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M. Qureshi[a]; S. Z. Qureshi[a]; J. P. Gupta[a]; H. S. Rathore[a]
[a] CHEMISTRY DEPARTMENT, ALIGARH MUSLIM UNIVERSITY, ALIGARH, U.P., INDIA

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REVIEW

Recent Progress in Ion-Exchange Studies on Insoluble Salts of Polybasic Metals

M. QURESHI, S. Z. QURESHI, J. P. GUPTA, and H. S. RATHORE

CHEMISTRY DEPARTMENT
ALIGARH MUSLIM UNIVERSITY
ALIGARH, (U.P.), INDIA

Zirconium phosphate is perhaps the first insoluble salt of a polybasic metal to be used as an ion exchanger. It is the most studied and probably the most useful of all the materials of this type. These materials are prepared by combining oxides of group IV with the more acidic oxides of groups V and VI of the periodic table, as shown in Table 1.

These new ion exchangers have high capacity, give high rates of ion exchange, and are superior to organic resins in their thermal stability and resistance to radiation. They also show high selectivity which can be modified by changing the chemical composition of the material. These substances have, therefore, attracted considerable attention from nuclear scientists, analytical chemists, physical chemists, and even pharmaceutical research workers. The growing interest in this field may be demonstrated by the fact that, when the book *Ion Exchange* by Helfferich (*1*) was published in 1962, only two pages were devoted to synthetic inorganic ion exchangers, of which only one page was devoted to the salts of polybasic metals and that 2 years later, a comprehensive monograph on *Inorganic Ion Exchangers* was published by Amphlett (*2*). This book is a classic in the field and has led to a revolutionary

TABLE 1

IV		V		VI	
C		N		O	
Si		P		S	
Ge	Ti	As	V	Se	Cr
Sn	Zr	Sb	Nb	Te	Mo
Pb	Hf	Bi	Ta	Po	W

upsurge of interest in inorganic ion exchangers, as is illustrated in Fig. 1.

In this review we sumarized the progress in the chemistry of inorganic ion exchangers of the generic type of zirconium phosphate from 1964 (when Amphlett's book was published) to August 1971.

It is not possible in a brief review to deal with all aspects of the subject. We have tried to include the more important studies, subject only to personal prejudice, and therefore, apologize for any omission of important papers.

STUDIES ON AMORPHOUS MATERIALS

Amorphous zirconium phosphate like ion-exchange materials, i.e., phosphates (*2–5*), arsenates (*6–9*), molybdates (*10–13*), tungstates

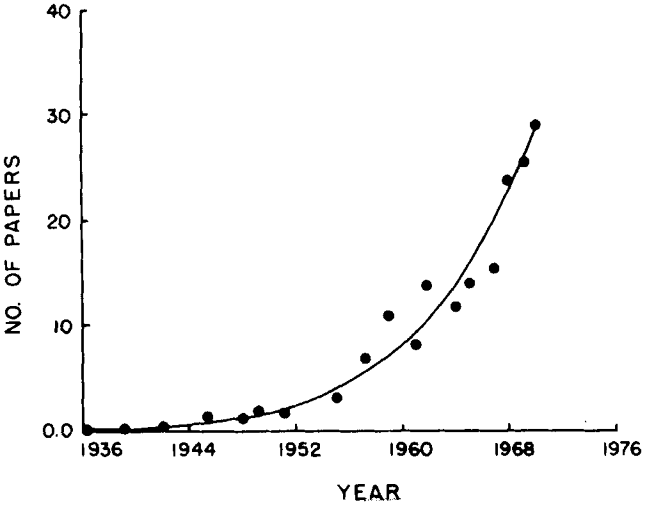

FIG. 1. Progress in ion-exchange investigations on insoluble salts of polybasic metals.

