THALLIUM DITHIZONATE

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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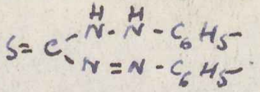
May 24, 1952

Attempts to establish a useful dithizone method in the determination of thallous ion have been carried on at Union College by Snyder (19). Because the previous work had not produced satisfactory results and because in general thallous dithizonates have not been studied, the following work, under Dr. W.G. Ewing's guidance, was undertaken.

Since dithizonates could be of keto or enol forms, or the mixture of both of them as will later be explained, Job's continuous variation method appeared to be applicable. In order to check the relative amount of thallous ion in thallous dithizonate, polarographic work seemed to be adequate. In addition, a few other methods were used as recommended by Mellon (10). Because the dithizone is soluble in strongly polar organic solvents, e. g. chloroform, carbon tetrachloride etc. but thallous carbonate is soluble in water, two phases had to be used and this caused serious inconvenience.

For advice and encouragement, special thanks are to be expressed to Dr. W. G. Ewing and to all the Chemistry Department staff at Union College, who in one way or the other made this work easier.

Emil Fischer prepared diphenylthiocarbozone, common name dithizone  $S=C\begin{matrix}-\overset{H}{N}-\overset{H}{N}-C_6H_5 \\ -N=N-C_6H_5\end{matrix}$ at the end of XIX century(3). He also noticed that the dithizone gave highly colored products with heavy metals. Hellmut Fischer (4) continued investigation and found that dithizone gave colored complexes even at very low concentration of the metal. But selectivity due to the similar colors was rather poor. Other chemists found that by proper choice of pH the selectivity could be increased because heavy metal dithizonates were formed at different pH's, and their solubilities in the organic phase varied markedly.

From a theoretical point of view, dithizone may be considered as a weak dibasic acid with much stronger monobasic acid character. The monobasic acid is prevalent up to pH 12 as it is observed by Buch (1).

Considering that dithizone dissociates in the following way :

$$H_2Dz \rightleftharpoons [H^+] + [HDz^-]$$
$$HDz^- \rightleftharpoons [H^+] + [Dz^=]$$

(For convenience dithizone is written as H_2Dz and dithizonate ion as HDz^- or $Dz^=$)

The dissociation constant for the first reaction is:

$$K_d = \frac{[H^+]_w \cdot [HDz^-]_w}{[H_2Dz]_w} \cdots 1$$

where subscript "o" stands for the organic phase and "w" for the aqueous phase.

The partition coefficient (P) between the organic phase and water is:

$$P_d = \frac{[H_2Dz]_o}{[H_2Dz]_w} \cdots 2$$

Considering that H^+ and $[H_2Dz]_w$ are constant and small following is true:

$$\frac{[H_2Dz]_o}{[HDz^-]_w} = \frac{P_d}{K_d}[H^+]_w$$

The value of $\frac{P_d}{K_d} = F = 3.6 \times 10^9$ as computed by Irwing and coworkers (7) and mentioned by Sandell (12).

If the metal dithizonate dissociates

$$MeHDz \rightleftharpoons [Me^+]_w\ [HDz^-]_w$$

then the equilibrium constant is:

$$K_m \quad \frac{[Me^+]_w [HDz^-]_w}{[MeHDz]_w}$$

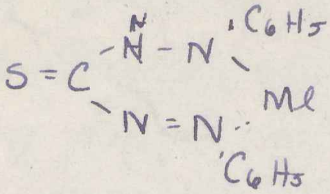
and the partition coefficient is:

$$P_m = \frac{[MeHDz]_o}{[MeHDz]_o}$$

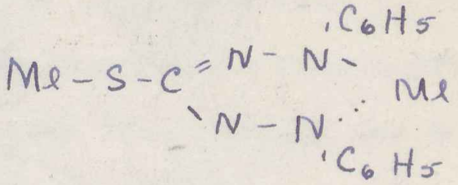
Dividing equation 5 by equation 4 and substituting equation 3 for $\frac{[H_2Dz]}{[HDz^-]}$ the following expression is obtained:

$$\frac{[MeHDz]_o}{[Me^+]_w} \qquad \frac{P_m}{K_m}\ \frac{[H_2Dz]_o}{F\ [H^+]_w}$$

Metal dithizonates formed by monobasic dithizone ion are known as keto complexes and are formed by all heavy metals which react with dithizone. Enol type complexes are easily formed by copper, mercury, and silver, but even so at higher pH and in the defficiency of dithizone (13). The structural formulas assigned by H. Fischer (5) are:

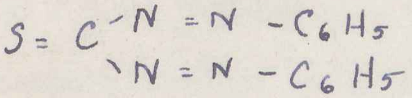


Keto metal
dithizonate



Enol metal
dithizonate

Dithizone is easily oxidized to diphenylthiocarbodiazone



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

Presumably the fading of complexes may be due to this oxidation.

The French Chemist P.Job (8),(9) successfully applied the colorimetric method in the study of complexes. Most of his publications appeared in the nineteen twenties in France. His work provoked some interest in the other countries. In the United States, Vosburgh & Cooper (21) studied the theoretical aspects and practical applications of the Job's continuous variation method in the investigation of the stability of complexes and their coordination numbers.

According to Job's continuous variation method, two reagents A and B, both M molar, are mixed in varying proportions, so that the concentration of A is dependant upon B as:

$A = M(1-x)$ ....1 where x is the volume of B

$B = Mx$ ....2 and x 1

At equilibrium this reaction may be expressed as:

$A + nB = AB_n$ 3

If the concentration of A, B, and AB_n are respectively c_1, c_2, c_3, than at equilibrium:

$c_1 = M(1-x) - c_3$ ..1. 4

$c_2 = Mx - nc_3$ 5

$Kc_3 = c_1 . c_2^n$ 6

c_3 is at a maximum when $\frac{dc_3}{dx} = 0$ 7

Differentiating equations 4, 5, 6 with respect to x and combining the resulting equations with 4 and 7 the coordination number "n" is obtained:

$$n = \frac{x}{1-x} \qquad \text{-----}\underline{8}$$

In order to show that a minimum or a maximum in the absorption of monochromatic light occurs when C_3 is at the maximum, consider that a_{m1}; a_{m2}; a_{m3} are the molar absorbancy indices of reagents and product at a given wave length. Then the absorbance (A) is:

$$A = l\,(a_{m1}\,C_1 + a_{m2}\,C_2 + a_{m3}\,C_3\,)$$ Where "l" is the thickness of the cell.

Denoting   as the difference between the absorbance observed and the absorbance of an identical solution if the reaction has not taken place. The following value is obtained:

$$Y = l\,\left[a_{m1}C_1 + a_{m2}C_2 + Ma_{m1}\,(1-x)\, - Ma_{m2}x\right] \qquad \text{----}\underline{9}$$

By differentiating this equation with respect to "x" it may be shown that "y" occurs at a maximum when C_3 is at the maximum provided that $a_{m3} > a_{m1}$; and "y" is at a minimum when C_3 is at a maximum if $a_{m3} < a_{m1}$. Consequently, as a maximum or mimimum in y will occur at the same value of "x" for various wave lenths, if there is only one complex formed.

In case a second complex is formed the equilibrium reaction is:

$$AB_n + qB \rightleftarrows AB\,(n+q)$$

When the equilibrium constant is:

$$K'' = \frac{C_3C_2^{q}}{C_4} \qquad \text{-------}\underline{10}$$ Where C_4 is the concentration of AB $(n+q)$

It may be shown that the coordination number "n" for this complex is:

$$n" = \frac{x}{1-x} + \frac{q(q+n)}{M\,(1-x)} \cdot c_4 \qquad \text{-----}\underline{11}$$

Incase there is only one complex formed or if the amount of the second complex is so small that it may be neglected and the maximum of C_3 occurs at $x = 0{,}5$ the slopes at $x = 0$ also at $x = 1$ are the same.

$$\Delta = \left(\frac{dA}{dx}\right)_{x=0} = -\left(\frac{dA}{dx}\right)_{x=1}$$

Then the absorbance (A) observed is related to the molar absorbancy index of the complex formed

$$A = a_{m_3}\left[\frac{c+1/k}{2} - \left(\left[\frac{c+1/k}{2}\right]^2 - c^2x(1-x)\right)^{1/2}\right] \ldots\ldots \underline{12}$$

as shown by Schwarzenbach (18) and Treadwell (20).

When $x = 0$ the expression of A becomes

$$\Delta = a_{m3}\,\frac{KC^2}{KC+1} \quad \ldots\ldots \underline{13}$$

Where C is the molar concentration of B at a given x value solving equations 12, and 13 simultaneously, we obtain the value of K - the equilibrium constant and also the value of the molar absorbancy index for the complex.

In this study of thallous dithizonates, it was decided to analyze only the organic phase. On account of this the computed value of the equilibrium constatn of thallous dithizonate in the chloroform solution is only proportional to the dissociation constant K_m as evaluated from the following equation:

$$\frac{[MeHDZ]_o}{[Me^+]_w} = \frac{P_m}{K_m}\,\frac{[H_2DZ]_o}{F\,[H^+]_w}$$

In determination of the absorbances and the relative amounts of thallous ion in thallous dithizonates the following apparatus has been used:

Beckman Model D U Photoelectric Quartz Spectrophotometer, serial no. 3210; during the absorbance measurments sensitivity was kept constant, only the slit opening was varied.

Elecdropode manufactured by Fisher Scientific Co. Roller-Smith, precision balance.

The materials used were:

Dithizone purchased from Eastman Kodak Co., original purity 84%. After purification according to the procedure described by Sandell (16) purity of dithizone was about 93-94%. The actual dithizone concentration was determined by measuring the absorbance of a chloroform solution of dithizone at the wave lengths 440, 505, 606 mμ and using Cooper & Sullivan (2) values of molar absorbancy indices as illustrated by the table I, Graph 1.

TABLE I

Mg of (H_2DZ)	Dissolved in ml $CHCl_3$	Absorbance 440	505	510	520	605	Av. Conc. of (H_2DZ)	Purity %
2.00	100	1.030	.401				6.55×10^{-5}	84.6
6.70	250	1.450	.539	.610	.790		9.88×10^{-5}	93.9(Av)
6.41	250	1.220	.469	.493	.629		7.90x	
5.18	250	0.990	.369	.387	.489	2.1	6.3x	
3.35	250	0.780	.300	.314	.394	1.96	4.9x	
1.34	250	0.310	.116	.124	.157	0.822	1.97x	
0.67	250	0.152	.058	.062	.078	.419	0.38x	

Molar absorbancy indices a_m for dithizone

440	mμ	16×10^3
505	mμ	6×10^3
605	mμ	41.5×10^3

Remaining impurities were probably the oxidation product of dithizone and some moisture. Since dithizone solutions decompose in light and above room temperature they were kept in the dark and in the refrigerator. Usually only the amount necessary for immediate use was prepared.

