

원자로 중성자에 의한 티탄, 지르코늄 및 니오브의 동시 정량

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Simultaneous Determination of Titanium, Zirconium and Niobium by Reactor Neutron Activation

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요 약. 핵분열 중성자에 의한 $^{47}\text{Ti}(n, p)^{47}\text{Sc}$ 및 $^{93}\text{Nb}(n, \alpha)^{90\text{m}}\text{Y}$ 의 반응과 열의 중성자에 의한 $^{96}\text{Zr}(n, \gamma)^{97}\text{Zr}$ 반응을 사용하여 합성혼합시료중에 함유된 티탄, 니오브 및 지르코늄을 동시 정량하였다. 그러기 위해서 시료용액을 중성자로 조사하기 전에 Dowex 50×8의 양이온 교환수지통에 가한 다음 0.5 M α -히드록시 이소부티르산(α -HIBA)을 용출제로 사용하여 티탄, 니오브 및 지르코늄을 함께 분리하였다.

중성자로 조사한 후에 생성된 핵종인 ^{97}Zr , ^{47}Sc 및 $^{90\text{m}}\text{Y}$ 을 같은 수지통을 통하여 0.5 M α -HIBA, 0.5 M α -HIBA-1 N HNO_3 및 0.5 M α -HIBA-2 N HNO_3 용액으로 용출함으로써 각각 차례대로 분리하였다. 감마선 분광법을 사용하여 용출된 핵종의 감마선 방사능을 측정하였다. 본 방법을 사용한 니오브, 티탄 및 지르코늄의 검출한계는 각각 0.2 %, 0.01 % 및 0.002 % 이었다.

Abstract. The fission neutron reactions of $^{47}\text{Ti}(n, p)^{47}\text{Sc}$ and $^{93}\text{Nb}(n, \alpha)^{90\text{m}}\text{Y}$, along with episcadmium neutron reaction of $^{96}\text{Zr}(n, \gamma)^{97}\text{Zr}$ were used for the simultaneous determination of Ti, Nb and Zr in synthetic mixture. Prior to neutron irradiation, Ti, Zr and Nb in the mixture were separated together in one group through the cation exchange column of Dowex 50×8 resin using 0.5 M α -hydroxy-*iso*-butyric acid as the eluent. After irradiation of the eluate the product nuclides, ^{97}Zr , ^{47}Sc and $^{90\text{m}}\text{Y}$, were eluted sequentially through the same column with 0.5 M α -HIBA, 0.5 M α -HIBA-1 N HNO_3 and 0.5 M α -HIBA-2 N HNO_3 solution, respectively. The gamma-ray spectrometry was used for the measurement of the gamma-ray activities of the eluted nuclides. The detection limits of Nb, Ti and Zr were found to be 0.2 %, 0.01 % and 0.002 %, respectively.

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1. Introduction

Several studies¹⁻³ have been reported on the determination of titanium and niobium by activation analysis technique. In most cases the short-lived radionuclides formed by the (n, γ) reaction are used for the determination of these elements. A major difficulty in the use of short-lived nuclides is that the induced activity decays rapidly with time, the energy of the γ -rays associated with the decay of the nuclides is low, and therefore subjects to serious interference from other nuclides in the sample.

Brooksbank, Leddicotte and Dean⁴ determined titanium in aluminum-based alloys with the reactions of $^{46}\text{Ti}(n, p)^{46}\text{Sc}$ and $^{48}\text{Ti}(n, p)^{48}\text{Sc}$. Gruverman and Henninger⁵ applied the reaction $^{48}\text{Ti}(n, p)^{48}\text{Sc}$ to determine high concentrations of titanium in corrosion residues. Athavale *et al.*⁶ reported the fast neutron activation analysis of titanium and niobium with $^{47}\text{Ti}(n, p)^{47}\text{Sc}$ and $^{93}\text{Nb}(n, \alpha)^{90\text{m}}\text{Y}$ reactions. In order to determine titanium and niobium, they measured the γ - and β -activities for ^{47}Sc and ^{90}Y , respectively. In their study, two different methods were required for the mutual separation of these two nuclides.

