

## SORPTION OF ZIRCONIUM AND HAFNIUM ON SILICA GEL IN THE PRESENCE OF PHOSPHORIC AND PHENYLARSENIC ACIDS AND OF IODATE\*

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The effect of phosphoric acid, of phenylarsenic acid ( $H_2L$ ) and of iodate on the sorption of zirconium and hafnium on silica-gel from solutions of sulphuric, oxalic and hydrochloric acids and from a mixture of HCl and KSCN was studied. It has been found that the sorption increases in media in which neutral complexes are formed; the stability constants for complexes  $B(HPO_4)_2$ ,  $B(HPO_4)_3^{2-}$  and  $B(L)_2$  were determined (B denotes the appropriate cation). In the presence of potassium iodate, sorption of complexes  $K_nB(IO_3)_{4+n}$  is assumed. A method for the separation of zirconium and hafnium from niobium and protactinium has been developed.

The present paper deals with the study of the sorption of zirconium and hafnium on silica gel in the presence of reagents with which they form sparingly soluble compounds. A similar problem was treated by Krtíl and Kolařík<sup>1</sup>, who studied the sorption of zirconium on silica gel from a  $HNO_3-H_3PO_4$  medium. However, zirconium is relatively easily sorbed in dilute nitric acid media and the interpretation of the experimental results is thus made difficult. Therefore, media containing sufficiently strong complexing agents were employed in this paper, where the element to be sorbed is masked, but reactions of the cations with the precipitant ions are not prevented. The concentrations of the elements were selected so that the solubility products were not exceeded.

Here the most suitable masking agents are solutions of sulphuric and oxalic acids; as reagents forming sparingly soluble compounds with zirconium and hafnium, phosphoric acid and phenylarsenic acid ( $H_2L$ ) and potassium iodate were employed.

The study of these systems is useful not only from the point of view of the behaviour of trace amounts of elements in the presence of ions capable of forming precipitates with macro-amounts of the particular elements, which constitutes an important problem in the field of "radiocolloids", but also from the point of view of separation procedures for substances present in low concentrations, which can be worked out on this principle.

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## EXPERIMENTAL

The sorption was studied on CH silica gel (Spolana, Neratovice). Its characteristics and pre-treatment have already been described<sup>2</sup>. Radiozirconium was freed of the daughter nuclide using the procedure described in an earlier paper<sup>3</sup>. Radiohafnium and protactinium were prepared by irradiating  $\text{HfO}(\text{NO}_3)_2$  and  $\text{Th}(\text{NO}_3)_4$  in the reactor. Protactinium was separated from thorium by sorption on silica gel<sup>4</sup>.

Stock solutions of the radionuclides were prepared by dissolving the original substances in 10M- $\text{H}_2\text{SO}_4$ , 12M-HCl and 0.1M- $\text{H}_2\text{C}_2\text{O}_4$ . The resulting concentration of hafnium was  $10^{-6}\text{M}$ ; zirconium, niobium and protactinium were used in carrierfree concentrations ( $\approx 10^{-10}\text{M}$ ). All other reagents used were of *p.a.* purity.

Experiments under static conditions involved stirring of 0.05 g silica gel with 2 ml of solution for 2 days at a temperature of 21–22°C. It was found that this time suffices for attainment of equilibrium. The other conditions were identical with those employed in ref.<sup>2</sup>.

For experiments under dynamic conditions, columns with an internal diameter of 5 mm were used and were packed with lg silica gel with an average grain size of 40  $\mu\text{m}$ . The elution conditions have been described in refs<sup>3,4</sup>.

## RESULTS

### *Sorption from Sulphuric Acid Solutions*

The determination of zirconium and hafnium from sulphuric acid solutions is depicted in Fig. 1. In 1M- $\text{H}_2\text{SO}_4$ , the sorption is virtually completely suppressed by the formation of stable sulphate complexes<sup>5</sup>. The retention of hafnium is somewhat higher than that of zirconium. The behaviour of these elements is affected not only by the sulphuric acid concentration, but also by the method employed for the preparation of the solutions. If the hafnium stock solution was diluted to 1.08M- $\text{H}_2\text{SO}_4$  and used for the preparation of experimental solutions only after 24 hour aging, the sorption increased considerably due to hydrolysis over the whole studied range of sulphuric acid concentrations. This fact suggests that the hydrolytic changes of sorbed hafnium (zirconium) are not identical with those occurring in solution. In subsequent experiments, stock solutions in 10M- $\text{H}_2\text{SO}_4$  were therefore always used; here hydrolysis does not occur even after prolonged storage. These solutions were diluted immediately before beginning an experiment.

