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QUANTITATIVE AND RAPID SEPARATION OF Zr(IV) AND Hf(IV) BY THIN-LAYER CHROMATOGRAPHY

SPECTROPHOTOMETRIC DETERMINATION OF Hf(IV) WITH CHLORANILIC ACID

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SUMMARY

By using a thin-layer chromatographic technique on Silica Gel G, Zr(IV) and Hf(IV) at different concentrations can be separated quantitatively in 45 min.

An HCl-H₃PO₄-H₂O (10:1:9) mixture was used to develop the plates.

Forty-three ions were chromatographed. Only Ag(I), Tl(I) and W(VI) remained in the spot area with Zr(IV). The R_F values of the other individual ions were higher than 0.6.

Zr(IV) and Hf(IV) were determined spectrophotometrically with chloranilic acid. The results were confirmed by a radiometric technique.

A spectrophotometric method was developed for the determination of Hf(IV) with chloranilic acid.

INTRODUCTION

Several methods for the separation of Zr(IV) from Hf(IV) by paper chromatography have been reported, but little is known about the separation of these ions by thin-layer chromatography. The best results were obtained on paper pre-treated with trioctylamine¹ by elution with HCl-HNO₃ in circular or horizontal chromatography. The differences in the R_F values were in both cases of the same order. Similar results were obtained by using butyl phosphate-butanol and xylene or benzene saturated with HNO₃ at various concentrations².

Separations performed with butanol-hydrochloric acid³, butanol-hydrochloric acid-hydrofluoric acid-water⁴, butanol-sulphuric acid-hydrofluoric acid-water⁴, acetone-hydrochloric acid-hydrofluoric acid-water⁴, dichloroethyleneglycol-nitric acid⁵ and diethyl ether-nitric acid on paper soaked with sodium nitrate⁶, were not as good as was desirable. Some results and operating conditions are summarized in Table I.

An HCl-H₃PO₄-water mixture (10:1:9, v/v/v), was used by QURESHI AND KHAN⁷ to separate Zr(IV) + Hf(IV) from other ions by ascending chromatography on paper. Zr and Hf were reported to be inseparable by this technique.

TABLE I

RESULTS AND OPERATING CONDITIONS AS SHOWN IN THE SEPARATION OF Zr(IV) AND Hf(IV) IN PAPER CHROMATOGRAPHY

Adsorbent	Solvent system	R_F value ^a		Observations	Reference
		Zr	Hf		
Paper-triethylamine	HCl-HNO ₃	0.25	0.80	Circular	1
		0.17	0.50	Descending	1
Paper	Bu ₃ PO ₄ -BuOH-xylene-H ₂ O	—	—	R_F value ratio	2
Paper	BuOH-HCl	0.28 t	0.30	13 h	3
Paper	BuOH-HCl-HF-H ₂ O	0.52 t	0.53 t		4
Paper	Acetone-HCl-HF-H ₂ O	0.48	0.46 t		4
Paper-NaNO ₃	Et ₂ O-HNO ₃	0.203 t	0.0204		6
Paper	Dichloroethyleneglycol-HNO ₃	0.2	0.1	18 h	5
Paper-triethylamine	HCl-HNO ₃	0.17	0.50	Descending	1
Silica Gel G-HR (TLC)	H ₃ PO ₄ -HCl-H ₂ O	0	0.90	45 min	This work

^a t = diffuse tail.

A thin-layer chromatographic technique on Silica Gel G-HR for the quantitative separation of Zr(IV) and Hf(IV), with HCl-H₃PO₄-water (10:1:9, v/v/v), as developer, is described in this paper. The process takes about 45 min.

EXPERIMENTAL AND RESULTS

All the reagents used were of analytical grade. Precautions were taken to avoid anomalous results due to eventual changes in the ions in solution, as both Zr(IV) and Hf(IV) form polymerized species. Before spotting the sample, it was kept in concentrated sulphuric acid and heated until fuming. With this treatment, both Zr and Hf ions from aged solutions behaved chromatographically in the same manner as those in fresh solutions.

For qualitative separation tests from other ions, 10 μ l of 0.1 M samples, prepared according to Table II, were spotted. A Desaga applicator was used to coat the 20 \times 20 cm plates with a 5:1 (v/w) mixture of water and cellulose powder (Whatman CC 41 of mean particle size (wet) 10-25 μ m), or with a 2:1 (v/w) mixture of water and Silica Gel G-HR (Macherey, Nagel & Co.). The height of the exit gate was set at 0.1 mm. After air-drying the plates, they were activated at 100-105° for 1 h, spotted with the standard and dried again with air under pressure. Special care was taken in drying the sample, because exceedingly hot air can immobilize some ions, particularly those of Hf(IV). The spot diameter was about 7 mm. The plates were placed vertically, developed in 20 \times 15 \times 35-cm tightly covered glass jars and maintained at 25-30°. A conditioning time of 10 min was used throughout. After 45 min, the solvent front reached a height of about 13 cm; in some instances on paper, the same height was reached only after 90 min.

