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SYNTHESIS OF A POORLY CRYSTALLINE TITANIUM TUNGSTATE

SEPARATION OF Hf^{4+} FROM Zr^{4+} AND OF La^{3+} FROM Ce^{3+} , Pr^{3+} , Nd^{3+} AND Sm^{3+}

MOHSIN QURESHI AND JAI PRAKASH GUPTA

Z. H. College of Engineering and Technology, and Chemistry Department, Aligarh Muslim University, Aligarh, U.P. (India)

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SUMMARY

A poorly crystalline titanium tungstate sample with a Ti:W ratio of 1:1.3 has been synthesised by mixing 0.5 M solutions of titanous chloride and sodium tungstate in the volume ratio 1:1. After precipitation at pH 0, the precipitate obtained was refluxed with its mother liquor for 12 h. A comparison of the ion-exchange properties of the various titanium tungstates shows that as the W:Ti ratio increases, the chemical stability and ion-exchange capacity (at 40° and 100°) also increase until the capacity becomes a maximum at W:Ti = 1.1.

INTRODUCTION

Some studies have been reported earlier^{1,2} on the synthesis and ion-exchange properties of titanium tungstate. It is difficult to say much about its structure until it has crystallised or unless it is crystalline. However, despite persistent efforts, titanium tungstate could not be crystallised, although a poorly crystalline phase was obtained. The present report summarises our results on this sample and correlates its properties with the other titanium tungstates synthesised earlier.

EXPERIMENTAL

Reagents

All the chemicals used were AnalaR grade from B.D.H. as reported earlier^{1,2}.

Apparatus

For IR, differential thermal and thermogravimetric analyses and flame photometry, a Perkin-Elmer IR spectrophotometer, an Aminco thermoanalyser (U.S.A.), and an Aimil flame photometer were used, respectively. Other measurements were carried out as described earlier^{1,2}.

Synthesis of titanium tungstate

3 l of 0.5 *M* titanitic chloride (diluted from a 15 % TiCl_4 solution containing 15 HCl) and 3 l of 0.5 *M* sodium tungstate solution (acidified with 100 ml of concentrated hydrochloric acid) were warmed separately. The titanitic chloride solution was then slowly added to the acidified sodium tungstate solution (volume ratio 1:1). A yellowish gel was formed which was heated to boiling with continuous stirring for 10 h. The mixture was cooled to room temperature and the supernatant liquid (pH 6) was decanted off. The precipitates were filtered under suction and dried at 40° and 80° separately (sample IV). They were immersed in 2 *M* nitric acid for 24 h. Excess of the acid was then removed by washing with demineralized water. The precipitates were then dried again at their respective temperatures.

Properties

Chemical analysis. The titanium and tungsten ratio was found to be 3:4 analysing sample IV as described earlier².

Chemical stability. The purpose of drying the ion-exchange material at 40° and 80° was to confirm that drying affects the stability². 500 mg samples were dissolved in 50 ml of water, nitric acid, hydrochloric acid or formic acid, adopting the earlier method². The results are summarized in Table I. The values of chemical stability used later in Fig. 10 are taken from Table I as 1/2 (amount of Ti dissolved + amount of W dissolved), in order to simplify the figure.

TABLE I

AMOUNT OF TITANIUM AND TUNGSTEN DISSOLVED IN WATER, FORMIC ACID, HYDROCHLORIC ACID AND NITRIC ACID FROM TITANIUM TUNGSTATE (SAMPLE IV) IN MG PER 50 ml

Solvent	Amount of Ti^{4+} dissolved		Amount of W^{6+} dissolved	
	Dried at 40°	Dried at 80°	Dried at 40°	Dried at 80°
Water	0.00	0.00	0.00	0.00
6 <i>M</i> nitric acid	2.05	0.55	0.80	0.40
1 <i>M</i> formic acid	—	0.00	—	0.00
1 <i>M</i> hydrochloric acid	—	0.16	—	0.00

The colour of the ion-exchanger beads was light yellow at the beginning but became very dark after heating for 6 h with 1 *M* HCl or 6 *M* HNO_3 .

Heat treatment. (a) Sample IV was further heated at 200° (Sample C), 250° (Sample D), 460° (Sample E), 600–700° (Sample F) and 800° (Sample G) in a mu furnace for 1 h. (b) Sample IV in the hydrogen, lithium, sodium, potassium, rubidium and caesium forms was subjected to thermogravimetric analysis (TGA) at a heat rate of 6°/min, 200 g of the samples being taken initially for the experiment. The results are shown in Fig. 1. (c) Differential thermal analysis (DTA) of sample IV in the hydrogen, sodium and potassium forms was carried out at the same heat rate as in thermogravimetry. The plots of ΔT versus T are given in Fig. 2.

