CHEMICAL AND RADIOMETRIC DETERMINATION OF URANIUM AND THORIUM IN ZIRCON SANDS AND PHOSPHORITES AFTER SEPARATION BY EXTRACTION CHROMATOGRAPHY

C. TESTA, D. DESIDERI
University of Urbino, Italy

S. BAZZARRI
ENEA, CRE Casaccia, Rome

INTRODUCTION

Zircon sands, essentially composed of zircon, are materials widely used in zirconium extraction industry, in foundry sands, in refractories and ceramics [1]; phosphorites are the starting material for the industrial production of phosphoric acid, fertilisers and plasters [2].

Zircon sands and phosphorites contain sensible concentration of uranium, thorium and radium representing a potential radiation risk for the professionally exposed staff [1, 3].

The measurements by gamma spectrometry give often too high uranium contents if compared with those obtained by other methods, because the members of uranium series are not always in radioactive equilibrium with the parents [4]. Consequently it is useful to operate both by analytical and radiochemical techniques which permit the determination of the elementary thorium and uranium and also of their isotopic composition.

The aim of the present work was to find out two different methods by Extraction Chromatography [5] for the separation of uranium, thorium and radium before their radiometric determination by ZnS(Ag) alpha counting (Ra-226) and by alpha spectrometry (U, Th).

ZIRCON SANDS

100 mg of powder were dissolved as described by Sill [6]; Zr, U and Th were precipitated as hydroxides adding concentrated NH_4OH up to pH 9. The precipitate was washed twice by centrifuging with diluted NH_4OH and dissolved in 5 ml 6M HNO_3; then 10 ml water and solid NH_4NO_3 up to saturation were added. The solution was percolated through a chromatographic column consisting of 5 g 50÷100 mesh microporous polyethylene (Microthene-710) supporting 4 ml 0.5 M tri-n-octylamine (TNOA). After washing with 40 ml 10M NH_4NO_3, uranium was eluted with 60 ml 6M HNO_3 and thorium with 60 ml 8M HCl, (Fig. 1). From the fraction containing uranium, 1 ml was taken for the fluorimetric analysis [7], and from that containing thorium 10 ml were withdrawn for colorimetric analysis with Arsenazo III [8]. The remainder of the two solutions was reserved for U and Th

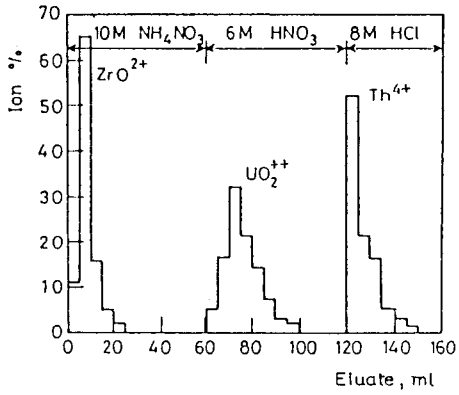

Fig. 1 - Elution diagram of zirconium, uranium and thorium by a Microthene-TNOA chromatographic column. Flow-rate: 1 ml·min^{-1}.

electrodeposition according to Talvitie [9]. Then the disks were counted by alpha spectrometry: Fig. 2 shows the alpha spectra of the isolated thorium and uranium.

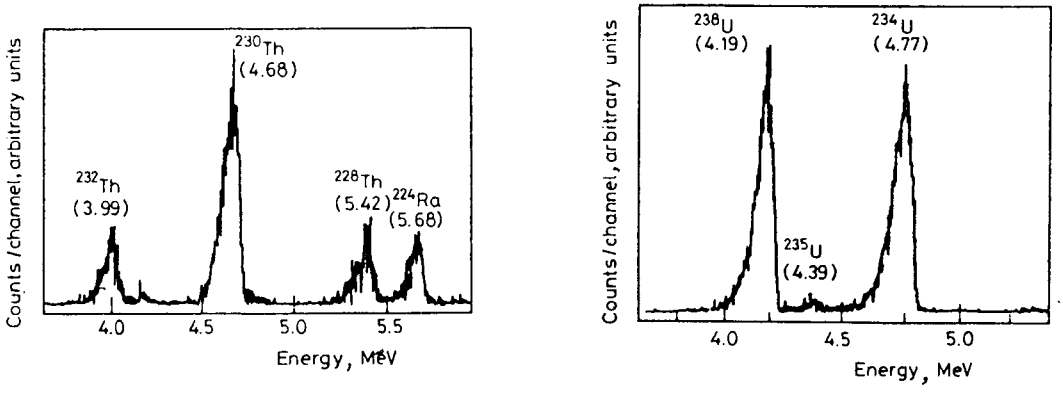

Fig. 2 - Alpha spectra of thorium and uranium isolated from a zircon sand sample.

Table I shows the results obtained for a zircon sand sample; a good agreement between the radiometric and the chemical-physical method can be derived.

Moreover these values are in good accordance with those obtained by other authors [10, 11] by radiometric techniques (0.023% for uranium and 0.017% for thorium). The alpha spectra also show that U-238 and U-234 are in secular equilibrium.

The analysis of the spectra also shows a complete decontamination of uranium from thorium and of thorium from uranium.

