a compound must be high enough at all temperatures so that some free surface is present. When part of the surface is covered with adsorbed ethylene, reaction is hindered, as the hypothesis would demand.

That these reaction conditions have some generality is shown by the work of Pease and Stewart,[2] who investigated the same reaction over calcium hydride and metallic calcium. The hydrogenation of ethylene over calcium does not go through the hydride stage, although this substance is an effective catalyst for the reaction.

One may not venture, however, to extend these principles, for Weichselfelder and Kossodo[3] have shown that in some cases of hydrogenation over nickel, and over nickel hydride, formation and decomposition of the hydride undoubtedly took place. It thus is impossible to predict the mechanism of such catalyzed reactions until further experimentation has furnished a clue.

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[2] Pease and Stewart, THIS JOURNAL, **47,** 2763 (1925).

[3] Weichselfelder and Kossodo, *Ber.*, **62B,** 769 (1929).

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THE USE OF THE IODINE MONOCHLORIDE END-POINT IN VOLUMETRIC ANALYSIS. I. THE TITRATION OF IODIDE

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Introduction

In the so-called "iodate methods"[1,2] of volumetric analysis there is usually added to a hydrochloric acid solution of the reducing substance to be analyzed a standard solution of an iodate until the iodine at first liberated is oxidized to iodine monochloride by the reaction $I_2 + 2HCl + O$ (from iodate) $= 2ICl + H_2O$. The end-point is determined by the disappearance of the iodine color in an immiscible organic solvent, usually carbon tetrachloride or chloroform, which is shaken in a closed flask with the aqueous solution. This end-point is sharp and permanent, and permits of back titration. According to Kolthoff[3] the sensitivity of the detection of free iodine by this method exceeds that by the conventional starch indicator, and a correction factor for the end-point is unnecessary. Results given below of tests which have been made under various conditions confirm this and show the extreme sensitivity of the end-points obtained.

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[1] Andrews, *Z. anorg. Chem.*, **36,** 83 (1903); THIS JOURNAL, **25,** 756 (1903).

[2] Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., New York, 1926.

[3] Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, New York, 1929, Vol. II, p. 352.

Adequate use does not seem to have been made of the fact that, by the addition of a small quantity of iodine monochloride to a hydrochloric acid solution of the substance to be titrated, this end-point, which depends only upon the oxidation of the iodine to iodine monochloride, can be used not only with iodate, but with any other standard oxidizing solution which rapidly and completely causes the formation of the monochloride. Iodide has, to be sure, been titrated with permanganate to iodine monochloride by McCulloch[4] and by Willard and Fenwick,[5] the latter having determined the end-point electrometrically. Willard and Young[6] have also titrated iodide to iodine monochloride with a ceric sulfate solution, but have determined the end-point electrometrically.

To ascertain what standard oxidizing agents could be used with the iodine monochloride end-point, there have been made a study and comparison of the titration of iodide with standard solutions of potassium iodate, potassium permanganate, ceric sulfate and potassium dichromate. These results, presented in this paper, show the conditions, especially as regards the concentration of hydrochloric acid, under which accurate titrations can be made with all of these solutions using the iodine monochloride end-point. It would thus seem possible under the proper conditions to substitute permanganate and ceric solutions, or dichromate if desired, for iodate in the titration of the numerous substances for which methods have been developed by the use of a standard iodate solution. Several advantages would be gained. Thus certain substances, notably arsenic and antimony, which are not readily titrated with permanganate or ceric solutions without the aid of catalytic agents, may be readily titrated with these solutions under the conditions of the iodine monochloride end-point; and the necessity of using electrometric end-points with ceric solutions is avoided. Moreover, the danger of loss of iodine, which is inherent when iodate is used and considerable amounts of iodine are liberated during the titration, is eliminated when only a small amount of iodine monochloride is added and another oxidizing agent substituted for the iodate. Finally, the possibility of standardizing several oxidizing solutions against the same primary standard under very similar conditions is gained. Thus there are presented in the following paper the results of a study of the standardization of solutions of permanganate and of ceric sulfate against arsenious oxide.

