

# THE TITRATION OF THALLOUS ION WITH POTASSIUM CHROMATE

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## THE TITRATION OF THALLOUS ION WITH POTASSIUM CHROMATE

By

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INTRODUCTION

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### INTRODUCTION

The gravimetric methods for the determination of thallium have been somewhat limited. The thallous chromate (6) or thallic oxide method (6) have been used for accurate work; but the precipitation of thallous iodide (6) has been used industrially because of its rapidity even though the results were not as accurate. Thionalide (2), thioglycollic aminonaphthalide, is specific for thallium in the presence of sodium hydroxide and potassium cyanide. The complex precipitate may be dried and weighed or titrated iodometrically.

The field of volumetric analysis has been explored by various workers in an attempt to find a rapid and accurate method. Several methods which depend upon a change in the oxidation state of thallium have been proposed (5,8). However, these methods have not proved entirely satisfactory. In two recently published articles, Mehrotra (10,11) attempted to solve the problem of an accurate volumetric method for thallium by proposing the use of bromphenol blue as an adsorption indicator in the precipitation of thallous iodide. On the basis of these two papers, it was decided to investigate the use of other indicators which might function as adsorption indicators in the precipitation of thallium.

The experimental problem was arranged to give special emphasis to the following: (1) sulforphthalein indicators other than bromphenol blue, (2) adsorption indicators listed by Fajans (13) as suitable for the titration of  $Ag^+$  and  $I^-$  ions, (3) chrysoidin derivatives as proposed by

Schulek and co-workers (14,15), and (4) congo red, which had been proposed by Mehrotra (12) as an adsorption indicator.

Fricke and Sammet (4) used sodium 2,6-dichlorobenzenoneindophenol as an adsorption indicator in the titration of lead with chromate. Since thallium forms an insoluble chromate, the use of various sodium benzenoneindophenol indicators was investigated as adsorption indicators in the precipitation of thallous chromate. Sodium 2,6-dichlorobensenoneindophenol was used successfully as an indicator in a volumetric precipitation of thallium. From the data obtained in these experiments, an accurate volumetric method for the determination of thallium was evolved. QUALITATIVE STUDY

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#### **WALITATIVE STUDY**

#### A. Adsorption Indicators

The qualitative study of the various adsorption indicators chosen was carried out as described below. A stock solution of thallous nitrate, approximately 0.04N, was prepared by dissolving 53 g. of C.P. grade thallous nitrate in 5 liters of redistilled water. The water, which was used in the preparation of all stock solutions, was redistilled from a Pyrex glass still.

A potassium iodide solution, approximately 0.04N, was prepared by dissolving 6.7 g. potassium iodide, C.P. grade, in redistilled water and diluting to one liter.

A potassium bromide solution of similar strength was prepared by dissolving 4.8 g. of C.P. grade potassium bromide in water and diluting to one liter.

Aqueous solutions of each indicator were prepared whenever possible, but in those cases where the indicator was not soluble in water, a 50% ethyl alcohol solution was used. The concentration of each indicator solution was 0.1 molar.

A sample of 20 ml. of stock thallous solution was titrated with potassium iodide or potassium bromide in the presence of each indicator listed in Table I. The direct and reverse titrations were attempted. The pH of the thallous solutions were adjusted to give the desired color form of the indicator. All possible color forms of each indicator were used. The results of these experiments are listed in Table I.

TABLE I

SUMMARY OF TITRATIONS OF THALLOUS NITRATE WITH POTASSIUM IDDIDE AND POTASSIUM BROWIDE USING VARIOUS ADSORPTION INDICATORS

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	Dia oi	LOTON	0	DeAleso	LIBCT	MITH	
Indicator	Solution	of Solution	Iodide		Bromide		11
Fluorescein	1.0	Greenish yellow	No color cha	nge	No colo	r change	
Eosin	7.0	Reddish yellow	No color cha	nge	No colo	r change	
Bromphenol Blue	5.0	Blue	Mehrotra's M	ethod	Slight	color change	
Bromphenol Blue	2.0	<b>Yellowish</b>	No color cha	agu	No colo	r change	
Bromcresol Green	6.0	Green	No color cha	nge	No colo	r change	
Bromcresol Green	3.0	Yellowish	No color cha	nge	No colo	r change	
Bromthymol Blue	7.7	Blue	No color cha	agu	No colo	r change	
Bromthymol Blue	3.0	Yellowish	No color cha	agu	No colo	r change	
Bromcresol Purple	0.7	Purple	No color cha	agu	No colo	r change	
Bromcresol Furple	3.0	Yellowish	No color cha	nge	No colo	r change	
Thymol Blue	1.2	Red	No color cha	nge	No colo	r change	
Thymol Blue	0.7	Yellowish	No color cha	nge	No colo	r change	
Thymol Blue	9.8	Blue	No color cha	nge	No colo	r change	
Cresol Red	6.5	Tellowish	No color cha	nge	No colo	r change	
Cresol Red	8.9	Red	No color cha	nge	No colo	r change	
Phenol Red	5.0	Yellowish	No color cha	age	No colo	r change	
Phenol Red	8.5	Red	No color cha	age	No colo	r change	
m-Cresol Furple	0.7	Yellowish	No color cha	nge	No colo	r change	
m-Cresol Furple	4.6	Purple	No color cha	agu	No colo	r change	
Chlorophenol Red	5.0	Yellowish	No color cha	nge	No colo	r change	
Methyl Violet	0.7	Purple	No color cha	nge	No colo	r change	
Crystal Violet	1.0	Purple	No color cha	nge	No colo	r change	
Methylene Blue	0.7	Blue	Slight color	change	Slight	color change	
p-Ethoxy Chrysoidin	3.2	Red	No color cha	nge	No colo	r change	
p-Ethoxy Chrysoldin	0.9	Yellow	Slight color	change	No colo	r change	
Chrysoldin R.	3.2	Red	No color cha	nge	No colo	r change	
Chrysoldin R.	2.0	Yellow	No color cha	nge	No colo	r change	
Sodium-alizarin Sulfonate	3.0	Yellow	No color cha	agu	No colo	r change	
Sodium-alizarin Sulfonate	0.7	Violet	No color cha	egu	No colo	r change	
Rhodamide 6 G	ONH NSO.	, Red orange	Color change	OVEL	No colo	r change	
			wide range				
Rhodamine B	ONH NZO.	Pink	Color change	not	No colo	r change	
			sharp				
Congo Red		Red	No color cha	age	No colo	r change	
Pheno safranine	OZN HNO.	Red	No color cha	agu	No colo	r change	1

The results of these experiments were completely negative. In those cases where a color change occurred, it was found to be unusable for analytical application.

