5-1-1973

An NMR Study of Substituent Effects in Ortho-Substituted Aryl Methyl Sulfides

Luba Anne Pacala

AN NMR STUDY OF SUBSTITUENT EFFECTS IN ORTHO-SUBSTITUTED ARYL METHYL SULFIDES

Luba Anne Pacala
May 1, 1973

Submitted to the faculty of Ursinus College
in partial fulfillment of the requirements for
Departmental Honors in Chemistry

Submitted: May 1st 1973

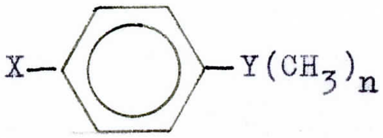
Approved: Roger P. Staiger
Ronald E. Hess

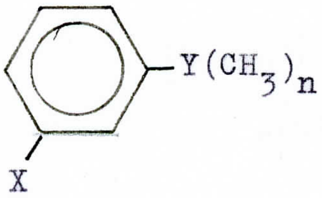
TABLE OF CONTENTS

I. INTRODUCTION

The correlation of Hammett sigma constants with various physical properties and spectral parameters in meta and para substituted benzene derivatives has been extensively investigated in the last few years. Correlations of nmr absorptions with these substituent parameters have been especially successful.[1]

For example, in 1969 an nmr study was undertaken to determine the effects of certain substituents on the nature of systems of the following types:[2]





Y =	n =
C	3
O	1
N	2
Si	3
Ge	3
P	2
S	1

X = NO_2, Cl, Br, H, CH_3, C_2H_5, t-C_4H_9, OCH_3, OC_2H_5, $N(CH_3)_2$

In these systems, the Y-methyl chemical shifts and carbon 13-proton coupling constants have been shown to be a function of the electronic environment of the absorbing proton. According to Bent's isovalent hybridization model,[3] the greater the electronegativity of Y in these systems, the greater the amount of s character in the carbon-hydrogen bonds of the methyl groups, and, therefore, the greater the magnitude of the coupling constant. Since coupling constants should be relatively free of solvent or anisotropy effects, they might better reflect substituent effects than do chemical shifts, which are not completely independent of such interactions.

Reasonably good linear correlations of Hammett sigma constants with carbon 13-proton coupling constant and chemical shift data were obtained.

For the system in which Y is S (Graph I), a plot of chemical shifts versus Hammett sigma constants resulted in a straight line with a correlation coefficient of 0.961 and a standard error of 0.950. When the σ^- constant is used in place of the σ constant for the nitro group, an even better correlation was obtained. The correlation coefficient was 0.989 and the standard error 0.512.

The σ^- constant takes into account the ability of the electron-withdrawing nitro group to enter into direct resonance interactions with the ring

A plot of the carbon 13-proton coupling constants versus Hammett sigma constants for the same system also gave a straight line with a correlation coefficient of 0.934 and a standard error of 0.205. Again the use of σ^- in place of σ for the nitro group resulted in a better correlation, with a correlation coefficient of 0.976 and a standard error of 0.12. This is shown in Graph II.

The slopes of these plots are believed to be indicative of the ability of Y to transmit the electrical effects of the substituent X to the methyl group. The slope equal to 1.38 obtained from the coupling constant data for the system in which Y is oxygen, as compared to the slope equal to 1.29 obtained for the system in which Y is sulfur, has been interpreted as being indicative of the greater ability of the oxygen atom to transmit the electrical effects of the substituent.[4] The ability of Y to transmit these effects is believed to be related to such factors as its size, electronegativity, polarizability, and the nature of the Y-aromatic bond.

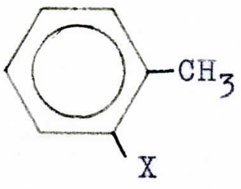
Up until the past fifteen years little of this type of work had been done with ortho substituents because it was believed that steric effects in such systems had to be considered in addition to electronic effects. At the present time more than thirty-two sets of ortho substituent constants have been defined by means of a Hammett-type linear free energy relationship:

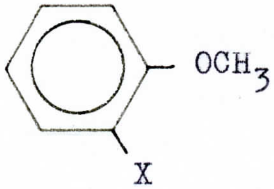
$$\log K_s / K_u = \rho \sigma + C$$

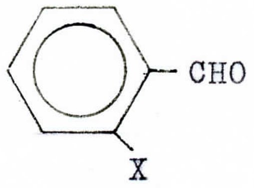
where ρ is the slope and C is the intercept obtained from the correlation of data for meta and para substituted compounds. K_s and K_u are physical or chemical constants for the substituted and unsubstituted compounds, respectively. Sigma is a measure of the effective electronegativity of the substituent group.

In 1969 Marvin Charton[5] undertook a study to determine whether or not these ortho sigma constants include steric effects and to invesitgate the possibility of representing the ortho effect by a single set of substituent constants. He was successful in correlating a good number of these substituent constants with an equation based on the Taft[6] separation of substituent effects into inductive and resonance contributions. Charton, therefore, concluded that the ortho effect is a pure electrical effect for most substituents. A study of the variability of the composition of the ortho substituent constants led Charton to conclude that no one set of ortho substituent constants can be defined. He also concluded that only in an exceptional case is the ortho electrical effect likely to have the same composition as the para electrical effect. In general, then, the ortho and para electrical effects may be expected to differ in both magnitude and composition.

In a more recent attempt to determine the electronic nature of ortho substituted aromatics, Hess, Schaeffer, and Yoder[7] examined the carbon 13-proton coupling constants of ortho substituted toluenes, anisoles, and benzaldehydes:







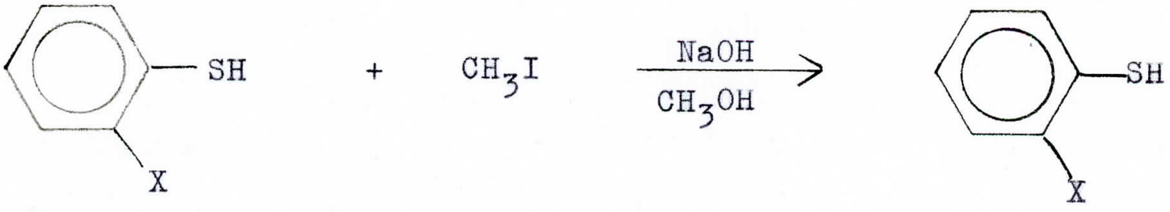
The results of this study, presented in Table I, showed that the ortho sigma constants for a particular substituent in all three series were roughly similar. The ortho sigma constants were generally greater than the related meta and para constants.

Since this appeared to be especially true for electron-attracting substituents, the authors believed this to be due to the greater inductive effect in the ortho position.

This project involved the synthesis of a series of ortho substituted methyl phenyl sulfides and the subsequent interpretation of their nmr spectra to see if a linear correlation of reported ortho sigma constants with carbon 13-proton coupling constants or S-methyl chemical shifts existed. It was also the object of this study to determine a new set of ortho substituent constants based upon these data.

II. SYNTHESIS

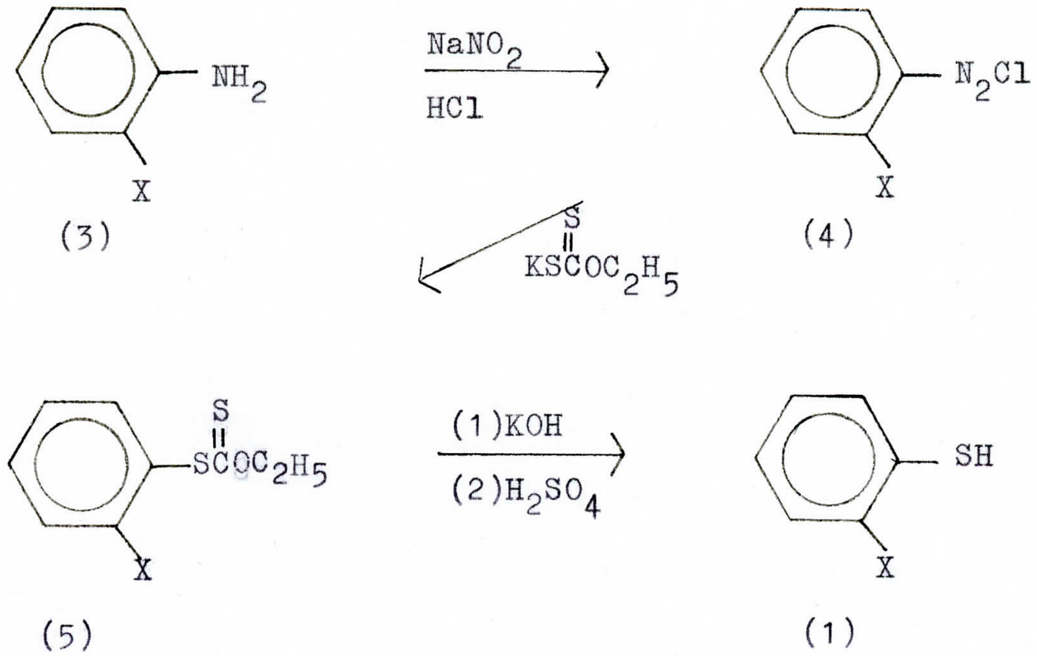
Because the ortho substituted methyl phenyl sulfides (2) either were not available commercially or were highly priced, most were prepared by methylation of the corresponding mercaptans (1) with methyl iodide in the presence of sodium hydroxide and methanol.



(1) (2)

The final products were isolated by vacuum distillations at pressures less than 20 mm Hg. The o-F, o-Cl, o-Br, o-OCH_3, o-COOH, and o-NH_2 members of the series were prepared in this manner.

The mercaptans (1) were obtained by a procedure similar to that suggested by Tarbell and Fukushima[8] in Organic Syntheses for the preparation of meta-toluenethiol. This involved treating the corresponding ortho substituted aniline (3) with sodium nitrite and hydrochloric acid to form the diazonium salt (4). The addition of excess potassium ethyl xanthate yielded the xanthate intermediate (5), which then underwent alkaline hydrolysis to give the mercaptan (1).

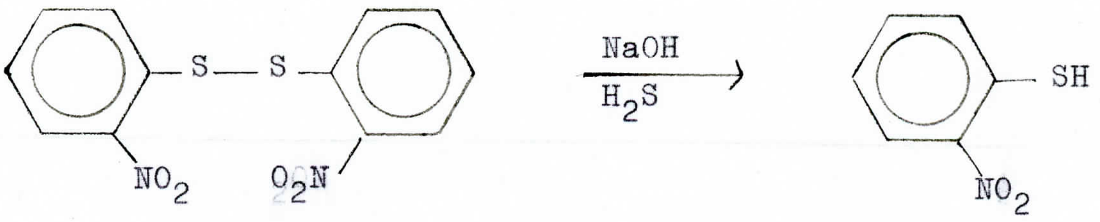


The mercaptans were isolated by steam distillation and were methylated without further purification.

It has been reported that even at low temperatures a diazonium solution may react explosively with a solution of a metallic polysulfide. Leukart[9] in 1890 reported such a reaction with xanthates. No unusual reactivity of this nature was observed during the preparation of the aryl methyl sulfides.

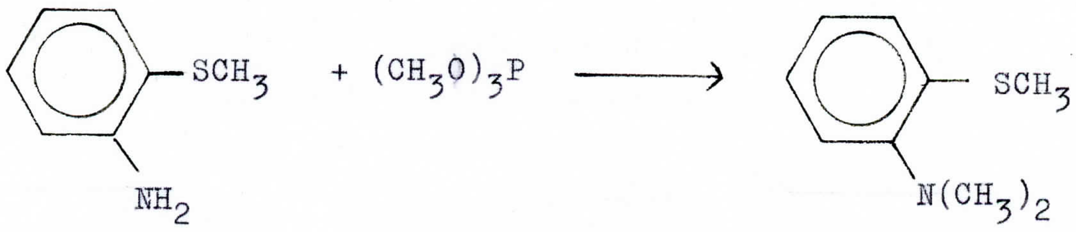
Prepared in the manner outlined above were *o*-methoxythiophenol, *o*-chlorothiophenol, *o*-fluorothiophenol, and *o*-bromothiophenol. *o*-tolylmethylsulfide, *o*-mercaptobenzoic acid, and *o*-aminobenzenethiol were obtained commercially.

The preparation of *o*-nitrothiophenol was attempted according to the procedures of Tarbell and Fukushima and of Foster and Reid.[10] Foster and Reid prepared *o*-nitrothiophenol (6) by the reduction of *o*,*o*'-dinitro-diphenyldisulfide (7) with sodium hydroxide and hydrogen sulfide.


(7) (6)

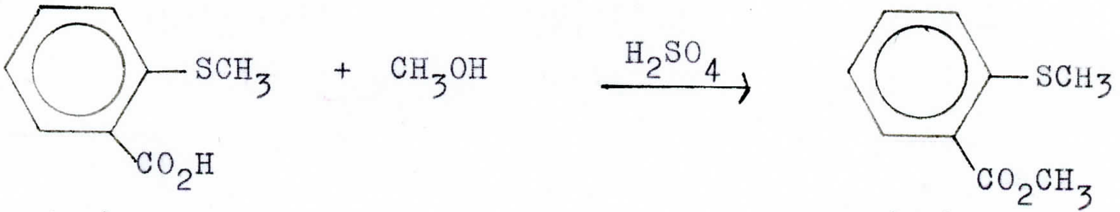
The o,o'-dinoitro-diphenyldisulfide was prepared by the method of Wohlfahrt.[11] Both Foster & Reid and Wohlfahrt found the yellow crystalline product to be quite stable. Both attempts on the part of the author to prepare o-nitrothiophenol were unsuccessful.

Methyl-o-(N,N-dimethylamino)phenylsulfide (8) was prepared by gently heating a mixture of methyl-o-aminophenyl sulfide (9) and an equimolar amount of trimethylphosphate.


(9) (8)

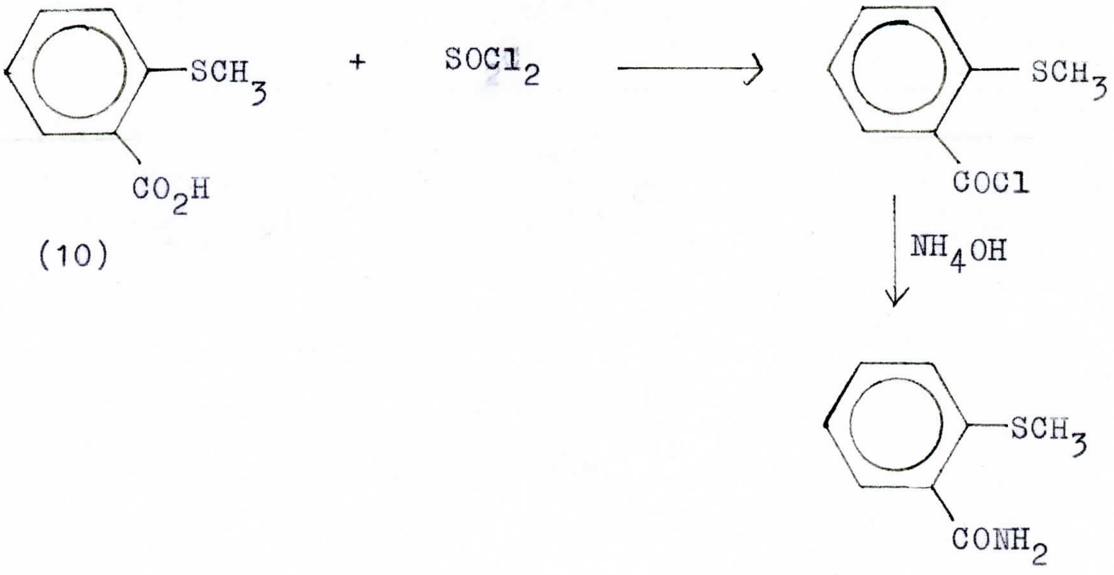
After the initial reaction had subsided, gentle reflux was carried out for a period of 2 hours and 45 minutes. Hydrolysis with aqueous sodium hydroxide followed by extraction with ether, removal of the solvent, and distillation at reduced pressure yielded a clear colorless product.

