Determination of thallium(III) using the dead-stop end point

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DETERMINATION OF THALLIUM(III) USING
THE DEAD-STOP END POINT

A Thesis
Presented to
the Faculty of the Department of Chemistry
University of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Richard Blount Williams
August 1963
The author wishes to thank three people who have helped in the preparation of this study: Dr. Hugh Wadman, who gave information on the toxic properties of thallium as absorbed through the skin and who gave a simple means for detecting thallium on the skin; Mr. James Larsen, a fellow student, who suggested and gave help in the preparation of the ultra sensitive ammeter used; and Dr. Herschel Frye, without whose guiding help this study could never have been undertaken. Dr. Frye provided just the right amount of help to stimulate rather than lead the study.
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CHAPTER I

INTRODUCTION

An accurate and fairly rapid method of analysis of thallium solutions is desirable in order to facilitate further investigation of the chemistry of thallium. The dead-stop titration method which has been successfully applied to other metals of Group 3b, will now be applied to the quantitative determination of the thallium(III) ion in aqueous solution.

The uses of thallium. There are no uses for the metal per se (Kirk and Othmer, 1954). Thallium sulfate is one of the most commonly used compounds, and it is used as a pesticide that is particularly effective against rodents. The toxic thallium salts are tasteless and odorless, and the combination of properties make thallium sulfate a particularly effective poison.

The following uses of thallium are those given by Kirk and Othmer (1954) and Hampel (1954). The use of thallium salts in the manufacture of glass results in a high index of refraction. "Thallofide" cells containing thallium oxysulfate are photosensitive and can be used to detect the presence of infrared radiation. A relatively new use derives from the infrared transmission of mixed
bromide-iodide crystals. Crystals with a 42 mole per cent thallium(I) bromide and 58 mole per cent thallium(I) iodide have a transmission of nearly 67 per cent from 10 to 14 microns. Still another use of the compounds is in scintillation counters.

**Occurrence and properties.** An estimate of the abundance of thallium in the earth's crust is 0.0004 per cent (Kirk and Othmer, 1954). Minerals having 16 to 20 per cent of thallium are so rare as to be of no commercial significance (Hampel, 1954). The major sources of commercial thallium lie in the recovery of the metal from trace amounts in sulfide ores during the roasting process for sulfuric acid or from the smelting of lead and zinc. The estimated yearly production is fifteen tons.

Thallium is a soft white metal and can be cut easily with a knife; the freshly cut surface is lustrous and silvery, but at room temperatures in air an oxide soon causes the surface to acquire a bluish tinge. The metal can be used to mark paper (Barnett, 1957). A heavy oxide coating will build up on the surface of metallic thallium that has been allowed to remain in contact with air at room temperature for a few weeks (Hampel, 1954). The physical properties of thallium are very similar to those of lead insofar as density, malleability, specific heat, and electrical conductivity are concerned. The most nearly unique
alloy of thallium is formed in an 8.5 per cent eutectic with a freezing point nearly sixty degrees below zero Celsius (Hampel, 1954).

The chemistry of thallium is unique among the group 3b elements in that it is usually found in the univalent state rather than the common tervalent state; the 6s electrons are said to be an "inert pair" (Cotton, 1962). Thallium in the plus three oxidation state is a powerful oxidizing agent as it reverts to the plus one state; this is readily apparent from the oxidation-reduction potential of -1.25 volts (Latimer, 1952).

Univalent thallium resembles lead(II) in the solubility of its salts. It resembles the element potassium in size and other physical properties, basic nature of the hydroxide, and lack of tendency to form complexes (Latimer and Hildebrand, 1940).

Tervalent thallium resembles the aluminum ion except that it is larger, and its hydroxide does not possess the acid properties of aluminum hydroxide (Latimer and Hildebrand, 1940).

Toxicity of thallium. The handling of metallic thallium with the hands is not advisable, for the metal can react with the moisture present on the skin to form soluble compounds which may be absorbed through the skin; soluble
salts may also be absorbed. The lethal dose for dogs is considered to be twelve to fifteen milligrams of the element when administered orally (Sax, 1951). Thallium resembles lead in its toxic properties, and it is also a cumulative poison.

Laboratory workers frequently use a simple test to detect accidental contact with thallium salts. The skin is wet with a solution of potassium iodide, and the formation of the insoluble yellow thallium iodide confirms contact. Such yellow areas should be abraded with soapstone until all traces of thallium salts have been removed.

Methods of analysis. Two long standing methods of analysis are the gravimetric determination of thallium(I) iodide and the volumetric determination of thallium(I) compounds by oxidation with standard permanganate solutions (Latimer and Hildebrand, 1940). A report of a more recent study recommends that the only gravimetric method worth retaining is that of the determination of thallium(I) chromate (Smith, 1948).

Two Russians have still more recently reviewed the analytical chemistry of thallium, and they have written books on the subject (Busev and Tipsova, 1960, 1961, and 1962).
Potassium hexacyanoferrate(II) has been used to determine thallium(I) volumetrically as thallium(I) calcium hexacyanoferrate(II) (Ripan and Popper, 1944, 1948).

Thallium(III) analysis. Thallium(III) can be detected by precipitation with tetrphenylarsonium chloride; the method is quantitative to the extent that it is recommended above all others (Smith, 1948).

Complexometric determinations have been made using Xylenol Orange as indicator and titrating with EDTA (Pribil, Vesely, and Kratochiv, 1961). Another titration is with 7-(5,7-disulfo-2-naphtylazo)-8 hydroxyquinoline-5-sulfonic acid using 7-(1-napthylazo)-8 hydroxyquinoline-5-sulfonic acid as indicator (Busev, 1962).

A photometric determination of small amounts of thallium(III) using primary aromatic amines has been reported (Pfrepper, 1963). A colorimetric determination using methyl violet has been recently reported (Kovarik and Moucka, 1963).

