

Titanium(IV) tungstosilicate and titanium(IV) tungstophosphate: two new inorganic ion exchangers

Zia Mahmood Siddiqi*, Deepak Pathania

Department of Applied Chemistry, Regional Engineering College, Jalandhar-144011, Punjab, India

Abstract

Crystalline phases of Ti(IV) tungstosilicate and Ti(IV) tungstophosphate have been synthesised. The ion-exchange capacities of Ti(IV) tungstosilicate and Ti(IV) tungstophosphate have been reported as 0.44 and 0.80 mequiv./g, respectively. Both materials show monofunctional ion-exchange characteristic and are stable in 0.1 M solutions of HNO₃, HCl, H₂SO₄ and acetone and benzene. Ti(IV) tungstosilicate is found to be more stable thermally than Ti(IV) tungstophosphate (loss in ion-exchange capacity was found as 58 and 80%, respectively for samples heated at 200 °C). The K_d values for heavy metals such as Pb, Hg, Cd, Sb, Co, Zn, Ni, Fe, Cr etc. have been reported in demineralised water and two surfactant media by batch processes. Cr³⁺, Fe³⁺ and Sn⁴⁺ are totally adsorbed on both the materials in demineralised water while a decrease in K_d value with increase in concentration of two surfactants is reported. On the basis of K_d values for metal ions, thirteen binary separations and five ternary separations on Ti(IV) tungstosilicate and thirteen different binary separations and four different ternary separations on Ti(IV) tungstophosphate have been achieved. Separation of methylamine from ethylamine has been done by GC on a column packed with Ti(IV) tungstophosphate.

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1. Introduction

Since the classical work of Amphlet, numerous inorganic ion exchangers have been synthesised under different conditions of synthesis and their properties studied [1]. The different types of inorganic ion exchanger and their applications in diverse fields are documented in a book by Clearfield [2]. Amorphous and crystalline forms of tetravalent metal acid salts, generally called single salts, with the general formula M(IV) (HXO₄)₂·nH₂O [where M represents Zr(IV), Ti(IV), Sn(IV) etc. and X represents P, W, Si, Mo, Se, As, etc.] have been studied.

Ti(IV)-based ion exchangers are known to be stable chemically and thermally in a comparative study under identical conditions of synthesis [3]. Ti(IV) tungstate (TiW) and its ion-exchange properties have been described previously [4]. An unusual and interesting feature of TiW is the negligible adsorption of tetravalent ions such as Fe³⁺, Al³⁺ and In³⁺ as compared to zirconium tungstate (ZrW), uranium tungstate (UW) and stannic tungstate (SnW), which show complete adsorption [5]. New phases of amorphous Ti(IV) tungstate with good ion-exchange properties have been recently reported [6]. Silicates of Ti(IV) are shown to have porous properties and are being used as molecular sieves [7]. A rapid method for the synthesis of Ti(IV) silicate ETS-10 has been reported which shows the use of TiCl₄ as

*Corresponding author.

E-mail address: siddiqizm@lycos.com (Z.M. Siddiqi).

the source of Ti(IV), produces highly crystalline and pure samples [8]. A semicrystalline potassium titanium silicate has been prepared under mild hydrothermal conditions [9]. Ti(IV) phosphates are probably the most widely studied materials amongst the Ti(IV)-based ion exchangers. Two new well crystalline phases of α -titanium phosphates with layered structures have been reported [10]. Lamellar α -titanium phosphate was studied for hydrogen–lithium and hydrogen–cesium ion exchange [11,12]. A new 2-D Ti(IV) phosphate $[\text{H}_3\text{NC}_2\text{H}_4\text{NH}_2]\text{TiOPO}_4$ has been prepared under solvothermal conditions [13]. The intercalation of octadecyltrimethylammonium ion into γ -titanium has been investigated. These host matrices exchange cationic surfactants to give organo inorganic composite materials, which may be used in heterogeneous catalysis [14]. A fibrous material $\text{Ti-M}_{0.5}\text{H}_{0.5}\text{TiOPO}_4$ ($\text{M}=\text{Na}, \text{K}$) has been synthesised recently [15]. A recent study reports the synthesis of spherically granular Ti(IV) phosphate via the gel method and characterisation of its ion-exchange properties [16].

Several studies show that mixed salts have better ion-exchange capacity, thermal and chemical stability as compared to single salts. These mixed salts may have tetravalent metals such as Zr(IV), Sn(IV), Ti(IV) etc. in combination with any two anions from W, P, Mo, Si, V etc. These mixed salts are called double salts. Ti(IV) vanadophosphate, a mixed type polybasic acid exchanger showed high resistance towards chemical attack, heat treatment and ionizing radiations and possess a good regeneration power. Nine representative binary separations of metal ions have been achieved on the column of Ti(IV) vanadophosphate [17]. Ti(IV) tungstoarsenate, Ti(IV) phosphosilicate and Ti(IV) molybdophosphate have been studied previously [18–20]. An amorphous form of Ti(IV) tungstophosphate has been prepared and studied for limited exchange properties [21]. Other titanium containing ion exchangers are Zr(IV)–Ti(IV) phosphate and Ti(IV)–Zr(IV) phosphate [22–24].

