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REVIEW

Synthetic Inorganic Ion-Exchangers

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Abstract

A review of the development of the synthetic inorganic ion exchangers during the 1970–1976 period has been made. Synthesis, properties, and analytical applications of the hydrated oxides, acidic salts of multivalent metals, heteropolyacid salts, and synthetic zeolite-type materials that are used as ion-exchangers have been included in the survey. Only the more important contributions during the 1970–1976 period are included.

During the last two decades, inorganic ion-exchangers have attracted analytical chemists. The synthetic inorganic ion-exchangers are fairly stable toward high temperature and ionizing radiation. Hence they are superior to commercially available organic or natural inorganic exchangers and suitable for use in the nuclear industry, hydrometallurgy, the preparation of ultrapure materials, the recovery of valuable materials from industrial waste, etc.

The book by Amphlett (*1*) and the review articles of Churms (*2*) and Materova et al. (*3*) on inorganic ion-exchangers cover the period up to 1965. The review by Vesely and Pekarek (*4*) covers 1965–1970. We thought it logical and useful to review the work done during 1970–1976.

In recent years, studies on synthetic inorganic ion-exchangers have increased at a phenomenal rate. Since 1970, review articles have been published by Rees (*5, 6*), Qureshi (*7, 8*), Fuller (*9*), Inczedy (*10*), Freund and Marcilly (*11*), Clearfield et al. (*12*), and Abe (*13*), Fuller (*9*) reviewed

ion-exchange chromatography on inorganic oxides and hydrous oxides. Abe, and Vesely and Pekarek reviewed the synthesis, properties, and analytical applications of inorganic ion-exchangers.

A large number of inorganic ion-exchangers have been synthesized during 1970–1976. The majority are amorphous when prepared at room temperature, but crystalline forms were obtained by refluxing, or by aging, or by digesting above a normal temperature. After preparation they have been subjected to different physicochemical investigations for elucidation of their nature, composition, and structure. For selective separation, the distribution coefficient (K_d) of different metal ions and anions have been measured. It was observed that inorganic ion-exchangers are selective for particular metal ions or anions.

Papers impregnated with inorganic ion-exchangers have been used for paper chromatography, electrochromatography, and thin-layer chromatography. The synthetic inorganic materials which exhibit ion-exchanging properties have been classified by Vesely and Pekarek (*4*) according to the following broad groups:

1. Hydrated oxides of metals
2. Acidic salts of polyvalent metals
3. Insoluble salts of heteropolyacids
4. Insoluble hydrated metal ferro- and ferricyanides
5. Synthetic zeolites
6. Other substances with weak exchange properties

HYDRATED OXIDES OF METALS

Hydrous aluminum oxide (*14*, *15*) and silicon dioxide (*16–19*, *168*), particularly in the form of a gel, are well known and still used in analytical separations. The elution sequences of four Co(III) complexes on a wide range of papers loaded with inorganic exchangers, hydrated oxides (*15*), were examined. Hydrous silica, both amorphous and gel, has been used in metal ion separations.

Hydrous stannic oxide (*15*, *20*, *21*, *168–172*), both the gel and crystalline forms, is a good cation as well as an anion exchanger above or below pH $\sim$ 4.8 to 6.3. It is amphoteric in nature. It has a great affinity for phosphate (*20*, *172*). It adsorbs Se and Te from HNO_3 (*21*). Recently a crystalline form of hydrous stannic oxide has been prepared in our laboratory (*172*) from sodium stannate solution with ammonium sulfate solution. It is α-stannic acid with greater chemical stability and selectivity

for phosphate. Paper chromatography, paper electrochromatography, and column chromatography have been performed for the separation of metal anionic species. The quantitative separation of Cr (VI), As(III), and V(V) from phosphate; V(V) and As(V) from Cr(VI); As(III) from As(V); etc. has been achieved.

Very few analytical applications (*15*, *22*, *23*) have been reported with zirconium dioxide (*173*, *174*).

Among the hydrous oxides, antimonic acid, both crystalline and amorphous, has found several uses (*15*, *24–39*). In a review article Fuller (*9*) reported some fundamental data on antimonic acid. It has a greater selectivity for sodium and hence is used in activation analysis to remove ^{24}Na activity (*25–28*). It is also selective for Sr (*29*, *39*), Ta (*30*), and Tl (*38*). The separation of ^{90}Sr (*39*) from a fission products waste solution in HNO_3 can be achieved with it.

