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The Synthesis and Reactions of Isatoic p-linear bis Anhydride

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The Synthesis and Reactions of Isatoic p-linear bis Anhydride

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Ursinus College
30 April 1969

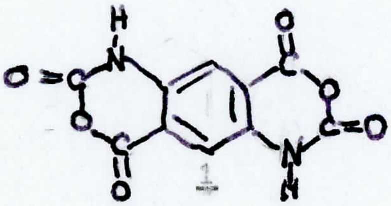
Submitted in fulfillment of the requirements for department honors.

Submitted by:
Willis G. Frick

Approved by:
Roger P. Staiger

The Synthesis and Reactions of Isatoic p-linear bis Anhydride

Isatoic anhydride and its reactions have been studied extensively at Ursinus in recent years.[1] The possibility of synthesizing what will be called a di-isatoic anhydride has,however, remained a challenge. Five possible isomers have been postulated:[2]



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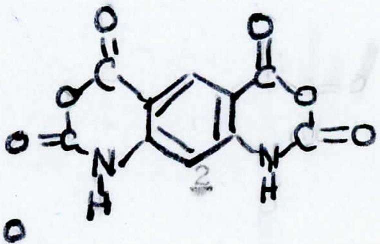

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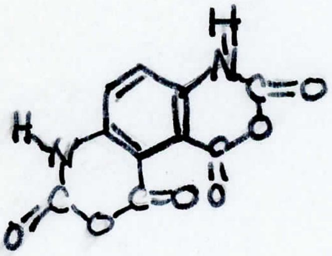

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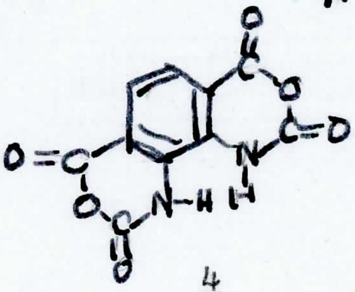

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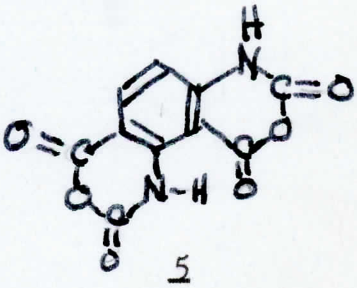

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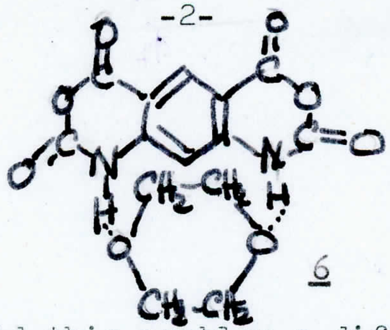
Three previous attempts to synthesis isatoic m-linear bis anhydride 2 [3,4,5] were unsuccessful in that the product defied positive confirmation. Among the difficulties encountered by these workers was the tendency for m-diIA to complex with dioxane, the solvent in the last step of the synthesis. The formation of this complex 6 has been postulated to be caused by a hydrogen bond between the -NH in the m-diIA and the oxygen in the dioxane.[6]



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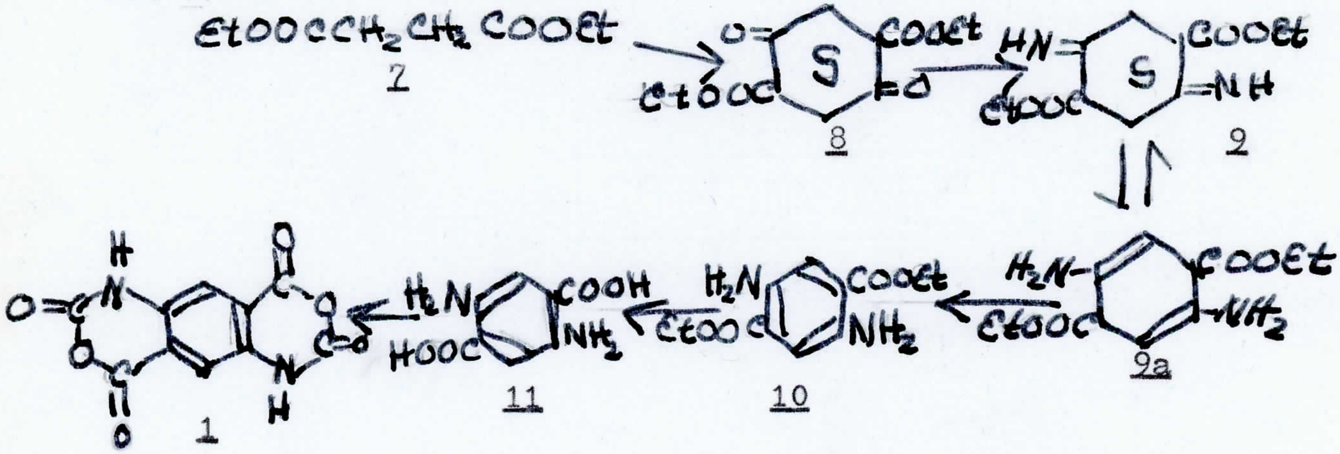
In order to avoid this problem a different isomer 1 was prepared, which would not be susceptible to such complexing.

Three schemes of synthesis were considered and two of these were utilized. One possibility would parallel the methods used by previous workers in the attempts to prepare m-diIA. This would involve the preparation of 1,4 dimethyl 2,5 dinitrobenzene, a reduction to the diamine, acetylation of the amine groups, oxidation of the methyl groups to carboxyls, and hydrolysis of the amides to yield 2,5p-diaminoterephthalic acid. The desired p-diI^{A} could be prepared by a final ring closure with phosgene. This approach was not attempted because of the difficulty encountered previously with the side chain oxidations. Two other independent synthesis were utilized to prepare the p-diaminoterephthalic acid, the last intermediate.

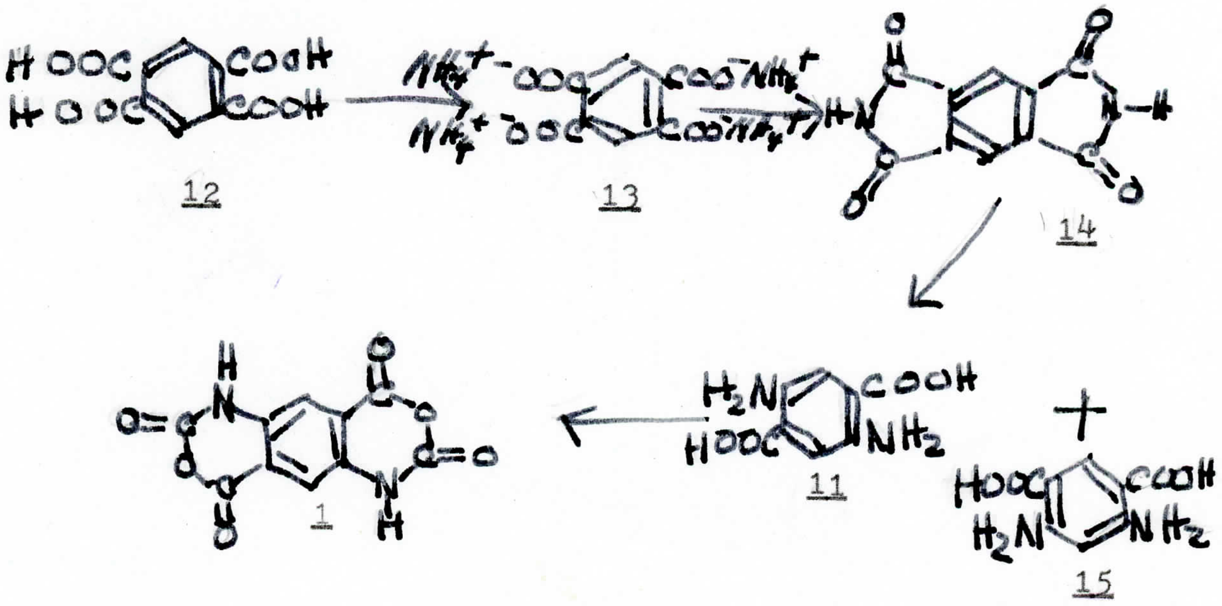
The first method shown below, was developed by Bogert and Dox[7].



Diethyl succinate 7 is treated with sodium ethoxide in absolute ethanol, promoting a base catalysed ring closure to yield succinylosuccinic acid diethyl ester 8. The ester is fused with ammonium acetate, and the resulting mass broken up and washed with water allowing the isolation of succinylosuccinic acid diethylester diimine 9.

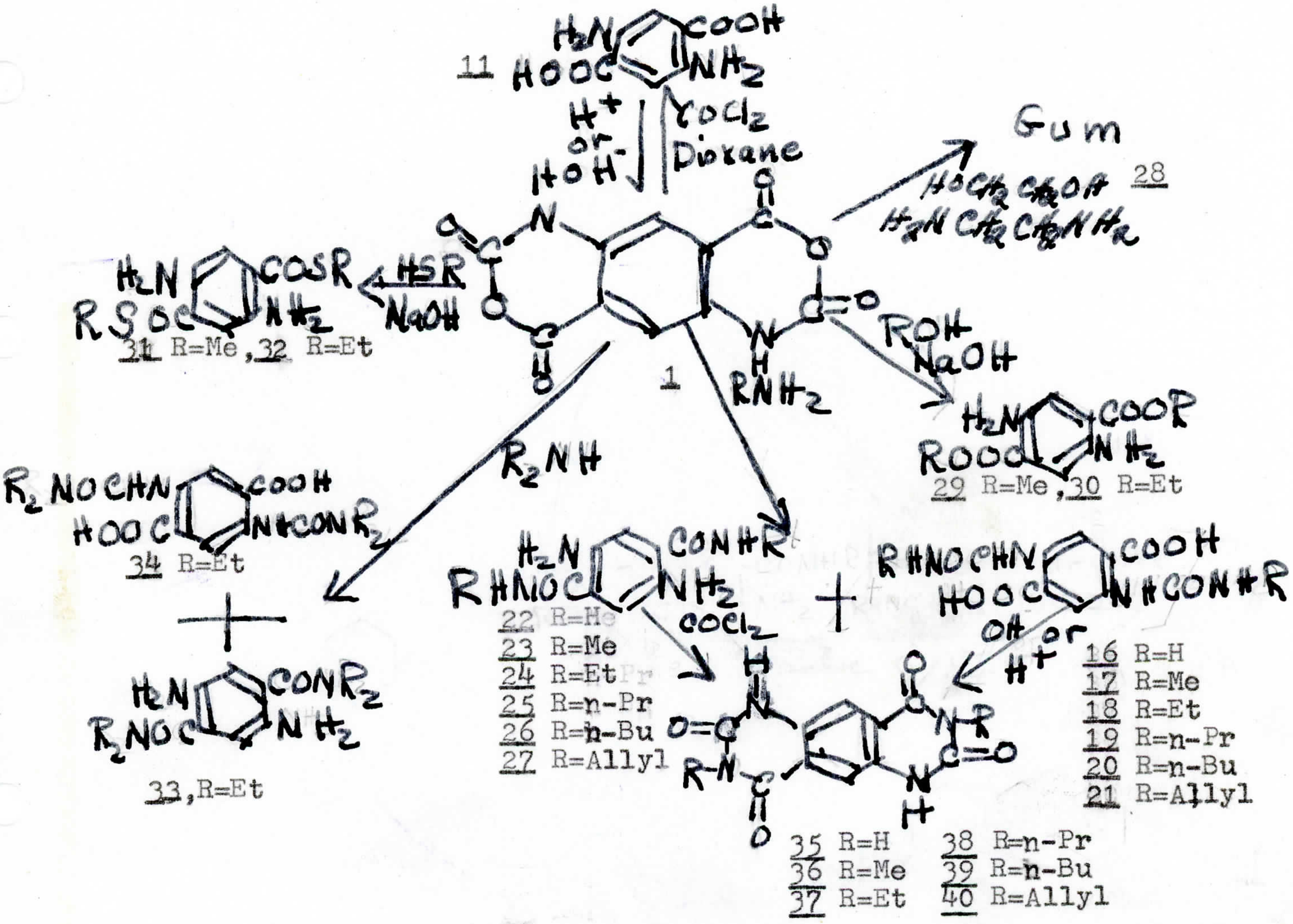
The presence of two sharp absorbtions at 2.90 and 3.0 in the I.R. spectrum suggest that the structure is actually a tautomer, 2,5 diamino 2,5 cyclohexadiene 1,4 dicarboxylic acid diethyl ester 9a. The diamine is oxidized in concentrated sulfuric acid with bromine yielding p-diaminoterephthalic acid diethyl ester 10 which is hydrolysed by 10% sodium hydroxide to yield p-diaminoterephthalic acid 11. The acid is suspended in dioxane and the double ring closures are achieved by treatment with phosgene after the method of Wagner and Fegley[8] yielding Isatoic p-linear bis anhydride, 2,4,7,9 tetraoxo 1,2,3,4,5,6,7,8 octahydro-benzo (1,2-d:-5, 4-d') bis 1,3 oxine, 1.[2] The I.R. spectrum of the material shows a single broad absorbtion near 3.2 u as expected for the hydrogen bonded -NH proton and two distinct carbonyl absorbtions at 5.7 and 5.8 u.

The second synthesis route was developed by Schoeter[9] for the synthesis of the p-diaminoterephthalic acid. This employed treatment of 1,2,4,5 benzene tetracarboxylic acid 12 with ammonium hydroxide to give the tetraammonium salt 13, which upon heating to 200°C in a stream of ammonia gives the diimide 14. The diimide, when treated with caustic and hypochlorite in a Hoffmann degradation, yields the desired p-diaminoterephthalic acid 11 among other products. According to Schoeter only the p-diaminoterephthalic acid is prepared and not the m-diamino-isophthalic acid 15. A second product, however, was isolated with both physical and spectral characteristics similiar to the p-diamino acid which indicated it was the second isomer 15. Repeated recrystallizations yielded the desired p-diamino isomer 10. Ring closure of 11 to 1 is achieved as previously described.



Reactions of Isatoic p-linear bis Anhydride

The reactions of p-diIA with nucleophiles closely parallel those of isatoic anhydride studied by Staiger and Miller.[10]



1. Reactions with NaOH and H_2SO_4

Treatment of p-diIA with either sodium hydroxide solution or dilute sulfuric acid converts it back to the p-diaminoterephthalic acid 11 which was confirmed by a comparison of its I.R. spectrum with the spectrum of a known analyzed sample. A side reaction of isatoic anhydride with NaOH to give anthranoylanthranilic acid was not observed with the p-diIA.

2. Reactions with Alcohols

Refluxing the p-diIA with primary alcohols in the presence of a catalytic amount of sodium hydroxide yields the diesters of p-diaminoterephthalic acid 29, 30. There compounds are characterized in Table I. Melting points correspond with those previously reported and the diethyl ester has an identical I.R. spectrum with a known sample. These spectra show the expected absorbtions, two peaks near 3.1 and 3.3 u for the amine groups and an ester carbonyl at 5.9 u, also a peak at 8.9 u for the C-O, which is absent for the thioesters.

Whereas isatoic anhydride will yield esters with aromatic and long chain aliphatic alcohols, attempts to prepare corresponding diesters with p-diIA were unsuccessful. In general the reactivity of p-diIA appears to be less than for isatoic anhydride.

TABLE I

DIESTERS OF p-DIAMINOTEREPHTHALIC ACID

Compound	R=	mp literature	mp found
29	methyl	168[a]	167
30	ethyl	185[b]	184-5

[a] Beilstein 14,560(641)

[b] Beilstein 14,560(641)

3. Reactions with Mercaptans

Refluxing p-diIA with primary thiols in the presence of a catalytic amount of sodium hydroxide yields brilliant red crystalline solids, the dithioesters of p-diaminoterephthalic acid 31, 32. These compounds have not been reported previously in the literature. (See TABLE II)

TABLE II

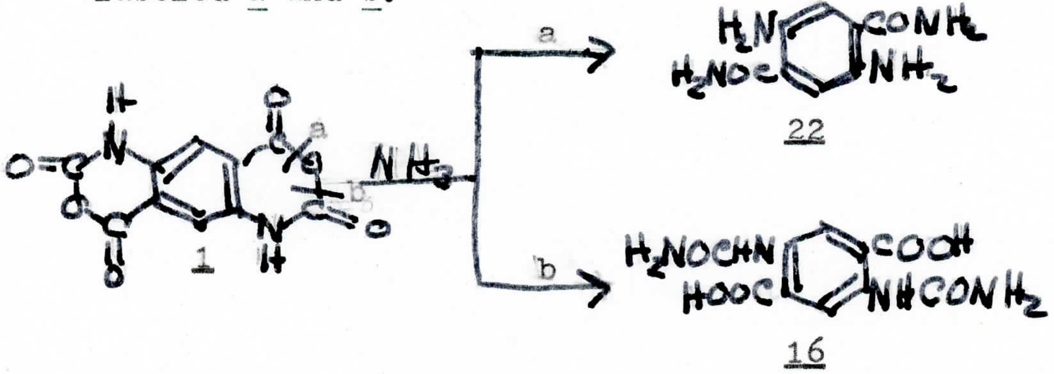
DITHIOESTERS OF p-DIAMINOTEREPHTHALIC ACID

R=	Compound	Formula	mp	Calcd,%				Found, %			
				C	H	N	S	C	H	N	S
Methyl[a]	31	$C_8H_{12}N_2O_2S_2$	174-5	41.70	5.18	12.00	27.60	41.81	5.22	11.95	27.35
Ethyl[a]	32	$C_{12}H_{16}N_2O_2S_2$	134-5	50.70	5.63	---	---	50.86	5.83	---	---

[a] of new composition

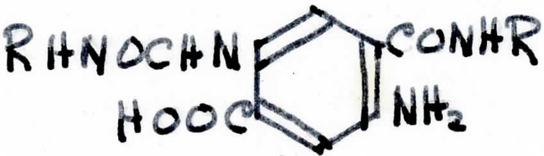
4. Reactions with Ammonia

Ammonia reacts with p-diIA in two routes, as shown below, in a manner parallel to isatoic anhydride. The routes may be labeled a and b.



