



Synthesis and characterization of a new cation exchanger-zirconium(IV)iodotungstate: Separation and determination of metal ion contents of synthetic mixtures, pharmaceutical preparations and standard reference material

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ABSTRACT

Samples of zirconium(IV)iodotungstate have been synthesized under varying mixing order and ratios of aqueous solution of potassium iodate, sodium tungstate and zirconium oxychloride at pH 1. A tentative formula was proposed on the basis of chemical composition, FTIR and thermogravimetric studies. The material shows a capacity of 0.68 meq g^{-1} (for K^+) which can be retained up to 200°C . pH titration data reveal its monofunctional behavior. The distribution coefficient values of metal ions have been determined in various solvent systems. A number of important and analytically difficult quantitative separations of metal ions have been achieved using columns packed with this exchanger. In order to demonstrate practical utility of this material, Hg^{2+} and Pb^{2+} have been selectively separated and determined in the synthetic mixtures. Assay of Al^{3+} and Mg^{2+} in commercial tablets and analysis of lead in the standard reference material have also been attempted.

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1. Introduction

Significant accumulation of toxic metals in the environment and their persistent nature have been the subject of great concern in recent years due to their over increased use in various industries. The hazardous heavy metal ions that pose potential dangers to human lives from the industrial effluents include lead, mercury, cadmium, chromium, copper, zinc and nickel. The toxicities of heavy metals may be caused by the inhibition and reduction of various enzymes, complexation with certain ligands of amino acids and substitution of essential metal ions from enzymes [1]. Their quantification in industrial effluents, various water and biological samples is important, especially in the environment monitoring and assessment of occupational and environmental exposure to toxic metals. Removal of toxic metals from the industrial effluents has special importance from the ecotoxicological point of view. Despite rapid development in the detectability of instrumental methods for analysis, a direct determination of trace metal ions in the samples of complex matrices still remains a difficult task because of insufficient sensitivity and selectivity of the methods used and strong interference from the sample matrix [2]. The matrix effects become more prominent when the limitations of

sophisticated analytical devices go unheeded [3]. Thus, the best way is to separate the metal ions from the matrix constituents prior to their determination. Solid phase extraction using inorganic ion exchanger for the separation of metal ions has been preferred over conventional solvent extraction and coprecipitation [4–6]. The possibility to extract selectively a number of analytes over a wide pH range, quantitative sorption and elution, kinetically faster sorption and desorption mechanisms, regenerability, simplicity in handling, higher thermal and resistivity to radiations are frequently quoted as an advantage [7]. During the last decades inorganic ion exchangers have also found applications in the field of sensor [8], wastewater treatment [9], radiochemical separation [10] and chromatographic separation of pesticides [11,12] because of their unusual selectivity towards certain ionic species. Synthesis of two component ion exchangers by introducing tetravalent metals (Zr and Sn) into phosphate, silicate, arsenate and molybdate have been the extensively studied groups owing to their variable coordination number [13]. Inorganic ion exchangers of three components have been found to exhibit enhanced ion exchange capacity and selectivity [14–17]. Tungstates of chromium, thorium, titanium, tin and zirconium exhibited low capacities that varied from 0.02 to 0.05 meq g^{-1} , poor selectivities and stability [18,19]. However, stannic(IV)tungstoselenate synthesized in our lab and stannic(IV)tungstoarsenate have shown higher capacities 0.88 and 1.06 meq g^{-1} , respectively [20,21]. Iodate containing exchangers zirconium(IV)iodophosphate and stannic(IV)iodophosphate have

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been found to show higher selectivities towards Pb^{2+} and Hg^{2+} , respectively [15,22]. Therefore, it is worthwhile to synthesize zirconium(IV)iodotungstate and investigate its ion exchange properties and applications in a systematic manner.

