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Identification of the products and mechanism of the disproportionation of DI(p-sulfonic acid)phenylthiocarbazide
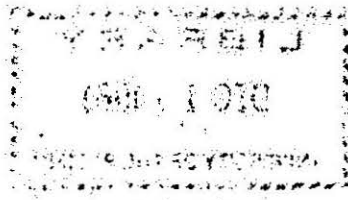
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IDENTIFICATION OF THE PRODUCTS AND MECHANISM OF
THE DISPROPORTIONATION OF
DI(p-SULFONIC ACID)PHENYLTHIOCARBAZIDE

A Thesis

Presented to

the Faculty of the Department of Chemistry

University of the Pacific

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Ralph Lee Riggs

August 1961

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Diphenylcarbazide, diphenylcarbazone, diphenylthio-
carbazide, and diphenylthiocarbazone are compounds that have
proved to be extremely valuable analytical reagents for the
determination of trace amounts of numerous heavy metal ions
by colorimetric methods. Diphenylthiocarbazone, commonly
known as dithizone, is the most widely used of the above
compounds. It was first synthesized by Emil Fischer in 1878
as a part of his study of phenylhydrazine derivatives.
Fischer observed that metal ions produced colors with
diphenylthiocarbazide but made no attempt to use it as an
analytical reagent. In 1925, Hellmut Fischer began his
studies using dithizone as an analytical reagent. Since
then, dithizone has been the subject of numerous papers,
and it has come into widespread use in colorimetric analysis.
However, as is the case with many colorimetric reagents, the
structure of the complexes formed by dithizone with the
heavy metal ions is still not clearly understood. Numerous
books, such as Iwantscheff (1958), include more than adequate
references to the uses of dithizone as a colorimetric
reagent.

The original method of preparation by Emil Fischer
has been modified, although these modifications are based

mainly on the solvent used in the coupling step of the synthesis. The solvent is usually benzene or diethyl ether. The method of preparation is shown below:

$$2 \; \varnothing NHNH_2 + CS_2 \longrightarrow \varnothing NHNHCS_2 \cdot \varnothing NHNH_2 \xrightarrow{95^\circ C} (\varnothing NHNH)_2 CS$$

and

$$(\varnothing NHNH)_2 CS \xrightarrow[MeOH]{KOH} dithizone$$
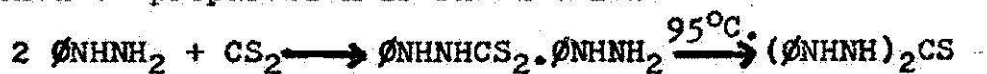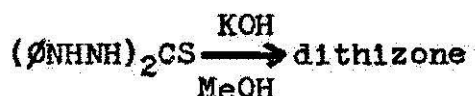
Even though it is extremely valuable as a reagent for heavy metal analysis, dithizone presents one serious problem; it is not soluble in aqueous solutions. Since metal analysis almost invariably involves aqueous solutions, a time consuming extraction with an organic solvent such as carbon tetrachloride or chloroform must be performed. In addition to the time and work involved, these procedures often introduce errors due to the partitioning of the complex between the organic and aqueous phases. The solution to the problem is obviously to solubilize the dithizone; for example, the addition of sulfonic acid or carboxyl group to the rings would accomplish this. Corwin, Jackson, and Webb (1945) patented a synthesis, to be described later, for this sulfonation, but their interest was in the use of this compound as an antidote for heavy metal poisoning. They made no use of it as an analytical reagent. Herzog (1951) used their method to prepare a sulfonated dithizone which she was unable to isolate in a pure form. The product she obtained

did possess some complexing properties with the heavy metal ions and she included substantiating analytical data.

Frye (1958) approached the apparent impossibility of separating and purifying the sulfonated dithizone from the point of view of using the sulfonated diphenylthiocarbazide as the reagent. This compound can be prepared, as shall be indicated later, in relatively pure form, and in the presence of strong base gives colors with several of the heavy metal ions.

By analogy with Emil Fischer's reactions for the production of dithizone in the presence of base, it was thought that the reaction involved was a disproportionation of the Cannizzaro type.

$$2 \ (HO_3S\emptyset NHNH)_2CS \ \xrightarrow[\text{MeOH}]{\text{KOH}} \ HO_3S\emptyset NHNHCSN:N\emptyset SO_3H \ +$$

$$HO_3S\emptyset NHNHCSNH_2 \ + \ HO_3S\emptyset NH_2$$
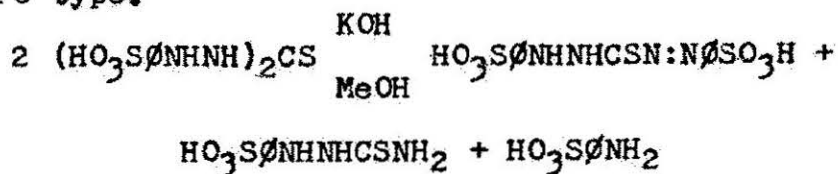
Frye thought that a sulfonated diphenylthiocarbazide could be prepared by the method of Corwin and Herzog, and that on treatment with strong base, this compound would disproportionate to yield di(p-sulfonic acid)phenylthiocarbazone, phenyl(p-sulfonic acid)thiosemicarbazide, and sulfanilic acid.

It is the purpose of this paper to separate and identify the products resulting from treatment of this compound with strong base. This will be done using both column

and paper chromatography, and through interpretation of infrared spectra. In addition, a discussion of the structure of the complexes of heavy metals with di(p-sulfonic acid) phenylthiocarbazide in basic solution will be presented.

CHAPTER II

HISTORY OF CHROMATOGRAPHIC METHODS

The classical methods used for separating substances from each other have been based upon the clumsy and wasteful operations such as crystallization, distillation, precipitation, and extraction by solvents. In chromatography we have both an analytical and preparative method based on the counter-current principle.

The name "chromatography" has been given to those processes which permit the resolution of mixtures by effecting the separation of some or all of their components in zones or phases other than those in which they are originally present, regardless of the nature of the process by which the substances are moved from one phase to another.

The ancient Greeks left records of purifying water with filters of sand, and Pliny mentions the use of papyrus in the determination of ferrous sulfate. There is no doubt, however, that M. Tswett (1906), the Russian biologist, should be given credit for discovering the principle of preferential adsorption. He studied the effect of a large variety of adsorbants and solvents on the separation of plant pigments.

The great popularity of present-day paper chromatography is due to A. J. P. Martin and his associates A. H. Gordon, R. Consden, and R. L. Synge.

Martin and Synge (1941), to effect the separation of acetylated amino acids, utilized the difference of partition coefficients with a series of solvent-solvent extractors. They found a much more efficient fractional solvent-solvent extraction was attained by packing columns with silica gel holding about 50 per cent water. A solution of the acid mixtures was placed on the column and developed with suitable solvents. Other materials capable of retaining water as a stationary phase include glass powder, Kieselguhr, starch, and cellulose. Martin and Synge, in this classical work, termed this "partition chromatography."

In order to avoid preparing silica gel, and to reduce the bulk of material used, Consden, Gordon, and Martin (1944) replaced silica gel with filter paper as the inert support. This technique, called "paper chromatography," is probably the most adaptable and widely used method employed for the separation of micro quantities of substances.

The theory developed by Martin and Synge (1941) considers partition chromatography to be analogous to fractional distillation. Assuming that diffusion in the column, or paper, is negligible, and that the partition of solute between the two phases is independent of the concentration, they derived and defined the R_f value, in which the movement of the zone is relative to that of the mobile phase:

$$R_f = \frac{A}{A + aA_1}$$

where a = partition coefficient $\frac{\text{(conc. in aqueous phase)}}{\text{(conc. in mobile phase)}}$

A = cross section area occupied by the stationary phase

A_1 = cross section area occupied by the mobile phase

R_f = $\frac{\text{distance traveled by the zone or spot}}{\text{distance traveled by the solvent front}}$

The measurement of the R_f value is relatively easy: the center of the original spot is marked as the origin and the distance to the center of the developed spot and that to the front of the mobile phase are measured. The R_f value is dependent upon many variables: temperature, the grade of paper, the nature of the solvent, and the nature of the mixture being separated, are but a few. The procedures employed in developing chromatograms will be discussed in a later chapter.

Partition, or paper, chromatography is thus a method of separating substances by distributing them between two liquid phases, one of which is mobile and the other essentially fixed by sorption to a support. It is now generally recognized, however, that although paper chromatography may function in some cases purely by partition, it more frequently combines partition, adsorption, and ion exchange. In paper chromatography the immobile phase is considered to be the water molecules bond to the cellulose fibers of the paper. The mobile phase may be any one of a number of pure or mixed solvents. Distribution of the solute between the aqueous and mobile phases results in movement of the solute.

Two methods of partition chromatography may be used: the column method, and that using sheets or strips of filter paper in either one- or two-dimensional runs. Block, Durrum, and Zweig (1957), and Lederer and Lederer (1958) provide a ready source of references to the innumerable studies concerning and employing paper chromatography. No mention is made in the literature of the separation of the present mixture, although Lederer and Lederer (1958) cite several references to the identification of one of the supposed components--sulfanilic acid. It is the purpose of this study then, to employ both column and paper partition chromatography in an attempt to separate and identify the disproportionation products of di(p-sulfonic acid)phenylthiocarbazide.

CHAPTER III

EXPERIMENTAL PROCEDURE AND RESULTS

Synthesis of Di(p-sulfonic acid)phenylthiocarbazide

The most logical solution to the problem of the solubilization of dithizone, or a similar compound, in water would be to sulfonate the compound. Herzog (1951) has shown this to be impractical because of possible cleavage or oxidation to the carbadiazone. Therefore the phenyl group must be sulfonated before preparation of the carbazide.

Several methods for this procedure are possible, either by analogy with the dithizone synthesis or by similar coupling reactions. Corwin, Jackson, and Webb (1945) have prepared this compound by coupling two moles of phenyl-hydrazinesulfonic acid with one mole of carbon disulfide in liquid ammonia.

This method of synthesis is valuable in that a fairly pure product of good yield is obtained with a minimum of side reactions if conditions are controlled accurately. One critical step involves the sulfonation of phenylhydrazine. The procedure followed is essentially that of Acree (1907), as modified by Frye (1958).

One hundred milliliters of concentrated reagent grade sulfuric acid contained in a 250 milliliter beaker was cooled in an ice bath to a temperature of 10-15° C.

