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Sequential radioanalytical method for the determination of U and Th isotopes, ^{226}Ra and ^{210}Po using alpha spectrometry in samples of the Brazilian phosphate industry

C. H. R. Saueia · B. P. Mazzilli · M. H. T. Taddei

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Abstract The phosphate rocks used for the production of phosphate fertilizers present in their composition radionuclides of the U and Th series. During the chemical attack, the radionuclides are distributed to final products and phosphogypsum. A sequential radiochemical procedure was implemented to determine the content of radionuclides alpha emitters in samples of fertilizers and phosphogypsum produced in Brazil. The results obtained show that the levels of radioactivity present in the fertilizers are of the same order of magnitude on those found in the phosphogypsum, reaching values up to 1158 and 457 Bq kg^{-1}, for the U and Th series, respectively.

Keywords Phosphate fertilizers · Phosphogypsum · Natural radionuclides · NORM/TENORM

Introduction

Uranium and thorium are known to be present in association with phosphate deposits of igneous and marine origin. Consequently, the various radionuclides of the natural occurring 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 on the distribution of natural radioactivity concentrations in the products, by-products and waste from the chemical process [1–5]. In Brazil, the phosphate rocks used as raw material for the phosphoric acid production is an igneous rock (phoscorite) made up of apatite, magnetite and olivine and cut by abundant carbonatitic veins.

The Brazilian phosphate fertilizer is obtained by wet reaction of igneous phosphate rock with concentrated sulphuric acid, giving as final product phosphoric acid and dihydrated calcium sulphate (phosphogypsum) as waste product. Phosphoric acid is the starting material for the production of the phosphate fertilizers: single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). During the chemical attack of the phosphate rock, the U and Th equilibria are disrupted and the radionuclides migrate to intermediate, final products, by-products and waste, according to their solubility and chemical properties.

While the fertilizers are commercialized, the phosphogypsum is disposed in stack piles and can cause an impact to the environment. In order to evaluate the alpha emitting radionuclides distribution in the industrial process of phosphate fertilizer production, samples of concentrated rock (CR), fertilizers (SSP, TSP, MAP and DAP) and phosphogypsum (PG) from three main national producers, Copebras (Cubatão facility) and Ultrafertil (Cubatão and Uberaba facilities), were analyzed.

The present paper deals with the implementation of a procedure to determine the content of radionuclides alpha emitting (^{234}U, ^{238}U, ^{230}Th, ^{232}Th, ^{228}Th, ^{226}Ra and ^{210}Po) in samples of phosphate rock, phosphate fertilizers and phosphogypsum produced by the Brazilian industries. The

C. H. R. Saueia · B. P. Mazzilli (✉)
Laboratório de Radiometria Ambiental, Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), Avenida Professor Lineu Prestes, 2242, Cidade Universitária, São Paulo, SP CEP 05508-000, Brazil
e-mail: mazzilli@ipen.br

M. H. T. Taddei
Laboratório de Poços de Caldas, Comissão Nacional de Energia Nuclear (LAPOC/CNEN-MG), Rodovia Poços de Caldas—Andradas, km 13, Poços de Caldas, MG CEP 37701-970, Brazil

investigation was directed specifically to the identification of optimum conditions necessary for complete sample dissolution, for efficient separation of radium, thorium and uranium isotopes from all other interfering components of the sample, and for preparing the final barium–radium fraction and Th, U and Po disks for alpha spectrometry. The experimental procedure adopted is a combination of the methodology proposed by Sill [6] for the determination of Ra by alpha spectrometry after a micro-precipitation of Ra with barium sulphate in the presence of a seeding suspension; the methodology already established by the authors for the determination of Th and U isotopes by electro deposition and alpha spectrometry [7]; and the methodology proposed by Mattheus [8] for the determination of Po by spontaneously deposition and alpha spectrometry.

Experimental

Analysis was carried out on samples of phosphate rock, fertilizers and phosphogypsum, obtained from the three main Brazilian facilities. After collection, the samples were dried at about 60 °C to remove moisture and crushed to fine powder (30–60 mesh). The radiochemical procedure was based on the total dissolution of 300 mg of the samples, by addition of concentrated acids under heating at 80 °C, in the presence of exact aliquots of ^{232}U, ^{229}Th, ^{209}Po and ^{133}Ba used as tracers. A volume of 10 mL of concentrated HNO_3 was added to the sample and the solution was evaporated carefully to near dryness. This procedure was repeated three times until complete dissolution of the sample. 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 was eluted in a Dowex 1X8 resin in 9 M HCl: U and Po are retained whereas Th isotopes and Ra flow through the resin. U was eluted with 0.1 M HCl and the final solution electroplated on a disc for alpha counting. For ^{210}Po determination, a modified methodology of Mattheus [8] was used. The Po was eluted with 1 M HNO_3 and the solution was evaporated to dryness. The residue was dissolved in 6.25 M HCl, filtered in Millipore 0.1 μm and 20% hydroxylamine hydrochloride, sodium citrate and stable Bi^{+3} was added. After the pH was adjusted to 1.5, polonium was spontaneously plated on the silver disc at 90 °C for 4 h, with agitation of the solution.