Hydrated cerium dioxide (*175*) is used for the sorption of amines of Co(III), Ni(II), Cu(II), Zn(II), and Cd(II). It has been synthesized under different conditions (*176*, *177*), and some selective separations of Mg, Zn, Co(II), and Mn(II) from Cu(II) have been achieved. Cu is adsorbed.

Antimony phosphoric oxide adsorbs Na from HCl solution (*178*), leaving K in the aqueous phase. Hydrous tungsten (VI) oxide (*228*) has been prepared under different conditions in our laboratory. The physicochemical properties have been studied and both cation-exchange and anion-exchange behavior observed. The separation of Zn, Cu(II), Ca, Sr, Mn(II), and Ni from Mg, and of Ni and Mn(II) from Co(II) has been achieved.

ACIDIC SALTS OF POLYVALENT METALS

Stannic phosphate (*40–43*, *179*, *180*) has been prepared in crystalline form. It has been used for the selective separation of Zr (*42*) and for paper chromatographic studies (*41*).

Stannic arsenate (*40*, *44–50*) in crystalline form has been used in column chromatography for the separation of alkali and alkaline earth metals. Lanthanides have a strong affinity toward it, and hence can be separated from each other. Pb and Al are strongly adsorbed (*45*, *46*) from HNO_3 solution. TLC (*49*) and paper chromatographic studies (*47*, *48*) have been reported for the separation of several metal ions. The K_{sp} values have been predicted from R_F values of the metal ions.

Papers impregnated with stannic molybdate have been used in electrochromatography (*52*) and paper chromatography (*47*, *53*). Numerous

metal ions have been separated from one another. Specific separation of Ga(III)–Au(III)–Mn(II) and Be–Al–Ga(III) have been reported in paper chromatography. Stannic molybdate gives good separation of Fe(III) from Al and Mn(II).

Stannic antimonate (*54–56*), stannic selenite (*57, 58*), and stannic ferrocyanide (*59, 60*) have been synthesized. A number of binary metal ion separations have been achieved. Lanthanides are separated on stannic selenite (*58*).

Stannous ferrocyanide (*61, 62*) is more stable than stannic ferrocyanide; the cation exchange capacity is 2.03 mequiv/1 g (dry weight). The probable formula is $[SnO \cdot H_4Fe(CN)_6 \cdot 2.5H_2O]_n$ as supported by thermogram, IR, and x-ray analysis. Five binary separations of metal ions by column and eight binary separations by impregnated paper chromatography have been achieved.

Ceric phosphate (*65–72*) has been prepared in crystalline form and is selective for Na. Cerium(IV) phosphosulfate (*70, 71*) is a new exchanger which is selective for Ag(I). TLC with ceric phosphosulfate gave R_F values of Ag(I), Na, Ca, Hg(II), Cd, Co(II), Ni, Cr(III), Fe(III), and Th with 0.2 *N* HCl or 0.2 *N* $HClO_4$ as the developing solvent.

Cerium(IV) arsenate (*72*), synthesized in crystalline form, is selective for alkali metals from HCl solution. Cerium(IV) antimonate (*73, 74*) and cerium(IV) molybdate (*75*), prepared in amorphous form, are new exchangers. Ceric antimonate is selective for Hg(II) whereas Pb is selectively separated by ceric molybdate.

Among the titanium-based exchangers, titanium phosphate (*39, 76–78, 181–183*), titanium arsenate (*51, 79–82, 183*), titanium antimonate (*81, 83–85*), titanium molybdate (*39, 86, 87, 184*), and titanium tungstate (*81, 86, 88–94*) continue to be used. Titanium phosphate (*39*) is used in crystalline form for fission product separation. Zr and Nb (*76*) are strongly adsorbed in it. When amorphous titanium phosphate is refluxed in H_3PO_4, it is converted into a crystalline $Ti(HPO_4)_2 \cdot H_2O$ (α-TiP), isomorphous with crystalline α-ZrP. Titanium arsenate (*82*) papers and columns are used for chromatographic separation of a number of alkaloids in aqueous and mixed solvent systems. Distribution coefficients of the alkaloids have been measured. The quantitative separation of codeine, atropine, strychnine, quinine, and cinchonine from nicotine has been achieved. It is a novel technique for alkaloid separation and a new approach for the separation of organic substances with the help of an inorganic cation-exchanger. It needs further systematic studies to elucidate the exchange reactions.

