

Thin-layer chromatographic behaviour and separation of zirconium(IV) and hafnium(IV) on silica gel in mineral acid–hydrogen peroxide media

KOJI ISHIDA*

Laboratory of Chemistry, Nippon Medical School, Kosugi, Nakahara-ku, Kawasaki, Kanagawa 211 (Japan)
and

SHUJI NINOMIYA, YOSHIAKI UCHIDA and MASUMI OSAWA

Department of Chemistry, Faculty of Education, Tokyo Gakugei University, Koganei, Tokyo 184 (Japan)

(Received July 11th, 1990)

ABSTRACT

The thin-layer chromatographic behaviour of Zr(IV) and Hf(IV) on silica gel in HNO₃, HCl and H₂SO₄ media containing various amounts of H₂O₂ was investigated as a function of the concentration of each component of the respective solvents. In all the systems, Zr(IV) gave much higher *R_F* values than Hf(IV) because of the stronger complexation of Zr(IV) with H₂O₂, so that the complete separation of the two metals, present in Zr:Hf weight ratios ranging from 20:1 to 1:40, could be accomplished simply and easily without any sample pretreatment.

INTRODUCTION

The complete separation of zirconium(IV) and hafnium(IV) is one of the most difficult tasks in inorganic analysis, because both metals exhibit almost the same chemistries owing to their similar outer electronic configurations and ionic radii, and is particularly troublesome when Zr(IV) is present in much higher proportions than Hf(IV), as in natural zirconium ores. In general, solvent extraction, ion-exchange and column chromatographic methods have effectively been utilized for this purpose [1]. Good results have also been obtained with several paper chromatographic methods [2]. However, much less information is available on the separation of these ions by thin-layer chromatography (TLC).

The TLC separation of Zr(IV) and Hf(IV) from each other was first achieved [3] using microcrystalline cellulose and diethyl ether–14 mol/dm³ HNO₃ (1:1, v/v). Shimizu and Muto [4] also accomplished the separation of the two metals by two-dimensional TLC on DEAE-cellulose by development with 0.1 mol/dm³ H₂SO₄–0.05 mol/dm³ (NH₄)₂SO₄ solution and 0.1 mol/dm³ H₂SO₄–1.0 mol/dm³ (NH₄)₂SO₄ solution. However, these two methods did not provide a sufficiently large resolution for this pair, having centred on the separation of equimolar amounts of the metals. In

contrast, Olsina *et al.* [5] quantitatively separated both metals present in a wide range of amounts and ratios on a silica gel layer by development with HCl-H₃PO₄-H₂O (10:1:9, v/v/v), in which both metals have been reported to be inseparable by paper chromatography [6]. This TLC method of separation, however, requires fuming of the sample solution with H₂SO₄ just before its application on the plate and special care in drying the spotted sample solution in order to avoid anomalous results caused by hydrolysed and polymerized species of these metals in aged solutions.

In this work, the TLC behaviour of Zr(IV) and Hf(IV) on silica gel in HNO₃, HCl and H₂SO₄ media containing various amounts of H₂O₂ was studied in order to establish simple and effective methods for the separation of these metals. All the TLC systems investigated allow the complete separation of both metals coexisting in a wide range of amounts (0.2–4 mg) and ratios (Zr:Hf = 20:1–1:40), without any pretreatment of aged sample solutions.

EXPERIMENTAL

Stock solutions

Stock solutions of Zr(IV) and Hf(IV) were prepared from their oxychlorides (99.99% purity), as follows, to give a concentration of 0.05 mol/dm³ with respect to each metal. The oxychloride solutions were obtained by dissolving suitable amounts of the respective compounds in a small volume of 6 mol/dm³ HCl, evaporating to dryness and dissolving the residues in the same acid. For oxynitrate and oxysulphate solutions, appropriate amounts of the oxychloride of each metal were dissolved in a small volume of 6 mol/dm³ HNO₃ or 3 mol/dm³ H₂SO₄ and evaporated to dryness, followed by dissolution of the residue in the same acid. When necessary, the stock solutions were diluted with the same acid of the same concentration.

Test solutions for the measurement of the R_F values were prepared by diluting the individual stock solutions to give a 1 mg/cm³ metal solution. Sample solutions were obtained by mixing suitable amounts of the stock solutions or by diluting the resulting mixtures.

