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DETERMINATION OF THALLIUM

BY A DITHIZONE MIXED-COLOR METHOD

By Roy S. Clarke, Jr., and Frank Cuttitta

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Trace Elements Investigations Report 667

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY





UNITED STATES  
DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY  
WASHINGTON 25, D. C.

April 4, 1958

AEC-425/8

Dr. Paul W. McDaniel, Acting Director  
Division of Research  
U. S. Atomic Energy Commission  
Washington 25, D. C.

Dear Dr. McDaniel:

Transmitted herewith is one copy of TEI-667, "Determination of thallium by a dithizone mixed-color method," by Roy S. Clarke, Jr., and Frank Cuttitta, December 1957.

We plan to submit this report for publication in *Analytica Chimica Acta*.

Sincerely yours,

*John H. Eric*  
for W. H. Bradley  
Chief Geologist

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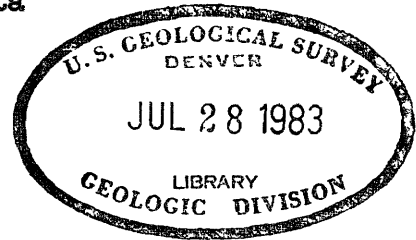
UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

DETERMINATION OF THALLIUM BY A DITHIZONE  
MIXED-COLOR METHOD\*

By

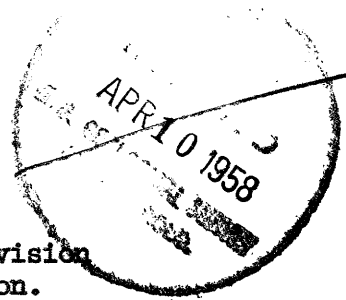
Roy S. Clarke, Jr., and Frank Cuttitta

December 1957



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## DETERMINATION OF THALLIUM BY A DITHIZONE MIXED-COLOR METHOD

by

Roy S. Clarke, Jr., and Frank Cuttitta

## ABSTRACT

The absorption spectra of the thallium-dithizone mixed-color system are presented and discussed. An analytical procedure based on this system is given which is applicable to pure solutions.

In the procedure thallium is extracted with a chloroform solution of dithizone from a citrate-sulfite-cyanide medium at a pH of 10.6 and then stripped from this chloroform solution with dilute nitric acid. The resulting acid solution is neutralized with sodium hydroxide and the pH again adjusted to 10.6 with potassium cyanide. A second extraction is made with dithizone and the absorbance determined at 505 m $\mu$ . Lead, bismuth, and tin (II) are serious interferences.

## INTRODUCTION

The present investigation was undertaken to find a direct and sensitive colorimetric method for the determination of thallium in relatively pure solutions. A procedure of this type was required for a contemplated study of the absorption of metal ions from solution by various minerals. Neither Anderson's<sup>1</sup> thorough review of the analytical chemistry of thallium nor a search of the more recent literature led to a procedure that seemed to satisfy our requirements.

The most commonly used colorimetric method for the determination of small quantities of thallium has been based largely on the reports of Haddock<sup>2</sup> and Sill and Peterson<sup>3</sup>. Thallium (III) is reacted with iodine and the final color measurement made on the starch-iodine system. This procedure has the disadvantages inherent in an indirect measurement of thallium concentration and the instability of the starch-iodine system.

Fischer and Weyl<sup>4</sup> presented the absorption spectrum of a carbon tetrachloride solution of thallium (I) dithizonate which had been extracted from a solution containing potassium cyanide. Subsequently, dithizone has been used as a means of separating thallium from other elements, but it has not been used as a colorimetric or spectrophotometric reagent for thallium. However, it has been used as a "limit test" by Bambach<sup>5</sup>, where total lead and thallium are determined together in pharmaceutical chemicals by colorimetric comparison of dithizone solutions.

Sandell<sup>6</sup> suggested that dithizone could be used as a reagent for the determination of thallium. An investigation of this system was undertaken because dithizone offers the advantages of a single reagent being used for the separation, concentration, and the direct measurement

of thallium. A procedure based on it would also be of comparable sensitivity to that found in other metal-dithizone systems.

