Synthesis and characterization of a new inorganic cation-exchanger—Zr(IV) tungstomolybdate: Analytical applications for metal content determination in real sample and synthetic mixture

Syed Ashfaq Nabi[*], Mu. Naushad, Inamuddin

Analytical Research Laboratory, Department of Chemistry, Faculty of Science, Aligarh Muslim University, Aligarh 202002, India

Abstract

An amorphous sample of inorganic cation-exchanger Zr(IV) tungstomolybdate was prepared by mixing varying ratios of 0.1 M aqueous solution of sodium tungstate and 0.1 M aqueous solution of sodium molybdate into 0.1 M aqueous solution of zirconium oxychloride at pH 1. This cation-exchanger was found to have a good ion-exchange capacity (2.40 mequiv. g^{-1} for Na^+), high thermal and chemical stability. A tentative structural formula was proposed on the basis of chemical composition, FTIR and thermogravimetric analysis. Distribution coefficients (K_d) values of metal ions in various solvent systems were determined. Some important and analytically difficult quantitative binary separations viz. Ni(II)–Pb(II), Ni(II)–Zn(II), Ni(II)–Cd(II), Mg(II)–Al(III), etc. were achieved. The practical applicability of the cation-exchanger was demonstrated in the separation of Cu(II)–Zn(II) from a synthetic mixture as well as from real samples of pharmaceutical formulation and brass alloy.
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Keywords: A new inorganic cation-exchanger; Zr(IV) tungstomolybdate; Column separations of metal ions; Thermal stability

1. Introduction

A good deal of interest has grown in the last decades in synthetic inorganic ion-exchangers [1] because of their greater resistance to high radiation and high temperature, which is of great importance in the nuclear technology [2–4]. Inorganic ion-exchangers have been widely used for the removal of heavy toxic metals from wastewater which are generated as untreated or partially treated by-product of various industries into public sewages, rivers, sea and on land which creates water pollution. The water pollution also arises due to the increasing use of copper, iron, zinc, lead and chromium in many industries. The heavy metals when present in water are injurious to the health. Hence, it is very important to treat such water to remove the metal ions before it is supplied for any useful purpose. When we need to remove a particular ion in the presence of other, we need a material specific for that particular metal ion. Thus, by synthesizing new inorganic cation-exchangers, having affinity and selectivity for a particular metal ion, one can separate the undesired metal from effluents.

Inorganic ion-exchangers also have applications in the development of ion selective electrodes [5–7], extraction of uranium from seawater [8], construction of ion-exchange membranes and their applications to electro-dialysis for metal ion separations. Two component ion exchangers of acidic salts of multivalent metals prepared in combination with phosphate, tungstate, arsenate, tellurate, selenite and molybdate anions were studied most intensively [9,10]. Three component inorganic ion-exchangers were found to show relatively increased ion-exchange capacity and selectivity [11–15]. Among the various inorganic ion-exchange materials of current importance, soluble acidic salts of tetravalent metals (Zr, Ti, Sn) occupied a pivotal position, so the synthesis of a new inorganic ion-exchanger Zr(IV) tungstomolybdate is worthwhile. The present paper describes the synthesis, characterization and ion-exchange behavior of a high thermally and chemically stable new inorganic cation-exchanger Zr(IV) tungstomolybdate. The material was used successfully for quantitative column separations of some binary mixtures of metal ions. Cu^{2+} and Zn^{2+} are also separated

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* Corresponding author. Tel.: +91 571 2404014.
  E-mail addresses: shad81@rediffmail.com,
sanabi@rediffmail.com (S.A. Nabi).

Table 1
Conditions of synthesis of different samples of Zr(IV) tungstomolybdate

Sample no.	Mixing volume ratios of reagents (v/v)			Total volume (mL)	pH	Condition	Appearance of beads in H$^+$ form after drying at $40 \pm 2\,^\circ$C	Yield (g)	IEC for Na$^+$ ion (mequiv. dry g^{-1}) exchanger
	ZrOCl$_2$·8H$_2$O (0.1 M)	Na$_2$MoO$_4$·2H$_2$O (0.1 M)	Na$_2$WO$_4$·2H$_2$O (0.1 M)						
S-1	2	1	1	200	1.0	Room temperature	White	2.87	1.10
S-2	4	1	1	300	1.0	Room temperature	Not precipitated	–	–
S-3	1	1	1	300	1.5	Room temperature	Yellowish	3.32	1.02
S-4	1	1	1	300	0.6	Room temperature	White	1.80	0.84
S-5	1	1	1	300	1.0	Room temperature	Yellowish	3.50	2.00
S-6	1	1	1	300	1.0	Refluxed for 6 h	Yellowish	3.80	2.40

