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A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS, (U)
MAY 79 J T BROWNRIGG, D A BUSCH, L P GIERING

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A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS

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125 Middlesex Turnpike
Bedford, MA 01730

CONDUCTED UNDER CONTRACT DOT-CG-91-78-1888

U.S. Coast Guard Research and Development Center
Avery Point, Groton, Connecticut 06340

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May 1979

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16. Abstract Room temperature luminescence (fluorescence) spectra of ninety-six toxic and hazardous materials corrected for instrument response and light output are presented. Eight additional spectra of non-fluorescent toxic and hazardous materials are also included. A brief literature review, estimated detection limits and a spectral code for preliminary identification of these materials are also provided.					
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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures		Approximate Conversions from Metric Measures		
Symbol	When You Know	Multiply by	To Find	Symbol
in ft yd mi	inches feet yards miles	LENGTH		inches inches feet yards miles
		2.5		
		30		
		0.9		
		1.6		
in ² ft ² yd ² mi ²	square inches square feet square yards square miles acres	AREA		square inches square meters square yards square miles acres
		6.5		
		0.09		
		0.8		
		2.6		
oz lb	ounces pounds short tons (2000 lb)	MASS (weight)		ounces pounds short tons
		28		
		0.45		
		0.9		
		2000		
tsp Tbsp fl oz c pt qt gal fl ³ yd ³	teaspoons tablespoons fluid ounces cups pints quarts gallons cubic feet cubic yards	VOLUME		fluid ounces pints quarts gallons cubic feet cubic yards
		5		
		15		
		30		
		0.24		
		0.47		
		0.95		
		3.8		
		0.03		
		0.76		
°F	Fahrenheit temperature	TEMPERATURE (exact)		°C
		5/9 (after subtracting 32)		
°C	Celsius temperature	TEMPERATURE (exact)		°F
		9/5 (then add 32)		



* For other exact conversions and more detailed tables, see *Handbook of Tables for Probability and Statistics*, 2nd Edition, National Bureau of Standards, Gaithersburg, MD, 1975, NBS Monograph 250.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1. INTRODUCTION	1-1
2. PREVIOUS WORK	2-1
3. EXPERIMENTAL	3-1
3.1 Samples and Sources	3-1
3.2 Sample Preparation	3-6
3.3 Data Acquisition	3-7
3.3.1 Absorption Spectra	3-8
3.3.2 Fluorescence Spectra	3-8
3.3.2.1 Standards	3-11
3.3.2.2 Fluorimeter Calibration	3-11
3.4 Data Reduction	3-16
3.4.1 Detection Limits	3-16
3.4.2 Spectral Code	3-17
4. INTERPRETATION	4-1
4.1 Introduction	4-1
4.2 Spectral Similarities and Interferences	4-5
4.2.1 Use of Absorption Spectra	4-5
4.2.2 Comparison of Available Fluorescence Spectra	4-5
4.2.3 General Comments on Samples	4-8

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TABLE OF CONTENTS (con't.)

<u>Section</u>		<u>Page</u>
4.2.4	Effect of Substituents on Aromatic Rings	4-15
4.2.4.1	Alkyl Substituents	4-15
4.2.4.2	Hydroxy Substituents	4-18
4.2.4.3	Amino Substituents	4-19
4.2.4.4	Cyano Substituents	4-19
4.2.4.5	Nitro Substituents	4-19
4.2.4.6	Halogen Substituents	4-20
4.2.4.7	Acid and Acid Chloride Substituents	4-20
4.2.4.8	Esters	4-24
4.2.5	Polynuclear Aromatic Hydrocarbons (PAH)	4-26
4.2.6	Heteroatom Compounds	4-28
4.2.7	Oils	4-29
4.2.8	Herbicides and Insecticides	4-32
4.2.9	Miscellaneous Compounds	4-37
5.	SUMMARY AND CONCLUSIONS	5-1
6.	REFERENCES	6-1
	COMPENDIUM	

LIST OF TABLES

<u>Table Number</u>		<u>Page</u>
TABLE 1.	Previously Published Absorption Spectra	2-2
TABLE 2.	Previously Published Fluorescence Spectra and Quantum Yields	2-6
TABLE 3.	Chemical Source List	3-2
TABLE 4.	Effect of Slit Width on 0.111 ppm Anthracene Signal in Cyclohexane	3-9
TABLE 5.	Comparison of Relative Vibronic Intensities of Anthracene in Ethanol	3-14
TABLE 6.	Relative Vibronic Intensities of Benzene and Fluoranthene	3-15
TABLE 7.	Summary of Fluorescent Toxic and Hazardous Materials	4-2
TABLE 8.	Comparison of Corrected Relative Fluorescence Intensities	4-6
TABLE 9.	Summary of Emission Region for Benzene Substituted Compounds	4-24
TABLE 10.	Oils Studied Under Contract	4-30
TABLE 11.	Summary of Herbicides and Insecticides Studied	4-33
TABLE 12.	List of Coded Spectra	4-41
TABLE 13.	Summary of Experimental Parameters and Results	4-44

LIST OF TABLES (con't.)

<u>Table Number</u>		<u>Page</u>
TABLE 14.	Effect of Solvent on Anthracene	5-2
TABLE 15.	Expected Influence of Substituents on the Luminescence of Aromatic Hydrocarbons	5-9

LIST OF FIGURES

<u>Figure Numbers</u>		<u>Page</u>
FIGURE 1	Undecyl Benzene 115.0 ppm in CH 5,5/5,5 nm Slits - Emission Scans	4-10
FIGURE 2	Undecyl Benzene 115.0 ppm in CH 5,5/5,5 nm Slits - Emission Scans	4-11
FIGURE 3	Undecyl Benzene 115.0 ppm in CH 5,5/5,5 nm Slits - TLS Contour	4-12
FIGURE 4	Undecyl Benzene 115.0 ppm in CH 5,5/5,5 nm Slits - TLS Contour	4-13
FIGURE 5	Anthracene 0.1 ppm in CH 5,5/5,5 nm Slits - TLS Contour	4-14
FIGURE 6	Zirconium Acetate - Emission Scan in 1.0 M H ₂ SO ₄	4-16
FIGURE 7	1.0 M H ₂ SO ₄ - Emission Scan	4-17
FIGURE 8	Emission Spectrum of Tannic Acid	4-23
FIGURE 9	Absorption Spectra of Several Herbicides and Pesticides	4-38
FIGURE 10	Absorption Spectra of Several Herbicides and Pesticides	4-39
FIGURE 11	P-Toluidine 10.0 ppm in CH 10,10/2,2 nm Slits - Emission Scan	5-3
FIGURE 12	P-Toluidine 10.0 ppm in EtOH 10,10/2,2 nm Slits - Emission Scan	5-4
FIGURE 13	P-Toluidine 10.0 ppm in 70% CH ₃ CN 10,10,2,2,nm Slits - Emission Scan	5-5
FIGURE 14	P-Tert Butylphenol 10.0 ppm in CH 10,10/2,2 nm Slit - Emission Scan	5-6
FIGURE 15	P-Tert Butylphenol 10.0 ppm in EtOH 10,10/2,2 nm Slit - Emission Scan	5-7
FIGURE 16	Dichlone 54 ppm/MCH Ex. 370 nm	5-11
FIGURE 17	Dichlone 54 ppm/MCH Ex. 490 nm	5-12

1. INTRODUCTION

This final report, prepared for the United States Coast Guard Research and Development Center at Groton, Connecticut, summarizes work performed by Baird Corporation on Contract No. DOT-CG-81-78-1888. Room temperature luminescence (fluorescence) spectra of 100 toxic and hazardous materials are presented. In addition, a brief literature review, estimated detection limits and a spectral code for preliminary identification of these materials are given.

The Coast Guard is charged with the responsibility of protecting the nation's waterways from accidental or deliberate discharge of petroleum products and other toxic and hazardous materials. In order to provide the capability to detect, identify and quantify hazardous substances found in navigable waterways, the Coast Guard intends to develop an in-house system of analytical techniques to handle this problem. It is the purpose of this report to demonstrate the utility of luminescence data for the identification and quantitation of hazardous materials and hopefully contribute to a successful methodology for a difficult problem.

The high sensitivity of luminescence plus the specificity afforded by the two spectral signatures of excitation and emission suggest that luminescence may afford a relatively simple and inexpensive approach to the identification of a significant fraction of unknown hazardous materials.

2. PREVIOUS WORK

As part of this contract, a brief literature review to determine existing corrected emission spectra for comparison with those developed in the program was conducted. This literature search was expanded to include both corrected and uncorrected emission and excitation spectra as well as available absorption spectra and fluorescence quantum yields.

In Table 1 previously published absorption spectra are tabulated. It was necessary to collect this data for as many of the 100 toxic and hazardous materials studied in this contract to compare with the absorption spectra obtained in our laboratories for these materials. Absorption spectra, taken on the toxic and hazardous materials, were used to aid in the selection of the appropriate concentration and excitation wavelength for fluorescence measurements and to check the purity by comparison with published data, of the compounds furnished by the Coast Guard. Compounds supplied by the Coast Guard which did not agree with the published data are tabulated in Section 4 of this report.

In Table 2 previously published uncorrected and corrected fluorescence spectra and fluorescence quantum yields are tabulated. This careful review of the literature showed that there exists very little corrected fluorescence data, especially for the hundred or more materials of interest to the Coast Guard. Where possible a comparison was made (same or similar solvent and concentration) with published corrected fluorescence spectra and corrected spectra obtained in this contract. The discussion of this comparison can be found in Section 4.

TABLE 1. PREVIOUSLY PUBLISHED ABSORPTION SPECTRA

	<u>Compound</u>	<u>Solvent</u>	<u>Reference</u>
1.	acenaphthene	cyclohexane ethanol methanol	5 9 21
2.	acetone	ethanol	4
3.	acridine	ethanol methanol	5,9 21
4.	aniline	ethanol cyclohexane isooctane	5 5,21 9
5.	anisoyl chloride	cyclohexane	21
6.	anthracene	cyclohexane methanol ethanol isooctane	5,9,21 10 11 11
7.	1,2 benzanthracene (benz (a) anthracene)	ethanol pentane methanol	9,10 12 21
8.	benzene	cyclohexane benzene vapor	5,9,21 5 21
9.	benzenesulfonic acid	methanol methanol/KOH methanol/HCl	21 21 21
10.	benzo (g,h,i) fluoranthene	cyclohexane	5
11.	benzonitrile	cyclohexane	21
12.	benzo (a) pyrene	ethanol dioxane methanol	10 21 19
13.	benzoyl chloride	cyclohexane	21
14.	benzyl alcohol	cyclohexane ethanol methanol	5 5,14 21
15.	benzylamine	isooctane methanol	9 21

TABLE 1. PREVIOUSLY PUBLISHED ABSORPTION SPECTRA (con't)

	<u>Compound</u>	<u>Solvent</u>	<u>Reference</u>
16.	benzyltriethyl ammonium chloride	methanol	21
17.	brucine	methanol	21
18.	p-tert-butylphenol	cyclohexane	21
19.	catechol	cyclohexane methanol	9 21
20.	m-chloroaniline	methanol	21
21.	p-chloroaniline	methanol	21
22.	1-chloronaphthalene	methanol	21
23.	2-chloronaphthalene	cyclohexane	5
24.	p-chlorophenol	methanol	21
25.	p-chlorotoluene	cyclohexane	21
26.	4-chloro-o-toluidine	methanol	21
27.	chrysene	cyclohexane ethanol methanol pentane	5 5,9 10,21 12
28.	m-cresol	cyclohexane methanol	9 21
29.	o-cresol	cyclohexane methanol methanol/KOH	9 21 21
30.	p-cresol	cyclohexane ethanol methanol	5,9 5 21
31.	cumene	cyclohexane	21
32.	cymene	cyclohexane	21
33.	dibenz(a,h)anthracene	benzene ethanol methanol	5 9 10
34.	dichlorodiphenylsilane	methanol	21

TABLE 1. PREVIOUSLY PUBLISHED ABSORPTION SPECTRA (con't)

	<u>Compound</u>	<u>Solvent</u>	<u>Reference</u>
35.	2,4-dichlorophenol	methanol methanol/KOH	21 21
36.	2,4-dimethylphenol (2,4-xylenol)	cyclohexane methanol	9 21
37.	3,5-dimethylphenol	methanol	21
38.	4,6-dinitro-o-cresol	methanol	21
39.	2,4-dinitrophenol	ethanol methanol	24 21
40.	diphenylamine	cyclohexane	21
41.	diphenylether	methanol	21
42.	1,1-diphenylhydrazine	methanol	21
43.	2,4-di-tert-butylphenol	methanol methanol/KOH	21 21
44.	2,6-di-tert-butylphenol	methanol	21
45.	dowtherm (4-biphenylphenylether)	methanol	21
46.	2,4-di-sec-butylphenol	cyclohexane methanol	5 21
47.	fluoranthene	cyclohexane methanol	5 21
48.	gallic acid, hydrate	methanol	21
49.	hydroquinone	methanol	21
50.	n-methylaniline	methanol	21
51.	α -methylstyrene	cyclohexane	21
52.	naphthalene	cyclohexane ethanol methanol	5 9 21
53.	1-naphthylamine	cyclohexane ethanol	5,21 5,9,14

TABLE 1. PREVIOUSLY PUBLISHED ABSORPTION SPECTRA (con't)

	<u>Compound</u>	<u>Solvent</u>	<u>Reference</u>
54.	2-nitroaniline	ethanol hexane water .01 M NaOH methanol	24 24 24 24 21
55.	o-nitrophenol	methanol methanol/KOH	21 21
56.	phenol	cyclohexane methanol	5,9 5
57.	p-nonylphenol	cyclohexane	21
58.	quinoline	ethanol cyclohexane	5 9
59.	resorcinol	ethanol methanol	9 21
60.	salicylic acid	ethanol	11
61.	styrene	cyclohexane	5,21
62.	tannic acid	methanol	21
63.	1,2,3,4,-tetrahydro- naphthalene	methanol	21
64.	toluene	cyclohexane methanol	5,9 21
65.	p-toluenesulfonic acid	methanol	21
66.	o-toluidine	isooctane	9
67.	p-toluidine	cyclohexane	21
68.	1,3,5-triethylbenzene	cyclohexane methanol	5 21
69.	m-xylene	cyclohexane	5,21
70.	o-xylene	cyclohexane	5,21
71.	p-xylene	cyclohexane	5,21

TABLE 2. PREVIOUSLY PUBLISHED FLUORESCENCE SPECTRA
AND QUANTUM YIELDS

<u>Compound</u>	<u>Quantum Yield</u>	<u>Solvent</u>	<u>Fluorescence Spectrum</u>	<u>Ref.</u>
1. acenaphthene	0.6(8)* 0.31(7) 0.39(6)	cyclohexane hexane ethanol	corrected em	(5)
2. acetone	.01±.003(2)	ethanol hexane	uncorrected em corrected em	(4) (20) (25)
3. acridine		ethanol	corrected em	(5)
4. aniline	0.08(5) (8) 0.08(2)	cyclohexane ethanol vapor	corrected em corrected em uncorrected em	(5) (5) (4)
5. anthracene	0.35(5) 0.27(7) (26) 0.31(7)	cyclohexane methanol ethanol hexane	corrected em corrected em corrected em	(5) (5) (10) (15) (26)
6. 1,2 benzanthracene	0.20(6) 0.20(2)	methanol diethylether ethanol hexane	uncorrected em uncorrected em	(13) (17)
7. benzene	0.07(5) 0.04(7) 0.04(6) (26)	cyclohexane neat hexane ethanol	corrected em corrected em corrected em	(5) (5) (26)
8. benzo(g,h,i) fluor- anthene	0.30(5)	cyclohexane	corrected em	(5)
9. benzo(a)pyrene		ethanol methanol	corrected ex/em uncorrected ex/em	(10) (19)
10. benzyl alcohol	0.08(5)	cyclohexane ethanol	corrected em corrected em	(5) (5)
11. t-butylphenol		methanol	uncorrected em/ex	(16)
12. catechol		water	uncorrected em/ex	(16)
13. p-chloroaniline	0.017(22)	water		
14. 1-chloronaphthalene	0.058(2)	cyclohexane ethanol-ether- 77°K	uncorrected em/ex	(16)
15. 2-chloronaphthalene		cyclohexane	corrected em	(5)
16. p-chlorophenol	0.0089(22)	water		

TABLE 2. PREVIOUSLY PUBLISHED FLUORESCENCE SPECTRA
AND QUANTUM YIELDS (con't)

<u>Compound</u>	<u>Quantum Yield</u>	<u>Solvent</u>	<u>Fluorescence Spectrum</u>	<u>Ref.</u>
17. p-chlorotoluene	0.02 (18)	ethanol		
18. chrysene	0.14 (5)	cyclohexane	corrected em	(5)
	0.17 (6)	ethanol	corrected em	(5)
		methanol	corrected ex/em	(10)
		pentane	corrected em	(12)
19. o-cresol		vapor	uncorrected em	(4)
20. m-cresol	0.25 (23)	water		
21. p-cresol	0.09 (5,8)	cyclohexane	corrected em	(5)
		ethanol	corrected em	(5)
	0.088 (8)	water		
22. dibenz (a,h) anthracene		benzene	corrected em	(5)
		methanol	corrected ex/em	(10)
23. 2,4-dimethylphenol		methanol	uncorrected ex/em	(16)
24. diphenylamine		cyclohexane	uncorrected ex/em	(16)
25. dowtherm (4-biphenyl-phenyl- ether)	0.09 (8)	cyclohexane		
26. ethylbenzene	0.18 (8)	cyclohexane	corrected em	(5)
27. fluoranthene	0.30 (8)	cyclohexane	corrected em	(5)
		methanol	corrected ex/em	(10)
28. gallic acid,hydrate		water	uncorrected ex/em	(16)
			uncorrected em	(15)
29. hydroquinone		water	uncorrected ex/em	(16)
30. methoxychlor		ethanol	uncorrected em	(15)
31. naphthalene	0.23 (5)	cyclohexane	corrected em	(5)
	0.10 (1)	hexane	uncorrected ex/em	(16)
	0.205 (1)	polar		
	0.19 (26)	ethanol	corrected em	(26)
32. 1-naphthylamine	0.38 (8)	cyclohexane	corrected em	(5)
		ethanol	corrected em	(5)
33. (PCB) 4,4-dichloro-biphenyl		cyclohexane	uncorrected ex/em	(16)

TABLE 2. PREVIOUSLY PUBLISHED FLUORESCENCE SPECTRA AND QUANTUM YIELDS (con't)

<u>Compound</u>	<u>Quantum Yield</u>	<u>Solvent</u>	<u>Fluorescence Spectrum</u>	<u>Ref.</u>
34. phenol	0.066 (8)	cyclohexane	corrected em	(5)
		methanol	corrected em	(5)
	0.22 (15)	water		
	0.19 (26)	ethanol	corrected em	(26)
35. quinoline		ethanol	corrected ex/em	(5)
36. salicylic acid, sodium salt		.0001N KOH	uncorrected ex/em	(16)
37. styrene		cyclohexane	corrected ex/em	(5)
38. toluene	0.17 (5)	cyclohexane	corrected em	(5)
	0.23 (7)	hexane		
39. p-toluidine		cyclohexane	uncorrected ex/em	(16)
40. 1,3,5-triethyl- benzene	0.12 (5)	cyclohexane	corrected ex/em	(5)
41. uranyl acetate	0.04 (15)	water		
42. uranyl sulfate		acid solution		(6)
43. m-xylene	0.17 (8)	cyclohexane	corrected ex/em	(5)
44. o-xylene	0.19 (8)	cyclohexane	corrected ex/em	(5)
45. p-xylene	0.40 (8)	cyclohexane	corrected ex/em	(5)
	0.20 (1)	polar		

*The numbers in parentheses are reference numbers for quantum yield measurements.

