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The Use of the Iodine Monochloride End-Point in Volumetric Analysis. III. The Titration of Thallous Salts with Permanganate, Iodate and Ceric Sulfate

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Introduction

Most of the methods which have been proposed for the volumetric determination of thallium have certain inherent defects. Many attempts have been made to use Willm's method¹ of titrating thallous salts with permanganate in hot hydrochloric acid solutions, but various investigators^{2,3,4,5} have shown the method to be subject to certain empirical corrections. In the course of this investigation an extensive study of this reaction was made, but no conditions were found which afforded precise titrations. The method used by Marshall⁶ which depends on heating the thallous salt with hydrochloric acid and a measured amount of standard bromate in excess, distilling off the residual bromine into potassium iodide solution and titrating the liberated iodine with standard thiosulfate, is involved and necessitates a special form of apparatus. Kolthoff⁷ and subsequently Zintl and Rienäcker⁸ developed a method for the titration of thallous salts in hot hydrochloric acid solution with a standard bromate solution using methyl orange as the indicator; and, although by careful titration precise results can be obtained, the end-point is irreversible. Willard and Young⁹ have used standard ceric sulfate in a hot hydrochloric acid solution, determining the end-point electrometrically or visually and applying a correction for the excess of ceric sulfate; their data indicate that the method is precise. Berry¹⁰ gives the result of a single titration of a thallous salt with standard ceric sulfate using the iodine monochloride end-point, but he states that the ceric sulfate should be standardized against a standard iodide solution using the iodine monochloride end-point. Berry¹¹ also made a few titrations of various thallous salts

with a standard iodate solution, using the iodine monochloride end-point, but his experiments are too limited to establish the value of the method. Other volumetric procedures¹²⁻¹⁷ all of which have some limitations, have been proposed at various times.

As the use of the iodine monochloride end-point with various oxidizing agents would considerably extend the conditions under which the determination of thallium could be made, an investigation of this method has been made and this paper presents the results of studies of the titration of thallous salts with iodate, permanganate and ceric sulfate solutions using the iodine monochloride end-point, and also of the closely related titration of thallous salts in hydrochloric acid solutions with permanganate using the visual end-point.

Experimental Methods and Results

Substances and Solutions.—The potassium permanganate solution was standardized against sodium oxalate obtained from the Bureau of Standards. The solution was restandardized near the end of the work and found to have been stable.

The potassium bromate solution was standardized against Bureau of Standards arsenious oxide.

The potassium iodate solution was prepared by direct weighing and dilution; the calculated value, 0.1008 *N*, was also obtained by standardization against Bureau of Standards arsenious acid using the iodine monochloride end-point.

The ceric sulfate solution was prepared by treating technical CeO₂ with concentrated sulfuric acid, diluting to the desired volume, and filtering through asbestos. It was 0.08350 *N* in ceric sulfate and 0.5 to 1 formal in sulfuric acid. It was standardized against Bureau of Standards sodium oxalate as recommended by Willard and Young¹⁸ the end-point being determined visually and corrected iodometrically or by comparison with prepared standards.

The thallous sulfate solution was prepared by converting C. P. thallous nitrate into the sulfate with sulfuric acid, recrystallizing, then dissolving the sulfate and diluting to volume. The solution was standardized by the method of

(1) Willm, *Bull. soc. chim.*, 352 (1863), and *Ann. chim. phys.*, [4] 5, 5 (1863).

(2) Noyes, *Z. physik. Chem.*, 9, 608 (1892).

(3) Hawley, *THIS JOURNAL*, 29, 300 (1907).

(4) Müller, *Chem. Ztg.*, 33, 297 (1909).

(5) Berry, *J. Chem. Soc.*, 121, 396 (1922).

(6) Marshall, *J. Soc. Chem. Ind.*, 19, 994 (1900).

(7) Kolthoff, *Rec. trav. chim.*, 41, 172 (1922).

(8) Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, 153, 276 (1926).

(9) Willard and Young, *THIS JOURNAL*, 52, 36 (1930).

(10) Berry, *Analyst*, 54, 463 (1929).

(11) Berry, *ibid.*, 51, 137 (1926).

(12) Nietzki, *Arch. Pharm.*, [2] 4, 385 (1871).

(13) Feit, *Z. anal. Chem.*, 28, 314 (1889).

(14) Sponholz, *ibid.*, 31, 519 (1892).

(15) Thomas, *Compt. rend.*, 134, 655 (1902).