Amperometric titrations are those using cerium sulfate (Singh and Agarwala, 1962); there is also an iodometric method (Singh and Agarwala, 1961), a trilonometric determination (Khadeev, 1962), and a semimicro iodometric determination (Bhatnagar, Bhatnagar, and Mathur, 1962).

The following potentiometric methods have been reported: with chromium(II) (Majundar and Bhatnagar, 1961);
with hydroquinone (Krejzova, Simon, and Zyka, 1959); with ascorbic acid (Bhatnagar, Bhatnagar, and Mathur, 1962); and finally with hydrazine sulfate (Berka and Busev, 1962).

An indirect determination of hypochlorite and hypobromite by ascorbimetric titration with thallium(III) ions has been reported (Erdey and Vigh, 1963).

The dead-stop end point method. Salomon (1897) originated the idea of using the change in current between two identical electrodes across which a constant small voltage is impressed in order that end points of titration might be detected. The method was further developed and the name "dead-stop end point method" proposed (Foulk and Bawden, 1926). More recently Jantti (1955) has proposed the name "diampereometric end point" for direct current dead-stop. The name is suitable since on one side of the equivalent point one electrode is the indicator electrode while on the other side of the equivalent point, the other electrode is the indicator electrode.

Two of the three metals in Group 3b have been determined by the dead-stop method. Gallium was first determined by Fetter and Swinehart (1956), and indium was determined at the University of the Pacific by Martens and Frye (1963).

Delahay (1954) in his text states, "... the advantage of a method such as the 'dead-stop end point' is
primarily in the simplification in the technique and possibly in improved accuracy, rather than in the possibilities of devising new titrations." Stone and Sholten (1952) state, "The applications are more numerous than originally proposed by Foulk and Bawden and depend on the ingenuity of the analytical chemist to have an electrolytic couple at the equivalence point of the titration."

The dead-stop method has been used to analyze ores and concentrates for more than one constituent, and iron, titanium, and vanadium have been titrated in the same solution using platinum electrodes (Jantti, 1955).

The apparatus needed for the dead-stop titration is shown in Figure 1. It may be seen that all components are those that might easily be found in a modest laboratory with the possible exception of the ammeter.

None of the electrical measurements demand a high degree of accuracy, for the equivalence point is simply indicated by an abrupt change in the current flowing through the ammeter.

Reagents needed are a standard solution of potassium hexacyanoferrate(II), and a solution of thallium(III) ions free from interfering substances. The potassium hexacyanoferrate(II) solution is easily made from the anhydrous salt (Martens and Frye, 1963). If the necessity arises, the
Figure 1. The dead-stop apparatus (Foulk and Bawden)

B, a 1.5 volt dry cell
R, a variable resistor or potentiometer
G, ammeter of approximately 50 microamperes full scale deflection
E, platinum electrodes
S, a beaker containing the solution to be titrated

not shown: a buret containing the titrant, and a stirrer
latter solution can be standardized against a known weight of ammonium hexanitratocerate(IV) (Smith and Fly, 1949).

An account of the preparation of the thallium(III) ion solution, and of the titration of the solution using the dead-stop apparatus follows.
CHAPTER II

THEORY

The dead-stop titration employs a pair of smooth identical platinum electrodes immersed in the solution to be titrated. A constant, low potential difference is impressed across the electrodes, and the resulting current flow measured. The equivalence point of the titration is characterized by an abrupt change in current flow.

Delahay (1954) discusses such amperometric titrations at constant voltage with two polarized electrodes. Consider the titration of a substance $R_1$ which is oxidized by the titrant $O_2$ according to the equation

$$R_1 + O_2 = O_1 + R_2$$

and assume that the couple $O_1 - R_1$ is reversible and $O_2 - R_2$ irreversible. All substances are assumed to be soluble.

Before the equivalence point both components of the reversible couple $O_1 - R_1$ are present in solution, and an appreciable current flows through the cell. Substance $R_1$ is oxidized at the anode and $O_1$ is reduced at the cathode. If there were no concentration polarization, the current before the equivalence point would be controlled only by
the resistance of the cell. Under these conditions the current flowing would be of the order of a few microamperes for the total resistance of the cell usually does not exceed a few hundred ohms. The current actually is reduced somewhat, for there is concentration polarization present.

The concentration of substance $R_1$ after the equivalence point is very low, and the current corresponding to the reversible couple $O_1 - R_1$ is virtually equal to zero. Both components of the couple $O_1 - R_2$ are present in solution, but practically no current flows through the cell inasmuch as the couple $O_2 - R_2$ is irreversible, and the impressed potential difference across the electrodes is too low to permit electrolysis. The titration curve where current is plotted as a function of volume of titrant added has the following shape.

\[ \text{Precipitation titrations.} \] If one of the reagents of the titrations forms a reversible couple, precipitation titrations are feasible (Delahay, 1950).
The couple hexacyanoferrate(II)-hexacyanoferrate(III) forms a reversible redox couple. The hexacyanoferrate(II) can be oxidized at the anode while the hexacyanoferrate(III) can be reduced at the cathode. There will be no change in concentration of the species, for the species occur in stoichiometric amounts.

\[
\text{Fe(CN)}_6^{4-} \rightleftharpoons \text{Fe(CN)}_6^{3-} + e^-
\]

The standard oxidation-reduction potential

\[
\text{Ti}^{1+} = \text{Ti}^{3+} + 2 e^- \quad E^0 = -1.25 \text{ volts}
\]

is too high for reduction to take place in the cell under the small impressed potential difference (Latimer, 1952).