(*14–17*), and antimonates (*18*, *19*) of Zr(IV), Sn(IV), Ti(IV), and Th(IV), continues to attract attention. Uranyl hydrogen phosphate (*20–24*), zirconium oxalate (*2*), zirconium vanadate (see Ref. *52*), chromium phosphate (see Ref. *53*), and hydrated tantalum pentoxide (*25*) have also been investigated. In four extensive papers, Vesely and co-workers have studied the sorption mechanism of cations on uranyl phosphate. The mechanism of the sorption of the di- and trivalent cations on uranyl hydrogen phosphate has been explained in terms of the formation of the metal uranyl phosphate and of the precipitation of the simple metal phosphates. The precipitation mechanism for the sorption of tetravalent elements on ammonium uranyl phosphate has been confirmed. For this purpose the solubility products of $UO_2HPO_4 \cdot 4H_2O$, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, $NH_4UO_2PO_4$, and $(NH_4)_xH_yMe^{IV}_{3-x-y}(PO_4)_{3-x-y}$ have been determined. However, the values of solubility products of the alkali uranyl phosphate found by Vesely et al. differ substantially from the values determined by Muraveva et al., and the

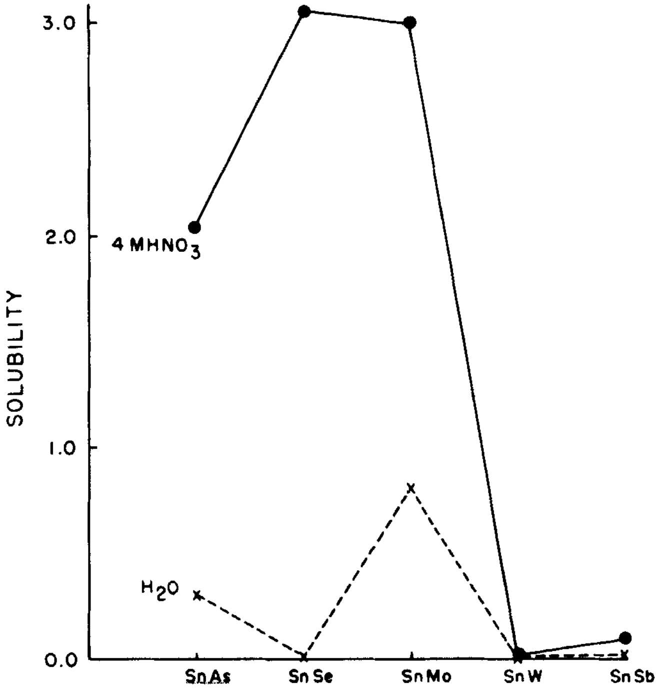

Fig. 2. Chemical stability of tin(IV)-based exchangers.

