ART. LII.—*An Iodometric Method for the Estimation of Telluric Acid*; by F. A. GOOCH and J. HOWLAND.

[Contributions from the Kent Chemical Laboratory of Yale College—xxxvii.]

IN his valuable and extended study of possible volumetric methods for the estimation of tellurium, Brauner* has investigated the action of iodine upon an alkaline tellurite and finds that the oxidation is slow and incomplete at ordinary temperatures, while at 100° C. and in presence of a sufficient excess of iodine complete oxidation takes place, though the difficulty of estimating the excess of iodine not directly utilized in the reaction is so great as to render the method practically inapplicable to the determination of tellurium. The difficulty in effecting oxidation in alkaline solution naturally suggests the reversal of the reaction in an attempt to reduce telluric acid by the action of hydriodic acid in acid solution. Upon putting the matter to the test we find the reduction of telluric acid does take place, but we have been unable to prevent its going too far. Thus, on boiling a solution made by adding 10 cm³ of sulphuric acid of half-strength and 3 gm. of potassium iodide in 90 cm³ of water containing a little more than 0.1 gm. of telluric acid, the liquid darkened, deposited dark gray crystalline scales and evolved iodine which, when collected and titrated with sodium thiosulphate proved to be twenty per cent in excess of the theoretical yield assuming that the reduction should result in the production of tellurous acid. A similar experiment made in like manner excepting that the liquid was heated for fifteen minutes in a closed bottle on the water-bath instead of being subjected to boiling, with the idea that the presence of the free iodine might tend to prevent excessive reduction of the tellurium, indicated a yield of free iodine about six per cent. in excess of what it should be if tellurous acid is the sole product of reduction. In this case the titration of the free iodine was made by sodium thiosulphate in the presence of the reduced tellurous acid, but we found by independent experiment that the determination of free iodine associated with tellurous acid may be accomplished with a fair degree of accuracy provided the solution be cold and dilute, and the final reaction secured by adding the thiosulphate in slight excess and restoring the color permanently by standard iodine. Even under the most favorable conditions the tellurous acid is somewhat acted upon by sodium thiosulphate even before the free iodine is entirely bleached and the reaction in the reverse titration by standard

* Jour. Chem. Soc., 1891, pp. 58, 238.

iodine is slow in coming, though finally definite; but if the solution is hot the thiosulphate precipitates tellurium in flocky condition.

The excessive action of the iodide suggested the substitution of potassium bromide—an agent which proved of value in reducing arsenic acid as described in a recent paper from this laboratory—and, the preliminary experimentation proving to be encouraging we set about the preparation of telluric acid of definitely known strength. We weighed out accurately tellurous oxide, prepared by oxidizing presumably pure crystallized tellurium with nitric acid and igniting the product at a low red heat, dissolved the weighed oxide in a few cubic centimeters of a strong solution of potassium hydroxide, precipitated the tellurous acid by the careful addition of dilute sulphuric acid, and dissolved the precipitate in 10 cm³ of sulphuric acid of half-strength. The solution thus obtained was treated with potassium permanganate in excess, the manganic oxide and the excess of permanganate were bleached by oxalic acid added to the hot solution, and the excess of oxalic acid was destroyed by the addition of a dilute solution of the permanganate until the faintest possible blush of color appeared. For the experiments involving the treatment of the larger amounts of tellurium every preparation was made individually in the manner described; for the experiments with smaller amounts a single preparation was made and the solution thus obtained was diluted to a half liter and portions of this standard solution were drawn from a burette as occasion required.

The equivalent of the so-called element tellurium is, as Brauner has shown* so variable with the mode of determining that constant and the preparation of material that we employed a preparation of tellurous oxide which had been tested as to its equivalent weight by Brauner's excellent method of oxidation by potassium permanganate. The results of these tests are recorded in the accompanying table. In series I the alkaline solution of the oxide was diluted to 100 cm³ and oxidation was effected in it by standard permanganate added in excess. Sulphuric acid of half-strength was added to neutralization and then 5 cm³ more, the liquid was heated, a solution of oxalic acid of known value was introduced to an amount slightly in excess of that needed to destroy the manganic oxide and excess of permanganate, and the surplus of oxalic acid was removed by standard permanganate. In series II the alkaline solution of the oxide was neutralized with dilute sulphuric acid and 1 cm³ of sulphuric acid of half-strength was

* Jour. Chem. Soc., 1889, 382.

added. The oxidation was accomplished from this point exactly as in series I, the only difference being that it took place in the presence of a slight excess sulphuric acid instead of in alkaline solution. The permanganate used in both series was standardized ultimately against lead oxalate.