Extraction with dithizone from an alkaline solution containing cyanide and citrate separates thallium from usual concentrations of elements other than lead, bismuth, and tin (II). These interferences would be insignificant in the solution in which we were interested and it was thought that by properly selecting separations this method could later be applied to materials of geologic interest. Maynes and McBryde<sup>7</sup> have shown that extraction with diethylammonium diethyldithiocarbamate can be used to separate thallium from lead and bismuth.

During the course of this work a number of papers have been published on the use of other colorimetric agents for the determination of thallium. Gur'ev<sup>8</sup> has reported a procedure using methyl violet and Gur'ev and Shkrobot<sup>9</sup> one using crystal violet. Voskresenskaya<sup>10</sup> has reported on the use of both methyl violet and Brilliant Green. Gladyshev and Tolstikov<sup>11</sup> have used p-aminophenol, and Pohl<sup>12</sup> has made use of the absorption of ether solutions of thallium carbamate. Onishi<sup>13</sup> has developed a procedure using Rhodamine B.

## APPARATUS AND REAGENTS

### Apparatus

Spectrophotometer. All absorbance measurements were made with a Beckman DU spectrophotometer using 1-cm corex cells. The absorption spectra were recorded with an automatic attachment.

pH meter. A line operated pH meter with a special high pH glass electrode and a sleeve-type calomel electrode was used.

Shaking machine. A wrist-action laboratory shaking machine was used.



## Reagents

Water. Redistill water from an all glass still.

Thallium nitrate solution. (1.00 mg Tl/ml). Dissolve 1.303 g of thallous nitrate in redistilled water and dilute to a liter. This solution is diluted to a convenient concentration just prior to use.

Sodium citrate, 25 percent (w/w). Dissolve 250 g of reagent grade sodium citrate in 750 g of redistilled water.

Sodium sulfite, 5 percent (w/w). Dissolve 25 g of reagent grade (A.C.S.) sodium sulfite in 475 g of redistilled water and store in a polyethylene bottle.

Potassium cyanide, 5 percent (w/w). A purified potassium cyanide solution is prepared according to the procedure of Sandell<sup>14</sup>. This solution should be stored in a polyethylene bottle.

Chloroform. Reagent grade (A.C.S.) chloroform is redistilled with an all glass still.

Dithizone. Purify dithizone by the procedure of Sandell<sup>15</sup>. Store dithizone solutions in red low actinic glass bottles in a refrigerator.

Dithizone solution no. 1. (1.2 mg dithizone/15 ml). Dissolve 80 mg of purified dithizone in 1 liter of redistilled chloroform.

Dithizone solution no. 2. (0.4 mg of dithizone/15 ml). Dissolve 27 mg of purified dithizone in 1 liter of redistilled chloroform.

Nitric acid, 0.08M. Dilute 5.0 ml of reagent grade nitric acid which has been redistilled with an all glass still to 1 liter with redistilled water.

Sodium hydroxide, 0.08M. Dissolve 3.2 g of reagent grade (A.C.S.) sodium hydroxide in 1 liter of redistilled water. Store in a tightly closed polyethylene bottle.

## RECOMMENDED PROCEDURE

The procedure found most successful is the double extraction procedure given in detail here.

Transfer an aliquot of a neutral thallium solution to a 60-ml separatory funnel which has a Teflon stopcock. Add 5.0 ml of 25 percent sodium citrate, 1.0 ml of 5 percent sodium sulfite, 2.0 ml of 5 percent potassium cyanide, and enough water to make a total volume of 20 ml (Tl solution plus  $H_2O$  equals 12 ml). Add 15.0 ml of dithizone solution no. 1 (1.2 mg of dithizone) and shake for 10 minutes on a shaking machine.

Allow the two layers to separate for several minutes and then drain the chloroform layer into a clean 60-ml separatory funnel. Rinse the stem of the first separatory funnel by passing 2 ml of chloroform through the funnel. Wash the water layer twice more by shaking by hand for about 10 seconds with 3 ml portions of chloroform. Collect all of the washings in the second separatory funnel taking care to empty the stem of the first separatory funnel each time chloroform solution is drained off.

Strip the thallium from the chloroform solution in the second separatory funnel by shaking with 0.08M nitric acid. To do this add 15.0 ml of 0.08M nitric acid to the separatory funnel containing the chloroform solution and shake on a shaking machine for 5 minutes. Allow the two layers to separate for several minutes and then drain off the chloroform layer and discard it. Wash the water layer as before by first rinsing with 2 ml of chloroform and then wash twice more with 3 ml portions of chloroform being careful not to lose any of the water layer.