If the attack occurs at a the amide of p-diaminoterephthalic acid is produced 22. (See TABLE III) If the attack occurs at b, then the uramidoterephthalic acid is prepared 16. This acid could however, not be isolated, since in the presence of either acid or base it undergoes ring closure to yield 2,4,7,9 tetra-oxo-octahydronaphthatetrazine 35. (See TABLE IV) If a separate sample of the amide is treated with phosgene in dioxane the identical tetrazine may be prepared, thus confirming the structure of both products. These have identical I.R. spectra and composition has been confirmed by elemental analysis. The tetrazine 35 thus produced is believed to be of new composition. The compound is mentioned in Beilstein but no record appears of preparation. The material exhibits an I.R. spectrum containing broad multiple absorbtions in the carbonyl region and two broad peaks at 3.1 and 3.3 as would be anticipated from the structure.

The ratio of the two products, amide 22 and acid 16, from the reaction with ammonia was found to depend on the ammonia concentration. At low ammonia concentrations (ca. .4 to 2M) the amide 22 was the major product. At high ammonia concentrations (ca. 4 to 15M) the major product was the acid 16. These findings parallel those of Staiger and Wagner.[11] There was no evidence for the production of mixed products of the form 41. There is need for a quantitative study of this reaction.



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5. Reactions with Primary Amines

Primary amines react in a manner similar to ammonia. The ratio of the two products is dependent in a similar manner on the amine concentration. The products were N,N' disubstituted amides of p-diaminoterephthalic acid 23, 24, 25, 26, 27 and the -substituted diuramidoterephthalic acids 17, 18, 19, 20, 21. (See TABLE III and TABLE IV) These latter acids underwent ring closure and were isolated as the 3,8 disubstituted 2,4,7,9 tetraoxo-octahydro 1,3,6,8 naphthotetrazines 36, 37, 38, 39, 40, which could be independently synthesized from the corresponding amide by the action of phosgene. (See TABLE IV)

The substituted amides and tetrazines thus prepared are of new composition. The amides show an amide I and amide II band in the I.R. at 6.1 and 6.3 respectively. Three absorbtions at 2.88, 2.90, and 3.08 may be assigned to the two amine and one amide protons respectively. The tetrazines show two carbonyl peaks at 5.8 and 6.05. They also have a peak at 2.95 for the NH stretch. The unsubstituted tetrazine also shows an additional absorbtion at 3.05 for the other NH stretch.

An unusual behavior was shown by the hindered amines. Analine does not yield the amide on direct reaction as with other simple amines, but if the product of direct fusion is treated with 10% sulfuric acid for several hours under reflux and the mixture made basic, a material with the I.R. of the amide but not the elemental conposition is prepared. Additional work is needed to clarify the nature of the action of these materials with p-diIA.

TABLE III

AMIDES OF p-DIAMINOTEREPHTHALIC ACID

R=	Compound	mp	Calcd, %		Found, %	
			C	H	C	H
H	22	280-2	47.50	5.20	47.71	5.30
Methyl[a]	23	276-8	54.14	6.30	54.10	6.38
Ethyl[a]	24	296-8	57.06	6.38	57.15	6.41
n-Propyl[a]	25	288-92	60.50	7.92	60.38	7.91
n-Butyl[a]	26	277-8	62.97	8.55	63.07	8.60
Allyl[a]	27	265-6	64.90	8.70	64.74	8.64

[a] of new composition

TABLE IV

3,8 DISUBSTITUTED 2,4,7,9 TETRA-OXO 1,3,6,8 NAPHTHATETRAZINES

R=	Compound	mp	Calcd, % C	Calcd, % H	Found, % C	Found, % H
H[a]	35	360	48.70	2.43	48.94	5.63
n-Propyl[a]	37	360	61.20	5.63	61.47	5.85

[a] of new composition

6. Reactions with Secondary Amines

Secondary amines react in a similar manner yielding both the N,N,N',N', tetrasubstituted amides of p-diaminoterephthalic acid 33 and the disubstituted diuramidoterephthalic acids 34. (See TABLE V) These acids cannot undergo ring closure as there are no hydrogens in the ω position. Thus they could be isolated and their N.E. and elemental analysis determined. The I.R. spectrum shows peaks at 5.78 and 6.10 for the carbonyls, as well as a broad NH peak.

TABLE V

DISUBSTITUTED DIURAMIDOTEREPHTHALIC ACIDS

R=	Compound	mp	Calcd N.E.	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Found N.E.
Ethyl[a]	34	360	178	63.00	7.53	62.81	7.59	174

[a] of new composition

7. Bifunctional Nucleophiles

With bifunctional nucleophiles such as ethylene diamine and ethyleneglycol a polymeric material resulted 28.

In general, p-diIA was found to react in a manner generally parallel to isatoic anhydride.[11] It appears to be somewhat less reactive toward nucleophiles. Further quantitative study is needed to elucidate the mechanism of these reactions, particularly those with amines and ammonia. Also, the nature of the product from the reaction of p-diIA with analine and hindered amines needs clarifying.

EXPERIMENTAL

Synthesis of Isatoic p-linear bis Anhydride

Method of Bogert and Dox

Succinylosuccinic acid diethyl ester: 8

500g of diethyl succinate and 175ml of absolute ethanol are placed in a 2 liter flask. 50g of sodium is gradually introduced slowly with shaking. After the initial reaction has subsided the mixture is refluxed for 4 to 8 hours. 95% ethanol is added to destroy excess sodium. The reaction mix is acidified with 10% sulfuric acid to precipitate the succinylosuccinic acid diethyl ester.

mp lit. 125-7, Beilstein 10,897, mp found 124-7. Yield 85-90%.

Succinylosuccinic acid diethyl ester diimide: 9

Succinylosuccinic acid diethyl ester is mixed with 5 to 7 times its weight of ammonium acetate. The mixture is heated until it forms a melt. The melt is heated until it begins to crackel and heating is continued for an additional 10 minutes. The melt is allowed to cool, crushed and washed with 2 times its weight in water. The diimide is removed by filtration as a yellow solid.

mp lit. 177-81, Beilstein 10,897, mp found 179-81. Yield 95-100%

p-diaminoterephthalic acid diethyl ester: 10

100g of the diimide is dissolved in 500ml of concentrated sulfuric acid. In a flask equipped with a condensor and vented to the hood, 20ml of bromine is added slowly. The mix is stirred and heated to 60°. This temperature is maintained for 30 minutes. The excess bromine is removed by a stream of air and the solution poured over ice wet with sulfurous acid. The sulfate salt of the p-diaminoterephthalic acid precipitates as a brown powder. Additional yield may be obtained by neutralizing the solution with ammonia.

mp lit. 168, Beilstein 14,560, mp found 167-169. Yield 20%.

p-diaminoterephthalic acid: 11

The ester is hydrolysed by heating with 10% sodium hydroxide and the product precipitated by addition of acetic acid. The acid may be further purified by redissolving in base and reprecipitating with acid.

mp lit. > 360, Beilstein 14.599, mp found > 360. Calc for $C_8H_8N_2O_4$: C 48.98, H 4.08, N 14.28, Found: C 48.77 H 4.13 N 14.11. Yield 90-100%.

Method of Schoeter[9]

1,2,4,5 Benzene tetracarboxylic acid (pyromellitic acid) 12 was purchased from the Aldrich Chemical Co.

Tetra ammonium salt of 1,2,4,5 Benzene tetracarboxylic acid: 13

100g of the acid is boiled with 50ml of concentrated ammonia. The ammonium salt precipitates on cooling. Additional crops may be obtained by evaporating and cooling. Yield 100%.

Pyromellic diimide: 14

The tetra ammonium salt is placed in a glass tube surrounded by heating tape. A stream of ammonia is passed through the tube while it is heated to 200°. The treatment is continued for 40 minutes. The imide may be purified by recrystallization from pyridine.

mp lit. 300, Beilstein 24,519, mp found 304-6. Yield 50%.

p-diaminoterephthalic acid: 11

5g of the diimide is suspended in 100g of H_2SO_4 acid and to this is added a solution containing 175ml of 2.5% NaOCl and 10g of NaOH. This mixture is stirred for one hour and then made acidic by the addition of SO_2. The resulting solid is purified by dissolving in NaOH and precipitating with acetic acid.

mp lit. >360, Beilstein 14,599, mp found>360. Yield 30%.

Isatoic p-linear bis anhydride: 1

25g of the dry p-diaminoterephthalic acid is suspended by stirring in 100ml of dioxane. Phosgene is passed through the mixture for 20 hours. Dry nitrogen is bubbled through to remove the excess phosgene. The mixture is filtered and the p-diIA is obtained as a yellow-green powder.

mp>360, $C_{10}H_4O_4N_2$ Calc: C 48.48 H 1.69, Found: C 48.50, H 1.85. Yield 100%.

Reactions with various nucleophiles:

1. NaOH and H_2SO_4: .5g of the p-diIA is refluxed with 10ml of acid or base for 5 hours. In the H_2SO_4 reflux the acid will precipitate. The NaOH mixture is made acidic with acetic acid to precipitate the acid.

2. Alcohols: 5ml of the alcohol, .5g of p-diIA and a small chip of NaOH are refluxed for 4 to 6 hours. The solution is boiled to dryness over a steam bath and the ester dissolved in benzene. They may be recrystallized from benzene and are characterized in TABLE I.

3. Thiols: 5ml of the thiol, .5g of p-diIA, 5 ml of dioxane and a small chip of NaOH are refluxed for 4 to 8 hours or until the p-diIA has dissolved. The mixture is diluted with water and the thioesters percipitate as brilliant red crystals. They may be recrystallized from EtOH and are characterized in TABLE II.

4. Ammonia: 5ml of ammonia of the appropriate concentration, dependent on the desired product, is heated with .5g of p-diIA in a beaker. The mix is chilled and the amide removed by filtration. The amide may be recrystallized from EtOH-HOH and is characterized in TABLE III. The mixture is made acidic with H_2SO_4 and the tetrazine precipitates as a brown powder. It is characterized in TABLE IV.

5. Primary amines: 5ml of an amine solution in water of the concentration appropriate to the product desired is heated with .5g of p-diIA until the solution boils. The amide precipitates on cooling, may be recrystallized from EtOH-HOH and is characterized in TABLE III. The tetrazines precipitate on the addition of H_2SO_4. They are characterized in TABLE IV.

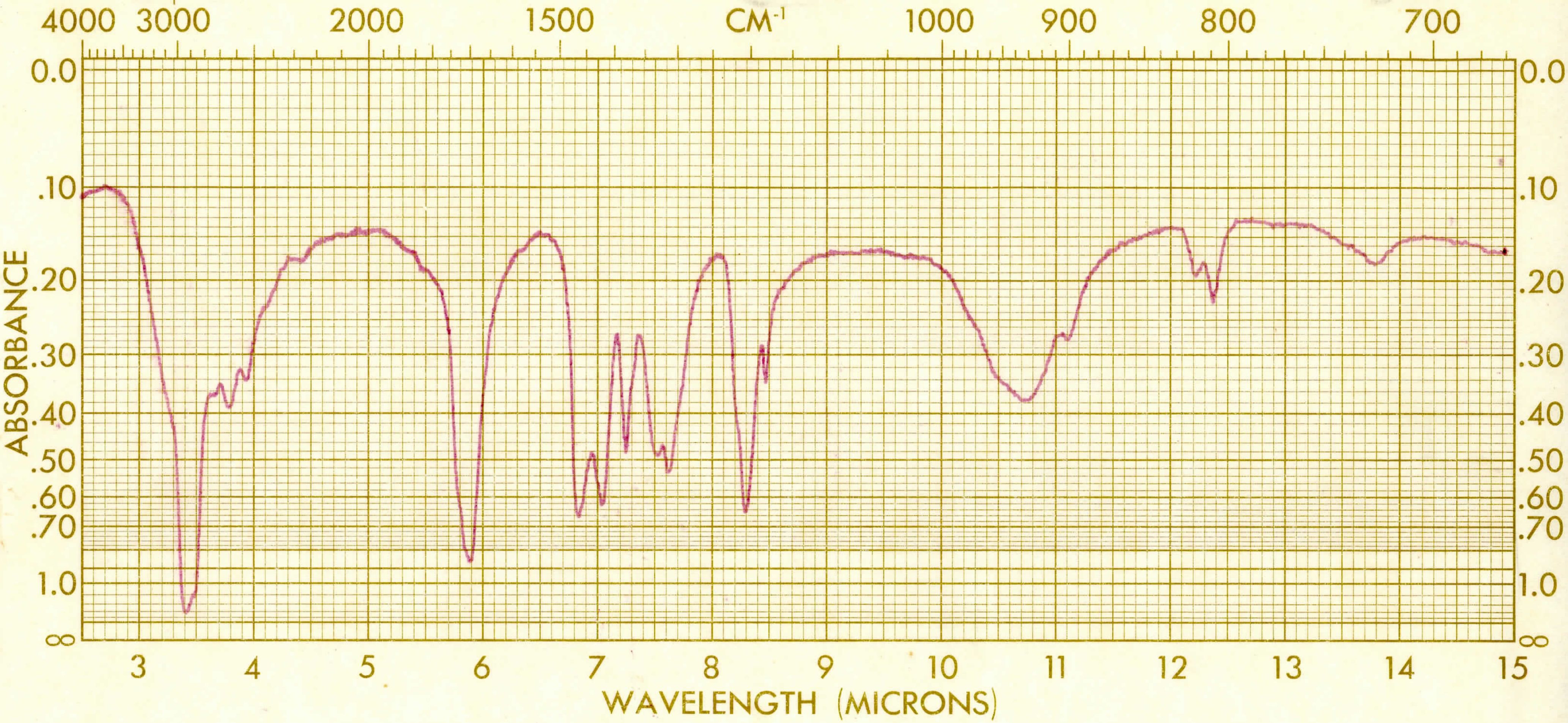
6. Secondary amines: 5ml of a water solution of the secondary amine of appropriate concentration and .5g of p-diIA are heated to a boil. The solution is acidified with 10% sulfuric acid and the ω substituted uramidoterephthalic acid precipitates. If the filtrate is treated with 20% NaOH the amine salt of the amide is destroyed and the secondary amide precipitates.

7. Bifunctional nucleophiles: .5g of the p-diIA is heated directly with the ethylene glycol or ethylene diamine. The resultant tar could not be characterized.

Independent synthesis of tetrazines: .5g of the amide is suspended in 25ml of dioxane and treated with phosgene for 4 to 10 hours. The tetrazines separate as a yellow ppt. which may be removed by filtration after the excess of phosgene has been removed by a stream of nitrogen. They are characterized in TABLE IV.

FOOTNOTES

1. R.P. Staiger and E.B. Miller, *J.Org.Chem.*, **24**,1214(1959).
2. Nomenclature developed by E.B. Miller, Maumee Chemical Co.
3. David A. Larson, Unpublished research at Ursinus College, 1965.
4. Calvin Moyer, Unpublished research at Ursinus College, 1963.
5. Mary Ann K. Haas, Unpublished research at Ursinus College, 1964.
6. Roger P. Staiger and Calvin Moyer, Unpublished research, 1963.
7. Bogart and Dox, *J.Am.Chem.Soc.*, **27**,1135.
8. *Organic Synthesis*, pg. 489, Horning Edt., ~~Weily~~ Wiley and Sons, N.Y., 1955.
9. Schoeter, *Chem.Ber.*, **57**,2024.
10. The Ring Index, **#3271**.
11. *Isatoic Anhydride III, Reactions with Primary Amines and Ammonia*, Staiger and Wagner, *J.Org.Chem.*, **18**,1427(1953). *Isatoic Anhydride IV, Reactions with Various Nucleophiles*, Staiger and Miller, *J.Org.Chem.*, **24**,1214(1959).



SPECTRUM NO. 4

SAMPLE Succinic Acid

ORIGIN Stock

PURITY

PHASE nujol moll

THICKNESS D.M.C.

LEGEND

1.

2.

