

An Improved Method for the Determination of Scandium by Neutron Activation Analysis

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(Received Jun. 3, 1964)

스칸듐정량을 위한 改良된 放射化分析法

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(1964. 6. 3 受理)

要 約

모나자이트中の 스칸듐농도를 더욱 簡便히 決定할 수 있도록 改良된 放射化分析法를 記述하였다. 即 熱中性
子束(10^{12} n/cm²/sec)에 照射된 試料에 스칸듐擔體와 黃酸을 넣고 加熱融解한 後 물로 稀釋한 試液에 암모니아水
를 加하여 稀土類元素를 沈澱分離하였다. 沈澱을 鹽酸에 녹인 다음 티오시아나이드를 넣어 스칸듐을 에테르
로 抽出하였다. 스칸듐의 化學的 回收率은 스칸듐을 만델린酸으로 沈澱시켜서 重量分析法에 依하여 決定하였다.
本分離法에 依한 스칸듐의 分離能과 共存元素의 放射能의 妨害與否는 이온交換樹脂를 使用하여 스칸듐을 分離
한 結果와 比較檢討하였다. 스칸듐의 放射能은 Gamma-scintillation spectrometry에 依하여 計測하였고 韓國産
모나자이트에는 約 12 p. p. m. 의 스칸듐이 含有되어 있음을 알았다.

Abstract

A rapid and simple method is described here for the determination of scandium in monazite by neutron activation analysis. The sample is irradiated for 20 hours at the neutron flux of 10^{12} thermal neutrons/cm²/sec in the TRIGA MARK II reactor, after which the sample is decomposed by fusion with concentrated sulfuric acid. The scandium-46 together with scandium carrier are separated from the irradiated sample by precipitating with ammonia, and are extracted by solvent extraction of the thiocyanate complex into ether. The induced radioactivity is measured by gamma scintillation spectrometry using the Multichannel Pulse Height Analyzer connected with 2' × 2' NaI(Tl). The chemical yield is determined gravimetrically by precipitating scandium with mandelic acid. In order to check the efficiency of scandium separation and the errors from interfering activities of the other elements, scandium was separated by the cation exchange resin column, and the results from both samples were compared each other, which showed that the chemical procedure used in this work was as selective as the ion-exchange method with respect to scandium separation. The scandium contents in Korean monazite were found to be about 12 p. p. m.

1. Introduction

Recently several reports^(1,2,3) have appeared on the determination of scandium by neutron activation analysis.

The chemical procedures used in these works are either time-consuming or too complicated to be used in monazite sample. This paper describes an improved method using simple chemical procedures for the

separation and determination of scandium in monazite. With extremely favorable nuclear data for scandium element, i. e., 100% isotopic abundance of scandium-45 and a relatively high activation cross section (23 barns) for thermal neutron to form Sc-46, scandium would appear to be one of the easiest element to determine by this method, however, there are a number of complications which must be confirmed by experiment. As pointed out by Smales *et al*, Sc-46 and a series of other radioactive scandium isotopes are formed by the following reactions on the other elements.

Target nuclide	Abundance of nuclide in natural element(%)	Product of irradiation	Half life	Nuclear reaction involved
Ti-46	8	Sc-46	85d	(n, p)
Ti-47	7.4	Sc-47	3.4d	(n, p)
V-50	0.25	Sc-47	3.4d	(n, α)
V-51	99.75	Sc-48	44h	(n, α)
Ti-48	73.8	Sc-48	44h	(n, α)

In this connection, they used rather too elaborate chemical procedure because of such interfering activities. It was, therefore, thought desirable to devise a somewhat simplified purification procedure. In order to avoid errors from interfering activities, ion exchange resin column was used in the present work to separate from monazite sample the rare earths including scandium. Comparison was made by irradiating an aliquot of the rare earths portion thus separated and monazite together with known quantities of scandium standard.

Activities of Sc-46 produced from 1 microgram of scandium after irradiation in a flux of 1×10^{12} thermal neutrons/cm²/sec.

After 10 hours irradiation	After 1 day irradiation	After 2 days irradiation
10×10^3	2.4×10^3	4.8×10^3
Activity, disintegrations/min. 99.9%		

2. Experimental

2.1. Reagents. Scandium carrier solution;—Weigh out accurately about 500 mg of scandium oxide, 99.9% (Wako Pure Chemical Industries, Ltd., Japan), dissolve with 10 ml of concentrated hydrochloric acid to give a clear solution and dilute with water to 100 ml in volumetric flask. 1 ml=5 mg scandium oxide.