3. EXPERIMENTAL

3.1 Samples and Sources

Table 3 contains a list of the chemicals used in this contract. Included in this list is the supplier of the chemical and the grade of the chemical used.

TABLE 3. CHEMICAL SOURCE LIST

<u>Compound</u>	<u>Source</u>	<u>Purity</u>
acenaphthene	Fluka	purum
acetone	Chem Service, Inc.	high purity
acridine	Fluka	≥ 98%
aniline	Fluka	99.5%
anisoyl chloride	MCB	--
anthracene	Fluka	≥ 99%
Aroclor 1242 1254	RFR Corporation	--
atrazine	Chemical Service	99%
azinphosmethyl	Chemical Service	96%
benz(a)anthracene	McKay	--
benz(a)pyrene	Aldrich	98%
benzene	Chemical Service	high purity
benzonitrile	Chemical Service	high purity
benzoyl chloride	Fluka	99.5%
benzyl alcohol	Chemical Service	high purity
benzyl amine	Fluka	≥ 99%
benzyl amine	MCB	--
benzyltriethylammonium chloride	MCB	practical
Bisphenol A	Aldrich	--
brucine	Fluka	purum
butylbenzylphthalate	Chemical Service	--
o-tert-butylphenol	Aldrich	99%
p-tert-butylphenol	Fluka	~99%
carbaryl	Chemical Service	--
carnauba wax	Fisher	#1 yellow
castor oil	MCB	USP
catechol	Chemical Service	high purity
4-chloroaniline	Fluka	≥ 99%

TABLE 3. CHEMICAL SOURCE LIST (con't)

<u>Compound</u>	<u>Source</u>	<u>Purity</u>
1-chloronaphthalene	Fluka	≥ 99%
4-chlorophenol	Fluka	≥ 99%
chloropyrifos	Chemical Service	98.5%
4-chlorotoluene	RFR Corporation	--
4-chloro-o-toluidine	MCB	practical
chrysene	Duke	(standard)
coconut oil	---	--
cod liver oil	Squibb	--
copper naphthenate	Chemical Service	lab assist.
cottonseed oil	---	--
coumaphos	Chemical Service	99%
o-cresol	Fluka	≥ 99%
p-cresol	Fluka	≥ 99%
cumene	Chemical Service	high purity
p-cymene	Chemical Service	high purity
DDD	RFR Corporation	--
DDT	RFR Corporation	--
diazinon	Chemical Service	92.4%
1,2,5,6-dibenzanthracene	Baird sample	--
dicamba	Chemical Service	94%
dichlone	Chemical Service	98%
dichlorobenil	Chemical Service	97%
diethylbenzene	Chemical Service	tech.
diethylene glycol	Fluka	≥ 99%
diethylphthalate	MCB	--
2,4-dimethyl phenol	Aldrich	99%
3,5-dimethyl phenol	Chemical Service	high purity
dimethyl terephthalate	Chemical Service	high purity
2,4-dinitroaniline	Fluka	puriss
4,6-dinitrocresol	Fluka	practical
2,4-dinitrophenol	Fluka	puriss, 20% H ₂ O
diphenylamine	Fluka	≥ 99%

TABLE 3. CHEMICAL SOURCE LIST (con't)

<u>Compound</u>	<u>Source</u>	<u>Purity</u>
diphenyldichlorosilane	Chemical Procurement Lab	
diphenylhydrazine	Fluka	puriss
diquat dibromide	Chemical Service	98%
diuron	Chemical Service	99%
dodecylbenzene	Fluka	\geq 97%
dowtherm	---	--
ethylbenzene	Chemical Service	high purity
fluoranthene	RFR Corporation	--
gallic acid	Fluka	\geq 99%
hydroquinone	Fluka	\geq 99%
indene	Fluka	\geq 90%
lard	Armour Star	--
linseed oil	Grumbacker	artist quality
methylene di-p-phenylene isocyanate	MCB	--
methylisobutylketone	Chemical Service	--
α -methylstyrene	Chemical Service	--
naphthalene	Fluka	puriss
α -naphthylamine	Chemical Procurement Lab	--
nitralin	Chemical Service	98%
m-nitroaniline	Chemical Service	high purity
nonylphenol	Chemical Service	--
olive oil	Filliop berio, Italy	pure
palm oil	---	--
parathion K	Chemical Service	98%
peanut oil	---	--
phenol	Fluka	\geq 98%
phenyl ether	Fluka	\geq 97%
phthalic acid	Fluka	puriss
piperazine anhydride	Fluka	puriss
polyethylated nonylphenol	Chemical Service	lab assist.

TABLE 3. CHEMICAL SOURCE LIST (con't)

<u>Compound</u>	<u>Source</u>	<u>Purity</u>
pyrogallol	Chemical Service	high purity
quinoline	Fluka	≥ 99%
sodium dodecylbenzene sulfonate	Chemical Service	lab assist.
soya bean oil	---	--
styrene	Chemical Service	high purity
tannic acid	Chemical Service	practical
1,2,3,4-tetrahydro naphthalene	Fluka	≥ 97%
p-toluidine	Fluka	≥ 99%
toluene		≥ 99.5%
p-toluene sulfonic acid		99%
1,1,1-trichloro-2,2-bis (p-methoxyphenyl)ethane Methoxychlor	Chemical Service	98.3%
tricresylphosphate	Chemical Service	tech.
1,3,5-triethylbenzene	Fluka	purum
trifluralin	Chemical Service	99%
turpentine	MCB	--
undecylbenzene	Chemical Procurement Labs	--
uranyl nitrate	Chemical Service	lab reagent
m-xylene	Eastman Kodak	--
o-xylene	Chemical Service	high purity
zirconium acetate	Chemical Service	--

3.2 Sample Preparation

During preliminary discussion with Coast Guard personnel, cyclohexane was selected as the primary solvent. If a particular compound was not soluble in cyclohexane, the following solvents were to be tried in order: water, methanol, ethanol, and acetonitrile. This was the order observed, with minor exceptions as noted below. The cyclohexane used was Matheson, Coleman, and Bell spectroquality grade. Variation in purity was noted between lots, although within a given lot good consistency was found. In general those lots currently available having the lowest background were used. The following lots of spectroquality cyclohexane were used: 10H24, K1H29B, and 6J23I. The water used was produced by a commercial (Continental Water Company) deionizing system equipped with particulate and carbon filters. The water produced by this system had a very low fluorescence background, comparable to that of distilled water. Samples of water from the deionizing system were run on the Baird spectrofluorimeter prior to running any toxic and hazardous materials. Commercially available ethanol (Graves, 95%) had fewer fluorescent impurities than methanol, and was used exclusively. (The solvation power of these two should be quite similar.)

The hazardous materials were weighed by difference into sample bottles equipped with screw caps and Teflon liners using an analytical balance. The balance was originally kept in the hood, but the front face velocity of the air moving in the hood make exact weighings difficult. The balance was moved to a special exhaust hood and set on a piece of granite. The balance used is accurate to $\pm 5\%$ at the 1 mg level, which was the weight range required for preparation of the stock solution. All sample bottles were allowed to come to equilibrium at the laboratory temperature before any weighings were made. Solvent volumes of 10 ml were added to the sample bottles using disposable pipettes (accuracy $\pm 1\%$). All hazardous materials were handled with care. Gloves and laboratory coats were worn by personnel in handling

these materials. All samples were prepared in the hood and all waste was disposed of properly.

Sample bottles were made of glass and had plastic screw caps with Teflon liners. Bottles were cleaned by soaking overnight in a dichromate - sulfuric acid bath, then scrubbed with a detergent solution (Micro) and rinsed with hot tap and deionized water. After oven drying, the bottles were rinsed with a portion of cyclohexane and dried with a stream of nitrogen gas. Teflon liners were cleaned with detergent solution, water, and then oven dried.

Solutions were stored in a refrigerator until being used. Generally, solutions more than one week old were discarded and a fresh solution prepared. Whenever possible, the solutions were run within one day of being prepared. Except for photochemical instabilities noted below, stock solutions of toxic and hazardous materials were stable.

3.3 Data Acquisition

Primary data consisted of both fluorescence and absorption spectra. Although absorption spectra were not specified in the original contract, they were considered important for two reasons. First, these provided an estimate of optimum excitation wavelengths, which is especially important for weak emitters. Second, these provide information on the purity of the material and thus, the origin of the observed emission. Many absorption spectra have been cataloged by Sadtler (21), and this data provided additional insights as to the purity of the materials studied.

A primary objective of this study was to obtain fluorescence spectra on one hundred toxic and hazardous materials. More

than one hundred compounds were obtained, of which several showed no detectable fluorescence, but an attempt was made to provide fluorescence spectra for one hundred materials.

3.3.1 Absorption Spectra

All absorption spectra were obtained using a Cary 14 double-beam spectrophotometer. Sample and reference (pure solvent) solutions were contained in standard 1 cm path quartz cuvettes. This spectrophotometer uses a hydrogen lamp in the ultraviolet (200-400 nm) and a tungsten-halogen lamp in the visible (400-700 nm) region. Serial ten-fold dilutions were made until the principal absorption bands were in the 0-2 absorbance range.

3.3.2 Fluorescence Spectra

Fluorescence spectra were obtained on a Baird FC-100 Fluoriscord spectrofluorimeter, equipped with an A/D converter and a PDP-8A computer. This system was originally structured for recording spectra in octal format on teletype paper tape, which could then be converted to computer cards. The card input was in turn used by an IBM 1130 computer for generating total luminescence spectra (TLS) in contour format. Spectral correction and graphics were accomplished using an IBM 1130 computer with Calcomp plotter. Additional details of this procedure are published elsewhere (27,28). In principle, this system could have been modified to produce corrected spectra in real time, without use of the IBM 1130 computer. The approach used, however, did have the advantage that the corrected spectra were available in digital format, facilitating data reduction.

The fluorimeter was equipped with a Hamamatsu R446 photomultiplier tube, whose response extended from approximately 185 to 870 nm. The wavelength range available on the Spectrofluorimeter is 200-

750 nm for both excitation and emission. A beam splitter located in the sample compartment, near the excitation slit, deflected a small portion of the excitation light through a quartz diffuser plate and onto a Hamamatsu 1P28 photomultiplier tube. This provided a reference ("monitor") signal proportional to the lamp intensity. A standard 150 watt Hanovia xenon lamp was used for the source.

Spectral bandwidths, selected in consultation with Coast Guard personnel, were 10 nm in excitation and 2 nm in emission. For this survey, it was decided to keep the analyzing (emission) slits reasonably narrow in order to resolve vibronic structure. Before actually running the toxic and hazardous materials for this contract a study of the effect of changing slit width on the spectrum of pyrene and anthracene was performed. In the case of pyrene the structure is very well defined when 10,10,1,1 slits are used. However, if 10,10,2,2 slits are used there is little loss in fine structure and a gain of at least a factor of four in signal. Changing the slits to 5,5,5,5 results in a gain in signal of over a factor of 10 but there is significant loss of structure. However, many of the compounds have structureless or less fine structure in emission, so that better sensitivities could have been achieved using greater slit widths (this also applied to the excitation bandwidth). Anthracene at .11 ppm in cyclohexane was run under varying slit conditions. The results are tabulated below.

TABLE 4. THE EFFECT OF SLIT WIDTH ON A
.11 PPM ANTHRACENE SIGNAL IN CYCLOHEXANE

<u>Slit Setting</u>	<u>Relative Signal at 380 nm</u>
10,10,1,1	99
10,10,2,2	468
10,10,5,5	2700
10,10,10,10	9100
5,5,1,1	33
5,5,2,2	143
5,5,5,5	820

In this case there was no significant loss in structure and in most cases there is significant gains in signal intensity.

The monochromator scan speed was 1 nm/sec., and the sample and monitor signals (two four-digit octal values) were teletyped and punched every second. Thus, data was taken at approximately 1 nm increments throughout the scan. Originally, a maximum wavelength span of 280 nm was possible (the limitations being available computer core memory), but this was later increased to 350 nm. Data collection on a particular scan was stopped when the apparent intensity had fallen to the background level, as established during preliminary scans. At the end of a scan, the source shutter was closed and several additional data points taken to establish appropriate dark current signals. These values were then subtracted from the preceding data prior to applying the correction factors (see below).

For each sample, at least two scans were recorded. If these appeared identical, they would be separately corrected and plotted. To improve signal-to-noise, the sum of these two scans was also plotted. If the two scans appeared to be different, a third scan was obtained, and the two most similar scans were retained. In this report, only the summed scans are reproduced in the Compendium.

The excitation wavelength chosen represented a compromise between reasonable intensity and freedom from scatter excitation light. This generally resulted in the use of a shorter excitation wavelength than the maximum excitation wavelength. In some cases use of the maximum excitation wavelength produced spectra that were distorted by scatter (Rayleigh and Raman) on the short wavelength side. For estimating detection limits, however (Section 3.4.1), the apparent excitation maximum was used.

3.3.2.1 Standards

Three fluorescence standards were selected for periodic measurement during the data collection phase of the contract. These standards were intended to function as reference materials in the calculation of detection limits, and also serve as monitors of instrumental sensitivity and calibration over long periods of time.

The three standards selected were naphthalene, anthracene, and fluoranthene at concentrations of 10, 1, and 1 ppm respectively in cyclohexane. These were originally run at weekly intervals as a check of the constancy of the calibration. No relative spectral changes were noted, so the frequency of measurement was extended to two weeks. Over the five month period during which data was taken, no significant (>2%) changes were observed in the relative intensities of the standards.

To obtain a daily measure of instrument sensitivity, and particularly lamp intensity, the cyclohexane Raman bands were recorded at excitation wavelengths of 250, 275, 300, and 350 nm. This procedure was followed prior to running a particular sample in the same cuvette, and also served as check of solvent purity and cuvette cleanliness. The wavelengths chosen spanned the excitation region most frequently used to excite the sample.

3.3.2.2 Fluorimeter Calibration

Fluorimeter calibrations involved the monochromator wavelengths and responsivity of the emission monochromator. The procedures used are detailed below.

Wavelength calibrations were performed with a low-pressure mercury lamp utilizing reference lines recommended by the ASTM (29). The emission monochromator was calibrated first. The lamp, in an aluminum housing equipped with a pinhole aperture

(to reduce light intensity to a useful level), was positioned in the sample compartment similar to an ordinary cuvette. The pinhole was aligned with the emission slit, selected to give the narrowest instrumental bandwidth, 1 nm. The slit near the photomultiplier was adjusted similarly. The wavelength dials were exposed by removing the instrument cover, and the orientation of the wavelength dial with respect to the drive shaft could be adjusted after loosening several screws. The dial was thus adjusted manually to give the closest correspondence with the reference mercury lines, as observed on a meter associated with the photometer.

Wavelength calibration of the excitation monochromator was done in a similar fashion. The excitation bandwidths were adjusted to 1 nm and the standard (xenon) lamp housing was removed. The mercury lamp, in a similar housing with a large slot, was placed near the external slit. A special cell having a thick layer of barium sulfate (white reflector) was placed at the sample location and served to diffuse the dispersed mercury light before entry into the emission monochromator. The emission monochromator was tuned to pass zero order light, so that the mercury lines were not re-dispersed. The excitation monochromator dial was adjusted manually as described previously for the emission dial.

An almost linear relation was noted between the dial wavelengths and the mercury wavelengths between 250 and 580 nm. Therefore, a linear regression analysis was performed to determine the least squares slope and intercept for both wavelength dials. These coefficients were stored in the 1130 computer and used to correct the values read from the dials.

These calibrations were repeated at intervals of 30-60 days to compensate for small drifts in the calibration; these were probably caused by wear of the wavelength cam. The wavelength calibration is accurate to ± 1 nm.

The other fluorimeter calibration involved a determination of the relative spectral responsivity of the emission monochromator. This "emission calibration" combines effects of optical efficiencies (mirrors and grating) and photomultiplier response as a function of wavelength. This calibration involves a measurement of the instrumental response to a source (or sources) of known relative spectral irradiance. The source(s) could be either materials whose emission spectra have been accurately corrected, or could be light sources of known relative spectral irradiance. In the present work, calibrated sources were used so that a wide spectral region could be covered easily, and the reference data was of greater accuracy. The source used in this work was a 200 watt tungsten-halogen lamp, electrically and geometrically equivalent to a type calibrated by the National Bureau of Standards(30). This lamp was positioned about 70 cm from the fluorimeter compartment and operated at the stated current (6.5 amps AC). The lamp current was adjusted by use of an autotransformer, which appeared to give good regulation; better stability could be achieved by operating the transformer from a constant voltage transformer.

An aluminum block containing a heavy layer of barium sulfate was placed in the sample compartment and served to diffuse the light before entry into the emission monochromator.

The tungsten-halogen lamp spectrum was digitized at approximately 2 nm intervals between 250 and 750 nm. This curve was divided by the known relative irradiance values (30) using linear interpolation to estimate values at wavelengths not covered in the reference data. The calibration curve obtained in this fashion was mainly featureless, but exhibited a sharp rise below about 300 nm. This rise is an artifact, probably due to increasing contribution of zero order light relative to the (much weaker) lamp intensity in this region. For this reason, this particular lamp is not well-suited for calibration at short wavelengths. In order to obtain calibration data at short wavelengths, the normal xenon lamp spectrum

was used. This "excitation calibration" was achieved by use of a concentrated rhodamine B solution (10 gm/liter in ethylene glycol), which functions as a quantum counter over the 250-600 nm region (31). This solution was contained in a triangular cell, and the rhodamine emission was monitored at 640 nm. To complete the calibration measurement, the excitation and emission monochromators were synchronously scanned at the same wavelength, with the barium sulfate cell serving as a diffusing surface. Division of this latter curve by that obtained from rhodamine yielded the desired calibration curve. The complete emission calibration curve was obtained by joining this curve to that obtained from the tungsten halogen lamp at about 350 nm.

As a check of the calibration, corrected spectra of anthracene in ethanol were obtained, the relative vibronic intensities compared with those available in the literature. These values (units of quanta per wavelength interval) are summarized in Table 5; wavelengths are approximate.

TABLE 5. COMPARISON OF RELATIVE VIBRONIC INTENSITIES OF ANTHRACENE IN ETHANOL

<u>λ (nm)</u>	<u>Ref. 10</u>	<u>Ref. 32</u>	<u>Ref. 6</u>	<u>This Work</u>
380	1.00	1.00	1.00	1.00
400	1.04	1.04	0.97	0.995
420	0.46	0.49	0.48	0.491
450	0.14	0.14	0.15	0.141

In general, the data obtained here is within 10% of that obtained by other workers. Differences from one laboratory to another are most probably a result of errors in instrument calibration.