DATE 2-24-67

OPERATOR W. Frick

REMARKS

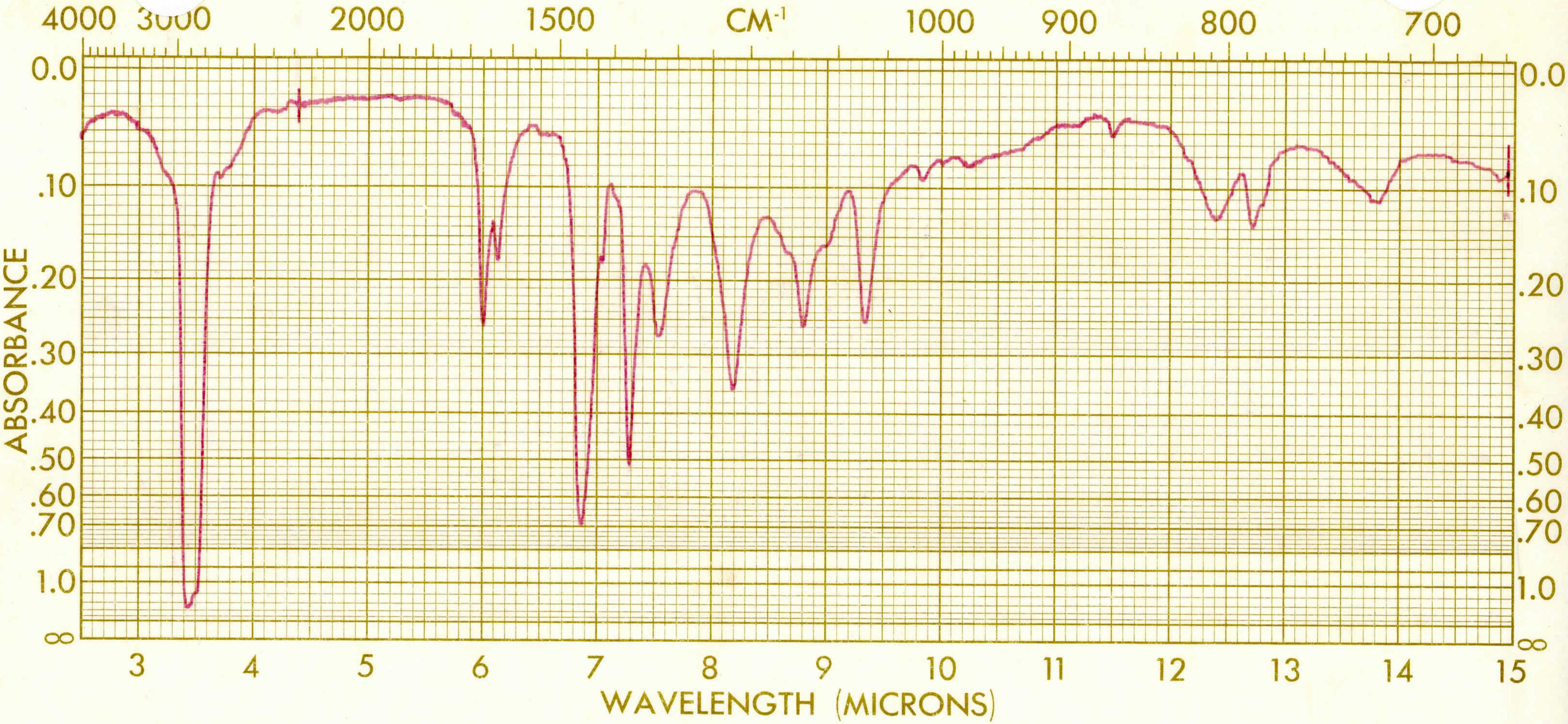
white ~~po~~ crystals.

SPECTRUM NO.

SAMPLE

PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 63

SAMPLE Succinylo

Succinic Acid

di Et ester.

ORIGIN Prep from.

Succinic Acid d. Et.

PURITY recry. acetone

PHASE nujol mull

THICKNESS

LEGEND

1.

2.

DATE 3/7/67

OPERATOR W. Frick

REMARKS note:

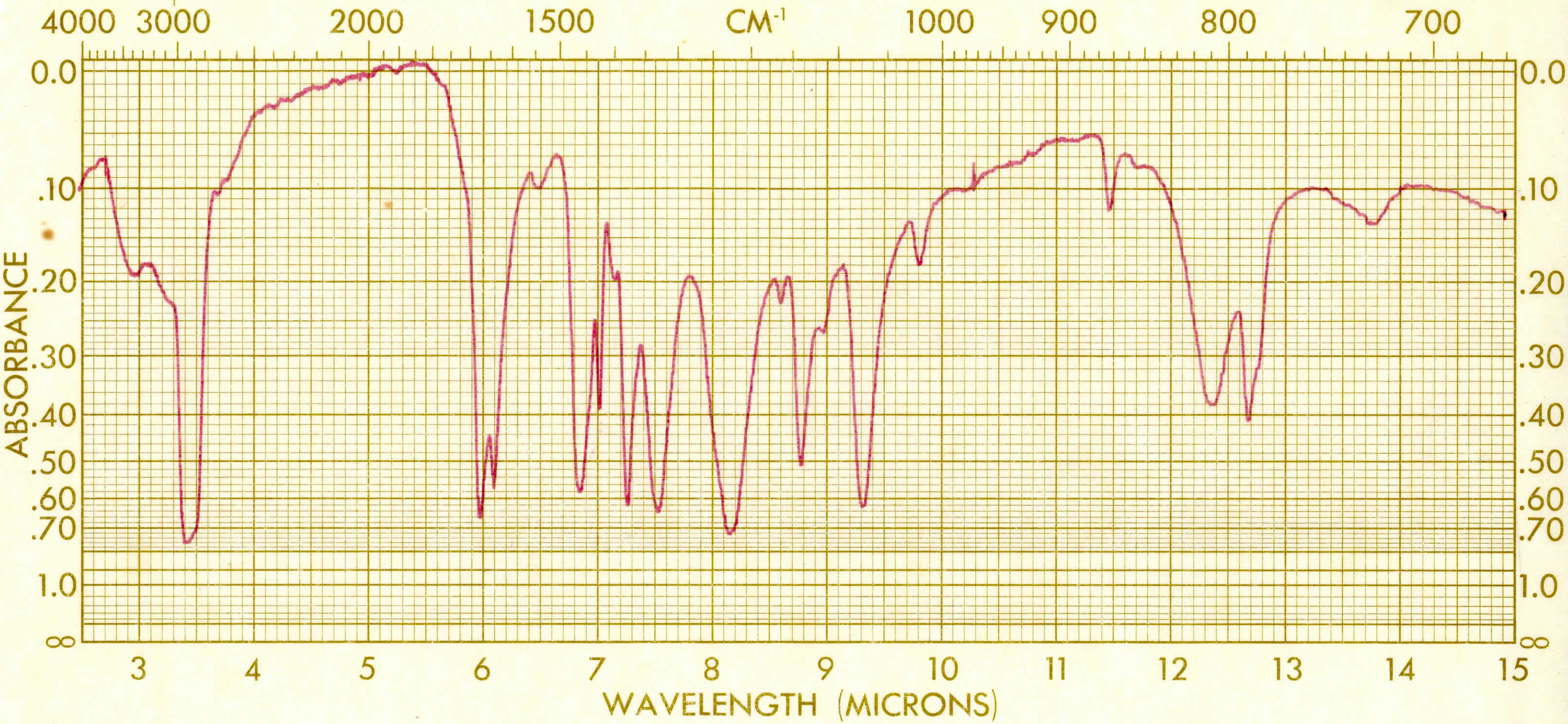
2 c=o peaks

SPECTRUM NO. 23

SAMPLE [illegible]

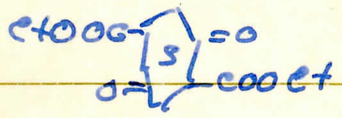
PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 15

SAMPLE



ORIGIN Exp'l

PURITY Recrystal. [illegible]

PHASE Nujol

THICKNESS

LEGEND

1.

2.

DATE 3/8/67

OPERATOR W-Frick

REMARKS Two C=O

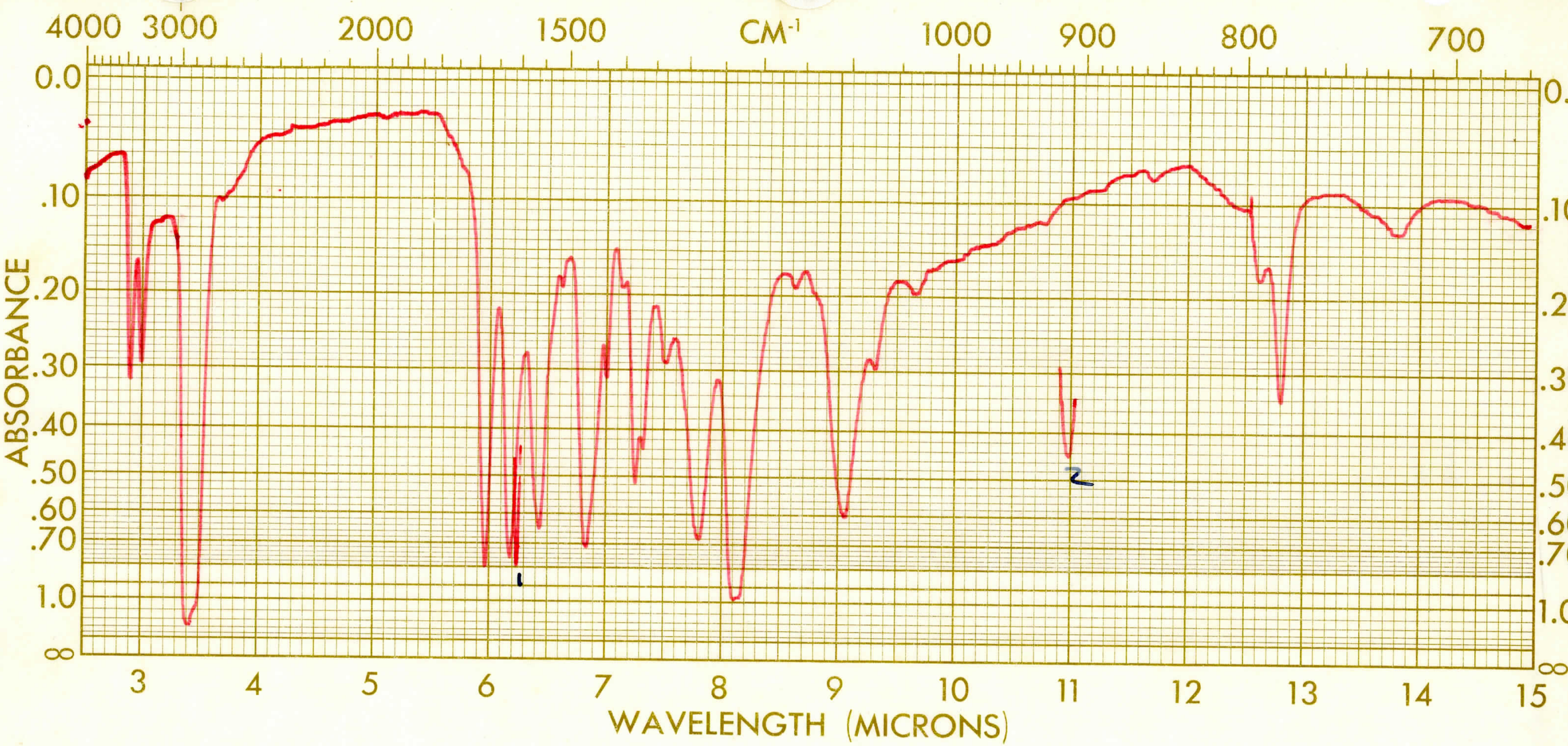
bands 5.9, 6.1

SPECTRUM NO. 15

SAMPLE SSDE

PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 2-1-8

SAMPLE

ORIGIN ~~Rx EtOH~~

Exp 2-1-8

PURITY Rx EtOH

PHASE nujol

THICKNESS –

LEGEND Polystyrene

1. 6.246

2. 11.032

DATE 2/10/08

OPERATOR W Fuij

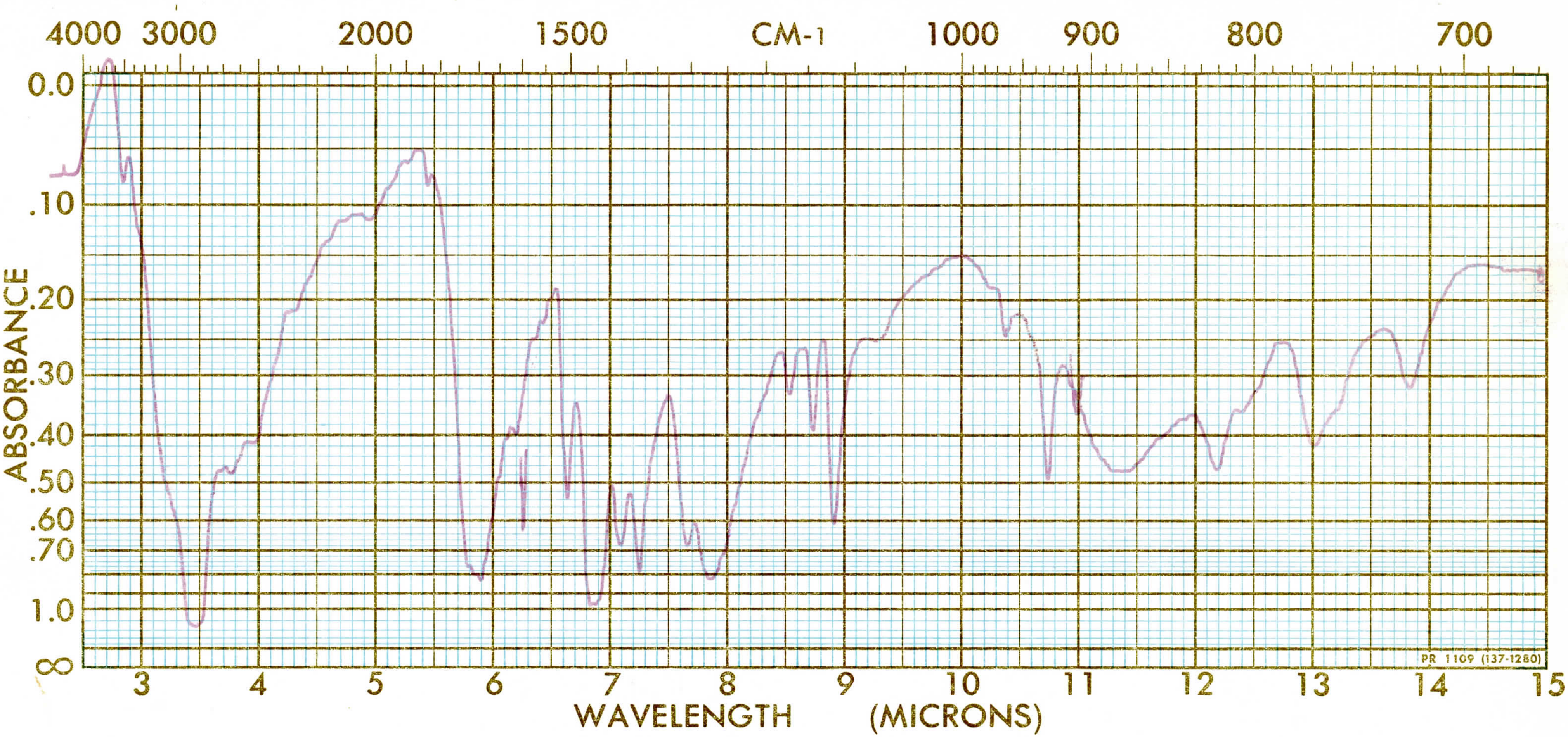
REMARKS

SPECTRUM NO. 2-1-8

SAMPLE SSPD

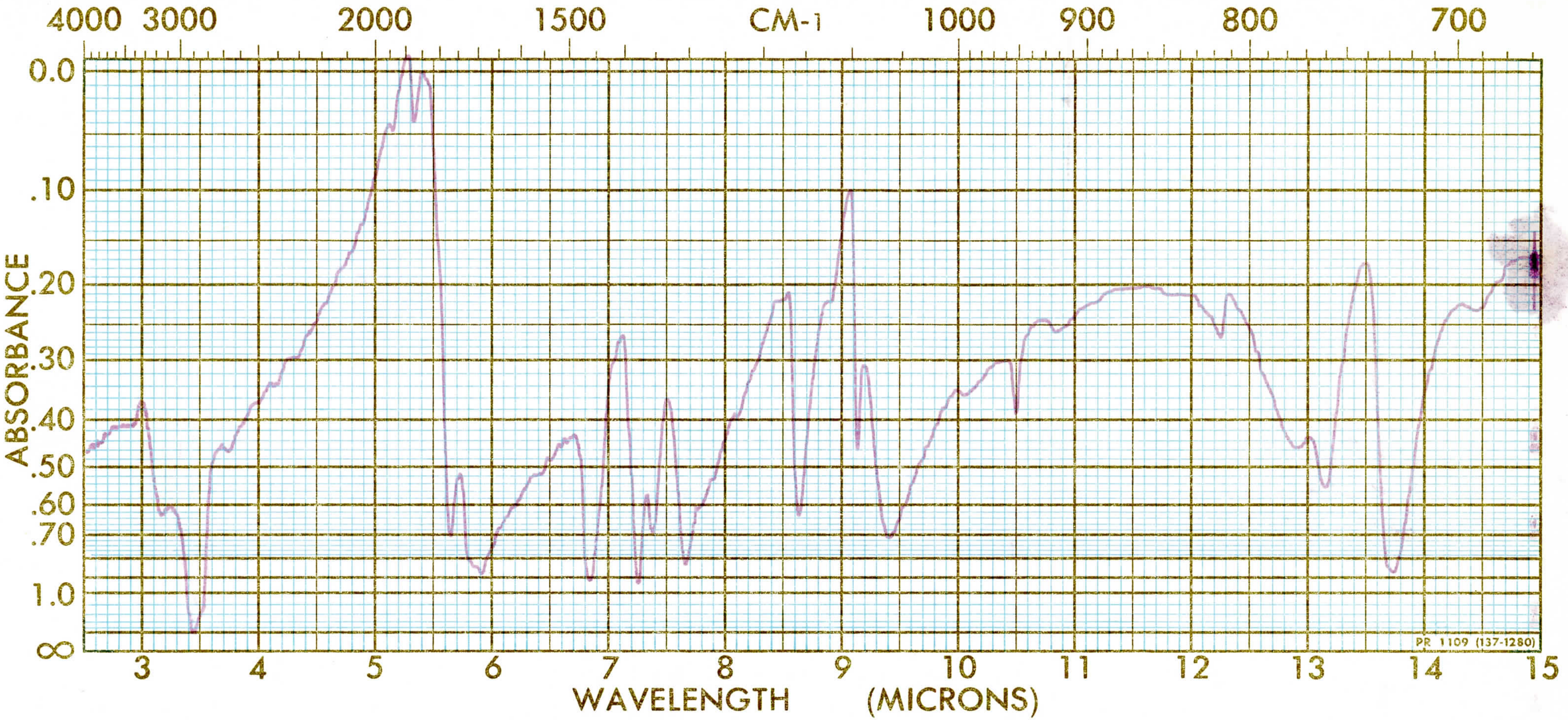
PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-9-87	ORIGIN Aldrich Chemical	LEGEND polystyrene	REMARKS
SAMPLE 1,2,4,5 benzene	Co.	1. 6.246	
tetracarboxylic acid	PURITY mp 282-4	2. 11.032	
	PHASE nujol mull	DATE 4/15/69	
	THICKNESS	OPERATOR W. Frick	

SPECTRUM NO.
SAMPLE



SPECTRUM NO. 4-9-86

SAMPLE pyromellitic diimide

ORIGIN Aldrich Chemical Co.

