

## A Simple Method for the Separation of Thorium in the Analysis of Monazite

by

Chull Lee and Koo Soon Chung

*Chemistry Division, Atomic Energy Research Institute, Seoul, Korea.*

*Department of Chemistry, Sogang University, P. O. Box 1142, Seoul, Korea.*

(Received Aug. 12, 1970)

---

### 모나자이트 분석을 위한 간편한 토륨분리법

원자력연구소 화학연구실 · 서강대학교 화학과

이 철 · 정 구 순

(1970. 8. 12. 접수)

### 요 약

모나자이트 시료종의 토륨만을 신속히 정량하기 위하여 양이온 교환지수법을 사용한 분리법을 고안하였다. 희토류 원소를 포함한 모든 공존 이온을 3N 염산으로 용출제거하고 남아있는 토륨을 5N 황산으로 용출한 다음 토린을 착색제로 사용하여 분광 광도 법을 써서 정량하였다. 방사성 동위원소 및 출광 분광법을 써서 용출된 토륨의 정량적인 회수 및 그의 화학적 순도를 확인하였다.

### ABSTRACT

A separation scheme using cation exchange procedure is designed specifically for the rapid determination of thorium in monazite samples. All the coexisting ions in monazite, including rare earth ions, are eluted with 3N hydrochloric acid. The remaining thorium is eluted from the resin column with 5N sulfuric acid prior to spectrophotometric determination with thorin reagent. The radioactive tracers and spectrographic methods were used to confirm the quantitative elution of thorium and also the chemical purity of the eluted thorium from the column.

### Introduction

In the course of radiometric determination of thorium in monazite, it was thought desirable to determine thorium by a chemical method as another independent means of checking the accuracy of radiometric procedure.

Generally, the determination of thorium in

monazite is complicated by the fact that thorium is associated not only with elements commonly encountered in rock and mineral analysis, but also with the rare earth elements, titanium, zirconium and uranium that present difficult analytical problem.

A number of gravimetric methods<sup>1-4</sup> have been used for the analysis of monazite. However those methods are likely to lead to loss of

materials since the separation of rare earth group, cerium and thorium from one another and from other elements present is made by precipitation.

Although the satisfactory use of ion-exchange resins are well established<sup>6</sup>, they do not appear to have been used for the single determination of thorium in monazite.

One of the present authors reported an analytical method for the total analysis of monazite, in which more than 30 elements were determined quantitatively after separating them into groups with cation exchange resin.

Although the ion-exchange separation developed in this method gave more satisfactory results than those achieved by precipitation, it took nearly 70 hours to elute thorium from the resin column. In the present work, the elution time of thorium has been greatly shortened with the modification of resin column and the whole procedure<sup>5)</sup> are specifically designed for the single determination of thorium in monazite.

This paper describes an analytical scheme for the separation of thorium from monazite using small scale cation exchange column. The thorium eluted from the column is determined spectrophotometrically using thorin as coloring agent.

## Experimental

**Apparatus.** The ion-exchange tube was constructed of 4 mm bore Pyrex tubing. It was constricted at its lower end, and a 5.5 cm column of the ion-exchange resin, Dowex, AG 50WX 12, 200 to 400 mesh, was supported on a glass wool plug. The flow rate of the packed column was 0.33 ml/min. The radioactivity was measured with Tracerlab Versa/matic V well type scintillation counter. A 100 channel gamma ray pulse height analyzer, TMC-102 Model, Tec-

hnical Measurement Corporation, which connected with 2'' × 2'' NaI(Tl) crystal.

A Beckman Model DU Spectrophotometer.

An Emission Spectrograph, Jarrel Ash (1.5 m), 15,000 grooves per inch.

**Reagent.** Standard thorium solution. Weigh out an appropriate amount of thorium nitrate A. R. (which has been gravimetrically standardized by ignition to oxide) to give 100 ml of solution containing 500 μg ThO<sub>2</sub>/ml.

Hydrochloric acid was twice distilled in an all-glass apparatus. Thorin solution. Dissolve 0.1 g of thorin (1-(0-arsono-phenylazo)-2-naphthol-3, 6-disulphonic acid sodium salt) in water, and dilute to 100 ml. Filter before use.

The radioactive tracer, Ce-143, La-140, Y-90, Eu-152, Sm-153 were used to check the elution pattern. They were prepared by irradiating of the individual spectrographically pure metals in the nuclear reactor and dissolving of the irradiated metals with concentrated nitric acid, which was diluted with water to contain about 10 μg each metal per ml.