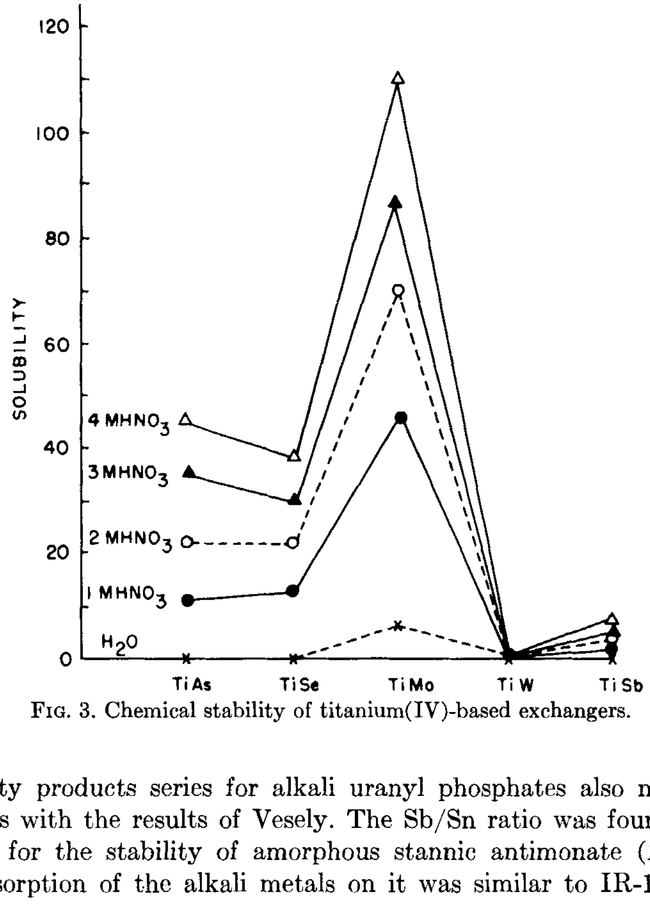

FIG. 3. Chemical stability of titanium(IV)-based exchangers.

solubility products series for alkali uranyl phosphates also markedly conflicts with the results of Vesely. The Sb/Sn ratio was found to be critical for the stability of amorphous stannic antimonate (*18*), and the adsorption of the alkali metals on it was similar to IR-120. Hydrated tentalum pentoxide (*25*) was found to be a good ion-exchange meterial to work at higher temperatures.

There are three major problems in analytical applications of inorganic ion exchangers. They are (*1*) chemical stability, (2) thermal stability, and (3) specificity.

The greater breakdown of inorganic ion exchangers in simple eluents as compared with organic resins seriously limits their use in practical work. Owing to the presence of interfering ions, K_d values are difficult to determine either by spectrophotometry or by complexometry. It is, therefore, very heartening to learn that titanium tungstate (*16*) shows unusual chemical stability even in 6 *M* HNO_3. The stability plots of

Sn(IV) and Ti(IV) based ion exchangers are shown in Fig. 2 and 3, respectively.

Thermal stability of an ion-exchange material depends upon the cation and the anion present in the exchanger. The comparative plots are shown in Fig. 4 and 5. From these it is clear that titanium vanadate (*26*), stannic arsenate (*7*), and stannic selenite (*27*) are the most stable materials.

The selectivity of an exchanger depends on ion pair formation (discussed above), size of the cavities, the hydrated radii, and the charge on the exchanging ion. The ion pair formation, in turn, depends upon the solubility product of the cation with the anion of the exchanger. The cations with low KSP values have low K_d values and vice versa. Since these materials have not been crystallized, it is not yet possible to say anything definite about the size of the cavities.

CRYSTALLIZATION AND CHARACTERIZATION OF ION-EXCHANGE MATERIALS

Crystallization of inorganic ion exchangers is difficult and tedious but it offers many advantages. It was found, for instance, that on crystallization thorium arsenate becomes specific for lithium (*9*) ions, whereas zirconium and tin phosphates (*28*, *29*) become more stable toward hydrolysis. Therefore, zirconium phosphate (*30*), zirconium arsenate (*31*), titanium phosphate (*4*), titanium arsenate (*32*), cerium phosphate (*33*), cerium arsenate (*34*), thorium arsenate (*9*), tin phosphate (*29*), and antimonic acid (*35*, *36*) were successfully crystallized. It was found in almost all cases that crystallization adds to the stability and the selectivity of the ion exchanger. Since crystallization ensures the purity of the product, it also facilitates many theoretical studies.

The crystal structure of zirconium phosphate was studied by Clearfield and co-workers (*30*) who showed that it has a layered structure. Each layer consists of sheets of zirconium atoms; the phosphate groups are above and below the sheets of metal atoms. They also explained the ion-exchange mechanism on this basis (*30*, *37*, *38*).