Neutralize the nitric acid solution in the separatory funnel by titrating with 0.08M sodium hydroxide. For this step add 0.05 ml of approximately 0.1 percent methyl red to the solution in the separatory funnel (the methyl red must be added carefully from a pipette as it contributes to the blank). Add the sodium hydroxide from a burette until the first definite yellow end point is reached. Add 2.0 ml of 5 percent potassium cyanide, followed by 15.0 ml of the dilute dithizone solution no. 2 (0.4 mg dithizone) which has been allowed to warm to near room temperature. Extract by shaking for 10 minutes on a shaking machine. Insert a filter plug made by rolling half a circle of 5.5 cm close textured filter paper into the stem of the funnel. Draw off and discard the first 1 to 2 ml of chloroform solution and collect most of remainder in a small glass stoppered flask. Measure the absorbance against chloroform as a reference solution at 505 m $\mu$  using 1-cm cells.

#### DISCUSSION OF EXPERIMENTAL CONDITIONS

In preliminary experiments the absorption spectra of the thallium-dithizone system were obtained at a number of thallium concentrations. These data were the basis for development of a procedure for determining thallium. A citrate-sulfite-cyanide medium was selected for the extraction of thallium dithizonate from aqueous solution and the effects of various factors on this system were studied.

A procedure involving two extractions with dithizone is recommended over a single extraction from the citrate-sulfite-cyanide medium for two reasons. The double extraction procedure is somewhat more sensitive and more reproducible results are obtained. The increase in reproducibility undoubtedly results from the more readily controlled conditions in the solution from which the final extraction is made.

## Preliminary experiments

### Absorption spectra

The absorption spectra of the thallium-dithizone mixed-color system obtained in preliminary experiments are given in Fig. 1. The solutions from which these curves were obtained were made by extracting an aqueous solution of thallium with 15.0 ml portions of a chloroform solution of dithizone which contained 0.3 mg of dithizone per 15 ml. The aqueous solutions were made to a total volume of 20 ml. They contained various amounts of thallium, 3 ml of 6 percent hydroxylamine hydrochloride, and their pH was adjusted to 10.2 by the addition of 2N sodium hydroxide. After the extraction was completed, the chloroform solutions were filtered through a filter paper plug in the stem of the separatory funnel into a glass stoppered flask. These solutions were used directly to obtain absorption spectra with a recording spectrophotometer.

Chloroform was used as a reference and measurement was made in 1-cm cells.

In Fig. 1, curve 1 represents the absorption spectrum of a chloroform solution of dithizone, and it has a minimum at 502 m $\mu$  and a maximum at 606 m $\mu$ . Curve 7 represents the absorption spectrum of pure complex, and it has a maximum at 512 m $\mu$  and a minimum at 400 m $\mu$  which is not shown in the figure. These curves are essentially the same as those given by Fischer and Weyl<sup>4</sup>. Curves 2 through 6 are for various levels of thallium.

In Fig. 1 there are isoabsorptive points shown at 438 and 555 m $\mu$ . A third isoabsorptive point was observed at 390 m $\mu$ . This type of absorption spectrum is a criterion for the existence of an equilibrium between two absorbing species (West<sup>18</sup>). This would indicate that equilibrium exists between a single thallium-dithizone complex and dithizone under the