Thin-layer chromatography of important α -amino acids in aqueous and mixed solvent systems has been performed on stannic tungstate and stannic(IV) selenoarsenate [25,26]. These studies show promising future utilisation of inorganic ion-exchange

materials for separation of organic molecules such as amines [27]. A fused-silica column was used for determination of very volatile amines by gas–solid chromatography [28]. The work reported here was stimulated by the following considerations;

1. The heteropolybasic acid salts are better ion exchangers than the corresponding single salts.
2. Ti(IV)-based exchangers are less studied as compared to zirconium and tin-based ion exchangers.
3. Ti(IV) tungstophosphate was not studied in the crystalline phase while Ti(IV) tungstosilicate has not been studied previously.
4. Inorganic ion exchangers were to be utilised more extensively for the separation of heavy metals and organic molecules in aqueous medium.
5. Gas–solid chromatography for amine has not been attempted utilizing a synthetic inorganic ion exchanger.
6. The inorganic ion exchanger may be utilised for separation of organic species by techniques (such as GC and HPLC) other than simple gravitational column chromatography.

2. Experimental

2.1. Reagents

Titanium(IV) chloride, tungstosilicic acid and tungstophosphoric acid were from Merck and of analytical reagent grade.

2.2. Apparatus

An ECIL atomic absorption spectrophotometry (AAS system) (model AAS 4129) and a Perkin-Elmer AAS (model 3100) system for the analysis of metals, an ECIL UV–Vis spectrophotometer (model UV 5704) for UV–Vis measurement, a Perkin-Elmer IR spectrophotometer for IR analysis, a Philips (The Netherlands) (model PW 1140/90) for X-ray diffraction, a LEO, UK (model VP 435) for scanning electron microscopy (SEM) and a Stanton Red Croft (UK) (model STA 780) for thermogravimetric analysis (TGA)/differential thermogravimetry (DTG)/differential thermal analysis (DTA) were used.

2.3. Syntheses

2.3.1. Titanium(IV) tungstosilicate (TiWSi)

This compound was prepared by adding a 0.1 M aqueous solution of tungstosilicic acid dropwise with constant stirring to an alcoholic solution of 0.1 M titanium(IV) chloride in a 1:1 molar proportion. After complete addition of the tungstosilicic acid, the pH was adjusted to 0–1 by the addition of 0.1 M HNO₃. The solution along with the precipitates, was stirred for 1 h. This mixture was stored overnight, then the precipitates were filtered, washed with distilled water and dried at 40 °C (overnight) in an oven. The product yield was found to be 80%. The material was converted to the H⁺ form by treating it with 0.1 M HNO₃ for 24 h. After washing with distilled water, excess acid was removed and finally, the material was dried at 40 °C in an oven.

2.3.2. Titanium(IV) tungstophosphate (TiWP)

This compound was prepared by adding a 0.1 M aqueous solution of tungstophosphoric acid dropwise with constant stirring to an alcoholic solution of 0.1 M titanium(IV) chloride in 1:1 molar proportion. The pH was adjusted to 0–1 by the addition of 0.1 M HNO₃ after complete addition of tungstophosphoric acid. The subsequent steps followed the procedure described in Section 2.3.1.

2.4. Ion-exchange capacity

A 1-g (dry mass) amount of TiWSi and TiWP in the H⁺ form was placed in two different glass columns having glass wool at the base. A 0.1 M KCl solution was passed slowly through these inorganic ion-exchange columns by adjusting the effluent to a rate of 20 drops/min. The effluent was carefully collected in a 250-ml conical flask. The complete replacement of H⁺ from the ion exchanger by the K⁺ of KCl was checked by pH meter. The collected acid was titrated with standard KOH, using phenolphthalein as indicator.

2.5. pH titration

The method used by Topp and Pepper was utilised for pH titration using a KCl–KOH system [29]. For

the purpose, 0.5 g (dry mass) of ion exchanger was treated with 50 ml of solution.

2.6. Chemical stability

The chemical stabilities of TiWSi and TiWP were assessed in several mineral acids, such as HCl, HNO₃, H₂SO₄ and bases, such as NaOH, KOH and organic solvents such as acetone and benzene. A 500-mg (dry mass) amount of each inorganic ion exchanger was placed in 50 ml of the solvent of interest and kept for 24 h with continuous shaking at room temperature. The metal ions released from the ion exchangers were analysed by AAS.

2.7. Thermal stability

The effect of heating on the ion-exchange capacity was studied by heating TiWSi and TiWP at various temperatures in range of 40–200 °C for 2 h each in a muffle furnace and then finding the ion-exchange capacity as described in Section 2.4.

2.8. Chemical composition

A 0.5-g (dry mass) amount of sample was dissolved in 15 ml hot concentrated mixture of three acids (16 M HNO₃, 18 M H₂SO₄, 11.6 M HClO₄, in volume ratio of 10:1:4). The solution was cooled and diluted. The metals were determined by AAS while other components were determined by titration or spectrophotometry using the procedure given in the literature [30].

