A STUDY OF THE THALLIUM DITHIZONE COMPLEX USING RADIOACTIVE TRACER TECHNIQUES

BY

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

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Date: May 29, 1953

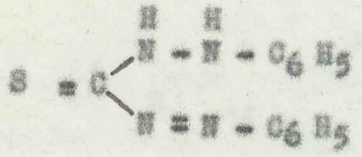
The author expresses his sincere appreciation to the members of the faculty of the Chemistry Department of Union College, in particular, to Dr. Galen W. Ewing for the encouragement, kind assistance and thoughtful suggestions which have contributed to make this work easier and more enjoyable.

INTRODUCTION

For some years now, work has been carried on at Union College, under the direction of Dr. Galen W. Ewing, on the study of the dithizone complex with thallium, with the aim of developing a simple, rapid and accurate colorimetric method for determining thallium. (6) (7) (15). Sandell describes a method of extracting and concentrating thallous ion from aquious solution using a chloroform solution of dithizone. The chloroform is evaporated, the thallium dithizone complex destroyed and then the thallium determined by some standard method such as iodide precipitation or another colorimetric procedure suggested by Sandell (12). This method, as a routine analysis, might be very long and tedious, involving many errors which are almost inevitable to a many-step procedure. Thallium in basic solution forms with dithizone in chloroform or carbon tetrachloride solution a bright red complex when extracted into the organic phase. The aim of this series of researches has been to investigate whether a quantitative extraction can be made of the thallium by the dithizone into the organic phase, to determine the nature of the thallium dithizone complex, to study the selectivity of the complex formation with regard to metallic ions other than those of thallium, and to investigate the optimum conditions under which extraction takes place. In the present work, use has been made of a radioactive isotope of thallium as a tracer in the study of the thallium dithizone complex.

HISTORICAL

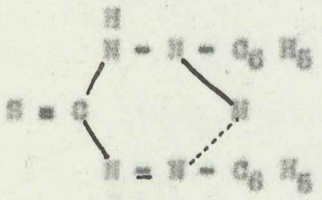
Diphenylthiocarbazone, abbreviated to "dithizone", was first prepared in the latter part of the last century by Emil Fischer (4). Dithizone is a relatively unstable organic compound, soluble in polar organic solvents such as chloroform and carbon tetrachloride and insoluble in water. (When a carbon tetrachloride solution of dithizone is shaken with concentrated hydrochloric acid, dithizone partially passes into the acid layer and imparts a violet-red color to it. In 6 N hydrochloric acid, dithizone is insoluble. On the other extreme, dithizone when added to a very concentrated solution of sodium hydroxide imparts a strong orange coloration to the solution.) The structural formula given to dithizone is:



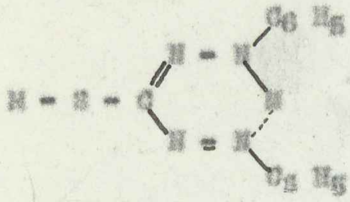
Emil Fischer also discovered that dithizone formed brilliantly colored compounds with heavy metals. Hellmut Fischer's continued investigations showed that dithizone formed the colored complexes at even very low concentrations of the metallic ion (5). H. Fischer and co-workers introduced the compound as an analytical reagent, described procedures for the detection and determination of traces of many heavy metals but noted that the selectivity of complex formation among the various metallic ions was rather poor.

It is now believed that the metal dithizonates can exist in two tautomeric forms, the keto form and the enol form. The following structural formulae are assigned to the two types of dithizone complexes (8) (17):

1. keto form



2. enol form



M represents the metal atom. The solid valence bond to the metal atom indicates the ordinary primary valence bonding, whereas the dashed valence bo bond to the metal atom indicates what is often called auxiliary or coordination type bonding. It is interesting to note that the complex forms a six-membered chelate ring complex, such a structure being well known as a stable configuration for inner complex compounds (14). The keto complexes are soluble in organic solvents and are much more important to the analytical chemist than are the enol complexes which are only sparingly soluble.

Bruno Jaselskis, working at Union College, reports in his thesis for the bachelor's degree, that dithizone forms with thallous ion at a pH of around 10, a one to one complex, that is a keto inner complex. His work involved applying the technique reported by the French chemist, P. Job, to the colorimetric method in the study of the complex (6).

APPARATUS

The usual method for forming the colored metal dithizone complex compound is to bring together in a separatory funnel a solution of dithizone in chloroform or carbon tetrachloride with an aqueous solution containing the metallic ion. The metal ion and the dithizone react, forming quantitatively under favorable conditions the metal dithizonate which is soluble in the organic phase. Whether a larger or smaller fraction remains in the aqueous phase depends mainly on the pH maintained.

In our present study of the thallium dithizone complex, the chief problems confronted were:

1) the necessity of working with two phases.
2) the instability of dithizone solutions.
3) the fading out of the red thallium dithizone complex.
4) the degree of extraction of the thallous ion into the organic solution of dithizone with the formation of the complex.
5) confirmation of the previously reported fact that the thallium dithizonate is a one-to-one complex.