The methyl ester of methyl-o-carboxyphenylsulfide (10) was prepared in a straightforward manner involving the esterification of a sulfuric acid solution of methyl-o-carboxyphenylsulfide with methanol. After a short period of reflux, neutralization with sodium bicarbonate, and the addition of the reaction mixture to water, the product separated as a white solid. (11)



(10) (11)

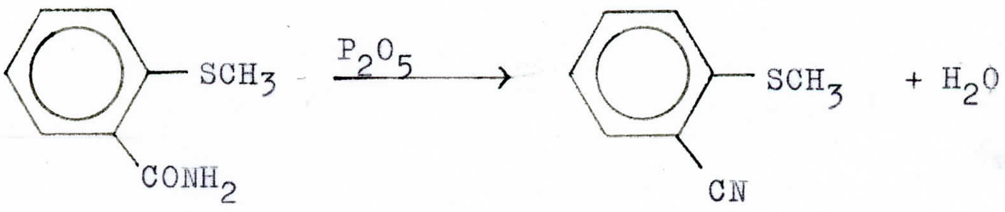
The amide (12) of methyl-o-carboxyphenylsulfide was prepared by simply treating the acid with thionyl chloride and then with ammonium hydroxide. A white crystalline product was isolated.



(10)

(12)

Upon treatment of the amide (12) with phosphorous pentoxide and application of heat, the cyano derivative (13) was prepared.



In none of these preparations were attempts made to maximize yields. With the exception of the carbomethoxy and cyano compounds, all products were liquids with a characteristic disagreeable odor. The physical constants of the products were consistent with those reported in the literature. No data were available for the fluorine compound, but an excellent elemental analysis was obtained. With the exception of the dimethyl amino compound, the purity of the products was verified by the absence of spurious signals in the nmr spectra. The dimethyl amino compound is estimated to contain approximately 10% impurity.

III. EXPERIMENTAL

o-fluorothiophenol. In a 1-liter, three-necked flask equipped with a mechanical stirrer, thermometer, and a pressure-equalizing dropping funnel, and immersed in an ice bath were placed 94 ml (3.1 moles) concentrated HCl and 94 g crushed ice. The stirrer was started, and 50.0 g (0.47 moles) o-fluoroaniline was added dropwise. The mixture was cooled to 2°C, and a cold solution of 34.5g (0.50 mole) $NaNO_2$ in 78 ml water was added dropwise so that the temperature remained below 4°C. The resulting diazonium solution was orange. A solution of 87.5g (0.54 mole) potassium ethyl xanthate in 113 ml water was placed in a 2-liter, 3-necked flask equipped with a thermometer, mechanical stirrer, and dropping funnel. The xanthate solution was heated to 40-45°C and the cold diazonium solution was added dropwise, the temperature being kept between 40-45°C with the exception of an occasional increase to approximately 50°C. A red oil was formed upon addition of the diazonium solution. The reaction mixture was heated at 45°C for 30 min. to insure complete decomposition of the intermediate. The red oil was separated from the aqueous layer, which was then extracted twice, using 100 ml portion of ether. The combined oil and extracts were washed once with 100 ml of 10% NaOH and then with two 100-ml portions of water. The final washing was neutral to litmus. The ether solution was dried over 25g anhydrous calcium chloride, and 110 ml ether was removed by distillation at atmospheric pressure. The red, oily residue was dissolved in 300 ml of 95% ethanol, and the solution was brought to a boil. The source of heat was removed, and 110g (1.96 moles) KOH pellets were added at a rate which kept the solution boiling. The solution was refluxed for 8 hours, after which a sample was soluble in water. Distillation at atmospheric pressure removed 184 ml ethanol. The red residue was taken up in 325 ml water. The resulting solution was extracted with several 50 ml portions of ether. The extracts were discarded. An exit hose leading from the reaction flask to the hood was assembled, and the aqueous solution was made strongly acidic to Congo red paper with 50 ml concentrated sulfuric acid. Copious amounts of carbon oxysulfide were liberated. Two grams of zinc dust were added to the acidified solution, and the mixture was steam distilled. After separating the yellow oil from the distillate, the aqueous layer was extracted with several 50 ml portions of ether (300 ml total). The extracts were added to the oil, and the combined solution was dried over anhydrous magnesium sulfate. Removal of the ether at atmospheric pressure yielded 17.9g of clear yellow product. (29.9%)

_o_-chlorothiophenol, **_o_-methoxythiophenol**, and **_o_-bromothiophenol** were prepared in a manner analagous to that for *o*-fluorothiophenol. The products were not isolated and purified. The percent yield of *o*-bromothiophenol was 35.8%. Other workers initiated the reactions for the preparation of *o*-chlorothiophenol and *o*-methoxythiophenol, and the data necessary for the calculation of % yields were not available.

Methyl-*o*-fluorophenylsulfide was prepared in the following manner. To a solution of 17.9g (0.140 mole) crude *o*-fluorothiophenol in 30 ml methanol was added with stirring a solution of 5.8g (0.14 mole) sodium hydroxide in 50 ml methanol. Methyl iodide (39.7g, 0.280 mole) was added dropwise to the reaction mixture over a period of 30 minutes. After refluxing for one hour, 72 ml of methyl iodide and methanol were removed by distillation at atmospheric pressure. The residue was washed with two 50 ml portions of water, and the washings were extracted with two 50 ml portions of benzene. The extracts and oil were combined and dried over anhydrous magnesium sulfate. After removal of the benzene by distillation at atmospheric pressure, 4.2g (20%) of clear yellow product were isolated by vacuum distillation (b.p. 51-55°C/1.7 mm). Data for this compound could not be found in the literature. An elemental analysis of the product yielded the following results: 59.26% Carbon, 5.04% Hydrogen (theoretical: 59.12% C, 4.97% H).

***o*-tolylmethylsulfide**, **methyl-*o*-chlorophenylsulfide**, **methyl-*o*-methoxyphenylsulfide**, **methyl-*o*-carboxyphenylsulfide**, **methyl-*o*-aminophenylsulfide**, and **methyl-*o*-bromophenylsulfide** were prepared by treatment of the corresponding sulfides with methyl iodide in the presence of NaOH and CH_3OH using the procedure outlined above for the preparation of methyl-*o*-fluorophenylsulfide. The boiling points and yields for these compounds are as follows: *o*-CH_3, bp 54-58/18mm (lit.[14] 96-97/17mm), 46.8%; *o*-Cl, bp 63-67/15mm (lit.[17] 116.5-117/15mm), 30.4%; *o*-OCH_3, bp 81-83/7mm (lit.[17] 127-128/18mm), 10%; *o*-CO_2H, mp 170.5-171.5°C (lit.[18] mp 169°C), 37%; *o*-NH_2, bp 93-95/1.7mm (lit.[19] 133-4/15mm), 39.4%; *o*-Br, bp 107/3.9mm (lit.[20] 81-83/0.3mm), 60%. An elemental analysis of *o*-tolymethylsulfide gave the following results: 69.73% C, 7.19% H (theoretical: 69.65% C, 7.31% H).

Methyl-*o*-carbomethoxyphenylsulfide was prepared in the following manner. Methyl-*o*-carboxyphenylsulfide (2.5g, 0.014 mole) was dissolved in 4.0 ml concentrated sulfuric acid. To this yellow reaction mixture was added 35.0 ml methanol (27.6g, 0.863 mole). After 15 minutes of reflux, the solution was neutralized with sodium hydrogen carbonate. Upon addition of 50 ml water, a white solid precipitated out of solution. The solid was collected by suction filtration, washed with water, and air dried. Recrystallization from aqueous methanol yielded 2.3g (88%) white crystals, mp 69.0-69.5 (lit.[18] 66-67).

***o*- thiomethylbenzamide** was prepared according to a method suggested by Shriner, Fuson, and Curtin.[21] Methyl-*o*- carboxyphenyl sulfide (19.1g, 0.114 mole) was added to 95.5 ml (1.33moles) thionyl chloride, and the reaction mixture was refluxed for 30 minutes. This dark brown solution was added dropwise to 290 ml (4.35 mole) of cold concentrated ammonium hydroxide. Dense white fumes were evolved, and a cream-colored solid was formed. The precipitate was collected by suction filtration and recrystallized from a 50:50 water-ethanol solution. 11.7g (61.3%) white crystals were isolated, mp 151.5-152.0.

_o_-thiomethylbenzonitrile was prepared by dehydration of *o*-thiomethylbenzamide. *o*-thiomethylbenzamide (12.1g, 0.0724 mole) and phosphorus pentoxide (6.9g, 0.048 mole) were placed in a 500 ml round-bottom flask and mixed well by shaking. The mixture was heated with a Fisher Burner and was distilled at reduced pressure (aspirator). The product, a colorless liquid, solidified on contact with the ice-cooled collection flask. The crude product was vacuum distilled to yield 5.9g product (55%), bp $149-152^{\circ}/4.1$mm, mp $37.5-39.0^{\circ}$ (lit.[18] mp 40-41).

An attempt to prepare **_o_-nitrothiophenol** according to the method of Tarbell and Fukushima was unsuccessful. Upon acidification of the reaction mixture with concentrated sulfuric acid, a tar was formed, and the distillation with steam yielded no product.

The reaction of sodium sulfide with *o*-chloronitrobenzene according to the procedure of Foster and Reid[10] was carried out in an attempt to synthesize **_o,o_'-dinitrodiphenydisulfide**, which was to be used in the preparation of *o*-nitrophenylsulfide. A mixture of 75.2g (0.313 mole) $Na_2S \cdot 9H_2O$ and 150 ml ethanol was refluxed for 3.5 hours. After this period of reflux some sodium sulfide still remained at the bottom of the reaction flask. Water (40 ml) was added to induce solution of the sodium sulfide. At this point there were two layers present in the reaction flask: a light yellow upper layer and a darker yellow-brown lower layer. Both layers were filtered free of precipitated iron sulfides, and 4.8g (0.019 mole) of finely ground sulfur was added to the combined layers. After a short time the sulfur dissolved. The solution was red-brown in color, the lower layer being darker than the upper. This solution was added to a boiling solution of 32.1g (0.204 mole) *o*-chloronitrobenzene in 50 ml of ethanol by means of a dropping funnel. The resulting red solution was refluxed for seven hours. When the light yellow precipitate of disulfide which was supposed to appear at this time was not observed, various unsuccessful attempts to isolate the product by extraction were made.

Methyl-*o*-N,N-dimethylaminophenylsulfide was obtained from the reaction of methyl-*o*-aminophenylsulfide with trimethyl phosphate. Methyl-*o*-aminophenylsulfide (16.2g, 0.116 mole) and 16.2g (0.116 mole) trimethyl phosphate were place in a 1-liter flask equipped with a water-cooled condenser. The reaction mixture was heated gently with a Bunsen burner until the exothermic reaction commenced. The reaction was allowed to proceed without additional heating until boiling ceased. At this time, heat was again applied for a period of 2.75 hours. The solution was then hydrolyzed with 19g NaOH in 150 ml water with vigorous magnetic stirring over a period of 1.5 hours. After the addition of 200 ml water, the amine was extracted into two 75 ml portions of ether. The extracts were combined and dried over NaOH in the refrigerator. The ether was removed by distillation at atmospheric pressure, and the orange-brown residual oil was fractionally distilled at reduced pressure (aspirator). 10.8 g (55.6%) of a clear, colorless product were obtained, bp 190-199°/Aspirator (lit.[19] 130/20mm). Analysis by nmr spectroscopy indicated the presence of approximately 10% impurity.

IV. SPECTROSCOPIC DATA

The nmr spectra were recorded by Mr. Richard Howell of Franklin and Marshall College using a Varian A-60D NMR Spectrometer. Carbon tetracholride was used as the solvent for all compounds, and the internal standard was tetramethylsilane. All spectra were recorded at a solution concentration of 30% (vol:vol or wt:vol) and a probe temperature of $38 \pm 2^{0}C$. The reported carbon 13-proton coupling constants and S-methyl chemical shifts are the averages of several traces and are believed to be accurate to ± 0.2 Hz and ± 0.3 Hz, respectively. See Table II.

IV. RESULTS

An attempt was made to correlate these spectral data with the ortho sigma constants recently reported in the literature by Traynham and Tribble,[12] who obtained their set of ortho sigma constants from the measurement of hydroxyl chemical shifts of ortho substituted phenols in dimethylsulfoxide solution. Table III. The strong intermolecular hydrogen bond between the phenolic OH and DMSO is believed to be oriented away from the ortho substituent, thereby minimizing steric effects.

With both the coupling constant and chemical shift data, correlations were poor. The plot of δ vs. σ_o had a correlation coefficient of 0.661 and a standard error of 4.12. The plot of J vs. σ_o had a correlation coefficient of 0.59 and a standard error of 0.611. Graphs III and IV. These poor correlations add additional weight to Charton's conclusion that no one set of ortho sigma constants can be defined.

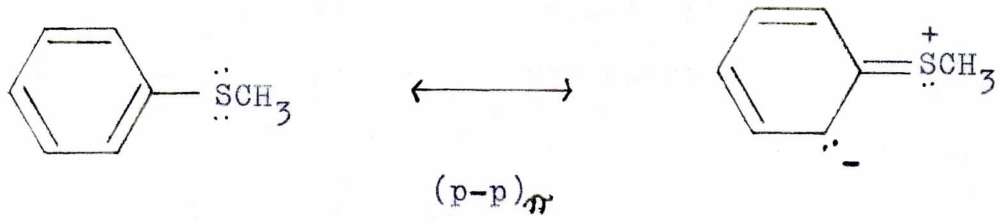
From an equation of the type:

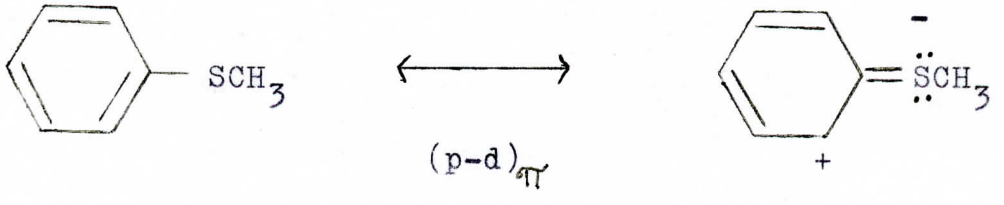
$$J = \rho\sigma + C$$

where J is the coupling constant and ρ and C are the least-square slope and intercept, respectively, of the J vs. σ plot for the appropriate meta and para series, a new set of ortho sigma constants was determined. An additional set of ortho sigma constants, denoted by $\sigma_o^{(*)}$, was determined using the appropriate parameters from the J vs. σ plot of the meta and para isomers, where σ^- was used in place of σ for the nitro group. Table IV.

Using the appropriate parameters from the δ vs. σ plots of the meta and para isomers, two new sets of ortho sigma constants were calculated. Table V. The results in both cases were not consistent with the general trends observed in previously reported ortho sigma constants or in those calculated using coupling constant data.

