

## SORPTION OF POLYVALENT ELEMENTS ON SILICA GEL. V.\* SEPARATION OF MACROAMOUNTS OF ZIRCONIUM AND HAFNIUM BY SORPTION ON SILICA GEL

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Separation of gram amounts of zirconium from hafnium traces has been studied using the sorption on silica gel from the hydrochloric acid solutions. The effects of the silica gel type used, of the hydrochloric acid concentration, of the concentration of the sorbed element, and of the temperature on the sorption of zirconium and hafnium have been determined. A column with the effective height of 100 cm can be used for a one-step purification of 10 g of  $ZrOCl_2 \cdot 8 H_2O$ /kg of silica gel. Optimum separation conditions were obtained with elution by 11.5–12M-HCl at a flow rate of  $1 \text{ ml cm}^{-2} \text{ min}^{-1}$  and with the specific surface area of silica gel of  $\sim 400 \text{ m}^2/\text{g}$ . Under these conditions the content of hafnium in zirconium can be reduced from original 1% to about 10 p.p.m.

Zirconium and hafnium can be separated on a silica gel column in the HCl solution. For trace- and milligram amounts it has been found<sup>1</sup> that in the 5–8M-HCl solution zirconium is sorbed better than hafnium, on the other hand in the concentrated HCl the sorption of hafnium is higher. Therefore the elution sequence of these two elements can be suitably changed changing the concentration of the acid in the eluent. The separation factor can be increased if a mixture of hydrochloric acid with lower aliphatic alcohols is used as an eluent.

In this study the optimum conditions for the preparation of gram quantities of pure zirconium with  $\leq 0.01\%$  of Hf from natural samples containing 1–3% of Hf have been determined. The two elements were separated in concentrated HCl solutions because zirconium, being the principal part of the mixture under separation, is practically not adsorbed on the column under these conditions and it is eluted first. The column capacity is thus better exploited.

### EXPERIMENTAL

*Reagents and apparatus.* Zirconium(IV) oxychloride of the analytical grade purity (Lachema) and hafnium(IV) oxychloride containing 99.3% of Hf (Sojuzchimreaktiv) were used in this study. The content of Hf in the Zr(IV) salt was found to be 1.1% by the activation analysis. The solution of zirconium used for the separation was prepared by shaking the oxychloride with 11.6M-HCl

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for three days. The concentration of zirconium in this solution was 0.327M, which is close to the values for the saturated solution<sup>2-4</sup>.

The hydrochloric acid used was of the analytical grade. The rectified 96% ethanol was used for separations from mixed solutions. The properties of the used types of silica gel are summarized in Table I. Silica gel was washed first by the concentrated HCl, then by distilled water until a neutral reaction was achieved and finally it was dried for 24 hours at 110°C. Before use the nuclide <sup>95</sup>Zr was always separated<sup>5</sup> from its daughter radionuclide <sup>95</sup>Nb. The radioactive hafnium <sup>175+181</sup>Hf was prepared by irradiating Hf(IV) oxide (of the spectral purity) by thermal neutrons in the nuclear reactor of the Nuclear Research Institute, Prague-Rež. The stock solutions of radioactive isotopes were prepared in 11.5M-HCl. The carrier was added at least 12 hours before use to ensure the establishment of the isotopic equilibrium. The concentration of zirconium and hafnium in solutions was determined by the complexometric titration: 0.25 ml of the analyzed solution in concentrated HCl was added to 1-2 ml of 0.05M complexon III. The mixture was diluted by 40 ml of distilled water, then 1 ml of 0.05% aqueous solution of xylenol orange was added and the excess amount of the complexon was titrated by 0.01M-Bi(NO<sub>3</sub>)<sub>3</sub> using a microburette. This procedure gives a sharp change of the indicator colour and presents reproducible results confirmed by gravimetry. The radioactivity of samples was measured using the NZQ 612 counter (Tesla) with the NaI(Tl) scintillator. In batch experiments the samples were shaken on a horizontal shaker in polyethylene stoppered glass tubes.