(16) Browning and Palmer, *Am. J. Sci.*, [4] 27, 379 (1909).

(17) Del Fresno and Valdés, *Z. anorg. allgem. Chem.*, 183, 258 (1929).

(18) Willard and Young, *THIS JOURNAL*, 50, 1332 (1928).

Zintl and Rienäcker⁸ using the above standard bromate solution with methyl orange as indicator. The average of four closely agreeing titrations gave 0.09892 *N*.

The iodine monochloride solution was prepared according to the method given by Jamieson.¹⁹ It was approximately 0.017 formal in iodine monochloride and 6 formal in hydrochloric acid.

The hydrochloric acid used (sp. gr. 1.18) was shown to be substantially free from chlorine and other oxidizing agents.

Titration of Thallous Salts in Hydrochloric Acid Solutions with Permanganate (Willm Method).—Using Willm's method¹ titrations were made varying the initial acid concentrations from 0.5 to 1 formal, the volume of the solution from 100 to 200 ml., and the temperature from 55 to 90°. The end-point was uncertain and faded slowly; results were from 0.6 to 0.7% high; the smell of chlorine or hypochlorous acid was observed. The addition of phosphoric acid, alone or with manganous salts, had no apparent effect. Solid potassium chloride (10–20 g.) improved the results to the point where they were about 0.4% high, but the end-point was transitory.

These experiments confirm the work of other investigators, particularly of Prosz²⁰ and of Bodnár and Terényi,²¹ who have noted the dependence of the results upon the acidity of the solution, but not the claims of Jílek and Lukáš²² that precise results can be obtained by the addition of solid potassium chloride.

Titration of Thallous Salts with Permanganate, Iodine Monochloride End-Point.—The iodine monochloride end-point has been discussed in a previous paper.²³ The procedure used was to pipet the thallous sulfate into a 250-ml. ground-glass stoppered flask ("iodine flask" type), then to add the necessary amount of 12 formal hydrochloric acid, followed by 4 ml. of carbon tetrachloride and 5 ml. of the iodine monochloride solution. The solution was then titrated with permanganate to the disappearance of the iodine color in the carbon tetrachloride.

The results of a few of the titrations made are shown in Table I and indicate the erratic nature of the end-point.

TABLE I
TITRATION OF THALLOUS SALTS WITH PERMANGANATE,
IODINE MONOCHLORIDE END-POINT

Expt.	Tl ₂ SO ₄ taken, ml.	HCl final formality	KMnO ₄ used, ml.	KMnO ₄ calcd., ml.
1	24.98	5	24.99	24.64
2	24.98	4	25.04	24.64
3	24.98	2	25.08 ^a	24.64
4	24.97	3.7	24.85 ^b	24.63
5	24.97	2	24.89	24.63
6	24.98	3.7	24.85 ^c	24.64

^a End-point slow. ^b CO₂ atmosphere. ^c Excess of ICl solution added before titrating.

The positive error is approximately twice as great in Experiments 1–3, in which the perman-

(19) Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, 1926.

(20) Prosz, *Z. anal. Chem.*, **73**, 401 (1928).

(21) Bodnár and Terényi, *ibid.*, **69**, 33 (1926).

(22) Jílek and Lukáš, *Chem. Listy*, **23**, 124 (1929).

(23) Swift, *This Journal*, **52**, 894 (1930).

ganate was added rapidly with little or no shaking, as in Experiments 4–6, in which it was added dropwise with shaking. The smell of chlorine or hypochlorous acid was observed, and upon passing the gases from the titration vessel through a trap, so as to eliminate spray or iodine vapor, into an acidified potassium iodide solution, an iodine color immediately developed; the possibility that this was caused by oxygen was eliminated by a control experiment.

It was thought that perhaps the end-point was being over-run and that the permanganate was oxidizing some of the iodine monochloride to iodine trichloride, but back-titrations made with 0.1 *N* potassium iodide required only about 0.02 ml. and disproved this. The results therefore indicate that there is a catalyzed reaction between permanganate and hydrochloric acid, and that the titration with permanganate using the iodine monochloride end-point is unsuitable for the volumetric determination of thallium.

Titration of Thallous Salts with Ceric Sulfate, Iodine Monochloride End-Point.—Berry¹⁰ made a single titration of a thallous salt with ceric sulfate using the iodine monochloride end-point and stated that the ceric sulfate factor obtained by standardization against sodium oxalate could not be used. In view of the fact that thallous salts can be titrated precisely with ceric sulfate in hot hydrochloric acid solution,⁹ it was thought to be of interest to discover if the iodine monochloride end-point could be employed.