and determined from a pharmaceutical sample and brass alloy sample by using packed column of this cation-exchanger.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were zirconium oxychloride (Loba Chemie, India), sodium molybdate and sodium tungstate (BDH, India) and all other chemicals and reagents used were of analytical reagent grade. A UV–vis spectrophotometer (Elico EI 301E, India), FTIR spectrophotometer (Perkin-Elmer spectrum BX, USA), an automatic thermal analyzer (V2.2A Du Pont 9900), a PW 1148/89 based X-ray diffractometer (Phillips, Holland), a water bath incubator shaker (MSW-275, India), muffle furnace (GI-111, India), brass alloy sample, antioxidant I-Vit (Elder, Bombay, India) were also used.

2.2. Preparation of reagents

Solution of 0.1 M Zr(IV) oxychloride was prepared in 0.01 M HCl, while the solutions of 0.1 M sodium tungstate and 0.1 M sodium molybdate were prepared in demineralized water (DMW).

2.3. Preparation of ion-exchange materials

In order to get a stable product with good ion-exchange properties, a number of samples of Zr(IV) tungstomolybdate were synthesized by adding a mixture of 0.1 M sodiumtungstate and 0.1 M sodium molybdate into 0.1 M Zr(IV) oxychloride solution gradually with continuous shaking of the mixture. The pH variation was adjusted by 1 M nitric acid or 1 M ammonia solutions to maintain the desired pH 1. The gelatinous precipitate so formed, was allowed to stand for 24 h in the mother liquor for digestion. It was divided into two parts. From the first part, the supernatant liquid was removed and the precipitate was washed with demineralized water several times, filtered by suction. The product was completely dried at $40 \pm 2\,^\circ$C in an oven. The dried product was then cracked into small granules by putting in demineralized water, dried and sieved to obtain particles of size 50–100 μm. The granules were converted into H$^+$ form by placing in 1 M HNO$_3$ for 24 h. It was experimentally determined that the equi-

librium was established in 6 h. During ion-exchange capacity determination experiments, it was found that H$^+$ adsorption and H$^+$ liberation capacities were equal. The material was finally washed with demineralized water to remove the excess acid and dried at $40 \pm 2\,^\circ$C. The second portion of the aliquot containing the precipitate was refluxed for 6 h and kept for 24 h at room temperature. Finally the material was cracked into small granules, sieved and converted into H$^+$ form by the procedure described above.

A number of samples of Zr(IV) tungstomolybdate were prepared under varying conditions. On the basis of ion-exchange capacity and yield sample S-6 was selected for detailed studies (Table 1).

2.4. Ion-exchange capacity

To determine the ion-exchange capacity, which generally taken as a measure of the hydrogen ion liberation by neutral salt, column process was used. 0.5 g dry cation-exchanger (sample S-6) in H$^+$ form was packed in column (35 cm in length, 0.9 cm i.d.) fitted with glass wool at the bottom. 1.0 M alkali and alkaline earth metal nitrates as eluent were used to elute the H$^+$ completely from the cation-exchanger column maintaining a flow rate of 0.5 mL min^{-1} till the effluent showed the absence of H$^+$ ions. The effluent was titrated against a standard solution of 0.1 M NaOH using phenolphthalein as indicator.

2.5. Thermal effect on ion-exchange capacity

To determine the effect of heating temperature on ion-exchange capacity, 1 g sample of the cation-exchange material (S-6) in H$^+$ form was heated at different temperatures in a muffle furnace for 1 h and Na$^+$ ion-exchange capacity was determined after cooling them at room temperature by standard column process as described above.

2.6. Chemical dissolution

To determine the extent of dissolution of the material in common mineral acids, bases and organic acids, a 0.5 g of exchange material was equilibrated with 50 mL of the solution of interest for 24 h at room temperature. Zirconium, molybdenum and tungsten released in the solution

were determined spectrophotometrically using alizarin red-s, phenyl hydrazine and hydroquinone [16] as coloring reagents, respectively.

2.7. Characterization

2.7.1. Chemical composition

To determine the chemical composition, 0.5 g of the exchanger was fused with a mixture of sodium nitrate and sodium carbonate (1:1). The fused mass was digested in demineralized water and made up upto 100 mL. Zirconium, molybdenum and tungsten contents of the solution were determined spectrophotometrically.