As stated earlier, use was made of a radioactive isotope of thallium as a tracer in our study of the thallium dithizone complex. The radioactive isotope was thallium, atomic mass 204, beta active, with a half-life of 2.7 years obtained by permission of the Atomic Energy Commission from the Oak Ridge National Laboratory in Tennessee. An aqueous stock solution of thallous ion was prepared from non-radioactive thallous carbonate to which was added a small amount of the tracer which was obtained as thallium nitrate in weak nitric acid. The dithizone was obtained from the Fisher Scientific company.

C.P. solvents were used in the preparation of the dithizone solutions.

Measurements of radioactivity were made with a Geiger tube and counter manufactured by Tracerlab, Inc. of Boston. The Geiger tube, model TGC1, was encased in chamber of lead 2.5 cm. thick and operated at a voltage of 1.5 kilovolts without the aluminum shield over the window of the tube which gave an average background of 30 counts per minute. Counts were made on ten milliliters of solution in 2-inch Pyrex petre dishes. The distance from the platform to the window of the Geiger tube was kept constant at 4.2 cm. The counting and indicating unit is designated as a "64" scaler, model SC - 2A.

In taking a count on a sample in one of the petri dishes, the following procedure was followed. The dish was centered under the window of the Geiger tube, and count was then taken for 3.2 minutes on a scale of 32. The activity of the sample in terms of counts per minute could thus be determined;

$$\text{activity} = \frac{(M)\ (32) + N \text{ counts}}{3.2 \quad \text{minutes}}$$

$$= M(10) + \frac{N \text{ counts}}{3.2 \text{ minute}}$$

That is, the number on recorder dial (M) multiplied by 10 plus the counts on the interpolating dial (N) divided by 3.2 gave the activity in counts per minute. For convenience in taking counts, a table was prepared of values of ratios of numbers from one through thirty-two divided by 3.2.

In order to check the stability of the Geiger tube and scaler, counts were taken every few days on a sample of uranium alloy which was kept as a standard specifically for this purpose:

Date	Specific count
11-17-52	1006
12- 4 -52	1068
12-11-52	1027
1- 5 -53	1104
1- 9 -53	1106
2- 9 -53	1021
2-16-53	1017
2-25-53	1091
3- 3 -53	1032
3-13-53	1106
3-30-53	1086
4-13-53	1083
4-21-53	1049

For quantitative colorimetric measurements, two instruments were used; namely, the Beckman Model DU Photoelectric Quartz Spectrophotometer (serial no. 3210) and the Cenco-Sheard Spectro-photelometer.

The buffer solutions were prepared according to the directions of Clark and Lubs (16).

DATA & RESULTS

The chief problems of our present work were outlined briefly in an earlier part of this thesis. The procedures used in attacking these problems and the data and results thus obtained will now be discussed more fully:

1. The necessity of working with two phases. The general procedure for the formation of the dithizone complex of thallium has already been mentioned. Throughout our work, equal volumes of the organic dithizone solution and of the aqueous solution of thallous ion were taken. Twenty-five milliliters of the organic solution of dithizone were added to twenty-five milliliters of the aqueous solution of thallium, adjusted to the desired pH, in a 125 ml. separatory funnel. The solutions were shaken with extraction of thallous ion into the organic phase and formation of the red thallium dithizone complex.

2. The instability of dithizone solutions. Because of the instability of dithizone, it cannot be obtained as a pure, dry product. The dithizone used in this work was recrystallized from chloroform according to the procedure described by Sandell (10). The solutions of dithizone made up from this recrystallized material were then standardized by the colorimetric method of Cooper and Sullivan and stored in the refrigerator in a dark, glass bottle (2) except for part 5 of our work, dithizone solutions were made up in 250 cc. lots on the basis of 0.0200 grams of recrystallized dithizone per liter of solution. The molar absorbancy indices, quoted from the paper by Cooper and Sullivan are:

Wave length (mμ)	Molar absorbancy index a_M
440	16.0×10^3
505	6.0×10^3
605	41.5×10^3

A solution of 0.0200 grams of dithizone per liter showed the following values of absorbance at the indicated wave lengths:

	440mμ	505mμ	605mμ
	1.08	0.391	3.00
	1.10	0.395	3.00
	1.08	0.393	3.00
	1.10	0.393	--
Average:	1.09	0.393	3.00

According to the Beer-Lambert Law, $A = a_M bc$, where A is the absorbance or optical density, a_M is the molar absorbancy index, b = length of path of light through the solution. We can then calculate c, the concentration of dithizone in solution, in terms of gram moles per liter:

$$c = \frac{A}{a_M b}$$

$$\text{At } 440\,m\mu,\ c = \frac{1.09}{(16\times10^3)(1)} = 6.71\times10^{-5}$$

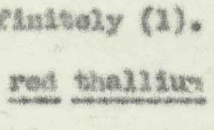
$$\text{At } 505\,m\mu,\ c = \frac{0.393}{(6.0\times10^3)(1)} = 6.55\times10^{-5}$$

$$\text{At } 605\,m\mu,\ c = \frac{3.00}{(41.5\times10^3)(1)} = 7.22\times10^{-5}$$

The average concentration of dithizone in solution is calculated to be 6.83×10^{-5} gram moles per liter. From the fact that 0.0200 grams of material were dissolved in preparing one liter of solution, we can determine the purity of the recrystallized dithizone to be 85.0%.