MECHANISM OF ION EXCHANGE

In two interesting papers (*39*, *40*), Clearfield discusses the mechanism of Li^+–H^+ and Na^+–H^+ exchange on γ-zirconium phosphate. He ex-

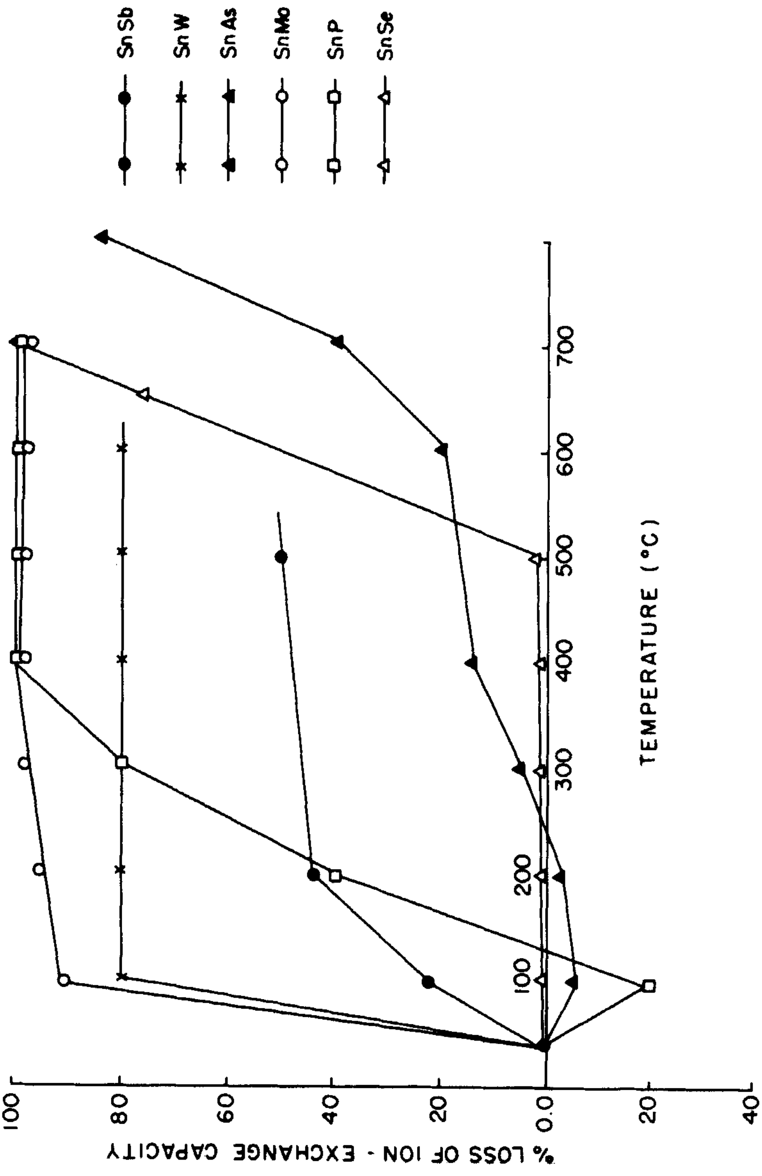

FIG. 4. Thermal stability of tin(IV)-based exchangers.

