ART. XII.—*The Determination of Tellurous Acid in presence of Haloid Salts;* by F. A. GOOCH and C. A. PETERS.

[Contributions from the Kent Chemical Laboratory of Yale University—LXXXIV.]

THE estimation of tellurous acid by oxidation with excess of potassium permanganate (either in acid or alkaline solution), destruction of the higher oxides of manganese or the manganate by standard oxalic acid in presence of sulphuric acid, and titration of the residual oxalic acid by more permanganate, has been shown by Brauner* to be feasible. The tendency of the permanganate to throw off too much oxygen when the oxidation is made in solutions strongly acidified with sulphuric acid (as must be the case if the tellurous oxide is to be held permanently in solution by sulphuric acid) necessitates the application of a considerable correction.† Fortunately, however, as has been shown in a former paper from this laboratory,‡ when the tellurous oxide is dissolved originally in an alkaline hydroxide and the solution made acid only to a limited degree with sulphuric acid either before or after oxidation by the permanganate, no correction appears to be necessary. Thus, when an excess of permanganate is added to the alkaline solution, followed by an excess of oxalic acid and sulphuric acid to an amount not exceeding 5^{cm^3} of the [1 : 1] mixture with water, the titration of the residual oxalic acid by more permanganate (after heating to 80° C.) leads to results which give no indication of over-decomposition of the permanganate; so also, when the process is similarly conducted excepting that before addition of the permanganate the original alkaline solution is acidified with sulphuric acid [1 : 1] to an amount 1^{cm^3} in excess of that necessary to re-dissolve the first precipitate, the results are theoretically accurate, and in close agreement with those obtained by the former procedure.

In the presence of free hydrochloric acid the action of the permanganate upon tellurous acid has been shown by Brauner§ to be irregular and excessive, and the irregularity cannot be corrected (as in the titration of ferrous salts in presence of hydrochloric acid) by the addition of a manganous salt according to the well-known procedure of Kessler‖ and Zimmermann.¶ So far as appears, however, there should be nothing to prevent the accurate determination of tellurium in tellurous compounds in the presence of chlorides by the permanganate process providing the first oxidation is made in alkaline solution, and the second oxidation carried out with such precautions

* Jour. Chem. Soc. 1891, p. 238.

† Loc. cit., p. 249.

‡ Gooch and Danner: this Journal, xliv, 301.

§ Loc. cit., p. 241.

‖ Ann. der Phys., cxviii, 48; cxix, 225, 226.

¶ Ann. der Chem., ccxiii, 302.

as are necessary to a correct determination of oxalic acid by permanganate in presence of hydrochloric acid; for, the special danger of over-action on the part of the permanganate cannot exist while the solution is alkaline, and has passed when the tellurite has become a tellurate and before the solution is made acid. As to the proper conditions for the titration of oxalic acid by permanganate we have shown recently* that the presence of a manganous salt is necessary and sufficient to secure regularity of action when a considerable amount of hydrochloric acid is in the solution; when the amount is small —so much as would be formed in the decomposition of a gram or two of halogen salt of tellurium—the disturbing effect under ordinary conditions of work is probably inappreciable, but even in such a case it is better to work in the presence of a manganous salt for the reason that the titration of the oxalic acid may then be made at the ordinary atmospheric temperature.

In the following table are gathered the results of experiments made with, and without, the addition of the manganous salt.

TABLE I.

O = 16, Te = 127·5.
Volume at beginning, 150^{cm^3}.
Temperature of titration, 60–80° C.

TeO_2 taken.	NaCl.	H_2SO_4 1:1.	$MnCl_2.4H_2O$.	TeO_2 found.	Error.
grm.	grm.	cm^3.	grm.	grm.	grm.
0·1000	·4	5	....	0·1003	+0·0003
0·1000	·4	5	....	0·1000	0·0000
0·1000	·4	5	....	0·1004	+0·0004
0·1000	1·0	5	....	0·1003	+0·0003
0·0650	1·0	5	....	0·0653	+0·0003
			B.		
		Temperature of titration, 20–26° C.			
0·0700	·4	5·7	1·0	0·0705	+0·0005
0·0700	·4	5·7	1·0	0·0698	−0·0002
0·0700	·4	5·7	·5	0·0701	+0·0001
0·1000	·4	5·7	·5	0·1008	+0·0008

The tellurium dioxide, made by the careful ignition of the crystallized basic nitrate obtained by oxidizing tellurium with nitric acid, was dissolved in a small amount of sodium hydroxide, the halogen salt was added to the amount shown, the permanganate standardized against ammonium oxalate was run in until its characteristic color appeared, standard ammonium oxalate was added in excess of the quantity required to reduce the excess of permanganate, manganate, and higher oxides, and

* This Journal.

the solution was heated with enough sulphuric acid [1 : 1] to neutralize the alkaline hydroxide and have an excess of about 5^{cm^3}. In the experiments of Section A the liquid was heated to 60°–80° C. to dissolve the oxides at the final titration begun at that temperature; in those of Section B, manganous chloride (0·5 to 1 gram) was added, so that the reduction of the higher oxides of manganese and the final titration of the excess of oxalic acid might take place at the ordinary temperature of the room.

Plainly the presence of the chloride does not interfere materially in the determination of the tellurium by this process whether the titration is made at a high or low temperature.