In the recent paper the present authors have shown the possibility of using $^{93}\text{Nb}(n, \alpha)^{90\text{m}}\text{Y}$ reaction for the determination of Nb⁷. This

possibility was explored in the present study for the simultaneous determination of titanium, niobium and zirconium using $^{47}\text{Ti}(n, p)^{47}\text{Sc}$, $^{93}\text{Nb}(n, \alpha)^{90\text{m}}\text{Y}$, $^{96}\text{Zr}(n, \gamma)^{97}\text{Zr}$ and $^{90}\text{Zr}(n, p)^{90\text{m}}\text{Y}$. In this work only the measurement of the gamma activity is required for the determination of these three elements, therefore the present method is simpler than the method by Athavale which required both γ and β counting for the determination of titanium and niobium.

2. Feasibility of the Method

The data relevant to the present study are given in Table 1. The nuclear reactions which produce short-lived nuclides are not listed as they are not utilized in the present work.

The yields from these reactions after irradiation of 1 mg of the elements for 1 hour at a fission flux of 7×10^{11} n per cm^2 per second are given in the fifth column of Table 1. As can be seen from this table, the yields are high enough to be of interest in activation analysis. The flux value is monitored by $^{58}\text{Ni}(n, p)^{58}\text{Co}$, with an assumed average fission cross section of 93 mb⁸. The application of ^{47}Sc , $^{90\text{m}}\text{Y}$ and ^{97}Zr - ^{97}Nb for the analysis of titanium, niobium and zirconium are described here.

3. Experiment

3.1. Reagents and Apparatus. Scandium

Table 1. Threshold nuclear reactions in fast neutron activation analysis
fission flux= 7×10^{11} n per cm^2 per sec. Irradiation time=1 hour

Element	Reaction	Average fission neutron cross section (mb)	Half-life	Yield(d per min. per mg.)	Radiation (MeV)
Ti	$^{47}\text{Ti}(n, p)^{47}\text{Sc}$	20	3.4 days	6.0×10^3	γ : 0.155
Nb	$^{93}\text{Nb}(n, \alpha)^{90\text{m}}\text{Y}$	0.018	3.1 hours	1.4×10^3	γ : 0.202 0.482
	$^{93}\text{Nb}(n, \alpha)^{90\text{m}}\text{Y}$	0.14	64 hours	4.2×10^2	β : 2.27
Zr	$^{96}\text{Zr}(n, \gamma)^{97}\text{Zr}$	0.033	3.1 hours	1.2×10^3	γ : 0.202 0.482
	$^{90}\text{Zr}(n, p)^{90\text{m}}\text{Y}$	0.83	64 hours	1.2×10^3	β : 2.27

and yttrium carrier solutions; About 30 mg each of scandium oxide(99.9%) and specpure yttrium oxide were dissolved separately in 2 ml of concentrated nitric acid and diluted to 25 ml (1 mg of oxide per 1 ml). Lanthanum carrier solution; 250 mg of lanthanum oxide was dissolved in 3 ml of concentrated nitric acid and diluted to 25 ml(10.0 mg La_2O_3 per ml).

One *N* nitric acid—0.5 *M* α -HIBA and 2 *N* nitric acid—0.5 *M* α -HIBA solutions; 25.0 g of α -HIBA, G. R., were weighed, dissolved in distilled water and diluted to 100 ml(2.4 *M* α -HIBA). Two 40 ml aliquots of α -HIBA solutions were each mixed with 7 ml and 14 ml of concentrated nitric acid and diluted to 100 ml with distilled water, respectively. The synthetic mixture solution was prepared by digesting and dissolving the solid mixture (ca. 50 mg of total metal per ml). The cation exchange column of Dowex 50 \times 8 resin(14 cm \times 6 mm dia., 200~400 mesh, H^+ form) were used.

3.2. Irradiation. 20 mg each of specpure titanium, niobium and zirconium metals were weighed and sealed in polyethylene vial. Each metal was wrapped in 0.8 mm thick cadmium foil along with nickel monitor. One ml of the synthetic mixture solution, wrapped with cadmium foil was irradiated for 1 hour in the pneumatic tube of TRIGA MARK II reactor. The samples were cooled for 30 minutes before they were processed to separate scandium and yttrium.