If the titrant be hexacyanoferrate(II), the concentration of the ion in solution is extremely low, for it is being removed by the precipitation reaction with the thallium(III); thus the current flowing in the cell is practically zero. Immediately after the equivalence point the concentration of hexacyanoferrate(II) ion increases rapidly, and a large increase in current is observed, for the hexacyanoferrate(II) - hexacyanoferrate(III) couple is reversible. If current be plotted as a function of volume of titrant added, a curve similar to the one below will be obtained.
The theory of the method underlying the dead-stop process has been presented by Reilley, Cooke, and Furman (1951), Stone and Sholten (1952), Kolthoff (1954), Delahay (1950 and 1954), and Kies (1955). The most rigorous study is that of Bradbury (1953 and 1954).
CHAPTER III

EXPERIMENTAL

The dead-stop apparatus of Foulk and Bawden was modified as shown in Figure 2. The electrodes consisted of two pieces of platinum wire sealed about four millimeters apart in the end of a soft glass tube. Mechanical connections inside the test tube permitted connecting wires to the ammeter. The original platinum electrodes were replaced as will be discussed later.

A fifty microampere full scale deflection ammeter, one microampere per millimeter, manufactured by the Beede Electrical Company of Penacook, New Hampshire, was used throughout the trials. Later it was found desirable to insert another ammeter in series with the Beede instrument. The latter ammeter had a three microampere full scale deflection or about twenty-five millimeters per microampere.

The potential difference impressed across the electrodes was measured using an Eico Model 232 vacuum tube voltmeter with an input resistance of eleven megohms and possessing an accuracy of plus or minus three per cent of full scale deflection.

In every case the thallium solution was placed in a fifty milliliter beaker which was supported in place under the electrodes. The volumes of the thallium solution were
Figure 2. The dead-stop apparatus used.

C = 1.5 volt dry cell
S = switch
R₁ = 1500 ohm variable resistor
R₂ = 300 ohm variable resistor
R₃ = 100 ohm fixed resistor
A = ammeter, 50 microampere full scale deflection
E = platinum electrode
dispensed using a ten milliliter volumetric pipet.

The apparatus was so arranged that a stirrer could be inserted into the beaker in which titration was being carried on. The stirrer had a fixed speed of rotation.

The titrant solution, in every case, was a $1.0000 \times 10^{-2}$ molar solution of potassium hexacyanoferrate(II). The titrant was dispensed from an uncalibrated, ordinary fifty milliliter buret which had an elongated tip so that the titrant was added directly into the beaker.

**Preparation of solutions.** Potassium hexacyanoferrate (II) (Baker and Adamson reagent grade crystal) was used. The hydrated salt was ground and dried in a drying oven at 100$^\circ$ Celsius until constant weight was reached as reported by Martens and Frye (1963). The necessary amount of anhydrous powdered salt was then weighed out and placed in a volumetric flask. Two grams per liter of reagent grade sodium carbonate monohydrate was added to stabilize the solution (Kolthoff and Sandell, 1952). The contents of the flask were then dissolved and diluted to volume.

Metallic thallium supplied by Fisher Scientific Company (lot #724476) of purified grade was used. The metal was encased in a type of metallic bag so that the metal could be extruded and retracted without the need for handling it with bare hands becoming necessary. Pieces of
metallic thallium varying in mass from about 0.9 to 2.6 grams were used.

The metal was covered with an oxide coating; so the samples were dropped into concentrated nitric acid to dissolve the oxide. Some dissolving of the metal was also noted. Deionized distilled water was used to remove all traces of nitric acid, and the samples were then dried and weighed. It has been reported (de Bruyne, 1962) that if two like metallic surfaces are clean, the pieces of metal will cling together. The pieces of thallium, while being washed with deionized distilled water, were observed to cling to one another; it was necessary to pull them apart.

The thallium samples were placed in a beaker and a small quantity of concentrated nitric acid was added to dissolve the metal. Heat was usually employed to speed the reaction. The thallium nitrate was evaporated to dryness and then dissolved in aqua regia. Either sodium chloride or calcium nitrate was added at this time in order to prevent possible hydrolysis (Cuta, 1933). The aqua regia solution was then carefully evaporated to dryness to bring about the quantitative oxidation of thallium(I) to thallium(III) (Pribil, Vesely, and Kratochvil, 1961). The residue after evaporation to dryness from aqua regia was then dissolved in sufficient nitric acid so that the final solution would be 0.2 molar HNO₃ (Busev and Tipsova, 1959).
Detection of equivalence point. The solution of potassium hexacyanoferrate(II) was placed in the fifty milliliter buret, and 10.000 milliliters of thallium(III) solution was transferred into the fifty milliliter beaker by means of a volumetric pipet.

The beaker was supported so as to immerse both the platinum electrodes and the mechanical stirrer. The needle of the ammeter almost always kicked far up scale indicating a momentary surge of current, but the needle quickly fell to a much lower value. The stirrer was next started, and titrant was permitted to flow at varying rates of one to three drops per second.

The ammeter fell to a minimum value as titrant was added. The current fluctuated somewhat during the initial addition of titrant, but the needle became steady when some fifty to sixty per cent of the equivalent volume of titrant had been added. Titration was stopped, although stirring was continued, when the ammeter read zero. The practice of waiting sixty seconds before recording the current was followed in every case (Martens, 1962).

Two or three drops of titrant were added, and again the current was recorded. A characteristic momentary kickup was usually noted just prior to the equivalence point. The addition of titrant was reduced to one drop at a time when there was reason to believe the end point was near, and
current was once again recorded after the customary sixty second wait. The current tended to increase linearly after the equivalence point; occasionally this linear relationship could be followed for as many as eight or nine drops of titrant.

Many graphs of current as a function of volume of titrant added were made, and they were all similar to Figure 4. The true equivalence point is found at the intersection of a straight line drawn through the minimum values and the line drawn through the points indicating the current after the equivalence point.

Occasionally negative currents were recorded by the ammeter as had been noted by Martens (1962); the significance of these observations will be discussed later.

Ultra sensitive current measurements. A Heathkit Operational Amplifier System Model EUW-19 was set up in connection with the previously mentioned Eico vacuum tube voltmeter (Malmstadt, Enke, and Toren, 1962). The combination provided three useful scales: zero to thirty microamperes, zero to ten microamperes, and most useful of all, zero to three microamperes full scale deflection.