## B. Sodium Benzenoneindophenol Derivatives

The qualitative experiments with sodium 2,6-dichlorobenzenoneindophenol were carried out in the manner described below.

A potassium chromate solution was prepared by dissolving 4.0 g. of C.P. grade potassium chromate in water and diluting to one liter. The calculated concentration of the potassium chromate solution was approximately 0.04M.

A 0.2% solution of sodium 2,6-dichlorobenzenoneindophenol, which was obtained from the Eastman Kodak Company, was prepared by dissolving 0.02 g. of the salt in 9.98 g. of water.

A sample of 20.0 ml. of stock thallous solution was pipetted into a 125 ml. Erlenmeyer flask. The sample was diluted to 30 ml. with redistilled water and 10 drops of the indicator solution was added. Upon the addition of the indicator, the solution was purple. The pH of the solution was lowered by adding one drop of 0.05N HNO<sub>3</sub> and the indicator changed to a scarlet. The potassium chromate solution was added slowly while the flask was swirled gently. A bright chrome yellow precipitate of thallous chromate was formed. The flask was swirled vigorously during the titration in order to coagulate the precipitate. After the addition of several milliliters of chromate solution, the flask was swirled strongly for several seconds. The solution at this point had an orange color when swirled. As the titration continued, it was noted that a

green color appeared where each drop of chromate solution entered, but disappeared upon mixing. As the end-point was approached, the entire solution became greenish, but reverted to orange after vigorous shaking for several seconds. At the end-point the entire solution became green and remained green after vigorous swirling. The precipitate was allowed to settle and the color of the supernatent liquid was observed. The supernatant liquid was colored purple. When this point was reached, standard potassium chromate was added a drop at a time. After the addition of each drop, the solution was swirled vigorously for 10 seconds. The precipitate was allowed to settle and the color of the supernatant liquid was again observed. The color of the supernatant liquid changed sharply from purple to blue. The observed color change occurred exactly as that described by Fricke and Sammet (b) in the titration of lead.

In view of the excellent color change which occurred when sodium 2,6-dichlorobenzenoneindophenol was used, several other substituted indophenols were tried.

A 0.2% solution of each indophenol was prepared. The titrations were carried out exactly as those for the sodium 2,6-dichlorobensenoneindophenol. The results are summarized in Table II.

Sodium 2,6-dichlorobenzenoneindophenol and sodium 2,6-dibromobenzenoneindophenol gave the best color changes when used as indicators during the qualitative tests. Therefore, both indicators were carried through the quantitative experiments.

# TABLE II

## SUMMARY OF RESULTS WITH VARIOUS SUBSTITUTED INDOPHENOLS

No.	Indicator	Formula	Results
1	Na 2,6-dichlorobensenone- indophenol	$N_a 0 \longrightarrow N = \langle \underbrace{\begin{array}{c} C1 \\ C1 \end{array}}_{C1} = 0$	The color change from red to blue was sharp, Further investigation was carried out
2	Na 2,6-dichlorobenzenone- 3'methylindophenol	$\mathbf{N}_{\mathbf{a}} \mathbf{O} \underbrace{\mathbf{C}}_{\mathbf{A}} \mathbf{N} = \underbrace{\mathbf{C}}_{\mathbf{C}} \mathbf{C} \mathbf{O}$	The color change from burnt orange to blue was not as good as No. 1. No further in- vestigation was attempt- ed.
3	Na 2,6-dichlorobenzenone- 3'chloroindophenol	$N_{a0}$ $\rightarrow N = $ $C1$ $C1$ $B_{T}$	The color change was not as sharp as No. 1. No further investiga- tion was attempted.
4	Na 2,6-dibromobenzenone- indophenol	$N_{a}O - N = 0$ Br	The color change from deep scarlet to blue was very sharp. Fur- ther investigation was carried out.
5	Na 2,6-dibromobensenone- 3'methylindophenol	$\mathbf{N}_{\mathbf{a}}\mathbf{O} \underbrace{\mathbf{C}}_{\mathbf{B}\mathbf{r}} \mathbf{H} = \underbrace{\mathbf{B}}_{\mathbf{B}\mathbf{r}} \mathbf{H} \mathbf{O} \\ \mathbf{B}\mathbf{r} \mathbf{H} \mathbf{O} \underbrace{\mathbf{C}}_{\mathbf{B}\mathbf{r}} \mathbf{H} \mathbf{O} \mathbf{O} \mathbf{H} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} O$	The color change from light orange to blue was not as distinct as No's 1 and 4. No further work was done.
6	Na 2,6-dibromobenzenone- 3'bromoindophenol	$\mathbf{N}_{\mathbf{q}} 0 \underbrace{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{R}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{r}}{\overset{\mathbf{B}\mathbf{R}}}{\overset{\mathbf{B}\mathbf{R}}{\overset{B}}{$	Indicator change is very poor due to ex- tremely light colors.
7	Na 2,6-dibromobenzenone- 2'methyl 5'isopropylindo- phenol	$N_{2}O \xrightarrow{CH_{3}} - N = \xrightarrow{Hr} O$ $HC \xrightarrow{CH_{3}} - N = \xrightarrow{Hr} O$ $Br = O$ $HC \xrightarrow{CH_{3}} O$	No visible color change occurred.
8	Na 2,6-dibromobenzenone- 3'methoxyindophenol	$N_a 0 $ $N$	No visible color change occurred

#### PRELIMINARY QUANTITATIVE STUDY

A set of weights was calibrated against weights which had been standardized by the National Bureau of Standards. A 20 ml. pipette, a 5 ml. pipette, a 50 ml. burette, and a 10 ml. burette were calibrated at 20° C. in the usual manner.

The exact concentration of the thallous nitrate solution was determined gravimetrically by the chromate method (6). The procedure follows:

A sample of 20.00 ml. of thallous nitrate stock solution was pipetted into a 400 ml. beaker. The solution was diluted to 200 ml. with redistilled water and 7 ml. of an ammonium hydroxide solution, which contained two parts of concentrated ammonium hydroxide to one part of water, was added. The solution was heated to  $70-80^{\circ}$  C. and 33 ml. of 10% potassium chromate solution was added slowly with stirring. Potassium chromate was added until the  $CrO_4^{--}$  concentration reached 2g./100 ml. solution. The precipitate was allowed to stand twelve hours and then was filtered through a Gooch crucible which had previously been prepared, dried at 120° C., and weighed. The precipitate was washed with a 1% solution of potassium chromate and then washed several times with a 50% methyl alcohol solution. The crucible and precipitate was weighed as  $Tl_2CrO_4$ . The results of these determinations are given in Table III. The concentration of the solution was taken as 189.7 mg. of thallium in 20.00 ml.