Taking into consideration the ability of the sulfur atom to undergo $(p-p)_\pi$ and $(p-d)_\pi$ resonance interactions,[13]





the following observations can be made:

(1) The σ_o constants for the CN, F, Cl, and CH_3 groups are considerably greater in magnitude than their σ_p constants. This may be attributed to the greater inductive effect in the ortho position.

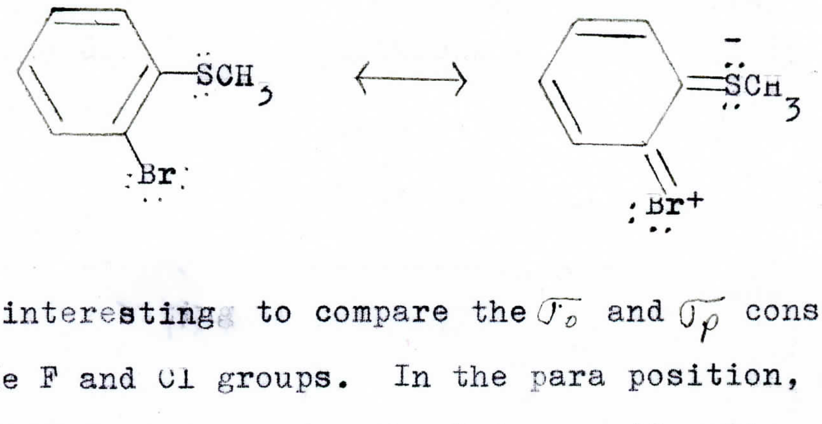
(2) The fact that the σ constant for the OCH_3 group is

considerably less negative than the σ_p constant indicates a greater influence of the electron-withdrawing inductive effect over the electron-releasing resonance effect in the ortho position.

(3) The less negative σ_o constant for the dimethylamino group, as compared to its σ_p constant, seems to indicate some steric inhibition of resonance in the ortho position, thereby reducing electron release by resonance. The increased electron-withdrawing effect of the nitrogen in the ortho position may also be considered to be effective in this case.

(4) The unexpectedly low value obtained for the CO_2CH_3 group may indicate that steric, as well as electrical, effects are involved.

(5) The relatively low σ_o value for the Br group indicated that bromine is a much less effective electron withdrawing group than F or Cl, possibly due to its increased donation of electrons by resonance in the ortho position.



(6) It is interesting to compare the σ_o and σ_p constants for the F and Cl groups. In the para position, the ortho sigma constant for the F is considerably smaller than the ortho sigma constant for the Cl group,

> indicating that the +R resonance effect of F is considerable. But in the ortho position, the sigma constant for F is greater in magnitude than that for the Cl, suggesting that the much greater inductive effect in the ortho position is relatively more important than the resonance effect.

Nmr spectroscopy, especially the measurement of coupling constants, represents an excellent method for investigating substituent effects, because the measurement depends on a transition that does not change the chemical character of the molecule.

TABLE I

σ_o Constants

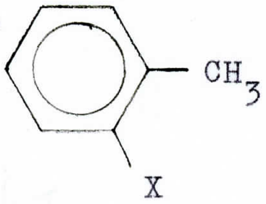
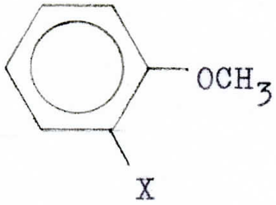
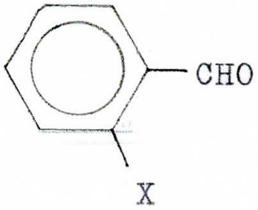
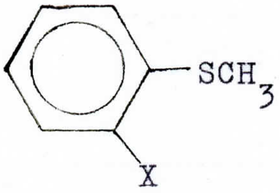
			
X	σ_o	σ_o	σ_o
NO_2	2.0	1.7	2.26
CHO	1.1	1.2	1.10
CO_2H	1.2		
CN	1.2		
F	1.2	0.8	1.04
Cl	1.2	0.8	1.08
Br	1.1	0.9	1.15
I	1.3	0.9	
OH	0.6		0.43
OCH_3	0.6	0.2	0.76
H	-0.06	0.0	0.076
CH_3	-0.12	0.0	-0.063
C_2H_5	-0.17		
NH_2	-0.17	0.2	-0.32
$N(CH_3)_2$	0.3		

TABLE II

S-Methyl Chemical Shifts (δ) and ^{13}C-H Coupling Constants (J)



X	δ (±0.3 Hz)	J (±0.2 Hz)
CN	151.0	140.8
F	142.4	139.9
Cl	140.1	139.8
Br	140.4	139.4
H	145.9	139.2
OCH_3	136.2	139.1
CH_3	137.8	139.0
$N(CH_3)_2$	136.0	138.8
CO_2CH_3	135.7	138.7

Instrument: Varian A-60D NMR Spectrometer

Internal Standard: Tetramethylsilane

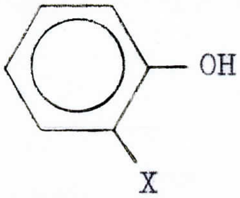
Solvent: Carbon tetrachloride

Solution Concentration: 30% (vol:vol or wt:vol)

Probe Temperature: 38 ± 2°C

TABLE III

σ_o of Traynham and Tribble



X	σ_o
CN	1.18
Br	0.55
Cl	0.50
F	0.29
H	0.00
CH_3	-0.13
$N(CH_3)_2$	-0.36
OCH_3	-0.37

Table IV.

$$J = \rho\sigma + C$$

X	σ_o	$\sigma_o^{(*)}$	σ_p^-	σ_p^+	σ_p
CN	1.085	0.990	1.00		0.628
F	0.386	0.594			0.062
Cl	0.310	0.495			0.227
Br	0.000	0.099			0.232
H	-0.155	-0.099			0.000
OCH_3	-0.233	-0.198			-0.268
CH_3	-0.310	-0.297		-0.78	-0.170
$N(CH_3)_2$	-0.465	-0.495		-1.7	-0.600
CO_2CH_3	-0.543	-0.594			0.39

σ_o values calculated from the equation $J = 1.29\sigma + 139.4$

$\sigma_o^{(*)}$ values calculated from the equation $J = 1.01\sigma + 139.3$

σ_p and σ_p^- values from Jaffe, *Chem. Rev.*, **53**, 191(1953).

σ_p^+ values from Okamoto, Inukai, and Brown, *J. Am. Chem. Soc.*, **80**, 4969(1958); and Brown and Okamoto, *J. Am. Chem. Soc.*, **80**, 4979(1958).

Table V

σ_o Constants

X	σ_o [a]	$\sigma_o^{(*)}$ [b]	σ_o [c]	$\sigma_o^{(*)}$ [d]
CN	1.085	0.990	0.759	1.041
F	0.386	0.594	-0.329	-0.380
Cl	0.310	0.495	-0.619	-0.760
Br	0.000	0.099	-0.582	-0.712
H	-0.155	-0.099	0.114	1.983
OCH_3	-0.233	-0.198	-1.115	-1.405
CH_3	-0.310	-0.297	-0.910	-1.140
$N(CH_3)_2$	-0.465	-0.495	-1.138	-1.438
CO_2CH_3	-0.543	-0.594	-1.176	-1.488

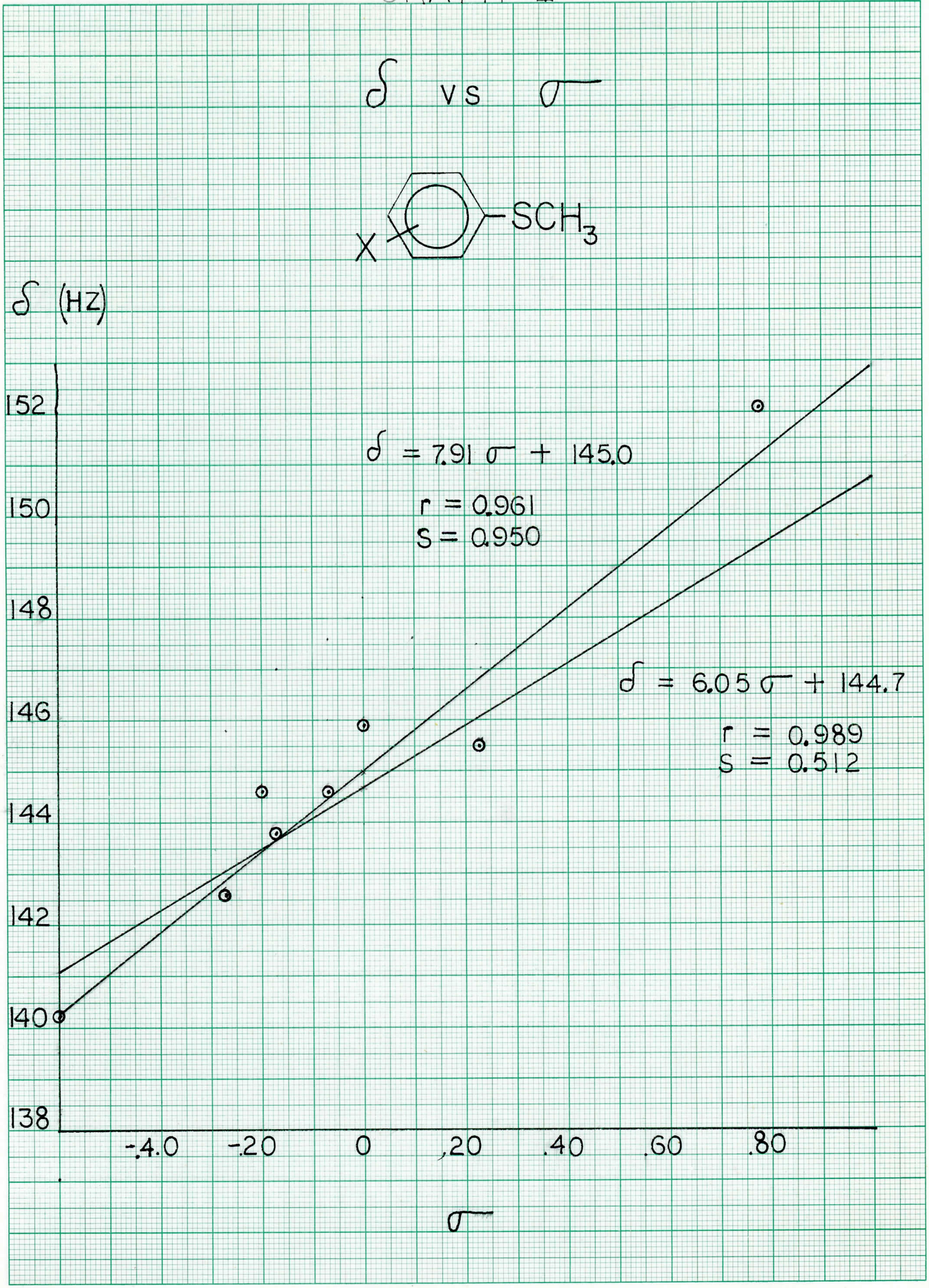
[a] From the equation $J = 1.29\sigma + 139.4$

[b] From the equation $J = 1.01\sigma + 139.3$

[c] From the equation $\delta = 7.91\sigma + 145.0$

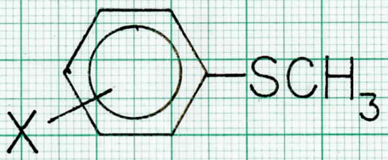
[d] From the equation $\delta = 6.05\sigma + 144.7$

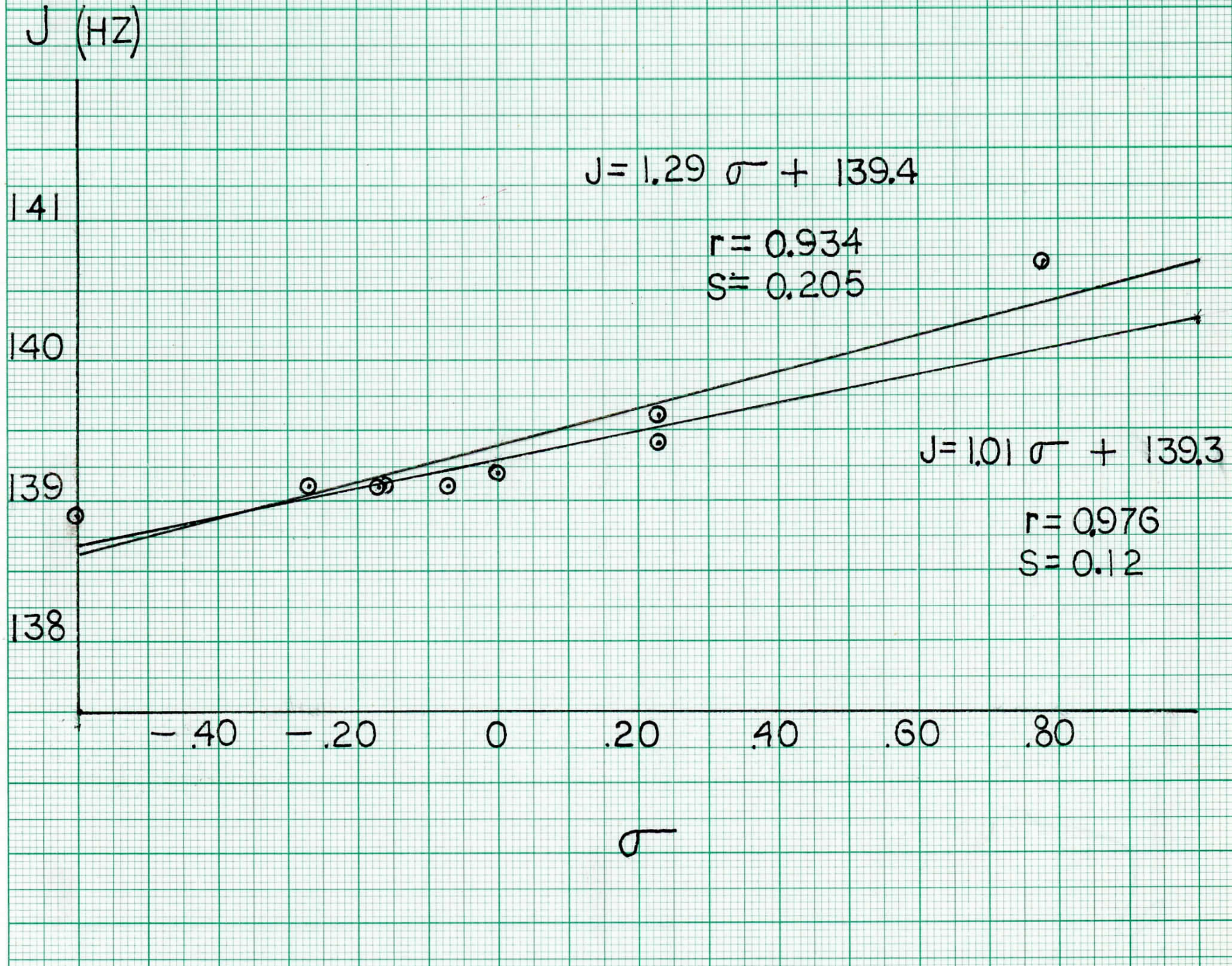
GRAPH I


δ vs σ
X
SCH3
δ (HZ)
152
150
148
146
144
142
140
138
δ = 7.91 σ + 145.0
r = 0.961
S = 0.950
δ = 6.05 σ + 144.7
r = 0.989
S = 0.512
-4.0
-.20
0
,20
.40
.60
.80
σ