In 1M and 2M- $\text{H}_2\text{SO}_4$ , addition of c.  $10^{-2}$  mol of phosphoric acid/litre sharply increases the sorption; on a further increase in the phosphoric acid content, the sorbed fraction of the cation again decreases (Fig. 2a,b). The retention of hafnium is always higher than that of zirconium and starts at a lower phosphoric acid content. In the range of low concentrations of phosphate ions, the differences in the behaviour of zirconium and hafnium are very pronounced, but they are negligible on the descending part of the sorption curve. In this region the concentration of sulphuric acid is also virtually without any effect. It has been also found that an increase in the zirconium concentration up to a value of  $10^{-6}\text{M}$  does not affect the character of the dependence of its sorption (these results are not given). The uptake of trace

amounts of niobium and protactinium in a medium of  $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$  is shown in Fig. 2c. Both these elements are relatively well sorbed on silica gel from solutions of dilute sulphuric acid<sup>2</sup>; phosphoric acid causes their desorption when present in a concentration exceeding  $0.1 \text{ mol l}^{-1}$ .

The effect of phenylarsenic acid on the deposition of zirconium and hafnium is illustrated in Fig. 3. Here no descending part was observed on the sorption curves at higher reagent concentrations. Higher concentrations of phenylarsenic acid cannot be used because of its relatively poor solubility. Hafnium also begins to deposit at a lower  $\text{H}_2\text{L}$  concentration under these conditions.

The results obtained in the presence of iodate ions have a somewhat different character. A sharp increase in the sorption of both studied elements occurs at practically the same concentration ( $0.1 \text{ mol l}^{-1}$ ) of potassium iodate (Fig. 4). If its content in the solution is increased, hafnium is deposited almost quantitatively ( $\sim 99\%$ );

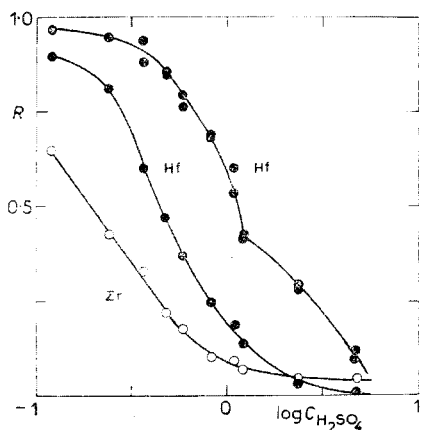


FIG. 1

Sorption of Zr and Hf on Silica Gel from Sulphuric Acid Solutions

$R$  the Zr (Hf) fraction sorbed.  $C_{\text{H}_2\text{SO}_4}$  is given in  $\text{mol l}^{-1}$ ; the sorption time is 48 hours;  $22 \pm 2^\circ\text{C}$ ; the upper curve represents sorption of hafnium from solutions after 24 hour ageing in  $1.08\text{M-H}_2\text{SO}_4$ .

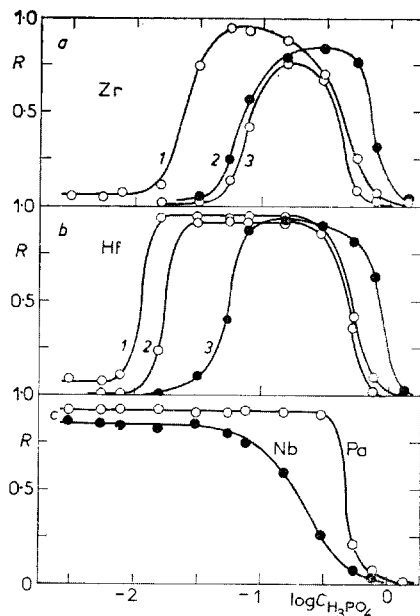


FIG. 2

Sorption of Zr, Hf, Nb and Pa on Silica Gel from Solutions of Sulphuric and Oxalic Acids in the Presence of Phosphoric Acid

$C_{\text{H}_3\text{PO}_4}$  is given in  $\text{mol l}^{-1}$ ; a, b: curve 1  $1.04\text{M-H}_2\text{SO}_4$ ; 2  $2.08\text{M-H}_2\text{SO}_4$ ; 3  $0.01\text{M-H}_2\text{C}_2\text{O}_4$ ; c:  $2.08\text{M-H}_2\text{SO}_4$ .

sorption of zirconium is only slightly lower ( $\sim 96\%$ ). However, when iodic acid up to  $2 \text{ mol l}^{-1}$  was used instead of potassium iodate, no increase in the sorption of zirconium and hafnium was observed.

During the sorption from solutions of  $1\text{M}$  and  $2\text{M-H}_2\text{SO}_4$ , containing up to  $0.5 \text{ mol/l}$  potassium cyanoferrate, the reagent decomposes to give Berlin blue. No increase in the sorption was observed when the sorption time was shortened to 10 hours. These results are not given in greater detail for the sake of brevity.

### Sorption From Oxalic Acid Solutions

Except for sulphuric acid, oxalic acid is the most common complexing agent used in analytical chemistry for masking zirconium and hafnium<sup>6</sup>. Hence experiments were carried out using  $0.01\text{M-H}_2\text{C}_2\text{O}_4$  as a masking agent. Under these conditions both the studied elements form oxalate complexes that are not sorbed on silica gel<sup>7</sup>. Addition of phosphoric acid in amounts from  $0.05$  to  $1 \text{ mol l}^{-1}$  has a similar effect as in sulphate solutions (Fig. 2). However, differences in the behaviour of zirconium and hafnium are minimal.

