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# CARRIER-FREE SEPARATION OF $^{228}\text{Th}$ FROM $\text{BaSO}_4(^{228}\text{Ra})$

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## ABSTRACT

This paper presents a procedure for the separation of  $^{228}\text{Th}$  from  $\text{BaSO}_4(^{228}\text{Ra})$ . Reasonably great amount of this material is stocked as a result of mesothorium decontamination of rare earth chlorides from the Brazilian industrial processing plant. Thorium-228 is selectively dissolved in nitric acid leaching of a  $^{228}\text{Th}$ -free barium sulfate. Carrier-free  $^{228}\text{Th}$  is obtained using a strong anion exchanger, thorium being retained as nitrate complex and eluted with 2.4M HCl.

## INTRODUCTION

The chemical treatment for breaking up monazite sand by the alkaline process has been in practice in Brazil (São Paulo) since 1948 on an industrial scale<sup>(6)</sup>. The production capacity is about 3000 metric tons of monazite per year for the production of thorium, rare earth chlorides (2000 tons) and phosphate as the main products. Uranium is an important by-product.

Decontamination of natural radioactivity from the lanthanides is a mandatory step. Mesothorium ( $^{228}\text{Ra}$ , 5.77y) is coprecipitated with  $\text{BaSO}_4$ . A large amount (tons) of this material has been accumulated as waste and represents a potential source of natural radionuclides as  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$  and their daughters, among them  $^{220}\text{Rn}$ ,  $^{222}\text{Rn}$ ,  $^{212}\text{Pb}$ ,  $^{210}\text{Pb}$ ,  $^{212}\text{Bi}$ ,  $^{210}\text{Bi}$  and  $^{208}\text{Tl}$ .

The demand for  $^{228}\text{Th}$ ,  $^{212}\text{Pb}$ ,  $^{212}\text{Bi}$  and  $^{208}\text{Tl}$  to use them as tracers in chemical work, for sources of alpha particles, for radiochemical educational purposes and specially the procurement of a high  $\gamma$ -ray isotope ( $^{208}\text{Tl}$ ) for heavy water analysis, justify the effort of this investigation for a reliable procedure for the recovery of such radionuclides from the  $\text{BaSO}_4(\text{Ra})$  matrix.  $^{228}\text{Th}$  is a convenient source not only for  $^{208}\text{Tl}$  (3.1 min) but also for  $^{220}\text{Rn}$  (55.6 s), used as tracer for the measurement of physical properties of some solids.

Some useful applications of activation methods using photons of high energy are based on the  $(\gamma, n)$  reaction for the determination of light elements like deuterium, beryllium, carbon, oxygen and nitrogen. Induced radionuclides like sodium-24 are employed as a source of energetic  $\gamma$ -rays, but it has the disadvantage of a short half-life. The activation method for beryllium and deuterium, counting the photoneutrons of the  $(\gamma, n)$  reaction has been considered as a promising analytical technique. It requires  $\gamma$ -rays source with energy greater than 1.67 MeV for beryllium and 2.23 MeV for deuterium. The main interest is the determination of deuterium in water.  $^{208}\text{Tl}$  in secular equilibrium with  $^{228}\text{Th}$  (1.9 y) is a good source of 2.61 MeV  $\gamma$ -rays for analysis of deuterium<sup>(7)</sup>. Of the naturally occurring radioactive elements the only one giving a high energy  $\gamma$ -rays is  $^{208}\text{Tl}$  (2.61 MeV).

An interesting application of  $^{220}\text{Rn}$ , another descendant of  $^{228}\text{Th}$ , is the study of the behavior of the spherical  $\text{UO}_3$  particles during heat treatment. Thorium-228 tracer was added to the uranium solution during the fabrication of the microspheres and the gas release was measured through the leakage of  $^{220}\text{Rn}$ <sup>(3)</sup>. The same type of application is being carried out in order to study the behaviour of gaseous fission products inside sintered microspheres of  $\text{UO}_2$  coated with pyrolytic carbon at the high temperature of gas-cooled reactors (HTGR) fuel elements.

