

# Separation of Zirconium-95 and Niobium-95 by Solvent Extraction using Acetylacetone

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The separation of  $^{95}\text{Zr}$  and  $^{95}\text{Nb}$  by the solvent extraction was studied using acetylacetone as a chelating agent. Zirconium acetylacetonate was almost quantitatively extracted with benzene at pH 5~7, whereas Nb was not extracted. Under the optimum condition the extraction recovery of  $^{95}\text{Zr}$  was 97% or more, and the decontamination factor for  $^{95}\text{Nb}$  was  $3 \times 10^2 \sim 1 \times 10^3$ . This extraction procedure would be convenient for the preparation of  $^{95}\text{Zr}$  tracer solution, because Zr can be easily back-extracted into 0.2N sulphuric acid solution.

## INTRODUCTION

Although the ion exchange method has been widely used for the separation of zirconium-95 and its daughter nuclide niobium-95<sup>1)</sup>, the liquid-liquid extraction has been studied by several workers as a rapid separation technique.

For the extraction of zirconium, tri-n-butyl phosphate is an excellent solvent<sup>2,3)</sup>, and the distribution coefficient of  $10^2$  was obtained on the extraction from 7N hydrochloric acid solution, and of  $10^3$  from 13N nitric acid solution<sup>4)</sup>. Alkyl phosphine oxide is also available. Zirconium could be extracted from hydrochloric or nitric acid solution into 0.01~0.02M tri-n-octyl phosphine oxide in cyclohexanone<sup>5)</sup>, and the separation of zirconium-95 from niobium-95 was made by extracting zirconium from 2N nitric acid solution with 0.005M tri-n-butyl phosphine oxide in carbon tetrachloride<sup>6)</sup>.

As chelating system, TTA extraction was commonly employed. Moore<sup>7)</sup> separated zirconium from other many elements by extracting with 0.5 M TTA in xylene from 1~6N hydrochloric acid or 2N nitric acid solution. The contamination with niobium and protactinium could be prevented by the addition of hydrogen peroxide or hydroxylamine. The distribution coefficient of zirconium-95 was measured on 0.05M TTA-benzene system<sup>8)</sup>. Benzene can be equally used as xylene, and the separation of zirconium-95 and niobium-95 was made by extracting zirconium with 0.5M TTA in benzene from 2N nitric acid solution<sup>9)</sup>. Marsh and collaborators improved Moore's procedure to give wide applicability to many kinds of samples<sup>10)</sup>. 8-Hydroxyquinoline was also a useful chelating reagent for the separation<sup>11)</sup>. Zirconium oxinate was extracted with chloroform at pH4.6, and niobium, at pH 6.9<sup>12)</sup>.

Acetylacetone reacts with zirconium to form an extractable chelate as well as in the case of many other metals. Steinbach<sup>13)</sup> reported that the recovery of

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zirconium was not quantitative but 70%, when the extraction was made at pH 2~3 with acetylacetone. However, according to a recent research on the separation of zirconium and niobium-95<sup>14)</sup>, zirconium could be almost completely extracted with chloroform containing 20% acetylacetone. With the same extracting solvent niobium was partially extracted.

In this investigation, the authors adopted such a procedure that acetylacetone was added into aqueous sample solution prior to the extraction, and therefore the hydrolysis of zirconium was minimized. Zirconium was almost quantitatively extracted into benzene at pH 5~7 from aqueous solution containing 5% acetylacetone, whereas niobium was not extracted, and the decontamination factor of  $3 \times 10^2 \sim 1 \times 10^3$  could be obtained. This extraction method would be convenient for the preparation of zirconium-95 tracer solution, because zirconium can be readily back-extracted into 0.2*N* sulphuric acid and furthermore acetylacetone is easily destroyed.

#### APPARATUS AND MATERIALS

A Kobe Kogyo NaI (Tl) ( $1 \frac{3}{4} \times 2'$ ) well type scintillation counter, Model PS-300, connected to a transistorised scaler, Model SA-230 was used for the measurements of gamma-rays, and the absorption curves of beta-rays were obtained with a Metro automatic deca-tron scaler, Model D-5, using a Philips halogen quenched G-M tube 1805, and with a Kobe Kogyo set of aluminium absorbers, Model EA-21. A Hitachi-Horiba glass electrode pH meter, Model M-3 was employed for the pH measurements.

Zirconium-95 mixture containing 0.5% oxalic acid was obtained from Radiochemical Center, Amersham, England. It was converted to sulphate by fuming with sulphuric acid, with or without the addition of carrier, before employment.

