the glass electrode is applicable. Furthermore we have observed that glass No. 6 shows steadier potentials in alkaline solution than any other that we have worked with. A comparison of two glasses under somewhat extreme conditions is given in the curves plotted in Fig. 4. The upper curve indicates the variation of the potential with time of the soft commercial glass, and the lower curve the corresponding variation of glass No. 6. It will be seen that the readings of the latter are roughly constant even in these strongly alkaline solutions.

Hughes[2] has shown, however, that these deviations in alkaline solutions depend upon the nature of the positive ions present. We have found, however, very small deviation at about $P_H$ 13 when the base present is tetramethylammonium hydroxide; this is shown in Point C of Fig. 3. We hope to be able to present in the near future a theory explaining these deviations.

## Summary

Using a form of glass electrode designed by the authors, the suitability of a series of specially prepared glasses for use as electrodes has been studied, and a few comparisons have been made with samples of glass of commercial origin. The electrodes were tested for "asymmetry potential," resistance and the amount of deviation in alkaline solutions of the measured potential from the theoretically predicted potential. The best of the glasses tested has the composition $SiO_2$, 72, $Na_2O$, 22 and CaO, 6%. The potential at the surface of this glass changes quantitatively with the hydrogen-ion activity up to $P_H$ values of 9.5, though this limit is lowered in strong salt solutions.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. X. THE DETERMINATION OF THALLIUM

BY H. H. WILLARD AND PHILENA YOUNG

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## Introduction

A number of volumetric procedures for thallium have been proposed. Willm's method based upon the titration of thallous salt in hot hydrochloric acid solution with potassium permanganate has been the one most extensively used.[1] Hawley[1] found that if the permanganate was standardized against pure thallous sulfate in hot solution, using exactly the same

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[1] Willm, *Bull. soc. chim.*, 352 (1863); Noyes, *Z. physik. Chem.*, **9**, 603 (1892); Dennis and Doan, THIS JOURNAL, **18**, 970 (1896); Marshall, *J. Soc. Chem. Ind.*, **19**, 994 (1900); Hawley, THIS JOURNAL, **29**, 300 (1907); Müller, *Chem.-Ztg.*, **33**, 297 (1909); Berry, *J. Chem. Soc.*, **121**, 394 (1922); Bodnár and Terényi, *Z. anal. Chem.*, **69**, 29 (1926); Jílek and Lucas, *Chem. Listy*, **23**, 124 (1929).

procedure as in a determination of thallium, and if 0.10–0.16 g. of thallium was present, the results were accurate. He showed by a graph that the weight of thallium oxidized by 1 cc. of permanganate was almost constant within this range, but dropped rapidly with less than 0.1 g. of thallium. Berry[1] used the electrometric end-point and found, in agreement with Hawley, that the method was a very empirical one. Jílek and Lucas[1] reported good results if considerable potassium chloride was added to the hydrochloric acid solution of the thallous salt before the titration with permanganate. Nietzki[2] titrated a thallous salt with standard potassium iodide as long as a precipitate formed, obviously an inaccurate method. Feit[3] added potassium iodide and an excess of standard arsenite to a thallic salt, filtered off the thallous iodide and titrated the excess arsenite with standard iodine. His results were low and the method involved a preliminary oxidation of thallous salt. Thomas[4] substituted standard thiosulfate for arsenite. Sponholz[5] titrated a thallous salt with standard bromine water to a visual end-point, an inaccurate method because of the instability of the oxidizing agent and the uncertainty of the end-point. Marshall[1] oxidized a thallous salt, to which bromide was added, with a measured excess of standard sodium bromate in a hydrochloric acid solution, distilled the bromine formed into potassium iodide solution and titrated the iodine with thiosulfate. He stated that the method was rapid and accurate, but it has the disadvantages of requiring a special form of apparatus and two standard solutions. Zintl and Rienäcker[6] simplified this procedure by titrating thallous salt in hydrochloric acid solution with standard potassium bromate, using the electrometric method or methyl orange as internal indicator. Their results were accurate, and the procedure was simple and rapid. These same authors showed that thallic salt could be titrated with standard titanous chloride in acetic acid solution. Browning and Palmer[7] oxidized thallous oxide with ferricyanide in alkaline solution, filtered off the thallic oxide formed, acidified the filtrate with sulfuric acid and titrated the ferrocyanide with standard permanganate. Berry[1] checked this method using recrystallized thallous sulfate, obtained good results by drying the thallic oxide, but found only a fairly good agreement by titrating the ferrocyanide in the filtrate. The color change at the end-point was not sharp. Berry[8] titrated thallous ion in strong

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

[3] Feit, *Z. anal. Chem.*, **28**, 314 (1889).

