

6-1953

Ultraviolet Spectrophotometric Determination of Metals with Thiocarbanilide

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ULTRAVIOLET SPECTROPHOTOMETRIC
DETERMINATION OF METALS WITH
THIOCARBANILIDE

BY

JOHN J. GRITMON

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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 Master of Science.

By John J. Gritmon

Approved by Galen W. Ewing

May 1953

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ACKNOWLEDGMENTS

I wish to express to Dr. Galen W. Ewing, my research supervisor, my sincere gratitude for his guidance and understanding during the performance of this work. Besides being profitable it was also most enjoyable for me to work with Dr. Ewing.

I also wish to thank Dr. Jerome Bigelow for his many helpful suggestions.

Gift of Author - 21 Nov. 1953

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ABSTRACT

The ultraviolet absorption spectra of thiocarbanilide (diphenylthiourea) were determined in aqueous solutions of varying acidity. The effect on the absorption spectra of thiocarbanilide of the addition of various cations (Ag^+ , Tl^+ , Ca^{++} , Fe^{++} , Fe^{+++} , Al^{+++} , La^{+++} , Au^{+++} and Ce^{++++}) was then determined. It was then necessary to establish whether complex formation had taken place. A correlation between the absorption spectra and data obtained has been attempted.

INTRODUCTION

Color is one of the physical properties of materials.

The analyst makes wide use of this property for identification and determination purposes. The beginning student in chemistry first feels the importance of color in the Qualitative Analysis laboratory. He soon realizes the information that can be gained and the time saved by careful observation of the colors of precipitates and solutions.

In recent years the use of colorimetric methods of measurements has been rapidly increasing on both a qualitative and quantitative scale (36).

Color according to approved definitions (35) is limited to the radiant energy (light) of the visible region of the spectrum. It should be understood that color is related to three things - the radiator, the object and the observer.

Absorptiometric Analysis in general terms applies to the invisible regions of the spectrum as well as the visible. A receptor of the radiant energy from the object is now a photocell in place of the human eye. In this case there will be no sensation of color. Since the work in this paper is concerned with the ultraviolet region of the spectrum, the term radiant energy will be used in place of light or color.

From the theoretical standpoint the problem of explaining the absorption of radiant energy of different frequencies in relation to structure is very difficult, to say the least.

Although a great deal of information has been obtained concerning the dependence of absorption of radiant energy on chemical

INTRODUCTION (Cont.)

constitution the majority of our knowledge is still empirical. By the use of the chemical-physical concept of resonance a correlation between molecular structure and absorption spectra can be arrived at on a qualitative basis. Since the mathematical basis for resonance lies in Quantum Mechanics, future advances in this field will be a great aid in clearing up present difficulties. Nevertheless a foundation for a modern theory of absorption has been laid (10).

The work in this paper was performed in the near-ultraviolet (200-400 $m\mu$) region of the spectrum. Previous work on the absorption spectra of thiocarbanilide was reported by J. E. Purvis (38). However, the information obtained was of little value to the present problem. Loh and Dehm (32) showed that thiocarbanilide formed definite addition compounds with various reagents. On this basis the present study was made to determine whether thiocarbanilide could be used as an analytical tool in the ultraviolet region of the spectrum.

HISTORICAL

The first major advance leading to our present theories of color was made in 1868 when Graebe and Liebermann (17) recognized that in order for a compound to be colored, visible light must be absorbed. The type of compounds exhibiting this phenomena must be unsaturated. Witt (47) in 1876 introduced the term chromophore. Chromophores are unsaturated linkages that have the potentiality for color. Examples of chromophores are the ethylene, azo, carbonyl and nitroso linkages. He also introduced the term auxochrome. The ability of a compound to be colored will be increased by the presence of such auxochromes as the hydroxyl and methyl groupings. Actually an auxochrome is a color aiding group. Hewitt (20) around the turn of the century proved that the color would deepen with an increase in the conjugated system.

The first promising solution of the origin of spectra was advanced by Bohr (1917). Bohr applied the quantum theory to the hydrogen spectrum. His theory accounted for the spectral lines of hydrogen as resulting from an electron moving from a high energy level to a lower energy level. As a result of this process radiant energy is emitted. Absorption is the reverse process. With the low atomic number elements, mathematical formulation of these excited states is possible. In the case of molecules this has not been realized as yet.

Bury (6) in 1935 pointed out the importance of resonance in affecting color and by the use of this theory the excited states of compounds may be approximated. Bury by combining the ideas of Witt and Bayer (1) in conjunction with the resonance

HISTORICAL (Cont.)

theory attempted to explain molecular spectra.

From the evidence presented up to the present day it can be concluded that absorption of light is due to vibrating electrons. Clar (7), Henrici (19), Lewis and Calvin (31) have presented empirical formulas whereby some quantitative generalizations can be made in regard to absorption spectra.

For a more detailed discussion of the historical background of absorption spectra the reader is referred to the following articles (14), (11), (28), (12) and (44).

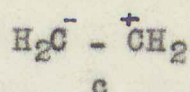
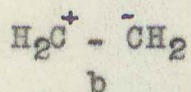
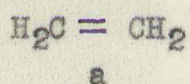
THEORY

Part I: Resonance and Molecular Structure

The largest amount of work on the absorption spectra of organic compounds has been obtained with solutions. In the case of the ultraviolet and visible regions of the spectrum where we are considering electronic spectra, the absorption bands are continuous. This is the result of the overlapping of many vibrational and rotational states (34), (3). The maximum in the band corresponds to the most likely transition.

In order to obtain a qualitative viewpoint of the excited states of molecules as the result of the absorption of radiant energy, the theory of resonance is invoked. Resonance energy is important in the consideration of both the ground and the excited state. It is not the magnitude of the resonance energy of the molecule that determines the wavelength of absorption but rather the difference of the resonance stabilization between the ground and excited state (15). In the case of conjugated systems, as the number of double bonds increases the number of structures for an excited state increases over the number of ground state structures. As a result the absorption will shift to lower frequencies. The fundamental idea in this case is that the more structures that can be drawn to represent a molecule in a certain state the greater is the resonance energy and hence the greater the stability of that state.

In the case of ethylene, the contributing structures can be written as follows

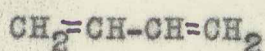


THEORY (cont.)

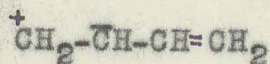
Structure (a) would be more stable than (b) or (c) (43).

We can consider (b) and (c) contributing to the resonance energy of the ground state, but the contribution is small. On the other hand the excited state may be represented by (b) and (c) with a small contribution from (a). In this excited state there are probably contributions from other structures. It is to the structure (b) and (c) that the absorption of light is attributed.

In the case of butadiene the structures may be written as follows:



A



B



C



D

Essentially the ground state can be represented by (A) with small contributions to the resonance energy from B to D (5). Obviously B-D are at much higher energies than A. The first excited state however can be represented by B, C and D. Now in comparing the two states it can be seen that the differences in energies of the structures representing the excited state as compared to the ground state is much less. Therefore the contribution to stabilization would be large. Although the effect of B may raise the energy a slight extent the net effect is a lower energy than would be expected if no resonance were possible. Also the stabilization in the excited state as a result of resonance is greater than in the ground state. It follows then that the energy of excitation is lower, and hence the absorption occurs at longer wavelengths than if there were no resonance. Since the resonance in butadiene is greater than that in ethylene it can be concluded (due to their similarity) that an increase in conjugation should

THEORY (cont.)

result in an increased wavelength of absorption. This is borne out experimentally.

The intensities, as well as the wavelengths of absorption are affected by the resonance. In the case of the conjugated systems the intensity per double bond increases as the length of the conjugated chain increases. The entire question of intensity is not very well understood at the present time.

For further information on resonance and absorption spectra the reader is referred to (14), (30), (2), (44), (28), (13) and (40).

THEORY (cont.)

Part II: Bouguer - Beer Law

When a ray of monochromatic light passes through an absorbing medium, the intensity of the emergent ray is less than the incident ray. The quantitative measure of this change in intensity is governed by two laws: Beer's and Bouguer's.

Bouguer's law states that the intensity of the incident beam decreases exponentially with an increase in the thickness of the absorbing medium traversed (46).

$$\log_{10} \frac{I_0}{I} = Kb$$

I_0 is the intensity of the incident ray.

I is the intensity of the transmitted ray.

K is a constant for any given wavelength.

b is the length of the absorbing layer in centimeters.

In the consideration of solutions where concentration must be taken into account, Beer's law applies. Beer's law states that the intensity of the incident beam decrease exponentially with an increase in the concentration of the absorbing medium traversed.

$$\log \frac{I_0}{I} = K'c$$

K' is a constant depending on the wavelength.

c is the concentration of absorbing solute.

Combining the two laws:

$$\log \frac{I_0}{I} = a_s cb = A_s$$

a_s is constant depending only on the wavelength of light and the nature of the solution. It is given the name absorbancy index according to the terminology of the National Bureau of

THEORY (cont.)

Standards (37). Previously it was known as the extinction coefficient.

A_s is the absorbancy or optical density, sometimes referred to as the extinction. The units for absorbancy are clearly dependent upon those of b and c . b is usually expressed in centimeters. The two most widely used units for c are grams per liter and gram-moles per liter. If grams per liter is chosen then the proportionality constant is given the symbol a_s . On the other hand if gram-moles per liter is chosen the constant is given the symbol a_m known as the molar absorbancy index.

In order for these laws to apply it is necessary to use monochromatic light. Bouguer's law has no exception but this cannot be said for Beer's law. Beer's law will be violated if dissociation, association or tautomeric behavior of the solute in solution and if the blank cell does not compensate for reflection losses. When applying Beer's law it is well to think of the words of Körtum (29) after summarizing evidence on this point, "the validity of Beer's law for ions must be considered as an exception rather than as a rule. Validity over large concentration ranges is not to be expected since Beer's law is a limit for low concentrations" (34).

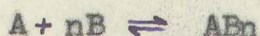
For further information concerning these laws the reader is referred to the following authors (16), (42), (4) and (18).

THEORY (cont.)

Part III: Job's Method of Continuous Variation

Job's method of continuous variation is applied to the identification of compounds or complex ions formed in solution. It consists in the determination of a physical property at various ratios of the two constituents. The property measured may be the absorbancy index, refractive index etc.

The reaction taking place in solution may be represented by the following equation



In order to determine n , solutions of A and B are mixed in varying proportions and a suitable property measured. The difference between each value found for the mixture and the corresponding values for A and B alone is plotted against composition. If no reaction has taken place, the plot will be a straight line. If a reaction has taken place the concentration value where AB_n is present in the largest amount will be indicated by a maximum or minimum in the curve obtained, depending on whether the compound formed has a lower or higher value (absorbancy index) than A and B alone. From the ratio of A to B it is possible to determine the compound formed.

The major condition in applying this method is that A and B are of the same molar concentration at the beginning so that on mixing the two solutions at various ratios, the final molar concentration will be the same for the various solutions. Otherwise the maximum or minimum obtained will be a function of the equilibrium constant as well as of n . Another condition is that the property measured be proportional to the concentration of the species.

THEORY (cont.)

For a more comprehensive discussion of this method the reader is referred to (24), (48) and (23).

EXPERIMENTAL

The absorption spectra obtained in this work were determined with a Model D U Beckman Spectrophotometer (8), Serial No. 3210.

The spectral band width obtained for each reading was within the approximate range of 1.7 to 0.40 mm. The sensitivity control was set at nearly minimum sensitivity in order to obtain wavelength readings down to $210\text{ m}\mu$.

Readings obtained were $5\text{ m}\mu$ apart with the exception of the mixture of silver and thiocarbanilide. In this case, as the maximum and minimum were approached, readings of $1\text{ m}\mu$ intervals were obtained. Since this method did not produce a better clarification of the peaks than the $5\text{ m}\mu$ interval, it was discontinued in the remaining spectra.

Matched, fused-silica cells of $10\text{mm} \pm 0.01\text{mm}$, square cross-sectional area were used.

The melting point determination of thiocarbanilide was made by means of a capillary tube attached to a thermometer that had been previously standardized with compounds of known purity.