*Procedure.* In batch experiments 0.05 g of silica gel (of the average granularity of 0.10 mm) was shaken for three days with 2 ml of the liquid phase at 25 ± 2°C. The adsorbed amount of zirconium or hafnium was determined from the decrease of the solution radioactivity after the sorption. If not stated otherwise, the initial concentration of the metal was always 10<sup>-6</sup>M. The separation experiments with zirconium and hafnium at various temperatures were carried out in columns with a heating jacket, the inner diameter of which was 5 mm, their height 8 cm. Gram quantities of zirconium were purified in a column of the inner diameter of 41.5 mm, containing 542 g of silica gel. The column height was 100 cm. Throughout the experiment samples of 50 ml were taken and analyzed. The start and the end of zirconium elution was continuously

TABLE I  
Separation Factors  $\alpha$

Type	Silica gel		$\alpha$ , at various HCl concentrations				
	specific surface area, m <sup>2</sup> /g	pore diameters, Å	7M	8M	9M	11.6M	
Ge <sup>a</sup>	800 <sup>e</sup>	780 <sup>f</sup>	21 <sup>e</sup>	0.48	0.55	0.70	2.37
CH <sup>b</sup>	400 <sup>e</sup>	360 <sup>f</sup>	80 <sup>e</sup>	0.53	0.60	0.87	4.17
Gw <sup>a</sup>	350 <sup>e</sup>	340 <sup>f</sup>	115 <sup>e</sup>	0.60	0.48	0.43	5.44
M <sup>c</sup>	—	340 <sup>f</sup>	—	0.56	0.44	0.79	6.40
HR <sup>d</sup>	—	315 <sup>f</sup>	—	0.66	0.57	0.74	14.8

<sup>a</sup>Grace GmbH, Bad Homburg; <sup>b</sup>Spolana, Neratovice; <sup>c</sup>silica gel prepared by freezing out of the silicic acid sol and kindly rendered by Dr J. Pitra; <sup>d</sup>Merck AG, Darmstadt; <sup>e</sup>data of the manufacturer; <sup>f</sup>estimated by us.

determined by a spot reaction on filter paper saturated with the Arsenazo III reagent. The zirconium concentration in the individual fractions was determined complexometrically, the hafnium concentration in the eluent was determined radiometrically by measuring the radioactivity of  $^{175,181}\text{Hf}$  nuclides that were previously added to the mixture of elements that had to be separated. After the separation the zirconium fraction, the radioactivity of which did not differ very much from the background radioactivity, were put together and concentrated to a minimum volume. The purified Zr(IV) oxychloride was isolated by crystallization at  $0^\circ\text{C}$ . The hafnium content in the washed and dried sample, muffled to the oxide, was determined by the activation analysis. The hafnium fraction was discarded.

## RESULTS

Fig. 1 presents the dependence on the HCl concentration of the adsorbed fractions of zirconium and hafnium ( $Y_{\text{Zr}}$  and  $Y_{\text{Hf}}$ , respectively) measured in batch experiments using various types of silica gel. The sorption of both these elements from the hydrochloric acid at concentrations  $< 4\text{M}$ -HCl does not depend on the type of silica gel used. Substantial differences in the behaviour of these elements on various types of silica

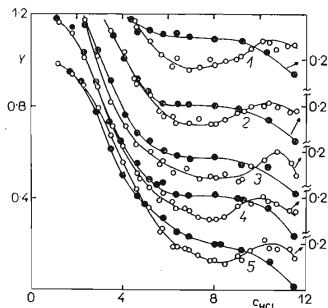


FIG. 1

Sorption of Zr and Hf from HCl Solutions on Various Types of Silica Gel

$Y$  The fraction of adsorbed Zr(Hf);  $c_{\text{HCl}}$  molar concentration of HCl; the ratio of the liquid to solid phases 40 ml/g; sorption time 75 h;  $25 \pm 2^\circ\text{C}$ ; metal concentration  $10^{-6}$ ; ● Zr; ○ Hf; 1 silica gel Ge; 2 CH; 3 Gw; 4 M; 5 HR. The  $Y$  scale is valid only for the curve 5, for curves 4–1  $Y$  is always 0.2.