The developed plates were dried with moderately hot air and sprayed, when necessary, with the appropriate chromogenic reagent (Table II), and finally dried again.

TABLE II

BEHAVIOUR OF VARIOUS INORGANIC IONS IN THIN-LAYER CHROMATOGRAPHY

Eluent HCl-H₃PO₄-H₂O (10:1:9); developing time 45 min.

Ion	Solvent	Chromogenic agent	<i>R_F</i> value ^a		Observations
			A	B	
Zr(IV)	HCl	1-nitroso-2-naphthol	0.00	0.00	
Hf(IV)	H ₂ SO ₄	b	0.90-1.0	0.90-1.0	
Nb(V)	H ₂ SO ₄ -H ₂ C ₂ O ₄	b	0.90-1.0	0.70-1.0	
Ge(IV)	HNO ₃	b	0.95-1.0	0.95-1.0	
Ga(III)	HNO ₃	b	0.95-1.0	0.95-1.0	
Rb(I)	HCl	b	0.91-0.98	0.91-0.98	
Cs(I)	HCl	b	0.91-0.98	0.91-0.98	
Al(III)	HNO ₃	Alizarin	0.85-1.0	0.86-1.0	
La(III)	HNO ₃	Alizarin	0.80-1.0	0.80-1.0	
In(III)	HNO ₃	Dithizone	0.88-0.95	0.88-0.96	
Cd(II)	HNO ₃	Dithizone	0.87-0.95	0.87-0.96	
Sb(III)	HCl	Dithizone	0.80-0.89	0.80-0.89	
Ag(I)	HNO ₃	(NH ₄) ₂ S	0.00-1.0	0.00-1.0	
Pb(II)	HNO ₃	(NH ₄) ₂ S	0.78-0.86	0.78-0.88	
Hg(II)	HNO ₃	(NH ₄) ₂ S	0.77-0.86	0.78-0.86	
Bi(III)	HNO ₃	(NH ₄) ₂ S	0.86-0.96	0.80-0.90	
Cu(II)	HNO ₃	(NH ₄) ₂ S	0.84-0.93	0.83-0.93	
Ti(IV)	HNO ₃	Chromotropic acid	0.60-1.0	0.60	Tail
Y(III)	HNO ₃	Oxine (fluorescent)	0.84-1.0	0.84-1.0	Tail
Cr(III)	HCl	H ₂ O ₂	0.84-0.92	0.84-0.92	
Selenite	H ₂ O	FeSO ₄ -H ₃ PO ₄	0.76-0.84	0.75-0.84	
Tellurite	H ₂ O	FeSO ₄ -H ₃ PO ₄	0.86-0.94	0.85-0.95	
Tl(I)	H ₂ SO ₄	KI	0.00-1.0	0.00-1.0	
Th(IV)	HNO ₃	Thoron	0.82-0.90	0.84-0.93	
Cr(VI)	H ₂ O	Not needed	0.84-0.92	0.69-1.0	
Au(III)	HCl	SnCl ₂	0.63-0.70	0.88-0.92	
Ba(II)	HNO ₃	Na rhodizonate	0.83-0.87	0.68-1.0	
Sr(II)	HNO ₃	Na rhodizonate	0.82-0.87	0.70-0.98	
Mg(II)	HNO ₃	Magneson I	0.90-1.0	0.85-1.0	
Pt(IV)	HCl	SnCl ₂	0.85-0.92	0.90-1.0	
Os(IV)	HCl	Not needed	0.80-0.88	0.95-1.0	
Sc(III)	HNO ₃	Oxine	0.87-0.92	0.85-0.91	
Arsenate	H ₂ O	AgNO ₃	0.91-0.99	0.91-1.0	
Fe(III)	HNO ₃	K ferrocyanide	0.82-0.92	0.82-0.93	
Sn(II)	HCl	HgCl ₂	0.81-0.90	0.80-0.90	
Sn(IV)	HCl	b	0.70-0.79	0.80-0.90	
W(VI)	H ₂ O	KSCN-SnCl ₂	0.40	0.35	Tail
Mo(VI)	H ₂ O	KSCN-SnCl ₂	0.93-1.0	0.85-0.88	
Ta(V)	HCl	Rhodamine B	0.85-0.92	0.85-0.95	
K(I)	HNO ₃	b	0.90-1.0	0.90-1.0	
Na(I)	HCl	b	0.95-1.0	0.95-1.0	
Li(I)	HCl	b	0.96-1.0	0.96-1.0	
Hg(I)	HNO ₃	SnCl ₂	0.00-1.0	0.00-1.0	

^a *R_F* values are given for the leading and trailing edge of the spot. A = cellulose; B = Silica Gel G.