2.9. IR analysis

For the quantitative IR analysis of sample TiWSi and TiWP, 10 mg (dry mass) of each material (H⁺ form) was separately taken at 40 °C. The ion-exchange material was then thoroughly mixed with 100 mg (dry mass) of KBr and ground to a very fine powder. A transparent disc was formed by applying a pressure of 80 000 p.s.i. (1 p.s.i. = 6894.76 Pa) in a moisture-free atmosphere. The transparent disc so formed contained 50–100 µg of the ion-exchange material. The IR absorption pattern was recorded between 200 and 4000 cm⁻¹.

2.10. Thermal analysis

The thermal analysis was performed with TiWSi and TiWP samples in H⁺ form. A 20-mg (dry mass) amount of each material was analysed for TGA, DTG, DTA with sample holder made up of Al₂O₃ in a atmosphere of N₂ and O₂ at a flow-rate of 50 ml/min. The heating rate and chart speed were maintained at 10 °C/min and 20 cm/h, respectively. Each analysis was done by heating the samples up to 1200 °C with Al₂O₃ as reference material.

2.11. X-ray analysis

For X-ray diffraction analysis manganese filtered CuKα radiations (λ = 0.1542 nm) at 298 K were used. The instrument was equipped with graphite monochromator and operating at 40 kV and 30 mA. The crystallinities of TiWSi and TiWP were ascertained by comparing the intensity of different peaks with the most intense peak at (25–26°) 2θ as strong (100%) peak. The study was done between 10 and 125° 2θ values with step size 0.05.

2.12. SEM analysis

Electron micrographs were recorded for TiWSi and TiWP by a scanning electron microscope operating at 15 kV. The details are shown in the SEM photographs.

2.13. Distribution studies

Distribution coefficients (K_d) for different metal ions such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺, Mo²⁺, Cd²⁺, Sn⁴⁺, Sb²⁺, Pb²⁺, Bi³⁺, Cr³⁺, Hg²⁺, As³⁺ and Fe³⁺ were determined in aqueous solutions by the batch process. K_d values of metal ions were also determined by using different concentrations of two surfactants, Triton-100 or sodium lauryl sulphate (SDS) as solvent. The K_d values for a few representative amines (*pri.*, *sec.*- and *tert.*-aliphatic amine) in water were also attempted.

For the studies, 0.5 g (dry mass) TiWSi or TiWP in H⁺ form (mesh size 50–100 μm) were put into flasks, each containing metal ion (concentration

range 0.01–0.1 M) or aliphatic amine (concentration; 0.1 M) solution. These solution mixtures were continuously shaken at 25±2 °C for up to 24 h. Blank solutions were prepared without ion exchanger, having the same concentration of metal ions or amines. This solution was treated in the same way as above. The solutions were then filtered and metal ions and amines were determined using AAS and UV-Vis. Spectrophotometry (with 2,4-dinitrofluorobenzene as coloring reagent) [30]. The distribution coefficients of different metal ions in different concentrations of surfactant were also determined by the same procedure. The K_d values were determined from formula:

$$K_d = \frac{(I-F)V}{F \times W} \text{ ml/g}$$

where I is the initial amount of metal ion in solution, F is the final amount of metal ion in solution, V is the initial volume of metal ion taken for analysis and W is the initial dry mass of ion-exchanger taken for analysis (0.5 g).

2.14. Separations

2.14.1. Binary separations of metal ions

A 1-g amount (dry mass) of TiWSi or TiWP in H⁺ form (mesh size 50–100 μm) was placed in glass column of inner diameter 1.1 cm with glass wool support. A mixture of the two metal ions (Tables 4 and 5) to be separated was then loaded by passing the mixture through the column at slow rate (maintaining a flow-rate of 20 drops/min) and recycled at least three times. The column was washed with distilled water so that the metal ions, which were not exchanged, could be removed. The metal ions adsorbed on the exchanger were then eluted with different concentrations of HNO₃ (0.1, 0.5, 1.0 and 1.5 M) after considering the K_d values. The flow-rate of effluent was maintained at 1 ml/min until the metal ions were completely eluted out of the column. The effluents were collected in 10-ml fractions and determined by AAS. Keeping the detection limit of particular metal by AAS in mind, the metal ion solutions were either concentrated or diluted as required so as to ensure detection.

2.14.2. Tertiary separations of metal ions

The same procedure was employed as in binary separations but in place of mixtures of two metal ions, three metal ions were passed through TiWSi and TiWP.

2.14.3. Binary separation of aliphatic amines

On the basis of K_d values two binary separations of amines were attempted on 1 g (dry mass) of TiWP as detailed in 2.14.1. The mixture of two different amines (methylamine + dimethylamine and methylamine + ethylamine) instead of the mixture of two metal ions, were loaded on the columns of TiWP. It was observed that the TiWP was decomposed after putting the 0.1 M solutions of two amines. The amount of unadsorbed amine was determined spectrophotometrically. The separation of methylamine from ethylamine was also attempted by GC using TiWP as column material. For that a steel column (1.75 m × 3.6 mm) was packed with TiWP (mesh size: 50–100 μm). After conditioning the column for 30 min at 100 °C, the aqueous mixture of (1 μl) of 0.1 M methylamine and 0.1 M dimethylamine was injected. The gas–solid chromatography was done with N_2 as carrier gas, isothermally at 75 °C with a flame ionisation detection system (fuel: hydrogen at 30 ml/min; oxidant: oxygen at 300 ml/min; injector temperature: 120 °C; detector temperature: 120 °C).