The presence of potassium hexacyanoferrate did not influence the sorption under these conditions, similar to sulphate solutions.

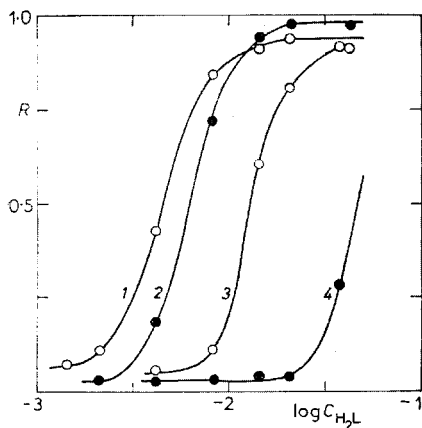


FIG. 3

Sorption of Zr and Hf on Silica Gel from Sulphuric Acid Solutions in the Presence of Phenylarsenic Acid ( $\text{H}_2\text{L}$ )

$C_{\text{H}_2\text{L}}$  is given in  $\text{mol l}^{-1}$ ; curves 1 and 3 Hf; 2 and 4 Zr; 1 and 2  $2.08\text{M-H}_2\text{SO}_4$ ; 3 and 4  $0.925\text{M-H}_2\text{SO}_4$ .

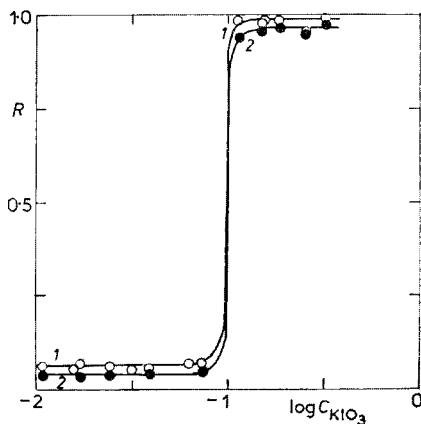


FIG. 4

Sorption of Zr and Hf on Silica Gel from  $1.04\text{M-H}_2\text{SO}_4$  in the Presence of  $\text{KIO}_3$

$C_{\text{KIO}_3}$  is given in  $\text{mol l}^{-1}$ .  $\circ$  Hf,  $\bullet$  Zr.

## Sorption from Thiocyanate Solutions

Among the most effective methods for the separation of zirconium and hafnium are those based on preferential extraction of hafnium thiocyanate complexes into organic solvents<sup>8</sup>. Therefore it was interesting to find whether there are differences in the behaviour of zirconium and hafnium thiocyanate complexes during their sorption on silica gel. Preliminary experiments have shown that the deposition of the studied elements is virtually suppressed in solutions containing potassium thiocyanate in an amount of  $2 \text{ mol l}^{-1}$  and  $1\text{M}$  to  $2\text{M}$  in  $\text{HCl}$  (Fig. 5). However, solutions of this composition are poorly stable and hence the sorption time was shortened to 10 hours in a medium of  $1\text{M-HCl} + 2\text{M-KSCN}$  and to two hours in  $2\text{M-HCl} + 2\text{M-KSCN}$ . The effect of phosphoric acid under these conditions is illustrated in Fig. 6*a,b*. However, no substantial differences in the behaviour of zirconium and hafnium have been found.

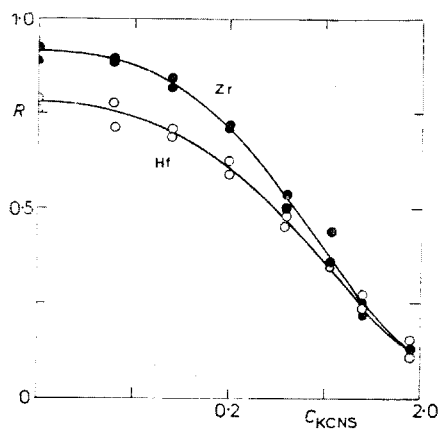


FIG. 5

Sorption of Zr and Hf on Silica Gel from Solutions of  $1.19\text{M-HCl}$  in Dependence on the Concentration of Potassium Thiocyanate

$C_{\text{KSCN}}$  is given in  $\text{mol l}^{-1}$ , the sorption time is 24 hours.

