

CHROM. 5920

**Bismuth tellurate; an inorganic ion exchanger**

In contrast to organic ion-exchange resins, inorganic ion exchangers are very stable under high temperatures and high doses of radiation. As a result, inorganic ion exchangers can be used in the recovery of highly radioactive fission products. During the last decade different inorganic compounds, especially zirconium salts, have been investigated as ion-exchange materials<sup>1,2</sup>. Our recent study<sup>3</sup> on zirconium tellurate prompted an investigation of other tellurates. The composition and some ion-exchange properties of bismuth tellurate are reported in this paper.

**Experimental**

**Preparation.** The sample was prepared similarly to zirconium tellurate<sup>3</sup>. Bismuth nitrate (900 ml of 0.1 M solution in 0.5 N HNO<sub>3</sub>) was added to 900 ml of 0.2 M sodium tellurate solution of pH 1, adjusted with nitric acid, and refluxed for 30 h. The precipitate was separated by filtration and washed with 0.1 N HNO<sub>3</sub> and dried at 90° until it broke into coarse particles. These particles were converted to the H<sup>+</sup> form by passing 0.1 N HNO<sub>3</sub> until there was no Na<sup>+</sup> in the effluent, and then washing free from acid and again drying at 90°.

**Analysis.** The sample is insoluble in alkali solution and in dilute acid solution up to 0.5 N. However, the sample is soluble in more concentrated acid solutions especially on warming. Analysis of the sample for tellurium and bismuth was made directly and indirectly. The indirect analysis was made by using known amounts of bismuth and tellurium while precipitating and then estimating the excess tellurium by a gravimetric method<sup>4</sup>, involving reduction of the tellurate ion to tellurium. The direct analysis was carried out by dissolving 1-g samples in 100 ml of 4.0 N HNO<sub>3</sub> solution, separating bismuth from tellurium by precipitating it as bismuth oxybromide, neutralizing the filtrate and analysing for tellurium by reducing it to metallic tellurium with sodium sulphite<sup>4</sup>. Bismuth was estimated in the precipitate, but the results were always low. As an alternative, bismuth was estimated by separating it from tellurium as bismuth oxalate precipitate. The precipitate was then redissolved and titrated against standard potassium permanganate solution<sup>5</sup>. In the absence of a thermobalance the weight loss at temperatures up to 200° was recorded by a Griffin-Grundy 2/300 electric oven and above 200° by a Karl Kolb KMR170 electric muffle furnace. The temperature fluctuation was within  $\pm 5^\circ$  and the constant weight at the given temperature was recorded each time.

**Exchange capacity and pH titration.** The total exchange capacity of the sample was determined by a batch method in strongly alkaline solution. The solid (0.5 g) was first equilibrated with 25 ml of distilled water to which 25 ml of strong sodium or potassium hydroxide solution was added and equilibrated. The strength of the sodium hydroxide in contact with the solid was 0.48 N and that of the potassium hydroxide was 0.28 N. The amount of H<sup>+</sup> released was determined by estimating the amount of alkali neutralized. During the experiment and the pH titration described below, due precaution was taken to keep the system free from atmospheric carbon dioxide.

To study the mode of dissociation of the exchangeable H<sup>+</sup>, 1.0 g of the solid

TABLE I

## ANALYSIS FOR Bi AND Te

Method	Bi in sample (g)	Te in sample (g)	Molar ratio Te:Bi
Indirect analysis	0.54	0.23	0.705
Direct analysis	0.50	0.21	0.686

was equilibrated by shaking at room temperature ( $25^{\circ}$ ) with 50 ml of 1.0 M NaCl or KCl solution and the equilibrium pH was recorded. After that a known amount of the standard solution of sodium or potassium hydroxide was added over a period and the pH was recorded after each addition. Sodium hydroxide solution was used in the sample/sodium chloride solution system and potassium hydroxide solution in the sample/potassium chloride solution system. The pH reading was taken to be constant when variation was less than 0.01 pH scale per 30 min. It took several minutes to several hours to obtain equilibrium readings. This experiment was carried out with a Beckman Electroscan TM30P. Before starting, the electrode system was calibrated using standard buffer solutions and the pH readings were corrected according to the calibration curve obtained.