X-ray studies. X-ray diffraction spectra for sample IV (dried at 40°) and samples C and F, and for sample IV (dried at 80°) in the hydrogen, lithium, sodium and potassium forms were recorded.

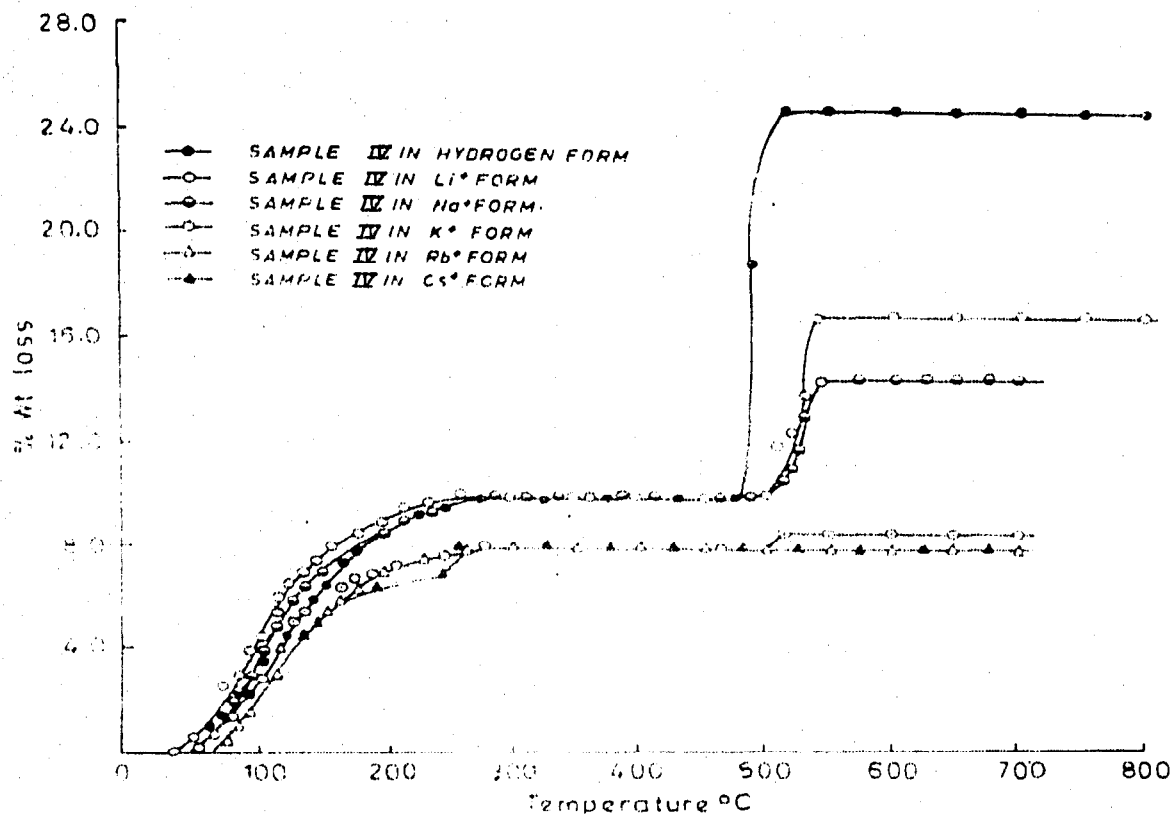


Fig. 1. Thermograms for titanium tungstate.

sium forms, using $\text{Cu-K}\alpha$ radiation with a nickel filter are shown in Fig. 3. The d spacings for sample F as calculated from the spectra are: 6.3203(w), 3.8635(vs), 3.7666(s), 3.6596(s), 3.5309(w), 3.3603(w), 3.1617(m), 2.6961(m), 2.6345(m), 2.4402(w), 2.1841(v.w), 2.1493(v.w), 1.9239(v.w), 1.8863(v.w), 1.8226(w), 1.6407(w), 1.5405(v.w) and 1.4955(v.w) (v = very, s = strong, m = medium and w = weak).

I.R. spectrophotometry. This study was carried out with NaCl discs and Nujol mulls with an NaCl blank disc. The spectrum is shown in Fig. 4.

Ion-exchange capacity. Titanium tungstate shows cation-exchange properties. The apparent ion-exchange capacity of sample IV for alkali metals (Fig. 5) and of samples D (0.25 mequiv./g), E (0.1 mequiv./g) and F (0.0 mequiv./g) for Cs^+ only was determined at pH 5-6 by the earlier method¹.