The same procedure was adopted as for the titrations with permanganate. The results of some of the titrations are given in Table II.

TABLE II
TITRATION OF THALLOUS SALTS WITH CERIC SULFATE

Expt.	Tl ₂ SO ₄ taken, ml.	HCl final formality	Ce(SO ₄) ₂ used, ml.	Ce(SO ₄) ₂ calcd., ml.
1	24.98	4	30.09 ^a	29.50
2	24.98	5	30.07 ^b	29.59
3	24.98	6	30.59 ^a	29.59
4	24.97	4	29.92 ^a	29.58
5	24.98	6	29.81 ^a	29.59
6	24.98	6	30.2 ^c	29.59
7	24.98	8	29.98	29.59

^a Rate fairly slow. ^b Excess of ICl solution added first.

^c Added excess ceric sulfate, solution allowed to stand with occasional shaking for one and one-half days, then back-titrated with standard KI.

In Experiments 1–3 the flask was not shaken during the titration and it is to be noted that the positive error is greater than in Experiments 4–5,

in which the flask was shaken; in Experiments 6-7, the ceric sulfate was added rapidly without shaking, and the positive error is again greater.

In addition to these experiments, two others were performed. In one, the ceric sulfate was added in 0.2-ml. excess under the conditions of Expt. 3, and the solution then shaken occasionally for two days; an iodine color was still present. This indicates that the high results are not due entirely to a slow rate of reaction. In the other experiment, in order to determine if chlorine or hypochlorous acid was being formed, the gases from the titration vessel were sent through the device used for the same purpose in the case of permanganate; none was found. This would seem to eliminate the explanation that the excess of ceric sulfate required is due to the oxidation of chloride to chlorine or hypochlorous acid.

Titration of Thallous Salts with Iodate. Iodine Monochloride End-Point.—Although Berry¹¹ titrated thallous salts with iodate using the iodine monochloride end-point, his data are of little value in establishing the precision of the method. The results of his preliminary experiments were about 2% low: the presence of chlorine in the hydrochloric acid used was given as the cause. He gives the results of several titrations using "purified hydrochloric acid," but the purity of the various thallous compounds titrated is not stated; he seems to have used a final hydrochloric acid concentration of about 7 formal. Apparently no systematic study has been made of this titration.

The same procedure was used as with the permanganate experiments, with the added precaution that the flask was cooled with tap water and a small amount of water poured around the stopper before opening it, to avoid possible loss of iodine vapor. Some of the results are given in Table III.

The rate of addition of iodate seemed to have no effect, and the titration is precise over the range of hydrochloric acid concentrations (from 1 to 5 formal) and the range of thallium content (from

TABLE III
TITRATION OF THALLOUS SALTS WITH IODATE, IODINE MONOCHLORIDE END-POINT

Expt.	Tl ₂ SO ₄ taken, ml.	HCl final formality	KIO ₃ used, ml.	KIO ₃ calcd., ml.
1	24.98	4	24.51	24.51
2	24.98	3	24.51	24.51
3	24.98	2	24.52 ^a	24.51
4	24.98	1	24.52 ^a	24.51
5	5.00	5	4.91	4.91

^a End-point slow.

0.078 to 0.42 g. Tl per 100 ml. of titrated solution) studied. The titration of thallous salts with iodate, using the iodine monochloride end-point, thus offers a rapid and precise method for the quantitative estimation of thallium; no end-point correction is required and the solution can be readily back-titrated with standard iodide solution if the titration is over-run.

Summary

Various modifications of the Willm method for the titration of thallous salts in hydrochloric acid solutions with permanganate, including the use of manganous sulfate, of phosphoric acid and of large amounts of potassium chloride, have been studied without finding conditions under which precise titrations could be made.

The titration of thallous salt with permanganate, using the iodine monochloride end-point, was found to be inaccurate due to the catalyzed oxidation of chloride by the permanganate.

Ceric sulfate cannot be used for the precise titration of thallous salts, using the iodine monochloride end-point; positive errors were found and the end-point was slow even in 4 to 8 formal hydrochloric acid solutions.

It was found that thallous salts can be precisely titrated with iodate solutions, using the iodine monochloride end-point, in solutions from 1 to 5 formal in hydrochloric acid; the end-point is more rapidly attained when the hydrochloric acid is 3 formal or greater.

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