ART. XVI.—*The Iodometric Estimation of Arsenic Acid;* by F. A. GOOCH and JULIA C. MORRIS.

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

THE interaction of a soluble arseniate and a soluble iodide in a suitably acidulated solution results, as is well known, in the reduction of the arsenic acid (more or less completely according to conditions of temperature and proportions of reagents and solvents) with the corresponding liberation of two atoms of iodine for every molecule of arsenic acid (H_3O_3AsO) reduced. Inasmuch, however, as the reaction of this process is reversible, it is necessary, in order that the reduction may be complete, to nullify the oxidizing action of the iodine liberated. Theoretically this end may be accomplished in either of two ways, by volatilizing the free iodine bodily or by destroying the oxidizing power of the iodine by converting it to hydriodic acid. The former method was followed in a process devised for the estimation of arsenic acid and elaborated in this laboratory.* This method, as originally put forward, consisted in adding to the solution of the arseniate potassium iodide in excess of the amount theoretically indicated, with 10^{cm^3} of sulphuric acid of half strength, and so arranging the dilution that the total volume of the liquid should be about 100^{cm^3}, boiling until the volume decreased to 40^{cm^3}, bleaching by the cautious addition of sulphurous acid the trace of free iodine still held by the hydriodic acids, diluting, cooling, neutralizing with acid potassium carbonate, and titrating with iodine, after adding the starch indicator. This process, depending upon the removal by volatilization of all but the last traces of liberated iodine and the conversion of this minute residue by sulphurous acid, involves no secondary reactions of a sort likely to influence the main effect. It is exact and fairly rapid.

The method of Williamson,† brought forward more recently, depends upon the conversion of the liberated iodine to hydriodic acid. The interaction at ordinary temperatures of a suitably strong acid, hydrochloric or sulphuric acid, upon the mixture of the arseniate and iodide sets free iodine, and the liberated iodine is converted to hydriodic acid by the action of sodium thiosulphate, the end point being the disappearance of the iodine color.

According to Williamson's directions, 25^{cm^3} portions of the solution of the arseniate are treated with potassium iodide and mixed with an equal volume of hydrochloric acid of sp. gr.

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* Gooch and Browning, this Journal, xl (1890), 66.

† Jour. Soc. Dyers and Colorists, 1896, 86–89.

1·16. The precaution is recommended that the strength of the solution of the arseniate shall not exceed the decinormal value, in order that the dilution consequent upon titration by the thiosulphate may not be too great—the reducing action brought about by the action of the strong acid upon the arseniate and iodide being reversible upon the dilution of liquid with water. This procedure thus limits the process to the determination of about 0·18 gram of arsenic acid in 25^{cm^3} of the solution to be treated with an equal volume of hydrochloric acid of sp. gr. 1·16. Obviously, however, the process should, so far as the reduction is concerned, be applicable to larger amounts of arsenic provided the strength of the acid is kept up proportionately. It is essential that the liquid at the end of the titration should contain approximately ten per cent of its mass of absolute hydrochloric acid or about one-third of its volume of the aqueous acid of sp. gr. 1·16.

The arsenic acid is measured either by the amount of standard thiosulphate required to bleach the iodine or by the amount of iodine required to reoxidize the reduced arsenious acid, after neutralizing with acid potassium carbonate. If the former alternative is followed, the end-reaction must be the disappearance of the yellow color of the iodine, since in solutions so strongly acid it is impossible to place dependence upon the starch indicator; in using the latter alternative, the starch indicator is, of course, permissible and preferable.

In the direct titration of the iodine by thiosulphate two sources of error present themselves as possibilities; first, the excessive liberation of iodine by the action of air upon the strongly acidulated iodide; and second, the liability of the thiosulphate,* if present even in momentary or local excess during the process of titration, to break down under the action of strong acid, thus changing its capacity to convert iodine to hydriodic acid. The latter contingency should be remote in proportion to the caution used in adding the thiosulphate and in keeping the liquid well stirred; the former must of necessity vary with the acidity of the solution containing the iodide, the time of exposure to atmospheric action, and the degree of contact with the air incidental to stirring. We have thought it desirable, therefore, to see how far each of these possibilities is likely to interfere in the practical conduct of an ordinary analysis.

