CONF-810203--5

Separation of Hafnium from Zirconium in Sulfuric Acid Solutions Using Pressurized Ion Exchange*

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*Research sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

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SEPARATION OF HAFNIUM FROM ZIRCONIUM IN SULFURIC ACID SOLUTIONS USING PRESSURIZED ION EXCHANGE*

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Summary

High-resolution pressurized ion exchange has been used successfully to study and separate hafnium and zirconium sulfate complexes by chromatographic elution from Dowex 50W-X8 (15-25 μm) resin with sulfuric acid solutions. Techniques were developed to continuously monitor the column effluents for zirconium and hafnium by reaction with fluorometric and colorimetric reagents. Since neither reagent was specific for either metal ion, peak patterns were initially identified by using the stable isotopes ^{90}Zr and ^{180}Hf as "fingerprints" of their elution position. Distribution ratios for both zirconium and hafnium decrease as the inverse fourth power of the sulfuric acid concentration below 2N and as the inverse second power at higher acid concentration. The hafnium-to-zirconium separation factor is approximately constant (~8) over the 0.5 to 3N range. Under certain conditions, an unseparated fraction was observed that was not retained by the resin. The amount of this fraction which is thought to be a polymeric hydrolysis product appears to be a function of metal and sulfuric acid concentrations. Conditions are being sought to give the highest zirconium concentration and the lowest acid concentration that can be used as a feed material for commercial scale-up in the continuous annular chromatographic (CAC) unit without formation of the polymer.

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Introduction

The increasing need for pure zirconium and pure hafnium in the nuclear industry has renewed interest in their separation and recovery. Of many methods developed, only three have been used on an industrial scale; fractional crystallization of ammonium and potassium fluorides, the hexone-thiocyanate system and the tributylphosphate-nitric acid system (1,2). The crystallization method was difficult and not very effective while both of the solvent extraction processes suffer disadvantages such as solvent degradation, excessive corrosion, and solids formation that interferes with continuous operation. The purpose of this study was to determine the feasibility of high pressure ion-exchange techniques, such as those described previously to separate cobalt and nickel (3), to define and effect this separation. Previous work has shown that a sulfuric acid treatment is the most economical way to dissolve the reaction product obtained after opening up the zircon sand feed with caustic (2). Electromigration and cation exchange experiments have shown that cationic species, present at low concentrations of H_2SO_4, are converted to uncharged and anionic species at high acid concentrations (4). In addition, the complex forming tendency of the zirconium and hafnium ions are quite different in the sulfate system and the minor constituent (Hf) is more strongly held by cation exchange resins which makes commercial scale separation more practical.

Lister (5) and Lister and MacDonald (6) have described the development of a cation exchange process whereby they effect the separation by taking advantage of the different complex-forming tendency of the ions HfO^{2+} and ZrO^{2+} with sulfuric acid. However, the overall throughput rate was much too slow for industrial application. A primary aim for this study was to determine whether or not the kinetics of this separation could be sufficiently improved by using very small beads, and thereby make the process attractive on an industrial scale.

At the start of this study, considerable effort was spent developing techniques for continuously monitoring the column effluents for zirconium and hafnium without the use of radioactive tracers. Radiochemical procedures used in past studies are cumbersome because of niobium daughter activity in the case of zirconium and because one can never be sure the tracers are completely representative of the true complexes in solution.

Experimental

Equipment

A schematic diagram of the pressurized ion-exchange system is shown in Figure 1. A positive displacement (Milton-Roy mini) pump was used to force solutions through Chromatronix Type LC columns. The 0.63 x 33 cm glass columns (500 psi pressure rating) were fitted with inlet and outlet plunger assemblies that allowed resin columns ranging from a few millimeters to about 25 cm in length. In chromatographic separations, 1 to 100 µl samples were injected directly onto the top of the resin bed using Cheminert Sample Injection Valve R605V for injection of dilute solutions or a Valco injection valve equipped with a calibrated 1 to 10 µl syringe for concentrated solutions.

The eluted metal ions were monitored continuously by two different methods as follows. In the method described in this paper, a fluorometric reagent was mixed with the column effluent in a "T" joint containing a small magnetic stirrer and the fluorescence of the mixed streams was measured in a flow fluorometer developed by Thacker (7). In the second method, a colorimetric reagent (Arsenazo III) was mixed with the column effluent and detection was made with a spectrophotometer. Although both methods were very effective, the fluorometric technique had a higher sensitivity and was preferred for this study.

Since neither of the reagents used were specific for either metal ion, we needed samples of pure zirconium (hafnium free) and pure hafnium (zirconium free) for initial identification of peak patterns. Because of the difficulty of obtaining these elements free from one another, we obtained samples of Calutron produced, isotopically pure, stable isotopes ^{90}Zr and ^{180}Hf for this purpose.