The eluate containing Th and Ra was passed through two columns: the first one (Dowex 1X8 resin in 8 M HNO_3) for the retention of Th and the second one (Dowex 1X8 resin in 0.75 M HBr) for the purification of Ra. Th was eluted with 9 M HCl and was electroplated for alpha counting. A seeding suspension of $BaSO_4$ was added to the solution containing Ra; the micro-precipitated $BaRaSO_4$ formed was retained in a polypropylene membrane filter of 0.1 μm and counted on the alpha spectrometer for the determination of ^{226}Ra. For the determination of the chemical yield the same precipitate was counted on a germanium detector for the determination of ^{133}Ba.

All the alpha measurements were performed on a surface barrier detector, E.G&G Ortec. The precision *and* accuracy of the method were determined by analyzing reference materials: soil IAEA-326, sediment IAEA-300 and sediment IAEA-368. The precision achieved was 6.7% for U isotopes, 7.9% for Th isotopes, 4.7% for ^{226}Ra and 4.3% for the ^{210}Po; the accuracy obtained was 5.4%, 7.6%, 4.4%, and 1.0%, 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, 5.9 mBq kg^{-1} for ^{210}Po, 1.0 mBq kg^{-1} for ^{232}Th and 1.0 mBq kg^{-1} for ^{228}Th, respectively.

Results and discussion

Results obtained for the radionuclides ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po, ^{232}Th and ^{228}Th on samples of phosphate rock (PR), fertilizers (TSP, SSP, MAP and DAP) and phosphogypsum (PG) obtained from the Brazilian three main factories are presented in Table 1.

In order to check the reliability of the sequential methodology proposed, the concentration of the radionuclides ^{238}U and ^{232}Th were determined by two different techniques: alpha spectrometry and neutron activation analysis; ^{226}Ra was measured by alpha spectrometry and gamma spectrometry. Details about the procedures are reported by Saueia [9]. Figures 1, 2 and 3 represent the correlation among the measurements carried out by different techniques. The values obtained for the correlation coefficient—*r* are high, indicating that the sequential radiochemical procedure implemented is suitable for the determination of the radionuclides and the results can be considered as representative of the activity concentrations.

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, reaching values up to 1868 and 1694 Bq kg^{-1}, respectively. SSP and TSP, which are obtained by reacting of phosphoric acid directly with phosphate rock, presented higher concentrations of all

Table 1 Activity concentration in Bq kg^{-1} for radionuclides in phosphate rock (PR), fertilizers (TSP, SSP, MAP and DAP) and phosphogypsum (PG) obtained from three industries

	PR		SSP		TSP		PG	
	(M ± e)[a]	Range	(M ± e)	Range	(M ± e)	Range	(M ± e)	Range
Industry Copebras—Cubatão								
U-238	1179 ± 48	841–1868	861 ± 30	706–1158	845 ± 43	834–861	50 ± 3	42–53
U-234	1260 ± 50	962–1841	881 ± 31	735–1167	859 ± 44	831–906	57 ± 5	13–63
Th-230	1145 ± 35	837–1694	722 ± 26	665–1169	697 ± 29	631–855	742 ± 19	655–978
Ra-226	1114 ± 31	948–1581	683 ± 24	626–879	546 ± 23	544–548	697 ± 24	550–940
Po-210	1480 ± 82	1205–1519	724 ± 17	719–756	757 ± 50	754–759	742 ± 47	541–777
Th-232	314 ± 11	250–462	197 ± 5	188–287	201 ± 10	189–222	239 ± 7	212–257
Th-228	296 ± 10	244–447	177 ± 5	170–243	208 ± 10	205–212	230 ± 7	205–253
	PR		MAP		TSP		PG	
	(M ± e)	Range	(M ± e)	Range	(M ± e)	Range	(M ± e)	Range
Industry Ultrafertil—Uberaba								
U-238	440 ± 26	289–705	332 ± 26	264–620	307 ± 21	261–377	20 ± 3	15–50
U-234	470 ± 27	320–736	309 ± 25	237–613	319 ± 22	276–378	21 ± 2	15–89
Th-230	287 ± 10	270–319	331 ± 10	248–476	295 ± 8	244–308	43 ± 2	32–68
Ra-226	143 ± 9	139–153	7 ± 1	2–14	95 ± 8	88–138	143 ± 11	104–215
Po-210	278 ± 25	262–285	6 ± 1	4–8	96 ± 12	90–97	174 ± 18	134–203
Th-232	339 ± 12	321–356	432 ± 12	339–511	400 ± 11	350–457	71 ± 4	57–102
Th-228	336 ± 12	318–353	249 ± 7	215–346	296 ± 8	284–302	76 ± 3	75–153
	PR		MAP		DAP		PG	
	(M ± e)	Range	(M ± e)	Range	(M ± e)	Range	(M ± e)	Range
Industry Ultrafertil—Cubatão								
U-238	527 ± 36	498–672	628 ± 43	520–799	647 ± 43	520–797	42 ± 5	31–58
U-234	575 ± 42	522–714	688 ± 47	592–822	707 ± 46	581–850	47 ± 5	37–52
Th-230	556 ± 19	492–636	159 ± 5	131–195	194 ± 6	155–290	298 ± 9	252–392
Ra-226	261 ± 10	222–296	3 ± 1	<1.5–10	<1.5	–	301 ± 3	280–329
Po-210	506 ± 15	503–510	8 ± 1	6–10	7 ± 1	4–9	279 ± 20	255–344
Th-232	393 ± 14	372–457	95 ± 4	81–121	125 ± 4	109–163	168 ± 3	159–218
Th-228	389 ± 13	360–473	60 ± 3	36–95	61 ± 3	46–102	192 ± 6	178–209