PURITY mp. >360°

PHASE nujol mull

THICKNESS

LEGEND

1.

2.

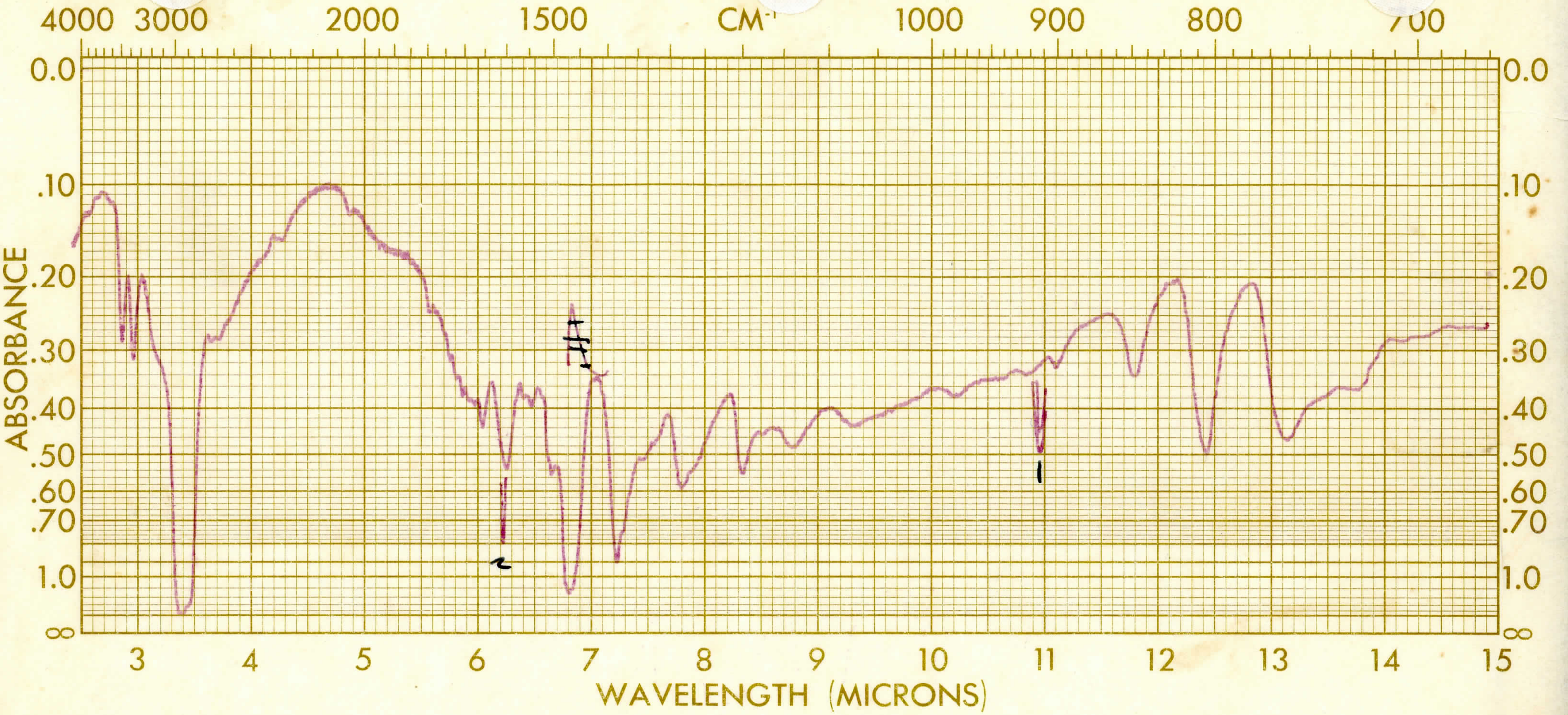
DATE 4/25/69

OPERATOR WFrick

REMARKS

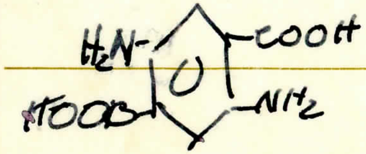
SPECTRUM NO.

SAMPLE



SPECTRUM NO. 9-10

SAMPLE



ORIGIN Purified.

p diaminoterephthalic acid

PURITY recry/.

PHASE Nujol

THICKNESS

LEGEND

1. 11.032

2. 6.246

DATE 4/18/67

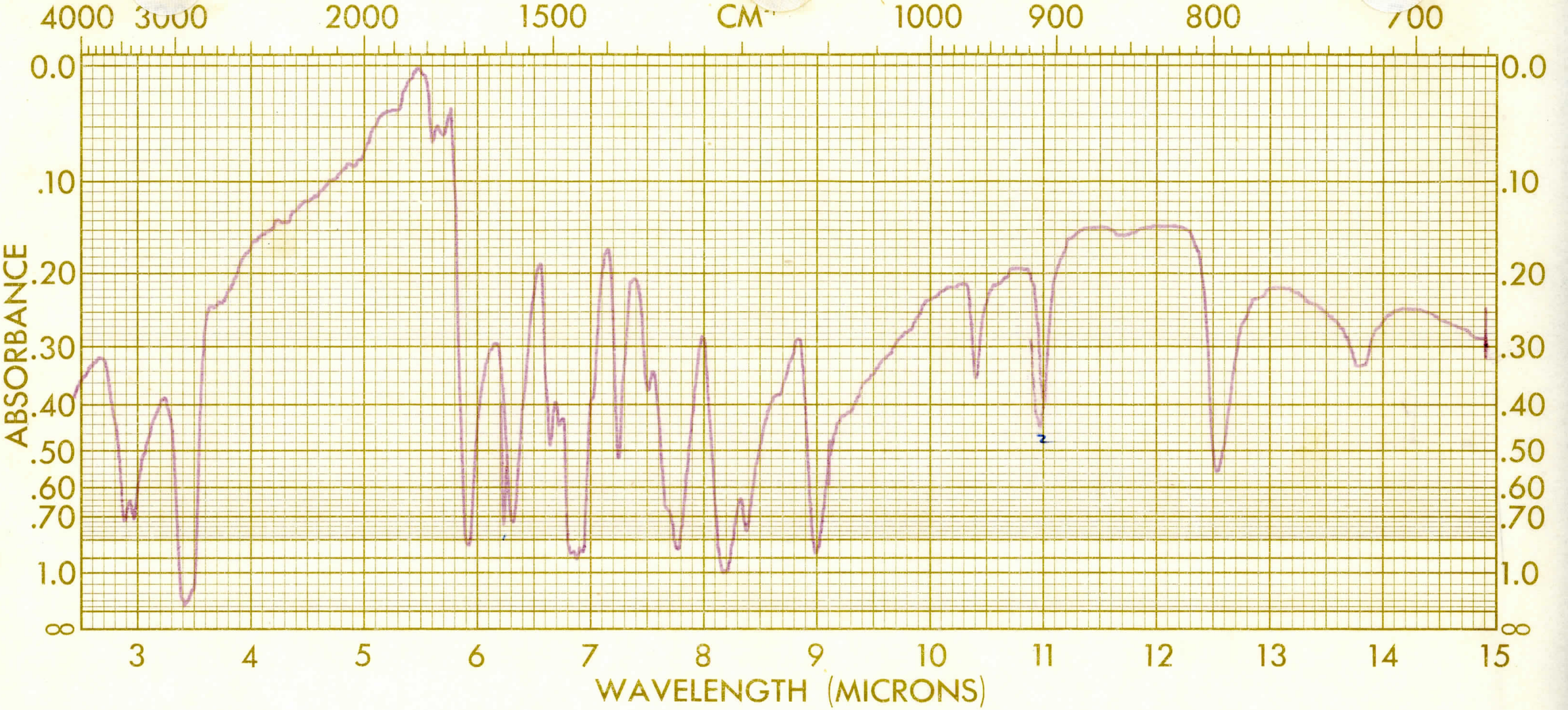
OPERATOR W Frick

REMARKS

SPECTRUM NO.
SAMPLE

PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-6-12

SAMPLE dimethyl ester

p-diamino phthalic acid

ORIGIN Exp 4-8-3

PURITY fair

PHASE nujol

THICKNESS -

LEGEND

1. 6.246

2. 11.032

DATE

OPERATOR

REMARKS

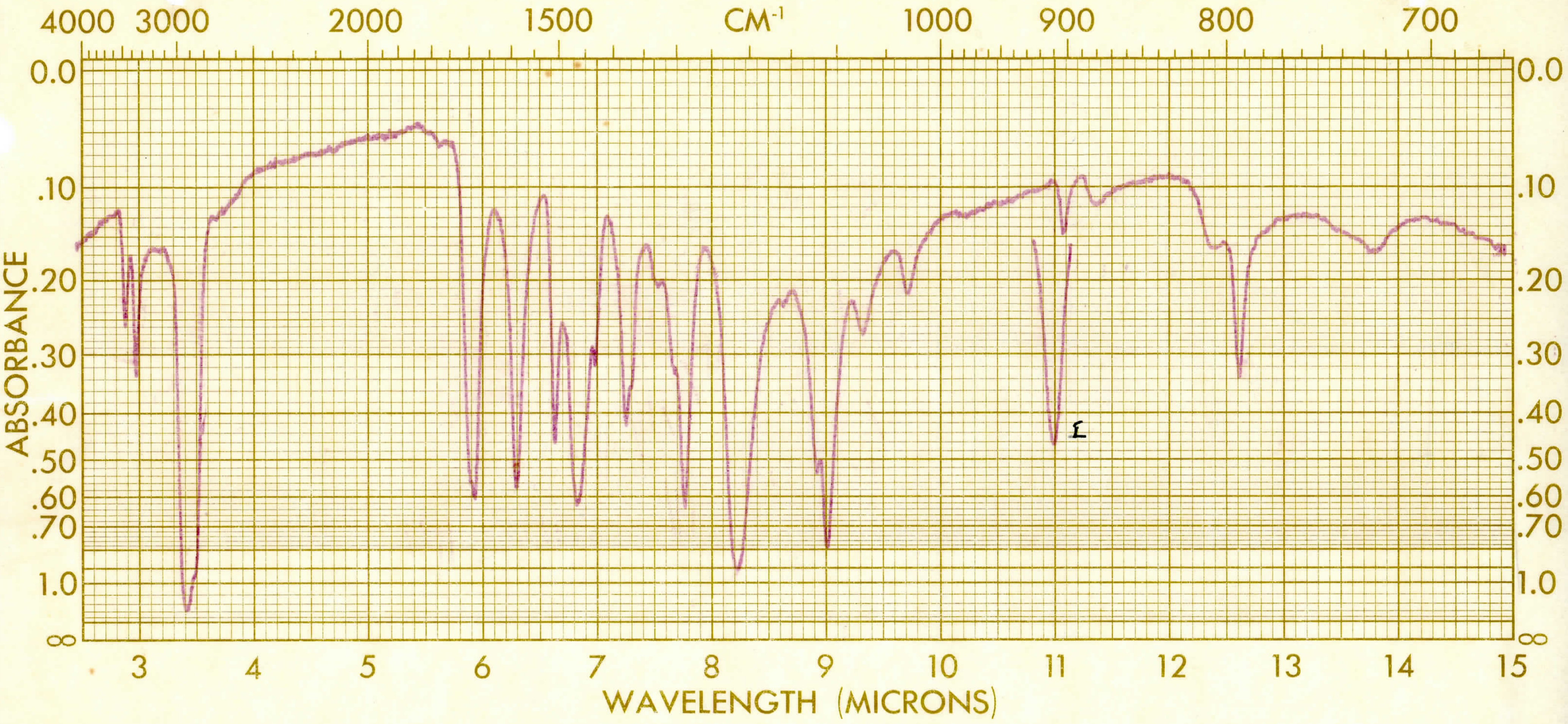
m.p. 187-4, lit 185

SPECTRUM NO. 4-5-12

SAMPLE dimeester

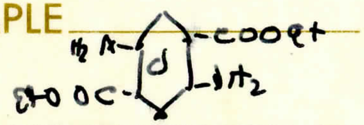
PART NO. 137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 32

SAMPLE



ORIGIN Prep Exp 6

PURITY crude

PHASE nujol

THICKNESS

LEGEND

1. Polystyrene 11.032

2.

DATE 7/21/67

OPERATOR W Frick

REMARKS

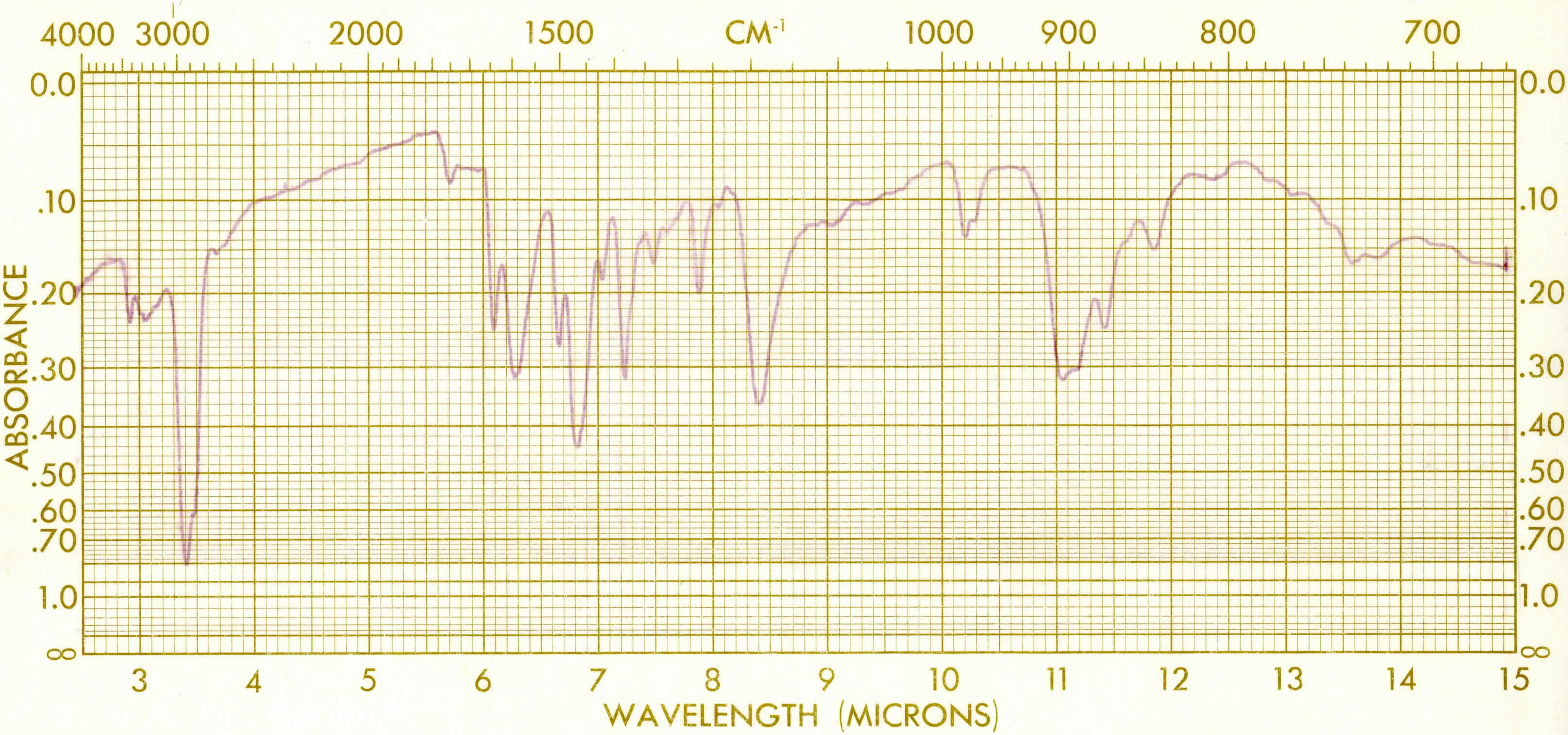
recryst. Benzene

SPECTRUM NO.