Further titrations were made using the ultra sensitive current reading after the customary sixty second wait. It was noted that the current no longer gave the
previous abrupt change in value, but that the equivalence point could be located only by graphing. Figures 3 and 4 should now be observed. Figure 3 shows a minimum value of about 0.1 microamperes before the equivalence point. The current increases through the equivalence point, and then it increases linearly past the equivalence point. The equivalence point was located by the intersection of the tangents drawn to the two portions of the curve.

The ultra sensitive ammeter which permitted estimates of the current to the nearest hundredth of a microampere was steady immediately prior to the equivalence point and for one drop of titrant past the end point. If the needle was observed to swing over a range of 0.04 microamperes, the equivalence point had been passed.

The equivalence point could now be detected in one of four ways: (1) intersection of linear increase from Beede ammeter, (2) the first kick-up noted on the Beede ammeter, (3) the intersection of the tangents to curves drawn from ultra sensitive ammeter data, and (4) the drop before the characteristic fluctuation of the ultra sensitive ammeter over a 0.04 microampere range. Reference to Figures 3 and 4 will show that all four of the equivalence points lie within one drop of titrant of one another; i.e., 0.04 milliliters.
Figure 3. Readings taken with 3 microampere full scale meter (ultra sensitive).

Figure 4. Readings taken with 50 microampere full scale meter (Beede).
Sufficient titrations were undertaken to confirm the location of the equivalent point; then further trials had only the equivalent point noted. This point was most easily noted from the kick-up of the Beede ammeter.

**Results obtained.** The majority of titrations were carried out with an impressed voltage of two hundred fifty millivolts across the electrodes, and all titrations were carried out at ambient temperatures which ranged from nineteen to thirty-four degrees Celsius.

A flocculent yellow precipitate could be seen forming after several drops of titrant were added. The precipitate became more dense as titration was continued, and the stirrer and electrodes were soon hidden from view.

Five thallium(III) solutions were prepared, and a total of thirty-seven titrations made. An average mole ratio of 1.247 to 1.000 was obtained. Tables I, II, III, IV, and V* give the values of the individual trials.

**Temperature.** No effort was made to control the temperature at which titrations were made. Thallium, like Indium (Martens, 1962) may be titrated at ambient temperature.

**Rate of titrant addition.** The most reproducible results were obtained when the titrant was added dropwise.

*See Appendix, page 44.*
The rate of addition could be fairly rapid during the initial stages of the titration; i.e., about one to three drops per second, but it was necessary to add drops slowly just before and after the end point. Presumably this was necessary in order that equilibrium might be reached. The sixty second delay in recording ammeter readings insured the attainment of equilibrium.

No significant differences in results were noted when drops were added as slowly as twenty seconds apart.

Very rapid addition of titrant caused an excess of the potassium hexacyanoferrate(II) solution to be used. Adsorption or occlusion of titrant by the forming precipitate could account for this observation. If the solution was not stirred during the time that the greater part of the titrant was added, a still greater volume of titrant solution was required.

**Impressed potential difference.** Table VI* lists the results obtained when potential differences other than the customary two hundred fifty millivolts was used.

The average mole ratio is somewhat lower, but there is reason to believe that titrations could be carried out at different potential differences. Changes in ammeter

readings were slight when only seventy-five millivolts were used, and the most abrupt changes were noted with the four hundred millivolt potential difference.

A reasonable assumption is that the operator becomes accustomed to the ammeter responses at a given potential difference, and that several practice runs at the new potential difference would be necessary to obtain consistent data.

**Concentration of solutions.** Each of the solutions was diluted by a factor of ten or more, and the results of titrations with the diluted solutions are to be found in Table VII.*

The familiar yellow precipitate was not easily seen, even at the end point. A more important factor was the low ammeter readings. The Beede ammeter failed to respond until the equivalence point was well past; however, the ultra sensitive ammeter could be used. Current readings taken with the zero to three microampere meter could be used to prepare a graph of current as a function of titrant added, and the equivalence point could best be detected in this manner.

---

**Electrode treatment.** The electrodes were customarily immersed in cleaning solution between titrations. The cleaning solution was the familiar potassium dichromate dissolved in concentrated sulfuric acid. Cleaning solution was removed by rinsing with deionized distilled water prior to use, and excess water blotted up. Failure to clean electrodes resulted in gradual lowering of current readings after the equivalence point, thus confirming the observations of Martens (1962).

An effort was made to vary electrode treatment, and they were scrubbed with an ordinary pipe cleaner which had been dipped into common scouring powder. The electrodes were washed and rinsed, but no improvements were observed.

Further comments on electrodes will be made under the heading of Discussion, page 27.

**Effect of oxidants.** The common oxidation state of thallium is the univalent, for the "inert pair" of 6s electrons are quite unreactive (Cotton, 1962). Early attempts to determine thallium(III) by the dead-stop method were not successful, for the ammeter simply climbed steadily to higher readings as titrant was added.

Failures were noted with ammonium peroxydisulfate, hydrogen peroxide, and with bromine as oxidizing agents. The literature, however, states that these reagents may be
used to oxidize thallium(I). See Busev and Talipova (1962), Smith (1948), and Bhatnagar, Bhatnagar, and Mathur (1962). Probable causes for failures are given under Discussion.

The oxidation of thallium(I) by evaporation to dryness from aqua regia insured two things: thallium(I) is quantitatively oxidized, and the excess oxidant is removed (Pribil, Vesely, and Kratochvil, 1961).

Oxidants were added to thallium(III) solutions in order to determine possible interference. Ten per cent by volume of saturated bromine water produced incorrect end points. The effect of hydrogen peroxide was even more noticeable; as little as one part in five hundred of the thirty per cent solution caused erratic results.
CHAPTER IV

DISCUSSION

The truly significant portions of this study are:
(1) the dead-stop titration can be used to determine thallium under appropriate conditions, and (2) a mole ratio of 5:4 is consistently obtained. Still other portions are of interest and will be discussed.

