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Abstract

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INVESTIGATION OF ION EXCHANGE IN HF SOLUTIONS. GROUP SEPARATIONS OF ELEMENTS BY MEANS OF ION-EXCHANGE RESINS

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In studies of ion exchange, along with the investigation of general regularities, systematic determination is being carried out of the distribution coefficients (K_d) of various elements between solutions containing complexing agents and ion-exchange resins. In this way, the absorption of practically all elements from aqueous HCl solutions (^{1}) and from HCl—HF solutions (^{2}) by the anion exchanger Dowex-1, and the absorption of cations from HCl (^{3}) on Dowex-50 resin, have been studied. The ion-exchange behavior of some elements in other acids has also been studied to varying degrees ($^{4-6}$). In the work of Faris (^{7}), K_d values were determined for many elements in hydrofluoric acid on the anion exchanger Dowex-1 × 10 under dynamic conditions on a column. Faris' data are very incomplete, and for many strongly sorbed elements the region of low HF concentrations, where especially strong sorption is observed, was not investigated.

In recent years, hydrofluoric acid has found increasing use as an eluent in chromatographic separations of hydrolyzing elements. On the basis of using mixtures of HCl—HF solutions as eluent, methods of analysis have been developed (^{8,9}) for alloys containing Ti, Nb, Ta, Mo, and W. A number of works are devoted to the chromatographic separation of microquantities of elements using HF and HF—HCl mixtures as eluents ($^{2,10-12}$).

We undertook a study of the absorption of a series of elements by ion exchangers from hydrofluoric-acid solutions, with the aim of finding optimal conditions for chromatographic separation of elements and determining certain regularities of ion exchange. In the present communication, distribution coefficients (K_d) are given for a number of elements, and possibilities are considered for their group chromatographic separation in hydrofluoric-acid solutions.

The work was carried out on domestic monofunctional resins: the anion exchanger AV-17 × 14 (F^- form) and the cation exchanger KU-2 × 6 (H^+ form). These resins possess high chemical stability; special experiments showed that their static exchange capacity does not change after prolonged treatment with $25M$ HF solution. Hydrofluoric acid was prepared by distillation (^{13}) of an ordinary commercial reagent. The work was conducted with the use of radioactive indicators of the elements under study, the purity of which was checked beforehand by radiochemical analysis. The initial solutions of the elements studied

Fig. 1. Absorption of elements from HF solutions by the anion exchanger AV-17 × 14. Solid line—no absorption; dashed line—absorption of metal chloro complexes from HF solutions

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Fig. 2. Absorption of elements from HF solutions by the cation exchanger KU-2 × 6. Notation as in Fig. 1

Figure 2: Fig. 2. Absorption of elements from HF solutions by the cation exchanger KU-2 × 6. Notation as in Fig. 1

were prepared by dissolving the corresponding metals, carbonates, oxides, or hydroxides in hydrofluoric acid; the initial concentration of the element in solution did not exceed 10^{-8} g/ml.

The distribution coefficients (K_d) were determined under static conditions (^{14,1}) from the ratio of the initial activity of the solution to the equilibrium activity of the resin, referred to unit volume of solution and weight of air-dry resin.

The distribution coefficients of the elements studied are presented in Figs. 1 and 2 in the coordinates $\lg K_d - C_{\mathrm{HF}}$. In studying the platinum metals and gold, we used solutions of their chlorocomplexes in hydrofluoric

acid, since the fluoro complexes of these elements are very unstable[^15] and can have no practical significance in ion-exchange chromatography. From consideration of the absorption curves of elements by the anion exchanger (Fig. 1) and the cation exchanger (Fig. 2), it is evident that most elements have a clearly expressed tendency to form, in hydrofluoric acid solutions, cations or anions possessing different capacities for sorption by ion exchangers. This

Fig. 1. Absorption of elements from HF solutions by the anion exchanger AV-17 × 14. Solid line—no absorption; dashed line—absorption of metal chloro complexes from HF solutions.

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makes it possible to separate practically all elements into groups according to their relation to ion-exchange resins in HF solutions. Verification of this proposition was carried out on chromatographic columns filled-

···anion exchanger AV-17 × 14 (F^- form) and cation exchanger KU-2 × 6 (H^+ form) on artificial mixtures of elements. When a mixture of elements in a solution of 1 M HF is placed on the column and the column is then washed successively with hydrofluoric acid of increasing concentration (and, for some elements, with other eluents), the elements are eluted in groups that are quite clearly separated from one another (Table 1).