In spite of the precautions taken in storing the dithizone solutions, usually only the quantity necessary for relatively immediate consumption was prepared at any one time. P. A. Clifford reports that dithizone solutions kept in a cold, dark place under a layer of SO_2-water of approximately 0.1N concentration will keep indefinitely (1).

3. __The fading of the red thallium dithizone complex.__ The fading out of the green solutions of dithizone and the red solutions of thallium dithizonate are believed to be due to the formation, under weak oxidizing conditions, of diphenylthiocarbodiazone (9):



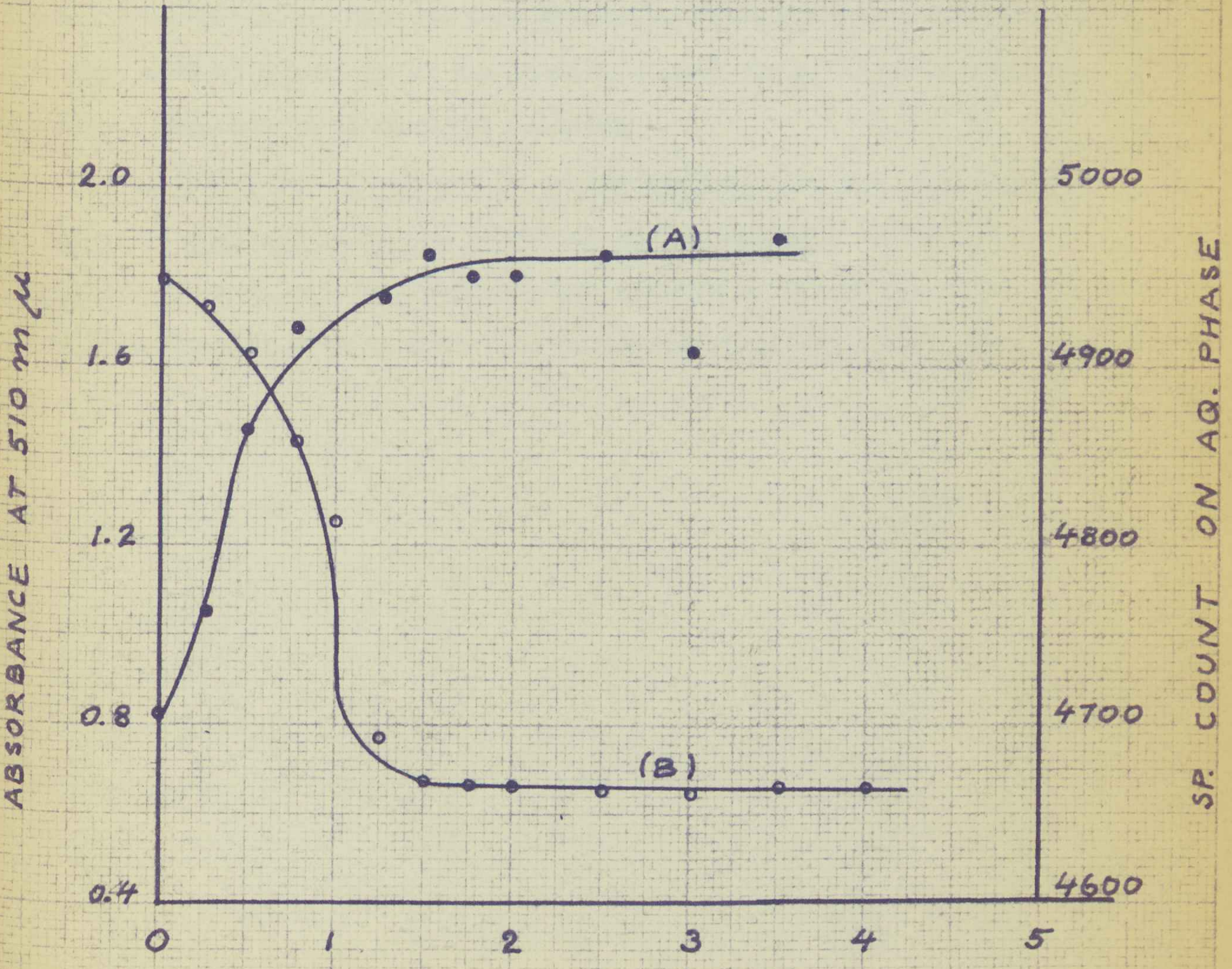
$$S{=}C\begin{cases} N{=}N{-}C_6H_5 \\ N{=}N{-}C_6H_5 \end{cases}$$