Ion-exchange potentiometric titrations. pH titrations of sample IV with lithium hydroxide, sodium hydroxide and potassium hydroxide were performed as described earlier². The effect of hydroxyl ions on the pH of the equilibrating solution is shown in Fig. 6.

Distribution studies. K_d values for 23 metal ions on sample IV in water and 0.1 M formic acid were determined by the earlier method¹ (see Fig. 7).

K_d values for some alkali metals on samples I, II, III and IV are shown in Fig. 8. The synthesis and ion-exchange properties of samples I and II (ref. 1) and III (ref. 2) have been described earlier. They have a Ti:W ratio of 2:1, 1:1 and 1:1.1,

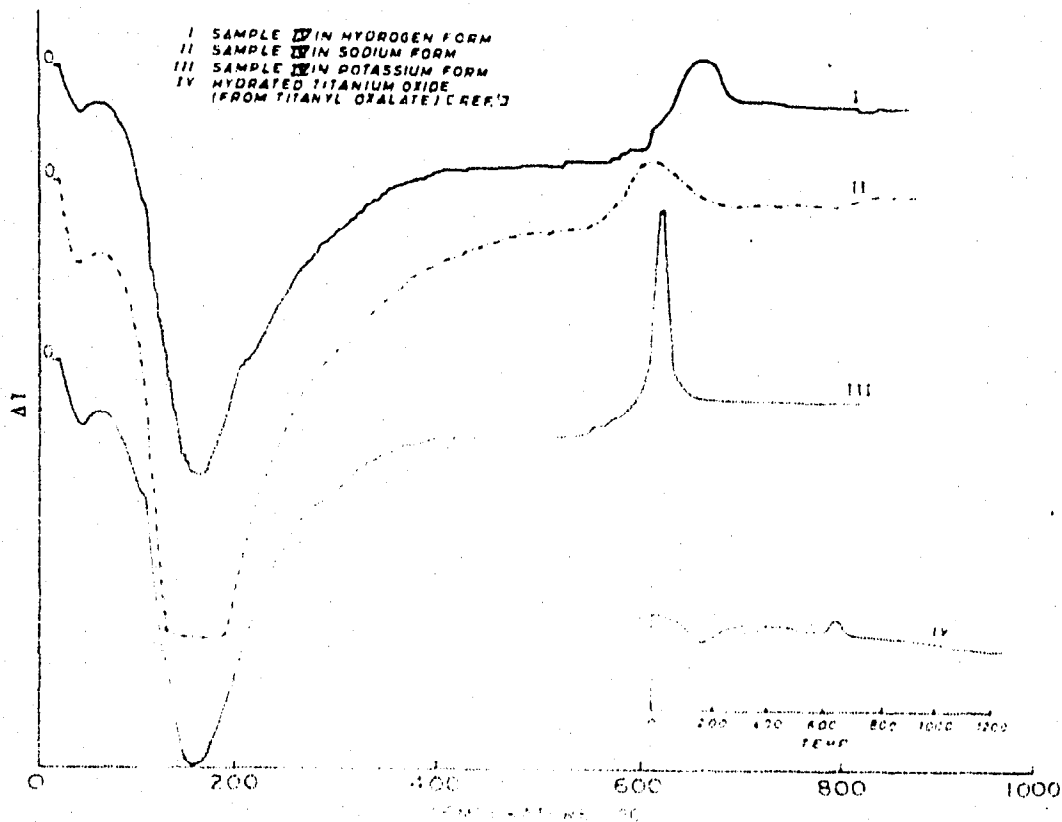


Fig. 2. DTA curves for titanium tungstate.