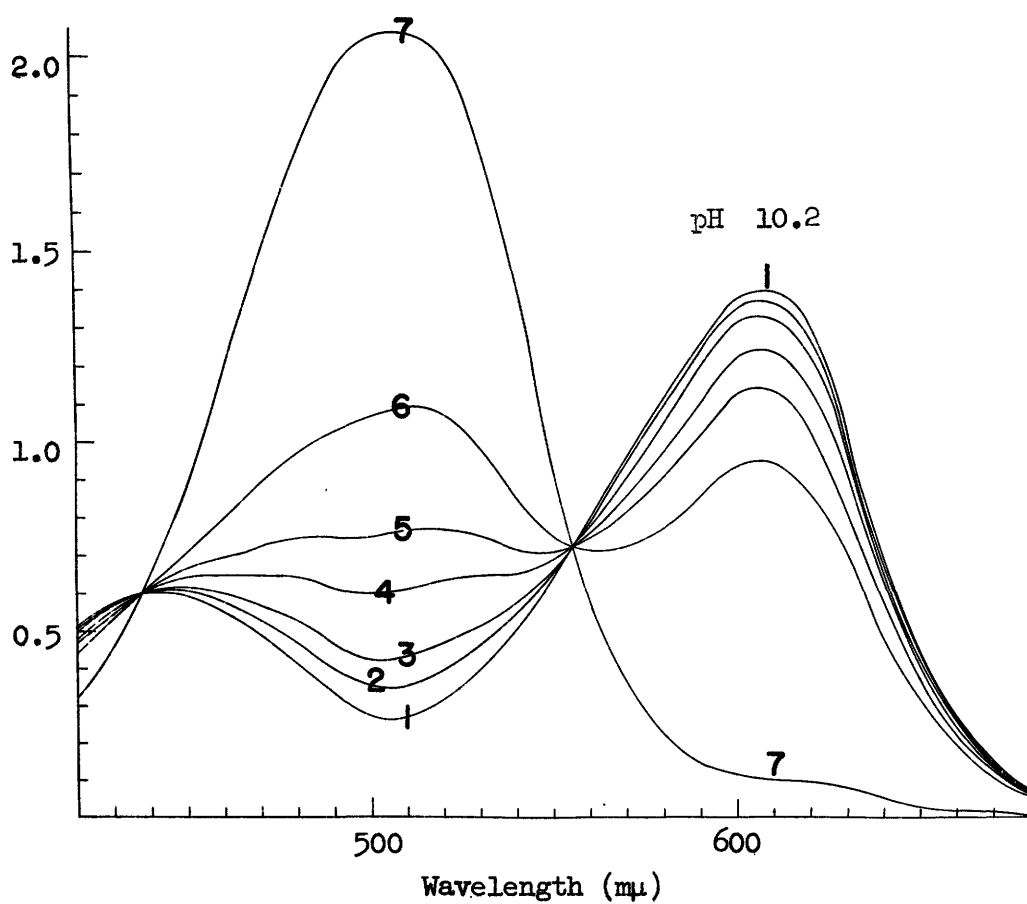


Fig. 1. Absorption spectra of Tl-dithizone mixed-color system. (Chloroform reference, 1-cm cells.)

<u>Curve</u>	<u>Tl, <math>\mu</math>g</u>
1	0
2	10
3	20
4	40
5	60
6	100
7	1000

conditions of this experiment.

Fig. 1 also shows that the absorption peaks for the thallium-dithizone complex and for dithizone are well separated. The region of each of these peaks is particularly suitable for relating absorbance measurements to thallium concentration. Measurement of the increase in absorbance due to complex formation can be made from 505 to 515  $m\mu$ . Measurement of the decrease in absorbance due to disappearance of dithizone can be made from 600 to 610  $m\mu$ . A plot of data taken from Fig. 1 at selected wave lengths within these regions is given in Fig. 2. The curve at 505  $m\mu$  is considerably more sensitive and conforms to Beer's law. The curve at 606  $m\mu$  shows slight deviation from Beer's law. For these reasons all subsequent work was done at 505  $m\mu$ .

#### Use of citrate and sulfite

The first extraction of thallium dithizonate is made from solutions approximately 0.2M in sodium citrate. The function of the citrate is to complex metals that would precipitate as hydroxides or phosphates at the high pH used (Welcher<sup>17</sup>). As the presence of citrate usually has no effect on the extraction of dithizonates, no specific test of its effect on the system was made. Ammonium citrate cannot be used to replace sodium citrate at the high pH used as ammonia is evolved and variations in pH result.

Sodium sulfite is used as a reducing agent to insure that thallium is present as thallium (I) and to reduce foreign ions that might otherwise oxidize dithizone. Hydroxylamine hydrochloride has been frequently used for this purpose but was found to be unsatisfactory in this instance.