This oxidation product dissolves in chloroform and carbon tetrachloride imparting a yellow or brown coloration to the solution. It does not react with metallic ions. Because of the relative ease of formation of the oxidation product upon exposure of solutions of dithizone and dithizonates to sunlight at room temperature, it was found that the complexes had to be studied almost immediately upon formation. A brief study was undertaken of the rate of decomposition of the thallium dithizone complex. In each case, twenty-five milliliters of a solution of dithizone in chloroform (0.0200 grams per liter) was shaken with an equal volume of aqueous solution of thallous ion (1.72×10^{-3} gram ions per liter, pH 10) and both phases placed in 1 x 8 in. Pyrex test tubes. The tubes were then suspended in a specially prepared box, equidistant from an AH-4 mercury vapor lamp, the distance being 7 inches (3). The temperature of the solutions reached 56°C. upon exposure to the radiations from the lamp. The time of exposure to the radiation was varied for the different samples and the rate of decomposition of the thallium dithizone complex was followed by the change in absorbance of the chloroform phase at 510 mμ. An alternative manner of studying the rate of decomposition of the complex consisted in determining the rate of change of thallium concentration in the aqueous phase after formation of the complex. The rate of change of thallium concentration in the aqueous phase was followed by taking the specific radioactive count on that phase at the various indicated intervals:

Time of exposure to mercury vapor lamp	absorbance at 510mμ	Specific average Count on the Aqueous phase
0 hr	1.80	4706
.25	1.75	4764
.5	1.65	4866
.75	1.45	4923
1	1.26	4927
1.25	.78	4940
1.5	.685	4963
1.75	.670	4954
2	.676	4951
2.5	.668	4965
3	.660	4903
3.5	.668	4972
4	.660	4928

FIGURE 1

THE DECOMPOSITION OF THALLIUM DITHIZONE COMPLEX FOLLOWED BY RATE OF CHANGE OF (A) CONCENTRATION OF THALLIUM IN THE AQUEOUS PHASE, (B) ABSORBANCE OF CHLOROFORM PHASE.



It is to be noted from the graphs, Fig. 1, that the rate of decomposition of the thallium dithizone complex is relatively rapid, reaching equilibrium in approximately 1.5 hours. It must be remembered, however, the conditions which apparently favor decomposition of the complex have been exaggerated here, the temperature being above normal room temperature and the illumination being more intense than under usual laboratory conditions. These illustrations, nevertheless emphasize the fact that conditions of temperature and illumination have to be closely regulated if reproducible results are to be obtained when the formation of the dithizone complex is to be used in the determination of thallium. Since normal room temperature ranges from 20°-25°C., the greatest precaution that should be taken in ordinary work on solutions of the complex appears to be to guard against prolonged exposure to ultraviolet radiation.

4. *The degree of extraction of the thallous ion into the organic solution of dithizone with the formation of the complex.* The original, undiluted stock solution of thallous ion containing tracer was standardized by iodide precipitation as described in Scott's *Standard Methods* (15):

	Sample I	Sample II
Volume of aliquot	25 ml	25 ml
Weight of empty sintered glass crucible	12.9133g.	12.8386g.
Weight of crucible plus precipitate of TlI	12.9500g.	12.8750g.
Weight of precipitate	.0367g.	.0364g.
Wt. of thallium in the sample	.0226g.	.0224g.
Conc. of thallium in grams per liter	.904	.896
Molar concentration of thallous ion	4.43×10^{-3}	4.40×10^{-3}
Average concentration	$4.42 \times 10^{-3} \frac{\text{g-ions}}{\text{liter}}$	

In all the subsequent studies, samples taken of the stock solution of thallous ion with tracer were buffered and diluted to two-fifths original strength so that the concentration of thallous ion in aqueous solution before reaction with dithizone in organic solution was equal to 1.72×10^{-3} gram-ions per liter. By measuring the radioactivity of the aqueous solution of thallous ion, it could be determined that the specific activity of 5,000 counts per minute per 10 ml corresponded to a concentration of thallous ion of 1.72×10^{-3} gram-ions per liter. The actual specific radioactive count on the solution of thallous ion varied somewhat here in actual practice, a count of 5,000 given for purposes of illustration.

In studying the partitioning of thallium between the organic phase and the aqueous phase, our first approach consisted in making a specific radioactive count on the organic phase and then a specific radioactive count on the aqueous phase after the thallium dithizone complex had been formed. It was then assumed that the partitioning followed this simple proportion:

