Studies on Solvent Extraction using Radioactive Isotope. X[1]*. Solvent Extraction of Zirconium-95 and Niobium-95 with Acetylacetone*

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The solvent extraction method has been successfully applied to the separation of zirconium - hafnium[2,3] and niobium - tantalum[4,5]. There have been a few reports on the separation of ^{95}Zr (^{95}Nb) from other fission products[6-8]. The present authors have previously reported that ^{144}Ce is nearly perfectly extracted with acetylacetone and that the extraction of ^{95}Zr (^{95}Nb) with the same reagent is possible. According to the literature, the percentage extraction of zirconium from aqueous phases of pH values ranging from 0.9 to 2.3 are 10~70, but the details are inaccessible[9]. Moreover, no study on niobium exists in the literature. In the present wark the extraction behaviors of zirconium and niobium are investigated, and the results of the extraction separation of ^{95}Zr and ^{95}Nb from each other are presented.

Experimental

Reagents.—*Stock Solutions of ^{95}Zr and ^{95}Nb.*—^{95}Zr and ^{95}Nb were separated, by means of the ordinary anion exchange separation procedure[10], from ^{95}Zr-^{95}Nb equilibrium mixture imported from the Oak Ridge National Lab., U. S. A., by an ion-exchange resin Dowex 2-X8 using a 0.1 M hydrochloric acid-0.01 M oxalic acid mixture as an eluant. The respective effluents were evaporated to fumes with sulfuric and nitric acids to give stock solutions. The acidity of the stock solutions was 9 N for ^{95}Zr and concentrated sulfuric acid for ^{95}Nb. As for ^{95}Zr, a solution less than 2 days old was used to eliminate the error due to the contamination of the ^{95}Nb daughter growth. The stock solutions prepared by potassium hydrogen sulfate fusion gave nearly the same results, but the results of ^{95}Nb were slightly less reproducible. For this paper, therefore, the stock solution prepared by the acid treatment was used.

Acetylacetone.—A commercial reagent was further purified by washing with ammonia water (1 : 10) and was distilled twice. The distillation fraction of 138°C was used.

Organic Solvents. — E. P. grade greagents were distilled twice.

Other Chemicals.—Guaranteed grade chemicals were used without further purification.

General procedure.—An acetate buffer solution containing ^{95}Zr and ^{95}Nb was shaken with an acetylacetone-chlorofrom mixture in a vessel for a suitable period. ^{95}Zr or ^{95}Nb was added just before shaking. The pH of the aqueous phase was adjusted with dilute nitric acid or sodium hydroxide, the ionic strength being kept at 0.6 with component salts. After separation of the layers, the radioactivity was measured* with a well-type scintillation counter made by the Kobe Kogyo Co., and the pH value was measured with a M-3 type glass-electrode pH meter made by the Horiba Instrument Co.

Concentration Effect of Acetylacetone.—To examine the effect of the concentration of acetylacetone, the extractions were carried out with acetylacetone-chloroform mixtures of various concentrations, the volume percentages of acetylacetone being 5, 10, 20, 30, 40, 50 and 100. To obtain the data for ^{95}Zr, the aqueous phase of pH 4.9 was shaken for two minutes. As is shown in Fig. 1, the extraction ratio is nearly constant above ca. 10% of acetylacetone in chloroform, but it drops in the case of pure acetylacetone. The lowering of the extractability in the case of pure acetylacetone

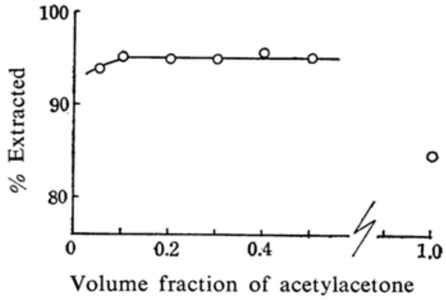

Fig. 1. Extraction of ^{95}Zr as function of volume fraction of acetylacetone in chloroform.