3. Results and discussion:

Table 1 shows that TiWP has a higher ion-exchange capacity than TiWSi under identical condition of synthesis (0.80 and 0.44 mequiv./g, respectively for K^+). An increase in the ion-exchange capacity is observed for TiWSi when this ion-ex-

changer in K^+ form is used for Ca^{2+} (the capacity is found to be 0.60 mequiv./g for Ca^{2+}). This is probably due to the strong affinity of silicate for the hydrogen ions. There was a remarkable increase in the ion-exchange capacity for TiWP (0.80 mequiv./g) as compared to Ti(IV) tungstate (0.58 mequiv./g) prepared under almost similar conditions [3]. It is observed from the pH titration curve that both the materials have a monofunctional ion-exchange characteristic.

The chemical stability studies (Table 2), in general, show that TiWSi and TiWP are highly stable up to 1 M concentrations of acids as well as for a few organic molecules, as has been cited in literature for Ti(IV) tungstate [3]. However, in basic media and in amine solutions above the 0.1 M concentration levels, these materials should not be used as they start decomposing. This is due to the hydrolysis of these exchange materials at the higher pH values. TiWSi is found to be more chemically stable than TiWP. However the ion exchangers synthesised as above, behave like strongly acidic cation exchangers, which agrees from the findings presented for other titanium(IV) based ion exchangers [3]. Hydrus metal oxides are known to be thermodynamically metastable and liable to lose their ion-exchange capacities at high temperature. Even binary hydrus metal oxides such as $\text{Si}^{4+}\text{--Ti}^{4+}$ and $\text{Ti}^{4+}\text{--Zr}^{4+}$ hydrus oxides, show such behaviours [31]. But as shown in Table 2, some ion-exchange capacity is observed even after heating these two ion-exchange materials up to 200 °C (although the decrease in mequiv. are 58% for TiWSi and 80% for TiWP). It is inferred that TiWSi and TiWP are thermally better than hydrus Ti(IV)–Si(IV) oxides and hydrus Ti(IV)–Zr(IV) oxides as these materials retain some ion-exchange capacity at 200 °C [31,32]. TiWSi is more stable than TiWP as the loss of ion-exchange capacity after heating exchanger up to 100 and 200 °C have been reported only 27 and 58% for TiWSi while 75 and 80% for TiWP.

The IR spectra of TiWSi and TiWP show three ranges of bands common to both materials.. The asymmetric absorption broad band between 3500 and 3000 cm^{-1} is attributed to water molecules and OH groups while a sharper peak in the region of 1700–1500 cm^{-1} with a maximum at 1650 cm^{-1} is a characteristic of interstitial water molecules. The

Table 1
Ion-exchange capacities after heating the materials at different temperatures

Temperature (°C)	TiWSi (mequiv./g)	TiWP (mequiv./g)
40	0.44	0.80
75	0.40	0.26
100	0.32	0.20
200	0.18	0.17

Table 2
Chemical stability of TiWSi and TiWP

Sr. no.	Solvent	Ti released (mg/l)	W released (mg/l)	Si released (mg/l)	PO ₄ ³⁻ released (mg/l)
1	4 M H ₂ SO ₄	2.35	18.54	13.20	20.20
2	2 M H ₂ SO ₄	1.98	2.24	5.4	4.20
3	1 M H ₂ SO ₄	0.70	0.00	0.00	0.18
4	4 M HCl	1.30	6.20	0.28	1.80
5	2 M HCl	0.56	0.66	0.14	1.56
6	1 M HCl	0.00	0.00	0.00	0.16
7	4 M HNO ₃	0.00	2.80	0.25	1.20
8	2 M HNO ₃	0.00	0.00	0.12	0.84
9	1 M HNO ₃	0.00	0.00	0.00	0.02
10	1 M NaOH	Dispersed	1480	28.24	1275
11	0.1 M NaOH	Dispersed	350	0.18	10.80
12	1 M KOH	Dispersed	1235	23.52	1126
13	0.1 M KOH	Dispersed	566	0.15	9.54
14	DMW	0.00	0.00	0.00	0.00

DMW, demineralised water.

presence of several low- and mid-intensity bands in the region of 1100–250 cm⁻¹ could be connected with metal–oxygen bonds. The bands at 1200 and 1000 cm⁻¹ may be assigned to symmetric and antisymmetric stretching of the P–O bond in PO₃ groups in the IR spectra of TiWP while the band at 900 cm⁻¹ may be due to Si–O stretching vibrations in TiWSi [33,34].

The thermal analysis curves show that TiWSi and TiWP contain adsorbed water.