$$\frac{C_o}{C_a} = \frac{(S.C.)_o}{(S.C.)_a}$$

where C_o = concentration of thallium in the organic phase

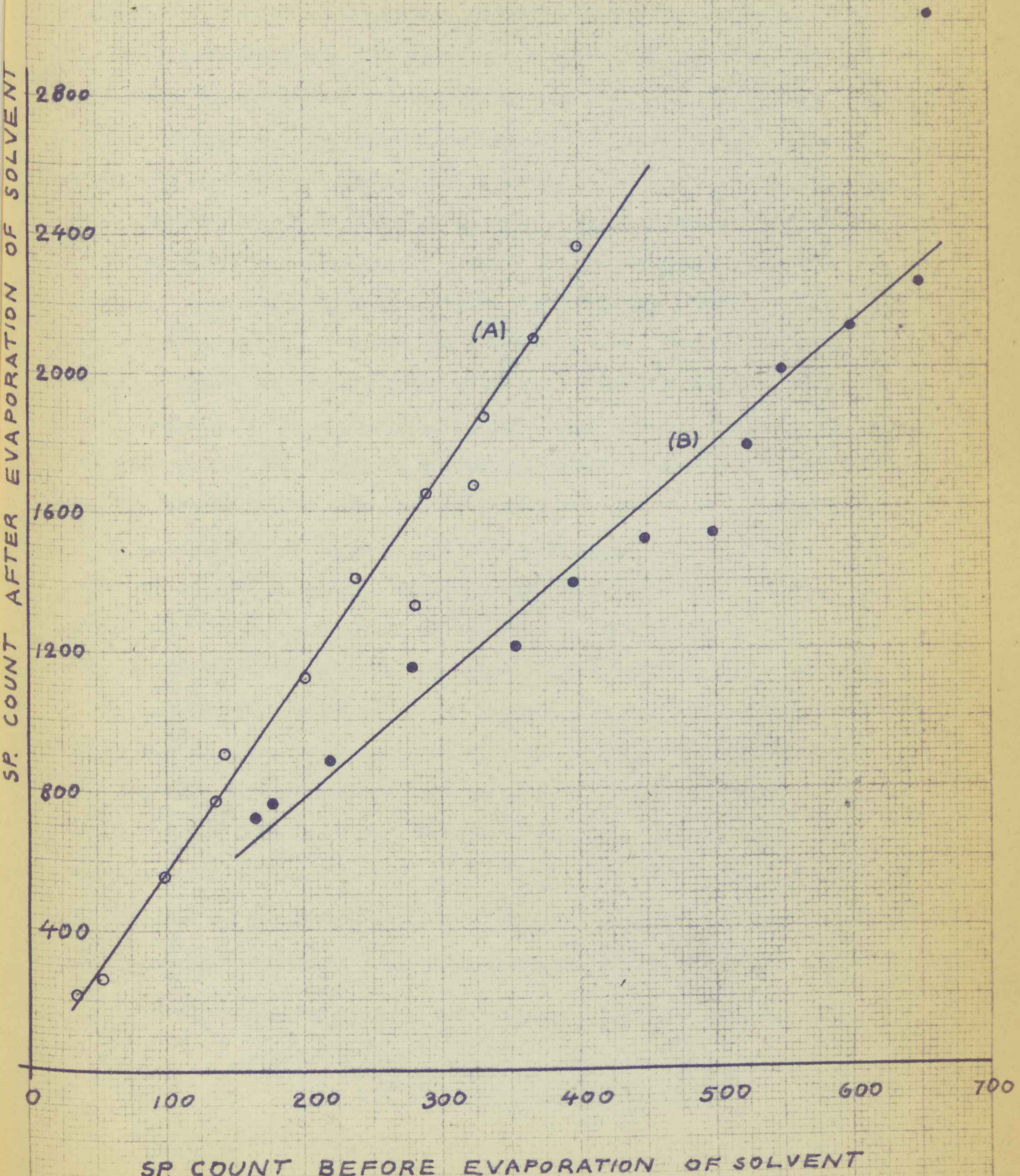
C_a = concentration of thallium in the aqueous phase

$(S.C.)_o$ = specific radioactive count on the organic phase

$(S.C.)_a$ = specific radioactive count on the aqueous phase

However, it was found that this relationship was not valid. The organic solvent, chloroform or carbon tetrachloride, being more dense than water has a greater power of absorption for beta radiation than does water. For example, a specific radioactive count of 1000 on the aqueous phase may represent a concentration of thallous ion of 3×10^{-6} gram ions per liter but a specific count of 1000 on the organic phase would correspond to a considerably greater concentration of thallium in that phase. The graph, Fig. 2, in which the specific count of solution is plotted against the specific count after the solvent has been evaporated further illustrate the fact that the solvent absorbs some of the radiation.

FIGURE 2
EFFECT OF SOLVENT ON RADIOACTIVITY OF SOLVENT:
(A) CHLOROFORM
(B) WATER



Curve (A) in which chloroform is the solvent was obtained by taking 10 milliliter samples of chloroform solution of thallium dithizonate containing radioactive thallium. The activity of each of the different samples was determined, the chloroform was evaporated, and the activity of the dry samples was also determined. The data for curve (B) was obtained in the same manner, the solvent in this case being water. It is to be noted that the activity of each sample appears to increase in both cases when the solvent is removed, indicating that the solvent has a masking or shielding effect on the beta radiation. With chloroform as solvent, the curve has a slope of 5.6; with water as the solvent, the curve has a slope of 3.5. Thus the samples in chloroform appear to be only 1/5.6 or 0.18 as active as when they are dry and the samples in water appear to be only 1/3.5 or 0.29 as active as when they are dry. We can conclude, therefore, that the shielding or absorbing power of chloroform for beta radiation is about 5.6/3.5 or 1.6 times as great as the absorbing power of water for beta radiation. (The specific gravity of chloroform at 20°C is 1.49.) Hence we must reject the simple relation that the ratio of the concentrations of thallium in each of the two phases is equal to the ratio of the specific radioactive count on the two phases.