The Roller-Smith torsion type balance (50 mg full scale) was used in all weighings.

The polarograms were determined by means of a Fisher Electrode.

All buffer solutions were checked with a Beckman Model - G pH meter.

EXPERIMENTAL (cont.)

Compounds Used

1. Thiocarbanilide was obtained in the pure state by recrystallization from an aqueous alcohol solution. This procedure was carried out twice and the melting point was found to be 152 - 153° C which checked with the literature.

The salts used in this work were obtained from the chemical stockroom unless otherwise stated. Purification of them did not seem essential because of the high dilution.

2. AgNO_3 - C.P. Percent of impurities not listed.

3. Tl_2SO_4 - Obtained from E. K. Bacon. Sample had been recrystallized twice previously.

4. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ - C. P. Per cent of impurities not listed.

5. AuCl_3 - A solution of unknown concentration obtained from C. B. Hurd. Analyzed by evaporating 10 ml. of solution to dryness and then weighing the gold.

6. $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ - C. P. Per cent of impurities not listed.

7. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ purity = 99.88%

8. $\text{Fe}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ purity = 99.86%

9. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ purity = 99.66%

10. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ purity = 99.79%

EXPERIMENTAL (cont.)

Preparation of Solutions

The stock solutions prepared varied in concentration between the limits 10 - 50 mg. per liter. The reference liquid used as the blank was identical with the solvent that contained the various components. In determining the absorption spectra, aliquot portions of the stock solutions were diluted to one liter so that the resulting concentration was in the range of from 1 to 3×10^{-5} molar, depending on the intensity. Results were reproduced with the maximum deviation being ± 0.004 for the optical density in the 230 - 255 $m\mu$ region.

Since thiocarbanilide only has a limited solubility in water it was necessary to effect solution by dissolving the sample in a few ml. of 95% ethonol. No effect on the absorption spectra was observed.

Clark and Lubs buffers (9) were used for alkaline solutions. In the pH range 2-6, the biphthalate salt in the Clark and Lubs buffers absorbs below 300 $m\mu$. It was therefore necessary to use Sorensen's glycine-hydrochloric acid buffers (43) since I preferred a pH between 2-3 for acid solutions.

The solutions for the determination of the polarograms were from 1 to 3×10^{-5} molar. A 0.02% gelatin solution (46) was added to suppress the maximum which might occur in the polarogram. Sodium sulfite was added in order to reduce the oxygen (46). All polarograms were obtained on neutral solutions.

In the "Job's Method of Continuous Variation" the molar concentrations of lanthanum and thiocarbanilide were identical (1×10^{-5}) at the beginning. For calcium and thiocarbanilide the concentrations

EXPERIMENTAL (cont.)

used were 1×10^{-4} molar.

Thiocarbanilide (diphenylthiourea) was oxidized to diphenylurea by means of sodium peroxide in an alkaline solution according to the method suggested by Loh and Dehm (32).

Thallous ion was oxidized to thallic by means of chlorine as suggested by Hopkins (21).

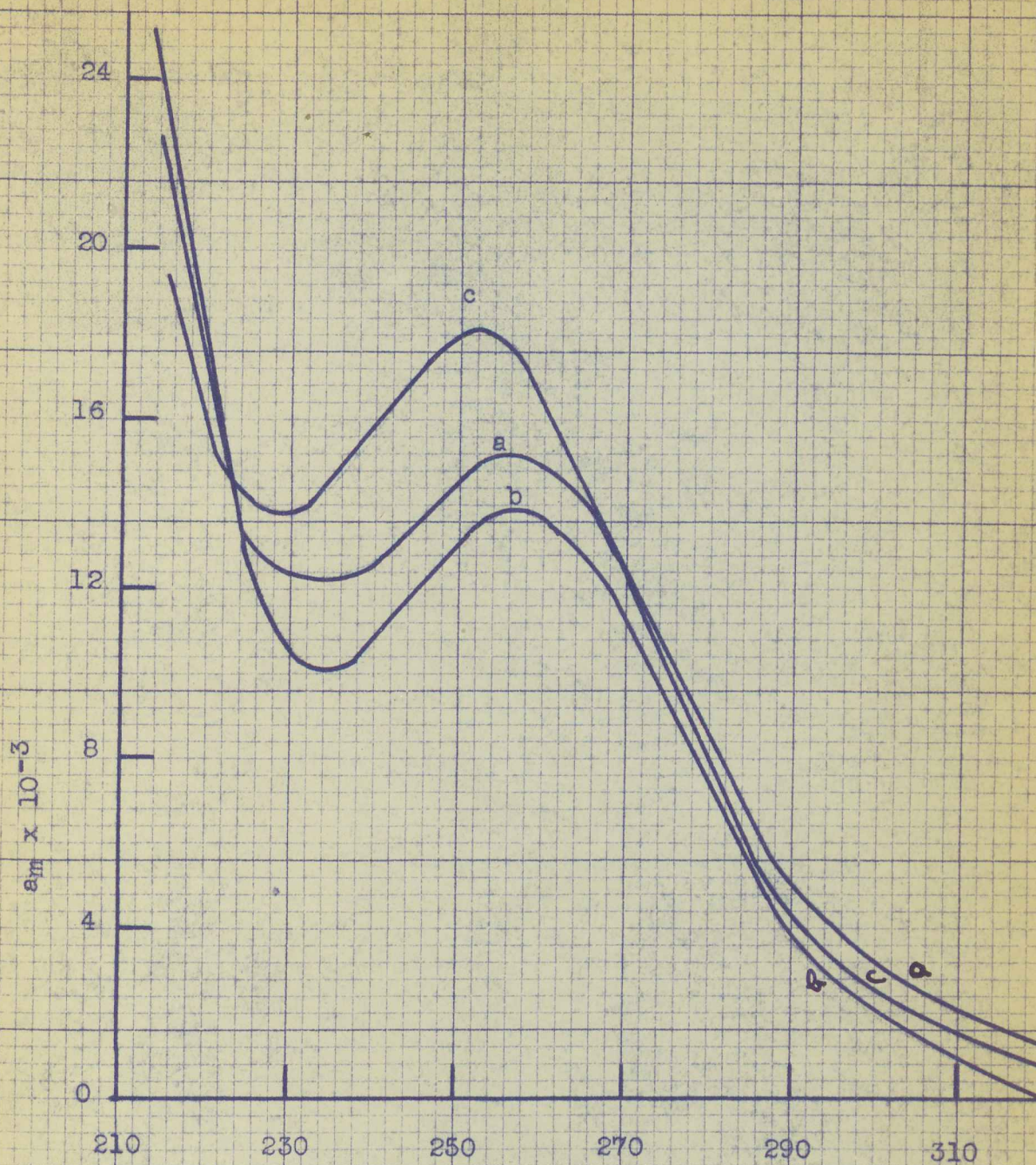
DISCUSSION

Thiocarbanilide

The ultraviolet absorption spectra of thiocarbanilide were determined in aqueous solutions of varying acidity. An increase of pH causes a hyperchromic (25, 26) (increased intensity) shift as shown by Graph I. There is also a hypsochromic (25, 26) (toward shorter wavelengths) shift of 4 m μ for maximum absorption in the basic solution as compared to the acid and neutral solutions.

It can be assumed that the main contributing structures of thiocarbanilide in acidic, neutral and basic solutions can be represented by I and II, III or V, VII and VIII respectively. (Roman numerals refer to the resonance structures in the appendix). The structures for the excited states for acid and basic solutions are difficult to realize qualitatively. For the basic solution IX and X represent excited states but the difference in energy between the ground and excited states is undoubtedly so large that these structures only offer a very small contribution to the excited state actually obtained. In the case of the acid solution the difference in energy would be even larger and it is difficult to draw a structure representing an excited state. A positive charge would probably be located on a carbon atom in the benzene ring.

For neutral solutions the problem of tautomerism comes into play. As pointed out by Sidgwick (41) there is evidence that thiocarbanilide exhibits this phenomena in solution (III and V). Certain reactions of thiocarbanilide indicate the presence of the thiol (-SH) group. Since there is no direct evidence of tautomerism Sidgwick offers the explanation for the reactions on the basis of the zwitterion formula (IV). For the purpose of this work it may



Absorption Spectra of
Thiocarbanilide

- (a) Neutral (no buffer)
- (b) pH 2.10 (buffer)
- (c) pH 11.32 (buffer)

DISCUSSION (cont.)

be assumed that the zwitterion represents a structure of the excited state. The enol tautomer's excited state could be represented by VI.

However, since the purpose of this work is not concerned so much with determining structure as seeking an analytical tool no step in the direction of solving this structural problem was taken. The zwitterion formula does simplify the explanation for reactions that do take place in this work. The structural formulas presented offer interesting speculation but it must be understood that correlation between resonance structures and observed spectra is mainly empirical and may be an inadequate explanation.

It may have been advantageous to determine the spectra of thiocarbanilide at other pH's. However it was felt that if a significant change should result, it would be in a strongly acidic or basic solution (although this does not necessarily hold). Another factor was the time involved.

Silver and Thiocarbanilide

The absorption spectra of a 1:1 molar ratio of silver and thiocarbanilide were determined at various pH's as shown in Graph II. The silver nitrate alone exhibited a slight absorption in the vicinity of 260-300 $m\mu$ which was attributed to the NO_3 radical (39) since the spectra of $\text{La}(\text{NO}_3)_3$ and $\text{Ca}(\text{NO}_3)_2$ were very similar (Graphs IV and IX). However, this would not account for the large hyperchromic shift with increasing pH (Graph II) as compared with thiocarbanilide alone (Table I). Also it should be noted that the wavelengths for maximum absorption are essentially the same in the three solutions (250 $m\mu$) although there is a hypsochromic shift of 7 $m\mu$ for acid and neutral and 3 $m\mu$ for basic as compared to thio-

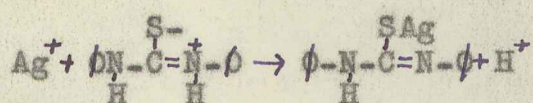
DISCUSSION (cont.)

carbanilide.

The problem resolves itself in determining whether or not complex formation has taken place. Yoe and Overholser (49) showed that Ag and thiocarbanilide in neutral, acid and basic solutions gave a tan, white and brown to black precipitate respectively. As a result the silver-thiocarbanilide complex was precipitated from a neutral solution by adding an excess of silver nitrate to a known amount of thiocarbanilide, allowed to air dry for a few hours (since it was found to decompose on standing for any large interval of time) and weighed. The results within the limits of experimental error showed the compound to be $\text{AgC}_{13}\text{H}_{11}\text{N}_2\text{S}$.

Complex formation is associated with a displacement of hydrogen ions (32). As a result metal complexes should be more stable at high pH and with the exception of the most stable should be extensively dissociated at low pH.

Considering the zwitterion the reaction in neutral solutions can be represented as follows



That the addition is not on the nitrogen is explained by the fact that diphenylurea is unable to form corresponding additive compounds (31).

Since the absorption maxima for the three solutions are at the same wavelength it can be assumed that the difference in structure is essentially the stability of the complex. As mentioned previously the question of changes in intensity is not very clear but it nevertheless can be seen from Graph II that as the stability of the complex increases the intensity increases.

In the final comparison of the two graphs it may be noted

DISCUSSION (cont.)

