioactive tracer (activity concentration of 1.7251 Bq g^{-1}) was added to 50 mL of the solution for the determination of the chemical yield.

The solutions obtained were eluted on a glass column filled with 3 g of Sr-Spec resin from EICHRON, which was previously conditioned with 100 mL of 2M HCl. The solution was percolated at a flow of one drop every 15 seconds. The Po retained in the resin was eluted with 60 mL of 6M HNO_3, at a flow of two drops every 30 seconds. After this process, 1 mL of concentrated HCl was added in the solution and heated almost to dryness, re-suspended with 10 mL of 0.5 M HCl + 5 mL of hydroxylamine hydrochloride 20 % + 5 mL of sodium citrate 25 % + Bi^{+3} carrier. The measurement of Po-210 was performed by spontaneous deposition on a silver disk (Figure 2), previously cleaned with acetone, on a water bath at 90 °C for about 4 h. At the end, the silver disk containing Po-210 was washed with deionized water, dried and counted on an alpha detector, from Canberra Alpha Analyst, for 80.000 seconds (Figure 3).

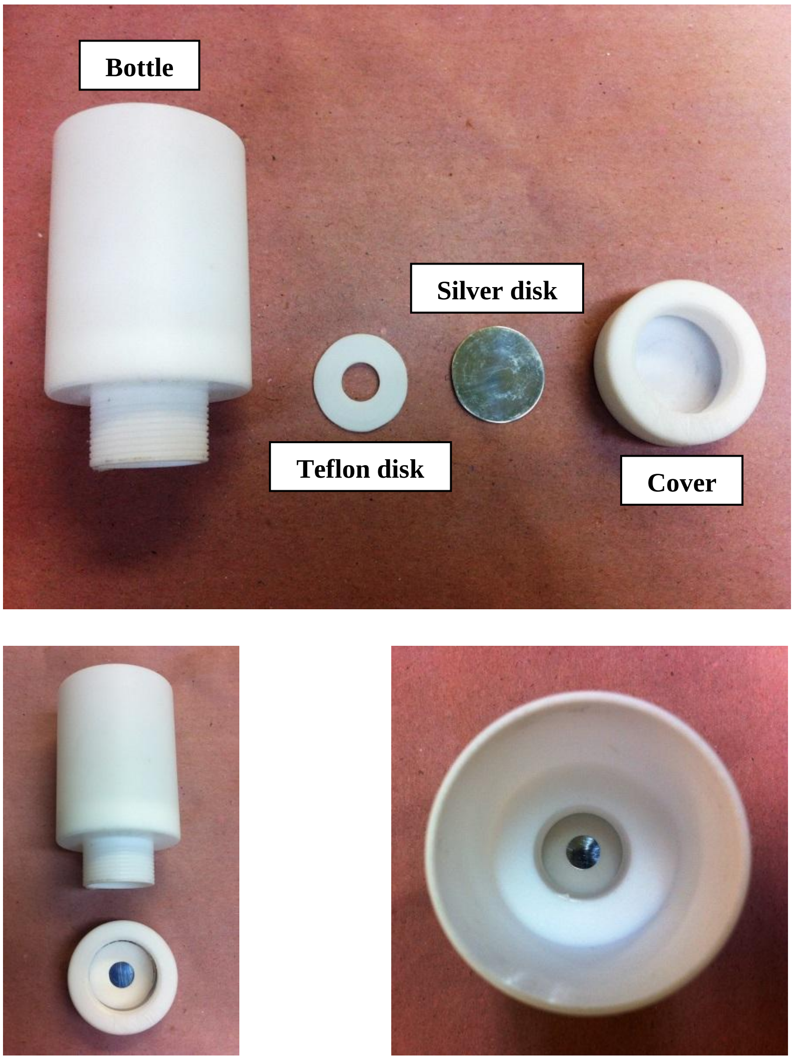

Figure 2: Apparatus used for spontaneous deposition of Po-210.

Figure 3: Alpha spectrometer used for the determination of Po-210.