[4] Thomas, *Compt. rend.*, **134**, 655 (1902).

[5] Sponholz, *Z. anal. Chem.*, **31**, 519 (1892).

[6] Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, **153**, 276 (1926).

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

[8] Berry, *Analyst*, **51**, 137 (1926). After this paper had been submitted for publication, further work by this author appeared [*ibid.*, **54**, 461 (1929)] in which he gave the results of a single titration of thallous chloride by ceric sulfate using iodine chloride

hydrochloric acid solution with potassium iodate, using chloroform as indicator.

Since nearly all of the volumetric methods for thallium except the bromate method of Zintl and Rienäcker[6] have serious disadvantages, the authors felt that a rapid and accurate procedure for thallium would be of value. The following material describes such a method based upon the direct titration of thallous salt with standard ceric sulfate.

## Experimental

Very pure thallous sulfate was recrystallized from water, dried at 150° and used to prepare a standard solution. The ceric sulfate solution was prepared by the method described by the authors[9] from high-grade ceric oxide obtained from the Welsbach Company of New Jersey and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate.[10]

**Titration in Hydrochloric Acid Solution.**—Measured volumes of the standard thallous sulfate solution were taken, diluted with water and acid, heated to the temperature indicated and titrated electrometrically at that temperature with standard ceric sulfate. A silver chloride–platinum

TABLE I

TITRATION OF THALLOUS SALT WITH 0.1 *N* CERIC SULFATE IN HYDROCHLORIC ACID SOLUTION. ELECTROMETRIC END-POINT

| Init. vol. soln., cc. | HCl, sp. gr. 1.18, cc. | Temp., °C. | Thallium | | Character of reaction |
|---|---|---|---|---|---|
| | | | Taken, g. | Found, g. | |
| 200 | 10 | 58–60 | 0.1008 | ? | Too slow, unsatis. |
| 200 | 20 | 58–60 | .1008 | 0.1008 | Slow, fairly satis. |
| 200 | 20 | 65–67 | .1008 | .1008 | Rapid, end-point poor |
| 200 | 30 | 58–61 | .1008 | .1008 | More rapid, satis. |
| 200 | 30 | 55–57 | .1008 | .1008 | More rapid, satis. |
| 200 | 30 | 48–51 | .1008 | .1008 | Slow, fairly satis. |
| 200 | 40 | 58–60 | .1008 | .1009 | Rapid, satisfactory |
| 200 | 40 | 44–46 | .1008 | .1008 | Little slow, satis. |
| 200 | 50 | 44–46 | .1008 | .1008 | Rapid, satis. |
| 200 | 50 | 34–36 | .1008 | .1009 | Little slow, satis. |
| 200 | 60 | 34–36 | .1008 | .1008 | More rapid, satis. |
| 200 | 60 | 30–31 | .1008 | .1005 | Little slow, satis. |
| 200 | 60 | 25–27 | .1008 | ? | Heavy TlCl ppt. |
| 200 | 60 | 25–27 | .0403 | .0403 | Little slow, satis. |
| 200 | 40 | 55–57 | .0403 | .0404 | Rapid, satisfactory |
| 100 | 20 | 55–57 | .0403 | .0402 | Rapid, satisfactory |
| 200 | 50 | 57–60 | .2016 | .2017 | Rapid, satisfactory |
| 200 | 30 | 55–57 | .3024 | .3026 | Heavy TlCl ppt., diss. during titrn., rapid, satis. |

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as catalyst and chloroform as indicator. He stated that under ordinary conditions ceric sulfate did not react with thallous salts and that even when iodine chloride was present the theoretical factor could not be used.