2.7.2. FTIR studies

For FTIR analysis, 10 mg (dry mass) of the exchanger in H$^+$ form was thoroughly mixed with 100 mg (dry mass) of KBr and grinded to a fine powder. A transparent disc was formed by applying a pressure of 80 psi (1 psi = 6894.76 Pa) in moisture free atmosphere. The IR absorption spectrum was recorded between 500 and 4000 cm^{-1}.

2.7.3. X-ray studies

X-ray diffraction pattern of the ion-exchange material sample S-6 was recorded by a PW 1148/89 based diffractometer with Cu Kα radiation.

2.7.4. Thermogravimetric analysis and differential thermal analysis studies (TGA–DTA)

TGA and DTA traces were obtained at a rate of 10 °C min^{-1} in nitrogen atmosphere.

2.8. Distribution studies

In order to get an idea of partition behavior of the exchanger towards the separation of metal ions of analytical interest, distribution coefficients (K_d) values were determined in several solvent systems. A, 0.4 g exchanger in H$^+$ form was treated with 40 mL solution of metal ions in required solvent medium in an Erlenmayer flask. The mixture was shaken for 6 h at 25 ± 2 °C in a temperature controlled incubator shaker. The amount of metal ions before and after adsorption was determined by titration against the standard solution of 0.01 M di-sodium salt of EDTA. The K_d values may be expressed as follows:

$$K_d = \frac{\text{metal ions (mequiv.)/ion-exchanger (g)}}{\text{metal ions (mequiv.)/solution (mL)}}$$

$$K_d = \frac{I - F}{F} \times \frac{V}{M} \qquad (1)$$

where I is the initial amount of the metal ion in the solution phase, F final amount of metal ion in the solution phase, V the volume of the solution (mL) and M is the amount of exchanger (g).

2.9. Quantitative separation of metal ions in binary synthetic mixtures

Quantitative separations of some important metal ions of analytical utility were achieved on Zr(IV) tungstomolybdate column. About 1.5 g of exchanger in H$^+$ form was packed in a glass column of 0.9 cm internal diameter with a glass wool support at the end. The column was washed thoroughly with demineralized water and the mixture of two metal ions having initial concentration 0.1 M of each with different volume ratio, was loaded on it and allowed to pass through the column at a flow rate of 0.25 mL min^{-1} till the solution level was just above the surface of the material. The column was then washed with demineralized water. Individual metal ions were eluted using the appropriate eluting reagents. The flow rate of the eluent was maintained 1 mL min^{-1} throughout the elution process. The effluent was collected in 10 mL fractions and was titrated against the standard solution of 0.01 M di-sodium salt of EDTA.

2.10. Separation of metal ion contents of commercially available pharmaceutical and brass alloy samples

2.10.1. Analysis of metal ions in pharmaceutical sample

Two tablets of antioxidant (I-Vit) were treated with 10 mL concentrated HCl and evaporated to remove excess acid. The aliquot was filtered by using Whattman filter paper number 1, and the clear filtrate obtained was diluted to 100 mL with demineralized water. Different amounts of stock solutions were poured into a glass column containing 1.0 g Zr(IV) tungstomolybdate with a glass wool support at the base. The solution was left to flow down the column with a flow rate of 0.25 mL min^{-1}. The effluent was recycled through the column to ensure the complete adsorption of metal contents. Cu^{2+} and Zn^{2+} were eluted with a 0.05 M HCONH$_2$.

2.10.2. Analysis of metal ions in brass alloy sample

A chip of commercially available brass sample (0.5 g) was dissolved in 10 mL of aquaregia solution. The mixture was stirred thoroughly and heated to remove excess acid. It was diluted to 100 mL with demineralized water and then used as a stock solution. Atomic absorption analysis for metal ions in the brass sample gave the results as Cu-70% and Zn-30%. The composition of brass sample was also determined after separation Cu^{2+} and Zn^{2+} on a cation-exchanger Zr(IV) tungstomolybdate column. Cu^{2+} and Zn^{2+} were eluted with a 0.05 M HCONH$_2$ from the method as described above.

3. Results and discussion

In the present work, various samples of new inorganic cation-exchanger Zr(IV) tungstomolybdate were prepared under varying conditions (Table 1). It was evident from Table 1 that the mixing ratio of the reactant and pH also affected the physical appearance and ion-exchange capacity of the material. It was found that anionic part contributed towards ion-exchange capacity as the replaceable groups are attached to this group and precipitation was decreased as cationic part was increased.

