

SOME METHODS FOR THE DETERMINATION OF THALLIUM

By

Ramon Frederick Rolf

A THESIS

Submitted to the School for Advanced Graduate Studies of Michigan
State University of Agriculture and Applied Science
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Department of Chemistry

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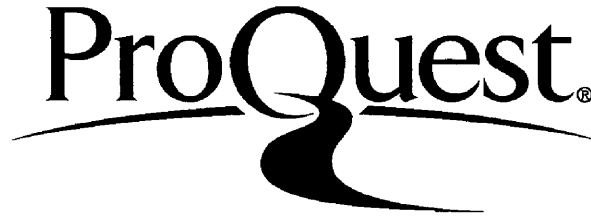
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Elmer Leininger

ABSTRACT

Methods have been developed for the rapid quantitative reduction of thallium (III) to thallium (I) in acid solution. The reduction is carried out by passing a dilute sulfuric acid solution of thallium (III) through a glass column reductor filled with finely divided cadmium, silver or bismuth metal. The reduction of thallium (III) was shown to be complete by determining the thallium (I) by the volumetric bromate procedure.¹ Blank determinations on the cadmium, silver and bismuth reducers were found to consume 0.05, 0.03 and 0.02 ml. of 0.1000 normal potassium bromate.

A method is proposed for the determination of 30 to 212 milligrams of thallium. The method consists of using a metallic reductor for the conversion of thallium (III) to thallium (I) followed by a volumetric bromate oxidation of the thallium (I). A number of thallium determinations were made using each reductor. The results using the bismuth reductor showed an average error of 0.2 per cent for 30 to 212 milligram samples of thallium while the cadmium and silver reducers showed an average error of 0.3 per cent.

Two volumetric methods are described for the determination of thallium (I). The direct method is based on the alkaline oxidation of thallium (I) to thallium (III) using hypobromite. The hypobromite is prepared extemporaneously by adding sodium hypochlorite to a thallium (I) solution containing a small amount of bromide ions. As soon as

¹ Zintl, E. and Rianacker, G., Z. anorg. Chem., 153, 276 (1926).

hypochlorite is formed it oxidizes thallium (I) to thallium (III) giving bromide ions which react with more sodium hypochlorite. The reaction between hypochlorite and bromide ions was found to be most rapid in the 7.5 to 8.5 pH range.

The indirect volumetric method is based on the alkaline oxidation of thallium (I) by an excess of standard sodium hypochlorite solution. The excess hypochlorite is titrated with standard sodium arsenite. Both the direct and indirect hypochlorite methods tended to give low results.

A method is described for the gravimetric determination of thallium. In this method thallium (I) is oxidized to thallium (III) oxide in an alkaline solution by adding an excess of sodium hypochlorite. Although hypochlorite gives a homogeneous precipitation of thallium (III) oxide, the use of hypochlorite does not appear to offer any advantages over potassium ferricyanide as an alkaline oxidant for the determination of thallium (III) oxide.

A modified procedure is recommended for the determination of thallium as thallium (III) oxide using potassium ferricyanide. Precipitation from a hot solution and digestion of the precipitate gives a more dense precipitate and eliminates the recommended 18 hour standing period. Using this modified procedure thallium can be determined with an average error of 0.4 per cent.

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INTRODUCTION

A large number of volumetric methods have been proposed for the determination of thallium while relatively few gravimetric methods have been proposed. Most of the methods require a preliminary reduction of thallium (III) so that all the thallium will be present in the plus one oxidation state. Sulfur dioxide is commonly used as the reducing agent. When thallium is to be determined by volumetric oxidation, sulfur dioxide has several disadvantages as a reducing agent. Since metallic reducers are more convenient as reducing agents, a study of the reduction of thallium (III) by metallic reducers was made.

As the work on the reduction of thallium (III) to thallium (I) proceeded, it became necessary to study the oxidation of thallium (I) to thallium (III). Thallium (III) oxide is the most easily prepared thallium (III) compound and potassium ferricyanide is the only alkaline oxidant proposed for the quantitative precipitation of thallium (III) oxide. Since potassium ferricyanide appeared to have disadvantages as an alkaline oxidant, a study of sodium hypochlorite was made.

A study of the oxidation of thallium (I) by sodium hypochlorite indicated that a standard solution of hypochlorite could be used for the volumetric determination of thallium. Direct and indirect volumetric methods for the determination of thallium were studied by using a standard solution of sodium hypochlorite.

During the volumetric work it appeared that sodium hypochlorite gave a homogeneous precipitation of thallium (III) oxide. A comparative study of the gravimetric determination of thallium as thallium (III)

oxide was made using potassium ferricyanide and sodium hypochlorite solutions as alkaline oxidizing agents.

HISTORICAL

Most of the methods for the determination of thallium require that the thallium be present in solution in one oxidation state only. For this reason the preliminary oxidation or reduction of thallium is of great importance. Therefore the literature on this subject is reviewed before the volumetric and gravimetric methods of determination are discussed. Since the work described in this thesis involves the use of metals as reductants, a brief historical review of metallic reducing agents is included.

A. Oxidation of Thallium (I) to Thallium (III)

Since oxidants utilized as standard solutions are discussed in Section C as part of the various volumetric determinations, the only oxidants included here are those which cannot be used as standard solutions.

Brown and McGlynn (10) treated a hot ammoniacal solution of thallium (I) sulfate with potassium persulfate. Upon boiling, the thallium (III) oxide coagulates and the excess ammonia is driven off.

Challenger and Masters (16) oxidized thallium (I) to thallium (III) with ozone. The excess ozone was removed by passing air through the solution.

B. Reduction of Thallium (III) to Thallium (I)

Sulfur dioxide is customarily used as the reducing agent for the quantitative reduction of thallium (III) to thallium (I), (19,30).

The advantage of sulfur dioxide is that no metal ions are introduced that would interfere in the determination of thallium (I). The major disadvantage is the difficulty of removing the excess sulfur dioxide. At least one hour of boiling is necessary to remove excess sulfur dioxide.

Strecker (62) treated an acidified solution of thallium (III) with potassium iodide and obtained thallium (I) iodide and iodine.

Berry (5,6) used hydroxylamine sulfate, iron (II) sulfate, sodium arsenite and metallic copper for the reduction of thallium (III) to thallium (I). Hydroxylamine sulfate gives quantitative reduction of thallium (III) in either acidic or basic solution.



The reduction proceeds more rapidly in alkaline solution but traces of nitrite were found.

Iron (II) sulfate will quantitatively reduce upon boiling a hot acidic solution of thallium (III) to thallium (I). The kinetics of the reduction of thallium (III) by iron (II) have been studied by Johnson (34) and by Forshheimer and Eppler (24).

Berry (6) treated thallium (III) oxide with an excess of standard sodium arsenite and found complete reduction of thallium (III) to thallium (I).

Thallium (III) in boiling solution was found to be quantitatively reduced to thallium (I) by the addition of copper metal (5).

Zintl and Rienacker (73) report the rapid quantitative reduction of thallium (III) to thallium (I) with titanium (III) chloride in hot acetate solution.

Brown and McGlynn (10) found that slow addition of hydrogen peroxide to an acid solution of thallium (III) gave quantitative reduction of thallium (III) to thallium (I).

Taimni (64) found that on the addition of potassium thiocyanate thallium (III) chloride is reduced to thallium (I) thiocyanate according to Equation 2.



When thallium (III) chloride is added to an excess of potassium thiocyanate, the results are in closer agreement with equation 2.

G. Volumetric Methods for Thallium

Hollens and Spencer (31) treated a thallium sample with chlorine gas until thallium (I) chloride dissolved. The solution was acidified and potassium iodide was added. The iodine liberated by the reduction of thallium (III), was titrated with standard sodium thiosulfate using the iodine color in chloroform as the indicator. They report excellent precision and accuracy.

Sill and Peterson (50) treated two to five milligram thallium samples with a bromine reagent and boiled the solution until only a faint bromine color remained. After cooling, the excess bromine was destroyed by the addition of a phenol solution. Potassium iodide was

added and the liberated iodine was titrated with standard thiosulfate using a special starch as indicator. Good results were reported for two to five milligrams of thallium. Larger concentrations of thallium gave low results. The addition of sufficient potassium iodide to precipitate thallium (I) iodide also gave low results. Presumably iodine is adsorbed or coprecipitated by the thallium (I) iodide.

Berry (6) treated a thallium (III) solution with an excess of standard sodium arsenite. The unreacted sodium arsenite was titrated with sodium hypochlorite using thallium (I) as the indicator. In alkaline solution, the first excess hypochlorite oxidizes thallium (I) to thallium (III) oxide. The results for thallium were approximately three per cent low. It appears that these low results were due to the slow reaction between hypochlorite and thallium (I).

Berry (5) determined thallium by reducing a thallium (III) solution with an excess of standard iron (II) sulfate solution. After quantitative reduction of the thallium (III) the excess iron (II) was titrated with standard potassium dichromate.

Zintl and Rienacker (73) titrated a hot acetate solution of thallium (III) with a standard titanium (III) chloride solution. The precipitation of titanium dioxide was prevented by the addition of ammonium fluoride. Hydrochloric acid was found to inhibit the reduction of thallium (III) by titanium (III).

Marshall (41) recommends the use of sodium bromate for the indirect volumetric determination of thallium (I). The method involves the addition of an excess of standard sodium bromate solution to a thallium

sample containing dilute hydrochloric acid and a small crystal of sodium bromide. The excess bromine was distilled over and treated with potassium iodide. The liberated iodine was titrated with sodium thiosulfate. Excellent precision and an accuracy of one part per thousand is reported. This method is slow because of the required distillation.

Zintl and Rienacker (73) propose a direct titration of thallium (I) in five to eight per cent hydrochloric acid with standard potassium bromate. The end point is detected potentiometrically or by the disappearance of methyl orange indicator at 50 to 60°C. Excellent precision and accuracy are reported. The bromate oxidation procedure is perhaps the best volumetric method for the determination of thallium (I). Rienacker and KnaueI (46) have adapted the bromate method to the micro titration of thallium for toxicology.

Hawley (27) proposed a permanganate titration of thallium (I) in 6 per cent hydrochloric acid. The method is of little use, since permanganate reacts with the hydrochloric acid.

Beale and co-workers (2) found that the chloride ion is necessary for the permanganate titration of thallium (I) and that thallium (I) is air oxidized in 0.8 normal hydrochloric acid. An alternate procedure is described for the determination of 6 to 100 milligrams of thallium. Sodium fluoride in hydrochloric acid is used to complex Mn (III) as the fluoride. This method is an improvement over Hawley's method but is inferior to the bromate method.

Willard and Young (70) propose the use of cerium (IV) sulfate for the volumetric oxidation of thallium (I) in hydrochloric acid.

This oxidation will not take place in the absence of hydrochloric acid. Elevated temperature is necessary for a rapid reaction. For usual end point detection, the solution must be between 85 and 100°C. This method is reported to yield good results but is not attractive due to the difficulty of detecting the equivalence point.

Tomicek and Josek (66) report the oxidation of thallium (I) to thallium (III) by sodium hypobromite in 1.5 to 2.0 normal sodium hydroxide. They proposed the use of thallium (I) carbonate for the standardization of hypobromite solutions. Excellent results were obtained.

Tomicek and Filipovic (65) state that calcium chlorohypochlorite is less suitable than hypobromite for the alkaline oxidation of thallium (I). They reported low results which could not be improved.

Berry (8) states that chloramine-T will quantitatively oxidize thallium (I) to thallium (III) in a dilute hydrochloric acid solution containing bromide ion. Methyl orange is used as the indicator.

Swift and Garner (63) determined thallium (I) in three to five normal hydrochloric acid solution by titration with a standard iodate solution using the iodine monochloride end point. Excellent results are reported.

Smith and Wilcox (54) titrated a 40 per cent hydrochloric acid solution of thallium (I) with a standard iodate solution using 0.05 ml. of dilute amaranth solution as indicator. The end point was detected by the destruction of the amaranth color by a slight excess of iodate. Excellent results are reported.

Singh and Singh (51) state that thallium (I) in five normal hydrochloric acid can be titrated with a standard potassium chlorate solution using iodine monochloride as catalyst.

Mehrota (42) states that a standard iodide solution can be titrated with a thallium (I) solution using bromphenolblue as an adsorption indicator. When the titration is kept out of bright light, the first excess thallium (I) causes a color change from violet to bright green. Good precision and accuracy are reported. This method has the disadvantage that the unknown is used as the titrant.

Browning and Palmer (13) estimated thallium by adding a measured volume of standard ferricyanide to an alkaline solution of thallium (I). The thallium (III) oxide was removed by filtration and the filtrate was acidified. The ferrocyanide was titrated with standard potassium permanganate. Berry (5) found the end point to be poor in the ferricyanide-permanganate titration.

D. Gravimetric Determinations of Thallium

One of the most popular gravimetric methods for the determination of thallium is based on the precipitation of thallium (I) from a dilute ammoniacal solution by the addition of potassium chromate (30). The precipitate is dense and easily handled. However, thallium (I) chromate is soluble in the precipitating solution to the extent of six milligrams per liter (43). This solubility loss would give a negative error of considerable magnitude with samples of low thallium content.

Mach and Lepper (40) treated a solution of thallium (I) with potassium hydroxide and potassium ferricyanide. The ferricyanide ion oxidizes the thallium (I) to thallium (III) which precipitates as thallium (III) oxide (Tl_2O_3) in alkaline solution. Oka (44) reports the solubility of thallium (III) oxide to be 5.93×10^{-4} milligrams per liter at 25°C ., while Sidgwick (48) reports 2.51×10^{-6} milligrams per liter at 25°C . The solubility of thallium (III) in alkaline solution is reported to be dependent on the method of precipitation (6,12). The black modification formed in strong alkali is less soluble than the brown modification. Duncan (21) states that on heating, thallium (III) oxide begins to lose oxygen at 100°C . Duval (22) reports that the oxide formed in alkaline solution may be used as a weighing form, if dried between 100 and 230°C . in the absence of carbon dioxide.