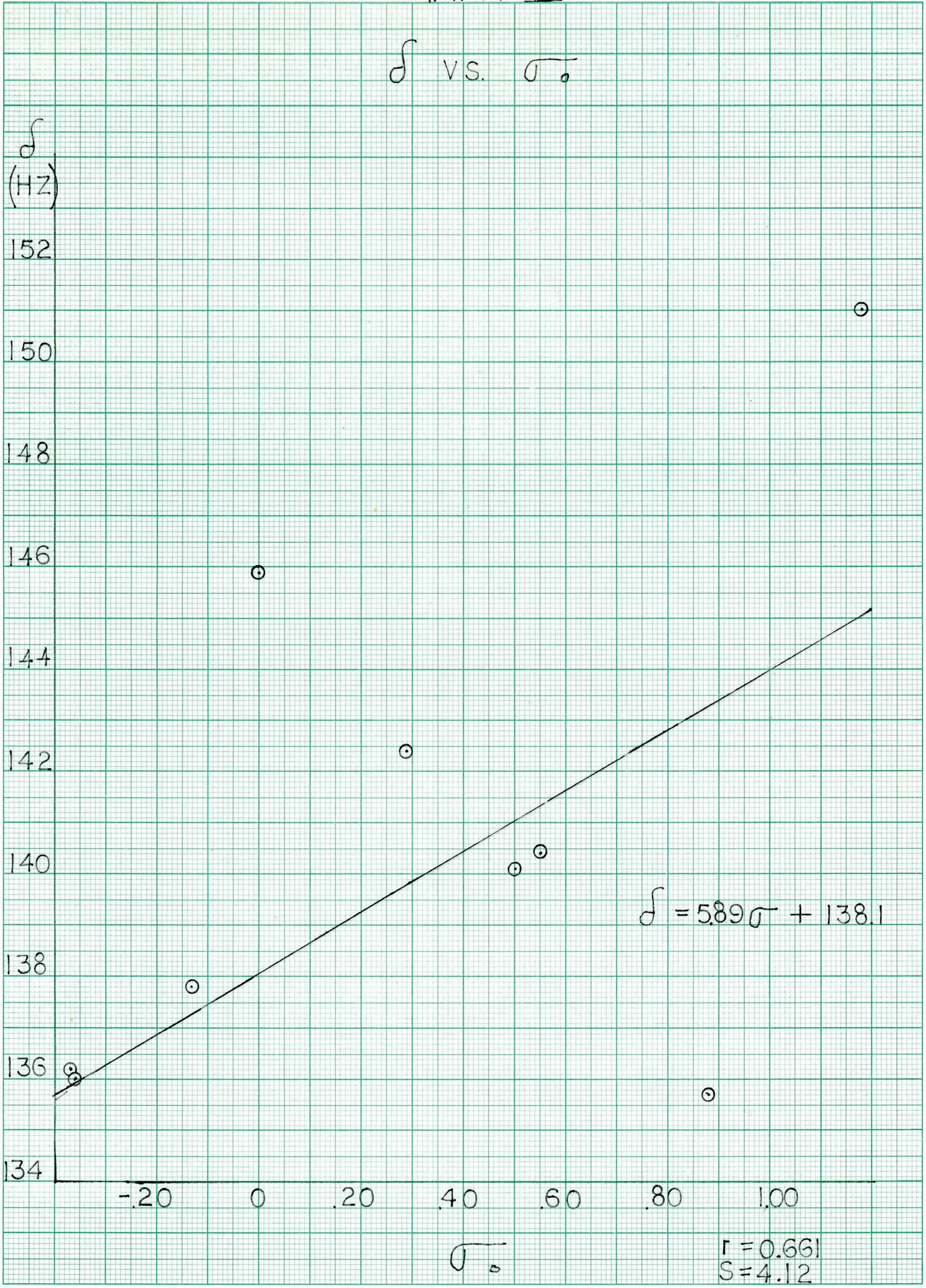
GRAPH II

J vs σ

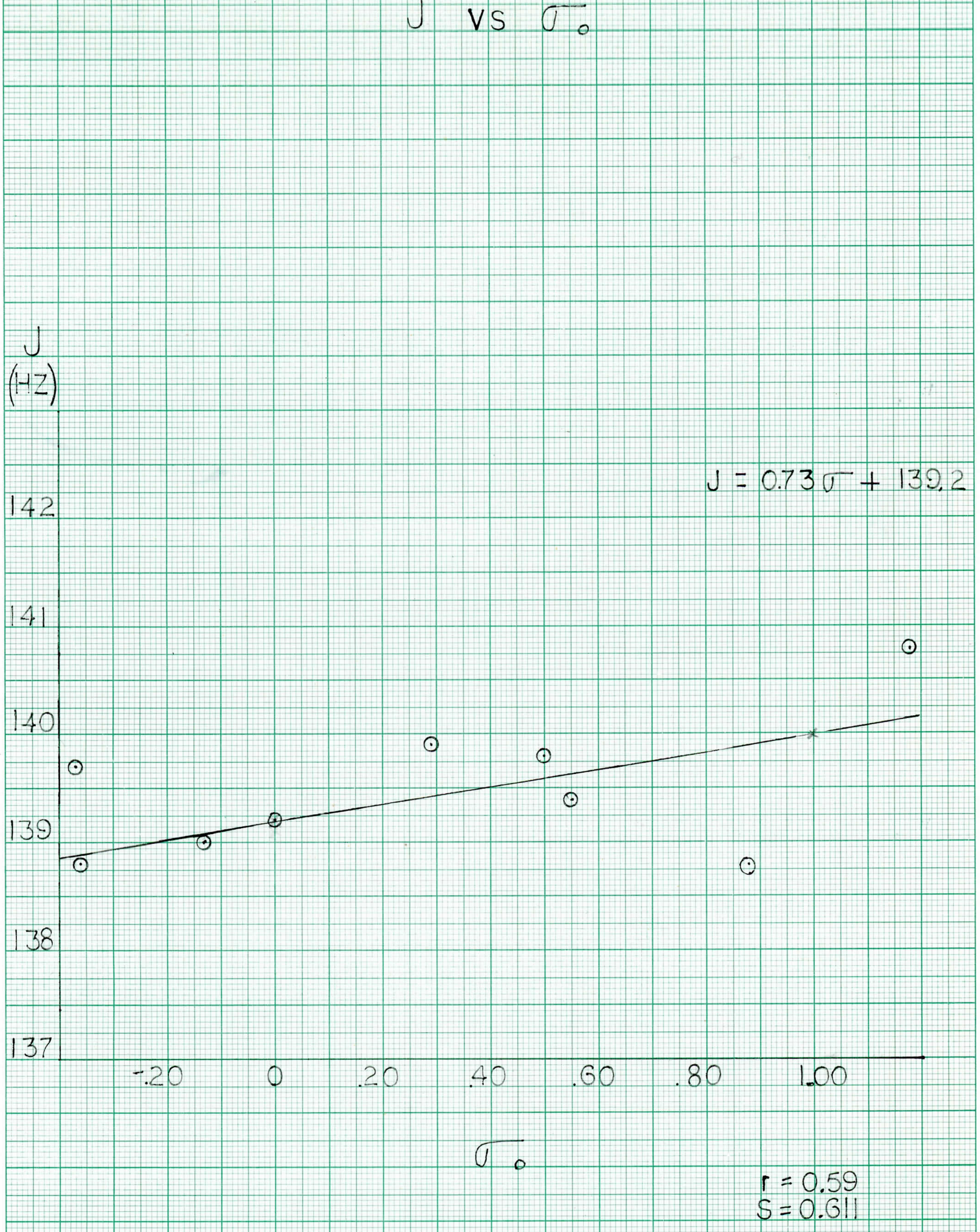




GRAPH III


δ VS. σ₀
δ (HZ)
152
150
148
146
144
142
140
138
136
134
-.20
0
.20
.40
.60
.80
1.00
σ₀
δ = 5.89 σ + 138.1
r = 0.661
S = 4.12

GRAPH IV


J vs σ₀
J (HZ)
142
141
140
139
138
137
-.20
0
.20
.40
.60
.80
1.00
σ₀
J = 0.73σ + 139.2
r = 0.59
S = 0.611

VII. ACKNOWLEDGEMENTS

The author gratefully acknowledges the financial support for this project given by Research Corporation. The author also wishes to thank Dr. Claude Yoder and Mr. Richard Howell of Franklin and Marshall College for providing the nmr data.

Above all, it was through the generous help and encouragement of Dr. Ronald E. Hess and the other members of the Chemistry Department that this paper was made possible. Sincere appreciation is extended to each of them.

VIII. REFERENCES

1. For example, see Yoder, Tuck, and Hess, *J. Am. Chem. Soc.*, **91**, 539(1969); Hess, Haas, Kaduk, Schaeffer, and Yoder, *Inorganica Chimica Acta*, **5**, 161(1971); Tribble and Traynham, *J. Am. Chem. Soc.*, **91**, 379(1969).

2. Yoder, Tuck, and Hess, *J. Am. Chem. Soc.*,**91**, 539(1969).

3. Bent, *Chem. Rev.*, **61**, 275(1961).

4. Hess, Haas, Kaduk, Schaeffer, and Yoder, *Inorganica Chimica Acta*, **5**, 161(1971).

5. Charton, *J. Am. Chem. Soc.*, **91**, 6649(1969).

6. Taft, *J. Phys. Chem.*, **64**, 1805(1960).

7. Hess, Schaeffer, and Yoder, *J. Org. Chem.*, **36**, 2201(1971).

8. Tarbell and Fukushima, *Org. Syn., Col. Vol. 3*, 809.

9. Leuckart, *J. prakt. Chem.*, **41**, 189(1890).

10. Foster and Reid, *J. Am. Chem. Soc.*, **46**, 1936(1924).

11. Wohlfahrt, *J. prakt. Chem.*, **66**, 551(1902).

12. Traynham and Tribble, *J. Am. Chem. Soc.*, **91**, 379(1969).

13. Price and Oae, *Sulfur Bonding* (New York: The Ronald Press Company, 1962), p. 8.

14. Jaffe, *Chem. Rev.*, **53**, 191(1953).

15. Okamoto, Inukai, and Brown, *J.Am. Chem. Soc.*, **80**, 4969 (1958).

16. Brown and Okamoto, *J. Am. Chem. Soc.*, **80**, 4979(1958).

17. *Chemical Abstracts*, 55, 9322(1961).

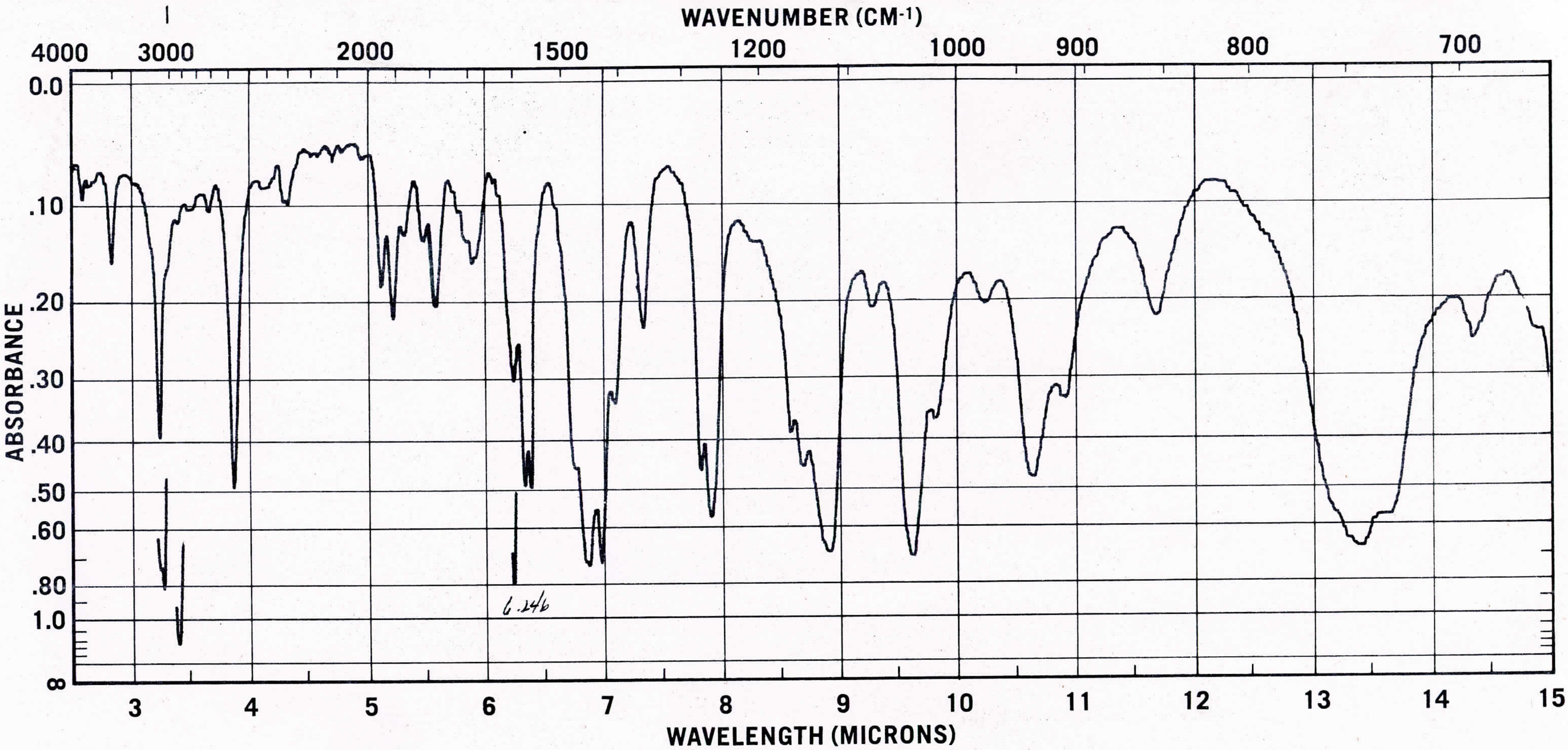
18. Heilbron, *Dictionary of Organic Compounds* (New York: Oxford University Press,1965), Vol. 4, p. 2239.

19. *Ibid.*, Vol. 1, p. 86.

20. *Ibid.*, Vol. 1, p. 420.

21. Shriner, Fuson, and Curtin, *The Systematic Identification*

of Organic Compounds (New York: J. Wiley and Sons, Inc., 1964), p.235.



