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Abstract

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ON THE COMPARATIVE SORBABILITY OF TRANSITION ELEMENTS OF THE FOURTH PERIOD BY MINERAL ION EXCHANGERS

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Along with synthetic ion-exchange resins, mineral ion exchangers with high exchange capacity are of practical interest. Kaolin, glauconite, and volkhonskoite ([1]), crystalline silicates ([2]), chromatographic aluminum oxide ([3,5]), zinc oxide ([6]), iron hydroxide ([7]), cadmium sulfide ([8]), and heteropoly acids ([9–13]) have been tested as mineral ion exchangers. Recently much attention has been devoted to the ion-exchange properties of zirconyl salts ([14,15]), zirconium hydroxide, zirconium and titanium dioxides ([16,17]). Great importance is attached to the synthesis of mineral polymers (polyphosphates, phosphonitrile hydroxides), as well as those possessing ion-exchange properties ([18]). Most of the sorbents listed have been used for the separation of alkali and alkaline-earth metals.

We undertook a comparative study of the sorbability by mineral ion exchangers of the transition elements of the fourth period, which are important not only in the analysis of alloys but also in the determination of trace elements in biological objects. Of particular interest was the search for sorbents with an exchange capacity higher than that of chromatographic aluminum oxide.

For these purposes the sorption properties of a number of salts $Zr(HPO_4)_2$, $CaHPO_4$, $BaHPO_4$, CaS, the hydroxides $Zr(OH)_4$, $Ti(OH)_4$, and the oxides ZrO_2, TiO_2, Nb_2O_5, Bi_2O_3, SnO were studied. Chromatographic aluminum oxide (TU MKhP 2962-54) served as the standard for comparison. $Zr(OH)_4$ and $Ti(OH)_4$ were obtained by the action of alkalis on salts ([19]), and TiO_2– according to Karyakin ([20]). The remaining sorbents were taken as commercial preparations (chemically pure or pure for analysis).

The absorption by sorbents of Cr(III), Fe(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) was investigated; these were taken only in the form of sulfates in order to exclude the influence of different anions on sorbability. All solutions were prepared with bidistilled water from chemically pure reagents.

The experiments were carried out under dynamic conditions. Into graduated glass tubes 7.0 mm in diameter, 1 g of air-dry sorbent was introduced, compacted, and wetted with bidistilled water. Solutions of precisely known concentration ($\simeq 0.3\,N$) were passed through the columns until "breakthrough" of the

sorbed cation, maintaining (with the aid of a stopcock) the same filtration rate. In the case of poor permeability of the sorbent (for example, $CaHPO_4$), an inert filler—crushed glass—was introduced into the columns. The "breakthrough" of cations and the filtrate were recorded using highly sensitive drop reactions ([21]): Cr(III)—with benzidine, Fe(III) and Co(II)—with thiocyanate, Mn(II)—with an ammoniacal solution of $AgNO_3$, Fe(II)—with ferricyanide, Ni(II)—with dimethylglyoxime, Cu(II)—with CdS, and Zn(II)—with ferrocyanide or with ammonium thiocyanatomercurate ([22]). The sorbability of the cations was expressed in milligram-equivalents per 1 g of sorbent. In addition, the sorption series of cations for each sorbent were determined by the generally accepted method. The mechanism of ion uptake by the sorbents was studied.

Table 1 gives quantitative data on the sorbability of the cations (arranged in order of increasing radii). It is evident from it that the cations studied are sorbed best of all by $Ti(OH)_4$. In addition, the exchange capacity of $Ti(OH)_4$, $Zr(OH)_4$, and $Zr(HPO_4)_2$ as a whole is much higher than that of chromatographic alumina. $CaHPO_4$ shows a sharply expressed selectivity with respect to Cu(II), and $BaHPO_4$ with respect to Fe(III). Cadmium sulfide absorbs only Cu(II). As for the oxides, ZrO_2, TiO_2, Bi_2O_3, and SnO, without any preliminary treatment (apart from wetting with bidistillate), do not sorb cations of the transition elements of the fourth period at all. From the data of the same table it follows that, although the sorbability of trivalent cations is higher than that of divalent ones, chromium in a number of cases constitutes an exception to this rule.

Investigation of the filtrates issuing from the columns showed that $Zr(HPO_4)_2$, $CaHPO_4$, and $BaHPO_4$ absorb cations by an ion-exchange mechanism accompanied by displacement of hydrogen cations. Consequently, sparingly soluble acid salts in general can behave as cation exchangers in the H-form. Therefore, along with the study of mineral polymers (18), investigations of the ion-exchange properties of other sparingly soluble acid salts are of undoubted interest. It is not excluded that some sparingly soluble basic salts will behave as anion exchangers in the OH-form. The selective absorption of Cu(II) by cadmium sulfide proved to be a purely chemical exchange reaction, in which copper displaces from the column an equivalent amount of cadmium.