A similar comparison of relative vibronic intensities for benzene and fluoranthene is summarized in Table 6 below.

TABLE 6. RELATIVE VIBRONIC INTENSITIES OF BENZENE AND FLUORANTHENE

<u>λ (nm)</u>	Benzene		<u>λ (nm)</u>	Fluoranthene	
	<u>Ref. 5</u>	<u>This Work</u>		<u>Ref. 10</u>	<u>This Work</u>
270	0.73	0.76	410	0.20	0.24
278	1.00	1.00	420	0.30	0.35
285	0.73	0.79	440	0.75	0.82
295	0.40	0.51	465	1.00	1.00
			495	0.65	0.74
			570	0.20	0.16

It should be noted that the benzene spectrum in Ref. 5, also obtained in cyclohexane solvent, was approximately 30 times more concentrated, so that distortions due to reabsorption may exist. The fluoranthene spectrum of Ref. 10 was in ethanol, whereas the spectrum here was in cyclohexane. Despite these differences, the overall agreement is satisfactory.

In order to obtain a more direct estimate of the accuracy of the calibration, the irradiance of the tungsten-halogen lamp between 270 and 700 nm was determined using a calibrated spectroradiometer. Although absolute values were lower than those of Ref. 10, the relative values agreed within $\pm 10\%$ above 300 nm. Below 300 nm, the lamp output is quite low, and the estimated uncertainty is approximately $\pm 15\%$.

In summary, the emission calibration should be accurate to $\pm 10\%$ between 300 and 700 nm, but may be less accurate ($\pm 15\%$) below 300 nm.

3.4 Data Reduction

Spectral data was obtained on 109 compounds. If no detectable fluorescence was observed, an alternate compound was used. Information contained in the fluorescence spectra is tabulated in Section 4. The data includes the code letters, excitation wavelength, wavelength of maximum emission, number of peaks, number of shoulders, width at half maximum and detection limits. Most of these parameters were used in the spectral code which is described below.

3.4.1 Detection Limits

The detection limit for the fluorescing material has been defined as the concentration at which the signal-to-noise ratio (S/N) at the fluorescence maximum is equal to two.

It should be noted that other techniques have been used to define detection limits. Hirschfield (40-42) chooses to use integral rather than peak ratios.

In practice, the stock solutions were serially diluted by factors of ten until the fluorescence signal became near or slightly below the detection limit. Signal-to-noise ratios were calculated for the two samples of lowest concentration, and the values linearly extrapolated to the concentration corresponding to the S/N of two.

In some cases, solvent background in the form of impurity emission or Raman peaks in the vicinity of the sample fluorescence resulted in greater uncertainty. In addition, certain compounds showed photochemical instability. For these cases, the detection limits must be regarded as approximate.

The units of concentration are given nominally in parts per million, although they are actually in units of mg/l. It should

emphasized that these values are dependent upon the characteristics of the instrumentation (light intensity, optical efficiency, and detector sensitivity) and thus, different equipment would give different absolute values. For this reason, the detection limits should be compared with one of the fluorescence standards (naphthalene, anthracene, and fluoranthene) whose emission occurs in approximately the same spectral region. This will provide a relative estimate which should be much less dependent upon the nature of the equipment.

3.4.2 Spectral Code

In establishing a spectral code, certain features of the fluorescence spectra must be selected for quantitation. Although the choice of these features is somewhat arbitrary, they should summarize the important spectral features and yet permit a non-specialist to construct an equivalent code for an unknown material. The following spectral parameters have been selected to be included in the code: wavelength at peak maximum, width at half maximum, number of distinct peaks, and the number of shoulders. The last two parameters sometimes constitute a "gray" area in that one observer may classify a peak as a shoulder (or conversely) and another observer may argue about the existence of a shoulder. For this contract, each spectrum of a toxic or hazardous material was examined by several people in an attempt to determine the code. Shoulders were chosen if they were not resolved as a peak from the peak in the spectrum. Certain materials (such as, the polynuclear aromatic hydrocarbons) have highly structured spectra, in which case measurement of half width is difficult to obtain. In cases of highly structured spectra, the half-width measurement was made based on the highest peak in the spectrum. For weakly or non-emitting compounds, the half-width measurements are denoted by N because of the difficulty and inaccuracy in measuring them. A typical code is illustrated below for N 1-Chloronaphthalene.

328-34-3(4) CNA

Wavelength of peak intensity _____
Half-width _____
Number of peaks _____
Number of shoulders _____
CHRIS code name _____

In the list of coded spectra, the entries are organized in order of increasing peak wavelength, so that this parameter functions as the primary identifier. The corresponding spectra are grouped alphabetically according to their CHRIS list code name.

The present code structure should be regarded as preliminary in nature, in that other spectral features or some algebraic combination of parameters might serve as more useful identifiers.

4. INTERPRETATION

4.1 Introduction

It was the purpose of this contract to investigate the fluorescence properties of one hundred toxic and hazardous materials and produce corrected emission curves and derive a spectral code for these materials. One hundred twenty-five potential compounds were selected based on structural and known properties for study, and of these, one hundred thirteen were received and studied.

Fluorescence spectroscopy is well regarded as an analytical tool because of its excellent sensitivity and added selectivity compared to other methods. An attempt has been made in this contract to examine the use of fluorescence for identification and quantitation of toxic and hazardous materials. There have been many studies which have examined the relationship between molecular structure and fluorescence and a number of generalities exist. A great majority of organic compounds which exhibit analytically useful fluorescence possess cyclic conjugated structures. The fact that a molecule possesses these structural characteristics however, does not guarantee that the species will fluoresce. The reverse is also true. The shape of the fluorescence spectrum, its position as a function of wavelength, and the intensity of the luminescence are sensitive to molecular structure, symmetry and the environment in which the molecule finds itself. Of the 113 materials supplied by the United States Coast Guard 96 compounds were fluorescent at room temperature, some very weakly however. Thirteen compounds were considered non-fluorescent at room temperature. The spectra of these compounds show little or no difference from the solvent background. The spectrum and solvent background for some of these thirteen materials can be found in the compendium. No digitized data was obtained for Diazinon, dimethylterephthalate, 2,4-dinitroaniline, 4,6-dinitro-o-cresol and m-nitroaniline. These materials were determined to be non-fluorescent from preliminary scans on the fluorimeter. Four compounds on the original list were not run. Table 7 summarizes these results. A complete table of experimental parameters and detection limits can be found at the end of this section (Table 13).

TABLE 7. SUMMARY OF FLUORESCENT TOXIC
AND HAZARDOUS MATERIALS

<u>Fluorescent</u>	<u>Non-Fluorescent</u>	<u>Not Run</u>
acenaphthene	atrazine	anisoylchloride
acetone	benzoylchloride	methylene diphenylene- isocyanate
acridine	butylbenzylphthalate	Nitralin
aniline	Diazinon	Trifluralin
anthracene	Dichlone	
Aroclor 1242	dimethylterephthalate	
Aroclor 1254	2,4-dinitroaniline	
azinphosmethyl	4,6-dinitro-o-cresol	
benzanthracene	2,4-dinitrophenol	
benzene	diphenylhydrazine	
benzonitrile	m-nitroaniline	
benzo(a)pyrene	Parathion	
benzyl alcohol	piperazine	
benzylamine		
benzyltriethylammon- iumchloride		
Bisphenol A		
brucine		
o-tert-butylphenol		
p-tert-butylphenol		
carbaryl		
carnauba wax		
castor oil		
catechol		
p-chloroaniline		
1-chloronaphthalene		
p-chlorophenol		
chloropyrifos		
4-chloro-o-toluidine		
p-chlorotoluene		
chrysene		
coconut oil		

TABLE 7. SUMMARY OF FLUORESCENT TOXIC
AND HAZARDOUS MATERIALS (con't.)

Fluorescent

cod liver oil
copper naphthenate
cottonseed oil
Coumaphos
o-cresol
p-cresol
cumene
p-cymene
DDD
DDT
1,2,5,6-dibenzanthracene
Dicamba
Dichlorobenil
dichlorophenoxyacetic acid
dichlorodiphenylsilane
diethylbenzene
diethylene glycol
diethylphthalate
2,4-dimethylphenol
3,5-dimethylphenol
dinitrophenol
diphenylamine
diphenylether
diquat dibromide
dodecylbenzene
Dowtherm
ethylbenzene
fluoranthene
gallic acid
hydroquinone
indene
lard
linseed oil
methyl isobutyl ketone
 α -methylstyrene

TABLE 7. SUMMARY OF FLUORESCENT TOXIC AND
HAZARDOUS MATERIALS (con't)

Fluorescent

methoxychlor
n-methylaniline
naphthalene
 α -naphthylamine
nonylphenol
olive oil
palm oil
peanut oil
phenol
phthalic acid
polyethoxylated nonylphenol
pyrogalllic acid
quinoline
resorcinol
salicylic acid
sodium dodecylbenzene sulfonate
styrene
tannic acid
tetrahydronaphthalene
toluene
p-toluene sulfonic acid
p-toluidine
tricresyl phosphate
1,3,5-triethylbenzene
turpentine
undecylbenzene
uranyl nitrate
m-xylene
o-xylene
zirconium acetate

Compounds were considered fluorescent if they exhibited a reproducible signal above the solvent background spectrum. In some cases (i.e., methyl isobutyl ketone) the fluorescence is extremely weak but consistent with what is found in the literature for a compound of similar structure (i.e., acetone).

4.2 Spectral Similarities and Interferences

4.2.1 Use of Absorption Spectra

In order to insure the integrity of the chemicals received, the absorption spectra of all the toxic and hazardous materials supplied were run. Not only did these spectra help in locating the proper wavelength for excitation but were used for comparison with literature spectra for detecting the presence of impurities. Only one compound, p-cymene showed no resemblance to the published Sadtler absorption spectrum. Four compounds (acridine, dodecylbenzene, quinoline and undecylbenzene) whose absorption spectra agreed with published work showed fluorescent impurities. The concentration of these impurities was either too low for identification using the absorption spectra or it overlapped with the primary compound absorption. For all other compounds where absorption spectra were available in the literature the agreement was very good.

4.2.2 Comparison of Available Fluorescence Spectra

It is difficult to compare the data obtained in this contract with most spectra appearing in the literature, since most of these are uncorrected. For example, an attempt was made to compare our spectra with those published by Sadtler, but there were many discrepancies. This is because uncorrected emission spectra reflect instrumental factors such as monochromator efficiency and detector response as a function of wavelength. Uncorrected excitation spectra, although not obtained under this contract, would be modulated by the spectral intensity

distribution of the light source. These instrumental factors introduce changes in wavelength and relative intensity into the spectra, making comparisons difficult. Although small differences among corrected spectra may exist due to calibration methods used, these will generally be minor in comparison with uncorrected data.

There are several advantages to using corrected data. The first is that spectra obtained on totally different instruments are more easily compared. Another is that accurate quantum yield measurements, which provide a measure of fluorescence intensity, require corrected data. Calibration of certain other spectral parameters, such as radiative lifetimes (related to fluorescence decay times) also require corrected spectral data.

In Section 3 of this report, comparisons of corrected fluorescence intensities in the literature with the data obtained for this contract for anthracene, benzene and fluoranthene were given. Below are tabulated results for other compounds for which corrected data exists. In most cases the agreement is good.

TABLE 8. COMPARISON OF CORRECTED RELATIVE FLUORESCENCE INTENSITIES

	<u>This Work</u>	<u>Ref. 10</u>	<u>Ref. 5</u>
Chrysene			
363	1.00	1.00	1.00
383	1.044	.975	1.16
404	.464	.425	.553
428	.125	.100	.160
 Benz (a) pyrene			
405	1.00	1.00	
428	.500	.506	
455	.123	.152	

TABLE 8. COMPARISON OF CORRECTED RELATIVE
FLUORESCENCE INTENSITIES (con't)

	<u>This Work</u>	<u>Ref. 5</u>
1,2,5,6 Dibenzanthracene		
396	1.00	1.00
418	.564	.480
442	.171	.133
Acenaphthene		
323	1.00	.978
328	.526	.615
338	.780	1.00
355	.289	.363
Benzene		
271	.76	.692
279	1.00	1.00
286	.794	.75
Benzylalcohol		
278	.817	.797
284	1.00	1.00
Ethylbenzene		
278	.943	.874
283	1.00	1.00
Naphthalene		
323	1.00	1.00
337	.879	.923

TABLE 8. COMPARISON OF CORRECTED RELATIVE
FLUORESCENCE INTENSITIES (con't)

	<u>This Work</u>	<u>Ref. 5</u>
Styrene		
294	.931	.849
303	1.00	1.00
Toluene		
278	.98	.890
284	1.00	1.00

4.2.3 General Comments on Samples

In general there were very few problems involved in running the samples of toxic and hazardous materials as previously mentioned. For a few samples there were problems of impurity emission and photochemical changes upon emission. Also, in several cases there was a change in the emission spectrum when the solvent was changed from cyclohexane to ethanol or some other specified solvent.

Acridine was prepared in both cyclohexane and ethanol. For both excitation wavelengths, 290 nm and 355 nm, the acridine emission was much stronger in ethanol. Impurity emission, however, was present when acridine was run in both solvents. A quick recrystallization of the acridine from ethanol did not produce any significant change. Acridine also showed photochemical decomposition.

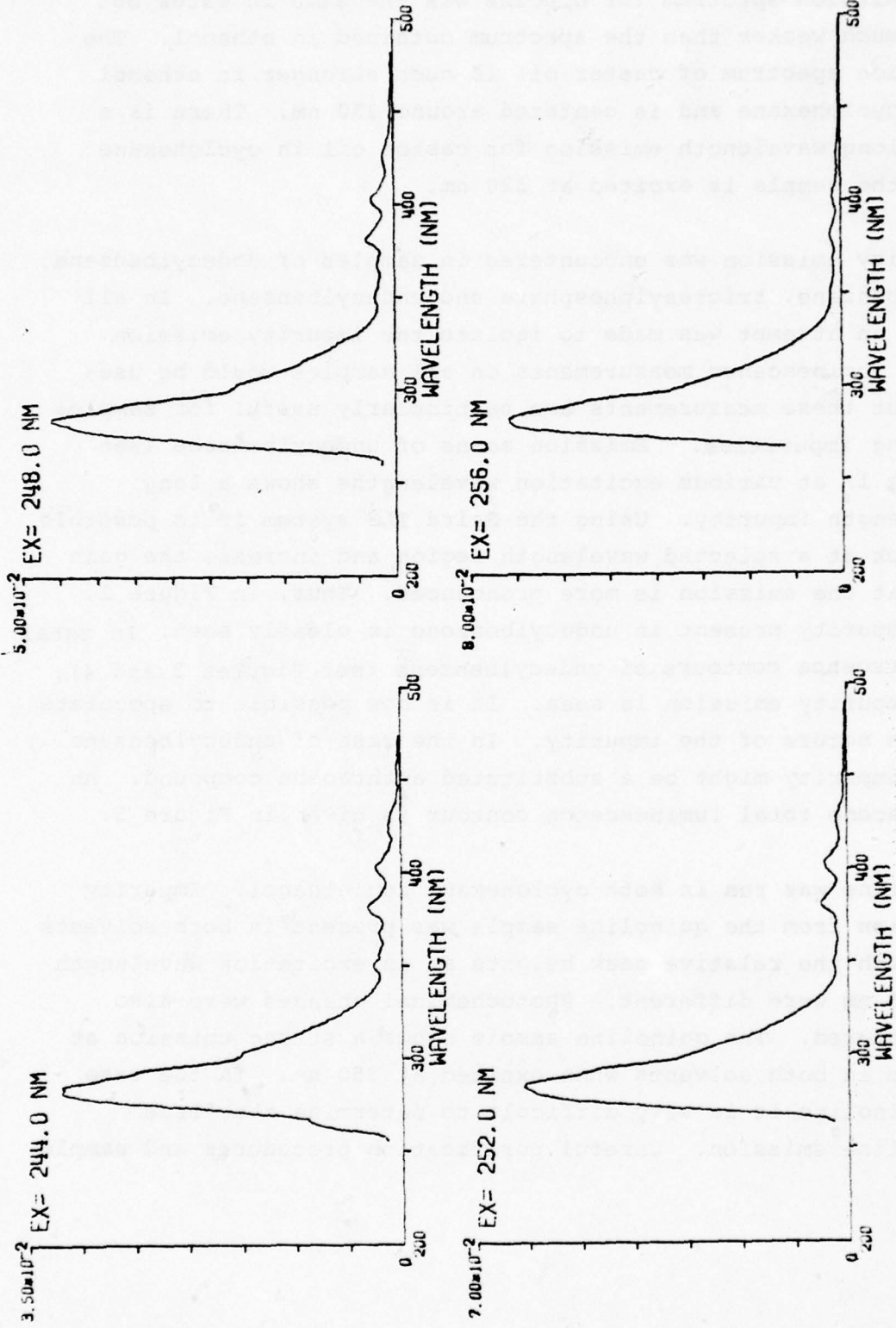
Azinphosmethyl was run in both cyclohexane and ethanol. There was little solvent dependence on the emission intensity and the emission maximum was entered around 430 nm in both solvents. Brucine was originally run in ethanol. However, the terms of the contract called for running the sample in water first.

The emission spectrum for brucine was the same in water but very much weaker than the spectrum obtained in ethanol. The emission spectrum of castor oil is much stronger in ethanol than cyclohexane and is centered around 330 nm. There is a weak long wavelength emission for castor oil in cyclohexane when the sample is excited at 320 nm.

Impurity emission was encountered in samples of dodecylbenzene, ethylbenzene, tricresylphosphate and undecylbenzene. In all cases an attempt was made to isolate the impurity emission. Total luminescence measurements on all samples would be useful but these measurements are particularly useful for samples showing impurities. Emission scans of undecylbenzene (see Figure 1) at various excitation wavelengths shows a long wavelength impurity. Using the Baird TLS system it is possible to look at a selected wavelength region and increase the gain so that the emission is more pronounced. Thus, in Figure 2, the impurity present in undecylbenzene is clearly seen. In total luminescence contours of undecylbenzene (see Figures 3 and 4), the impurity emission is seen. It is now possible to speculate on the nature of the impurity. In the case of undecylbenzene this impurity might be a substituted anthracene compound. An anthracene total luminescence contour is given in Figure 5.