Mole ratio. A review of the literature reveals no suggested empirical formula for the precipitate resulting from the reaction of the thallium(III) ion and the hexacyanoferrate(II) ion.

Many efforts were made to determine the molar relationship, and finally a technique for producing reproducible results was attained. These suggest an empirical formula of $Tl_5K[Fe(CN)_{6}]_4$. Later studies in the laboratory suggest that the precipitate is a hydrate of the empirical composition $Tl_5K[Fe(CN)_{6}]_4\cdot nH_2O$, where $n$ may have the approximate value of sixteen. It is of interest to note that the aluminum hexacyanoferrate(II) has seventeen molecules of water of hydration.

Inasmuch as the literature reveals no suggested empirical formula, the empirical formula for the corresponding indium precipitate might be expected to be consistent
with the above findings. A mole ratio of 5:4 was found by two groups of earlier workers, Bray and Kirschmann (1927), and Martens and Frye (1963). If two adjoining metals in the same group might be expected to possess similar properties, then the 5:4 mole ratio for thallium is justified.

**Characterization of precipitate.** The yellow flocculent precipitate formed by the reaction of the thallium(III) ion with the hexacyanoferrate(II) ion will slowly settle to the bottom of a beaker. After a wait of twenty-four hours, most of the clear supernatant liquid can be separated, but not all, for the precipitate does not compact on standing.

Most of the precipitate passes through ordinary filter paper; a considerable portion passes through a fine sintered glass crucible.

The precipitate has a property which distinguishes it from many thallium compounds, for it is one of several thallium compounds that is photosensitive. Workers in the field report photosensitivity for heavy metal, such as lead and thallium, colloidal solutions of the hexacyanoferrate(II) and hexacyanoferrate(III) salts with exposure to ultraviolet light to precipitate iron(III) hydroxide (Nanobashvilli and Bakhtadze, 1960). They do not, however, suggest an empirical formula.
An aqueous suspension of the precipitate was kept in an ordinary glass bottle exposed to indoor light for more than one week, and no photosensitivity was noted. However, a sample exposed, still within ordinary glass, to direct sunlight for thirty minutes changed from yellow to blue; a green color was intermediate. The above workers report that Fe(OH)$_3$ is precipitated by ultraviolet light. The blue color could be accounted for by the formation of Prussian Blue by the reaction of Fe$^{3+}$ and free hexacyanoferrate(III) ions. The color change suggests a sensitivity to wavelengths longer than the ultraviolet.

An attempt was made at verification of the simple empirical formula of the precipitate by dehydration. A whole number of moles of water should be associated with the precipitate.

Two hundred milliliter volumes each of the thallium (III) and hexacyanoferrate(II) solutions were mixed to provide an ample quantity of precipitate which was filtered using a fine sintered glass crucible. The precipitate filtered rapidly at first and some of the precipitate passed through the crucible, but a layer of precipitate forming on the crucible soon slowed down the rate of filtering. The precipitate turned greenish blue as noted under photosensitivity. The residue was washed with 0.2 molar HNO$_3$ and then with alcohol. The alcohol caused the precipitate to
break into small lumps. The lumps were air dried and weighed. The lumps were then placed in a drying oven at 100°C Celsius overnight and weighed again. Data presented in Table VIII* suggests approximately fifteen molecules of water of hydration.

**Techniques of dead-stop titration.** Clean identical platinum electrodes are necessary for consistently reproducible results.

The original electrodes used presented difficulty in maintaining a constant potential difference across the electrodes. The measured potential difference would vary as much as fifty millivolts from one trial to the next.

Examination of the electrodes with a hand lens revealed that they were badly scratched; presumably this came about from attaching an alligator clip for current measurement. Also a cavity in the glass existed just at the entrance of the electrodes into the supporting glass test tube. The cavity may have been formed by the bending and subsequent straightening of the electrodes causing small portions of the supporting glass to be chipped away. The supporting glass also had cracks in it, but no evidence of seepage of electrolyte into the cracks was observed.

*ibid.*
New electrodes consisting of approximately ten millimeter lengths of smooth platinum wire were sealed into separate pieces of six millimeter soft glass tubing, and connection to a copper wire was made with a drop of mercury. The potential difference across the new electrodes remained stable for periods of time up to twelve hours.

Observation of the zinc hexacyanoferrate(II) precipitate revealed the fact that the precipitate was somewhat gelatinous. The scratched electrodes could hardly have remained identical under these conditions, for precipitate could collect in the scratched areas. Provision was made with the new electrodes to measure the potential difference at the point where the copper wire entered the glass tubing. Examination of the new electrodes after more than one hundred titrations had been run showed no scratching of the electrodes.

Negative currents. The Beede ammeter showed occasional negative currents just prior to the equivalence point. Explanations of the observed phenomena could be based upon the formation of a cell caused by collection of precipitate on the electrodes giving rise to a back electromotive force or by a faulty ammeter. The ultra sensitive ammeter failed to reveal negative currents, but it did provide a basis for understanding the negative currents.
The procedure for determining the equivalence point calls for adding one or two drops of titrant at a time as the equivalence point is approached and waiting one minute to record the current. The needles of the meters connected in series would occasionally kick violently with the addition of a new drop. The deflection was sometimes up scale and sometimes down scale. The ultra sensitive ammeter always had its needle return to a point very near the last position, but occasionally the needle of the Beede meter would deflect below the zero point and remain there.

A third ammeter matching the Beede instrument in characteristics was placed in series with the other two at this time, and similar deflections were noted on the third meter, but the third needle always returned from negative readings.

The conclusion was reached that the Beede ammeter had a faulty restoring mechanism, for two other ammeters failed to yield negative currents. Confirmation of this conclusion came from the fact that the Beede ammeter was difficult to zero; the needle did not respond smoothly to changes in the zero adjusting movement.