Table 2
Ion-exchange capacity of various exchanging ions on Zr(IV) tungstomolybdate cation-exchanger

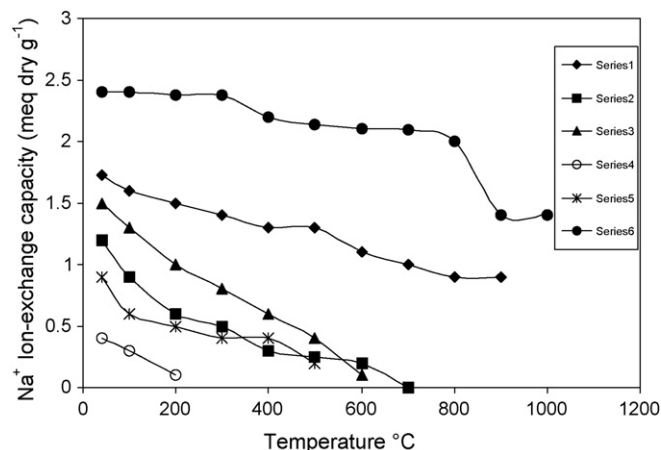| Exchanging ions	Ionic radii (Å)	Hydrated radii (Å)	IEC (mequiv. dry g^{-1}) exchanger
Li$^+$	0.68	10.0	1.09
Na$^+$	0.97	7.90	2.40
K$^+$	1.33	5.30	2.80
Mg^{2+}	0.78	10.80	0.98
Ca^{2+}	1.06	9.60	1.16
Sr^{2+}	1.27	9.40	1.90
Ba^{2+}	1.43	8.80	2.10

Fig. 1. Comparison of the ion-exchange capacity of different ion-exchange materials after drying at different temperatures. Series 1, stannic silicomolybdate; series 2, stannic molybdoarsenate; series 3, zirconium iodomolybdate; series 4, titanium tungstosilicate; series 5, stannic tungstoselenate; series 6, zirconium tungstomolybdate.

Table 4
Solubility of Zr(IV) tungstomolybdate in various solvents (500 mg of the material was initially taken for the treatment)

Solvents used	Amount released (mg)/50 mL of the solvent		
	Zr	W	Mo
DMW	0.0	0.0	0.0
1.0 M HCl	0.15	2.5	2.75
1.0 M H$_2$SO$_4$	0.25	2.8	3.00
1.0 M HNO$_3$	0.12	1.5	2.55
1.0 M NaOH	0.30	3.8	3.2
1.0 M KOH	0.40	5.00	4.5
1.0 M CH$_3$COOH	0.04	0.52	0.82
1.0 M HCOOH	0.08	0.80	1.12

Improvement in ion-exchange capacity and chemical stability was observed when the precipitate was refluxed for 6 h. On the basis of good yield, better ion-exchange capacity and both chemical and thermal stability as compared to others, sample S-6 was chosen for detailed studies.

Ion-exchange capacity of alkali and alkaline earth metal ions were shown in Table 2. It was evident from the table that affinity sequence for alkali metal ions were $K^+ > Na^+ > Li^+$ and for alkaline earth metal ions were $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. This sequence was in accordance with the hydrated ionic radii [17,18]. The ion-exchange capacity should increase with decreasing hydrated radii and increases with electrode potential. The ions with smaller hydrated radii easily enter the pores of exchanger, resulting in higher adsorption [19]. Ion-exchange capacity of the material was also affected by heating. On heating at different temperatures for 1 h, the mass, physical appearance and ion-exchange capacity of Zr(IV) tungstomolybdate (S-6) were changed (Table 3). One interesting property Zr(IV) tungstomolybdate that differentiated it from other exchange materials was that it can withstand temperature as high as 1000 °C with a loss of only 18% in ion-exchange capacity. Stannic tungstoselenate, stannic molybdoarsenate, zirconium iodomolybdate and stannic silicomolybdate [19–22] experience a drastic loss in ion-exchange capacity on heating in the temperature range of 100–1000 °C. A comparison of ion-exchange capacity data as a result of heating for different inorganic ion-exchangers was depicted in Fig. 1. Zr(IV) tungstomolybdate was found to be superior to other inorganic ion-exchangers.

The solubility experiment (Table 4) showed that the material was quite stable in common mineral acids, organic acids and alkalies. It was difficult to dissolve the material in 5 M NaOH, 5 M KOH, pure HCl, HNO$_3$, H$_2$SO$_4$ and aquaregia even on heating which showed that material was highly chemically stable.