3.3. Chemical Separation of Scandium and Yttrium. Because of low activities of ^{47}Sc and $^{90\text{m}}\text{Y}$, these two elements were separated from the synthetic mixture after irradiation. The successive separation of scandium and yttrium is difficult when using α -HIBA system through a cation exchange column because a band is formed due to scandium precipitation⁹.

In the present study the separation of these two elements was achieved with the α -HIBA- HNO_3 system using radioactive tracers of scandium and yttrium as follows.

The radioactive tracer solutions of ^{46}Sc and $^{90+90\text{m}}\text{Y}$ were prepared by irradiating the carrier solutions in the pneumatic tube for 5 minutes. 0.5 ml of this solution were loaded on the cation exchange column which was pre-equilibrated with 5 ml of 0.5 *M* α -HIBA solution (pH 1.8). The column was then eluted sequentially with 6 ml of 0.5 *M* α -HIBA, 15 ml of 1 *N* nitric acid—0.5 *M* α -HIBA and 30 ml of 2 *N* nitric acid—0.5 *M* α -HIBA solutions. The eluates were collected in 1 ml by means of a fraction collector. Each test tube was counted for the γ -activity with a well type scintillation counter. The elution curve was drawn for the activities vs. the volume of eluate as shown in Fig. 1, which indicates that scandium and yttrium were not eluted until 10 ml eluates of 0.5 *M* α -HIBA (pH 1.8). The sequential elution of scandium and yttrium was achieved by eluting with 1 *N* nitric acid—0.5 *M* α -HIBA

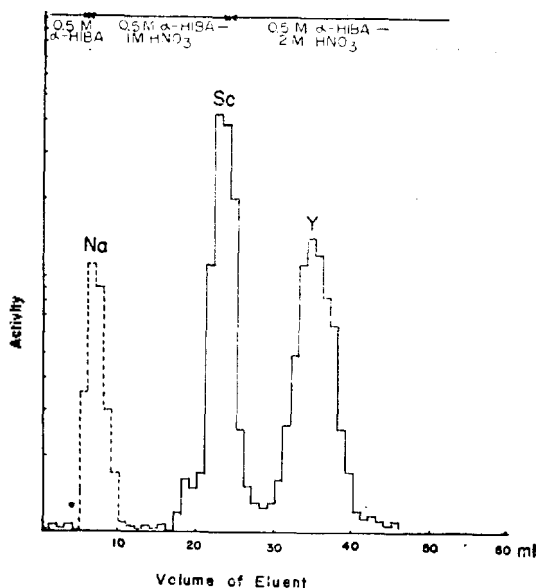


Fig. 1 Elution curve of Sc and Y

and 2 *N* nitric acid—0.5 *M* α -HIBA solutions. The yield was found to be quantitative for both elements eluted.

3.4. Standardization. Twenty mg each of titanium, niobium and zirconium metal were irradiated along with nickel monitor as described under the section of "Irradiation." The irradiated metals were each transferred into a platinum crucible of 50 ml capacity and dissolved by treating with 2 ml of conc. nitric acid and a few drops of concentrated hydrofluoric acid. One hundred λ of yttrium carrier solution (ca. 0.1 mg of Y) were added to each of the irradiated solutions of niobium and zirconium. One hundred λ of scandium solution (ca. 0.1 mg of Sc) were added to the irradiated solution of titanium.