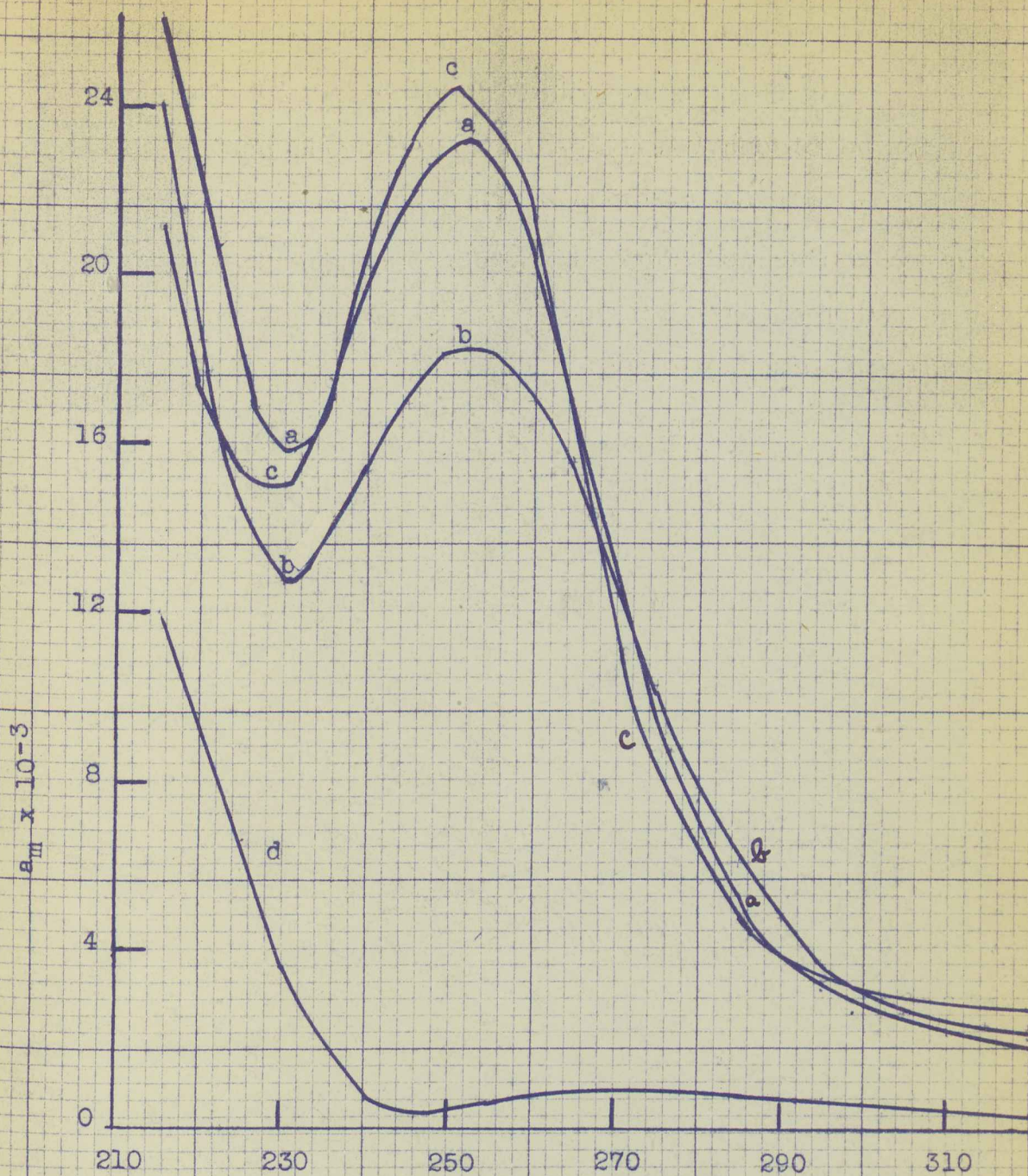
that the changes resulting from the addition of silver nitrate to thiocarbanilide result in an increased intensity and a decrease in wavelength of maximum absorption to $250\text{ m}\mu$ for the three solutions. The hypsochromic shift can be accounted for by the decrease in the resonating property of sulfur due to the silver. The added mass of silver may account for the increase in intensity.

Thallium and Thiocarbanilide

The absorption spectra of a 1:1 molar ratio of thallium (ous) and thiocarbanilide were determined in solutions of varying acidity (Graph III).

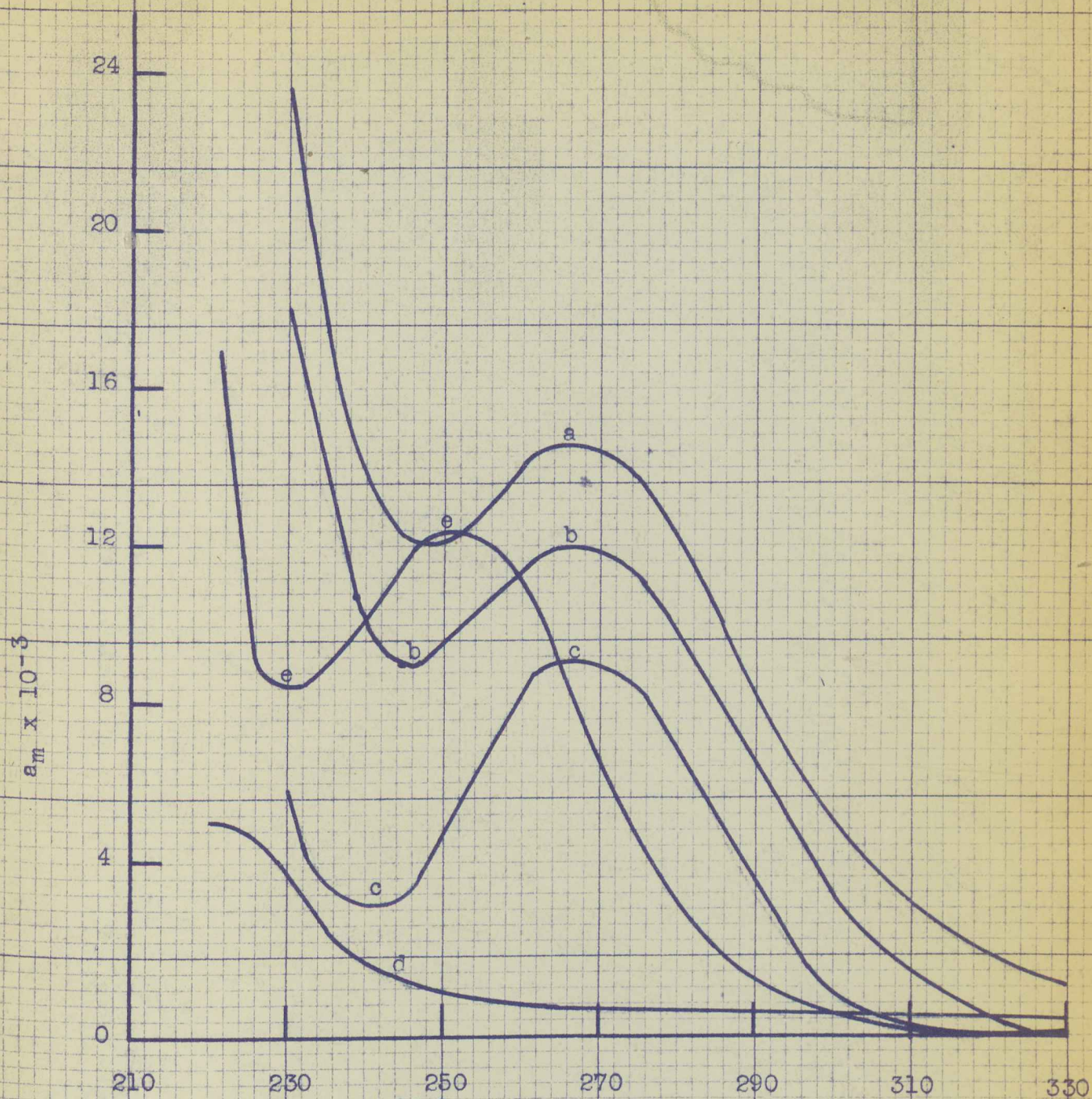
In this case there is a hypochromic (decreased intensity) shift as compared to thiocarbanilide. In an acid medium the change is slight (Table I) whereas in a neutral solution the difference is negligible since it falls within the experimental error. However, the decrease in molar absorbing index in the basic solution is very large (Note Table I) whereas the variation in wavelength is very small, $\pm 2\text{ m}\mu$.

In order to account for the large discrepancies it was first necessary to determine if complex formation had taken place. Thallium and thiocarbanilide will precipitate from a basic solution (49) but decomposition takes place in a very short time. Therefore the polarographic method (46) was chosen in which the maximum for the diffusion current was obtained at various concentrations. A plot of I_d against c in moles per liter was then made (Graph XIII). The dotted line indicates a solution of 3×10^{-5} moles of thallous and 1×10^{-5} moles of thiocarbanilide. Since it corresponds very closely to 2×10^{-5} moles of thallous ion alone,



Absorption Spectra of
Silver and Thiocarbanilide
1:1 Molar Ratio

- (a) Neutral (no buffer)
- (b) pH 2.10 (buffer)
- (c) pH 11.90 (buffer)
- (d) AgNO_3 Aqueous solution



Absorption Spectra of
Thallium and Thiocarbamilide

1:1 Molar Ratio

(a) Neutral (no buffer)

(b) pH 1.07 (buffer)

(c) pH 11.32 (buffer)

(d) Tl_2SO_4 Aqueous solution

(e) Tl^{+++}

DISCUSSION (cont.)

the conclusion can be drawn that one mole of thallous ion reacted with one mole of thiocarbanilide.

Since the complex $Tl(C_{13}H_{11}N_2S)$ should be more stable in basic solutions this would probably account for the large decrease in molar absorbandy index. The question arises however as to why silver causes a hyperchromic shift while thallium causes a hypochromic shift. This question will be considered later.

The absorption spectra of thallic ion has also been determined (curve e of Graph III) mainly out of curiosity since to my knowledge no previous spectrum has been obtained for it. The procedure for oxidation was that of Hopkins (21).

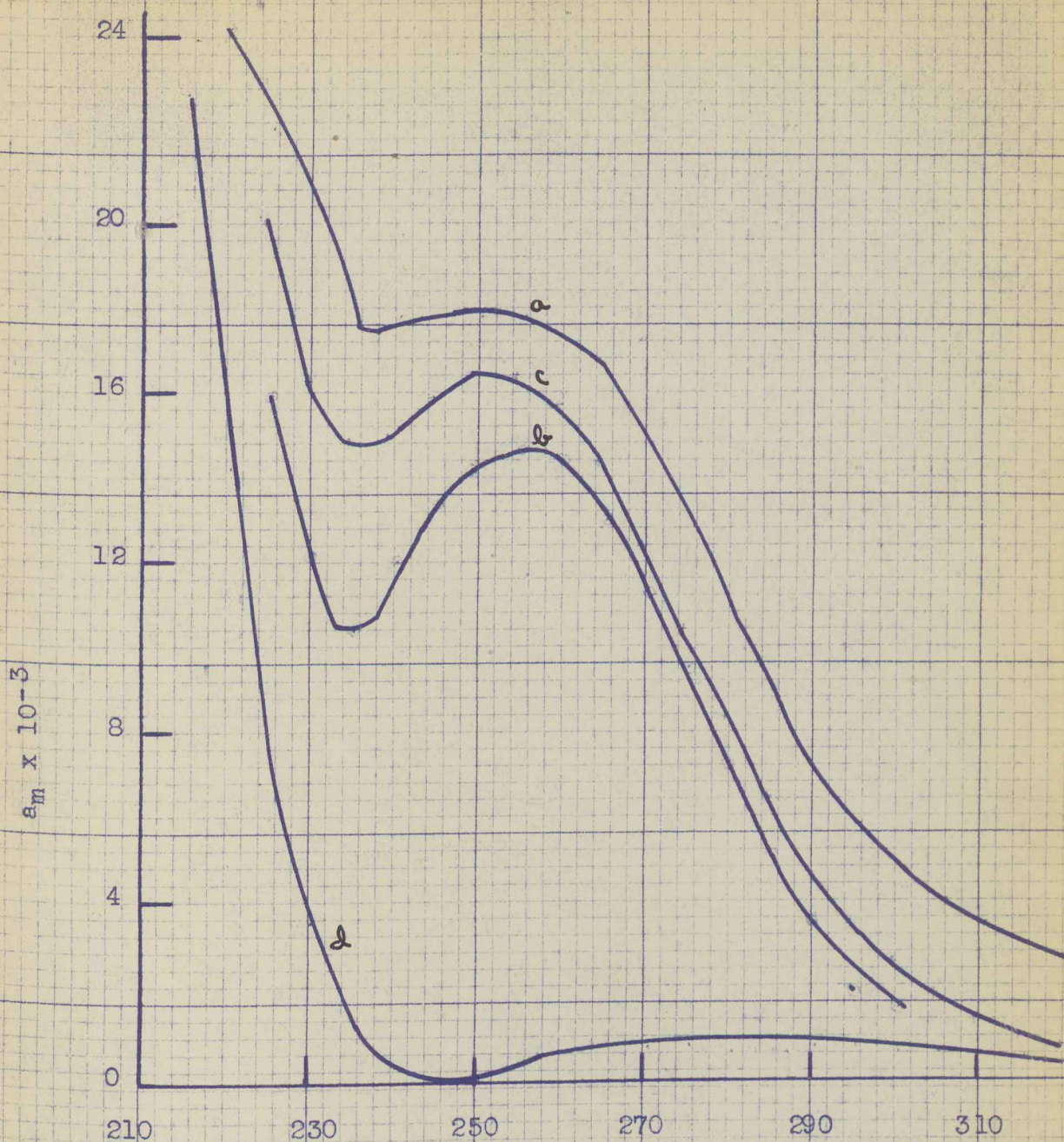
Lanthanum and Thiocarbanilide

The procedure of lanthanum is similar to that for silver and thallium. A hyperchromic shift for the acid and neutral solutions is exhibited while the basic solution shows a hypochromic shift as compared to thiocarbanilide alone (Graph IV). The main point of interest is that in the neutral solution there is an extreme flattening of the absorption peak.