The radiochemical purity of tracer solution was confirmed with gamma ray spectrometer. The cation exchange resin, Dowex, AG 50WX 12, 200 to 400 mesh, H-form, was washed with water to remove "fines", and then warm it on the boiling water bath with 3N hydrochloric acid for 1 hour to remove iron or any cations. The acid washings were repeated twice. The resin was then packed into the column and the resin column was rinsed acid-free with water.

**Procedure.** About 0.1 g of the finely ground monazite (dried at 110°C) was accurately weighed out into a platinum crucible fitted with a cover. The content was digested with 1 ml of concentrated sulfuric acid for 3 hours on a hot plate at ca. 250°C. When cool, the digested mass was quantitatively transferred with a jet of water into a 150 ml beaker containing ca.

60 ml of water. The solution was filtered into a 100ml volumetric flask through a hardened filter (Whatman No. 542) using gentle suction. The clear filtrate was diluted to 100 ml with water. A 15 ml aliquot of the solution was allowed to pass through the ion-exchange column, and the column was washed with 60 ml of 3N hydrochloric acid to remove all the coexisting cations from the column except thorium. The elution speed was regulated by applying the compressed air to the head of the column with a pump. The eluate was rejected. The thorium was eluted from the column using 25 ml of 5N sulfuric acid. The eluate was evaporated to dryness in Pyrex beaker under infra-red heater. The evaporation was continued until the fume of sulfuric acid was no longer visible. The evaporated residue was dissolved with 10 ml of 60% perchloric acid and 10ml of water, and diluted to 25ml with water.

The 5 ml aliquot of this solution and 5 ml of thorium solution were pipetted into a 25 ml volumetric flask, and thorium was determined spectrophotometrically at 547 m as described elsewhere<sup>6</sup>.

### Results and Discussion.

(1). The analytical scheme used in the present

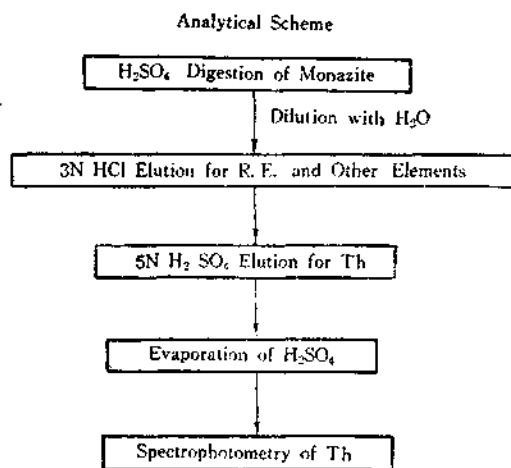


Fig. 1 Analytical Scheme

work is shown with block diagrams in Fig. 1.

At the beginning of this investigation, the elution behaviors of the coexisting cations were confirmed by counting the radioactivity of tracer in each eluate, i. e., Ce-143, La-140, Y-90, Eu-152, and Sm-153. The elution method with radioactive tracers were similar to the above procedure. The amount of each tracer added to the column was about 10 $\mu$ g. The elution results indicate, as shown in Table I, that all the cations, with the exception of thorium, were eluted with 60 ml of 3N hydrochloric acid. Thorium was quantitatively eluted from the column with 25 ml of 5N sulfuric acid solution. The

Table I. Elution of Rare Earths and Thorium with 3N HCl and 5N H<sub>2</sub>SO<sub>4</sub>

Eluent	Element	% Recovery in 10ml portions of 3N HCl								
		1	2	3	4	5	6	7	8	Total
3N HCl	La(III)	0.02	4.66	57.7	32.0	6.84	0.17	0	0	101
	Ce(III + IV)	35.4	5.33	45.5	13.6	0.2	0	0	0	100
	Y(III)	80.2	19.7	0.1	0	0	0	0	0	100
	Sm(III)	45.8	53.0	0.1	0	0	0	0	0	99
	Eu(III)	2.3	60.4	37.0	0.2	0	0	0	0	100
	Th(IV)	0	0	0	0	0	0	0	0	0
		% Recovery 5 ml portions of H <sub>2</sub> SO <sub>4</sub>								
5N H <sub>2</sub> SO <sub>4</sub>	Th(IV)	1	2	3	4	5	6	7	Total	
		66.7	23.4	7.3	2.6	0.1	0	0	99.9 $\pm$ 0.2	

leution behavior of thorium was evaluated by determining thorium content in each eluate spectrophotometrically as follows. The known amount of pure thorium as nitrate was loaded on the column and eluted with each of 5 ml portion of 5N sulfuric acid solution. (Table I). The amount of thorium eluted in each eluate was determined similarly by the colorimetric method as described above under the section of the Experimental procedure.