SAMPLE

PART NO.137-1280 PE®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-9-67

SAMPLE Dimethyl thiomercaptan

p-diaminoterephthalate

ORIGIN p-diIA and methyl

PURITY 3Rx from EtOH

PHASE nujol mull

THICKNESS -

LEGEND

1.

2.

DATE 3/20/69

OPERATOR W. Frick

REMARKS

for % analysis

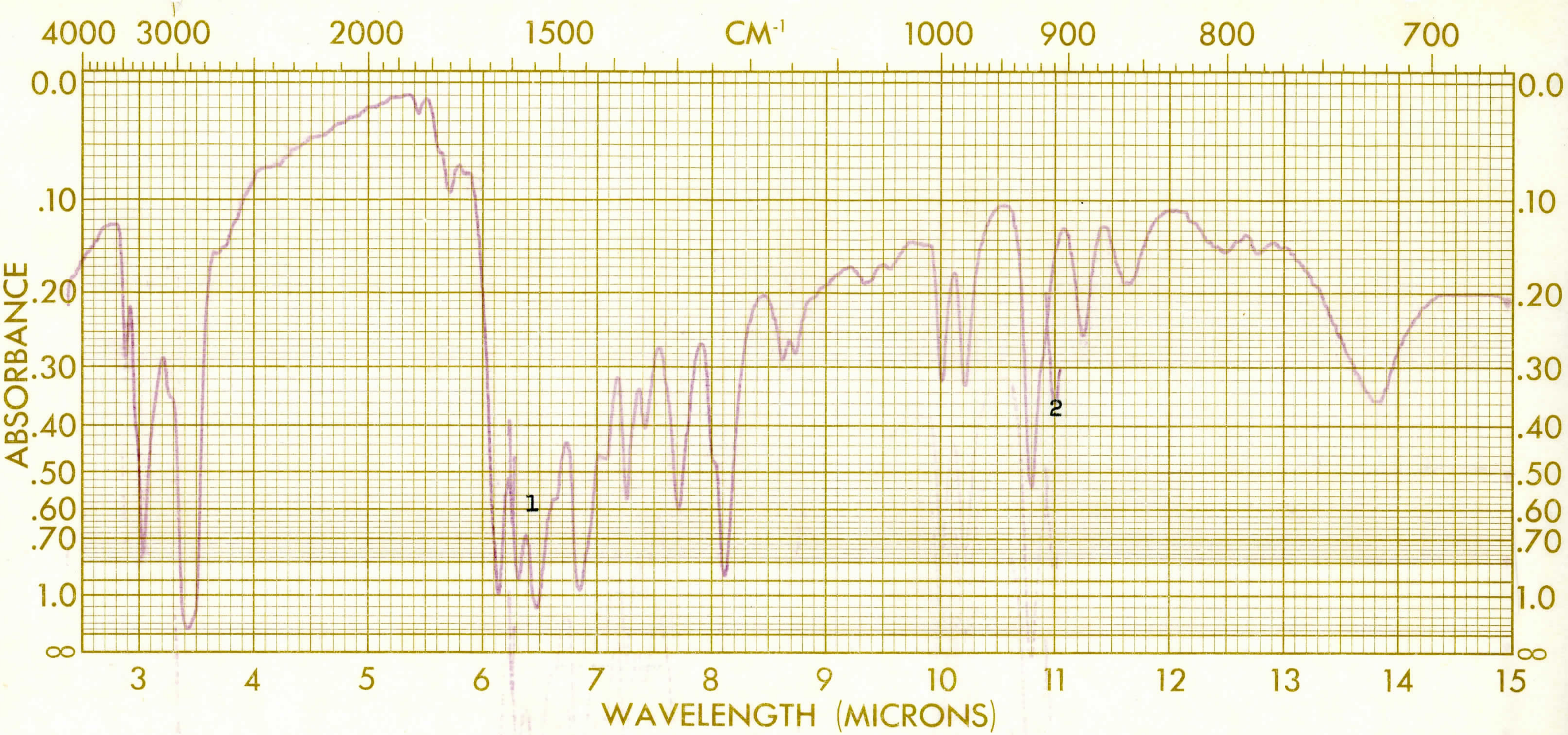
	theo	found
C	42.7	41.81
H	5.18	5.22
N	12.00	11.95
S	27.60	27.35

SPECTRUM NO.

SAMPLE

PART NO. 137-1280

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-9-49

SAMPLE NNdiallyl p-diaminoterephthalic acid diamide

ORIGIN p-diisotoic anhydride and allyl amine

PURITY 3 rx from water

PHASE nujul mull

THICKNESS

LEGEND polystyrene

16.246

2. 21.032

DATE 3/6/69

OPERATOR

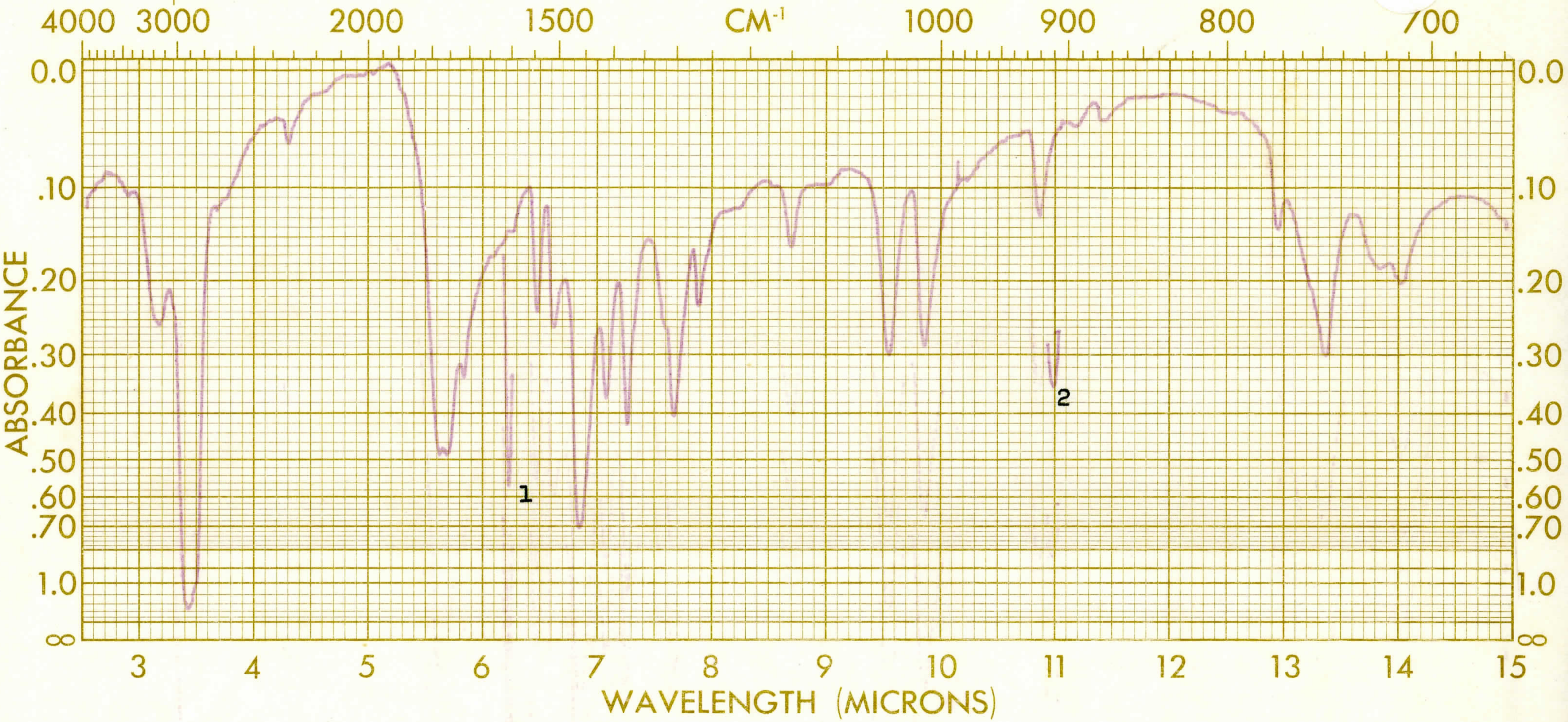
REMARKS %analysis

	theo.	found
C	64.9	64.74
H	8.7	8.64

SPECTRUM NO. SAMPLE

PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-9-47

SAMPLE p-diisotoic anhydride ,Rx NNDimethyl formamide, washed with acetone and wther

ORIGIN p-diaminoterephthalic acid and $COCl_2$

PURITY

PHASE nujul mull

THICKNESS

LEGEND polystyrene

1. 6.346

2. 11.032

DATE 3/6/69

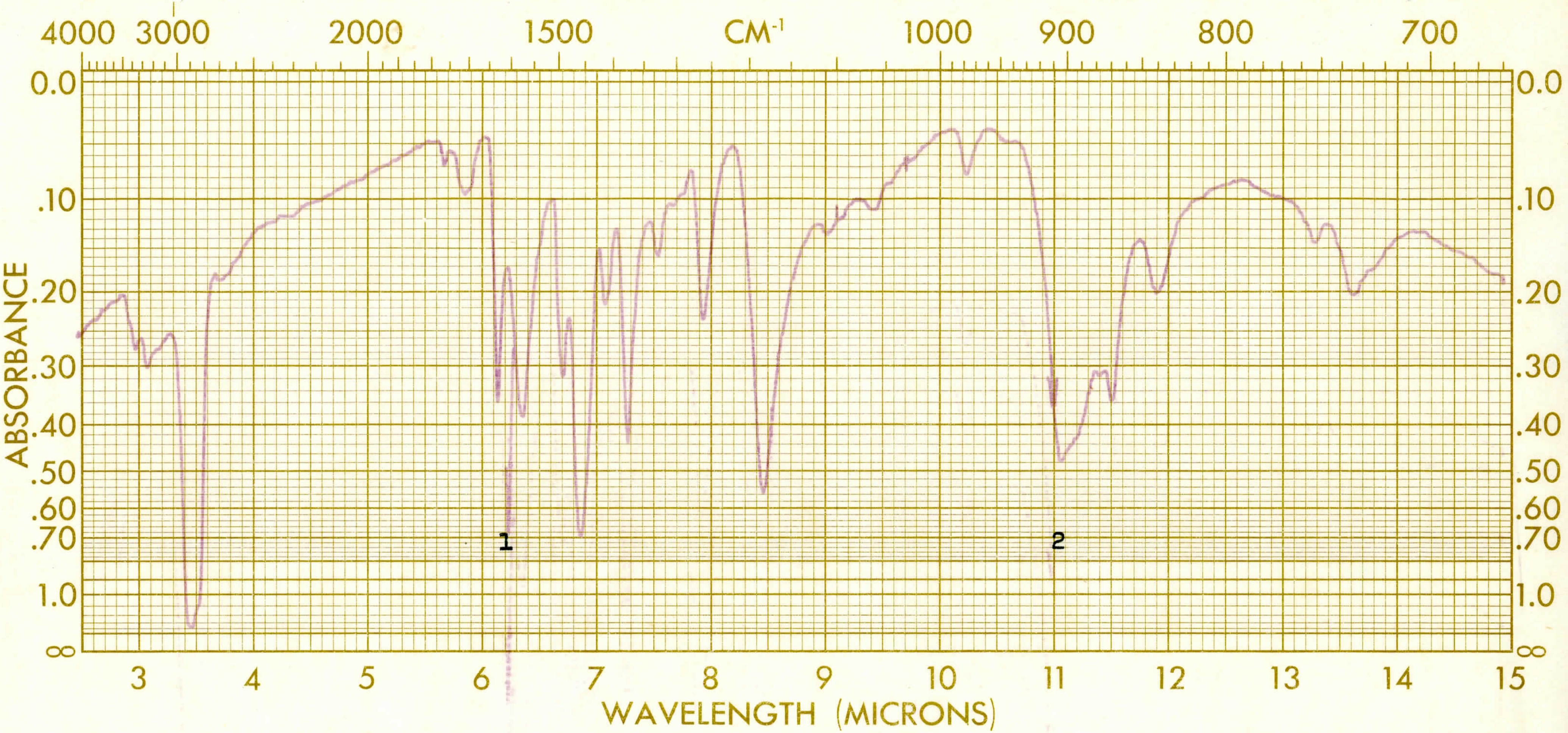
OPERATOR W/.Frick

REMARKS
seht for % analysis

	THEO	FOUND	
C	48.48	42.4	42.50
H	1.69	2.30	1.85

SPECTRUM NO.
SAMPLE

PART NO.137-1280 PE ®
THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-9-71

