ART. III.—*The Estimation of Sulphites by Iodine*; by
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[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxxxvi.]

VOLHARD'S method for the determination of sulphur dioxide and sulphites is accurate and reliable, but involves the inconvenience of making up every solution to be examined accurately to a standard volume of which portions are to be drawn from a burette and made to react with definite amounts of a standardized solution of iodine. The method consists in running the unknown sulphite or sulphurous acid solution into a known amount of a standardized solution of iodine, acidified with hydrochloric acid, to the disappearance of the iodine reaction with starch. This procedure rests upon the facts that the oxidation of sulphite is brought about in the acidified solution and that, as Bunsen showed, no more than a small proportion of hydriodic acid should be present at the point at which the bodies are made to react. The reaction for the oxidation of sulphur dioxide proceeds normally in dilute solutions according to the equation

In solutions too concentrated, however, the secondary reaction

takes place as Vollhard has shown*, and vitiates the indications.

To avoid the inconvenience of the Vollhard method it has been proposed by Rupp† to bring about the oxidation of sulphites by treatment with an excess of standardized iodine in a solution made alkaline by acid sodium carbonate, and then, after fifteen minutes, to titrate the excess of iodine by sodium thiosulphate. This procedure, however, is, as has been shown by Ruff and Jaroch‡ and by the present writer,§ faulty in principle and practice, and gives correct results only by a chance balancing of opposing errors. Theoretically it might be possible to overcome the difficulties by treating with acid the alkaline mixture of iodine and sulphite and acid sodium carbonate

* Ann. Chem. 242, 93.

† Ber. Dtsch. Chem. Ges. xxxv, 3694.

‡ Ber. Dtsch. Chem. Ges. xxxviii, 409.

§ This Journal, vol. xiv, p. 237.

before attempting to titrate by sodium thiosulphate the excess of iodine.

In the experiments recorded in the table the following procedure was followed: the sulphite was treated with 1 grm. of acid sodium carbonate and an excess of standardized iodine solution. The solution was then acidulated with a safe amount of hydrochloric acid, it having been found by experiment that the presence of 10^{cm}³ of 1:4 hydrochloric acid in 125^{cm}³ of water was without effect upon the determination of iodine by sodium thiosulphate. The excess of iodine after acidification was titrated by standardized sodium thiosulphate. It will be noticed that in the experiments recorded under A of the table, the excess of iodine used was small and in these experiments large negative errors are obtained; while in the experiments recorded under B, in which a large excess of iodine was employed, the results are better. They are best when at least twice as much iodine is added as is theoretically required to oxidize the sulphur dioxide. The length of time during which the iodine may act does not affect the results to any very marked degree.

A

Iodine value of SO ₂ taken. grm.	Iodine taken. grm.	Iodine value of Na ₂ S ₂ O ₃ used. grm.	Error.		Excess of HCl 1:4. cm ³ .	Vol. at titra- tion. cm ³ .
			In terms of Iodine. grm.	In terms of SO ₂ . grm.		
0·2197	0·3143	0·0978	—0·0032	—0·0008	7·5	125
“	“	0·0965	—0·0019	—0·0005	“	“
“	“	0·0970	—0·0024	—0·0006	“	“
0·1535	0·1913	0·0464	—0·0086	—0·0022	“	“
“	“	0·0467	—0·0089	—0·0022	“	“
“	“	0·0472	—0·0094	—0·0024	“	“
“	“	0·0465	—0·0087	—0·0022	“	“
0·2366	0·3194	0·0903	—0·0075	—0·0019	“	“
0·2906	0·3825	0·1132	—0·0213	—0·0054	“	“
0·3825	0·4463	0·0750	—0·0112	—0·0028	“	“

