Sequential determination of U and Th isotopes *and* ^{226}Ra by alphaspectrometry in phosphate fertilizers samples and phosphogypsum

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Abstract. The Brazilian phosphate fertilizer is obtained by wet reaction of igneous phosphate rock with concentrated sulphuric acid, giving as final product phosphoric acid and calcium sulphate (phosphogypsum) as by-product. Phosphoric acid is the starting material for the production of the majors' phosphate fertilizers: triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). The phosphate rock used as raw material is enriched in radionuclides of the U and Th natural series. During the chemical attack these radionuclides are distributed among products and by-products. A sequential procedure was implemented to determine the content of radionuclides alpha emitters (^{234}U, ^{238}U, ^{230}Th, ^{232}Th, ^{228}Th and ^{226}Ra) in samples of phosphate rock, phosphogypsum and phosphate fertilizers produced by the Brazilian industries. The experimental procedure consisted of a chemical attack with strong acids, followed by sequential chromatography extractions in column with ionic resins. Depending upon the conditions of percolation U isotopes are separated, followed by Th isotopes and ^{226}Ra. The solutions containing U and Th are electroplated on stainless steel disks and counted on a surface barrier detector for alpha spectrometry. To the Ra final solution, a $BaSO_4$ seeding suspension was added to allow the formation of a micro precipitated of $BaRaSO_4$. This precipitate is filtered in a polypropylene membrane and counted on the same detector. The precision and accuracy of the method were determined by analyzing reference materials: soil IAEA-326 and sediment IAEA-300. SSP and TSP, which are obtained by reacting phosphoric acid with phosphate rock in different proportions, presented higher concentrations of all studied radionuclides. Brazilian phosphate fertilizers, which are produced directly from phosphoric acid, MAP and DAP, present in their composition low concentrations of radionuclide ^{226}Ra. As for the radionuclides U and Th, the concentrations observed are higher.

1. Introduction

Uranium is known to be present in association with phosphate deposits of marine origin. Consequently, the various radionuclides of the natural occurring uranium decay series would be expected to be present with this mineral and to be partitioned by physical and chemical means during phosphate mining and subsequent processing. Several groups of researchers throughout the world have reported the distribution of natural radioactivity concentrations in the products, by-products and waste from the chemical process [1-5]. In Brazil, the phosphate rock used as raw material for phosphoric acid production is an igneous rock (phoscorite) made up of apatite, magnetite and olivine and cut by abundant carbonatitic veins. This rock is associated with uranium, thorium and their decay products. The Brazilian phosphate fertilizer is obtained by wet reaction of this igneous phosphate rock with concentrated sulphuric acid, giving as final product phosphoric acid and calcium sulphate (phosphogypsum) as by-product. Phosphoric acid is the starting material for the production of the majors' phosphate fertilizers: triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). Although several publications were found related with the characterization of Brazilian phosphate rock and phosphogypsum [6-9], no specific reference was found concerning the radiological characterization of the Brazilian phosphate fertilizers.

The present paper deals with the implementation of a sequential procedure to determine the content of radionuclides alpha emitters (^{234}U, ^{238}U, ^{230}Th, ^{232}Th, ^{228}Th and ^{226}Ra) in samples of phosphate rock, phosphogypsum and phosphate fertilizers produced by the Brazilian industries. The investigation was directed specifically at identification of optimum conditions necessary for complete sample dissolution, for efficient separation of radium, thorium and uranium isotopes from all other components of the sample, and for preparing the final barium-radium fraction and Th and U electroplated for alpha spectrometry. The experimental procedure adopted is a combination of the methodology proposed by Ref. [10] for the determination of Ra by alpha spectrometry after a micro precipitation of Ra with barium sulphate in the presence of a seeding suspension; and of a methodology already established by the authors for the determination of Th and U isotopes electroplated by alpha spectrometry [11].