The molar composition of Zr(IV) tungstomolybdate was found as Zr:W:Mo::1:4:3, which shows that the anionic part is

Table 3
Effect of temperature on ion-exchange capacity of Zr(IV) tungstomolybdate on heating time for 1 h

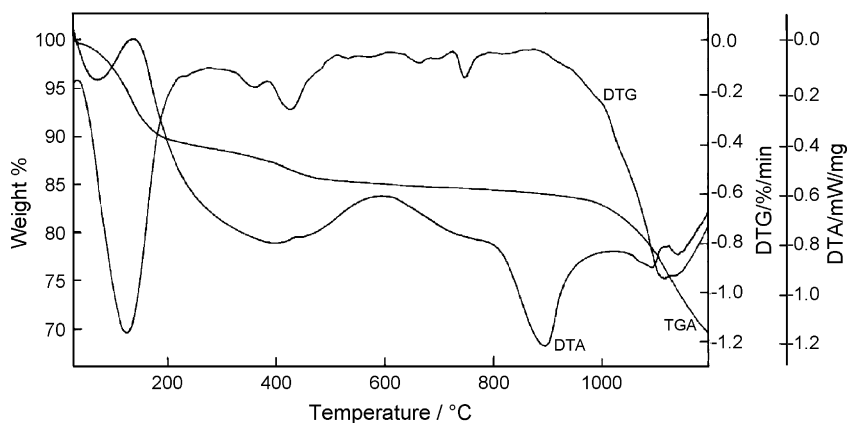| Heating temperature (°C)	Appearance (color)	IEC for Na$^+$ ion (mequiv. dry g^{-1}) exchanger	% Retention of ion-exchange capacity
100	Light yellow	2.40	100
200	Light yellow	2.38	99.16
300	Light yellow	2.38	99.16
400	Light gray	2.20	91.66
500	Light brown	2.14	89.16
600	Brownish blue	2.10	87.50
700	Brownish blue	2.09	87.00
800	Dull white	2.00	83.33
900	White	1.96	81.66
1000	White	1.96	81.83

Fig. 2. Simultaneous TGA–DTA curves of Zr(IV) tungstomolybdate.

higher than cationic one. As it was observed earlier from Table 1 that anionic part contributed towards ion-exchange capacity for this cation-exchanger. Therefore, Zr(IV) tungstomolybdate showed high ion-exchange capacity.

The thermogravimetric curve (Fig. 2) shows a continuous weight loss of mass (about 8%) upto 150 °C, which was due to removal of external water molecule [23]. Gradual weight loss of about 3.7% observed between 351 and 550 °C was due to the removal of interstitial water molecules removed by condensation of –OH groups together with external water molecule from the material. Further weight loss only 0.34% from 550 to 748 °C indicating the start of condensation due to the removal of the lattice water from the material. Further weight loss after 1000 °C, may be due to the formation of mixed oxides of zirconium, tungsten, and molybdenum. Only 23% weight loss takes place upto 1120 °C, which indicated that Zr(IV) tungstomolybdate was highly thermally stable cation-exchanger. DTA analysis (Fig. 2), which was used as a complimentary technique also supports of these conclusions. Therefore, it was observed from thermal treatment that no significant structural changes were encountered upto 1000 °C. The ion-exchange capacity data also supported these findings as the material lost only 18% ion-exchange capacity even at 1000 °C.

The FTIR spectrum of Zr(IV) tungstomolybdate (Fig. 3) indicated the presence of extra water molecule in addition to –OH groups and metal oxides present in the material. A strong and broad peak around 3200 cm^{-1} corresponds to the presence of interstitial water and hydroxyl groups [24]. A sharp peak at 1617 cm^{-1} corresponds to the deformation vibration of free water molecules, while the sharp peak at 1348 cm^{-1} was due to the deformation vibration of hydroxyl groups. A broad peak in the region around 734 cm^{-1} was due to metal–oxygen bond [25].

The X-ray diffraction pattern (Fig. 4) showed weak intensities thereby suggested that of Zr(IV) tungstomolybdate is amorphous in nature.