B

0·1143	0·3143	0·1990	+0·0010	+0·0003	5·0	125
“	“	0·1982	+0·0018	+0·0004	“	“
“	“	0·1992	+0·0008	+0·0002	“	“
“	“	0·1986	+0·0014	+0·0003	“	“
0·1482	0·3187	0·1708	—0·0003	—0·0001	7·5	“
0·1576	0·3187	0·1586	+0·0025	+0·0006	“	“
“	“	0·1643	—0·0032	—0·0008	“	“
“	“	0·1598	+0·0013	+0·0003	“	“
“	“	0·1606	+0·0005	+0·0001	“	“
“	“	0·1602	+0·0009	+0·0002	“	“

(B)

Iodine value of SO ₂ taken. gram.	Iodine taken. gram.	Iodine value of Na ₂ S ₂ O ₃ used. gram.	Error.		Excess of HCl 1 : 4 cm ³ .	Vol at titra- tion. cm ³ .
			In terms of Iodine. gram.	In terms of SO ₂ . gram.		
0.1576	0.3187	0.1622	-0.0011	-0.0003	7.5	125
0.1560	0.3195	0.1660	-0.0025	-0.0006	"	"
0.1992	0.4460	0.2482	-0.0014	-0.0003	"	"
0.1915	0.3825	0.1919	+0.0009	-0.0002	"	"
0.2056	0.3771	0.1701	+0.0014	+0.0003	"	"
"	"	0.1697	+0.0018	+0.0004	"	"
"	"	0.1707	+0.0008	+0.0002	"	"
"	"	0.1709	+0.0006	+0.0002	"	"
[0.2131	0.4470	0.2412	-0.0073	-0.0018]	"	"
0.2354	0.3825	0.1490	-0.0019	-0.0005	"	"
0.2597	0.4463	0.1869	-0.0003	-0.0001	"	"
0.2638	0.4463	0.1847	-0.0022	-0.0005	"	"
0.2908	0.6375	0.3505	-0.0038	-0.0009	"	"
0.3187	0.4463	0.1326	+0.0050	+0.0012	"	"
0.3395	0.6275	0.2842	+0.0038	+0.0009	"	"
"	"	0.2852	+0.0028	+0.0007	"	"
"	"	0.2844	+0.0036	+0.0009	"	"
"	"	0.2855	+0.0025	+0.0006	"	"

Ruff and Jaroch* take the ground that in the favorable results occasionally obtained by Rupp's process, an error due to the over-oxidation of the tetrathionate normally formed in the action of sodium thiosulphate upon the residual iodine is apparently balanced by some oxidation of sulphur dioxide by dissolved air, the iodine in solution acting catalytically as well as directly. The theory, however, is quite at variance with the evidence supplied in the table: for, if it were true, under no conditions could iodine in the presence of air act as a correct measure of sulphur dioxide, as it apparently does when used in a sufficiently large excess; nor does the theory of the catalytic action of iodine explain the fact that when a greater mass of iodine is used, under conditions otherwise similar, we get a larger oxidation of sulphur dioxide.

The most obvious explanation is that at a low concentration of iodine an intermediate oxidation product may be formed and that the formation of this product may be prevented by sufficient concentration of the iodine. It is not unreasonable to suppose that the formation of a small amount of dithionate instead of sulphate is the occasion of the deficient expenditure of iodine noted when the concentration of this element is low, and that the dithionate is not formed appreciably when the

* Loc. cit.

iodine concentration is high. The dithionate once formed is but slowly attacked by iodine, and that is apparently the reason why long standing of the mixtures containing a small proportion of iodine does not result in complete oxidation of the sulphite to sulphate. From these considerations it will be seen that the secondary error of Rupp's process may very probably be due to the formation of some dithionate from the sulphite where the concentration of the iodine is low.

The practical estimation of sulphurous acid or a soluble sulphite may, then, be accomplished with a reasonable degree of accuracy by adding to the solution of the substance, not exceeding 100^{cm}³ in volume and containing a gram of acid sodium carbonate, at least twice as much iodine as is theoretically necessary to effect oxidation, acidifying cautiously with hydrochloric acid, and determining with standard sodium thiosulphate the excess of iodine remaining in the acidified solution.

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