Preparation of Telluric Acid from Tellurium Dioxide by Oxidation with Potassium Permanganate

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General Statement

Tellurium dioxide, TeO_2, although periodically similar to sulfur dioxide, cannot be oxidized by nitric acid to the valence of six, i.e., to telluric acid, $H_2TeO_4.2H_2O$. Among the many stronger oxidizing agents that will produce this oxidation, potassium permanganate in a nitric acid solution is quite satisfactory. This paper gives directions and data for the preparation of telluric acid by this reaction.

The making of telluric acid is a desirable laboratory experiment because (1) tellurim dioxide is available in large quantities and is easily obtained, (2) the telluric acid is a stable compound, easily purified, easily crystallized, and non-corrosive, and (3) students are interested in experimenting with the rarer elements.

The small soluibility of telluric acid and the high solubility of both manganese and potassium nitrates in nitric acid[1] gives a sufficient difference in properties for successful purification by crystallization of the telluric acid.

Methods of Analyses

Tellurium dioxide can be volumetrically[2] titrated in a sulfuric acid solution by an excess of standard potassium permanganate, followed by enough standard oxalic acid to decolorize the excess of permanganate. The excess of oxalic acid must then be titrated by more of the permanganate.

The telluric acid can be titrated, like any ordinary monobasic acid,[3] with standard sodium hydroxide using phenolphthalein as an indicator, if an equal volume of glycerine is added. If any nitric acid is present, it must be neutralized first with sodium hydroxide, using methyl orange as indicator. Test analyses on purified telluric acid showed that this method was satisfactory, although there were some small variations in the check determinations.

Preparation of Material

The lead and copper electrolytic refining plants have large stocks of crude tellurium dioxide. Some of this material which contained 84.8% of TeO_2 was treated with a slight excess of sodium hydroxide and filtered. This removed sand, dirt, iron and all the other things that were insoluble in alkalies. The sodium tellurite, Na_2TeO_3, in the filtrate was decomposed

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[1] Mathers and Rice, this volume, p. 117 (1942).

[2] Brauner, J. Chem. Soc., **59**:238 (1891).

[3] Rosenheim and Weinheber, Z. Anorg. Chem., 69:266-9; Chem. Abst., 5:378 (1911).

and tellurium dioxide was precipitated by addition of hydrochloric acid until almost neutral, and then by acetic acid until slightly acid. It was found best to allow the precipitate to stand a few days before washing (by decantation) and filtering. The filtered residue, after drying, was white, soft, bulky, chalky and pure tellurium dioxide.

Experimental

The quantities of the materials to be used and the conditions of operation in the preparation of the telluric acid are not critical. All that is needed is a slight excess of permanganate on tellurium dioxide in a hot solution containing sufficient nitric acid to prevent a permanent precipitation of much manganese dioxide. At the end of the reaction, sufficient hydrogen peroxide should be added to make the remaining manganese dioxide dissolve. The rest of the process is simply a crystallization of the telluric acid and its purification by recrystallization.

The equation for the reaction in strong nitric acide is:

$$5TeO_2 + 2KMnO_4 + 6HNO_3 + 2H_2O = 5H_2TeO_4 + 2KNO_3 + 2Mn(NO_3)_2.$$

If only a little nitric acid is present, the reaction seems to be:

$$3TeO_2 + 2KMnO_4 + 2HNO_3 + 2H_2O = 3H_2TeO_4 + KNO_3 + 2MnO_2.$$

Due to the necessity of purifying the telluric acid from the by-products of the reaction, the first reaction is preferable because a smaller ratio of permanganate is needed. The theoretical quantity of potassium permanganate for 10 gms. of tellurium dioxide is 3.95 gms. It was found desirable to use a little excess of the permanganate, to compensate for some loss of oxygen, if the permanganate was added too rapidly or without sufficient stirring.

After many preliminary experiments, which need not be discussed, the following quantities and conditions were chosen:

> Four grams of $KMnO_4$, dissolved in 100 ml. of H_2O, were added slowly, about 5 ml. at a time with vigorous stirring, to a boiling mixture of 10 gms. TeO_2, 40 ml. of HNO_3 and 100 ml. of water.

Some manganese dioxide was present during this entire process. It was possible, but not necessary, to cause the black manganese dioxide to react, except near the end, by boiling for a sufficient time after each addition of permanganate. The amount of manganese dioxide remaining in the reaction mixture at the end depends upon (1) the excess of permanganate used, (2) the rate of adding the permanganate, and (3) the time of boiling between additions of the permanganate.

As the insoluble tellurium dioxide was oxidized to the soluble telluric acid, the solution gradually became free of any precipitate except for some manganese dioxide.

After all the permanganate was added, the solution was kept at the boiling point for fifty minutes, in order to have maximum reaction of the manganese dioxide which remained from the excess of permanganate. Then enough hydrogen peroxide was added to make the remaining manganese dioxide go into solution.

The clear solution was evaporated to a weight of 60 grams and 10 ml. of HNO_3 were added; then the solution was allowed to crystallize for twenty-four hours, preferably at 10° C. The mother liquor yielded a second crop of crystals after evaporation to a weight of 25 gms. and the addition of 10 ml. of nitric acid.

These crystals, after uniting, were washed with three portions of 10 ml. each of nitric acid and drained as completely as possible after each washing. In later experiments, a centrifuge was found desirable in conducting this washing operation.

These crystals were purified by dissolving in 25 ml. of water after which 17 ml. of conc. nitric acid were added. The crystals, which formed after twenty-four hours, were washed three times with nitric acid as described above. These crystals were then recrystallized a third time in the same way. The nitric acid and water were removed from these final crystals by heating to about 100° C.

The final crystals had a purity of 99.85 per cent, and the overall material yield from the tellurium dioxide used was 77 per cent. If well formed crystals are desired, these crystals should be crystallized slowly from water—the solubility of the telluric acid in nitric acid is too small for large crystals to be produced easily. Also crystals from water solutions are more easily freed from solvent than those from nitric acid.

If a high material yield is not an aim of the work, it is recommended that the crystallizations should be from water, after one recrystallization from the nitric acid—strong nitric acid solutions are not pleasant to work with.

Crude tellurium dioxide can be used with equally good results, if the sand and other insoluble material is filtered out following the addition of the hydrogen peroxide.

The material yield could have been increased somewhat by reworking the mother liquors and by using still more concentrated nitric acid to reduce further the solubility of telluric acid.