Fig. 1. Change in the sorbability of divalent cations as a function of the atomic number of the element: 1 —on chromatographic alumina, 2 —on Nb_2O_5, 3 —on $Zr(HPO_4)_2$, 4 —on $Zr(OH)_4$, 5 —on $Ti(OH)_4$, 6 —on $CaHPO_4$.

The very high exchange capacity of $Ti(OH)_4$ makes it possible to suppose that in titanium, as also in zirconium (14), the formation of approximate chains is possible,

$$-\mathrm{Ti}-\mathrm{O}\ldots-\mathrm{Ti}-\mathrm{O}-\mathrm{Ti}-\ldots\mathrm{O}-\mathrm{Ti}-,$$

bearing one or another ion-exchange group. The mechanism of cation absorption

by Nb_2O_5 remains, for the present, the least understood. It is possible that, for this case, the concepts concerning the sorption properties of other oxides (5, 6) are applicable.

The curves in Fig. 1 show how the absorption by mineral sorbents of divalent cations changes as a function of the position of the elements in the periodic system, i.e., of the atomic number of the element.

It is characteristic that the minimum sorbability by all sorbents occurs for the nickel cation, which is distinguished by the smallest radius (0.78 Å), and consequently by the greatest degree of hydration and the poorest entry into sorbents. The maximum uptake for most sorbents occurs for the copper cation and, in some cases, for the cobalt cation. The simple dependence between ionic radii and their uptake is complicated here by phenomena of selective sorbability.

Table 1

Comparative sorbability (in mg-equiv/g) of cations by mineral ion exchangers

Sorbent	Cr^{3+}	Fe^{3+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Mn^{2+}
Chromatographic alumina	0.35	0.48	0.24	0.31	0.35	0.26	0.25	0.25
$Zr(HPO_4)_2$	0.11	2.61	0.41	0.78	0.76	0.65	0.66	0.71
$CaHPO_4$	0	1.50	0	0.30	5.64	0.24	0.24	0.45
$BaHPO_4$	0	1.14	0	0	0	0	0	0
CdS	0	0	0	0	13.8	0	0	0
$Zr(OH)_4$	0.84	2.15	0.41	0.56	0.96	0.80	0.68	0.81
$Ti(OH)_4$	1.59	2.25	0.90	1.69	1.59	1.24	1.76	1.46
Nb_2O_5	0.34	0.53	0.16	0.18	0.28	0.20	0.16	0.17
ZrO_2	0	0	0	0	0	0	0	0
TiO_2	0	0	0	0	0	0	0	0
Bi_2O_3	0	0	0	0	0	0	0	0
SnO	0	0	0	0	0	0	0	0

The sorption series of cations established by us for different mineral sorbents are not identical in form. Only the sorption series of cations on chromatographic alumina as a whole agrees with the literature data ([3], [5]):

$$Cr^{3+} > Fe^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Ni^{2+} = Fe^{2+} > Mn^{2+}.$$

The sorption series of the same cations on zirconium hydrophosphate looks quite different:

$$Fe^{3+} > Cu^{2+} > Mn^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Ni^{2+} > Cr^{3+}.$$

For $CaHPO_4$ a sorption series was obtained that differs in the following features:

$$Fe^{3+} > Cu^{2+} > Fe^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+} > Ni^{2+} = Cr^{3+}.$$

The sorption series of cations on $Ti(OH)_4$ proved to be very similar

$$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$$

and on $Zr(OH)_4$:

$$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}.$$

However, they differ substantially from the sorption series of ions on niobium pentoxide

$$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} = Ni^{2+}.$$

The varied character of the sorption series opens up possibilities for choosing mineral sorbents for each particular case of cation separation. Bearing in mind the concentration and analytical separation of elements

of the fourth period, the most promising mineral sorbents may be considered to be $Ti(OH)_4$, $Zr(OH)_4$, $Zr(HPO_4)_2$, and $CaHPO_4$, whose exchange capacity is much higher than that of chromatographic alumina. In addition, for these purposes one can make use of the sharply pronounced selectivity of $BaHPO_4$ with respect to Fe(III), as well as the selectivity of $CaHPO_4$ and CdS with respect to Cu(II).

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Note: Figure translations are in progress. See original paper for figures.