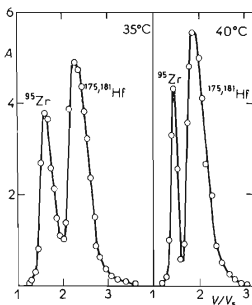


FIG. 2

Separation of Micro Amounts of Zr and Hf in 11.5M-HCl at Various Temperatures

$A$  The eluate radioactivity ( $10^3$  cpm/ml);  $V$  volume of the eluate solution;  $V_s$  the column free volume; silica gel CH, average granularity 0.07 mm; column dimensions  $5 \times 80$  mm; flow rate  $0.5 \text{ ml cm}^{-2} \text{ min}^{-1}$ .

gel appear only at higher concentrations of the hydrochloric acid. The separation factors  $\alpha$ , calculated according to the relation

$$\alpha = \frac{D(\text{Hf})}{D(\text{Zr})} = \frac{Y_{\text{Hf}}(1 - Y_{\text{Zr}})}{Y_{\text{Zr}}(1 - Y_{\text{Hf}})},$$

(where  $D(\text{Me})$  denotes the distribution coefficient of the respective element), at various concentrations of HCl, are given in Table I. From these results it follows that in 11.5M-HCl the separation factor increases with the decrease of the specific surface area of the silica gel used. This conclusion agrees with the results of ref. 1 in which it has been found that the best separation of microquantities of zirconium and hafnium is achieved using a column of silica gel with wide pores, with the specific surface area of 345 m<sup>2</sup>/g. However, in preliminary experiments it has been found that silica gel with extremely wide pores is less advantageous for the separation of macroamounts of these elements. Hence, all the subsequent experiments were carried out using silica gel CH that fulfils best the requirements both on the quality of separation and on the quantity of the elements separated in one cycle. The effect

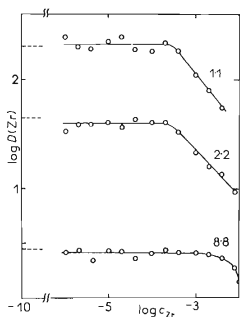


FIG. 3

The Dependence of the Distribution Coefficient  $D(\text{Zr})$  on the Initial Concentration of Zr in the Solution

$C_{\text{Zr}}$  The initial concentration of Zr in the solution (mol/l); silica gel CH; for the sorption conditions see Fig. 1. Numbers at curves: molar concentrations of HCl; dotted lines: sorption of trace amounts of the <sup>95</sup>Zr nuclide ( $\log C_{\text{Zr}} \approx -10$ ).

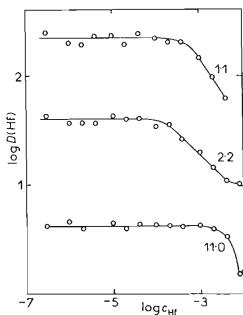


FIG. 4

The Dependence of the Distribution Coefficient  $D(\text{Hf})$  on the Initial Concentration of Hf in the Solution

$C_{\text{Hf}}$  The initial concentration of Hf in the solution (mol/l); for the sorption conditions see Figs 1 and 3.

of temperature on the separation of zirconium and hafnium in 11.5M-HCl is shown in Fig. 2. The increase of temperature causes a narrowing of the elution peaks and a decrease of the eluent volume necessary for a complete removal of both elements from the column. The separation of the two elements is somewhat better at higher temperatures. This positive effect is, however, not strong enough to counterbalance the negative effect connected with the higher volatility of the hydrochloric acid. It would be therefore necessary to make the chromatographic column perfectly leakless if high amounts of zirconium were separated at higher temperatures. Figs 3 and 4 present the plots of the distribution coefficients of zirconium and hafnium *vs* their concentrations. In the 1M- and 2M-HCl solutions the value of *D* does not depend on the element concentration if its value is lower than  $2 \cdot 10^{-4}$  mol/l. In concentrated hydrochloric acid solutions the values of *D* are constant for both elements already for the metal concentrations  $\leq 2 \cdot 10^{-3}$  mol/l. The partial increase of *D*(Hf) in the case of sorption from solutions containing  $\geq 10^{-2}$  mol Hf/l is presumably