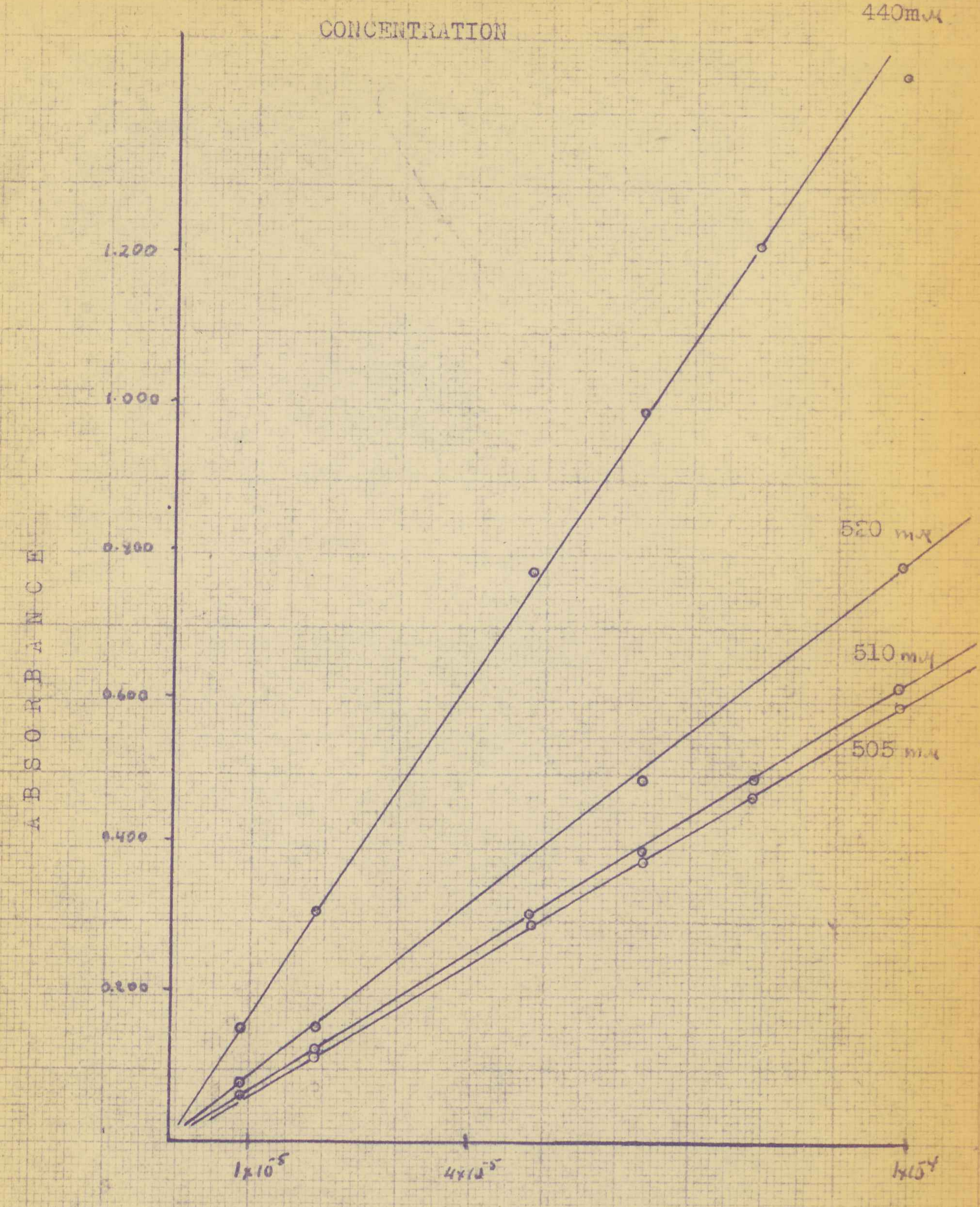
Dithizone is soluble in polar organic solvents: for the purposes of this work chloroform ($CHCl_3$) was employed. USP and CP grades of chloroform were used without further purification.

Thallous carbonate (Tl_2CO_3) (CP) purchased from Fairmount Chemical Co. was found by the gravimetric method described by Scott (17) to be 99.92% pure. This analysis was confirmed by the volumetric determination of thallous ion by the titration with standard ceric sulfate as recommended by Willard and cO-workers (23, 24). The foregoing is illustrated

GRAPH No 1

ABBORBANCE OF DITHIZONE VERSUS

CONCENTRATION



in the data below:

	I sample	II sample
Weight of sample Tl_2CO_3	0.2344 gr.	0.2344 gr
Weight of $Tl_2C_rO_4$	0.2609 gr.	0.2608 g
Weight of Tl in $Tl_2C_rO_3$ samples	0.2043 gr.	0.2043 gr
Weight of Tl in $Tl_2C_rO_4$	0.2037 gr.	0.2036 gr
Total volume of washings and solution	75 ml	75 ml

The amount of Tl in $Tl_2C_rO_4$ must be increased by approximately 0.0004 gr. due to the loss in washing.

Therefore, the purity of thallous carbonate is 99.92% -- -- 99.91%

In volumetric determinations solutions were prepared in the following way:

Hydrochloric acid concentrated	15.25 ml
Iodine chloride (catalyst)	10.00 ml
Water	74.75 ml

Standardization of ceric sulfate with sodium oxolate:

Weight of $Na_2C_2O_4$	Ml of $Ce(SO_4)_2$	Normality of $Ce(SO_4)_2$
6.01 mg	7.94	
6.01 mg	7.92	
6.01 mg	7.95	Av. 0.1124 N

Titration of thallous carbonate:

Weight of Tl_2CO_3	Ml of $Ce(SO_4)_2$
0.2344 gm	8.85 ml
0.2344 gm	8.88 ml

Purity of the sample is 99.71%.

The buffer solutions were prepared according to the directions of Clark & Lubs (22).

The water was redistilled for the solutions used in Job's continuous variation method.

2, 3 dimercaptopropanol* was used in the recursion method. This is also known as "British anti-Lewisite" abbreviated (BAL)

The mixed color method was applied, while studying absorption of thallous dithizonates. The volumes of two phases: Chloroform and aqueous phase were kept constant.

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* Obtained through the courtesy of J. E. Fagel, Jr. General Electric Research Laboratories.

TABLE II

Absorption spectra of dithizone, thallous dithizonates, thallous dithizonates with (BAL) and the decolorized (in the sun light) thallous dithizonate are illustrated in 2 following graphs. 2A and 2B.

Wave Length	Absorbance						
mμ	(a)	(b)	(c)	(d)	(e)	(f)	(g)
250	.319	.213					.440
260	.351	.233					.460
270	.339	.226			.266	.712	.390
280	.305	.204			.232	.627	.325
290	.239	.163			.212	.482	.282
300	.196	.133			.195	.401	.257
310	.165	.113			.165	.335	.243
320	.138	.098			.167	.270	.225
330	.118	.084			.163	.216	.195
340	.108	.077			.137	.198	.150
350	.105	.075			.110	.191	.137
360	.102	.074			.100	.181	.125
370	.096	.071			.107	.157	.113

Wave Length	Absorbancy						
mμ	(a)	(b)	(c)	(d)	(e)	(f)	(g)
380	.090	.067			.124	.126 ~~.23~~	.107
390	.087	.065			.156	.106	.099
400	.089	.067			.200	.100	.093
410	.098	.078			.244	.111	.087
420	.111	.083			.285	.142	.085
430	.131	.094		.500	.325	.193	.077
440	.157	.110	.548	.530	.328	.262	.075
450	.188	.128	.737	.560	.320	.350	.069
460	.225	.148	.980	.550	.294	.458	.063
470	.267	.172	1.220	.530	.261	.588	.054
480	.311	.195	1.360	.510	.218	.700	.048
490	.349	.217	1.580	.480	.172	.800	.091
500	.384	.239	1.680	.458	.147	.802	.034
505			1.710	.468			
508			1.720				
510	.399	.247	1.721		.147	.878	.030
512			1.680				

Wave Length	Absorbance						
mμ	(a)	(b)	(c)	(d)	(e)	(f)	(g)
520	.389	.245	1.610	.490	.178	.810	.026
530	.358	.230	1.350	.500	.222	.662	
540	.296	.199		.508	.275	.473	
550	.239	.168	.634	.548	.357	.302	
560	.187	.138		.622	.440	.182	.018
570	.141	.114	.257		.518	.106	
580	.116	.102	.187	.810	.590	.080	
590	.110	.098	.165	.930	.678	.063	
600	.106	.096	.158	1.020	.741	.060	
605			.156	1.050			
610	.101	.088	.150	1.000	.735	.055	
620	.086	.079	.120	.630	.050		
625				.740			
630	.068	.062			.305	.048	
640					.128	.043	
650	.038	.031	.030	.264	.075	.040	
660					.052	.038	
670							

Wave Length mμ	Absorbance (a)	(b)	(c)	(d)	(e)	(f)	(g)
675	.015	.016	.010	.058			
680					.040		
690							
700	.011	.011			.032	.028	

Absorption spectra of:

a) Unknown thallous dithizonate 1:1

b) " " " 1:2

c) 1.4 mg of unknown thallous dithizonate per 50 cc of shloroform

d) 1.4 mg of unknown thallous dithizonate per 50 cc of chloroform with (BAL)