Werther (68) and Long (39) precipitated thallium (I) iodide from a hot dilute acetic acid solution of thallium (I) by the addition of potassium iodide. The sample solution must be free of substances such as silver or copper that precipitate as iodides or substances such as titanium that hydrolyze in dilute acetic acid. All the thallium must be in the plus one oxidation state prior to precipitation. This is achieved by reduction with sulfur dioxide and boiling to remove the excess. The solubility of thallium (I) iodide in water is reported to be 0.0847 grams per liter at 26°C . (35). The solubility is decreased in solutions containing a little potassium iodide, acetic acid, or alcohol. This method is not recommended due to the appreciable solubility of the precipitate.

Cushman (20) used chloroplatinic acid for the precipitation of thallium (I) from dilute acid solution. Thallium (I) chloroplatinate is the least soluble of the chloroplatinates. Duval (22) recommends drying the precipitate between 65 and 155°C.

Hawley (28,29) reported the use of sodium tetrasulfostannate as a precipitating reagent for the determination of thallium (I) in dilute acid. The precipitate has the formula Tl_4SnS_4 . The excess tin (IV) sulfide is removed as the soluble thioestannate ion by adding a sodium sulfide solution and boiling. The precipitate is dried at 150°C. Duval (22) states that the precipitate is not a suitable weighing form.

Smith (55) proposed tetraphenyl arsoniumchloride for the quantitative precipitation of thallium (III) as tetraphenylarsonium chlorothallate $((C_6H_5)_4AsTlCl_4)$. The precipitation is carried out in 0.2 to 0.5 normal hydrochloric acid. An accuracy of one part per thousand is reported. Smith states that potassium chromate is the best reagent for the gravimetric determination of thallium, and in spite of the fact that it tends to give low results due to the solubility of thallium (I) chromate.

Berg and Fahrenkamp (4) recommend the use of thionalide (-mercapto-N-naphthylacetamide) under controlled conditions as a specific reagent for the estimation of thallium (I). The reagent is specific for thallium (I) when precipitation is carried out in an alkaline cyanide solution. The precipitate is thoroughly washed with water to remove cyanide and then washed with acetone to remove the excess thionalide. Duval (22) states that the precipitate may be dried between 69 and 156°C.

Browning (11) proposed weighing thallium (I) as the sulfate or acid sulfate after isolation of the thallium. He states that the acid sulfate may be dried to constant composition between 220 and 240°C. Weighing as the sulfate requires drying in platinum to a dull red heat. Duval (22) states that the sulfate may be dried between 92 and 355°C.

E. Trace Methods

A number of methods have been proposed for the determination of small amounts of thallium.

Pavelka and Morth (45) determined thallium in concentrations of 0.004 mg. per ml. by measuring the color of the thallium (I) phosphomolybdate hydrosol. Lead, bismuth, mercury (II) and cadmium ions do not interfere, but potassium and ammonium ions must be absent since they form insoluble salts with the phosphomolybdic acid. An accuracy of one to five per cent is reported.

Shaw (47) separated thallium (III) chloride by an ether extraction. The thallium (III) chloride was treated with potassium iodide and the liberated iodine was extracted in carbon disulfide. The carbon disulfide extracts were compared to standard series. This method is applicable to concentrations of 0.04 to 0.16 milligrams of thallium per ml. of carbon disulfide.

Haddock (26) modified Shaw's method by extracting thallium (I) in chloroform with dithizone, conversion of thallium to trivalent state, reduction with potassium iodide, and measuring the starch iodine color with similarly treated samples. The method is applicable for 0.005 to

0.2 milligram of thallium in the presence of 0.5 gram of silver, copper, cadmium, antimony, chromium and iron.

Sill and Peterson (49) measured the fluorescence of microgram quantities of thallium (I) in 1 to 2 normal hydrochloric acid. A large number of interferences must be removed prior to measurement.

Flaschka (23) treated solutions containing from 0.025 to 5.0 milligrams of thallium with solid magnesium versene complex. The displaced magnesium was titrated with standard versene in the presence of eriochrome black as indicator.

Buck, Farrington and Swift (14) determined thallium (I) by coulometric titration using generated bromine or chlorine. The end point was determined by a rotating platinum electrode having an applied e.m.f. of 200 millivolts. An error of 0.2 per cent is reported for thallium concentrations from 93 to 1900 micrograms.

F. Metallic Reductors

Metallic reductors are often used for preparative work prior to a volumetric oxidation. Analysis by volumetric oxidation assumes that all of the species being determined are present in the same oxidation state. Preliminary treatment, for example dissolving the sample, may effect quantitative conversion of the species to the desired oxidation state. In most cases, quantitative reduction is necessary before the measured reaction is carried out. Two requirements are necessary for reducing agents that are to be used prior to volumetric oxidation.

1. The reducing agent employed must be stable in the oxidized form in

order that it will not consume the standard oxidant being used.

2. The excess reducing agent must be removed prior to the measured reaction. The first condition is easily satisfied by using a reducing agent having only one stable oxidation state in solution. The method to be used for removing the excess reducing agent is dependent on the material being used. Metallic reductors satisfy both of the above conditions. In the column reductor, the removal of excess reducing agent is automatic. The column reductor also offers the advantage of rapid reduction due to the large surface area of the metal.

Liquid amalgams are not used extensively as reducing agents due to the difficulty of separating the amalgam from the aqueous phase.

Hillebrand, Lundell, Hoffman and Bright (30) describe in detail the preparation and uses of the Jones and silver reductors.

Cooke and co-workers (18) describe the preparation of a lead reductor and its use for the reduction of uranium (VI) to uranium (IV). The lead reductor has the advantages that amalgamation is not necessary and ammonium ions and acetate ions do not interfere. When sulfuric acid solutions are used, an adherent film of lead sulfate forms on the lead, which rapidly decreases the reducing action of the reductor. The formation of a lead sulfate film can be prevented by hydrochloric acid, if the hydrochloric acid concentration is 2.5 normal or greater.

Treadwell and co-workers (67) describe the preparation and uses of a cadmium reductor. The cadmium reductor can be used in hydrochloric or sulfuric acid and has been recommended for the following reductions:

Fe (III) to Fe (II), Ti (IV) to Ti (III), Mo (VI) to Mo (III), V (V) to V (II) and U (VI) to U (IV) and U (III).

Brinn (9) recommends the use of a cadmium rod for the reduction of Fe (III) to Fe (II) in either hydrochloric or sulfuric acid.

Yoshimura (72) proposes the use of a bismuth column for the reduction of Fe (III) to Fe (II), Ti (IV) to Ti (III) and U (VI) to U (IV).

Metallic nickel in a carbon dioxide atmosphere at room temperature can be used as a reducing agent for Cu (II), Fe (III), Sn (IV), Ti (IV), U (VI), W (VI), V (V) and Mo (IV) (71). Boiling solutions of the above ions in a carbon dioxide atmosphere can be reduced by metallic antimony (71).

Smith and Wilcox (53) recommend the use of Woods metal for the reduction of Fe (III) to Fe (II) in dilute hydrochloric or sulfuric acid. Woods metal is an alloy of 50 per cent bismuth, 25 per cent lead, 12.5 per cent tin and 12.5 per cent cadmium. The alloy melts at 65.5°C . and can conveniently be removed by letting it cool and separating the solid.

A series of papers by Someya (56,57,58,59,60,61) describe the preparations and uses of zinc, bismuth, cadmium, lead and tin amalgams.

Smith and Kurtz (52) recommend carrying out amalgam reductions in an Erlenmeyer flask. After reduction, they add 50 ml. of carbon tetrachloride which forms a layer separating the amalgam from the aqueous phase. Titrations using indicators can be performed on the aqueous phase by gentle swirling so that the amalgam does not contact the aqueous phase.

Hope and co-workers (32) describe a glass reduction cell useful for amalgam reduction in an atmosphere of carbon dioxide.

EXPERIMENTAL

I Standard Solutions

All reagents used in this work were, unless otherwise stated, analytical reagent grade.

All pipets and burets were calibrated and corrections were applied where necessary.

All weighings were made with calibrated weights.

Sodium arsenite, 0.1000 normal, was prepared from Baker and Adamson Primary Standard Analytical Reagent arsenious oxide, which had been dried at 110°C . for two hours. Approximately 16 grams of sodium hydroxide pellets and 60 ml. of water were added to 9.8910 grams of the dried reagent. After the mixture dissolved, it was diluted with water to 300 ml., neutralized with dilute sulfuric acid, treated with 6 grams of sodium bicarbonate, and diluted to two liters.

Potassium bromate, 0.1000 normal, was prepared from Mallinckrodt Analytical Reagent Grade potassium bromate which had been dried at 110°C . for two hours. The Mallinckrodt assay was 99.8 per cent. Two liter batches were prepared by dissolving 5.5792 grams of the dried reagent in distilled water and diluting to two liters.

Sodium hypochlorite solutions were prepared by diluting various quantities of commercial bleaches. The preparation of two liter solutions of 0.1 normal sodium hypochlorite required 130 ml. of Clorox, 130 ml. of Roman Cleanser or 190 ml. of Fleecy White Bleach. These diluted solutions were stored in amber bottles and kept out of direct sunlight. The bottles were equipped with siphons and soda lime traps.

Sodium hypochlorite, 0.1 normal, pH of 12, was prepared by diluting 130 ml. of commercial Clorox to two liters and adding sodium hydroxide pellets until the required pH was registered on a Beckman H2 line operated pH meter. The solution was stored in an amber bottle and kept out of direct sunlight.

Sodium hypochlorite, 0.1 normal, and 0.6 normal in hydroxide was prepared by diluting 130 ml. of commercial Clorox to two liters and adding 48 grams of sodium hydroxide pellets. The solution was stored in an amber bottle and kept out of direct sunlight.

A gallium solution, 0.0158 molar, was prepared by dissolving 0.1102 grams of Fisher Scientific gallium metal in a mixture of 2 ml. of concentrated sulfuric acid and 1 ml. of concentrated perchloric acid and diluting to 100 ml.

An iron (II) chloride solution, containing 0.174 milligrams of iron (II) per milliliter, was prepared by dissolving 0.0870 grams of Mallinckrodt standard iron wire in 10 ml. of 6 normal hydrochloric acid and diluting to 100 ml.

Bordeaux. A 0.2 per cent aqueous solution was prepared from Bordeaux, British Color Index 88, G. Frederick Smith Chemical Company.

Diphenylamine sodium sulfonate, 0.01 molar was prepared (69) by dissolving 0.32 grams of diphenylamine barium sulfonate in 100 ml. of water and adding 0.5 grams of sodium sulfate. After standing over night, the clear solution was decanted from the precipitated barium sulfate.

Sodium hypochlorite, 0.1 normal, was standardized by the following procedure which is essentially that of Kelthoff and Stenger (36). To 24.94 ml. of the standard sodium arsenite solution in a 125 ml. Erlenmeyer flask were added 1.0 gram of potassium bromide, 1.0 gram of sodium bicarbonate and one drop of Bordeaux indicator. The sodium arsenite solution was titrated with the hypochlorite solution until the indicator faded. One more drop of indicator was added and the titration continued until a fraction of a drop caused the indicator color to flash from pink to colorless or pale yellow. An indicator blank of 0.01 ml. of 0.1 normal sodium hypochlorite was subtracted from the volume of hypochlorite used.

II Stability Studies of Sodium Hypochlorite Solutions

Aqueous hypochlorite solutions are known to be strong oxidizing agents, but reasonably stable solutions have been prepared by many investigators.

Jellinek and Kristeff (33) prepared sodium hypochlorite by passing chlorine into a 0.1 normal sodium hydroxide solution. The resulting solution was stored in a clear glass bottle and in 17 days the normality changed from 0.1352 to 0.1330. The authors infer that sunlight accelerates the decomposition of hypochlorites.

Chapin (17) studied the decomposition of sodium hypochlorite as a function of pH and found that a pH of 13.1 gave maximum stability. Buffer mixtures containing acetate, borate, carbonate and phosphate ions were found to accelerate the decomposition of hypochlorite solutions.

Kolthoff and Stenger (36) used H.T.H., calcium hypochlorite manufactured by Mathieson Alkali Works, for the preparation of hypochlorite solutions. These solutions were adjusted to a pH of 11 to 12 and stored in glass bottles painted black to protect the solutions from light. The solutions were quite stable, showing normality changes from 0.1047 to 0.1035 in six months, 0.0895 to 0.0881 in six months and 0.1262 to 0.1230 in 16 months. Calcium hypochlorite solutions have the disadvantage that on standing a precipitate of calcium carbonate settles out.

Goldstone and Jacobs (25) used Clorox, a commercial bleach, as a source of hypochlorite. They adjusted the diluted Clorox solution to a pH of 12.5 and stored these solutions in dark bottles out of direct sunlight. Their solutions showed normality changes from 0.00500 to 0.00498 in 56 days and 0.00557 to 0.00554 in 175 days.

A number of variables such as pH, foreign ions and exposure to light have been shown to affect the stability of hypochlorite solutions. Calcium hypochlorite solutions have been reported to be more stable than sodium hypochlorite solutions (36). Most of the stability studies were made on sodium hypochlorite solutions which were prepared by passing chlorine gas into sodium hydroxide solutions. Goldstone and Jacobs (25) used commercial Clorox while Belcher (3) used B.D.H. sodium hypochlorite for the preparation of standard hypochlorite solutions. Carlyen (15) used Clorox as a source of hypochlorite and found that 0.1 normal solutions with a pH of ten were reasonably stable. Goldstone and Jacobs

were the only investigators who used commercial sodium hypochlorite for stability studies, and their solutions were quite dilute.

In view of the conflicting literature on the effect of pH and the lack of information on the stability of various commercial bleaches the following stability studies were designed.

Sodium hypochlorite solutions prepared from various commercial bleaches were stored in amber bottles, which had been thoroughly rinsed with a dilute solution of sodium hypochlorite. These solutions were periodically standardized by titration against 0.1000 normal sodium arsenite. In triplicate standardizations of a given hypochlorite solution, the normalities obtained by the first standardization were uniformly low. This was attributed to incomplete conditioning of the buret surface. In order to obtain a constant normality, the buret was filled with hypochlorite solution and allowed to stand 20 minutes, drained and refilled before titrations were performed. The results in Table I are averages of duplicate standardizations which agreed within two parts per thousand.