SAMPLE diethyl thio ester if p-diaminoterephthalic acid

ORIGIN p-diIA and ethyl mercaptan

PURITY 3Rx from EtOH

PHASE nujol mull

THICKNESS

LEGEND polystyrene

1. 6.246

2. 11.032

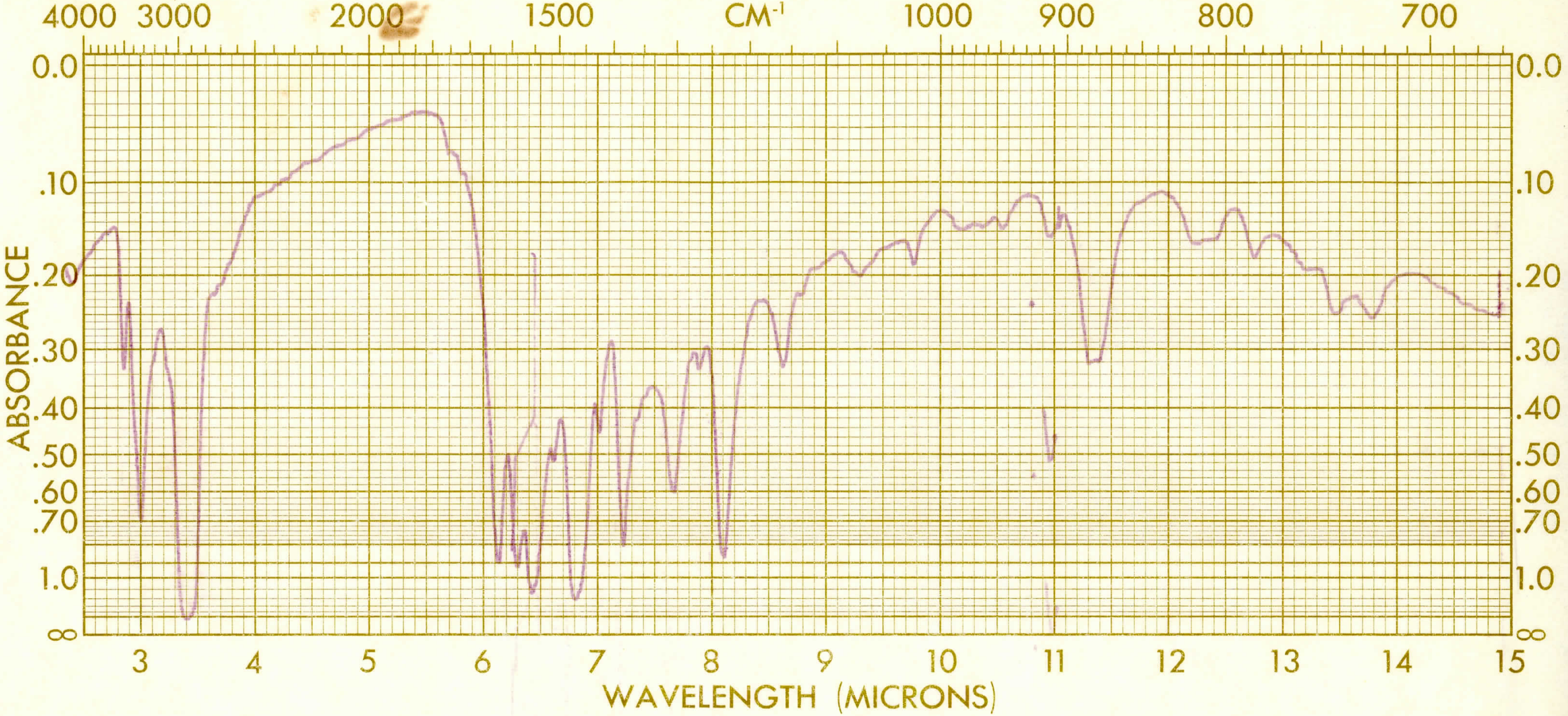
DATE 3/21/69

OPERATOR W. Frick

REMARKS for % analysis

	theo	found
C	50.70	50.86
H	5.63	5.83

SPECTRUM NO.
SAMPLE



SPECTRUM NO. 4-9-65

SAMPLE di n-butylamide of p-diaminoterephthalic acid

ORIGIN p-diIA and n-butyl amine

PURITY Rx EtOH, HOH

PHASE nujol mull

THICKNESS

LEGEND polystyrene

1. 6.246

2. 11.032

DATE 3/19/69

OPERATOR W. Frick

REMARKS % analysis

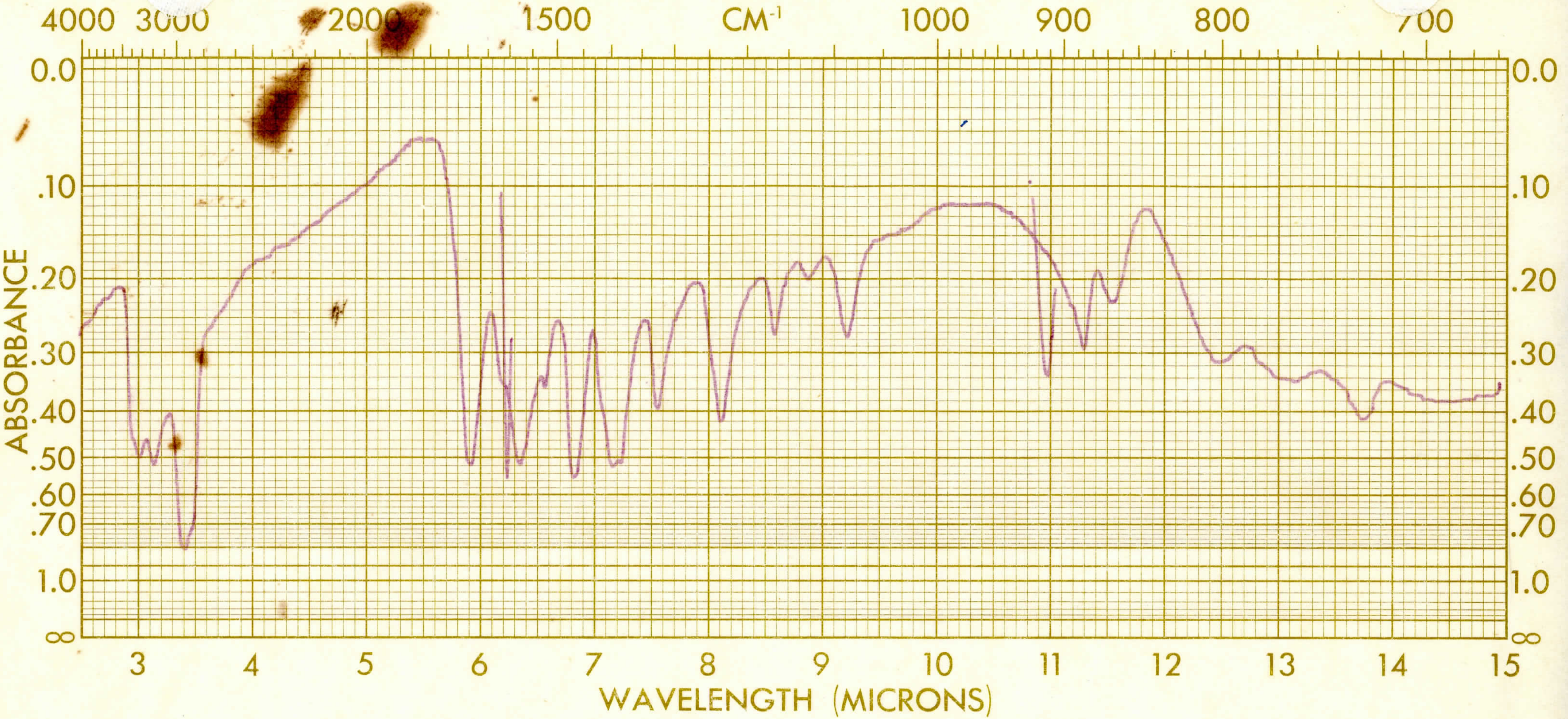
	theo	found
C	62.97	63.07
H	8.55	8.60

SPECTRUM NO.

SAMPLE

PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-9-36

SAMPLE p-diamino terephthalic acid diamide

ORIGIN di-isatoic anhydride and ammonia

PURITY 3 Rx from water

PHASE nujol mull

THICKNESS

LEGEND

1. 6.246

2. 11.032

DATE 2/11/67

OPERATOR W. Frick

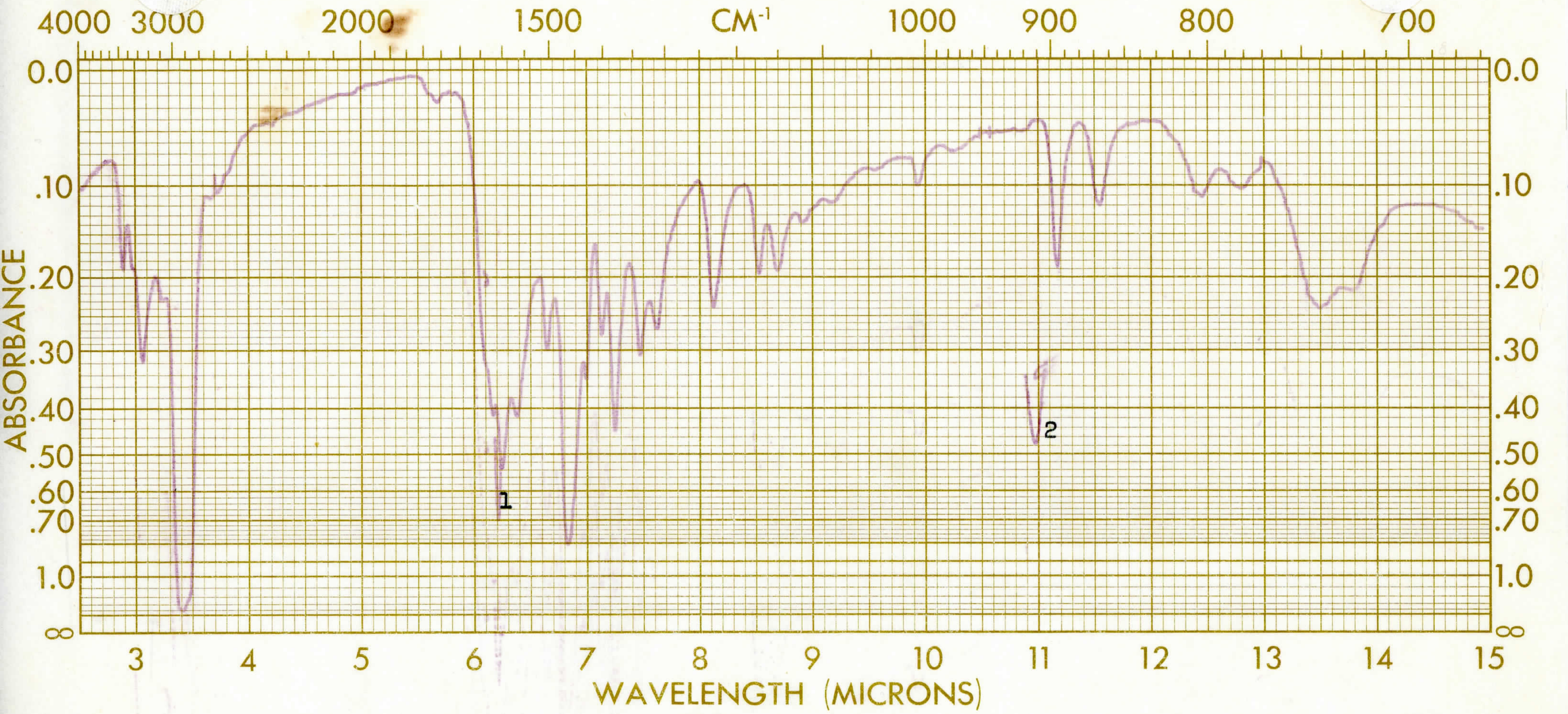
REMARKS % analysis

	theo	found
C	49.5	47.51
H	5.2	5.3

SPECTRUM NO.
SAMPLE

PART NO. 137-1280

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-9-50

SAMPLE NNdimethyl p-di-
amino terephthalic acid
diamide

ORIGIN p-diisotoic
anhydride and methyl
amine

PURITY 3rx water

PHASE nujul mull

THICKNESS

LEGEND polystyrene

1. 6.246

2. 11.032

DATE 3/7/69

OPERATOR W. Frick

REMARKS for % analysis

	theo	found
C	54.1	54.1
H	6.30	6.38

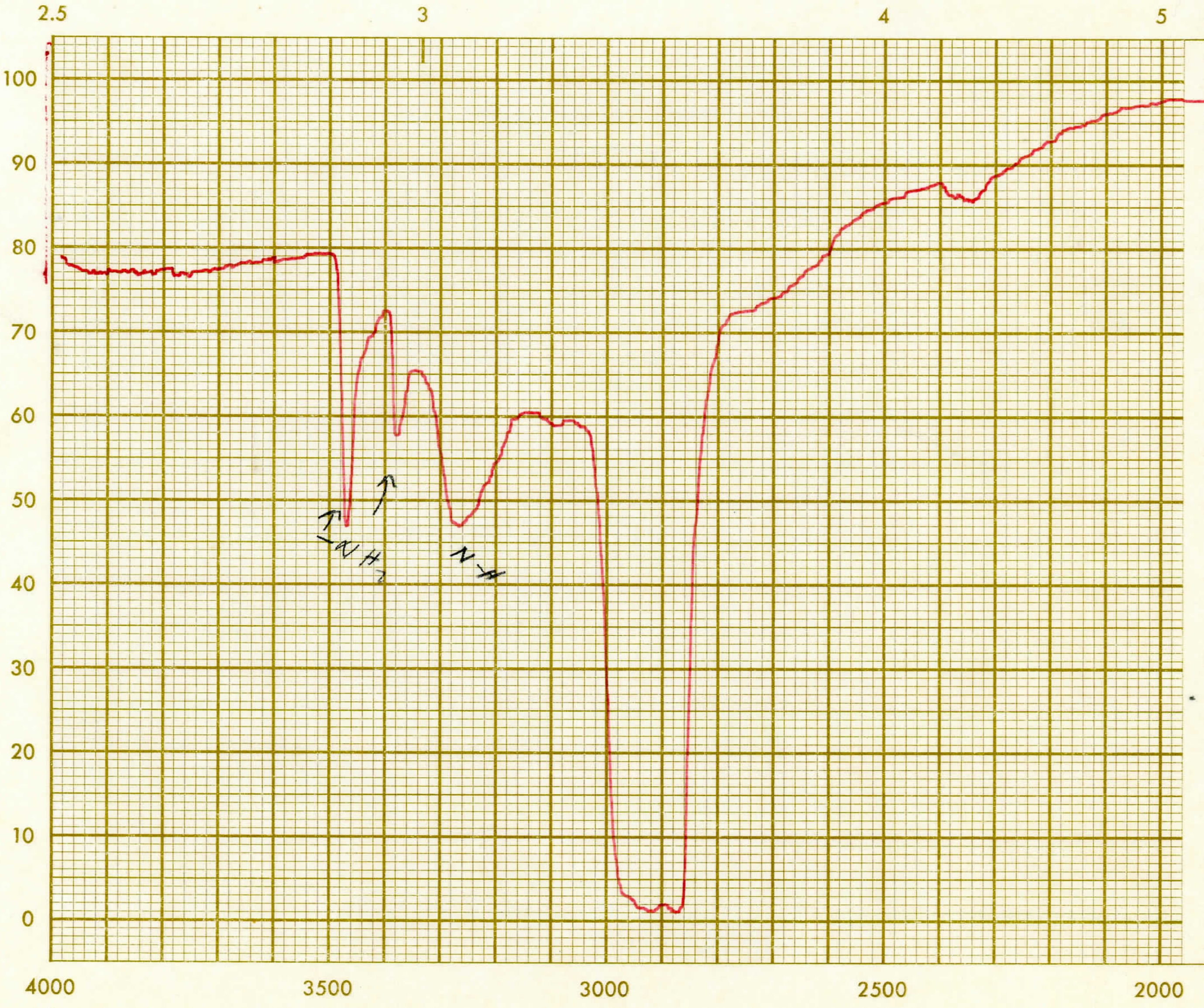
SPECTRUM NO.

SAMPLE

PART NO.137-1280

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

59


2.5
3
4
5
100
90
80
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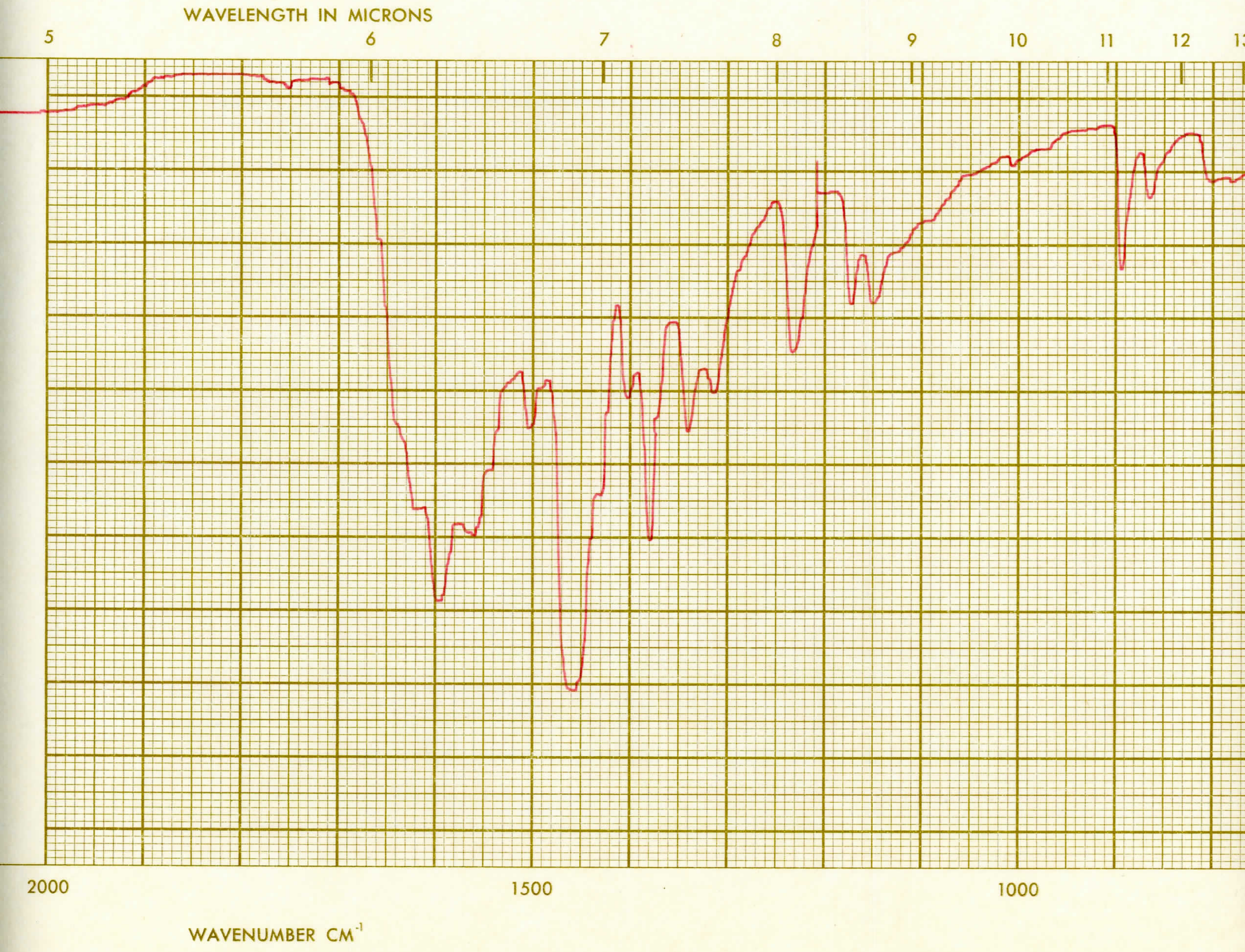
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
-NH2
N-H