Zirconium carrier solution (10 μg/ml) was prepared by fusing zirconium oxide with potassium bisulphate, followed by dissolving with 2*N* sulphuric acid. Niobium carrier solution (10 μg/ml) was made by dissolving niobium metal with sulphuric acid and hydrogen peroxide.

Reagent grade of acetylacetone and TTA were used without further purification. Acetylacetone was dissolved with water to make 10% and 16% aqueous solution, and TTA was dissolved with benzene to give 0.5*M* solution.

Chloroform was purified by washing with diluted sodium hydroxide solution, water, diluted hydrochloric acid and then three times with water, followed by distillation. Benzene and butyl acetate were also purified by washing with water and by distillation.

All other reagents used in the experiment were the reagent grade materials.

#### PREPARATION OF ZIRCONIUM-95 AND NIOBIUM-95 TRACER

Zirconium-95 tracer was prepared by Moor's TTA extraction method<sup>15)</sup>, using benzene as solvent.

An aqueous 2*N* nitric acid solution containing about 100 μC of zirconium-niobium-95 mixture is added with a few drops of 30% hydrogen peroxide, and is

shaken with an equal volume of 0.5M TTA-benzene for 15 minutes. After benzene phase is separated and washed with an appropriate volume of 2N nitric acid, organic solvent is evaporated at room temperature and organic matter is decomposed by fuming with perchloric acid. The residue is dissolved with water to make zirconium-95 solution. Aqueous phase by the above extraction is evaporated and fumed with perchloric acid, after shaken with 0.5M TTA-benzene. Niobium-95 solution is then prepared by dissolving the residue.

The concentration of zirconium-95 and niobium-95 solution was about  $1\mu\text{C}/\text{ml}$ , and the purity was confirmed by estimating the maximum beta energy by absorption measurement.

### EXTRACTION OF ZIRCONIUM

The extraction behaviour of zirconium acetylacetonate was studied by the following procedure.

To the sample solution containing about  $1\mu\text{C}$  of zirconium-95 and  $10\mu\text{g}$  of zirconium carrier, except in the case of the carrier-free separation, 2ml of 1M acetic acid and 2ml or 10ml of 10% acetylacetonate solution or 12.5ml of 16% acetylacetonate solution are added (the final concentration of the reagent is 1%, 5% and 10%, respectively). pH of the solution is controlled to a desirable value with diluted sodium hydroxide solution or diluted sulphuric acid, and the volume is adjusted to 20ml in a 100ml separating funnel. The resulting solution is shaken with 20ml of chloroform, benzene or butyl acetate for 10 minutes\*. Two millilitres of each phase are pipetted into a test tube having the same diameter, and gamma activity was measured in the NaI well type scintillation counter.

Extraction curves of zirconium were shown in Fig. 1, Fig. 2 and Fig. 3. In the calculation of the distribution ratio, counts of aqueous phase were corrected for build up activity of niobium-95, because it became evident from data of the following experiment, that niobium could not be extracted under the condition studied.

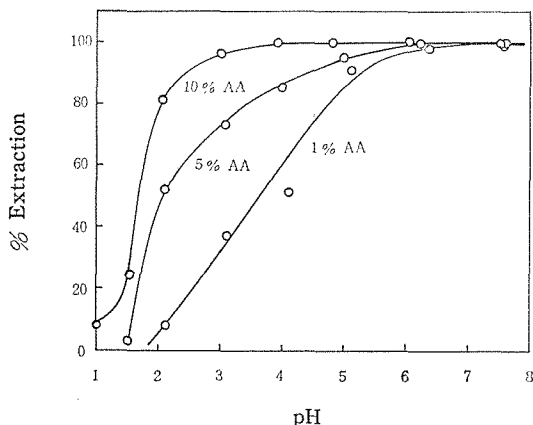


Fig. 1. Extraction curves of  $^{95}\text{Zr-AA-CHCl}_3$  system.

\* Distribution is sufficiently equilibrated by shaking for 5 minutes.

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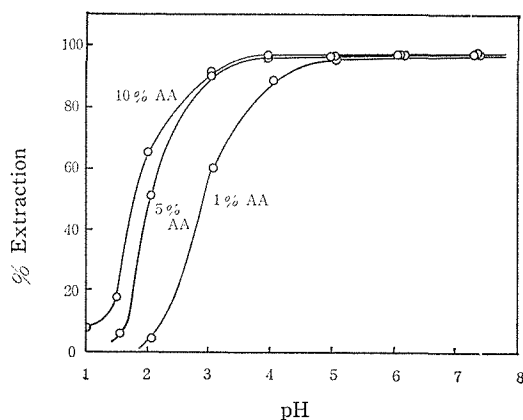


Fig. 2. Extraction curves of <sup>95</sup>Zr-AA-C<sub>6</sub>H<sub>6</sub> system.