The procedure presented in this paper for  $^{228}\text{Th}$  separation is based on the principle that thorium is solubilized by concentrated nitric acid, while radium and barium are retained in the solid  $\text{BaSO}_4$  (Ra). It seems that no rapid method for leaching thorium from a quite insoluble  $\text{BaSO}_4$  (Ra) matrix, avoiding its solubilization via fusion, has been reported in the literature.

### SEPARATION OF $^{228}\text{Th}$ FROM $^{228}\text{Ra}$

Radium-228 is the first radioactive daughter of the  $^{232}\text{Th}$  decay series and it can easily be separated from thorium. The  $^{228}\text{Ra}$  content in secular equilibrium with natural is about 0.5 mg/1000 kg of thorium-232<sup>(4)</sup>. As it was mentioned above, in the industrial processing plant, the rare earth chlorides are decontaminated from radium by coprecipitation of radium with barium sulphate. Submicrogram quantities of thorium in mineralogical and biological samples are also separated by coprecipitation with barium sulfate<sup>(8)</sup>. Of the several radium isotopes of the  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  series collected on barium sulfate during the decontamination of lanthanide chlorides, the main activity is contributed by  $^{226}\text{Ra}$  (1602 y),  $^{228}\text{Ra}$  and also its descendant  $^{228}\text{Th}$ . This is the only thorium isotope that appears as decay product from these thorium isotopes.

It is known that barium sulfate as well barium and radium nitrates are insoluble in concentrated nitric acid<sup>(5)</sup> while thorium nitrate is soluble. Having this in mind, the possibility of leaching  $^{228}\text{Th}$  from  $\text{BaSO}_4$  ( $^{228}\text{Ra}$ ), without solubilization of the matrix, was considered and a very simple procedure based on nitric acid leaching of  $\text{BaSO}_4$  ( $^{228}\text{Ra}$ ) was developed.  $^{228}\text{Th}$  is recovered from the solution.

### SELECTIVE DISSOLUTION OF $^{228}\text{Th}$

The counting equipment used was a  $\gamma$ -ray spectrometer with a 512-channel analyser and a 3" x 3" NaI(Tl), well-type detector.

Experiments confirmed that thorium is selectively leached from  $\text{BaSO}_4$  (Ra) by hot concentrated nitric acid. Figures 1 and 2 show the  $\gamma$ -ray spectra of  $\text{BaSO}_4$  (Ra) and the solution, respectively. As a proof that  $^{228}\text{Ra}$  is not leached, the solution spectrum exhibits no  $^{228}\text{Ac}$  photopeaks after 24 hours. The same spectrum and the activity variation with time (firstly, the decay of some leached  $^{212}\text{Pb}$  and then its regrowing, generated from  $^{228}\text{Th}$ ) evidenced that the solution contains  $^{228}\text{Th}$ .

It was observed, however, that the barium sulfate obtained during the decontamination of rare earth chlorides contained other impurities like  $^{232}\text{Th}$  and cerium, both leached from the  $\text{BaSO}_4$  (Ra) as well. Therefore, from the first solution,  $^{228}\text{Th}$  could be easily separated from cerium but not from  $^{232}\text{Th}$ . Thus, it was required a previous treatment of  $\text{BaSO}_4$  ( $^{228}\text{Ra}$ ) with hot nitric acid to remove  $^{232}\text{Th}$ ,  $^{228}\text{Th}$  and cerium.

The growth of  $^{228}\text{Th}$  in pure  $^{228}\text{Ra}$  reaches a maximum in about five years but about 25% of the maximal activity is attained after six months<sup>(4)</sup>.

A second leach, after waiting enough time for  $^{228}\text{Th}$  regrowing and accumulation still gave a small residue after evaporation of the solution. This indicated the need of a final purification to obtain carrier-free thorium-228.

### CARRIER-FREE $^{228}\text{Th}$ PREPARATION

The purification of  $^{228}\text{Th}$  was performed using the anionic character of thorium in nitric acid solutions and its sorption on strong anionic ion exchangers since thorium is desorbed from the resin with 2.4M HCl<sup>(1,2)</sup>.