Solutions

Sulfuric acid stock-solutions of pure zirconium and pure hafnium were prepared from the oxides of the isotopes ^{90}Zr (H-1) and ^{180}Hf (H-2). These samples were used as fingerprints to identify zirconium and hafnium peaks in chromatograms produced using solutions described below.

A stock solution of hafnium (H-3) was prepared by dissolving hafnium metal in a 1:4 mixture of 48% HF and cp H_2SO_4. The fluoride was removed by repeated fuming with sulfuric acid. The solution was then diluted with water, precipitated with NH_4OH, and redissolved in sulfuric acid. This step was found to be necessary to ensure complete removal of fluoride ion which can cause significant changes in distribution coefficients when present even in trace quantities.

Stock solutions of zirconium (plus ~2.5 wt/% Hf) were prepared by dissolving reagent grade zirconyl sulfate in water and adding sulfuric acid to the desired acidity (H-4) and by treating zircon sand ($ZrSiO_4$). For preparation from zircon sand, one part by weight of zircon sand was reacted with 1.2 parts of sodium hydroxide by heating the mixture for 1.5 hr at 600°C in an iron crucible (8). The light, granular solids were washed with water to remove soluble silicate and excess caustic and then dissolved in sulfuric acid (H-5). In one case, a solution was prepared in which a Hf spike was made by adding precipitate from the hafnium solution (H-3) to the sand-caustic mixture (H-6).

Table I gives details of the sulfuric acid solutions.

Table 1. Zr-Hf Stock Solutions

Solution Number	Source	Concentration g/L Zr	Concentration g/L Hf	Concentration $\underline{N}$ H_2SO_4
H-1	^{90}Zr oxide	4.65	0	0.7
H-2	^{180}Hf oxide	0	4.20	0.7
H-3	Hf Metal	1.00	34.80	1.6
H-4	$ZrOSO_4 \cdot H_2SO_4$	95.0	1.55	1.0
H-5	$ZrSiO_4$	38.3	0.33	7.5
H-6	$ZrSiO_4$ (Hf spike)	9.86	0.88	1.7

Procedure

Much of the experimentation involved the injection of small samples of the liquor (usually less than 3% of the column capacity) onto a 0.3 to 6 cc bed of Dowex 50W-X8 resin hydraulically graded to 15 to 25 microns and elution of the species with varying concentrations of sulfuric acid. In most tests the pumps were set to give column feed rates, F_c, of 0.5 to 1 ml/min and reagent feed rates, F_R, of 0.2 to 0.5 ml/min (Figure 1). The samples (1 to 100 μl) were injected through the sample injection valve into the eluent flow at the same time that the recorder was started. Peak distances were measured in millimeters from this point.

Calculations

Distribution ratios, K_d, were calculated from the chromatograms using equation 1:

$$K_d = (V_R - V_o)/V_o \qquad (1)$$

where V_R is the retention volume or that volume necessary to elute the peak of a band and V_o is the void volume of the column, which was assumed to be 38% of the bed volume (9). V_R was calculated from the measured peak distances in millimeters, d, as given in equation 2:

$$V_R = \left(\frac{d}{c} - \frac{V_1}{F_c} - \frac{V_2}{F_T}\right) F_c \qquad (2)$$

where c is the chart speed (mm/min); V_1 is the volume of the tubing between the sample injection valve and the top of the column plus the volume between the bottom of the column and the mixer; V_2 is the volume from the stirrer to the flow-through cell in the fluorometer; F_c is the feed rate of the eluent and F_T is the total flow rate ($F_c + F_R$). The last two terms in parentheses are corrections for volumes of the system other than the column.

Analysis

X-ray fluorescence (XRF) and neutron activation analyses (NAA) were used to analyze solutions H-1 through H-6 for zirconium and hafnium and to confirm separations in some of the chromatographic tests. Theoretical detection limits by XFR are 0.4 ppm zirconium and 1.2 ppm hafnium (10) and by NAA are 1.0 ppm Zr and 0.001 ppm Hf (11).

Morin (2',4',3,5,7-pentahydroxyflavone) is a very sensitive reagent for the detection of zirconium and hafnium and can be used in quantitative fluoresence analysis once the peaks are identified (12). Beer's law holds at low concentrations so that quantitative measurements can be made in the parts per million range. Detection limits were ~2 ppm for zirconium and ~8 ppm for hafnium. Best results were obtained when a 0.035% solution of morin in 95% ethanol was fed into the mixing "T" at a flow rate equal to ~30% of the eluent flow rate.