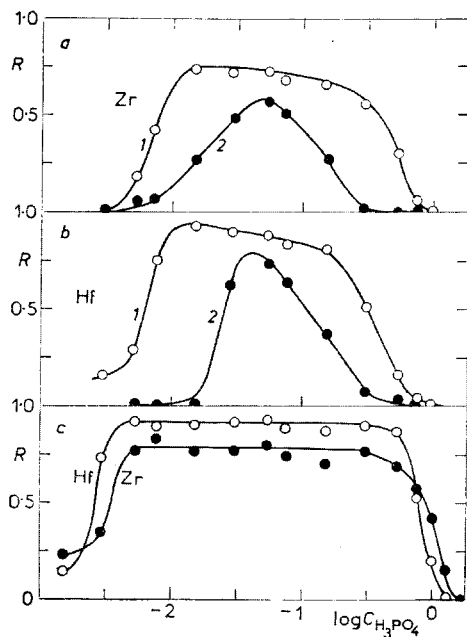


FIG. 6

Sorption of Zr and Hf on Silica Gel from Solutions of  $\text{HCl} + \text{KCNS}$  and  $5.95\text{M-HCl}$   
*a, b*: curve 1  $1.19\text{M-HCl} + 2.00\text{M-KCNS}$ ;  
 2  $2.38\text{M-HCl} + 2.00\text{M-KCNS}$ ; *c*:  $5.95\text{M-HCl}$ .

### *Sorption from Hydrochloric Acid Solutions*

When the above-described experiments had already been completed, a paper by Olšina, Dapas and Marone<sup>9</sup> appeared dealing with the separation of zirconium and hafnium on a thin layer of silica gel. Using the elution mixture, HCl-H<sub>3</sub>PO<sub>4</sub>-water (10 : 1 : 9 by volume), the authors achieved very good separation of the elements. Zirconium remains at the start, while hafnium moves with the eluent front. Considering the higher tendency of hafnium to be sorbed on silica gel in the presence of phosphoric acid, the reverse elution order might be expected. It should be mentioned that an elution mixture of this composition has already been employed for the separation of zirconium and hafnium by means of ascending paper chromatography<sup>10</sup>; however, unsatisfactory results were obtained.

The exact composition of the elution solution is not given in the paper<sup>9</sup>. If the ratio given relates to concentrated acid solutions, it can be assumed that 5.5 to 6M-HCl and c. 1.4M-H<sub>3</sub>PO<sub>4</sub> were used. Therefore, the sorption of zirconium and hafnium on silica gel was studied using solutions of 5.9M-HCl with varying contents of phosphoric acid. As follows from Fig. 6c, zirconium is actually somewhat better sorbed than hafnium in the given phosphoric acid concentration range, but it is not probable that this difference would enable the perfect separation mentioned in the cited paper<sup>9</sup>. In fact, an attempt to separate the two elements in a chromatographic column using H<sub>3</sub>PO<sub>4</sub> concentrations of 0.7--2M was unsuccessful.

### *Experiments Under Dynamic Conditions*

In addition to the separation of zirconium and hafnium in a medium of HCl-H<sub>3</sub>PO<sub>4</sub>, separation in a H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub> medium was also attempted. The phosphoric acid concentration was selected so that zirconium alone would be eluted first; hafnium was then eluted with 2M-H<sub>2</sub>SO<sub>4</sub>. During these experiments, two perfectly separated elution zones were always obtained, but  $\gamma$ -spectrometric analysis indicated only enrichment and not separation of the components of the mixture. The reason for this behaviour is probably the formation of mixed phosphate complexes of zirconium and hafnium<sup>5</sup>. On the other hand, perfect separation of these elements from niobium and protactinium was achieved. An example of the separation under dynamic conditions is given in Fig. 7. The possibility of separating zirconium and hafnium under these conditions is being further studied.

## DISCUSSION

The explanation of the experimental results is based on the assumption that molecular sorption occurs in the given systems<sup>1</sup>. Equilibrium distribution of element B between the solid phase (sorbent) and the solution (sorbate) can be characterized by the distribution ratio,  $D_m$ , expressed by the relationship

$$D_m = R(1 - R)^{-1} Vm^{-1}, \quad (1)$$

where  $R$  is the fraction of element B sorbed,  $V$  is the solution volume and  $m$  is the sorbent mass.

For a system containing the studied element,  $B^{z+}$ , a buffer ligand,  $X^-$ , and a complexing ligand,  $A^-$ , the  $D_m$  values are given by the equation

$$D_m = \frac{K_D(B) + \sum_1^N K_B(BA_n) \beta(BA_n) [A]^n + \sum_1^U K_D(BX_u) \beta(BX_u) [X]^u}{1 + \sum_1^N \beta(BA_n) [A]^n + \sum_1^U \beta(BX_u) [X]^u}, \quad (2)$$

where the  $K_D$  denotes the distribution constants and  $\beta$  the stability constants for the species specified in brackets after the symbols.

For molecular sorption it holds that all the distribution constants equal zero except for  $K_D(BA_z)$ , which can be defined by the relation

$$K_D(BA_z) = [C(BA_z)_s / C(BA_z)] (V/m), \quad (3)$$

where  $C(BA_z)_s$  and  $C(BA_z)$  denote the concentration in the sorbent and solution, respectively.

