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THE USE OF THE IODINE MONOCHLORIDE END-POINT IN VOLUMETRIC ANALYSIS. II. THE TITRATION OF ARSENIOUS ACID WITH PERMANGANATE AND WITH CERIC SULFATE

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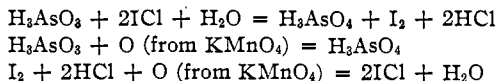
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Introduction

The advantages of the use of the iodine monochloride end-point and of its use with standard oxidizing solutions other than iodate have been discussed in the preceding paper. The titration of arsenious acid with permanganate solutions has presented a troublesome problem, of which the literature is too voluminous to be discussed in detail here.¹ Briefly, it may be stated that in sulfuric acid solution the rate of the reaction as the end-point is approached becomes very slow and various colored compounds form to such an extent that the titration is not recommended, even at 100°. In a hydrochloric acid solution at room temperature the same difficulties are encountered, but the titration may be made if the solution is heated to boiling. It has also been found by several workers² that small amounts of iodine or bromine compounds catalyze the reaction.

In view of the fact that arsenious acid can be titrated rapidly and accurately at room temperature with standard iodate solution using the iodine monochloride end-point, and in view of the just mentioned catalysis by iodine compounds, it seemed quite probable that permanganate could be substituted for iodate if a little iodine monochloride were added to serve as an indicator. This was found to be the case. The results of a study of this titration and of the standardization of a permanganate solution against arsenious oxide are shown below.

The successive reactions involved in the process may be represented as follows



The titration of arsenious acid with ceric sulfate solution has been studied by Willard and Young.³ They found the reaction in a hydrochloric acid solution to be too slow for use at room temperature, but to be

¹ For reviews of this subject see Hall and Carlson, *THIS JOURNAL*, **45**, 1615 (1923), or Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1929, pp. 2, 285, 304.

² (a) C. Lang, *Chem.-Ztg.*, **37**, 774 (1898); *Chem.-Ztg. Rep.*, p. 48 (1905); (b) R. Lang, *Z. anorg. allgem. Chem.*, **152**, 203 (1926); (c) O. Cantoni, *Ann. chim. appl.*, **16**, 153 (1926); (d) Pročke and Svěda, *Chem. Zentr.*, **I**, 1859 (1926).

³ Willard and Young, *THIS JOURNAL*, **50**, 1372 (1928).

sufficiently rapid if the temperature were above 70° and if 15 ml. of concentrated hydrochloric acid per 100 ml. of solution were present. They also found that this reaction was catalyzed by bromine or iodine compounds and adopted the use of iodine monochloride since it theoretically would require no correction factor when used in a hydrochloric acid solution. Titrations could be made at room temperature. They then studied the standardization of ceric sulfate solutions against arsenious oxide; and while very reproducible results were obtained, they were consistently about 0.3% lower than the normality for the ceric sulfate solution found by standardization against electrolytic iron and sodium oxalate. They consequently recommend a correction factor of 1.003 for the titration. End-points were determined electrometrically.

The experiments to be described here show that the iodine monochloride end-point can be used in titrating arsenite with ceric sulfate, and that a correction factor is not necessary in the standardization of ceric sulfate against arsenious oxide, either in using the iodine monochloride or the electrometric end-point, if a sufficiently high concentration of hydrochloric acid is maintained in the solution.

We wish to thank Dr. A. H. Kunz for his generous assistance and for the use of the apparatus with which the electrometric titrations were made.

Experimental Methods and Results

Substances and Solutions.—The potassium permanganate solution was standardized against sodium oxalate obtained from the Bureau of Standards. Weight burets were used. The values obtained were 0.09930 and 0.09921 equivalents per 1000 grams of solution.

The ceric sulfate solutions were prepared by treating technical CeO_2 with concentrated sulfuric acid and then diluting the mixture to the desired volume. A small insoluble residue was removed by filtration through asbestos. The solutions were approximately 0.5 molal in sulfuric acid.

The arsenious acid used was of "analytical chemical" grade, accompanied by an analysis of the other constituents present. It was dried over sulfuric acid, the proper amount weighed out, dissolved in sodium hydroxide, the solution nearly neutralized with hydrochloric acid and then diluted to volume. The weight of the solution was also taken.

The iodine monochloride solution was prepared by adding to 20 ml. of 0.025 molal potassium iodate 25 ml. of 0.04 molal potassium iodide and 40 ml. of 12 molal hydrochloric acid. A few ml. of carbon tetrachloride was then added and the solution titrated with iodate or iodide until a barely perceptible iodine color remained in the carbon tetrachloride. The solution was thus approximately 0.017 molal in iodine monochloride and 5.5 molal in hydrochloric acid.