Titanium antimonate is selective for V(V) and Mg (*83*).

Titanium molybdate-impregnated paper (*87*) is used for the separation of metal ions in an aqueous HNO_3 medium.

Titanium tungstate is a good exchanger and useful for many binary quantitative separations in a HNO_3 medium. Stannous ion is separated from stannic ion in an acetate medium by impregnated titanium tungstate (*93*) paper. Sn(IV) ions move faster.

Titanium vanadate (*95*) and titanium selenite (*81, 92, 96*) have been newly synthesized in an amorphous form. Titanium vanadate is selective for Sr, and titanium selenite is selective for Cd.

Zirconium phosphate (*36, 97–108, 184–202*) is a well-used and well-studied inorganic exchanger. It is prepared in different hydrated crystalline forms (*196*). The relative amounts of the hydrated phases in the mixture are largely dependent on the method of preparation. Under appropriate experimental conditions, 100% of a phase having an interlayer distance of 10.4 Å in $Zr(HPO_4)_2 \cdot 8H_2O$ (called *v*-ZP) has been obtained. Zirconium phosphate has a special affinity toward alkali metals and is used for the separations of alkali metals from each other (*102*), from alkaline earths and other metal ions, and in biosamples (*36*).

Zirconium arsenate is used as an adsorbent for gas chromatography in the quantitative separation of aliphatic amines (*108*). Zirconium antimonate (*111, 112*) is selective for alkali metals. Its selectivity scale is $Na \geqslant K > NH_4 > Rb > Cs > Li$. The crystal structure of basic zirconium molybdate (*113*) has been studied. The separation factor of Zn and Cd is large with zirconium tungstate (*203, 204*). Zirconium tellurate (*205, 206*), a new exchanger, has been prepared.

Zirconium ferrocyanide (*59, 114*), an amorphous exchanger, has been prepared and its ion-exchange properties have been studied. A few separations have been reported. It is selective for Cs (*115*). It can withstand a γ-radiation dose of 10^9 rads.

Thorium phosphate (*116*) in the form of fibrous sheet has been reported. It has also been prepared in a crystalline form (*117–119*). It is selective for Pb and Bi, and these two metal ions have been separated from others. Paper and electrochromatographic techniques have been used for the separation of several metal ions.

Thorium arsenate (*120, 121*), thorium antimonate (*176, 207*), thorium molybdate (*122*), and thorium tungstate (*123, 124*) have been prepared and used for metal ions separation. Thorium arsenate crystal is selective for Li. Thorium antimonate is used for the separation of Cu(II) from Mg, Ni, Co(II), and Mn(II); and of Mg from Zn and Cd. Selective ion-

exchange separations of Bi and Hg from other metal ions have been achieved on a column of thorium tungstate.

Exchangers based on chromium(III) have been studied including phosphate (*125–132*), arsenate (*133*), antimonate (*133, 134*), molybdate (*133*), tungstate (*133*), and ferrocyanide (*135*). Chromium polyphosphate glasses, a linear polymer, absorb sodium strongly (*126, 130*). Chromium phosphate exchangers have a strong affinity toward alkali metals. Other chromium(III)-based exchangers are useful for selective binary separations.

Ferric phosphate is selective for Pb, Eu(III), and Ga(III) (*136*). Ferric arsenate (*137*) is selective for Li, Na, and K. Ferric antimonate is effective for a few rare earth separations (*138*). It is very stable both thermally and chemically. The distribution coefficients of 27 metal ions have been determined.

Niobium phosphate (*208*) and arsenate (*139*) have been synthesized. TGA and x-ray studies are reported and compared with Nb_2O_5. The separations of Mg from Al and Mn(II), Ge(III) from Al, and Hg(II) from Cd have been achieved. A plot of $pK_{sp} \cdot r^\circ$ vs K_d is a straight line.

Tantalum phosphate (*209*), tantalum arsenate, (*140, 210*) and tantalum antimonate (*141*) have been reported as new exchangers. Tantalum arsenate is selective for Ba, K, and Na whereas tantalum antimonate is selective for the VO_2^+ ion.