The effects likely to result simply from the strong acidification of the solution containing potassium iodide and their variation for conditions of dilution representing the beginning and the end of a titration on the lines laid down are shown in

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* Norton, this Journal, vii, 287.

the following table. The solution of potassium iodide was diluted as indicated before the addition of the acid and the iodine set free was titrated by thiosulphate.

HCl Sp. gr. 1·16 taken. cm³.	KI taken. gm.	Total volume. cm³.	$Na_2S_2O_3$ added at once. In terms of H_3O_3AsO. gm.	$Na_2S_2O_3$ added after 5 minutes. In terms of H_3O_3AsO. gm.	$Na_2S_2O_3$ added after stirring 5 minutes. In terms of H_3O_3AsO. gm.
25	2	50	0·0013		
25	2	75	0·0004		
25	2	50		0·0035	
25	2	75		0·0019	
25	2	50			0·0042
25	2	75			0·0021
50	2	100	0·0017		
50	2	150	0·0004		
50	2	100		0·0035	
50	2	150		0·0019	
50	2	100			0·0035
50	2	150			0·0014

The proportionate strength of acid and the time before titration are, obviously, the essential factors. The absolute amount of acid present and the stirring seem to make little difference.

As to the action of the hydrochloric acid on small amounts of the thiosulphate, we have the evidence of the experiments detailed in the following statements, in which 1, 2, and 5^{cm^3} of nearly $\frac{n}{10}$ thiosulphate are exposed to the action of 25^{cm^3} hydrochloric acid, sp. gr. 1·16, without dilution or diluted with

HCl Sp. gr. 1·16. cm³.	Volume before titration. cm³.	$Na_2S_2O_3$ nearly $\frac{n}{10}$ cm³.	in terms of H_3O_3AsO. gram.	Iodine to color without dilution in terms of H_3O_3AsO. gram.	Error of titration without dilution in terms of H_3O_3AsO. gram.	Iodine to color after diluting to 75^{cm^3} in terms of H_3O_3AsO. gram.	Error of titration after dilution in terms of H_3O_3AsO. gram.
25	26	1	0·0071	0·0062	—0·0009	0·0071	0·0000
25	50	1	0·0071	0·0071	0·0000	0·0071	0·0000
25*	50	1	0·0071	0·0079	+0·0008	0·0079	+0·0008
25	50	2	0·0141	0·0146	+0·0005	0·0146	+0·0005
25*	50	2	0·0141	0·0157	+0·0016	0·0157	+0·0016
25	30	5	0·0353	0·0336	—0·0017	0·0374	+0·0024
25	50	5	0·0353	0·0359	+0·0006	0·0359	+0·0006
25*	50	5	0·0353	0·0411	+0·0058	0·0411	+0·0058

*In these experiments the acid stood in contact with the thiosulphate 5 minutes before titration.

an equal volume of water, were titrated with nearly $\frac{n}{10}$ iodine. The condition of acidity when the volume of 50^{cm^3} contains 25^{cm^3} of hydrochloric acid, sp. gr. 1·16, is that of the beginning of titration of Williamson's process. In order that the effect of error due to such action upon the determination of arsenic acid may appear immediately, the thiosulphate and iodine used are expressed in terms of that acid.

These two sources of error, the one due to a liberation of iodine and the other due to decomposition of the thiosulphate, would naturally tend to overcome one another, but the completeness of such neutralization would naturally be largely a matter of chance in the varying conditions of actual analysis. The experiments of the following table, however, in which $\frac{n}{10}$ thiosulphate, to the amount of 1, 2, and 5^{cm^3}, was added to the liquid, 50^{cm^3} and 75^{cm^3}, containing 25^{cm^3} acid, and titrated with iodine at once, and after five minutes, were made to test the matter for the conditions of dilution at the beginning and at the end of a titration.