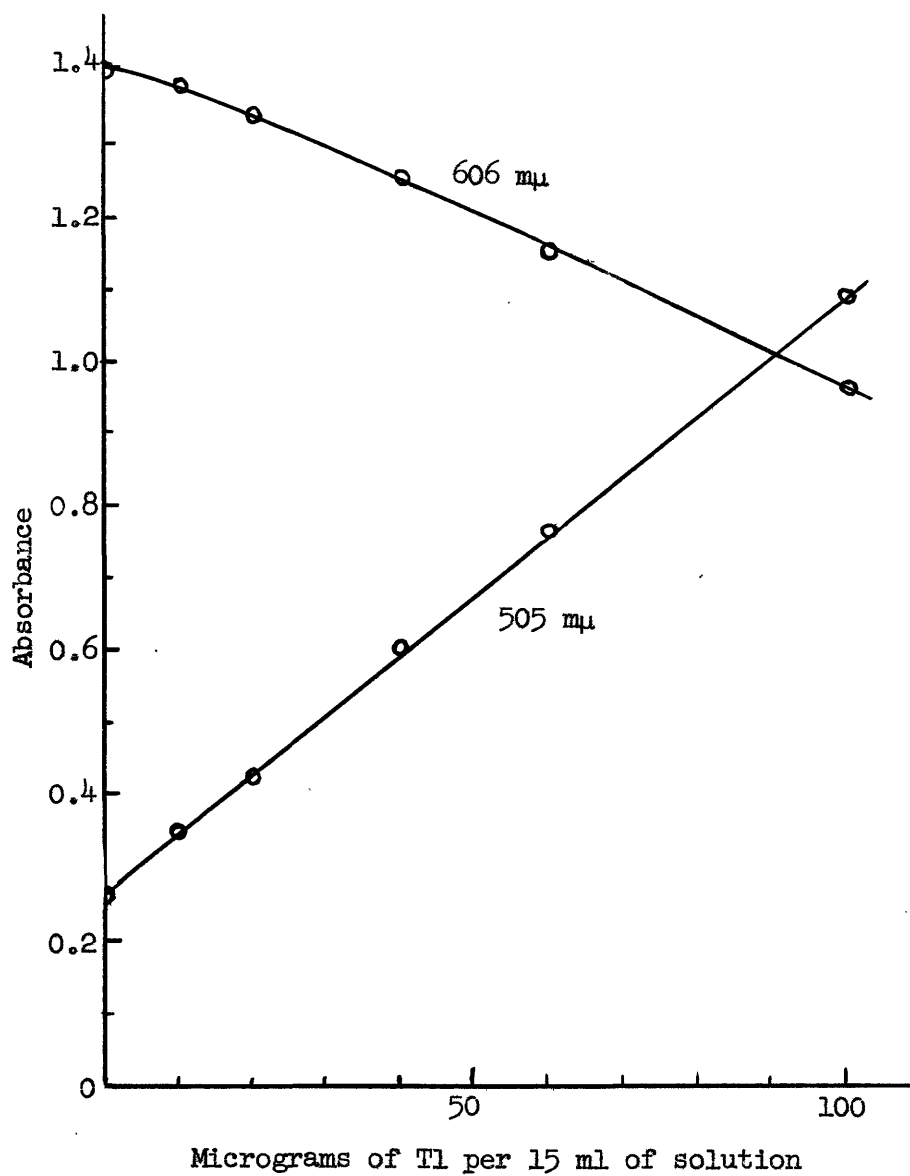


Fig. 2. Relationship of absorbance at 505 and 606 mμ to thallium concentration. (Chloroform reference, 1-cm cells.)

It gives poorly reproducible blanks and occasional erratic absorbance readings for the thallium-dithizonate solutions.

### Study of experimental variables

Studies, using single extraction with the dilute dithizone solution, were made of the factors considered in selecting the conditions recommended in the procedure. The single extraction studies gave sufficiently accurate data at a considerable saving of time.

#### Effect of pH and potassium cyanide concentration

Wichman<sup>18</sup> presented curves that relate the percent metal extracted by a chloroform solution of dithizone to the pH of the solution from which the metal was extracted. According to the curve given for thallium (I), thallium can be extracted somewhat at a pH slightly above 8 and completely at pH values of 10.5 or greater. Our experimental data indicated an optimum pH range of 10.3 to 11.5 for the chloroform extraction of thallium (I). It also showed no extraction of thallium (I) at a pH less than 7.7, thus confirming the curve Wichman had given earlier.

Preliminary experimental data also indicated that close control of pH would be necessary for an accurate and precise method. Within the optimum pH range, the absorbance of both the thallium complex and the reagent blank varied slightly with change of pH, the absorbance of the blank decreasing with increasing pH.