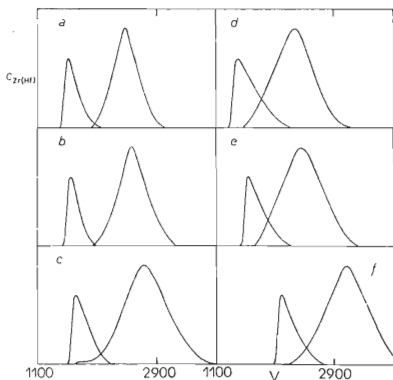


FIG. 5

Elution Curves for the Separation of Gram Amounts of Zr and Hf on Silica Gel CH

$C_{Zr(Hf)}$  Relative concentrations of Zr(Hf) in the eluate; *V* the eluate solution volume (ml); column dimensions  $4.15 \times 100$  cm; silica gel granularity 0.20–0.22 mm. Separation conditions:  $C_{HCl}$  (mol/l), flow rate  $E_v$  ( $\text{ml cm}^{-2} \text{min}^{-1}$ ), feed volume  $V_f$  (ml of 0.327M-Zr in 11.6M-HCl): a 11.6; 0.5; 50; b 11.6; 1.0; 50; c 11.6; 1.5; 50; d 11.6; 0.5; 100; e 11.6; 1.0; 75; f 10.9; 0.5; 50. The mean value of  $C_{Zr}$  in the maximum was  $\approx 0.07$  mol/l (the first elution peak), the mean value of  $C_{Hf}$  in the maximum corresponded to the specific radioactivity  $\approx 1.5 \times 10^2$  c.p.m./ml (the second elution peak).

given by the lower solubility of Hf in the hydrochloric acid<sup>2-4</sup>. The elution curves obtained for the separation of gram quantities of natural zirconium from hafnium traces are given in Fig. 5. In these experiments the concentration of the hydrochloric acid in the eluent, its flow rate and the total feeding volume (*i.e.* the amount of the purified zirconium) have been varied. From the given examples it is evident that the best separation is achieved using 11.5–12M-HCl solution for the elution. At higher concentrations of the hydrochloric acid better results can be expected but at the same time the higher volatility of HCl would cause a disadvantageous effect, similarly as in experiments at higher temperatures. From Fig. 5 it also follows that the optimum flow rate under the given conditions is about  $1 \text{ ml cm}^{-2} \text{ min}^{-1}$ . Higher values of the flow rate lead to a larger volume of the acid that is necessary for the complete elution of hafnium and to a lower quality of separation.

The saturated solution of Zr(IV) oxychloride in the hydrochloric acid was used for the separation so that the optimum feeding volume (50 ml) corresponds to 9.7 g of  $\text{ZrOCl}_2 \cdot 8 \text{ H}_2\text{O}$  per kg of silica gel. Further increase of the column load leads to less successful separation. Altogether ten separation cycles were made under the determined favourable conditions (*i.e.*, 50 ml of the feeding volume, 0.327M solution of Zr in 11.6M-HCl, eluted by 11.6M-HCl at the flow rate of  $1 \text{ ml. cm}^{-2} \text{ min}^{-1}$ ). 50 g of  $\text{ZrOCl}_2 \cdot 8 \text{ H}_2\text{O}$  with 30 p.p.m. of hafnium have been obtained, which corresponds to the yield of about 95%. It has been found that the content of hafnium in the first 70% of the zirconium fraction does not exceed 8–10 p.p.m. The average concentration of zirconium in the maximum of the elution peak was 0.07M and the ratio of the pure zirconium fraction volume to the feeding volume was about 8–9. In no case a substantial retention of hafnium has been observed that could cause any contamination of zirconium during the next separation cycle. A complete column regeneration was achieved by elution with about two litres of 11.6M-HCl. The position of individual elution peaks and their shapes were well reproducible throughout the entire series of experiments. It was also found that both the specific surface area of silica gel and the column efficiency did not change even after 15 operations which corresponded to elution with about 50 l of HCl within one month. By the described procedure zirconium can at the same time be separated also from several other elements, namely from iron, thorium, rare-earth elements, *etc.* These elements are not adsorbed on the column and they are eluted before the elution of zirconium.