Dilute standard scandium solution;—Dilute 0.4 ml of the above carrier solution with water and a few drops of hydrochloric acid in a 100-ml volumetric flask to give a final concentration of a approximately 20 micrograms of scandium per ml.

Mandelic acid solution;—8% solution in water.

Other chemicals used were of analytical reagent grade and were used without further purification.

2.2. Irradiation. About 0.1 g of monazite samples, in the form of finely ground powder, was accurately weighed, and duplicate quantities of dilute aqueous standard solution of scandium were sealed in polyethylene tube of 5 mm internal diameter. Sample and standard were packed side by side into the 13.5×2.8 cm plastic container, and irradiated for 20 hours in the rotary specimen rack of the TRIGA MARK II nuclear reactor, which permits irradiations at thermal neutron fluxes of about 10^{12} neutrons/cm²/sec.

2.3. Radiochemical separation. After irradiation, the samples and standards were put through a radiochemical procedure to separate scandium-46 free from interfering activities. Several radiochemical procedures for scandium separation have been described in monographs⁴⁻⁶. These methods are either too elaborate because of the very low scandium content of the samples, or not suited to the monazite analysis because the methods are mainly concerned with the separation of scandium from cyclotron bombarded metals, such as copper and titanium etc. The radiochemical methods used in the present work were largely based on the procedures of Fisher and Bock⁽⁷⁾ with regard to scandium extraction and also that of Alimarin and Shen⁽⁸⁾ for gravimetric determination of scandium using mandelic acid.

2.4. Radiochemical separation procedure.

(1) Open the Nylon Rabbit and transfer the irradiated samples into 40-ml platinum crucible. Ignite the crucible carefully on the burner in order to incinerate the paper in which the sample is enclosed. Cool, and add 5 ml of concentrated sulfuric acid and about 20 mg of inactive scandium oxide as carrier. Ignite on a Meker burner for about ten minutes to assist decomposition of samples. Cool and add water drop by drop into the crucible while warming it over an alcohol lamp until the digested samples is completely dissolved. Filter the solution into 35 ml centrifuge tube and

discard the residue. Precipitate the scandium (and other cations) by adding excess 3N-ammonia solution until the white permanent precipitates are formed, which is collected by centrifugation. Dissolve the precipitate with 3N HNO₃ and add 2 ml of saturated zirconyl nitrate reagent in order to separate phosphate ion as white precipitate. Add ammonia into the supernatant solution to precipitate the rare earths completely, (2) Centrifuge, decant and dissolve the white precipitate in dilute hydrochloric acid and repeat the precipitation and centrifugation etc once more. Evaporate the hydrochloric acid solution of the sample to a moist mass, add 60 ml of 0.5 M HCl and 53 g of ammonium thiocyanate. Adjust the volumes of the solution to 100 ml and add 100 ml of ethyl ether. Extract for 5 minutes. Separate the phases and add 5 ml of 2 M hydrochloric acid to the aqueous phase; extract again with 100 ml of ethyl ether. Evaporate the combined ether extracts after the addition of a few milliliters of hydrochloric acid. (3) Add nitric acid cautiously drop by drop at water bath temperature to destroy thiocyanate. Finally, boil the residue with a little concentrated nitric acid until the orange-red decomposition products of thiocyanic acid are destroyed. Dilute with water to about 50 ml. Centrifuge the solution and discard the residue*¹. Add 15 ml of an 8% solution of mandelic acid. After heating in a water bath for 30 minutes and cooling to room temperature, adjust the pH of the solution with hydrochloric acid between 1.8 to 2.5 to form the white scandium mandelate*². Centrifuge, discard the supernatant solution and dissolve the precipitate with concentrated ammonia into the test tube. Dilute with water to about 20 ml and neutralize with hydrochloric acid to an acid reaction with methyl orange. Count the activity with the Multichannel Pulse Height Analyzer. (4) For the chemical recovery of scandium, precipitate again scandium mandelate as described above. Warm the solution on a water bath for 30 minutes to complete the precipitation. After cooling, filter the precipitate through Toyo 5 B paper which is then ignited and

weighed in the platinum crucible. The chemical yields throughout the entire procedure were usually ca. 60% for scandium.

2.5. Measurement of radioactivity. The scandium mandelate was dissolved as described above and transferred into the test tube (1.5 × 12 cm). The gamma spectra of samples and standards were measured with the 256 multichannel pulse height analyzer connected with 2" × 2" NaI(Tl) crystals. As the half life of Sc-46 is too long to make its determination practical, the gamma spectra of both samples and standards were checked with respect to gamma energies and relative peak height as a confirmation of radiochemical purity.