2. Experimental

2.1. Reagents and chemicals

Zirconium(IV)oxychloride and sodium tungstate were obtained from S.D. fine Chem. Ltd. (India) and potassium iodate was obtained from E. Merck (India). Pharmaceutical preparations Gelusil MPS (aluminium hydroxide gel 300 mg/tablet, magnesium hydroxide 150 mg/tablet, magnesium aluminium silicate hydrate 75 mg/tablet), Logascid (dried aluminium hydroxide gel 200 mg/tablet, magnesium hydroxide 200 mg/tablet) and acidin MPS (magnesium hydroxide 250 mg/tablet, dried aluminium hydroxide gel 250 mg/tablet) by Parke Davis, Astra-IDL and East India, respectively, were used. Standard reference material (Rompin Hematite, JSS 800-3) was used from Japan Steel Society. All other chemicals and reagents used were of anal R grade.

2.2. Instrumentation

An Electronic India-III E digital pH meter and a Spectronic 20 Genesis spectrophotometer were used to measure pH and absorbance, respectively. Powder X-ray diffraction pattern was recorded using a diffractometer PW 1820 with $\text{Cu K}\alpha$ radiation ($\alpha = 1.5418 \text{ \AA}$). A PerkinElmer FTIR 1730 spectrometer was used for recording FTIR spectra using KBr disc method. TGA analysis was carried out with a general V2.2 A Du Pont 9900 thermal analyzer at a rate of $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere. A temperature controlled shaker (SICO-India) was used for shaking. Muffle furnace (Narang Scientific works-India) was used for heating samples at different temperatures. Atomic absorption spectrophotometric measurements were performed on PerkinElmer 3100 model.

2.3. Synthesis of the ion exchange material

Samples of zirconium(IV)iodotungstate (ZIW) were synthesized either by adding a mixture of aqueous solution of 0.2 M potassium iodate and sodium tungstate into aqueous solution of 0.2 M zirconium(IV)oxychloride solution or by reverse order with continuous stirring to obtain a gel under varying mixing ratios. The desired pH was adjusted by adding dilute HCl solution. The precipitate so formed was allowed to settle overnight at room temperature and then filtered under suction. The excess acid was removed by washing with demineralized water (DMW) and it was kept in an oven at $50 \pm 1^\circ\text{C}$ for drying. The dried product was then cracked into small granules by putting in DMW, which was then treated with 1 M HCl for 24 h to ensure complete conversion to H^+ form at room temperature ($25 \pm 2^\circ\text{C}$). The material was finally washed with DMW to remove any excess of acid.

2.4. Ion exchange capacity

The ion exchange capacity (IEC) of the material was determined by the column process. The 0.5 g of the exchanger in H^+ form packed in a column (internal diameter of 0.8 and 35 cm of length) with glass wool support and washed with DMW to remove any excess of acid remained sticking on the particles. Metal nitrate solutions were used to elute the H^+ ions completely from the exchanger column at a flow rate of 1 mL min^{-1} . The effluent was collected and titrated against a standard NaOH solution to determine the total H^+ ions released. To study the effect of drying temperature on the IEC the

material was heated at different temperature in a muffle furnace for 1 h and IEC was determined by column method.

2.5. pH-titration

Topp and Pepper's batch method [23] was used for pH-titration of the material using 0.1 M solution of KCl–KOH systems. The 0.5 g of exchanger was equilibrated with 50 mL of the mixed solution of KCl and KOH in an Erlenmeyer flask for 4 h at $25 \pm 1^\circ\text{C}$.

2.6. Chemical stability and composition

To study the chemical stability, 0.5 g exchanger was equilibrated with 50 mL of desired solutions at $25 \pm 2^\circ\text{C}$ for 24 h with occasional shaking. For the determination of chemical composition of the sample ZIW-5, 0.1 g of exchanger was dissolved in minimum amount of concentrated HNO_3 . The solution was diluted to 100 mL with DMW. Zirconium, tungstate and iodate released in the solutions were determined spectrophotometrically using alizarin red-S, sodium metavanadate [24] and pyrogallol [25], respectively, as coloring reagents.