(2). The optimum flow rate was calculated by equating the first (doubled) term with the third in Glueckauf's equation of effective height of theoretical plate<sup>7)</sup>. Molar distribution coefficients of Th(IV) and La(III) were taken as 114 and 18.8 respectively<sup>8)</sup> for this purpose. The elution speed thus calculated and used in this experiment was 0.33ml/min.

The optimum height was also determined by multiplying the number of theoretical plate which was calculated graphically<sup>7)</sup> by the effective height of theoretical plate. The length of the actual column was 5.5cm long which was much longer than ca. 1cm that was roughly obtained by this calculation.

(3). The quantitative recoveries of thorium and other cations are confirmed as shown in Table I. In general, the elution sequence of the rare earths are known to be in the reverse order<sup>10)</sup> of the atomic number of these elements. Therefore, if Eu, Sm, Ce, La, and Y are completely eluted with 60 ml of 3N hydrochloric acid as described in Table I, it is reasonable to expect that all the rare earths are eluted in this portion. Therefore, it is unlikely that the rare earth elements will cause any interfering effect on the present method.

(4). It is known that many cations including iron, tin, uranium, alkaline earths etc., are contained in monazite. However, the distribution coefficients of these elements on the cation

exchange resin are much smaller than rare earths<sup>8)</sup> and therefore they are eluted with 3N hydrochloric acid from the resin before the rare earths. This was also confirmed by the present author in the previous work<sup>6)</sup>.

Zirconium which exists in monazite as impurity, is known to interfere in thorium-thorium complex. However, zirconium is contained in the insoluble residue from the sulfuric acid digestion of monazites. This residue, which is free of thorium, may contain a number of oxide minerals, such as rutile, quartz, magnetite and ilmenite, together with silicate minerals<sup>6)</sup>. Therefore zirconium is unlikely to interfere in the present method.

(5). In order to confirm the purity of thorium, the eluted thorium was examined with spectrograph as follows. The monazite sample was eluted by the present procedure as described above. After the elution, the following two samples were examined spectrographically, i. e., the rare earths portion of the eluate and the resins after 3N hydrochloric acid elution in which thorium were expected to remain absorbed. These two samples were evaporated to dryness under an infra-red lamp before the spectrographic examination.

The spectrographic results show that the rare earths portion of the eluate was free of thorium which was indicated by the emission spectra being devoid of thorium lines. After the elution of rare earths, the resin containing thorium was also examined with spectrograph and it was found that the eluted thorium was free from rare earth impurity.

With the above spectrographic results and with the data in Table I, it was concluded that the separation of thorium from monazite is quantitative.

(6). In the present work, the elution time for thorium has been shortened by means of a

shorter column to about 5 hours in contrast to 70 hours which were taken in the previous work<sup>6)</sup>.

Three monazite samples were analyzed for thorium content and the results in Table II show that the present scheme for the separation and spectrophotometric determination enables one to determine the thorium content with the

**Table II** Thorium Content in Monazite(%)

This Work	Radiometric Method
5.26	
5.29	5.3±0.1
5.25	
Mean 5.27±0.02	

relative standard deviation of 0.02%.

The results by radiometric analysis<sup>9)</sup> for thorium content show a good agreement with that obtained by the present method.

#### Reference

- 1) R. De Oliveira, *Anais Assoc. Brasil. Quim.*, **9**, 65 (1950)
- 2) A. E. Williams, *Chem. Eng. Mining Rev.*, **33**, 112 (1941)
- 3) W. R. Schoeller and A. R. Powell, *The Analysis of the Minerals and Ores of the Rare Elements*, London, 1955.
- 4) J. Rodden in *Standard Methods of Chemical Analysis*, ed. by N. H. Furman, vol. 1, p. 1058, D. Van Nostrand, 1962.
- 5) P. Grimaldi, *Treatise on Analytical Chemistry*, ed. by I. M. Kolthoff and P. J. Elving, p. 139. Part II, vol. 5, Interscience, 1962.
- 6) K. S. Chung and J. P. Riley, *Anal. Chim. Acta*, **28**, 1 (1963)
- 7) F. W. Helfferich, "Ion Exchange", McGraw-Hill Book Co., 1962, p. 452-461.
- 8) F. W. E. Strelow, *Anal. Chem.* **32**, 1185 (1960).
- 9) M. Sankar Das, W. I. Kim, and Ch. Lee, *Annual Report, Office of Atomic Energy, Korea*, vol. 5, No. 1, 191-217 (1968).
- 10) M. M. Woyski and R. E. Harris, *Treatise on Analytical Chemistry*, ed. by Kolthoff and Elving, p. 84, Part II, vol. 8. Interscience, 1963.