[a] Mean value ± uncertainty

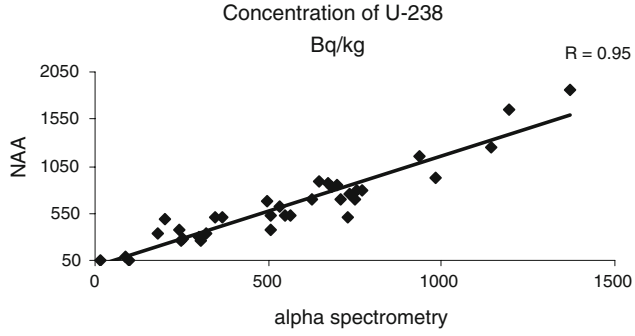

Fig. 1 Correlation among ^{238}U measurements by alpha spectrometry and neutron activation analysis (NAA)

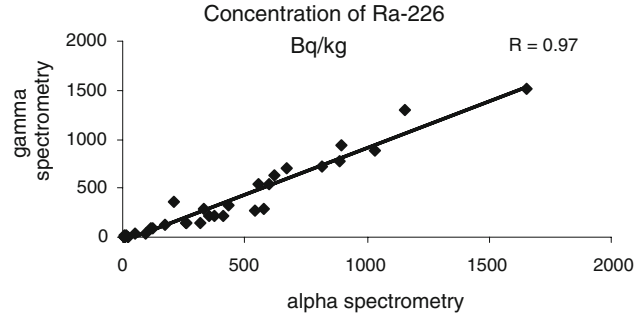

Fig. 2 Correlation among ^{226}Ra measurements by alpha spectrometry and gamma spectrometry

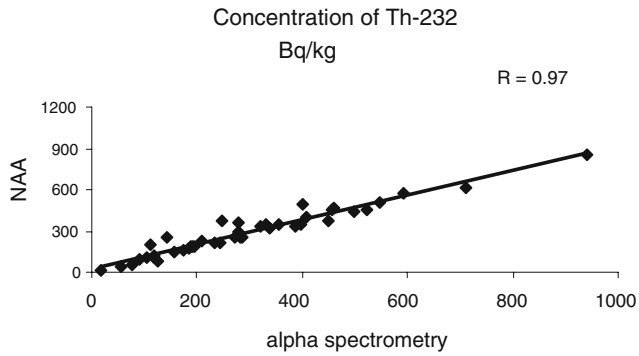

Fig. 3 Correlation among ^{232}Th measurements by alpha spectrometry and neutron activation analysis (NAA)

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, 759 Bq kg^{-1} for ^{210}Po, 457 Bq kg^{-1} for ^{232}Th and 346 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 as those found in the phosphogypsum.

While the fertilizers are commercialized, providing a dilution of their radioactivity, the phosphogypsum is stored in piles at open air, posing serious problems to the surrounding environment [10]. One of the main problems, which prevents its reutilization, is the level of impurities, including radioactivity, although it presents the same radioactivity content as the fertilizers. The results presented here for the activity concentration of radionuclides, both in fertilizers and phosphogypsum should be taken into account in decision-making on the final destination of phosphogypsum. After all, the question is: should phosphogypsum be considered a waste or a by-product? The radiological impact caused by the phosphogypsum piles in the surrounding environment is certainly more relevant than those caused by its reutilization.

Conclusions

A sequential radiochemical procedure was implemented to determine the content of radionuclides alpha emitters in samples of fertilizers and phosphogypsum produced in Brazil. The results obtained show that the levels of radioactivity present in the fertilizers are of the same order of magnitude on those found in the phosphogypsum, which raises the question of its ultimate disposal.

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