HCl Sp. gr. 1·16.	KI.	Volume.	$Na_2S_2O_3$ nearly $\frac{n}{10}$	in terms of H_3O_3AsO.	Iodine in terms of H_3O_3AsO, at once.	Iodine in terms of H_3O_3AsO, after 5 min.	Error in terms of H_3O_3AsO.
cm³.	gm.	cm³.	cm³.	gram.	gram.	gram.	gram.
25	2	50	1	0·0071	0·0057		−0·0014
25	2	75	1	0·0071	0·0071		0·0000
25	2	50	2	0·0141	0·0131		−0·0010
25	2	75	2	0·0141	0·0143		+0·0002
25	2	50	5	0·0353	0·0322		−0·0021
25	2	75	5	0·0353	0·0357		+0·0004
25	2	50	1	0·0071		0·0028	−0·0043
25	2	75	1	0·0071		0·0067	−0·0004
25	2	50	2	0·0141		0·0116	−0·0025
25	2	75	2	0·0141		0·0139	−0·0002
25	2	50	5	0·0353		0·0314	−0·0041
25	2	75	5	0·0353		0·0361	+0·0008

It is clear that under the conditions covered by the experiments of the two preceding tables the decomposition of the thiosulphate is likely to occur in greater or less degree, and that when the acid of sp. gr. 1·16 is not much diluted, the products of decomposition are not oxidized by the iodine completely. The latter observation is quite in harmony with the fact that sulphur dioxide bleaches iodine in strong hydrochloric acid only slowly and incompletely. In such cases dilution favors further action of the iodine, but results obtained by titration with iodine in the acid solution diluted with an equal amount of water are unmodified by further dilution.

In the following tables are recorded actual determinations of arsenic according to Williamson's process. To each 25^{cm^3} of the arseniate were added 1, 2, or 3 grams of potassium iodide and 25^{cm^3} hydrochloric acid, sp. gr. 1·16. The iodine was bleached by nearly decinormal thiosulphate without addition of the starch indicator, which loses all delicacy in the presence of strong acid. The time occupied by each titration was about five minutes. The standards of the arseniate were determined by the vaporization process,* the purity of reagents employed in that process having been proved by trying the process in the estimation of a solution of arsenic acid made by oxidizing pure decinormal arsenious acid by iodine.

HCl cm³.	KI. gram.	Volume at beginning of titration. cm³.	Volume at end of titration. cm³.	H_2KAsO_4 in terms of H_3O_3AsO. gram.	H_3O_3AsO found. gram.	Error. gram.
25	2	50	51	0·0062	0·0085	+0·0023
25	2	50	52	0·0125	0·0156	+0·0031
25	2	50	55	0·0312	0·0350	+0·0038
25	2	50	55	0·0624	0·0666	+0·0042
25	2	50	73	0·1559	0·1588	+0·0029
25	2	50	73	0·1559	0·1587	+0·0028
25	2	50	73	0·1559	0·1591	+0·0032
25	2	50	73	0·1559	0·1595	+0·0036
25	3	50	73	0·1559	0·1595	+0·0036
25	1	50	73	0·1559	0·1581	+0·0022
25	2	50	73	0·1559	0·1581	+0·0022
25	2	50	73	0·1559	0·1588	+0·0029

The range of error in these results is from +0·0023 gram to +0·0042 gram with a mean of +0·0031 gram—not very different from what might be expected from the effect of the interaction of the strong hydrochloric acid and the iodide alone. The counter-effect due to the decomposition of the thiosulphate is not large, yet it is probably real, as will appear in the sequel. In the following series of determinations, made with new solutions and new standards throughout, the arsenic acid was determined, first, by titrating the iodine set free by 25^{cm^3} of hydrochloric acid, sp. gr. 1·16 and 3 grams potassium iodide, the solution having a total volume of 50^{cm^3} at beginning and of 75^{cm^3} at the end of titration and, secondly, the arsenious acid produced in the first reaction was titrated, after being neutralized with acid potassium carbonate by iodine in the presence of the starch indicator.

