

## Ti, Zr 및 Nb 의 원통크로마토그래프 분리

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(1972, 12, 26 접수)

## Column Chromatographic Separation of Titanium, Zirconium and Niobium

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(Received Dec. 26, 1972)

요 약.  $\alpha$ -HIBA 물 용리제로한 양이온 교환 수지층을 사용하여 철, 코발트, 니켈, 이트륨 및 희토류 원소와 같은 여러가지 금속의 공존이온으로부터 티탄, 니오브 및 지르코늄을 함께 분리하는 방법을 발전시켰다. 본 연구의 결과 르코늄의 꼬리끌기현상은 용리전에 행한 수산화침전에 기인하고 있음을 알았다. 예를 들면 지르코늄을 수산화나트륨으로 침전시킬 때 다른 지자들의 보고와는 달리 지르코늄은 심한 꼬리끌기현상을 나타낼수 있었다. 본 연구에서는 이러한 꼬리끌기현상을 없애고 또한 이 이온들을 함께 분리하기 위한 목적으로 이온교환법을 적용하였다. 본 방법을 사용한 결과 조사된 지르코늄으로부터 생성된  $^{90m}\text{Y}$ 와  $^{90}\text{Y}$ 을 방사화학적 순도로 분리할 수 있었다.

**Abstract.** A method was developed for the separation of titanium, niobium and zirconium together in a group from the coexisting ions of various metals such as iron, cobalt, nickel, yttrium and rare earths by means of the cation exchange column using  $\alpha$ -hydroxyisobutyric acid as the eluent.

In the course of the present investigation, it was found that the tailing phenomena of zirconium were attributable to the hydroxide precipitation which was made prior to the elution. For example, if zirconium was precipitated by sodium hydroxide, the tailing of zirconium became very serious in contrast to the results reported by others. This paper describes how these tailing phenomena of zirconium were prevented and how a practical procedure for the separation of these ions was achieved using ion-exchange method. Using the present method the nuclides of  $^{90m}\text{Y}$  and  $^{90}\text{Y}$  were separated with radiochemical purity from the irradiated zirconium.

### 1. Introduction

In the course of determinations of titanium, zirconium and niobium by fast neutron activation analysis, it was necessary to separate some product nuclides from the coexisting ions<sup>1-3</sup>. For this purpose, an attempt was made to

develop an ion exchange method using  $\alpha$ -hydroxy isobutyric acid as eluent. In this connection, Perdue et al.<sup>4</sup> have reported that after the hydroxide precipitation of titanium, niobium and zirconium, these metal ions have been eluted rapidly from the ion exchange column with 0.5 M  $\alpha$ -hydroxyisobutyric acid ( $\alpha$ -HIBA) solution at pH 1.80 giving the quantitative

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separation from rare earths and other elements. Contrary to this report, however, when this procedure was applied, the present authors were never able to reproduce the clear separation of zirconium and found that zirconium tailing became very serious and that the tailing activities of  $^{97}\text{Zr}$  from the column were still high enough to interfere with the subsequent elution of  $^{47}\text{Sc}$  and  $^{90\text{m}+90}\text{Y}$ . These phenomena of tailing appear to be attributable to the hydroxide precipitation of zirconium which is made prior to the elution. This was proved to be the case, *i. e.*, when the zirconium was directly loaded on the column without prior hydroxide precipitation, it was found that zirconium was eluted quantitatively without any tailing.

It was also found that even after the hydroxide precipitation, however, the quantitative elution of zirconium, without tailing, could be achieved if the  $\alpha$ -HIBA solution of zirconium was irradiated in a thermal neutron flux for about 10 min. Using the present method the nuclides of  $^{90\text{m}}\text{Y}$  and  $^{90}\text{Y}$  were separated with radiochemical purity from the irradiated zirconium.

Aqueous solutions containing the ions of these metals were passed through a column containing Dowex 50 cation exchange resin. The column was eluted with  $\alpha$ -HIBA by which these metal ions were separated together in a group from the coexisting metals, such as scandium, yttrium, rare earths, iron, cobalt and nickel.