Ferrocyanides of copper (*211*), zinc (*142, 143*), cobalt (*144, 145*), and nickel (*146, 147*) are useful for Cs metal separation. Cobalt and zinc ferrocyanides strongly adsorb the Ag(I) ion. Nickel ferrocyanide is used for the binary separation of other metal ions in HCl solution. Mo is separated from Tc in acetic acid solution. These separations were used for activation analysis of various metals, e.g., determination of nickel in iron and chromium. Bismuth tellurate (*212*) and lead strontium-phosphate (*213*) are reported as exchangers.

HETEROPOLYACID SALTS

Ammonium phosphomolybdate (*148–157*) continues to be used as an exchanger. It is selective for Cs and can be used for the isolation of Cs from seawater. The separation of actinides (*148, 149*) was reported. Np has been separated from Th, U, and Pu,

Stannic tungstoarsenate (*158*), a new exchanger, has been prepared with the composition Sn:W:As = 12:5:2. A comparison of the ion-exchange properties of tin(IV) tungstoarsenate with those of tin(IV) tungstate and

tin(IV)-arsenate has been made. It has greater thermal and chemical stability and a high K_d values after heating at 500°C. Quantitative separation of Cu(II) from others has been achieved.

Zirconium phosphosilicate is a good exchanger for the separation of radioisotopes (*159–162*). Pu (*159*) in the fission product is reduced to Pu(III) by ascorbic acid during elution and passes out, while others remain adsorbed in the column. Bk is separated from Pu and other metals in HNO_3 solution (*161*). In the separation of Np(IV) from Pu(III) and Am(III), Np(IV) is adsorbed and then eluted with 8 *M* HNO_3 (*162*).

ZEOLITE-TYPE EXCHANGERS

These types of exchangers have been well known for many years. Now a few applications have been reported. Noteworthy separations are thiamine (*164*) from other organic compounds, Cs (*163*) from Na and K in nonaqueous medium, and Hg from organic mercury compounds (*165–167*).

The work on hydrated metal oxides, acidic salts of polyvalent metals, heteropoly acid salts and zeolite-type exchangers with reference to the nature, composition, selectivity, and separation of metal ions are summarized in Table 1.

EQUILIBRIUM AND KINETICS

In order to understand the theoretical aspects of exchange processes, thermodynamic equilibrium and kinetic studies are essential. Such studies are usually made with crystalline inorganic exchangers (*214, 215*). The synthetic zeolites have known structures with different types of cavities. Some cavities allow small counterions but not large ones, which are sieved.

Equilibrium in different synthetic inorganic exchangers, including zeolites, has been examined in aqueous (*204–222*) and mixed solvents (*106, 203, 223*). Ion exchange in fused nitrate salts with zirconium phosphate (*200*) and zeolites (*224*) is a reversible process. Kinetic studies with an exchange of isotopes reveal that two kinds of exchange sites are present in zeolites (*225, 226*). The exchange of cations on exchangers in the H^+ form, as well as in the Na^+ or NH_4^+ forms, was studied by several workers. The slow step which determines the rate of exchange of these hydrated ions is diffusion through the particles (*210, 227*). The diffusion

TABLE 1

Summary of Work Done on Synthetic Inorganic Ion Exchangers

Exchanger	Nature/ composition	Separations/ selectivity sequence	Remarks	References
		Hydrous Oxides of Metals		
Aluminum oxide	Crystalline; amphoteric	SO_2 separated from SO_4^{2-} and $S_2O_3^{2-}$		*14, 15*
Hydrous silicate	Gel, amorphous, cation exchanger	Zn and Pd separated from various cations	Eluting agent, HCl	*16–19*
		Th separated from U	Eluent, NTA. Elution order, Th–U	
		Ni separated from Cu	Eluent, CH_2Cl_2–CH_3CN. Elution order Ni–Cu	
		Separation: Na–Rb–Cs–Fr		
Stannic oxide	Dried gel, crystalline, amphoteric	Selectivity: $PO_4^{3-} > C_2O_4^{2-} > SO_4^{2-} > Cr_2^{2-}O_7 > MnO_4^-$; $Cl^- > Br^- > I^-$	Eluent, HNO_3	*15, 20, 21*
		Separations: Se–Te and Tc–Mo	Eluent, HNO_3	
Zirconium dioxide		Separations: Cu–Ni, In^{113m}–Sn^{113}	At high temperature Cu adsorbed	*15, 22, 23*
Antimonic acid	Crystalline, amorphous	Separations: alkali metals, each other	Eluent, HNO_3–NH_4NO_3. Li eluted first	*12, 24–39*
		Na–K, Na-other elements	Eluting agent, HCl, etc. applied to activation analysis, Na adsorbed	
		Sr-water	Sr adsorbed	
		Ta-others	Ta adsorbed; HNO_3 as eluent	