For the distribution ratio a simplified relationship can then be obtained

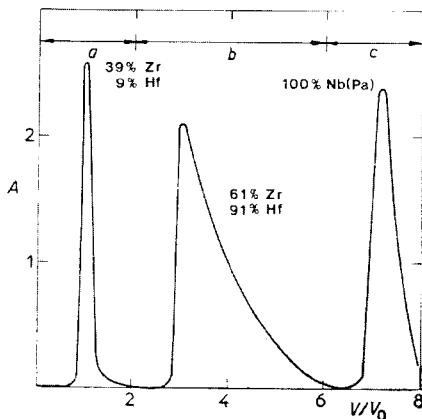
$$D_m = K_D(BA_z) \delta_z, \quad (4)$$

where  $\delta_z$  expresses the fraction of neutral complex  $BA_z$  in the solution, *i.e.*

FIG. 7

Separation of Zr, Hf, Nb and Pa on Silica Gel under Dynamic Conditions

$A$  the eluate radioactivity in  $10^3$  imp/min per drop;  $V$  the eluate volume;  $V_0$  the column dead volume (1.07 ml); flow-rate of 0.4 ml/cm<sup>2</sup> min; Zr and Hf concentration sampled  $10^{-3}$  mol/l. The values given with the individual elution bands specify percentages; the composition of the elution solutions:  $a$  2.08M-H<sub>2</sub>SO<sub>4</sub> + 5.3 · 10<sup>-2</sup>M-H<sub>3</sub>PO<sub>4</sub>;  $b$  2.08M-H<sub>2</sub>SO<sub>4</sub>;  $c$  2.08M-H<sub>2</sub>SO<sub>4</sub> + 0.76M-H<sub>3</sub>PO<sub>4</sub>.



$$\delta_z = \beta(\text{BA}_z) [\text{A}]^z \left\{ 1 + \sum_1^N \beta(\text{BA}_n) [\text{A}]^n + \sum_1^U \beta(\text{AX}_u) [\text{X}]^u \right\}^{-1}. \quad (5)$$

Equation (5) can readily be modified when ligand  $\text{X}^-$  or  $\text{A}^-$  is the anion of a polybasic acid; introducing the dissociation constant for these ions, the  $\delta_z = f(\text{pH})$  dependence can be obtained. Equations (2) and (5) can be modified analogously to provide for hydrolysis of ion  $\text{B}^{z+}$  or for the formation of mixed complexes.

When it is assumed that only complexes  $\text{BA}_{z-1}$ ,  $\text{BA}_z$  and  $\text{BA}_{z+1}$  are formed, equation (5) is simplified to give

$$\frac{1 - \delta_z}{\delta_z} = \frac{K_D(\text{BA}_z)}{D_m} - 1 \approx \frac{Q}{\beta(\text{BA}_z) [\text{A}]^z} + \frac{\beta(\text{BA}_{z-1})}{\beta(\text{BA}_z) [\text{A}]} + \frac{\beta(\text{BA}_{z+1}) [\text{A}]}{\beta(\text{BA}_z)}, \quad (6)$$

where  $A = 1 + \sum_1^U \beta(\text{BX}_u) [\text{X}]^u$ .

This simplification is justified in the region where the neutral complex predominates, in view of the stepwise complex formation.

For further analysis it is convenient to define the value of the concentration of ligand  $\text{A}^-$ ,  $[\text{A}]_{1/2}$ , at which 50% of element B is converted into complex  $\text{BA}_z$ ; the relationship,  $(1 - \delta_z) \delta_z^{-1} = 1$ , is then valid. The concentration of ligand  $\text{A}^-$  at which  $\delta_z \approx 1$  (corresponding as a first approximation to the presence of 100% B in complex  $\text{BA}_z$ ) can be termed  $[\text{A}]_1$ . As the dependence,  $(1 - \delta_z) \delta_z^{-1} = f([\text{A}])$ , can be represented by a simple curve with a minimum, the  $[\text{A}]_{1/2}$  value is attained twice, on the descending and the ascending branches; the  $[\text{A}]_1$  value corresponds to the minimum value.

If the values of the individual stability constants,  $\beta(\text{BA}_n)$ , are sufficiently different, which is almost always true for stable complexes, then two cases can be encountered assuming that only two complexes coexist in solution:

a) If  $A \ll \beta(\text{BA}_{z-1}) [\text{A}]^{z-1}$ , the concentration of complexes  $\text{BX}_u$  is negligible and the numerical value of  $A_{1/2}$  on the descending part of dependence (6) corresponds to the consecutive dissociation constant for complex  $\text{BA}_z$ , *i.e.*

$$\text{p}A'_{1/2} = \text{p}K(\text{BA}_z), \quad (7)$$

b) If, on the other hand,  $Q \gg \beta(\text{BA}_{z-1}) [\text{A}]^{z-1}$ , the concentration of complex  $\text{BA}_{z-1}$  can be neglected and for the descending part of the curve can be written

$$\text{p}A'_{1/2} = 1/z \{ \log \beta(\text{BA}_z) - \log Q \}. \quad (8)$$

If the concentration of the competing buffer ligand,  $\text{X}^-$ , is selected so that most of the studied element is present in the form of complex  $\text{BX}_u$  in the absence of com-



