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## NOTE

# Synthesis and Ion-Exchange Properties of Lanthanum Tungstate, A New Inorganic Ion Exchanger

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### Abstract

Amorphous samples of a new inorganic ion exchanger, lanthanum tungstate, have been prepared under varying conditions. The material prepared by mixing 0.05 *M* lanthanum nitrate and 0.05 *M* sodium tungstate in a ratio of 1:2 was studied in detail for its ion-exchange capacity, chemical stability, IR, thermogravimetry, and $K_d$ values. Its columns have been used for the separation of $CD^{2+}$ from $Pd^{2+}$, $Mn^{2+}$, and $Cu^{2+}$, and $Ni^{2+}$ from $Pd^{2+}$.

## INTRODUCTION

During the last few years considerable advances in ion exchange have been in the area of inorganic ion exchangers. New synthetic inorganic ion exchangers have been reported which show high selectivities toward certain elements (*1–5*). Very few studies have been made on lanthanum-based ion exchangers. Lanthanum tellurate has been reported to show ion-exchange properties (*6*). In an earlier paper (*7*) we reported the separation of toxic metals on thin layers of lanthanum tungstate, a new inorganic ion exchanger, but no further studies were made. The present paper describes the synthesis, ion-exchange properties, and analytical applications of lanthanum tungstate.

## EXPERIMENTAL

**Reagents.** All the chemicals were of analytical grade (B.D.H. or E. Merck).

**Apparatus.** The thermogravimetric analysis was performed on a Stanton thermobalance-type 750/770 and x-ray studies were made with a Philips unit. A Perkin-Elmer IR spectrophotometer and a Zeiss Atomic Absorption spectrophotometer were used for IR studies and determinations.

**Synthesis of Lanthanum Tungstate.** Lanthanum tungstate was prepared by mixing sodium tungstate and lanthanum nitrate solutions under the conditions given in Table 1. The pH of the reaction mixture was adjusted by adding either HCl of NaOH. On standing for 24 h, the gel settled. It was then filtered off, washed three times with demineralized water, and dried in an oven at 50°C. The material was converted into the $H^+$ form.

**Ion-Exchange Capacity.** The ion-exchange capacity of each sample was determined by the standard method as before (*8*). Results are given in Table 1.

**Chemical Composition.** 100 mg portions of the ion-exchanger sample were fused with 5 g of $Na_2CO_3$ for an hour at about 1000°C. The fused masses were digested with dilute acid and filtered. Tungsten (*9*) and lanthanum (*10*) were determined in these solutions, and the results are recorded in Table 1.

**Chemical Stability.** All the samples are insoluble in water, alcohol, and

TABLE 1

Synthesis and Properties of Lanthanum Tungstate[a]

| | Conditions of synthesis | | | | Properties | | |
|---|---|---|---|---|---|---|---|
| | Concentration of reagents (*M*) | | Mixing volume ratio | pH | Composition, La:W | Ion exchange capacity meq/g | Color in $H^+$ form |
| Sample | LN | ST | | | | | |
| 1 | 0.1 | 0.1 | 1:1 | 6 | 1:1.40 | 0.71 | WY |
| 2 | 0.1 | 0.1 | 1:2 | 8 | 1:2.20 | 0.72 | WY |
| 3 | 0.1 | 0.1 | 1:2 | 2–3 | 1:2.00 | 0.85 | LY |
| 4 | 0.05 | 0.05 | 1:1 | 6 | 1:2.20 | 0.74 | LY |
| 5 | 0.05 | 0.05 | 1:2 | 7 | 1:2.30 | 0.61 | WY |
| 6 | 0.05 | 0.05 | 1:2 | 2–3 | 1:1.20 | 1.04 | Y |

[a] LN = lanthanum nitrate, ST = sodium tungstate, WY = whitish yellow, LY = light yellow, Y = yellow.

benzene. When heated for 1 h with concentrated $H_2SO_4$, $HNO_3$, $CH_3COOH$, and HCl, none of them was dissolved. They are appreciably soluble in alkalies and ammonia solution. Quantitative studies on the stability of the ion exchanger (Sample 6) in different solvents were made by shaking 500 mg in 50 mL of the solvents for 6 h at 25°C. Lanthanum (*11*) and tungsten (*12*) were determined spectrophotometrically in the solutions. The results are recorded in Table 2.

**Distribution Coefficients.** The $K_d$ values for metal ions were determined as reported earlier (*8*). In this case a 25-mL solution containing 50 ppm of the element was equilibrated at 25 ± 1°C for 24 h with occasional shaking. The elements were determined by atomic absorption methods under standard conditions.

## RESULTS

### X-Ray Analysis

X-ray photographs of samples dried at 50°C, nickel-filtered Cu-$K_\alpha$ radiation being used, show that they are all noncrystalline (glassy).