The disadvantages of this method of determining the end-point are the necessity for vigorous shaking of the solution in flasks with ground-glass stoppers and the rather large quantities of hydrochloric acid required. The first is minimized by the fact that one accustomed to the

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[4] McCulloch, *Chem. News*, **57**, 135 (1888).

[5] Willard and Fenwick, THIS JOURNAL, **45**, 624 (1923).

[6] Willard and Young, *ibid.*, **50**, 1368 (1928).

method can approximate the position of the end-point both by the change in the color of the aqueous layer and by the intensity of the iodine color in the organic solvent, and by the fact that a back titration is readily made. It has also been found that the concentration of hydrochloric acid, 3.5–4 molal, thought to be the minimum[7] for obtaining this end-point can be somewhat reduced in certain titrations.

Experimental Methods and Results

Substances and Solutions.—The potassium iodide used was of "analytical chemical" grade and was proved to be free from iodate and from an appreciable quantity of alkali. The calculated weight of the dried salt was dissolved and diluted to the proper volume to make the resulting solution 0.04 molal.

The potassium iodate was of the same grade and was proved to be free from iodide. The solution was prepared as above to be 0.025 molal.

The potassium permanganate solution was standardized against sodium oxalate obtained from the Bureau of Standards.

The ceric sulfate solution was supplied through the courtesy of Dr. A. H. Kunz of this Laboratory. It had been prepared by ignition of C. P. ceric oxalate to oxide and dissolving the oxide in sulfuric acid. It was 0.05950 molal in ceric salt and 0.5 molal in sulfuric acid. It had been standardized against Bureau of Standards sodium oxalate under the conditions recommended by Willard and Young,[8] the end-point being determined electrometrically.

The potassium dichromate solution was prepared by weighing the proper amount of the "analytical chemical" grade of material, dissolving it and diluting the solution to make it 0.1 *N*.

Sensitivity of the Detection of Iodine by Carbon Tetrachloride.—To 50 ml. of 1 molal hydrochloric acid were added 0.1 ml. of 0.04 molal potassium iodide and 5 ml. of carbon tetrachloride and the solution was then titrated with 0.00025 molal potassium iodate. Upon adding 0.12 ml. a barely perceptible color was observed, most apparent against a white background. With 0.16 ml. the color was very definite and with 0.24 ml. it was obvious. The total amount of iodine present when its detection was definite was approximately 0.03 mg., its concentration being 2.4×10^{-6} molal. It should be noted that this test, unlike the starch test, is made somewhat less sensitive by the presence of large amounts of iodide; also that when the titration is made with iodate

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[7] Andrews (Ref. 1) states, apparently as the result of experiments in which iodide was titrated with "chlorine water" and successively larger volumes were found to be required as the acid concentration was reduced below 5.5 molal, that a high concentration of hydrochloric acid is necessary because of the hydrolysis of the iodine monochloride according to the equation $ICl + H_2O = IOH + HCl$, and "the iodous hydroxide ('hypoiodous acid'), which is formed, undergoing spontaneous conversion into iodic acid, etc." Since this decomposition would seem to result in the formation of iodine and some higher valence form of iodine, since the constant K for $(I_2)(ICl_3) = K(ICl)^3$ has been found to be at 1.1×10^{-11} and practically independent of the acid concentration down to 4 molal hydrochloric acid [Forbes, Glass and Fuoss, THIS JOURNAL, **47**, 2892 (1925)], and since it was found that iodine monochloride solutions could be largely diluted without appreciable formation of iodine, it appeared that the effect might be one of rate rather than one of hydrolysis. Experiments, the results of which are shown, seem to confirm this belief.

[8] Willard and Young, *ibid.*, **50**, 1332 (1928).

and large quantities of iodine monochloride are present, the yellow color of the iodine monochloride makes the test somewhat less sensitive. Even so, 50 ml. of a solution which was approximately 0.02 molal in ICl and 6 molal in hydrochloric acid could be consistently titrated back and forth with 0.06–0.08 ml. of solutions of potassium iodide and iodate which were 0.004 and 0.0025 molal, respectively.

Titration of Iodide with Iodate.—To afford a check on the concentration of the potassium iodide solution and to study the effect of the concentration of the hydrochloric acid present it was titrated with the standard iodate solution.

