Note

Zirconium isotope separation by means of cation-exchange chromatography

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Zirconium is an important material in the nuclear power reactor because of its low thermal neutron capture cross-section. Zirconium has five stable isotopes, *viz.* ^{90}Zr (51.45), ^{91}Zr (11.22), ^{92}Zr (17.15), ^{94}Zr (17.38) and ^{96}Zr (2.80)[1] (numbers in parentheses are the percentage atomic fractions) for which the thermal neutron capture cross-sections have been estimated to be 0.032, 1.14, 0.21, 0.056 and 0.020[2] barns, respectively. From the point of view of the isotopic abundance ratio, ^{90}Zr is the most important isotope of zirconium. In 1979, Smith[3] reported a new value for the thermal neutron capture cross-section of ^{90}Zr of 0.0144 barns.

For the reactor in-core component, the use of isotopes which have low thermal-neutron-capture cross-sections can not only extend uranium resources (improve the neutron economy), but also improve the life-time of pressure tubes. The new value indicates that enrichment of ^{90}Zr can provide these improvements effectively. However, there has been no report on zirconium isotope separation, and there are no suitable chemical forms of zirconium for which mechanical isotope separation methods, such as gaseous diffusion and ultracentrifuge, can be used.

In the present work, the separation of zirconium isotopes has been investigated by means of cation-exchange chromatography, and the elemental separation coefficients for zirconium-90 have been evaluated.

EXPERIMENTAL

Ion-exchange resin, equipment and reagents

The cation-exchange resin was LS-6 (100–200 mesh) (Asahi), a strongly acidic cation-exchange resin of a highly porous type. The resin was packed into a pressure-resistant Pyrex column (420 × 1 cm I.D.) which had a water jacket through which water from a thermostatted bath was circulated. To avoid the influence of light, the column was covered with black sheeting. The packed resin was conditioned to the H^+ form by passing through 2 M hydrochloric acid solution. At this stage, the height of the resin bed was *ca.* 400 cm.

A single plunger pump was used to introduce a solution into the column with a constant flow-rate.

The stock solution of zirconium was prepared by dissolving commercial zir-

conyl chloride, $ZrOCl_2 \cdot 8H_2O$, into a 1 M perchloric acid solution and a triammonium citrate solution was prepared by dissolving a commercially available reagent in water. All other reagents were of analytical-reagent grade.

Reverse breakthrough chromatography

Prior to the experiments on the chromatographic separation of zirconium isotopes, a series of preliminary experiments was carried out to find the most appropriate conditions, *i.e.*, the kind of eluting reagents, concentration and pH of eluent, under which reverse breakthrough chromatography with a sharp boundary could be realized. On the basis of the results from the preliminary experiments, 0.1 M triammonium citrate solution (pH $\approx$ 8) was selected as one of the eluents.

The resin bed (*ca.* 400 cm) was fed with 0.3 M zirconyl chloride solution to convert the resin into a zirconium form. After washing with water, reverse breakthrough chromatography was carried out by feeding the 0.1 M aqueous solution of triammonium citrate, adjusting its pH to *ca.* 8 with ammonium hydroxide. The effluent from the bottom of the column was collected in small fractions. Three chromatographic runs were performed, at 10, 25, and 40°C.

Analysis

For each fraction, the pH and the concentration of zirconium were measured using a pH meter and an inductively coupled plasma spectrophotometer (Shimadzu, Model ICPS 50S), respectively.

The atomic fraction of zirconium isotopes in the fraction was determined from the isotopic ratio measured by a mass spectrometer (Varian MAT, Model CH-5) using a surface ionization technique. Details of the measurement will be published elsewhere[1]. To measure the isotopic ratios, the fractions were converted into zirconium sulphate as follows. To decompose the organic components, the fraction sample was heated to above 1000°C when the zirconium in the sample was converted into zirconium dioxide. The dioxide was then dissolved in concentrated hot sulphuric acid in a quartz crucible. After evaporating the excess acid, the resulting zirconium sulphate was diluted with dilute sulphuric acid until the concentration of zirconium was *ca.* 10 $\mu g/\mu l$.

RESULTS AND DISCUSSION

The chromatograms obtained from the three runs are shown in Figs. 1–3, and the experimental conditions are listed in Table I.