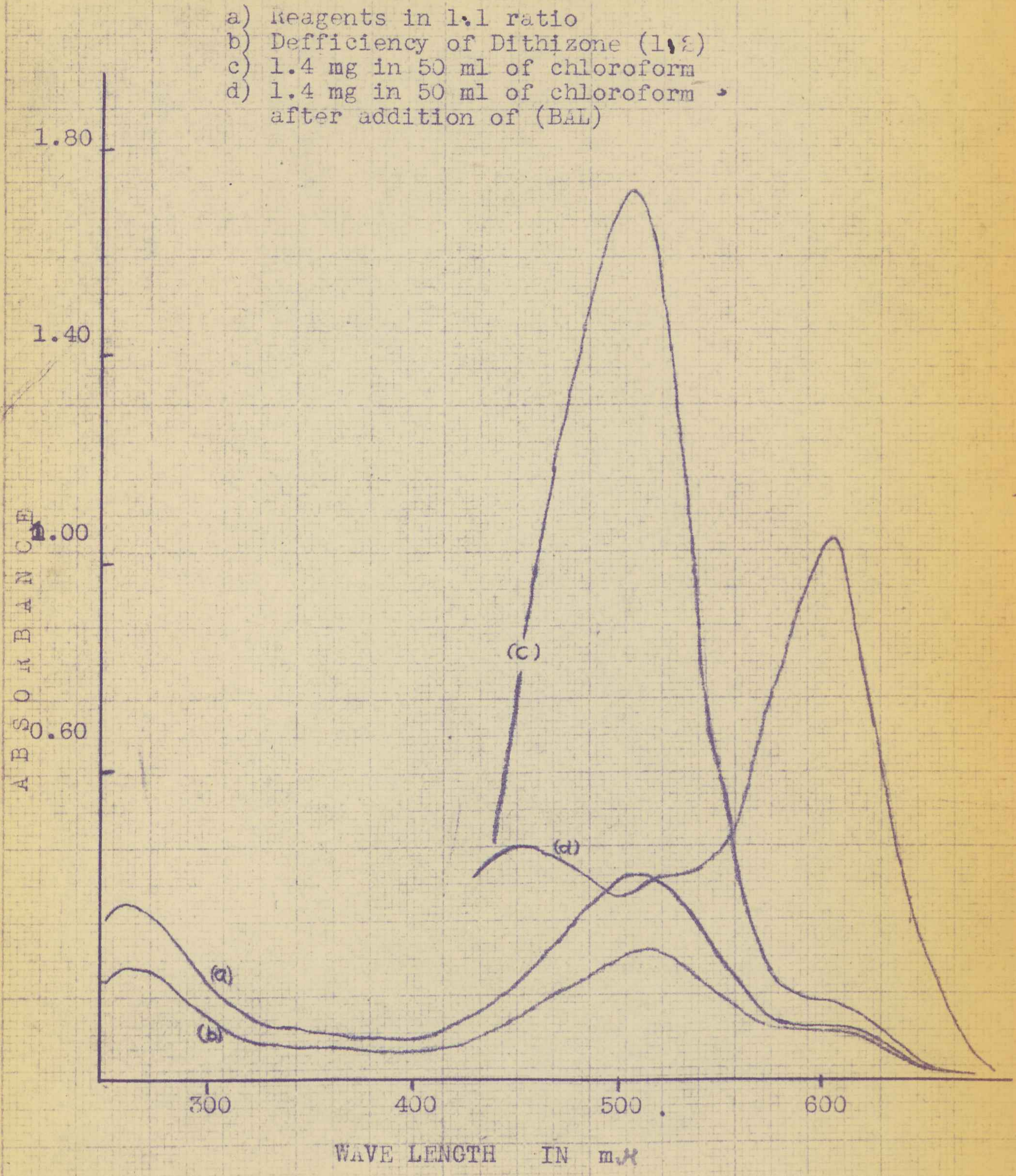
e) Dithizone in chloroform

f) Unknown dithizonate in chloroform

g) Decolorized thallous dithizonate.

GRAPH No 2A

ABSORPTION SPECTRUM OF UNKNOWN THALLOUS DITHIZONATE



GRAPH No 2B

ABSORPTION SPECTRA OF

e) Unknown thallous dithizonate
f) Dithizone in chloroform
g) Decolorized Thallous dithizonate

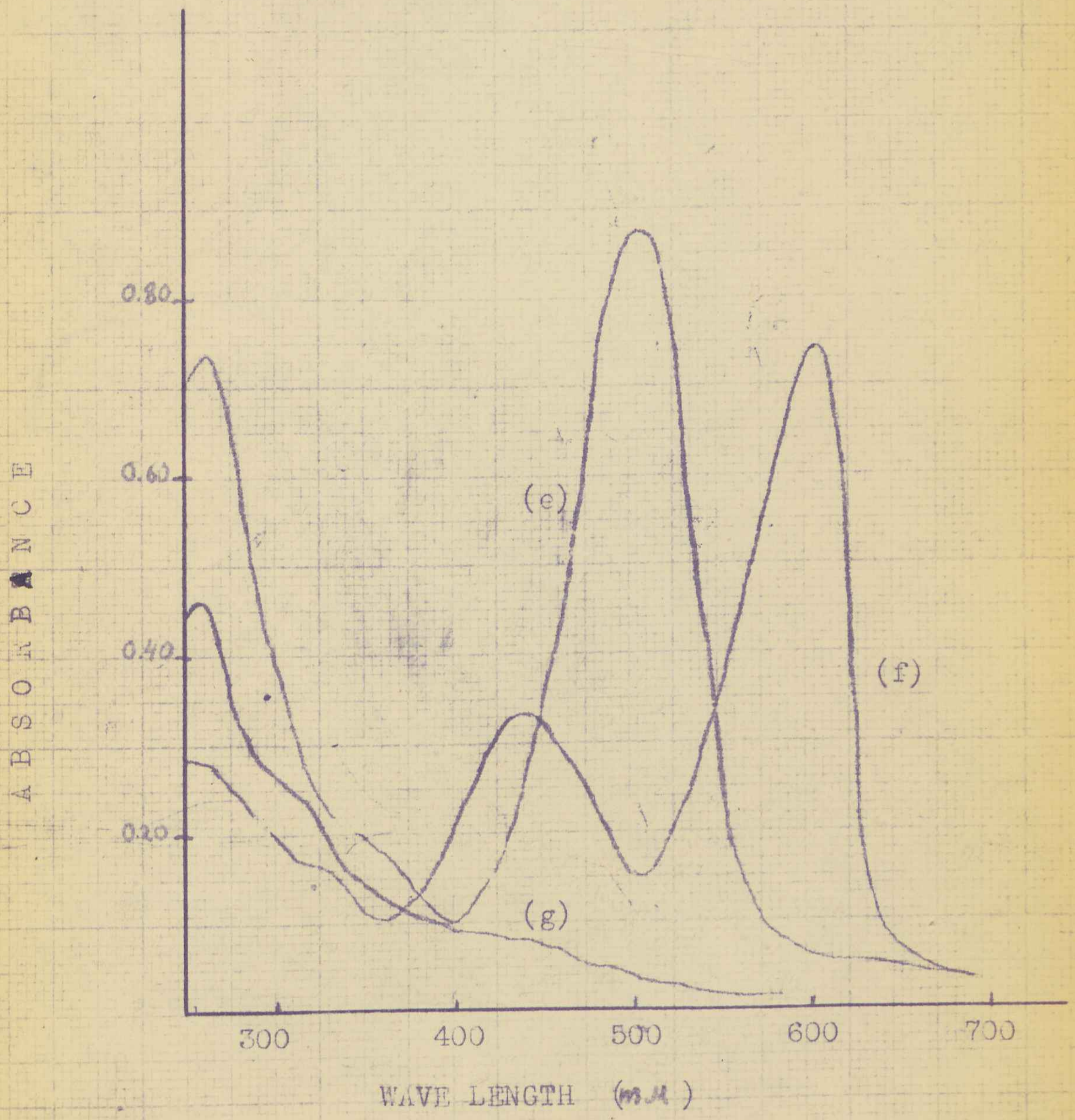


TABLE III

Graph 5

Job's Continuous variation method

pH 9.4

T 20° C

$(1-x) = 8.5x\ 10^{-7}m$ when $x = 0$

Solutions were kept at 20° for 30-35 minutes before measuring absorbance.

Serial No.	Moles of H_2DZ	H_2DZ ml $4.25\times10^{-5}m$	$CHCl_3$	Moles of Tl^+	Tl^+ ml $5.0\times10^{-4}N$	Buffer ml	Water ml	Resulting Mol. Of H_2DZ in $CHCl_3$
1	6.4×10^{-7}	15.0	-	2.1×10^{-7}	0.42	8.0	1.58	$4.25x\ 10^{-5}$
2	6.0x	14.1	0.9	2.5x	0.50	8.0	1.50	4.00x
3	5.5x	13.0	2.0	3.0x	0.60	8.0	1.40	3.77x
4	5.5x	13.0	2.0	3.0x	0.60	8.0	1.40	3.77x
5	5.1x	12.0	3.0	3.4x	0.68	8.0	1.32	3.40x
6	4.5x	10.6	4.4	4.0x	0.80	8.0	1.20	3.00x
7	4.25x	10.0	5.0	4.25x	0.81	8.0	1.19	2.84x
8	4.00x	9.6	5.4	4.5x	0.90	8.0	1.10	2.66x
9	3.40x	8.0	7.0	5.1x	1.02	8.0	1.08	2.26x
10	2.95x	7.0	8.0	5.55x	1.11	8.0	0.89	1.98x
11	2.55x	6.0	9.0	5.95x	1.19	8.0	0.81	1.70x
12	2.10x	5.0	10.0	6.40x	1.28	8.0	0.72	$1.31x\ 10^{-5}$
13	1.26x	3.0	12.0	7.24x	1.48	8.0	0.52	$8.00x\ 10^{-6}$

No.	Absorbance at 510	GmC_1		Absorbance (A) at 510 with (BAL)	Incriment
1	.648	.268	.380	.560	.088
2	.658	.250	.408		
3	.688	.237	.451	.510	.178
4	.715	.237	.477		

No.	Absorbance at 510	$a_m c_1$	Y	Absorbance at 510 with (BAL) (A)	Incriment (D)
5	.740	.213	.527	.490	.250
6	.761	.188	.573		
7	.770	.179	.591	.430	.340
8	.742	.167	.575		
9	.635	.143	.492	.371	.264
10	.568	.123	.443	.317	.251
11	.497	.108	.389	.264	.233
12	.394	.081	.313	.198	.196
13	.245	.050	.195	.092	.153

TABLE IV (Graph 5)

Job's continuous variation method

pH 9.6 ; T 20° C ; $(1-x) = 8.5 \times 10^{-7}$ When $x = 0$

Solutions were kept at 20° for 30-35 minutes before measuring the absorbance (A).

No.	Moles of H_2Dz ml	H_2DZ ml 4.25×10^{-5} m	$CHCl_3$ ml	Moles of Tl^+	Tl^+ 5.0×10^{-4} m	Buffer ml	Water ml	Resulting mol H_2DZ in $CHCl_3$
1	6.5×10^{-7}	14.95	0.05	2.0×10^{-7}	0.40	8.9	1.60	4.28×10^{-5}
2	5.5 ×	12.95	2.05	3.0x	0.60	8.0	1.40	3.77x
3	4.50x	10.35	4.65	4.0x	0.80	8.0	1.20	3.00x
4	4.00x	9.40	5.60	4.5x	0.90	8.0	1.10	2.66x
5	3.50x	8.35	6.65	5.0x	1.00	8.0	1.00	2.36x
6	3.00x	7.05	7.95	5.5x	1.10	8.0	0.90	1.98x
7	2.50x	5.88	9.12	6.0x	1.20	8.0	0.80	1.66x

No.	Moles of H_2Dz	H_2Dz 4.25×10^{-5}	$CHCl_3$ ml	Moles Te^+	Te^+ ml	Buffer ml	Water ml	Resulting mol. (H_2Dz)
8	1.00×10^{-7}	2.35	12.65	7.5x	1.50	8.0	0.50	0.67×10^{-5}

	Absorbance (A) at 510 mμ	$a_m C_1$	Y
1	.620	.268	.352
2	.737	.236	.501
3	.790	.190	.600
4	.755	.168	.587
5	.688	.148	.540
6	.608	.122	.486
7	.445	.102	.343
8	.220	.041	.161

TABLE V (Graph 5)

Job's Continuous variation method

pH 9.6 ; T = 20°C ; (1-x) = 8.5 x 10^{-7}m when x = 0

Solutions were kept at 20°C for 30-35 minutes before measuring the absorbance (A).