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* A correction for the difference in the counting efficiency between the two phases was made by multiplying the counting rate of counting rate of the organic phase by the factor 1.027.

is presumed to be due to the decrease in the partition of the chelated compounds between the two phases. Based on these results, a 20% acetylacetone solution was chosen for further experiments.

Effect of Shaking Time.—The effect of the shaking time on the extraction of ^{95}Zr and ^{95}Nb using a 20 per cent acetylacetone solution was studied. The results are shown in Fig. 2, where no perceptible change in the extraction ratio of ^{95}Zr is seen by the extension of the shaking time up to an hour. On contrary, the the extraction ratio of ^{95}Nb from the aqueous phase having the same pH value of 5.7 decreases remarkably with the length of the shaking time. The lowering of the extractability of ^{95}Nb can be accounted for by hydrolysis, as will be seen in the results of an extraction curve given later. The lowering of the pH value will prevent the hydrolysis, and, in fact, the effect of the shaking time was not appreciable when the pH value was reduced to 3. Based on these results, the shaking time was chosen to be two minutes for ^{95}Zr and one minute for ^{95}Nb for further studies.

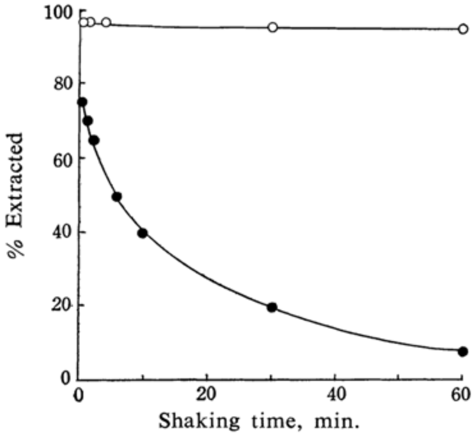

Fig. 2. Extraction of ^{95}Zr and ^{95}Nb with 20% acetylacetone in chloroform as function of shaking time.
-○- ^{95}Zr at pH 5.6
-●- ^{95}Nb at pH 5.7

Extraction Curve.—To examine the relation between the pH value of the agueous phase and the extractability of ^{95}Zr and ^{95}Nb, extraction with 20% acetylacetone in chloroform was carried out. The extraction curves are shown in Fig. 3, where it is seen that 98% of the ^{95}Zr was extracted at a pH range of from 3 to 8, and 92% of ^{95}Nb was extracted at a pH range of from 2 to 5 by a single extraction. Thus, the optimum pH range for ^{95}Nb is slightly narrower than that for ^{95}Zr because of hydrolysis. It is doubtful, however, that these extraction curves represent the true equilibrium state over the entire pH range examined; the pH range is at least partially in such an unstable condition that hydrolysis is probably occuring.

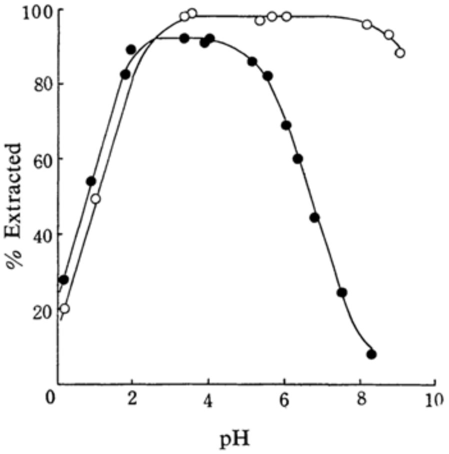

Fig. 3. Extraction of ^{95}Zr and ^{95}Nb with 20% acetylacetone in chloroform as function of pH.
-○- ^{95}Zr -●- ^{95}Nb

Extraction by Various Solvents. — Acetylacetone can be used both as a solvent and as an extractant, and in a number of cases various organic solvents are used as a diluent. For example, carbon tetrachloride(1), chloroform(9), and benzene(11-13) were used as a diluent. In the preceding chapter it was reported that an acetylacetone-chloroform mixture showed a higher extractability than pure acetylacetone. The results of the extractions using 20 vol.% solutions of acetylacetone in various solvents are shown in Table I, were the pH values