The procedure was to pipet the iodide solution into a 250-ml. conical flask provided with a ground-glass stopper, and then to add 5 ml. of carbon tetrachloride and the hydrochloric acid. The flask was cooled with tap water and the carbon tetrachloride examined just before beginning the titration to be sure that it was colorless. The iodate was usually run in rapidly until within approximately 1 ml. of the end-point. After shaking the solution, the flask was cooled with tap water and a small amount of water poured around the stopper before opening it, so that as the stopper was withdrawn any iodine vapor or solution around it would be drawn into the flask and not expelled. The amounts of the reagents used and the results are shown in Table I.

TABLE I

TITRATION OF IODIDE WITH IODATE

Expt.	KI, ml.	12 M HCl, ml.	KIO_3, ml.	HCl, final molality	KI, molality found
1	25	25	20.02	4.3	0.04004
2	25	25	20.01	4.3	.04002
3	50	50	40.00	4.3	.04000
4	50	50	39.99	4.3	.03999
5	25	20	20.00	3.5	.04000[a]
6	25	10	20.01	2.1	.04002[b]
7	25	20[c]	20.01	1.8	.04002[b]
8	50	20[c]	40.04[d]	1.0	.04004[b]
9	25	20[c]	20.01	1.8	.04002[b]

[a] After reaching the end-point 65 cc. of water was added. No return of iodine color. One drop of 0.04 M KI restored the color. [b] End-point slow. [c] Six M HCl used. [d] 39.93 ml. of KIO_3 was added and the solution allowed to stand for two hours before finishing the titration.

The results of Expts. 5–8 in the above table seem to show that the necessity for a high acid concentration is not due to hydrolysis of the iodine monochloride, but to a slow rate of reaction as the end-point is approached. To further confirm this, after completing the titration of Expt. 8, an excess of 0.10 ml. of potassium iodate was added and the solution allowed to stand for an hour; then upon titrating with iodide the first drop, 0.03 ml., caused an iodine color which faded only after shaking for five to ten minutes. This was repeated until 0.03 ml. excess of iodide had been added, after which the color remained permanent. In another experiment 10 ml. of a solution approximately 0.02 molal in iodine monochloride and 6 molal in hydrochloric acid was pipetted into a flask and 5 ml. of carbon tetrachloride and 90 ml. of water were added. The faint color of the iodine in the carbon tetrachloride seemingly increased very slightly. Another 100 ml. of water was added with no appreciable change in the color even on standing for one hour. Upon adding 0.1 cc. of 0.025 molal iodate this color slowly but completely disappeared. In another experiment 10 ml. of the same stock solution of iodine monochloride was very carefully titrated with iodate solution until the carbon tetrachloride solution showed no perceptible iodine color. To it was added 190 ml. of water and the solution was allowed to stand for an hour. No iodine color developed in the carbon tetrachloride. It then required only one drop of 0.04 molal potassium iodide solution to produce an immediate and permanent color.

In Expt. 9 the total amount of iodate was added and the solution then shaken intermittently until the end-point was attained; this required four and one-half minutes. The solution was then let stand for ten minutes, after which 0.03 ml. of 0.05 molal potassium iodide was added; a permanent color was produced in the carbon tetrachloride. It should be noted that during the four and one-half minutes it was evident after each period of shaking, usually ten to fifteen seconds, that the iodine color was decreasing, so that the probability of overrunning the end-point can be minimized. Likewise, the solution can be back titrated with iodide solution to a permanent color. It is thus possible under certain conditions to titrate successfully iodide with iodate in 2 molal hydrochloric acid; however, where a quick end-point is desired, a higher concentration is advisable. Below 2 molal acid the rate of the reaction is too slow to be of practical use.

Titration of Iodide with Permanganate.—Table II shows the results obtained upon titrating iodide with standard permanganate solution. The procedure was essentially the same as in the iodate titrations. It should

TABLE II

TITRATION OF IODIDE WITH PERMANGANATE

Expt.	KI, ml.	$KMnO_4$, ml.	HCl, final molality	KI, molality found
1	25	20.18	4.2	0.04008
2	50	40.34	4.2	.04006
3	25	20.16	4.2	.04004
4	25	20.16	4.2	.04004
5	25	20.32	1.1	.04035[a]
6	25	20.15	1.8	.04002[b]
7	25	20.15	3.0	.04002
8	50	40.30	3.3	.04002
9	25	20.18	6.3	.04008

[a] End-point very slow. [b] $KMnO_4$ added all at once; required five minutes for appearance of end-point.

be noted that, even upon adding a slight excess, the usual color of the permanganate is not obtained in the solution, but the excess is reduced, the iodine monochloride probably being oxidized to trichloride.