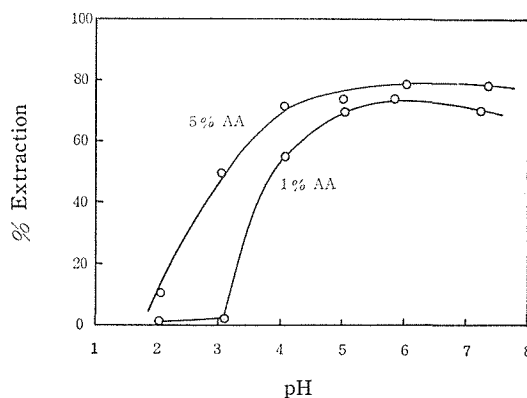


Fig. 3. Extraction curves of <sup>95</sup>Zr-AA-BuOAc system.

As extracting solvent, chloroform and benzene are useful, while butyl acetate is not desirable as shown in figures. Extraction recovery of zirconium is 97% or more, when the extraction is made under the condition; 5% acetylacetone, pH6~7, with chloroform; 5% acetylacetone, pH5~7, with benzene; 10% acetylacetone, pH4~7, with benzene. Benzene is superior in the pH range to chloroform, whereas it is reverse with respect to the extractability. With the increase of the reagent concentration the pH region where zirconium can be extracted expands, but the extractability almost remains constant.

In the extraction with chloroform from the solution containing 1% acetylacetone, sum of the radioactivities of organic and aqueous layers varies remarkably and shows deficiency. It may be due to the formation of colloidal particles suspended in the boundary of two layers.

Extraction recovery of carrier-free zirconium-95 was estimated by comparing radioactivity of organic layer to a standard, which was prepared in the same manner as the sample solution but without extraction, in consideration of the adsorption of zirconium on the wall of the apparatus in carrier-free state. Extraction recovery of 80~95% can be obtained, when the extraction are made on

aqueous solution of pH5~6, containing 5% acetylacetone.

#### BACK EXTRACTION OF ZIRCONIUM

After zirconium was extracted at pH 6 with chloroform or benzene, back extraction was examined by shaking organic layer with equal volume of diluted sulphuric acid or sulphuric acid containing oxalic acid. As shown in Table 1, zirconium can be easily stripped with 0.2*N* sulphuric acid.

Table 1. Stripping of zirconium.

Solvent	Stripping solution	% Back extrn.
Chloroform	1 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	99.9 <sub>4</sub>
	0.1 <i>N</i> -H <sub>2</sub> SO <sub>4</sub> , 1% H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	99.9 <sub>5</sub>
	0.1 <i>N</i> -H <sub>2</sub> SO <sub>4</sub> , 0.1% H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	99.8 <sub>2</sub>
	0.5 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	99.9 <sub>3</sub>
	0.2 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	99.9 <sub>1</sub>
	0.1 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	99.7 <sub>9</sub>
Benzene	1 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	99.9 <sub>6</sub>
	0.1 <i>N</i> -H <sub>2</sub> SO <sub>4</sub> , 1% H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	99.9 <sub>6</sub>
	0.1 <i>N</i> -H <sub>2</sub> SO <sub>4</sub> , 0.1% H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	99.9 <sub>1</sub>
	0.5 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	100.0
	0.2 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	99.9 <sub>0</sub>
	0.1 <i>N</i> -H <sub>2</sub> SO <sub>4</sub>	99.7 <sub>2</sub>

#### EXTRACTION OF NIOBIUM

Extraction behaviour of niobium-95 was studied by the same procedure as in the case of zirconium. Niobium remains almost quantitatively in aqueous phase over the pH region from 3 to 8, and the decontamination factors are  $1\sim 3\times 10^2$  in the extraction with chloroform and  $3\times 10^2\sim 1\times 10^3$  with benzene.

#### SEPARATION OF ZIRCONIUM AND NIOBIUM

From the results obtained in the preceding experiments, the separation of zirconium-95 and niobium-95 seemed to be possible by the extraction procedure. As shown by the decontamination factor, benzene is better than chloroform for the separation. Therefore the following experiment was designed.