On the basis of chemical composition, thermogravimetric and FTIR studies, a tentative formula for Zr(IV) tungstomolybdate may be written as $(ZrO)(OH)_2(H_2WO_4)_4(H_2MoO_4)_3 \cdot 8H_2O$. The formula showed that H$^+$ ions attached to tungstate and molybdate groups are responsible for the exchange character-
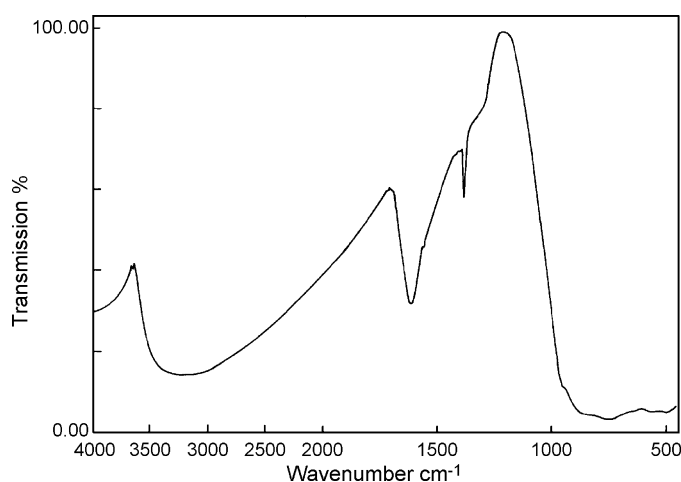

Fig. 3. FTIR spectra of Zr(IV) tungstomolybdate.

istic of the material as it was earlier observed that anionic part contributed toward ion-exchange capacity for this cation-exchanger.

It was observed from thermogravimetric analysis that the weight loss of 8% mass upto 150 °C is due to the removal of external water molecules. The number of water molecules per mole of the material as calculated from Alberti's equation [26] is found to be 8:

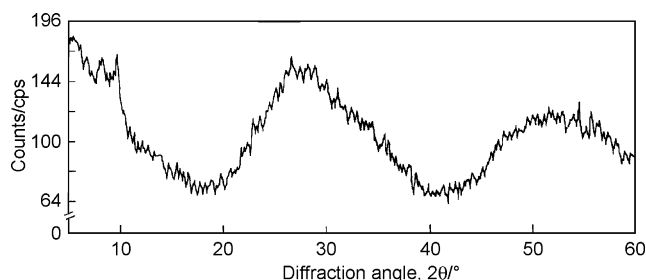$$\% \text{ Weight loss} = \frac{18n}{M + 18n} \times 100$$

Fig. 4. Powder X-ray diffraction pattern of Zr(IV) tungstomolybdate.

Table 5
Distribution coefficient (K_d) values of different metal ions on Zr(IV) tungstomolybdate in different solvent systems

Metal ions	0.05 M HCONH$_2$	0.1 M HCONH$_2$	1.0 M HCONH$_2$	0.05 M HCOOH	0.3 M HCOOH	1.0 M HCOOH	0.05 M HCONH$_2$ + 0.05 M HCOOH (1:1)	0.05 M HCONH$_2$ + 0.05 M HCOOH (2:1)	DMW	0.05 M DMF	1.0 M DMF
Ag$^+$	215	122	84	106	82	60	150	180	120	80	66
Mg^{2+}	45	60	70	30	35	44	38	45	112	140	168
Ca^{2+}	127	140	281	107	132	204	112	116	288	144	180
Sr^{2+}	180	260	340	220	312	412	204	188	328	238	418
Ba^{2+}	412	740	844	328	700	944	387	398	528	418	610
Pb^{2+}	1014	1112	2218	358	358	456	714	790	1628	1516	1580
Cd^{2+}	328	620	917	414	726	1600	380	388	298	188	422
Zn^{2+}	227	710	1712	920	1102	1428	480	512	828	516	580
Ni^{2+}	50	128	240	728	1152	1282	360	410	1188	270	308
Cu^{2+}	40	188	414	298	644	802	120	150	84	260	282
Co^{2+}	318	450	662	1022	1126	1244	590	640	1217	290	320
Cr^{3+}	518	996	2228	218	722	876	382	318	4450	616	818
Al^{3+}	619	712	1124	2218	1652	678	1448	1918	3218	6628	3656
Fe^{3+}	328	510	600	470	650	710	360	390	1368	300	450
Bi^{3+}	10,900	18,600	24,300	2400	2800	3200	7400	1600	23,900	24,500	24,500
La^{3+}	3120	4160	5200	1180	900	600	2600	2440	2840	20,500	21,340
Zr^{4+}	4550	5500	8742	1280	1180	980	3800	3200	4000	45,000	45,500
Th^{4+}	428	592	618	444	298	160	415	420	560	442	496

where $M + 18n$ is the molecular weight of the material, and n is the number of water molecule per mole of the material.