Twenty-seven milliliters of reagent grade phenylhydrazine was added from a dropping funnel with constant adequate mechanical stirring. The temperature was never allowed to rise above $50^{\circ}C.$; the addition required from thirty to forty minutes. When all the phenylhydrazine had been added, the mixture, which was black with white cumuli, was placed on a steam bath and allowed to warm to 80° C. After heating for fifteen minutes at a temperature between 80 and 85° C., the mixture, which now contained no white solid, was poured into 200 milliliters of cold distilled water. The temperature was lowered to 10° C. in an ice bath, upon which treatment crystals of phenylhydrazinesulfonic acid separated and were collected on a Buchner funnel with the aid of a vacuum. The filtrate was discarded and the crystals were washed sparingly with cold water.

The crystals of the sulfonic acid were dissolved in a clear solution of reagent grade sodium carbonate, which was used sparingly to avoid excessive addition of acid for neutralization later in the synthesis. The yellowish solution was heated to 85° C., four or five grams of decolorizing carbon were added with stirring, and the whole was filtered immediately with the aid of vacuum. The carbon was washed with a little dilute sodium carbonate solution. The filtrate was cooled, made just acid with 6N sulfuric acid, and again cooled to a temperature of 10° C. The crystals were filtered

with a Buchner funnel and washed with small amounts of dis-
tilled water; the filtrate was discarded. Decolorization
with the activated carbon was repeated once, or twice when
necessary, and the white crystals were air dried in the dark.
The yield was 37 grams or 79 per cent of the theoretical
based on phenylhydrazine. The melting point was sharp at
288° C.

It was found that failure to adhere to the temperature
limits set forth above gave a product which was over-
sulfonated. The reagent resulting from this over-sulfonated
compound tended to be less stable than that produced accord-
ing to the instructions given.

The acid is both light and air sensitive and should
be used as soon as possible after preparation or should be
preserved in a dark, air-tight bottle kept in a cool, dark
place. Recrystallization yielded slender needles which
turned yellow on standing in air.

Thirteen grams of the phenylhydrazine sulfonic acid
added with continuous stirring to sixty grams of liquid
ammonia in a 250 milliliter Dewar flask; the resulting solu-
tion was orange-red in color. Ten milliliters of purified
carbon disulfide was added slowly over a period of about
fifteen minutes, and the solution was stirred for one hour.
Departure from the method of Corwin, Jackson, and Webb
occurred here. The resulting scarlet solution was poured

into several large porcelain evaporating dishes (about 50-60 milliliters of solution per dish), and the contents were swirled while the liquid ammonia was being evaporated in order to form a thin film of the yellow compound over the entire interior of the dish. The dishes were allowed to stand for three days, at which time no odor of hydrogen sulfide was apparent; this material had little activity with zinc ion. The dishes and contents were then heated for one hour on a steam bath at a temperature not in excess of 95° C., and the tenaciously adhering yellow material was scraped into the center of the dish with a porcelain spatula. This yellow powder was then heated for an additional four hours with occasional working with the spatula and pulverization of the larger flakes. The powder was then collected and stored in an amber bottle. This material showed good activity with zinc ion. The yield was 32 grams, or 88 per cent of the theoretical based on phenylhydrazine sulfonic acid. The melting point was 322-324° C. Elemental analysis of the compound showed the following:

Calculated:

	% C	% H	% N	% S	% Ash
	27.92	4.79	16.71	27.36	

Found:

	% C	% H	% N	% S	% Ash
1.	31.43	4.35	17.54	25.93	
2.	27.50	4.61	16.53	27.68	
3.	27.91	4.38	22.58	33.69	0.71

The analytical data for sample three above was for a sample of the compound which had been prepared using fifteen milliliters of carbon disulfide rather than the ten previously used. This compound appeared to be, and in its reactions with zinc ion was, identical with the compound formed as stated in the original synthesis. The only two explanations that can be offered are that (1) the compound was over-sulfonated, and (2) that the analyses for nitrogen and sulfur are grossly inaccurate--this would appear to be borne out by the additionally inexplicable presence of ash in the sample.
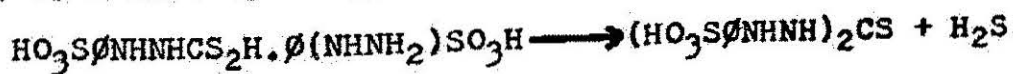
The reactions involved in the synthesis are shown below:

$$\phi NHNH_2 + H_2SO_4 \longrightarrow HO_3S\phi NHNH_2 + H_2O$$
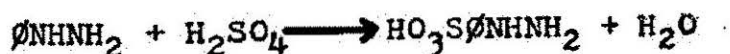
in which the substitution of the sulfonic acid group is para to the hydrazino group. If the temperature limits are not observed, some disulfonic acid is formed. The coupling step may be written:

$$2\ HO_3S\phi NHNH_2 + CS_2 \xrightarrow{NH_3} HO_3S\phi NHNHCS_2H.\phi(NHNH_2)SO_3H$$

and, upon heating to 95° C.:

$$HO_3S\phi NHNHCS_2H.\phi(NHNH_2)SO_3H \longrightarrow (HO_3S\phi NHNH)_2CS + H_2S$$
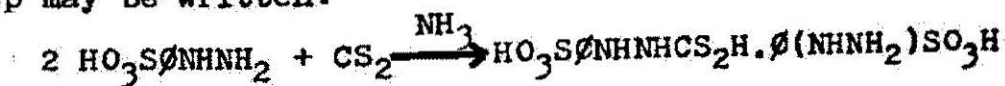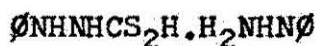
or, in this case, the ammonium salt.

Thermal Stability and Structure

The analytical data indicate that there is a molecule of hydrogen sulfide present for each molecule of di(p-sulfonic acid)phenylthiocarbazide. There is doubt as to the

placement of this extra molecule in the structure. Two possibilities exist which would account for this hydrogen sulfide. It might possibly be a "hydrogen sulfide of crystallization" similar to a monohydrated compound. Due to the lack of analogous examples and the nature of the compound this view seems unlikely, but because of the similarity of hydrogen sulfide and water it cannot be totally ignored.

The second explanation which presents itself lies in the phenylhydrazine salt of β-phenyldithiocarbazic acid, which is an intermediate in the analogous dithizone synthesis.

$$\emptyset NHNHCS_2H \cdot H_2NHN\emptyset$$

This compound becomes dithizone through loss of hydrogen sulfide when heated to $95°$ C. The adding of sulfonic acid groups to the para positions of the benzene rings should stabilize the xanthate structure. The ammonium salt of the sulfonated compound conforms closely to the analytical data for such a compound. The increased stability is shown by reference to the following: the unsulfonated compound decomposes at $95°$ C. while the sulfonated compound is fairly stable up to about $165°$ C. Figure 1 shows weight loss as a function of temperature for the sulfonated compound. Constant weight was achieved at each temperature. The loss of hydrogen sulfide appears to be complete at about $165°$ C. Figure 2 shows the relation of weight loss to the optical activity of the compound. Samples of the carbazide heated

to 120° C. for several hours retained activity fairly well.
Samples heated to higher temperatures were less active but
retained a greater degree of activity than indicated by
Frye (1958), thus supporting the second of the above hypo-
theses.

Disproportionation of Di(p-sulfonic acid)phenylthiocarbazide to Di(p-sulfonic acid)phenylthiocarbazone

Emil Fischer (1878) postulated the formation of
dithizone from diphenylthiocarbazide in basic solution as
follows:

$$2 \ (\emptyset NHNH)_2 CS \longrightarrow \emptyset NHNHCSN{:}N\emptyset + \emptyset NHNHCSNH_2 + \emptyset NH_2$$
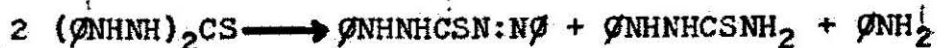
One mole of the carbazide is oxidized to the carbazone and
the second mole is cleaved through reduction to phenylthio-
semicarbazide and aniline. He substantiated this postulate
mainly through identification of the aniline produced.
Corwin and Jackson (1949) also have identified aniline and
phenylthiosemicarbazide as the reduction products.

It appears logical to assume that the disproportiona-
tion of the sulfonated carbazide should proceed in the same
manner, the products in this case being di(p-sulfonic acid)
phenylthiocarbazone, (p-sulfonic acid)phenylthiosemicarbazide,
and sulfanilic acid. The sulfanilic acid should be identi-
fiable by chromatographic means to be discussed later.

Samples of the di(p-sulfonic acid)phenylthiocarbazide
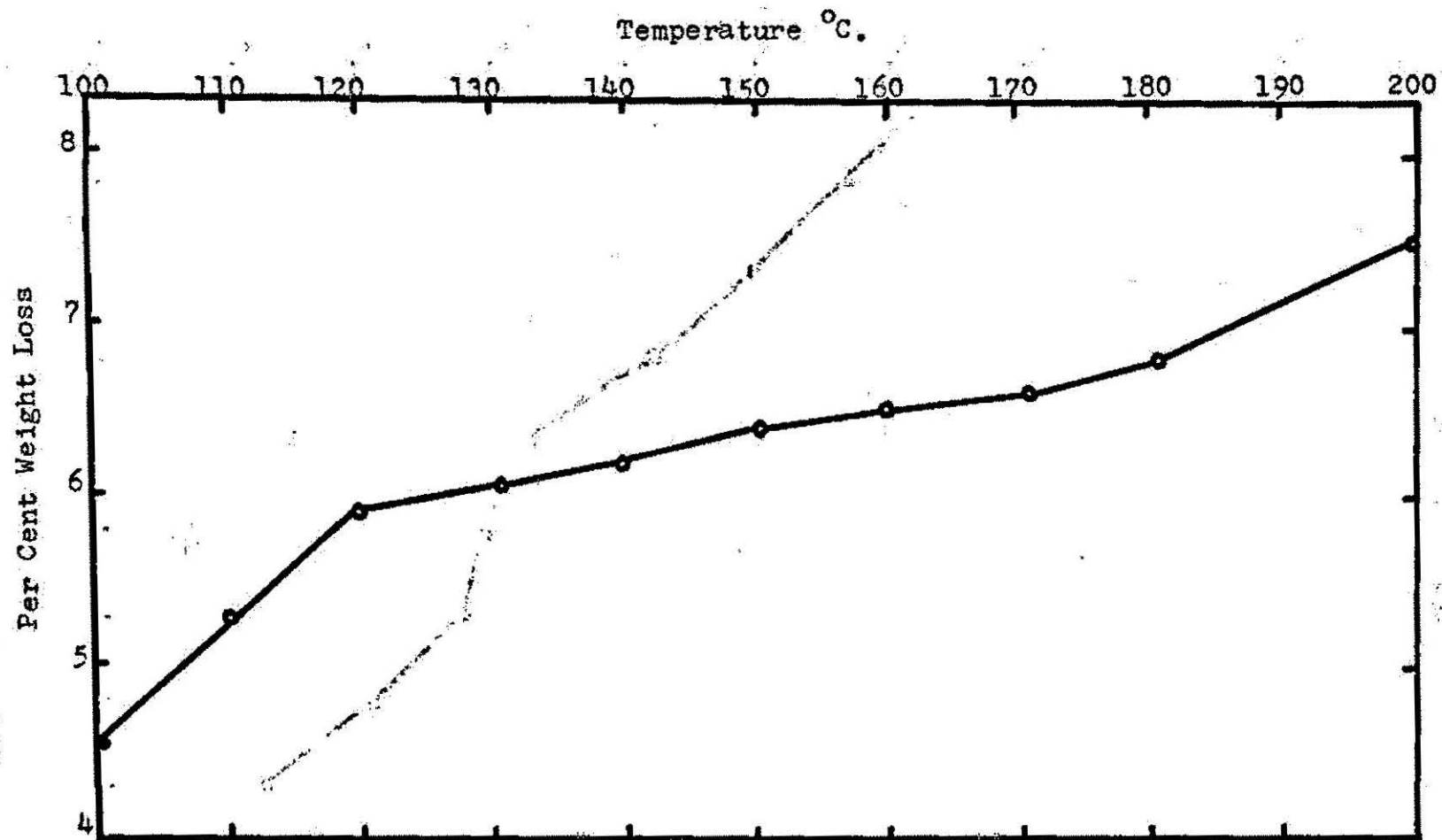were oxidized in both methanolic and aqueous potassium