Selection of potassium cyanide for controlling pH was based primarily on its ability to buffer within the pH range chosen for the chloroform extraction. A further consideration was the desirability of having cyanide ion present to prevent the extraction of metals other than



thallium (I), lead, tin (II) and bismuth (Sandell<sup>19</sup>). Subsequent work on the simultaneous effect of pH and potassium cyanide concentration, was in the pH range of 9.9 to 11.1, the latter pH requiring use of more cyanide than would be convenient in practice.

The study of the effect of variation in potassium cyanide concentration upon extraction was made with two series of solutions each containing the recommended amount of citrate and sulfite. One series was a reagent blank and the other contained 50 micrograms of thallium. Amounts of 5 percent potassium cyanide varying from 0.5 to 10 ml were added to each series, and the volumes were adjusted to a total of 20 ml with water. These solutions were extracted with 15 ml of dilute dithizone solution.

Absorbance measurements were made on the chloroform-dithizone extracts, and pH measurements were made on the aqueous phase. Results are shown in Fig. 3.

The curves in Fig. 3 diverge over the pH range presented and do not show the complete relationship between pH and absorbance. This incomplete picture results from the limitation in pH attainable with potassium cyanide. Earlier work using sodium hydroxide to attain higher pH values shows that the curves reach a maximum divergence at about a pH of 11.5 and then converge rapidly. At pH 12.5, the difference in absorbance between a reagent blank and the chloroform extract of the thallium (I) dithizonate is about 50 percent of the difference at pH 11.5.

Although consideration of Fig. 3 indicates that the greatest sensitivity would be obtained when using 10.0 ml of the cyanide solution (pH 11.1), 2.0 ml of 5 percent potassium cyanide (pH 10.5) was selected for the recommended procedure. Experience showed that any increase in sensitivity obtained when using larger than 2 ml amounts of cyanide