## Results and discussion

The supernatant liquid of the bismuth tellurate gave a negative test for bismuth but a positive test for tellurium. This indicates that during precipitation tellurium was in excess. Table I shows the estimated molar ratio Te:Bi. The lesser amounts

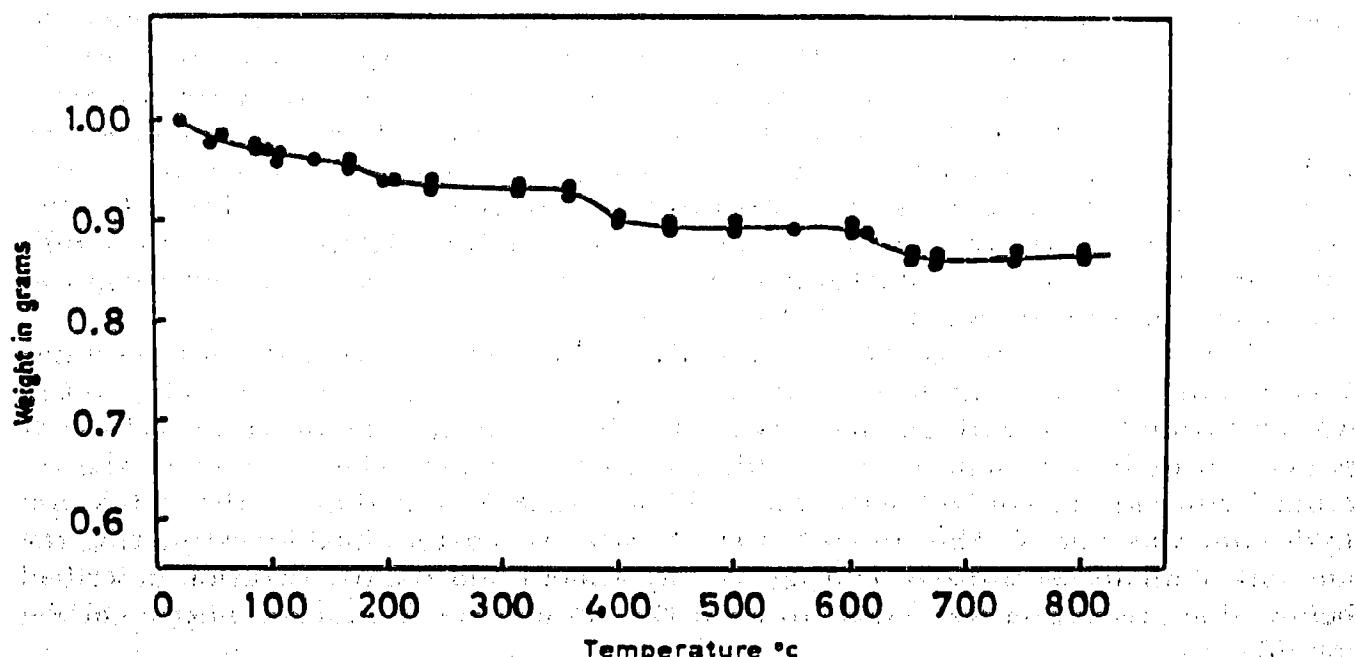


Fig. 1. Thermograms for Bi-Te sample (maximum spread of repeated observations is shown).

of bismuth and tellurium per gram of the sample as estimated by direct analysis are probably due to absorption of moisture by the stored sample.

Fig. 1 shows the thermogram of bismuth tellurate. If the composition corresponding to constant weight at temperatures above 650° is assumed to be  $2\text{Bi}_2\text{O}_3 \cdot 3\text{TeO}_3$ , then the calculated composition of the product reported in this paper becomes  $2\text{Bi}_2\text{O}_3 \cdot 3\text{TeO}_3 \cdot 12\text{H}_2\text{O}$ .

Considering that the recently proposed formula of oxytelluric acid is  $\text{H}_6\text{TeO}_6$  and that it forms monoclinic salts such as  $\text{KH}_5\text{TeO}_6$ ,  $\text{Li}_2\text{H}_4\text{TeO}_6$  and  $\text{Ag}_6\text{TeO}_6$ , where more than two protons of the acid are substituted<sup>6</sup>, it is likely that the molecular formula of the compound reported in this paper is  $\text{Bi}_4(\text{H}_2\text{TeO}_6)_3 \cdot n\text{H}_2\text{O}$ , where  $n$  is 9. However, this will vary with absorbed moisture. This formula best explains all the experimental results. According to this formula the molar ratio Te:Bi should be 0.75, which is in agreement with the observed value of about 0.7.

Fig. 1 shows that there has been continuous water loss up to 180°, with a loss of four moles of water. The constant compositions at different temperature ranges are 210–370° for  $\text{Bi}_4(\text{H}_2\text{TeO}_6)_3 \cdot 3\text{H}_2\text{O}$ ; 410–600° for  $\text{Bi}_4(\text{H}_2\text{TeO}_6)_3$ ; above 650° for  $2\text{Bi}_2\text{O}_3 \cdot 3\text{TeO}_3$ . The thermogram has some similarity to that of zirconium tellurate, except that up to 450° water loss was continuous in the case of zirconium tellurate while in the case of the present compound water loss in this range was in two stages. The distinct weight loss at 600–650° is probably due to loss of water of constitution, and this is identical with the loss of water of constitution of zirconium tellurate at 650–670°. Water loss of three molecules at 600–650° indicates the transformation of  $\text{Bi}_4(\text{H}_2\text{TeO}_6)_3$  to  $2\text{Bi}_2\text{O}_3 \cdot 3\text{TeO}_3 \cdot 3\text{H}_2\text{O}$ . The residue above 700° was a homogeneous liquid mass. Most probably there would be further weight loss if the temperature could be raised above 900°, due to decomposition of  $2\text{Bi}_2\text{O}_3 \cdot 3\text{TeO}_3$ , followed by evaporation of both  $\text{Bi}_2\text{O}_3$  and  $\text{TeO}_3$ .