The proof of the formation of a complex was determined by "Job's Method of Continuous Variation" (Graph XII). The $La(NO_3)_3$ and thiocarbanilide solutions were made up at the same molar concentrations (1×10^{-6}) so that on mixing them at various ratios the final molar concentration would be the same (1×10^{-6}). Since a definite peak is formed at 0.5 for the different wavelengths it can be concluded that a 1:1 complex was formed. The explanation for the variation at other ratios lies in the low concentrations which meant a low optical density.

Considering the molar absorbandy index for the three cations

Graph IV



Absorption Spectra of
Lanthanum and Thiocarbanilide

1:1 Molar Ratio

- (a) Neutral (no buffer)
- (b) pH 1.30 (buffer)
- (c) pH 11.20 (buffer)
- (d) $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ Aqueous solution

DISCUSSION (cont.)

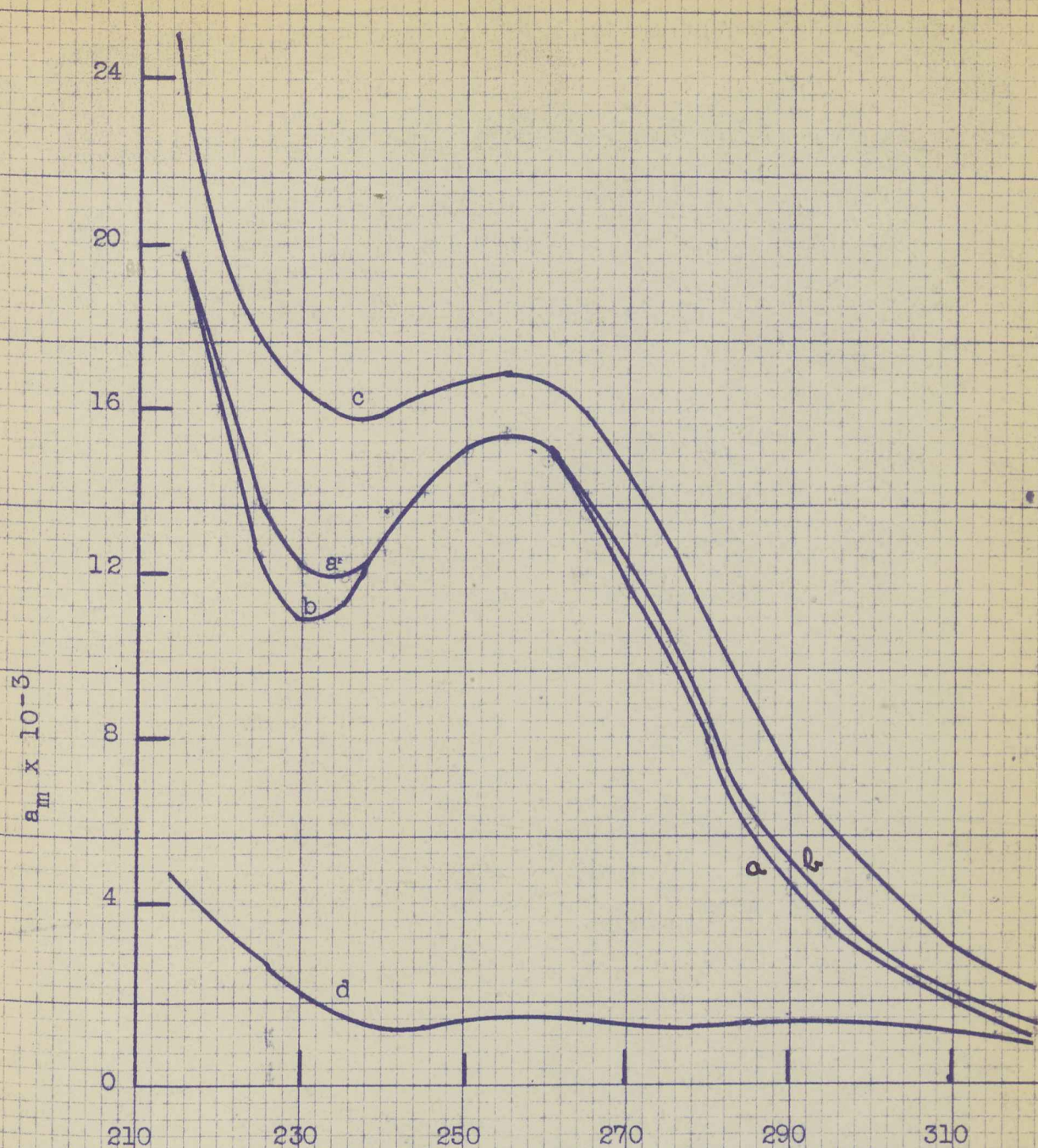
in solution of varying acidity it can be seen that no definite pattern has been followed. The variation with acidity is different for the three. The only explanation is that the difference lies in the properties of the cations and in the stability of the complex.

Cerium and Thiocarbanilide

Cerium (Ic) and thiocarbanilide exhibits the same molar absorbancy index in acid and neutral solutions and shows a slight increase in basic solutions (Graph V). Although the ceric salt alone possesses considerable power for absorption of radiant energy, this can be disregarded since complex formation takes place as proven polarographically (Graph XIII). Again it is found in a basic solution that the molar absorbancy index for the complex is lower than for thiocarbanilide alone. (This is similar to La and Tl but not to Ag).

Gold and Thiocarbanilide

AuCl_3 absorbs to a large degree as can be seen from Graph VI. In the case of the neutral solution no definite peak is produced. However, gold and thiocarbanilide do not form a complex (Graph XV) to any significant degree of stability. Therefore since absorption is additive the AuCl_3 curve was subtracted (22) from the neutral curve (Graph XVI). The maximum and minima are then obtained and the behavior of the three solutions is now similar to silver (Table I). In order to explain the peaks for the acid and basic solutions it must be assumed that some degree of complexing is taking place. As Yoe and Overholser state there is a decolorization in concentrated solutions but no precipitate is formed. On this basis and in considering the spectra obtained I would say



Absorption Spectra of
Cerium and Thiocarbanilide

1:1 Molar Ratio

- (a) Neutral (no buffer)
- (b) pH 1.70 (buffer)
- (c) pH 11.65 (buffer)
- (d) $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$

DISCUSSION (cont.)

some degree of complexing has no doubt taken place in the acid and basic medium.

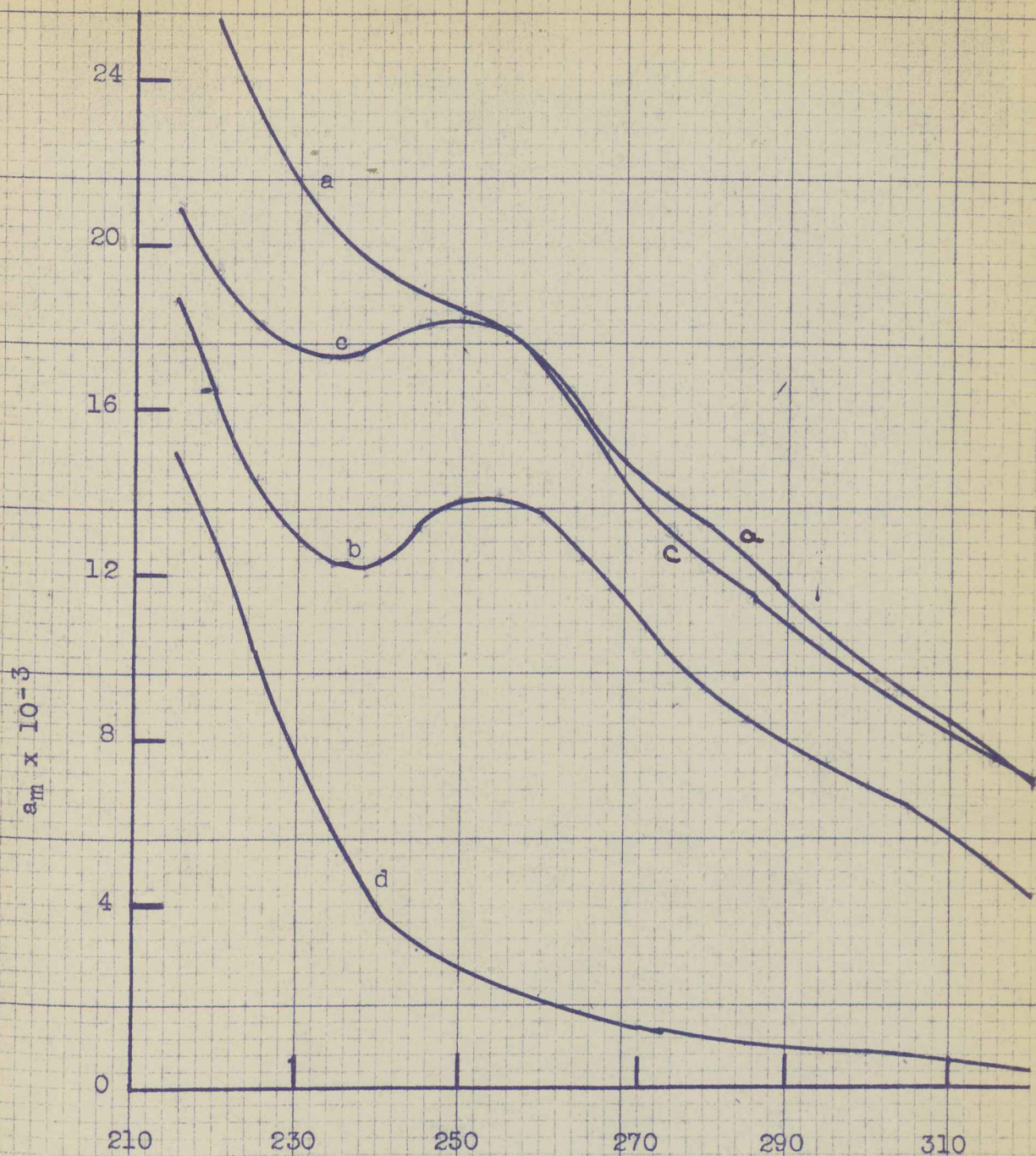
Fe^{++} , Fe^{+++} , Ca^{++} , Al^{+++} and Thiocarbanilide

The last four ions will be considered together since their individual spectra are very similar (Graphs VII, VIII, IX, X). The molar absorbancy index for these ions increases with increasing pH, although the change from acid to neutral is very slight.

Complex formation does not take place as can be seen from Graphs XIII, XIV and XV. It was necessary to determine calcium by Job's method because the polarogram exhibits a maximum which cannot be suppressed.