Additional work is needed to refine these analytical techniques and this information will be reported separately.

Results and Discussion

Elution of Stable Isotopes ^{90}Zr and ^{180}Hf with H_2SO_4

When a sample (~0.02 mg) of ^{90}Zr was injected on a column of Dowex 50W-X8 (15-25 μm) resin and eluted with 1.2 N H_2SO_4, the chromatogram showed a single peak with a distribution ratio of 1.2 (Fig. 2A). In a similar test with a sample (~0.02 mg) of ^{180}Hf, a single peak with a K_d of 10 was observed (Fig. 2B). This indicates a hafnium/zirconium separation factor (α) of ~eight.

Identification of Zr-Hf Peaks Using ^{90}Zr and ^{180}Hf

A sample containing a mixture of zirconium and hafnium prepared from zircon sand spiked with hafnium (H-6) was eluted with 1.2 N H_2SO_4 to give the chromatogram shown in Fig. 3A. Figure 3B shows the growth of the zirconium in a similar chromatogram after spiking the solution with ^{90}Zr and Fig. 3C shows the growth of hafnium after spiking the solution with ^{180}Hf. In each case the K_d for zirconium was 1.2 and the K_d for hafnium was 10 as expected from chromatograms of the pure isotopes described above. The hafnium/zirconium separation factor (α) was 8.

Figure 4A shows a chormatogram of the liquor prepared from zircon sand. In this case, the zirconium K_d was 1.2 and the hafnium K_d was 10 to give a hafnium/zirconium separation factor of 8. Figure 4B shows the chromatogram after solution was spiked with ^{90}Hf. The hafnium peaks are the same in each case. In order to have sufficient concentration in the unspiked sample (4A) for the hafnium peak to be seen (∿ .006 mg hafnium) the zirconium peak (∿ 0.2 mg zirconium) went off scale.

Effect of Sulfuric Acid Concentration

As shown in Fig. 5, distribution ratios for both zirconium and hafnium decrease as the approximate inverse fourth power of the sulfuric acid concentration over the range 0.5 to 1.5 N acid and as the approximate inverse second power over the range 1.5 to 3.0 N. The hafnium to zirconium separation factor is approximately constant (~8) over the entire range.

Process Application

As an extension of our small-scale laboratory studies, scale-up tests on more concentrated solutions were initiated by the Chemical Technology Division in their pressurized continuous annular chromatograph (13). The results of these tests indicated the presence of an unseparated fraction not retained by the resin. The amount of this fraction, which is thought to be a polymeric hydrolysis product, appears to be a function of the concentrations of metal and sulfuric acid. Although in commercial application this fraction could possibly be recycled, we are carrying out tests to devise ways to prevent its formation.

It has been reported that a small fraction of both species have passed through ion exchange beds in the first few column volumes, suggesting that in solution zirconium and hafnium form mixed polymers (14). This was ascribed to colloidal forms held weakly by the resin. It is well known that zirconium ions exhibit strong tendencies toward polymerization, hydrolysis, and colloid formation, particularly at low acidities and high metal ion concentrations.

Measurements with concentrated zirconium solutions have been made in our laboratory HPLC system to try and duplicate those made in the CAC unit. Timed chromatographs show that the polymerized material, as indicated by the initial peak in Figure 6, disappears within 6-7 hours after dilution indicating that the equilibrium is slowly reversible. The response of the fluorometer is much less for the polymer than for the ionic zirconium complex so that its peak height is not indicative of the relative amounts present. Parameters affecting the formation of this material are thought to be sulfuric acid and zirconium concentration. Conditions will be optimized to give the highest zirconium concentration and the lowest sulfuric acid concentration that can be used as a feed material for the CAC unit without formation of the polymer. In order to accomplish this task, we have had to purchase additional equipment in order to better quantify the data and determine the fraction of zirconium that exists as a polymer under various conditions. For this reason, this study will be published later.

Conclusions

The present results demonstrate that pressurized ion exchange chromatography using elution development with small resin beads can successfully separate zirconium from hafnium in sulfuric acid solutions. Because of the relatively low distribution ratios in sulfuric acid concentrations sufficiently high to prevent or minimize hydrolysis and polymerization it is doubtful that the simpler and cheaper preparative ion exchange techniques, such as displacement or breakthrough chromatography, can be used to make this separation on a commercial scale. However, the values obtained here are sufficient for effective separation in the CAC unit being developed by the Chemical Technology Division. Scale-up tests in their unit have been very encouraging from the standpoint of industrial application and confirmed the separation reported here. One problem that remains to be solved is the formation of an unseparated zirconium-hafnium fraction that is not retained by the resin. Although in commercial application this fraction could possibly be recycled, we are carrying out tests to devise ways to prevent its formation.