The chromate solution was standardized by comparison with a standard potassium dichromate solution. The comparison was made by means of a ferrous sulfate solution.

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TABLE	III
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## STANDARDIZATION OF 20,00 ML. OF STOCK THALLOUS NITRATE SOLUTION

Sample Number	Thallous Chromate Method (Mg. Tl. Found)
1	189.80
2	189.71
3	189.65
14	189.61
5	189.62
6	189.59
7	189.60
8	189.64
Average	189.70

A standard potassium dichromate solution was prepared by weighing out 2.5505 g. of National Bureau of Standards Sample #136, potassium dichromate, which had been previously dried for two hours at  $105^{\circ}$  C. The weighed potassium dichromate was dissolved in 500 ml. of redistilled water and then diluted to one liter at  $20^{\circ}$  C. in a volumetric flask which had been calibrated by the National Bureau of Standards. The standard dichromate was calculated to be 0.052245N in the reaction listed below.

$$K_2 Cr_2 O_7 + 6F_8 SO_4 + 7H_2 SO_4 \longrightarrow Cr_2 (SO_4)_2 + 3Fe_2 (SO_4)_2 + K_2 SO_4 + 7H_2 O$$
(1)

A ferrous sulfate solution was prepared by dissolving 10 g. of ferrous annonium sulfate in water containing 10 ml. of concentrated sulfuric acid. The solution was diluted to one liter in a volumetric flask and was approximately 0.025 N.

The potassium chromate solution was standardized by comparison with the standard potassium dichromate solution in the following manner (18):

A 40.0 ml. sample of the ferrous sulfate solution was pipetted into a 500 ml. Erlenmeyer flask. The acidity of the solution was adjusted by adding 5 ml. of dilute sulfuric acid (1:1) and 5 ml. of dilute phosphoric acid (1:1). The solution was diluted to 200 ml. and 0.3 ml. of 0.01M diphenylaminesulfonic acid was added as indicator. The ferrous solution was titrated with the standard potassium dichromate solution.

An identical sample of the ferrous sulfate solution was measured into a 500 ml. Erlenmeyer flask and treated as described above. However, this sample was titrated with the potassium chromate solution of unknown concentration. Therefore, the concentration of the potassium chromate solution was determined by titrating both the standard potassium dichromate solution and the potassium chromate solution against equal volumes of the ferrous sulfate solution.

The normality of the potassium chromate solution must be calculated in terms of equation (2).

$$2T1NO_3 + K_2CrO_4 \longrightarrow \underline{T1_2CrO_4} + 2KNO_3$$
 (2)

Simple calculations show that the normality of the potassium chromate solution in terms of equation (2) is equal to two thirds of the normality of the potassium chromate solution as determined experimentally on the basis of equation (1).

The initial conditions, which were chosen, were those used by Fricke and Sammet (4) in the determination of lead. A 20,00 ml. sample of the standardized thallous nitrate solution, which contained 189.7 mg.  $\text{Tl}^{+1}$ , was pipetted into a 125 ml. Erlenmeyer flack. The sample was diluted to 30 ml. and 10 drops of a 0.2% aqueous indicator solution were added. The sample solution was purple after addition of the indicator, but by adding 4 drops of 0.01N nitric acid, the color of the solution changed to red. The samples were titrated with standard potassium chromate solution. The indicator changed color exactly as described previously under the qualitative experiments. The quantitative results when using either sedium 2,6-dichlorobenzenoneindophenol or sodium 2,6-dibromobenzenoneindophenol were very poor. At this point, it was noticed that the end-point could be shifted by varying the amount of nitric acid which was added at the beginning of the titration. Thus it became essential to determine the nature of the end-point.

#### Experiments to Determine the Nature of the End-point

Fricke and Sammet (4) stated that sodium 2,6-dichlorobenzenoneindophenol acted simultaneously as an adsorption indicator and a pH indicator in their procedure for determining lead. In view of the fact that the amount of nitrie acid added at the beginning of the titration caused the indicator to change color and the end-point to be shifted, it was decided to follow the pH of the solution during the entire reaction.

A Beckman Model H-2 line operated pH meter, which employed a saturated calomel electrode as a reference electrode and a glass electrode as an indicator electrode, was used. A mechanical stirrer was also used to obtain the necessary agitation.

The pH meter was standardized by using a potassium acid phthalate buffer, pH 4.0 (3), prepared by dissolving 10.212 g. of reagent grade petassium acid phthalate in 600 ml. of water and diluting to one liter in a volumetric flask.

The sample solutions were prepared by measuring 40.00 mls. of standard thallous solution into a 250 ml, beaker and diluting to 60.0 ml. The initial pH of each solution was adjusted with 0.01M mitric acid and 0.01M ammonium hydroxide. No indicator was added during these titrations. The pH values vs. ml. of standard potassium chromate are plotted in Graph 1.



GRAPH NO.I

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Graph 1 showed a definite pH change occurring during the titration. It also showed that the point of color change for a pH indicator could be shifted by varying the initial pH of the solution. Thus the amount of standard chromate necessary to cause a sharp change in the pH of the solution was dependent upon the initial pH of the solution.

Similar curves were developed for titrations in which the indicator was present. These titrations were carried out in the same manner as those described above except that 10 drops of a 0.2% indicator solution were added. Both indicators, sodium 2,6-dichlorobenzenoneindophenol and sodium 2,6-dibromobenzenoneindophenol, change color from red to blue at a pH of 5.7. On the basis of Graph 1, an initial pH of 3.8 was chosen because the pH at which the indicators change color was located approximately at the equivalence point on the curve with an initial pH of 3.8. The results of these titrations are plotted on Graph 2.

Graph 2 showed that the pH curve of the titration was unchanged in the presence of either indicator. It also showed that the indicator might be functioning only as a pH indicator. Therefore a titration was made upon 30,00 ml. of redistilled water containing an amount of potassium nitrate equivalent to that formed during the titration of 189.7 mg. of thallous ion. Titrations were carried out in the absence of either indicator and also in the presence of 2 drops of a 0.2% solution of sodium 2,6-dichlorobenzenoneindophenol or 2 drops of a 0.2% solution ef sodium 2,6-dibromobenzenoneindophenol. Both indicators changed from red to blue exactly as when thallium was present. The results of these titrations are plotted in Graph 3.