Table 1

Elution of elements from the column by successively used eluents

Ion-exchange resin	1 M HF	5 M HF	10 M HF	15 M HF	20 M HF	HNO_3 + H_3BO_3	1 M HF + 4 M NH_4Cl	3 N $HClO_4$
Cation exchanger KU-2 (H^+ form)	anions	Cr, Fe, Ca, As, Cd, In	Na, Rb, Cs, Mn, Pb, Bi	Ni, Zn, Tc, Hg	Co, Cu, Tl	REE, TPE	–	–
Anion exchanger AV-17 (F^- form)	cations and Cr, Fe, Zn, Pb	Al, Si, P, Co, As	Be, Sc, V, Se	Br, Mo, Tl, Bi, U	Ti, Zr, Tc, Pd, Sn, Hf, W, Ir, Re	–	Nb, Ta	Ag, Sb, Pt, Au, Hg, Po

Each of the groups includes elements eluted by an eluent taken in an amount not exceeding 10 free column volumes. Dashes in the columns of the table mean that the given eluent is not used. The groups of elements obtained in this way can subsequently easily be separated into individual elements by known methods of ion-exchange chromatography (see, for example, (16)).

On the basis of the data presented in Figs. 1 and 2 and in Table 1, we developed original procedures for separating complex mixtures of fission and deep-spallation products formed upon irradiation of targets made of Ta, Hf, W, and U with 660 MeV protons. The irradiated target was dissolved in concentrated hydrofluoric acid with the addition of several drops of HNO_3; the solution was diluted to 1 M in HF and passed through a column filled with the cation exchanger KU-2. Rare-earth elements, alkali and alkaline-earth metals, and other elements that do not form anions under these conditions are quantitatively sorbed by the ion exchanger. Ta, Hf, W, and U form anions in HF solutions and are not sorbed by the cation exchanger. The elements sorbed by the resin were then extracted according to the scheme set out in Table 1, and the rare-earth elements isolated in this way were further separated on a cation-exchange column with ammonium lactate. In this procedure a high degree of purification of Ta, Hf, W, and U from microquantities of rare-earth elements is achieved. In particular, for uranium the purification coefficient reaches $\sim 10^5$.

The examples given show the great possibilities of the above method of group separation of elements using ion-exchange resins in hydrofluoric acid solutions.

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REFERENCES

1. K. A. Kraus, F. Nelson, *Chemistry of Nuclear Fuel*, Moscow, 1956, p. 353.
2. F. Nelson, K. A. Kraus, R. Rush, *J. Am. Chem. Soc.*, **82**, 339 (1960).
3. F. W. E. Strelow, *Anal. Chem.*, **32**, 1185 (1960).
4. L. R. Bunney, N. E. Ballou et al., *Anal. Chem.*, **31**, 324 (1959).
5. L. Wish, *Anal. Chem.*, **31**, 326 (1959).
6. E. C. Freiling, J. Pascual, A. A. Delucchi, *Anal. Chem.*, **31**, 330 (1959).
7. J. P. Faris, *Anal. Chem.*, **32**, 520 (1960).
8. C. U. Wetlesen, *Anal. chim. acta*, **22**, 189 (1960).
9. D. H. Wilkins, *Talanta*, **2**, 355 (1959).
10. U. Schindewolf, J. W. Irvine, *Anal. Chem.*, **30**, 906 (1958).
11. K. A. Kraus, *J. Am. Chem. Soc.*, **73**, 2900 (1951).
12. O. V. Larionov, M. K. Nikitin, *Vestn. Leningr. Univ.*, No. 10, 73 (1961).
13. I. G. Rys, *Chemistry of Fluorine and Inorganic Fluorine Compounds*, Moscow, 1956, p. 104.
14. J. Schubert, *J. Phys. Coll. Chem.*, **52**, 340 (1948).
15. A. K. Babko, *ZhNKh*, **4**, 1067 (1959).
16. B. K. Preobrazhenskii, in: *Radiochemistry and Chemistry of Nuclear Processes*, Moscow, 1960, p. 384.

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