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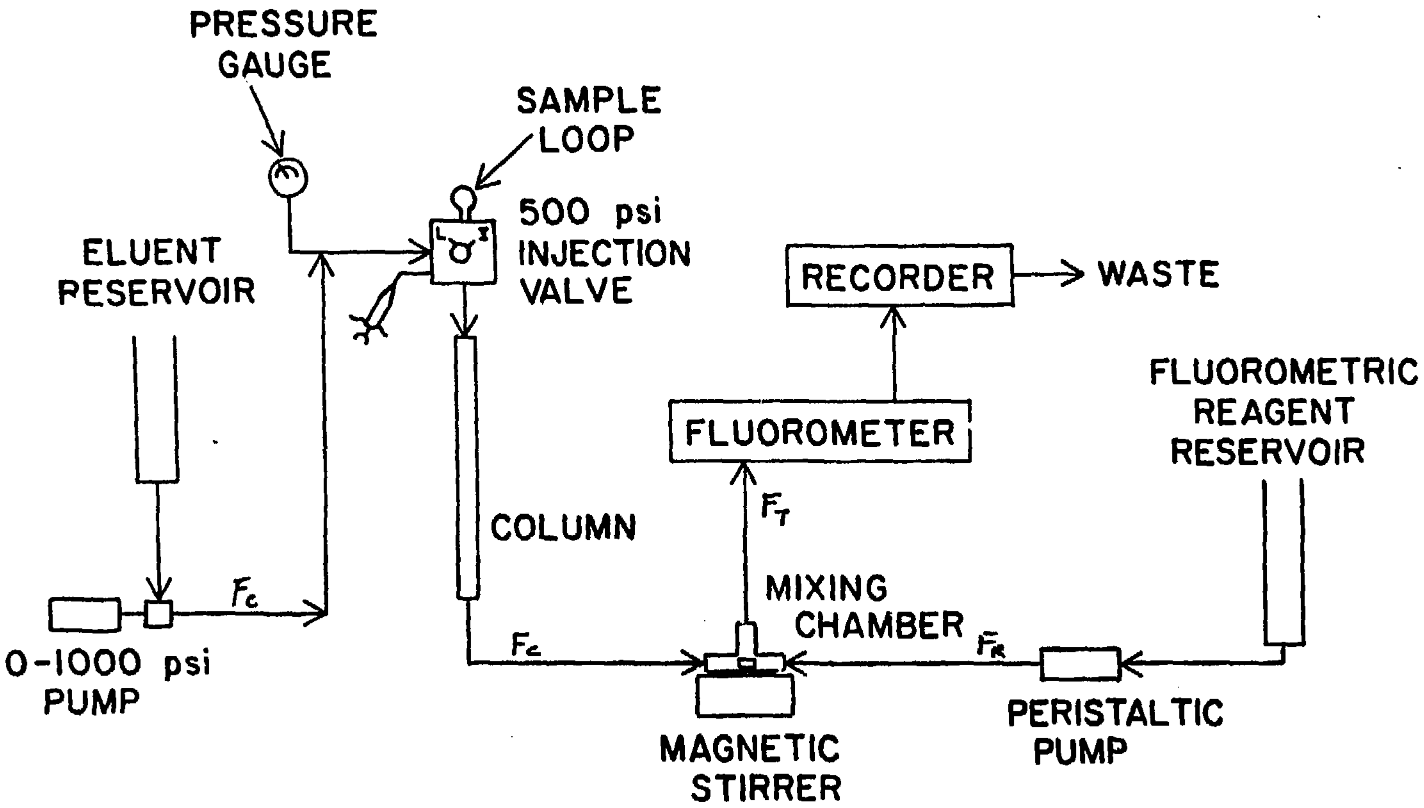
Figure Captions

DWG. NO.	FIG. NO.	Title
79-1262	1	Pressurized Ion Exchange System.
	2	Elution of Stable Isotopes ^{90}Zr and ^{180}Hf from Dowex 50W-X8 Resin with 1.2 N H_2SO_4. Column: 0.63 x 10.7 cm; 3.34 ml of resin. Flow rate: 2 ml cm^{-2} min^{-1}.
	3	Identification of Zr and Hf Peaks Using Stable Isotopes ^{90}Zr and ^{180}Hf. Conditions are the same as Fig. 2.
	4	Chromatogram of Liquid from Zircon Sand. Conditions are the same as Fig. 2.
80-727	5	Effect of H_2SO_4 Concentration on Sorption of Zirconium and Hafnium Complexes by Dowex 50W-X8 Resin.
	6	The Effect of Aging Time on Depolymerization.