The main point of interest is that the spectra obtained for basic solutions differs considerably from all previous spectra. Previously the difference in spectra at various pH's was mainly in the absorbancy index. However, in these cases the peaks are very sharp, the minimum is much lower and displaced approximately 5 $\text{m}\mu$ to lower wavelengths (Table II).

Loh and Dehm state that it is possible to oxidize diphenylthiourea to diphenylurea by various reagents in alkaline media, e.g. HgCl_2 . The reaction is practically quantitative with Na_2O_2 . In order to determine whether oxidation (replacement of $-\text{SH}$ by $-\text{OH}$) has taken place, thiocarbanilide was oxidized with Na_2O_2 and a spectrum obtained (Graph XVI). In comparing this spectrum with that for Ca^{++} , Fe^{++} , Fe^{+++} and Al^{+++} and thiocarbanilide for basic solutions, it can be seen that they are very similar. The degree of similarity is brought out even more by Table II. It therefore can be concluded that a certain degree of oxidation has taken place.

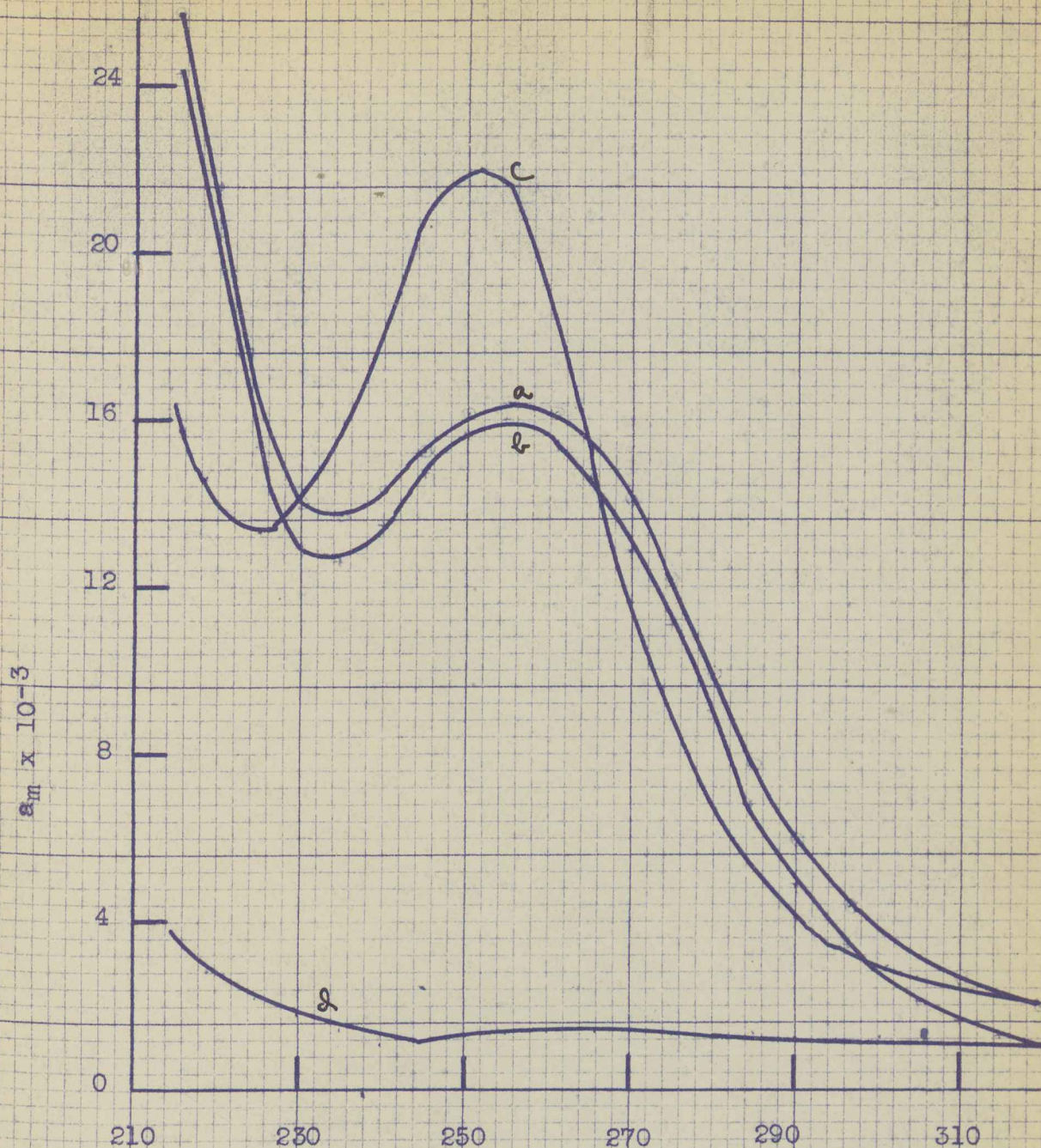


Absorption Spectra of
Gold and Thiocarbanilide

1:1 Molar Ratio

- (a) Neutral (no buffer)
- (b) pH 1.30 (buffer)
- (c) pH 11.00 (buffer)
- (d) AuCl_3

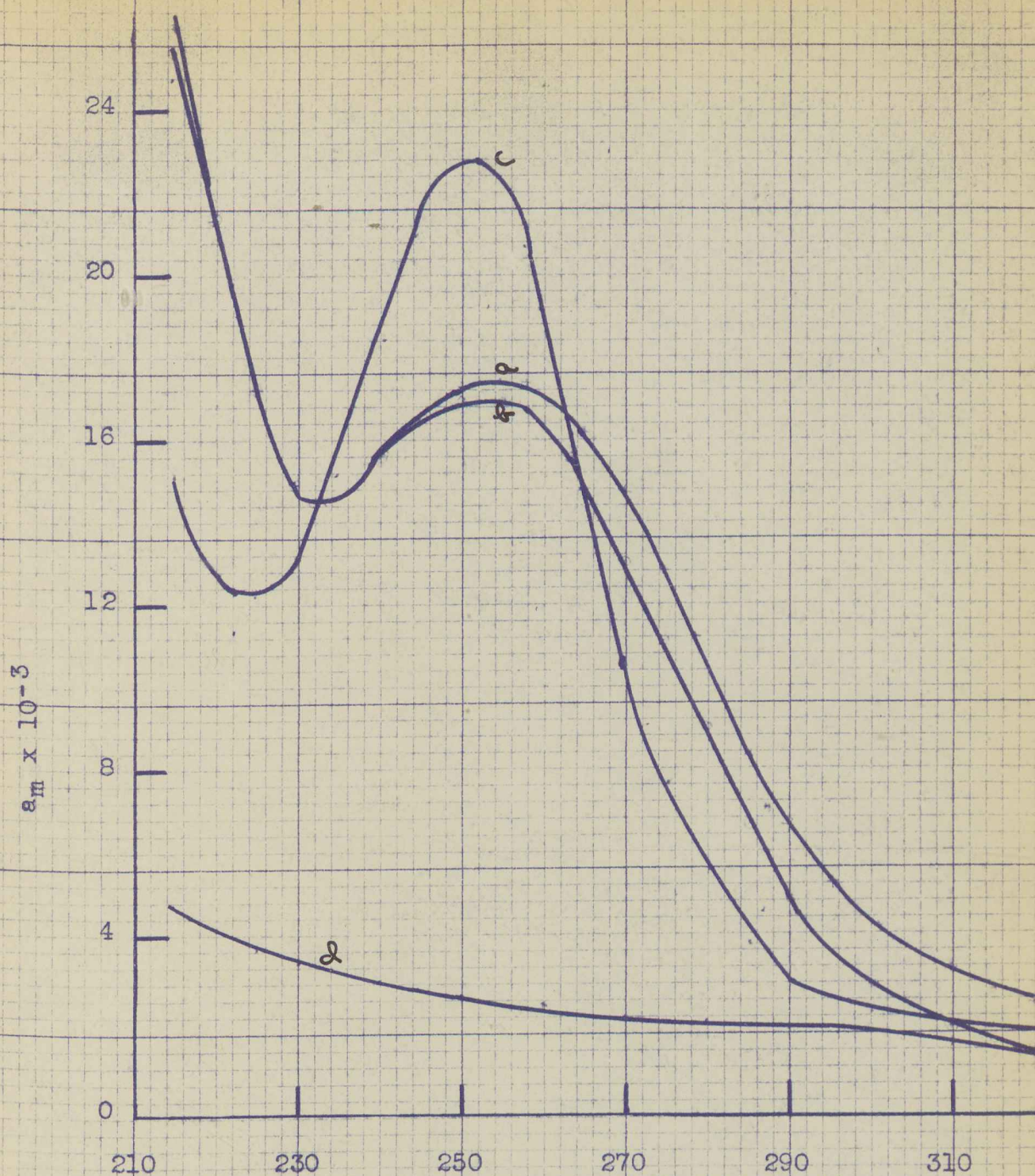
Graph VII



Absorption Spectra of
Ferrous ion and Thiocarbanilide

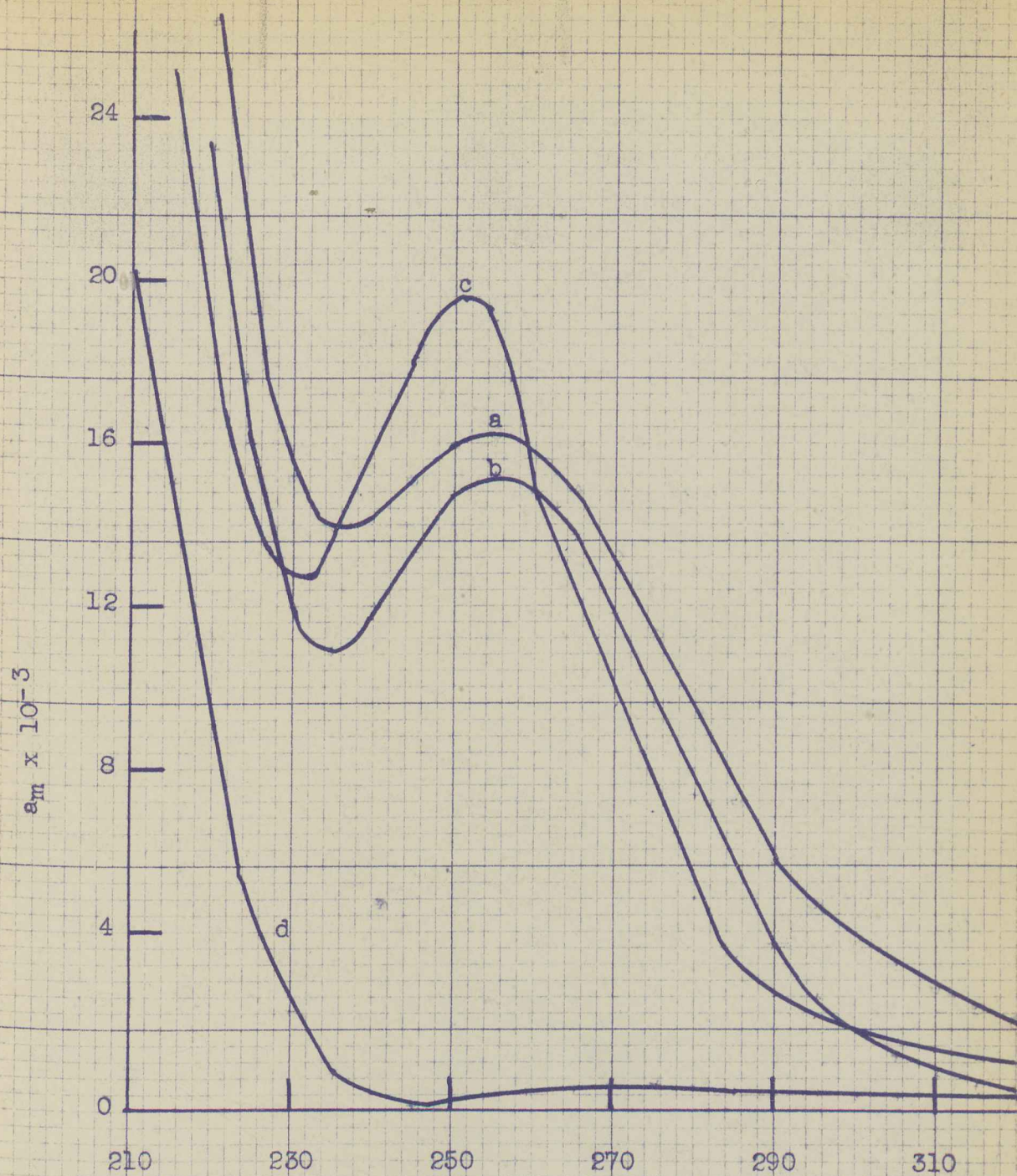
1:1 Molar Ratio

- (a) Neutral (no buffer)
- (b) pH 1.22 (buffer)
- (c) pH 11.54 (buffer)
- (d) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$