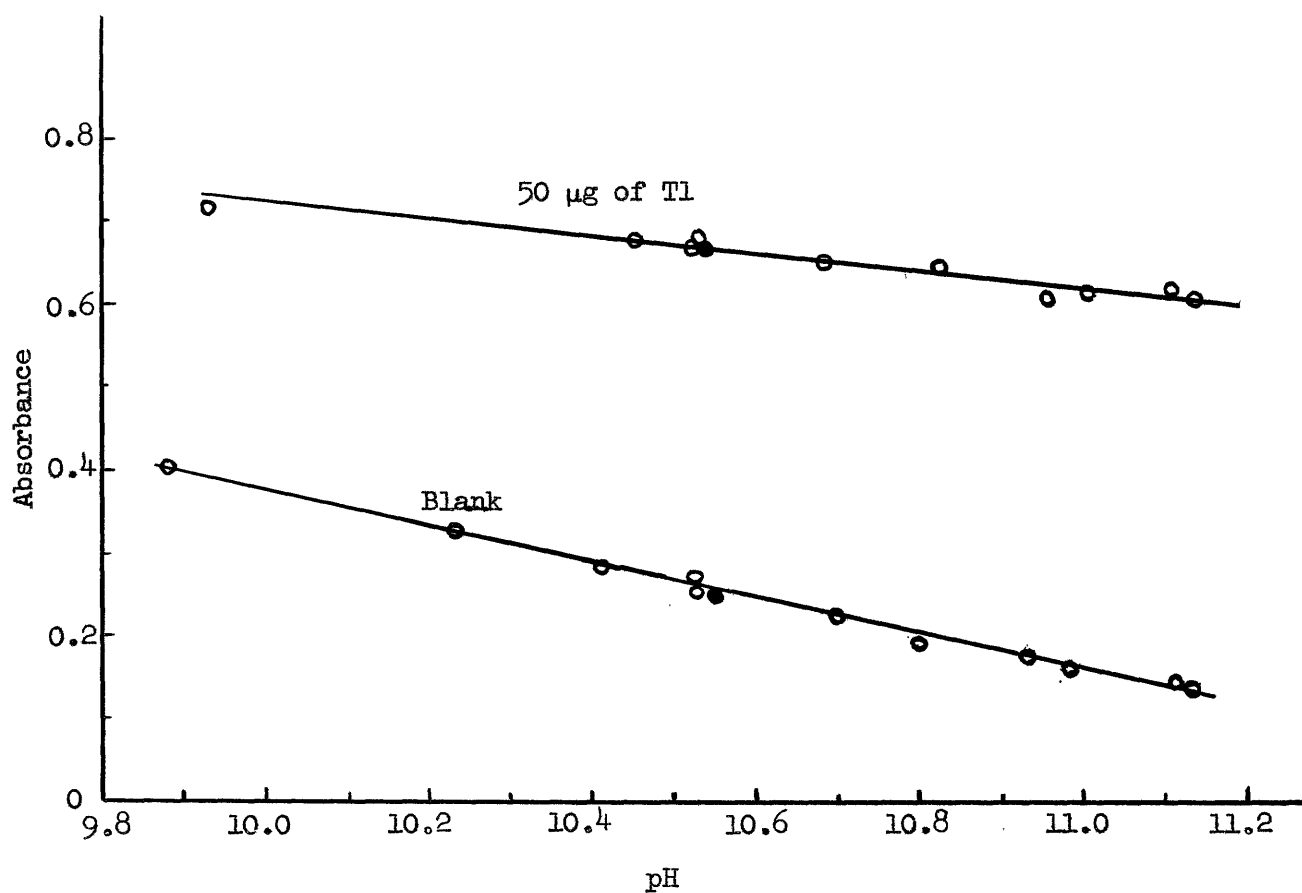


Fig. 3. Relationship between pH adjusted by variation of KCN concentration and absorbance of blanks and solutions containing 50 micrograms of Tl per 15 ml. (Chloroform reference, 1-cm cells, 505 m $\mu$ .)

solution was more than offset by loss in reproducibility of the reagent blank.

#### Dithizone concentration

Single extraction experiments from the citrate-sulfite-cyanide medium were performed to study the effect of variation of dithizone concentration. The differences in absorbance between samples and reagent blanks were measured. They reached a constant value at a concentration of 0.2 mg of dithizone per 15 ml of solution when 50 micrograms of thallium were present, and at a concentration of 0.4 mg of dithizone per 15 ml of solution when 90 micrograms of thallium were present.

#### Shaking time

The effect of shaking time on extraction was studied using blanks and solutions containing 20 and 60 micrograms of thallium. Shaking was done on a wrist-action shaker for 5 minute time intervals over a period of 30 minutes. The resulting absorbance values were essentially constant from 5 to 15 minutes. The values seemed to rise slightly during the period from 15 to 30 minutes. A 10 minute shaking period was selected, although shorter periods would undoubtedly be equally satisfactory.

#### Stability of complex

The stability of the complex was tested by reading absorbance values on dithizone extracts of a blank, a solution containing 50 micrograms of thallium, and one containing 1 mg of thallium. The latter corresponds to the solution used for pure complex in Fig. 1. Readings were made every 30 minutes over a six-hour period. The cell holder containing the

solutions stood exposed to the artificial light of the laboratory except when readings were being taken. Absorbance values decreased rather evenly during this period for a total of about two percent. Readings made within the first two hours, however, were essentially constant and within instrumental reading error.

#### Acid-strip and final pH adjustment

When a chloroform solution of thallium dithizonate is shaken with 0.08M nitric acid, the complex is destroyed and the thallium reverts to the water layer. This acid solution is titrated with 0.08M sodium hydroxide in the separatory funnel to the first definite yellow color immediately after adding 0.05 ml of 0.1 percent methyl red solution from a pipette. Care must be taken in the addition of the methyl red solution prior to titration. An experiment was made using different amounts of indicator dispensed from a dropping bottle. Two drops of solution gave blanks with an average absorbance value of 0.130, while 3 drops gave 0.150 and 4 drops 0.171. If the indicator is allowed to stand in the solution too long before titration, it may extract into the small volume of chloroform that is present in the bottom of the funnel and cause difficulty in seeing the end point.

Titration of the acid solution according to the recommended procedure results in a pH very near the neutral point. The addition of 2.0 ml of 5 percent potassium cyanide to these solutions leads to closely controlled pH in the vicinity of 10.6. The observed pH variation for a given set of experiments was no more than 0.1 of a pH unit. The resulting solutions are then ready for final extraction of the thallium-dithizone complex and subsequent measurement of absorbance.

The thallium is extracted from these solutions by shaking with 15.0 ml of dithizone solution added carefully from a pipette. A concentration of 0.4 mg of dithizone per 15 ml of chloroform was selected for the second extraction as experiments given above established this would complex at least 90 micrograms of thallium. The dithizone concentration selected for the first extraction is three times that used in the second. This was done to insure a large excess of the reagent in the initial separation step.