2.7. Distribution studies

The distribution coefficients (K_d) of metal ions on ZIW were determined by the batch method in demineralized water (DMW), hydrochloric acid (HCl), aqueous solutions of ammonium chloride (NH_4Cl) and dimethyl sulphoxide (DMSO). The ion exchange capacity of metal ions in DMW is also determined by batch method. The 0.4 g exchanger was equilibrated continuously with 40 mL solution of concerned metal ions ($1.25 \times 10^{-3} \text{ mol L}^{-1}$) in appropriate solvent for 4 h in a shaker at $25 \pm 1^\circ\text{C}$. The amount of metal ion left in the solution was determined by titrating against standard solution of the disodium salt of ethylenediaminetetra acetic acid (EDTA). The distribution coefficient was calculated using the following equation.

$$K_d = \frac{\text{mmoles of metal ions/g of exchanger}}{\text{mmoles of metal ions/mL of solution (after sorption)}} (\text{mL g}^{-1})$$

2.8. Sample preparation

For the preparation of synthetic samples of metal ions, different amounts of Pb^{2+} and Hg^{2+} were mixed with Mn^{2+} (0.549 mg), Ni^{2+} (0.587 mg), Zn^{2+} (0.654 mg), Cd^{2+} (1.124 mg) and Mn^{2+} (0.549 mg), Ni^{2+} (0.587 mg) Al^{3+} (0.269 mg), Co^{2+} (0.589 mg), respectively.

For the determination of Al^{3+} and Mg^{2+} in pharmaceutical preparation, three tablets were powdered and were digested in a beaker with 2 mL of concentrated HNO_3 by slowly increasing the temperature until a solid residue remained. After cooling, the residue was dissolved in 12 mL of concentrated HNO_3 . The solution was gently evaporated on a steam bath till a residue was again left. After adding 10 mL of distilled water to it, concentrated HNO_3 was added drop wise with moderate heating until a clear solution was obtained. It was then filtered and the clear solution was diluted to 100 mL with DMW.

The solution of standard reference material (Rompin Hematite, JSS 800-3) was prepared by dissolving 0.5 g of the substance in 20 mL of hydrochloric acid (1 + 1) by heating on a water bath and then 2 mL of 30% hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the solution on a water bath. The solution was cooled, filtered and the filtrate was diluted to 25 mL with DMW. The concentration of Pb in this stock solution will be $4.4 \mu\text{g}$.

Table 1
Synthesis and few properties of zirconium(IV)iodotungstate.

Sample	Mixing ratio Z:I:W ^a	Order of mixing	IEC for K ⁺ ions (meq g ⁻¹ exchanger)	Appearance after drying at 50 ± 1 °C
ZIW-1	1:1:1	Z is added to mixture of I and W	0.49	Light yellow
ZIW-2	1:1:2	Z is added to mixture of I and W	0.56	White
ZIW-3	1:2:1	Z is added to mixture of I and W	0.54	Off white
ZIW-4	1:1:1	Mixture of I and W is added to Z	0.60	Brown
ZIW-5	1:1:2	Mixture of I and W is added to Z	0.68	White
ZIW-6	1:2:1	Mixture of I and W is added to Z	0.62	Light yellow
ZIW-7	1:2:2	Z is added to mixture of I and W	0.52	Off white
ZIW-8	1:2:2	Adjusted the pH of mixture of I and W and Z is added	0.51	Very light pink
ZIW-9	1:2:2	Mixture of I and W is added to Z	0.66	White
ZIW-10	1:2:2	Adjusted the pH of Z, then mixture of I and W is added	0.66	White
ZIW-11	1:2:2	ZIW-2 refluxed for 12 h	0.38	Yellow
ZIW-12	1:2:2	ZIW-5 refluxed for 12 h	0.54	Light yellow

^a Concentration of Z (zirconium(IV)oxychloride), I (potassium iodate) and W (sodium tungstate) was 0.2 M and pH was adjusted to 1 ± 0.05.