For the determination of the detector alpha counting efficiency, a calibrated source of Am-241 with a known activity of 5.55 kBq was counted for 300 seconds. The efficiency results obtained for the detector varied from 22.54% to 26.96%.
The counting efficiency was obtained by the equation:

$$E_f = \frac{C_f}{A_f}$$

Where:

E_f = Efficiency (cps dps^{-1})
C_f = Calibrated source counts (cps)
A_f = Activity of the calibrated source (Bq)

The activity concentration of Po-210 was determined by the equation:

$$A_t = \frac{C - Bg}{t \,.\, ef \,.\, cy \,.\, m}$$

Where:
At = Activity concentration of Po-210 (Bq kg^{-1})
C = Total counts of Po-210
Bg = Background counts
t = Counting time (s)
ef = Efficiency of alpha spectrometer (cps dps^{-1})
cy = Chemical yield
m = Mass (kg)

The chemical yield was determined by adding 300 μL of Po-209 radioactive tracer in the solution and counting in a using a surface barrier detector for 80.000 seconds.

The lower limit of detection was determined by following the same methodology and using deionized water. The equation used to determine the lower limit of detection is presented below:

$$LID = \frac{4.66\ x\ \sqrt{Bg}}{ef\ .cy\ .m\ .t}$$

Where:
LID = Lower limit of detection (Bq L^{-1})
Bg = Background counts
ef = Efficiency of alpha spec (cps/dps)
cy = Chemical yield
m = Mass (L)
t = Time (s)

Typical lower limit of detection obtained for Po-210 was 4.32 10^{-3} Bq L^{-1}. The accuracy of the method was determined by the equation below:

$$RE = \left| \frac{x - \bar{x}}{x} \right| .100$$

Where:
RE = Relative Error
x = Certified value
$\bar{x}$ = Average value

The Precision was determined by the following equation:

$$RSD = \frac{S}{\bar{x}}\ .100$$

Where:
RSD = Relative Standard Deviation
S = Standard deviation
$\bar{x}$ = Average value

3. RESULTS AND CONCLUSION

The experimental results obtained for the determination of Po-210 by alpha spectrometry and spontaneous deposition using the reference material IAEA 385 and Po-210 standard solution are presented in Table 1.

The results obtained for precision 2.2 and 7.6, accuracy 1.5 and 17.5 for IAEA 385 and Po-210 standard solution, respectively, were satisfactory. The chemical yield achieved, from 62.2 to 77.7 was high, showing that the methodology chosen is suitable for the determination of Po-210 in sediment and water.

It is concluded that the methods performance is suitable for application in the study of the availability of radionuclides in tropical soils amended with phosphogypsum.

Table 1: Accuracy and precision obtained for the determination of Po-210

Reference Material	Activity concentration of Po-210 (Bq kg)	Chemical Yield (%)	Information Value (Bq kg)	95% Confidence Interval	Accuracy (%)	Precision (%)
IAEA 385 - Irish Sea Sediment	33.8±3.28	70.6	32.9	31.2 - 35.3	1.5	2.2
	33.9±3.44	77.7				
	33.3±2.56	74.4				
	32.1±2.83	73.6				
	33.2±2.90	73.2				
	34.2±4.23	72.5				
IRD - Standard Solution	1.59±0.09	62.2	1.43±0.21	-	17.5	7.6
	1.76±0.11	72.9				

ACKNOWLEDGMENTS

The authors would like to thank FAPESP for sponsoring this project (project number 2010-10587-0) and CNPq grant.

REFERENCES

1. B. P. Mazzilli, V. Palmiro, C. Saueia, M. B. Nisti., "*Radiochemical characterization of Brazilian phosphogypsum*" Journal of Environmental Radioactivity 49 (2000) pg. 113-122.
2. B. P. Mazzilli, C. H. R. Saueia., "*Radiological impact of the application of phosphogypsum in agriculture" RADIOPROTEÇÃO*, volume II, nº 20, (2012) pg. 191-197. http://www.sppcr.online.pt/.
3. A. J. G. Santos, P. S. C. Silva, B. P. Mazzilli and D. I. T. Fávaro., "*Radiological characterization of disposed phosphogypsum in Brazil: evaluation of the occupational exposure and environmental impact*" Radiation protection Dosimetry (2006), doi: 10.1093/rpd/ncl1011, Vol. 121, No. 2, pp 179-185.
4. Comissão Nacional de Energia Nuclear (CNEN), "Resolução nº 147/13 Nível de isenção para o uso de fosfogesso na agricultura ou na indústria cementeira," http://www.cnen.gov.br/seguranca/normas/pdf/Nrm488.pdf (2013).
5. IAEA, "A procedure for the sequential determination of polonium-210, lead-210, radium-226, thorium and uranium isotopes in phosphogypsum by liquid scintillation counting and alpha spectrometry," http://nucleus.iaea.org/rpst/ReferenceProducts/Analytical_Methods/PG_procedure_ver_12.pdf (2011).