The solution was heated on a hot plate to evaporate the excess acid. Each solution was quantitatively transferred from the platinum crucible into 10 ml volumetric flask and diluted to the volume with distilled water. One ml each of the irradiated solution of titanium, niobium and zirconium was loaded on three separate columns of the Dowex 50 \times 8 resin (14 cm \times 6mm dia., 200~400 mesh, H⁺ form), which were previously equilibrated with 5 ml of 0.5 *M* α -HIBA (pH 1.8). Each column was eluted with 6 ml of 0.5 *M* α -HIBA (pH 1.8) in order to elute titanium, niobium and zirconium, respectively¹⁰. The 6 ml eluates from both columns, each containing titanium and niobium respectively, were discarded, whereas the eluate from the zirconium column containing ⁹⁷Zr was collected into 25 ml of volumetric flask and diluted with distilled water to the volume. The activity of ⁹⁷Zr-⁹⁷Nb was counted for the photo-peak area of 0.663 \pm 0.75 Mev. γ -rays after 1 day's cooling. The results are in good agreement with the one previously reported¹⁰, i.e., niobium, zirconium, and titanium were quantitatively eluted through the

column with 6 ml eluent of 0.5 *M* α -HIBA (pH 1.8).

The remaining scandium was eluted from the titanium column by eluting with 20 ml of 0.25 *M* α -HIBA (pH 1.8). Yttrium was eluted in similar manner from both niobium and zirconium columns. The flow rate was always adjusted to 0.3 ml per minute. The eluate in fraction of 1 ml was taken into the test tube by means of a fraction collector. The activity of each tube was measured for 1 minute with a well type scintillation counter and was plotted against the number of the test tube.

The scandium portions of the eluate from the titanium column were collected into 50 ml beaker. The two yttrium eluates each from the latter two columns were collected similarly. Two ml of the La³⁺ carrier solution (10 mg of La₂O₃ per ml) were added to all the eluates. Scandium and yttrium ions were coprecipitated with lanthanum at pH 4~5 after the addition of 2 ml of saturated oxalic acid solution. Each precipitate was filtered through a demountable glass filter containing a Whatman No. 42 paper, washed with water and finally with acetone. Each paper containing the oxalate precipitate was removed, dried under an infrared lamp and mounted on a 1/32 inch thick aluminum plate with Scotch tape. Each sample was counted for 1 hour with 3'' \times 3'' NaI(Tl) crystal coupled with 400 channel analyzer. After counting, the yield corrections were made by igniting and weighing as lanthanum oxides.

The γ -activities of ⁴⁷Sc, ^{90m}Y and ⁹⁷Zr-⁹⁷Nb were each corrected for the flux differences with the ⁵⁸Co activities of nickel monitor⁷. The photo-peak areas obtained for the characteristic γ -rays are shown in Table 2.

3.5. Simultaneous Determination of Titanium, Niobium and Zirconium in Synthetic Mixture. One ml of the synthetic sample solution (50 mg of total metal per ml) was

Table 2. Standardization

Target	Reaction	Isotope produced	cpm/mg	Cooling time	Radiation (MeV)
Ti	$^{47}\text{Ti}(n, p)^{47}\text{Sc}$	^{47}Sc	714 ± 20	25 hours	$\gamma: 0.155$
Nb	$^{92}\text{Nb}(n, \alpha)^{89\text{m}}\text{Y}$	$^{90\text{m}}\text{Y}$	95.2 ± 5	3.2 hours	$\gamma: 0.202$
Zr	$^{90}\text{Zr}(n, p)^{90\text{m}}\text{Y}$	$^{90\text{m}}\text{Y}$	102 ± 7	3.2 hours	$\gamma: 0.202$
Zr	$^{96}\text{Zr}(n, \gamma)^{97}\text{Zr}$	$^{97}\text{Zr}-^{97}\text{Nb}$	$9,525 \pm 85$	24 hours	$\gamma: 0.663$ 0.75

The ratio of the photo-peak area of $^{97}\text{Zr}-^{97}\text{Nb}$ to $^{90\text{m}}\text{Y}$ (obtained from zirconium) = $9,525 \pm 85 / 10 \pm 7 = 9.30 \pm 0.74$

loaded on the cation column which was pre-equilibrated with 5 ml of 0.5 M α -HIBA (pH 1.8). The column was eluted with 6 ml of 0.5 M α -HIBA (pH 1.8) for the separation of titanium, niobium and zirconium in one group. The eluate was diluted to 10 ml. Two ml of the eluate were taken into a polyethylene vial of 2.5 ml capacity. The vial which was wrapped with cadmium foil was irradiated for 1 hour along with the nickel monitor.