plexing ligand  $A^-$ , then  $Q \approx \beta(BS_u) [X]^u$  and equation (8) is converted to give

$$pA'_{1/2} = 1/z \{ \log \beta(BA_z) - \log \beta(BX_u) + u(pX) \}. \quad (8a)$$

c) Both the presence of complex  $BA_{z-1}$  and of complex  $BS_u$  can be neglected on the ascending branch of dependence (6), *i.e.* in the region of higher concentrations of ligand  $A^-$ . The deposition of element B is then affected only by the formation of neutral complex  $BA_z$  and of anionic complex  $BA_{z+1}$ . It then holds that

$$pA''_{1/2} = pK(BA_{z+1}), \quad (9)$$

where  $K(BA_{z+1})$  is the consecutive dissociation constant of complex  $BA_{z+1}$ . If element B does not form anionic complexes, the ascending branch is absent on the curve for the dependence,  $(1 - \delta_z) \delta_z^{-1} = f([A])$ .

d) The relationship between the  $[A]_1$  value and constants  $\beta(BA_n)$  and  $\beta(BX_u)$  can be found by solving equation  $\partial(1 - \delta_z) \delta_z^{-1} / \partial[A] = 0$ . It follows for  $Q \ll \ll (BA_{z-1}) [A]^{z-1}$  that

$$pA_1 = 1/2 [\log \beta(BA_{z+1}) - \log \beta(BA_{z-1})], \quad (10)$$

for  $Q \gg \beta(BA_{z-1}) [A]^{z-1}$  that

$$pA_1 = 1/z + 1 [\log \beta(BA_{z+1}) - \log z - \log \dot{A}]. \quad (11)$$

It follows from the above discussion that, from known values of  $\beta(BA_n)$  and  $\beta(BX_u)$ , the concentration of ligand A can be calculated at which the maximum deposition is attained and the region of deposition of the studied element can be determined. In the opposite case the stability constants of complexes  $BA_n$  can be calculated from the experimental results. The value of distribution constant  $K_D(BA_z)$  can be determined from equation (4) if the experimental value of  $D_m$  at point  $[A]_1$  is known.

The sorption, of course, also depends on the concentration of masking ions  $X^-$ . The formation of complexes  $BX_u$  causes a shift of the sorption curves,  $\log D_m = f(\log [A])$ , towards higher  $[A]$  values and also results in a change in their shape. In extreme cases, the sorption is entirely suppressed, *i.e.* perfect masking occurs. The effect of the  $Q$  value on the formation of complexes  $BA_z$  and hence on the deposition of element B can be assessed by comparing the  $\beta(BA_z) [A]^z$  and  $Q$  values. In order that the formation of complexes  $BA_z$  not be suppressed by the masking reaction, the inequality,  $Q < \beta(BA_z) [A]^z$ , must be valid.

If two elements,  $B_1$  and  $B_2$ , capable of forming sorbable neutral complexes with ligand  $A^-$ , are present in the solution, then differences in the corresponding  $pA_{1/2}$  values can be employed as a criterion of their separability. By suitable choice of the

experimental conditions, effective separation can usually be achieved even for elements with very similar properties. The most advantageous conditions involve the region around  $[A']_{1/2}$ , where the sorption is affected by the formation of both  $BA_z$  and  $BX_u$  complexes. In the region around  $[A'']_{1/2}$ , the sorption and consequently the separation factor for the two elements depend only on the formation of  $BA_n$  complexes. For univalent elements  $B_1$  and  $B_2$  it follows from equation (8) that

$$(\text{p}A'_{1/2})_1 - (\text{p}A'_{1/2})_2 = 1/z \left\{ \log \frac{[\beta(BA_z)]_1}{[\beta(BA_z)]_2} - \log Q_2/Q_1 \right\}. \quad (12)$$

In practice, especially in analytical applications, it is often more advantageous to employ the sorption ratio,  $R$ , instead of the distribution ratio,  $D_m$ , (or the  $K_D \cdot (BA_z) D_m^{-1} - 1$  value); their relationship is determined by equation (1). The  $R = f(\text{p}A)$  dependence can usually be represented by a symmetrical sigmoid curve. If it is experimentally possible to reach a concentration of  $A^-$  at which the studied element is virtually completely converted into complex  $BA_z$  (i.e.  $\delta_z \approx 1$ ) and if the distribution constant,  $K_D(BA_z)$ , is sufficiently high, then  $R_{\text{max}}/2$  corresponds to the  $[A]_{1/2}$  values. The  $[A]_1$  value can be determined graphically or by determining the geometric centre of the  $\text{p}A'_{1/2}$  and  $\text{p}A''_{1/2}$  values.

The  $\text{p}A_{1/2}$  and  $\text{p}A_1$  values, obtained for zirconium and hafnium from the experimental values under the condition,  $R_{\text{max}}/2$  and  $R_{\text{max}}$ , or under the condition,  $\text{p}A_1 = 1/2(\text{p}A'_{1/2} + \text{p}A''_{1/2})$ , are given in Tables I and II. The stability constants were in some cases calculated on the basis of these data, using the above equations. The formation of various complexes of zirconium and hafnium is discussed below.