The use of silica gel type M under otherwise similar conditions allows to decrease twice the optimum feeding volume in comparison with silica gel CH. In good agreement with the already published results<sup>1</sup> it can be concluded that the silica gel with wide pores is suitable only for the separation of microamounts of zirconium and hafnium. For the separations of larger amounts of these elements silica gel with the specific surface area of about  $400 \text{ m}^2/\text{g}$  is more suitable. The separation of zirconium and hafnium on silica gel with narrow pores is incomplete due to the lower value of  $\alpha$  and slower kinetics of sorption. In the previous paper<sup>1</sup> it was also found that the separation factor  $\alpha$  can be increased by the presence of methanol or ethanol. However, from the experiments with larger amounts of zirconium it follows that the use of mixed solutions is inconvenient under the given conditions. The presence of alcohols decreases substantially the solubility of oxychlorides and therefore also

the total amount of the raw zirconium in the feed. The separation was not complete even in the case when 50 ml of 0.327M-ZrOCl<sub>2</sub> in 11.6M-HCl was adsorbed on the column and eluted by the mixture of 90% of 11.6M-HCl with 10% of ethanol. The presence of ethanol causes evidently the precipitation of the crystalline oxychloride in the upper part of the column and therefore also a broadening of the individual zones.

## DISCUSSION

The nature of the distribution of zirconium and hafnium in concentrated hydrochloric acid solutions as illustrated by Fig. 1 does not correspond to the ion-exchange mechanism. The assumption of the molecular sorption of neutral chlorido complexes of zirconium and hafnium, supported by the salting-out effect of hydrochloric acid, seems much more probable. The decrease of sorption in saturated hydrochloric acid solutions is probably due to the formation of the complex acid H<sub>x</sub>MeOCl<sub>2+x</sub> or, eventually, H<sub>x</sub>MeCl<sub>4+x</sub>. The differences in the sorption of individual complexes and therefore also the differences in the behaviour of zirconium and hafnium can be explained not only by the different stability of the respective complexes but first of all by the different solvation of these complexes. This explanation can be corroborated by the results obtained by solubility studies of Zr(IV)- and Hf(IV) oxychlorides in hydrochloric acid<sup>2-4</sup>. It has been found that the solubility of these compounds decreases with the increase of the hydrochloric acid concentration up to 8-9M. If this concentration is increased still further, the solubility of both oxychlorides increases, the Zr(IV) salt being more soluble than the Hf(IV) salt. In the paper<sup>4</sup> the fraction insoluble at the high concentration of HCl has been analyzed. In the case of zirconium the composition of this solid phase corresponds to the formula ZrOCl<sub>2</sub>·2 HCl·10 H<sub>2</sub>O ( $C_{\text{HCl}} \geq 10\text{M}$ ), in the case of hafnium to the formula HfOCl<sub>2</sub>·HCl·6.5 H<sub>2</sub>O ( $C_{\text{HCl}} > 10.5\text{M}$ ). The changes of hydration of the individual complexes play evidently an important role even in the presence of organic solvents in the eluents.

The increase of *D* values in the concentrated hydrochloric acid has been observed even in the sorption of zirconium and hafnium<sup>6,7</sup> on Dowex-50. Also in this case the sorption of hafnium is somewhat higher than the sorption of zirconium. This effect has been exploited for the separation of zirconium and hafnium on catex KU-2 from the mixed solutions of the hydrochloric acid with certain organic solvents<sup>8</sup>. It has been found that the column efficiency is influenced not only by the solution composition but also by the catex cycle (the NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, and Ba<sup>2+</sup> cycles have been studied). It is however probable that at the high concentration of the acid the ion exchange between NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, or Ba<sup>2+</sup> ions and the hydrogen ions proceeds in the system. Little soluble complex chlorides Me<sub>2</sub>Me<sup>IV</sup>Cl<sub>6</sub> or, eventually, Me<sup>II</sup>Me<sup>IV</sup>Cl<sub>6</sub> (ref.<sup>9,10</sup>) are formed in the solution and they are adsorbed on the surface of the catex

due to the molecular adsorption. It can be assumed that the molecular sorption plays an important role even in the separation of zirconium and hafnium on silica gel from the solutions of their tetrachlorides<sup>11</sup> or oxychlorides<sup>12</sup> in methanol.

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