## 2. Experimental

**2.1. Apparatus.** The column for the  $\alpha$ -HIBA system was 6 mm-i. d. glass tube, stuffed at the tip with glass wool and filled with resin bed of 14 cm length, with a reservoir above the resin holding approximately 20 ml volume. During the elution an air compressor was applied to maintain the elution rate to 0.3 ml

per min., The eluate in fraction of 24 drops (1 ml) was taken into the test tube by means of a fraction collector. A well type NaI(Tl) scintillation counter was used to count  $\gamma$ -rays of each test tube. Gamma ray spectra from 3'' $\times$ 3'' NaI(Tl) crystal, connected with 400 channel analyzer, were used to determine the purity of sample at various stages.

**2.2. Reagents.** Dowex 50 $\times$ 8 (200-400 mesh, H form) cation exchange resin was used without further purification. The G. R. grade reagent was used to prepare the aqueous solution of  $\alpha$ -HIBA with various concentrations. pH was adjusted with 6 N  $\text{NH}_4\text{OH}$  using Beckman Zeromatic pH meter.

**2.3. Elution procedure, with hydroxide precipitation after irradiation.** 50 mg of specpure titanium, zirconium and niobium metals were each weighed and sealed separately into a polyethylene vial of ca. 1 ml capacity and were irradiated in the pneumatic tube of TRIGA MARK II for 1 hour. During the irradiation  $^{46+47+48}\text{Sc}$  and  $^{90\text{m}+90}\text{Y}$  were produced from Ti and Zr-Nb by fast neutron, respectively.  $^{97}\text{Zr}$ - $^{97}\text{Nb}$  nuclides were also produced by ( $n, \gamma$ ) reaction on zirconium. These metals were each dissolved in platinum crucible with 3 ml of concentrated nitric acid and a few drops of concentrated hydrofluoric acid. The excess acid was evaporated by heating on a hot plate. The solutions were diluted with water to 10 ml (5 mg of metal per ml) and used as the irradiated stock solutions. Two ml of this solution were taken into centrifuge tube and precipitated by adding 6 N NaOH. The filtrate was discarded. Each precipitate was dissolved with 2 ml of concentrated hydrochloric acid. The reprecipitation was made at pH 8 by adding 6 N ammonium hydroxide solution. The precipitate was centrifuged, washed once with slightly basic water, centrifuged again and then disso-

ived by adding 5-6 drops of concentrated  $\text{HNO}_3$ . Each solution was transferred to resin bed with 2 ml of  $\alpha$ -HIBA solution (pH 1.8). The elution was made at pH 1.8 with 0.5 M  $\alpha$ -HIBA solutions and 1 ml each of the eluate was collected into the test tube by the fraction collector. Each tube was counted for  $\gamma$ -activity with a well type scintillation counter and plotted the no. of counts *vs.* the eluate volumes. The curve 1 of Fig. 1 shows the elution pattern of zirconium.

**2.4. Elution procedure, without hydroxide precipitation.** One ml each of the irradiated stock solution, which was prepared as described above under the section of 2-3, was transferred directly to the column without hydroxide precipitation. The elution was made at pH 1.8 with 0.5 M  $\alpha$ -HIBA solutions and the elution curve, the curve II in Fig. 1, was obtained in a similar manner.

**2.5. Elution procedure, with hydroxide precipitation before irradiation.** 50 mg of zirconium were digested and dissolved with 3 ml of concentrated nitric acid and a few drops of concentrated hydrofluoric acid. The excess acid was expelled by heating on a hot plate. The solution was transferred into centrifuge tube and precipitated with 6 N sodium hydroxide.

The reprecipitation was made as described above and the washed precipitate was dissolved with 5-6 drops of concentrated nitric acid, and the solution was diluted into a 10 ml volumetric flask with 0.5 M  $\alpha$ -HIBA (pH 1.8).

One ml of this solution was pipetted into a polyethylene tube of 2 ml capacity. The vial was then irradiated for one hour in the pneumatic tube of TRIGA MARK II. One ml of the irradiated solution was pipetted and transferred to the resin bed which was previously equilibrated with 0.5 M  $\alpha$ -HIBA (pH 1.8). The elution was made at pH 1.8 with 0.5 M  $\alpha$ -HIBA and the elution curve III (Fig. 1) was similarly obtained.