No.	Moles of H_2O_2	H_2O_2 4.25×10^{-5} ml	$CHCl_3$ ml	Moles Te	Te^+ 5.0×10^{-4}	Buffer ml	Water ml	Resulting mol (H_2O_2)
1	6.5x10^{-7}	14.95	0.05	2.0x10^{-7}	0.40	8.0	1.6	4.25 x10^{-5}
2	6.0x	14.10	0.90	2.5x	0.50	8.0	1.5	4.0x
3	5.5x	12.95	2.05	3.0x	0.60	8.0	1.4	3.77x
4	5.0x	11.80	3.20	3.5x	0.70	8.0	1.3	3.30x
5	4.50x	10.35	4.65	4.0x	0.80	8.0	1.2	2.92x
6	4.00x	9.40	5.60	4.5x	0.90	8.0	1.1	2.66x
7	3.50x	8.35	6.65	5.0x	1.00	8.0	1.0	2.34x
8	3.00x	7.05	7.95	5.5x	1.10	8.0	0.9	2.00x
9	2.50x	5.88	9.12	6.0x	1.20	8.0	0.8	1.66x
10	2.00x	4.70	10.30	6.5x	1.30	8.0	0.7	1.33x
11	1.50x	3.55	11.45	7.0x	1.40	8.0	0.6	1.00x
12	1.00x	2.35	12.65	7.5x	1.50	8.0	0.5	0.65x

No.	Absorbance (A) at 510	a_mC_1	
1	.603	.268	.335
2	.625	.250	.375
3	.727	.236	.491
4	.758	.208	.550

No.	Absorbance (A) at 510	a_mC_1	Y
5	.810	.190	.620
6	.764	.168	.596
7	.695	.148	.547
8	.603	.122	.481
9	.453	.102	.351
10	.383	.081	.302
11	.302	.062	.240
12	.204	.041	.163

TABLE VI (Graph 3,4)

Job's continuous variation method.

pH 10.0 T = 20°C ; $1-x = 10. \times 10^{-7}$m when $x = 0$

Solutions were kept at 20°C for 30-35 minutes before measuring absorbance (A).

No.	Moles of H_2Dz	H_2Dz (ml) 59×10^{-5}	$CHCl_3$ ml	Moles Te^+	Te^+ (ml) 5×10^{-4}	Buffer ml	Water ml	Resulting mol. H_2Dz.
1	7.5×10^{-7}	12.75	1.25	2.5×10^{-7}	0.50	8.0	1.50	5.0×10^{-5}
2	6.5x	11.00	4.00	3.5x	0.70	8.0	1.30	4.34x
3	6.0x	10.20	4.80	4.0x	0.80	8.0	1.20	4.00x
4	5.5x	9.30	5.70	4.5x	0.90	8.0	1.10	3.66x
5	5.5x	9.30	5.70	4.5x	0.90	8.0	1.10	3.66x
6	5.0x	8.50	6.50	5.0x	1.00	8.0	1.00	3.35x
7	4.5x	7.60	7.40	5.5x	1.10	8.0	0.90	3.00x
8	4.5x	7.60	5.5x	1.10	1.10	8.0	0.90	5.00x

No.	Moles of H_2Dz	H_2Dz (ml) 5.9×10^{-5}	$CHCl_3$ ml	Moles Tl^+	Tl^+ (ml)	Buffer ml	Water ml	Resulting Mol H_2Dz
9	4.0x	6.80	8.20	6.0x	1.20	8.0	0.80	2.66x
10	4.0x	6.80	8.20	6.0x	1.20	8.0	0.80	2.66x
11	3.0x	5.10	9.90	7.0x	1.40	8.0	0.60	2.00x
12	2.0x	3.40	11.60	8.0x	1.60	8.0	0.40	1.33x

No.	(A) 440 mμ	a_mC_1	D	(A) 505 mμ	a_mC_1	D	(A) 510 mμ	a_mC_1	D
1	.660	.770	-.110	.825	.395	.430	.757	.312	.445
2	.506	.666	-.160	.876	.255	.621	.884	.270	.614
3	.418	.612	-.194	.974	.234	.740	.980	.250	.730
4	.344	.561	-.217	.990	.217	.773	1.000	.230	.770
5	.355	.561	-.225	.982	.217	.765	.983	.230	.753
6	.330	.520	-.190	.950	.198	.752	.980	.211	.769
7	.290	.460	-.170	.840	.175	.665	.850	.188	.662
8	.298	.460	-.162	.857	.175	.682	.865	.188	.677
9	.255	.410	-.155	.810	.153	.657	.815	.167	.648
10	.249	.410	-.161	.798	.153	.645	.803	.167	.636
11	.202	.307	-.105	.690	.115	.575	.695	.125	.570
12	.132	.205	-.073	.438	.078	.360	.455	.083	.377

* (A) is absorbance observed.

(D) is the difference

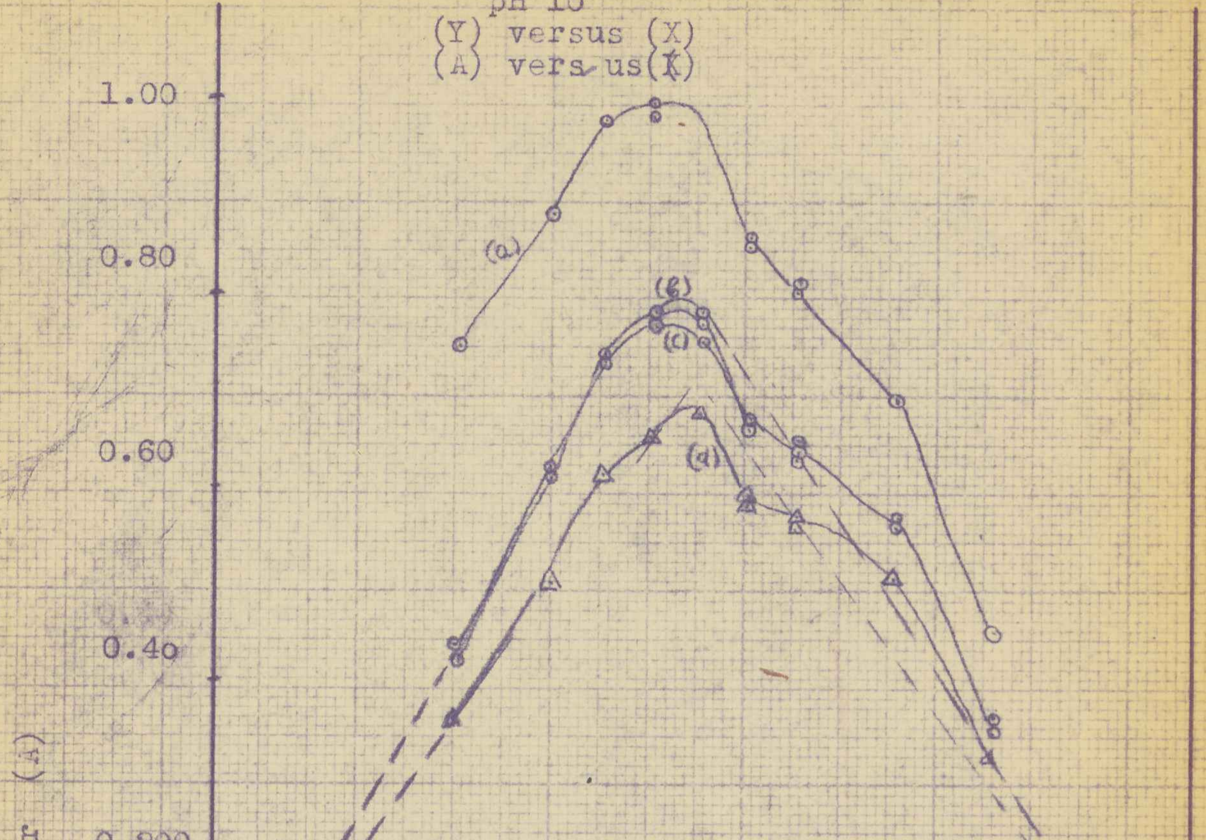
No.	(A) 520 mμ	a_mC_1	ν
1	.760	.395	.365
2	.845	.343	.502
3	.936	.315	.621
4	.950	.290	.660
5	.943	.290	.653
6	.948	.265	.683
7	.820	.235	.585
8	.827	.235	.592
9	.788	.210	.578
10	.776	.210	.566
11	.675	.158	.517
12	.445	.106	.339
~~13~~			

(BAL) added ; TABLE VII (Graph 4)

	(A) 440 mμ	D	(A) 505 mμ	D	(A) 510 mμ	D	(A) 520 mμ	D
	~~2~~	~~.622~~	~~.116-~~	~~.390~~	~~.486~~			
2	.662	.116	.390	.486	.402	.482	.461	.384
3	.580	.162	.418	.556	.430	.550	.468	.468
4	.565	.220	.410	.580	.420	.580	.455	.495
6	.518	.188	.343	.607	.355	.625	.390	.558
7	.440	.150	.405	.435	.408	.442	.408	.412
9	.435	.180	.278	.532	.283	.532	.315	.473
11	.363	.161	.265	.425	.264	.431	.285	.473
12	.220	.088	.150	.288	.156	.299	.175	.270

GRAPH No 3

JOB'S CONTINUOUS VARIATION METHOD
pH 10
(Y) versus (X)
(A) versus (X)