#### Conformity to Beer's law

Fig. 4, curve A, is a Beer's law plot of data obtained using the recommended double-extraction procedure. Values for differences in absorbance between sample and reagent blank used to plot this curve are averages of data from four experiments performed on different days. The pH values for the solution from which the extractions were made ranged from 10.6 to 10.8, although for a given day varied by no more than 0.1 of a pH unit.

The 60-microgram level is the only one determined on all four days. At this thallium level the individual values for difference in absorbance differed from their average value by a maximum of 3.6 percent and an average of 2.3 percent. Four values for difference in absorbance were also obtained at the 60-microgram level in a single experiment. These individual values for difference in absorbance differed from their average by a maximum of 2.7 percent and an average of 1.4 percent..

Satisfactory thallium values for some purposes could be obtained by a single extraction from the citrate-sulfite-cyanide medium which has a pH

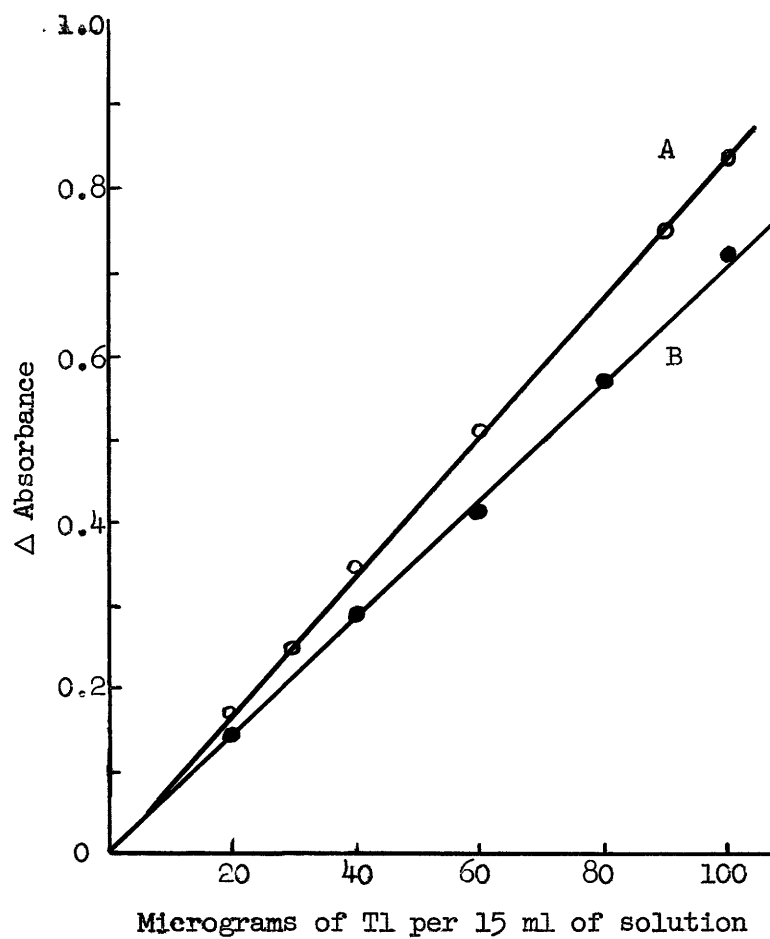


Fig. 4. Beer's law curve showing comparison of extraction procedures.

A. Double extraction

B. Single extraction

of approximately 10.6. An experiment using dithizone solution no. 2 (0.4 mg dithizone per 15 ml) where the more concentrated solution is normally used gave the Beer's law curve, curve B, in Fig. 4. This curve represents a loss in sensitivity of 13 percent over the double-extraction procedure. On the basis of the data at hand, the single-extraction procedure lacks the reproducibility that can be obtained with a double extraction.

#### CONCLUSION

Use of the thallium-dithizone mixed-color system has been shown to be a reproducible and sensitive method for thallium under properly controlled conditions. The only elements that would be significant interferences are lead, bismuth, and tin (II). A combination of this dithizone method of determination with published methods of separation should result in a useful analytical method for thallium in a wide variety of materials including those of geologic interest.

#### ACKNOWLEDGMENT

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