FIGURE 1
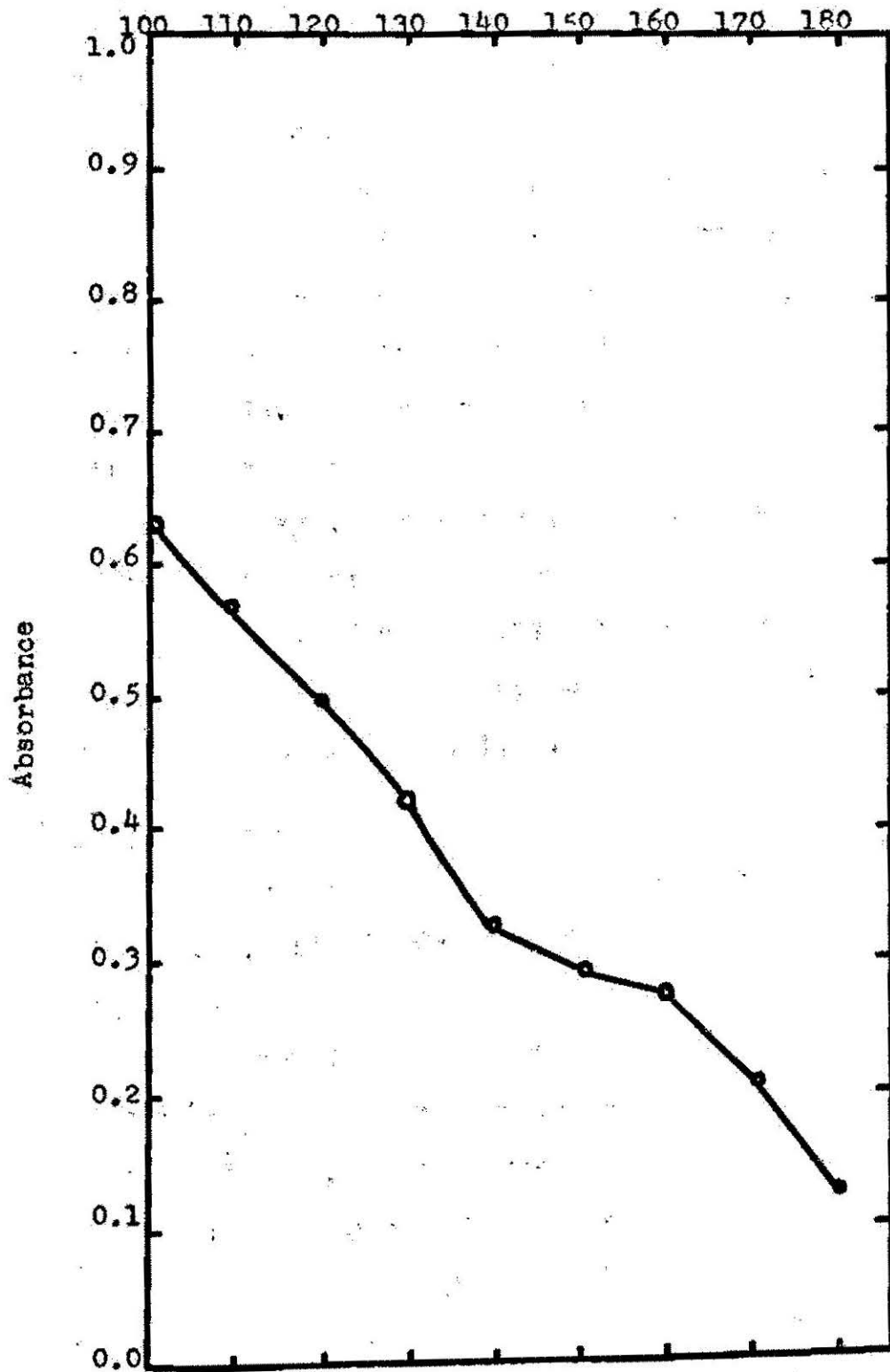
WEIGHT LOSS AS A FUNCTION OF TEMPERATURE

16

FIGURE 2

ABSORBANCE AS A FUNCTION OF TEMPERATURE

hydroxide solutions of various pH's. The resulting yellow to orange solutions were then analyzed chromatographically. Solutions of the carbazide made basic with potassium hydroxide do not keep well. To prevent oxidation, all solutions used in the research were prepared by first dissolving the needed amount of sodium bisulfite in water or methanol and then adding the carbazide. Even when protected with 1×10^{-3} molar bisulfite ion, the solutions lost their complexing ability in four to five days. Attempts at recovery of the carbazone from basic solution yielded a purple compound which showed no complexing ability. The fact that, apparently, only strongly basic solutions of the carbazide complex with metallic ions supports the postulated oxidation.

Chromatographic Analysis

The mixture obtained through treatment with base, sulfanilic acid, phenylhydrazinesulfonic acid, and other reagent blanks were spotted on pieces of Whatman No. 1 washed filter paper four by twenty inches. The papers were hung in a suitable chromatographic chamber in a manner so as to produce descending chromatograms. The papers were equilibrated for one hour by exposure to the vapors of a solvent prepared by saturating normal butanol with an aqueous buffer solution which was 1.5 N in both ammonium carbonate and ammonium hydroxide. After equilibration, 100 milliliters

of the solvent was poured into the trough and the chromatograms were allowed to run for 24 hours. The resulting chromatograms were air dried, heated at 110° C. for a few minutes, and developed with suitable colorimetric reagents. The identification of the various components of the resolved mixture left much to be desired. Evidently the amount of sulfanilic acid present was often too minute to detect. Better results were obtained with the following procedure and much practice. A column of powdered Whatman No. 1 filter paper was prepared by pouring a slurry of the powdered cellulose and the solvent into a column 4 cm. in diameter and 100 cm. long. The bottom of the column was supported with a sintered glass filter and fitted with a stopcock. The column was gently tamped and slight suction was applied to pack it. Four to five milliliters of the mixture were introduced to the column and as the material descended more eluent was added as needed. The bands which were separated on the column were eluted and the solvent evaporated. The residues were then dissolved in aqueous and methanolic solutions and subjected to strip chromatography with accompanying reagent blanks as above. Figure 3 shows the positions of the bands on the column. Band No. IV was usually, but not always, present.

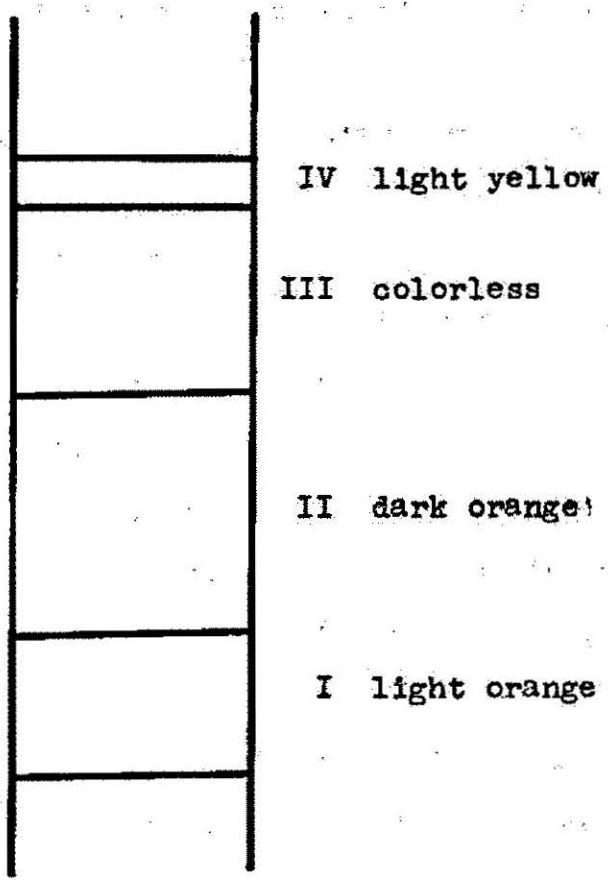Table I indicates the reagent blanks and mixture components which were run, and assigns them a reference

FIGURE 3

POSITION OF BANDS ON THE COLUMN

number for ease of identification in the following pages.
Table II shows the colorimetric test, the color of the spot,
and the R_f value obtained for each of the various compounds.
The following spot tests were used in developing the chroma-
tograms:

1. Methyl red was prepared by diluting one part of a
   0.1 per cent methanolic solution of indicator
   with two parts of a potassium dihydrogen phosphate-
   dipotassium hydrogen phosphate buffer at pH 7.0.
   Sulfanilic acid was developed as a pink spot on a
   yellow background.

2. Diazotization with 0.2 per cent ice cold sodium
   nitrite-0.1 N hydrochloric acid and coupling with
   0.2 per cent beta naphthol or 0.2 per cent alpha
   naphthylamine in ethanol produced red to purple
   spots on a brown background with sulfanilic acid.

3. An aqueous solution of 0.2 per cent ferric chloride
   solution produced reddish-brown spots on a yellow
   background with sulfanilic acid.

4. The semicarbazides were identified by their reaction
   with a 0.1 N hydrochloric acid solution of selenious
   acid, followed by coupling with an acetic acid
   solution of alpha naphthylamine. The various semi-
   carbazides appear as red to purple spots.