WAVELENGTH IN MICRONS
5
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11
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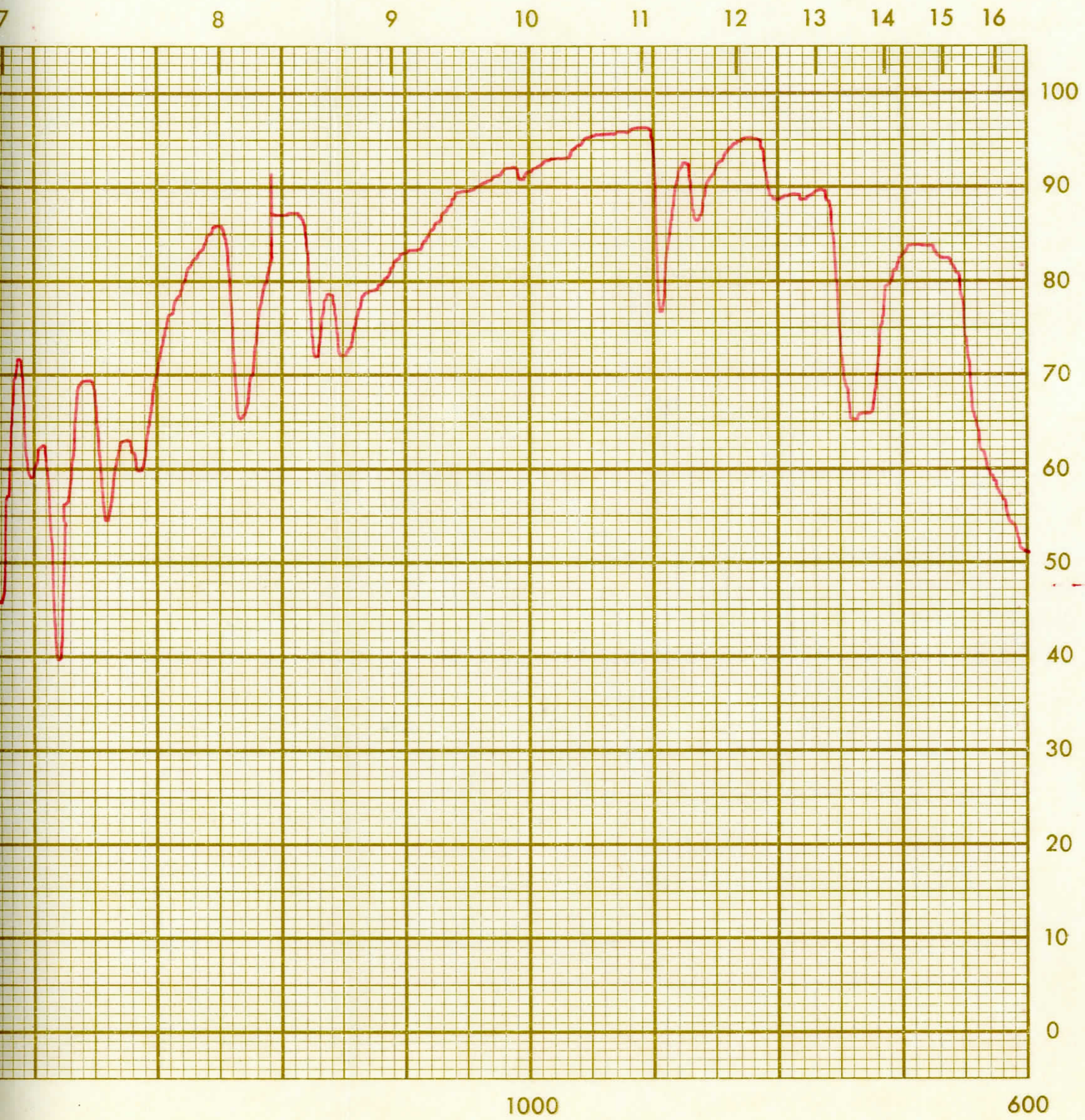
2000
1500
1000
WAVENUMBER CM⁻¹



SPECTRUM NO. 4-9-50a

DATE 3/7/69

SAMPLE Dimethyl amide of p-diamoni terephthalic acid

SOURCE p-diIA +Meamine

STRUCTURE

PATH mm

SOLVENT none

CONCENTRATION -

PHASE nujul mull

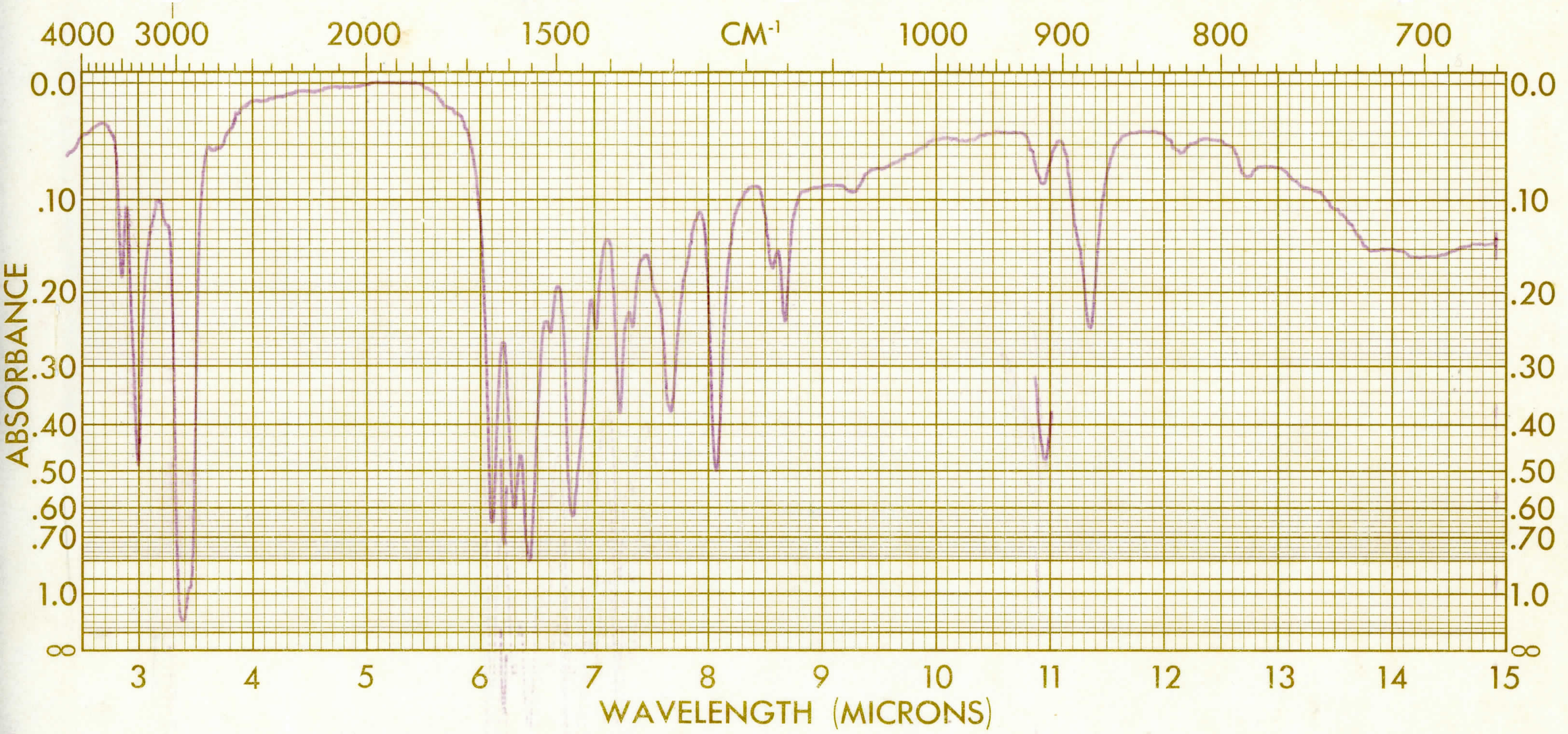
COMMENTS

note 3 NH bands

ANALYST W Frick

Beckman®

INFRARED SPECTROPHOTOMETER



SPECTRUM NO. 4-9-53

SAMPLE NNdiethyl p-di aminoterephthalamide

ORIGIN p-diisotoic anhydride and Etamine

PURITY 3 Rx water-EtOH

PHASE nujul mull

THICKNESS

LEGEND polystyrene

1. 6.246

2. 11.032

DATE 3/7/69

OPERATOR W. Frick

REMARKS for % analysis

	theo	found
C	51.06	51.15
H	6.38	6.41

SPECTRUM NO.
SAMPLE

PART NO.137-1280 PE®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

PRINTED IN U.S.A.

59


WAVELENGTH IN MICRONS
5
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2000
1500
WAVENUMBER CM^{-1}

RUMENTS, INC., FULLERTON, CALIFORNIA, U.S.A.

SPECTRUM NO. 4-9-53a

DATE 3/7/69

SAMPLE NNdiethyl p-diamino-
terephthamide

SOURCE p-diIA and Et amine

STRUCTURE

PATH ______ mm ______

SOLVENT

CONCENTRATION

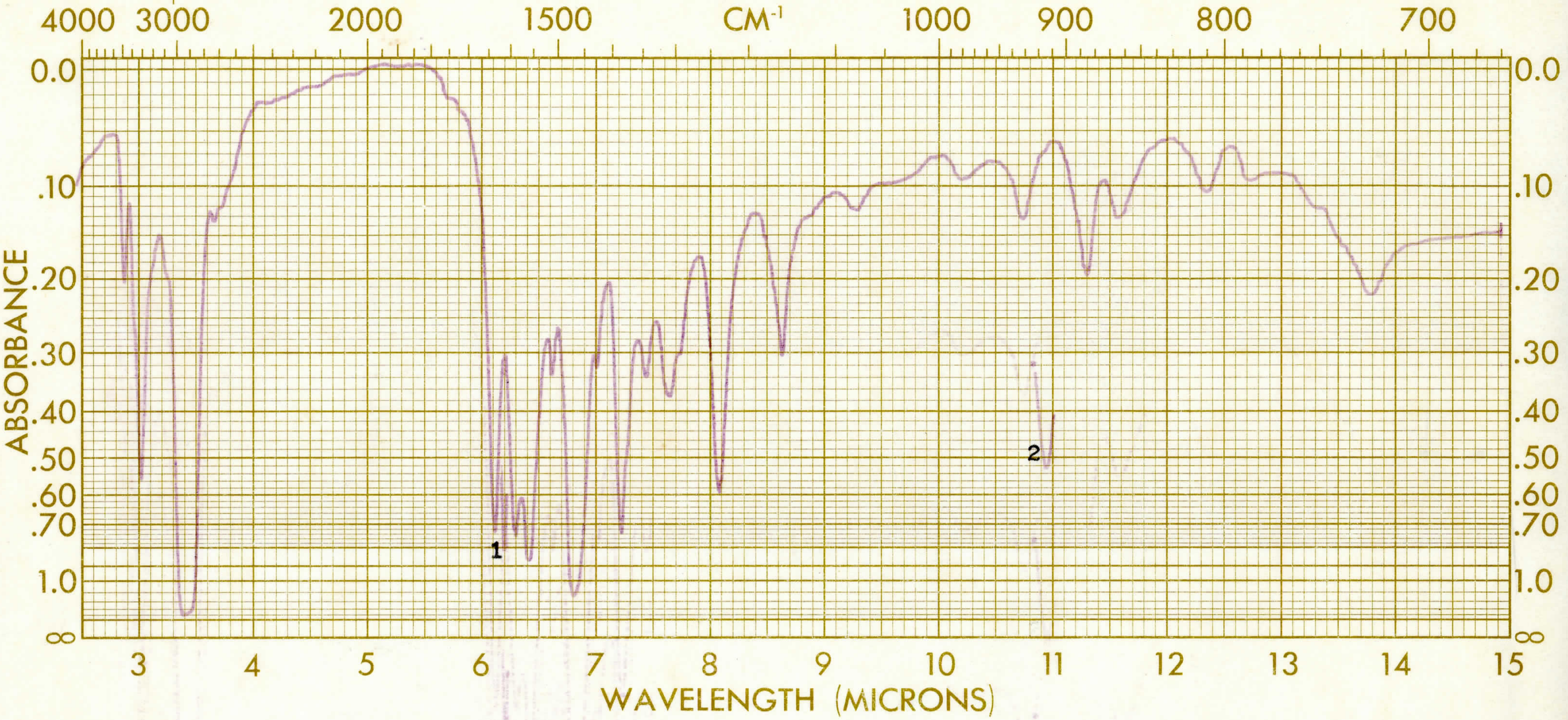
PHASE nujul mull

COMMENTS

ANALYST W. Frick

Beckman®

INFRARED
SPECTROPHOTOMETER



SPECTRUM NO. 4-9-68

SAMPLE diN-propyl amide of p-diaminoterephthalic acid

ORIGIN p-diIA and n-Pr amine

PURITY 4Rx HOH,EtOH

PHASE nujol mull

THICKNESS -

LEGEND polystyrene

1. 6.246

2. 11.032

DATE 3/20/1969

OPERATOR W. Frick

REMARKS for % analysis

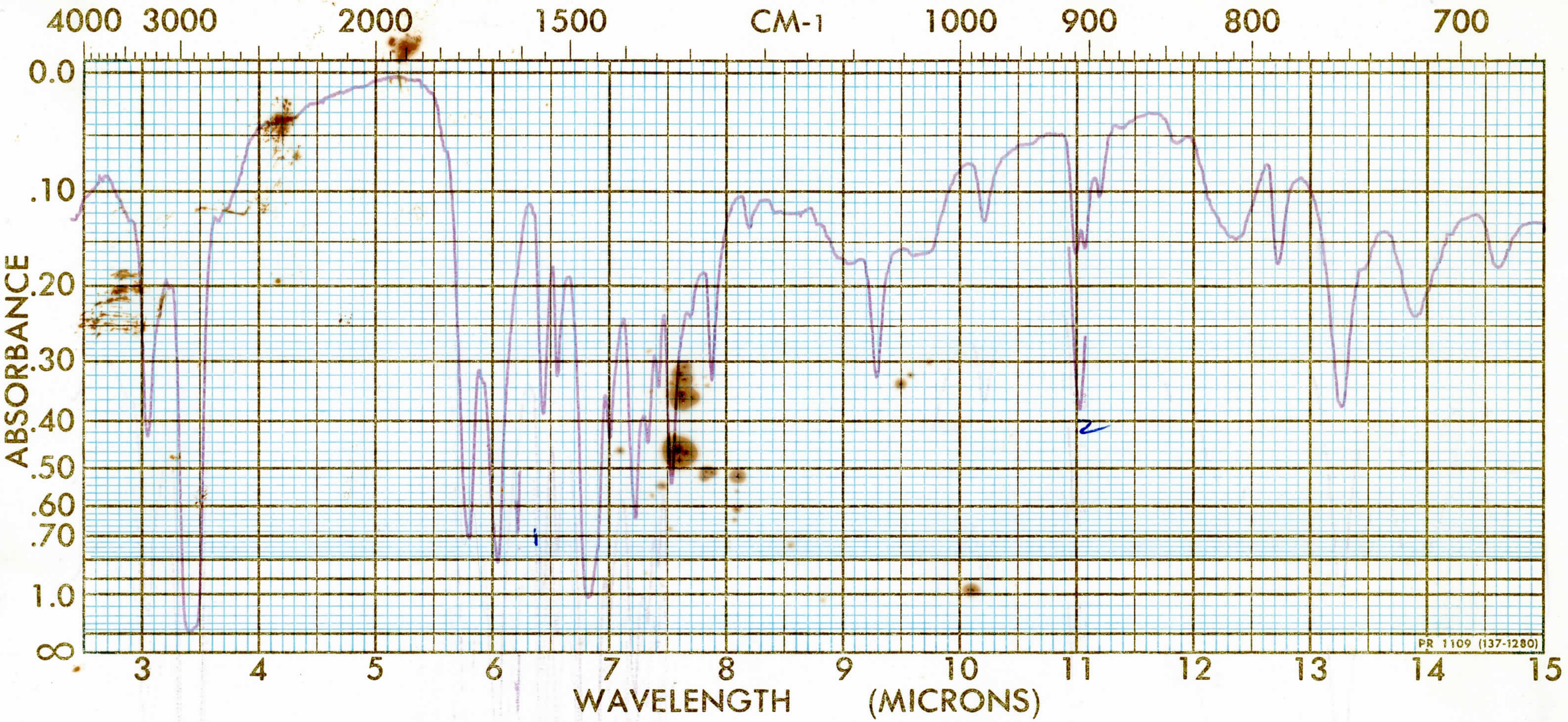
	theo	found
C	60.5	60.30
H	7.92	7.91

SPECTRUM NO.