After irradiation 2 ml of the mixture solution were loaded on a cation column. The column was eluted with 6 ml of 0.5 M α -HIBA (pH 1.8) for the matrix element¹⁰. The column was further eluted with 15 ml of 1 M nitric acid-0.5 M α -HIBA and 30 ml of 2 N nitric acid-0.5 M α -HIBA solution for the separation of scandium and yttrium as described above. One ml portions of the eluate were successively collected into a test tube by means of a fraction collector. Each tube was counted with a well type scintillation counter and the activities were plotted vs. volumes of the eluate. An elution curve was obtained as shown in Fig. 2.

The eluates with 0.5 M α -HIBA containing $^{97}\text{Zr}-^{97}\text{Nb}$ were collected into a 25 ml volumetric flask and counted for the γ -activities with multichannel analyzer. Each eluate containing scandium and yttrium respectively was collected into a 100 ml beaker. Two ml of La^{3+} carrier solution were added to both beakers and pH was adjusted to about 3 with 6 N ammonium

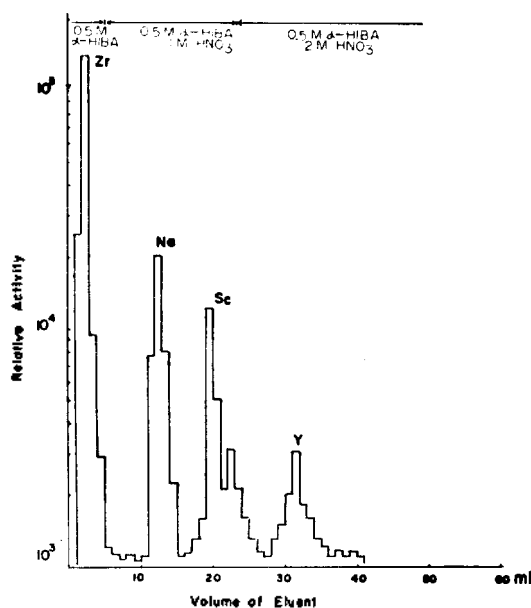


Fig. 2 Elution curve of synthetic mixture.

hydroxide. Two ml of saturated oxalic solution were added. The oxalate precipitates formed were filtered, counted for the γ -activities and weighed for the chemical yield after ignition. The γ -activities of ^{48}Sc , $^{90\text{m}}\text{Y}$ and $^{97}\text{Zr}-^{97}\text{Nb}$ were corrected for the flux difference with the ^{58}Co activity of nickel monitor as previously described⁸.

The radiochemical purities of ^{48}Sc , $^{90\text{m}}\text{Y}$ and $^{97}\text{Zr}-^{97}\text{Nb}$ were confirmed by their γ -ray spectrum and half-lives. The zirconium contents in the synthetic sample were determined by comparing the photo-peak area of (0.663+0.75) Mev. γ -rays from $^{97}\text{Zr}-^{97}\text{Nb}$ with the cpm per mg of standard zirconium as shown in Table 2. The

titanium content was determined by comparing the photo-peak area of 0.155 Mev. γ -ray, from ^{47}Sc , with the cpm per mg of titanium in Table 2.

The content of niobium was determined as follows. The total photo-peak area, $A(\text{total})$, of 0.202 Mev. γ -ray of $^{90\text{m}}\text{Y}$, which originated from both niobium and zirconium, was measured. Since $^{90\text{m}}\text{Y}$ is formed from both niobium and zirconium, the following additivity holds in photo-peak area.

$$A(\text{total}) = A(\text{Nb}) + A(\text{Zr})$$

In this equation, $A(\text{Zr})$, the photo-peak area of $^{90\text{m}}\text{Y}$ contributed only from zirconium, was evaluated by cpm of $^{90\text{m}}\text{Y}$ per mg of zirconium (in Table 2) as well as by the zirconium content determined as described above. The net photo-peak area contributed only from niobium, $A(\text{Nb})$, was thus calculated using this equation. From this calculated value, $A(\text{Nb})$, the contents of niobium was determined by comparing with the cpm/mg of Nb in Table 2.