In these three runs, the concentration and pH of the eluent were almost the same, while the operating temperatures were 10, 25 and 40°C. At the rear portion of the chromatograms for runs 1 and 2, displacement chromatograms were realized; however, a small but significant degree of tailing was observed in the case of run 3 (see Fig. 3). This may arise from the instability of triammonium citrate at the relatively high temperature of *ca.* 40°C. During these chromatograms, a series of reactions took place. At the rear boundary of the zirconium-adsorbed band, zirconium species in the resin phase were exchanged with ammonium ion in the eluent, and zirconium–citrate complexes were formed. At present, it is impossible to identify these reactions which took place during chromatography, because little is known about
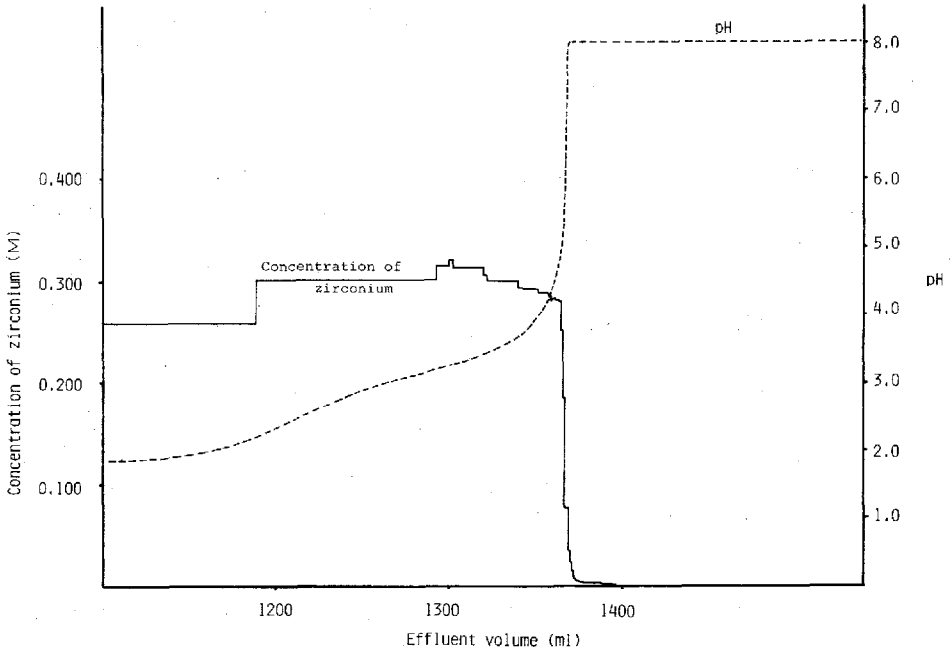
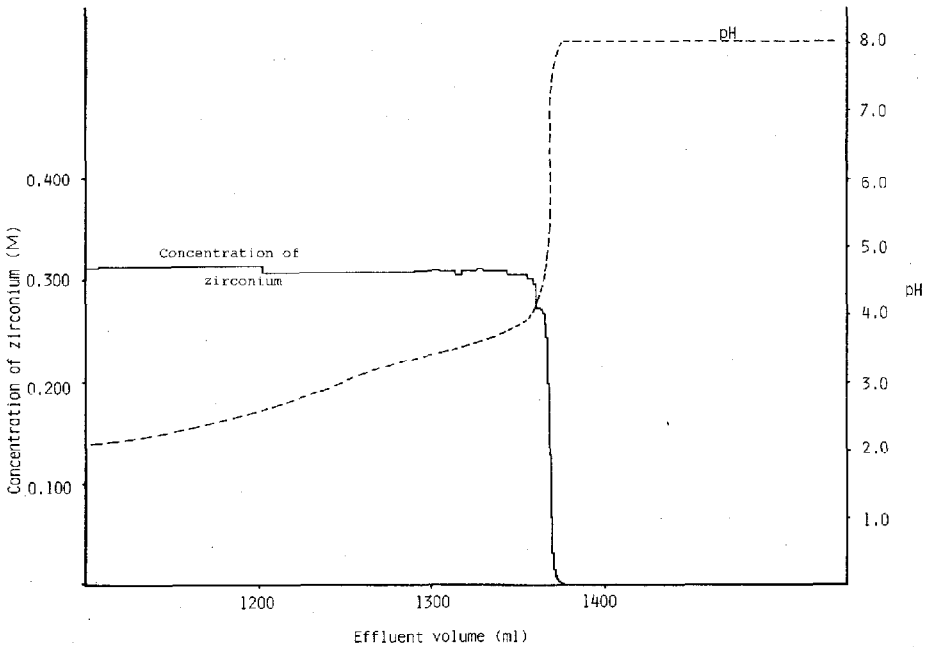Fig. 1. Chromatogram for zirconium–citrate system of run 1. Flow-rate, 6 ml/h; temperature, 10°C.