2. Experimental

Analysis was carried out on samples of phosphate rock (12), phosphogypsum (8) and fertilizers (18), obtained from the three main Brazilian factories, named A, B and C. After collection, the samples were dried at about 60^{o}C to remove moisture and crushed to fine powder (30 to 60 mesh). The radiochemical procedure was based on the total dissolution of 250 mg of the samples, by addition of concentrated acids under heating at 80^{o}C, in the presence of exact aliquots of ^{133}Ba, ^{232}U and ^{229}Th tracers. A volume of 10 mL of concentrated HNO_3 was added to the sample and the solution was evaporated carefully to near dryness. The residue was treated with 1 mL H_2O_2 to eliminate organic matter and with concentrated HF to eliminate silica. The final solution was conditioned with concentrated HCl to eliminate nitrates and the elements of interest separated and purified by sequential chromatography extractions in column with DOWEX 1x8 ionic resins. In the first column the solution is eluted in a Dowex 1x 8 resin in 9M HCl: U is retained whereas Th isotopes and Ra flow through the resin. U is eluted with 0,1M HCl and the final solution electroplated on a disk for alpha counting. The eluate containing Th and Ra is passed through two columns: the first one (Dowex 1x8 resin in 8M HNO_3) for the retention of Th and the second one (Dowex 1x8 resin in 0,75M HBr) for the purification of Ra. Th is eluted with 9M HCl and is electroplated for alpha counting. A seeding suspension of $BaSO_4$ is added to the solution containing Ra; the $BaRaSO_4$ micro precipitated formed is retained in a Polypropylene membrane filter and counted on the alpha spectrometer for the determination of ^{226}Ra. For the determination of the chemical yield the same precipitate is counted on a germanium detector for the determination of ^{133}Ba. All the alfa measurements were performed on a surface barrier detector, EG&G Ortec. The precision *and* accuracy of the method were determined by analyzing reference materials: soil IAEA-326 *and* sediment IAEA-300. The precision achieved was 6.7% for U isotopes, 7.9 % for Th isotopes *and* 4.7 % for ^{226}Ra; the accuracy obtained was 5.4 %, 7.6 % *and* 4.4 % respectively. Typical lower limits of detection for the alpha measurement of the radionuclides were 1.4 mBq kg^{-1} for ^{238}U, 1.3 mBq kg^{-1} for ^{234}U, 0.9 mBq kg^{-1} for ^{230}Th, 0.8 mBq kg^{-1} for ^{226}Ra, 1.0 mBq kg^{-1} for ^{232}Th and 1.0 mBq kg^{-1} for ^{228}Th, respectively.

3. Results and discussion

Results obtained for the radionuclides, ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{232}Th and ^{228}Th on samples of phosphate rock, phosphogypsum and fertilizers (TSP, SSP, MAP and DAP) obtained from the Brazilian three main factories, named A, B and C, are presented in figure 1.

Brazilian phosphate fertilizers, which are produced directly from phosphoric acid, MAP and DAP, present in their composition low concentrations of radionuclides ^{226}Ra. As for the radionuclides U and Th, the concentrations observed are higher, reaching values up to 822 and 850 Bq kg^{-1}, respectively. SSP and TSP, which are obtained by reacting phosphoric acid with phosphate rock in different proportions, presented higher concentrations of all studied radionuclides, reaching values up to 1158 Bq kg^{-1} for ^{238}U, 1167 Bq kg^{-1} for ^{234}U, 1169 Bq kg^{-1} for ^{230}Th, 879 Bq kg^{-1} for ^{226}Ra, 521 Bq kg^{-1} for ^{232}Th, and 302 Bq kg^{-1} for ^{228}Th. The results obtained show that the levels of radioactivity present in the fertilizers are of the same

order of magnitude of those found in the phosphogypsum. Whereas, the fertilizers are commercialized, providing a dilution of their content of radioactivity, the phosphogypsum is storage in piles at open air, posing serious problems to the surrounding environment. One of the main problems is the levels of impurities, including radioactivity, which prevent its reutilization, although it presents the same radioactivity content as the fertilizers. It should be emphasized that it is a common practice in environmental radioprotection to minimize the effect of a punctual contamination to dilute spatially and temporally the source in order to reduce the environmental impact. The phosphogypsum piles are a typical example of such situation, since the radiological impact caused to the environment in the surrounding area is certainly more relevant than those caused by its reutilization.