Quinoline was run in both cyclohexane and ethanol. Impurity emission from the quinoline sample was present in both solvents although the relative peak heights at an excitation wavelength of 275 nm were different. Photochemical changes were also encountered. The quinoline sample shows a strong emission at 430 nm in both solvents when excited at 350 nm. In the case of quinoline it is very difficult to determine the "true" quinoline emission. Careful purification procedures and sample

5 / 9 / 79

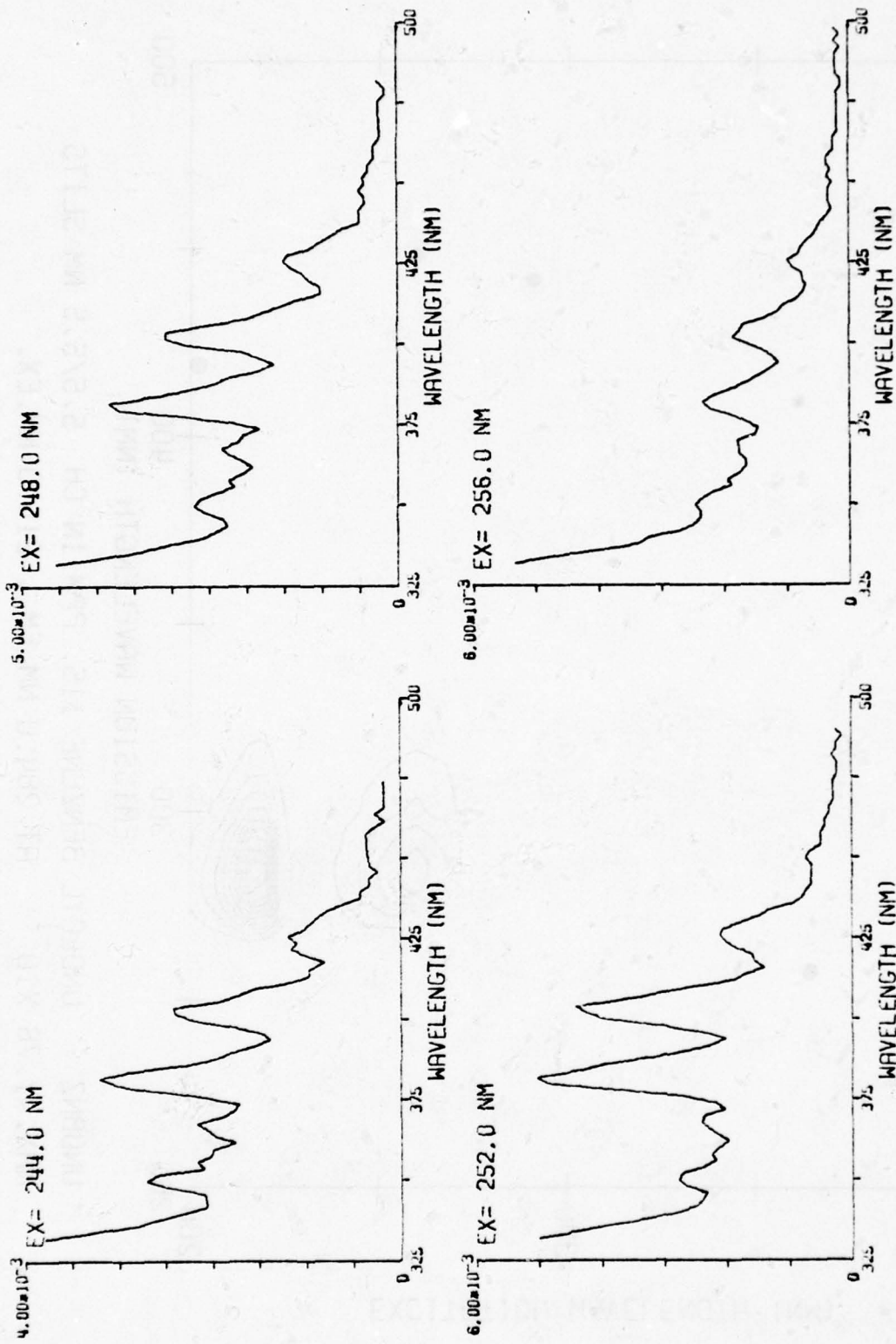


4-10

UNDBNZ UNDECYL BENZENE 115. PPM IN CH 5,5/5,5 NM SLITS

FIGURE 1

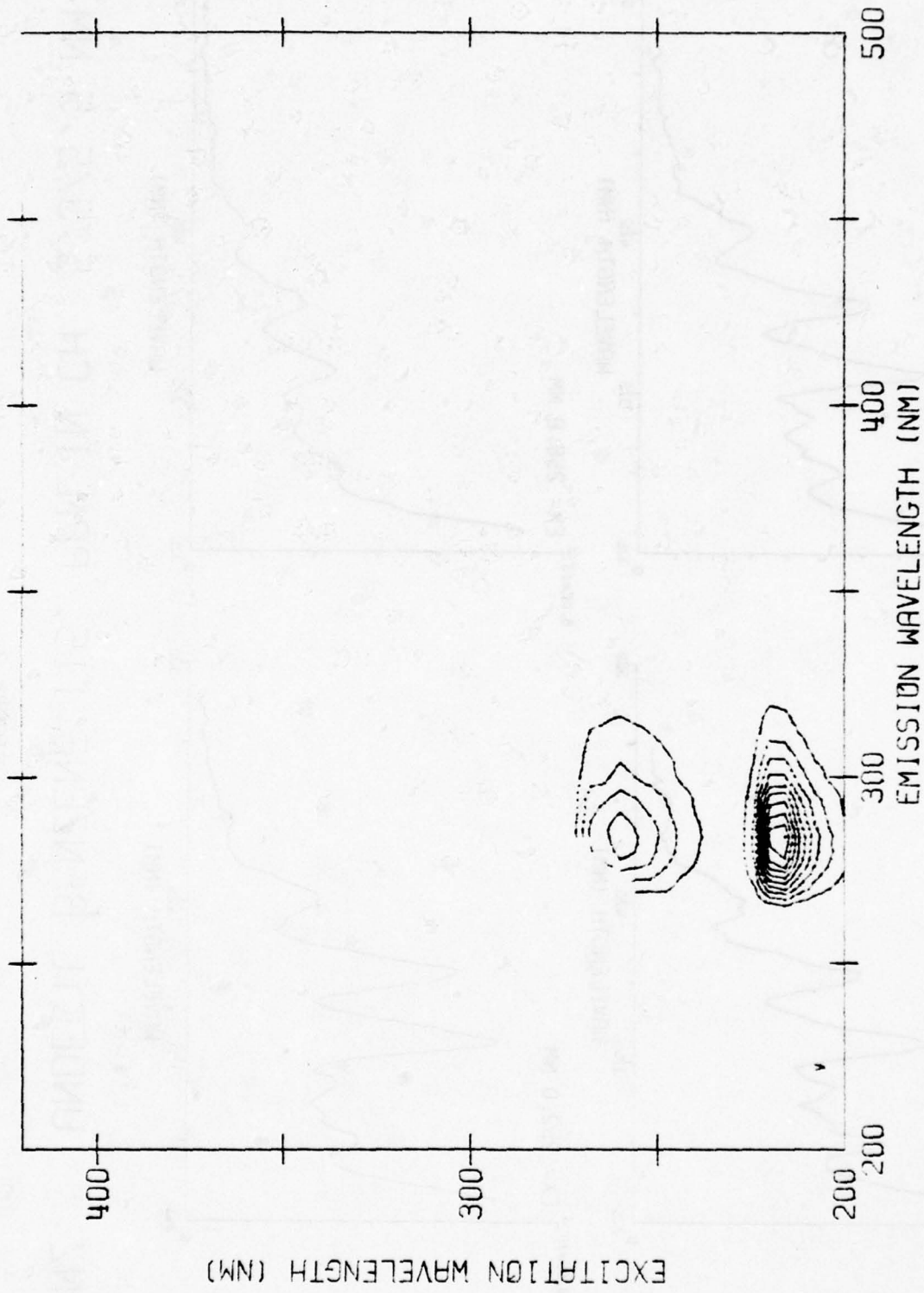
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4 - 11

UNDBNZ UNDECYL BENZENE 115. PPM IN CH₂CL₂ 5.5/5.5 NM SLITS

FIGURE 2

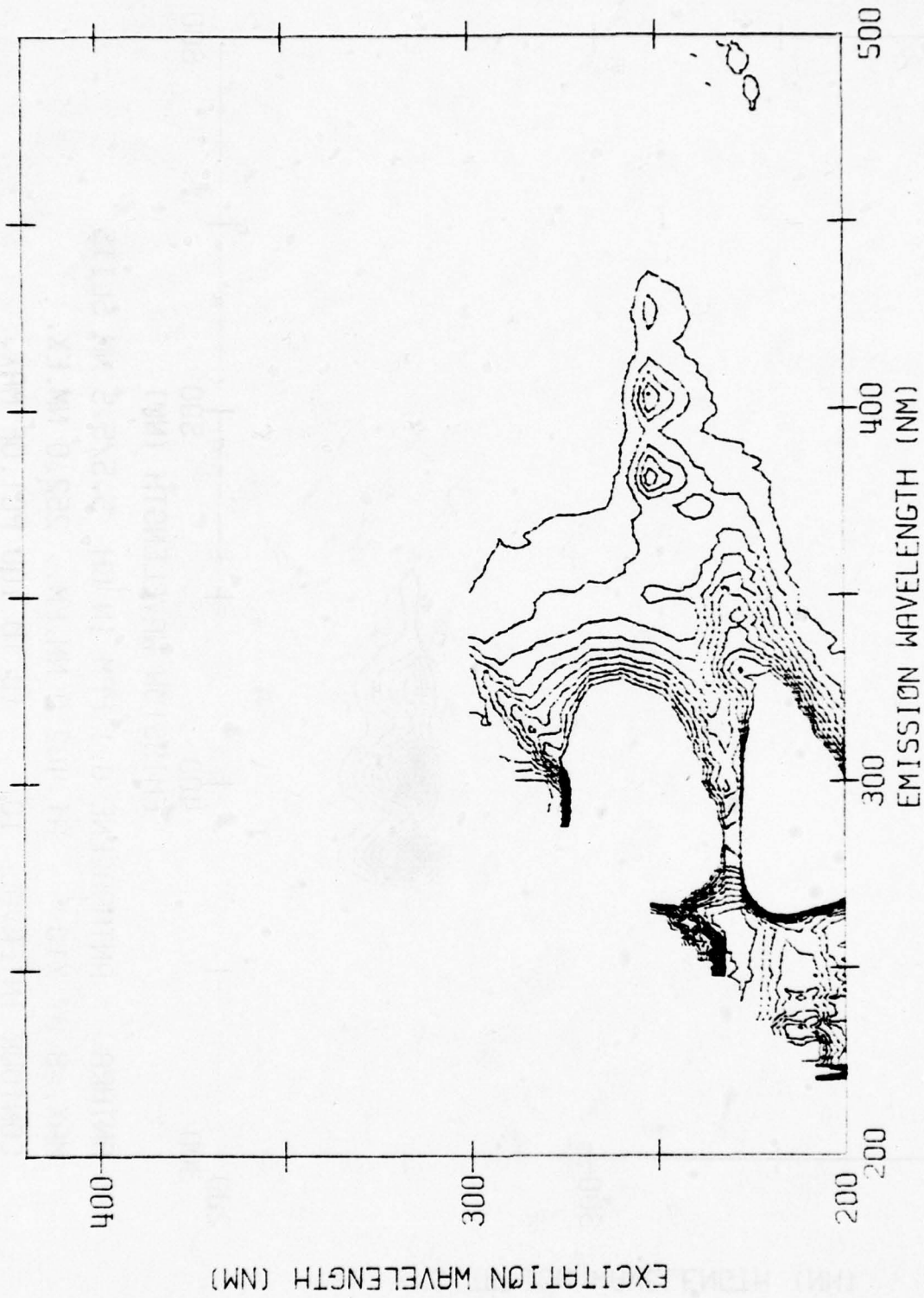


UNDBNZ UNDECYL BENZENE 115. PPM IN CH 5.5/5.5 NM SLITS
MAX. = 1.76×10^{-1} AT 284.0 NM. EX., 216.0 NM. EX.
CONTOUR INTERVAL = 10 10 TO 100 PCT. OF MAX.

FIGURE 3

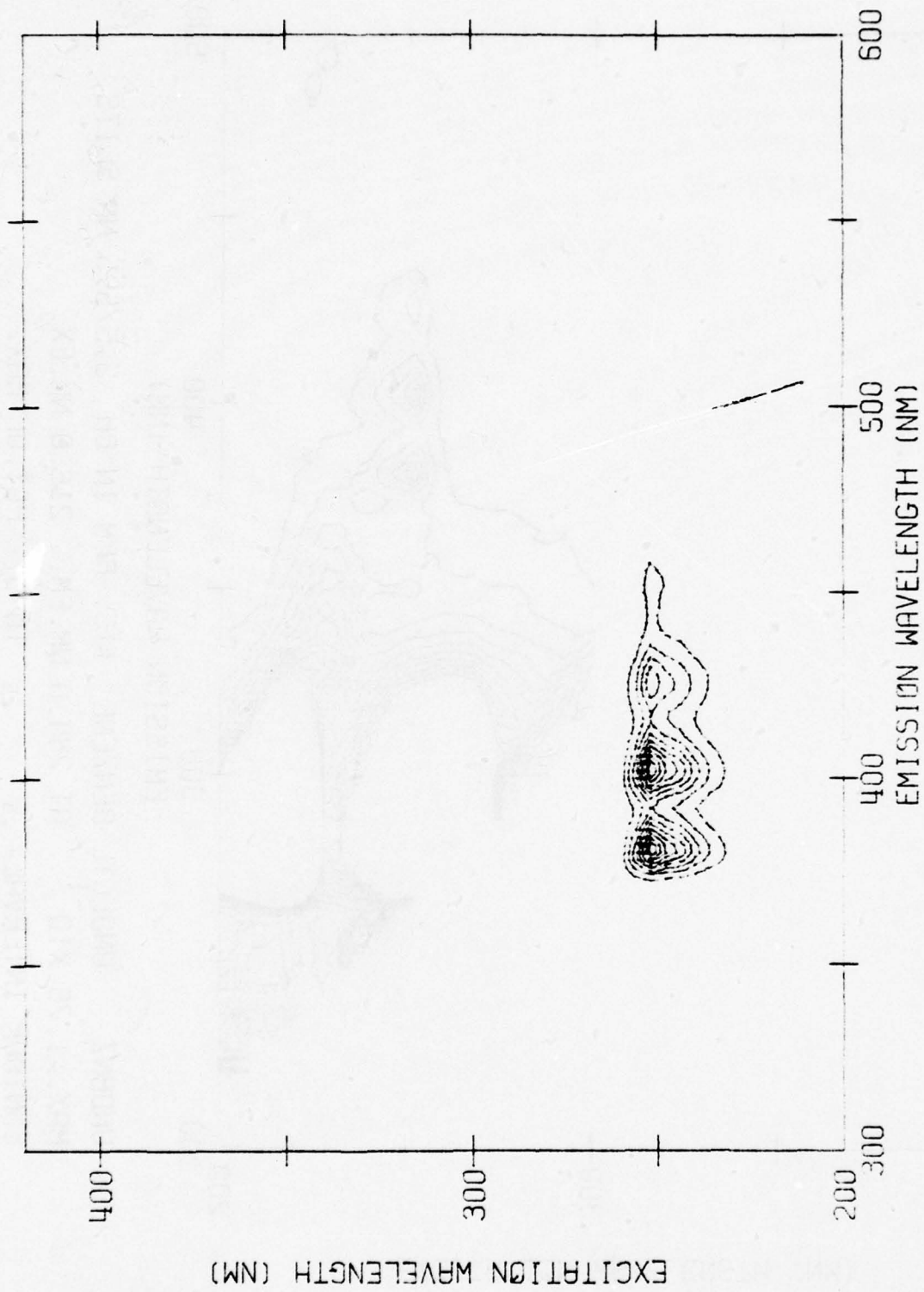
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4-13



UNDBNZ UNDECYL BENZENE 115. PPM IN CH 5.5/5.5 NM SLITS
MAX. = 1.76×10^{-1} AT 284.0 NM. EM., 216.0 NM. EX.
CONTOUR INTERVAL = .5 .5 TO 5 PCT. OF MAX.

FIGURE 4



ANTHRA ANTHRACENE 0.1 PPM IN CH 5.5/5.5 NM SLITS
 MAX. = 8.07×10^{-1} AT 402.0 NM. EM. 252.0 NM. EX.
 CONTOUR INTERVAL = 10 10 TO 100 PCT. OF MAX.

FIGURE 5

handling techniques (nitrogen atmosphere) are necessary to obtain the correct spectrum for quinoline.

In addition to acridine and quinoline photochemical changes were encountered with diphenylamine, Dicamba and the Aroclor mixtures. This made the determination of a detection limit difficult in some cases. Those compounds on the Chris and EPA lists which undergo photochemical changes require further study if the photoproduct(s) are to be identified.

Zirconium acetate was insoluble in all the solvents used which included cyclohexane, water, ethanol and acetonitrile. It was soluble in a 1.0 M H_2SO_4 solution. The fluorescence spectrum of a 216 ppm sample and solvent background are given in Figures 6 and 7. The fluorescence is very weak. No detection limits were determined for this sample.