ORNL DWG 79-1262



PRESSURIZED ION EXCHANGE SYSTEM

Fig 1

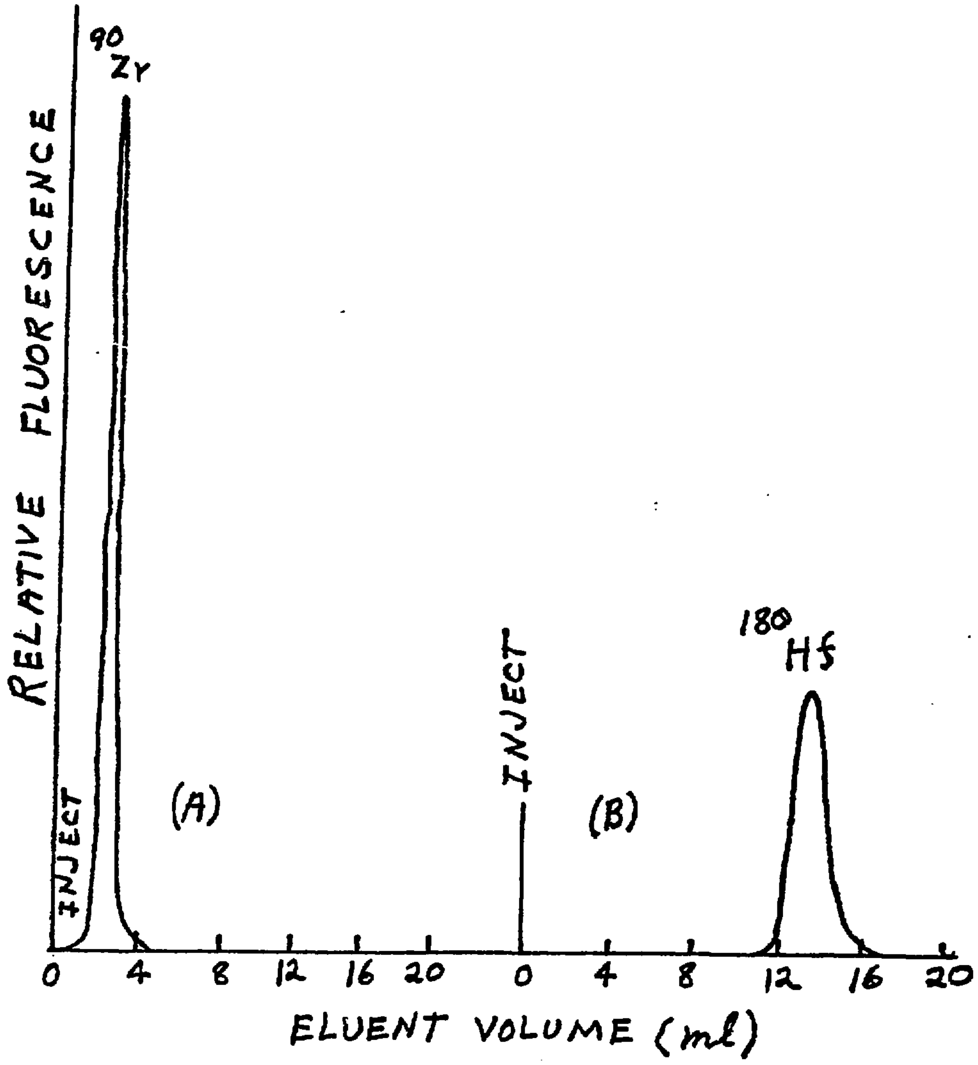


FIG 2. Elution of stable Isotopes ^{90}Zr and ^{180}Hf with 1.2 N H_2SO_4. Column: 0.63 X 10.7 cm ; 3. 34 mL of resin. Flow rate: 2mL cm^{-2} mi