NUMBER 6

NOTES Neat

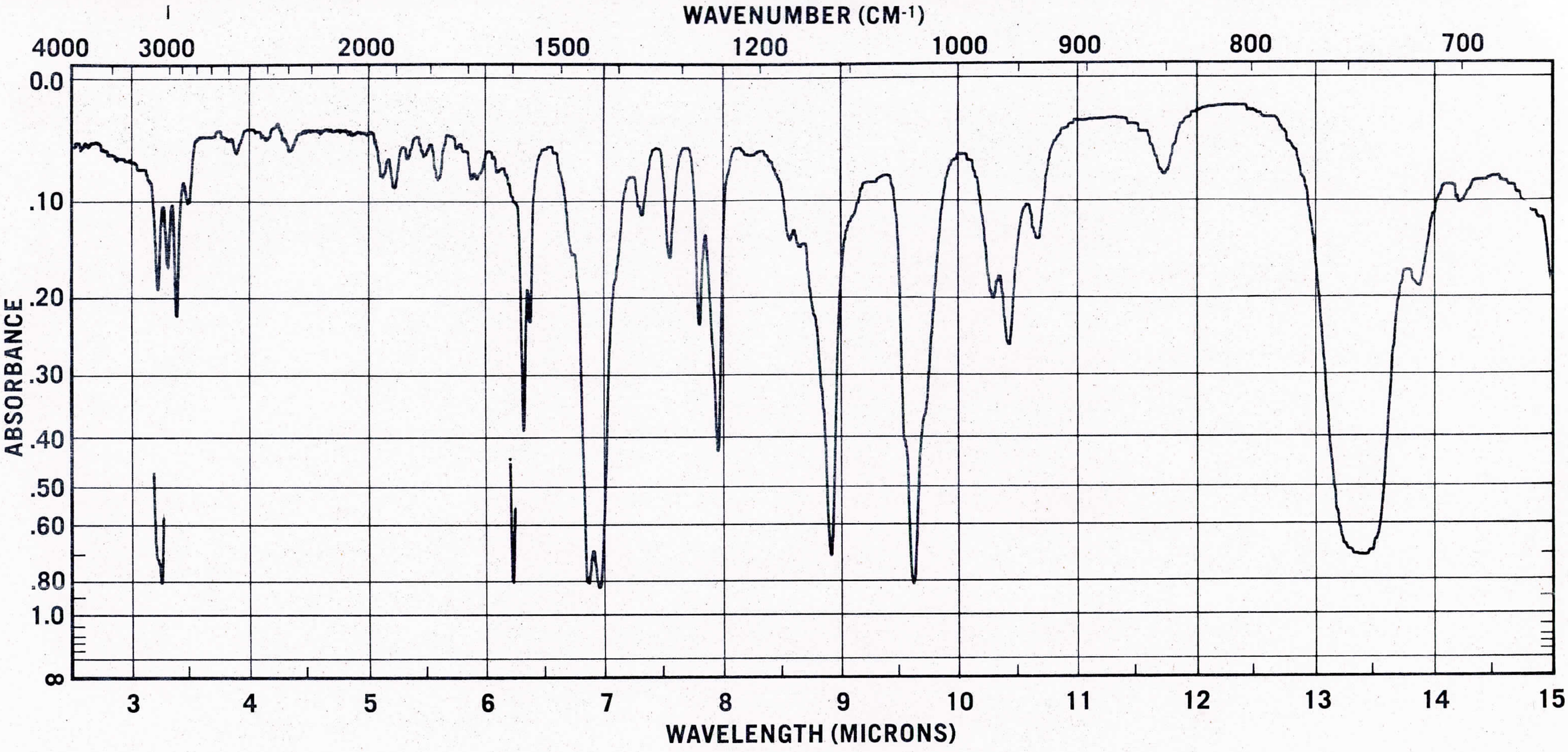
DATE 21 Je 1972 PATHLENGTH

SAMPLE o-Chlorothiophenol fraction 2

ANALYST

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

999•0013



NUMBER 10

NOTES Neat

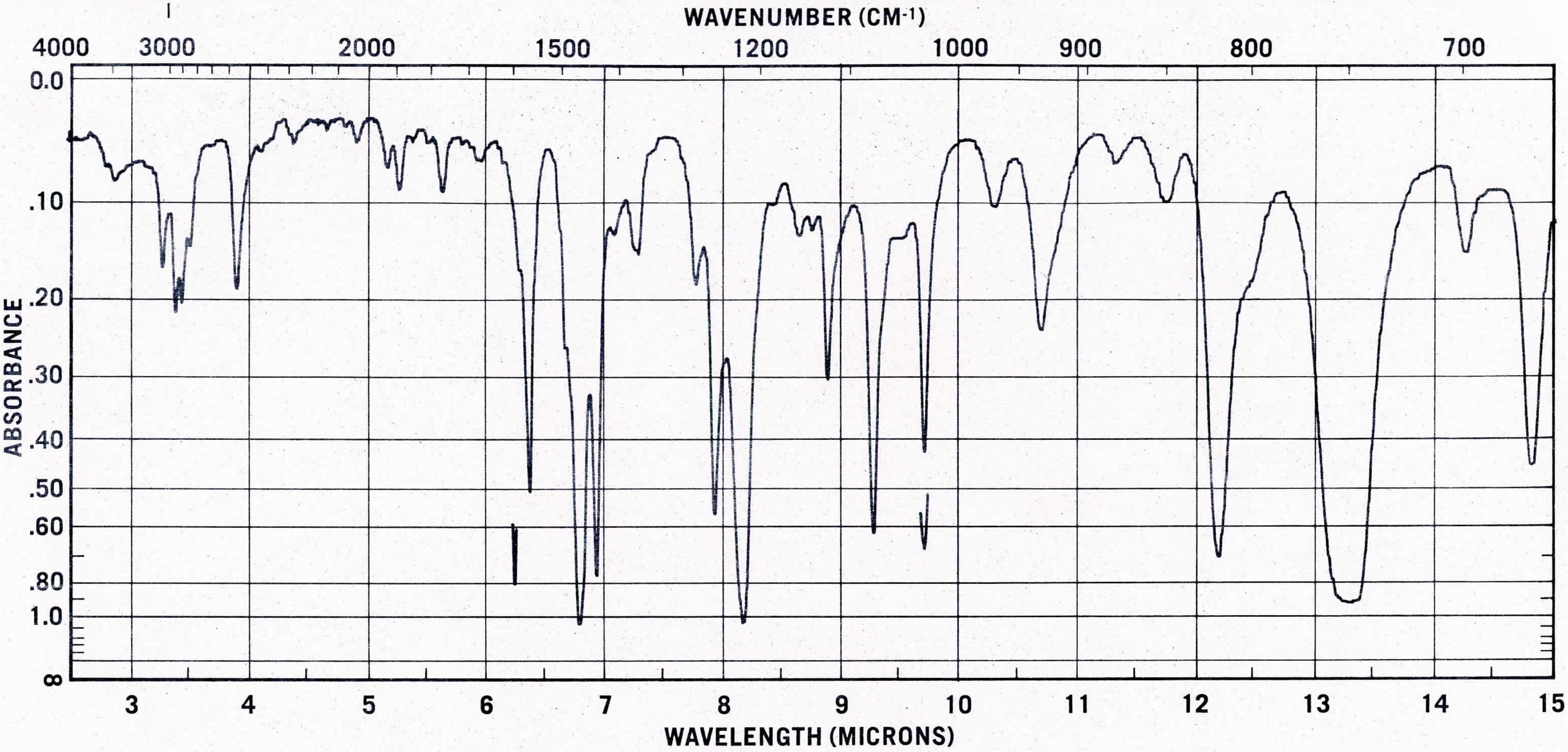
DATE 5 Ju 1972 PATHLENGTH

SAMPLE methyl-o-chlorophenylsulfide fraction 2

ANALYST

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

999•0013



NUMBER 17

NOTES Neat

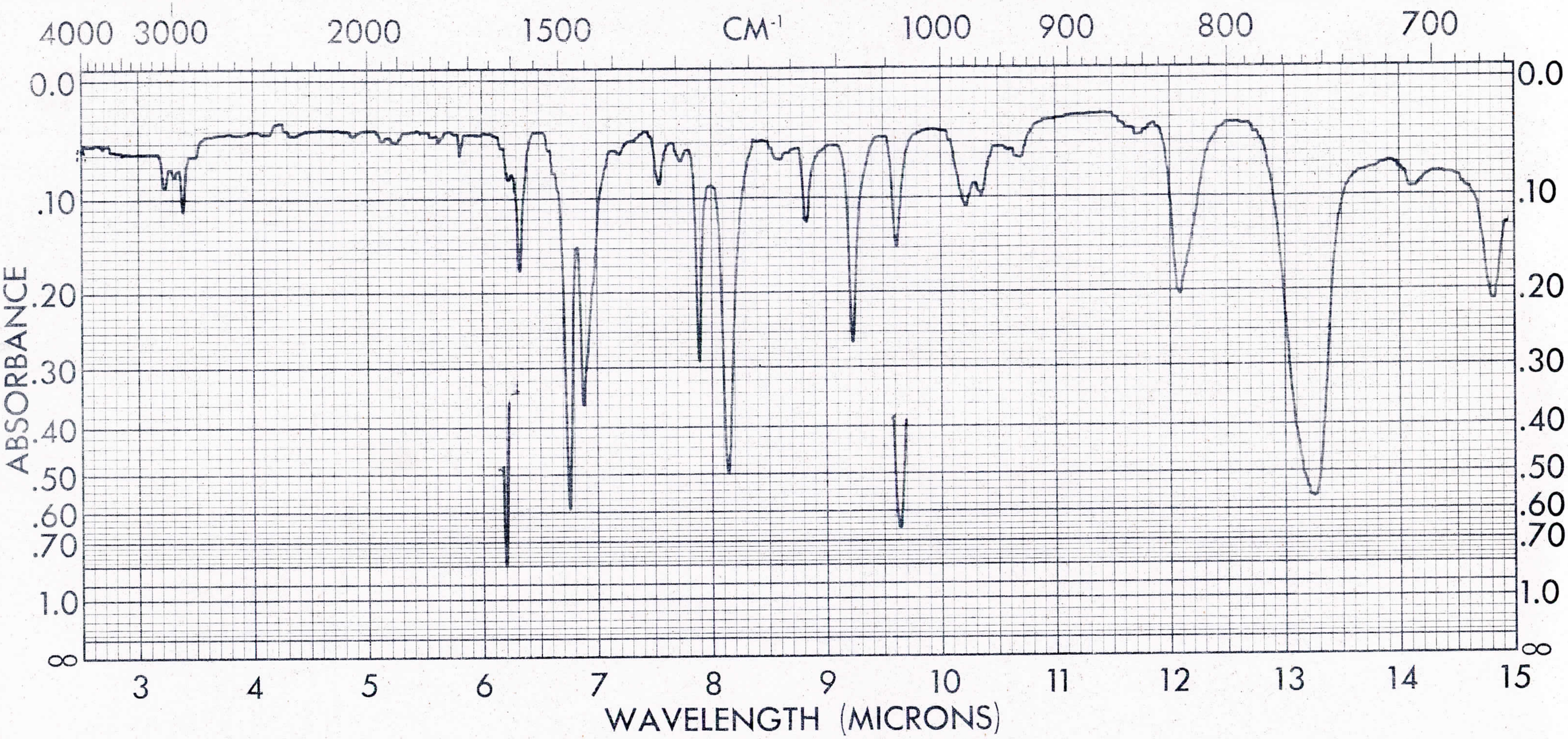
DATE 11 Ju 1972 PATHLENGTH

SAMPLE o-fluorobenzenethiol

ANALYST

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

999•0013



SPECTRUM NO. 31

SAMPLE

methyl o-fluorophenyl sulfide II

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2. 2+ ⊣

DATE 21 July 1972

OPERATOR

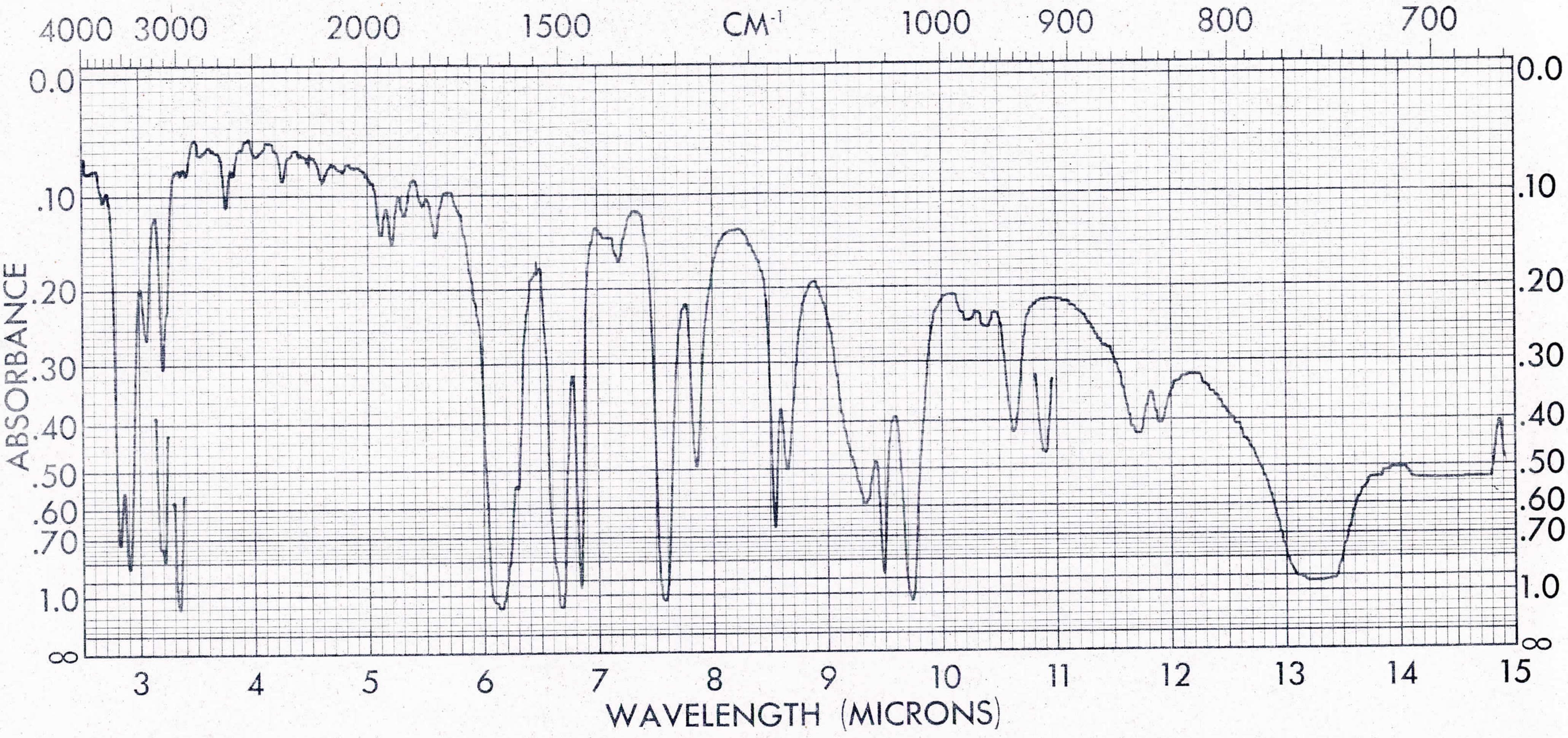
REMARKS Neat

SPECTRUM NO.