Preparation of thin-layer plates

A 10-g portion of silica gel without binder (Wakogel B-O; Wako, Osaka, Japan) was thoroughly blended with 22.5 cm³ of distilled, deionized water. The slurry was spread to a thickness of 250 μm on glass plates (20 × 20 cm) with an applicator. The plates were allowed to stand for 30 min at room temperature and then dried in an oven at *ca.* 70°C for 30 min.

In order to remove inorganic impurities from the silica gel used, the plate was thoroughly washed by developing overnight up to the upper edge of the plate by the ascending technique with 30 cm³ of 1 mol/dm³ HCl-3% (w/v) H₂O₂ solution, using a sandwich type of chamber made of plastic. Subsequently, the plate was dried on a hot-plate at *ca.* 90°C for 20 min. After cooling, they were stored in a desiccator containing saturated sodium chloride solution, until ready for use.

Procedure

A 0.5-μl portion of the test or sample solution was applied to the plate by means of a microcap (Drummond, Broomall, PA, U.S.A.) at a point 2.5 cm from one edge

and the spots were dried in air for 10 min. The plate was immediately placed in a chromatographic chamber (22 × 10 × 22 cm), equipped with a small tank (21 × 5 × 4 cm) containing 30 cm³ of a developing solvent, and developed up to 10 cm from the starting point by the ascending technique at room temperature. The developing solvents used were HNO₃, HCl and H₂SO₄ containing H₂O₂ at various concentrations.

Detection

After development, the plate was dried on a hot-plate at *ca.* 90°C and the positions of the metals were revealed by spraying with a 0.02% aqueous arsenazo III solution. Both metals were detected as green spots on a pink background.

RESULTS AND DISCUSSION

Adsorption behaviour

HNO₃-H₂O₂ system. The R_F values of Zr(IV) and Hf(IV) on silica gel in HNO₃-H₂O₂ media are summarized as a function of the concentration of each component of the solvents in Table I, where the separation factors (α) and the resolutions (R_s), each defined as follows, are also given to clarify the effectiveness of the system for the separation of the metals:

$$\alpha = \left[R_{F(\text{Hf})}^{-1} - 1 \right] / \left[R_{F(\text{Zr})}^{-1} - 1 \right]$$

TABLE I

R_F VALUES (× 100) OF Zr(IV) AND Hf(IV) ON SILICA GEL IN HNO₃-H₂O₂ MEDIA

Concentration of HNO ₃ (mol/dm ³)	Concentration of H ₂ O ₂ (% w/v)	$R_F \times 100$		Separation factor (α)	Resolution (R_s)
		Zr(IV) ^a	Hf(IV) ^a		
0.1	0	1-11	1-5	2	0.4
0.1	0.6	75-97	0-4	300	6.5
0.1	1	84-99	2-7	230	8.7
0.1	3	91-100	1-8	450	11
0.1	6	88-100	0-9	330	8.5
0.1	10	92-100	2-25	150	5.3
1	0	0-9	0-7	1	0.1
1	0.3	2-93	2-8	17	0.9
1	0.6	33-95	2-11	26	1.6
1	1	62-98	2-11	58	3.3
1	3	87-100	1-20	120	5.2
1	6	92-100	1-23	180	5.6
1	10	92-100	3-38	93	3.5
0.1	3	91-100	1-8	450	11
0.5	3	90-100	2-11	270	9.3
1	3	87-100	1-20	120	5.2
3	3	91-100	3-35	90	3.7
6	3	92-100	4-44	76	3.0
9	3	91-100	12-33	71	5.0

^a Oxynitrate used.

where R_F is the average of the R_F values of the rear and the front of each spot; and

$$R_S = 2[D_{(Zr)} - D_{(Hf)}]/[W_{(Zr)} + W_{(Hf)}]$$

where D is the migration distance of the centre of each spot and W is the width of each spot in the longitudinal direction.

When the concentration of HNO_3 was kept constant at 0.1 or 1.0 mol/dm³, Zr(IV) migrated near the solvent front even in the presence of a small amount of H_2O_2 and gave more compact spots as the concentration of H_2O_2 became higher. In contrast, Hf(IV) remained near the point of application in almost all the solvents tested and showed longer spots at higher concentrations of H_2O_2 .