		F^--others	F^- adsorbed; HCl as eluent	
		Na-acids, Na–Zn, Na–Se	Na adsorbed	
		Selectivity: Na > Rb > Cs > K > Li at low pH		
		Separations: Na-biosamples, Re–Mo, Re–W, Tl-others, and ^{90}Sr-fission products	Na adsorbed. Eluent, HNO_3 + acetone, Mo and W adsorbed. Eluent, HNO_3	
		Acidic Salts of Polyvalent Metals		
Stannic phosphate	Crystalline, P/Sn = 1.25–1.50	Separations: alkali metals and each other	—	*40–44*
		Zr-other metals	Paper chromatography	
Stannic arsenate	Crystalline, amorphous, Sn/As = 1.8	Separations: Cu–Pb, Cu–Fe(III), Fe(II)–Pb, Fe(II)–Cu, Fe(II)–Fe(III), Sr–Ba, Mg–Ba, Ca–Ba, Co(II)–Fe(III), Al–Fe(III), Mn–Fe(III), Ca–Fe(III), Ni–Fe(III), Al–In, and Mg–Al	Eluent, HNO_3 and NH_4NO_3. TLC mixed with silica gel. Paper chromatography. K_{sp} value predicted from R_F value	*45–51*
Stannic molybdate	Amorphous, Sn/Mo = 1:1	Separations: Sm–Tm, Eu(III)–Dy(III), Fe(II)–Cu, Fe(II)–UO_2(II), Hg(II)–Ag(I)–V(IV), Cs–Rb, Ba–Sr, Co–Ni, Mo(VI)–W(VI), Ti(IV)–V(IV), and Th(IV)–Tm(III)–Lu(III)	Electrochromatography. Background electrolyte $NaNO_3$ solution, HNO_3	*52*

(*continued*)

TABLE 1 (continued)

Exchanger	Nature/ composition	Separations/ selectivity sequence	Remarks	References
		In–Al, Ti–Zr, Hf–Ti, Dy–Lu–Gd, and Th–Y–Gd	Paper chromatography	*47*
		Fe(III)–Al, Mn(II)–Fe(III). Specific separation of Ga, Au(III), and Mn(II), Be–Al–Ga		*53*
Stannic antimonate	—	Rare earths, actinides, and alkaline earth metals	Paper chromatography, mobile phase, 0.1–4 *M* HNO_3 or 0.1 *M* HNO_3–1 *M* NH_4NO_3, DMSO	*54–56*
Stannic selenite	Amorphous, Sn/Se = 1.33	Separations: Fe–Pb, Se–V, Fe–Cu, Cu–Ni, Cu–In, lanthanides, and each other	—	*57, 58*
Stannic ferrocyanide		Selectivity: Li > K > Na > NH_4^+, Ba > Ca > Mg	Effect of γ-radiation examined	*59, 60*
		Separations: Zr–Th, UO_2(II)–Th, and Ba–La	Th and La adsorbed. Eluting agent, 0.5 *M* NH_4Cl + 0.1 *M* HCl	
Stannous ferrocyanide	Sn/Fe = 1:1	Separations: Mg–Ba, Mg–Ca, Mn–Co, and Mn–Ni. 36 metals studied. Y–Th	Paper chromatography	*61, 62*
Cerium phosphate	Amorphous, P/Ce = 1.03–1.93. Microcrystalline, P/Ce = 1.5	Separations: Na–Li, Na–K, and Na–Cs. Cs > Rb > K > Na > Li. Cs > Na > Ag	Na adsorbed at pH 4	*63–72*