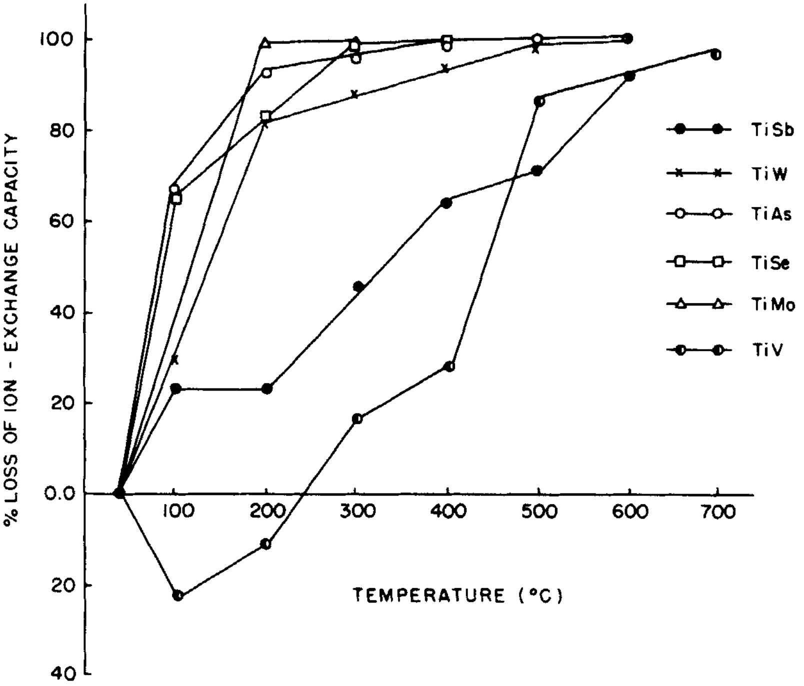

FIG. 5. Thermal stability of titanium(IV)-based exchangers.

plains the formation of a hysteresis loop in both cases by the existence of two phase systems containing the unexchanged and the semiexchanged exchanger. The phases present during the forward and the backward reactions are different and give rise to a hysteresis loop. It is probable that similar studies on crystalline products may give equally valuable results.

THERMODYNAMICS OF ION EXCHANGE

Nancollas and co-workers studied the thermodynamics of cation exchange on zirconium phosphate (*41–43*). They determined the values of ΔS, ΔH, and ΔF for the exchange reaction,

$$R^-H^+ + M^+ \rightleftharpoons R^-M^+ + H^+$$

They interpreted the thermodynamical functions in terms of the nature of the bonding between the alkali metal ion and the matrix of the ion exchanger. It is hoped that such studies will be continued so that a better understanding is obtained of the ion-exchange process. Similar studies have also been reported on anion exchange (*44*, *45*).

KINETICS OF ION EXCHANGE

Nancollas also studied the kinetics of Na^+–H^+ exchange on crystalline zirconium phosphate. The rate of exchange is initially fast and then becomes slow, suggesting a change in crystal structure (*46*). Fuga and Kikenda studied the kinetics of ion exchange between alkali metals and zirconium antimonate (*45*) in hydrogen form at 25°C. They found that the rate of the reaction increases with the atomic number of the cation. It was slower than that for sulfonated resins but more rapid than that for carboxylic resins.

ION EXCHANGE IN FUSED SALTS

Unfortunately very few studies have been reported on ion exchange in molten salts. Alberti and Alluli (*47*) treat ion exchange on amorphous zirconium phosphate in molten nitrates. They found that lithium ion is greatly preferred over potassium ions by the exchanger.

ION EXCHANGE BETWEEN SOLIDS

A recent paper by Clearfield and Troup (*48*), points to many interesting possibilities. They found that ion exchange between two solids is possible. Thus if zirconium phosphate in hydrogen form is heated with a salt, e.g., $CoCl_2$, then the following equilibrium exists:

$$CoCl_2 + 2RH \rightleftharpoons R_2Co + 2HCl$$

As the volatile acid is removed the reaction proceeds to the right and ion exchange occurs. Such exchanges should be possible whenever one of the products of ion exchange is volatile at the reaction temperature and can be removed.

SURFACE PROPERTIES OF GELS

Many interesting points emerge from the studies of Murray and Fuerstenau (*49*) on the surface properties of zirconium phosphate gels.

They found that the charge on these gels depends on the exchanger composition and on the pH of the solution. Uptakes of electrolytes, such as K^+ and Li^+, are lowest at the zero point of charge and at pH values where the solid is positively charged. These ions are not adsorbed until the gel has a negative surface charge. These phenomena suggest that surface charge is principally responsible for the sorptive and exchange properties of these gels. However, if the exchange leads to the formation of an insoluble phosphate, e.g., Ag^+–H^+ exchange, then the surface charge is less important. In this case Ag^+ ions are chemisorbed even when the solid is positively charged.