TABLE I

STABILITY OF 0.1 NORMAL SODIUM HYPOCHLORITE SOLUTIONS
PREPARED FROM VARIOUS COMMERCIAL BLEACHES

Days	Glorox	Roman Cleanser	Fleecy White
—	0.1084	—	0.1117
4	—	0.1073	—
9	0.1077	—	0.1109
18	0.1073	0.1065	0.1112
19	0.1081	0.1070	0.1113
32	0.1080	0.1069	0.1104
53	0.1078	0.1067	0.1105
78	0.1077	0.1067	0.1104

The results from Table I indicate that sodium hypochlorite solutions prepared from various commercial bleaches have similar stabilities.

The effect of pH on the stability of sodium hypochlorite solutions was determined by periodic standardization of 0.1 normal Chlorox solutions adjusted to varying alkalinity. The results in Table II are averages of duplicate determinations which agreed within two parts per thousand.

TABLE II
EFFECT OF pH ON STABILITY OF 0.1 NORMAL CLOROX SOLUTIONS

Time in Days	Normality of Hypochlorite Solutions		
	0.638N NaOH	pH = 12	pH = 10
0	0.1016	0.1047	0.1042
2	0.1015	0.1044	--
8	0.1015	0.1044	--
14	0.1012	0.1040	--
15	--	--	0.1041
28	0.1010	0.1039	--
43	0.0999	0.1034	0.1035
69	0.0998	0.1038	0.1035
105	0.0997	0.1027	0.1021

The solutions studied in Table II were stored in amber glass bottles which were not rinsed with hypochlorite preliminary to use. This lack of rinsing may account for the decreased stabilities of the solutions in Table II compared to the more stable solutions in Table I. A change of hydroxide concentration from 0.0001 to 0.64 normal appears

to have little effect on the stability of 0.1 normal sodium hypochlorite solutions.

A sodium hypochlorite solution with a pH of 12, after being stored in a translucent polyethylene bottle for 28 days, showed a normality change from 0.1042 to 0.0977. This was a larger normality change than noted for the solutions stored in amber glass bottles. It appears that translucent polyethylene is unsuitable for the storage of hypochlorite solutions.

A hypochlorite solution, which was stored in an amber bottle previously used for hypochlorite storage, had a normality decrease from 0.1014 to 0.1005 in 155 days. It appears that conditioning of a container aids in the stability of sodium hypochlorite solutions.

The data in Table I indicate that 0.1 normal solutions of sodium hypochlorite, prepared from various commercial bleaches, have nearly equal stability. The data in Table II indicate that hydroxide concentrations from 0.0001 to 0.64 normal have a negligible effect on the stability of 0.1 normal hypochlorite solutions. Three successive solutions of 0.1 normal hypochlorite were stored in an amber bottle. It was noted that the second and third solutions were more stable than the first. This increased stability may be due to conditioning of the glass surface. It was found that for accurate titrations with hypochlorite, the buret should be conditioned with the hypochlorite solution for 15 to 30 minutes before use. When the buret is not conditioned, the volumes of hypochlorite used in titrations are found to be too large.

Several precautions are necessary when preparing stable 0.1 normal solutions of sodium hypochlorite. A 0.1 normal solution is easily prepared by diluting 130 ml. of commercial Clorox (5.25 per cent sodium hypochlorite) to two liters. The solution should be stored in an amber glass bottle which has been cleaned and thoroughly rinsed with 0.1 to 0.2 normal hypochlorite solution. The prepared solution should stand over night before being standardized against a standard arsenite solution by the method of Kolthoff and Stenger (36).

III The Use of Metallic Reductors for the Reduction of Thallium (III) to Thallium (I)

Most of the methods for the determination of thallium require a preliminary reduction of thallium (III) to thallium (I), and sulfur dioxide is commonly used as the reducing agent. The disadvantages of sulfur dioxide were discussed in section B. Copper metal is the only metallic reducing agent mentioned in the literature for the reduction of thallium (III). In view of the advantages of metallic reductors in analysis, it seemed desirable to investigate their use for the reduction of thallium (III) to thallium (I).

In order to study methods for the reduction and determination of thallium it was necessary to prepare a stable standard solution of a thallium compound. Fisher Scientific Company C.P. thallium (I) nitrate was used as a thallium source, since primary standard thallium salts are not commercially available.

Approximately 75 grams of Fisher Scientific C.P. thallium (I) nitrate was recrystallized twice from water, air dried and finally

even dried at 110°C . for two hours. Spectrographic analysis of the recrystallized salt showed lead to be absent.

A thallium (I) nitrate solution was prepared by dissolving 6.6826 grams of the dry reagent in 100 ml. of distilled water and diluting to 500 ml. Weight calibration of this volumetric flask showed the true volume to be 499.92 ml. Assuming the thallium (I) nitrate to be pure, the calculated normality of this solution was 0.10036.

As a check on the purity of the thallium (I) nitrate the 0.10036 normal solution was analysed in triplicate for thallium (I) by the chromate procedure (30) and the thallium (III) oxide procedure (40).

Three 24.94 ml. aliquots of the thallium solution yielded thallium (I) chromate precipitates of 0.3260, 0.3264 and 0.3261 grams. After applying the correction for the solubility loss, the average normality is 0.10029.

Three 24.94 ml. aliquots of thallium solution gave weights of thallium (III) oxide of 0.2863, 0.2861 and 0.2863 grams, giving an average normality of 0.10050.

The normalities obtained by analysis and weight-volume measurements agree to one part in a thousand. This close agreement indicates that the minimum purity of the recrystallized thallium (I) nitrate is 99.9 per cent.

A large volume of thallium (I) nitrate solution was prepared for the following studies. Six-hundred ml. of water containing 36.3981 grams of the dry reagent was diluted to the mark in a two liter volumetric flask. This solution was transferred to a clean dry seven liter bottle.

To the unrinsed volumetric flask was added 600 ml. of water containing 19.4550 grams of the dry reagent. The flask was diluted to volume and its contents were added to the solution in the seven liter bottle. The calculated normality of this solution is 0.1048.

Since the 0.1048 normality of the thallium solution was questionable, the solution was analyzed by the bromate and chromate procedures.

In standardization by the chromate method, five 24.94 ml. aliquots of the thallium solution yielded thallium (I) chromate precipitates weighing 0.3405, 0.3407, 0.3405, 0.3421 and 0.3409 grams. After applying the correction for the solubility loss, the average normality is 0.1048.

The volumetric bromate method of Zintl and Reinacker (73) was used to standardize the reference thallium solution. Two 19.97 ml. aliquots required 20.95 and 20.95 ml. of the standard 0.1000 normal potassium bromate solution, giving a normality of 0.1049. Duplicate 29.97 ml. aliquots required 31.39 and 31.47 ml. of the standard bromate solution, giving an average normality of 0.1049. The equivalence point was detected potentiometrically by the use of a platinum-calomel couple and a Fisher Titrimeter. The normality, 0.1049 obtained by the bromate method agrees well with the calculated normality of 0.1048.

Thallium (III) sulfate, 0.1 normal, was prepared from thallium (I) nitrate in the following manner. Fifty-four grams of the thallium (I) nitrate was dissolved in 900 ml. of water and the solution made basic with sodium hydroxide pellets. The basic solution was treated with 350 ml. of commercial Clorox and digested on a steam bath.

The thallium (III) oxide precipitate was washed twice by decantation and then dissolved in 220 ml. of concentrated sulfuric acid. The solution was heated to fumes of sulfur trioxide and on cooling, the sides of the beaker were washed down with distilled water. The solution was heated to sulfur trioxide fumes a second time and on cooling was diluted to four liters.

The thallium (III) sulfate solution was analyzed for total thallium content by the volumetric bromate method (73). Two 19.97 ml. aliquots were reduced with sulfur dioxide and boiled for one hour to expell the excess. These aliquots required 20.88 and 20.84 ml. of 0.1000 normal potassium bromate. Three blanks were run in order to determine the amount of sulfur dioxide remaining after one hour of boiling. The blanks required 0.04, 0.07 and 0.05 ml. of 0.1000 normal potassium bromate, giving an average blank of 0.05 ml. After subtracting the 0.05 ml. blank, these determinations give an average normality of 0.1043 for total thallium in the thallium (III) sulfate solution.

The thallium (I) concentration in the thallium (III) sulfate solution was determined by titrating two 19.97 ml. aliquots with 0.1000 normal potassium bromate. These titrations required 0.74 and 0.76 ml. of standard bromate solution, giving a normality of 0.0038 for thallium (I). Since the total thallium concentration is 0.1043 normal and the thallium (I) concentration is 0.0038 normal, the thallium (III) normality is 0.1005.

A. Cadmium Reductor

A cadmium reductor was prepared in the following manner. Small cadmium filings were obtained by filing a cadmium rod (Fisher Scientific Company) with a coarse file. The filings, approximately 30 mesh in size, were washed in one normal hydrochloric acid and in one normal sulfuric acid. The washed filings were placed in a Pyrex glass reductor fitted with a glass wool plug and equipped with a glass stopcock. These reducers are commonly used as silver reducers and can be purchased from the G. F. Smith Chemical Company. The 20 cm. cadmium column was washed by passing one normal sulfuric acid through the reductor. When not in use the reductor was filled with one normal sulfuric acid,

Measured quantities of the 0.1043 normal thallium (III) sulfate solution were treated with varying amounts of one normal sulfuric acid and diluted. Samples containing 212.8 milligrams of thallium were diluted to 100 ml. and the smaller samples were diluted to 50 ml. These acid solutions were passed through the cadmium reductor at a measured rate. The column was washed with three 50 ml. portions of dilute sulfuric acid. Since the volumetric bromate method requires the solution to be five to eight per cent in hydrochloric acid, the solutions were treated with 30 ml. of six normal hydrochloric or with 12 grams of potassium chloride. The thallium (I) solution was titrated with 0.1000 normal potassium bromate and the equivalence point was detected by the use of a Fisher Titrimeter with platinum and calomel electrodes. Five blanks were run on the cadmium reductor and 0.06, 0.05, 0.04, 0.06 and 0.05 ml. of 0.1000 normal potassium bromate were

consumed. An average blank of 0.05 ml. was subtracted from the volume of 0.1000 normal potassium bromate used. The results obtained using the cadmium reductor are tabulated in Table III.

B. Silver Reductor

A silver reductor was prepared in the same manner as the cadmium reductor by replacing the cadmium metal with granular silver (G. F. Smith Chemical Company). The 16 cm. silver column was washed by passing one normal sulfuric acid through the reductor. When not in use the reductor was filled with one normal sulfuric acid.

Measured quantities of the 0.1043 normal thallium (III) sulfate solution were treated with varying amounts of one normal sulfuric acid and diluted. Samples containing 212.8 milligrams of thallium were diluted to 100 ml. and the smaller samples were diluted to 50 ml. These acid solutions were passed through the silver column at a measured rate. The column was washed with three 50 ml. portions of dilute sulfuric acid. The reduced solutions were treated with 30 ml. of six normal hydrochloric acid or with 12 grams of potassium chloride. The thallium (I) was titrated with 0.1000 normal potassium bromate. The equivalence point was detected by using a Fisher Titrimeter equipped with platinum and calomel electrodes. Five blanks were run on the silver reductor giving values of 0.02, 0.03, 0.03, 0.02 and 0.04 ml. of 0.1000 normal potassium bromate. An average blank of 0.03 ml. of 0.1000 normal potassium bromate was subtracted from the volumes of bromate used. When hydrochloric acid is added silver chloride precipitates, but apparently thallium chloride is not coprecipitated since

TABLE III
REDUCTION OF THALLIUM (III) TO THALLIUM (I)
USING A CADMIUM REDUCTOR

Sample Number	Acidity of Diluted Solutions	Acidity of Washings	Flow Rate (ml./min.)	Milligrams of Thallium		Error (mg.)
	(N)			Taken	Found	
1	1.0	1.0 N	30-50	32.0	32.1*	+0.1
2	0.1	0.01N	30-50	32.0	31.7	-0.3
3	1.0	0.01N	25-35	32.0	31.7	-0.3
4	1.0	0.01N	25-35	32.0	31.9	-0.1
5	1.0	0.01N	20-30	32.0	32.0	0.0
6	1.0	1.0	30-50	53.1	53.1*	0.0
7	0.2	0.01	30-50	53.1	53.2	+0.1
8	1.0	0.01	25-35	53.1	52.9	-0.2
9	1.0	0.01	20-30	53.1	52.9	-0.2
10	1.0	0.01	20-30	53.1	52.5	-0.6
11	0.8	1.0	40-50	106.4	106.3*	-0.1
12	1.6	1.0	40-50	106.4	106.6*	+0.2
13	2.0	1.0	40-50	106.4	106.0*	-0.4
14	0.24	1.0	40-50	106.4	106.3*	-0.1
15	1.5	1.0	40-50	106.4	106.3*	-0.1
16	0.4	0.01	20	106.5	106.4	-0.1
17	0.4	0.01	20-30	106.5	106.3	-0.2
18	1.0	1.0	25	212.8	213.3*	+0.5
19	0.6	1.0	15-20	212.8	212.8*	0.0
20	1.0	1.0	25	212.8	212.6	-0.2
21	1.0	0.01	43	212.8	212.2	-0.6
22	1.0	0.01	20-25	212.8	212.7	-0.1

*12 grams of KCl added

Samples 1-17 diluted to 50 ml., 18-22 diluted to 100 ml.

results for thallium tend to be high. The results are given in Table IV.