In order to explore the potentiality of the new inorganic cation-exchange material in the separation of metal ions, distribution studies for 18 metal ions were performed in different solvent systems (Table 5). It was observed that for most of the metals K_d values increased with the increase in concentration of formamide. Similar behavior was observed for formic acid and dimethyl formamide systems. However, in mixed formic acid and formamide systems the K_d value increased with increasing the formamide concentration. This effect is more prominently

observed in the case of Al^{3+}, Pb^{2+}, Ca^{2+}, Sr^{2+} and Cr^{3+}. Exceptional behavior was observed for La^{3+}, Zr^{4+}, Th^{4+} and Ag$^+$ metal ions in these systems. It is apparent from Table 5 that K_d values in 0.05 M DMF are relatively high for most of the metal ions except Ag$^+$, Cd^{2+}, Co^{2+} and Fe^{3+} as compared to 0.05 M HCONH$_2$. This may be due to more basic nature of DMF than formamide, due to which more hydrogen ions were released and metal ions were adsorbed by this cation-exchange material in this solvent system. The differential behavior of the exchanger for the uptake of metal ions in these solvent systems showed the separation possibilities of certain metal ions of analytical interest from a given mixture. High K_d values of Pb^{2+} enable

Table 6
Quantitative separation of metal ions from a binary mixture using Zr(IV) tungstomolybdate column at room temperature

S. no.	Metal ions separation	Amount loaded (mg)	Amount found (mg)	% Recovery	% Error	Volume of eluent used (mL)	Eluent used
1	Ni^{2+}	2.93	2.91	99.32	−0.68	45	0.05 M HCONH$_2$
	Pb^{2+}	10.36	10.34	99.80	−0.20	55	0.05 M HCOOH
2	Ni^{2+}	2.93	2.91	99.32	−0.68	45	0.05 M HCONH$_2$
	Zn^{2+}	3.27	3.28	100.30	+0.30	45	0.05 M HCONH$_2$
3	Zn^{2+}	3.27	3.28	100.30	+0.30	45	0.05 M HCONH$_2$
	Pb^{2+}	10.36	10.34	99.80	−0.20	55	0.05 M HCOOH
4	Mg^{2+}	1.22	1.24	101.64	+1.64	40	0.3 M HCOOH
	Pb^{2+}	10.36	10.34	99.80	−0.20	55	0.05 M HCOOH
5	Ni^{2+}	2.93	2.91	99.32	−0.68	45	0.05 M HCONH$_2$
	Cd^{2+}	5.62	5.58	99.28	−0.72	50	0.05 M DMF
6	Fe^{3+}	2.79	2.74	98.20	−0.80	40	0.05 M DMF
	Al^{3+}	1.35	1.30	96.29	−3.70	60	0.05 M HCONH$_2$
7	Mg^{2+}	1.22	1.24	101.64	+1.64	40	0.3 M HCOOH
	Al^{3+}	1.35	1.30	96.29	−3.70	60	0.05 M HCONH$_2$
8	Cu^{2+}	3.18	3.14	98.74	−1.26	35	0.05 M HCONH$_2$
	Zn^{2+}	3.27	3.28	100.30	+0.30	35	0.05 M HCONH$_2$

S. no.: serial number.

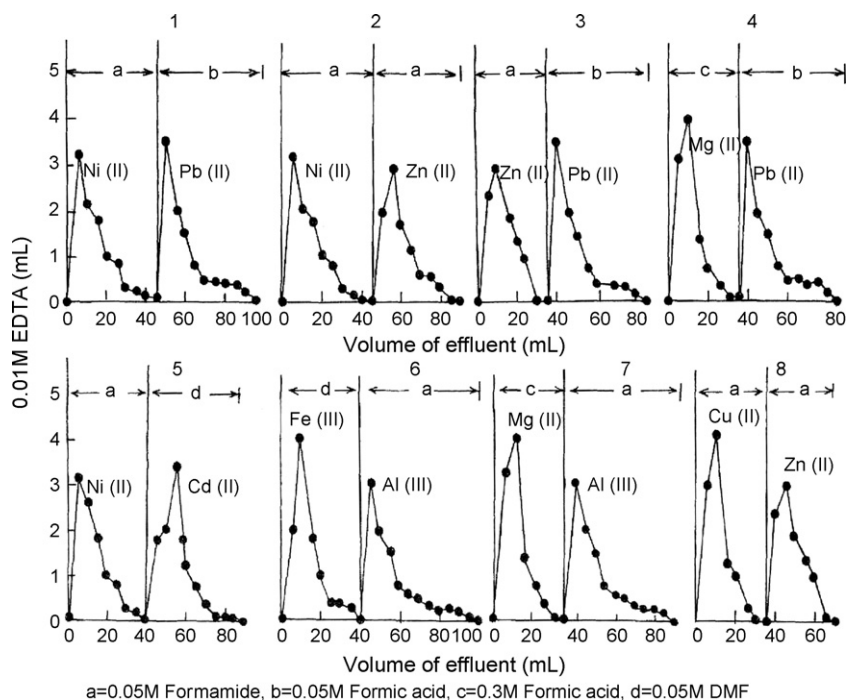a=0.05M Formamide, b=0.05M Formic acid, c=0.3M Formic acid, d=0.05M DMF