The problem presented by the different degrees of absorbance for beta radiation shown by the organic solvent and water was solved in the following way: Let us suppose that the specific count on the aqueous solution of thallous ion before treatment with the organic solution of dithizone was determined to be X and this represents a thallous ion concentration of C_x gram-ions per liter. After some of the thallium has been extracted into the organic phase with formation of the compex, a specific count of Y is determined again on the aqueous phase, and this corresponds to a concentration of thallous ion C_Y where:

$$C_Y = \frac{(CxXY)}{X}$$

We know that the diminution in concentration of thallous ion in the aqueous phase is due to the fact that some of it has been taken up into the organic phase with formation of the thallium dithizone complex. Having known the original concentration of thallium in the aqueous phase and the concentration in that phase after extraction has occurred, we can now calculate the amount of thallium that has been transferred to the organic phase and, provided the volumes of the two phases are kept equal, the following relationship can be be set up:

$$\frac{C_o}{C_a} = \frac{X - Y}{Y}$$

where C_o = concentration of thallous ion in the organic phase

C_a = concentration of thallousion in the aqueous phase

X = specific count on the aqueous phase before extraction

Y = specific count on the aqueous phase after extraction

This relationship made it possible to study the effect of pH on the formation of the thallium dithizone complex and the degree of extraction of thallium from the aqueous phase. Each aqueous solution had to be carefully buffered and then twenty-five milliliters of each phase were shaken together in a separatory funnel, and after equilibrium had been reached, specific count taken on the aqueous phase. The data and results obtained are given below:

The specific count on the aqueous solution of thallium before treatment with the chloroform solution of dithizone was 5501 counts per minute per 10 ml. Therefore:

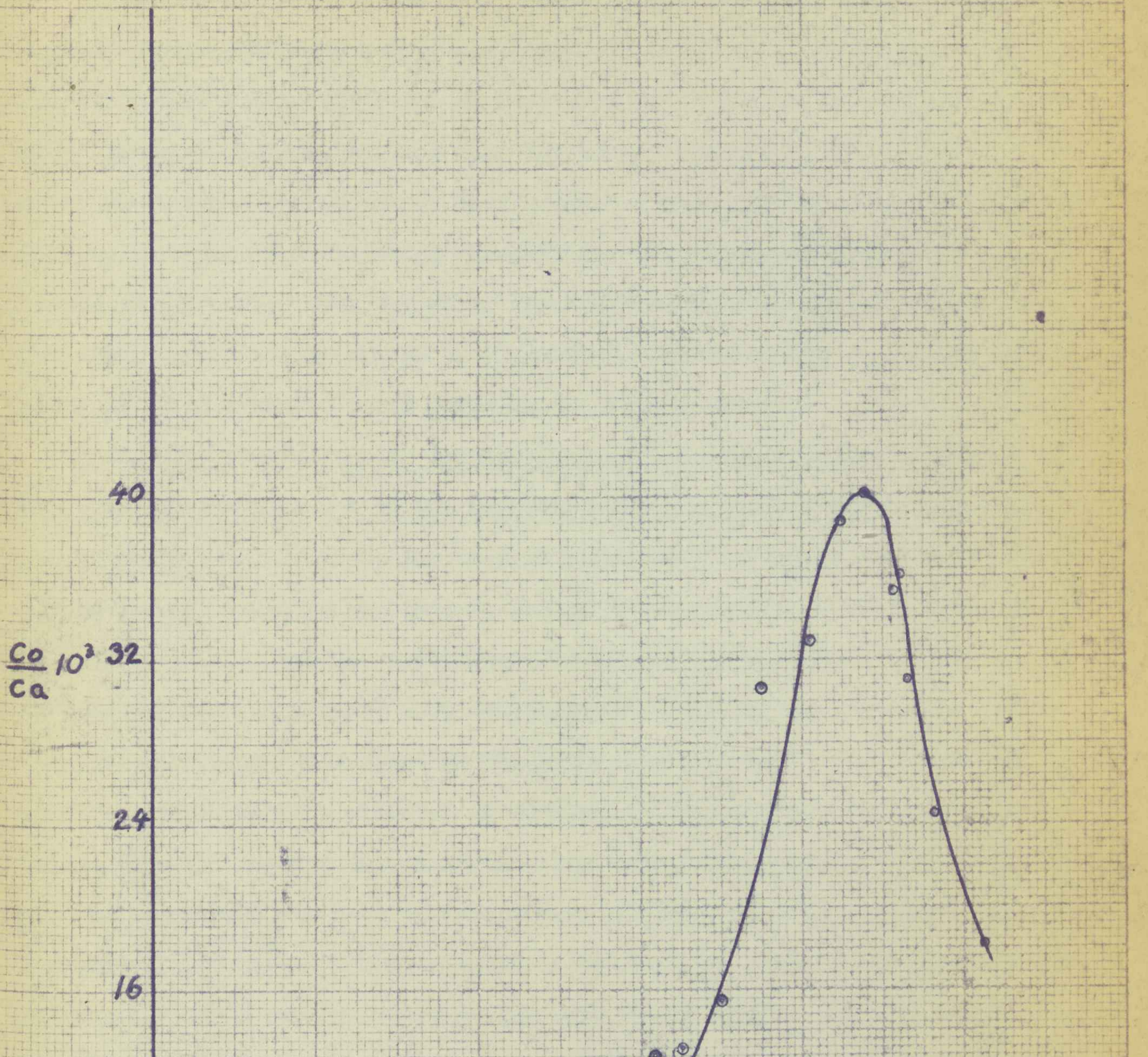
$$\frac{C_o}{C_a} = \frac{5501 - X}{Y}$$

where Y = specific count on the aqueous phase after treatment with dithizone.