GRAPH NO. 3



The pH of the 0.0435N potassium dichromate solution was 8.10. This was due to the hydrolysis of the potassium chromate according to equations (3) and (4).

$$K_{a}CrO_{a} + H_{a}O \longrightarrow HCrO_{a}^{*} + OH^{*} + 2K^{*}$$
(3)

Several titrations were made in which the pH of the chromate solution was varied by the addition of nitric acid or potassium hydroxide. The pH curves of these titrations varied greatly from those in which the pH of the chromate solution was a function only of the concentration. These curves are reproduced in Graph 4. In the case of the acidified chromate solution, the precipitate formed during the titration was orange instead of yellow. However, when potassium hydroxide was added to the chromate solution, the pH of the sample increased steadily. It was obvious, that in both instances, a marked variation from the other curves had occurred.

In summary, any theory in regards to the nature of the end-point must take into consideration the following: (1) The pH of the solution remained fairly constant until the equivalence point was approached. (2) The color change of the indicator was independent of the presence of thallium and was dependent upon the pH of the solution. (3) The amount of standard chromate which must be added to cause the color change of the indicator was dependent upon the amount of thallium and the initial pH of the solution. (4) The addition of acid or base to the standard chromate solution caused wide variations in the subsequent pH curves.

# GRAPH NO. 4

TITRATION OF 379.4 MG TL WITH 0.0463 N K2CRO4 OF VARYING PH

CURVE I, PH OF STD  $K_2 C_R O_4 = 6.60 \bullet$ CURVE 2, PH OF STD  $K_2 C_R O_4 = 6.95 \times$ CURVE 3, PH OF STD  $K_2 C_R O_4 = 10.15 \bullet$ 



The above mentioned experimental facts can be explained by considering that the color change of the indicator was due to a change in pH caused by hydrolysis of the excess potassium chromate. The nearly constant pH of the solution prior to the color change was caused by the removal of essentially all chromate ion from solution.

In order to verify the above statements, a single drop of 0.0435N potassium chromate was added to 15 ml. of stock thallous nitrate solution containing 23.7 mg. of thallium. A precipitate of yellow thallous chromate was formed and did not dissolve upon standing for five hours. The formation of the precipitate was considered likely even though the solubility product were not exceeded. However, calculation of the solubility product from the solubility of thallous chromate given in the literature (16), subsequently showed that the solubility product of thallous chromate was exceeded. The required calculations are reproduced below.

The solubility of  $Tl_{g}CrO_{4}$  given was 0.0427 g.  $Tl_{g}CrO_{4}$  per liter of saturated solution. Therefore the molar concentration was  $8.14 \times 10^{-5}$ .

$$K_{g,p} = [16.3 \times 10^{-6}]^3 \cdot [8.14 \times 10^{-6}]$$

$$K_{s.p.} = 1.75 \times 10^{-18}$$
  
Tl<sub>g</sub>Cr<sup>O</sup><sub>4</sub>

Fifteen milliliters of solution contained 23.7 mg. of thallium or 7.7 x  $10^{-3}$  millimoles/ml.

From the solubility product of thallous chromate calculated above, the concentration of chromate ion necessary to cause precipitation was calculated as shown below.

$$[7.7 \times 10^{-3}]^3$$
 .  $[Cr0_4^{-1}] = 1.75 \times 10^{-13}$ 

Neglecting the small change in volume, the molar concentration of chromate ion was calculated when one drop of 0.0435N potassium chromate was added to 15 ml. of solution.

According to the above calculation, the solubility product of thallous chromate was exceeded by the addition of one drop of 0.0435N potassium chromate solution to 15 ml. of a thallous nitrate solution which contained 23.7 mg. of thallium. These calculations substantiate the theory that in the initial phase of the titration, essentially all chromate was effectively removed from solution by the formation of thallous chromate according to the reaction below.

$$2T_{1NO} + K_{C}CrO_{A} = T_{1}CrO_{A} + 2KNO_{A}$$

The potassium nitrate, which was the other product formed, did not affect the pH of the solution. Thus, the increase in pH at the equivalence point was caused by the hydrolysis of potassium or thallous chromate.

Note should be made at this point that during further experimentation, it was found that some adsorption of the indicator probably occurred. In attempting to establish optimum conditions for carrying out the titration, attempts were made to match the blue color in the supernatant liquid with a color blank. The color blank was prepared by adding the indicator being used to a buffer solution with a pH of 5.7. The buffer was composed of potassium acid phthalate and sodium hydroxide in quantities which were specified by Clark (3). The volume of buffer solution was approximately that of the sample after titration and identical amounts of indicator were used in each instance. However, it was noted that the color blank was more highly colored than the supernatant liquid of the sample after titration. It was assumed from this data that some adsorption of the indicator had occurred. However, when thallous chromate was filtered from a sample which had been previously titrated in the presence of indicator, no difference in color was noted when compared with thallous chromate which was precipitated in the absence of indicator. This fact may be due to the large amount of bright yellow thallous chromate and the small amount of indicator which was probably adsorbed.

QUANTITATIVE METHODS

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#### QUANTITATIVE METHODS

After establishing the color change of sodium 2,6-dichlorobenzenonaindophenol and sodium 2,6-dibromobenzenoneindophenol to be that of a pH indicator, it was necessary to determine the initial pH of the solution which was required in order that the indicator change color at the equivalence point. From Graph 1 and Graph 2, it was apparent that the initial pH should be somewhere between 3.7 and 4.2. It was also desirable at this point to determine the amount of indicator which must be added to obtain the sharpest end-point. Since the indicator used was the sodium salt of a weak acid, it had basic properties upon hydrolysis. Therefore, if it were added at any point in the titration, the pH of the solution would be affected. By experimentation, it was found that the addition of two drops of a 0.2% aqueous solution of the indicator to 30.00 mL of solution was sufficient to give a good color change.

Titrations were carried out in which the initial pH of the solution was varied between 3.7 and 4.2. The initial pH was adjusted by using 0.01M and 0.1M mitric acid and ammonium hydroxide solutions in conjunction with the Beckman Model H-2 pH meter which was standardized as described previously. It was found that if 30.00 ml. of thallous mitrate solution was adjusted to a pH of 3.85 to 3.90 and two drops of a 0.2% indicator solution added, the color change could be used to establish the equivalence point. Attempts were made to titrate the solution to a color blank which has been described previously, but it was found more satisfactory to titrate to a pure blue color in the supernatant liquid.