TABLE IV
REDUCTION OF THALLIUM (III) TO THALLIUM (I)
USING A SILVER REDUCTOR

Sample Number	Acidity of Diluted Solution (N)	Acidity of Wash Solution (N)	Flow Rate (ml./min.)	Milligrams of Thallium		Error (mg.)
				Taken	Found	
1	1.0	1.0	20-30	32.0	32.0*	0.0
2	1.0	0.01	25	32.0	32.0	0.0
3	1.0	0.01	25	32.0	31.8	-0.2
4	1.0	0.01	25	32.0	32.0	0.0
5	1.0	1.0	20-30	53.1	53.8*	+0.7
6	1.0	0.01	25	53.1	53.0	-0.1
7	1.0	0.01	25	53.1	53.1	0.0
8	1.0	0.01	25	53.1	53.0	-0.1
9	0.4	1.0	40	106.4	106.6*	+0.2
10	2.0	1.0	30-40	106.4	106.7*	+0.3
11	0.4	1.0	30-40	106.4	107.0*	+0.6
12	1.6	0.01	30-40	106.4	107.3*	+0.9
13	1.0	0.01	25	106.5	106.6	+0.1
14	1.0	0.01	25	106.5	106.4	-0.1
15	1.0	1.0	10	212.8	212.8*	0.0
16	1.0	0.01	17	212.8	213.4	+0.6
17	1.0	0.01	26	212.8	213.3	+0.5
18	1.0	0.01	25	212.8	213.2	+0.4
19	1.0	0.01	20	212.8	212.8	0.0

*12 grams of KCl added.

C. Bismuth Reductor

A bismuth reductor was prepared by the same procedure used for the cadmium reductor, but the cadmium was replaced with 99.98 per cent lump bismuth (Fisher Scientific Company). The large lumps of bismuth were removed leaving smaller particles of approximately 30-100 mesh. The 20 cm. bismuth column was washed by passing one normal sulfuric acid through the reductor. When not in use the reductor was filled with one normal sulfuric acid.

Measured quantities of the 0.1043 normal thallium (III) sulfate solution were treated with varying amounts of one normal sulfuric acid and diluted. Samples containing 212.8 milligrams of thallium were diluted to 100 ml. and the smaller samples were diluted to 50 ml. These acid solutions were passed through the bismuth column at a rate of 38 ml. per minute and the column was washed with three 50 ml. portions of 0.01 normal sulfuric acid. The solutions containing the reduced thallium were treated with 30 ml. of six normal hydrochloric acid and titrated with 0.1000 normal potassium bromate. Three blanks were run on the bismuth reductor and each was found to consume 0.02 ml. of 0.1000 normal potassium bromate. A reductor blank of 0.02 ml. of 0.1000 normal potassium bromate was subtracted from the volumes of bromate used. The data on the bismuth reductor are tabulated in Table V.

TABLE V
REDUCTION OF THALLIUM (III) TO THALLIUM (I)
USING A BISMUTH REDUCTOR

Sample Number	Acidity of Solution (N)	Milligrams of Thallium		Error (mg.)
		Taken	Found	
1	1.0	32.0	31.9	-0.1
2	1.0	32.0	32.1	+0.1
3	1.0	32.0	32.0	0.0
4	1.0	32.0	31.9	-0.1
5	1.0	53.1	53.1	0.0
6	0.2	53.1	52.8	-0.3
7	1.0	53.1	53.2	+0.1
8	1.0	53.1	53.1	0.0
9	1.0	106.5	106.1	-0.4
10	1.2	106.5	106.4	-0.1
11	1.2	106.5	106.5	0.0
12	1.2	106.5	106.6	+0.1
13	1.0	212.8	212.8	0.0
14	1.3	212.8	213.3	+0.5
15	1.3	212.8	213.1	+0.3
16	1.3	212.8	213.2	+0.4

Samples 1-12 diluted to 50 ml., 13-16 diluted to 100 ml.

D. Nickel Reductor

A nickel reductor was prepared from 99 per cent 18 gauge nickel wire (Driver Harris Co., Harrison, New Jersey). Shears were used to cut the wire into one to two millimeter lengths in order to increase the surface area. The reductor was prepared in the same manner as the cadmium reductor. The reductor was washed by passing one normal sulfuric acid through the column. When not in use the reductor was filled with one normal sulfuric acid.

Measured quantities of 0.1043 normal thallium (III) sulfate solution were treated with varying amounts of one normal sulfuric acid and diluted. Samples containing 212.8 milligrams of thallium (III) were diluted to 100 ml. and the smaller samples were diluted to 50 ml. The diluted solutions were one normal in sulfuric acid. These solutions were passed through the nickel reductor at varying rates and the reductor was washed with three 50 ml. portions of 0.01 normal sulfuric acid. The solutions containing the reduced thallium were treated with 30 ml. of six normal hydrochloric acid and titrated with 0.1000 normal potassium bromate. Blanks were run on the nickel column and reproducible results could not be obtained. The blanks ranged from 0.22 to 0.03 ml. of 0.1000 normal potassium bromate. An average blank of 0.13 ml. was subtracted from the volume of potassium bromate used. The results using the nickel reductor are tabulated in Table VI.

TABLE VI
REDUCTION OF THALLIUM (III) TO THALLIUM (I)
USING A NICKEL REDUCTOR

Sample Number	Flow Rate ml./Min.	Milligrams of Thallium		Error (Mg.)
		Taken	Found	
1	21	32.0	31.5	-0.5
2	6	53.1	52.0	-1.1
3	23	53.1	53.6	+0.5
4	13	106.5	106.1	-0.4
5	15	212.8	213.1*	+0.3
6	19	212.8	213.4*	+0.6

*Samples 1-4 diluted to 50 ml., 5-6 diluted to 100 ml.

E. Lead Reductor

A lead reductor was prepared by the same procedure used for preparing the cadmium reductor. Thirty mesh granular lead (Fisher Scientific Company) was washed with six normal hydrochloric acid before being placed in the reductor. The 18 cm. lead column was washed by passing one normal sulfuric acid through the reductor. The reductor was filled with one normal sulfuric acid when not in use.

Measured quantities of the 0.1043 normal thallium (III) sulfate solution were treated with dilute sulfuric acid and diluted to known volume. The 212.8 milligram sample was diluted to 100 ml. and the smaller samples were diluted to 50 ml. The diluted solutions were passed through the lead reductor at a rate of approximately 25 ml. per minute. The reductor was washed with three 50 ml. portions of one normal sulfuric acid and the washings were added to the reduced thallium solution. The combined solution was treated with 12 grams of potassium chloride and titrated with 0.1000 normal potassium bromate. A Fisher Titrimeter equipped with platinum and calomel electrodes was used to detect the equivalence point. The results obtained using the lead reductor are tabulated in the order in which they were carried out and are listed in Table VII.

Two 106.9 milligram samples of thallium (I) nitrate were treated with dilute sulfuric acid and diluted to 50 ml. These samples were passed through the lead reductor and treated in the same manner as the thallium (III) samples. Titration with 0.1000 normal potassium bromate yielded 105.7 and 106.7 milligrams of thallium.

TABLE VII
REDUCTION OF THALLIUM (III) TO THALLIUM (I)
USING A LEAD REDUCTOR

Sample Number	Acidity of Diluted Solution (N)	Milligrams of Thallium		Error (Mg.)
		Taken	Found	
1	0.4	106.4	105.3	-1.1
2	0.4	106.4	105.2	-1.2
3	0.4	106.4	100.7	-5.7
4	0.2	106.4	85.3	-21.1
5	0.4	212.8	4.72	-208.1

F. Aluminum Reductor

An aluminum reductor was prepared in the same manner as the cadmium reductor by using 30 mesh granular aluminum (J. T. Baker Company). The 18 cm. aluminum column was washed by passing 0.01 normal sulfuric acid through the reductor. When not in use the reductor was filled with 0.01 normal sulfuric acid.

A 4.99 ml. aliquot of the 0.1043 normal thallium (III) sulfate solution was diluted to 50 ml. and passed through the aluminum reductor at the rate of 12 ml. per minute. The reductor was washed with three 50 ml. portions of 0.01 normal sulfuric acid. The thallium solution and the washings were treated with 30 ml. of six normal hydrochloric acid. Titration of the sample with 0.1000 normal potassium bromate required 5.00 ml. The reaction was slow. If the thallium (III) was quantitatively reduced to thallium (I), the calculated volume of 0.1000 normal potassium bromate would be 5.20 ml.

To a second 4.99 ml. sample of 0.1043 normal thallium (III) solution was added 50 ml. of one normal sulfuric acid. This solution was passed through the reductor at the rate of 11 ml. per minute, but the rate of flow was erratic due to the evolution of hydrogen. The thallium solution and the washings were treated with 30 ml. of six normal hydrochloric acid and titrated with 0.1000 normal potassium bromate. The titration required 5.18 ml. of bromate solution. The reaction was slow and detection of the equivalence point was difficult.

G. Zinc Reductor

A zinc reductor was prepared from 30 mesh zinc (Mallinckrodt Analytical Reagent) by the same procedure used for the cadmium reductor. The zinc was washed in one normal sulfuric acid before being placed in the reductor. The 16 cm. zinc column was washed by passing 0.01 normal sulfuric acid through the reductor. When not in use the reductor was filled with 0.01 normal sulfuric acid.

A 9.98 ml. sample of the 0.1043 normal thallium (III) sulfate solution was adjusted to an acid concentration of one normal with sulfuric acid and diluted to 100 ml. After passing the solution through the zinc reductor and adding 12 grams of potassium chloride, a titration of the thallium (I) required 0.21 ml. of 0.1000 normal potassium bromate. The solution was then passed through the cadmium reductor. The solution required less than 1.00 ml. of 0.1000 normal potassium bromate.

A second sample of 9.98 ml. of thallium (III) sulfate was adjusted to 0.2 normal with sulfuric acid and diluted to 100 ml. After passing

the solution through the zinc reductor and adding 12 grams of potassium chloride a titration required approximately 0.3 ml. of 0.1000 normal potassium bromate solution. If the thallium (III) solution was quantitatively reduced to thallium (I), the calculated volume of 0.1000 normal potassium bromate would be 10.41 ml.

H. Amalgamated Zinc Reductor

An amalgamated zinc reductor was prepared in the following manner. One-hundred and thirty-five grams of 30 mesh zinc (Mallinckrodt Analytical Reagent) was washed for several minutes with one normal hydrochloric acid. The washed zinc was treated with 28 ml. of 0.25 molar mercury chloride (22) and stirred for three minutes. The one per cent amalgamated zinc was placed in a reductor column and washed with one normal sulfuric acid. The 20 cm. amalgamated zinc reductor was filled with one normal sulfuric acid when not in use.

A 9.98 ml. sample of the 0.1043 normal thallium (III) sulfate solution was diluted to 50 ml. and then adjusted to one normal with dilute sulfuric acid. After passing the solution through the amalgamated zinc reductor and adding 12 grams of potassium chloride, a titration required 0.09 ml. of 0.1000 normal potassium bromate solution. If the thallium (III) was quantitatively reduced to thallium (I), the calculated volume of 0.1000 normal potassium bromate would be 10.41 ml. After the bromate titration sulfur dioxide was bubbled through the solution and the excess was removed by boiling the solution for one hour. A titration with 0.1000 normal potassium bromate required less than 0.10 ml.

I. Cadmium Amalgam

A cadmium amalgam, three per cent cadmium, was prepared by mixing three grams of cadmium metal (Fisher Scientific Company), 7.4 ml. of Cenco triple distilled mercury and 15 ml. of six normal sulfuric acid. This mixture was heated several hours on the steam bath and cooled. The amalgam was separated from the undissolved cadmium by use of a separatory funnel and stored under one normal sulfuric acid.

A 10.00 ml. sample of 0.1043 normal thallium solution was added to 100 grams of cadmium amalgam and shaken for two minutes in a separatory funnel. The amalgam was drawn off and washed twice with 20 ml. portions of one normal sulfuric acid. The reduced thallium solution and the washings were combined and filtered through a Sela crucible. Ten grams of potassium chloride was added to the combined solution and titration with 0.1000 normal potassium bromate required less than 2.0 ml.

J. Lead Amalgam

A three per cent lead amalgam was prepared by mixing three grams of Mallinckrodt Analytical Reagent granular lead, 7.4 ml. of Cenco triple distilled mercury and 15 ml. of six normal hydrochloric acid. After heating several hours on the steam bath the amalgam was cooled, separated from the undissolved lead and stored under one normal hydrochloric acid.

A 10.00 ml. sample of 0.1043 normal thallium (III) solution was added to 100 grams of lead amalgam and shaken for two minutes in a

separatory funnel. A dense white precipitate of lead sulfate appeared in the aqueous phase. The amalgam was drawn off and washed twice with 20 ml. portions of one normal sulfuric acid. Ten grams of potassium chloride was added to the combined washings and the reduced thallium solution. Titration with 0.1000 normal potassium bromate required approximately 7.5 ml. If the thallium (III) was quantitatively reduced to thallium (I) the calculated volume of 0.1000 normal potassium bromate would be 10.43 ml.

K. Bismuth Amalgam

A three per cent bismuth amalgam was prepared by the same procedure used for lead amalgam by substituting Fisher Scientific Company bismuth metal for lead. The bismuth amalgam was stored under one normal sulfuric acid.

Three 10.00 ml. samples of 0.1043 normal thallium (III) sulfate solution were pipetted into separatory funnels containing 100 grams of three per cent bismuth amalgam. The funnels were stoppered and shaken for one-half, one and two minutes and the amalgams were drawn off. The amalgams were washed twice with 20 ml. portions of one normal hydrochloric and the washings were added to the reduced thallium solutions. The combined solutions were diluted to 150 ml. with one normal hydrochloric acid and titrated with 0.1000 normal potassium bromate. The samples that were shaken for one and two minutes required almost identical volumes of standard bromate, while the sample shaken one-half

minute required a smaller volume. Two 20 ml. washings of the amalgam were found to be sufficient for the complete removal of thallium.

Three blanks were run in the following manner. Fifty ml. of two normal sulfuric acid was added to 100 grams of bismuth amalgam and shaken for two minutes. The amalgam was drawn off and washed three times with 50 ml. portions of two normal sulfuric acid. Ten grams of potassium chloride was added to the solution which was then titrated with 0.1000 normal potassium bromate. The same procedure was repeated with one and 0.6 normal sulfuric acid. The respective blanks for two, one and 0.6 normal sulfuric acid were 0.03, 0.03 and 0.05 ml. of 0.1000 normal potassium bromate.