Fig. 2. Chromatogram for zirconium–citrate system of run 2. Flow-rate, 4 ml/h; temperature, 25°C.
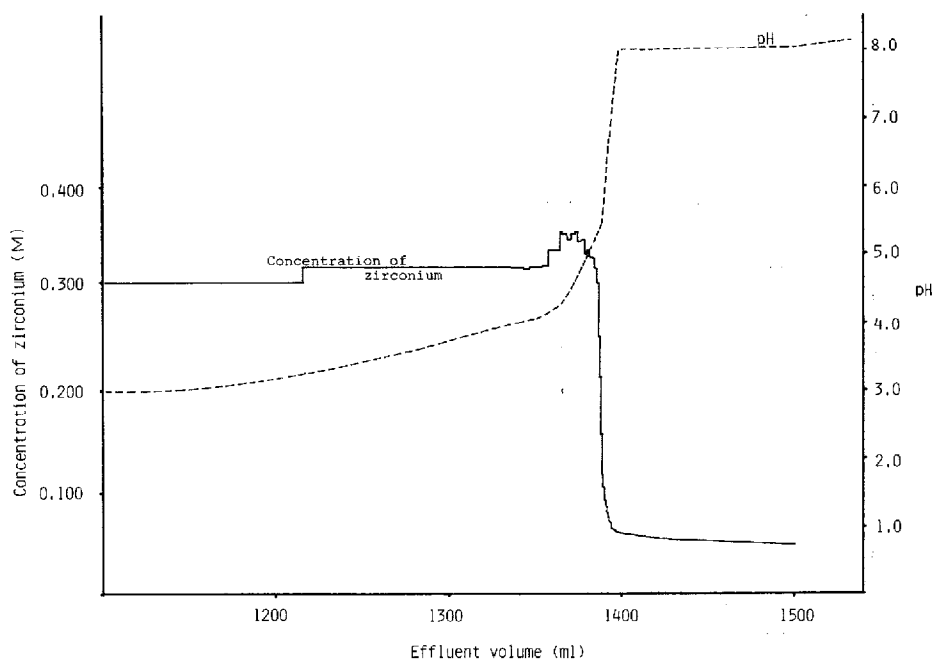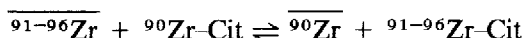
Fig. 3. Chromatogram for zirconium–citrate system of run 3. Flow-rate, 6 ml/h; temperature, 40°C.

zirconium species in resin and aqueous phases. Hence, the isotopic exchange reaction can only be expressed by

$$\overline{^{91-96}\mathrm{Zr}} + {}^{90}\mathrm{Zr}\text{–Cit} \rightleftharpoons \overline{^{90}\mathrm{Zr}} + {}^{91-96}\mathrm{Zr}\text{–Cit}$$

where ——— represents the zirconium species in the resin phase, and Zr–Cit the zirconium–citrate complexes.

The $^{96}\mathrm{Zr}/^{90}\mathrm{Zr}$ isotopic ratios obtained in the fractions are illustrated in Figs. 4–6. The deviations in isotopic ratio obtained from the original ratio are small but appreciable. It is apparent that the lightest isotope, $^{90}\mathrm{Zr}$, was enriched at the rear

TABLE I

EXPERIMENTAL CONDITIONS FOR REVERSE BREAKTHROUGH CHROMATOGRAPHY

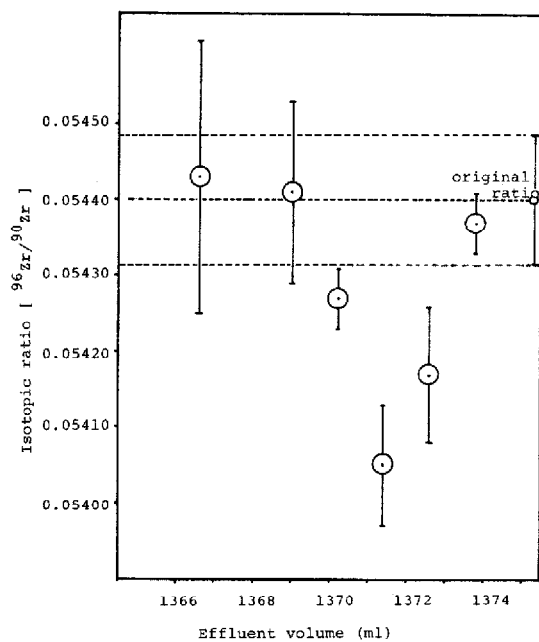|	Run No.		
	1	2	3
Cation-exchange resin	LS-6	LS-6	LS-6
Bed height (H⁺ form, cm)	411	400	400
Eluent	Triammonium citrate, 0.1 M, aqueous solution		
Eluent pH	8.1	8.1	8.2
Eluent flow-rate (ml/h)	6	4	6
Operating temperature (°C)	10	25	40