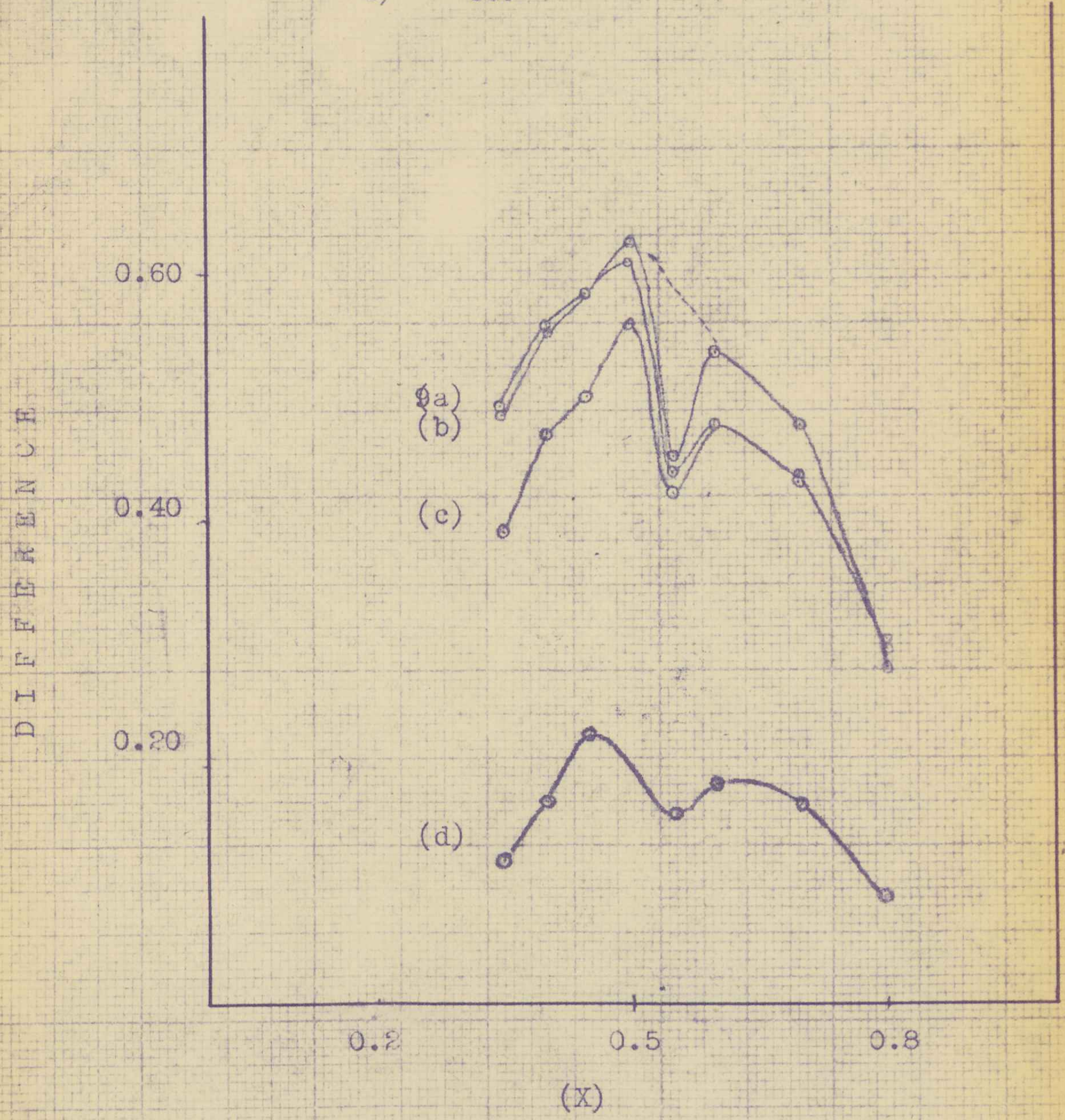


a) (A) a t 510 mμ
b) (Y) 510 "
c) (Y) 505 "
d) (Y) 520 "
e) (Y) 440 "

GRAPH No 4

DIFFERENCE BETWEEN ABSORBANCE
WITHOUT (BAL) AND WITH (BAL)
VERSUS (X)

a) at 510 mμ
b) 505 "
c) 520 "
d) 440 "

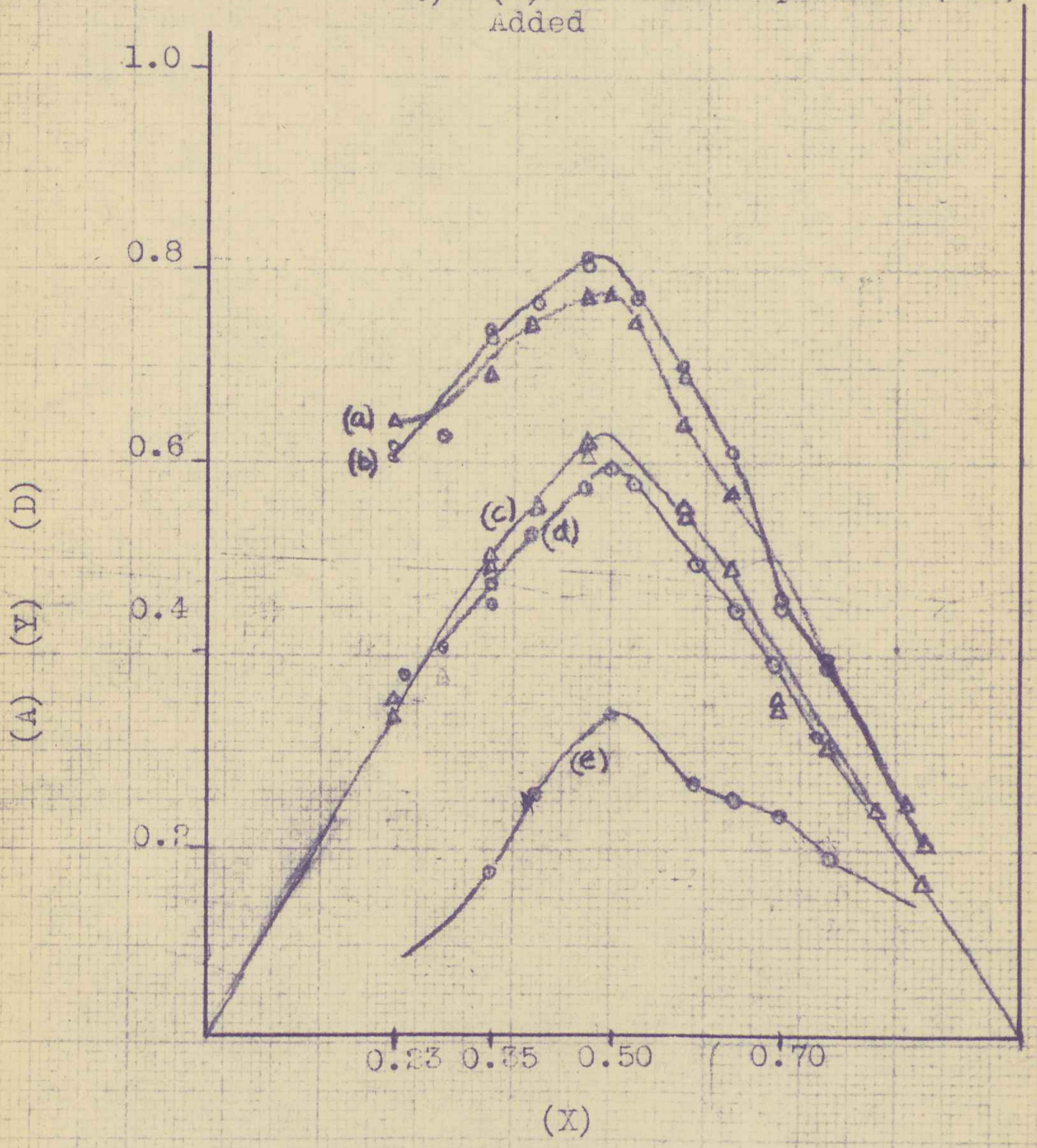


GRAPH No 5

JOB'S CONTINUOUS VARIATION METHOD
pH 9.4 and pH 9.6

(Y) Versus (X)
(A) Versus (X)
(D) Versus (X)

a) (A) at 510 mμ pH 9.6
b) (A) at 510 " pH 9.4
c) (Y) at 510 " pH 9.6
d) (Y) at 510 " pH 9.4
e) (D) at 510 " pH 9.4 (BAL)
Added



(D) Is difference between absorbances

TABLE VIII (Graph 6)

H_2DZ constant varying amount of thallous ion added

H_2DZ = approximately 4.25×10^{-7} moles

pH 9.4

Chloroform phase 15 ml ; aqueous phase 10 ml

	Tl Moles	Tl ml 8×10^{-4}	Absorbance at 510 mμ	at 440 mμ
1	$1x10^{-7}$	0.20	.338	.425
2	2x	0.43	.475	.334
3	3x	0.60	.600	.310
4	4.0	0.80	.742	.291
5	6.0x	1.20	.804	.277
6	8.0x	1.40	.804	.278
7	10.0x	2.00	.810	.275
8	9.0x	1.80	.810	
9	12.0x	2.40	.815	

H_2DZ = approximately 4.20×10^{-7} moles

pH 9.8

Chloroform phase 15 ml ; aqueous phase 10 ml

1	$1x10^{-7}$	0.20	.432	.372
2	2x	0.40	.519	.344
3	3x	0.60	.620	.317
4	4x	0.80	.740	.297
5	5x	1.00	.775	.298
6	6x	1.20	.788	.292
7	8x	1.60	.796	.291
8	10x	2.00	.800	.290

GRAPH No 6

ABSORBANCE VERSUS THALLOUS ION CONCENTRATION
DITHIZONE CONCENTRATION
CONSTANT

a) pH 9.4 (A) at 510 mμ
b) pH 9.4 (A) at 440 "
c) pH 9.6 (A) at 510 "
d) pH 9.6 (A) at 440 "