Absorption Spectra of
Ferric ion and Thiocarbanilide
1:1 Molar Ratio

- (a) Neutral (no buffer)
- (b) pH 1.30 (buffer)
- (c) pH 11.50 (buffer)
- (d) $\text{Fe}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$



Absorption Spectra of
Calcium and Thiocarbanilide

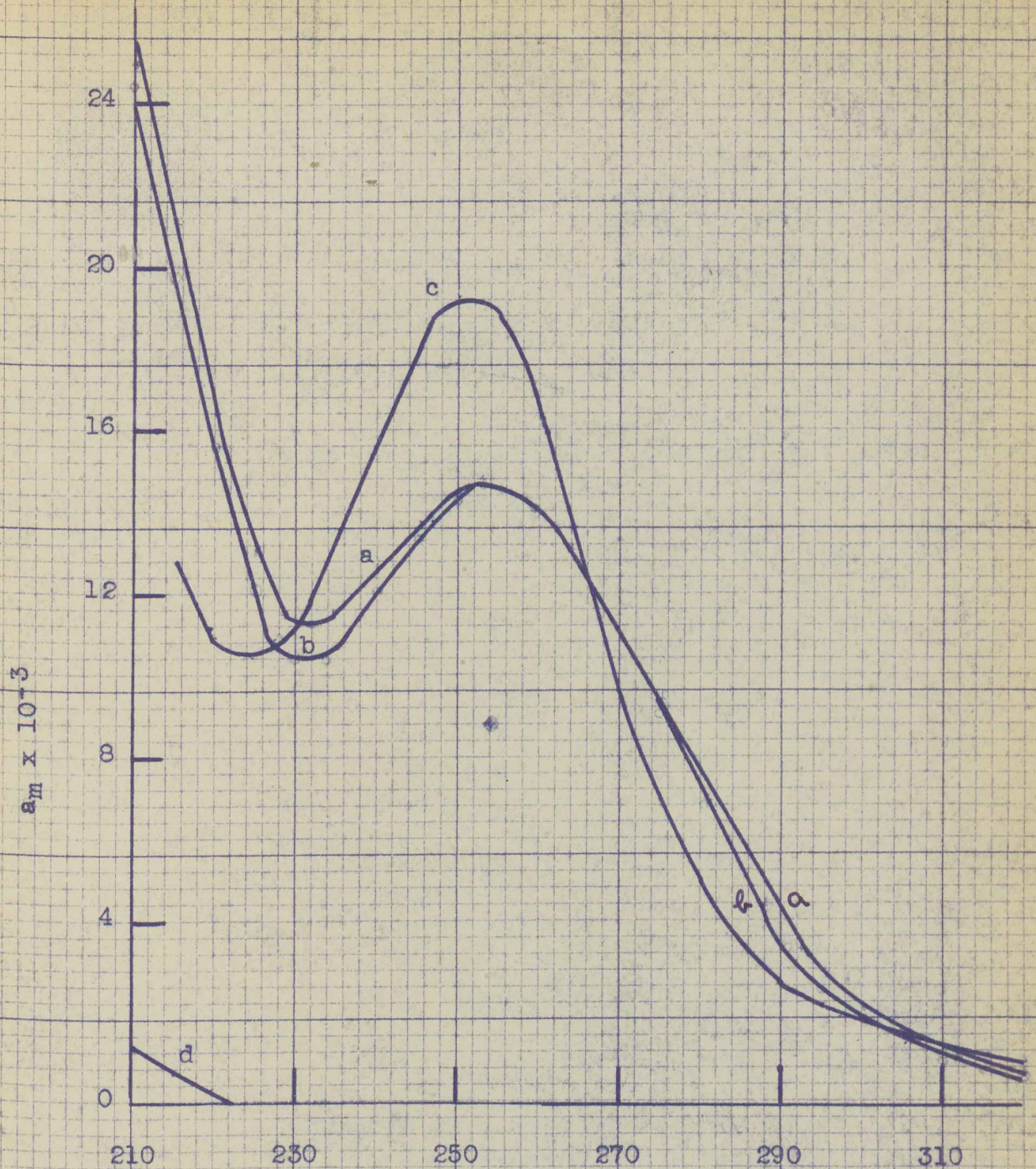
1:1 Molar Ratio

(a) Neutral (no buffer)

(b) pH 1.22 (buffer)

(c) pH 11.60 (buffer)

(d) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

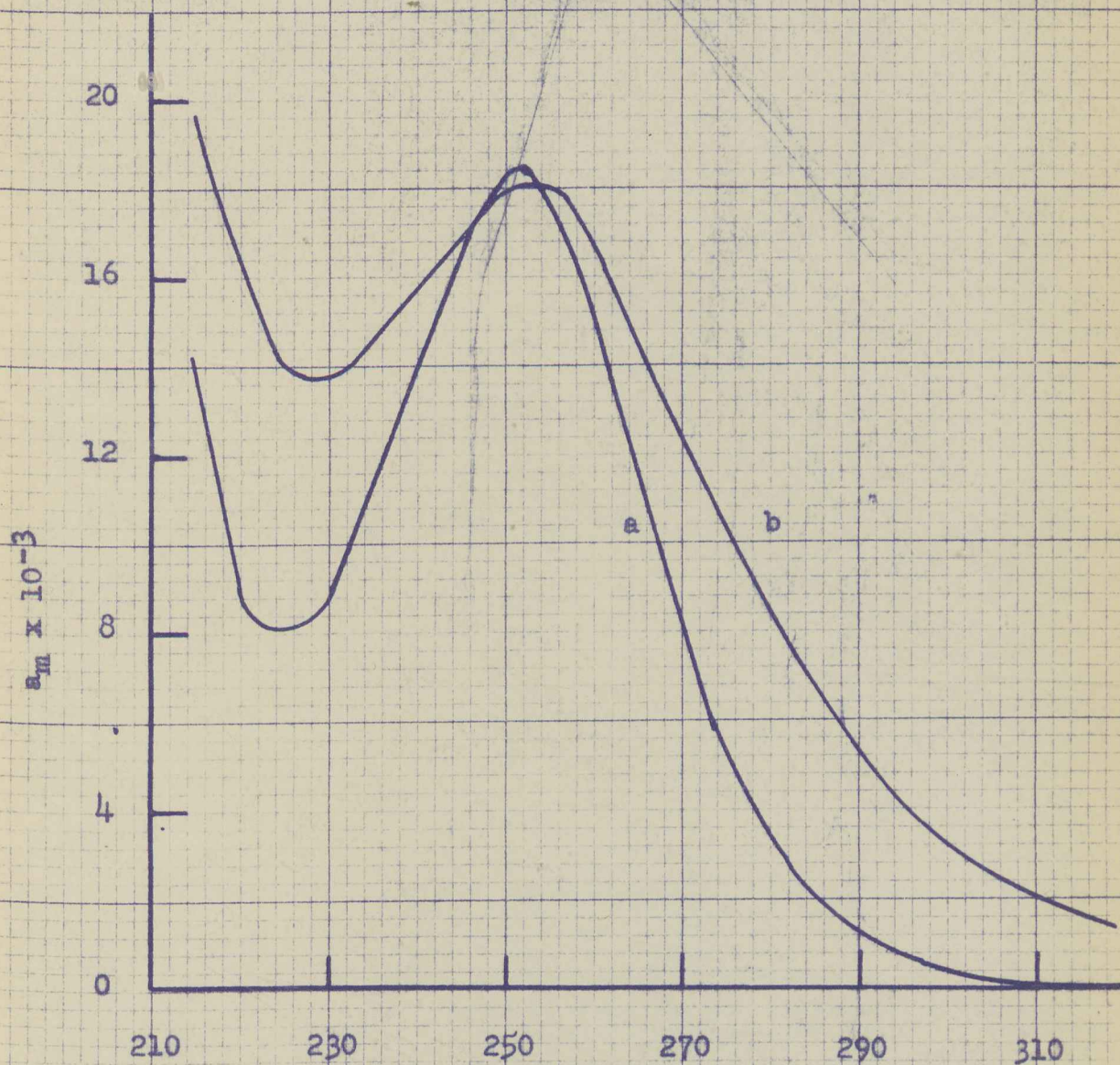


Absorption Spectra of
Aluminum and Thiocarbanilide

1:1 Molar Ratio

- (a) Neutral (no buffer)
- (b) pH 1.21 (buffer)
- (c) pH 11.58 (buffer)
- (d) $\text{Al}(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