SAMPLE

PART NO. 137-1280 PE®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 43

SAMPLE

o-bromoaniline (Aldrich)

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

DATE 1 Aug 1972

OPERATOR

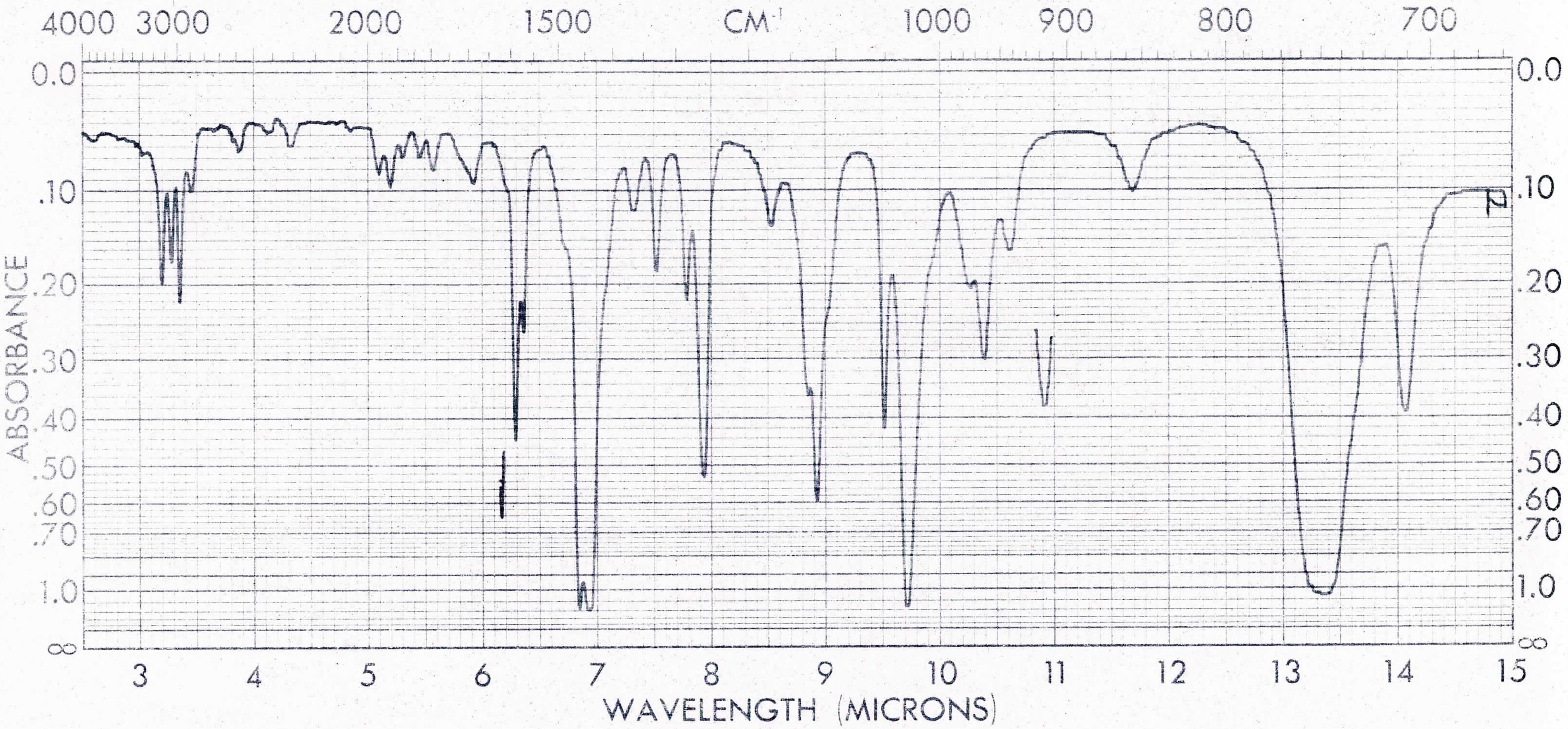
REMARKS Neat

SPECTRUM NO.

SAMPLE

PART NO.137-1280

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 65

SAMPLE

methyl-o-bromo phenyl sulfide

III

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

DATE 11 December 1992

OPERATOR

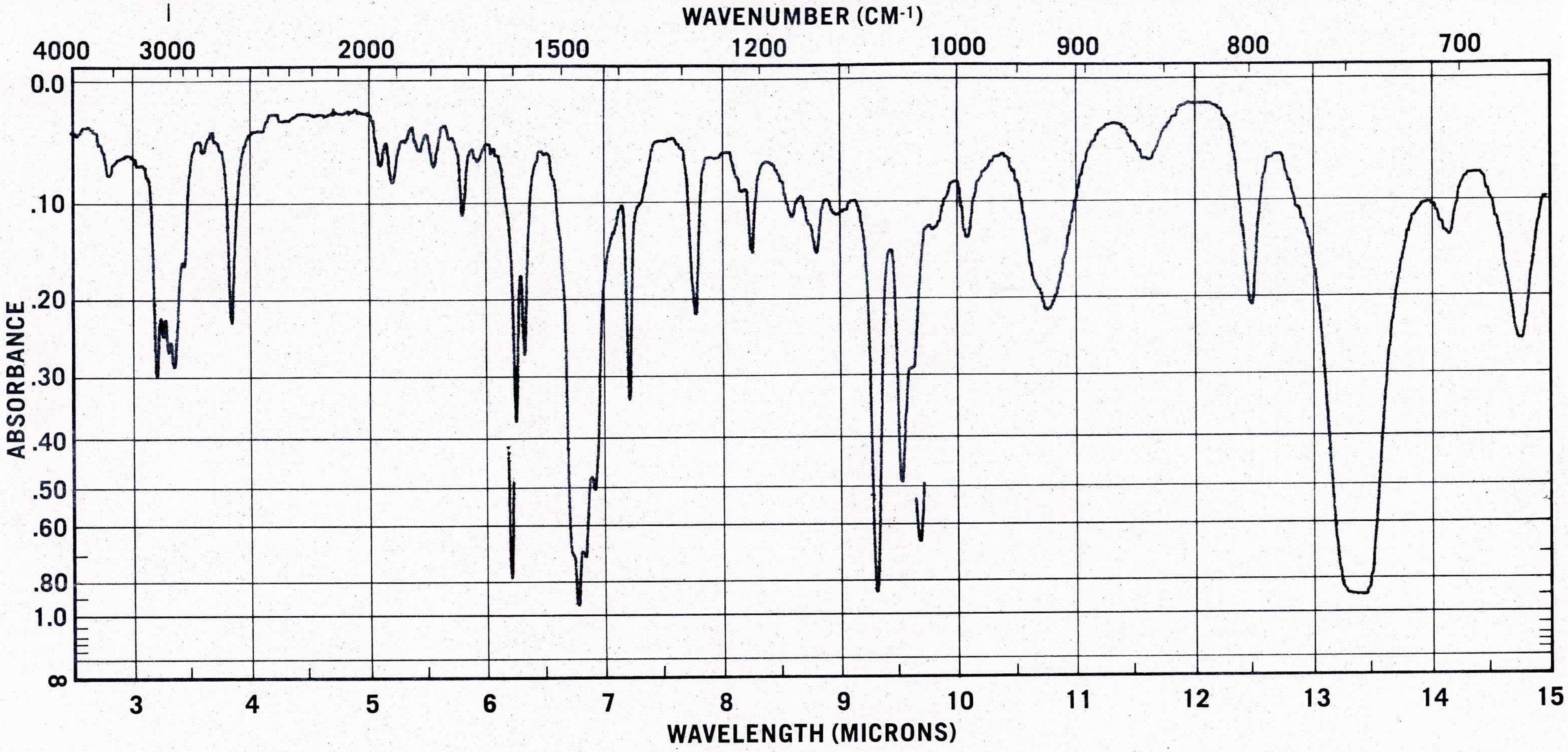
REMARKS Neat

SPECTRUM NO.

SAMPLE

PART NO.137-1280

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



NUMBER 1

NOTES Neat

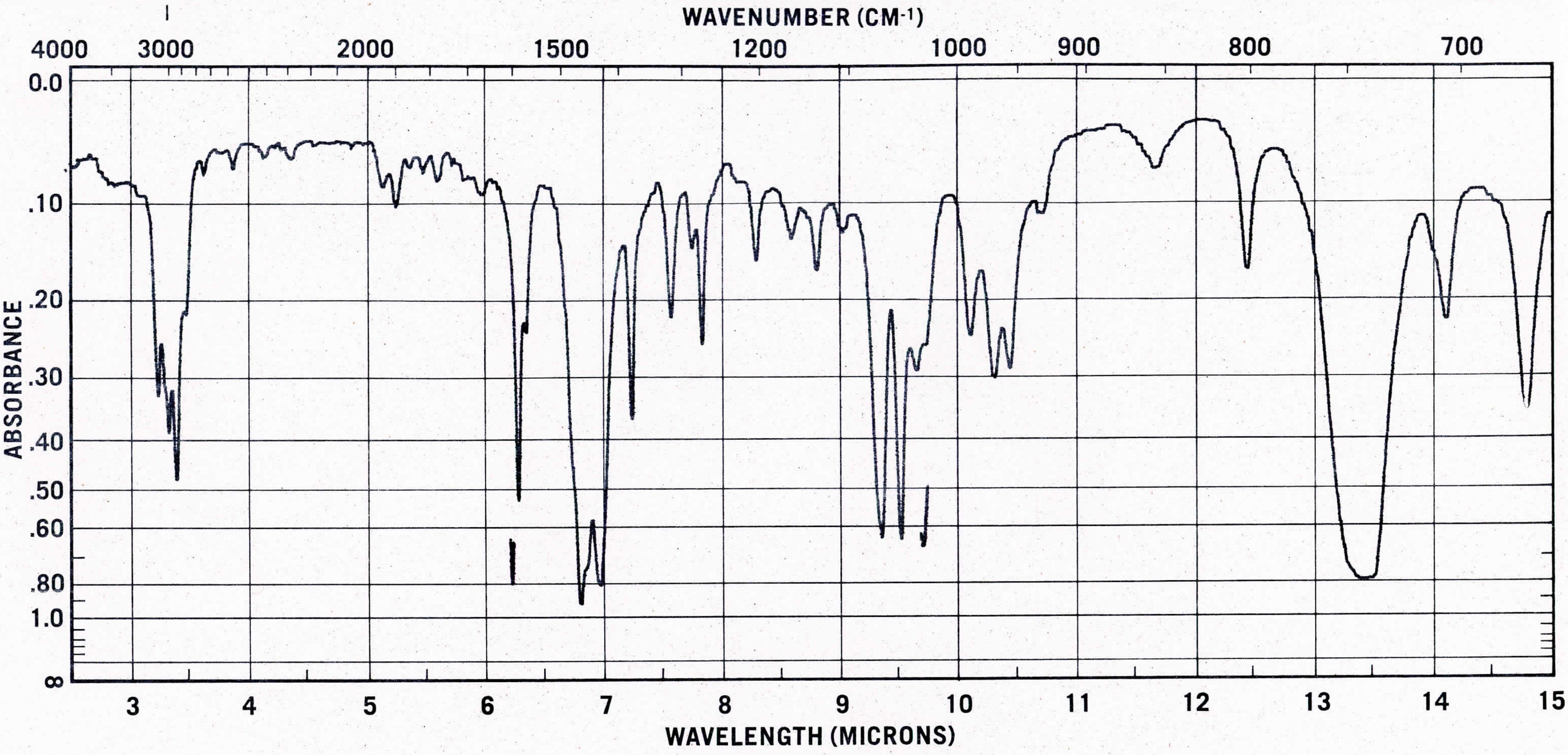
DATE 23 Je 1972 PATHLENGTH

SAMPLE o-toluenethiol (Eastman)