It appears, also, upon putting the matter to the test, that fairly good determinations of tellurous acid may be made similarly in the presence of a bromide, provided the titration is made at the atmospheric temperature in the presence of a sufficiency (0·5 gram to 1 gram) of a manganous salt and of an excess of sulphuric acid limited to about 5^{cm^3} or less of the 12·5 per cent mixture. At the higher temperatures bromine is liberated at once from the acid solution by the permanganate. The experimental results are given in Table II.

TABLE II.

O = 16, Te = 127·5.
Volume at beginning, 150^{cm^3}.
Temperature of titration, 24°–26° C.

TeO_2 taken. grm.	NaCl. grm.	KBr. grm.	H_2SO_4 12·5 %. cm^3.	$MnCl_2 . 4H_2O$. grm.	TeO_2 found. grm.	Error. grm.
[0·1000	----	0·5	20	1·0	0·1022	+0·0022]
[0·3000	----	1·5	25	1·0	0·3030	+0·0030]
0·0650	----	0·5	1	1·0	0·0661	+0·0011
0·0650	----	0·5	1	1·0	0·0647	−0·0003
0·1000	----	0·5	1	1·0	0·1002	+0·0002
0·3000	----	0·5	5	0·5	0·3010	+0·0010
0·0650	0·5	0·5	1	1·0	0·0661	+0·0011

It is obvious, therefore, that tellurous acid may be determined with a fair degree of accuracy by the permanganate method in the presence of chlorides and bromides, provided the first oxidation is made in alkaline solution and the final titration of the residual oxalic acid is made at ordinary temperatures in the presence of a manganous salt and restricted amounts of free sulphuric acid.

In the presence of an iodide, however, the case is different. Upon acidifying the mixture of iodide and the higher oxygen compounds of manganese, produced in the action of the permanganate upon the solution, iodine is at once set free, and oxalic acid does not suffice to reconvert it. In the presence of an excess of potassium iodide the higher manganic compounds are completely reduced with rapidity and the iodine liberated is the measure of the excess of permanganate over that required to oxidize the tellurous acid; the difference between the amount of permanganate thus indicated and that originally introduced should determine the amount of the tellurous acid. It is upon this basis that Norris and Fay* have founded their excellent iodometric determination of tellurous acid. This process consists in treating the alkaline solution of tellurous acid with standard permanganate until the meniscus of the liquid shows a deep pink color, then diluting the solution with ice-water, adding potassium iodide and sulphuric acid, and titrating with sodium thiosulphate. The results are excellent.

It is plain that any agent capable of converting the iodine to hydriodic acid without at the same time reducing telluric acid should be capable of measuring the excess of the permanganate, and so the amount of tellurous acid originally present. We find that the standard arsenite made, as usual, by dissolving 4·95 grams of pure resublimed arsenious oxide to the liter of water containing potassium bicarbonate answers the purpose admirably, and possesses the further advantage of fixing at once the entire standard of the process, the strength of the permanganate $\left(\text{approximately } \frac{n}{10}\right)$ being determined by running a definite volume of its solution into water containing potassium iodide (1 gram) with 2 to 3^{cm^3} of dilute sulphuric acid and titrating by the standard arsenite the iodine (set free by the action of the excess of permanganate and higher oxides) after neutralization with acid potassium bicarbonate. In this titration of iodine by the arsenite we find it best to dispense with the starch solution usually employed to secure the end reaction. The color of the free iodine itself is sufficiently definite, even at a dilution so much as 300^{cm^3}, and its disappearance under the action of the arsenite is much sharper than that of the blue starch iodide.

In Table III are recorded results obtained by adding the alkaline solution of tellurous oxide to 100^{cm^3} of water containing 0·5 gram or 1 gram of potassium iodide, introducing the standardized potassium permanganate until the green color of the manganate appears (about 30^{cm^3} of the $\frac{n}{10}$ solution for every 0·1 gram of TeO_2), adding a few cubic centimeters of dilute sulphuric acid followed, when the solution has cleared and separated iodine, by an excess of acid potassium carbonate,

* Am. Chem. Jour., xx, 278.

and titrating to the destruction of color with the standard solution of arsenic. It is essential in order that oxygen may not go to waste in the breaking down of the oxides, that more than enough iodide should be present when the solution is acidified to complete the reduction of the manganese oxides, or else, that the arsenious acid should be present in suitable amount before the sulphuric acid is put in. This latter procedure may be used in case, for any reason, it is preferred not to introduce more iodide into the solution than may be present originally: when, for example, a direct determination of the iodine present is to follow.

TABLE III.

O = 16, Te = 127·5.

TeO_2 taken. grm.	NaCl. grm.	KBr. grm.	KI. grm.	Total volume at end. cm³.	NaOH present during oxidation. grm.	TeO_2 found. grm.	Error. grm.
0·1000	----	----	·5	160	0·1	0·1005	+ ·0005
0·1000	----	----	·5	160	0·1	0·1001	+0·0001
0·1000	----	----	·5	160	0·1	0·1003	+0·0003
0·1000	----	----	1·0	250	0·1	0·1007	+0·0007
0·2000	----	----	1·0	250	0·2	0·1997	−0·0003
0·1000	.5	·5	·5	250	0·1	0·1000	0·0000
0·2100	1·0	1·0	1·0	225	0·2	0·2105	+0·0005
0·1000	----	----	·5	160	1·0	0·1011	+0·0011
0·2000	----	----	1·0	300	2·0	0·2009	+0·0009

These results are reasonably good. Like those of Table I they would be brought practically in the average to the figure demanded by theory if the value of the Committee of the German Chemical Society, Te = 127, were to be taken instead of Te = 127·5, the value of Clarke and of Richards.