Fig. 5. Chromatograms of binary separations of metal ions on Zr(IV) tungstomolybdate column.

Table 7
Selective separations of Al^{3+} from a synthetic mixture of Co^{2+}, Fe^{3+}, Mg^{2+} and Ca^{2+}

S. no.	Amount of Al^{3+} loaded (mg)	Amount of Al^{3+} found (mg)	% Recovery	% Error	Eluent used 0.05 M $HCONH_2$ (mL)
1	1.34	1.32	98.50	−1.50	50
2	2.01	2.03	100.99	+0.99	60
3	2.68	2.70	100.75	+0.75	75
4	3.35	3.32	91.10	−0.90	90

their separation from Mg^{2+}, Ni^{2+}, Cu^{2+} and Sr^{2+} by use 0.05 M $HCONH_2$. On the other hand the high K_d values of Al^{3+}, Bi^{3+}, La^{3+} and Zr^{4+} in all solvent systems was found to be useful for selective separation of these metal ions from the mixture of the other metal ions. The separation capability of the material has been demonstrated by achieving a number of binary separations of some important metal ions (Table 6). The sequential elution of ions through column depends upon the metal-eluting ligand

(eluent) stability. The weakly retained metal ions eluted first. The order of elution and eluents used for binary separations are also shown in Fig. 5. The separations are quite sharp and recovery was quantitative and reproducible. The practical utility of these separations was also demonstrated by separating metal ions quantitatively from a commercially available pharmaceutical preparation I-Vit (antioxidant) and brass alloy sample as shown in Tables 7–9.

Table 8
Separation of Cu^{2+} and Zn^{2+} in a commercially available pharmaceutical formulation on a column of Zr(IV) tungstomolybdate

S. no.	Separations achieved	Amount loaded (mg)	Amount found (mg)	% Recovery	% Error	Volume of eluent used	Eluent
1		0.16	0.15	93.75	−6.25	45	
2	Cu^{2+}	0.24	0.23	95.83	−4.17	55	0.05 M $HCONH_2$
3		0.32	0.30	93.75	−6.25	60	
4		0.40	0.38	95.00	−5.00	70	
1		3.2	3.16	98.75	−1.25	60	
2	Zn^{2+}	4.8	4.76	99.16	−0.84	70	0.05 M $HCONH_2$
3		6.4	6.38	99.68	−0.32	75	
4		8.4	7.8	97.50	−2.50	85	

Table 9
Separation of Cu^{2+} and Zn^{2+} in brass sample on a column of Zr(IV) tungstomolybdate

S. no.	Separations achieved	Amount loaded (mg)	Amount found (mg)	% Recovery	% Error	Volume of eluent used	Eluent
1		3.50	3.40	97.14	−2.86	45	
2	Cu^{2+}	5.25	5.20	99.04	−0.96	55	0.05 M HCONH$_2$
3		7.00	6.98	99.71	−0.29	60	
4		8.75	8.72	99.65	−0.35	70	
1		1.50	1.41	93.33	−6.67	50	
2	Zn^{2+}	2.25	2.23	99.11	−0.89	55	0.05 M HCONH$_2$
3		3.00	2.98	99.33	−0.67	65	
4		3.75	3.73	99.46	−0.54	75	

4. Conclusion

An amorphous cation-exchanger Zr(IV) tungstomolybdate was found to have good ion-exchange capacity, high chemical and thermal stability and selectivity for metal ions. The differential behavior of the exchanger towards metal ions in different solvent systems showed the separation possibilities of metal ions of analytical interest from a given mixture. So this cation-exchange material can be conveniently utilized for the removal and isolation of heavy toxic metal ions, released from wastewater stream.

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