### IR Absorption Spectra

IR spectra of samples were measured by the standard KBr disk technique. The IR spectrum of Sample 6 in $H^+$ form is recorded in Fig. 1.

### Thermogravimetric Studies

Thermogravimetric analysis of various samples in the $H^+$ form was performed at a heating rate of 10°C/min. The thermogram for Sample 6 is given in Fig. 2.

TABLE 2

Stability of Lanthanum Tungstate (Sample 6) in Different Solvents. Values in mg/50 mL

| Solvent | Lanthanum dissolved (mg) | Tungsten dissolved (mg) |
|---|---|---|
| 4 *M* $HNO_3$ | 0.85 | 6.60 |
| Demineralized water | 0.00 | 0.00 |
| 4 *M* $H_2SO_4$ | 0.00 | 3.40 |
| 1 *M* NaOH | 2.92 | 50.00 |
| 1 *M* Oxalic acid | 1.65 | 34.50 |

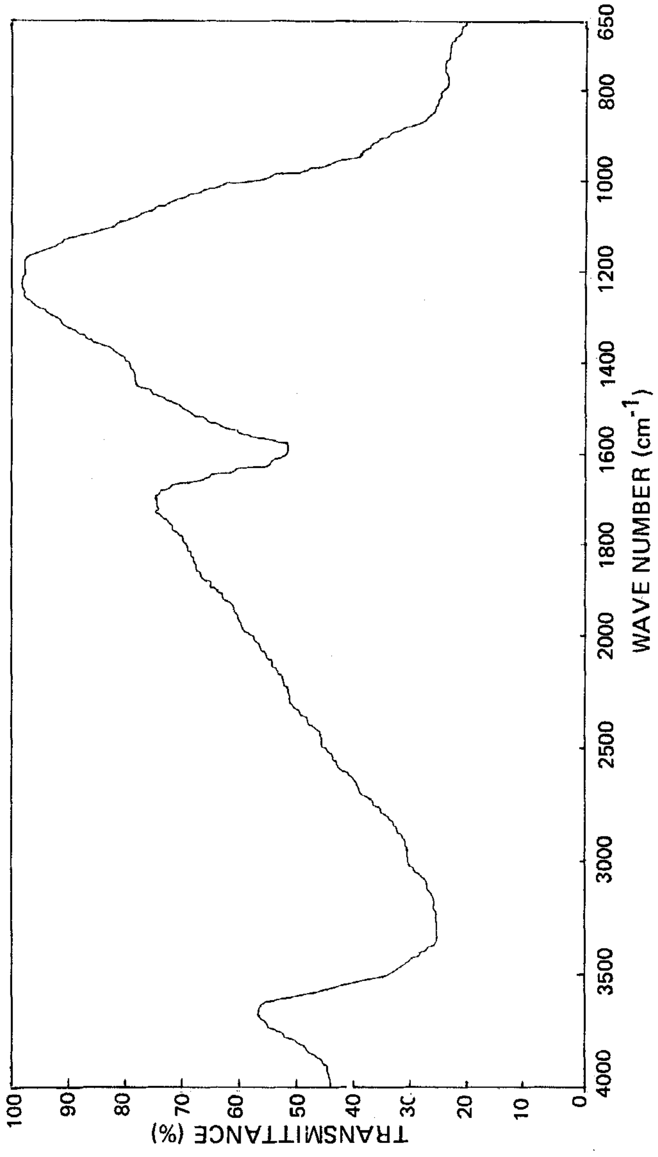

FIG. 1. Infrared spectrum of lanthanum tungstate.