Twenty millilitres of zirconium-95-niobium-95 mixture solution (ca. 10 $\mu$ C) containing 5% acetylacetone is shaken with an equal volume of benzene at pH6. After organic layer is washed with 20ml of 0.1*M* acetic acid solution whose pH is controlled to 5~6, zirconium is stripped by shaking with two portion of 10ml of 0.2*N* sulphuric acid, — Zirconium-95 fraction. Aqueous layer is again shaken with benzene after addition of a few millilitres of 10% acetylacetone solution and adjustment of pH, and is separated, — Niobium-95 fraction. Both fraction of zirconium-95 and niobium-95 are evaporated and fumed with sulphuric acid or perchloric acid, and then diluted to appropriate volume.

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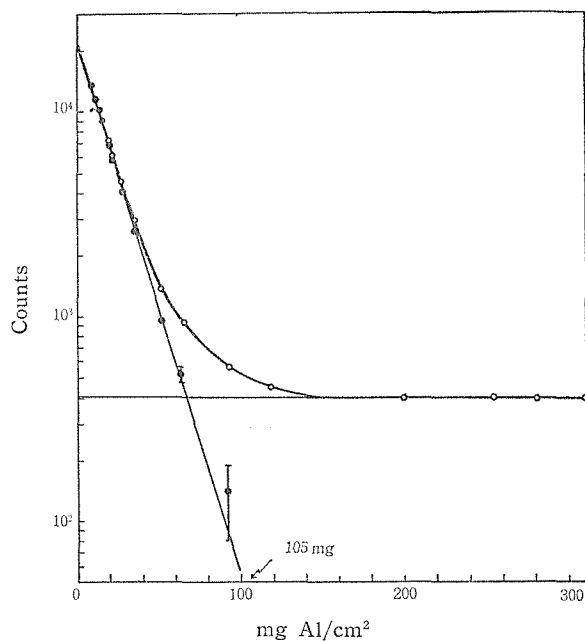


Fig. 4. Absorption curve for <sup>95</sup>Zr, extracted into C<sub>6</sub>H<sub>6</sub>.

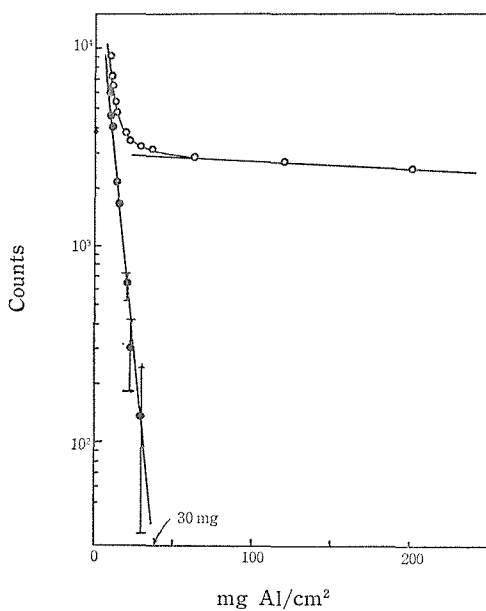


Fig. 5. Absorption curve for <sup>95</sup>Nb, left in aqueous phase.

Aluminium absorption curves of zirconium-95 and niobium-95 fractions were measured with a point source on thin mylar film, and the results were shown in Fig. 4 and Fig. 5.

These absorption curves indicate that the extraction using acetylaceton is

successfully applied to the separation of zirconium-95 and niobium-95.

Extraction behavior of zirconium is almost the same as Suzuki and Omori's results<sup>(14)</sup>, although the extractability obtained in the present work is somewhat high, especially in the extraction with benzene. It may be due to the fact that the relatively high concentration of acetylacetone in aqueous phase eliminates the hydrolysis by pH adjustment. Extraction of niobium was quite different. In the previous report<sup>(14)</sup> it was shown that niobium was considerably extracted, showing a curious property; the extractability decreased remarkably with the length of shaking time. The contamination of niobium on zirconium did not diminish to negligible value, and therefore hydrogen peroxide had to be added for remaining niobium in aqueous layer. By the procedure presented in this paper niobium is not extracted and the separation of zirconium-95 and niobium-95 can be smoothly made without the use of hydrogen peroxide.

In comparison with TTA method, the acetylacetone procedure has such an advantage that zirconium extracted in organic solvent is readily stripped with diluted sulphuric acid and furthermore the reagent is easily decomposed therefore zirconium-95 solution can be easily prepared. It has however, a weak point that niobium can not be obtained as salt-free unless some further treatment is made, because sodium hydroxide or ammonia is used for the adjustment of pH value.

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