### Phosphate Complexes

In addition to hydroxide and fluoride ions, phosphate ions belong among the ligands with the highest affinity for zirconium<sup>11</sup>. However, the stability constants of phosphate complexes of zirconium and hafnium are still not reliably known. In a single paper<sup>12</sup>, the values,  $\log \beta(\text{Zr}(\text{HPO}_3)_3^{2-}) = 36.83$  and  $\log \beta(\text{Hf}(\text{HPO}_3)_3^{2-}) = 37.09$ , are given for complexes of the  $\text{B}(\text{HPO}_4)_3^{2-}$  type.

The deposition of zirconium on silica gel from phosphate-containing media has been explained by Krtíl and Kolařík<sup>1</sup> by molecular sorption of the  $\text{Zr}(\text{HPO}_4)_2$  complex. The values of constants  $\beta_2$  and  $\beta_3$  (Table I)<sub>j</sub>, were calculated using this assumption. The last value differs considerably from the data given in ref.<sup>12</sup>, but satisfactory agreement exists among the results obtained in the present paper under various conditions. Solutions of 0.01M- $\text{H}_2\text{C}_2\text{O}_4$  form an exception. It should be emphasized that here the  $Q$  values were calculated from the  $\beta(\text{BX}_u)$  values determined

\* The subscript used here and in Table I denotes the number of ligands in the complex.

TABLE I  
The Stability Constants of Phosphate Complexes

Medium	Element	log A	$-\log C'/pA_{1/2}$	log $\beta_2$	$-\log C'/pA_{1/2}^f$	log $\beta_3^a$	$-\log C_1/pA_1$	log $\beta_3^b$
1.04M-H <sub>2</sub> SO <sub>4</sub>	Zr	1.55	1.58/ 9.67	20.9	0.19/8.27	29.2	—/8.97 <sup>c</sup>	28.8
	Hf	1.15	1.96/10.04	21.2	0.30/8.37	29.6	—/9.21 <sup>c</sup>	29.1
2.08M-H <sub>2</sub> SO <sub>4</sub>	Zr	2.87	1.13/ 9.38	21.6	0.40/8.65	30.4	—/9.01 <sup>c</sup>	30.2
	Hf	1.66	1.77/10.03	21.7	0.33/8.58	30.3	—/9.31 <sup>c</sup>	29.9
0.11M-H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Zr	~10.74	1.20/ 7.40	~25.8	0.12/7.01	~32.8	—/7.21 <sup>c</sup>	~32.7
	Hf	~10.7	1.25/ 7.43	~25.8	0.08/7.02	~32.8	—/7.23 <sup>c</sup>	~32.7
5.95M-HCl	Zr	1.51	2.45/10.55	22.6	—0.04/8.10	30.7	—/9.33 <sup>c</sup>	29.8
	Hf	1.35	2.57/10.67	22.6	—0.07/8.17	30.7	—/9.42 <sup>c</sup>	29.9
2M-HNO <sub>3</sub> <sup>d</sup>	Zr <sup>e</sup>	0.80	—	—	0.36/8.50	—	1.36/9.50	29.6
	Zr <sup>f</sup>	0.80	2.00/10.25	21.3	0.36/8.50	29.8	1.36/9.50	29.6

<sup>a</sup> The  $\beta_3$  value was calculated from the relationship,  $\log \beta_2 + pA_{1/2}^f$ ; <sup>b</sup> The  $\beta_3$  value was calculated according to equation (11); <sup>c</sup> determined from the condition,  $pA_1 = 1/2(pA_{1/2}^f + pA_{1/2}^g)$ ; <sup>d</sup> see ref. 1; <sup>e</sup> deposition on silica gel; <sup>f</sup> deposition on Teflon.

Symbols  $C'$ ,  $C''$  and  $C_1$  denote the concentrations of phosphoric acid at points  $[A]_{1/2}$ ,  $[A]_{1/2}^f$  and  $[A]_1$ , respectively;  $\beta_2$  and  $\beta_3$  are the stability constants for complexes  $B(HPO_4)_2$  and  $B(HPO_4)_3^{2-}$ . During the calculations, dissociation constants of acids and complexes, determined, if possible, under analogous conditions, were used.<sup>18</sup>

TABLE II  
The Stability Constants of the Phenylarsenate Complexes

Medium	Element	$\log Q$	$-\log C' : \rho A_{1/2}$	$\log \beta(BL_2)$
0.925M-H <sub>2</sub> SO <sub>4</sub>	Zr	1.56	2.22/14.15	29.9
	Hf	1.19	2.37/14.36	29.9
2.08M-H <sub>2</sub> SO <sub>4</sub>	Zr	2.87	1.35/14.00	30.9
	Hf	1.66	1.90/14.53	30.7
2M-HNO <sub>3</sub> <sup>a</sup>	Zr <sup>b</sup>	0.80	2.26/14.86	30.5

<sup>a</sup> See ref.<sup>17</sup>; <sup>b</sup> deposition on paraffin and crushed glass.  $C'$  denotes the experimentally determined concentration of H<sub>2</sub>L at point [A]<sub>1/2</sub>.

under different conditions and the hydrogen ion concentration was not determined but calculated. As the stability constants for thiocyanate complexes are not known, the results obtained under these conditions were not treated further.