4. Result and Discussion

The principle of the present method for the determination of niobium requires that the ratio of the *epi*-cadmium to fast neutrons should be constant since both ^{97}Zr - ^{97}Nb and $^{90\text{m}}\text{Y}$ are formed by *epi*-cadmium and fast neutrons, respectively. Therefore, an attempt was made to examine this ratio. As shown in Table 2 the ratio of ^{97}Zr - ^{97}Nb to the $^{90\text{m}}\text{Y}$ activities was found to be always 9.30 ± 0.74 indicating that the ratio of the *epi*-cadmium to fast neutrons was constant inside the cadmium foil.

As shown in Table 1 the dpm of $^{90\text{m}}\text{Y}$ per mg of niobium are higher than that obtained by β -counting of ^{90}Y . This indicates that the present method based on the γ -counting of $^{90\text{m}}\text{Y}$ has the following two advantages, better sensi-

tivities and less interferences, when compared with other method using the β -counting of ^{90}Y . The possible interferences of $^{92}\text{Zr}(n, p)^{92}\text{Y}$ can be neglected as reported previously⁷. The interference of vanadium is negligibly small on the determination of titanium⁶. Hafnium might be eluted together with zirconium,¹¹ however, this interference could be eliminated when using γ -ray spectrometry.

In the activation analysis of titanium and niobium, Athavale *et al.* have wrapped the sample with cadmium foil in order to cut down the interfering activities of ^{46}Sc and ^{90}Y which were produced by the following thermal neutron reactions, $^{45}\text{Sc}(n, \gamma)^{46}\text{Sc}$ and $^{89}\text{Y}(n, \gamma)^{90}\text{Y}$. When this procedure was applied, however, the present authors were never able to eliminate completely these interfering activities if the content of scandium and yttrium were high in the sample, i. e., even with cadmium wrapping the residual activities of these interfering nuclides were considerably high, which caused serious interferences in subsequent determination. In the present study, therefore, these elements of scandium and yttrium together with the other interfering elements such as, iron, nickel, cobalt and cerium were eliminated before irradiation.

When niobium was counted for 1 hour by the present method, the number of count was found to be ca. 6×10^3 . From this number, the detection limit of niobium was calculated¹² to be about 0.01 mg. When using 50 mg of the synthetic mixture this limit is equivalent to ca. 0.2%. According to the similar calculation the detection limits of titanium and zirconium were 0.01% and 0.004%, respectively. As shown in Table 3 the results on the determination of the synthetic mixture are reasonably consistent with the amounts added, and the reproducibility of the determinations are also satisfactory. The deviation ranges about 10% which is probably

Table 3. Analysis of synthetic mixture

Element	Amount added(mg)	Value obtained(mg)				Average value
		(1)	(2)	(3)	(4)	
Ti	2.14	2.12	2.14	2.17	—	2.14±0.03
Nb	2.13	1.99	2.23	2.49	2.19	2.23±0.26
Zr	1.84	1.82	2.02	1.81	1.81	1.87±0.11
Fe	30.2	—	—	—	—	—
Ni	5.05	—	—	—	—	—
Co	4.95	—	—	—	—	—
Ce	1.0	—	—	—	—	—
Y	1.0	—	—	—	—	—

due to the fluctuation of neutron flux in the reactor and also to the errors inherent to the chemical separations and the counting of the radioactivities.

The drawback of the present method is the low sensitivity for the determination of niobium as indicated in Table 2. Furthermore the precision of niobium seems to be critically dependent on the amount of zirconium which also produces the same nuclide. According to Table 2, it appears that niobium could not be determined by the present method with a reasonable accuracy when the ratio of Zr/Nb exceeds about three. However, the present method, despite of its low sensitivity, suggests the possibility of determining niobium by the $^{93}\text{Nb}(n, \alpha)^{90\text{m}}\text{Y}$ reaction. On the other hand, when zirconium and titanium are to be determined, the present method could be an adequate alternative because of its high sensitivity and its simplicity. The present method could be considered applicable for the determination of Ti, Nb and Zr in alloys or samples having a similar composition as described in Table 3.

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