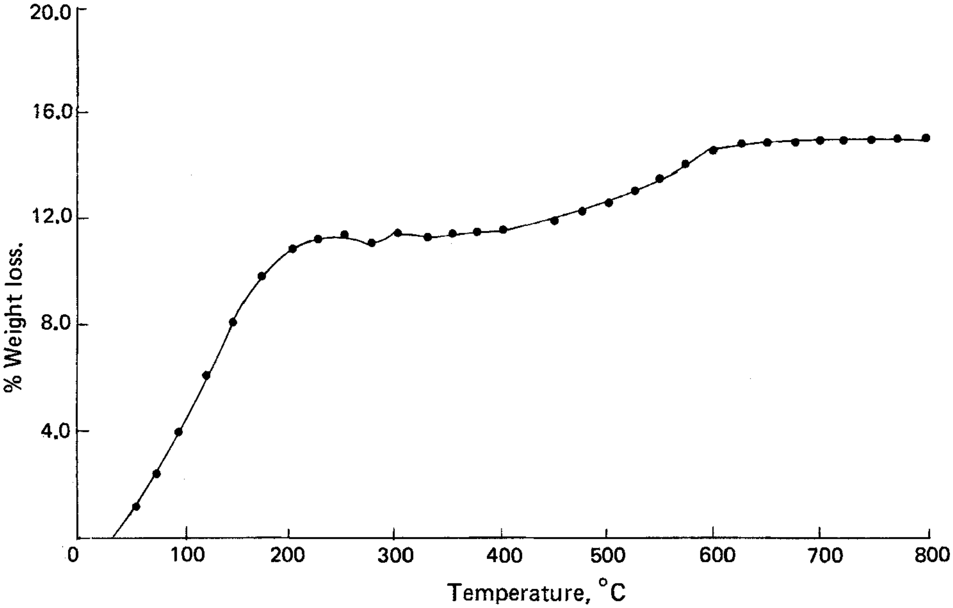

FIG. 2. Thermogram of lanthanum tungstate (Sample 6) in $H^+$ form. Heating rate: 10°C/min.

## DISCUSSION

The chemical composition and the degree of hydration of amorphous inorganic ion-exchangers depend considerably on the method of their preparation (*13*). These two factors are responsible for the size and shape of the cavities inside the exchanger and its chemical stability (*14*). Out of six different samples of lanthanum tungstate prepared (Table 1), Sample 6 shows good ion-exchange capacity, is easy to prepare, and is very stable in water and dilute mineral acids. It can be prepared with reproducible exchange properties (Table 3), and therefore it has been studied in detail.

The IR spectrum of lanthanum tungstate (Fig. 1) shows three absorption peaks. On the basis of IR data for tungstates (*2*, *15*), we can say that the first peak between 2900–3500 $cm^{-1}$ with a maximum at 3300 $cm^{-1}$ is due to interstitial water and hydroxyl groups, the second sharp peak at 1600 $cm^{-1}$ is probably due to the deformation vibration of free water molecules, and the third broad band between 650–900 $cm^{-1}$ corresponds to metal–oxygen bonds, presumably in a polymeric compound.

The thermogram for Sample 6 given in Fig. 2 suggests that the weight loss of the ion exchanger up to 180° is due to the removal of free external water

TABLE 3

Data of Reproducibility of Lanthanum Tungstate (Sample 6)

| Four samples prepared at different dates | Ion-exchange capacity (meq/g) of exchanging ion | | Distribution coefficient (mL/g) for | | | |
|---|---|---|---|---|---|---|
| | $Na^+$ | $Mg^{2+}$ | $Cu^{2+}$ | $Sr^{2+}$ | $Pd^{2+}$ | $Cd^{2+}$ |
| I | 1.09 | 0.98 | 60.13 | 209.87 | 0.00 | T.A.[a] |
| II | 1.04 | 0.88 | 58.69 | 200.00 | 0.00 | T.A. |
| III | 0.93 | 0.92 | 50.40 | 187.21 | 0.00 | T.A. |
| IV | 1.04 | 0.85 | 60.00 | 212.00 | 0.00 | T.A. |

[a] Total adsorption.

molecules. At higher temperatures, 320–610°C, condensation takes place, resulting in the removal of interstitial water molecules. Above 610°C the weight becomes constant owing to the formation of oxides.

The $K_d$ values given in Table 4 show that lanthanum tungstate is a useful ion exchanger, and this has also been demonstrated by thin-layer chromatographic studies in our laboratories (*7*). The cadmium is highly adsorbed on this ion exchanger, and therefore its quantitative separation from $Mn^{2+}$, $Cu^{2+}$, and $Pd^{2+}$ has been easily achieved (Fig. 3). Elution of cadmium is easier due to the formation of a complex anion $CdCl_4^{2-}$ in the presence of

TABLE 4

Distribution Coefficients for Metal Ions on Lanthanum Tungstate (Sample 6)

| Metal ion | Salt used | Equilibrium concentration of external solution (ppm) | $K_d$ value (mL/g) |
|---|---|---|---|
| Mg(II) | Sulfate | 7.00 | 307.14 |
| Ca(II) | Carbonate | 5.00 | 450.00 |
| Mn(II) | Nitrate | 20.00 | 75.00 |
| Ni(II) | Nitrate | 1.00 | 2450.00 |
| Cu(II) | Nitrate | 23.00 | 58.69 |
| Sr(II) | Nitrate | 10.00 | 200.00 |
| Pd(II) | Chloride | 50.00 | 0.00 |
| Cd(II) | Acetate | 0.00 | Total adsorption |
| Ba(II) | Nitrate | 7.99 | 263.00 |
| Pb(II) | Nitrate | 11.00 | 177.27 |