pH	Average Specific Count on Aqueous Phase (Y)	$\frac{C_o}{C_a}$
2.00	5519	0
2.50	5512	0
3.45	5503	0
4.09	5495	.0011
5.56	5497	.0007
6.32	5498	.0005
6.82	5491	.0018
7.20	5473	.0061
7.81	5470	.0067
7.93	5463	.0070
8.12	5432	.0127
8.35	5442	.0107
8.48	5429	.0133
9.00	5416	.0167
9.44	5333	.0316
10.10	5329	.0323
10.42	5296	.0388
10.50	5298	.0384
10.75	5288	.0404
11.10	5312	.0356
11.14	5309	.0361
11.22	5335	.0312
11.66	5369	.0244
12.15	5395	.0182

FIGURE 3

THE EFFECT OF pH ON THE FORMATION OF THE THALLIUM DITHIZONE COMPLEX.



Hellmut Fischer reports that the pH for the most favorable formation of the thallium dithizone complex is 11.0. On the other hand, P. Kammerman reports a pH of 9.0 as the one most favorable for formation of the complex (11). Using our method, varying only the pH, we obtained a value of 10.8 as the pH at which optimum extraction occurs as shown by the graph of Fig. 3. It is well to note the following observations made during this specific section of our work: when the pH of the aqueous phase was 3, the color of the organic phase was green; pH of 8 produced a crimson color in the organic phase; pH of 12 produced a red color in the organic phase.

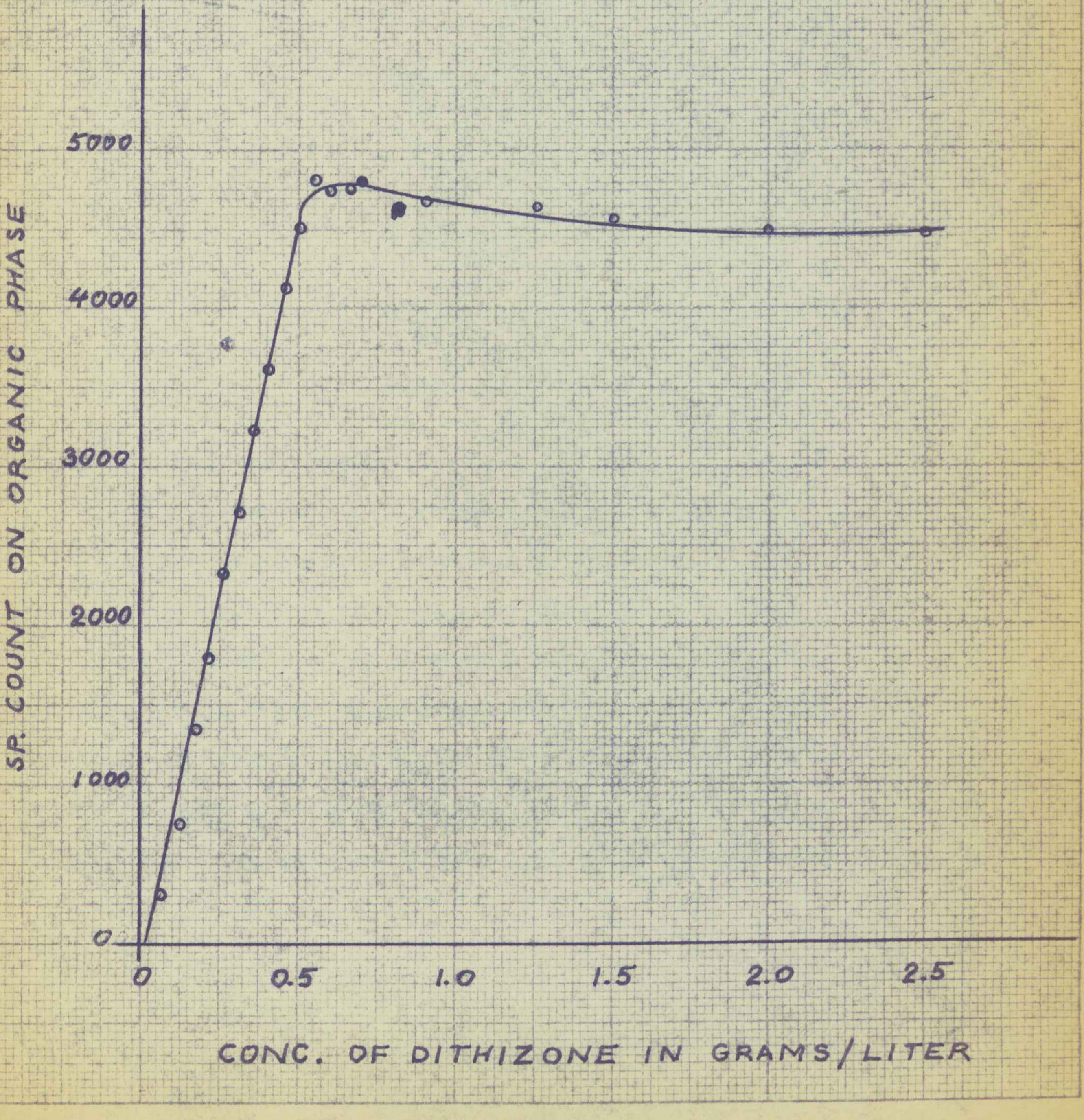
5. Confirmation of the previously reported fact that the thallium dithizone complex is a one to one complex, employing a different procedure than formerly used. A study was made in which only the concentration of dithizone in organic solution was varied, the pH of the aqueous phase being kept constant at 10. Solutions of dithizone in chloroform were made up varying the concentration of the 85% pure dithizone from zero to 2.5 grams per liter of solution. Thespecific count on the aqueous phase was taken after treatment with the chloroform solution of dithizone. Using equal volumes of both phases, (X - Y) would be the specific count on the chloroform phase if its power of absorbance for beta radiation were the same as that of water (where, as previously, X is the specific count on the aqueous phase before any thallium had been extracted from it by treatment with the dithizone solution and Y is the specific count on the aqueous phase after extraction has occurred.) The value of (X - Y) is proportional to the concentration of thallium in the organic phase. The graph, Fig. 4, is plotted as (X - Y) versus concentration of dithizone, showing at what concentration of dithizone all the thallium has been extracted from the aqueous phase that can be extracted from a solution