CHROMATOGRAPHY ON PAPERS IMPREGNATED WITH ZIRCONIUM PHOSPHATE AND SIMILAR MATERIALS

Chromatography on papers impregnated on inorganic ion exchangers of the zirconium phosphate type was reported recently, and a number of interesting separations have been developed. In some studies at our laboratories (*50*), it was observed that these papers are highly selective and give rapid separations with simple aqueous systems. These papers are useful in rapid evaluation of the analytical potential of an ion-exchange material. The use of mixed solvent systems increases the selectivity of these materials because now both solvent extraction and ion-exchange mechanisms play an important role. The spots are more compact than in aqueous systems. The importance of mixed solvent systems for paper chromatography on inorganic papers was first reported by Qureshi and co-workers (*51*). It is hoped that these solvents will find increasing use in column chromatography also. Some important separations achieved with these papers are listed in Table 2.

ANALYTICAL APPLICATIONS

The counterion matrix interactions are more important in inorganic ion exchangers than in organic resins. They sometime lead to irreversible adsorption (when the ion is incorporated in the matrix) and often lead to selective or specific separations. Stannic molybdate (*11*) and stannic tungstate (*15*) are specific for lead; zirconium vanadate (*52*) adsorbs K, Na, Ba, Sr, Mg, Cd, Fe, Co, Ni, Pb, Zn, Cu, and Ag but does not absorb Al, Mn, Bi, Ti, and Hg; and chromium tripolyphosphate glass is suitable for column operations (*53*) and can be used for alkali

TABLE 2

Some Important Binary, Ternary, and Quarternary Separations on papers Impregnated with Inorganic Ion Exchangers[a]

Solvent system	Separations achieved	Paper
Acetone + aceic acid + *n*-butanol + 4 *M* HCl (1:1:1:1)	Al^{3+}–In^{3+}–Ga^{3+}–Tl^{3+}	Titanium tungstate
Acetone + acetic acid + *n*-butanol + 4 *M* HCl (1:1:1:1)	Al^{3+}–Be^{2+}–Ga^{3+}–Tl^{3+}	Titanium tungstate
Acetone + acetic acid + *n*-butanol + 4 *M* HCl (1:1:1:1)	Fe^{2+}–Fe^{3+}	Titanium tungstate
Ethyl methyl ketone + acetone + 50% HCl (1:6:1)	Al^{3+}–Be^{2+}–Fe^{3+}	Titanium tungstate
Acetyl acetone + acetone + 50% HCl (6:3:1)	Tl^{+}–Zn^{2+}–Ga^{3+}	Titanium tungstate
Ethyl methyl ketone + *n*-butanol + 50% HCl (6:3:1)	As^{3+}–Sb^{3+}–As^{3+}–Bi^{3+}	Stannic tungstate
1 *M* Ammonium formate	Mg^{2+}–Sr^{2+}–Ba^{2+}	Stannic tungstate
Dioxane + satd. solution of NaF + 1 *M* HCl (3:1:6)	Zr^{4+}–Th^{4+}	Stannic tungstate
Acetyl acetone + acetone + 50% HCl (7:3:1)	Zn^{2+}–Mn^{2+}–Ni^{2+}	Stannic tungstate
n-Butanol + 50% HNO_3 (6:4)	Ag^{+}–Cu^{2+}–An^{3+}	Stannic tungstate
0.1 *M* ammonium tartarate in 4 *M* NH_4OH	Se^{4+}–Te^{4+}	Stannic tungstate
Me—OH + 10 *M* HCl + HCOOH (6:2:2)	Cs^{+}–Rb^{+} or K^{+}	Stannic selenite
0.1 *M* H_2SO_4	Mo^{6+}–Cr^{3+}	Stannic selenite
0.1 *M* $HClO_4$	Al^{3+}–Cr^{3+}	Stannic selenite
1 *M* $HClO_4$	VO_2^{2+} – V^{4+} – Th^{4+}	Stannic selenite
Me—OH + 10 *M* HCl + acetic acid (6:1:4)	An^{3+} – Ag^{+} – Pt^{4+}	Stannic selenite
2 M HCl + 2 *M* orthophosphoric acid (1:1)	Sb^{3+}–Sb^{5+}	Stannic phosphate
n-Butanol + HCl (8:2)	W^{6+}–Mo^{6+}	Stannic phosphate

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[a] From Quneschi (*50*).