SERIES I.			
TeO ₂ taken. grm.	Oxygen required for oxidation.	Molecular weight of TeO ₂ when 0=16.	Mean.
0.1200	0.01202	159.7	158.88
0.0783	0.00785	159.6	
0.0931	0.00940	158.7	
0.1100	0.01119	158.	
0.0904	0.00909	159.5	
0.1065	0.01078	157.8	

SERIES II.			
0.0910	0.00935	159.2	159.03
0.0910	0.00910	159.9	
0.0911	0.00924	157.7	
0.0913	0.00915	159.6	
0.0912	0.00915	159.4	
0.0914	0.00923	158.4	

The mean value of these determinations assigns to the tellurous oxide which we employed a molecular weight of about 159 and to the element tellurium an atomic weight of 127, when oxygen is 16. Brauner advocates the application of a correction made necessary by the excessive decomposition of the permanganate in the oxidation; but inasmuch as the oxidation in series I took place in alkaline solution under conditions in which we have no absolute proof that unused oxygen is liberated to any considerable degree from the permanganate, while in series II, the excess of sulphuric acid was purposely restricted to the lowest limit—the sulphuric acid having been shown in a previous paper from this laboratory* to be the chief agent in inducing the excessive decomposition of the permanganate—we incline, provisionally at least, to accept in this case the result of the analysis without correction.

In the test experiments the telluric acid, prepared in the manner described, was introduced into the apparatus for distillation with 3 grms. of potassium bromide, care being taken to insure in the 50 cm³ or more of liquid the presence of 10 cm³ of sulphuric acid of half strength. A current of carbon dioxide was passed through the apparatus, the solution was boiled to set free the bromine which was absorbed in

* Gooch and Danner, this Journal, xliv, 301.

potassium iodide and estimated by standard sodium thiosulphate. In handling the larger amounts of tellurium we found it desirable to make the preparation of the telluric acid in the distilling flask and to boil out the oxygen and ozone set free in the preparation before proceeding with the operation. The apparatus which we used consisted of a Voit's gas-washing flask, with sealed-in inlet tube and ground-in outlet tube, used as the distillation flask, to which was joined by a sealed joint the inlet tube of a Drexel washing bottle to the outlet tube of which was sealed a Will and Varrentrapp absorption apparatus. The washing bottle and attached bulbs contained a solution of 3 grams of potassium iodide and the former was kept cool by standing it during the distillation in a vessel of cold water. The absorption of the bromine took place almost entirely in the bottle, only traces of iodine being set free in the bulbs. The results of our experiments are recorded in the accompanying statement; $\text{Te}=127, 0=16$.

	Initial volume. cm ³ .	Final volume. cm ³ .	TeO ₂ taken. gm.	TeO ₂ found. gm.	Error. gm.
(1)	50	20	0.0102	0.0098	0.0004—
(2)	50	20	0.0102	0.0099	0.0003—
(3)	50	20	0.0102	0.0098	0.0004—
(4)	50	20	0.0102	0.0098	0.0004—
(5)	100	40	0.1000	0.0994	0.0006—
(6)	80	40	0.1001	0.1001	0.0000
(7)	100	20	0.1002	0.1001	0.0001—
(8)	50	20	0.1000	0.1003	0.0003+
(9)	50	25	0.5011	0.5008	0.0003—
(10)	50	25	0.5002	0.5006	0.0004+
(11)	50	25	0.5000	0.4998	0.0002—
(12)	50	20	0.5000	0.4994	0.0006—

The results of experiment agree fairly well with one another and with theory based upon the assumption that the atomic weight of the tellurium which we employed was 127. It is evident that the reducing action of the hydrobromic acid developed in the distillation is regular and that that agent is well adapted to the reduction of telluric acid to tellurous acid. The formation of tellurium tetrabromide in the concentrated acid liquid makes it impossible to tell by the color when all the bromine has been distilled, but the evidence of the experiments goes to show that the boiling of the liquid from a volume of 50 cm³ to 25 cm³ is sufficient, while concentration from 100 cm³ to 20 cm³ apparently does no harm.