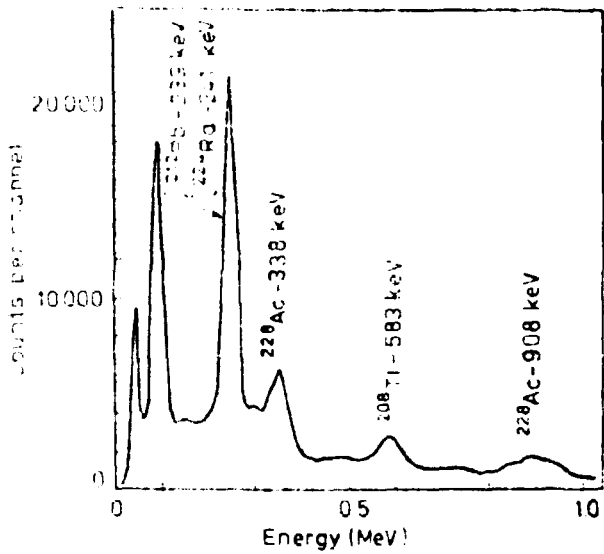


Figure 1 - Gamma-ray spectrum of  $\text{BaSO}_4(^{228}\text{Ra})$

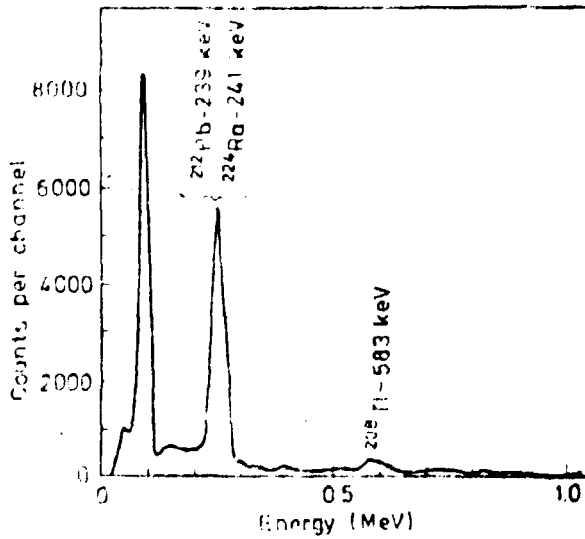


Figure 2 - Gamma-ray Spectrum of Nitric Acid Liquor from  $\text{BaSO}_4(^{228}\text{Ra})$

A set of successful experiments allows to recommend the following procedure for the preparation of carrier-free  $^{228}\text{Th}$ :

- 1) Leach  $^{232}\text{Th}$  and  $^{228}\text{Th}$  from the  $\text{BaSO}_4(\text{Ra})$  precipitate with hot concentrated nitric acid;
- 2) Wait the growing of  $^{228}\text{Th}$  in the  $\text{BaSO}_4(\text{Ra})$  precipitate (about three months);
- 3) Leach the  $^{232}\text{Th}$ -free  $\text{BaSO}_4(\text{Ra})$  with hot concentrated nitric acid;
- 4) Dilute the solution to 7-8M  $\text{HNO}_3$ ;
- 5) Percolate the solution through a strongly basic anion exchanger column (Lewatit M-500, 30-50 mesh, 3 ml of resin), previously washed with 7-8M  $\text{HNO}_3$ ;
- 6) Wash the column with 7-8M  $\text{HNO}_3$ ;
- 7) Elute the carrier-free  $^{228}\text{Th}$  with 2.4M  $\text{HCl}$ .

The residue was observed after the evaporation of this eluate. Its activity growth and the  $\gamma$ -ray spectrum showed that only carrier-free radiothorium ( $^{228}\text{Th}$ ) and its descendants were present. Figures 3 and 4 show the  $\gamma$ -ray spectra of  $^{228}\text{Th}$  immediately after eluted from the resin and after reaching radioactive equilibrium, respectively.