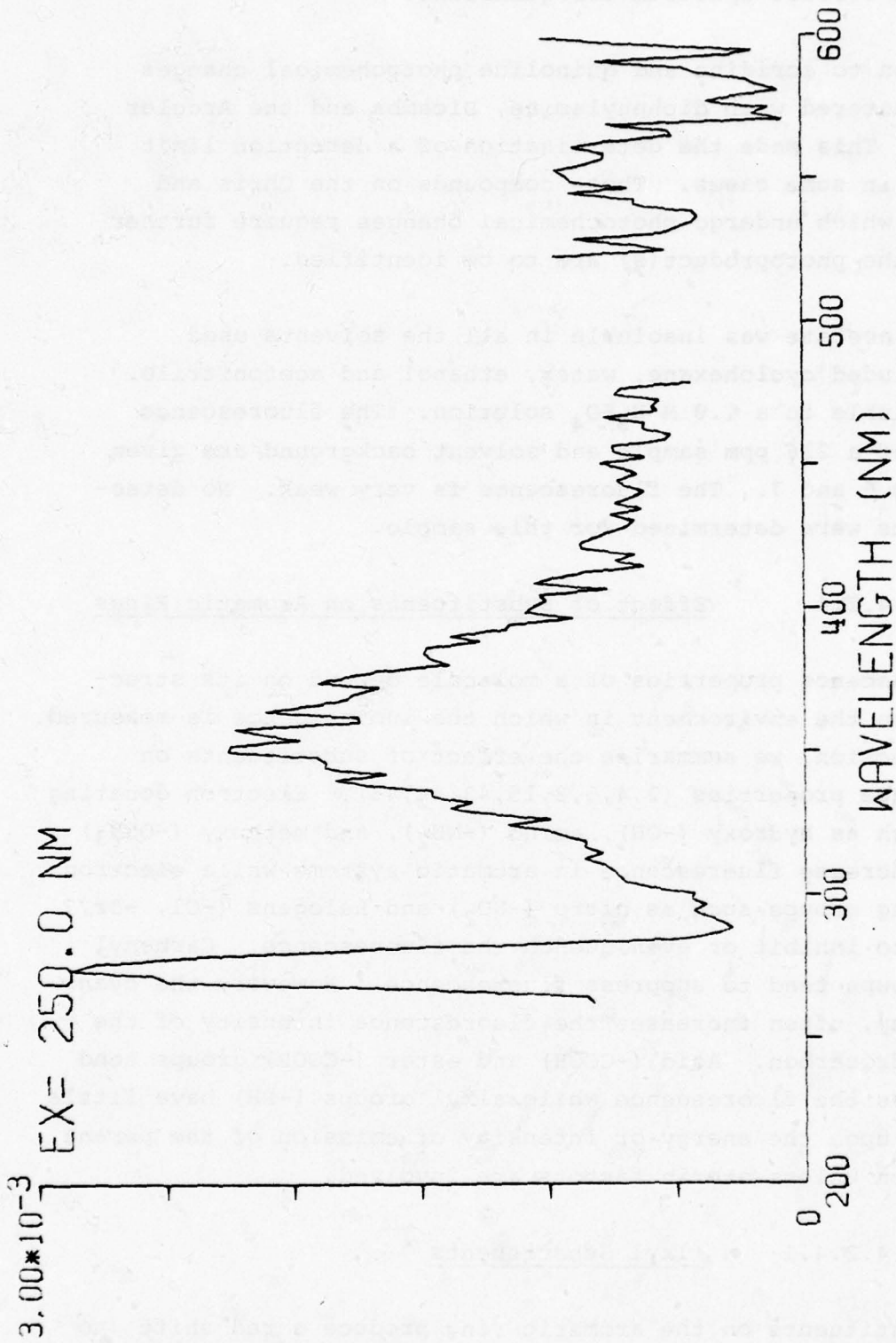
4.2.4 Effect of Substituents on Aromatic Rings

The luminescence properties of a molecule depend on its structure and on the environment in which the luminescence is measured. In this section, we summarize the effect of substituents on fluorescence properties (2,4,5,8,15,43,44,45). Electron donating groups such as hydroxy (-OH), amino (-NH₂), and methoxy (-OCH₃) tend to increase fluorescence in aromatic systems while electron withdrawing groups such as nitro (-NO₂) and halogens (-Cl, -Br, -I) tend to inhibit or even quench the fluorescence. Carbonyl (>C=O) groups tend to suppress fluorescence. However, the cyano (-CN) group, often increases the fluorescence intensity of the parent hydrocarbon. Acid (-COOH) and ester (-COOR) groups tend to suppress the fluorescence while alkyl groups (-RH) have little influence upon the energy or intensity of emission of the parent hydrocarbon unless steric factors are involved.

4.2.4.1 Alkyl Substituents

Alkyl substituents on the aromatic ring produce a red shift (to longer wavelengths) in both absorption and fluorescence(2,4,5,8).

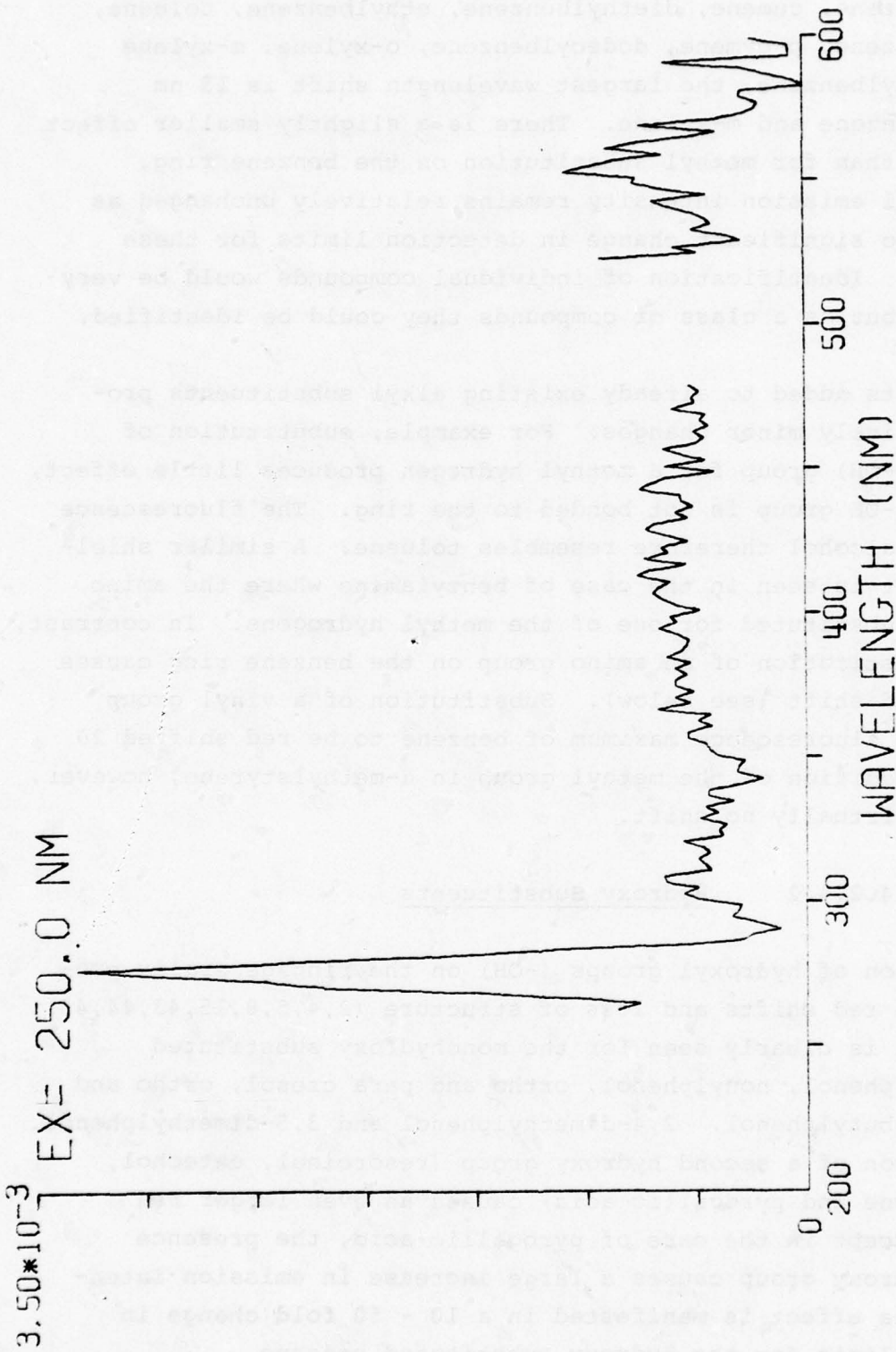
5 / 8 / 79



ZIRCONIUM ACETATE IN 1. M H₂SO₄ 10,10/2,2 NM SLITS

FIGURE 6

5 / 8 / 79



1.0 M SULFURIC ACID 10,10/2,2 NM SLITS

FIGURE 7

For the alkyl-substituted benzenes studied under this contract, namely benzene, cumene, diethylbenzene, ethylbenzene, toluene, undecylbenzene, p-cymene, dodecylbenzene, o-xylene, m-xylene and triethylbenzene, the largest wavelength shift is 15 nm between benzene and m-xylene. There is a slightly smaller effect for ethyl than for methyl substitution on the benzene ring. The overall emission intensity remains relatively unchanged as there is no significant change in detection limits for these compounds. Identification of individual compounds would be very difficult but as a class of compounds they could be identified.

Substituents added to already existing alkyl substituents produce relatively minor changes. For example, substitution of hydroxyl (-OH) group for a methyl hydrogen produces little effect, since the -OH group is not bonded to the ring. The fluorescence of benzyl alcohol therefore resembles toluene. A similar shielding effect is seen in the case of benzylamine where the amino group is substituted for one of the methyl hydrogens. In contrast, direct substitution of an amino group on the benzene ring causes a large red shift (see below). Substitution of a vinyl group causes the fluorescence maximum of benzene to be red shifted 20 nm. The addition of the methyl group in α -methylstyrene, however, produces virtually no shift.

4.2.4.2 Hydroxy Substituents

Substitution of hydroxyl groups (-OH) on the ring generally produce large red shifts and loss of structure (2,4,5,8,15,43,44,45). This shift is clearly seen for the monohydroxy substituted benzenes; phenol, nonylphenol, ortho and para cresol, ortho and para-tert-butylphenol, 2,4-dimethylphenol and 3,5-dimethylphenol. Substitution of a second hydroxy group (resorcinol, catechol, hydroquinone and pyrogalllic acid) causes an even larger red shift. Except in the case of pyrogalllic acid, the presence of the hydroxy group causes a large increase in emission intensity. This effect is manifested in a 10 - 50 fold change in detection limit for the hydroxy substituted benzene.

4.2.4.3 Amino Substituents

Substitution of the amino ($-NH_2$) group for hydrogen on the benzene rings results in a large red shift, an increase in emission intensity and a loss of structure in the fluorescence spectrum (2,4,5,8,15,43,44,45). These effects are clearly demonstrated in benzene/aniline and naphthalene/ α -naphthylamine. The peak emission is shifted from 279 nm to 316 nm for benzene/aniline and from 323 nm to 377 nm for naphthalene/ α -naphthylamine. In both cases the structure of the unsubstituted compound is lost with the addition of the amino group but the detection limit is improved by a factor of 50 to 100. The effect of added substituents after the initial amino group is quite small. There is no significant wavelength shift or change in the fluorescence yield for methylaniline, p-toluidine, p-chloroaniline and 4-chloro-o-toluidine.

4.2.4.4 Cyano Substituents

Benzonitrile, with its electron releasing cyano ($-CN$) group is only slightly shifted to longer wavelength compared to benzene (2,4,5,8,15,43,44,45). The cyano group results in an increase in emission intensity and this can be seen in the factor of 10 lower detection limit for benzonitrile compared to benzene.

4.2.4.5 Nitro Substituents

Nitro ($-NO_2$) groups tend to totally quench the fluorescence of aromatic hydrocarbons (2,4,5,8,15,43,44,45). No fluorescence emission was observed for 2,4-dinitroaniline, m-nitroaniline, 4,6-dinitro-cresol and 2,4-dinitrophenol. At 77°K in methylcyclohexane and ethanol, p-nitrophenol and p-nitroaniline do not exhibit fluorescence but do show phosphorescence in each solvent with the ethanol spectrum being red shifted from that of methylcyclohexane (33). Nitrobenzene, p-nitrotoluene, p-chloro-nitrobenzene and p-nitroanisole have a lowest triplet ($n-\pi^*$) state but do not exhibit phosphorescence at low temperature. The

reason for this is not understood. Heavy atom effects and predissociation have been used to explain the fluorescence quenching of nitro substituted aromatic compounds.

4.2.4.6 Halogen Substituents

There are only a few examples of halo-substituted compounds (X=F, Cl, Br, I) in this contract. Direct substitution of a halogen increases the rate of intersystem crossing due to the internal heavy atom effect, resulting in a reduction in the fluorescence efficiency (2,4,5,8,15,43,44,45). In addition to this decrease in fluorescence intensity there is a shift to longer wavelength. The effect is not as great for toluene and p-chlorotoluene, $\lambda_{\max} = 284$ nm and $\lambda_{\max} = 288$ nm, respectively. A more dramatic shift in wavelength can be seen for phenol and p-chlorophenol, $\lambda_{\max} = 288$ and $\lambda_{\max} = 305$ nm respectively.

4.2.4.7 Acid and Acid Chloride Substituents

Acid substituents (-COOH) and acid chlorides (-COOCl) result in a decrease in emission frequency and a large decrease in emission intensity (2,4,5,8,15,43,44,45). The simplest acid substituted benzene derivative, benzoic acid, does not fluoresce at room temperature (5). The lack of fluorescence of benzoic acid in solution is attributed to the fact that the lowest excited state is n, π^* in character. The presence of the acid group deactivates the benzene ring by withdrawing π electrons and reducing their mobility. At low temperature a very weak fluorescence is observed. All of the benzene substituted carboxylic acids (except phthalic acid) studied under this contract had other substituents attached to the benzene ring. This altered the fluorescence characteristics of the molecule. Phthalic acid, a benzene dicarboxylic acid, exhibited a weak fluorescence with

an emission maximum some 60 nm shifted to the red of benzene. The fact that benzoic acid does not fluoresce at room temperature coupled with the presence of the second acid group suggests that the observed luminescence may be due to an impurity. Room temperature phosphorescence on silica gel has been reported recently by Hurtubise(34). Addition of hydroxy groups to the benzene carboxylic acid structure counteracts the effect of the acid. If intramolecular hydrogen bonding occurs between substituents this may modify the fluorescence. Hydrogen bonding with other phenolic hydroxy substituents may be the reason salicylic, gallic and tannic acid all exhibit enhanced fluorescence emission which is red shifted from benzene.

Salicylic acid has a detection limit similar to phenol indicating that the carboxylic acid may not have a large diminishing effect on the emission intensity in the case. Gallic acid which is the carboxylic acid derivative of pyrogallol shows the wavelength shift associated with the acid group. The emission maximum of pyrogallol occurs at 335 nm while the emission maximum of gallic acid occurs at 346 nm. The fluorescence of tannic acid in water is weak and as a result very noisy. It is possible to apply a smoothing routine to this data to get better results. The smoothing algorithm is based upon a moving least-squares fit to a small number of data points. A quadratic cubic smoothing polynomial with a minimum of five points is used. The number of points in the smoothing function is an odd integer value to preserve symmetry about the central point, and is normally much smaller than the total number of points. Edwards and Wilson (38) in a study of noise-free gaussian lines, concluded that the smoothing range (number of data points times the data interval) should be ≤ 0.7 the full width at half maximum (FWHM) for a peak distortion of $< 10\%$. Enke and Meman(39) conclude that for a single pass smooth, the maximum signal to noise improvement is obtained by a smoothing range equal to approximately twice the FWHM. Generally band distortion was avoided at the expense of poorer signal to noise. In most cases the number of points which spans the FWHM of the narrowest band present was chosen. If the narrowest band is a Raman band

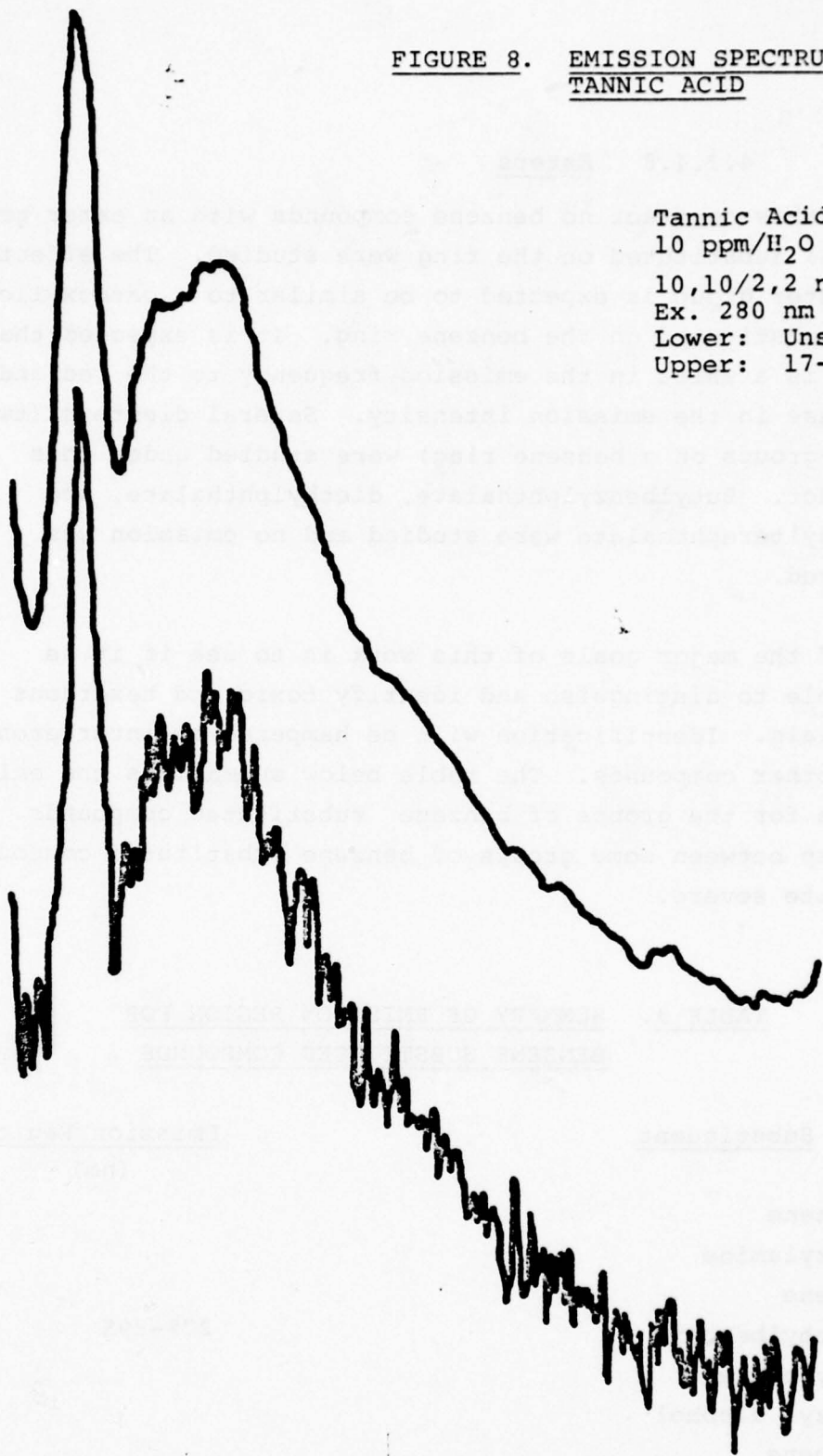
or other less interesting feature, the smoothing range might be enlarged to match that of the analyte (i.e. the tannic acid spectrum, Figure 8). Figure 8 shows both the unsmoothed and smoothed fluorescence curve for tannic acid.

The (-SO₃H) group has no effect on the emission frequency or emission intensity. This effect can be seen in the data for toluene and p-toluene sulfonic acid. The emission maxima for these compounds occur at the same point within experimental error and the detection limits for both of these compounds is similar.

Anisoyl chloride and benzoylchloride showed no fluorescence emission. This result is not surprising due to the presence of the acid and halogen substituents on the benzene ring.

FIGURE 8. EMISSION SPECTRUM OF TANNIC ACID

Tannic Acid
10 ppm/H₂O
10,10/2,2 nm Slits
Ex. 280 nm
Lower: Unsmoothed
Upper: 17-Point Smooth



300 | 400 | 500 | 600
Wavelength (nm)

4.2.4.8 Esters

Under this contract no benzene compounds with an ester group ($-\text{CO}_2\text{R}$) substituted on the ring were studied. The effect of the ester group is expected to be similar to a carboxylic acid substituted on the benzene ring. It is expected that there is a shift in the emission frequency to the red and a decrease in the emission intensity. Several diesters (two ester-groups on a benzene ring) were studied under this contract. Butylbenzylphthalate, diethylphthalate, and dimethylterephthalate were studied and no emission was observed.