	Fibrous crystalline, crystalline, Ce:P:S = 2:1:2	Separations: Li–Na–K, Ni–Ag–Tl, and Co–Eu–Fe	TLC. Eluting agent 0.2 *N* HCl or 0.2 *N* $HClO_4$	
	Molar ratio Ce:P:S = 2:2.5:0.5	Separation: ^{110m}Ag–^{22}Na	Ag strongly adsorbed. Na eluted with 0.01 *N* HCl or 1 *N* $HClO_4$	
Cerium arsenate	Crystalline, As/Ce = 2.0	Separations: Alkali metals and each others	Eluting agent, HCl. Elution order, Na–K–Rb–Cs	*72*
Cerium antimonate	Amorphous, Sb/Ce = 0.30–0.32	Separations: Hg–Cd, Hg–Zn, Hg–Tl, Hg–Pb, Th–Zr, Al–Fe, and Mn–Cu	Hg adsorbed. Various eluting agents used	*73*, 74
Cerium molybdate	Amorphous, Mo/Ce = 2.33–8.29	Separation of Mg, Zn, Co, and Cu from Pb. Selective separation	Pb adsorbed strongly	*75*
Titanium phosphate	Crystalline P/Ti = 0.6–2.0	Separations: Zr and Nb from others. ^{137}Cs and ^{90}Sr from fission products	Eluting agent, HNO_3. Zr and Nb adsorbed.	*39*, *76–78*
Titanium arsenate	Crystalline	Separations: Pb from bivalent metal ions. Ba–Mg, Ba-Ca, and Ba–Sr	Paper chromatography of 48 cations in HNO_3	*51*, *79–82*
		Quantitative separation of codeine, atropine, strychnine, quinine, and cinchonine from nicotine	Paper and column chromatography, in mixed solvent system	
Titanium antimonate	Semicrystalline and amorphous, Sb/Ti = 1–3.6	Separations: VO(II) from Fe(III), Al, Mn(II), UO_2(II), Sr, and Hf. Mg–Sr, Mg–Ca, Mg–Al, Mn(II)–Al, Al–Cr(III),	When compared, selectivity depends on exchanger	*81*, *83–85*

(*continued*)

TABLE 1 (continued)

Exchanger	Nature/ composition	Separations/ selectivity sequence	Remarks	References
		Al–Fe(III), Co–Ni, Co–Mn(II), UO_2(II)–Th(IV), Zn–Hg(II), and Zn–Cd		
Titanium molybdate	Amorphous, Mo/Ti = 0.5–2.0	Na–Rb, K–Cs, Na–Cs, and Ba–Ca	Paper chromatography	*39, 86, 87*
Titanium tungstate	Amorphous, Ti:W = 3:4	Ca from Sr, Mg, Ba, and Zr–Hf.	Eluting agent, formic acid	*81, 86*
		Na–Rb, K–Cs, and Na–Cs	Eluting agent, HNO_3	
		Ga from Fe, Al, and In	Elution order, Al–In–Fe–Ga	
		Be–Al	Paper chromatography in nonaqueous solvent	*88–94*
		Sn(II)–Sn(IV)	Paper chromatography in acetate medium. Sn(IV) moves faster.	
Titanium vanadate	Amorphous, V/Ti = 4.0	Selective for Sr. Separations: Sr–Mg, Sr–Ca, and Sr–Ba	Sr adsorbed. Eluent, HNO_3	*95*
Titanium selenite	Amorphous, Ti/Se = 1.39	Selective for Cd. Separations: Cd–Zn, Cd–Ca, and Cd–Al	Eluent, NH_4Cl	*81, 92, 96*
Zirconium phosphate	Crystalline	Separations: Cs and Na from others	Eluent, HCl. Cs adsorbed. Exchangers compared	*36*
		Separations: Ca, Sr, Ba, and each other	Eluent, HCl and CDTA. Sr eluted first in HCl	*97–108*
		Separations: Am(V)–Cm(III)	Eluent, HNO_3. Elution order, Am(V)–Cm(III) Eluent, NaOAc	

		Separations: alkali metals from each other, from Ca, Sr, Ba, and bio samples. Sb–U and Sb–Sn	Eluent, NH_4Cl Eluent, HCl. Sb(III) and Sb(V) adsorption studied in HCl-alcohol medium	
	$ZrNaH(PO_4)_2 \cdot 5H_2O$, crystalline	Selectivity: K > Cs > Na > Li		
		Mercaptans and chlorocarbons are well separated in gas chromatography	—	
Zirconium arsenate	Crystalline	Aliphatic amines quantitatively separated by gas chromatography. Ba strongly adsorbed	Partition coefficients of Zn, Cd, Ba, Sr, and Ca measured	*108–110*
Zirconium antimonate	Crystalline and amorphous	Selectivity: Na > K > NH_4^+ > Rb > Cs > Li	—	*111, 112*
Zirconium molybdate	Amorphous	—	—	*113*
Zirconium ferrocyanide	Amorphous	Separation of Zn from Cd, Mn(II), and Co(II); UO_2(II) from Th(IV) and Zr(IV); Ca–Ba Cs from seawater	—	*114, 115*
Thorium phosphate	Crystalline, $PO_4/Th = 1.6–2.1$	Separations: Cu, Mg, Mn, Zn, Cd, Co, Hg, and Ca from Pb. Zn, Cu, Co, Cd, Hg, and Ni from Bi	Pb and Bi selectively adsorbed Paper chromatography and electrochromatography, performed	*116–119*
Thorium arsenate	Amorphous and crystalline, As/Th = 1.53–1.96	Selective for Li. Separation: Li–Na	Li adsorbed	*120, 121*