TABLE II

## EXCHANGE CAPACITY

Room temperature: 25°. Capacity in mequiv./g.

Ions	Total capacity	Plateau capacity <sup>a</sup> at pH ranges	
		11–12	12–13
$\text{Na}^+$	3.2	1.6	1.8
$\text{K}^+$	3.4	1.6	1.9

<sup>a</sup> Calculated from the titration curves.

According to the composition of the compound proposed above the total exchange capacity should be six moles per mole and there should be two plateaux in the pH titration curves. Considering the proposed formula the capacity of six moles per mole should yield a capacity of 3.5 mequiv./g and 1.7 mequiv./g should correspond to each plateau of the titration curves.

The observed total capacities shown in Table II are 3.4 and 3.2 mequiv./g for  $\text{Na}^+$  and  $\text{K}^+$ , respectively. These values are in agreement with the theoretical values. Fig. 2 also shows two plateaux for both  $\text{Na}^+$  and  $\text{K}^+$  ions and the capacity corresponding to each plateau is also in agreement with the expected theoretical values.

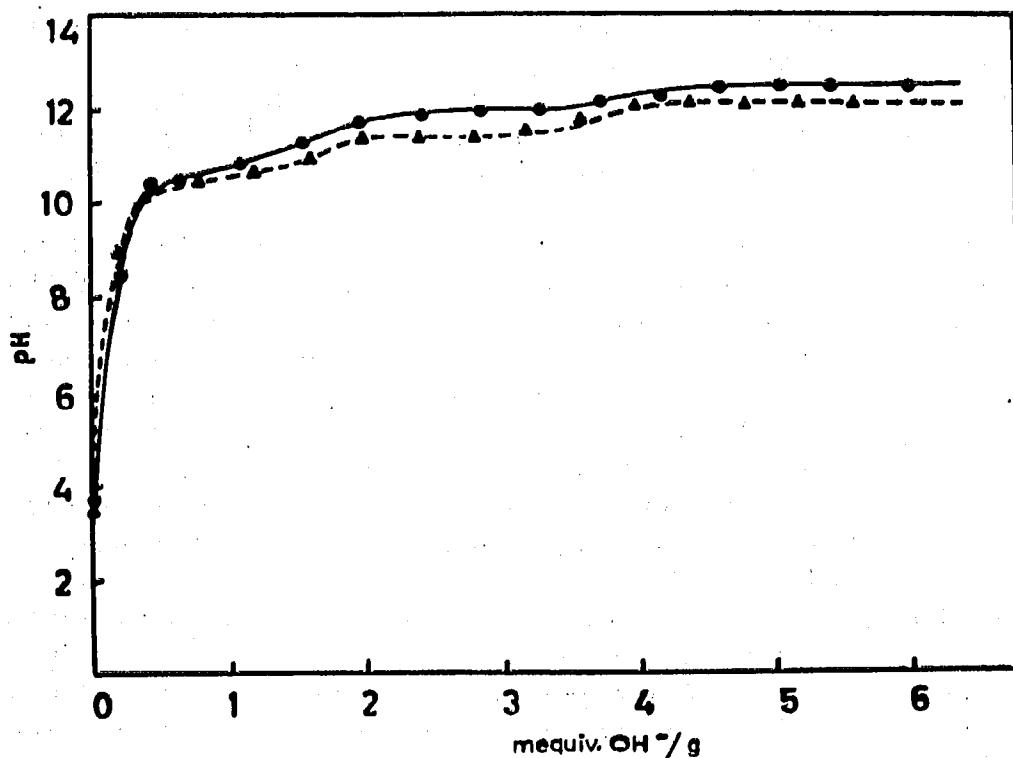


Fig. 2. Titration curves of bismuth tellurate with different salts and alkalis: ●, KCl + KOH; ▲, NaCl + NaOH.

The titration curves indicate that each stage of the dissociation of the exchangeable  $H^+$  ion takes place at a slightly higher pH for KCl and KOH systems compared to that for NaCl and NaOH systems.

Comprehensive investigations for evaluating the distribution of different ions, especially those which constitute fission products are under way.

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