Titration of Arsenious Acid with Permanganate.—The procedure used

was to pipet the arsenite solution into a 250 ml. conical flask fitted with a ground-glass stopper (if weight burets were used this solution was then weighed), and then to add the volume of 12 molal hydrochloric acid necessary to give the desired acid concentration at the end-point. There were then added 3-4 ml. of carbon tetrachloride and 5 ml. of 0.017 molal iodine monochloride solution and the solutions titrated with permanganate until the iodine color in the carbon tetrachloride disappeared. Vigorous shaking of the solution is necessary as the end-point is approached in order to be sure that an equilibrium is attained between the carbon tetrachloride and aqueous layer. In Table I are shown the results of titrations as the hydrochloric acid concentration was varied. In each case 25 ml. of the arsenite solution was taken. The volume of permanganate calculated to be required was 20.14 ml.

TABLE I
TITRATION OF ARSENITE WITH PERMANGANATE

Expt.	HCl (sp. gr. 1.18) added, ml.	Final molal concn. of HCl	KMnO ₄ used, ml.
1	4.5	1	20.27 ^a
2	10	2	20.13
3	16.7	3	20.15
4	25	4	20.14

^a End-point very slow.

It is thus seen that it is possible to titrate arsenious acid by this method in as low as 1 molal hydrochloric acid, although at this concentration the solutions have to be shaken for two to four minutes after each addition of permanganate. In view of the tendency of one not familiar with the method to over-run the end-point, a higher concentration of acid is advisable for accurate work. At no time during the titration were there any colored compounds formed in the solution even though most of the permanganate was run in very rapidly.

Using weight burets and a solution 4 molal in hydrochloric acid the permanganate solution was standardized against the solution of the arsenious acid with the results shown in Table II.

TABLE II
STANDARDIZATION OF PERMANGANATE AGAINST ARSENIOUS OXIDE

Expt.	As ₂ O ₃ soln., g.	KMnO ₄ soln., g.	Normality KMnO ₄ equiv./1000 g.
1	25.06	20.15	0.09922
2	25.08	20.18	.09915
3	25.10	20.16	.09933
4	25.10	20.15	.09938
5	25.11	20.18	.09927
Average			.09927

It is very probable that the somewhat lower values for the first two results are due to slightly over running the end-point, as this was more

carefully guarded against in the subsequent titrations. It is thought that these results are in such close agreement with the value, 0.09930 equivalent per 1000 g., obtained by the sodium oxalate method, as to warrant recommending this method for the standardization of permanganate solutions against arsenious oxide.

Standardization of the Ceric Sulfate Solutions against Sodium Oxalate.—The desired amount of sodium oxalate was weighed, dissolved and diluted in a volumetric flask. Aliquot portions were then taken out with a 50-ml. pipet. The flask had been calibrated against this pipet. The titration was carried out under the conditions recommended by Willard and Young,⁴ the solution being kept above 70° and 5 ml. of sulfuric acid (sp. gr. 1.83) being used. The end-points were determined by several methods. The first detectable yellow color given by an excess of the ceric solution was noted and this estimated by matching the color in another beaker containing the same volume of acid and water. The excess was also determined by cooling the solution under carbon dioxide, adding potassium iodide and then titrating the iodine liberated with 0.01 normal thio-sulfate. The end-points were found to be unstable if this titration was made without excluding the air. Finally, the end-point was determined electrometrically. The excess required in visually determining the end-point was approximately 0.1 ml. of a 0.04 molal ceric solution. The values obtained by the various methods agreed to 0.01 ml. The values obtained for the concentration of the ceric sulfate solution are shown in Table III. The weight of sodium oxalate taken was in each case 0.093269 g. A weight buret was used for the ceric sulfate.

TABLE III
STANDARDIZATION OF CERIC SULFATE AGAINST SODIUM OXALATE

Number	Ce(SO ₄) ₂ used, g.	Ce(SO ₄) ₂ per 1000 g., mole
1	37.47 ^a	0.03715
2	37.48 ^{c, b}	.03714
3	37.47 ^b	.03715
4	37.48 ^c	.03714
	Average	.03714

End-point noted visually, corrected by blank. ^b End-point noted visually, corrected iodometrically. ^c End-point determined electrometrically, also iodometrically.

Titration of Arsenious Acid with Ceric Sulfate.—The experiments given in Table IV show the effect of the hydrochloric acid concentration on the titration. The procedure was the same as that used in titrating arsenious acid with permanganate. The volume of arsenious acid taken was in every case 10 ml., then sufficient 12 molal hydrochloric acid was added to make the final concentration that shown. Five ml. of iodine

⁴ Willard and Young, *THIS JOURNAL*, 50, 1322 (1928).

monochloride solution was used. The volume of ceric sulfate calculated to be required was 20.57 ml.