TABLE I

COMPOUNDS IDENTIFIED BY CHROMATOGRAPHIC PROCEDURES

Compound	Reference Number
Dithizone	1
1,5 diphenyl 3 thiocarbahydrazide	2
1,4 diphenylsemicarbazide	3
1 phenylsemicarbazide	4
4,4 diphenylsemicarbazide	5
1, 5 diphenylcarbohydrazide	6
Diphenylcarbazone	7
Phenylhydrazinesulfonic Acid	8
Sulfanilic Acid	9
Band I	10
Band II	11
Band III	12
Band IV	13

TABLE II

CHROMATOGRAPHIC COMPARISON OF COMPOUNDS

Solvent: n-Butanol saturated with 1.5 N NH_4OH and 1.5 N $(NH_4)_2$ CO_3

Compound No.	Developing Test	Color	R_f Value
1	zinc ion	pink	0.65
2	base: zinc ion	pink	0.70
3	selenious acid	purple	0.68
4	selenious acid		0.74
5	selenious acid		0.64
6	–	lt. pink	0.55
7	–	orange	0.50
8	methyl red	pink	0.07
9	methyl red	pink	0.12
10	–	lt. orange	0.53
	zinc ion	–	0.53
11	–	dk. orange	0.40
	zinc ion	pink	0.40
12	methyl red	pink	0.12
13	methyl red	pink	0.07

TABLE III

R_f VALUES OF SULFANILIC ACID AND BAND III

Compound	Solvent[*]	Developing Test	Color	R_f Value
Sulfanilic Acid	A	methyl red	pink	0.12
		a-naphthylamine	red	0.12
Band III	A	methyl red	pink	0.12
		a-naphthylamine	red	0.12
Sulfanilic Acid	B	methyl red	pink	0.13
Band III	B	methyl red	pink	0.13
Sulfanilic Acid	C	methyl red	lt. pink	0.54
		a-naphthylamine	dk. red	0.53
Band III	C	methyl red	lt. pink	0.53
		a-naphthylamine	purple	0.54
Sulfanilic Acid	D	methyl red	-	
		a-naphthylamine	purple	0.24
Band III	D	a-naphthylamine	purple	0.23

[*]Solvents: A n-Butanol, 1.5 N NH_4OH, and 1.5 N $(NH_4)_2CO_3$

B n-Butanol, 1.5 N NH_4OH

C Ethanol, 1.5 N NH_4OH

D n-Butanol, 1.5 N HAc

5. Dithizone and diphenylthiocarbazide were identified
by their reaction with strong base, followed by
zinc ion.

Several of the reagent blanks produced colored solutions and
colored spots on the paper. For example, the dithizone solu-
tion was green and the semicarbazide solutions were various
shades of yellow. The colorimetric tests in these cases
served as the second identification test. Table III compares
the R_f values of sulfanilic acid and the residue from Band
III in several solvents. The R_f values obtained experimentally
were in close agreement with those given by Lederer and
Lederer (1958) for these solvents. It is evident from the
experimental data that sulfanilic acid was present in the
mixture. It follows that the thiocyanate suggested by
Williams (1961), which he identified by spraying with ferric
chloride solution, was not thiocyanate but sulfanilic acid.
It also appears from the chromatographic evidence that the
residue from Band IV, when present, was unreacted phenyl-
hydrazinesulfonic acid. There is no record of any previous
chromatographic analyses of phenylhydrazinesulfonic acid,
di(p-sulfonic acid)phenylthiocarbazone, or (p-sulfonic acid)
phenylthiosemicarbazide. A sample of (p-sulfonic acid)phenyl-
thiosemicarbazide synthesized by Frye (1958) was run as a
blank in the buffered n-butanol solvent and was found to
have an R_f value of 0.49. This was not run simultaneously

with the mixture, however, so a more precise correlation can-
not be assumed, although the values are within the reason-
able limits of error (10 per cent). It was hoped that
infrared analyses of the residues from the column, when
compared with reference samples run by Williams (1961),
would aid in the identification of the disproportionation
products.

Job's Method of Continuous Variation

The stoichiometric ratio of reagent to zinc ion was
investigated using the continuous variation method of Job
(1928). The volume of zinc ion (1×10^{-3} M) was varied
from zero to ten milliliters per ten milliliter sample. The
concentration of the reagent, which was protected by bisulfite
ion, was also 1×10^{-3} M. The reagent solution was adjusted
to pH 10.0 with NaOH. The absorbance of the reagent-zinc
complex was measured at 550 mu on a Beckman (model DU)
spectrophotometer. The maximum composition in equimolar
solution was found to be 2:1 (reagent: zinc). Figure 4
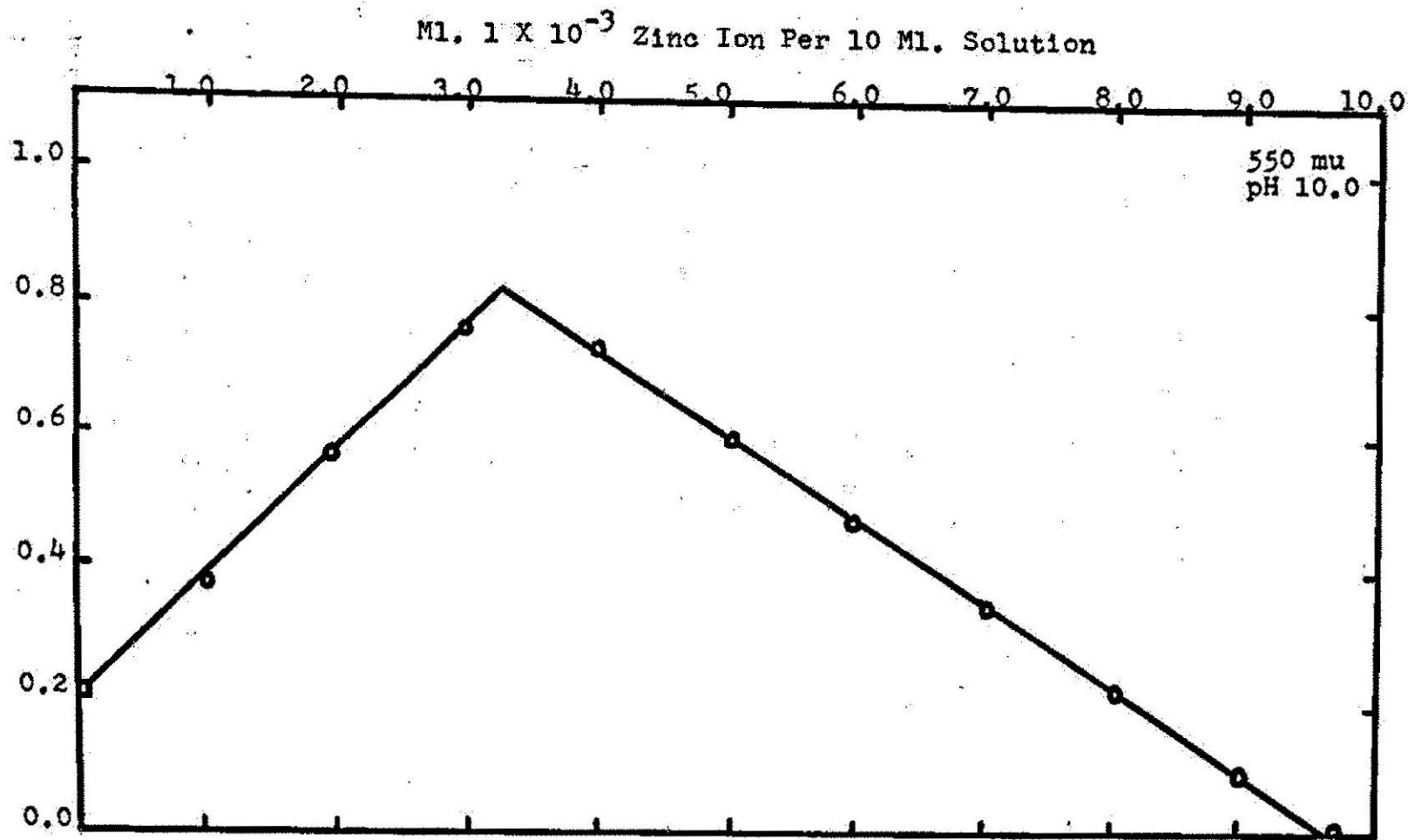shows absorbance as a function of the composition.

FIGURE 4

STOICHIOMETRIC RATIO REAGENT TO ZINC ION

27

CHAPTER IV

INFRARED SPECTROPHOTOMETRY

The infrared curves, Figures 5 through 9, were run on a Perkin-Elmer Model 121 Infrared Spectrophotometer. The samples were run at a concentration of approximately 1 per cent in a 1.5 mm. potassium bromide pellet. The curves were run at a speed of 2.0 microns per minute using air as a reference. The following compounds were run in the hope of finding correlations between their spectra and those of known substances run by Williams (1961):

	Figure
Di(p-sulfonic acid)phenylthiocarbazide	5
Band I	6
Band II	7
Band III	8
Band IV	9

The curves of the infrared spectra are shown in Figures 5 through 9. The peaks of the curves of di(p-sulfonic acid)phenylthiocarbazide, Band III and Band IV appear to be almost identical with the respective curves for "thiazate," sulfanilic acid, and phenylhydrazinesulfonic acid obtained by Williams. The curve of Band I appears to be representative of the curves of several of the various semicarbazides. The curve of Band II shows little

correlation with those of dithizone and diphenylcarbazone.
The peaks of Band II appear to be representative of those
obtained for the di(p-sulfonic acid)phenylthiocarbazide.
The fine structure seen in the dithizone and diphenylcarba-
zone curves in the region from 1300 to 2000 cm^{-1} is lacking
entirely. Although evidence for a sulfonated phenylthiocarba-
zone resembling dithizone in resonance is lacking, it is
apparent that sulfanilic acid and a compound having a curve
very similar to the semicarbazides are present. Due to the
similarity between Band II and the di(p-sulfonic acid)phenyl-
thiocarbazide, it is assumed that the compound obtained from
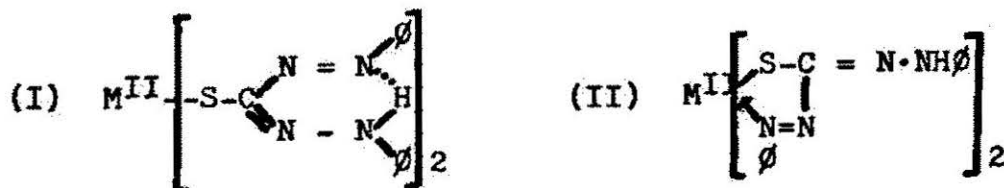the residue of Band II is di(p-sulfonic acid)phenylthiocarba-
zone.