The violent kicks of the ammeter needle immediately prior to the equivalent point were undoubtedly associated with concentration polarization.
Initial contact of the thallium(III) solution with the electrodes consistently resulted in a kick up scale, sometimes as much as fifty microamperes, but the needle rapidly fell to a much lower value in the range of five to ten microamperes. Writers in the field state that concentration polarization is responsible for the initial drop in the current (Delahay, 1954).

The wait of sixty seconds to record current readings allowed the solution to come to equilibrium. The addition of one new drop of titrant that was swept past the electrodes by the stirrer could easily have changed the concentration and thus provided an opportunity for the deflection of the needle.

Examination of the smooth platinum electrodes with a hand lens revealed no adhering precipitate, nor were bubbles of any gas noted on the electrodes at any time.

**Oxidation of thallium.** Oxidation of metallic thallium presented two problems: (1) a reasonably pure sample of the metal had to be obtained and weighed, and (2) thallium(I) nitrate needed to be oxidized to provide thallium(III) ions.

Early samples of thallium were obtained after placing the thallium, weighing bottles, knife, and other materials in a plastic glove bag which had provisions for an inert atmosphere, e. g. nitrogen. The thallium metal was exposed,
and the layer of oxide scraped away to reveal the silvery metal. A piece of thallium was cut off and placed in a tared weighing bottle that was filled with nitrogen. The weight of the thallium was found by difference in weighings.

Later samples of thallium were cut off and placed in concentrated nitric acid to remove the oxide and thus expose fresh metal. Distilled water removed traces of nitric acid, and the metal was weighed. An effort was made to estimate the amount of oxide formed on the surface of the thallium prior to weighing. A sample of thallium was prepared and weighed, and the sample was then exposed to the air for twenty minutes and weighed again. The increase in weight was only 0.3 milligrams. The error, about three parts in ten thousand, was less than ten per cent of the average deviation from the mean of the 5:4 ratio; so it was concluded that the latter technique provided samples of sufficient purity for analytical purposes.

Thallium metal samples were usually dissolved in concentrated nitric acid in order that a salt might be obtained in as little time as possible. Reaction with concentrated nitric acid took approximately five minutes. Corresponding times for concentrated sulfuric, concentrated hydrochloric, and aqua regia were approximately twenty minutes, twelve or more hours, and about four hours. Hydrochloric acid and aqua regia were eliminated unless a special
need existed. Reaction with hot concentrated sulfuric acid produced hydrogen sulfide fumes and also a residue that appeared to be elemental sulfur.

Difficulties were encountered in attempts to oxidize thallium(I) salts in a manner that yielded suitable solutions for analysis with the dead-stop apparatus.

The use of ammonium peroxodisulfate and hydrogen peroxide may or may not have been successful in oxidation, but the resulting solutions were unsuitable for titration. Experiments showed that the presence of free hydrogen peroxide in solution caused the current to steadily climb. The steady climb may have been caused by the oxidation of hexacyanoferrate(II) to the hexacyanoferrate(III), for an attempt to titrate using a solution of potassium hexacyanoferrate(III) produced similar readings on the ammeter.

The addition of near stoichiometric amounts of ammonium peroxodisulfate provided solutions that gave characteristic deflection of the ammeter, but this method could hardly be used for the determination of thallium, for the concentration of thallium would have to be known in order to use stoichiometric proportions.

Non-reproducible results from early evaporations to dryness from aqua regia can now be accounted for by the thermal decomposition of thallium(III) salts. The appearance of a brown, or even black, residue following evaporation
from concentrated nitric acid can be attributed to the formation of an oxide. Both oxides of univalent and tervalent thallium are colored black. The black residue, however, dissolved very rapidly after the addition of aqua regia. Presumably the chloride was formed by this action.

Thallium(III) chloride has a melting point of only 25°C, and it decomposes before boiling. There is reason to believe that thallium(III) nitrate may also have a low melting point. Care needed to be exercised in evaporating to dryness from aqua regia to avoid the appearance of a yellow material which signified decomposition.

The dry white residue was dissolved in sufficient concentrated nitric acid to make the final solution 0.2 molar in HNO₃. If a yellow color had been noted after evaporating to dryness from aqua regia, a yellow salt was observed at the bottom of the volumetric flask, and a considerable time was necessary for the salt to dissolve. The literature supports the following proposed reaction during the final heating of the residue.

\[ 4 \text{TlCl}_3 = \text{Tl}^{III} \text{Tl}^{I} \text{Cl}_6 + 3 \text{Cl}_2 \]

Evidence of the proposed reaction lies in the low solubility of the thallium sesquichloride in water and also in its slow reaction with nitric acid.
Reproducible results could only be obtained when there was no evidence of the formation of thallium sesquichloride. Deliberate efforts to produce the sesquichloride invariably gave high mole ratios. Some sort of direct relationship was suggested: the more yellow color, the higher the mole ratio.

Six samples of thallium were prepared to give data for this study. Five of the six yielded wholly white salts which readily dissolved; the results are to be found in Tables I through V.* The sixth sample yielded a very small amount of yellow residue, and predictably the mole ratio for this sample was higher, 1.27 to 1.

**Topics for future study.** This study has shown that reproducible results can be obtained under controlled and appropriate conditions, but at least three areas for future study are indicated. These are: (1) the need for and amount of carrier salt, (2) the successful use of oxidants other than aqua regia, and (3) the characterization of the precipitate.

Cuta (1933) has suggested that a soluble chloride be added to prevent possible hydrolysis. Sodium chloride and calcium nitrate were used in amounts from equal in weight to the thallium metal to four times the weight. In every case

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reproducible results followed. Can other salts be used? If so, in what amounts?

The literature suggests that chlorine gas might be used to bring about oxidation of thallium(I). Chlorine gas could easily be removed by evaporation to dryness.