ANALYST

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

999•0013



NUMBER 3

NOTES Neat

DATE 23 Je 1972

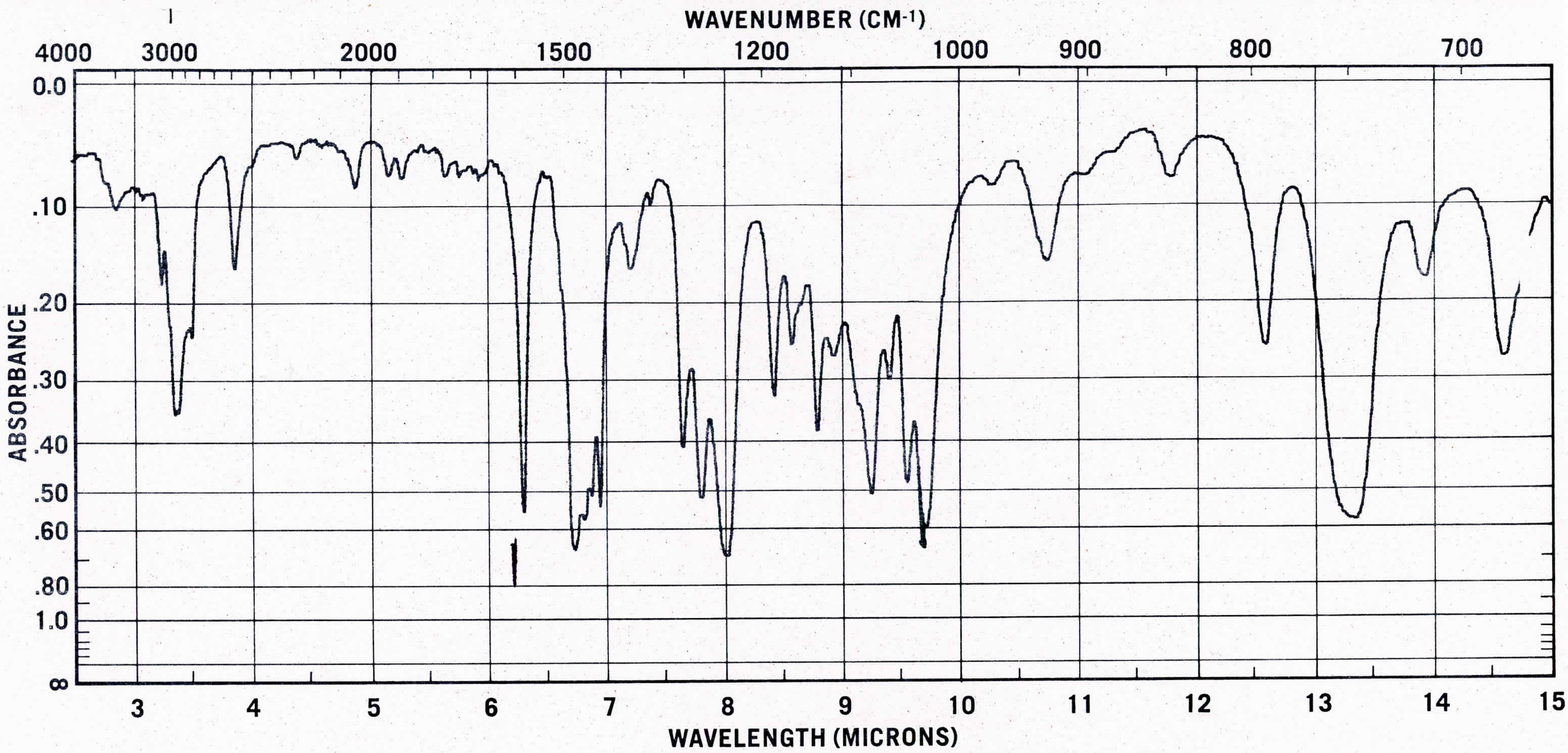
PATHLENGTH

SAMPLE o-tolyl methyl sulfide fraction 2

ANALYST

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

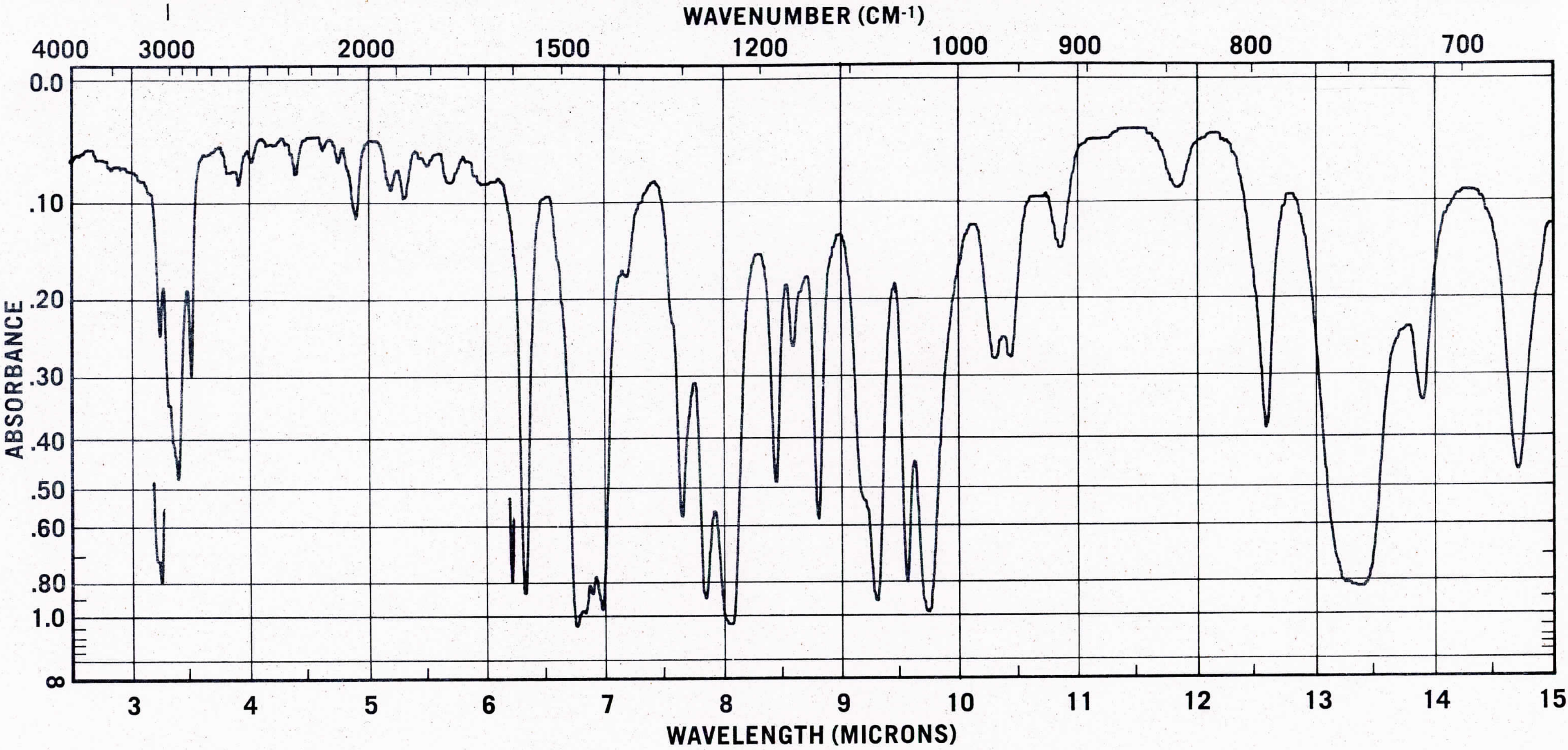
999•0013



NUMBER 11	NOTES Neat
DATE 29 Je 1972 PATHLENGTH	
SAMPLE o-methoxy thiophenol	
ANALYST	

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

999•0013



NUMBER 15

NOTES Neat

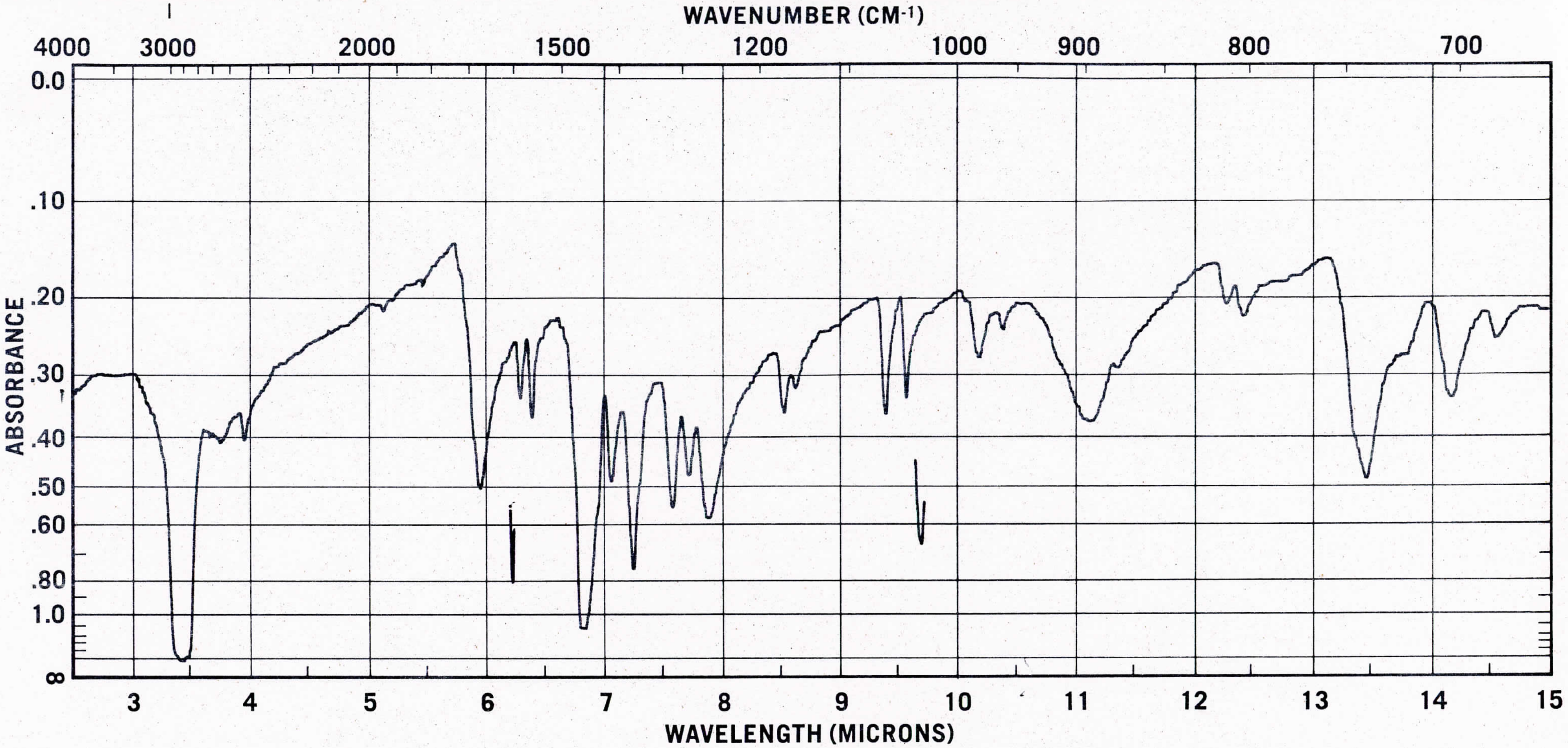
DATE 6 Ju 1972 PATHLENGTH

SAMPLE methyl-o-methoxyphenyl sulfide fraction 2

ANALYST

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

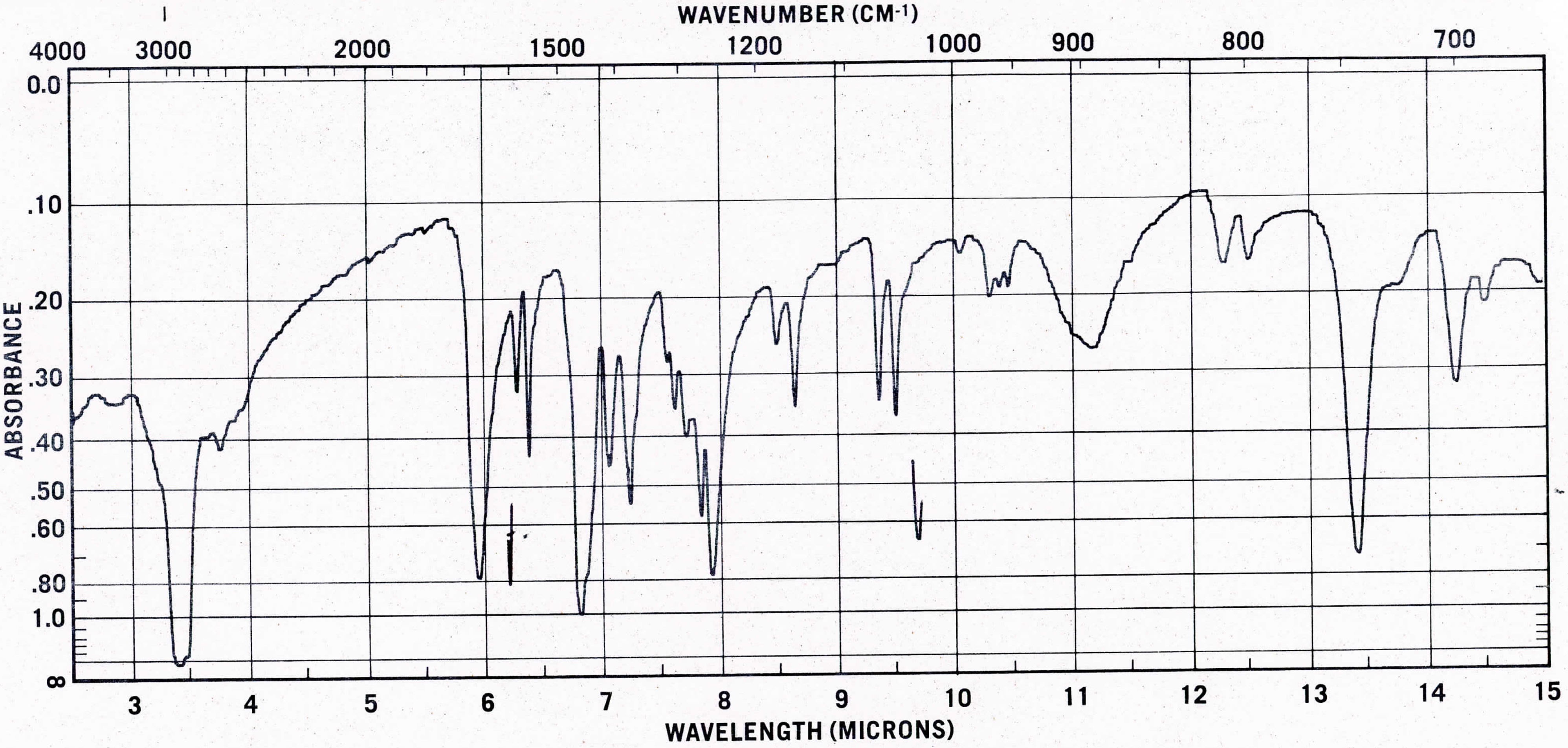
999•0013



NUMBER	16
DATE	10 Jn 72
PATHLENGTH	
SAMPLE	o-mercaptobenzoic acid (Aldrich)
ANALYST	
NOTES	Nujol mull

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

999•0013



NUMBER 18

NOTES Nujol mull

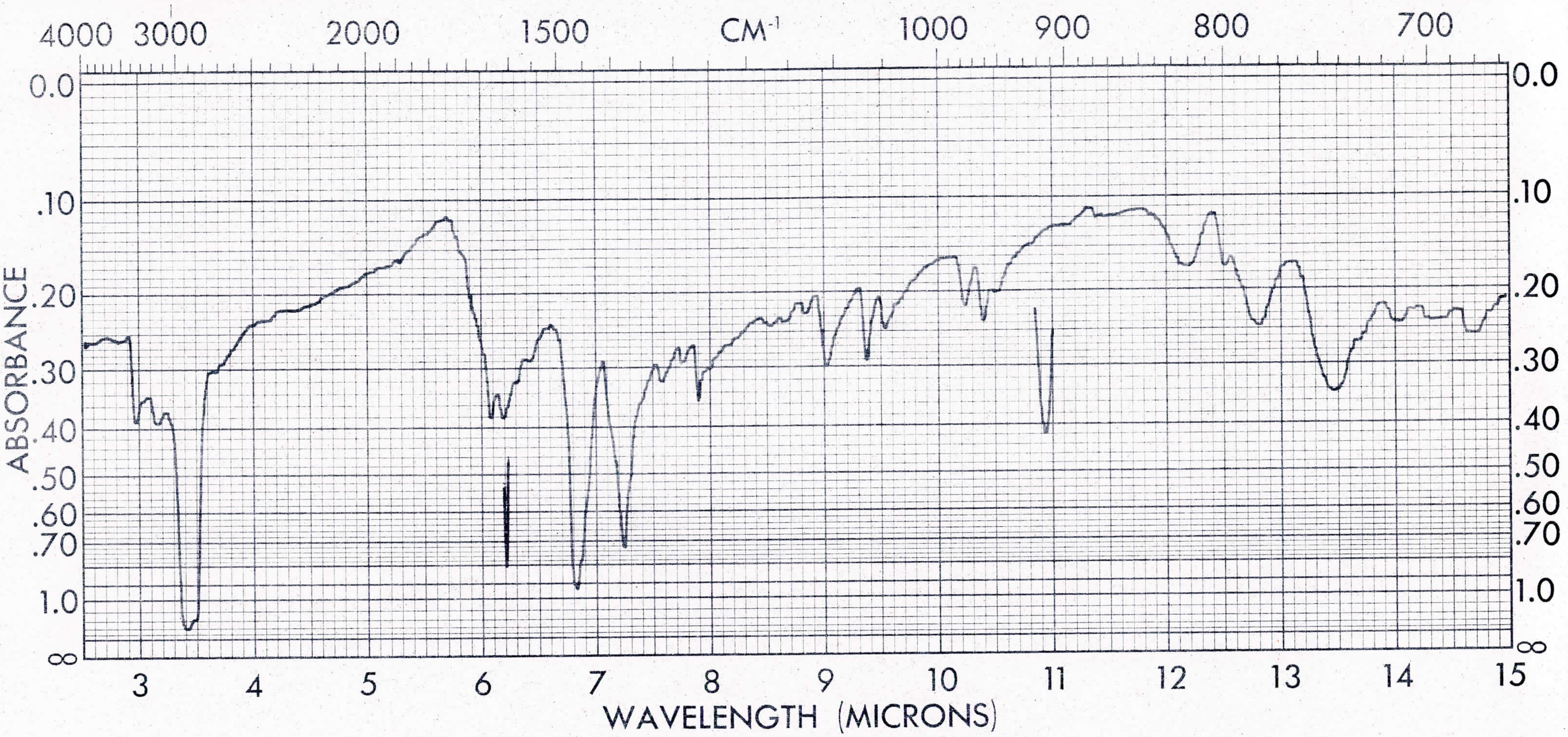
DATE 11 Ju 1972 PATHLENGTH

SAMPLE methyl-o-carboxyphenyl sulfide

ANALYST

BARNES ENGINEERING COMPANY • INSTRUMENT DIVISION • STAMFORD, CONNECTICUT

999•0013



SPECTRUM NO. 29

SAMPLE

(Amide)