(*continued*)

TABLE 1 (continued)

Exchanger	Nature/ composition	Separations/ selectivity sequence	Remarks	References
Thorium molybdate	Amorphous	Separation: Co(II), Zn, and Cu from Fe(III)	—	*122*
Thorium tungstate	Amorphous and crystalline, W/Th = 2.0–6.4	Separations: La from Ba, Sr, Ca, and Y; VO_2(I) from Fe(III) and Mn; Cu, Zn, Cd, Mg, Ca, Mn, Ni, and Pb from Bi	—	*123, 124*
Chromium phosphate	Amorphous, P/Cr = 0.6–1.0	Separations: K–Cs, Rb–Cs, Rb–Sr, Mn–Fe(III), Co–Fe(III), Te–Mo, Sn–In	—	*125–128*
		Alkali metals from di- and trivalent metal ions	Li–Cs adsorbed	
Chromium poly phosphate	Glass solid, Cr/P = 1.2–0.48	Na–K–Rb–Cs, Rb–Sr	Na strongly adsorbed. Eluent, HCl	*129–132*
Chromium arsenate	Amorphous, As/Cr = 1.98	Separations: Zr–Hf	—	*133*
Chromium antimonate	Amorphous, Sb/Cr = 2.95	Separations: Pb–Co	K_d values of 27 metals determined	*133, 134*
Chromium molybdate	Amorphous, Mo/Cr = 1.90	Separations: Pb–Ga	—	*133*
Chromium tungstate	Amorphous, W/Cr = 1.92	Separation: Th–Hf	—	*133*
Chromium ferrocyanide	Amorphous, Cr/Fe = 0.327	—	Exchange capacity = 3.65 mequiv/g	*135*
Ferric phosphate	Amorphous, P/Fe = 2.0	Selective for Pb, Eu, and Ga	—	*136*
Ferric arsenate	Amorphous	Selective for K, Na, and Li	—	*137*

Ferric antimonate	Amorphous Sb/Fe = 2.4	Separation: Mg–Sr, Al–Ga, Y–La, Mg–Cd–Zn, and Th–Sm	Excellent thermal and chemical stability. Distribution coefficients of 27 metal ions determined	*138*
Aluminum phosphate	Amorphous, Al/P = 0.5–0.66	—	—	*136*
Niobium arsenate	Amorphous, Nb/As = 1.96	Separation: Mg from Al and Mn; Ga from Al; Hg from Cd	—	*139*
Tantalum arsenate	Amorphous, Ta/As = 1.30	Selective for Ba, K, and Na	—	*140*
Tantalum antimonate	Amorphous, Ta/Sb = 1.30	Separation: VO_2(I)–Al–Ti, VO_2(I)–Fe(III)–Ti, and UO_2(II)–Ti	—	*141*
Zinc ferrocyanide	—	Cs from soil Ag from others	Cs adsorbed Ag adsorbed	*142, 143*
Cobalt ferrocyanide	—	Selective for Ag(I)	—	*144, 145*
Nickel ferrocyanide	—	Separation: Cs-alkali earth metals, As–Sb, Mn–Ni, and Mo–Tc	Eluent, HCl and HOAc. Distribution coefficients measured	*146, 147*
		Heteropoly Acid Salts		
Ammonium phosphomolybdate		Separations: Y–Th	Y eluted with 1 *M* NH_4NO_3	*148–157*
		Th–U–NP; NP from U, Th, and Pu	Th eluted with 4 *M* HNO_3	
		Rb, Cs from K, Ag, and Tl	Eluent, HNO_3	
		Cs from seawater	^{133}Cs adsorbed	