2.9. Quantitative separation and determination of metal ions

Quantitative separations of metal ions were achieved on the columns having an internal diameter of 0.8 and 35 cm of length. The column was packed with 2.0 g of exchanger and washed thoroughly with DMW. Sample of metal ions (0.2–1.5 mL) to be separated was loaded on it. After recycling three times to ensure complete adsorption of the mixture on the column, the separation was achieved by passing a suitable solvent through the column as eluent at a flow rate of 1 mL min⁻¹. The metal ions in the effluent were determined titrimetrically using standard disodium salt of EDTA.

2.10. Analysis of lead in the standard reference material

In the case of standard reference material, 5 mL of stock solution was loaded onto a column packed with 2.0 g of zirconium(IV)iodotungstate. After complete sorption by recycling three times, less strongly adsorbed metal ions were eluted by passing 50 mL of DMW. The remaining strongly adsorbed metal ions were eluted by passing 50 mL of 0.1 M HCl and subsequently lead was determined in this effluent by atomic absorption spectrophotometric method at 217.0 nm.

3. Results and discussion

Table 1 describes the preparation of samples of zirconium(IV)iodotungstate. It is clear from the table that the order of mixing affects the IEC which is higher when mixture of iodate and tungstate is added to zirconium(IV)oxychloride. On increasing the tungstate content of the mixture increases the ion exchange capacity of the materials to a better extent than iodate. However, increasing both the contents of iodate and tungstate at one time could not increase the ion exchange capacity any further. Adjusting the pH of either the mixture of tungstate and iodate or zirconium by adding HCl before mixing have no significant effect on ion exchange capacity. Refluxing the bulk mixture does not improve the yield but significant loss of ion exchange capacity was observed. This loss of ion exchange capacity may be ascribed to the fact that some of the surface hydroxyl groups disappeared from the exchanger after refluxing in the bulk mixture [26]. The variation in colours of the products was also observed which may be due to the redox reactions of IO₃⁻ groups of the material [14]. Sample ZIW-5 (in H⁺ form) was chosen for detailed studies owing to its higher IEC and reported as ZIW hereafter.

Data from Table 2 reveals that the ion exchange capacity for alkali metals increases from Na⁺ to K⁺ due to a decrease in their hydrated ionic radii as expected. The attraction between anions and cations in ionic crystals, obeys coulombs law which demands that for cations of equal charge a small ion be attracted with a

greater force and held more tightly than a large ion. The ions with smaller hydrated radii easily enter the pores of exchanger, resulting in higher adsorption [15,27]. Strangely enough the alkaline earth metals exhibit a reverse relationship except barium. This is similar to the investigation reported by Nachod and Wood [28] for the exchange of alkali and alkaline earth metal ions on a carbonaceous zeolite. Perhaps factors other than ionic radius are responsible for this unusual uptake of ions.

The pH titration studies (Fig. 1) reveals monofunctional weak acid behavior of the material and the exchange capacity was found to be 0.63 meq g⁻¹ for K⁺ which is in close agreement with capacity data obtained by column method.

It is apparent from Table 3 that material is fairly stable in lower concentrations of HCl, HNO₃, NH₄Cl, dimethyl sulphoxide (DMSO) and also quite stable in organic acids like formic acid.

Based on the chemical composition analysis the molar ratio of Zr, IO₃ and WO₄ was found to be 4:3:2.

The FTIR spectrum of the exchanger (Fig. 2) shows a broad but strong peak in the region 3500–3000 cm⁻¹ which represent O–H stretching of lattice water molecule [29]. Another strong and sharp peak at 1650 cm⁻¹ may be due to H–O–H bending. A sharp peak in the region 550–500 cm⁻¹ may be ascribed to the coordinated IO₃⁻

Table 2
IEC of ZIW for alkali and alkaline earth metal ions.