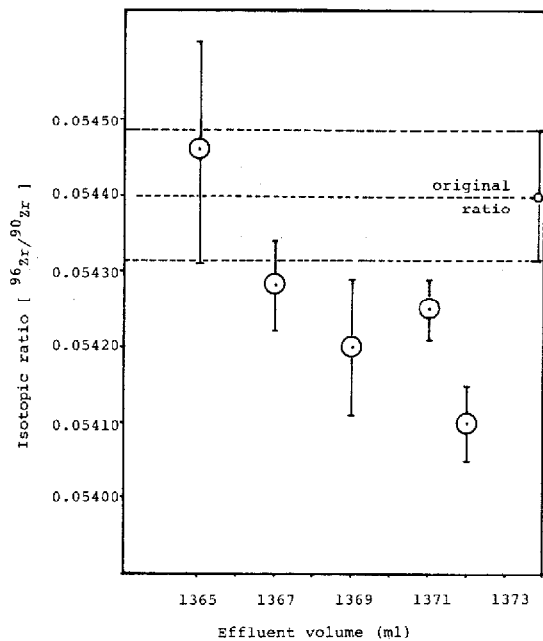Fig. 4. Isotopic ratio (^{96}Zr/^{90}Zr) obtained from run 1. Vertical bars denote uncertainty (95% confidence limit).

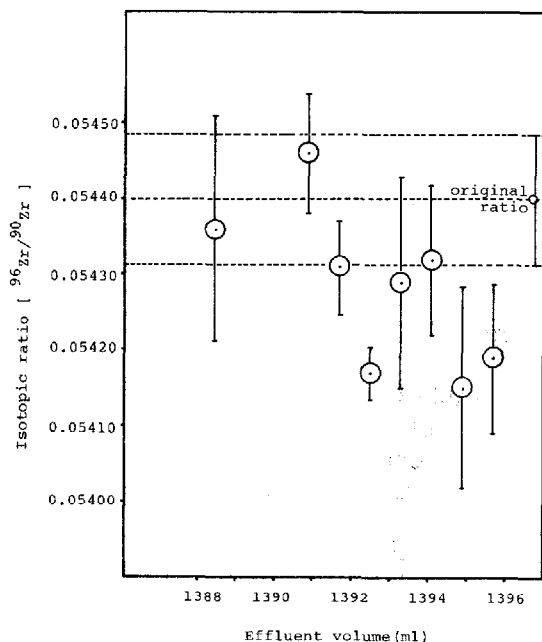Fig. 5. Isotopic ratio (^{96}Zr/^{90}Zr) obtained from run 2. Vertical bars denote uncertainty (95% confidence limit).

Fig. 6. Isotopic ratio (^{96}Zr/^{90}Zr) obtained from run 3. Vertical bars denote uncertainty (95% confidence limit).

boundary of the zirconium band, *i.e.* ^{90}Zr is preferentially retained in the zirconium species adsorbed onto the resin rather than in the zirconium–citrate complexes. This tendency of the heavier isotope being preferentially retained in the complexes agrees with the results of uranium isotope separation using uranous complex formation reactions[4].

The influence of operating temperature on the changes of the ^{96}Zr/^{90}Zr isotopic ratio was not appreciable in the present study.

The isotope effect obtained by the present system was evaluated as the elemental separation coefficient, ε, defined as

$$\varepsilon = S - 1 = \frac{[^{90}Zr] \, [^{91-96}Zr]}{\overline{[^{90}Zr]} \, \overline{[^{91-96}Zr]}}$$

where S is the elemental separation factor, [   ] denotes the concentration of the isotopes in the aqueous phase and $\overline{[]}$ represents the concentration of the isotopes in the resin phase. The elemental separation coefficient was calculated from the analytical data using the equation[7]

$$\varepsilon = \sum_i f_i \, (R_i - R_0)/Q R_0 \, (1 - R_i)$$

where f_i is the amount of zirconium in the ith fraction, R_0 is the atomic fraction of

TABLE II

ELEMENTAL SEPARATION COEFFICIENTS (ε)

Run No.	ε
1	$9.5 \cdot 10^{-7}$
2	$1.6 \cdot 10^{-6}$
3	$8.6 \cdot 10^{-7}$

^{90}Zr, R_i is the atomic fraction of ^{90}Zr in the ith fraction and Q is the total exchange capacity of the resin bed.

The ε values calculated are listed in Table II. These values are much smaller than those of uranium[5,6,8] which were obtained by similar ion-exchange chromatographic processes using uranyl and/or uranous complex formation reactions; however, they are the first values obtained by an experimental study of zirconium isotope separation.

Further discussion and an exact and quantitative interpretation of the small isotope effect is impossible because the chemical species of zirconium can not at present be determined.

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