TABLE 1

Uranium and thorium contents obtained with radiometric and chemical-physical methods

Sample number	Th % by colorimetry	Th % by α spectrometry	U % by fluorimetry	U % by α spectrometry
1	0.022	0.018	0.021	0.025
2	0.021	0.022	0.023	0.024
3	0.016	0.016	0.023	0.025
4	0.019	0.019	0.020	0.023
5	0.016	0.017	0.024	0.022
6	0.022	0.019	0.029	0.023
Mean±σ	0.019±0.003	0.018±0.002	0.023±0.003	0.024±0.001

PHOSPHORITES AND THEIR DERIVATIVES

100 mg of phosphorite, plaster ($CaSO_4.2H_2O$), or H_3PO_4 were dissolved in 6M HNO_3; some fluorimetric measurement were carried out direclty [7]. As for as the separation of Ra-226 and uranium is concerned a chromatographic column was prepared consisting of 3 g Microthene-710 supporting 2.5 ml 0.2M Tri-n-octyl-phosphine-oxide (TOPO). Fig. 3 shows the elution diagrams for the two radio-nuclides; radium was coprecipitated [12] as $Ba(Ra)SO_4$ and counted by a ZnS(Ag) detector up to equilibrium (20 days); uranium was electroplated [9] and counted by alpha spectrometry.

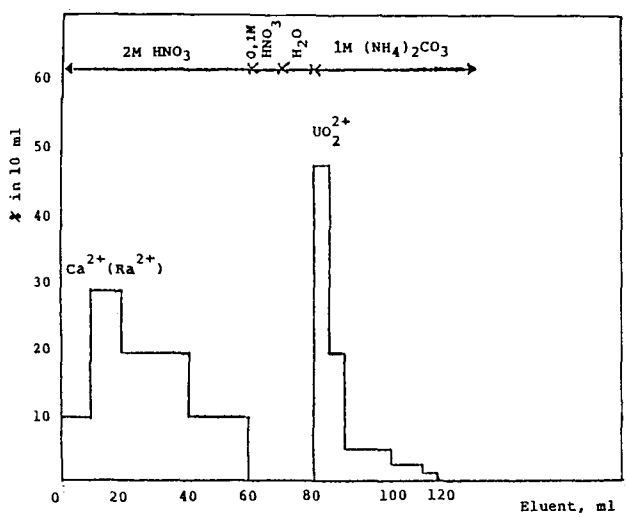

Fig. 3 - Separation Ra^{++}-UO_2^{++} in a phosphorite by a Microthene-TOPO column.

The uranium concentrations found in four different phosphorites (Morocco, Togo, Giordania, Boucraa) was respectively 0.010, 0.009, 0.006 and 0.009%; in 30% H_3PO_4 (Boucraa) the concentration was found to be 0.0045%.

The uranium concentration found by alpha spectrometry (Fig. 4) and calculated by adding a known activity of U-232 as on yield internal standard, was in good agreement with the fluorimetric results. Also in this case the uranium isotopes were found to be in a secular radioactive equilibrium.

Radium-226 concentration were found 1.22 KBq/Kg for phosphorite Morocco (σ = 0.23), 0.69 KBq/Kg for plaster Togo (σ = 0.03) and 0.35 KBq/Kg for plaster Boucraa (σ = 0,06); Radium-226 in H_3PO_4 was not detectable.

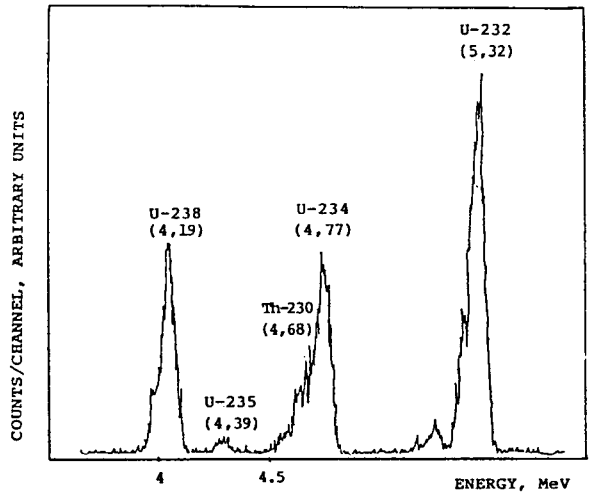

Fig. 4 - Alpha spectrum uranium isolated from a phosphorite sample.

References

1) G.F. BOOTHE et al.: Health Phys, 38 (1980), 393.
2) E.J. BOUWER and J.W. McKLEEN: Health Phys, 34 (1978), 345.
3) G. BOOTHE: Health Phys, 32 (1977), 285.
4) C.W. SILL: Health Phys, 33 (1977), 393.
5) T. BRAUN and G.GHERSINI: "Column Extraction Chromatography", Ed. Elsevier Sequoia, 1974.
6) C.W. SILL: Anal. Chem., 33 (1961), 1684.
7) F.A. CENTANNI et al.: Anal. Chem., 28 (1956), 1651.
8) S.B. SAVVIN: Talanta, 8 (1961), 673.
9) N.A. TALVITIE: Anal. Chem., 44 (1972), 280.
10) P. SPEZZANO: ENEA RT/COMB/85/1, (1985).
11) Nat. Group for Stud. Radiol. Impl. in the Use of Zircon Sand. The Science of the total Environment, 45 (1985), 135.
12) J.M. HARLEY et al.: Nucleonics, 10 (1952), 45.