TABLE 3

Important Separations on Inorganic Ion-Exchange Columns

Cations	Separations from	Exchanger	Eluents	Elution order	Ref.
Cu^{2+}	Zn^{2+}, Co^{2+}	Hydrous tin oxide	H_2SO_4	Cu^{2+} last	*54*
Zn^{2+}	Mn^{2+}	Hydrous tin oxide	H_2SO_4	Mn^{2+}, Zn^{2+}	*54*
Co^{2+}	Fe^{3+}	Hydrous tin oxide	$(COONH_4)_2$	Fe^{3+}, Co^{2+}	*54*
Na^+, K^+	Each other and other elements	Ammonium molybdophosphate	NH_4NO_3	Na^+, K^+	*55*
Na^+, Cs^+	Sr^{2+}, Ca^{2+}	Hydrous tin oxide	HNO_3, NH_4NO_3	Sr^{2+}, Ca^{2+} last	*56*
Cs^+	Na^+	Hydrous tin oxide	NH_4Cl	Cs^+, Na^+	*56*
Mn^{7+}	Cr^{6+}	Hydrous tin oxide	HNO_3, NH_4NO_3	Mn^{7+}, Cr^{6+}	*56*
Ca^{2+}	Mg^{2+}, Sr^{2+}	Titanium tungstate	HNO_3, NH_4NO_3	Ca^{2+} las$_4$	*57*
Ga^{3+}	Al^{3+}, In^{3+}, Fe^{3+}	Titanium tungstate	H_2O, HNO_3	Ga^{3+} last	*16*
Pb^{2+}	Numerous metal ions	Titanium tungstate	NH_4NO_3, HNO_3	Pb^{2+} last	*16*
Hf^{4+}	Zr^{4+}	Titanium tungstate	NH_4NO_3, HNO_3	Hf^{4+} first	*58*
La^{3+}	Ce^{3+}, $Pr^{3+}Nd^{3+}$, Sm^{3+}	Titanium tungstate	NH_4NO_3, HNO_3	La^{3+} last	*58*
Zn^{2+}, Bi^{3+}	Pb^{2+}, Tl^+	Titanium molybdate	HNO_3, HCl, NH_4NO_3, NH_4Cl	Zn^{2+}, Bi^{3+} first	*12*
Cu^{2+}	Pb^{2+}, Fe^{3+}	Stannic arsenate	H_2O, HNO_3, NH_4NO_3	Cu^{2+} first	*7*
Fe^{2+}	Fe^{3+}, Cu^{2+}, Pb^{2+}	Stannic arsenate	H_2O, HNO_3, NH_4NO_3	Fe^{2+} first	*7*
Fe^{3+}	Ni^{2+}, Co^{2+}, Mn^{2+}, Ca^{2+}, Al^{3+}	Stannic arsenate	H_2O, HNO_3, NH_4NO_3	Fe^{3+} last	*59*
Al^{3+}	In^{3+}, Mg^{2+}	Stannic arsenate	H_2O, HNO_3, NH_4NO_3	Mg^{2+}, Al^{3+}, In^{3+}	*59*
Pb^{2+}, UO_2^{2+}, Cr^{3+}	Numerous metal ions	Stannic arsenate	H_2O, HNO_3, NH_4NO_3	Pb^{2+}, UO_2^{2+}, Cr^{3+} last	*60*

(*continued*)

TABLE 3 (continued)