Graph XI

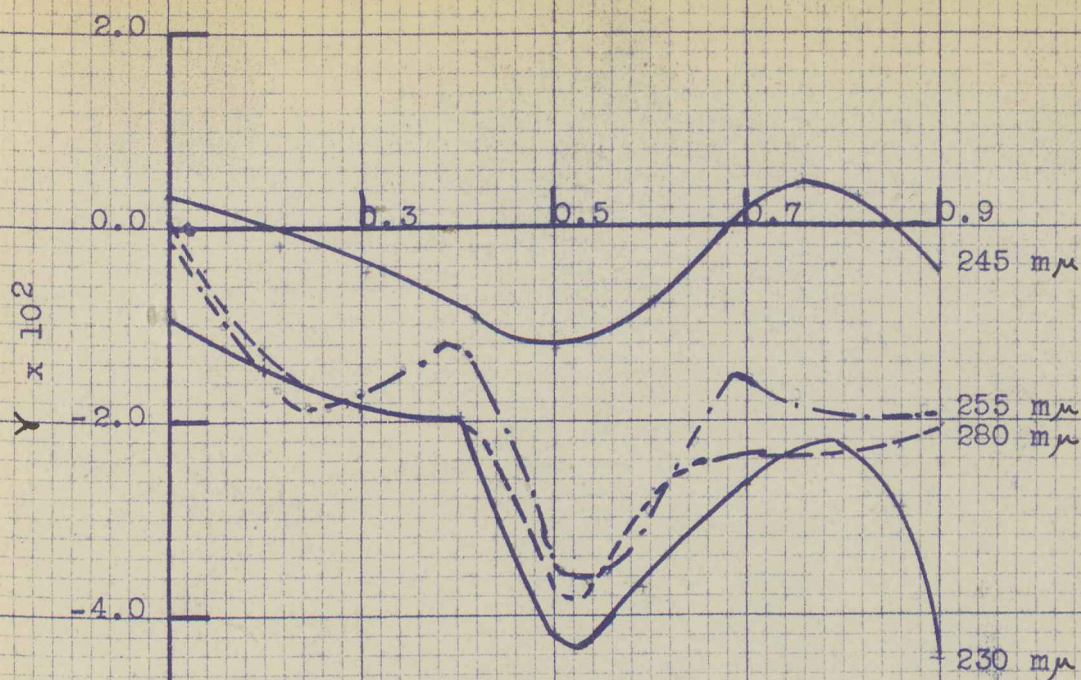


Absorption Spectra of Diphenylurea
as compared to Diphenylthiourea

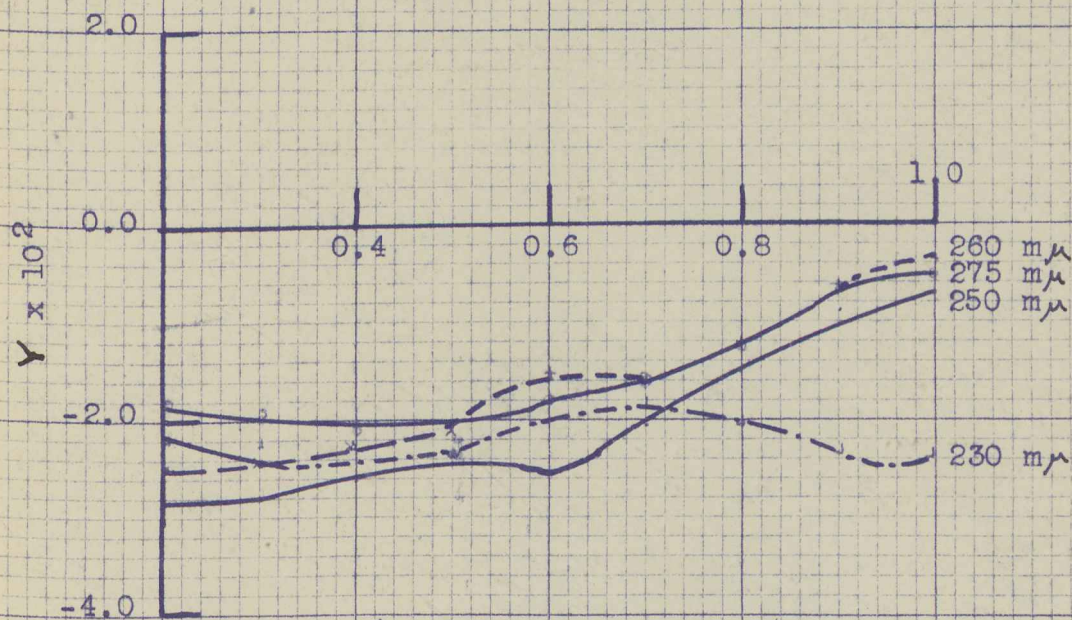
(a) Diphenylurea pH 11.5 (buffer)

(b) Diphenylthiourea pH 11.5 (buffer)

Job's Method of Continuous Variation



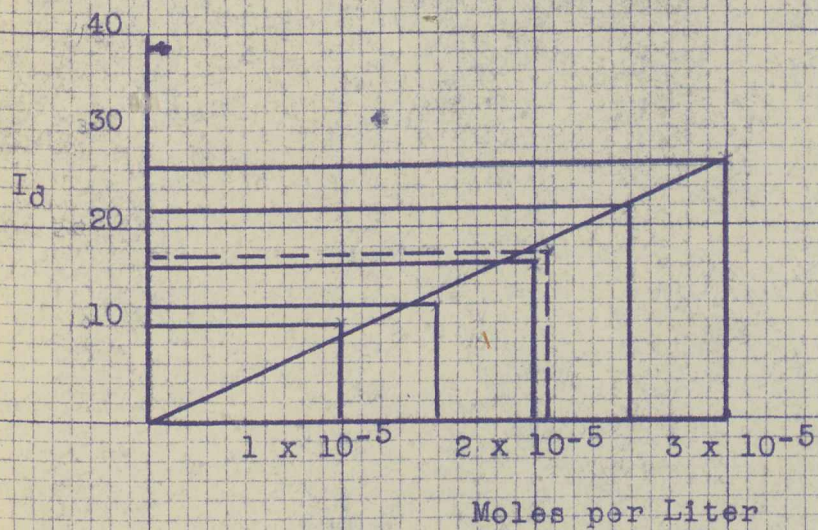
Lanthanum and Thiocarbanilide



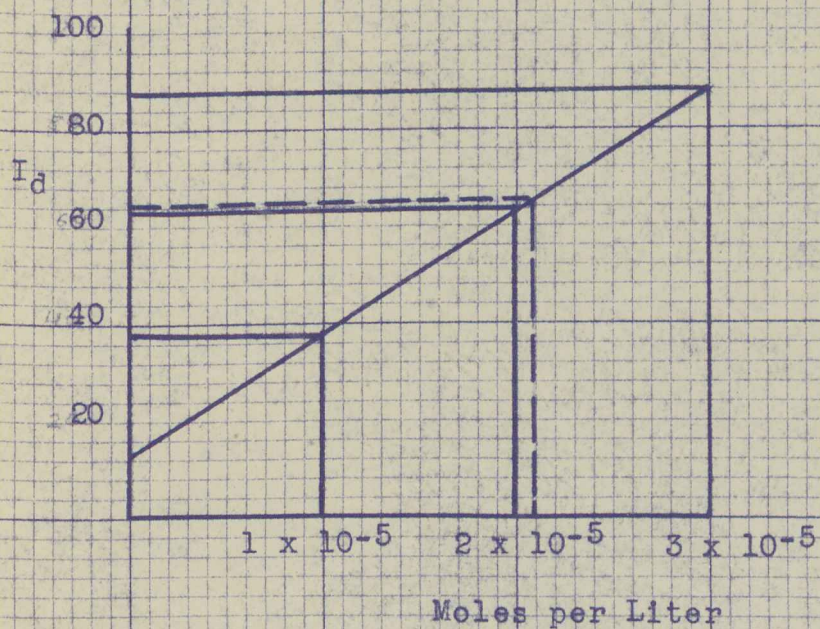
Calcium and Thiocarbanilide

Graph XIII

Wave Height - Concentration Plots



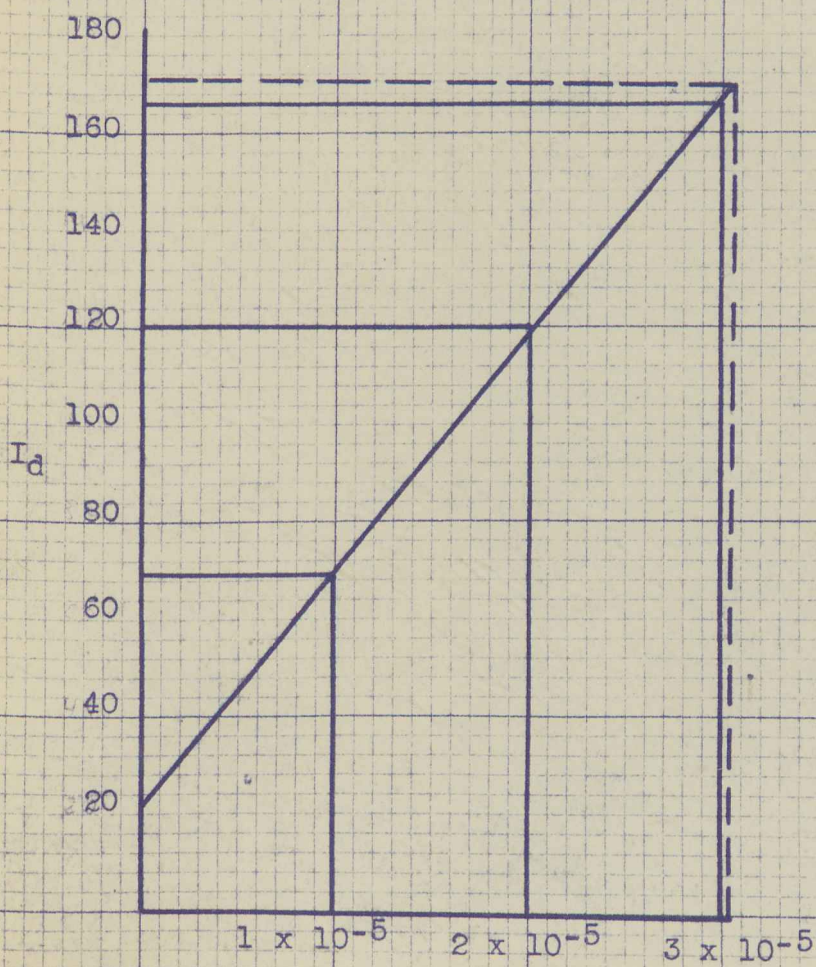
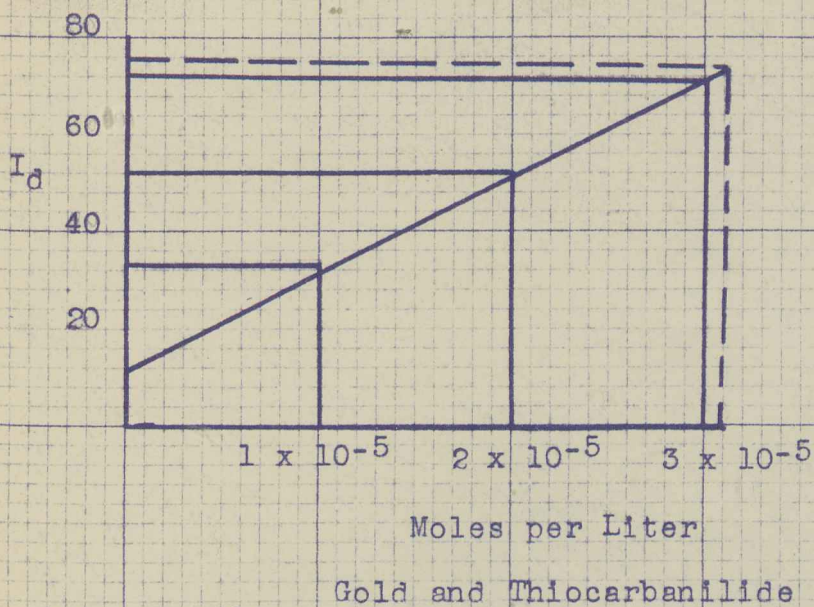
Thallium and Thiocarbonyl