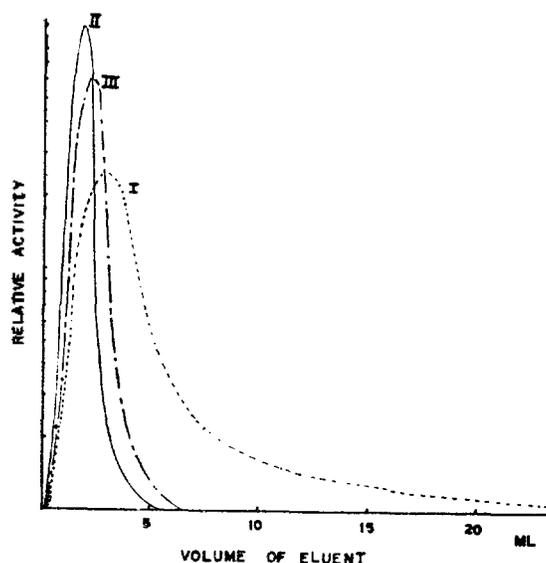


Fig. 1. Elution curves of zirconium  
 curve I: With hydroxide precipitation after irradiation  
 curve II: Without hydroxide precipitation  
 curve III: With hydroxide precipitation before irradiation

### 3. Results and Discussion.

The elution behaviors of zirconium at different experimental conditions, which are described above, are shown in Table 1 and Fig. 1. At these conditions, both titanium and niobium were always eluted quantitatively with 6 ml of the eluting agent. This was confirmed by the radioactivities which were induced from the

Table 1. The recoveries (%) of Zr, Ti and Nb in 6 ml eluate of 0.5 M  $\alpha$ -HIBA (pH 1.8)

Ele-	With hydroxide precipitation after irradiation	Without hydroxide precipitation	With hydroxide precipitation before irradiation
Zr	80	99.9	99.9
Nb	99.9	99.9	99.9
Ti	99.9	99.9	99.9

( $n, \gamma$ ) reactions by reirradiating each eluate for about 1 minute. The complete elution of these two metals is in accordance with the previous report<sup>4</sup>.

When the hydroxide precipitation was made after the irradiation, according to the procedure by Perdue et al.<sup>4</sup>, the present authors found that the elution of zirconium was not quantitative as the tailing of zirconium became serious, *i. e.*, when the column was eluted with 15 ml of 0.5 M  $\alpha$ -HIBA (pH 1.8), the zirconium recovery was ca. 90% and the tailings were continued as shown on the curve I of Fig. 1. In order to rectify the tailing, the following attempts were made without success. When the 0.5 M  $\alpha$ -HIBA solution of zirconium was overnighted or heated on a boiling water bath for 1 hour after the hydroxide precipitation the recoveries were not improved and the tailings were still continued. When the elution was made with 0.5 M  $\alpha$ -HIBA at higher pH, the tailings were more serious. When the column was eluted at the lower pH solution (pH 1.0) the recovery was still not improved. In contrast with the results obtained by Perdue et al., the tailings of zirconium were always observed at all these conditions.

However, when the zirconium solution was directly loaded on the column without hydroxide precipitation, the elution of zirconium was completed in 6 ml portions of eluate as shown in Fig. 1 and <sup>97</sup>Zr was not detected in the succeeding portions of the eluate.