Metal ions	Hydrated ionic radii (Å ⁰)	IEC (meq g ⁻¹ exchanger)
Na ⁺	7.90	0.63
K ⁺	5.30	0.68
Mg ²⁺	10.80	0.68
Ca ²⁺	9.60	0.46
Sr ²⁺	9.40	0.44
Ba ²⁺	8.80	0.58

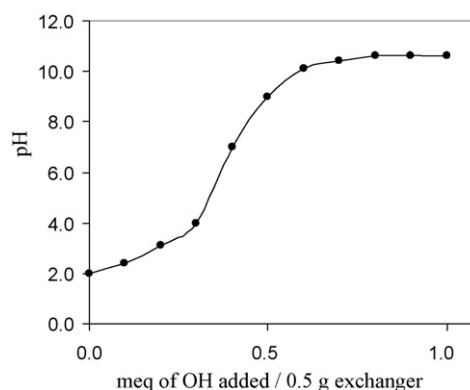


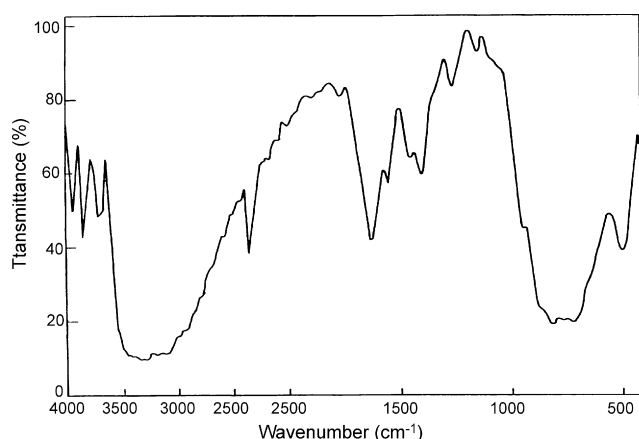
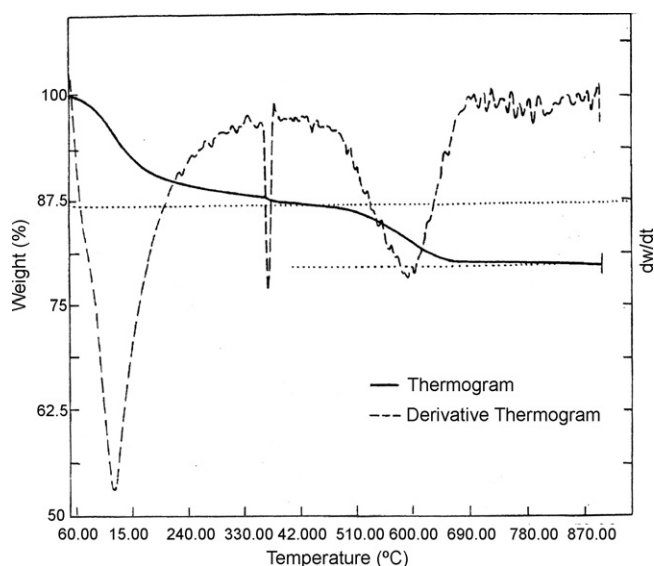
Fig. 1. pH titration curve of zirconium(IV)iodotungstate.

Table 3
Chemical stability of ZIW in some solvents.

Solution	Amount released (mg/50 mL)		
	Zr(IV)	IO ₃	WO ₄
DMW	0.00	0.15	0.05
0.1 M HCl	0.00	0.55	0.25
0.5 M HCl	2.50	9.10	6.00
1.0 M HNO ₃	6.00	14.05	6.50
1.0 M Formic acid	3.00	8.30	6.00
1.0 M NH ₄ Cl	2.50	6.00	5.50
10% DMSO	0.25	1.35	0.45
0.05 M NaOH	26.50	2.50	33.05

group. Spectrum also shows broad and weak bands in the region 830–780 and 900–825 cm⁻¹ which can be assigned to the presence of WO₄²⁻ and metal oxide groups, respectively [30–32].