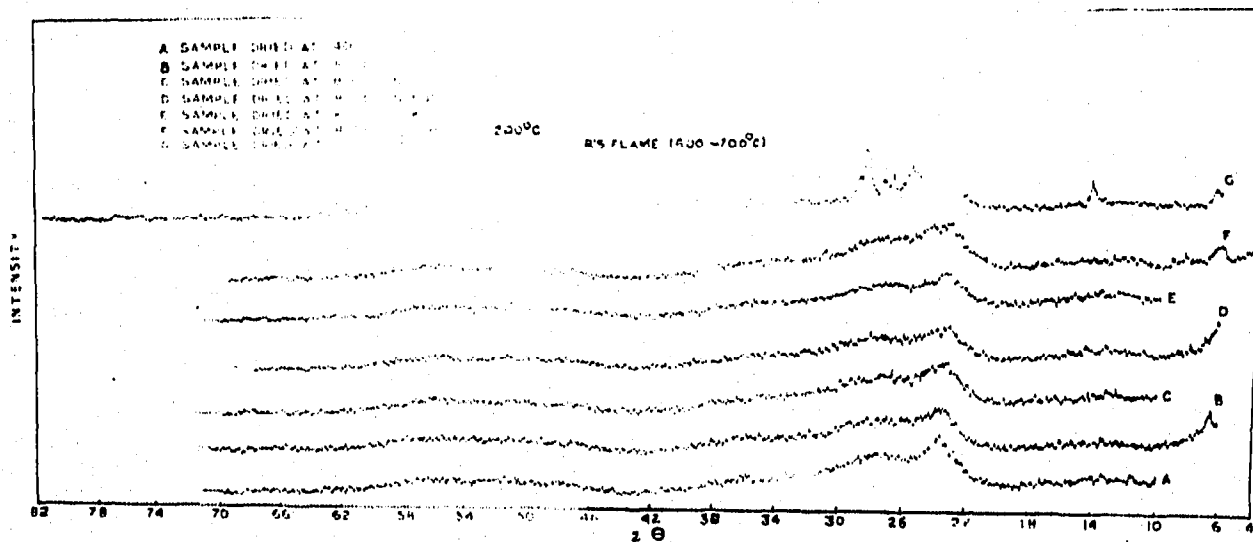


Fig. 3. X-ray diffraction patterns for titanium tungstate.

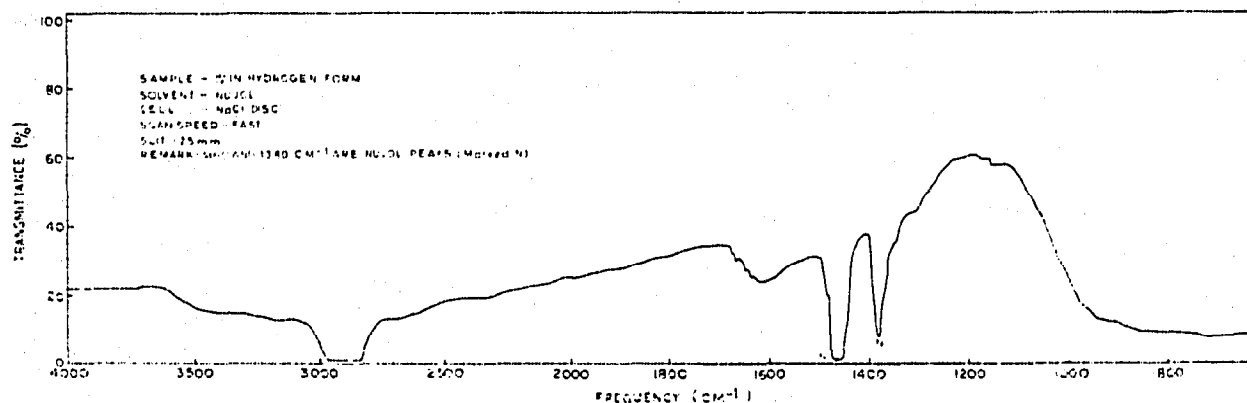


Fig. 4 IR spectrum for titanium tungstate.

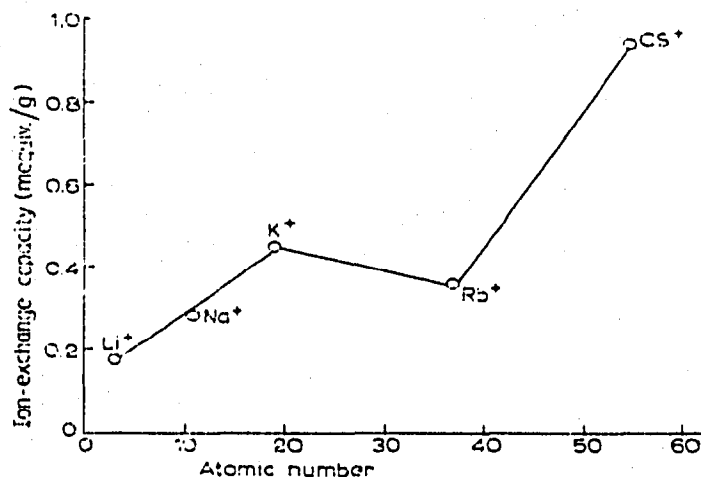


Fig. 5. Plot of apparent ion-exchange capacities of titanium tungstate (sample IV) vs. the atomic numbers of alkali metals.

respectively. Lithium was determined by spectrophotometry⁹ while sodium and potassium were estimated by flame photometry.