The photosensitivity of the precipitate with the empirical formula $\text{Ti}_5\text{K}[\text{Fe(CN)}_6]_4$ was not anticipated, and suitable precautions were not followed to prevent decomposition. The precipitate could be formed in dark bottles by the mixing of appropriate solutions in a 5:4 molar ratio. The filtration could be carried out in subdued light, and the washing with alcohol eliminated by longer air drying of the precipitate. The drying oven itself would provide a site with absence of light.
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TABLE I

TITRATION OF THALLIUM SOLUTION 3Q WITH POTASSIUM HEXACYANOFERRATE(II)

Ten milliliters of $1.682 \times 10^{-2}$ molar thallium(III) solution used yielding $16.820 \times 10^{-5}$ moles of Tl(III) ions.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Milliliters of 0.01 M $K_4Fe(CN)_6$</th>
<th>$Fe(CN)_6^{4-}$ moles times $10^5$</th>
<th>Mole Ratio $Tl^{3+}:Fe(CN)_6^{4-}$</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.61</td>
<td>13.61</td>
<td>1.236</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>13.64</td>
<td>13.64</td>
<td>1.233</td>
<td>-4</td>
</tr>
<tr>
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<td>13.59</td>
<td>13.59</td>
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<tr>
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<td>13.56</td>
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<td>1.240</td>
<td>+3</td>
</tr>
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<td>13.63</td>
<td>13.63</td>
<td>1.234</td>
<td>-3</td>
</tr>
<tr>
<td>7</td>
<td>13.56</td>
<td>13.56</td>
<td>1.240</td>
<td>+3</td>
</tr>
</tbody>
</table>

Average mole ratio 1.237:1.
Average deviation from the mean two parts per thousand.
TABLE II

TITRATION OF THALLIUM SOLUTION 3R WITH POTASSIUM HEXACYANOFERRATE(II)

Ten milliliters of 1.3428 x 10^{-2} molar thallium(III) solution used yielding 13.428 x 10^5 moles of Tl(III) ions.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Milliliters of 0.01 M K₄Fe(CN)₆</th>
<th>Fe(CN)₆⁴⁻ moles times 10^5</th>
<th>Mole Ratio Tl³⁺:Fe(CN)₆⁴⁻</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.75</td>
<td>10.75</td>
<td>1.249</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>10.83</td>
<td>10.83</td>
<td>1.240</td>
<td>-10</td>
</tr>
<tr>
<td>3</td>
<td>10.67</td>
<td>10.67</td>
<td>1.258</td>
<td>+8</td>
</tr>
<tr>
<td>4</td>
<td>10.83</td>
<td>10.83</td>
<td>1.240</td>
<td>-10</td>
</tr>
<tr>
<td>5</td>
<td>10.70</td>
<td>10.70</td>
<td>1.255</td>
<td>+5</td>
</tr>
<tr>
<td>6</td>
<td>10.74</td>
<td>10.74</td>
<td>1.250</td>
<td>0</td>
</tr>
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</tr>
<tr>
<td>8</td>
<td>10.70</td>
<td>10.70</td>
<td>1.255</td>
<td>+5</td>
</tr>
<tr>
<td>9</td>
<td>10.71</td>
<td>10.71</td>
<td>1.254</td>
<td>+4</td>
</tr>
</tbody>
</table>

Average mole ratio 1.250:1.
Average deviation from the mean five parts per thousand.
TABLE III
TITRATION OF THALLIUM SOLUTION 38 WITH POTASSIUM HEXACYANOFERRATE(II)

Ten milliliters of 1.7423 x 10^-2 molar thallium(III) solution used yielding 17.423 x 10^-3 moles of Tl(III) ions.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Milliliters of 0.01 M K₄[Fe(CN)₆]</th>
<th>Fe(CN)₆⁻₄ moles times 10⁵</th>
<th>Mole Ratio Tl³⁺:Fe(CN)₆⁻₄</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.12</td>
<td>14.12</td>
<td>1.234</td>
<td>-4</td>
</tr>
<tr>
<td>2</td>
<td>14.12</td>
<td>14.12</td>
<td>1.234</td>
<td>-4</td>
</tr>
<tr>
<td>3</td>
<td>14.04</td>
<td>14.04</td>
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<td>+3</td>
</tr>
<tr>
<td>5</td>
<td>14.02</td>
<td>14.02</td>
<td>1.243</td>
<td>+5</td>
</tr>
<tr>
<td>6</td>
<td>14.01</td>
<td>14.01</td>
<td>1.244</td>
<td>+6</td>
</tr>
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<td>14.11</td>
<td>14.11</td>
<td>1.235</td>
<td>-3</td>
</tr>
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<td>14.06</td>
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</tr>
<tr>
<td>9</td>
<td>14.08</td>
<td>14.08</td>
<td>1.237</td>
<td>-1</td>
</tr>
</tbody>
</table>

Average mole ratio 1.238:1.
Average deviation from the mean four parts per thousand.
TABLE IV

TITRATION OF THALLIUM SOLUTION 3T WITH POTASSIUM HEXACYANOFERRATE(II)

Ten milliliters of $1.3205 \times 10^{-2}$ molar thallium(III) solution used yielding $13.205 \times 10^{-5}$ moles of $\text{Tl}^{3+}$ ions

<table>
<thead>
<tr>
<th>Trial</th>
<th>Milliliters of $0.01 \text{ M } \text{K}_4\text{Fe(CN)}_6$</th>
<th>$\text{Fe(CN)}_6^{4-}$ moles times $10^5$</th>
<th>Mole Ratio $\text{Tl}^{3+}:\text{Fe(CN)}_6^{4-}$</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.51</td>
<td>10.51</td>
<td>1.256</td>
<td>-4</td>
</tr>
<tr>
<td>2</td>
<td>10.46</td>
<td>10.46</td>
<td>1.262</td>
<td>+2</td>
</tr>
<tr>
<td>3</td>
<td>10.47</td>
<td>10.47</td>
<td>1.261</td>
<td>+1</td>
</tr>
<tr>
<td>4</td>
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</tr>
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<td>10.49</td>
<td>10.49</td>
<td>1.260</td>
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<tr>
<td>6</td>
<td>10.46</td>
<td>10.46</td>
<td>1.262</td>
<td>+2</td>
</tr>
</tbody>
</table>