CHAPTER V

CONCLUSIONS

Although the stoichiometric ratio of the zinc complex
has been established, the structure of the complex is still
in doubt. Two forms of dithizone, enol (I) and keto (II),
seem to exist. The enol form has been found to exist in

(I) $HS-C\begin{smallmatrix} N = N \diagdown \phi \\ \\ N - N \diagdown \phi \end{smallmatrix} H$ (II) $S = C\begin{smallmatrix} N = N \cdot \phi \\ \\ NH \cdot NH\phi \end{smallmatrix}$

basic solutions, while the keto form exists in both acid and
neutral solutions. Irving and Bell (1952) have shown that
metal keto dithizonates are derived by replacement of the
hydrogen of the mercapto group rather than that of the imido
group. Irving and Cox (1961) believe that more likely
structures involve metal-sulfur bonds. In the formazan
structure (I) below, the ring system is formed by hydrogen
bonding and each dithizone molecule would occupy only one
co-ordination position. In another structure (II), the

(I) $M^{II}\left[-S-C\begin{smallmatrix} N = N \diagdown \phi \\ \\ N - N \diagdown \phi \end{smallmatrix} H \right]_2$ (II) $M^{II}\left[\begin{smallmatrix} S-C = N \cdot NH\phi \\ | \\ N=N \\ \phi \end{smallmatrix} \right]_2$
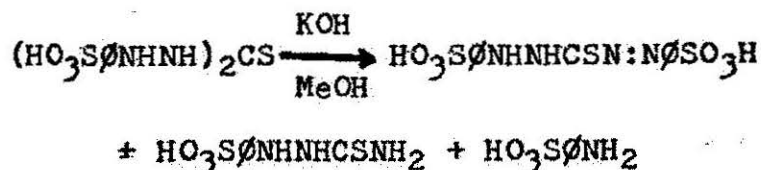
five-membered chelate ring would occupy two cis co-ordination
positions. Irving and Cox, basing their argument on the
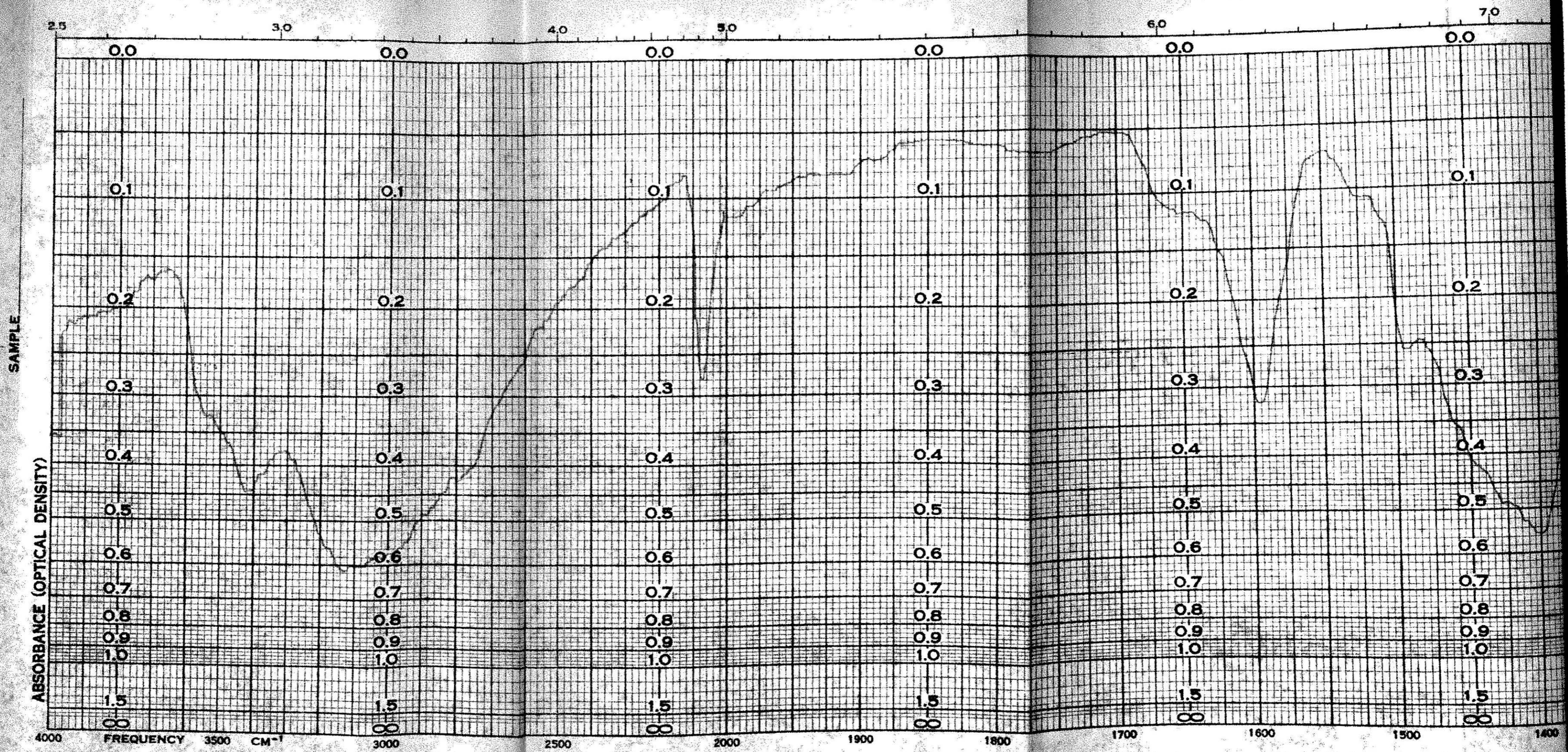complexes of Sn(II), Pb(II) and Hg(II), believe that dithizone

acts as a bidentate ligand and also predict this type of
chelation for Zn(II) ion. By analogy with dithizone, it is
possible that the zinc complexes with di(p-sulfonic acid)
phenylthiocarbazone as shown below.

$$Zn^{II} \left[\begin{array}{c} S-C=N \cdot NH\emptyset SO_3H \\ | \quad | \\ N=N \\ \emptyset \\ SO_3H \end{array} \right]_2$$
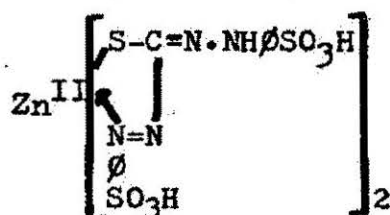
The results of the paper chromatography and infrared
spectrophotometry indicate that the disproportionation of
di(p-sulfonic acid)phenylthiocarbazide proceeds in a manner
analogous to that of dithizone, yielding the corresponding
thiocarbazone, semicarbazide, and sulfanilic acid as follows:

$$(HO_3S\emptyset NHNH)_2CS \xrightarrow[\text{MeOH}]{\text{KOH}} HO_3S\emptyset NHNHCSN:N\emptyset SO_3H$$