Some chemical separations. The following quantitative separations were achieved on the column (I.D. 0.6 cm), using 1 g of sample IV. The column was washed with dilute nitric acid and then with water.

(a) *Separation of Hf⁴⁺ from Zr⁴⁺.* A mixture of Zr⁴⁺ (341 μ g) and Hf⁴⁺ (417.6 μ g) was applied to the column. The effluent was recycled on the column. Hafnium was then eluted with 25 ml of 0.1 M formic acid at a flow rate of 7–8 drops per minute. Hf⁴⁺ was determined volumetrically with EDTA after removing formic acid by evaporation to dryness. Zirconium could not be eluted with 1 N nitric acid or with 4 M ammonium nitrate in 0.5 M nitric acid.

To find out whether or not zirconium was sorbed by ion exchange several conical flasks were taken containing 500 mg of the exchanger beads and 50 ml of zirconium solution containing 0–400 μ g of Zr⁴⁺. After shaking for 6 h, Zr and Ti were determined in the supernatant liquid. Both were found to be absent.

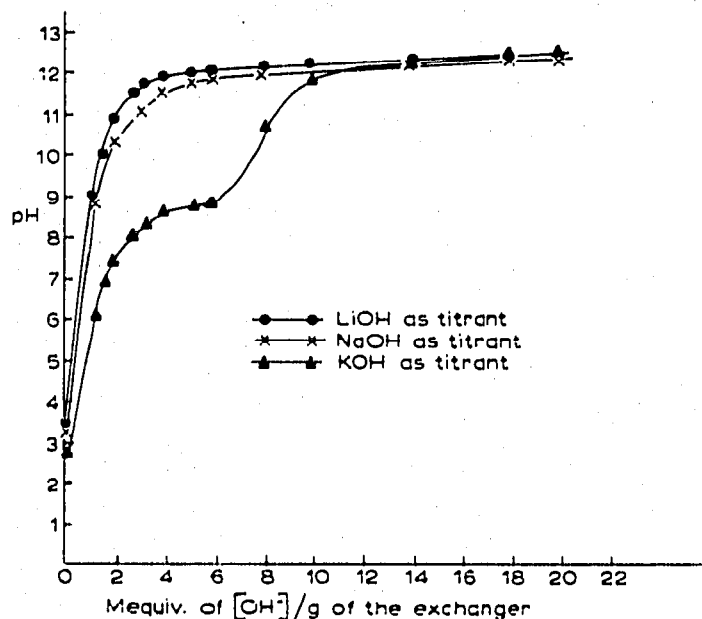


Fig. 6. Ion-exchange potentiometric titration curves for titanium tungstate (sample IV).