TABLE I. EXTRACTION OF ^{95}Zr AND ^{95}Nb WITH VARIOUS SOLVENTS

Solvent	% Extracted	
	^{95}Zr	^{95}Nb
Benzene	88.6	61.5
Xylene	—	55.8
Carbon tetrachloride	88.5	37.6
Chloroform	97.7	89.8
Methylene chloride	96.5	79.9
Isopropyl ether	51.5	1.0
Methyl isobutyl ketone	65.4	4.2
Ethyl acetate	71.6	44.3
Isoamyl acetate	64.8	49.0
Tri-*n*-butyl phosphate	64.3	53.5
Kerosene	13.9	10.0

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after the extraction covered the range from 5.7 to 5.8 for ^{95}Zr and from 4.2 to 4.3 for ^{95}Nb. Chloroform showed the highest extractability for both ^{95}Zr and ^{95}Nb, and methylene chloride came next.

Effect of Coexisting Salts.—The coexisting salts show a considerable influence upon the extraction of ^{95}Zr and ^{95}Nb. The results in the presence of a substance such as sodium chloride, sodium nitrate, ammonium sulfate, sodium hydrogenphosphate, potassium thiocyanate, sodium acetate, hydrogen peroxide, hydroxylamine, oxalic acid, citric acid and disodium ethylenediaminetetraacetate (EDTA) are shown in Table II, where the concentrations in the table denote those of the substances present in the aqueous phase. No effect was observed when the concentration of sodium acetate used as a buffer component was raised to 0.75 M. The extractions of both ^{95}Zr and ^{95}Nb were remarkably interfered with sodium hydrogenphosphate, oxalic and citric acids. In general, ^{95}Nb is more sensitive to the interference from coexisting salts. The use of hydrogen peroxide or hydroxylamine as a masking agent has been found in the literature[6,8]. As is seen in the present results, the extraction ratio of ^{95}Zr was reduced only slightly in the presence of hydrogen peroxide, whereas ^{95}Nb was perfectly masked by it. In Table III, the extraction ratios obtained in the presence of hydrogen peroxide in various concentrations at pH 5 are given. ^{95}Nb is not extracted under coexistence with hydrogen peroxide, while the extraction ratio of ^{95}Zr increases with the decreasing concentration of hydrogen peroxide. ^{95}Zr could be extracted as high as 98% by successive extraction from the aqueous phase containing a considerable amount of hydrogen peroxide, but it is not practical to extract ^{95}Nb from the residual aqueous layer because 2% of the ^{95}Zr is still left in the aqueous layer.

TABLE II. EFFECT OF COEXISTING SUBSTANCES

Substance	Concn. in aq. phase M	% Extracted	
		^{95}Zr	^{95}Nb
$NaNO_3$	2	97.0(8.3)	79.0(3.7)
NaCl	2	97.6(8.5)	81.7(3.7)
$(NH_4)_2SO_4$	2	98.1(6.3)	69.6(4.1)
Na_2HPO_4	0.2	1·1(—)	1.7(4.7)
KSCN	1	94.3(4.5)	80.0(4.3)
CH_3CO_2Na	0.75	98.2(7.0)	90.9(3.4)
H_2O_2	2%	78.1(5.0)	0.3(5.1)
NH_2OH-HCl	1	96.0(4.6)	59.2(3.8)
	0.1	96.2(8.1)	61.7(3.8)
Oxalic acid	0.04	4.7(4.2)	4.5(5.0)
Citric acid	0.2	3.9(4.0)	0.3(4.6)
EDTA	0.001	2.1(4.4)	6.3(5.0)

Parentheses show the pH of aqueous phase at equilibrium with organic phase.

TABLE III. EFFECT OF HYDROGEN PEROXIDE

Concn. of H_2O_2 %	% Extracted	
	^{95}Zr	^{95}Nb
0	98.0(99.5)	91.4
0.004	93.5(97.7)	0.5
0.2	87.3	0.3
2	78.1(94.6)	0.3

Parentheses show total percentage of two-successive extraction.