of that concentration in thallium. If the thallium dithizonate is a one-to-one complex, when the point is reached where the molar concentration of dithizone and the molar concentration of thallous ion are equal, a further increase in concentration of dithizone in the organic phase will not increase the concentration of thallium in the organic phase because the source in the aqueous phase has been exhausted.

Concentration of dithizone in grams per liter	(X - Y) Counts on organic phase corrected to the absorbance of water
0	-512
.05	356
.10	767
.15	1360
.20	1865
.25	2379
.30	2771
.35	3243
.40	3675
.45	4179
.50	4559
.55	4881
.60	4734
.65	4756
.70	4821
.80	4632
.90	4639
1.00	4622
1.50	4529
2.00	4538
2.50	4497

FIGURE 4

EFFECT OF INCREASING CONCENTRATION OF DITHIZONE IN THE CHLOROFORM PHASE.



The curve shows that a maximum extraction of thallium from aqueous solution of thallous ion of concentration 1.72×10^{-3} gram-ions per liter occurs when the concentration of dithizone in the chloroform phase is 0.55 grams of 85% dithizone per liter of solution. This is true for one extraction with equal volumes of both phases. This results in 94% extraction of the thallium into the chloroform phase and the partition coefficient, K, is calculated to be 15.1:

$$
\begin{aligned}
K &= \frac{C_o}{C_a} \\
&= \frac{X - Y}{Y} \\
&= \frac{5204 - 323}{323} \\
&= \frac{4881}{323} \\
&= 15.1
\end{aligned}
$$

where, as previously stated,

C_o = concentration of thallium in the organic phase

C_a = concentration of thallium in the aqueous phase

X = specific count on aqueous phase before extraction

Y = specific count on aqueous phase after extraction

The molar concentration of dithizone when 0.55 grams of 85% material are dissolved per liter of solution is 1.82×10^{-3} gram moles per liter. (The molecular weight of dithizone is 256.32.) The ratio of the concentration of dithizone to thallous ion is thus 1.07, which corresponds quite well to a one-to-one complex. It is not apparent why the curve takes on a slight negative slope after the concentration of 0.55 grams of dithizone per liter is exceeded, that is, why an increase in dithizone concentration beyond this point causes a decrease in concentration of thallium in the organic phase. An investigation of this anomalous behavior might be very informative.

SUMMARY

Our objective has been the study of dithizone as an organic reagent for the analysis of thallium. We have attempted to point out some of the difficulties in the use of dithizone as an analytical reagent in general, and as a complexing agent for thallium, in particular. The nature of the thallium dithizone complex and the most suitable conditions for its formation have been investigated by using a radioactive isotope of thallium as a tracer.

Based on work of the past and on our own investigations we have noted:

1. the necessity of working with two phases
2. the preparation, standardisation and storage of dithizone solutions.
3. the relative instability of solutions of dithizone and the thallium dithizone complex
4. the thallium dithizone complex is formed most favorably from solutions of pH 10.8
5. the thallium dithizone complex is a one to one complex, that is, a keto inner complex.

Throughout, we have tried to emphasize the important, new techniques available through the use of radioactive isotopes as tracers.

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