The characteristics of the titration with permanganate were very similar to those with iodate. The rate at which the end-point was attained with the same acid concentration was perhaps slightly slower with the permanganate. This was contrary to what had been expected. It appears that about 0.1% too much permanganate is required. This may be due to slightly overrunning the end-point or some irregularity in the reaction. The magnitude of the effect is too close to the possible experimental error to draw definite conclusions.

Titration of Iodide with Ceric Sulfate.—Table III shows the results obtained upon titrating iodide with ceric sulfate solution by the same procedure.

TABLE III

TITRATION OF IODIDE WITH CERIC SULFATE

Expt.	KI, ml. taken	$Ce(SO_4)_2$, ml. used	HCl, final molality	KI, molality found
1	20	26.90	6	0.04001
2	10	13.43	6.5	.03995
3	10	13.41	6.5	.03989
4	10	13.42	5.5	.03992
5	10	13.43	5.5	.03995
6	25	33.53	3.6	.03990
7	25	33.59	3.6	.03997
8	10	13.43	5.5	.03995
9	10	13.44	4.8	.03998
10	10	13.43	4.0	.03995
11	10	13.43	3.5	.03995[a]
12	10	...	3.0	......[b]

[a] End-point slow. [b] No end-point even after fifteen minutes.

When titrating iodide with ceric sulfate in 3 molal hydrochloric acid the iodine monochloride end-point is so slow as to be impracticable; with 3.5 molal acid care has to be taken not to overrun the end-point. These results are in approximate agreement with those of Willard and Young[6] using an electrometric end-point. The slightly low molality of the potassium iodide may be due to a loss of iodine, as reported by these authors, although this effect has not been apparent in the iodate and permanganate titrations and is much smaller than the effect noted by them. Special precautions, such as cooling the solutions, the use of glass-stoppered flasks with small mouths, and not shaking or stirring the solution except when the flask was closed, were taken to avoid serious error from this source.

Titration of Iodide with Potassium Dichromate.—The same procedure was used in these titrations as in those with the other oxidizing solutions. The results are shown in Table IV.

TABLE IV

TITRATION OF IODIDE WITH POTASSIUM DICHROMATE

Expt.	KI, ml. taken	$K_2Cr_2O_7$, ml. used	HCl, final molality	KI, molality found
1	25	20.04	7.5	0.04008[a]
2	25	20.02	8.5	.04004
3	25	19.99	7.5	.03998[b]
4	10	8.01	8.8	.04005

[a] End-point very slow. [b] End-point overrun, back titrated with iodide.

In other experiments not shown in the table satisfactory end-points were not obtained until the solution was approximately 8 molal in hydrochloric acid.

Summary

The advantages have been pointed out of using the iodine monochloride end-point in the titration of reducing substances with standard oxidizing solutions. This process depends upon the oxidation of iodine in a hydrochloric acid solution to iodine monochloride by the reaction $I_2 + 2HCl + O = 2ICl + H_2O$, the disappearance of the iodine color being determined by shaking with an immiscible solvent.

The use of iodine monochloride as an indicator with standard oxidizing solutions other than iodate is suggested. This substitution avoids the liberation of large amounts of iodine in the solution being titrated; for then the addition of only sufficient iodine monochloride to serve as an indicator is necessary. No correction factor is necessary either for the iodine monochloride added or the sensitivity of the end-point.

Experiments have determined the conditions under which iodide can be accurately titrated to iodine monochloride with iodate, permanganate, dichromate and ceric salt solutions. The titration with dichromate requires a solution approximately 8 molal or more in hydrochloric acid.

The results indicate that a high concentration of acid is necessary in titration of this type mainly because of the slow rate at which iodine is oxidized to iodine monochloride.

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