It is interesting to observe that even after hydroxide precipitation, the quantitative recovery of zirconium was also obtained if the precipitation was made prior to the irradiation, *i. e.*, when the zirconium solution of 0.5 M  $\alpha$ -HIBA (pH 1.8) which was prepared after the hydroxide precipitation, was irradiated, the zirconium was quantitatively eluted with 6 ml

Table 2. Irradiation effect of Zr

Irradiation time	Recovery (%)
0	80
5 minutes	95
10 "	99.9
30 "	99.9

of the eluate. In order to confirm this, the experiments were carefully repeated several times as shown in Table 2. The results indicate that when the solution is irradiated for about 5 minutes the recovery of 95 % is obtained. If the irradiation time is extended to about 10 minutes, the complete recovery of zirconium is obtained. These results show that if the certain species of zirconium are once formed, which are not elutable with  $\alpha$ -HIBA, it is difficult to transform the species into the elutable form by ordinary chemical treatments. When, however, the  $\alpha$ -HIBA solution of zirconium, which was prepared after hydroxide precipitation, was irradiated in the reactor for more than 10 minutes the zirconium are transformed into the elutable form. These phenomena, which appear to be a kind of irradiation effect on zirconium elution, seem rather an interesting observation. The present authors have been able to reach no definite conclusions as to the exact nature of the eluted species of zirconium which were formed by the irradiation.

It was confirmed with tracer work that Fe, Ni, Co, Ce and Y were not eluted until 15 ml of eluates of 0.5 M  $\alpha$ -HIBA. These results are in accordance with the previous report<sup>4</sup>. In order to confirm the validity of the present method, the proposed procedure was applied to an irradiated solution of zirconium containing ions of <sup>97</sup>Zr-<sup>97</sup>Nb and <sup>90m+90</sup>Y and the following results were obtained.

After eluting <sup>97</sup>Zr-<sup>97</sup>Nb through the column

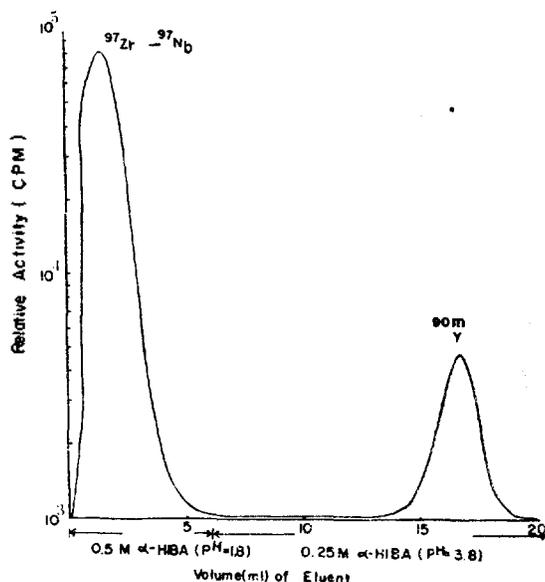


Fig. 2. Separation of  $^{90m}\text{Y}$  from irradiated Zirconium.

with 6 ml of 0.5 M  $\alpha$ -HIBA at pH 1.8, the remaining yttrium was eluted with 0.25 M  $\alpha$ -HIBA at pH 3.8<sup>5</sup>. The elution curve of Fig. 2 was obtained similarly as described above under the section of 2-3. The radiochemical purity of  $^{90m}\text{Y}$  was also confirmed by  $\gamma$ -ray spectra and half-life determination. The results of the present investigation suggest that the proposed method may be conveniently utilized especially in the field of radiochemistry where  $^{90m+90}\text{Y}$  and  $^{97}\text{Zr}$ - $^{97}\text{Nb}$  are to be separated from the irradiated zirconium. The present authors have successfully applied the proposed method for the separation of these metals in order to determine fission neutron cross section for the

following nuclear reactions,  $^{90}\text{Zr}(n, p)^{90}\text{Y}$  and  $^{90}\text{Zr}(n, p)^{90m}\text{Y}$ . The detailed accounts of these works will be published.

#### 4. Conclusion

The metal ions of titanium, zirconium and niobium have been eluted together in a group with 0.5 M  $\alpha$ -hydroxyisobutyric acid solution at pH 1.80 giving the quantitative separation from rare earths and other elements. If the hydroxide precipitation of zirconium is made, zirconium showed extensive tailing during the elution.

Even after the hydroxide precipitation, however, the quantitative elution of zirconium, without tailing, could be achieved if the  $\alpha$ -HIBA solution of zirconium, which was prepared after the hydroxide precipitation, was irradiated in a thermal neutron flux for about 10 minutes.

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