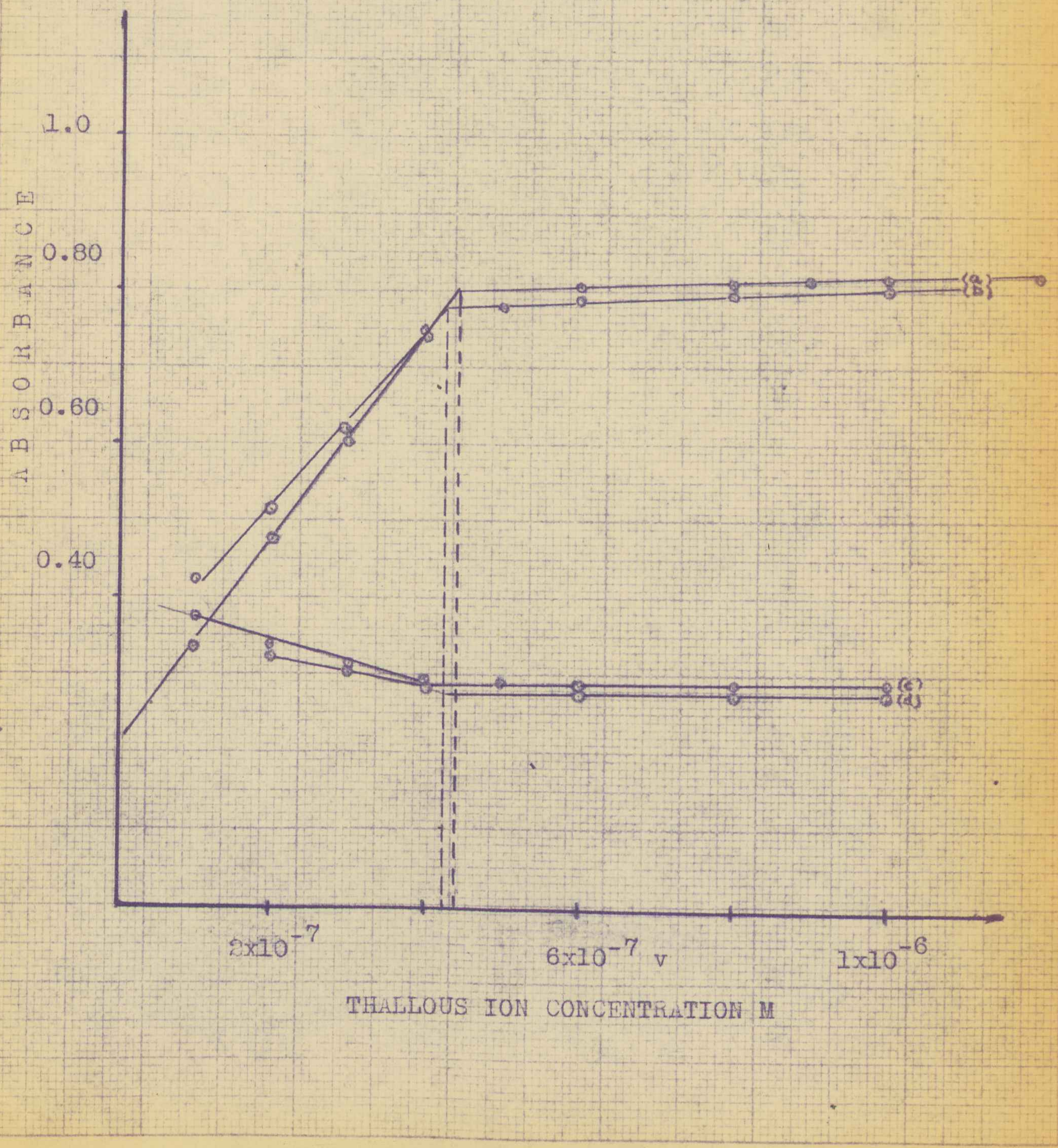


TABLE IX (Graph 7)

Effect of pH on absorbance

Dithizone and thallous ion concentrations constant.

H_2DZ moles	H_2DZ (ml)	Tl^+ moles	$Tl^+ (5x10)^{-4}$ ~~cc~~ ml	Buffer ml	pH	(A) at* 510 mu
6.5x10-7	11.0	6.5x10-7	1.30	12.7	6.0	0.545
6.5x	11.0	13.0x	2.60	11.4	6.0	0.555
6.5x10-7	11.0	6.5x10-7	1.30	12.7	8.0	0.575
6.5x	11.0	13.0x	2.60	11.4	8.0	0.700
6.5x10-7	11.0	6.5x10-7	1.30	12.7	9.0	1.100
6.5x	11.0	13.0x	2.60	11.4	9.0	1.240
6.5x10-7	11.0	6.5x10-7	1.30	12.7	9.6	1.430
6.5x	11.0	13.0x	2.60	11.4	9.6	1.550
6.5x10-7	11.0	6.5x10-7	1.30	12.7	10.0	1.640
6.5x	11.0	13.0x	2.60	11.4	10.0	1.750

* (A) --- absorbance

TABLE X (Graph 8)

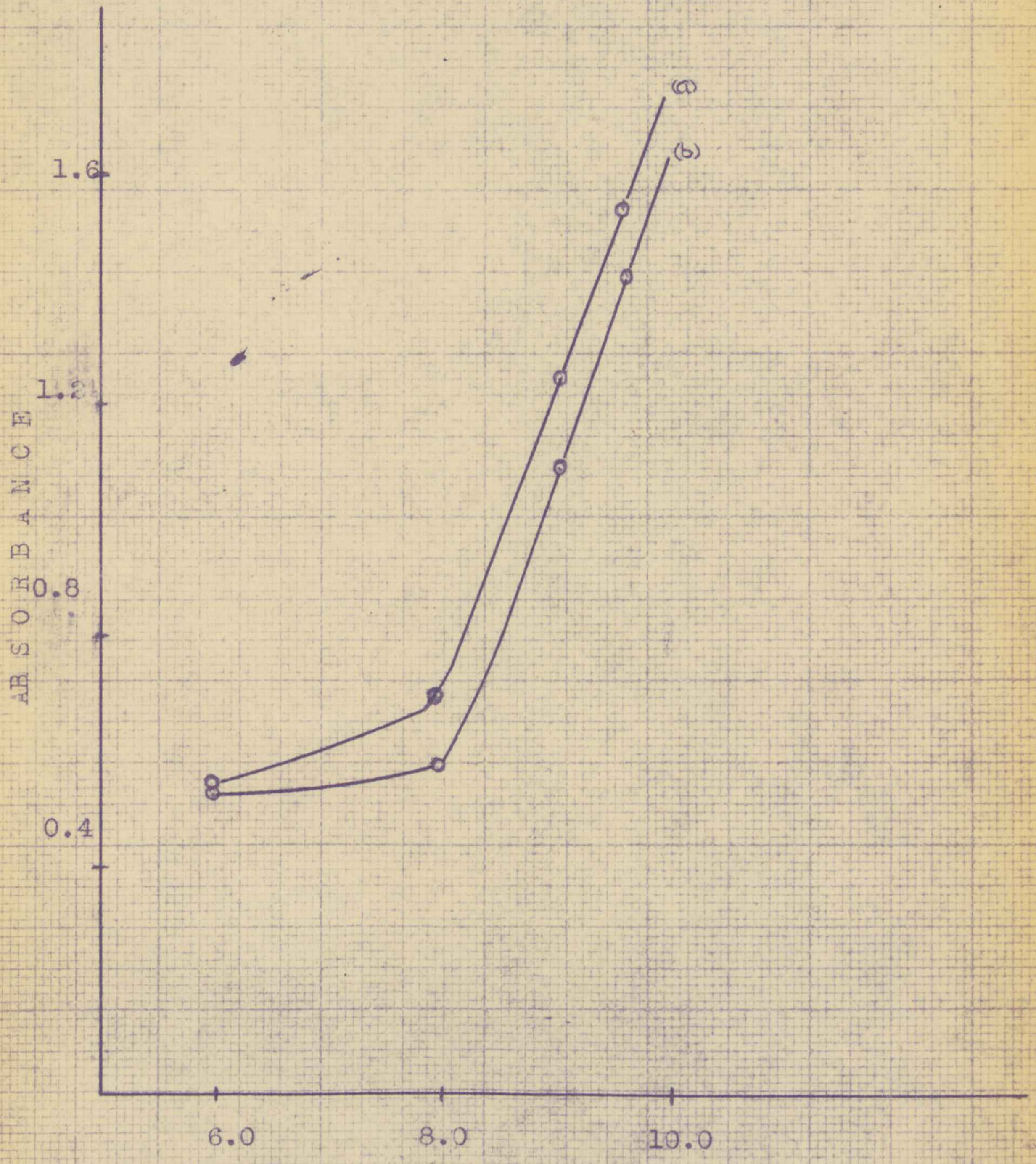
Weight of (TlxDz)	Chloroform (ml)	Absorbance at 510 mu	Molar (Tl H_2Dz)	a_m*
1.40 mg	50.0 cc	1.730	3.04x10-5	5.69x10+5
1.12 mg	50.0 cc	1.413	2.43x	6.14x
0.84 mg	50.0 cc	1.060	1.82x	5.82x
0.56 mg	50.0	0.703	1.21x	5.80x
0.39 mg	50.0	0.500	0.85x	5.82x
0.28 mg	50.0	0.330	0.61x	5.41x
				Av. 5.78x10-5

a_m is computed assuming that thallous dithizonate is of keto form having molecular weight of 459.7.

GRAPH No 7

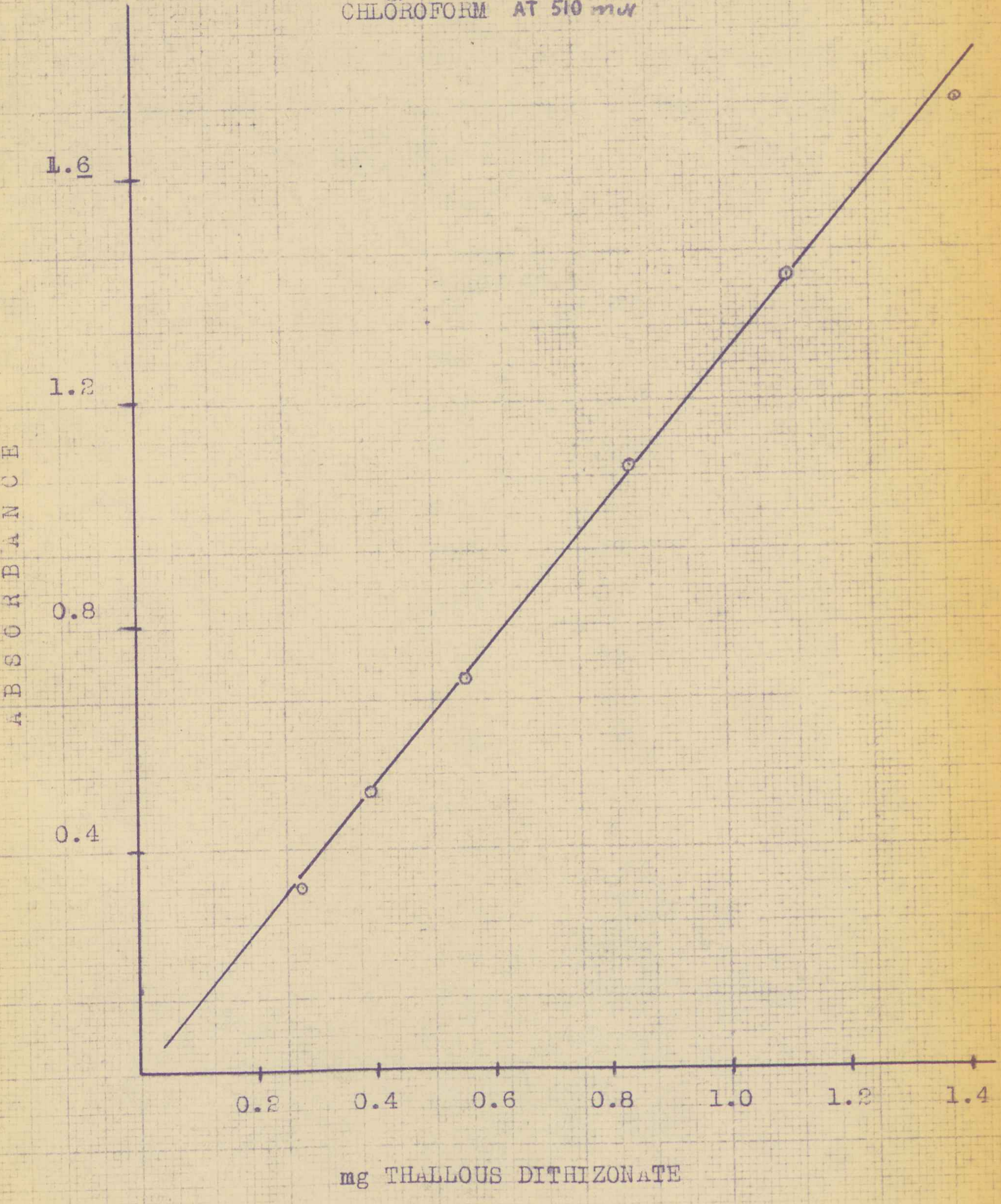
ABSORBANCE VERSUS PH

a) Thallous ion excess
b) Equivalent amount of thallous ion



GRAPH No 8

ABSORBANCE VERSUS THALLOUS DITHIZONATE
mg/50 ml IN
CHLOROFORM AT 510 mμ



Solutions for polarographic work were:

0.1 M in potassium chloride (KCl)

0.002% w/v in gelatin

Purified nitrogen was bubbled through the solution for 15 min.