Thermogram of ZIW (Fig. 3) shows some interesting information. The derivative curve exhibits three endothermic peaks with T_{max} at 121.3, 379.0 and 585.9 °C corresponding to three distinct weight losses. The external water molecule is lost up to 150 °C as indicated by the first peak of the derivative curve which corresponds to a weight loss of 10%. Only a little gradual loss in weight (2.7%) is observed from 150 to 401.86 °C owing to the removal of interstitial water molecules by condensation of –OH groups and

**Fig. 2.** FTIR spectrum of zirconium(IV)iodotungstate.**Fig. 3.** Thermogram of zirconium(IV)iodotungstate.**Table 4**
Effect of drying on IEC and color of ZIW.

Heating temperature (°C)	IEC for Mg ²⁺ (meq g ⁻¹ exchanger)	Color
50	0.68	White
100	0.68	Off white
200	0.67	Light brown
300	0.64	Very light brown
400	0.54	Brown
500	0.46	Pale yellow
600	0.32	Light pink
700	0.30	Pink (brownish)
800	0.24	Pink

volatilization of IO₃⁻ groups [15]. This loss is supported by an endothermic peak at 379.0 °C. The weight loss beyond 401.86 °C which continues up to 690 °C due to the loss of tungsten. This has been indicated by an endothermic peak at 585.9 °C. The weight becomes almost constant above 690 °C owing to the formation of metal oxides as final product. The heating effect on ion exchange capacity (Table 4) also justify the loss of iodate and tungsten as the IEC (for Mg²⁺) of the material at 400 and 600 °C decreases to 0.48 and 0.32 meq g⁻¹, respectively. However, only 6% of capacity was observed to be lost when the exchanger dried at 300 °C. The corresponding mass loss from the thermogram was only 12%. These facts makes zirconium(IV)iodotungstate more thermally stable compared to other iodate and tungstate containing inorganic exchanger [15,18–19,22].

X-ray diffraction pattern of ZIW showed no peaks at all thereby suggesting an amorphous nature of the material.

On the basis of chemical composition, IEC, FTIR and TGA, a tentative formula for zirconium(IV)iodotungstate may be written as [(ZrO₂)₄ (HIO₃)₃ (H₂WO₄)₂].nH₂O. It was observed from thermogravimetric analysis that the weight loss due to the presence of water molecules in the gel is 10%. The number of such molecules (*n*) per mole of exchanger can be computed from Alberti's equation [33].

$$18n = \frac{X(M+18n)}{100}$$

where *X* is the percent water content and *M* + 18 is the molecular weight of the material. It gives the value of '*n*' as 9.38.

It is clear from Table 5 that *K_d* values vary with the composition and nature of the solvent system. It decreases with the increase in concentration of hydrochloric acid. The *K_d* values of almost all the

Table 5
K_d values of metal ions on ZIW in different solvent systems (×10² mL g⁻¹).

Metal ions	<i>K_d</i> values (×10 ² mL g ⁻¹)					IEC (mg g ⁻¹)
	DMW	HCl (0.01 M)	HCl (0.1 M)	NH ₄ Cl (0.05 M)	DMSO (10%)	
Mg ²⁺	2.89	0.23	0.16	0.08	3.07	0.90
Ca ²⁺	0.55	0.18	0.00	0.07	1.00	0.71
Sr ²⁺	0.44	0.30	0.27	0.23	0.55	1.34
Ba ²⁺	2.00	0.37	0.23	0.50	2.00	4.60
Zn ²⁺	0.20	0.18	0.00	0.70	0.22	0.56
Cd ²⁺	0.46	0.16	0.21	0.00	0.56	1.78
Cu ²⁺	0.75	0.16	0.07	0.07	0.93	1.36
Ni ²⁺	0.10	0.08	0.00	0.00	0.16	0.27
Pb ²⁺	8.50	1.16	0.10	3.00	9.00	9.27
Al ³⁺	0.22	0.18	0.11	0.00	0.40	0.24
Hg ²⁺	7.00	3.00	0.00	0.00	12.00	8.78
Bi ³⁺	5.00	4.00	0.00	4.00	0.71	8.73
Co ²⁺	0.30	0.18	0.00	0.07	1.50	0.68
Fe ³⁺	3.00	1.00	0.25	1.50	3.79	2.09
Zr ⁴⁺	2.50	2.50	0.25	7.00	2.58	3.26
Th ⁴⁺	1.80	1.50	1.33	3.00	1.90	7.47
La ³⁺	0.71	0.33	0.00	0.44	1.16	2.88
Mn ²⁺	0.30	0.08	0.07	0.16	0.57	0.63

