

3. While in general increased temperature means increased precipitation, yet with the low current strength and low temperature used, the reverse is the case above  $70^{\circ}$ , no doubt on account of the rapidly increasing solvent action of the acid.

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## THE GRAVIMETRIC DETERMINATION OF TELLURIUM.

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Of all the methods proposed for the precipitation of tellurium perhaps the one which is most used is a modification of the original method of Berzelius. He used sulphurous acid as a precipitating agent.

The method of procedure as commonly carried out consists in adding to the hydrochloric acid solution of tellurium a strong aqueous solution of sulphur dioxide and allowing this mixture to remain in a warm place for a few days in order to effect a complete precipitation. It has been shown by Schroetter,<sup>1</sup> Brauner,<sup>2</sup> Norris and Fay,<sup>3</sup> Crane,<sup>4</sup> Frerichs,<sup>5</sup> and others that the precipitation by means of sulphur dioxide is far from satisfactory. Brauner has pointed out that part of the precipitated tellurium undergoes oxidation in the liquid, becoming converted into the tetrachloride, in which form it remains in solution. Crane has suggested that the main cause of the incomplete precipitation by means of sulphur dioxide is the very rapid increase in the ratio of the acids to the unprecipitated tellurium in solution, two-thirds of this being due to the hydrochloric acid set free, and one-third to the sulphuric acid formed. He thought if these could be removed the reduction would be complete. The hydrochloric acid could be eliminated by evaporation, but the continuous increase in sulphuric acid would soon interrupt the reaction. This might, however, be kept under control by the addition of sodium or potassium hydroxide.

Whitehead has suggested a remedy in the use of acid sodium sulphite. He advises a moderately concentrated solution of the sulphite and that the quantity added to the tellurium solution be sufficient only to just neutralize the acids present and that formed during the reaction. When the solution is thoroughly agitated and then allowed to stand in a warm place, the precipitate will form and settle evenly. He states that "while acid sodium sulphite does not completely remove all of the tellurium from the solution in the cold, that if not used in great excess and the

<sup>1</sup> Chem. News, 87, 17.

<sup>2</sup> J. Chem. Soc., 55, 392.

<sup>3</sup> Am. Chem. J., 20, 278.

<sup>4</sup> *Ibid.*, 23, 408.

<sup>5</sup> J. für pr. Chem., 66, 261.

mixed solutions be raised to the boiling point, toward the end of the action the precipitation will be perfect, and the tellurium will be obtained in a state of aggregation favorable to easy filtration."

Frerichs has worked on the basis that hydriodic acid and sulphur dioxide cause immediate and complete separation of tellurium from a tellurous solution even in the cold, and McIvor<sup>1</sup> has confirmed this method.

Norris and Fay<sup>2</sup> have demonstrated that under ordinary working conditions precipitated tellurium increases in weight about 0.5 per cent., owing to oxidation and that this increase is balanced by the quantity of the elements left behind as tellurium tetrachloride in the strongly acid solution in which the precipitate is formed by sulphur dioxide. They believe that it is more accurate to weigh tellurium dioxide than to weigh tellurium in the elementary state.

McIvor<sup>3</sup> and Donath<sup>4</sup> have studied the precipitation of tellurium by hydrosulphurous acid. This method possesses the disadvantage of a precipitate of tellurium contaminated by more or less sulphur. The method hardly possesses any advantages over the sulphurous acid precipitation.

Stolba<sup>5</sup> in 1873 and later Kastner<sup>6</sup> have proposed the precipitation of tellurium from an alkaline solution by means of grape sugar.

Later, Gutbier<sup>7</sup> described the precipitation of tellurium by means of hydrazine as a method for its determination. His method of procedure is to dissolve telluric acid in warm water in a porcelain dish covered with a glass cover and add by means of a pipette a 10 to 20 per cent. solution of hydrazine hydrate. A dark blue almost black color is noted and after heating a short time, elementary tellurium is precipitated in a flocculent condition, the liquid becoming colorless. He continues the addition of hydrazine hydrate until the fluid is no longer colored by further addition of the reagent.