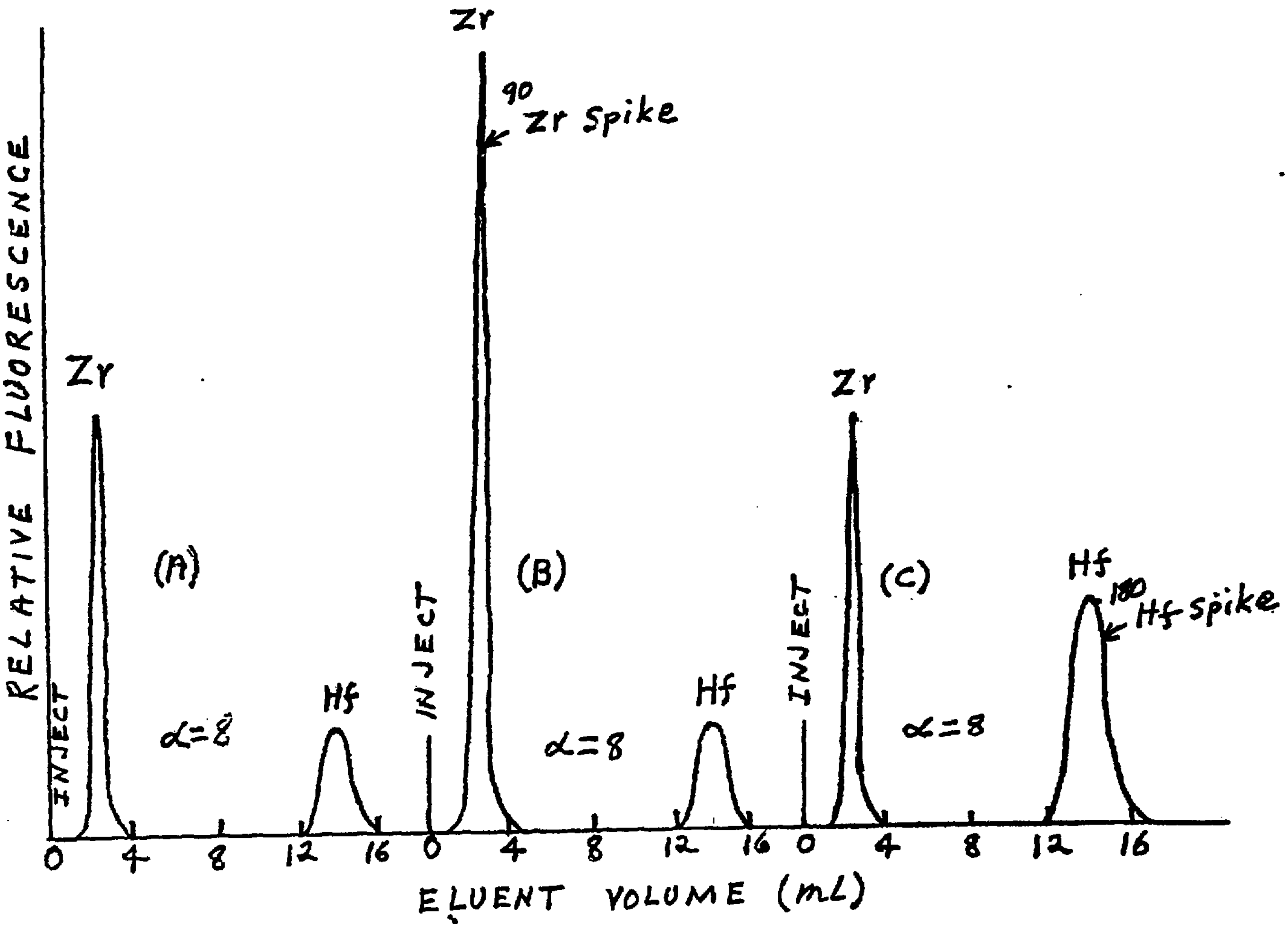


FIG 3. Identification of Zr + Hf peaks using stable Isotopes ^{90}Zr + ^{180}Hf

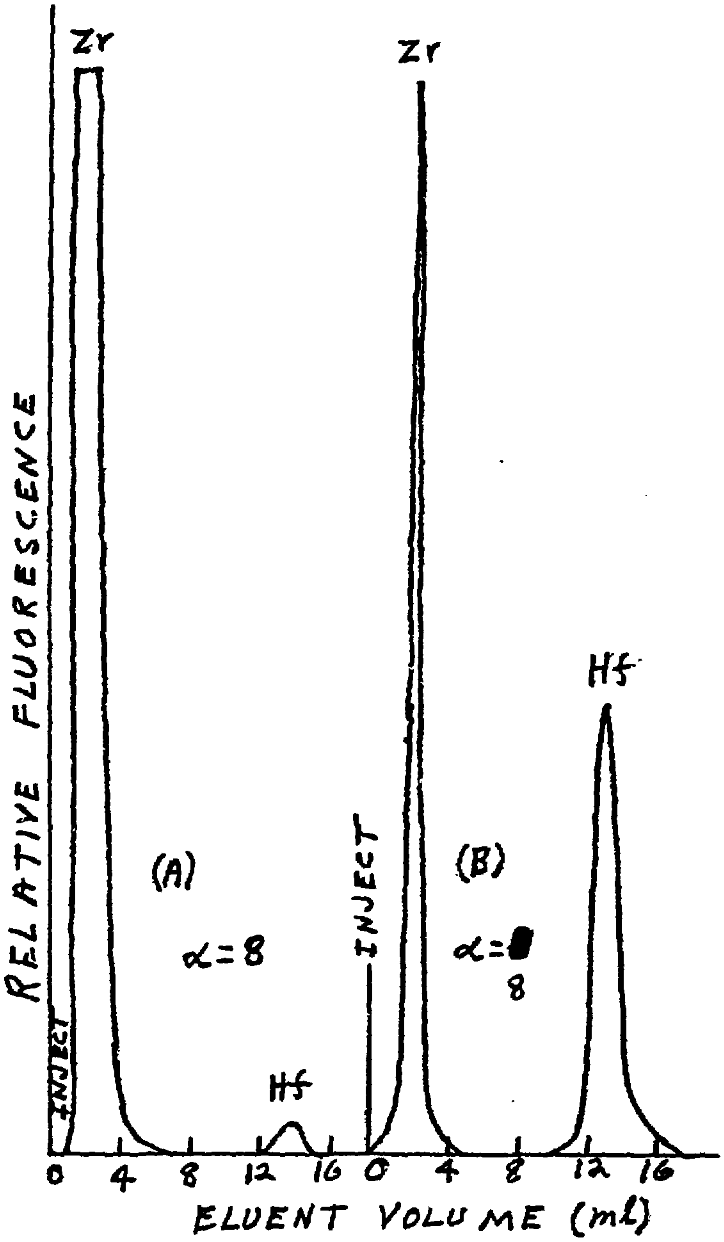