On the other hand, when the concentration of H_2O_2 was kept constant at 3.0% (w/v), Zr(IV) displayed well defined and compact spots in contact with the solvent front, regardless of the concentration of HNO_3 , whereas Hf(IV) showed low R_F values and gave longer spots as the concentration of HNO_3 increased.

In addition, without any H_2O_2 , the adsorption behaviour of Zr(IV) and Hf(IV) were very similar; they adsorbed very tightly on silica gel in all the HNO_3 solutions within the concentration range 0.1–6.0 mol/dm³, and showed a slightly increasing tendency in their R_F values with further increase in HNO_3 concentration, although all the data obtained are not quoted in Table I.

Hence in this system Zr(IV) gives extremely high R_F values even in the presence of small amounts of H_2O_2 , but Hf(IV) remains near the point of application, although

TABLE II

R_F VALUES ($\times 100$) OF Zr(IV) AND Hf(IV) ON SILICA GEL IN HCl- H_2O_2 MEDIA

Concentration of HCl (mol/dm ³)	Concentration of H_2O_2 (% w/v)	$R_F \times 100$		Separation factor (α)	Resolution (R_s)
		Zr(IV) ^a	Hf(IV) ^a		
0.1	0	1–11	1–5	2	0.4
0.1	0.6	44–97	2–6	57	2.3
0.1	1	91–100	0–6	690	12
0.1	3	95–100	0–6	1300	17
0.1	6	94–100	1–11	510	12
0.1	10	96–100	1–15	560	10
1	0	–1–8	–1–6	1	0.1
1	0.3	0–55	0–12	6	0.6
1	0.6	41–99	0–17	25	1.6
1	1	86–100	0–16	150	5.6
1	3	90–100	0–16	220	6.7
1	6	94–100	2–26	200	5.5
1	10	95–100	0–26	260	5.5
0.1	3	95–100	0–6	1300	17
0.6	3	92–100	1–16	260	7.6
1	3	90–100	0–16	220	6.7
3	3	83–100	0–46	36	2.2
6	3	88–100	55–76	8	1.7

^a Oxynitrate used.

both metals adsorb very strongly on silica gel in pure HNO_3 without H_2O_2 . Therefore, the complete separation of the two metals can be achieved over a wide range of concentrations of HNO_3 and H_2O_2 .

HCl-H₂O₂ system. The R_F values, the separation factors and the resolutions for Zr(IV) and Hf(IV) on silica gel in HCl-H₂O₂ media are listed as a function of the concentration of each component of the solvents in Table II.

In general, the TLC behaviour of the two metals in this system was very similar to that in the HNO_3 - H_2O_2 system, although the former offered larger separation factors and resolutions than the latter. However, when the stock solution of Zr(IV) oxychloride, aged for at least 4 h, was applied to the silica gel layer, another very weak spot was observed, just at the point of application. On the other hand, when that of the oxynitrate, aged for at least 6 months, was used, Zr(IV) did not show any abnormal adsorption. Fortunately, the abnormal adsorption of Zr(IV) oxychloride could easily be eliminated by adding a few drops of 3% (w/v) H_2O_2 and allowing the solution to stand for at least 4 h or by pretreating the sample solution three times with small amounts of 6 mol/dm³ HCl-3% (w/v) H_2O_2 solution or aqua regia. These observations suggest that the oxychloride solutions can produce more hydrolysed and polymerized species for a long aging period than the oxynitrate solutions and that it is very difficult to dissociate rapidly the resulting species to less hydrolysed and