### Experimental.

*Precipitation by Hydrazine.*—In our hands the method of Gutbier gave fairly good results. The fact should be noted, however, that the addition of an excess of the hydrazine does not at once precipitate all of the tellurium. It is preferable to add a small amount of the precipitating agent from time to time. This necessitates several hours for complete precipitation. The following results were obtained by Gutbier's method in hydrochloric acid solution:

<sup>1</sup> Chem. News, 87, 163.

<sup>2</sup> Am. Chem. J., 20, 278.

<sup>3</sup> Chem. News, 87, 163.

<sup>4</sup> Z. angew. Chem., 1890, 214.

<sup>5</sup> Z. anal. Chem., 11, 437.

<sup>6</sup> *Ibid.*, 13, 142.

<sup>7</sup> Ber., 34, 2724.

TeO <sub>2</sub> . Gram.	Te required. Gram.	Te obtained. Gram.
0.2247	0.1795	0.1790
0.1988	0.1588	0.1577
0.2006	0.1603	0.1596
0.2056	0.1643	0.1637

*Precipitation by Sodium Acid Sulphite.*—In order to completely precipitate the tellurium by this reagent from a hydrochloric acid solution of a tellurous compound, the solution must contain excess of the reagent and must be allowed to stand in a warm place for twenty-four hours. In the following experiments, the sodium acid sulphite was prepared freshly for this purpose by passing sulphur dioxide into a solution of sodium carbonate. It has been our experience that when acid sodium sulphite which has not been freshly prepared is used for the precipitation of tellurium, the precipitated element frequently contains sulphur.

That it is necessary for the solution to stand a considerable length of time is apparent from the following experiments, all of which experiments were made under exactly the same conditions. The solution of the dioxide in hydrochloric acid was brought to boiling, a saturated solution of acid sodium sulphite was added, the solution allowed to stand the requisite length of time, then brought on a Gooch platinum filter washed with water until the filtrate no longer showed chlorides, after which it was washed with 15 cc. of alcohol and dried at 105°.

	Te required. Gram.	Te obtained. Gram.	Error. Gram.
Solution allowed to stand two hours.....	0.1609	0.1586	—0.0023
“ “ “ “ .....	0.1609	0.1590	—0.0019
“ “ “ “ .....	0.1767	0.1744	—0.0023
Allowed to stand six hours.....	0.1609	0.1600	—0.0009
“ “ “ “ .....	0.1609	0.1603	—0.0006
“ “ “ “ .....	0.1374	0.1366	—0.0008
“ “ “ “ .....	0.1527	0.1517	—0.0010
Allowed to stand twenty-four hours.....	0.1609	0.1615	+0.0006
“ “ “ “ .....	0.1609	0.1618	+0.0009
“ “ “ “ .....	0.1726	0.1730	+0.0004
“ “ “ “ .....	0.1286	0.1289	+0.0003

After tellurium, which has been precipitated by means of sodium sulphite and hydrochloric acid, has been washed thoroughly with water, and alcohol, it oxidizes very slowly when heated as high as 200° as evidenced by the following data:

Length of time of heating.	Temperature.	Te(1).	Te(2).
15 minutes.....	105°	0.1619	0.1620
15 “ .....	105°	0.1619	0.1620
1 hour.....	120–130°	0.1620	0.1622
1 “ .....	200°	0.1620	0.1623

*Precipitation by Means of Sulphur Dioxide.*—By the treatment of tellurium dioxide dissolved in hydrochloric acid with a freshly saturated

solution of sulphur dioxide and allowing to stand for 24 hours, the following results were obtained:

Te required. Gram.	Te obtained. Gram.
0.1607	0.1617
0.1609	0.1613
0.1609	0.1615
0.1609	0.1613

Unless the acidity in this precipitation is ten per cent., the tellurium is not likely to be completely precipitated or it will be precipitated in a very fine state of division. The solution should also be hot in order to secure satisfactory precipitation.