Back Extraction.—The following experiments were carried out to find the optimum condition for the back extraction of ^{95}Zr and ^{95}Nb from the solvent phase. A 20% acetylacetone-chloroform solution containing ^{95}Zr or ^{95}Nb-acetylacetonate complex was prepared by the standard method, and an aliquot of this solution was shaken with various concentrations of nitric, hydrochloric, and sulfuric acids and hydrogen peroxide solution. The results are shown in Table IV. Sulfuric acid was most effective for the back extraction, both ^{95}Zr and ^{95}Nb being nearly perfectly stripped into the aqueous phase. Nitric and hydrochloric acids were not so effective. ^{95}Nb was more easily

TABLE IV. BACK EXTRACTION WITH VARIOUS AQUEOUS SOLUTIONS

Stripping soln.	Shaking time, min.	% Back-extracted	
		^{95}Zr	^{95}Nb
0.1 N HNO_3	1	50.9	17.9
	10	43.5	61.1
1 N HNO_3	1	67.4	35.6
	10	69.6	83.9
2.5 N HNO_3	1	77.4	51.3
	10	78.2	68.1
5 N HNO_3	1	71.6	46.3
	10	69.8	27.6
10 N HNO_3	1	28.3	12.4
	10	—	12.8
0.1 N HCl	1	72.3	21.2
	10	81.0	55.3
1 N HCl	1	96.3	62.9
	10	99.0	89.2
6 N HCl	1	97.2	34.6
	10	97.3	35.7
1 N H_2SO_4	1	98.3	81.6
	10	99.0	91.3
5 N H_2SO_4	1	98.4	87.9
	10	99.5	96.1
9 N H_2SO_4	10	99.8	—
0.3% H_2O_2*	1	0.6	33.7
	10	4.0	66.5

* pH 4.9 acetate buffer

stripped than ^{95}Zr in the pesence of hydrogn peroxide. However, the back extraction ratio of ^{95}Nb was still as high as 66.5% after being shaken for ten minutes. This fact shows that the acetylacetonate complex formed is rather stable.

Mutual Separation of ^{95}Zr and ^{95}Nb.—The experimental results mentioned above suggest two methods for the separation of ^{95}Zr and ^{95}Nb from each other, one being based on the different behavior of ^{95}Zr and ^{95}Nb at a suitable pH value, and the other on the masking of ^{95}Nb with hydrogen peroxide. In the former method, the intention is to make use of the facts that at a high pH value ^{95}Nb is not extracted and that an extension of the shaking time diminishes its extraction ratio. It was not practical, however, to separate ^{95}Zr perfectly by this method, because a small percentage of ^{95}Nb is always accompanied with ^{95}Zr.

Practically, pure ^{95}Zr, free from ^{95}Nb, can be prepared by the latter method. An oxalic acid solution of ^{95}Zr-^{95}Nb was treated with sulfuric and nitric acids, or by potassium hydrogensulfate fusion. The pH value was adjusted to about 5, and hydrogen peroxide was added until the concentration come to 0.2%. Then the solution was repeatedly shaken with a 20% acetylacetone-chloroform mixture. After washing the organic phase with a dilute hydrogen peroxide solution, the aqueous phase was discarded and the organic phase was shaken with 9 N sulfuric acid for ten minutes to strip ^{95}Zr. The acid solution was then washed with chloroform to remove the acetylacetone. The yield was about 96%. The ^{95}Zr obtained was proved to be radiochemically pure by taking a β-ray absorption curve, which showed normal chemical behavior.

Summary

The extraction of ^{95}Zr and ^{95}Nb with an acetylaceton-echloroform mixture was investigated. The percentage extraction of ^{95}Zr with a 20% acetylacetone solution was 98% at pH valves ranging from 3 to 8, and that of ^{95}Nb was 90% at pH values from 2 to 5. The extraction ratio of ^{95}Nb was lowered by the extension of the shaking time. As an diluent, chloroform and methylene chloride were recommended. Phosphate, oxalic acid, citric acid and EDTA interfered remarkably. Sulfuric acid was most efficient for the back extraction. A high purity of ^{95}Zr was obtained by using hydrogen peroxide as a masking agent. The yield was satisfactorily high.

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