[9] Willard and Young, THIS JOURNAL, **51**, 149 (1929).

[10] Willard and Young, *ibid.*, **50**, 1322 (1928).

electrode system was used and a thermionic voltmeter, Type DP-2, from the General Electric Company. The silver chloride electrode in 0.1 *N* potassium chloride was placed directly in the liquid to be titrated. The quantities of the various substances and the results are indicated in Table I. One-tenth gram of thallium required about 10 cc. of 0.1 *N* ceric sulfate.

These results show that the titration of thallous salt with ceric sulfate is quantitative and satisfactory over a wide range of conditions: (a) room temperature if a large amount of hydrochloric acid is present and if the thallium content is not too high, (b) higher temperature if the volume of hydrochloric acid used is decreased or if the thallium content is large enough to cause much thallous chloride to be precipitated by the hydrochloric acid present, (c) a variation in volume of solution, (d) a variation in amount of thallium from 0.04–0.30 g. Experiments were not carried out beyond this range in thallium content. In many of the reactions, when within 0.1 cc. of the end-point the equilibrium was reached rather slowly. A sudden break in potential was followed by a slow increase for a minute or two. A complete titration never took more than ten minutes, and with a little experience required less time. At temperatures below 60°, the end-point break amounted to 200–250 mv. per 0.02 cc. of 0.1 *N* ceric sulfate, but in titrations made above 60°, the break was decreased to 40–100 mv. The type of titration curve obtained is illustrated in Fig. 1.

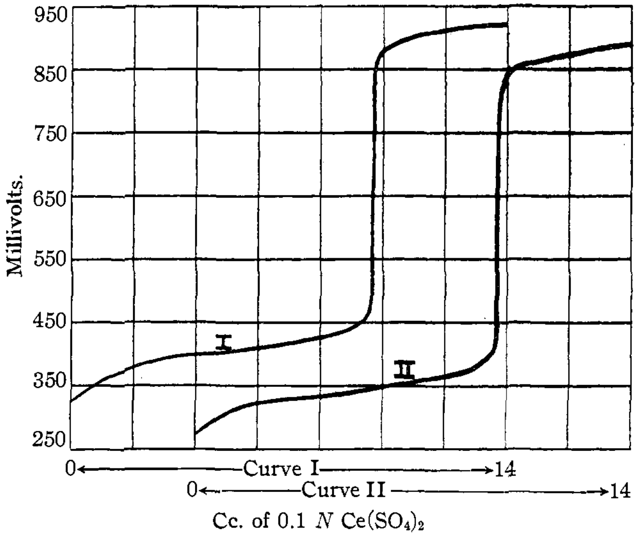

Fig. 1.—Curve I—25 cc. of Tl$_2$SO$_4$ (0.1008 g. Tl) + 145 cc. H$_2$O + 30 cc. concd. HCl titrated at 55–57° with 0.1 *N* Ce(SO$_4$)$_2$. Curve II—25 cc. of Tl$_2$SO$_4$ (0.1008 g. Tl) + 115 cc. H$_2$O + 60 cc. concd. HCl titrated at 34–36° with 0.1 *N* Ce(SO$_4$)$_2$.

To test this method further, the thallous sulfate solution was standardized volumetrically by the method of Zintl and Rienäcker.[6] Twenty-five cc. of the standard thallous sulfate was mixed with 165 cc. of water and 10 cc. of hydrochloric acid (sp. gr. 1.18), the solution heated to 50° and titrated electrometrically at that temperature with a standard potassium bromate solution, the oxidizing power of which had been accurately determined in this Laboratory against Bureau of Standards arsenious oxide. A comparison of the weights of thallium in 25-cc. portions of the standard thallous sulfate solution is given in Table II.