*Simultaneous Precipitation by Means of Sulphur Dioxide and Hydrazine.*—By bringing both sulphur dioxide and hydrazine into a tellurium solution the whole of the element is thrown out of the solution almost instantaneously. The solution should have an acidity of 5 to 10 per cent. and it is desirable to have the solution in a high degree of concentration. The solution is brought to boiling and 15 cc. of a saturated solution of sulphur dioxide is added, then 10 cc. of a 15 per cent. solution of hydrazine hydrochloride and again 25 cc. of the sulphur dioxide solution. The solution is boiled for a few minutes when the elementary tellurium will settle in such a way that it can be rapidly washed. The precipitate is then transferred to a platinum Gooch filter and washed first with hot water until all of the chlorine is removed, and then with 15 cc. of alcohol. The crucible and contents are then dried at 100–105° and finally weighed.

The following results were obtained by the process as outlined above, using 10 cc. of solutions of hydrazine hydrochloride of different strengths with sulphur dioxide. Tellurium dioxide was used for the analysis:

Strength of hydrazine hydrochloride. Per cent.	Te required. Gram.	Te obtained. Gram.	Error. Gram.
20	0.1731	0.1735	+0.0004
20	0.2065	0.2068	+0.0003
20	0.1638	0.1641	+0.0003
20	0.1608	0.1608	0.0000
15	0.2212	0.2210	—0.0002
15	0.1435	0.1434	—0.0001
15	0.1605	0.1607	+0.0002
15	0.1072	0.1070	—0.0002
10	0.1658	0.1656	—0.0002
10	0.1642	0.1637	—0.0005
10	0.1268	0.1264	—0.0004
10	0.1422	0.1420	—0.0002

That hydrazine must be there in sufficient quantity is evidenced by the following series of tests in which a 6 per cent. solution was used along

with sulphur dioxide and the solution boiled only a few minutes, other conditions being exactly the same as in the preceding series of experiments.

Te required. Gram.	Te obtained. Gram.	Error. Gram.
0.1508	0.1374	—0.0134
0.1701	0.1443	—0.0258
0.1608	0.1535	—0.0073
0.1521	0.1140	—0.0381
0.1903	0.1781	—0.0122

The following two experiments were made with a large excess of sulphur dioxide water along with a 6 per cent. solution of hydrazine and the solution heated six hours.

Te required. Gram.	Te obtained. Gram.	Error. Gram.
0.1680	0.1545	—0.0135
0.1516	0.1416	—0.0100

The method which has been used in this laboratory for a number of years and which has proven the most satisfactory for the gravimetric determination of tellurium is as follows: The tellurium either as derivative of the dioxide or as a tellurate, should be present in a solution which has an acidity of approximately ten per cent. of hydrochloric acid and it is preferable to have the solution sufficiently concentrated, otherwise the fine state of division of the precipitate will render it unsatisfactory for washing. The solution is heated to boiling and 15 cc. of a saturated solution of sulphur dioxide added, then 10 cc. of a 15 per cent. solution of hydrazine hydrochloride, and again 25 cc. of a saturated solution of sulphur dioxide. The boiling is continued until the precipitate settles in such a way that it can be easily washed. This boiling should not take more than five minutes. The precipitated tellurium after being allowed to settle is washed with hot water on a Gooch filter until all of the chlorine is removed, after which the water is displaced by alcohol and the crucible and contents dried at 105°.

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## LOSS OF PHOSPHORIC ACID IN ASHING OF CEREALS.

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Recent work in this laboratory on the determination of phosphoric acid in the ash of wheat has brought to the attention of the writers the fact that whereas the temperature below fusion, at which ashing of grain is carried on, makes very little difference in the percentage of ash, there is a loss in the corresponding values of phosphorus, varying with the temperature.