Five 9.98 ml. samples of the 0.1043 normal thallium (III) solution were treated with varying amounts of sulfuric acid and diluted to 50 ml. The diluted samples were shaken in a separatory funnel with 100 grams of bismuth amalgam for two minutes. The amalgam was drawn off and the aqueous phase was filtered through a Selas filtering crucible to remove globules of the amalgam. The amalgam was washed three times with 50 ml. portions of one normal sulfuric and the filtered washings were added to the respective samples. Ten grams of potassium chloride was added to each sample, which was then titrated with 0.1000 normal potassium bromate using a Fisher Titrimeter equipped with platinum and calomel electrodes. A blank of 0.03 ml. of 0.1000 normal potassium bromate was subtracted from the volume of bromate used. The results obtained using a bismuth amalgam reduction are tabulated in Table VIII.

TABLE VIII
REDUCTION OF THALLIUM (III) TO THALLIUM (I)
USING A BISMUTH AMALGAM

Sample Number	Acidity of Diluted Solution	Milligrams of Thallium		Error (Mg.)
		Taken	Found	
1	0.4	106.4	107.4	+1.0
2	0.5	106.4	107.1	+0.7
3	1.0	106.4	107.0	+0.6
4	2.0	106.4	107.0	+0.6
5	2.0	106.4	107.1	+0.7

L. Discussion

The following values from Latimer's "Oxidation Potentials" indicate that certain reducing agents might be useful for the reduction of thallium (III) to thallium (I) (37).

		E° (volts) NHE
Tl	= $Tl^{+} + e$	+0.3363
$Tl^{+} + Cl^{-}$	= $TlCl + e$	+0.557
Tl^{3+}	= $Tl^{3+} + 2e$	-1.25
$TlCl + 2.5Cl$	= $TlCl_{2.5} + 2e$	-0.980
Ag	= $Ag^{+} + e$	-0.7991
$2Ag + SO_4^{2-}$	= $Ag_2SO_4 + 2e$	-0.653
$Bi + H_2O$	= $BiO^{+} + 2H^{+} + 3e$	-0.32
Pb	= $Pb^{++} + 2e$	+0.126
$Pb + SO_4^{2-}$	= $PbSO_4 + 2e$	+0.356
Ni	= $Ni^{++} + 2e$	+0.250
Co	= $Co^{++} + 2e$	+0.277
Cd	= $Cd^{++} + 2e$	+0.403
Zn	= $Zn^{++} + 2e$	+0.763

Lingane (38) reports the reduction potential of thallium (I) to thallium (0) at a dropping mercury electrode to be -0.217 volts.

The increased ease of reduction noted by Lingane is attributed to the large solubility of thallium metal in mercury.

In acid solution cadmium amalgam reduces thallium (I) to thallium (0), due to the solubility of thallium (0) in mercury.

Chloride ions must be absent when metallic reductors are used to reduce thallium (III) to thallium (I), since the separation of the insoluble thallium (I) chloride from the metallic reductor is difficult.

The results shown in Tables III, IV and V show that the cadmium, silver and bismuth reductors may be used for the quantitative reduction of thallium preliminary to its volumetric oxidation. These reductors gave quantitative reduction of 50 ml. of 0.02 to 0.006 normal thallium (III) solutions. The results from the cadmium, silver and bismuth reductors give average errors of 0.20, 0.25 and 0.17 milligrams respectively. These results correspond to average relative per cent errors of 0.29, 0.27 and 0.17 for samples containing from 30 to 212 milligrams of thallium. Acid concentration of the solution may vary from 0.01 to one normal without effecting the completeness of reduction. The rate of flow through the reductors is dependent on the surface area of the metal being used. These reductors were prepared with finely divided metal and flow rates of 20 to 25 ml. per minute gave complete reduction. Blank corrections on the cadmium, silver and bismuth reductors of 0.05, 0.03 and 0.02 ml. of 0.1000 normal potassium bromate were necessary.

When determining thallium by the volumetric bromate method, the use of a cadmium, silver or bismuth reductor is superior to sulfur dioxide

for the reduction of thallium (III) to thallium (I). The blanks on the metallic reducers are smaller and more consistent than the blanks on sulfur dioxide. The time required for the reduction of thallium (III) to thallium (I) with a suitable metallic reductor is approximately five minutes, but reduction with sulfur dioxide and removal of the excess requires at least one hour.

The bismuth reductor is preferable to the cadmium reductor, since finely divided high purity bismuth metal is commercially available whereas cadmium metal must be machined to a small particle size. A bismuth reductor can be prepared more economically than a silver reductor.

The erratic results obtained using the nickel reductor were probably due to the impurities in the nickel metal (Table VI). Blanks on the nickel reductor consumed from 0.02 to 0.22 ml. of 0.1000 normal potassium bromate. The reductor had a relatively small surface area and small flow rates were necessary to achieve complete reduction of thallium (III) to thallium (I). It is probable that a finely divided high purity nickel reductor would give a constant blank and would be suitable for the quantitative reduction of thallium (III) to thallium (I).

The lead reductor is not suitable for the reduction of thallium (III) to thallium (I). When sulfuric acid is used in a lead reductor the insoluble lead sulfate forms a film on the lead. The results in Table VII indicate that the lead reductor rapidly loses its reducing capacity. If the sulfuric acid is 2.5 normal in hydrochloric acid,

the lead sulfate film will not form. Thallium solutions 2.5 normal in hydrochloric acid precipitate thallium (I) chloride which would be trapped in the lead reductor.

The reduction of thallium (III) to thallium (I) using an aluminum reductor was slow. A 0.01 normal thallium (III) solution that was 0.2 normal in sulfuric acid was not quantitatively reduced when a flow rate of 12 ml. per minute was used. A 0.01 normal thallium (III) solution, that was one normal in sulfuric acid, was quantitatively reduced by the aluminum reductor, but hydrogen evolution was quite vigorous and some of the aluminum was forced into the reductor reservoir.

The zinc and Jones reductors are unsuitable for analytical use since they reduced thallium (III) to thallium metal.

Amalgams are not convenient for the reduction of thallium (III) to thallium (I) due to the difficulty of separating the amalgam from the aqueous phase. When carrying out the reduction in a separatory funnel, the amalgam is drawn off, but small beads of amalgam remain attached to the glass wall of the funnel. These beads of amalgam must be removed from the aqueous phase prior to the volumetric oxidation, since they would reduce thallium (III). Addition of carbon tetrachloride to separate the amalgam from the aqueous phase is only useful when manual stirring is used.

Saturated bismuth amalgam gives a quantitative reduction of thallium (III) to thallium (I) in two to 0.6 normal sulfuric acid solutions. The results in Table VIII indicate consistently high results.

Lead sulfate precipitates when lead amalgam is used as a reducing agent in the presence of sulfuric acid. The lead sulfate coprecipitates thallium (I) sulfate and low results for thallium are obtained.

IV Volumetric Determination of Thallium (I) Using a Standard Sodium Hypochlorite Solution

A. Direct Method

Sodium hypobromite is known to react more rapidly than sodium hypochlorite. Standard hypobromite solutions can be prepared extemporaneously by adding a standard hypochlorite solution to a slightly alkaline solution containing bromide ions. If the hypobromite ion reacts rapidly, only a trace of bromide ions would be necessary; since the reduction product of the hypobromite ion is the bromide ion which could react with more hypochlorite to yield hypobromite. The oxidation of thallium (I) to thallium (III) by hypochlorite yields the chloride ion as a product and the precipitation of thallium (I) chloride would retard the rate of thallium (I) oxidation. In a solution containing 4.2 grams of sodium nitrate per 100 ml., the solubility of thallium (I) chloride is increased from 0.38 to 0.61 grams per 100 ml. of solution.

1. Salt Effect

Titration of thallium (I) with extemporaneously generated hypobromite were performed with and without the addition of sodium nitrate. The addition of four grams of sodium nitrate to 100 ml. of thallium solution was found to increase the rate of oxidation of thallium (I) by hypobromite, thus increasing the potential change at the end point.

In the following titrations of thallium (I) with extemporaneously generated hypobromite the solutions were first treated with an inert salt in order to increase the solubility of thallium (I) chloride.

2. pH Effect

The effect of pH on the rate of reaction between hypochlorite and bromide ions was determined by the following procedure. Measured quantities of thallium (I) solution were treated with 50 ml. of various buffers and diluted to 100 ml. Each sample was treated with ten drops of a one per cent potassium bromide solution, four grams of sodium nitrate, and titrated with a standard sodium hypochlorite solution. Throughout this section all equivalence points were detected potentiometrically by the use of a Sargent wide range potentiometer, equipped with a platinum and saturated calomel electrode system. The titrations were carried out by adding small increments of standard hypochlorite solution and waiting 30 seconds before the potential was measured. The change in potential per 0.10 ml. of standard hypochlorite at the equivalence point is a measure of the rate of formation of hypobromite. The pH values of the sample solutions were measured before and after the hypochlorite titrations with a Beckman Model G pH meter. The results are tabulated in Table IX, and indicate that the reaction between hypochlorite and bromide ions is most rapid in the pH range from 7.5 to 8.5. Sodium bicarbonate was found to be the most suitable buffering agent and was used throughout this section.

TABLE IX
EFFECT OF pH ON FORMATION OF HYPOBROMITE FROM
HYPOCHLORITE AND BROMIDE IONS

Buffer	pH		Change in Millivolts per 0.10 ml. of 0.1 N ClO^-
	Before	After	
1% NaHCO_3	7.73	8.00	97
2% NaHCO_3	7.73	8.09	95
Phosphate (1)	6.50	6.50	29
Phosphate (2)	7.18	7.12	18
Phosphate (3)	7.23	7.19	28
Borate (1)	7.68	7.63	53
Borate (2)	8.29	8.11	45
1% Na_2CO_3	10.93	10.80	--
1 N NaOH	--	--	--

3. Effect of Sodium Bicarbonate Concentration

The effect of the sodium bicarbonate concentration was determined in the following manner. Four 10.00 ml. samples of thallium (I) nitrate were diluted to 100 ml. and treated with four grams of sodium nitrate and ten drops of a one per cent solution of potassium bromide. One, two, three and four gram portions of sodium bicarbonate were added to the respective samples. Titrations were carried out using 0.1080 normal sodium hypochlorite. The results of these titrations are recorded in Table X.

The results in Table X indicate that thallium (I) solutions containing bicarbonate concentrations of one to three per cent require nearly identical volumes of standard hypochlorite. The change in potential at the equivalence point appears to increase as the sodium bicarbonate concentration is increased from one to three per cent. The largest

TABLE I

EFFECT OF SODIUM BICARBONATE CONCENTRATION ON THE OXIDATION
OF THALLIUM (I) BY HYPOCHLORITE

Concentration of Sodium Bicarbonate (Per cent)	Change in Millivolts 0.10 ml. of 0.1 N ClO^-	Ml. ClO^- Req.	Milligrams Thallium Taken	Found	Error (Mg.)
1	91	9.15	102.2	101.0	-1.2
2	100	9.15	102.2	101.0	-1.2
3	126	9.14	102.2	100.9	-1.3
4	100	9.10	102.2	100.5	-1.7

error was found in solutions containing four per cent sodium bicarbonate. In the following work in this section two per cent sodium bicarbonate solutions were used.

4. Effect of Bromide Ion Concentration

The effect of bromide ion concentration on the oxidation of thallium (I) by a sodium hypochlorite titration was estimated in the following manner. Two 10.00 ml. samples of 0.1048 normal thallium (I) nitrate solution were treated with two grams of sodium bicarbonate, four grams of sodium nitrate and diluted to 100 ml. To one sample was added ten drops and to the other 50 drops of a one per cent solution of potassium bromide. These samples were titrated with 0.1080 normal sodium hypochlorite by adding small increments and reading the potential at regular time intervals until successive values agreed to within five millivolts. Within 30 seconds after the addition of one ml. increments, the potential values were constant in both solutions. When within 0.3 ml. from the

equivalence point, the waiting time was 90 seconds for the solution containing 50 drops and 120 seconds for the solution containing ten drops. Another sample was run in a similar manner, except one drop of one per cent potassium bromide was added. When titrating this sample, several minutes were required before constant potential values were obtained. The investigation on the effect of bromide ion concentration indicates that ten drops of a one per cent potassium bromide solution are sufficient to give a rapid conversion of hypochlorite to hypobromite. Throughout the remaining work in this section ten drops of a one per cent potassium bromide solution were used.

5. Determination of Thallium

Having established the proper pH and the minimum bromide ion concentration which were necessary for a rapid oxidation of thallium (I) to thallium (III), a number of samples were run using the following procedure. Measured thallium (I) samples were diluted and treated with sufficient sodium bicarbonate to yield a two per cent solution and sufficient sodium nitrate to yield a four per cent solution. Each sample was treated with ten drops of one per cent potassium bromide solution for each 100 ml. of diluted volume. The samples were titrated with standard sodium hypochlorite by adding small increments and waiting one minute before measuring the potential. The results are tabulated in Table XI.