Two compartment cell with agar-gel salt bridge and S.C.E. reference cell on one side--was used.

TABLE XI (Graph 9,10,11)

Volts	Deflections (A)	(B)	(C)	(D)	(E)	(F)	(G)
(−)	S=2	S=2	S=2	S=2	S=2	S=2	S=2
0.00	-3.5	-2.5	-2.0	-2.2	-2.5	0.0	0.0
0.05	0.9	2.0	1.0	2.0	1.0	4.0	4.0
0.10	7.1	8.5	6.8	12.0	7.2	9.9	9.9
0.15	9.1	11.1	9.5	16.0	10.5	13.0	13.0
0.20	10.6	13.0	11.0	18.1	12.1	16.0	15.9
0.25	12.0	14.5	12.0		13.5	17.4	17.5
0.30	13.2	15.5	12.6	21.5	14.7	19.0	18/8
0.35	16.0	17.0	14.0	22.7	15.5	21.0	20.0
0.375	19.2	19.8	16.0	23.6			
0.40	25.7	23.5	20.0	25.1	16.0	23.0	21.3
0.425	45.0	53.2	26.9		25.0	23.2	
0.450	75.0	48.6	38.4	35.7	16.8	28.0	25.0
0.475	S=5 50.5	73.0	56.7	45.6		32.0	29.0
0.500	65.0	92.0	73.0	54.1	17.8	36.5	33.0
0.525	74.5	S=5 42.5	82.7	59.5			
0.55	78.6	44.8	87.5	62.0	18.5	41.0	37.5
0.60	81.2	46.4	90.3	64.0	19.0	43.5	40.0
0.65	82.2	47.0	91.2	65.3	19.8	44.2	41.5

0.70	89.8	47.5	92.3	67.0	20.9	45.6	43.0
0.75	83.0	48.0	93.3	68.8	22.3	47.0	44.5
0.80	83.2	48.5	94.4	70.5	23.8	49.0	45.8
0.85	83.8	49.6	95.4	72.6	25.3	51.0	47.8
0.90	84.5	50.0	96.4	75.0	26.8	53.0	49.5
0.95	85.1	50.5	97.4	78.5	28.9		
1.00	85.5	51.0	98.2	80.5	30.2		
1.05					32.0		
1.10					33.3		
1.15					34.5		

a) Tl ion concentration 9.80x10^{-4} M

b) " " " 5.00x10^{-4}M

c) " " " 4.00x10^{-4}M

d) " " " 2x10^{-4} M

e) o.1M KCl--supporting electrotyte.

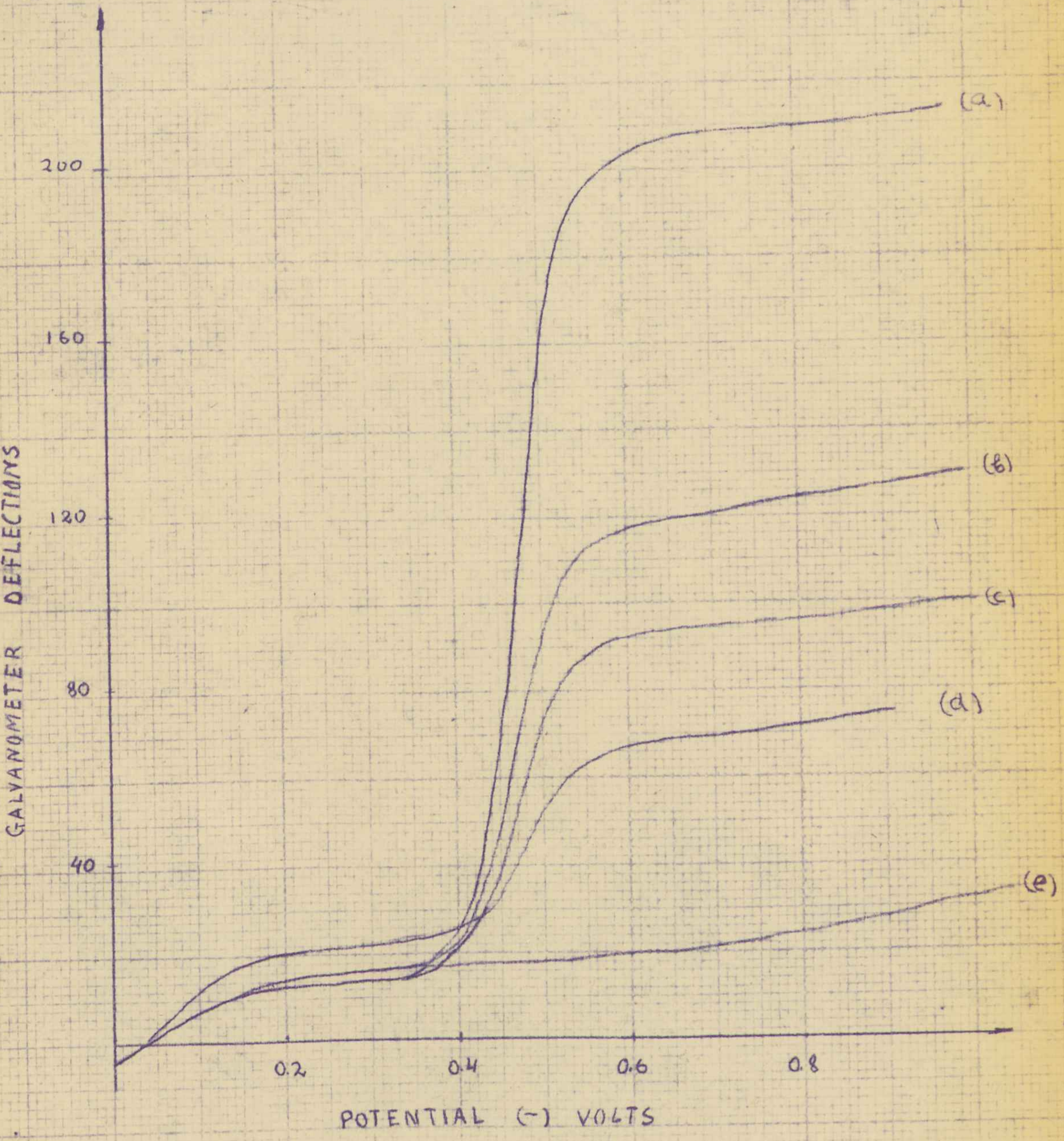
f) 2.24 mg of unknown thallous dithizonate

g) 1.86 mg of unknown thallous dithizonate.

GRAPH No 9

GALVANOMETER DEFLECTIONS VERSUS POTENTIAL

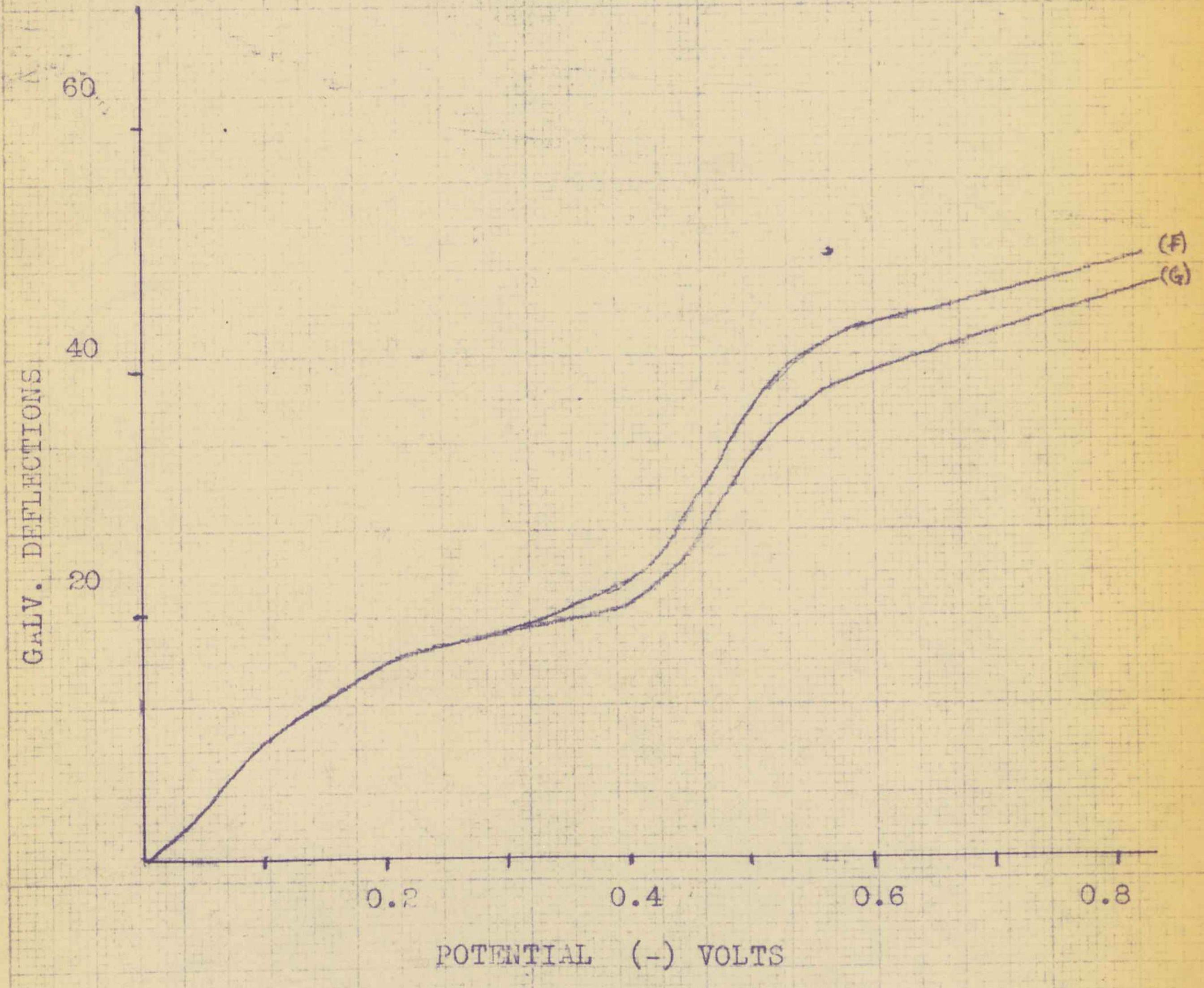
a) THALLOUS ION CONCENTRATION 9.8×10^{-4}
b) " " " $8.0 \times$
c) " " " $4.0 \times$
d) " " " $2.0 \times$
e) 0.1M KCl SUPPORTING ELECTROLYTE