Table 3 shows the X-ray diffraction patterns for TiWSi and TiWP. Both the materials are found to be crystalline in nature, which may be due to the method of preparation adopted. Earlier studies on Ti(IV) tungstate, Ti(IV) silicate and Ti(IV) phosphate show that the majority of these samples are

Table 3
X-ray data for TiWSi and TiWP

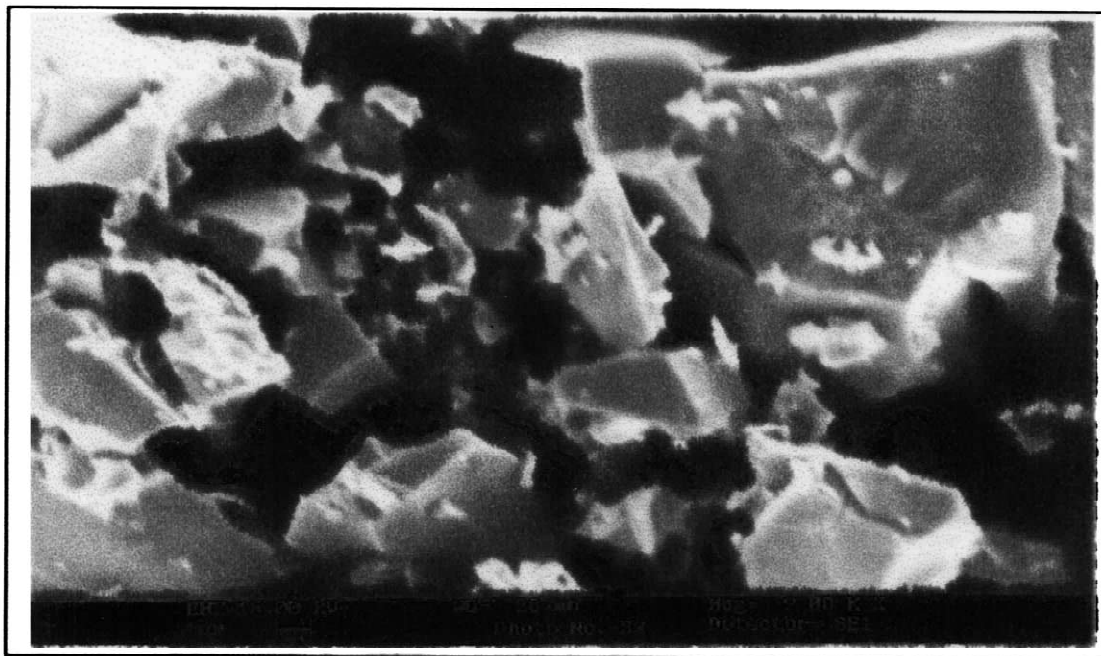
Sr. no.	TiWSi			TiWP		
	θ	d (Å)	Intensity	θ	d (Å)	Intensity
1	12.75	3.50	S	12.75	3.50	S
2	19.13	2.357	M	17.30	2.59	VW
3	21.05	2.147	M	19.00	2.37	M
4	21.50	2.106	M	23.50	1.937	M
5	27.52	1.687	M	24.00	1.899	M
6	31.25	1.488	W	27.25	1.687	M
7	–	–	–	31.25	1.488	W

S, sharp; M, medium; W, weak; VW, very weak.

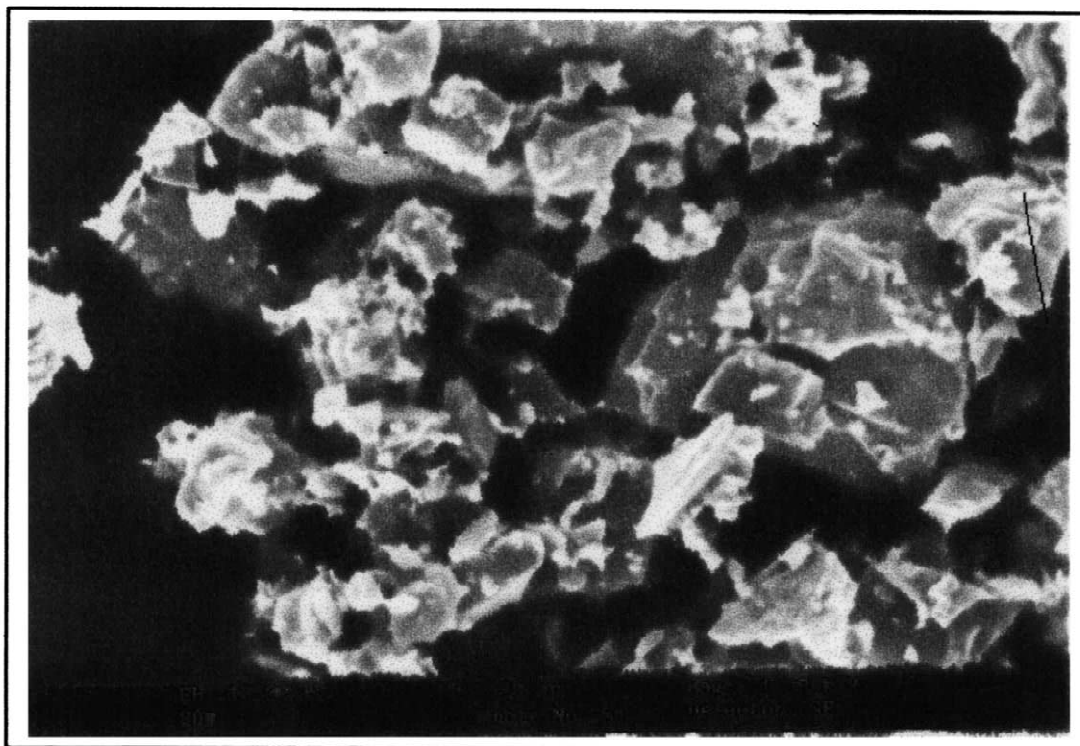
amorphous, except one sample of Ti(IV) phosphate [3,35,36]. The present crystalline samples show reversibility, stability and rigidity in structure so that mechanism of ion-exchange process is more easily understandable with such materials. Therefore the syntheses of the crystalline form of TiWSi and TiWP have definite advantage (in terms of reversibility, stability and rigidity in structure, understanding mechanism) over amorphous ion-exchange, as ion-exchange studies could be done in a better way.

