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Anion Exchange Characteristics of Zirconium Tellurite

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Zirconium tellurite anion exchanger is stable in acids, bases and salts and has anion uptake capacity of 0.98 meq/g. It has a great affinity for chromate and can be used for the separation and recovery of the same from aqueous solutions.

Tellurides of rare earth metals[1], tellurates of zirconium[2], lanthanum[3] and chromium[4], and tellurite of cerium[5] etc. have been used with different degrees of success for the separation of cation pairs of analytical interest. The preparation of zirconium tellurite under the conditions, when the gel exhibits anion exchange characteristics, is reported in this note. Analysis of the product, its stability, selectivity and utility in column operations have also been investigated.

Zirconium oxychloride (E. Merck), potassium tellurite (BDH) and other chemicals used were of analytical grade. Doubly distilled water was used for the preparation of solutions. *p*H measurements were made with an ELICO *p*H meter model LI 10. A Unicam SP 500 spectrophotometer was used for the estimation of some ions. Thermogravimetric analysis of the product was done on Stanton Redecraft TG 750 thermobalance and infrared spectra in KBr matrix were recorded at room temperature (30°C) on a Beckmann IR 20 spectrophotometer. A Phillips X-ray diffractometer employing $M_0 - K_\alpha$ radiation was used for X-ray diffraction studies.

Preparation, ion exchange capacity and analysis of exchanger material

A solution of zirconium oxychloride (0.025 *M*) was mixed slowly with potassium tellurite (0.05 *M*), prepared in highly acidic medium[5] (pH ~ 0), in equal volumes. The precipitate obtained was digested for 70 hr at 70°C, washed with distilled water to remove absorbed electrolyte and dried in an air oven at 60°C for 6-8 hr. The chloride uptake capacity of this sample was 0.98 meg g^{-1}.

Ion exchange capacity was determined by batch method. Since, reproducible results could not be obtained for anion release capacity, the anion uptake capacity was measured by observing the uptake of ^{36}Cl radiometrically.

Zirconium in the exchanger material was precipitated as hydroxide by adding concentrated sodium hydroxide to a solution of the known amount of the sample in aqua regia. The precipitate of zirconium hydroxide was dissolved in hydrochloric acid and zirconium estimated by alizarin red-S, spectrophotometrically[6] at 510 nm. The filtrate was made upto 100 ml with distilled water and tellurite estimated as thiourea complex of tellurium at 360 nm spectrophotometrically[6].

Distribution coefficients

Distribution coefficients (K_d) for different anions were determined by the batch equilibration method by shaking exchanger (0.1 g) with 10 cm^3 of anion solution (0.002*N*) for 48 hr. The estimation of Cl^- was done by radiometric method while SO_4^{2-}, PO_4^{3-}, AsO_4^{3-} and Br^- were estimated volumetrically. The concentrations of SCN^-, $Fe(CN)_6^{4-}$, VO_3^-, CrO_4^{2-} and MoO_4^{2-} were determined spectrophotometrically.

Column operation

A column ($6\,cm \times 0.5\,cm$) containing 1 g of the exchanger material of 100-200 mesh size was loaded with a mixture of pair of ions till these were completely adsorbed. Elution was started after 15 min at a flow rate of 0.2 cm^3/min. The eluted ions were determined in 2 cm^3 fraction of the column effluent.

The preparation of the exchanger material described above gives the product with maximum anion exchange capacity (0.98 meq g^{-1}). It is a white amorphous solid (X-ray) and can be easily sieved. It is quite stable in water, acids (1-5 *M*), alkali (1-3 *M*) and in salt solutions (upto ~ 5 *M*).

The product analysed for $ZrO.TeO_3.3H_2O$ (Found: Te, 37.5; ZrO, 31.2; H_2O, 16.5. Reqd: Te, 37.8; ZrO, 31.8; H_2O, 16.8%). The number of water molecules have been calculated by the method of Alberti *et al.*[7] The IR spectrum of zirconium tellurite exhibits strong absorption bands at 3400 (νOH) and 1620 (δOH), 700-760 (TeO_3^{2-}) and 421 ($\nu Zr-O$) cm^{-1}.

The time and concentration of solution, required for maximum uptake of ions have also been determined and it is found that an equilibration time of 38 hr and 0.8-0.9 *M* concentration of bathing solution is necessary for saturation.

The product has a significant affinity for chromate ions and the distribution coefficient values for various anions (given in parentheses) follow the order: CrO_4^{2-} (4455) > MoO_4^{2-} (769) > SO_4^{2-} (392) > PO_4^{3-} (361) > AsO_4^{3-} (277) > $Fe(CN)_6^{4-}$ (200) > Br^- (105) > Cl^-

Table 1—Binary Separation of CrO_4^{2-} from Various Other Anions on Zirconium Tellurite Column

Mixture	Amount taken μg	Recovery %
CrO_4(II)	463.9	96.0
+		
SCN(I)	232.0	100.0
CrO_4(II)	463.9	95.6
+		
MoO_4 (II)	639.0	100.0
CrO_4 (II)	463.9	95.2
+		
PO_4 (III)	379.9	100.0
CrO_4 (II)	463.9	95.8
+		
$Fe(CN)_6$ (IV)	423.9	100.0

(31). The uptake of some cations has also been observed. The distribution coefficient values for Rb^+, Cs^+, Tl^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cr^{3+}, Th^{4+} etc. range between zero to fifteen.

On the basis of distribution coefficient values a variety of separations are possible on a column prepared from this material. Large number of binary separations, involving chromate ions, have actually been performed on this material and the results are reported in Table 1. Elution of chromate ions is done with $3\,M$ NH_4OH and the recovery is almost 96%. Other anions can be easily eluted with 1 to $2\,M$ NaCl. All the separations are clean and no cross contamination occurs. One column can be used upto five cycles without any loss in separation efficiency.

The utility of this product in the separation and recovery of Cr^{6+} from tannery waste has also been explored. Waste samples from a tannery containg CrO_4^{2-}, 5000; tannic acid 1600; Cl^- 1500; and Ca^{2+} 1200 mg/litre were tried on the columns of this exchanger material. The retention of chromate was 100% but only 95% could be eluted with eluants mentioned above.

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