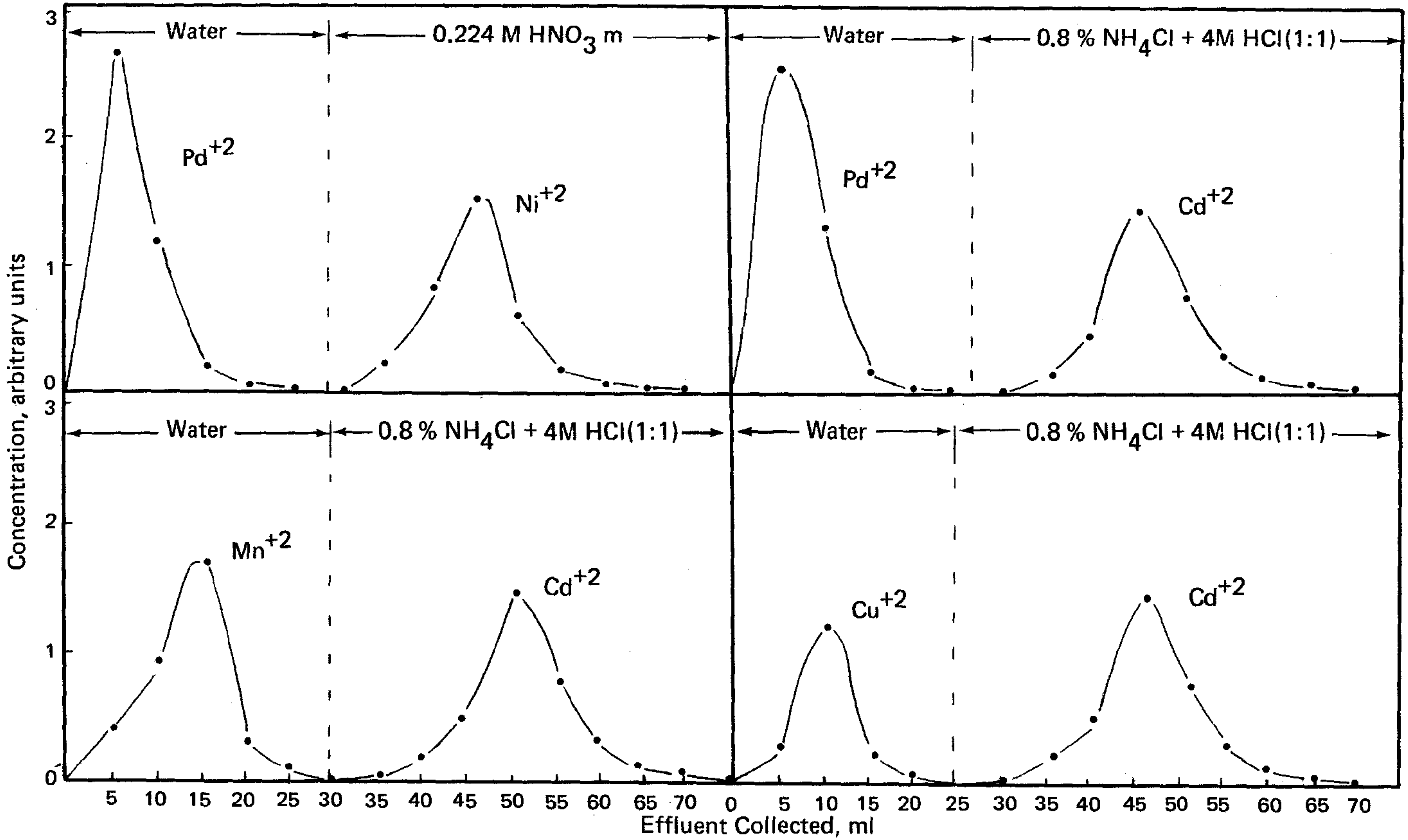

FIG. 3. Separations on lanthanum tungstate (Sample 6). Exchanger, 1.0 g; column 72 × 0.43 cm i.d.; flow rate, 4 drops/min; feed, 10 mL containing 50 ppm (Ni or Mn or Cd) or 60 ppm (Pd) or 25 ppm (Cu) as binary mixtures.

excess chloride (*16, 17*). Cadmium is toxic to humans and animals (*18*), and its removal from biomatrices lacks selective methods (*19*). This ion exchanger may prove useful in this regard. Very few methods are available for the quantitative separation of platinum metals such as palladium (*20*). Here palladium, as it is not adsorbed on the exchanger, is easily separated from its strongly interfering base, metal nickel. Nickel is eluted later by dilute nitric acid due to the formation of weakly charged species. This idea is supported by the weak electrophoretic migration of nickel in dilute $HNO_3$ (*21*) and its negligible adsorption from dilute $HNO_3$ on other ion exchangers (*22*).

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