Fig. 1 shows the surface properties of TiWSi and TiWP at different magnifications. Both materials have irregular particle shapes with narrow pore size distribution and enormous ranges of particle size, which shows that the precipitated materials are not suitable for HPLC or packed column in its present form. Therefore synthesizing these materials in granular form with a spherical shape may be attempted as recently done in synthesizing titanium tungstate and sodium aluminophosphate silicate in spherically granulated forms via the gel method [37].

Table 4 shows the K_d values. When compared with the K_d value of different metal ions on titanium tungstate, it has been observed that the K_d of all metal ions show higher values when TiWSi and TiWP have been used. Fe³⁺ is adsorbed totally on TiWSi and TiWP in accordance with the behaviours of other ion-exchangers reported earlier. This is a marked reversal as Ti(IV) tungstate is reported to



(A)



(B)

Fig. 1. SEM photograph for (A) TiWSi (2080 \times) (B) TiWP (1980 \times).

Table 4
 K_d values of different metal ions for TiWSi and TiWP at room temperature (batch process)

Sr. no.	Metal ion	TiWSi									TiWP								
		H ₂ O	Triton X-100 (mg/50 ml)				SDS (mg/50 ml)				H ₂ O	Triton X-100 (mg/50 ml)				SDS (mg/50 ml)			
			106	212	318	424	10	20	30	40		106	212	318	424	10	20	30	40
1	Mg ²⁺	52	312	308	236	210	401	321	205	205	113	110	96	83	43	105	104	75	34
2	Ca ²⁺	15	806	715	613	215	80	32	14	6	13	10	8	5	4	12	10	10	6
3	Cr ³⁺	TA	124	130	142	155	130	134	137	138	TA	314	324	326	401	118	113	54	4
4	Mn ²⁺	51	38	29	24	17	36	27	26	20	150	128	97	86	50	114	82	65	32
5	Fe ³⁺	TA	TA	TA	TA	TA	TA	TA	TA	TA	TA	1386	2236	TA	TA	1637	TA	TA	TA
6	Co ²⁺	39	266	272	288	285	209	250	717	TA	314	TA	TA	TA	TA	816	1883	TA	1642
7	Ni ²⁺	65	68	81	91	102	61	64	84	101	1162	1595	1736	1867	1880	1180	1300	1430	1550
8	Zn ²⁺	33	27	23	15	8	24	21	18	13	97	894	830	850	471	115	112	114	112
9	As ²⁺	422	–	–	–	–	–	–	–	–	1066	–	–	–	–	–	–	–	–
10	Mo ²⁺	3049	378	122	99	92	132	116	104	94	116	112	92	84	85	93	92	97	83
11	Cd ²⁺	789	638	3280	TA	TA	1450	1760	1850	TA	1809	1800	1825	1980	TA	1606	1750	1950	TA
12	Sn ⁴⁺	TA	–	–	–	–	–	–	–	–	TA	–	–	–	–	–	–	–	–
13	Sb ²⁺	1352	644	3436	TA	TA	294	2105	4729	TA	2650	1135	1020	886	983	2523	2112	1934	1230
14	Hg ²⁺	400	–	–	–	–	–	–	–	–	300	–	–	–	–	–	–	–	–
15	Pb ²⁺	500	TA	TA	TA	TA	TA	TA	TA	TA	1567	TA	TA	TA	TA	TA	TA	TA	TA
16	Bi ³⁺	1984	48	173	210	324	202	277	280	320	2074	2180	2195	2205	2260	1250	1402	1618	1905

TA, total adsorption/ion exchange.