The change in potential during a titration of thallium (I) by hypochlorite is shown in Figure 1. This titration was carried out by

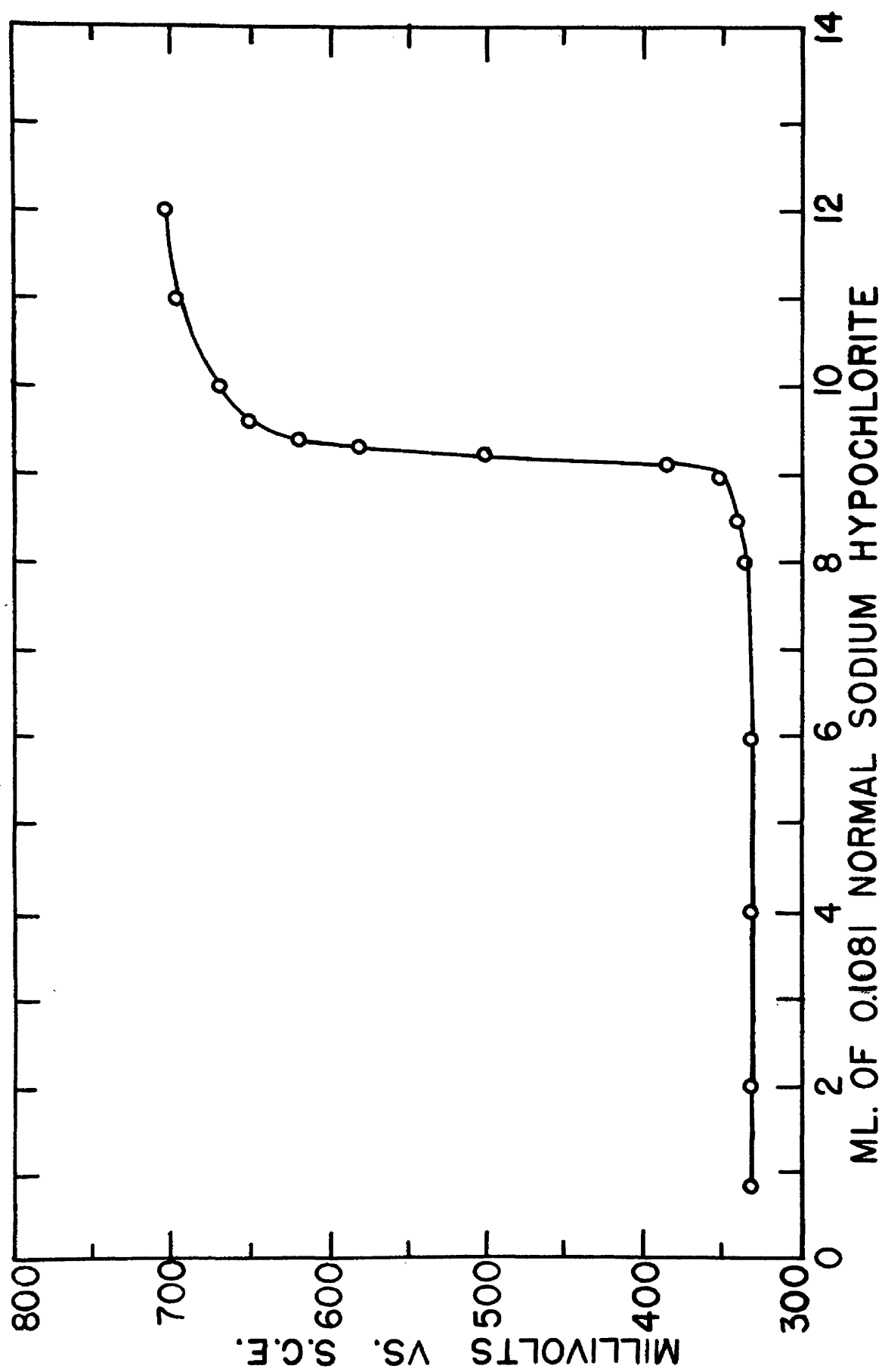


FIGURE 1. TITRATION OF THALLIUM (I) WITH SODIUM HYPOCHLORITE

TABLE XI

DIRECT TITRATION OF THALLIUM (I) WITH STANDARD
SODIUM HYPOCHLORITE SOLUTIONS

	Diluted Volume (ML.)	<u>Hypochlorite Required</u>		<u>Milligrams of Thallium</u>		Error (Mg.)
		(ML.)	(N)	Taken	Found	
1	100	9.60	0.1038	102.2	101.8	-0.4
2	100	9.17	0.1082	102.2	101.4	-0.8
3	100	9.24	0.1082	102.2	102.2	0.0
4	100	9.17	0.1081	102.2	101.3	-0.9
5	100	9.18	0.1081	102.2	101.4	-0.8
6	100	9.63	0.1081	107.1	106.4	-0.7
7	100	9.28	0.1081	102.6	102.5	-0.1
8	150	9.25	0.1081	102.6	102.2	-0.4
9	125	11.90	0.1081	132.6	131.4	-1.2
10	100	11.98	0.1082	133.6	132.5	-1.1
11	100	22.86	0.1082	254.9	252.7	-2.2
12	100	22.88	0.1081	255.9	252.7	-3.2
13	100	22.91	0.1081	255.9	253.1	-2.8
14	250	22.99	0.1081	255.9	254.0	-1.9
15	250	24.02	0.1081	267.2	265.4	-1.8

adding small increments of sodium hypochlorite and measuring the potential at regular time intervals until constant values were obtained. Near the equivalence point a ten minute stirring period was required to obtain a constant potential.

6. Determination of Thallium (I) After Using Metallic Reductors

Measured quantities of 9.98 ml. of 0.1043 normal thallium (III) sulfate solution were treated with sulfuric acid, diluted to 50 ml. and passed through a cadmium or silver reductor. The reductors were washed with dilute acid and the washings were added to the reduced thallium solution. These solutions were partially neutralized with two normal

sodium hydroxide and treated with sodium bicarbonate, sodium sulfate, and bromide ions as previously described. The thallium (I) was determined by potentiometric titration with 0.1077 normal sodium hypochlorite. The results are tabulated in Table XII. The results with the cadmium reductor indicate that some of the thallium (I) is lost. Since cadmium precipitates as the carbonate or the hydroxide when the solution is made alkaline some of the thallium (I) may be lost by co-precipitation. The unexpected results obtained with the silver reductor will be discussed later.

TABLE XII

DIRECT HYPOCHLORITE TITRATIONS OF THALLIUM (I)
REDUCED BY METALLIC REDUCTORS

Reductor Used	Acid Normality Before Reduction	Milliliters of 0.1074 Normal Hypochlorite	Milligrams Thallium		Error (Mg.)
			Taken	Found	
Cadmium	0.4	9.46	106.4	104.3	-2.1
Cadmium	0.4	9.39	106.4	103.7	-2.7
Cadmium	0.06	9.50	106.4	104.8	-1.6
Cadmium	0.01	9.50	106.4	104.8	-1.6
Cadmium	0.01	9.58	106.4	105.6	-0.8
Silver	0.2	19.10	106.4	210.6	+104.2

B. Indirect Method

The oxidation of thallium (I) by hypochlorite in alkaline media is too slow for a direct titration with sodium hypochlorite. It was thought that an excess of standard sodium hypochlorite could be added

to a thallium (I) solution and upon standing the unreacted hypochlorite could be determined by a titration with standard sodium arsenite. The oxidation of arsenite by thallium (III) oxide should be negligible due to the slight solubility of thallium (III) oxide.

1. Time Required for Oxidation of Thallium (I) by Excess Hypochlorite

The following procedure was used to determine the time required for the complete oxidation of thallium (I) by an excess of sodium hypochlorite. A 19.97 ml. sample of the 0.1048 normal thallium (I) nitrate solution was diluted to 250 ml. and treated with six grams of sodium bicarbonate, nine grams of sodium sulfate and 49.88 ml. of 0.1014 normal sodium hypochlorite. The solution was stirred with a magnetic stirrer. The potential was recorded as a function of time. It was found that one hour of stirring was required to obtain a potential above 700 millivolts. One hour of stirring was considered sufficient, since a two ml. excess of sodium hypochlorite in the direct titration of thallium (I) (Figure 1) gave a potential of 710 millivolts.

2. Determination of Thallium (I)

Measured quantities of the 0.1048 normal thallium (I) nitrate solution were diluted and treated with sufficient sodium bicarbonate to yield a two per cent solution and sufficient sodium sulfate to yield a four per cent solution. To each solution was added 49.88 ml. of 0.1014 normal sodium hypochlorite. After stirring the solutions for one hour the unreacted hypochlorite was titrated with 0.1000 normal sodium arsenite. The results of these determinations are tabulated in

Table XIII. A plot of one of these titrations is given in Figure 2.

TABLE XIII

INDIRECT DETERMINATION OF THALLIUM (I) BY SODIUM ARSENITE
BACK TITRATION OF EXCESS SODIUM HYPOCHLORITE

Volume of Diluted Solution (Ml.)	Milliliters of Arsenite Required	Milligrams of Thallium		Error (Mg.)
		Taken	Found	
150	40.10	107.1	107.1	0.0
300	37.91	129.9	129.5	-0.4
300	37.88	129.3	129.8	+0.5
250	35.41	155.3	155.0	-0.3
300	35.33	155.3	155.9	+0.6
300	33.67	173.6	172.8	-0.8
300	33.65	173.8	173.0	-0.8
300	29.83	213.9	212.2	-1.7
300	29.83	213.9	212.2	-1.7

3. Determination of Thallium (I) After Using Metallic Reductors

Measured samples of 9.98 ml. of 0.1043 normal thallium (III) sulfate were acidified, diluted to 50 ml. and passed through metal reductors. The reductors were washed and the washings were added to the reduced thallium solutions. The combined solutions were neutralized, treated with six grams of sodium bicarbonate, nine grams of sodium sulfate, and diluted to 300 ml. To each sample was added 49.88 ml. of 0.1014 normal sodium hypochlorite and the resulting solutions were stirred for one hour. The unreacted hypochlorite was then titrated with 0.1000 normal sodium arsenite. The results of these titrations are recorded in Table XIV.

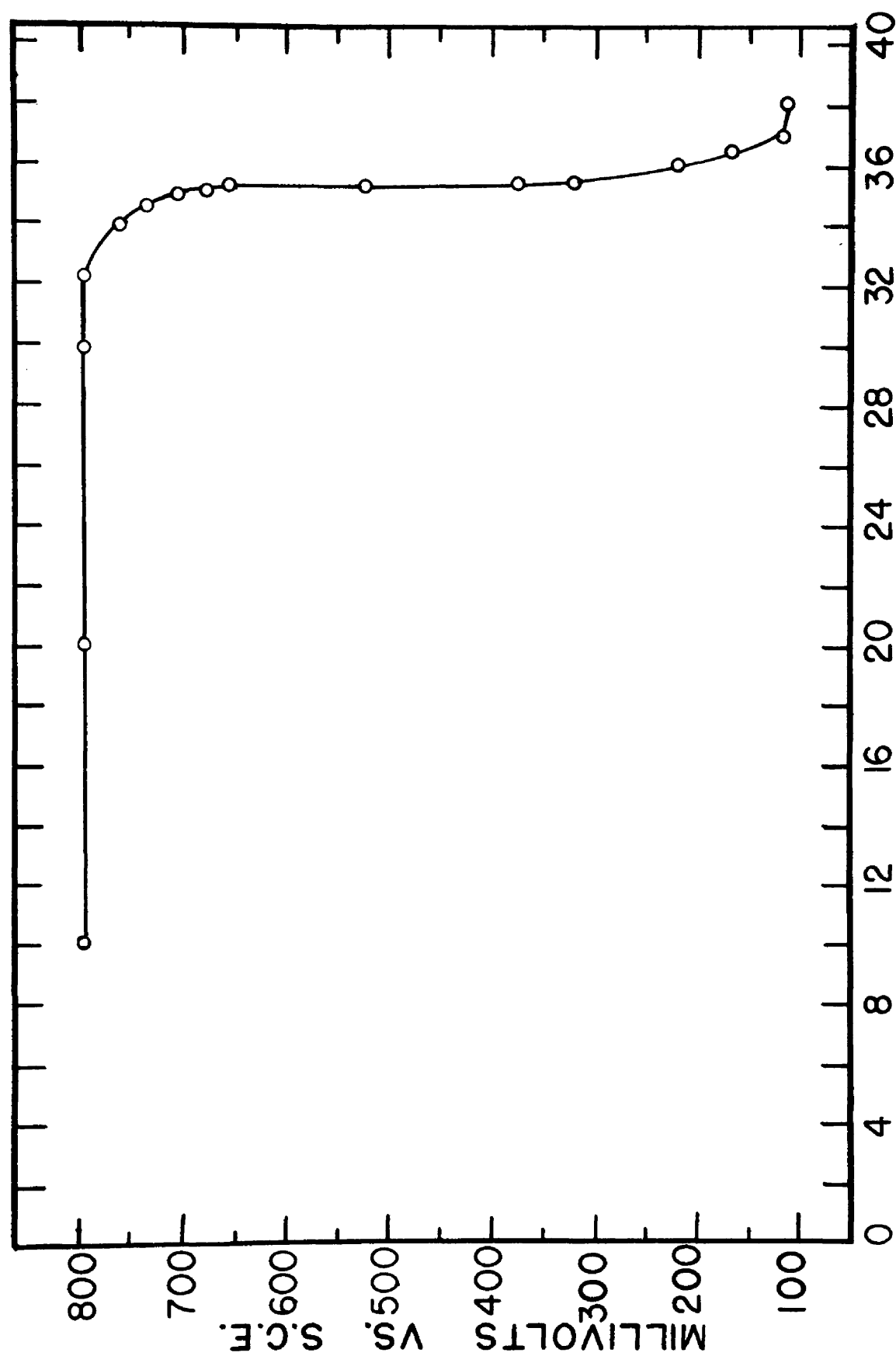


FIGURE 2. TITRATION OF EXCESS SODIUM HYPOCHLORITE

TABLE XIV
INDIRECT TITRATION OF THALLIUM (I) REDUCED BY METALLIC REDUCTORS

Reductor Used	Acid Normality Before Reduction	Milliliters of Arsenite Required	Milligrams Thallium Taken	Found	Error (Mg.)
Cadmium	0.4	15.55	0.1064	0.1186	+12.2
Cadmium	0.01	15.20	0.1064	0.1197	+13.3
Silver	0.4	15.55	0.1064	0.1161	+ 9.7

C. Discussion

The rate of oxidation of thallium (I) by sodium hypochlorite in alkaline media is slow and the reaction is not suitable for a direct titration. Since hypobromite reacts more rapidly than hypochlorite, a direct titration of thallium (I) using hypobromite was found to be satisfactory when carried out under the proper conditions. The extemporaneous preparation of hypobromite from hypochlorite and bromide was found to be pH dependent. The reaction was found to be rapid between pH values of seven and nine (Table IX). Sodium bicarbonate was found to be most convenient for maintaining the proper pH. Concentrations of sodium bicarbonate of one to four per cent by weight were found to be satisfactory. Only a small amount of bromide ion was found to be necessary since the bromide ion is returned as soon as hypobromite reacts with thallium (I). The experimental work indicates that one milligram of bromide is sufficient for the rapid oxidation of thallium (I), when a 0.1 normal sodium hypochlorite solution is used as a titrant.

When sufficient bromide ions are added to convert all of the hypochlorite to hypobromite, thallium (I) bromide precipitates and the rate of oxidation of thallium (I) by hypobromite is decreased. The addition of an inert salt such as sodium nitrate or sodium sulfate increases the solubility of thallium (I) chloride thereby increasing the rate of reaction between thallium (I) and hypobromite.