o-thiomethylbenzamide

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

DATE 19 July 1972

OPERATOR

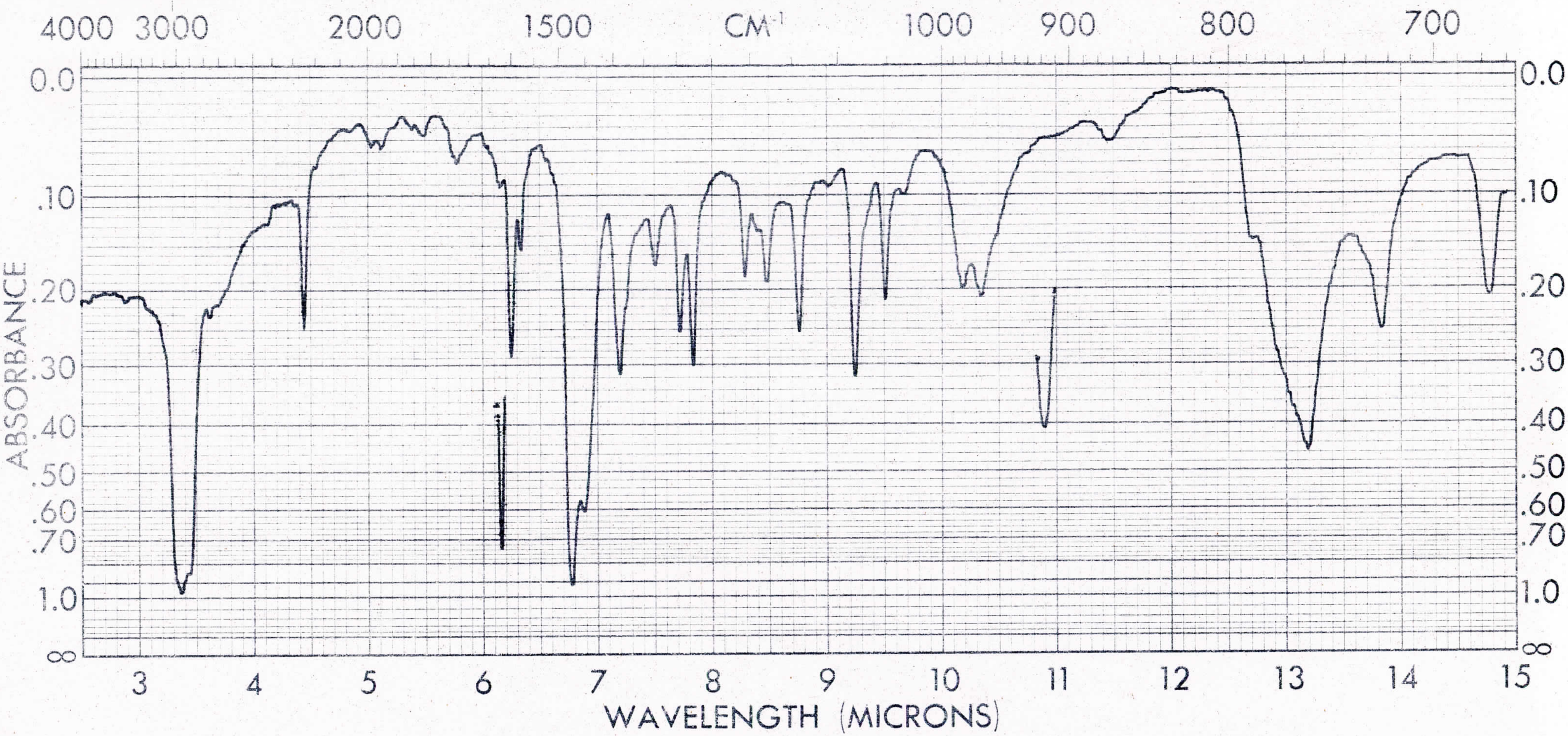
REMARKS Nujol Mull

SPECTRUM NO.

SAMPLE

PART NO. 137-1280

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 52

SAMPLE

Nitrile

o-thiomethylbenzonitrile

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

DATE 15 Aug 1972

OPERATOR

REMARKS

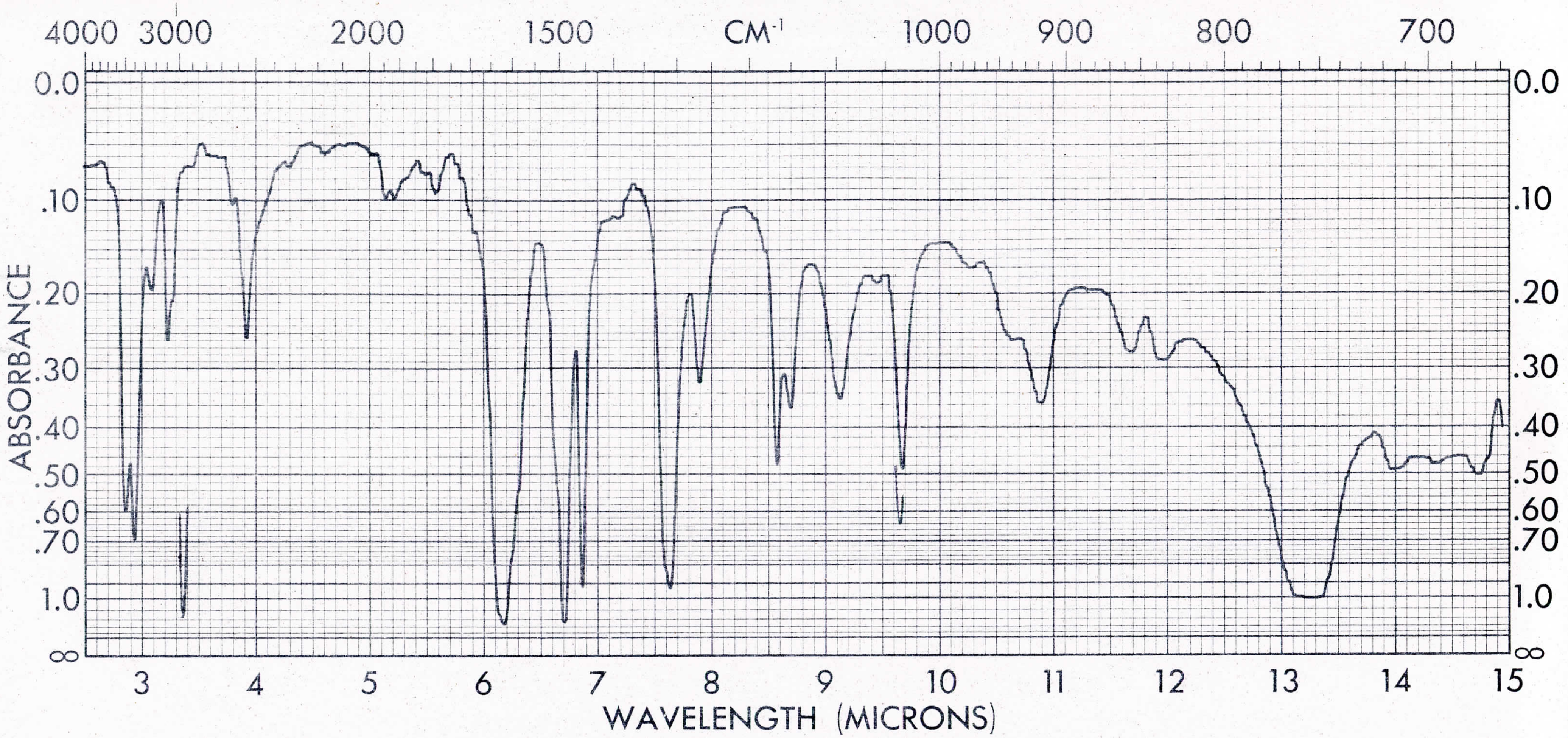
Nujol Mull

SPECTRUM NO.

SAMPLE

PART NO.137-1280

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



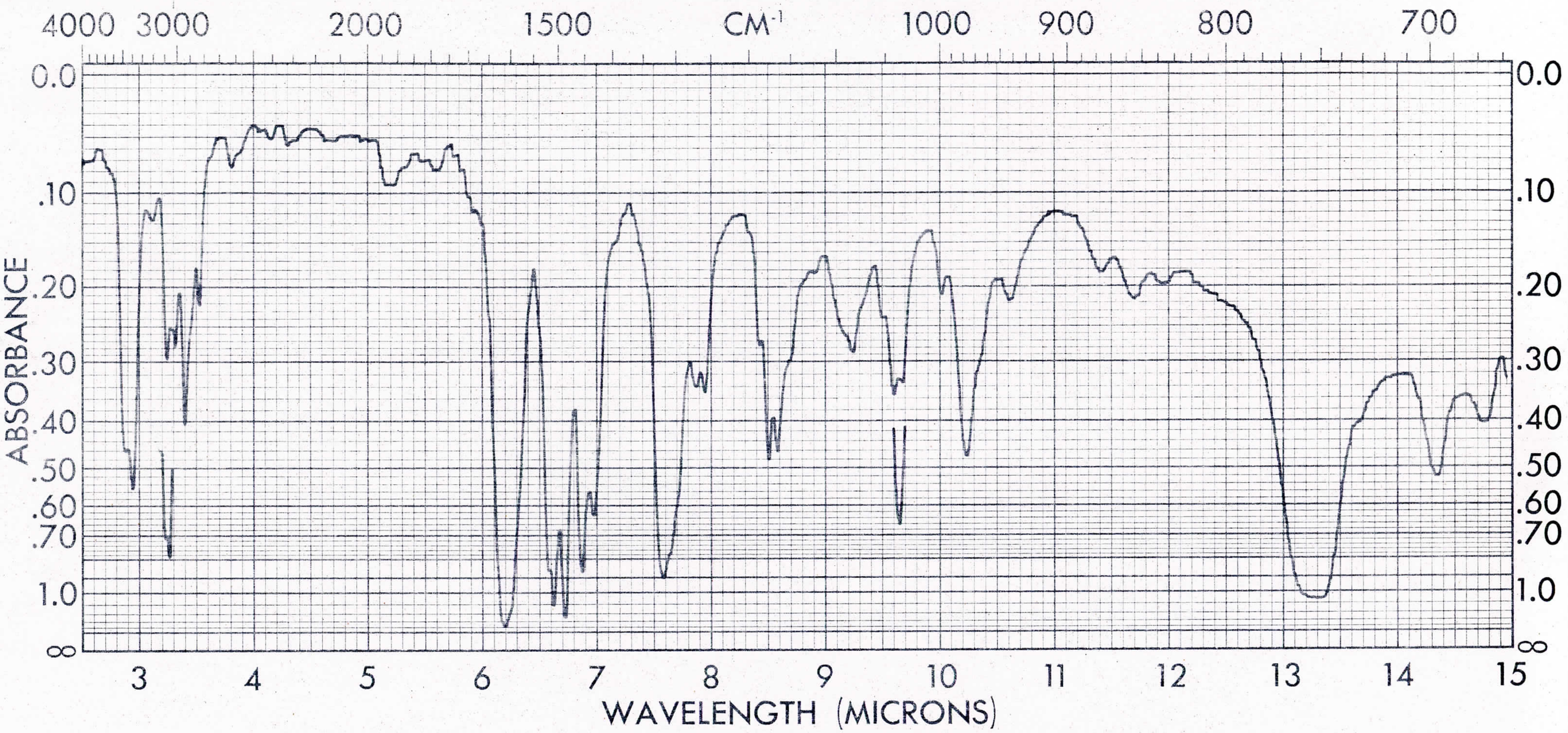
SPECTRUM NO. 26	ORIGIN Eastman	LEGEND	REMARKS Neat
SAMPLE		1.	
o-aminobenzenethiol	PURITY	2.	
	PHASE	DATE 1-18-72	
	THICKNESS	OPERATOR	

SPECTRUM NO.

SAMPLE

PART NO.137-1280 ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 32

SAMPLE

Methyl-o-aminophenyl sulfide I

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

DATE 21 July 1972

OPERATOR

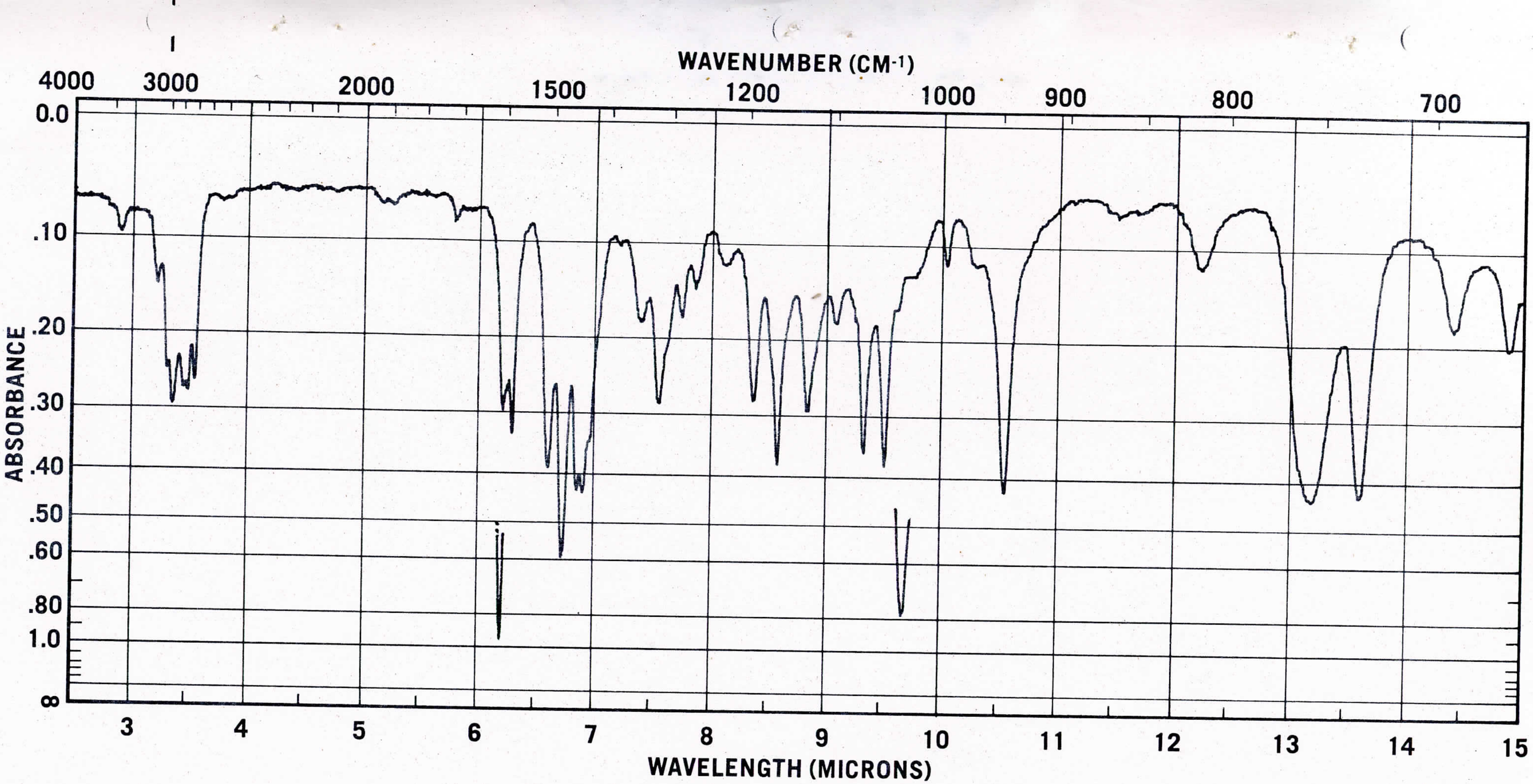
REMARKS Neat

SPECTRUM NO.

SAMPLE

PART NO. 137-1280 PE®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

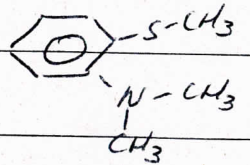


NUMBER 67

NOTES Neat

DATE 11 Jan 1973 PATHLENGTH

SAMPLE



Fraction I

ANALYST

BARNES ENGINEERING COMPANY • 30 COMMERCE ROAD • STAMFORD, CONNECTICUT 06902

0022-004