Table 6
Quantitative separation of metal ions on ZIW column.

Metal ions	Amount loaded (mg)	Amount found (mg)	RSD ^a (%)	Recovery (%)	Eluent used	Volume of eluent (mL)
Zn ²⁺	0.65	0.62	4.04	95.00	DMW	30.0
Pb ²⁺	2.07	2.07	1.83	100.00	0.1 M HCl	45.0
Ni ²⁺	0.58	0.54	2.79	93.00	DMW	25.0
Pb ²⁺	2.07	2.00	1.25	97.00	0.1 M HCl	45.0
Al ³⁺	0.26	0.25	5.95	93.00	DMW	25.0
Pb ²⁺	2.07	2.03	1.77	98.00	0.1 M HCl	50.0
Cd ²⁺	1.12	1.07	1.94	95.99	DMW	40.0
Pb ²⁺	2.07	2.06	1.28	99.8	0.1 M HCl	35.0
Ni ²⁺	0.58	0.53	4.99	91.99	DMW	30.0
Bi ²⁺	2.08	1.88	3.52	90.00	0.1 M HCl	35.0
Cd ²⁺	1.12	1.07	3.37	96.00	DMW	40.0
Hg ²⁺	2.00	1.96	1.84	97.99	0.1 M HCl	35.0
Al ³⁺	0.26	0.25	5.95		DMW	35.0
Hg ²⁺	2.00	1.92	2.46	93.99	0.1 M HCl	45.0
Al ³⁺	0.26	0.24	4.16	92.30	DMW	30.0
Mg ²⁺	0.24	0.23	6.45	95.83	0.1 M HCl	40.0

^a Mean of three replicate determinations.**Table 7**
Selective separation of Hg²⁺ from a synthetic mixture of Al³⁺, Ni²⁺, Mn²⁺ and Co²⁺ on ZIW column.

Amount loaded (mg)	Amount found (mg)	RSD ^a (%)	Recovery (%)	Eluent used	Volume of eluent (mL)
6.02	5.92	2.48	98.43	0.1 M HCl	40.0
10.03	9.74	2.01	97.15	0.1 M HCl	40.0
14.04	13.61	2.89	97.00	0.1 M HCl	50.0

^a Mean of three replicate determinations.

metal ions are high in DMSO as compared to other solvent systems studied. This may be due to its more basic nature, which favours the release of the hydrogen ions from the exchanger and metal ions were sorbed on it. DMSO plays a very important role in reflecting

differential behavior of metal ions towards ion exchange materials. The Pb²⁺, Hg²⁺, Bi³⁺ and Zr⁴⁺ have high K_d values in almost all the solvent systems studied. However, Zn²⁺, Ni²⁺, Al³⁺, Cd²⁺ and Cu²⁺ have low K_d values.

Table 8
Selective separation of Pb²⁺ from synthetic mixture of Zn²⁺, Cd²⁺, Ni²⁺ and Mn²⁺ on ZIW column.

Amount loaded (mg)	Amount found (mg)	RSD ^a (%)	Recovery (%)	Eluent used	Volume of eluent (mL)
4.14	4.00	2.74	96.62	0.1 M HCl	45.0
8.29	8.29	2.83	100.00	0.1 M HCl	50.0
12.43	11.86	2.59	94.41	0.1 M HCl	55.0

^a Mean of three replicate determinations.**Table 9**
Column chromatographic separation of Al³⁺ and Mg²⁺ in three pharmaceutical preparations on zirconium(IV)iodotungstate.