One of the major goals of this work is to see if it is possible to distinguish and identify toxic and hazardous materials. Identification will be hampered by interferences from other compounds. The table below summarizes the emission region for the groups of benzene substituted compounds. Overlap between some groups of benzene substituted compounds is quite severe.

TABLE 9. SUMMARY OF EMISSION REGION FOR
BENZENE SUBSTITUTED COMPOUNDS

<u>Substituent</u>	<u>Emission Region</u> (nm)
Alkyl	
benzene	
benzylamine	
cumene	
diethylbenzene	279-295
ethylbenzene	
benzyl alcohol	
toluene	
undecylbenzene	
p-cymene	

TABLE 9. SUMMARY OF EMISSION REGION FOR BENZENE
SUBSTITUTED COMPOUNDS (con't.)

<u>Substituent</u> (Alkyl con't.)	<u>Emission Region</u> (nm)
dodecylbenzene	
o-xylene	
triethylbenzene	279-295
m-xylene	
Hydroxy	
mono-hydroxy	
phenol	
nonylphenol	
o-cresol	
p-cresol	
o-tert-butylphenol	288-300
p-tert butylphenol	
2,4-dimethylphenol	
3,5-dimethylphenol	
dihydroxy	
hydroquinone	
resorcinol	303-326
catechol	
trihydroxy	
pyrogallol	395
Cyano	
benzonitrile	287

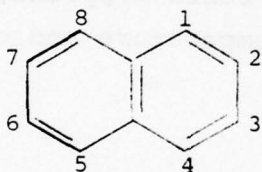
TABLE 9. SUMMARY OF EMISSION REGION FOR BENZENE
SUBSTITUTED COMPOUNDS (con't.)

<u>Substituent</u>	<u>Emission Region (nm)</u>
Amino	
aniline	
methylaniline	
p-toluidine	316-328
4-chloro-o-toluidine	
p-chloroaniline	
Halo	
p-chlorotoluene	288-305
p-chlorophenol	
Acid	
phthalic	
gallic	340-409
salicylic	


4.2.5 Polynuclear Aromatic Hydrocarbons (PAH)

In general, PAH have high quantum efficiencies of fluorescence allowing detection at low levels and tend to have sharp vibronic structure even at room temperature. The sharp vibronic structure and high quantum efficiency can be seen in compounds like benzo(a)pyrene, benzanthracene and dibenzanthracene. The fusing together of benzene rings in a sequence such as benzene, naphthalene, and anthracene, results in a decrease in energy between the lowest excited singlet and ground states. This results in a progressive movement of the fluorescence from the ultraviolet to the visible with anthracene emitting in the blue.


The emission maxima for benzene, naphthalene and anthracene show the expected shift: 279 nm, 323 nm, and 378 nm, respectively. Within this same series of linear polynuclear aromatic hydrocarbons the fluorescence yield increases as evidenced by the change in detection limit. There is greater than a 1000 fold change in quantum yield from benzene to anthracene. In most cases there is no significant wavelength shift for linear polynuclear aromatic hydrocarbons when the solvent is changed from a non-polar solvent like cyclohexane to a polar one like ethanol. The lack of solvent effect can be seen in the results for anthracene (section 3) where data was taken in both cyclohexane and ethanol. Alkyl substitution on a polynuclear aromatic hydrocarbon causes a red shift in the fluorescence spectrum. In large systems like naphthalene and anthracene this shift is dependent upon the positions of the substituent groups and are usually additive. Substituents placed in 2,3,6 and 7 positions of naphthalene have a larger effect on shifting spectra to



longer wavelengths than substituents in the 1,4,5, and 8 positions (5). Anthracene which can be considered a 2,3, or 6,7 substituted naphthalene causes a 50 nm shift in emission maxima.

Acenaphthalene,  which can be considered an alkylbridged

naphthalene has little effect on the emission maxima of

naphthalene. Fluoranthene,  which can be considered a

substituted naphthalene (35) causes a large shift in emission maxima primarily due to the effect of the benzene ring. The amino group in 1-naphthylamine produces a large (50 nm) red

shift, a loss in structure and a 20-fold decrease in detection limit. Heavy atom substitution as in chloronaphthalene produces no significant wavelength shift but does cause a reduction in the fluorescence efficiency. This can be seen in the five-fold poorer detection limit for chloronaphthalene. Tetrahydronaphthalene is structurally more like an alkyl substituted benzene. Its emission maximum is only slightly shifted from benzene and its width at half maximum is similar. There is a slight improvement in detection limit for tetrahydronaphthalene when compared to benzene similar to other alkyl substituted benzenes.

The other PAH studied in this contract can be considered bent systems. Naphthalene and anthracene are linear systems whereas benzanthracene, chrysene, 1,2,5,6-dibenzanthracene and benzo(a)pyrene are bent systems. Anthracene, benzanthracene, chrysene, 1,2,5,6-dibenzanthracene and benzo(a)pyrene exhibit sharp vibronic structure at room temperature and can be detected at 1-10 ppb levels.

4.2.6 Heteroatom Compounds

The presence of a heteroatom greatly affects the luminescence of aromatic compounds. Heteroatoms possess lone pairs of nonbonding electrons which can undergo photochemical changes and compete with luminescence. Heterocyclic compounds (heteroatom incorporated in a ring) are usually very basic and the fluorescence and phosphorescence will be dependent on the choice of solvent. Under this contract both heterocyclic and heteroatom compounds were studied.

In several samples the heteroatom separated two benzene rings. These samples included diphenylether, diphenylamine, diphenyldichlorosilane and diphenylhydrazine. The results for these samples are varied. Diphenyldichlorosilane is much like benzene.

There is little change in the emission maximum and the detection limit is similar to benzene. In the case of diphenylether and diphenylamine there is a slight red shift from benzene, 13 and 45 nm respectively, with a small improvement in the detection limit for diphenylether. Diphenylamine underwent photochemical changes as the spectrum was being run. Diphenylhydrazine exhibited no fluorescence which may be related to the instability of the compound to oxidation.

Piperazine, acridine and quinoline were the heterocyclic compounds studied under this contract. Piperazine was non fluorescent. This result is not unexpected for saturated heterocyclic systems. Both acridine and quinoline were fluorescent. The fluorescence bands of acridine in neutral solution are located in the same spectral region as anthracene. The spectrum of acridine at room temperature is more diffuse but the structure becomes resolved at low temperature. The fluorescence emission of acridine is complicated by the presence of impurities and may be undergoing photochemical changes. The acridine emission is stronger in ethanol than in cyclohexane which is consistent with the increase in polarity of the solvent (36). Quinoline in non-polar solvents has an $n-\pi^*$ lowest excited state and is virtually non-fluorescent. In polar solvents the position of the $\pi-\pi^*$ and $n-\pi^*$ state reverses and gives rise to fluorescence emission. Quinoline was studied in cyclohexane, a non-polar solvent, and ethanol. The true emission is complicated by the presence of an impurity making identification of quinoline fluorescence difficult.

4.2.7 Oils

It is not surprising that the oils studied under this contract, (castor, coconut, cod liver, lard, linseed, olive, palm, peanut and soya bean) were for the most part weakly

fluorescent. The major constituents of these oils are saturated and unsaturated fatty acids which are not likely to fluoresce. Most of the oils had to be studied at fairly high concentrations (200-400 ppm) in order to see any fluorescence at all. This weak fluorescence is probably due to certain proteins or other natural products which are fluorescent and present in these oils. Since oils are complex mixtures it was important to excite at several different wavelengths. In several cases, two different emissions were obtained.

The results for the oils studied are tabulated below.

TABLE 10. OILS STUDIED UNDER CONTRACT

<u>Oil</u>	<u>Conc.</u> (ppm)	<u>Solvent</u>	λ_{ex} (nm)	λ_{em} (nm)	<u>O.D.</u>	<u>Comment</u>
Castor Oil	390	ethanol	290	328	.025	Relatively strong single emission.
	286	cyclohexane	280	---	.051	Weak emission shoulder on solvent Raman.
	286	cyclohexane	320		>.01	Weak emission at 420 nm.
Coconut Oil	286	cyclohexane	290	330	>.01	Weak fluorescence occurs at both 280 and 290 nm excitation wavelengths, no emission occurs at 350 nm excitation.
Cod Liver Oil	323	cyclohexane	260	320	.027	Excitation at 260 nm and 280 nm produce similar emission spectra. Excitation at 350 nm produces a long wavelength emission centered at 500 nm.
	323	cyclohexane	280	320	.029	
	323	cyclohexane	350	500	.021	

TABLE 10. OILS STUDIED UNDER CONTRACT (con't.)

<u>Oil</u>	<u>Conc.</u> (ppm)	<u>Solvent</u>	$\frac{\lambda_{ex}}{(\text{nm})}$	$\frac{\lambda_{em}}{(\text{nm})}$	<u>O.D.</u>	<u>Comment</u>
Cottonseed Oil	305	cyclohexane	280	320	.119	Excitation at 280 nm and 320 nm produced weak and different emissions for both wavelengths.
	305	cyclohexane	320	380	>.01	
Lard	287	cyclohexane	270	330	.045	Only a very weak emission was seen when the sample was excited at 270 nm. Long wavelength excitation did not produce any long wavelength emission.
Linseed Oil	355	cyclohexane	300	418	.036	Shows relatively strong emission when excited at 300 nm.
Olive Oil	237	cyclohexane	260	320	.076	Shows very weak emission at both excitation wavelengths.
	290	cyclohexane	310	---	.01	
Palm Oil	300	cyclohexane	260	320	.012	Shows two different and relatively weak emissions when excited at 260 and 350 nm.
	310	cyclohexane	350	500	>.01	
Peanut Oil	249	cyclohexane	260	320	.038	Very weakly emitting oil, almost no detectable emission.
	249	cyclohexane	290	320	.011	
Soya bean Oil	290	cyclohexane	270	---	.037	Very weakly emitting oil; almost no detectable emission.
	290	cyclohexane	320	---	.01	

4.2.8 Herbicides and Insecticides

Fluorescence has been used for the identification and quantitation of herbicides and insecticides. Solution methods have been developed and can be very sensitive in certain cases but care must be taken that impurities do not interfere with the measurement. In general, fluorescence analysis of herbicides and insecticides usually involves preparation on thin layer chromatography (TLC) (37). Thin layer chromatography relies on four methods for analysis. These include 1) the native fluorescence of the compound, 2) fluorogenic labelling, 3) release of a fluorescent chelating agent through complexation with the herbicide or insecticide or 4) conversion of a non-fluorescent compound to a fluorescent compound by means other than addition of a labelling agent. The TLC method incorporates several errors such as reproducibility of spot size, uniformity of the spot and weighing and integration to quantitate the amount of herbicide or insecticide present. Direct analysis would be the best way to analyze these materials. Several herbicides and insecticides studied under this contract can be measured directly. The results of our findings are tabulated below. (See Table 11.)

TABLE 11. SUMMARY OF HERBICIDES AND INSECTICIDES STUDIED

COMPOUND	TYPE	STRUCTURE	λ ex (nm)	λ em (nm)	DETECTION LIMIT (PPM)	COMMENT
Atrazine	herbicide		290	350	300	Very weakly fluorescent.
Azinphosmethyl	insecticide		340	420	4	More strongly fluorescent in ethanol than cyclohexane.
Carbaryl	insecticide		285	335	.01	-----
Coumaphos	insecticide		320	377	0.3	-----

TABLE 11. SUMMARY OF HERBICIDES AND INSECTICIDES STUDIED (Con't.)

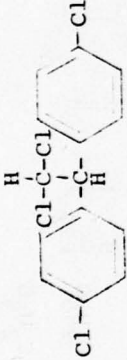
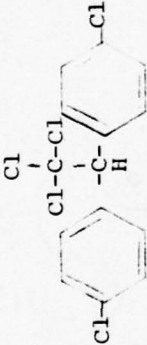
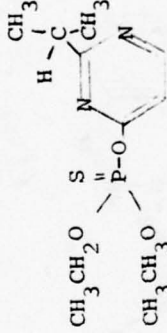
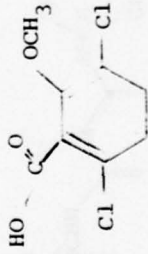
COMPOUND	TYPE	STRUCTURE	λ_{ex} (nm)	λ_{em} (nm)	DETECTION LIMIT (PPM)	COMMENT
DDD	insecticide		240	294	4	
DDT	insecticide		245	291	7	Separation of DDD and DDT by fluorescence would be difficult.
Diazinon	insecticide		---	---	---	
Dicamba	herbicide		310	420	0.9	

TABLE 11. SUMMARY OF HERBICIDES AND INSECTICIDES STUDIED (Con't.)

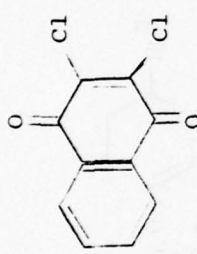
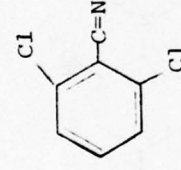
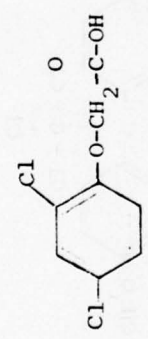
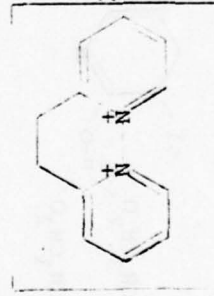
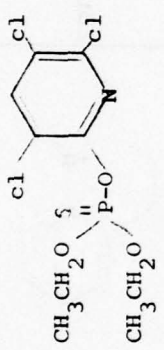
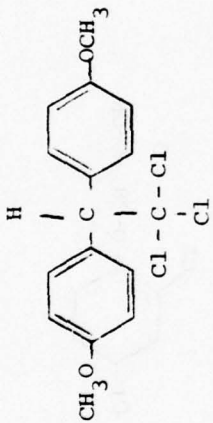
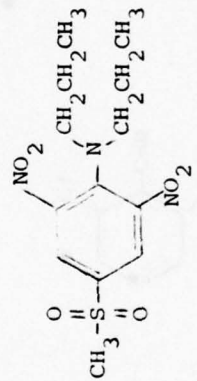
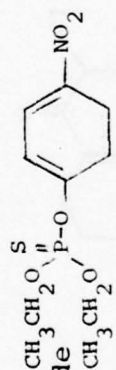
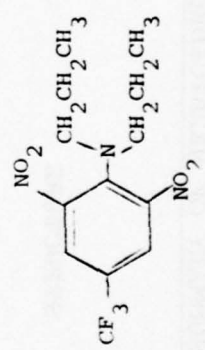
COMPOUND	TYPE	STRUCTURE	λ ex (nm)	λ em (nm)	DETECTION LIMIT (PPM)	COMMENT
Dichlone	herbicide		---	---	---	Non-emitter at room temperature, exhibits phosphorescence at 77°K.
Dichlorobenzil	herbicide		285	312	0.6	
2,4,-D 2,4-Dichloro- phenoxyacetic acid	herbicide		270	310	30	
Diquat dibromide	herbicide		310	348	.05	

TABLE 11. SUMMARY OF HERBICIDES AND INSECTICIDES STUDIED (CON'T)

COMPOUND	TYPE	STRUCTURE	λ ex (nm)	λ em (nm)	DETECTION LIMIT (PPM)	COMMENT
Durban (Chloropyrifos)	insecticide		280	326	0.5	
Methoxychlor	insecticide		270	299	0.8	
Nitralin	herbicide		---	---	---	Not run-presence of nitro groups strongly quenches fluorescence.
Parathion	insecticide		---	---	---	
Trifluralin	herbicide		---	---	---	Not run-presence of nitro groups strongly quenches fluorescence.

Several of the pesticides studied should not fluoresce based on their structure. It is possible that the emission is due to an impurity. Spectra run on ultra pure compounds would be the best way to determine if the fluorescence measured is attributed to the structure. A careful examination of the onset of absorption and the location of the fluorescence may help clarify this problem. In Figures 9 and 10 the absorption spectra of several of the herbicides and insecticides studied in this contract are superimposed. From these figures it is clear that selective excitation of a single compound in a mixture of these compounds would be very difficult. However, if only one material was present fluorescence or possibly phosphorescence would be a convenient and direct method for detection.

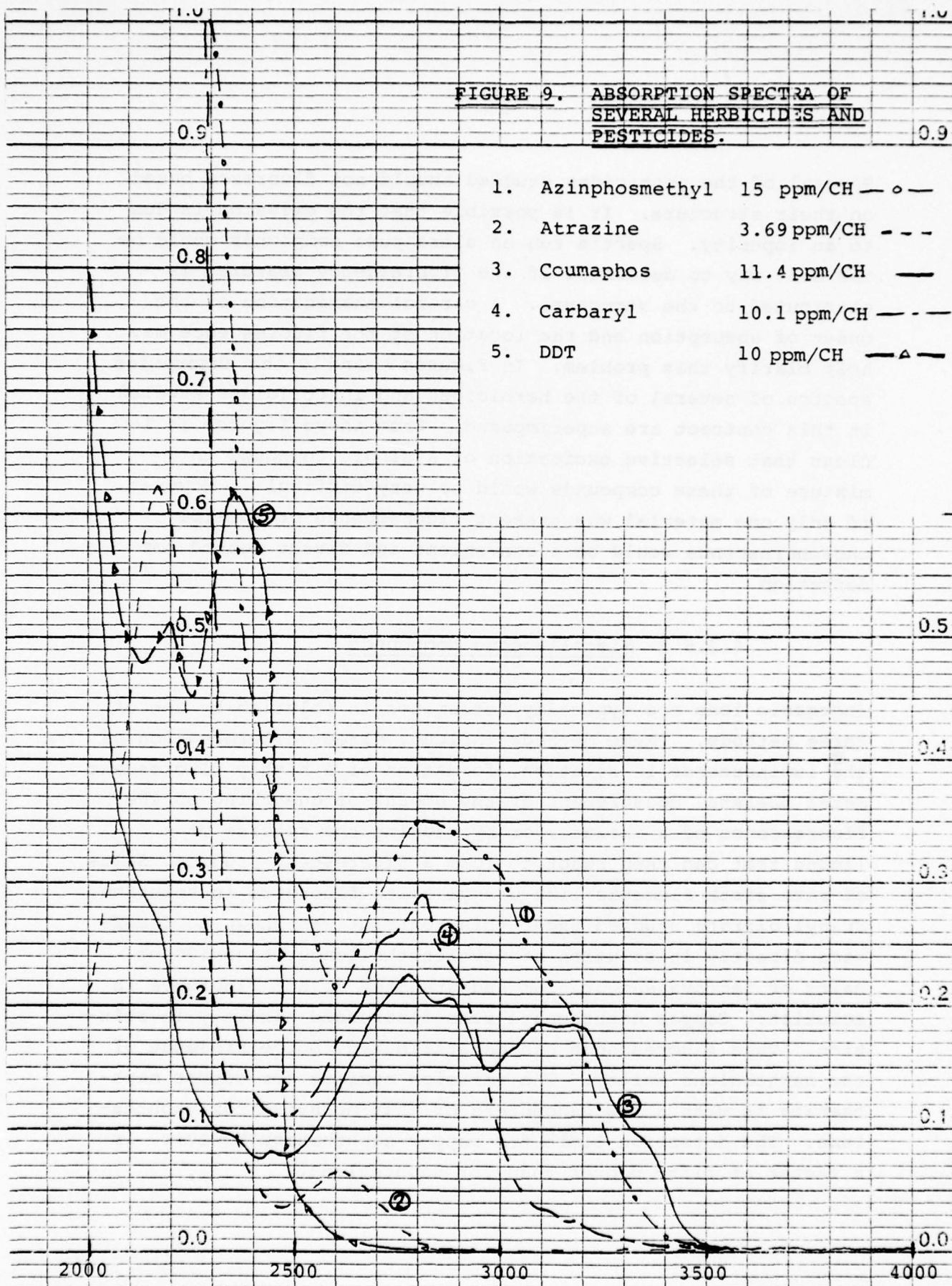
4.2.9 Miscellaneous Compounds

Inorganic ions are typically determined in solution by one of three methods. These methods include, direct determination of the luminescence in solution, formation of a highly fluorescent metal chelate, measurement of the amount of quenching of the fluorescence of a chelate, or by causing the release of a ligand that can then react to form a fluorescent product. Salts of rare earth elements like uranyl salts fluoresce in solution. Uranyl nitrate studied under this contract was shown to fluoresce directly in solution at wavelengths longer than 500 nm. Salts of tetravalent uranium and uranates do not fluoresce in solution. Copper naphthenate also fluoresced directly in solution. This fluorescence can be attributed to the presence of the naphthalene moiety. The emission maximum for copper naphthenate is with a few nanometers of that measured for naphthalene. The detection limit for copper naphthenate however, is a factor of fifty poorer than for naphthalene.