2.6. Separation using ion exchange column. In order to check the errors from the interfering activities and that from the scandium separation by the proposed method, the ion exchange column was used, as an independent mean, to separate scandium. Resin and column: Strongly acidic cation exchange resin, Amberlite IR-120, cross linked with 8% divinyl benzene (52-100 mesh). The ion-exchange column used was constructed of 1.3 cm bore Pyrex tubing. It was supported on a glass wool plug. The flow rate of the packed column was 60 ± 10 ml/hour. Eluting reagents: Hydrochloric acid (1 and 3 N). Sulphuric acid (ca. 3.6 N).

Ion exchange: Allow the solution of the sulphuric acid digest from 1 g of monazite (volume ca. 400 ml) to pass through the ion-exchange column. Elute with 1970 ml of 1 N hydrochloric acid. Reject the effluent and the eluate. In this eluate, the following elements are included; aluminium, calcium, magnesium, iron, lead, titanium and uranium*³. Elute the rare earth elements from the column using 750 ml of 3 N hydrochloric acid; collect the eluate in a liter graduated flask and dilute to volume. Scandium is contained in this portion, which was proved by eluting radioactive scandium tracer through the column. The thorium remaining on the column was eluted using 800 ml of 3.6 N sulphuric acid, after which the resin column was reused.

*1. No activity was detected in the residue.

*2. The rare earth elements and thorium do not give a precipitate with mandelic acid at pH 2-3 and hence they can be separated from scandium.

*3. The conditions selected for the elution of the cations from the sulphuric acid digests of the monazites were previously reported by the author (Cf. Ref. 9).

Results and discussion

The quantitative precipitation of scandium with mandelic acid was confirmed to be satisfactory as shown in the following table.

Sc ₂ O ₃ mg		Error	
Taken	Found	mg	%
17.37	17.33	0.04	0.23
17.37	17.34	0.03	0.17
17.37	17.34	0.04	0.23

This was also proved using radioactive scandium tracer, i.e., by the absence of radioactivity in the supernatant after precipitation. Twenty samples were analyzed on scandium content, and the results are shown in Table 1. The eluted portion, the first column in Table 1, is the results obtained from the scandium sample that separated using ion-exchange column. The second column shows the results obtained from the same sample, which are determined from irradiated monazite without prior separation. The third and the fourth column are the values determined from different monazite samples without prior separation. Good agreement between the values of the first and that of second column imply sufficient proof to confirm radiochemical purity of this method with respect to scandium separation. Fig 1 shows the standard spectra, and which was compared with two other spectra of scandium, obtained respectively from irradiated monazite and from its eluted portion. Identity among three spectra was also observed, which indicates that the separation procedure are clean enough for scandium determination.

Table 1. Sc Content p.p.m. in monazite

笠 Ip Chang (Eluted portion)	笠 Ip Chang (Sand)	谷 Kok Sung (Sand)	德 Tukryong (Sand)
12.54	12.01	12.59	11.81
12.32	12.05	11.90	11.20
11.69	12.38	11.62	10.30
11.71	11.46	11.70	
	11.60		
11.8±0.4	11.9±0.3	11.9±0.4	10.8±0.3

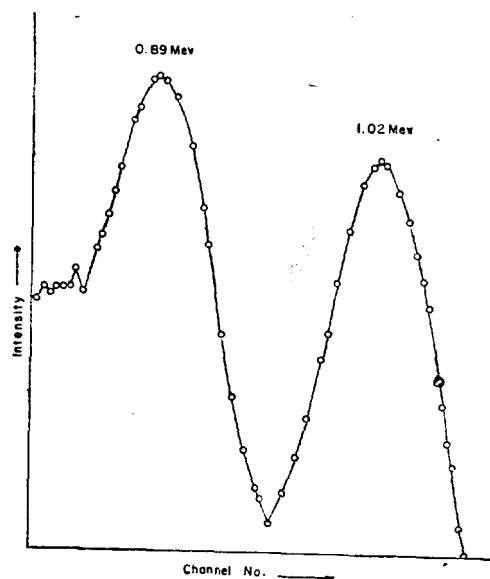


Fig 1. Gamma ray spectrum of a standard scandium-46, measured with a 2 × 2 inch NaI(Tl) crystal connected with 256 channel pulse height analyzer.

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