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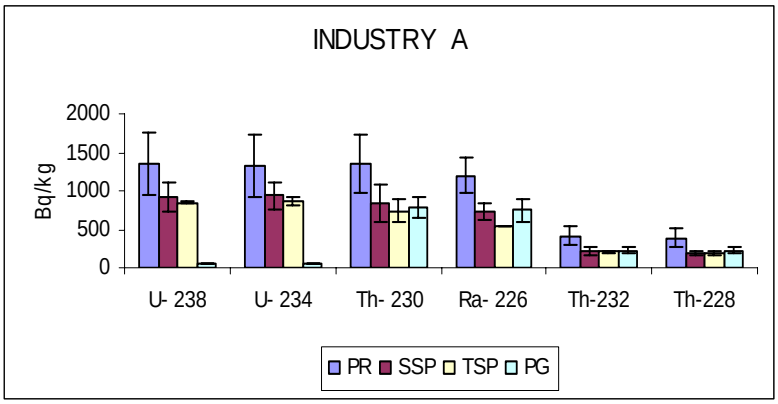

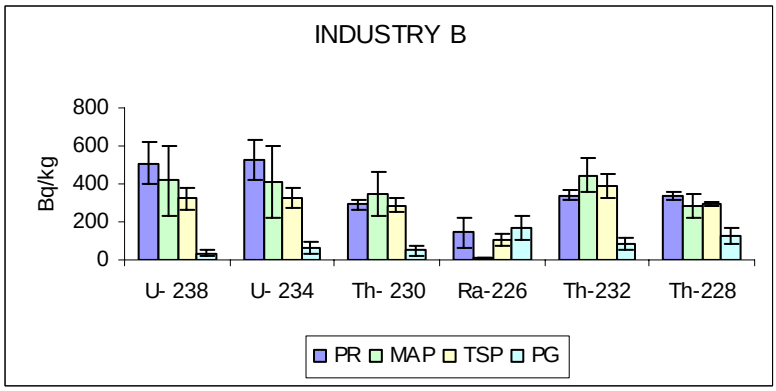

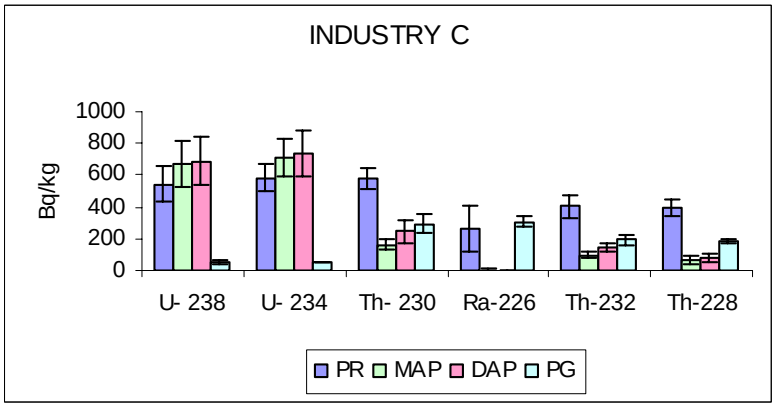

Figure 1. Activity concentration of radionuclides of the U and Th series and ^{226}Ra in samples of phosphate rock (PR), phosphogypsum (PG) and phosphate fertilizers (SSP, TSP, MAP, DAP) in Bq kg^{-1}.