^b Heated in air at 120°.

Spectrophotometric readings were made with a Beckman DU unit, and radio-metric measurements using Zr⁹⁵ and Hf¹⁸¹ as tracers, with a Radiochromatograph Scanner Model 7.200.

Quantitative studies

Chromatographic separations for quantitative studies were performed by using Silica Gel G-HR plates. Spectrophotometric determinations of both Hf(IV) and Zr(IV) were made with chloranilic acid. As it is a strong acid, chloranilic acid retains its complexing properties even in the highly acidic solutions that are necessary in order to keep easily hydrolyzable ions in solution.

Zr(IV) was determined by THAMER AND VOIGT's method⁸, while the method of JOHNSON AND FREUND⁹ for Hf(IV) was tested and modified so as to give a higher sensitivity.

Strips of the adsorbent on the developed plates containing the ions under investigation were removed. Each fraction was then ground in a small agate mortar and fused with 3 g of Na₂CO₃ in a platinum crucible. When cool, the melt was dissolved in hot water, kept in a steam-bath for 20 min, cooled again and then centrifuged. The bulk of the Zr(IV) and Hf(IV) remained in the precipitate, retaining an appreciable amount of phosphate; most of it was then separated by a second fusion and subsequent leaching and centrifugation.

In order to recover most of the Zr(IV) and Hf(IV), the supernatant liquid from the first centrifugation was re-evaporated. The residue was fused with Na₂CO₃, and the hot water and centrifugation process was repeated. Both precipitates were dissolved in perchloric acid and the colour developed as described in Table III. Spectrophotometric readings were made by previous adjustment of the null point, by using a blank solution. This was obtained according to the method described above by using a portion of a parallel strip of the plate developed without sample, and obtained at the same level of the chromatogram.

TABLE III

OPERATING CONDITIONS IN THE SPECTROPHOTOMETRIC DETERMINATIONS OF Zr(IV) AND Hf(IV) WITH CHLORANILIC ACID

<i>Ion</i>	<i>λ (nm)</i>	<i>Acidity (HClO₄)</i>	<i>Developing time (min)</i>
Zr(IV)	340	2 <i>M</i>	15
Hf(IV)	335	1 <i>M</i>	60

To determine the location of the separated ions after development, samples containing 123 μg of Zr(IV) and 421 μg of Hf(IV) were individually chromatographed on two different plate runs, simultaneously. The adsorbent on the plates was divided in horizontal strips 1 cm wide, and each was used for the spectrophotometric determination of Zr(IV) and Hf(IV).

The results (Fig. 1) proved that Zr(IV) did not move appreciably, while Hf(IV) is spread over a portion of the plate, 4 cm from the solvent front. Thus, over the 13 cm traveled by the solvent, the separation distance between Zr(IV) and Hf(IV) was 6 cm.

The resolution remained equally satisfactory when Zr(IV) and Hf(IV) ions were present in the sample in proportions ranging from 1:100 to 100:1, within the absolute amounts given in Table IV.

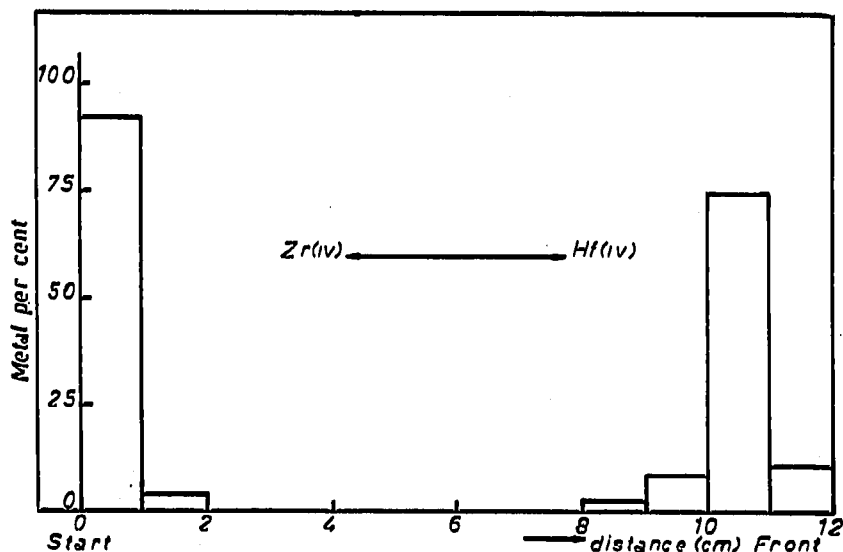


Fig. 1. Distribution of Zr(IV) and Hf(IV) on Silica Gel G-HR chromatographic plate, eluted with $\text{HCl}-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$ (10:1:9). Spotting: Zr(IV) = Hf(IV) = 100 μmoles . Developing time, 45 min; temperature, 25–30°. Spectrophotometric evaluation.