Average mole ratio 1.260:1.
Average deviation from the mean two parts per thousand.
TABLE V
TITRATION OF THALLIUM SOLUTION 3U WITH POTASSIUM HEXACYANOFERRATE(II)

Ten milliliters of $1.1428 \times 10^{-2}$ molar thallium(III) solution used yielding $11.428 \times 10^{-5}$ moles of Tl$^{3+}$ ions

<table>
<thead>
<tr>
<th>Trial</th>
<th>Milliliters of 0.01 M $K_4Fe(CN)_6$</th>
<th>$Fe(CN)_6^{4-}$ moles times $10^5$</th>
<th>Mole Ratio Tl$^{3+}$:Fe($CN)_6^{4-}$</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.16</td>
<td>9.16</td>
<td>1.248</td>
<td>-5</td>
</tr>
<tr>
<td>2</td>
<td>9.10</td>
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<td>1.256</td>
<td>+3</td>
</tr>
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<td>3</td>
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</tr>
<tr>
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<td>9.12</td>
<td>9.12</td>
<td>1.254</td>
<td>+1</td>
</tr>
<tr>
<td>6</td>
<td>9.10</td>
<td>9.10</td>
<td>1.256</td>
<td>+3</td>
</tr>
</tbody>
</table>

Average mole ratio 1.253:1.
Average deviation from the mean two parts per thousand.
TABLE VI
TITRATIONS AT DIFFERENT POTENTIAL DIFFERENCES

<table>
<thead>
<tr>
<th>Potential Millivolts</th>
<th>Tl$^{3+}$ moles times $10^5$</th>
<th>Fe(CN)$_6^{4-}$ moles times $10^5$</th>
<th>Mole Ratio Tl$^{3+}$:Fe(CN)$_6^{4-}$</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>13.428</td>
<td>10.92</td>
<td>1.231</td>
<td>-10</td>
</tr>
<tr>
<td>150</td>
<td>13.428</td>
<td>10.84</td>
<td>1.240</td>
<td>-1</td>
</tr>
<tr>
<td>250</td>
<td>13.428</td>
<td>10.74</td>
<td>1.250</td>
<td>+9</td>
</tr>
<tr>
<td>400</td>
<td>13.428</td>
<td>10.83</td>
<td>1.241</td>
<td>0</td>
</tr>
</tbody>
</table>

Average mole ratio 1.241:1.
Average deviation from the mean five parts per thousand.
Ten milliliters of a thallium(III) solution which had been diluted to a molarity of 9.2360 × 10⁻⁴ was titrated with a potassium hexacyanoferrate(II) solution which had been diluted to a molarity of 1.0000 × 10⁻³.

<table>
<thead>
<tr>
<th>Moles of Tl(III) times 10⁶</th>
<th>Milliliters of K₄Fe(CN)₆ solution</th>
<th>Moles of Fe(CN)₆⁴⁻</th>
<th>Mole Ratio Tl³⁺:Fe(CN)₆⁴⁻</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.236</td>
<td>7.41</td>
<td>7.41</td>
<td>1.246</td>
<td>-7</td>
</tr>
<tr>
<td>9.236</td>
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<td>1.245</td>
<td>-8</td>
</tr>
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<td>1.263</td>
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</tr>
<tr>
<td>9.236</td>
<td>7.38</td>
<td>7.38</td>
<td>1.251</td>
<td>-2</td>
</tr>
</tbody>
</table>

Average mole ratio 1.253:1.
Average deviation from the mean seven parts per thousand.
TABLE VIII
CHARACTERIZATION OF PRECIPITATE

The 5:4 molar relationship suggests a possible empirical formula \( \text{Tl}_5\text{K}[\text{Fe(CN)}_6]_4 \cdot n\text{H}_2\text{O} \) for the precipitate.

Heating of the precipitate yielded the following:

weight of hydrate = 0.2979 g  
weight of anhydride = 0.2615 g  
weight of water = 0.0363 g

If the reaction for the dehydration is assumed to be:

\[ \text{Tl}_5\text{K}[\text{Fe(CN)}_6]_4 \cdot n\text{H}_2\text{O} = \text{Tl}_5\text{K}[\text{Fe(CN)}_6]_4 + n\text{H}_2\text{O} \]

\[ \text{or} \quad 0.2615 \text{g} = 0.0364 \text{g} + n \times 0.001370 \text{moles} \]

The water relationship can be expressed:

\[ 0.0364 \text{g} = n \times 0.001370 \text{moles} \times 18 \text{ grams} \]

\[ = n \times 0.00247 \text{g} \]

solving \( n = 14.7 \) or nearly 15.
Figure 5. Ultra sensitive ammeter

\[ R_1 = 500,000 \text{ ohms} \]
\[ R_2 = 10,000 \text{ ohms} \]
\[ G = \text{common ground} \]
\[ e_o = \text{D. C. voltage probe} \]
\[ \text{O.A.} = \text{operational amplifier} \]

Figure 6. Balance circuit for ammeter

\[ R_3 = 100,000 \text{ ohms} \]
\[ R_4 = 10,000 \text{ ohms} \]
\[ G = \text{common ground} \]
\[ e_o = \text{D. C. voltage probe} \]
\[ \text{O.A.} = \text{operational amplifier} \]

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**USE OF OPERATIONAL AMPLIFIER**

1.5 volt D. C. equivalent to 3 microamperes full scale
5.0 volt D. C. equivalent to 10 microamperes full scale
15.0 volt D. C. equivalent to 30 microamperes full scale