SAMPLE

PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO 4-9-83

SAMPLE 3,8 din-propyl 2,4,7,9tetraoxo-octahydro 1,3,6,8 naphthotetraazine

ORIGIN din-Pr amide and COCl$_2$

PURITY crude, out of pot

PHASE nujol mull

THICKNESS

LEGEND polystyrene

1. 6.246

2. 11.032

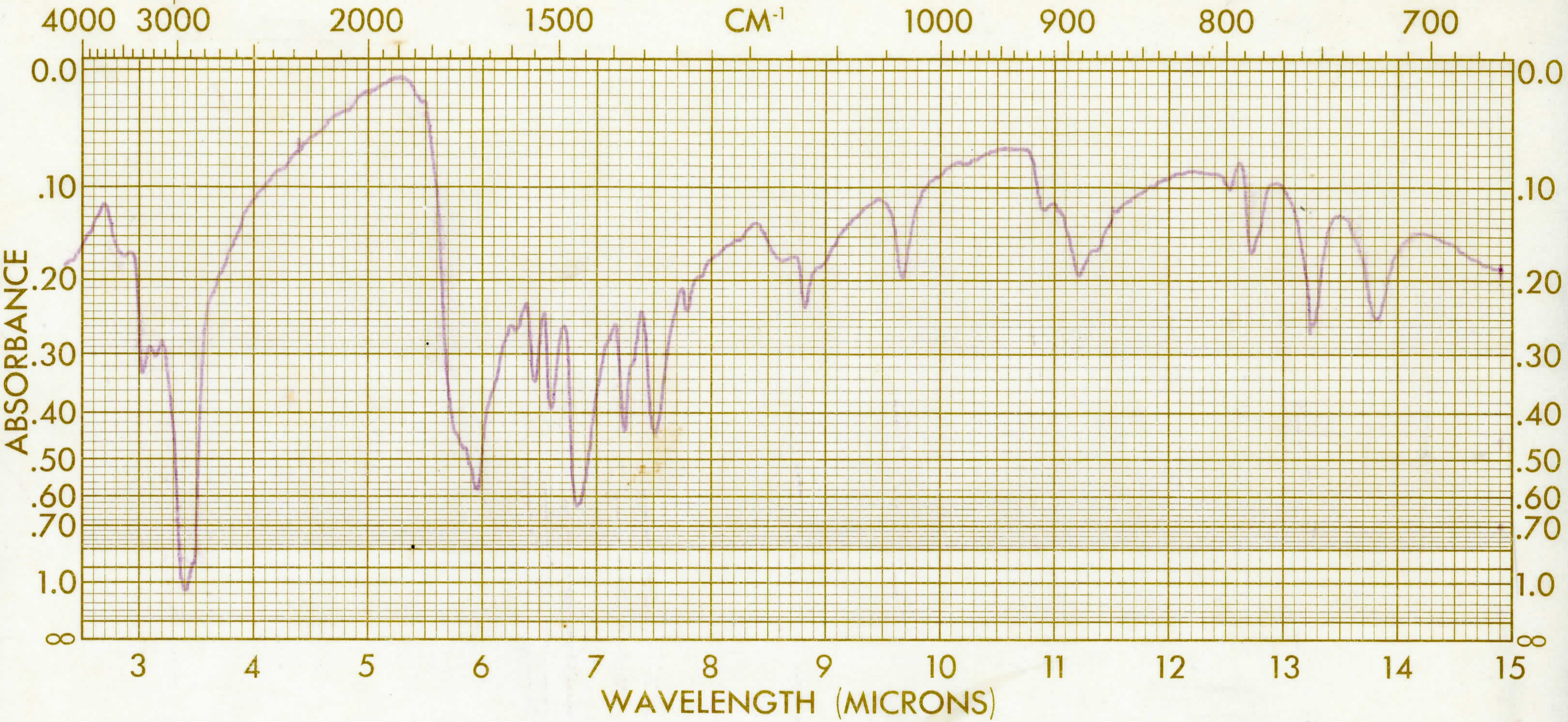
DATE 4/5/69

OPERATOR W. Frick

REMARKS for % analysis

	C	H
theo	61.2	5.63
found	61.47	5.85

SPECTRUM NO.
SAMPLE



SPECTRUM NO. 49-9-66

SAMPLE 2,4,7,9tetraoxo-
octahydro-1,3,6,8naphth
atetrazine

ORIGIN amide and
phosgene

PURITY

PHASE nujol mull

THICKNESS

LEGEND

1.

2.

DATE

OPERATOR

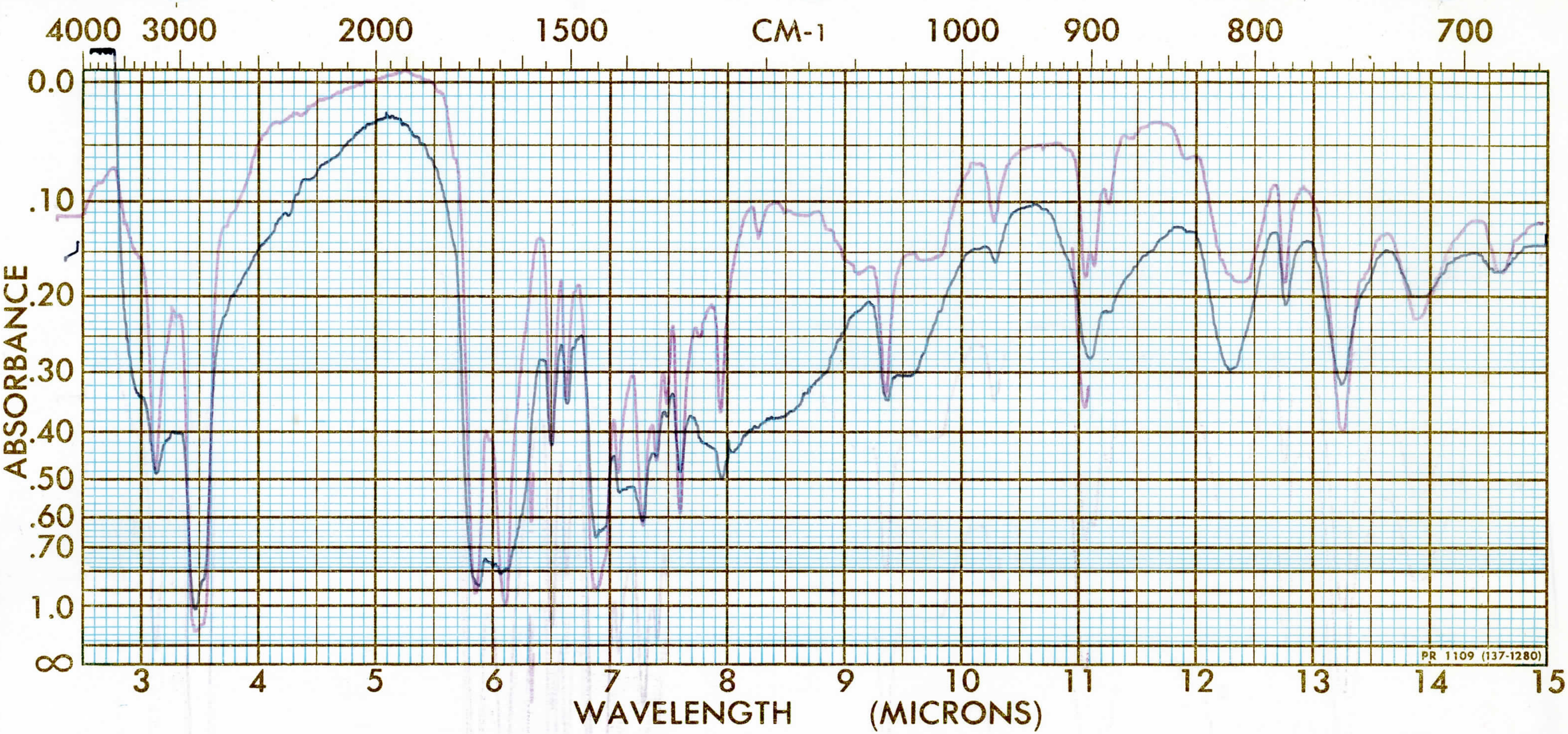
REMARKS

for % analysis
theo found
48,70 C 48.94
2.43 H 2,28

SPECTRUM NO.
SAMPLE

PART NO.137-1280 PE ®

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4-9-84

SAMPLE 3,8 di n-Propyl 2,4,7,9 tetraoxo octahydro 1,3,6,8 naphthatetrazine

ORIGIN black-H^+ ring closure, Red-Phosgene closure

PURITY crude

PHASE nujol mull

THICKNESS

LEGEND polystyrene

1. 6.246

2. 11.032

DATE 4/5/69

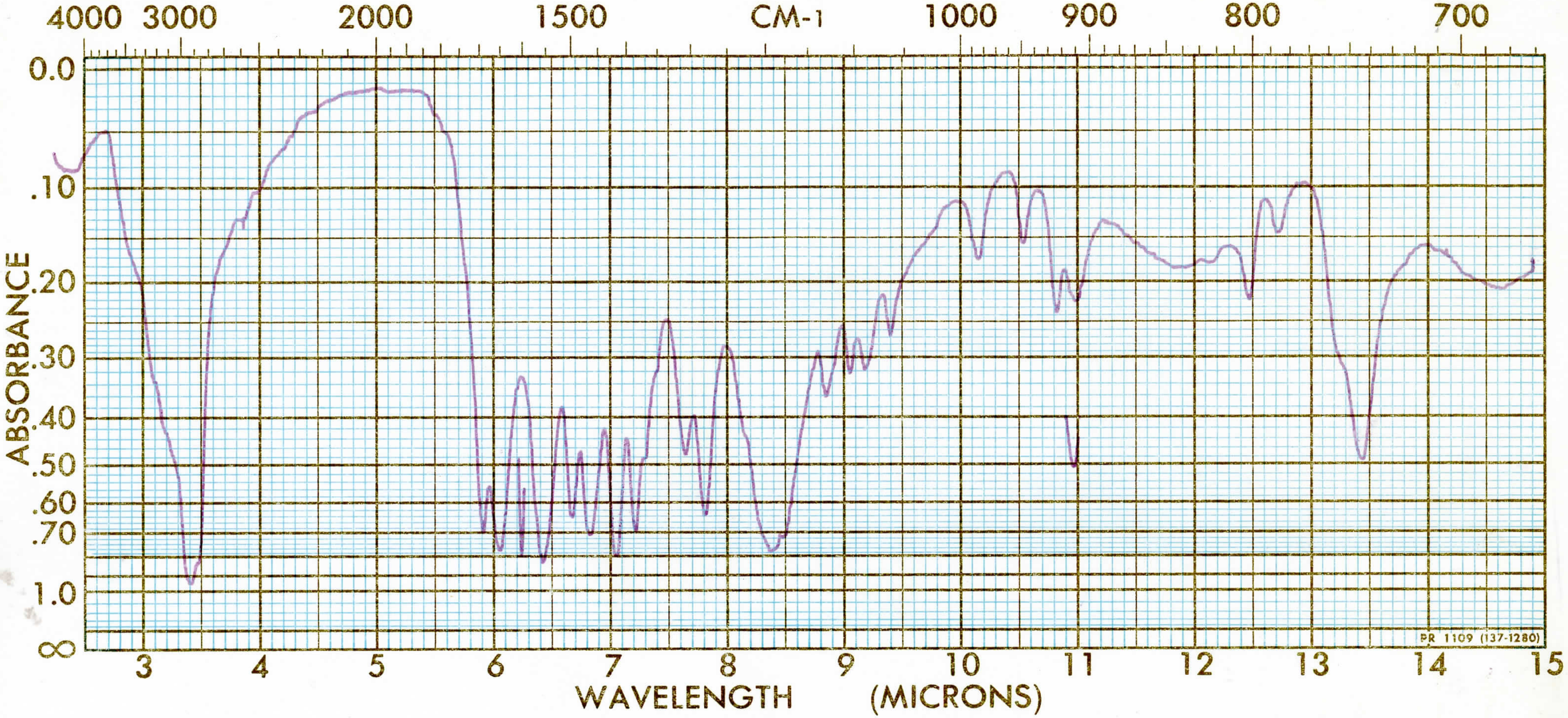
OPERATOR W. Frick

REMARKS

Both show the same compound

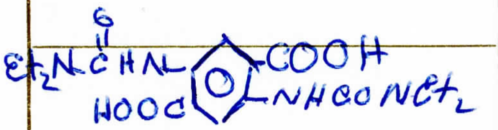
SPECTRUM NO.

SAMPLE



SPECTRUM NO. 4-9-80

SAMPLE N,Ndiethyl diuram dobenzoic acid



ORIGIN p-diIA and/diEthyl amine

PURITY 3Rx EtOH

PHASE nujol mull

THICKNESS

LEGEND polysytrene

1. 6.246

2. 11.032

DATE 4/5/69

OPERATOR W. Frick

REMARKS

	theo	found
N.E.	178	170

for % analysis

	C	H
theo	63.00	7.53
Found	62.71	7.59

SPECTRUM NO.

SAMPLE

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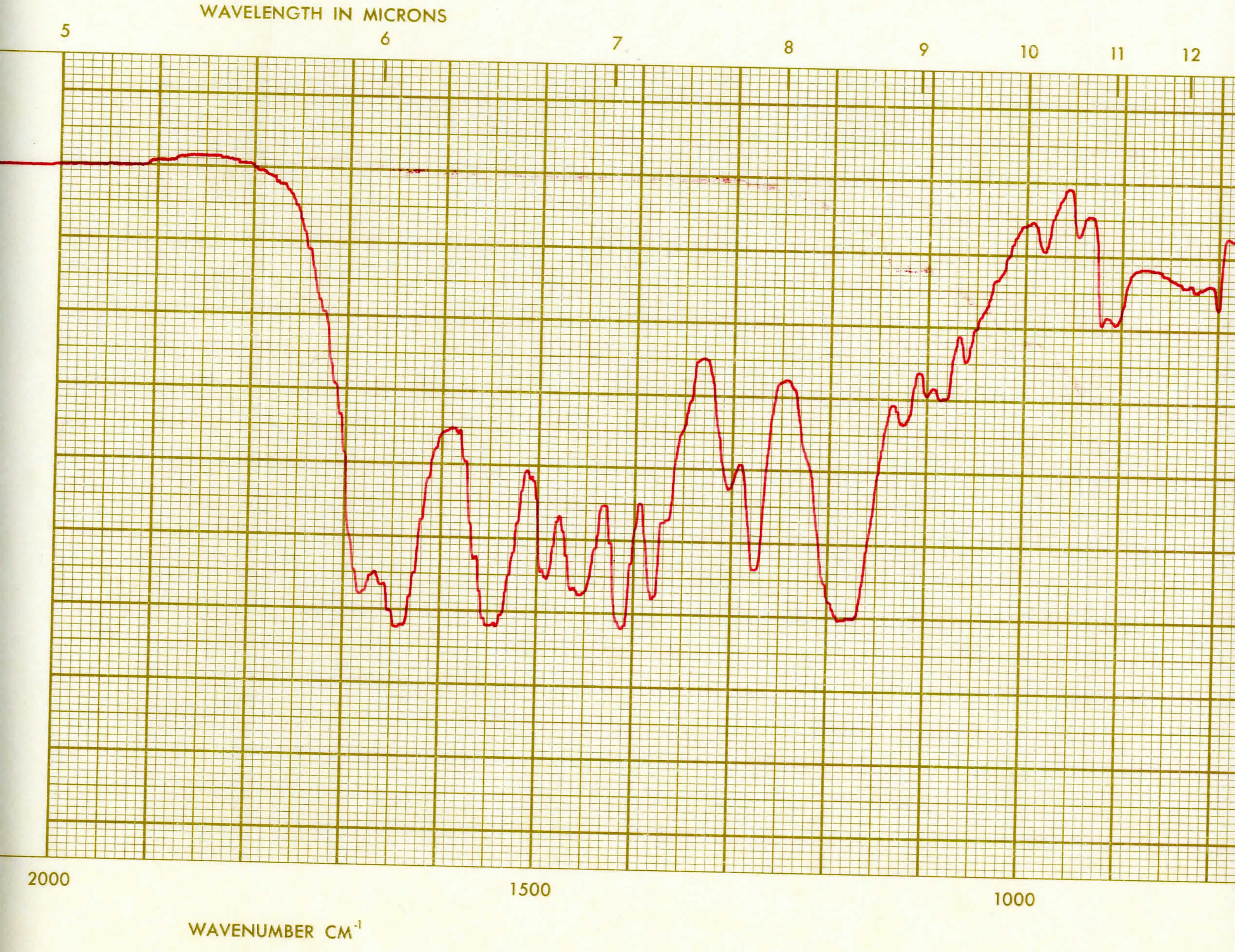
WAVELENGTH IN MICRONS
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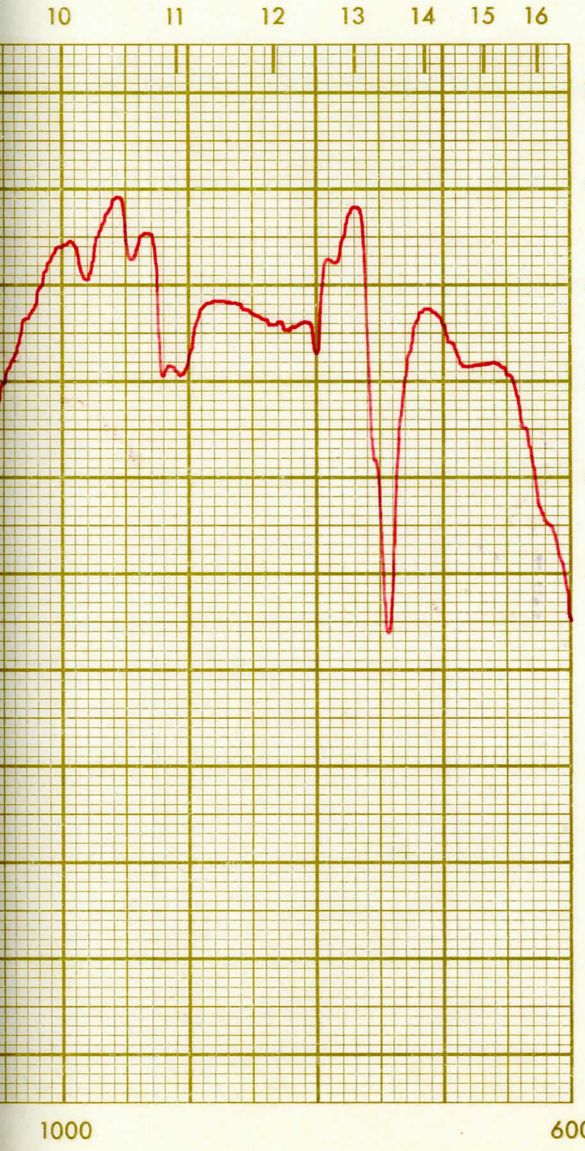
WAVENUMBER CM⁻¹

RTON, CALIFORNIA, U.S.A.



SPECTRUM NO. 4-9-80a

DATE 9/5/69

SAMPLE di Et acid

SOURCE

STRUCTURE

PATH — mm

SOLVENT —

CONCENTRATION —

PHASE nujol mull

COMMENTS

ANALYST W Fink

Beckman®

INFRARED
SPECTROPHOTOMETER