FIG 4. Chromatogram of Liquor from zircon sand

ORNL DWG 80-727

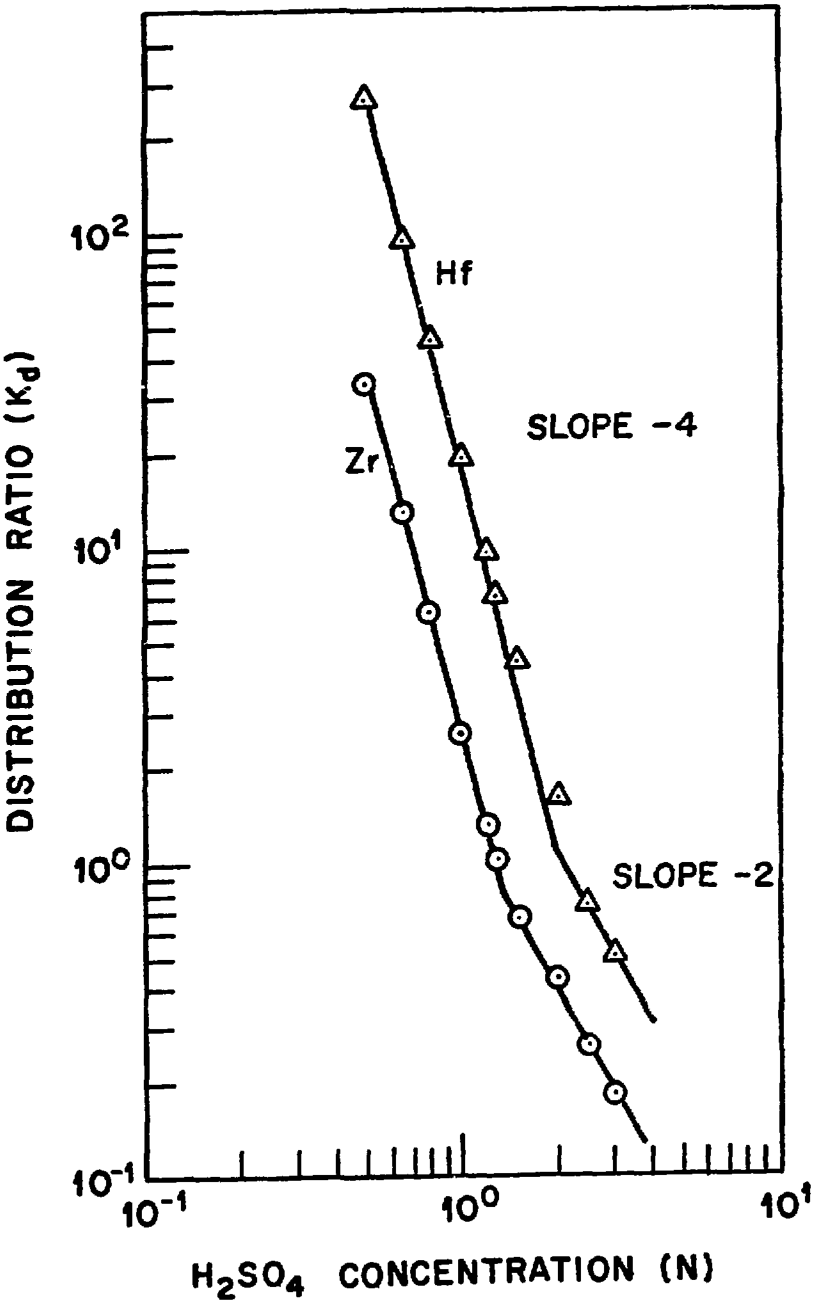
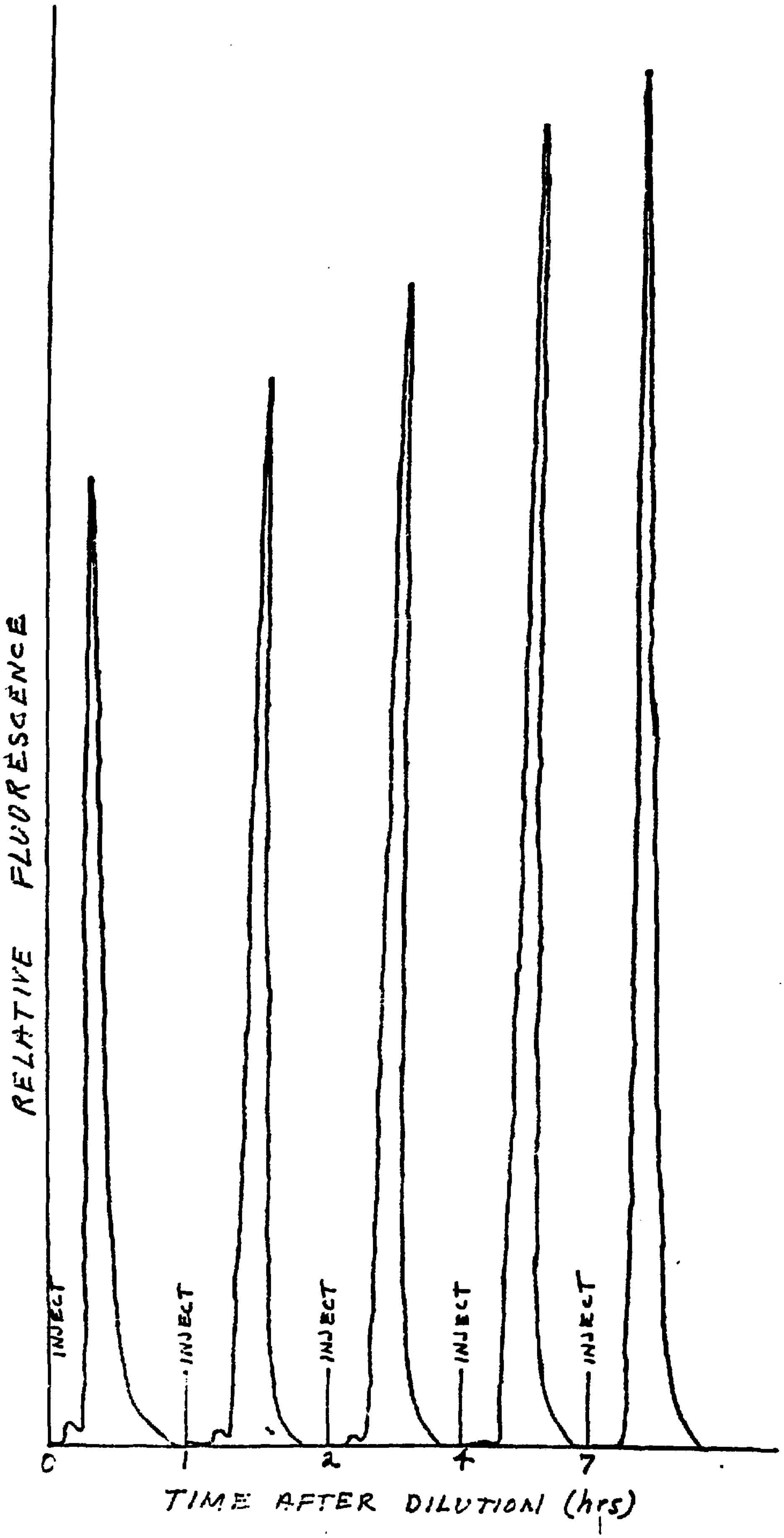


Fig 5


RELATIVE FLUORESCENCE
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1
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7
TIME AFTER DILUTION (hrs)

fig 6