$$\pm HO_3S\emptyset NHNHCSNH_2 + HO_3S\emptyset NH_2$$

It appears obvious that the disproportionation
products resemble in no way whatsoever the decomposition
products reported by Williams (1961). It is also obvious
that further work should be directed toward the purification
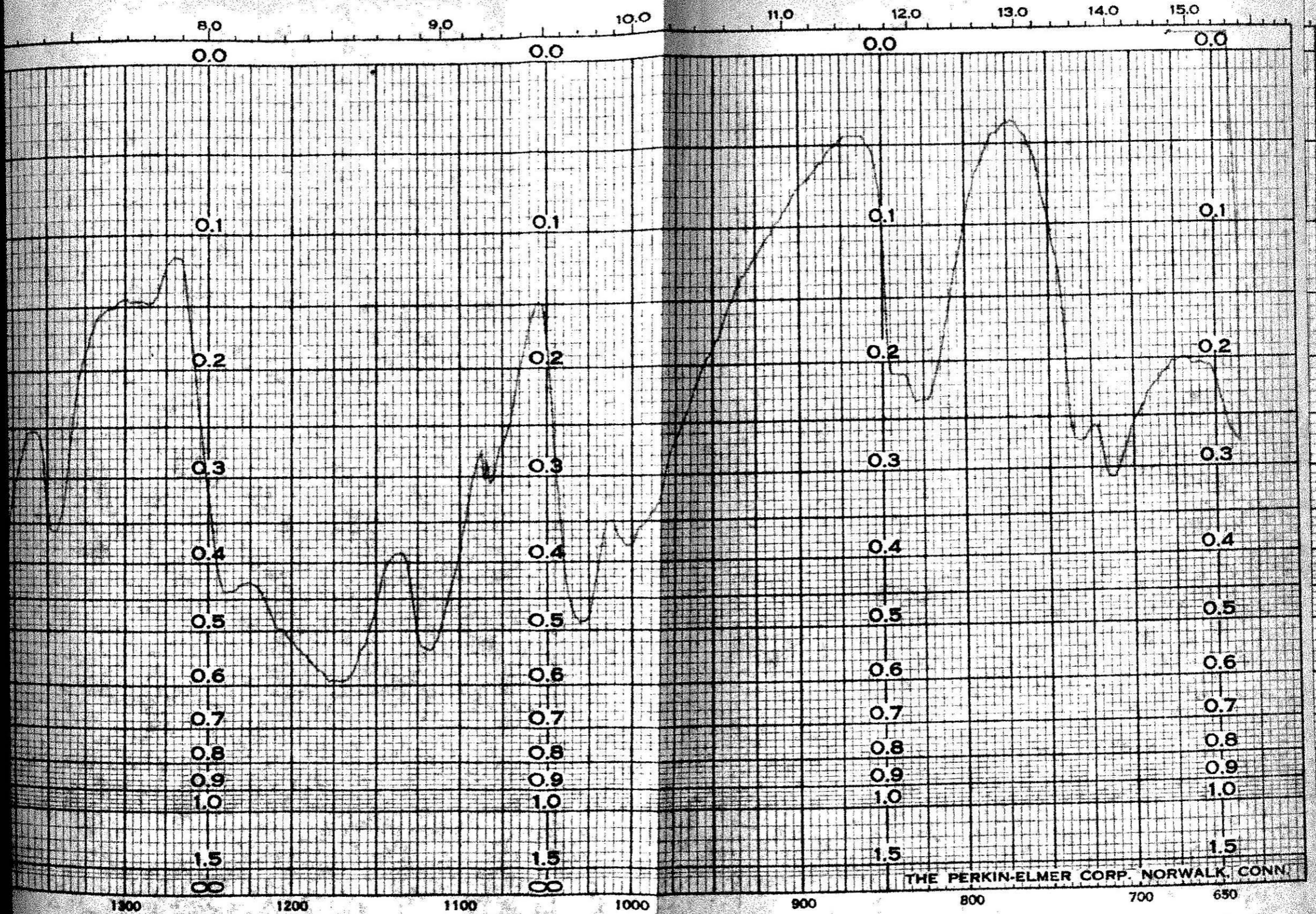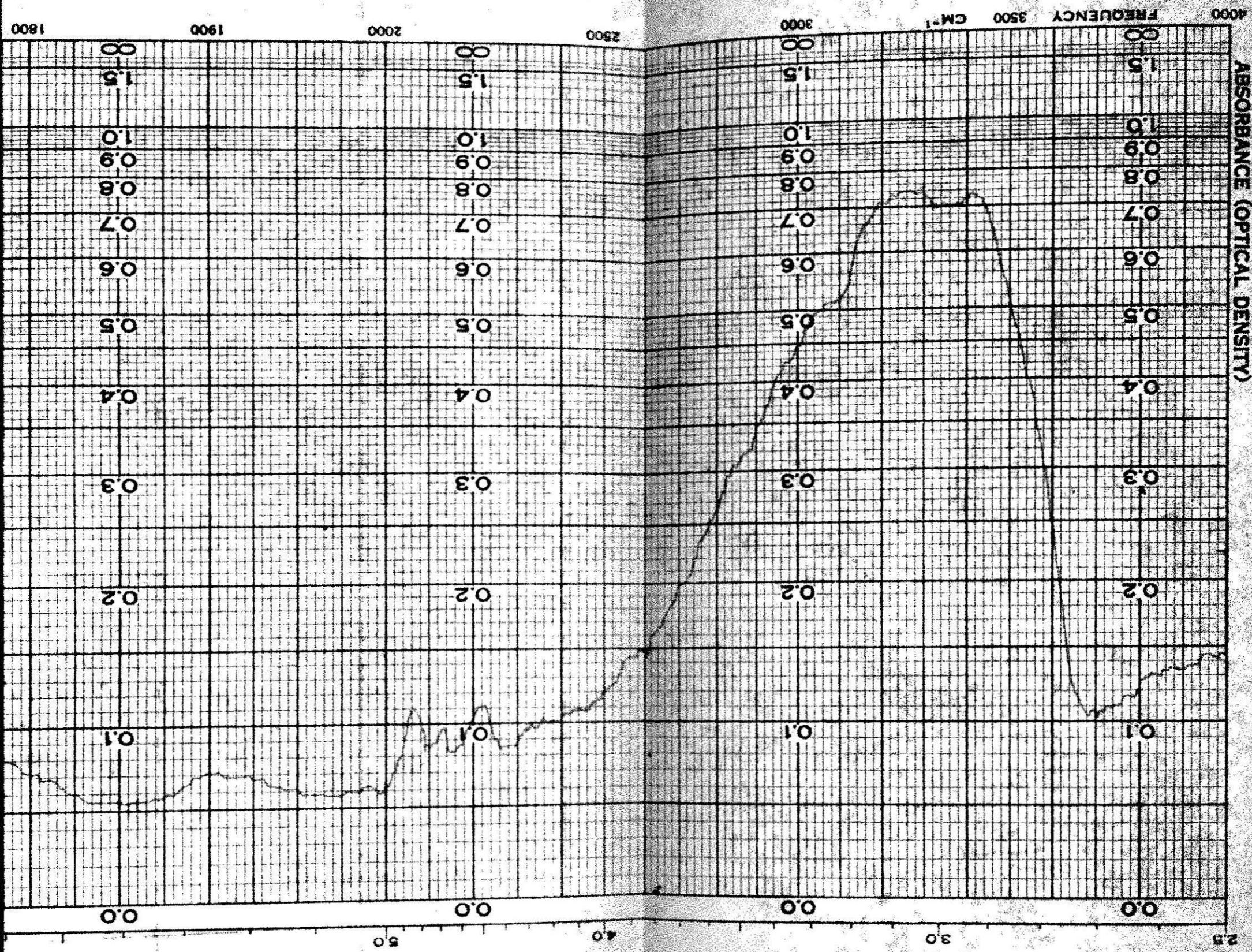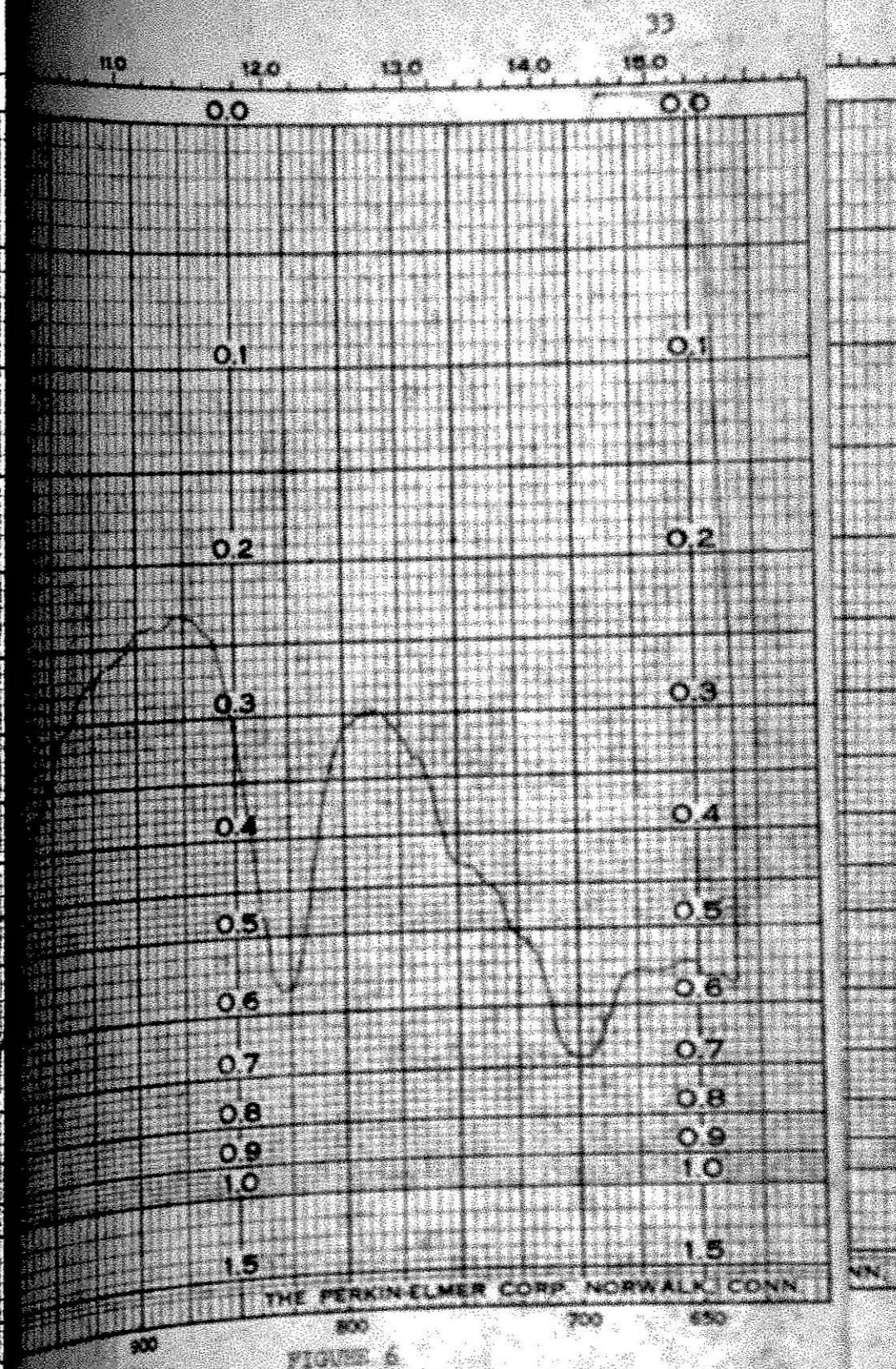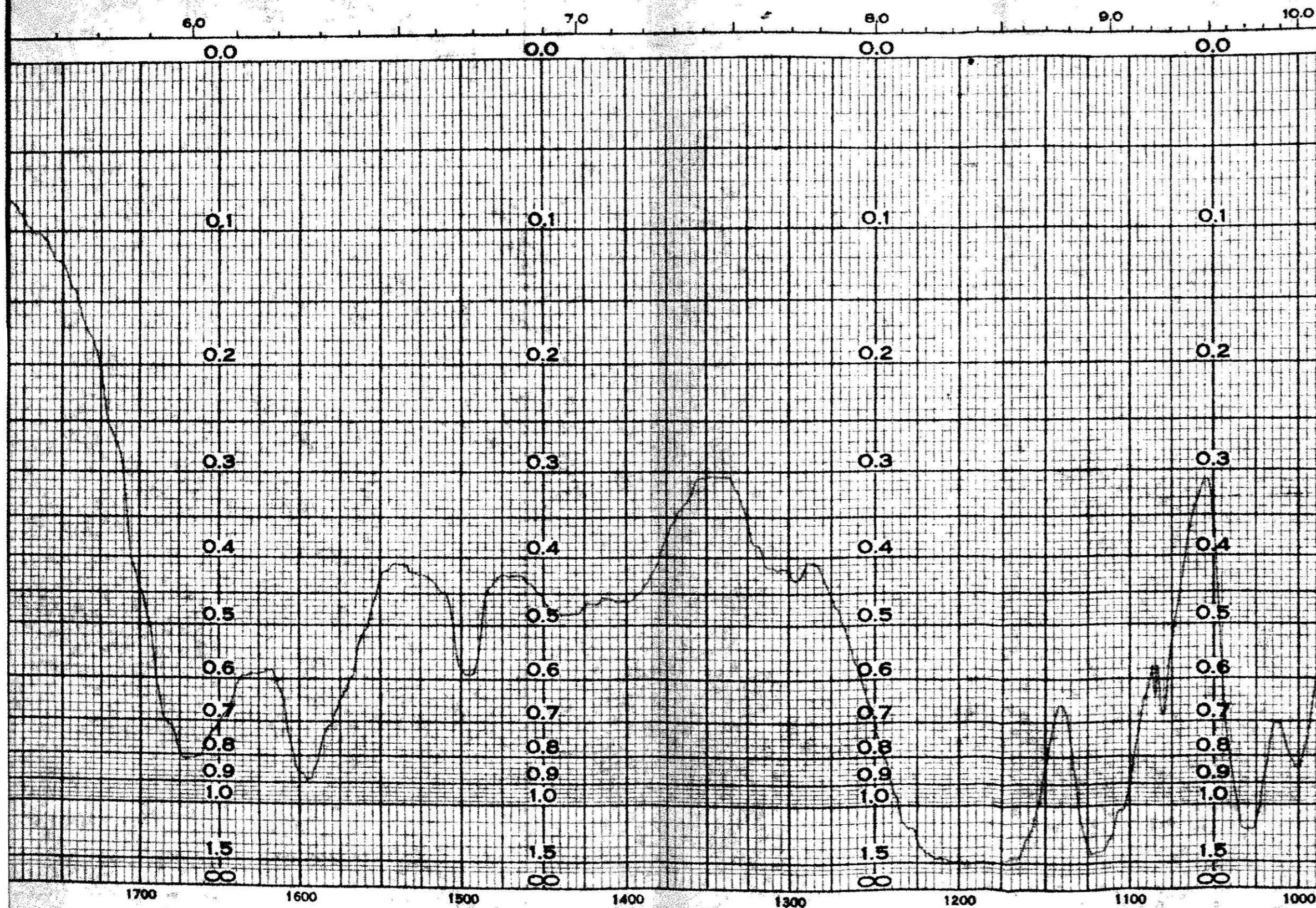and isolation of the sulfonated thiocarbazide and the respec-
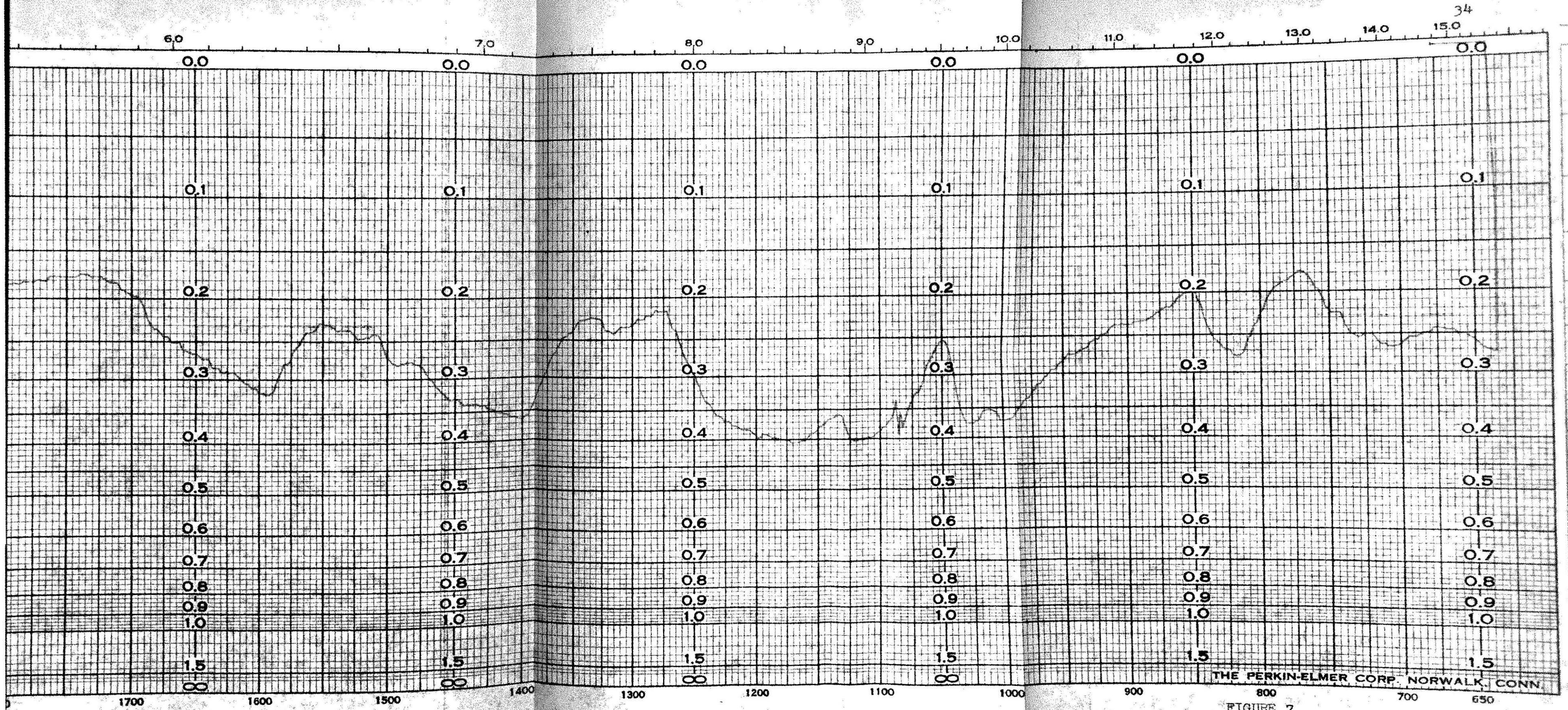tive thiocarbazone.