In order to make the method more widely applicable, it was considered desirable to adjust the original pH of the solution by means of a second indicator. Methyl orange was chosen because it changed color at the desired pH and also because the yellow color of the basic form would not interfere with the color change of the indophenol. It was determined that two drops of a solution containing 0.2 g. of the sodium salt of methyl orange per liter was sufficient. The color was matched with a freshly prepared blank which was made by adding two drops of the methyl orange solution to 30.00 ml. of a solution which was buffered to a pH of 3.85-3.90. The 3.85 buffer was prepared in the following manner (3). A 0.1 molar solution of potassium acid phthalate was prepared by dissolving 20.42 g. of C.P. anhydrous potassium acid phthalate in redistilled water and diluting to one liter. An HCl selution which was standardized in the usual manner was also used. The buffer was prepared by mixing 50 ml. of the 0.1 molar potassium acid phthalate solution with 0.233 milliequivalents of HCl. The solution was then diluted to 100 ml.

From the above data, conditions were tentatively established for carrying out the titration in order to determine the effective concentration range of thallium over which the method would work. Titrations were made with varying amounts of thallium present and it was found that the concentration of the thallium must be taken into consideration. The smount of thallium present aid not affect the action of the indicator; but, if the concentration of thallium was too low, the precipitated thallous chromate did not coagulate and the end-point was obscured.

Thus the initial volume of solution to be titrated must be regulated. This was also true of the amount of indophenol indicator added. It was found that if the thallium concentration were 94 to 190 mg, an initial volume of 30 ml.and two drops of the indophenol indicator was satisfactory. However, if the amount of thallium being titrated were 23 to 94 mg., the initial volume should be 15 ml. and one drop of the indophenol indicator should be used. The limits given above in regards to initial volume are not highly critical, but must be observed within reason.

It was found that it was not necessary to reduce the two drops of methyl orange to one drop when titrating only 15 ml. of solution. The yellow color of the basic form of methyl orange did not interfere even when two drops were used in adjusting the initial pH of 15 ml. of thallous solution.

During these experiments, the use of sodium 2,6-dibromobenzenoneindophenol was unsatisfactory. The failure of this indicator was apparently due to adsorption of the indicator by the precipitate. Thus at the equivalence point, very little indicator was left in solution and the color change was poor. Therefore all further work employed only sodium 2,6-dichlorobenzenoneindophenol as indicator.

The use of a pH meter to adjust the initial pH of the solution was also investigated. The initial pH of the solution was adjusted by means of a Beckman Model G pH meter which was standardized in the same manner as described previously for the Beckman Model H-2 pH meter. Although experimental results show that a pH meter may be used successfully, some difficulty was encountered in keeping the volume of solution within set

TABLE .
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TITRATIONS	<b>T</b> 0	DETERMINE	EXPERIMENTAL	CONDITIONS
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Titration Number	Mg Tl Present	Mls. of Soln.	Drops of M.O.	Drops of Indophenol	Mg Tl Calc.	Error pp/1000
1	189.7	30	2	2	189.11	-2.5
2	189.7	30	2	2	189.29	-1.5
3	189.7	30	2	2	189.38	-1.0
Ĩ,	94.85	30	2	2	94.69	-1.0
5	94.85	30	2	2	95.13	+3.3
6	94.85	30	2	2	94.42	-3.8
7	47.42	30	2	2	47.7	+5.0
8	47.42	30	2	2	47.9	+10.0
9	47.42	30	2	2	46.4	-20.0
10	47.42	15	2	2	47.2	-4.0
11	47.42	15	2	2	47.6	+3.0
12	47.42	15	2	1	47.4	0.0
13	47.42	15	2	1	47.4	0.0
11	23.71	15	2	1	23.4	-15.0
15	23.71	15	2	1	23.7	0.0
16	23.71	15	2	1	23.4	-15.0
17	94.85	15	2	1	94.70	-2.0
18	94.85	15	2	1	94.39	-5.0

limits due to the quantitative transfers between the titrating flask and the pH meter, and the necessity of rinsing the electrodes. The results are tabulated in Table V.

The final conditions for carrying out the volumetric determination of thallium by precipitation of thallous chromate were established to be as follows;

## A. Titration of 94 to 190 mg. of thallium.

The sample containing the thallium in the thallous state was placed in a 125 ml. Erlermeyer flask. The total volume of the solution was adjusted to approximately 30 ml. and two drops of methyl orange solution, 0.2 g. of the sodium salt per liter, were added. The pH of the thallous solution was adjusted to 3.85-3.90 by using 0.1N and 0.01N solutions of nitric acid and ammonium hydroxide. The color of the solution was matched with a color blank which was prepared weekly by adding two drops of methyl orange to 30.00 ml. of the 3.85-3.90 buffer previously discussed. After adjusting the initial pH as described above, 2 drops of a 0.2% aqueous solution of sodium 2,6-dichlorobenzemoneindophenol were added. At this point the solution was scarlet. Standard potassium chromate was added slowly while the flask was rotated vigorously. The bright yellow thallous chromate precipitated causing the suspension to have an orange color. The flask was rotated continually during the titration to coagulate the thallous chromate. After the addition of several milliliters of petaesium chromate, the titration was stopped and the flask swirled for about 60 seconds. At the end-point, the thallous chromate should be

## TABLE V

# TITRATIONS OF VARYING AMOUNTS OF THALLIUM. INITIAL PH ADJUSTED TO 3.85-3.90 BY BECKMAN MODEL G PH METER

Titration Number	Ml. Solution	Mg Tl Present	Mg <b>Tl</b> Calculated	Error pp/1000
Number 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 14	30 30 30 30 30 30 30 30 30 30 30 30 30 15 15 15 15 15 15	189.70 189.70 189.70 189.70 189.70 94.85	189.4 189.3 189.3 189.5 189.4 94.51 94.42 94.33 94.33 94.33 47.3 47.3 47.1 23.4	-1.5 -2.0 -2.0 -1.0 -1.5 -2.5 -3.5 -4.5 -4.5 -4.5 -4.5 -4.5 -4.5 -4.5 -4
18 17 18	15 15 15	23.71 23.71 23.71	23.8 23.3 23.2	-8.0 -10.0

almost completely coagulated. Near the end-point a green color appeared where each drop of chromate entered, but disappeared upon mixing. Upon further addition of potassium chromate, the entire solution became greenish, but reverted to orange upon shaking for several seconds. At the endpoint, the suspension remained green when it was swirled vigorously. The solution was allowed to stand for several seconds. The yellow precipitate settled and the color of the supernatant liquid was observed. The endpoint was reached when the supernatant liquid exhibited a true blue color. If a purple color existed, the end-point had not been reached and if a green color existed, the end-point had been overstepped.