TABLE III

R_F VALUES ($\times 100$) OF Zr(IV) AND Hf(IV) ON SILICA GEL IN H_2SO_4 - H_2O_2 MEDIA

Concentration of H_2SO_4 (mol/dm ³)	Concentration of H_2O_2 (% w/v)	$R_F \times 100$		Separation factor (α)	Resolution (R_s)
		Zr(IV) ^a	Hf(IV) ^a		
0.05	0	0-78	0-13	9	0.7
0.5	0	55-99	0-44	12	1.3
1	0	83-98	58-82	4	1.1
2	0	93-100	87-98	2	0.4
3	0	95-100	89-96	3	0.8
0.05	3	91-100	0-34	100	3.7
0.5	3	92-100	26-59	33	2.6
1	3	90-100	69-90	5	1.0
2	3	91-100	78-95	3	0.7
3	3	90-100	89-100	1	<0.1
0.05	0.6	72-98	4-29	29	2.7
0.05	1	92-100	3-33	110	4.1
0.05	3	91-100	0-34	100	3.7
0.05	6	92-100	0-39	99	3.2
0.05	10	92-100	0-52	68	2.3
0.5	0.3	88-100	10-42	45	3.1
0.5	0.6	89-100	12-50	38	2.6
0.5	1	88-100	19-53	28	2.5
0.5	3	92-100	26-59	33	2.6
0.5	6	90-100	26-76	18	1.5
0.5	10	90-100	42-83	11	1.3

^a Oxysulphate used.

polymerized species during chromatography. In addition, Hf(IV) always remained at or near the point of application with or without any treatment. Therefore, all the data in Table II are given with respect to the oxynitrates.

In conclusion, this system also allows the complete separation of Zr(IV) and Hf(IV) to be achieved simply and effectively, as with the $\text{HNO}_3\text{-H}_2\text{O}_2$ system, if the oxynitrates of the metals are used as the starting material.

H₂SO₄-H₂O₂ system. The R_F values, the separation factors and the resolutions for Zr(IV) and Hf(IV) are given as a function of the concentration of each component of the solvents in Table III, and those in pure H_2SO_4 without H_2O_2 are also listed for comparison.

In H_2SO_4 without H_2O_2 , the TLC behaviour of these metals was notably different from those in pure HNO_3 and pure HCl ; Zr(IV) showed weaker adsorption than Hf(IV), as with the cation-exchange resin-dilute H_2SO_4 system [7]. With lower concentrations of H_2SO_4 , these two metals could be separated on silica gel only with difficulty, because the resolutions were not satisfactory owing to long tailing of the peaks of the metals. On the other hand, with higher concentrations of H_2SO_4 , both metals were hardly adsorbed, because they occurred as less hydrolysed and polymerized species produced by the complexation with sulphate ions.

In contrast, in the H_2SO_4 media with H_2O_2 , Zr(IV) showed a compact spot in contact with the solvent front, irrespective of the change in the concentration of H_2SO_4 , whereas Hf(IV) gradually moved upwards as the concentrations of both H_2O_2 and H_2SO_4 increased. Thus, the addition of suitable amounts of H_2O_2 to H_2SO_4 solutions was very effective for the separation of Zr(IV) and Hf(IV), particularly when the concentration of H_2SO_4 was kept constant at 0.5 mol/dm^3 .

Hence, in all of the present systems the R_F values of Zr(IV) increase significantly with increasing concentration of H_2O_2 , but those of Hf(IV) are hardly affected, so that Zr(IV) always provides much higher R_F values than Hf(IV). This observation can be explained by the fact that Zr(IV) forms much more stable peroxo complexes than Hf(IV) [8]. Another particularly interesting characteristic common to the present systems is that the sequence of adsorption is contrary to those in systems consisting of silica gel and $\text{HCl-H}_3\text{PO}_4\text{-H}_2\text{O}$ (10:1:9, v/v/v) [5] and of a strongly basic anion-exchange resin and $2.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4\text{-}0.1\% \text{ H}_2\text{O}_2$ solution [9]. These facts and the present results suggest that in the present systems cation-exchange adsorption of hydrolysed and polymerized species of both metals and desorption of Zr(IV) based on the formation of peroxo complexes participate in determining the R_F values of the metals. Consequently, it is clear that the presence of appropriate amounts of H_2O_2 is essential to obtain better resolutions and separation factors for this pair of metals.