FIGURE 5

DI(p-SULFONIC ACID)PHENYLTHIOCARBAZIDE

FIGURE 6
BAND I

THE PERKIN-ELMER CORP. NORWALK, CONN.

SAMPLE _____

ABSORBANCE (OPTICAL DENSITY)

2.5   3.0   4.0   5.0

0.0   0.0   0.0   0.0

0.1   0.1   0.1   0.1

0.2   0.2   0.2   0.2

0.3   0.3   0.3   0.3

0.4   0.4   0.4   0.4

0.5   0.5   0.5   0.5

0.6   0.6   0.6   0.6

0.7   0.7   0.7   0.7

0.8   0.8   0.8   0.8

0.9   0.9   0.9   0.9

1.0   1.0   1.0   1.0

1.5   1.5   1.5   1.5

∞   ∞   ∞   ∞

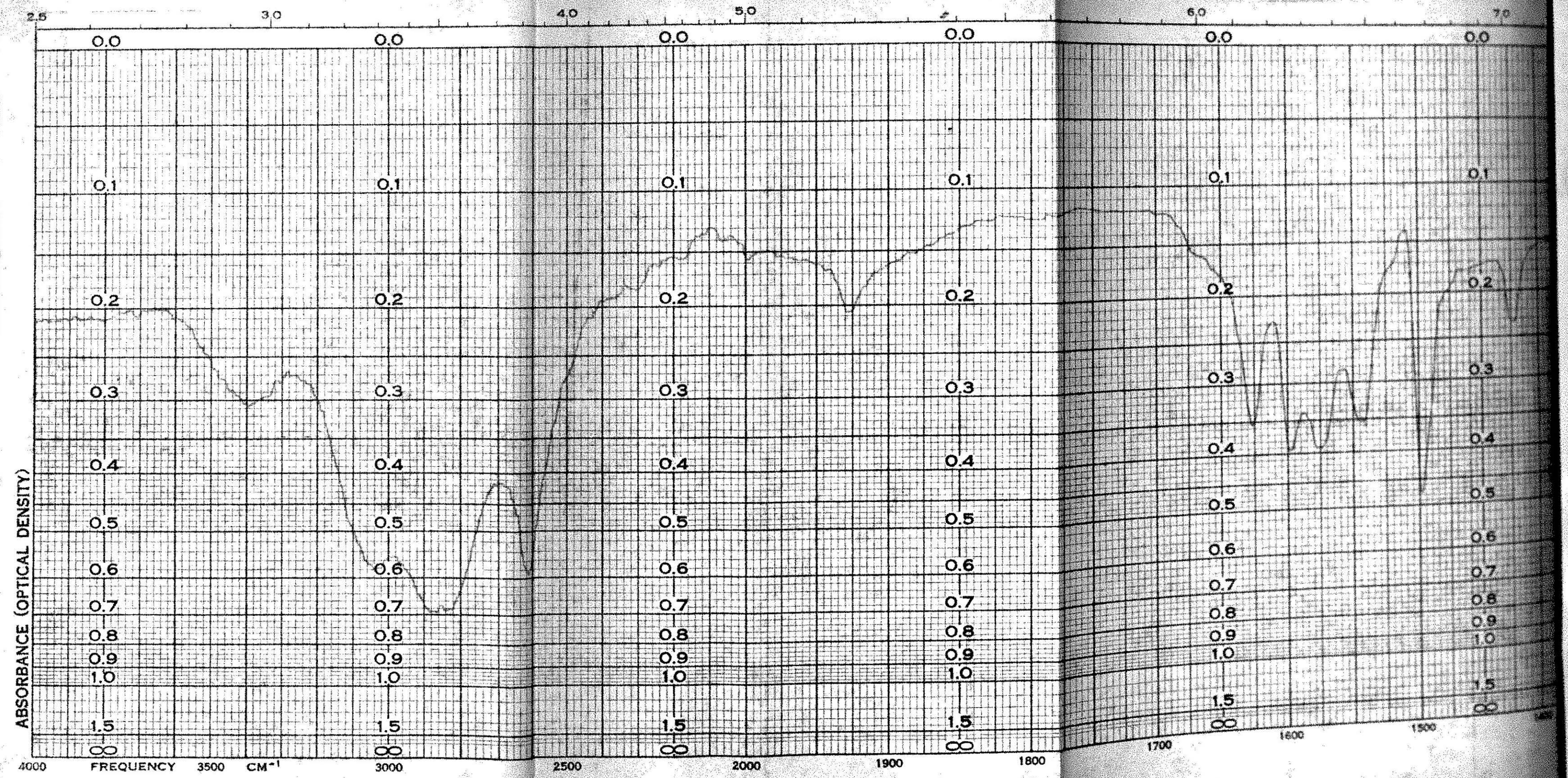4000   FREQUENCY   3500   CM⁻¹   3000   2500   2000   1500