The data in Table XI on the direct titration of thallium (I) with hypochlorite indicate that this method yields consistently low results. Since precipitation from a more dilute solution tends to decrease the amount of coprecipitation, one would expect to obtain better results by titrating thallium (I) in more dilute solutions. Samples 11 through 14 in Table XI, which contained nearly the same amount of thallium, were diluted to different volumes and titrated with a standard hypochlorite solution. Samples 11, 12 and 13 were diluted to 100 ml. and showed negative errors of 2.2, 3.2 and 2.8 milligrams of thallium, while samples 14 and 15 were diluted to 250 ml. and showed negative errors of 1.8 and 1.9 milligrams of thallium. The consistently low results in Table XI appear to be due to coprecipitation of thallium (I) by thallium (III) oxide.

The data in Table XIII on the indirect determination of thallium indicate a trend toward low results with increasing amounts of thallium. Coprecipitation of thallium (I) by thallium (III) oxide is probably responsible for the low results obtained. A maximum error of 0.8 per cent can be expected for the indirect determination of 100 to 200 milligrams of thallium. The change in potential during a typical indirect titration of thallium (I) is shown in Figure 2.

Considering the variables of pH, bromide ion concentration and the solubility of thallium (I) halides the following procedure is recommended for the direct volumetric determination of thallium (I) using hypochlorite as a standard oxidant. Dilute a solution of thallium (I) to 300 ml. This solution must be free of substances that would precipitate or reduce thallium (III), react with hypochlorite or hypobromite or precipitate thallium (I) in alkaline solution. Neutralize the solution and add six grams of sodium bicarbonate, nine grams of sodium sulfate and one ml. of a one per cent potassium bromide solution. Titrate the solution by adding small increments of a standard sodium hypochlorite solution. Measure the potential in the solution with a titrimeter or potentiometer equipped with a platinum-calomel electrode system. The solution should be vigorously stirred for 30 seconds after the addition of each increment before the potential is measured. The equivalence point is detected by a change in potential of approximately 100 millivolts per 0.10 ml. of 0.1000 normal sodium hypochlorite added.

For the indirect determination of thallium (I) using an arsenite titration of excess hypochlorite the following procedure is recommended. Dilute a solution of thallium (I) to 300 ml. This solution must be free of substances that would precipitate or reduce thallium (III), react with hypochlorite or precipitate thallium (I) in alkaline solution. Neutralize the solution and add six grams of sodium bicarbonate and nine grams of sodium sulfate. Add a measured quantity of standard sodium hypochlorite (five milliequivalents) and stir the solution for

one hour. Titrate the excess hypochlorite with standard sodium arsenite. The equivalence point can be easily detected potentiometrically with a platinum-calomel electrode system since the addition of 0.10 ml. of 0.1000 normal sodium arsenite gives a change in potential of approximately 300 millivolts.

The direct and indirect methods give equally accurate results with a maximum error of approximately 0.8 per cent for 100 to 200 milligram thallium samples. An advantage of the direct method is that it is more rapid than the indirect method due to the one hour of stirring required in the latter. However, the titration in the indirect method is more rapid due to the instantaneous reaction between hypochlorite and arsenite, while the reaction between hypobromite and thallium (I) is somewhat slower. The change in potential at the equivalence point is larger in the indirect method thereby allowing a more accurate estimation of the end point. The indirect method has the disadvantage that two standard solutions are required whereas the direct method requires only one standard solution. A minor advantage of the indirect method is that arsenite is used as a titrant where the direct method requires an alkaline solution of hypochlorite.

When a solution containing thallium in the plus three oxidation state is encountered a reduction of thallium(III) to thallium (I) is necessary before a titration with hypochlorite can be performed. Sulfur dioxide can be used to reduce thallium (III) since the excess can be removed and the reaction product is the sulfate ion which does not interfere in the hypochlorite titration. Metallic reducers and

amalgams are not satisfactory for the reduction of thallium (III) to thallium (I), when a titration in alkaline solution is to be used. These reductors introduce metal ions to the system, which precipitate when the solution is made alkaline for the titration. The effect of these precipitates depends on whether the direct or indirect hypochlorite method is used for the determination of thallium (I).

In the indirect determination these precipitates appear to catalyze the decomposition of the excess hypochlorite. This decomposition of hypochlorite yields high results for thallium as shown in Table XIV.

In the direct determination the cadmium hydroxide precipitate appears to coprecipitate some of the thallium (I), thus giving low results for thallium (Table XII).

The direct determination of thallium (I) reduced from thallium (III) in a silver reductor gave unexpected results (Table XII). The thallium sample consumed nearly twice the calculated volume of hypochlorite expected. Each milliequivalent of thallium (III) reduced introduces a milliequivalent of silver (I) ion, which precipitates as the carbonate upon the addition of sodium bicarbonate. The result obtained suggest that silver (I) may be oxidized to silver (II) by hypobromite in a slightly alkaline solution.

V. Gravimetric Determination of Thallium Using Sodium Hypochlorite

The gravimetric determination of thallium as thallium (III) oxide is based on the alkaline oxidation of thallium (I) to thallium (III), which precipitates as anhydrous thallium (III) oxide. Potassium

ferricyanide is the only oxidant proposed for the gravimetric determination of thallium as thallium (III) oxide. A disadvantage of potassium ferricyanide is that the filtrate would be unsuitable for subsequent analysis due to the large amount of iron present.

It appeared that sodium hypochlorite might be preferable to potassium ferricyanide for the oxidation of thallium (I) to thallium (III), since the studies on the volumetric determination of thallium by hypochlorite showed the reaction to be slow. This slow alkaline oxidation of thallium (I) by hypochlorite appeared to offer a method for the homogeneous precipitation of thallium (III) oxide. Any cations that form insoluble oxides or hydroxides in alkaline solution, would interfere regardless of the oxidizing agent. Cations, that are soluble in alkaline solution but form insoluble ferricyanides or ferrocyanides in alkaline solution, constitute interferences unique to the ferricyanide procedure. Unfortunately, data are not available on the alkaline solubilities of metallic ferricyanides or ferrocyanides.

A. Washing the Precipitate

The determination of thallium as thallium (III) oxide necessitates precipitation from an alkaline solution. Since precipitates formed in alkaline solution must be thoroughly washed to remove excess alkali, an efficient method must be devised for washing the thallium (III) oxide. In order to determine the efficiency of successive washes the following procedure was used.

Measured quantities of the 0.1048 normal thallium (I) solution were treated with varying amounts of sodium hydroxide and diluted to known volumes. Each sample was then treated with 25 ml. of Clorox reagent prepared by diluting 30 ml. of commercial Clorox to 150 ml. The samples were digested two hours, washed six times by decantation with hot water and transferred to tared Gooch crucibles. Approximately 500 ml. of distilled water was used for the total washing of each precipitate. The precipitates were dried under a nitrogen atmosphere for two hours at 200°C. Completeness of washing was followed on a Beckman Model G. pH meter by measuring the pH of successive washings. The results on washing thallium (III) oxide are given in Table XV.

From the results in Table XV it was concluded that six washings of thallium (III) oxide were sufficient since samples two and three gave almost identical weights of the dried oxide.

B. Effect of Hydroxide Concentration

Aliquots of 19.97 ml. of 0.1048 normal thallium solution were treated with varying quantities of one normal sodium hydroxide. After dilution precipitation was made by the addition of 25 ml. of the Clorox reagent. The samples were digested two hours and allowed to stand over night. The precipitates were washed six times by decantation using a total of 500 ml. of hot water. The washed precipitates were transferred to tared Gooch crucibles and muffle dried one hour under nitrogen at 200°C. The results are tabulated in Table XVI.

TABLE XV

EFFECT OF HOT WATER WASHING OF THALLIUM (III) OXIDE

1	2	3	4	ML. of 1N NaOH Added	Diluted Volume	Concentration of Sodium Hydroxide (N)	pH of Washes				Milligrams Thallium Taken	Thallium Found	Error (Mg.)
							3rd	4th	5th	6th			
1	10	400		.025	8.62	8.42	8.05	7.90	213.9	215.4	+1.5		
2	10	400		.025	9.28	8.92	8.75	8.30	213.9	215.5	+1.6		
3	25	400		.0625	9.35	9.30	8.99	8.89	213.9	215.6	+1.7		
4	50	400		.125	—	9.47	9.39	9.34	213.9	217.3	+3.4		

TABLE XVI

EFFECT OF HYDROXIDE CONCENTRATION ON THE PRECIPITATION OF
THALLIUM (III) OXIDE BY SODIUM HYPOCHLORITE

Ml. of 1N NaOH	Diluted Volume	Concentration of Sodium Hydroxide (N)	Milligrams of Thallium		Error (Mg.)
			Taken	Found	
10	400	0.025	213.9	215.1	+1.2
10	400	0.025	213.9	215.1	+1.2
10	400	0.025	213.9	215.4	+1.5
10	400	0.025	213.9	214.9	+1.0
10	400	0.025	213.9	215.0	+1.1
25	400	0.0625	213.9	215.4	+1.5
25	400	0.0625	213.9	216.1	+2.2
25	400	0.0625	213.9	215.6	+1.7
50	400	0.125	213.9	217.1	+3.2
50	400	0.125	213.9	217.3	+3.5
50	400	0.125	213.9	217.3	+3.4
25	100	0.25	213.9	217.6	+3.7
25	100	0.25	213.9	217.6	+3.7
25	100	0.25	213.9	216.9	+3.0

The results in Table XVI indicate that precipitation of thallium (III) oxide by alkaline hypochlorite oxidation yield consistently high results for thallium. The data also indicate that precipitation from more alkaline solutions yields larger errors. The thallium (III) oxide formed in 0.25 normal base was a dense black powder which settled rapidly. The oxide formed in 0.025 normal base was a chocolate brown fluffy powder which settled slowly.

C. Interferences

Aliquots of 19.97 ml. of the 0.1048 normal thallium (I) solution were treated with varying amounts of sodium hydroxide and diluted to known volumes. Measured quantities of foreign ions were added to the alkaline thallium (I) solutions. Precipitation was carried out by adding 25 ml. of the Clorox reagent. The solutions were digested several hours on the steam bath and allowed to stand over night before filtration. The thallium (III) oxide precipitates were washed six times by decantation with hot water and transferred to tared Gooch crucibles.

The precipitates were muffle dried under nitrogen for one hour at 200°C. Results are tabulated in Table XVII.

The data in Table XVII indicate that solutions 0.01 molar in aluminum, 0.002 molar in gallium and 0.1 molar in phosphate ions do not interfere in the alkaline hypochlorite precipitation of thallium. Solutions 0.001 molar in zinc and one molar in base interfere.

D. Effect of Drying Conditions

Some of the precipitates from previous work were saved and dried in air for one hour at 150°C. No effort was made to exclude carbon dioxide. The results in Table XVIII confirm the statement of Mack and Lepper (40), that thallium (III) oxide gains weight when dried in air.

E. Discussion

In basic solution, the rate of oxidation of thallium (I) by hypochlorite appears to be slow. Several minutes elapsed after the addition

TABLE XVII
EFFECT OF FOREIGN IONS

Interference Ion	Ml.	Diluted Volume (Ml.)	Concentration of Sodium Hydroxide (N)	Mg. of Thallium		Error (Mg.)
				Taken	Found	
Aluminum	27	100	0.25	213.9	212.8	-1.1
Aluminum	27	100	0.25	213.9	213.7	-0.2
Zinc	65	100	0.25	213.9	277.6	+63.7
Zinc	65	100	0.25	213.9	274.6	+60.7
Zinc	65	100	0.25	213.9	278.3	+64.4
Zinc	65	100	1.0	213.9	221.0	+ 7.1
Zinc	65	100	1.0	213.9	218.9	+ 5.0
Zinc	65	100	1.0	213.9	218.4	+ 4.5
Zinc	16	100	0.5	213.9	220.3	+ 6.4
Zinc	16	100	0.5	213.9	221.0	+ 7.1
Zinc	16	100	0.5	213.9	220.7	+ 6.8
Zinc	16	100	1.0	213.9	217.9	+ 4.0
Zinc	16	100	1.0	213.9	217.7	+ 3.8
Zinc	16	100	1.0	213.9	218.8	+ 4.9
Zinc	6.5	100	1.0	213.9	216.4	+ 2.5
Zinc	6.5	100	1.0	267.1	269.7	+ 2.6
Zinc	6.5	100	1.0	267.1	270.7	+ 3.6
Gallium	5.5	100	0.04	213.9	213.7	- 0.2
Gallium	11.0	100	0.04	213.9	215.1	+ 1.2
Phosphate	940	200	0.05	213.9	217.0	+ 3.1
Phosphate	94	200	0.05	213.9	215.2	+ 1.3
Phosphate	94	200	0.05	213.9	215.3	+ 1.4

of hypochlorite before any noticeable amount of thallium (III) oxide was formed. Thallium (III) solutions give an immediate precipitation of thallium (III) oxide when neutralized. This slow oxidation of thallium (I) by hypochlorite in alkaline solution gives a homogeneous precipitation of thallium (III) oxide.

The results in Table XV on the washing of thallium (III) oxide indicate that six washings by decantation did not completely remove

TABLE XVIII

WEIGHTS OF THALLIUM (III) OXIDE UNDER VARYING DRYING CONDITIONS

Milligrams of Tl_2O_3 Dried for One Hour	
Under Nitrogen at $200^\circ C$.	Under Air at $150^\circ C$.
242.0	242.1
244.7	244.9
243.1	243.5
243.2	243.7
242.4	242.7
237.8	238.8
238.8	239.8
247.0	247.3
244.6	245.0
244.0	244.5
238.8	238.6
240.4	240.2
237.5	237.3

excess base. However, samples containing 10 and 25 ml. of one normal sodium hydroxide gave almost identical precipitate weights; therefore, six washings were considered reasonable.

The data in Table XVI on the effect of alkalinity indicate, that the weights of thallium (III) oxide precipitates increase with increasing alkalinity. However, precipitates were more dense when formed in stronger alkaline solution. It is apparent that in stating a procedure for analysis a compromise must be made between the alkalinity of the precipitating solution and a reasonable number of washings.