Cerium and Thiocarbonyl

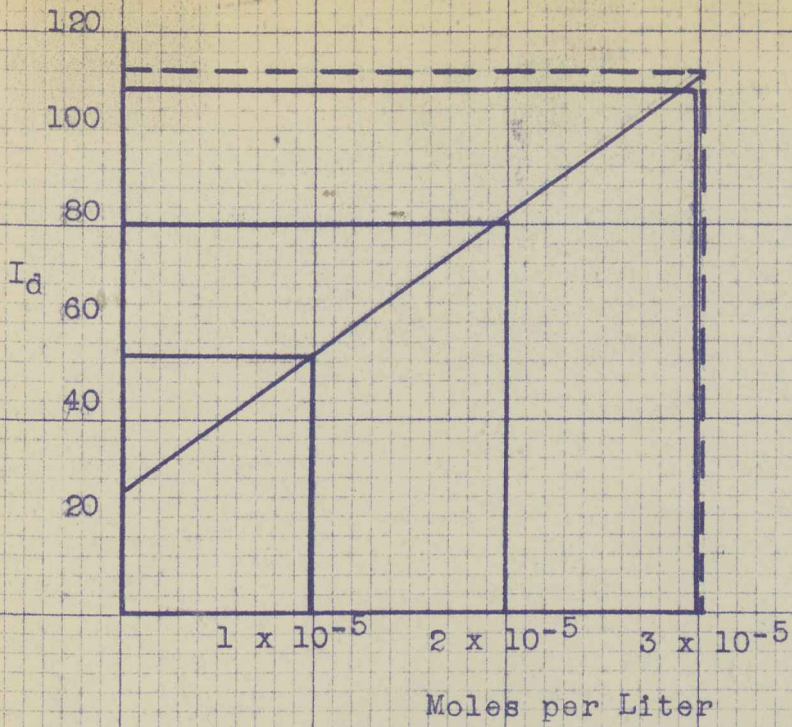
Graph XIV

Wave Height - Concentration Plots

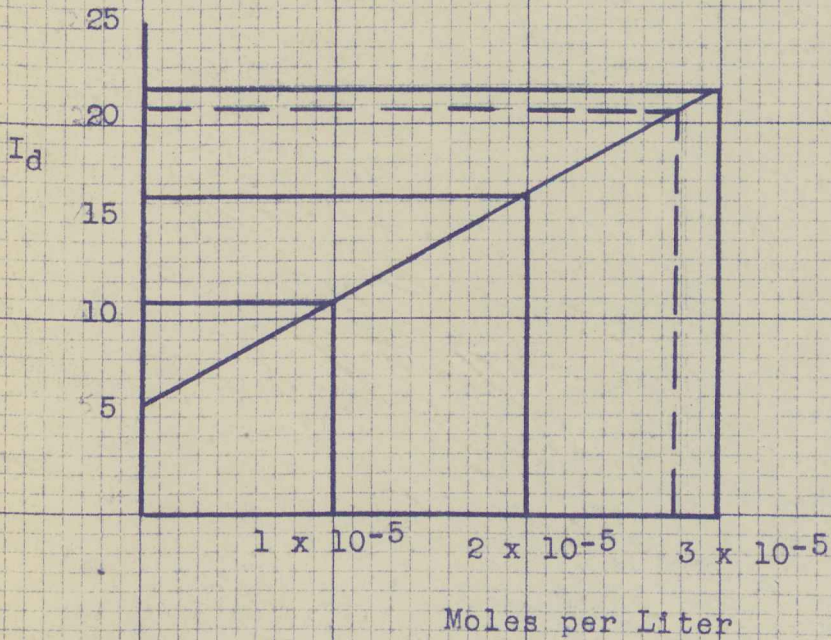


Moles per Liter
Aluminum and Thiocarbanilide

Wave Height - Concentration Plots

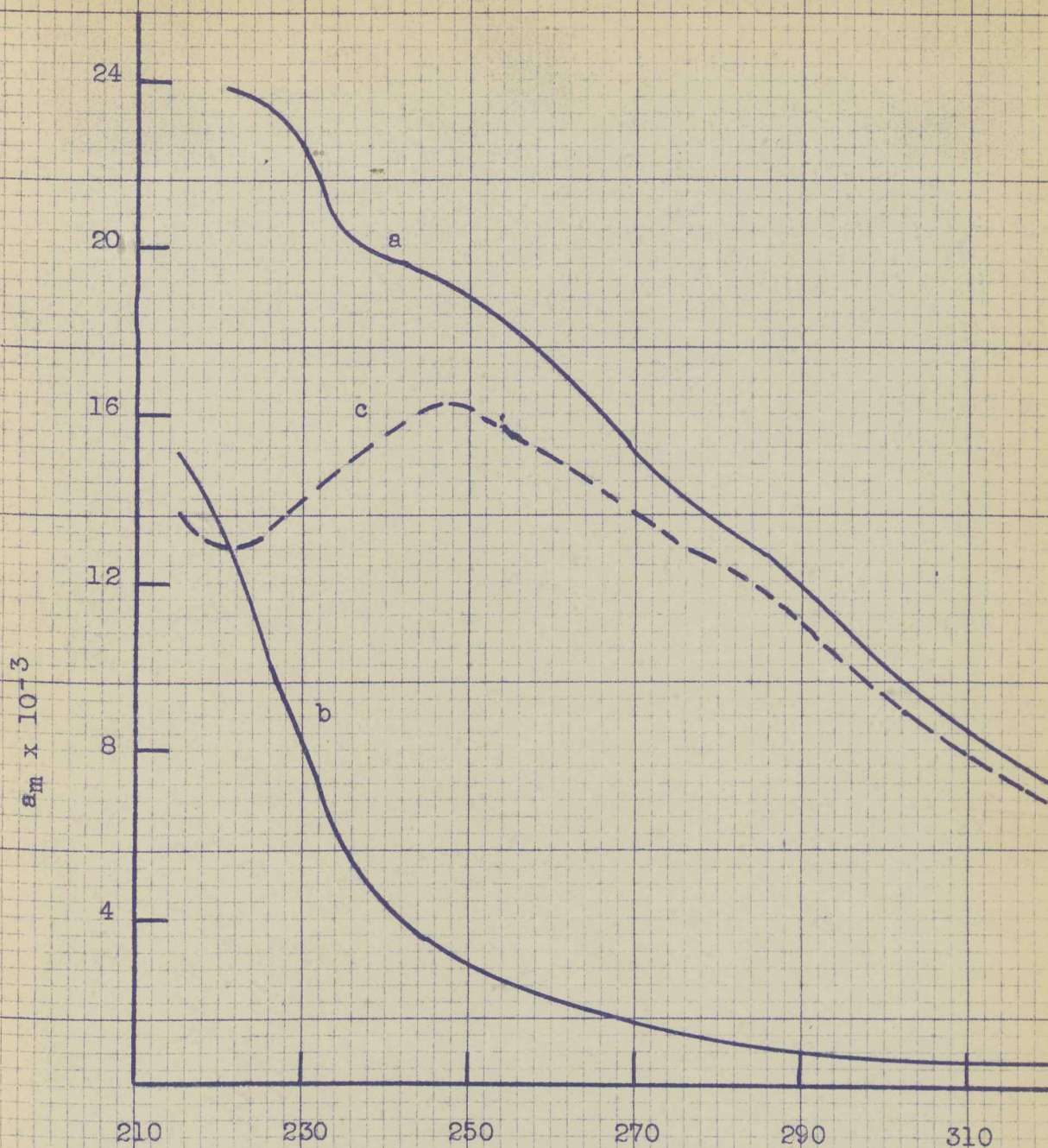


Ferrous ion and Thiocarbanilide



Ferric ion and Thiocarbanilide

Graph XVI



Absorption Spectra of

- (a) Gold and Thiocarbanilide 1:1 Molar Ratio
Neutral (no buffer)
- (b) AuCl_3 - Aqueous Solution
- (c) The curve for gold and thiocarbanilide
obtained by subtracting graphically
(b) from (a).

TABLE I

Values of a_m and wavelengths for maximum absorption peaks.

	Complex Detected	Acid		Neutral		Basic	
		$a_m \times 10^{-3}$	m μ	$a_m \times 10^{-3}$	m μ	$a_m \times 10^{-3}$	m μ
(1) Thiocarbanilide ---		13.8	257	15.2	257	18.2	253
(2) Ag ⁺ and T *	yes	18.4	250	23.4	250	24.9	250
(3) Tl ⁺ and T	yes	12.4	255	15.0	255	9.5	255
(4) La ⁺⁺⁺ and T	yes	14.8	255	18.0	250	16.7	253
(5) Ce ⁺⁺⁺⁺ and T	yes	15.7	255	15.7	255	16.2	255
(6) Au ⁺⁺⁺ and T	?	14.4	252	18.8	252	18.6	252
Au ⁺⁺⁺ (Graph XVI)---		----	---	16.2	248	----	---
(7) Fe ⁺⁺ and T	no	16.0	255	16.4	255	22.0	252
(8) Fe ⁺⁺⁺ and T	no	17.4	255	17.5	255	23.5	252
(9) Ca ⁺⁺ and T	no	15.5	255	16.5	255	20.0	252
(10) Al ⁺⁺⁺ and T	no	15.2	253	15.2	253	19.8	252

TABLE II

Values of a_m and wavelengths for minimum absorption (in basic solutions)

	$a_m \times 10^{-3}$	m μ
Diphenylthiourea	13.7	230
Diphenylurea	8.0	225 (Max. -18.4, 252)
Fe ⁺⁺ T *	13.2	225
Fe ⁺⁺⁺ T	12.4	225
Ca ⁺⁺ T	12.8	232
Al ⁺⁺⁺ T	10.8	222

T * - Denotes thiocarbanilide and cation in 1:1 molar ratio

DISCUSSION (cont.)

Of the metals which form complexes it has been noted that in acid and neutral solutions there has been an increase or no change within the experimental error and a decrease in basic solutions of the molar absorptancy index. Silver however showed an increase in basic solution. The spectrum is however similar to that of diphenylurfa in the large difference between the maximum and minimum peaks. The explanation for this discrepancy may be that partial oxidation has taken place. Since Ce^{++++} is a stronger oxidizing agent than Fe^{++} , Ca^{++} etc., the reason why oxidation does not take place in basic solution with Ce^{++++} must be that complex formation interferes with the oxidation. This would be the same for the other complexing ions.

The explanation for complex formation may lie in the fact that an addition compound is less stable the smaller the ionic radius of the cation. (The Experimental evidence in support of this statement is the separation of the rare earths by ion-exchange columns) (27).

The oxidation and complexing explains the difference in spectra between Fe^{++} , Fe^{+++} , Ca^{++} , Al^{+++} and La^{+++} , Tl^{+} , Ag^{+} , Ce^{++++} . Other slight differences may be attributed to differences in the extent of oxidation, stability of complexes, and characteristic properties (e.g. mass) of the cations.

However, gold does not fall into this pattern. Gold exhibits no complex formation of any stability, no oxidation to any extent yet its ionic radius is larger than La or Ag and it is a stronger oxidizing agent than for example Al^{+++} or Ca^{++} . The information that has been obtained offers no reasonable explanation for this phenomena.

SUMMARY

1. The question of resonance structures of thiocarbanilide for ground and excited states was mentioned but no attempt to clarify the problem was attempted since the main interest of this work was to determine the analytical applicability of thiocarbanilide for cations in the ultraviolet region of the spectrum.
2. Upon comparing the wavelengths of maximum molar absorbancy index for the various spectra no large displacement of any value was found.
3. By oxidizing thiocarbanilide to diphenylurea by means of Na_2O_2 in an alkaline medium it has been shown that Fe^{++} , Fe^{+++} , Ca^{++} and Al^{+++} also cause oxidation to take place. The extent of the oxidation was not determined. This would explain the variation in spectra for these basic solutions. It has also been assumed that the discrepancy for Ag^+ as compared to the other complexing agents in basic solution is due to partial oxidation of thiocarbanilide.
4. The complexes formed were explained by the fact that the larger the ionic radius the greater the stability of the addition compound.
5. Gold has proved to be an exception from the data obtained and no explanation is offered at this time.
6. The spectra for the non-complexing ions are not additive because although there may be a certain degree of addition, the instability ratio is probably large.
7. Loh and Dehm state that in anhydrous solvents (alcohol, methylethyl ketone or toluene) definite additive compounds

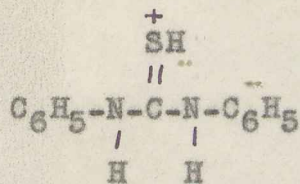
SUMMARY (cont.)

are formed. It would be interesting for future work to investigate the spectra of thiocarbanilide and various cations using these solvents.

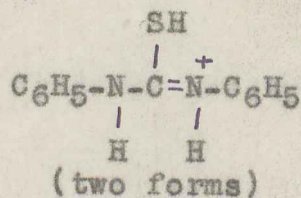
APPENDIX

Resonance Structures of Thiocarbanilide at various pH's.

Acid:

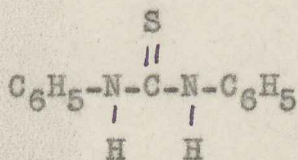


I

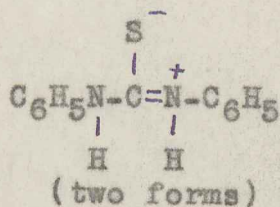


II

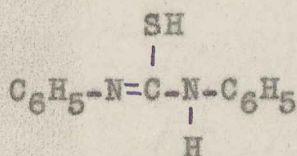
Neutral: (two tautomers)



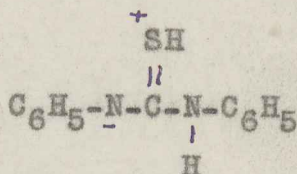
III



IV

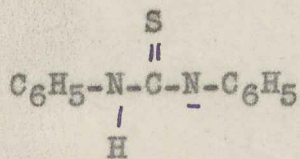


V

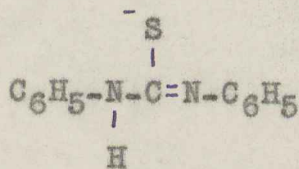


VI

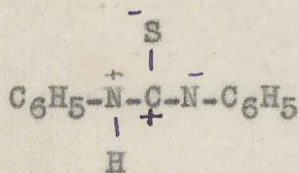
Basic:



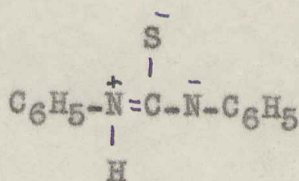
VII



VIII



IX



X

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