TABLE II

CONCENTRATION OF THALLOUS SULFATE SOLUTION

| Method of determination | Weight of Tl in 25 cc. of solution |
|---|---|
| From the weight of $Tl_2SO_4$ | 0.1008 |
| Titration with standard $KBrO_3$ | 0.1008 and 0.1009 |
| Titration with standard $Ce(SO_4)_2$ | 0.1008 (average value from Table I) |

Since in the titration of thallous salt the solution is colorless until an excess of ceric sulfate is present, the possibility of using a visual end-point was investigated. An initial volume of 200 cc. containing the amount of hydrochloric acid indicated in Table III was used, the solution heated to the given temperature and titrated without further application of heat. If an equal volume of water is taken as a comparison liquid, the slightest change in color at the end-point is easily seen. Blank determinations made at 70 and 80° on 200 cc. of water containing 20 cc. of hydrochloric acid (sp. gr. 1.18) and 3–5 cc. of sulfuric acid, sp. gr. 1.83 (since sulfuric acid is present in the ceric sulfate added), showed that 0.05 cc. of 0.1 *N* ceric sulfate was required to give a pale yellow color. Unless sulfuric acid was added, the ceric sulfate was reduced by the hydrochloric acid. This blank correction has been applied to the results given in Table III.

TABLE III

TITRATION OF THALLOUS SALT WITH 0.1 *N* CERIC SULFATE IN HYDROCHLORIC ACID SOLUTION. VISUAL END-POINT

| HCl, sp. gr. 1.18, present, cc. | Temperature, °C. Init. | Temperature, °C. Final | Tl taken, g. | Tl found, g. | Character of reaction |
|---|---|---|---|---|---|
| 40 | 55 | 50 | 0.1008 | 0.1008 | Rapid |
| 20 | 65 | 55 | .1008 | .1009 | Too slow |
| 60 | 35 | 34 | .1008 | .1008 | Rapid |
| 20 | 90 | 75 | .1008 | .1009 | Very rapid |
| 20 | 98 | 80 | .1008 | .1009 | Very rapid |

Thus it is seen that for a visual end-point the results are most satisfactory when a smaller volume of acid is used and the titration made in a very hot solution. Under these conditions the color produced by the excess ceric sulfate is more permanent.

If 5 cc. of sulfuric acid (sp. gr. 1.5) or 5 cc. of perchloric acid (70–72%) was added to a volume of 200 cc. containing 40 cc. of hydrochloric acid (sp. gr. 1.18) and thallous salt, the reaction with ceric salt was slower than in the absence of these acids, but the results were quantitative. With larger amounts of these acids the reaction was too slow. Nitric acid, even in small amounts, caused the results to be erratic. Titrations in which no hydrochloric acid was present were not possible.

The effect of the presence of various metals which occur with thallium in ores was tested. The volume of solution at the beginning of the titration was 200 cc. in every case. Results are shown in Table IV.

TABLE IV

EFFECT OF THE PRESENCE OF VARIOUS METALS ON THE VOLUMETRIC DETERMINATION OF THALLIUM

| Metallic ions added, g. | HCl (sp. gr. 1.18) present, cc. | Temp. during titrn., °C. | Tl taken, g. | Tl found, g. | Character of reaction |
|---|---|---|---|---|---|
| 0.5 Fe (as $FeCl_3$) | 30 | 55–57 | 0.1008 | 0.1011 | Rapid, satis. |
| .1 Cu (as $CuSO_4$)<br>.1 Cd (as $CdCl_2$)<br>.1 Bi (as $BiCl_3$)<br>.1 Sn (as $SnCl_4$)<br>.1 Pb (as $PbCl_2$)<br>.1 Hg (as $HgCl_2$)<br>.1 Zn (as $ZnCl_2$) | 30 | 55–57 | .1008 | .1008 | Slightly slow, satis. |
| .1 Cr (as $CrCl_3$) | 60 | 34–35 | .1008 | .1007 | Rapid, satis. |
| .1 Cr (as $CrCl_3$) | 30 | 55–57 | .1008 | ? | Results high |
| .1 Te (as $K_2TeO_3$) | 60 | 33–35 | .1008 | .1007 | A little slow at end-point |
| .1 Te (as $K_2TeO_3$) | 30 | 55–57 | .1008 | .1010 | A little slow at end-point |
| .1 Se (as $H_2SeO_3$) | 60 | 33–35 | .1008 | .1006 | A little slow at end-point |
| .1 Se (as $H_2SeO_3$) | 30 | 55–57 | .1008 | .1008 | A little slow at end-point |
| .1 As (as $H_3AsO_4$) | 60 | 33–35 | .1008 | .1009 | Rapid, satis. |
| .1 Sb (as $SbCl_5$) | 60 | 33–35 | .1008 | .1007 | Rapid, satis. |