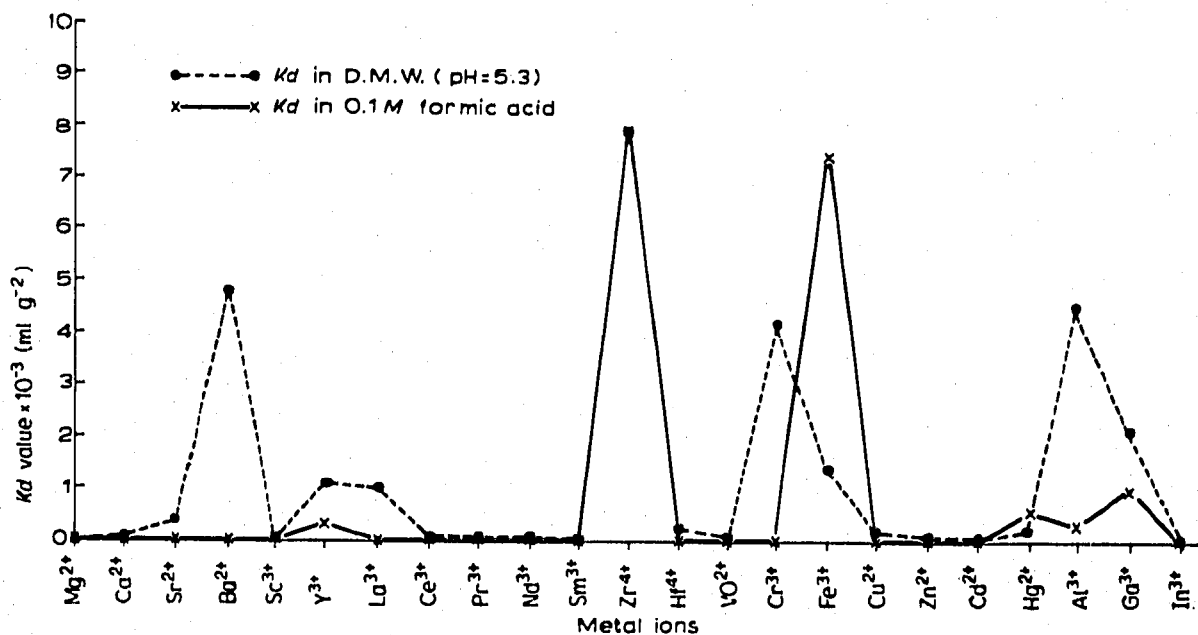


Fig. 7. Distribution coefficients of metal ions on titanium tungstate (sample IV).

(b) Separation of rare earths La-Ce, La-Pr, La-Nd and La-Sm were quantitatively separated on sample IV (Fig. 9). In every case, 248 μg of La were applied while the quantities of Ce, Pr, Nd and Sm applied were 883, 1410, 1442 and 1503 μg , respectively. 0.01% NH_4NO_3 solution was used as eluent for Ce, Pr, Nd and Sm. La was stripped off with 1% HNO_3 (flow rate 7-8 drops per minute).

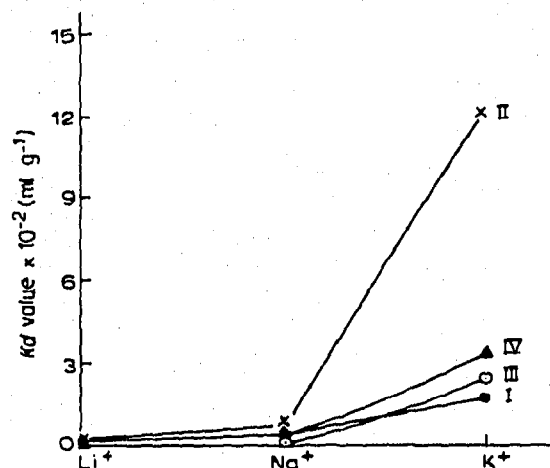


Fig. 8. Adsorption behaviour of Li, Na and K on some samples of titanium tungstate.

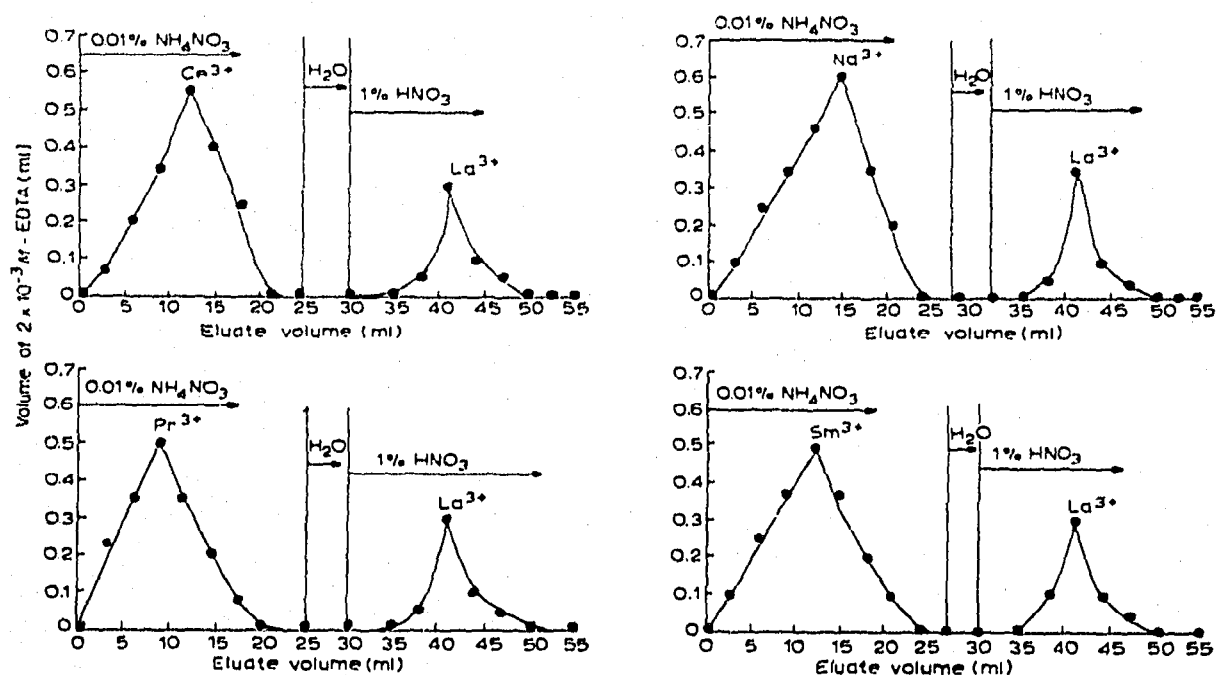


Fig. 9. Elution curves for Ce-La, Pr-La, Nd-La and Sm-La.