Separation

The most outstanding characteristic of the present TLC systems is that the separation factors and the resolutions for Zr(IV) and Hf(IV) are large enough to separate them clearly. The R_F data in Tables I and II suggest that all of the HNO_3 and HCl media, containing H_2O_2 in concentrations of 0.6% (w/v) or more, allow the complete separation of both metals present in a wide range of amounts and ratios to be accomplished simply and easily. The maximum separation factor ($\alpha = 1300$) and the best resolution ($R_s = 17$) can be obtained in $0.1 \text{ mol/dm}^3 \text{ HCl-}3\% \text{ (w/v) H}_2\text{O}_2$ solution, whereas in $0.1 \text{ mol/dm}^3 \text{ HNO}_3\text{-}3\% \text{ (w/v) H}_2\text{O}_2$ solution the values are $\alpha = 450$ and $R_s = 11$.

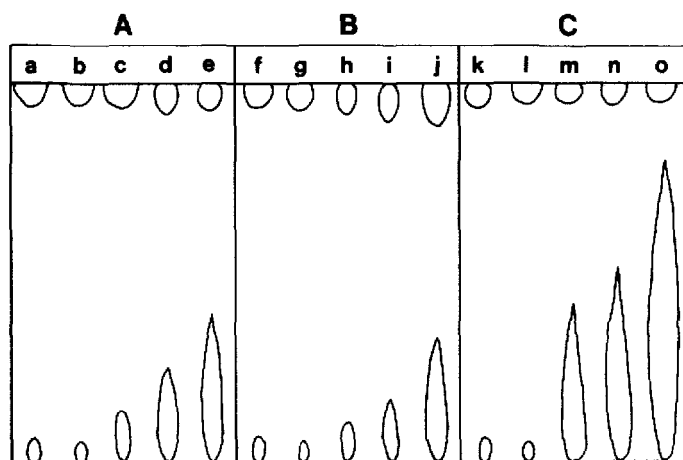


Fig. 1. Separation of Zr(IV) (upper spots) and Hf(IV) (lower spots). Solvent: (A) 0.1 mol/dm³ HNO₃-3% (w/v) H₂O₂; (B) 0.1 mol/dm³ HCl-3% (w/v) H₂O₂; (C) 0.05 mol/dm³ H₂SO₄-3% (w/v) H₂O₂. Amounts of metals taken (mg): a, f and k, Zr 4, Hf 0.2; b, g and l, Zr 2, Hf 0.2; c, h and m, Zr 0.2, Hf 2; d, i and n, Zr 0.2, Hf 4; e, j and o, Zr 0.2, Hf 8. Metal: (A) and (B) oxynitrate used; (C) oxysulphate used.

On the other hand, in H₂SO₄-H₂O₂ media the resolution and the separation factors are smaller, viz., $\alpha = 110$ and $R_s = 4.1$ with 0.05 mol/dm³ H₂SO₄-1% (w/v) H₂O₂ solution.

Typical thin-layer chromatograms for the separation of Zr(IV) and Hf(IV), coexisting in a wide range of amounts (0.2-4 mg) and ratios (Zr:Hf = 20:1-1:40), are given in Fig. 1. The validity of the separation of each mixture was confirmed by visual comparison with the same amounts of standards chromatographed alongside the sample on the same plate. The R_F values of the metals separated were in good agreement with those obtained individually.

In conclusion, it can be expected that the present systems, consisting of silica gel and acidic media containing H₂O₂, will be applicable not only to the TLC separation of Zr(IV) and Hf(IV) coexisting in a more extended range of amounts and ratios, but also to the column separation of these two metals.

REFERENCES

- 1 J. Korkisch, *Modern Methods for the Separation of Rarer Metal Ions*, Pergamon Press, Oxford, 1969, p. 415.
- 2 J. Michal, *Inorganic Chromatographic Analysis*, translated by J. F. Tyson, Van Nostrand Reinhold, London, 1973, p. 75.
- 3 K. Ishida and M. Miyazaki, *Bunseki Kagaku*, 21 (1972) 1518.
- 4 T. Shimizu and A. Muto, *J. Chromatogr.*, 88 (1974) 351.
- 5 R. Olsina, R. Dapas and C. Marone, *J. Chromatogr.*, 75 (1973) 93.
- 6 M. Qureshi and F. Khan, *Anal. Chem.*, 39 (1967) 1329.
- 7 B. A. Lister, *J. Chem. Soc.*, (1951) 3123.
- 8 S. Kiciak, *Talanta*, 36 (1989) 711.
- 9 F. W. E. Strelow and C. J. C. Bothma, *Anal. Chem.*, 39 (1967) 595.