FIGURE 9. ABSORPTION SPECTRA OF SEVERAL HERBICIDES AND PESTICIDES.

- | | | | |
|----|----------------|-------------|-------|
| 1. | Azinphosmethyl | 15 ppm/CH | —○— |
| 2. | Atrazine | 3.69 ppm/CH | - - - |
| 3. | Coumaphos | 11.4 ppm/CH | — |
| 4. | Carbaryl | 10.1 ppm/CH | — · — |
| 5. | DDT | 10 ppm/CH | —△— |

OPTICAL DENSITY



WAVELENGTH

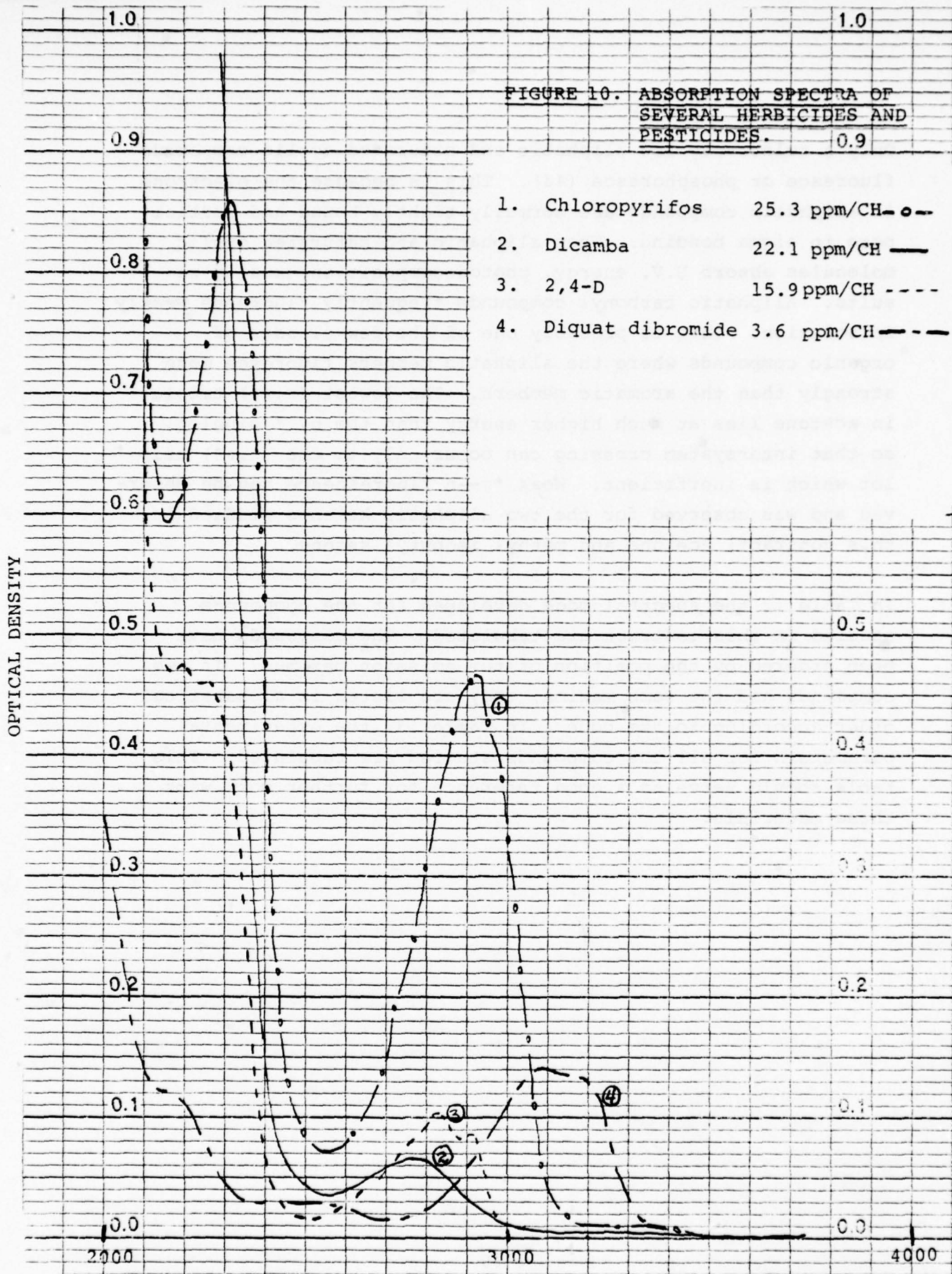


FIGURE 10. ABSORPTION SPECTRA OF SEVERAL HERBICIDES AND PESTICIDES.

1. Chloropyrifos 25.3 ppm/CH-o--
2. Dicamba 22.1 ppm/CH —
3. 2,4-D 15.9 ppm/CH ----
4. Diquat dibromide 3.6 ppm/CH - - -

OPTICAL DENSITY

WAVELENGTH 4-39

Only a relatively few aliphatic and saturated cyclic compounds fluoresce or phosphoresce (43). This is because the electrons in aliphatic compounds are normally tightly bound and participate in sigma bonding. When aliphatic and saturated cyclic molecules absorb U.V. energy, photodecomposition usually results. Aliphatic carbonyl compounds frequently fluoresce weakly in solution. This is probably one of the few classes of organic compounds where the aliphatic members fluoresce more strongly than the aromatic members. The lowest (π, π^*) triplet in acetone lies at much higher energy than the n, π^* singlet, so that intersystem crossing can occur only to the (n, π^*) triplet which is inefficient. Weak $\pi^* \rightarrow n$ fluorescence can be observed and was observed for the two aliphatic ketones studied in this contract; acetone and methyl isobutyl ketone.

In Table 12 the spectral code developed for the compounds studied in this contract are tabulated. The compounds have been ordered by the position of the emission maximum. If two compounds had the same maxima, they are listed in alphabetical order according to the code. In Table 13, the experimental parameters for all the compounds studied are tabulated. This table should serve as a good reference for further work with these materials.

TABLE 12. LIST OF CODED SPECTRA

<u>Spectral Code</u>	<u>Compound</u>
279-24-3(2)-BNZ	Benzene
280-28-1(3)-BMA	Benzyltriethylammonium Chloride
283-27-1(2)-BZA	Benzylamine
283-28-2(1)-CUM	Cumene
283-28-1(2)-DEB	Diethylbenzene
283-26-2(2)-ETB	Ethylbenzene
283-34-1(2)-TPT	Turpentine
284-27-2(1)-BAL	Benzyl alcohol
284-27-2(2)-THN	Tetrahydronaphthalene
284-27-2(2)-TOL	Toluene
284-32-2(3)-UDB	Undecylbenzene
285-28-1(2)-CMP	p-Cymene
285-30-2(2)-DDS	Dichlorodiphenylsilane
285-30-3-DDB	Dodecylbenzene
285-28-1(1)-TAP	p-Toluene sulfonic acid
285-30-1-XLO	o-Xylene
287-28-2(1)-BZN	Benzonitrile
288-29-1(3)-CTN	p-Chlorotoluene
288-30-1(2)-PHN	Phenol
288-62-1(1)-TCP	Tricresyl phosphate
291-26-1(2)-DPE	Diphenylether
291-28-1(1)-DDT	DDT
292-28-1(2)-TEB	1,3,5-Triethylbenzene
293-30-1-CRO	o-Cresol
294-30-1(2)-DDD	DDD
295-30-1(1)-BOP	o-tert-Butylphenol
295-31-1(1)-BTP	p-tert-Butylphenol
295-28-1(1)-DPM	3,5-Dimethylphenol
295-28-1-XLM	m-Xylene
297-30-1(1)-PEN	Polyethoxylated nonylphenol
298-28-1-NNP	Nonylphenol
299-30-1(2)-CRP	p-Cresol
299-30-1(1)-MTC	Methoxychlor
300-31-1-DMH	2,4-Dimethylphenol

TABLE 12. LIST OF CODED SPECTRA (con't.)

<u>Spectral Code</u>	<u>Compound</u>
303-39-1(1)-RSC	Resorcinol
304-30-1(1)-BPA	Bisphenol A
305-30-1-CPN	p-Chlorophenol
305-30-2(2)-DOW	Dowtherm
306-32-2(2)-STY	Styrene
307-48-1-DEP	Diethylphthalate
307-35-1(2)-MSR	α -Methylstyrene
310-46-1-CTC	Catechol
310-46-1(1)-DCA	2,4-Dichlorophenoxyacetic acid
310-N-2-DEG	Diethylene glycol
310-64-1-WCA	Carnauba Wax
312-30-1(2)-DIB	Dichlorobenil
316-32-1-ANC	Aniline
317-35-1(1)-PC4	Aroclor 1242
317-35-2(1)-PC5	Aroclor 1254
320-N-1-DEP	Diethylphthalate (Ex. 280nm)
320-N-1-OCL	Cod Liver Oil (Ex. 260nm)
320-N-1-OCL	Cod Liver Oil (Ex. 280nm)
320-N-1(1)-OCS	Cottonseed Oil (Ex. 280nm)
320-N-1-OOL	Olive Oil
320-60-1-OPM	Palm Oil (Ex. 260 nm)
320-N-1-OPN	Peanut Oil
323-20-4(3)-ACN	Acenaphthene
323-24-2(3)-NPT	Naphthalene
325-35-1-MAN	n-Methylaniline
325-34-1(1)-TLI	p-Toluidine
326-60-1(2)-CNN	Copper naphthenate
326-52-1-DUR	Chloropyrifos (Dursban)
326-38-1(1)-HDQ	Hydroquinone
327-56-1-BRU	Brucine
328-38-1-CAP	p-Chloroaniline
328-34-3(4)-CNA	1-Chloronaphthalene
328-39-1(1)-COT	4-Chloro-o-toluidine
328-43-1-OCA	Castor Oil

TABLE 12. LIST OF CODED SPECTRA (con't.)

<u>Spectral Code</u>	<u>Compound</u>
330-N-1(1)-OCC	Coconut Oil
330-N-1-OLD	Lard
333-37-1(2)-DAM	Diphenylamine
335-36-2(3)-CBY	Carbaryl
335-86-1(1)-PGA	Pyrogallic acid
340-100-1-PHA	Phthalic acid
340-100-1-TNA	Tannic acid
346-77-1-GLA	Gallic acid
347-52-1(1)-SDB	Sodium dodecylbenzene sulfonate
348-41-1(1)-DOD	Diquat dibromide
369-32-2(3)-IND	Indene
377-74-1-COU	Coumaphos
377-55-1(1)-NAD	α -Naphthylamine
378-31-3(2)-ATH	Anthracene
380-N-1-OCS	Cottonseed oil (Ex. 320nm)
383-27-5(3)-CRY	Chrysene
386-28-4(1)-BAT	1,2-Benzanthracene
396-26-4(2)-DBA	1,2,5,6-Dibenzanthracene
400-N-1-MIK	Methyl isobutyl ketone
405-5-6(2)-BAP	Benzo(a)pyrene
409-64-1-SLA	Salicylic acid
410-N-1-ACT	Acetone
410-58-2-AZP	Azinphosmethyl/CH
418-105-1-OLS	Linseed Oil
420-52-2(1)-ACD	Acridine/ETOH
420-82-1-AZP	Azinphosmethyl/ETOH
420-70-1-DIC	Dicamba
430-94-2-ACD	Acridine/CH
464-91-2(3)-FLA	Fluoranthene
500-150-1-OCL	Cod Liver Oil (Ex. 330nm)
500-141-1-OPN	Palm Oil (Ex. 350nm)
520-56-3-UAN	Uranyl Nitrate

TABLE 13. SUMMARY OF EXPERIMENTAL PARAMETERS AND RESULTS.

CODE	CONC (PPM)	SOL-VENT	λ_{exc} (nm)	λ_{max}^{em} (nm)	# PEAKS	WIM (nm)	# SHOULDER	DETEC-TION LIMIT (D.L.) (PPM)	λ_{DL} (nm)	COMMENTS
Acenaphthene	1.03	CH	290	323	4		3	.001	290	
Acetone	227	CH	290	410	1			212	290	
Acridine	96	CH	285/355	386/422	4/2		2/0			
ACR	9.6	ETOH	290/355	357/415	2/2		1/1	.02/.04	290/355	
Aniline	15.5	CH	280	316	1			.037	280	No fluorescence data taken
Anisoyl Chloride										
Anthracene	1.03	CH	355	378	4		1	.001	355	
ATH	1.55	ETOH	355	380	4		1	.001	355	
Aroclor 1242	131	CH	270	317	2	35	1	.3	270	
PC4	129	CH	270	317	2	36	1	2	270	
PC5	369	CH	290	350	1	--		300	290	
AT2	112	CH	350	410	2	60		10	350	
AZP	122	ETOH	340	420	2	80		4	340	
Benz(a)anthracene	1.1	CH	280	386	4		1	.003	280	
Benzene	79	CH	250	279	3	24	1	2/4	250/265	
BNZ	9.9	CH	260	287	2	28	1	.1/.1	260/270	
Benzo(a)pyrene	0.088	CH	370	405	6		2	.002	370	Non-fluorescent
BAP	104	CH	260							
Benzoyl chloride										
BAL	99	CH	250	284	2	27	1	.1/.1	250/260	
Benzyl alcohol	118	CH	250	283	1	27	2	3/2	250/260	
BAM	210	H2O	250	280	1	28		59	250	
Benzyl triethyl-ammonium chloride										
BPA	10.5	ETOH	270	304	1	30	1	.04/.02	270/285	
Bisphenol A	13.5	ETOH	280	327	1	56		2/2	280/295	Non-fluorescent
Brucine										
Butyl benzylphthalate										
BBP	21	CH	265	295	1	30	1	.1/.1	265/275	
0-Tert-Butylphenol	17.5	CH	260	295	1	31	1	.6/.4	260/280	
p-Tert-Butylphenol	1.0	CH	285	335	2	36	2	.01	285	
Carbaryl	63.5	CH	260	310	1	64		42	260	
Carnauba Wax	390	ETOH	290	328	1	43	2	20	290	
Castor Oil	286	CH	280/320		1			180/300	280/320	
Catechol	8.7	H2O	265	310	1	46		.4/.2	265/280	
4-Fluoromiline	17.2	CH	290	328	1	36	1	.2	290	
1-Chloro-2,3-dichloro-benzene	11.3	CH	290	328	3	34	4	.1	290	

TABLE 13. SUMMARY OF EXPERIMENTAL PARAMETERS AND RESULTS (cont.).

CODE	CONC (PPM)	SOLVENT	λ_{exc} (nm)	λ_{em}^{max} (nm)	# PEAKS	MHM (nm)	# SHOULDER	DETECTION LIMIT (DL) (PPM)	λ_{DL} (nm)	COMMENTS
p-Chlorophenol	101	CH	260	305	1	30		1/.1	260/285	
Chlorpyrifos (Dursban)	25.3	CH	280	326	1	52		1/.5	280/295	
p-Chlorotoluene	23.8	CH	265	298	1	29	3	1/.8	265/275	
p-Chloro-o-toluidine	25	CH	290	328	1	39	1	.09	300	
Chrysene	1.0	CH	270	383	5			.002	270	
Cocaine Oil	286	CH	290	330				100	290	
Coal Liver Oil	323	CH	260/280 340	300/320 340	1/1	150		500/140 65	260/280 310	
Copper Naphthenate	98	CH	260	326	1	60	3	3/1	260/280	
Cottonseed Oil	305	CH	280/320/380		-			165,300	80,320	
Coumaphos	11.4	CH	320	377	1	74		.3	320	
o-Cresol	12.0	CH	265	293	1	30	1	.04	280	
p-Cresol	10.3	CH	265	299	1	30		.03	280	
Cumene	101	CH	250	283	2	28	1	3	250	
p-Cymene	11.8	CH	260	285	1	28	2	.4/.2	260/270	
DDD	61.	CH	240	294	1	30	2	4	240	
DDE	87	CH	245	291	2	28	2	7	245	Non-fluorescent
DZN										
1,2,5,6-Dibenzanthracene	.015	CH	300	396	4		2	.001	300	
Dicamba	22.2	H2O	310	420	1	70		.9	310	
Dichloroacetic acid	2.8	CH	280							Non-fluorescent
Dichlorobenzil	108	CH	285	312	1	30		.6	285	
2,4-Dichlorophenoxy-	159	CH	270	310	1	46	1	30	270	
Diethylbenzene	100	CH	255	283	1	28	2	.2/.1	255/270	
Diethylene glycol	202	CH	265	310	2			202	265	
Diethylphthalate	145/289	CH	260/280	300/320	1/1				280	
2,4-Dimethylphenol	10.5	CH	265	300	1	31	1	.2/.04	265/280	
3,5-Dimethylphenol	10.5	CH	265	295	1	28	1	.07/.03	265/280	
Dimethyl terephthalate										Non-fluorescent
2,4-Dinitroaniline										Non-fluorescent
4,6-Dinitro-cresol										Non-fluorescent
2,4-Dinitrophenol	10.4	H2O	270	350						Non-fluorescent
Diphenylamine	11.2	CH	290	333	1	37	2		290	Photochemical change
	1.2	CH	290	333	1	37	2		290	