TABLE IV

RECOVERY OF Zr(IV) AND Hf(IV) FROM MIXTURES IN VARIOUS PROPORTIONS, AFTER SEPARATION BY THIN-LAYER CHROMATOGRAPHY

Molar ratio, Zr(IV):Hf(IV)	Amount taken (μg)		Amount found (μg)	
	Zr(IV)	Hf(IV)	Zr(IV)	Hf(IV)
1:1	2.5	2.5	2.45	2.45
50:1	100	2	98.2	1.80
1:50	2	100	1.92	97.0
100:1	100	1	97.2	0.92
1:100	1	100	0.95	96.0

In the confirmatory tests with radioactive tracers, the samples under study were prepared in the same way as used in spectrophotometry, using Zr^{90} or Hf^{181} .

After developing the chromatograms, the dry chromatographic plates were sprayed with Neo-Natan, dried again and finally protected with glued cellophane.

When Zr^{90} was used, an aluminium foil 18 mm thick was placed between the plate and detector to eliminate the Nb radiation from Zr^{90} decay.

The results (Fig. 2) confirmed those obtained when the effectiveness of the separation was spectrophotometrically evaluated.

Spectrophotometric determination of Hf(IV)

By a spectrophotometric method, VARGA AND VEATCH¹⁰ found two complex species with 1:1 and 3:1 molar ratios of chloranilic acid to Hf(IV). The reagent was

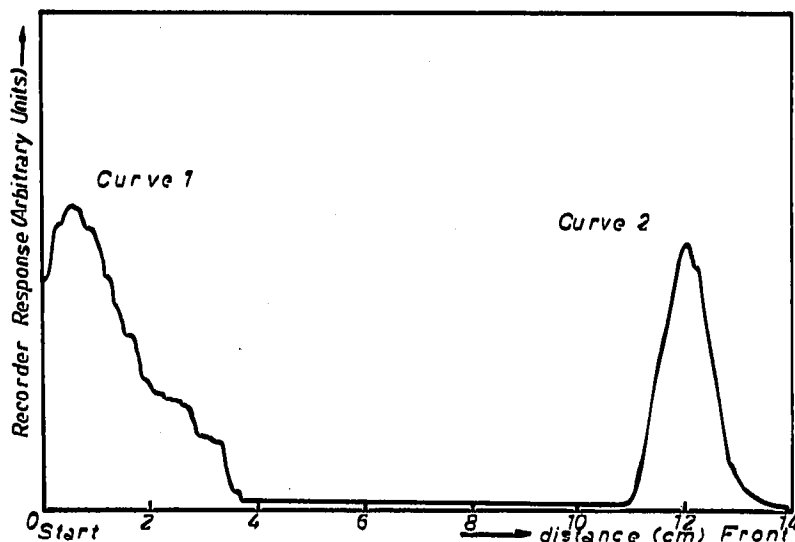


Fig. 2. Distribution of $Zr^{90}(IV)$ and $Hf^{191}(IV)$ on Silica Gel G-IR chromatographic plate eluted with $HCl-H_3PO_4-H_2O$ (10:1:9). Curve 1, Zr:Hf ratio 100:1; curve 2, Zr:Hf ratio 1:100. Developing time, 45 min; temperature, 25–30°. Radiometric evaluation.

previously applied to the spectrophotometric determination of Hf(IV) in a method having the same sensitivity as that attained by THAMER AND VOIGT⁸ for the Zr(IV)-chloranilic acid system. The present authors studied the method, as indicated below, in a search for higher sensitivity.

Absorption spectra and effect of the acidity

Absorption spectra of a series of solutions containing a fixed amount of Hf(IV) and a large excess of ligand, at different concentrations of perchloric acid between 0.1 and 3 M, were recorded in comparison with the corresponding blank. The curves showed an absorption maximum at 332–337 nm regardless of acidity; the highest absorptivity corresponds to 1 M $HClO_4$.

Effect of the reagent: Hf(IV) molar ratio and rate

The absorbance of the chloranilic acid-Hf(IV) system increased with the concentration of the reagent, reaching a stable value at a molar ratio of 80:1.

The absorptivity, under the described conditions, increased for 1 h and then remained unaltered for at least 48 h.

Conformity to Beer's law, sensitivity and accuracy

A straight-line calibration curve showed agreement with Beer's law within the concentration range considered, *i.e.* 0.21–4.55 p.p.m. of Hf(IV).

The molar absorptivity calculated was 38,000 and the mean sensitivity (Sandell's method) was 0.0046 $\mu g/cm^2$. The optimum concentration range, as obtained from the curves drawn according to RINGBOM¹¹, was 1.0–3.80 p.p.m.

The relative error for 1% absolute photometric error was 2.80.

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