(*continued*)

TABLE 1 (continued)

Exchanger	Nature/ composition	Separations/ selectivity sequence	Remarks	References
Stannic tungstoarsenate	Sn: W: As = 12: 5: 2	Separation: Cu(II)–Ni(II), Cu(II)–Mg, and Ba–Mg;	—	*158*
Zirconium phosphosilicate		Separation: Pu from Zr, Nb	Eluent, HNO_3; ascorbic acid reduces to Pu(III) which passes out	*159–162*
		Fission products	Eluent, various	
		Bk from Pu, Cs, and Ce	Eluent, HNO_3	
		Np(IV) from Pu(III) and Am(III)	Np(IV) adsorbed, Pu and Am pass through. Np eluted with 8 *M* HNO_3	
		Zeolite-Type Exchangers		
Zeolite	Na–A–Zeolite, K–A–Zeolite	Separation: Cs from Na and K	Nonaqueous medium, Cs adsorbed	*163–166*
	Zeolite S/F	Thiamine from others		
	Corasil I	Hg from organic mercury compounds	Eluent, $HClO_4$	
Zeolite A	SiO_2/Al_2O_3 = 1.8			
Zeolite X	SiO_2/Al_2O_3 = 2.7	Selectivity Cu > Zn;	—	
Zeolite Y	SiO_2/Al_2O_3 = 4.7	Na > Ni, Co		
Soda-calcium glass	—	Hg(II) separated from organomercurial compounds	Hg(II) selectively adsorbed. Eluent, phosphate buffer (pH 7.1)	

coefficients, energies of activation, and entropies of activation have been calculated for a few cations with tantalum arsenate.

The exchange of cations with crystalline zirconium phosphate is well studied (*185–202*). Zirconium phosphate is a biprotic acid. Two distinct inflections are observed in the titration curve, and complex structural changes accompany ion exchange. The equilibrium curves for K–H (*218*) and K–Na (*217, 219*) exchanges show two kinds of exchange sites in crystalline zirconium phosphate. The effect of temperature in ion-exchange equilibria has been studied with zirconium phosphate (*186, 194, 195, 220, 221*), zirconium oxide (*174*), and tin dioxide (*170*). A selectivity reversal of the sulfate and chloride anion pair between 25 and 80°C has been observed. Sulfate is preferred at higher temperatures whereas chloride is preferred at lower temperatures.

The exchange reaction rate of alkaline earth metals with crystalline zirconium phosphate is catalyzed by partly loading with Na^+ ion (*197*). Ba(II) ions are more rapidly taken up than Ca and Ba by the exchanger in a single transition step until the fully converted Ba-form is obtained. The conversion of $Zr(HPO_4)_2 \cdot H_2O$ into $ZrHNa(PO_4)_2 \cdot 5H_2O$ followed by regeneration with dilute hydrochloric acid yields a mixture of zirconium phosphate materials with various degrees of hydration and different interlayer distances (*196*). Interlayer distances also increase discontinuously with alkali metal loading (*199*). The relative amounts of hydrated phases in the mixture are strongly dependent on the method of preparation of $Zr(HPO_4)_2 \cdot H_2O$. The ion-exchange properties of $Zr(HPO_4)_2 \cdot 8H_2O$ (ν-ZP) (interlayer distance, 10.4 Å) for alkali, alkaline earth, and some divalent transition metal ions have been investigated in detail, and a comparison with ion-exchange properties of $Zr(HPO_4)_2 \cdot H_2O$ has been made. ν-ZP and other highly hydrated dihydrogen phases, because of their large interlayer distances, can exchange with several cations, whereas the monohydrated dihydrogen form cannot (or only slowly) exchange due to steric hindrance. Crystalline ceric phosphate (*66*) has a small pore zeolitic-type structure.

The mechanism of the ion-exchange process and the nature of the functional groups of amorphous stannic phosphate (*43*) have been studied by IR and Mössbauer spectroscopy. The phosphate group participates in ion-exchange processes only at pH 6 to 7, and the stannate group participates in acidic media.

The sorption of ammine complexes of Co(III), Ni, Cu(II), Zn, and Cd on hydrated metal oxides (*168, 169, 175*) has been studied at different pH values and ionic concentrations of the external solutions. The rate of exchange follows the order $ZrO_2 > SnO_2 > SiO_2$.

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