Table 5
Separation of metal ions on TiWSi at room temperature

Sr. no.	Metal ions separated	Amount loaded (μg)	Amount found (μg)	Total elution volume (ml)	Eluent used ($M \text{ HNO}_3$)
1	Cd^{2+}	9500	9400	80	0.1
	Pb^{2+}	15500	11 200	90	0.5
2	Ni^{2+}	4100	4100	70	0.1
	Bi^{3+}	15 000	14 000	90	0.5
3	Mg^{2+}	6800	6700	50	0.1
	Pb^{2+}	10 000	10 000	120	0.5
4	Mg^{2+}	8000	7900	60	0.1
	Mo^{2+}	3500	3500	340	1.5
5	Pb^{2+}	10 200	10 100	160	0.5
	Mo^{2+}	3700	3700	190	1.5
6	Mg^{2+}	3000	3000	50	0.1
	Bi^{3+}	15 000	14 500	260	1
7	Pb^{2+}	22 000	21 800	200	0.5
	Bi^{3+}	94 500	9400	90	1
8	Mn^{2+}	11 000	11 000	90	0.1
	Pb^{2+}	15 100	15 100	100	0.5
9	Zn^{2+}	1800	1800	40	0.1
	Bi^{3+}	7000	6900	220	1
10	Mn^{2+}	14 500	14 400	90	0.1
	Mo^{2+}	3000	3000	210	1.5
11	Cd^{2+}	2300	2200	90	0.1
	Bi^{3+}	3900	3900	160	1
12	Mn^{2+}	3800	3800	70	0.1
	Bi^{3+}	4800	4800	220	1
13	Ca^{2+}	5400	5300	40	0.1
	Bi^{3+}	7000	6900	240	1
14	Mg^{2+}	5600	5600	50	0.1
	Bi^{3+}	14 000	13 600	140	1
	Mo^{2+}	4600	4600	60	1.5
15	Cr^{3+}	2200	2200	50	0.1
	Pb^{2+}	16 000	15 700	240	0.5
	Bi^{3+}	22 000	21 000	100	1
16	Mn^{2+}	1500	1300	30	0.1
	Bi^{3+}	11 000	10 600	180	1
	Mo^{2+}	3500	3000	90	1.5
17	Zn^{2+}	1200	1500	30	0.1
	Pb^{2+}	12 000	11 100	170	0.5
	Bi^{3+}	15 000	13 000	90	1
18	Cd^{2+}	1000	700	30	0.1
	Pb^{2+}	8300	8200	200	0.5
	Bi^{3+}	16 000	15 100	290	1

Table 6
Separation of metal ions on TiWP at room temperature

Sr. no.	Metal ions separated	Amount loaded (μg)	Amount found (μg)	Total elution volume (ml)	Eluent used
1	Hg ²⁺	5000	4100	80	0.1
	Pb ²⁺	2500	2300	90	0.5
2	Ca ²⁺	40 000	30 500	80	0.1
	Bi ³⁺	6000	5700	170	1
3	Cd ²⁺	2000	1800	60	0.1
	Bi ³⁺	10 000	9500	240	1
4	Zn ²⁺	11 000	10 600	80	0.1
	Bi ³⁺	7000	6900	170	1
5	Mg ²⁺	10 800	10 800	90	0.1
	Pb ²⁺	15 000	14 000	80	0.5
6	Ca ²⁺	15 000	14 200	70	0.1
	Cd ²⁺	4000	3300	90	0.5
7	Mg ²⁺	12 000	10 600	100	0.1
	Cr ³⁺	3500	3200	40	0.5
8	Zn ²⁺	7300	7300	70	0.1
	Ni ²⁺	5500	5500	130	0.5
9	Mg ²⁺	13 000	12 700	100	0.1
	Cd ²⁺	3500	3300	50	0.5
10	Mo ²⁺	5400	5400	100	0.1
	Pb ²⁺	7100	7100	100	0.5
11	Mg ²⁺	2500	2500	40	0.1
	Bi ³⁺	2500	2400	200	1
12	Mn ²⁺	2000	1600	50	0.1
	Bi ³⁺	1500	1500	170	1
13	Cr ³⁺	2000	1950	140	0.5
	Bi ³⁺	12 000	12 000	180	1
14	Zn ²⁺	1400	1300	30	0.1
	Ni ²⁺	2800	2750	130	0.5
	Bi ³⁺	5000	4950	110	1
15	Mg ²⁺	1100	1100	40	0.1
	Pb ²⁺	8000	7950	130	0.5
	Bi ³⁺	7000	7000	100	1
16	Zn ²⁺	1000	700	20	0.1
	Cr ³⁺	2500	2500	180	0.5
	Bi ³⁺	2600	2550	80	1
17	Mn ²⁺	3200	3200	100	0.1
	Pb ²⁺	8900	8900	100	0.5
	Bi ³⁺	3500	3300	80	1

have negligible adsorption [3]. High K_d values have been observed for Mo²⁺, Sb²⁺, and Bi³⁺ on TiWSi and Ni²⁺, As³⁺, Cd²⁺, Sb²⁺, Pb²⁺ and Bi³⁺ on TiWP. Fe³⁺, Cr³⁺ and Sn⁴⁺ are totally adsorbed on

TiWSi and TiWP, which may indicate that these metal ions are going to the ion-exchange framework. It has been observed that heavy metals like Pb²⁺, Hg²⁺ and Sb²⁺ have high K_d values as compared to

alkaline earths on both materials—TiWSi and TiWP. Mo^{2+} has an exceptionally high K_d value on TiWSi, which have been utilised for separation. Binary separation of As^{3+} – Hg^{2+} may be attempted on a TiWP column. The effect of concentration of surfactant (Triton X-100 and SDS) on K_d values of metal ions was studied. The K_d values decrease in general with an increase in concentration of both ionic and neutral surfactants, while the reversed order is observed with Cr^{3+} , Ni^{2+} and Bi^{3+} . However Fe^{3+} and Pb^{2+} are totally adsorbed on TiWSi in the presence of the surfactants. The K_d values for all metal ions except Fe^{3+} , Co^{2+} , Cd^{2+} , Sb^{2+} and Pb^{2+} have been reported to decrease with increased concentrations of both surfactants.