The data in Table XVII indicate the degree of interference exhibited by various foreign ions. When foreign ions were added to the alkaline

thallium (I) solutions no noticeable precipitation occurred. Solutions 0.01 molar in aluminum and 0.001 molar in gallium did not interfere. In the case of zinc, a more basic solution was required to reduce interference. Solutions 0.001 molar in zinc and one normal in base gave a one per cent positive error in the determination of thallium. Solutions 0.01 molar in phosphate do not interfere. Larger concentrations of phosphate do not interfere but tend to disperse the precipitate making washing difficult.

The data in Table XVIII indicate that thallium (III) oxide dried under nitrogen exhibits a slight increase in weight when heated in air. Thallium (III) oxide, when heated above $100^{\circ}\text{C}.$, is reported to begin decomposition to thallium (I) oxide with the evolution of oxygen (21). The increase of weight by heating thallium (III) oxide is reported to be due to the absorption of carbon dioxide by the thallium (I) oxide.

Considering the data on the washing of thallium (III) oxide, the alkalinity of the precipitating solution, the interference of foreign ions and the effect of air drying, the following procedure is recommended.

Neutralize a solution containing not more than 200 milligrams of thallium and dilute to 350 ml. Add 25 ml. of one normal sodium hydroxide and filter. Add 25 ml. of Clorox reagent (prepared by diluting 30 ml. of commercial Clorox to 150 ml.) and digest the solution for two hours. Decant the supernatant liquid through a tared Gooch crucible and wash the precipitate six times by decantation using 80 ml. portions of hot water. Transfer the precipitate to the crucible and dry for one hour at $200^{\circ}\text{C}.$ in an atmosphere of nitrogen. The results for thallium will be approximately one per cent high.

It appeared that sodium hypochlorite would be more suitable than potassium ferricyanide for the gravimetric determination of thallium as thallium (III) oxide. However, the results obtained indicate that sodium hypochlorite offers no advantage over potassium ferricyanide for the alkaline oxidation of thallium (I) to Thallium (III). The thallium (III) oxide precipitates obtained by using potassium ferricyanide are more dense and more easily handled than precipitates obtained by using sodium hypochlorite. The density and ease of handling the precipitates appears to be related to the color of the thallium (III) oxide. The darker colored precipitates are more dense and easier to handle.

In the section on metallic reductors the chromate (30) and the potassium ferricyanide (40) methods were used to analyze a standard thallium solution. The results from these standardisations indicate that the chromate and ferricyanide procedures yield more accurate results than the sodium hypochlorite method.

VI. Improvements on the Precipitation of Thallium (III) Oxide by Potassium Ferricyanide

The gravimetric determination of thallium by the ferricyanide procedure of Mack and Lepper (40) appears to be superior to the gravimetric chromate method (30). The ferricyanide procedure does not define interferences or the specific conditions for precipitation. No statement is made concerning digestion of the precipitate or precipitation from a hot solution. Concerning interferences the procedure states

that elements forming alkali insoluble ferricyanides or ferrocyanides must be removed prior to precipitation.

A. Effect of Precipitation from Hot Solution and Digestion of the Precipitate

The effect of precipitating thallium (III) oxide from a hot solution and digestion of the precipitate was studied in the following manner. Twelve 19.97 ml. samples of 0.1048 normal thallium (I) nitrate solution were diluted to 70 ml. and treated with 25 ml. of one normal potassium hydroxide. Six of the samples were heated on a steam bath before precipitation was made by adding 25 ml. of an eight per cent potassium ferricyanide solution. The six precipitates formed in hot solution were digested for two hours. The remaining six samples were treated with 25 ml. of the eight per cent ferricyanide. These samples were precipitated at room temperature and no digestion was made. The potassium hydroxide and ferricyanide solutions were freshly prepared and filtered before being used. After standing 18 hours the twelve precipitates were each washed six times with 50 ml. portions of hot water and transferred to tared Gooch crucibles. The thallium (III) oxide precipitates were dried under a nitrogen atmosphere for one hour at 200°C. The results of these precipitations are given in Table XIX.

The 0.1043 normal thallium (III) sulfate solution was assayed by the thallium (III) oxide procedure (40). Precipitations were carried out at room temperature and the precipitates were not digested. Five 19.97 ml. samples of the thallium (III) sulfate solution yielded

TABLE XIX
EFFECT OF PRECIPITATING FROM HOT SOLUTION AND
DIGESTION OF THE PRECIPITATES

Digestion and Precipitation From Hot Solution			Precipitation from Cold Solution and No Digestion		
Milligrams of Thallium			Milligrams of Thallium		
Taken	Found	Error	Taken	Found	Error
213.9	214.2	+0.3	213.9	212.4	-1.5
213.9	214.4	+0.5	213.9	212.5	-1.4
213.9	213.3	-0.6	213.9	213.2	-0.7
213.9	214.0	+0.1	213.9	213.5	-0.4
213.9	215.1	+1.2	213.9	213.2	-0.7
213.9	214.0	+0.1	213.9	213.2	-0.7

precipitates of thallium (III) oxide weighing 0.2399, 0.2406, 0.2398, 0.2399 and 0.2387 grams. Assuming the thallium (III) sulfate to be 0.1043 normal the calculated weight of precipitates should be 0.2377 grams. The precipitates were easily dispersed by washing and difficult to handle.

Two 19.97 ml. samples of the thallium (III) sulfate solution were assayed by the thallium (III) oxide procedure. Precipitation was carried out in a hot solution and the precipitates were digested two hours. This modification of procedure yielded thallium (III) oxide precipitates weighing 0.2388 and 0.2383 grams, giving an average error of plus 0.8 milligrams of thallium (III) oxide. These precipitates dispersed on washing and were difficult to handle.

Six 19.97 ml. samples of the thallium (III) sulfate solution were reduced by bubbling sulfur dioxide through the solutions for ten minutes.

After standing over night on the steam bath to remove excess sulfur dioxide, the samples were made alkaline by adding 30 ml. of filtered one normal potassium hydroxide. Precipitation was carried out by adding 25 ml. of a filtered eight per cent potassium ferricyanide solution to each sample. These hot solutions were then digested for two hours. After standing 18 hours the precipitates were washed six times by decantation, transferred to tared Gooch crucibles, and dried under nitrogen for one hour at 200°C . The weights of thallium (III) oxide were 0.2386, 0.2394, 0.2375, 0.2382, 0.2384 and 0.2388 grams, giving an average error of plus 0.8 milligrams. The precipitates were dense, easily handled, and did not disperse on washing.

B. Interferences

A study of the interference of foreign ions was made in the following manner. Samples of 19.97 ml. of 0.1048 normal thallium (I) nitrate solution were diluted to 50 ml. and made alkaline with 25 ml. of filtered one normal potassium hydroxide. Measured quantities of foreign ions were added to the solutions. Precipitation was carried out by adding 25 ml. of a filtered eight per cent solution of potassium ferricyanide. The precipitates were digested about two hours on a steam bath and allowed to stand 18 hours before filtration. The precipitates were washed six times by decantation with 50 ml. portions of hot water, transferred to tared Gooch crucibles, and dried for one hour under nitrogen at 200°C . The results are tabulated in Table XX.

TABLE XX

EFFECT OF FOREIGN IONS ON THE DETERMINATION OF THALLIUM
BY THE POTASSIUM FERRICYANIDE METHOD

Ion Added	Milli- grams Added	Diluted Volume	Potassium Hydroxide Conc.	Milligrams Thallium		Error (Mg.)
				Taken	Found	
Aluminum	27	100	0.25	213.9	213.0	-0.9
Zinc	65	100	0.25	213.9	272.7	+58.6
Zinc	65	100	0.25	213.9	270.9	+57.0
Gallium	5.5	100	0.40	213.9	213.3	-0.6
Gallium	11	100	0.40	213.9	213.1	-0.8

The results in Table XX indicate that 0.002 molar gallium or 0.01 molar aluminum concentrations do not interfere while 0.01 molar zinc concentrations do interfere.

G. Contamination of the Precipitate By
Potassium Ferricyanide

Thallium (III) oxide precipitated by the ferricyanide procedure (36) was analyzed for iron by the following procedure. Two 19.97 ml. samples of 0.1048 normal thallium (I) nitrate solution were diluted to 50 ml. One solution was treated with 25 ml. of filtered one normal potassium hydroxide and 25 ml. of a filtered eight per cent potassium ferricyanide solution. The other sample was treated with 50 ml. of a filtered mixture containing 25 ml. of one normal potassium hydroxide and 25 ml. of an eight per cent solution of potassium ferricyanide. After the two samples were allowed to stand 18 hours, the precipitates

were washed six times by decantation with 50 ml. portions of hot water and transferred to a clean Sela filtering crucibles. The crucibles containing the precipitates were placed in beakers containing 70 ml. of distilled water and the precipitates were dissolved by bubbling sulfur dioxide through the solutions. The crucibles were removed and washed and the solutions were boiled 30 minutes to expel the excess sulfur dioxide. The solutions were transferred to 100 ml. volumetric flasks and diluted to volume. A blank of 19.97 ml. of 0.1048 normal thallium (I) nitrate was treated with sulfur dioxide, boiled 30 minutes and diluted to 100 ml. in a volumetric flask. Twenty ml. aliquots of the diluted solutions were treated with two ml. of a ten per cent solution of hydroxylamine hydrochloride and ten ml. of a 0.1 per cent solution of 1,10-phenanthroline. These solutions were treated with dilute ammonium hydroxide to adjust the pH to five and diluted to 100 ml. in volumetric flasks. The color of the iron (II) phenanthroline complex was measured in one cm. Corex cells at a wavelength of 515 millimicrons with a Beckman Model B spectrophotometer. A calibration curve was constructed using a standard iron solution (0.174 milligrams per ml.). The thallium blank was found to contain 0.08 milligrams of iron. The thallium (III) oxide precipitated by adding hydroxide and ferricyanide separately contained 0.15 milligrams of iron, and the sample precipitated by adding the mixture contained 0.12 milligrams of iron.

D. Discussion

The procedure of Mack and Lepper (40) does not mention precipitation from a hot solution or digestion of the precipitate. The results in Table XIX indicate that more accurate results are obtained when thallium (III) oxide precipitates are formed in hot solution and digested for several hours. Reduction of thallium (III) to thallium (I) before precipitation is recommended, since thallium (III) solutions when treated with base and potassium ferricyanide yielded precipitates that were easily dispersed and difficult to handle. The precipitates that were formed in hot solution and digested for two hours settled rapidly. The 18 hour settling period recommended does not seem warranted when precipitation is carried out in a hot solution and a two hour digestion is used.

The data on interferences indicate that aluminum and gallium do not interfere, but a ten millimolar concentration of zinc does interfere.

A 0.23 gram sample of thallium (III) oxide, which was precipitated by the potassium ferricyanide procedure, was shown to contain 0.07 milligrams of iron. This contamination of 0.07 milligrams of iron from the potassium ferricyanide has a negligible effect on the accuracy of the determination.

In view of the results obtained using a precipitation from hot solution and a two hour digestion of the precipitate, the following modified procedure is recommended. Prepare 50 to 100 ml. of an acid solution of monovalent thallium, free of reducing substances and

substances precipitated by potassium hydroxide, potassium ferricyanide or ferrocyanide and ions that react with thallium such as iodides or chromates. Neutralize the solution with one normal potassium hydroxide and add 25 ml. excess. Heat the alkaline solution and add 25 ml. of a filtered eight per cent solution of potassium ferricyanide and digest for two hours on a steam bath. Wash the precipitate six times by decantation with 50 ml. portions of hot water and transfer the precipitate to a tared Gooch crucible. Dry the precipitate for one hour at 200°C . in an atmosphere free of carbon dioxide. Weigh as Tl_2O_3 .

SUMMARY

Methods for the quantitative reduction of thallium (III) to thallium (I) have been developed. Metallic reductors made from finely divided cadmium, silver or bismuth metal, quantitatively reduce thallium (III) to thallium (I) under proper conditions. The thallium in these reduced solutions was determined by the volumetric bromate method. An average relative error of less than ± 0.3 per cent was found for samples containing from 30 to 212 milligrams of thallium. Bismuth amalgam was found to give a quantitative reduction of thallium (III) to thallium (I). A number of metallic reductors and amalgams were found to be unsatisfactory for the reduction of thallium (III) to thallium (I).

Two volumetric methods for the determination of thallium (I) were developed. The direct volumetric method is based on the oxidation of thallium (I) to thallium (III) oxide by extemporaneously generated hypobromite. The titrant used is a standard solution of sodium hypochlorite which instantaneously reacts with bromide ions to yield hypobromite ions.

The indirect volumetric method is based on the addition of an excess of standard sodium hypochlorite solution to a sample containing monovalent thallium. After complete oxidation of the thallium (I), the excess sodium hypochlorite is titrated potentiometrically with a standard sodium arsenite solution. Both of these volumetric methods require that the thallium be present in the plus one oxidation state. Metallic reductors or amalgams cannot be used for the reduction of thallium (III),

since the metal ions introduced during the reduction, interfere in the alkaline oxidation of thallium (I).

Comparison of the gravimetric chromate, gravimetric thallium (III) oxide, and the volumetric bromate methods indicate that the bromate method yields the most accurate results. The volumetric bromate method in conjunction with the proposed methods for the reduction of thallium (III), is the most accurate and the most rapid method for the determination of thallium.

A modified procedure was developed for the gravimetric determination of thallium (I) using potassium ferricyanide. The modification consists of precipitating the thallium (I) from a hot solution and digestion of the precipitate. This modified procedure eliminates the 16 hour standing period, yields more accurate results and gives a more easily handled precipitate. A study on the interference of foreign ions indicated that thallium solutions 0.01 molar in aluminum or 0.002 molar in gallium do not interfere, but zinc does interfere and must be removed.

A gravimetric method for the homogeneous precipitation of thallium (III) oxide was developed. This method is based on the alkaline oxidation of thallium (I) to thallium (III) by a solution of sodium hypochlorite. The slow rate of oxidation of an alkaline solution of thallium (I) to thallium (III) oxide by hypochlorite effectively gives a homogeneous precipitation. A study of foreign ion interferences indicates that 0.001 molar concentrations of zinc or gallium interfere slightly and solutions 0.01 molar in aluminum or phosphate ions do not interfere.

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