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THE VOLUMETRIC DETERMINATION OF TELLURIUM BY THE DICHROMATE METHOD

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The only attempts to use titration with dichromate in the determination of tellurium which are recorded are the experiments of Brauner[1] who after a number of unsuccessful trials concluded that the method is unsuitable for volumetric analysis, and the experiments of Lenher and Tibbals[2] on tellurium and telluride minerals. In these latter experiments no attempt was made to work out the details of a volumetric procedure.

Under proper conditions the oxidation of a tellurous solution to the telluric state by the use of a dichromate solution can be made an accurate volumetric procedure. The method proposed is based upon the following reaction: $3TeO_2 + K_2Cr_2O_7 + 8HCl = 3H_2TeO_4 + 2KCl + 2CrCl_3 + H_2O$. Since, however, hydrochloric and telluric acids also react with production of chlorine, it is necessary to control the direction of the reaction. To this end the titration must be carried on in a manner like that

Table I

Titration Data

0.0996 g. of TeO_2 taken; 1 cc. excess of 0.1 N $K_2Cr_2O_7$ solution

Time Hours	TeO_2 found G.	Difference Mg.
1/2	0.0994	−0.02
3/4	.0994	− .02
1	.0995	− .01
1 1/4	.0996	.00
1 1/2	.0996	.00
2	.0996	.00
2 1/2	.0996	.00
3	.0997	+ .01

0.1046 g. of TeO_2 taken; time, 30 minutes

Excess 0.1 N $K_2Cr_2O_7$ of solution; cc.	TeO_2 found G.	Difference Mg.
2	.1036	− .10
3	.1037	− .09
4	.1042	− .04
5	.1044	− .02
7	.1043	− .03
9	.1044	− .02

0.1988 g. of TeO_2 taken; 0.3 cc. excess of 0.1 N $K_2Cr_2O_7$ solution; time 30 minutes

TeO_2 found G.	Difference Mg.
0.1988	0.00
.1989	+ .01
.1989	+ .01
.1987	− .01
.1989	+ .01
.1989	+ .01

0.2971 g. of TeO_2 taken; 1.0 cc. excess of 0.1 N K_2CrO_7; time, 30 minutes

TeO_2 found G.	Difference Mg.
.2971	.00
.2977	+ .06
.2978	+ .07
.2971	.00
.2970	− .01
.2974	+ .03

0.2983 g. of TeO_2; time, 30 minutes

Excess of 0.1 N $K_2Cr_2O_7$ of solution; cc.	TeO_2 found G.	Difference Mg.
1	.2992	+ .09
1	.2986	+ .01
2	.2986	+ .03
3	.2986	+ .03

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

[2] Lenher and Tibbals, *Econ. Geology*, **4**, 554 (1909).

for the permanganate titrations of selenious and tellurous acids, in which it is essential to add an excess of standard permanganate solution, followed by a measured excess of standard oxalic acid, and titrate the surplus of oxalic acid by means of standard permanganate.

In the dichromate method for tellurium the hydrochloric acid solution of the tellurium dioxide is treated with an excess of standard dichromate solution and allowed to react for at least a half hour, after which a measured excess of standard ferrous ammonium sulfate is added, and the excess of ferrous salt titrated with standard dichromate. Table I shows a typical series of results.

Conditions.—*The size of the sample to be used* should preferably correspond to 0.1–0.3 g. of tellurium. Smaller amounts will obviously give greater inaccuracies in weighing while greater amounts of tellurium than 0.3 g. in the form of the dioxide are likely to give high results. The temperature used is ordinary room temperature. In our experiments a dilution of 200 cc. was maintained. Any material variation from this volume will necessitate relative variations in acidity. The *acidity* of the solution should be close to 2% of hydrochloric acid or 10 cc. of concd. acid (d., 1.2) to 200 cc. of solution. When the amount of free acid is less, the speed of the reaction is retarded, while with greater amounts of free acid there is likely to be liberation of free chlorine. In such cases when excessive amounts of acid cause the formation of free chlorine the apparent results may be either higher or lower than the correct figure depending on the length of time of the experiment. In the case of high acidity and a short duration of the experiment the free acid probably causes reversion of the telluric acid to the tellurous with subsequently lower results, or it may be considered that excessive acidity actually prevents the dichromate from acting as an oxidizing agent on tellurium dioxide. Actually, a dichromate solution with tellurium dioxide remains red a longer time with greater amounts of free hydrochloric acid present and turns green more rapidly when the acidity is low.

When a solution of high acidity stands for a few minutes free chlorine begins to escape and part of the oxidizing power of the dichromate is destroyed. At the end of an hour, at ordinary temperature, sufficient chlorine has been lost to reduce measurably the quantity of ferrous salt that is later oxidized, with the result that more dichromate is consumed in the final titration. In such a case the result is higher than the true one. This loss of free chlorine from such solutions of high acidity can be readily demonstrated by subjecting the solution to diminished pressure, when the direct chlorine loss can be followed.

This variation from the real value has been found to take place in as low acidity as $3^1/_4$% of free hydrogen chloride or 15 cc. of concd. hydrochloric acid (d., 1.2), in the 200 cc. volume used, and since Brauner used as great amounts as 40 cc. of concd. acid to 200 cc. of titrating liquid or an acidity of $8^1/_2\%$ of free acid, it is easily understood why he could not develop a method.

The length of time of the titration varies with the size of the sample. At least $^1/_2$ hour's contact of the tellurium dioxide with the dichromate should be allowed in the first instance. The amount of titrating solutions to be used can vary within wide limits; a considerable excess of dichromate added in the first instance, however, insures more rapid oxidation with subsequent reduction of time.

Application of the Method

A sample of the material containing from 0.1 g. to 0.3 g. of tellurium dioxide is dissolved in 10 cc. of concd. hydrochloric acid and diluted to 200 cc. with water. A measured excess of 1 to 5 cc. of 0.1 *N* dichromate is added from a buret and the solution allowed to stand for a half hour. A measured excess of standard ferrous sulfate solution is then added and the surplus of ferrous salt titrated with 0.1 *N* dichromate using potassium ferricyanide as an outside indicator in the usual manner.

With tellurium compounds the preliminary treatment consists either in dissolving in hydrochloric acid at a temperature sufficiently low to prevent loss of tellurium by volatilization, or when treatment with aqua regia is necessary in removing the excess of nitric acid with hydrochloric acid on a water-bath.

Summary

The potassium dichromate titration can be successfully applied to tellurium as a volumetric procedure.

Tellurium dioxide is oxidized to trioxide in hydrochloric acid solution. Certain very definite steps in the procedure are essential. The weight of tellurium dioxide should be less than 0.3 g. The solution should contain 2% of free hydrochloric acid. The volume of solution should be approximately 200 cc. To the acid solution of tellurium dioxide an excess of 0.1 *N* potassium dichromate solution is added, followed by a known excess of standard ferrous iron solution, the surplus of which is subsequently titrated by dichromate using ferricyanide as an outside indicator.

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