## B. Titration of 23 to 94 mg. of thallium.

The titration was carried out in exactly the same manner as above, except that the initial volume was 15 ml. and one drop of the indophenol indicator was used. A 15 ml. methyl orange color blank was also used, but two drops of methyl orange solution were added.

The results of the titrations carried out according to the above procedures are summarized in Tables VI and VII.

## TABLE VI

Titration Number	Ml. Soln.	Ml. K-CrO.	N. K-CrO.	Mg	T1 Found	Error pp/1000
						PF/
1	30	21.26	0.04350	189.70	189.0	-3.5
2	30	21.28	0.04350	189.70	189.2	-2.5
. 3	30	21.35	0.04350	189.70	189.8	+0.5
<u>Ā</u>	30	21.27	0.04350	189.70	189.1	-3.0
5	30	21.29	0.04350	189.70	189.3	-2.0
6	30	21.30	0.04350	189.70	189.4	-1.5
7	30	21.32	0.04350	189.70	189.6	-0.5
8	30	21.27	0.04350	189.70	189.1	-3.0
9	30	21.29	0.04350	189.70	189.3	-2.0
10	30	21.30	0.04350	189.70	189.4	-1.5
11	30	10.61	0.04350	94.85	94.33	-6.0
12	30	10.61	0.04350	94.85	94.33	-6.0
13	30	10.70	0.04350	94.85	95.13	+3.0
14	30	10.68	0.04350	94.85	94.95	+1.0
15	<b>3</b> 0	10.65	0.04350	94.85	94.69	-2.0
16	30	10.63	0.04350	94.85	94.51	-4.0
17	30	10.66	0.04350	94.85	94.78	-0.5
18	30	10.65	0.04350	94.85	94.69	-2.0
19	<b>3</b> 0	10.70	0.04350	94.85	95.13	+3.0
20	30	10.62	0.04350	94.85	94.42	-4.5
21	15	5.32	0.04350	47.42	47.3	-2.0
22	15	5.26	0.04350	47.42	46.8	-12.0
23	15	5.32	0.04350	47.42	47.3	-2.0
24	15	5.32	0.04350	47.42	47.3	-2.0
25	15	5.31	0.04350	47.42	47.2	-4.0
26	15	5.28	0.04350	47.42	47.0	-8.0
27	15	5.30	0.04350	47.42	47.1	-6.0
28	15	5.33	0.04350	47.42	47.4	0.0
29	15	5.34	0.04350	47.42	47.4	0.0
30	15	2.66	0.04350	23.71	23.7	0.0
31	15	2.59	0.04350	23.71	23.0	<b>-3</b> 5.0
32	15	2.64	0.04350	23.71	23.6	-5.0
33	15	2.64	0.04350	23.71	23.6	-5.0
34	15	2.63	0.04350	23.71	23.4	-15.0
35	15	2.64	0.04350	23.71	23.6	-5.0
36	15	2.65	0.04350	23.71	23.7	0.0
37	15	2.63	0.04350	23.71	23.4	-15.0
38	15	2.66	0.04350	23.71	23.7	0.0
39	15	2.63	0.04350	23.71	23.4	-15.0

# TITRATION OF VARIOUS AMOUNTS OF THALLIUM WITH POTASSIUM CHROMATE USING Na 2,6-DICHLOROBENZENONEINDOPHENOL AS INDICATOR

# TABLE VII

SUMMARY OF TITRATIONS WITH Na 2,6-DICHLOROBENZENONEINDOPHENOL

Number of	Mg Tha	llium	Av. Error	Max. Dev.
Titrations	Present	Found	pp/1000	pp/1000
10	189.7	189.30	-2	Ц.О
10	94.85	94.47	-4	8.5
9	47.42	47.21	-4	12.0
8 (Omit #22)	47.42	47.31	-3	8.0
10	23.71	23.5	-10	35.0
9 (Omit #31)	23.71	23.6	-8	15.0

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# THE EFFECT OF FOREIGN SALTS

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#### THE EFFECT OF FOREIGN SALTS

The effect of foreign salts upon the titration was investigated. Titrations were carried out with the addition of varying amounts of foreign salts, which were most likely to be present. The pH of each titration was adjusted to pH 3.85-3.90 after the addition of the foreign salt but prior to the titration. The results of these titrations are given in Table VIII.

The addition of modium or momonium nitrate did not affect the determination. On the other hand, the amount of sulfate present affected the end-point. The presence of a large sulfate concentration caused high results. The addition of even a small amount of phosphate or acetate caused very high results. These high results were probably due to the buffering action of the phosphate and acetate ions. The results obtained in the presence of 500 mg, of perchloric acid were excellent. Thus perchloric acid in large amounts does not interfere. However, the addition of even a small amount of potassium fluoride decolorized the indicator completely.

## TABLE VIII

Salt	Mg	Mls.	Mg.	, T1	Error
Added	Added	Soln.	Present	Calculated	pp/1000
Na-SO	100	30	189.7	189.9	+1.0
Na SO	200	30	189.7	191.7	+10.0
Na.50	500	30	189.7	193.2	+18.0
	100	30	189.7	189.9	+1.0
(NH_) 30	200	30	189.7	190.7	+5.0
NaNOa	100	30	189.7	189.9	+1.0
NaNO 2	200	<b>3</b> 0	189.7	189.5	-1.0
NaNOa	<b>5</b> 00	<b>3</b> 0	189.7	189.2	-2.5
NH_NO_	100	30	189.7	189.8	+0.5
NH NO	200	<b>3</b> 0	189 <b>.7</b>	189.6	-0.5
NH NO	<b>50</b> 0	30	189.7	189.2	-2.5
MapPO	10	<b>3</b> 0	189.7	190.5	+4.0
Na <sub>3</sub> PO4	20	30	189.7	193.4	+18.5
Na PO	50	<b>3</b> 0	189.7	197.6	+39.5
NaC <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	10	30	189.7	191.1	+6.5
HH_CIO	<b>5</b> 85	<b>3</b> 0	189.7	189.8	+0.5
N <sup>°</sup>	100	<b>3</b> 0	189 <b>.7</b>	decolorized i	ndicator
					completely

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THE EFFECT OF FOREIGN SALTS UPON THE TITRATION

INTERFERENCES

#### INTERFEILENCES

Several different interferences were noted during the experimental work and the literature survey. One of the most troublesome interferences is iron. Iron is commonly found with thallium and constitutes an interference when present in either the ferrous or ferric state. Titrations were made in which ferrous iron was added as ferrous ammonium sulfate. The initial pH was adjusted after the ferrous iron was introduced. The results of these titrations were high and the precision was very poor. The results are reproduced in Table IX.