Thus salts of $Cu^{++}$, $Fe^{+++}$, $Cd^{++}$, $Bi^{+++}$, $Sn^{4+}$, $Pb^{++}$, $Hg^{++}$, $Zn^{++}$, $SeO_3^{--}$, $TeO_3^{--}$, $AsO_4^{---}$, $Sb^{5+}$ and $Cr^{+++}$ cause no interference in the titration of thallous ion with ceric sulfate. If $Cr^{+++}$ is present, the acid concentration should be kept high and the temperature low to prevent any oxidation of chromium.[11] Trivalent arsenic and antimony interfere, as would be expected.[12] Zintl and Rienäcker[6] in their bromate method for thallium found that $Fe^{+++}$ caused their results to be low and erratic. They did not test the effect of selenium and tellurium, which may occur with thallium in ores.

## Summary

1. Thallium may be rapidly and accurately determined by titration of thallous salt in hydrochloric acid solution with standard ceric sulfate.

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[11] Willard and Young, THIS JOURNAL, **51**, 139 (1929).

[12] Willard and Young, *ibid.*, **50**, 1372 (1928).

The end-point may be determined electrometrically, or visually if the solution is colorless. In the former case the titration may be made at room temperature if the concentration of hydrochloric acid present is high or at temperatures up to 60° if the concentration of hydrochloric acid is decreased. Above 60° the end-point break is usually unsatisfactory. For the visual end-point the most satisfactory conditions are low concentration of hydrochloric acid and a temperature of 80° or higher.

2. Results obtained by this method and by the bromate titration method of Zintl and Rienäcker agree very closely.

3. $Fe^{+++}$, $Cu^{++}$, $Bi^{+++}$, $Cd^{++}$, $Pb^{++}$, $Sn^{4+}$, $Hg^{++}$, $Zn^{++}$, $SeO_3^{--}$, $TeO_3^{--}$, $AsO_4^{---}$, $Sb^{5+}$ and $Cr^{+++}$ are without effect.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUCKNELL UNIVERSITY]

# THE QUANTITATIVE DETERMINATION OF OSMIUM BY MEANS OF STRYCHNINE SULFATE[1]

BY S. C. OGBURN, JR., AND L. F. MILLER

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The analytical separations of osmium and ruthenium from the other metals of the platinum group have been based largely on the volatility of their tetroxides from acid and alkaline solutions, respectively. The use of certain organic complexes in the formation of stable coördinated salts with the metals of this group is well known and in some cases they have been used to effect their quantitative removal.[2] Those of the oximes, aromatic nitrosoamines and hydroxyquinolines are especially useful in this connection with platinum and palladium, and 6-nitroquinoline has recently been added to the list as a quantitative reagent for palladium.[3]

In studying the analytical reactions of the platinum metals, one of us[2] found that when a saturated aqueous solution of strychnine sulfate was added to a slightly acidulated solution of sodium chlorosmate, a heavy canary-yellow precipitate was produced, which on settling left a clear supernatant liquid which gave no test for osmium with hydrogen sulfide on boiling, nor with thiourea—a test which will detect one part of osmium in one hundred thousand parts of solution. Following this evidence, the work upon which this paper is based was started with the view of determining whether or not this reagent could be used as a means of quantitatively separating osmium from solutions of its pure salts or from mix-

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[1] This paper is based upon a thesis submitted by L. F. Miller to the Faculty of Bucknell University in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

[2] Ogburn, THIS JOURNAL, **48**, 2493 (1926), and other references given therein; also, Ogburn, *ibid.*, **48**, 2507 (1926).

[3] Ogburn and Riesmeyer, *ibid.*, **50**, 3018 (1928).