GRAPH No 10

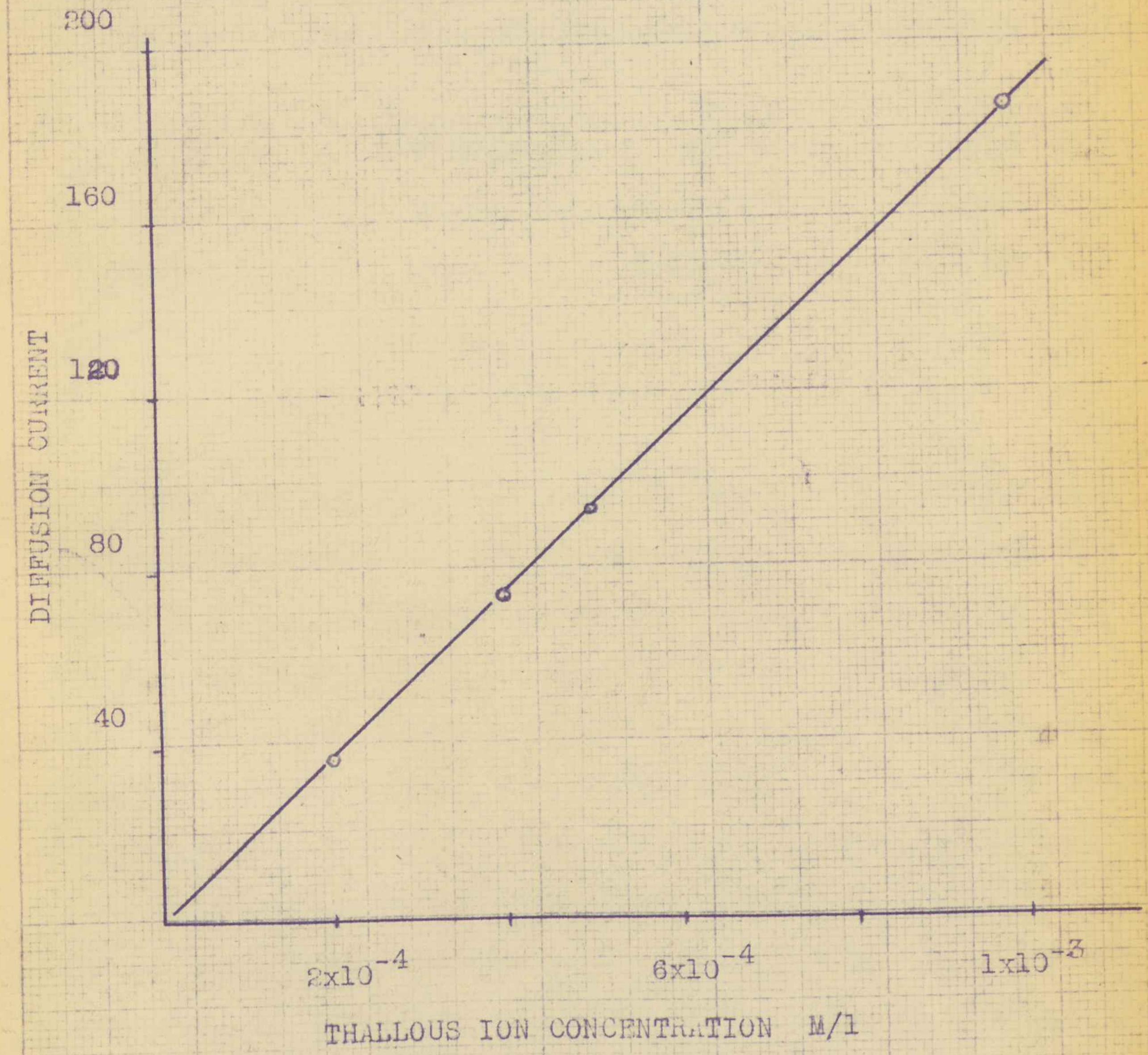
UNKNOWN THALLOUS DITHIZONATE
GALVANOMETER DEFLECTIONS VERSUS
POTENTIAL APPLIED

f) 2.24 mg of Thallous dithizonate
g) 1.86 mg " "



GRAPH No 11

DIFFUSION CURRENT VERSUS THALLOUS ION CONCENTRATION



From graph 11 we can evaluate the concentration of thallous ion. Two samples of unknown thallous dithizonate prepared as will be described were decomposed with hot sulfuric acid and hydrogen peroxide. In order to reduce thallium III back to thallium I hydroxyl ammonium chloride was used. The completeness of reduction was checked by measuring the absorbance of aqueous solution at 215 mμ and 240 mμ as recommended by Gritman (6).

By polargraphic work the following results were obtained:

Weight of sample mg	Galv. Deflections	Tl M/1 observed	Tl M/1 computed
2.24	16.5	0.94×10^{-4}	0.96×10^{-4}
1.86	13.7	0.79×10^{-4}	0.80×10^{-4}

From graphs 2A and 2B, curves a and b, it is evident that thallous dithizonate in chloroform solution has a maximum absorption at 510 mμ regardless of the ratio of reagents mixed. The curve c confirms that thallous dithizonate prepared as will be described later in chloroform solution gives a maximum absorption at 510 mμ. After addition of (BAL) to thallous dithizonate the absorption curve d becomes almost identical to that of the dithizone in chloroform solution (curve f). Thallous dithizonate in chloroform solution upon being exposed to strong sun light fades to a yellowish solution. This absorption spectrum (curve g) resembles that of the oxidation product of dithizone (diphenylthiocarbondiazone) (14). Besides, it is worth mentioning that the maximum absorption for thallous dithizonate 510 mμ almost coinside with a minumum for dithizone which is at 505 mμ .

In the application of Job's continuous variation method it is seen in graph 3 curves b, c, d, e ; that minima or maxima in (Y) occur almost at the same value of (x). This confirms the point of view that only one complex is formed where the "n" value is unity. The slightly higher values of (Y) and (A) when $x = 0.5$ are probably due to the greater solubility of keto-thallous dithizonate (TlH_4Dz) But from previous observations on the effect of relative ratios of reagents it is impossible to conclude that the enol complex might be formed.

The maximum in (A) occurs when $\frac{dc3}{dx} = 0$ which is seen from the graph to fall at the point where $x = 0.48$ and

$$n = \frac{x}{1-x} = 1.$$

From graph 4 it is evident that the difference between absorbances observed without (BAL) and after the addition of (BAL) gradually increases up to $x = 0.5$ and then reaches a minumum at approximately $x = 0.6$ and again returns to the expected level. This behavior, probably is due to the formation of enol thallous dithizonate, but there is no further substantiating evidence to prove it.

In graph 5 curves a, b, give maximum at x = 0.5, which confirms that there is only one complex present in chloroform solution at pH 9.4 and pH 9.6. Also the plot of Y against (x) shows a maximum at x = 0.5.

In order to establish the effect of one reagent on the formation of the colored product the measurements of absorbance may be used as recommended by Mellon (10). Keeping dithizone concentration constant and varying the amount of thallous ion the curves a, be, c, and d, in graph 6 are abtained. It is evident that in the beginning absorbance increases considerably until it reaches the point where the reagents are in 1:1 ratios. On further addition of thallous ion the absorbance increases very slightly which is probably due to the greater solubility of thallous dithizonate in chloroform. If there were another complex formed the slope would change at another equivalence point where the reagents would be in ratio (1:2) but this is not noticed.

The pH of the solution is of great importance in the study of metal dithizonates with respect to both: their formation and their solubility in the organic phase. By varying the pH and keeping dithizone and thallous ion concentrations and volumes constant curves a and b in graph 7 were obtained. Between pH 6--8 there is only a small amount of thallous dithizonate in chloroform phase, above pH 8 it increases rapidly. Besides, the excess thallous ion gives higher absorbance probably due to the increased solubility of thallous dithizonate in chloroform.

For determination of molar absorbancy index solid thallous dithizonate was prepared as follows:

Dithizone chloroform solution was shaken with thallous carbonate buffered at pH 9.6. After a few minutes the chloroform solution was separated from the aqueous phase and chloroform was evaporated slowly in the dark at room temperature, until a precipitate formed and only a few ml. of chloroform were left. Then it was filtered and the precipitate washed with cold alcohol and chloroform mixtures. The product was dried in a desiccator and was used for determinations, of molar absorbancy index as shown in graph 8, and polarographic studies.

On account of time limitations work could not be carried to the extent planned. One of the interestes of this work was to establish the equilibrium constant

$$K_m = \frac{[M^+]_w \, [HD_z]_W}{(Ml \, HD_z)_w}$$

for thallous dithizonates between two phases: chloroform and water. As already mentioned in previous discussion K_m could be computed from the relationship

$$\frac{(Ml \, HD_z]_o}{[M^+]_w} = \frac{P_m}{K_m} \qquad \frac{[H_2 DZ]_o}{F[H^+]_w}$$

if the partition coefficient (P_m), the amount of metal dithizonate in chloroform, the concentration of metal ion in water and the undissociated dithizone concentration in chloroform were known.

Having prepared keto-thallous dithizonate (TlHDZ) it is possible to determine the partition coefficient by absorbance measurements of chloroform solution or by using a radioactive isotope of thallium and determining by tracer methods.

Thallous ion concentration (Tl^+) in the aqueous phase might be determined by measuring the absorbance at 215 $m\mu$ of there are interfering substances present.

The amount of keto-thallous dithizonate $(TlHDZ)_o$ may be determined by measuring the absorbance at 510 $m\mu$. Since the molar absorbancy index for dithizone is about 100 times less than that for keto thallous dithizonate, the correction of observed absorbance is unnecessary, unless dithizone is in excess.

The amount of free dithizone $(H_2DZ)_o$ in the organic phase might be determined by extraction of thallous dithizonate with dilute acid, and measuring the absorbance of chloroform solution at 610 $m\mu$.

The (H^+) concentration of the solution may be measured by a pH meter. The "F" value is computed by Irving and co-workers as already mentioned.

From this data K_m may be evaluated.

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