The constants calculated from the experimental data by Krtil and Kolařík are also given in Table I. Good agreement was also found here, both for the sorption on silica-gel and for that on teflon. The non-symmetry of some curves in the cited paper<sup>1</sup> can be ascribed to the deposition of the Zr(OH)<sub>2</sub>HPO<sub>4</sub> complex or, when using the catex, to the deposition of ZrHPO<sub>4</sub><sup>2+</sup> cations.

The reason for different behaviour during the sorption from HCl-H<sub>3</sub>PO<sub>4</sub> solutions observed here and in ref.<sup>9</sup> cannot be found in possible differences in the characteristics of the silica gel used, since these differences would have to affect both the deposition of zirconium and that of hafnium. Therefore, the effect of differences in the separation methods is more probable. Ascending chromatography, employed in ref.<sup>9</sup>, basically enables non-uniform transport of hydrochloric and phosphoric acids during the elution. It has been found<sup>13</sup> that zirconium is sorbed more effectively than hafnium in solutions of 6M-HCl. This fact and the higher mobility of hydrochloric acid might cause the chloride complexes of hafnium to move with the front of the eluent, where there was a low concentration of phosphoric acid, while zirconium remained deposited at the start in the form of phosphate complexes.

#### Phenylarsenate Complexes

The reaction of zirconium with phenylarsenic acid was studied in many papers (refs<sup>6,14-17</sup> and references cited therein). For ZrL<sub>2</sub> complexes, Mikhailov<sup>14</sup> gives a value of  $\log \beta(ZrL_2) = 30.0$  and Kyrš and coworkers<sup>15</sup> a value of 30.6. The results given in Table II, calculated on the basis of the sorption of hafnium and zirconium on silica gel and on the basis of the results obtained during the study of the sorption

of zirconium on paraffin and crushed glass<sup>17</sup>, agree well with these data. The formation of higher complexes is rather improbable here.

### *Iodate Complexes*

The slope of the sorption curves at point  $[A]_{1/2}$  depends on the number of ligands in the molecule of the sorbed complex, which is assumed to be neutral. As iodic acid is monobasic, steeper sorption curves should be expected than, *e.g.*, for phosphoric acid complexes. Actually, the curves obtained were so steep that they indicated the formation of sorbed species containing even more than four  $\text{IO}_3^-$  particles. Moreover, differences in the behaviour of the studied elements in the presence of  $\text{HIO}_3$  and  $\text{KIO}_3$ , which might suggest the participation of potassium ions in the deposition, also indicate that sorption of  $\text{B}(\text{IO}_3)_4$  molecules is improbable. Therefore, it cannot be excluded that neutral particles of complex iodates,  $\text{K}_n\text{B}(\text{IO}_3)_{4+n}$ , where  $n = 1 - 2$ , are sorbed under these conditions. It should be noted that compounds of the type  $\text{Zr}(\text{IO}_3)_{4 \cdot n} \text{IO}_3$  have been prepared in the solid state<sup>6</sup>.

It follows from equation (12) that the distribution coefficients of the two elements depends not only on the difference in constants  $\beta(\text{BA}_n)$  and  $\beta(\text{BX}_n)$  but also on the number of ligands in the corresponding complexes. This fact is clearly manifested in the sorption of zirconium and hafnium from solutions containing potassium iodate, where the high number of ligands eliminates differences in the stability of sulphate complexes of zirconium and hafnium.

### *Hexacyanoferrite Complexes*

It can be concluded from the results obtained that in solutions of  $1\text{M-H}_2\text{SO}_4$  and  $0.1\text{M-H}_2\text{C}_2\text{O}_4$  neutral hexacyanoferrite complexes of zirconium and hafnium are either not formed or their distribution constants,  $K_D$ , are very low.

As the stability constant values for complexes  $\text{B}(\text{HPO}_4)_3^{2-}$  found here do not satisfactorily agree with the literature data, the validity of the given equations cannot be considered to be unambiguously proven. However, it should be pointed out that ref.<sup>12</sup> does not mention the sorption of zirconium and hafnium on the vessel walls, which necessarily plays an important role in the presence of phosphate ions. On the other hand, the agreement of the constants for the phenylarsenate complexes and the general character of the individual sorption dependences indicate the validity of the molecular adsorption mechanism. Although the attempt to separate zirconium and hafnium was not quite successful, it can be assumed that a more detailed study will lead to the determination of suitable conditions. Sorption of this type can be used for the isolation of a mixture of zirconium and hafnium or of one of them in the absence of the other. The main advantage of this method lies in the relatively high sensitivity.

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