Cations	Separations from	Exchanger	Eluents	Elution order	Ref.
Mg^{2+}	Ca^{2+}, Sr^{2+}, Al^{3+}	Titanium antimonate	HCl, HNO_3, NH_4Cl	Mg^{2+} first	*19*
Mn^{2+}	Al^{3+}	Titnium antimonate	HCl, HNO_3, NH_4Cl	Mn^{2+}, Al^{3+}	*19*
VO^{2+}	Fe^{3+}, Al^{3+}, Mn^{2+}, UO_2^{2+}, Zr^{4+}, Hf^{4+}	Titanium antimonate	HCl, HNO_3, NH_4Cl	VO^{2+} first	*61*
Pb^{2+}	Cu^{2+}, Zn^{2+}, Mg^{2+}, Ga^{3+}	Titanium arsenate	H_2O, NH_4NO_3, HNO_3	Pb^{2+} last	*8*
Fe^{3+}	Al^{3+}, Mg^{2+}, Ni^{2+}, Mn^{2+}	Stannic molybdate	NH_4Cl, HNO_3	Fe^{3+} last	*62*
Ce^{3+}	Pr^{3+}, Nd^{3+}	Stannic molybdate	NH_4Cl, HNO_3	Ce^{3+} last	*62*
La^{3+}	Ca^{2+}, Sr^{2+}, Ba^{2+}, Y^{3+}	Thorium tungstate	H_2O, NH_4Cl, HCl	La^{3+} last	*17*
VO^{2+}	Cr^{3+}, Mn^{2+}, Fe^{3+}	Thorium tungstate	H_2O, NH_4Cl, HCl	VO^{2+} first	*17*
Fe^{3+}	Zn^{2+}, Co^{2+}, Cu^{2+}	Thorium molybdate	H_2O, NH_4Cl, HCl	Fe^{3+} last	*13*
Cm^{3+}	Am^{5+}	Zirconium phosphate	HNO_3	Am, Cm	*63*
Na^+	K^+, Cs^+	Stannic phosphat	NH_4Cl	Na^+, K^+, Cs^+	*3*
Na^+	K^+	Zirconium phosphate		Na^+, K^+	*64*
Cs^+	Rb^+	Zirconium phosphate		Rb^+, Cs^+	*64*
Cd^{2+}	Numerous metal ions	Titanium selenite	2×10^{-4} HNO_3, 0.4% NH_4Cl	Cd^{2+} last	*65*

metal separations. Distribution coefficients for actinides on zirconium phosphate were determined as a function of HNO_3 concentration; K_d values of alkali metals on antomonic acid in ammonium nitrate and HNO_3 have also been determined. On the basis of above studies, ammonium nitrate was found to be good a eluent for alkali metals. Numerous difficult separations have been achieved on synthetic inorganic ion-exchangers, and some of the more important are given in Table 3.

MISCELLANEOUS

Reference must also be made to a very thorough study on the hydrolysis of zirconium phosphate by Ahrland and co-workers (*66*). They found that at low pH the phosphate release is not primarily due to hydrolysis but rather is the washing out of the phosphoric acid that adheres very stubbornly to the gel. They also found that high affinity of the exchanger for Fe^{3+} is probably due to the incorporation of iron into the exchanger matrix. The latter explanation may hold good in many other cases also.

Two important points emerge from the lengthy studies of Szirtes et al. (*67*). They found that the capacity increases with increase in the precipitation temperature and also with an increase in the proportion of the precipitating anions. Biochinova published a number of papers on inorganic ion exchangers. One of his exchangers, zirconiumphthalophosphate (*68*), may be of some practical value since it ratains ion-exchange properties up to 700°C.

Finally a few novel applications of inorganic ion-exchange beads may be mentioned. Stannic molybdate beads give a black color (*69*) with iron(II) and are specific for this ion. Stannic arsenate beads in the Fe(III) form have been used as an indicator (*70*) for the titration of zinc with potassium ferrocyanide.

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