In order to study the interference of iron in the ferric state, one milliliter of a ferric nitrate solution, which contained one milligram of iron per milliliter, was added to several samples of thallous nitrate. During the subsequent determination, ferric hydroxide precipitated. The freshly precipitated hydroxide immediately removed all indicator from solution. Apparently the removal of the indicator by the ferric hydroxide was due to adsorption. It might be expected that aluminium and chromium (III) would act in a similar manner.

The buffering effect of phosphate and acetate has been mentioned previously. Therefore it was assumed that any ion which will establish a buffered system similar to that established by phosphate and acetate would constitute ion interference. Mention has also been made that sulfate ion acts as an interference.

Several cations and anions are obvious interferences. Thallous iodide and bromide were precipitated in the initial phase of this work and thallous

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Titration	Mg. Fe <sup>+2</sup>	Mg T1		Error
Number	Added	Present	Found	pp/1000
1	10	189.7	194.3	+23.0
2	10	189.7	192.8	+15.5
3	10	189.7	193.7	+20 <b>_0</b>
4	10	189.7	193.9	+21.0

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TITRATION	IN	THE	PRESENCE	OF	FERROUS	IRON
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TABLE IX

chloride is insoluble. Therefore, Cl<sup>\*</sup>, Br<sup>\*</sup> and I<sup>\*</sup> would constitute interferences. The commonly used hydrogen sulfide Qualitative scheme employs the precipitation of lead chromate and barium chromate as confirmatory tests while insoluble silver chromate is used as an indicator in the Mohr method for the determination of chloride ion. Therefore it is readily apparent that barium, lead and silver constitute interferences in this method.

## COMPARISON WITH MEHROTRA'S METHOD

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#### COMPARISON WITH MEHROTRA'S METHOD

Mehrotra (10,11) proposed the determination of thallium by precipitation of thallous iodide using bromphenol blue as an adsorption indicator. Since this research problem was initially based upon Mehrotra's work, a comparison between the two methods was desirable. The comparison was carried out in the following manner.

A standard KI solution was prepared by dissolving 8.35 g. of C.P. potassium iodide in redistilled water and diluting to one liter. The solution was standardized (7) by measuring 20.00 ml. of the potassium iodide into a 400 ml. beaker. The solution was diluted to 200 ml. and made alkaline by the addition of a dilute ammonium hydroxide solution which was prepared from 2 part of concentrated ammonium hydroxide and one part water. Silver nitrate, 0.05N, was added slowly with stirring until the precipitation was complete. The precipitation was carried out in diffuse light. Mitric acid was added in 1% by volume excess. The precipitate was filtered and washed with 1% by volume nitric acid. The final washing was made with water to remove all nitrie acid. Water was sparingly used because it tended to render the iodide colloidal. The precipitate was dried at 100-110° C, for one hour and then at 130-150° C, for one hour. The results of the standardization are given in Table X.

Mehrotra stated that the end-point was reversible, but that it was much sharper if iodide ion was titrated with a standard thallous solution. Titrations were attempted in both directions, but in titrating thallous ion

## TABLE X

Sample Number	Mg AgI	Mg of KI per 20.00 ml.	Normality of KI Solution
l	294.4	208.1	0.06267
2	294.5	208.2	0.06273
3	294.3	208.1	0.06267
<u>h</u>	295.3	<b>2</b> 08 <b>.8</b>	<b>0.062</b> 86

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STANDARDIZATION OF POTASSIUM IODIDE SOLUTION

with potassium iodide, the end-point was so very poor that it was unusable. However, in titrating iodide ion with thallous nitrate a fair end-point was found. The titrations were carried out by pipeting varying amounts of standardized potassium iodide solution into a 125 ml. flask and adding 4 drops of 0.1% alcoholic solution of bromphenol blue. The pH of the solution was 5.0. The total volume of the solution was adjusted to 30.0 ml. with distilled water. Standard thallous nitrate solution was added with vigorous agitation. The titration was continued until the precipitate turned a dark green. The titration had to be carried out in very diffuse light because strong light turns the precipitated thallous iodide from a yellow to a green color. The results of these titrations are given in Table X.

In comparing methods, the following facts should be taken into consideration. The proposed chromate method is a direct titration of thallium while the Mehrotra method involves a reverse titration. The standardisation of the chromate solution was carried out volumetrically while the standardization of the potassium iodide solution was done gravimetrically. However, the iodide solution might have been standardized volumetrically using an adsorption indicator as proposed by Fajans (13). The end-point of the chromate method was sharper and clearer than that of the Mehrotra method. In view of the above cited facts, it is believed that the proposed chromate method is superior to the Mehrotra method.

TABLE	I
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DETERMINATION OF THALLIUM BY MEHROTRA METHOD

Sample	Ml. of	Ml.	Milliequiv.	Ml. of	Mg. Thal	lium	Error
Number	KI	Soln.	KI	Tl Soln.	Present	Found	pp/1000
1	20.0	30	1.254	27.08	256 <b>.3</b>	<b>2</b> 56 <b>.7</b>	+2
2	20.0	<b>3</b> 0	1.254	27.13	256.3	257.1	+4
3	20.0	30	1.254	27.08	256 <b>.3</b>	25 <b>7.</b> 1	+2
4	10.0	<b>3</b> 0	0.6269	13.60	128.2	128.8	+6
5	10.0	<b>3</b> 0	0.6269	13.58	128.2	128.6	+4
6	10.0	<b>3</b> 0	0 <b>.62</b> 69	13.63	128.2	129.3	+11
7	5.0	30	0.3135	6.84	64.1	65.8	+28
8	5.0	<b>3</b> 0	0.3135	6.85	64.1	66.0	+32
9	5.0	<b>3</b> 0	0.3135	6.82	64.1	65.0	+15