Tablet; metal ions	Amount loaded (mg)	Amount found (mg)	RSD ^a (%)	Recovery (%)	Volume of eluent (mL)	Eluent used
Gelasil MPS						
Al ³⁺	1.02	1.01	2.83	99.03	45.0	DMW
	2.04	2.01	2.58	98.52	50.0	DMW
	3.06	2.98	2.52	97.39	55.0	DMW
Mg ²⁺	0.65	0.65	3.12	100.00	30.0	0.1 M HCl
	1.30	1.27	2.00	97.69	35.0	0.1 M HCl
	1.95	1.86	2.84	95.39	40.0	0.1 M HCl
Acidin MPS						
Al ³⁺	0.78	0.77	3.51	98.72	40.0	DMW
	1.30	1.28	2.94	98.46	45.0	DMW
	2.59	2.54	2.12	98.07	50.0	DMW
Mg ²⁺	0.63	0.62	3.00	98.41	30.0	0.1 M HCl
	1.55	1.53	2.75	98.71	40.0	0.1 M HCl
	2.50	2.44	2.06	97.60	45.0	0.1 M HCl
Logascid						
Al ³⁺	1.04	1.03	3.74	99.04	45.0	DMW
	2.07	2.05	2.91	99.03	50.0	DMW
	3.11	3.10	4.03	99.68	55.0	DMW
Mg ²⁺	0.50	0.49	2.55	99.20	25.0	0.1 M HCl
	1.25	1.23	2.93	98.40	35.0	0.1 M HCl
	2.00	1.96	3.44	98.00	40.0	0.1 M HCl

^a Mean of three replicate determinations.

Table 10Analysis of Pb²⁺ in the standard reference material.

Sample	Certified composition ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	RSD ^a (%)
Rompin Hematite, JSS-800-3	Pb: 210; Mn: 2200; Cu: 640; Zn: 1030; Bi: 230; V: 60; As: 330; Sn: 120	Pb: 210	4.42

^a Mean of three replicate determinations.

On the basis of distribution studies, the most promising property of this material was found to be selectivity for Pb²⁺ and Hg²⁺ in DMSO and DMW medium which are major polluting metals. The potential of this material has been demonstrated by achieving some important binary separations such as Zn²⁺–Pb²⁺, Ni²⁺–Pb²⁺, Al²⁺–Pb²⁺, Cd²⁺–Pb²⁺, Ni²⁺–Bi³⁺, Cd²⁺–Hg²⁺ and Al³⁺–Hg²⁺. The details are summarized in Table 6. These separations can be utilized in the removal of particular metal ions which may interfere in the determination of certain other metal ions. Different amounts of lead and mercury have been selectively separated from a synthetic mixture containing other metals on a small column of this exchanger. The sequential elution of ions through column depends upon the metal-eluting power of the eluent. The weakly retained metal ions eluted first. A striking feature of these selective separations is that Pb²⁺ and Hg²⁺ could be recovered at more than 95% (with less than 3% RSD) using a common acid (HCl) as evident from Tables 7 and 8. Assay of Al³⁺ and Mg²⁺ in two commercial available pharmaceutical tablets has been checked by column chromatography using this material (Table 9). To check the accuracy and applicability of the method, standard reference material was also analysed for the separation and determination of lead (Table 10).

4. Conclusion

A new amorphous ion exchanger, zirconium(IV)iodotungstate, has been synthesized which exhibits monofunctional cation exchange behavior. Cation exchange capacity is found to be highest (0.68 meq g⁻¹) for K⁺ ions. The material was found to be quite stable in mineral and organic acids. On the basis of differences in *K_d* values of metal ions, a few binary separations of metal ions have been achieved utilizing the columns of this material. It is selective for lead and mercury. Hence, the exchanger can be used to remove Pb²⁺ and Hg²⁺ selectively from industrial effluent and to preconcentrate from various water, environmental and biological samples.

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