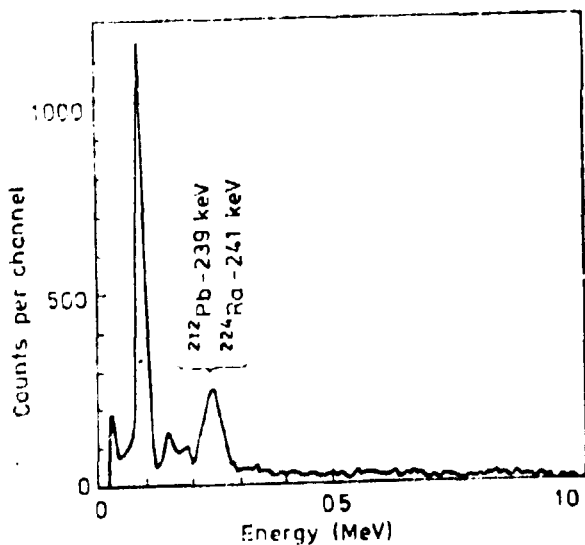


Figure 3 - Gamma-ray Spectrum of  $^{228}\text{Th}$  Immediately After Eluted from the Resin

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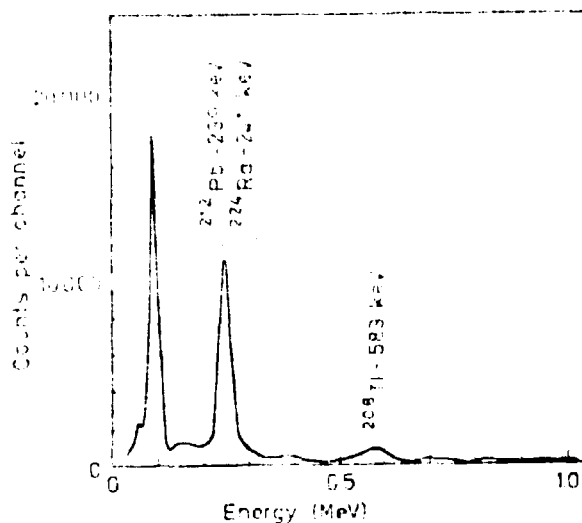


Figure 4 — Gamma-ray Spectrum of Eluted  $^{228}\text{Th}$  in Equilibrium with its Daughters

## RESUMO

Estudou-se um procedimento para a obtenção de  $^{228}\text{Th}$ , livre de carreador, a partir de  $\text{BaSO}_4(^{228}\text{Ra})$  proveniente da industrialização da monazita.

O  $^{228}\text{Th}$  é separado do sulfato de bário isento de  $^{232}\text{Th}$  por dissolução seletiva com ácido nítrico concentrado. A Purificação da lixívia nítrica por meio de uma coluna de resina aniônica forte permite a obtenção de  $^{228}\text{Th}$  livre de carreador isotópico.

## REFERENCES

1. CARSWELL, D. J. Separation of thorium and uranium nitrates by anion exchange. *J. Inorg. Nucl. Chem.*, London, **3**:384-7, 1957.
2. DANON, J. Separation of thorium and rare-earth elements in nitric acid media by anion exchange. *J. inorg. nucl. Chem.*, London, **5**:237-9, 1958.
3. FURTHMANN, R. et alii. *Investigations of the preparation of  $\text{UO}_2$  microspheres by internal gelation of a  $\text{UO}_2$  sol and from a uranium(VI) solution.* Jülich, Kernforschungsanlage, Apr. 1970. (JUL-655-RW).
4. HYDE, E. K. et alii. *The nuclear properties of the heavy elements. 2. Detailed radioactivity properties.* Englewood Cliffs, N. J., Prentice Hall, 1964.
5. KIRBY, H. W. & SALUTSKY, M. L. *The radiochemistry of radium.* Washington, National Academy of Sciences, 1964. (NAS-NS 3057).



6. KRUMHOLZ, P. & GOTTDENKER, F. The extraction of thorium and uranium from monazite. In: UNITED NATIONS, New York. *Proceedings of the international conference on the peaceful uses of atomic energy, held in Geneva, 8 August-20 August 1955, v.8: Production technology of the material used for nuclear energy.* New York, 1956. p.126-8
7. LYON JR, W. S., ed. *Guide to activation analysis.* Princeton, N. J., Van Nostrand, 1964.
8. SILL, C. W. & WILLS, C. P. Precipitation of submicrogram quantities of thorium by barium sulfate and application to fluorometric determination of thorium in mineralogical and biological samples. *Analyt. Chem.*, Easton, Pa., 36:622-30, 1964.