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METHYL RED AS A POSSIBLE INDICATOR

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#### METHYL RED AS A POSSIBLE INDICATOR

Methyl red was tried as an indicator because of the relative unavailability of sodium 2,6-dichlorobenzenoneindophenol and because it changed color over the desired pH range. Several titrations were made upon 20 ml. of standard thallous nitrate solution which was diluted to 30 ml. The solution contained 189.7 mg. of thallium. The pH of the solution was adjusted to 3.85-3.90 with methyl orange in the same manner as described previously. Four drops of a prepared methyl red solution were added. Standard potassium chromate was added with vigorous swirling as described under the directions for carrying out the titration using sodium 2.6-dichlorobensenoneindophenol. A color change in the supernatant liquid from red to yellow took place. The color change was fairly sharp. However, some of the methyl red underwent adsorption because the precipitated yellow thallous chromate had no orange cast. This caused the suspension to appear orange upon swirling, but if the precipitate was allowed to settle, the supernatant liquid underwent a fairly sharp color change from red to yellow.

The quantitative results of this experiment were extremely poor. However, if the proper experimental conditions were determined, the methyl red color change probably could be used to mark the equivalence point in the precipitation of thallous ion with potassium chromate.

# SEPARATION OF THALLIUM

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### SEPARATION OF THALLIUM

Wada (17) proposed that thallic bromide could be separated from the salts of all other metals except gold by shaking a hydrobromic acid solution with ether. McBryde and Yoe (9) used the ether extraction from hydrobromic acid to separate gold. According to McBryde and Yoe the percent of extraction of iron was dependent upon the approximate molarity of the hydrobromic acid and the ether used. The smallest amount of iron was removed if the molarity of the hydrobromic acid was maintained at 2-2.5 molar and isopropyl ether was used.

In view of the two papers cited above, an attempt was made to separate thallium from iron by extraction with isopropyl ether.

Eastman Kodak technical grade isopropyl ether was purified in the following manner. The ether was shaken in a large separatory funnel with acidified ferrous ammonium sulfate solution to remove the peroxides which might be present in the ether. The ether layer was separated and stored over sodium to remove all alcohols and water. After drying for several days, the ether was redistilled from copper turnings and placed in a dry bottle whose stopper contained a calcium chloride tube filled with anhydrous magnesium perchlorate.

The following procedures were used in attempting to separate thallium from iron by extraction with isopropyl ether.

## A. With continuous extraction apparatus.

A continuous extraction apparatus as described by Ashley and Murry (1)

was used. A 5 ml, sample of stock thallous nitrate solution which contained 47.41 mg, of thallium, and 1 ml. of a ferric nitrate solution which contained 10 mg, of iron were placed in the apparatus. Bromine water was added in excess to oxidize the thallium from the thallous to the thallic state. The molarity of the solution with respect to hydrobromic acid was adjusted by the addition of 18.5 ml. of 34% HBr. The solution was diluted to 50 ml. The isopropyl ether was added and the extraction carried out for eight hours.

After extraction, the ether solution was evaporated on a steam bath to 5 ml. and transferred to a 50 ml. Erlenmeyer flask. The solution was diluted to 10 ml. and 0.15 ml. of 70-72% perchloric acid was added. The solution was evaporated to dryness on a steam bath and then taken to fumes of perchloric acid to remove any bromine.

The residue was taken up in 10, ml. of water and 1 ml. of a 20% sodium sulfite solution was added to reduce the thallium to the thallous state. The solutions were boiled for one minute and then cooled to room temperature. The initial pH was adjusted against the color buffer and one drop of a 0.2% solution of sodium 2,6-dichlorobensenoneindophenol was added. The solution was titrated with standard chromate as described before. The results are summarized below.

Sample No.	Mg. Tl Present	Mg Tl Found
1	47.42	48.0
2	47.41	49.4

## B. With mechanical shaker.

A 5 ml. sample of thallous nitrate solution which contained 47.41 mg. of thallium was pipetted into a 300 ml. iodine flask. Iron was introduced by the addition of 1 ml. of a ferric nitrate solution which contained 10 mg. of iron per milliliter. Bromine water was added until the color of free bromine was observed. After the oxidation, 18.5 ml. of a 34% hydrobromic acid solution was added and the volume of the solution was made up to 50 ml. The extraction was carried out by the addition of 50 ml. of purified isopropyl ether to the water solution. The flask was tightly stoppered and shaken for 30 minutes by means of a mechanical shaker. The flask was then removed from the shaker and the contents placed in a 250 ml. separatory funnel. The two layers were separated. The water layer was replaced in the iodine flask and three more extractions were made upon that particular solution. The ether extracts were combined and evaporated over a steam bath to 5 ml. of solution. The samples were then treated identically as those which underwent continuous extractions. The results of these extractions are given below.

Sample No.	Mg. Tl Present	Mg. Tl Found	
1	47.41	49.1	
2	47.41	<b>5</b> 0.5	

From the above results, it can easily be seen that this method was not successful. The high results are probably caused by iron being extracted along with the thallium.

DISCUSSION AND CONCLUSION

#### DISCUSSION AND CONCLUSION

The titration of thallous ion with potassium chromate proved successful when sodium 2,6-dichlorobenzenoneindophenol was used as indicator. The error was less than 8 parts per thousand when titrating approximately 20 to 190 mg. of thallium. A comparison of the proposed chromate method with the Mehrotra (10,11) method was made and the chromate method was found to be superior.

Contrary to the proposal of Fricke and Sammet (h) which stated that sodium 2,6-dichlorobenzenoneindophenol functioned as a pH and an adsorption indicator in the titration of lead with potassium chromate, sodium 2,6-dichlorobenzenoneindophenol functioned only as a pH indicator in the titration of thallous ion with potassium chromate. Several other substituted indophenols were also tried, but they proved unsuccessful.

Experiments were carried out in which methyl red was substituted as the indicator instead of sodium 2,6-dichlorobenzenoneindophenol. A color change was observed, but it did not occur at the equivalence point. However, it is believed that methyl red could be used as the indicator by adjusting the initial conditions.

Common interferences of the proposed method were noted and studied. An attempt was made to separate thallium from iron by extraction from a hydrobromic acid solution with isopropyl ether. The method used was not satisfactory. However, further investigation of this separation might yield a successful procedure.

Several additional experiments were carried out using various indicators and dyes as adsorption indicators in the titration of thallous ion with potassium iodide or potassium bromide. The results of these experiments were completely negative. LITERATURE CITED

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