FIGURE 7

BAND II

THE PERKIN-ELMER CORP. NORWALK, CONN.
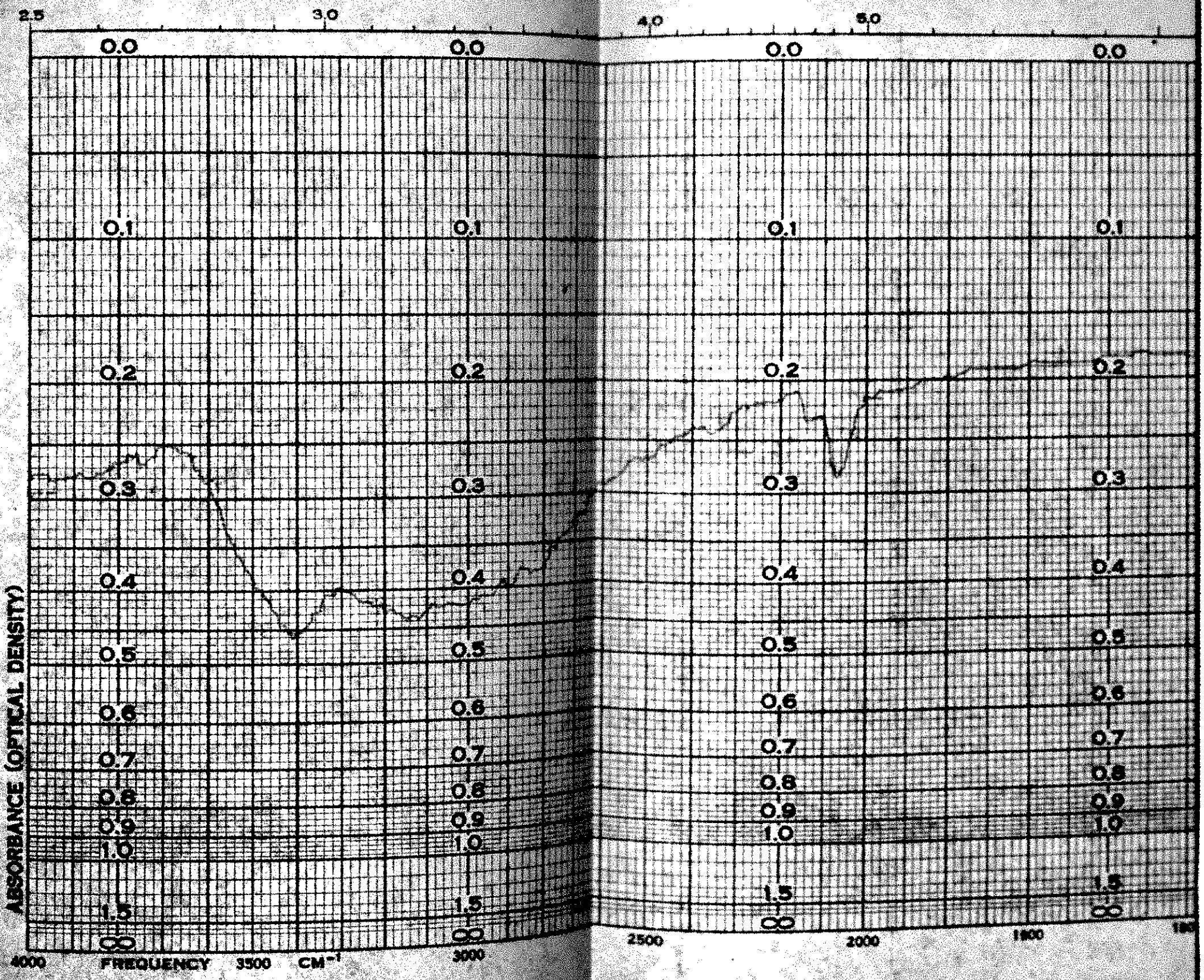
THE PERKIN-ELMER CORP. NORWALK, CONN.

FIGURE 8

BAND III

FIGURE 9

BAND IV

THE PERKIN-ELMER CORP. NORWALK, CONN.
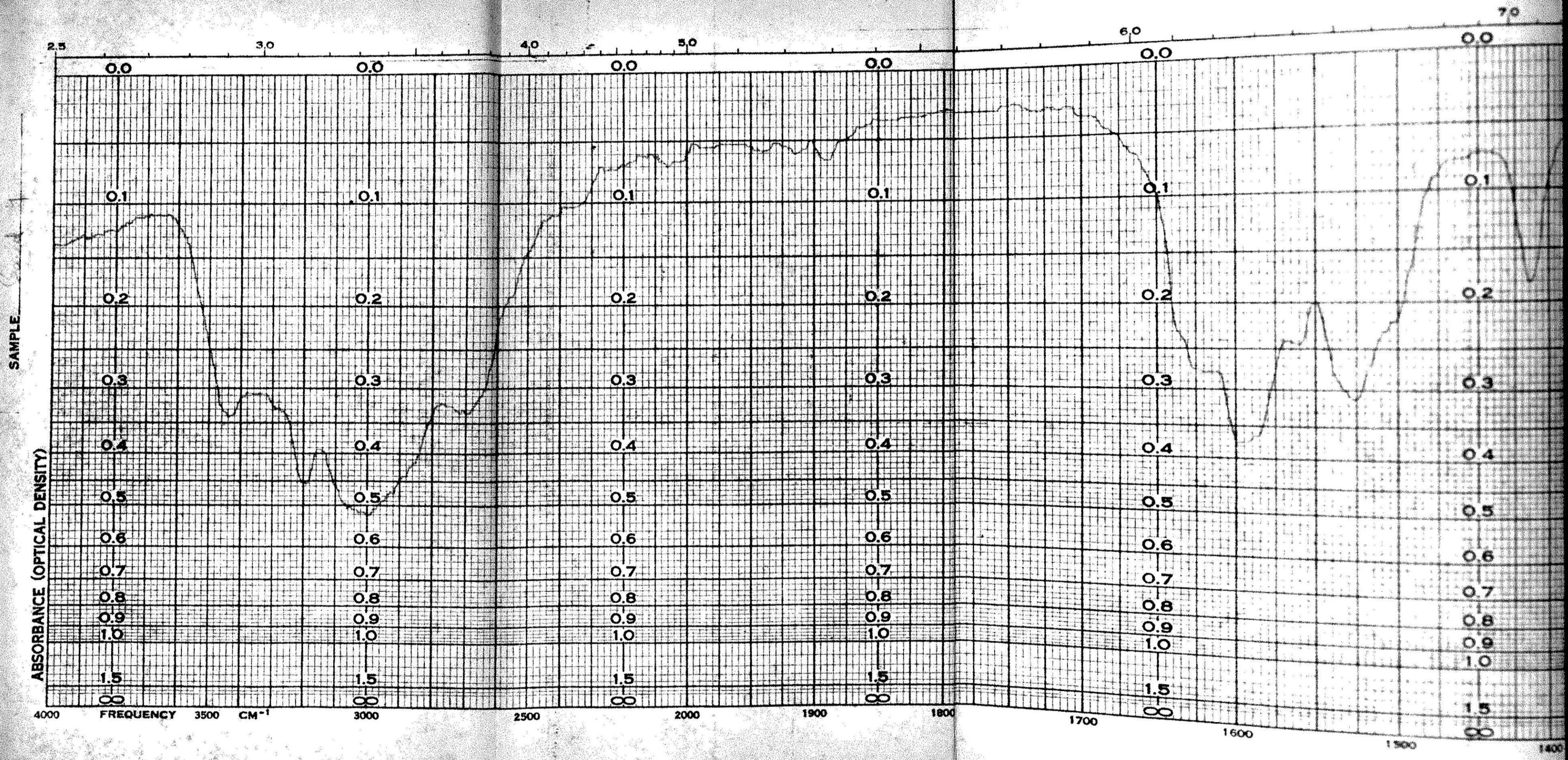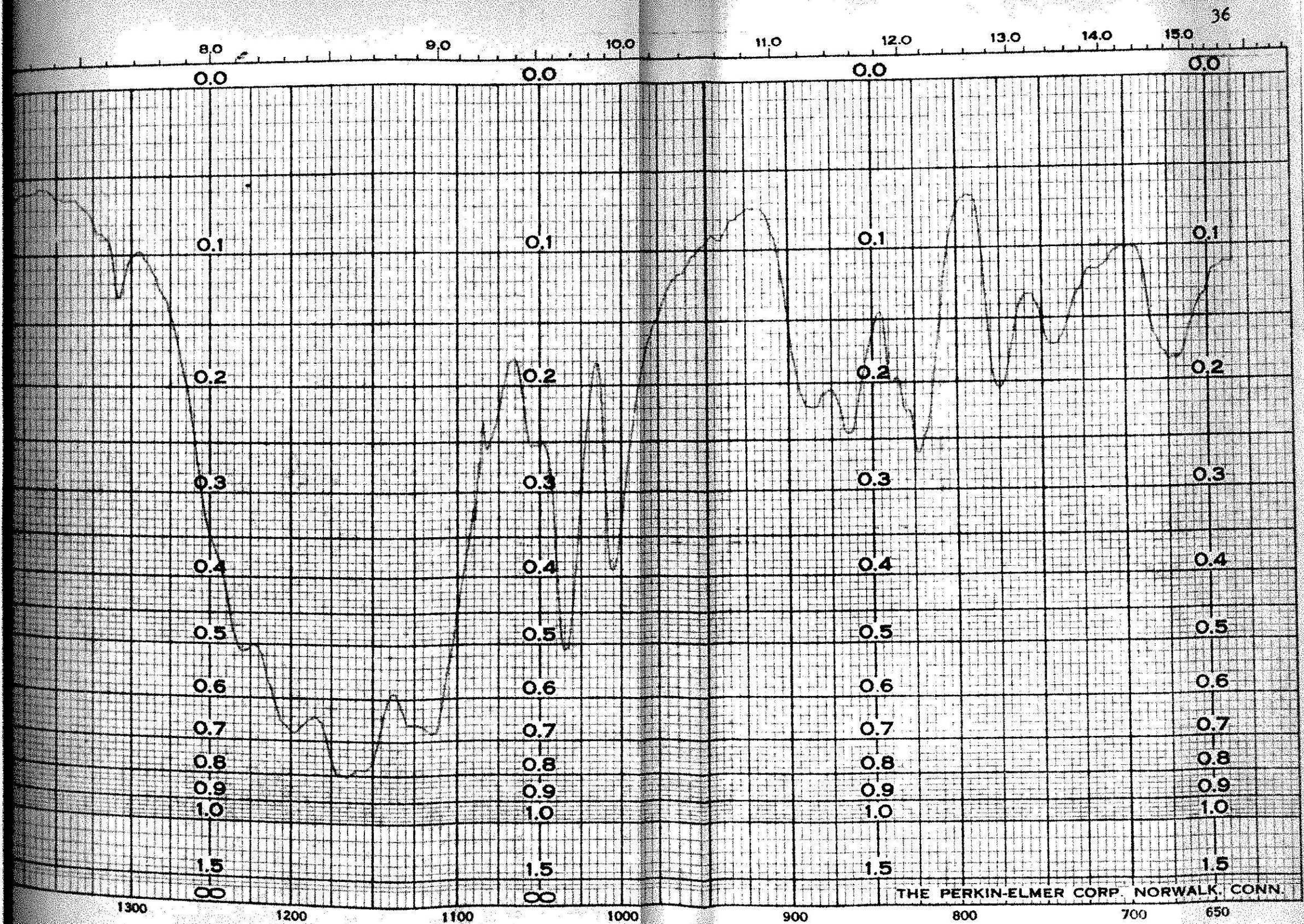
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