RESULTS AND DISCUSSION

The new phase of titanium tungstate has some unusual characteristics. It has the highest W/Ti ratio and is poorly crystalline. All other samples were completely amorphous. The other important points are discussed below.

TGA and DTA

Thermograms for sample IV in the hydrogen, lithium, sodium, potassium and caesium forms are shown in Fig. 1. The increase is sharp up to 160° and becomes

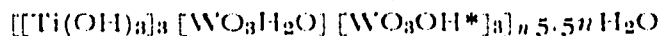
very slow in the temperature range 160–260°. No further weight loss occurs up to 470° (in the case of samples in the potassium, rubidium and caesium forms, the weight loss is constant from 260° to 800°). Between 480° and 510° the weight loss is very sharp for the samples in the hydrogen, lithium and sodium forms. Above 510°, the weight loss becomes constant. This can be explained as follows: we believe that up to 160°, the weight loss is due to the elimination of the interstitial (or free) water, and at higher temperatures (160–480°) condensation of exchangeable hydroxyl groups takes place. Between 480° and 510°, the sharp weight loss is probably due to the condensation of hydroxyl groups attached to titanium. This is confirmed by the fact that the order of the weight loss is $H^+ > Li^+ > Na^+ > K^+ > Rb^+ = Cs^+$ according to the hydrated radii. Above 510°, the constant weight loss is due to the formation of the oxides of titanium and tungsten. The removal of interstitial water at 160–260° is confirmed by the DTA curves (Fig. 2); there is an endothermic change in this temperature range. The exothermic peak in the DTA curves also explains the formation of the oxides between 520° and 700°. A similar DTA curve is also obtained for the hydrated titanium oxide (curve IV in Fig. 2). These structural changes in TGA are supported by X-ray and ion-exchange capacity data: the ion-exchange capacity at 460° is 0.1 mequiv./g for Cs^+ .

X-ray studies

The X-ray patterns do not give quantitative results because the sample is not very crystalline. As the temperature increases, the ion-exchange capacity decreases because of the slow formation of crystalline oxides. Sample F, which shows a number of lines in the X-ray spectrum, is a mixture of oxides of titanium and tungsten, since the d spacings of most of the lines coincide with the patterns of WO_3 (ASTM card No. 5-0363) and TiO_2 (ASTM card No. 3-0380). The formation of oxides at this temperature is also supported by the TGA and DTA results.

IR spectra

There are three peaks in the IR spectrum of titanium tungstate (sample IV) (cf. Fig. 4). The first peak lies between 2800 and 3000 cm^{-1} (maximum at 2900 cm^{-1}), the second occurs between 1500 and 1650 cm^{-1} (maximum at 1620 cm^{-1}), and the third is a broad band which lies between 400 and 800 cm^{-1} . On the basis of the data for hydrated titanium oxide⁴ and sodium tungstate⁵, we can say that the first peak is due to the interstitial water and hydroxyl groups, the second corresponds to the interstitial water only, and the third broad band is due to the metal-oxygen bonds. From the above results and the aqueous chemistry of titanium and tungsten, we can postulate the formula of sample IV as follows:



The water of crystallization was calculated by the method of ALBERTI *et al.*⁶. The exchangeable hydrogen ions are marked with an asterisk.

Ion-exchange capacity and pH titrations

The ion-exchange capacity of sample IV for alkali metals is in the order $Cs > K > Rb > Na > Li$. This may be explained in terms of the hydrated radii of the ions. The ion-exchange potentiometric titrations show that ion exchange in-

creases with increase in the pH of the solution. The ion-exchange capacity as calculated from these titrations is the same as that obtained experimentally.

Distribution studies

The adsorption behaviour of alkali metals and alkaline earths depends on the hydrated radii of the cations. Thus the smaller the radius, the larger is the Kd value in the order $K^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The decrease in the Kd values in 0.1 M formic acid may be due to the fact that in acidic medium (or low pH), the exchange and adsorption decreases⁷. This is further confirmed by the ion-exchange potentiometric titrations (Fig. 6).