Tables 5 and 6 show separations attempted on the ion-exchangers. As a result of high K_d value for Mo^{2+} , Bi^{3+} and Pb^{2+} in aqueous medium on TiWSi, thirteen binary metal separations and five ternary metal separations have been achieved on the TiWSi column. Bi^{3+} has been selectively separated from Ca^{2+} , Cd^{2+} , Mn^{2+} , Zn^{2+} , Pb^{2+} , Mg^{2+} , Ni^{2+} and Pb^{2+} from Mn^{2+} , Mo^{2+} , Mg^{2+} and Cd^{2+} while Mo^{2+} is separated from Mg^{2+} and Mn^{2+} . Similarly high K_d values for Bi^{3+} , Cd^{2+} , Pb^{2+} , Ni^{2+} and Cr^{3+} on TiWP resulted in thirteen binary and four ternary metal ion separations using TiWP as the column material. Bi^{3+} – Ca^{2+} , Bi^{3+} – Cd^{2+} , Bi^{3+} – Zn^{2+} , Bi^{3+} – Cr^{3+} , Bi^{3+} – Mn^{2+} , Bi^{3+} – Mg^{2+} , Cd^{2+} – Ca^{2+} , Cd^{2+} – Mg^{2+} , Pb^{2+} – Mo^{2+} , Pb^{2+} – Mg^{2+} , Mg^{2+} – Cr^{3+} , Zn^{2+} – Ni^{2+} , Hg^{2+} – Pb^{2+} and Mn^{2+} – Pb^{2+} – Bi^{3+} , Zn^{2+} – Cr^{3+} – Bi^{3+} , Mg^{2+} – Pb^{2+} – Bi^{3+} , Zn^{2+} – Ni^{2+} – Bi^{3+} separations have been observed on TiWP. The metal ions which are totally or highly adsorbed on TiWSi and TiWP in water (batch process) show rapid elution (column process) because of HNO_3 used as eluent and continuous removal of effluent. The availability of H^+ in HNO_3 medium facilitates the ion-exchange process between exchanger phase (with metal ions) and mobile phase (with H^+ ions) and continuous removal of effluent (with metal ions) favours the rapid elution of metal ions from the column. A number of these separations may be actually done for practical samples of alloys, minerals and heavy metals/trace metals etc. utilizing these new inorganic ion-exchange materials.

Since both ion-exchange materials are hydrolysed on treatment with 0.1 M solutions of different amines

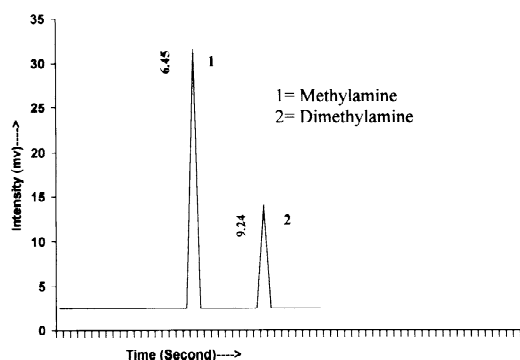


Fig. 2. Separation of methylamine and dimethylamine on TiWP.

in an aqueous medium, it was not possible to determine the reproducible K_d values (batch process). During the separation process it was observed that considerable amounts of the amines were adsorbed or absorbed differentially on TiWP. The separation of methylamine from dimethylamine by GC column packed with TiWP (Fig. 2), was the result of the differential adsorption of two amines. The heavy metals such as Pb^{2+} , Hg^{2+} , Cd^{2+} , Ni^{2+} , Cr^{3+} , Zn^{2+} , Fe^{3+} etc. are dangerous for human health, even if they are present in microlevel quantities. The synthesised ion exchangers (TiWSi and TiWP), are more effective in separating microlevel quantities. Thus these ion-exchangers could be utilised for removal, recovery and separation of metals such as Cd^{2+} – Pb^{2+} , Hg^{2+} – Pb^{2+} etc. in aqueous media. TiWP can also be utilised to separate amines like methylamine and dimethyl amine (known to be environmentally hazardous) by liquid–gas chromatography.

4. Conclusion

Two new heteropolybasic acid salts based on titanium(IV), namely Ti(IV) tungstosilicate (TiWSi) and Ti(IV) tungstophosphate (TiWP) were synthesised in crystalline forms. These ion-exchange materials have better chemical and thermal stabilities compared to Ti(IV) tungstate, Ti(IV) silicate and Ti(IV) phosphate. These materials were utilised for separating heavy metals in aqueous medium and show potential applications in the presence of surfactants. The separation of methylamine from di-

methylamine by GC on a column packed with TiWP shows promise for future utilisation of the material for separation of various aliphatic amines by HPLC and GC, after preparing TiWP in a spherically granulated form by the gel method.

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