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* Gooch and Browning, loc. cit.

H_2KAsO_4 taken, in terms of H_3O_3AsO. gram.	H_3O_3AsO found by the thiosulphate. gram.	Error. gram.	H_3O_3AsO found by titration of H_3O_3As with iodine. gram.	Error. gram.
0·1767	0·1798	+0·0031	0·1776	+0·0009
0·1767	0·1798	+0·0031	0·1777	+0·0010
0·1767	0·1795	+0·0028	0·1785	+0·0018
0·1767	0·1793	+0·0026	0·1785	+0·0018
0·1767	0·1794	+0·0027	0·1780	+0·0013
0·1767	0·1798	+0·0031	0·1785	+0·0018

The average error of the first operation is 0·0029 gram, not far from that of the previous series; the error of the second operation, the titration of the arsenious acid, amounts on the average to 0·0014 gram. In the second operation the error due to over-use of the thiosulphate by iodine set free outside the main reaction is obviously eliminated. The tetrathionate present after neutralization with acid potassium carbonate is unaffected by iodine, as we have found by titrating 25^{cms} $\frac{n}{10}$ iodine mixed with 25^{cm^3} hydrochloric acid, sp. gr. 1·16, by the thiosulphate, neutralizing with acid potassium carbonate,* adding starch and getting the starch blue with a single drop of $\frac{n}{10}$ iodine. The average error of this process, therefore, 0·0014, is probably due to the products of decomposition of the thiosulphate in the first operation.

From the foregoing experiments it is clear that an arbitrary correction of about 0·0030 gram must be deducted from the indications of Williamson's process of direct titration by thiosulphate, made with the greatest care under the conditions mentioned; and that a correction varying from one-half that amount (0·0015 gram) to nothing (according to the amount of arsenious acid present) when the determination is made by iodine after neutralization with acid potassium carbonate. After making these arbitrary corrections in the results of the preceding table, the individual variations fall within reasonable limits.

On the other hand, the vaporization process, in which the arseniate is reduced by boiling with sulphuric acid and potassium iodide in the manner described,† gives indications reason-

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*It is worthy of note, that, as we have found by experience, it is not possible to substitute an alkaline hydroxide for the carbonate in the early stages of the process of neutralization, on account of the decomposing effect of the former reagent upon the tetrathionate. This effect is in proportion to the heating of the solution, but is never wholly absent even when ice is intermixed with the liquid and the greatest care taken to prevent a rise of temperature.

† Loc. cit.

ably regular and accurate without the application of an arbitrary correction. This process, moreover, may be shortened by restricting the volume at which heating begins so that the boiling need not be extended beyond five or six minutes. According to this slight modification, the solution of the arseniate is heated in an Erlenmeyer flask with potassium iodide to an amount about 0·5 gram in excess of the amount theoretically required and 10^{cm^3} of sulphuric acid of half strength in a total volume of between 50^{cm^3} and 75^{cm^3}. The liquid is boiled till the iodine vapors are no longer visible in the flask above the liquid, the iodine color in the still hot liquid is bleached by the cautious addition of sulphurous acid, the whole is diluted with cold water, and cooled quickly. The solution is nearly neutralized with potassium hydroxide and the neutralization is completed with acid potassium carbonate. The reduced acid is titrated with iodine after adding the starch indicator. By this procedure the results of the following table were obtained.

Volume. cm^3.	H_3O_3AsO taken. gram.	H_3O_3AsO found. gram.	Error. gram.
35	0·1559	0·1559	0·0000
35	0·1559	0·1560	+0·0001
40	0·1559	0·1559	0·0000
65	0·1559	0·1559	0·0000
50	0·2495	0·2499	+0·0004
50	0·2557	0·2449	−0·0008
60	0·3119	0·3117	−0·0002
60	0·3119	0·3120	+0·0001
75	0·3119	0·3124	+0·0005
75	0·3119	0·3132	+0·0013
75	0·3119	0·3121	+0·0002
75	0·3119	0·3115	−0·0004
75	0·3119	0·3124	+0·0005