Separation potential

This ion exchanger is very useful for the separation of Hf^{4+} from Zr^{4+} . Zr^{4+} is irreversibly adsorbed. However, the uptake of Zr^{4+} is not followed by the release of titanium and it appears that zirconium-titanium tungstate is formed. Owing to a large difference between the Kd values of La^{3+} and those of Ce^{3+} , Pr^{3+} , Nd^{3+} and Sm^{3+} , the separation of lanthanum from these metals has been achieved (Fig. 9). The other possible separations are Ba^{2+} from Sr^{2+} , Ca^{2+} and Mg^{2+} , Sc^{3+} from Y^{3+} , Cr^{3+} from VO^{2+} , Fe^{3+} and Cu^{2+} and Al^{3+} from Ga^{3+} , In^{3+} and Hg^{2+} .

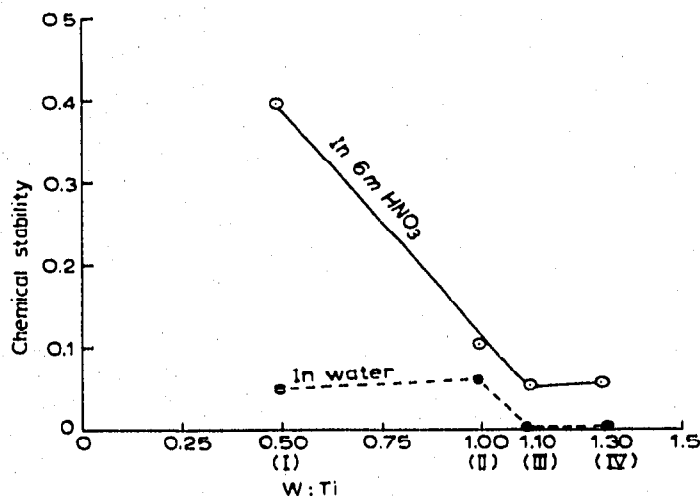


Fig. 10. Plot of chemical stability in water and 6 M HNO_3 versus W:Ti ratio of titanium tungstate.

It is useful to compare the various titanium tungstate samples synthesized in our laboratories. Such a comparison illustrates the effect of composition on the ion-exchange properties of the inorganic ion exchangers (Figs. 8, 10 and 11). It is clear from Fig. 10 that as the tungsten content increases, the sample becomes more stable in water and in 6 N HNO_3 . The Ti:W ratio also affects considerably the ion-exchange capacity of the sample. At 40° and 100°, the chemically most stable sample has the highest ion-exchange capacity. Above 100°, the sample with the smallest W content has the highest ion-exchange capacity. This may be explained as follows. Up to 100°, the loss in weight is due almost entirely to the removal of water of hydration. Hence there is a net gain in ion-exchange capacity (curves 1 and 2 of Fig. 11). The maxima

in curves 1 and 2 are due to the fact that the ion-exchange capacity depends on the tungsten content of the sample. At 200° and above, condensation of hydroxyl groups begins. The larger the number of hydroxyl groups, the easier is the condensation and hence there is an abrupt fall in the ion-exchange capacity as the W:Ti ratio increases. The W:Ti ratio also affects the Kd values (Fig. 8). Although the order is not affected, there is a considerable difference in the magnitude. Sample II can be very useful for the separation of K^+ from Na^+ and Li^+ .

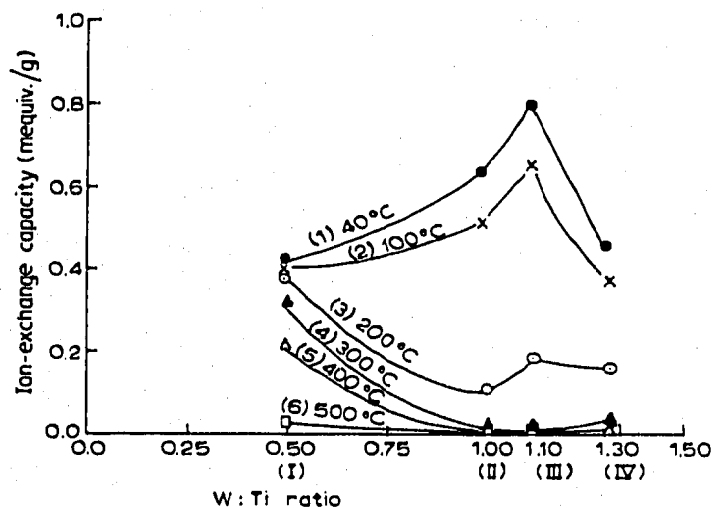


Fig. 11. Ion-exchange capacity as a function of W:Ti ratio.

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