TABLE IV
EFFECT OF HYDROCHLORIC ACID ON THE TITRATION OF ARSENIOS ACID WITH CERIC SULFATE

Final concn. of HCl, <i>M</i>	Ce(SO ₄) ₂ used, ml.	Character of end-point
2	20.61	Very slow, impractical
3	20.54	Slow
4	20.54	Rapid
4	20.55	Rapid
4	20.55	Rapid
4	20.55	Rapid

It is seen that the necessary concentration of hydrochloric acid is higher than that for the permanganate titration, and that it corresponds to that required in the titration of iodine with ceric sulfate.

By standardizing the ceric sulfate solution against arsenious acid, maintaining the hydrochloric acid at 4 molal and using weight burets, the results shown in Table V were obtained.

TABLE V
STANDARDIZATION OF CERIC SULFATE AGAINST ARSENIOS ACID

Arsenious acid, g. of soln.	Ceric sulfate, g. of soln.	Concn. of Ce(SO ₄) ₂ , mole per 1000 g.
20.005	42.94	0.03717
19.985	42.90	.03717
19.985	42.92	.03715
	Average	.03716

This value agrees to better than 0.1% with the value given by the sodium oxalate standardization and indicates that ceric sulfate solutions can be standardized very accurately against arsenious acid. It is to be noted that the deviation is in the opposite direction from that observed by Willard and Young.³ In their standardization the concentration of the hydrochloric acid at the end-point was less than 2 molal. In view of the slow rate at which an equilibrium was established in our experiments at 2 molal acid, it seemed probable that their deviation might be caused by a similar effect. Accordingly, a different ceric sulfate solution was standardized against sodium oxalate, the end-points being determined electrometrically, and its normality found to be 0.05658. It was then titrated against the arsenious acid solution, using the iodine monochloride end-point. Finally, duplicating closely the conditions of Willard and Young, the end-point was determined electrometrically with the final acid concentration 4 and 1.8 molal. The results are shown in Table VI. In all cases 20 ml. of arsenite was taken. In Expts. 1-2, 5 ml. was used, but in Expts. 3-7 only 2 ml. of the iodine monochloride solution.

TABLE VI

TITRATION OF CERIC SULFATE AGAINST ARSENIOUS ACID UNDER VARIOUS CONDITIONS

Expt.	Final vol., ml.	Final concn., HCl <i>M</i>	Method of detg. end-point	Ce(SO ₄) ₂ used, ml	Ce(SO ₄) ₂ , <i>M</i>
1	75	4	Iodine	28.24	0.05659
2	75	4	Iodine	28.26	.05655
3	130	4	Electrometric	28.24	.05659
4	130	4	Electrometric	28.23	.05661
5	130	1.8	Electrometric	28.28	.05642
6	130	1.8	Electrometric	28.35	.05630
7	130	1.8	Electrometric	28.36	.05628

A deviation similar to the one noted by Willard and Young is to be found in Expts. 5-7. A constant reading was attained much more slowly in Expts. 5-7 and the break at the end-point, which amounted to 180-200 mv. in Expts. 3-4, was about 140 mv. in Expt. 5 and 80-100 mv. in Expts. 6-7. Expt. 5 was run more slowly than the others. It is thus recommended that the hydrochloric acid concentration be made 4 molal when titrating arsenious acid with ceric solution using either the iodine monochloride end-point or using iodine monochloride as a catalytic agent and determining the end-point electrometrically.

Summary

Experiments have shown that by the addition of a small amount of iodine monochloride and using the iodine monochloride end-point arsenious acid can be rapidly and accurately titrated in a hydrochloric acid solution at room temperature with permanganate solutions. The effects of varying the acid from 1 to 4 molal are shown; below 2 molal the end-point is attained very slowly. The values obtained from standardizing a permanganate solution against arsenious oxide by this method are found to be in close agreement with those obtained using sodium oxalate.

It has also been shown that arsenious acid can be titrated with ceric sulfate solutions by the same method. Rapid end-points are attained if the solution is 4 molal in hydrochloric acid. Close agreement is found in standardizing a ceric solution against arsenious oxide by this method and against sodium oxalate. It has also been found that if the solution is 4 molal in hydrochloric acid, arsenious acid can be accurately titrated with ceric sulfate solutions, using iodine monochloride as a catalyst and determining the end-point electrometrically. The electrometric method is liable to error if the acid concentration is as low as 2 molal.

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