CODE	CONC (PPM)	SOLVENT	λ_{exc} (nm)	λ_{max}^{em} (nm)	# PEAKS	WHM (nm)	# SHOULDERS	DETECTION LIMIT (D.L.) (PPM)	λ_{DL} (nm)	COMMENTS
DDS	157	CH	260	285	2	30		3/2	260/270	
DPH	32.6	ETOH								Non-fluorescent
DQD	35.5	H2O	310	348	1	41	1	.055	310	
DIU										Not received
DDB	116	CH	250	285	3	30		*	250	Strong impurity
	116	CH	220	285	3	30		11.6	220	
DTH	10.8	CH	260	305	2	33	2	.035	260	
ETB	10.1	CH	250	281	2	26		3.1/1.5	250/260	
FLA	1.0	CH	360	465	2	91	3	.005	360	
GLA	103	H2O	290	346	1	77		.70	290	
HDQ	1.1	H2O	290	326	1	38	1	.025	290	
IND	175	CH	260	309	2	32	3	.12	260	
OLD	340	CH	270	330					270	
OLD	287	CH	280	330	1				280	
OLS	355	CH	300	418	1	105		32.	300	
MOC	95	CH	270	299	1	30	1	1.3/0.8	270.280	
MAN	10.8	CH	290	325	1	35		.01	290	No fluorescence data taken
Methylene di-p-phenylene diisocyanate										
Methyl isobutyl ketone	158	CH	290	400	1				290	
-Methyl styrene	105	CH	255	307	1	35	2	.12	255	
Naphthalene	10.5	CH	280	323	2	24	3	.02	280	
N-Propylamine	1.85	CH	325	377	1	55	1	.0012	325	
Nitroline										No fluorescence data taken
m-Nitroaniline										
Nonyl phenol	17.1	CH	265	298	1	28		.09	265	
Olive Oil	237	CH	260	320	1				360	
OOL	290	CH	310						310	
OPM	300	CH	260	320	1	60		218	260	
Palm Oil		CH	350	500	1	140		300	350	Non-fluorescent
Parathion K	3.5	CH	280							
Peanut Oil	249	CH	260, 290	320	1					
Phenol	11.9	CH	265	288	1	30	2	.011/.007	265/275	
Phenyl ether	20.4	CH	265	291	1	36	1	.10	265	

TABLE 13. SUMMARY OF EXPERIMENTAL PARAMETERS AND RESULTS (cont.)		CODE	CONC (PPM)	SOLVENT	λ_{exc} (nm)	λ_{max}^{em} (nm)	# PEAKS	WIM (nm)	# SHOULDER	DETECTION LIMIT (D.L.) (PPM)	λ_{DL} (nm)	COMMENTS
Phthalic acid	PHA	97	H2O	280	330	1	100			84	280	
Phthalic acid	PHA	228	H2O	270	340	1	100			114	270	
Piperazine	PPZ	235	CH	280	350	1						
Polyethoxylated nonylphenol	PEN	9.5	CH	265	297	1	30			.08/.33	265/280	
Pyrosalol	PGA	152	H2O	270	335	1	86		1	17	270	
Quinoline	QNL	113	EtOH	275	321	5			2			
		113	EtOH	355	420	1	70		0			Photolyzes
		95	CH	275	336	3			2	.37	275	Photolyzes
		95	CH	350		2	57		1			Photolyzes
Resorcinol	RSC	10.1	H2O	265	303	1	39		1	.135/05	265/280	
Salicylic acid	SLA	1.5	H2O	300	409	1	64			.005	300	
Sodium dodecylbenzenesulfonate	SDB	90	CH	290	347	1	52		2	.90	290	
Soya Bean Oil	SOB	290	CH	270, 320						.300	270, 320	
Styrene	STV	1.1	CH	270	306	2	32		2	.03	270	
Tallow	TLO											No fluorescence data taken
Tannic acid	TNA	13	H2O	280	340	1	100			.63	280	
1,2,3,4-Tetrahydro- naphthalene	TTH	12.3	CH	260	284	1	27		2	.21/.13	260/270	
p-Toluidine	TLI	14.1	CH	290	325	1	34			.03	290	
Toluene	TOL	107	CH	250	284	2	27		1	2.1/1.6	250/215	
p-Toluene sulfonic acid	TAP	120	H2O	260	285	1	28		1	2.1/1.5	260/265	
Tricresylphosphate	TCP	123	CH	260	288	1	66		1	.55/.35	260/270	
1,3,5-Trisubstituted benzene	TIB	122	CH	250	292	1	28		3	12.5/1.5	250/270	
Trifluorin	TFL											No fluorescent data taken
Turpentine	TPT	301	CH	260	283	1	34		3	31/13	260/270	
Undecylbenzene	UBB	87.3	CH	250	284	2	33		2	6.0	250	
Uranyl nitrate	UNN	61.	H2O	290	520	3	56		2	6.1/10.5	290/340	
m-Xylene	XIM	114	CH	260	285	1	28		1	2.0/1.4	260/270	
o-Xylene	XIO	92	CH	260	295	1	30			1.5/1.3	260/270	
Zirconium acetate	ZCA											See text

5. SUMMARY AND CONCLUSIONS

The results obtained in this contract showed that fluorescence offers a useful analytical tool for identifying and quantifying toxic and hazardous materials. One hundred-nine compounds were studied and ninety-six compounds were determined to be fluorescent. Some compounds (i.e., non-petroleum oils) fluoresced very weakly. However, in many cases, the emission was strong and offered detection at reasonably low levels, <1 ppm.

Several compounds were studied in two solvents; cyclohexane and ethanol. For some compounds changing the solvent to a more polar one can lead to dramatic effects on peak location. This change can be explained in terms of the Franck-Condon principle. An electronic transition must occur while the photon is in the vicinity of the absorbing molecules in about 10^{-15} sec. This is 10^3 - 10^4 times faster than the rate of bond stretching so that an electronic transition occurs before any change in interatomic distance will occur. The molecule now in a Franck-Condon excited state readjusts to its new environment by a solvent reorientation in 10^{-12} sec and reaches an equilibrium excited state. Emission then occurs in 10^{-8} sec. Thus, in solution, the molecule enters into one excited state and leaves from another excited state of slightly different energy levels. This is why fluorescence and absorption spectra are subject to different solvent effects. For polar molecules the excited state is more polar than the ground state. Increasing the polarity of the solvent produces a greater stabilization of the excited rather than the ground state. Hence, a shift to longer wavelength is observed. This type of behavior is observed for almost all cases even when the solute and solvent are not polar because of the induced dipole in the excited state. The magnitude of this shift is not great. Table 14 below summarizes the effect of solvent on anthracene absorption and fluorescence.

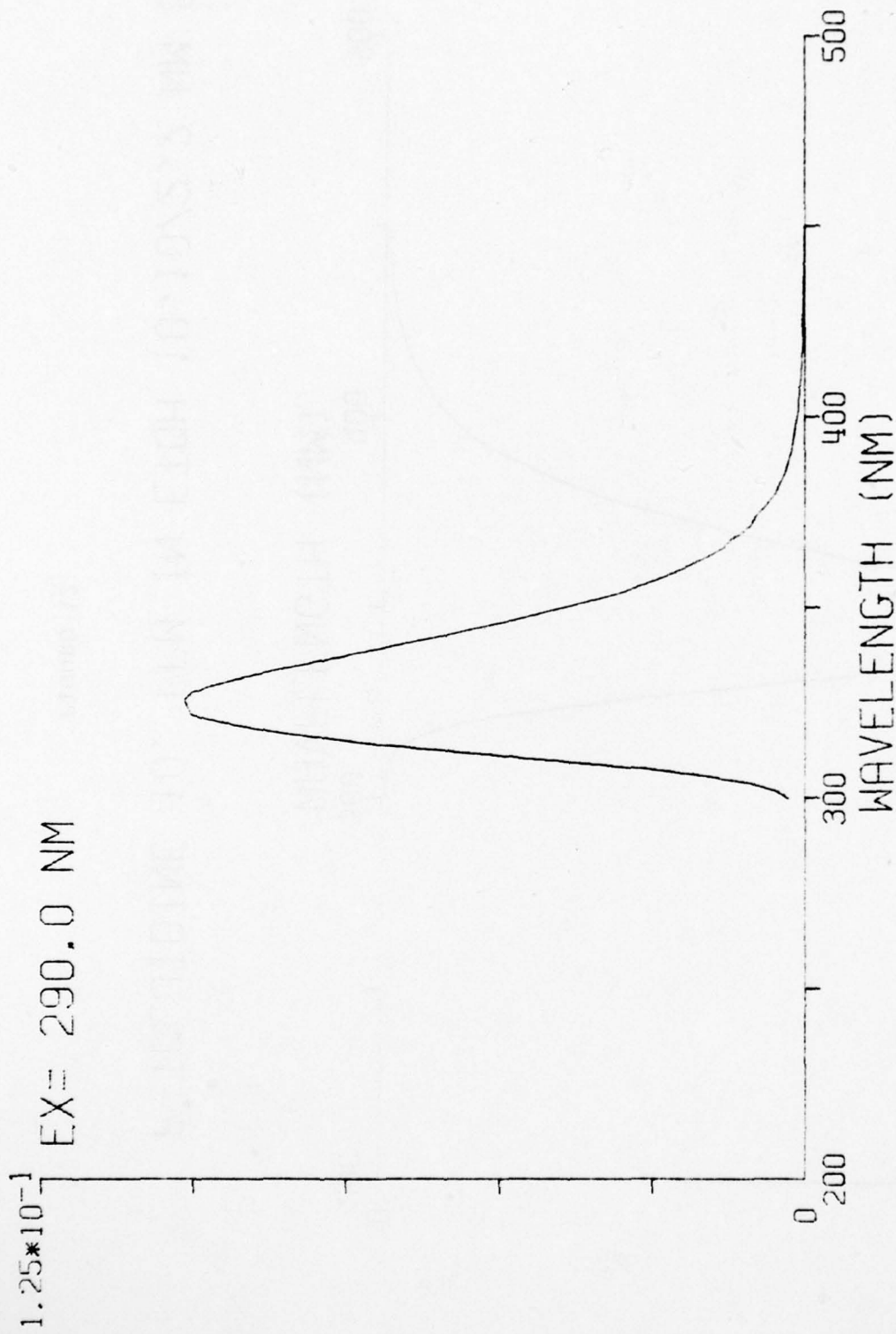
TABLE 14. EFFECT OF SOLVENT ON ANTHRACENE (45)

<u>Solvent</u>	\sqrt{F} cm^{-1}	λ_F nm
Vapor	27380	365
Hexane	26517	377
Methanol	26461	378
Dioxane	26220	381
Toluene	26170	382
Benzene	26116	383
Chlorobenzene	26064	384
Acetonitrile	25972	385
Formamide	25508	392
N-Methylformamide	25112	398

As further examples of this effect two other molecules were run in several solvents. Figure 11 shows the emission of p-toluidine in cyclohexane. The shift of the emission maximum to longer wavelength is clearly seen for p-toluidine in ethanol (Figure 12) and for a seventy percent solution of acetonitrile and water (Figure 13). A similar but not nearly as dramatic effect can be seen for p-tertbutylphenol in cyclohexane and ethanol (Figure 14 and 15). This solvent effect should be studied in great detail. It offers another parameter which may lead to further selectivity of the fluorescence method.

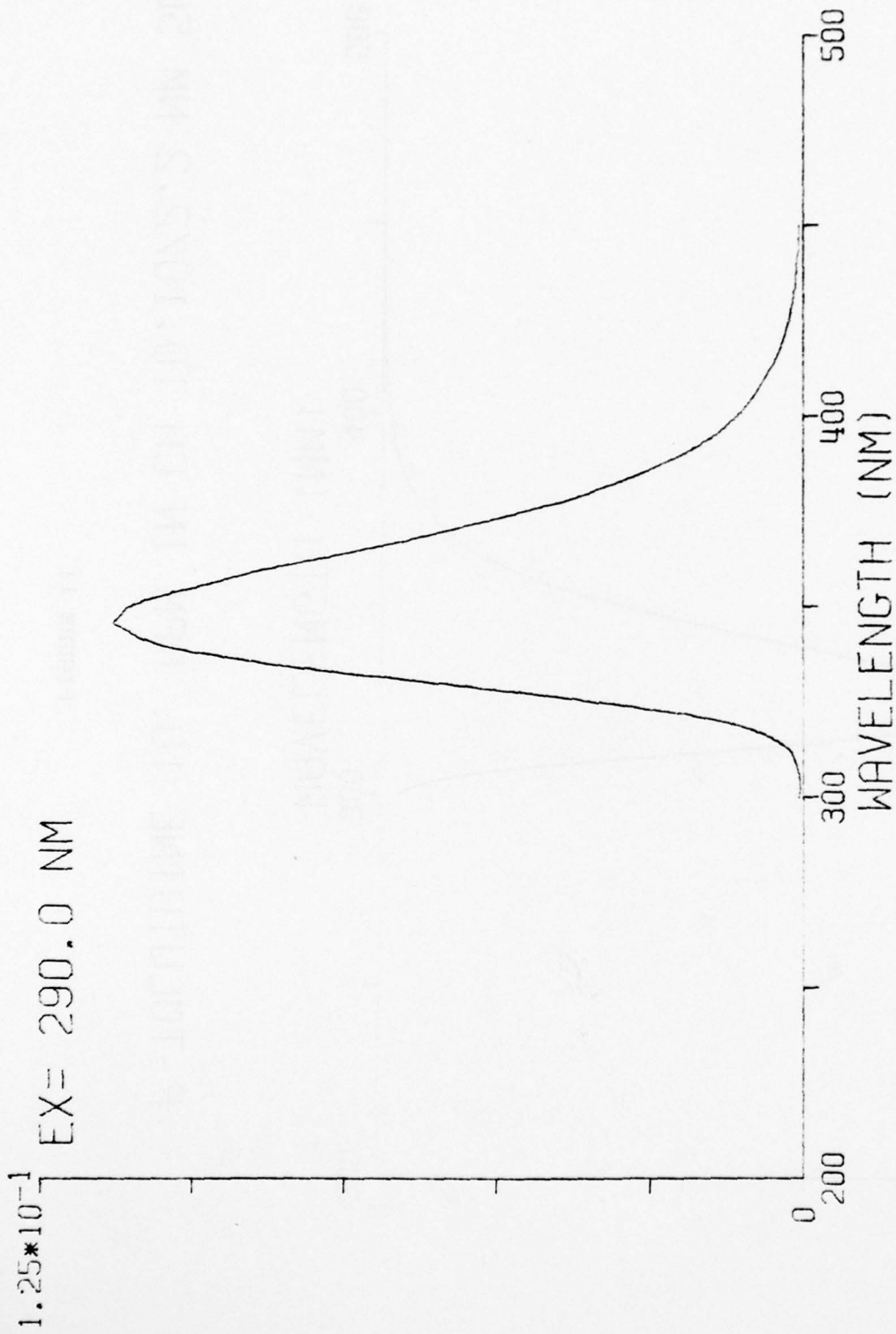
Impurities always present problems in analytical measurements. Several compounds studied under this contract showed fluorescing impurities. Attempts were made to separate the impurity emission from pure compound emission. This was not possible in all cases. Several compounds were determined to be fluorescent which based on their chemical structure should not be. This type of possible misassignment is due to the dominance of impurity emission. A careful examination of the absorption and fluorescence data may shed light on this problem.

1 / 24 / 79



P-TOLUIDINE 10. PPM IN CH 10,10/2,2 NM SLITS

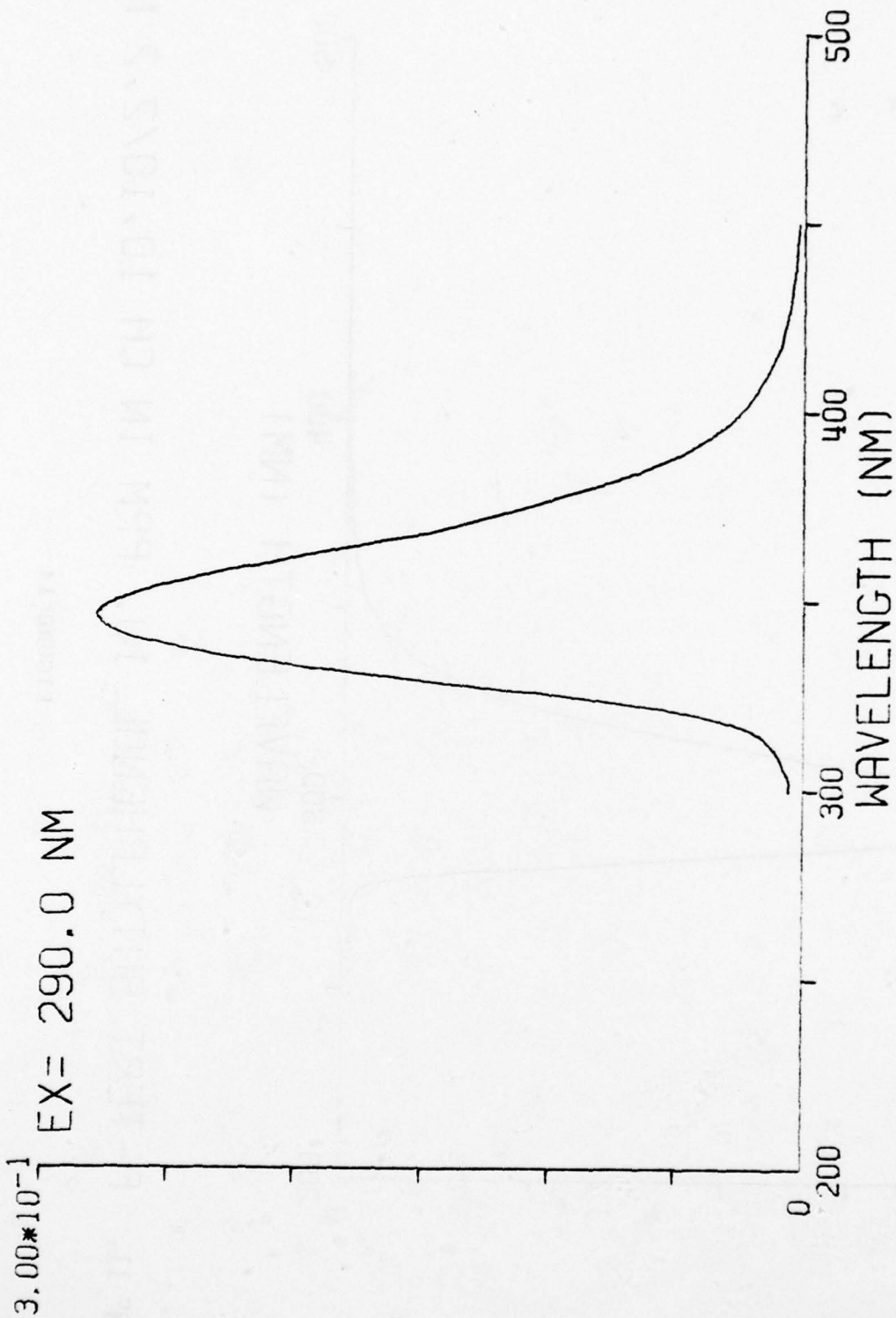
FIGURE 11



P-TOLUIDINE 10. PPM IN ETCH 10,10/2,2 NM SLITS

FIGURE 12

5 / 9 / 79



P-TOLUIDINE 10 PPM IN 70% CH₃CN IN H₂O 10,10/2,2

FIGURE 13

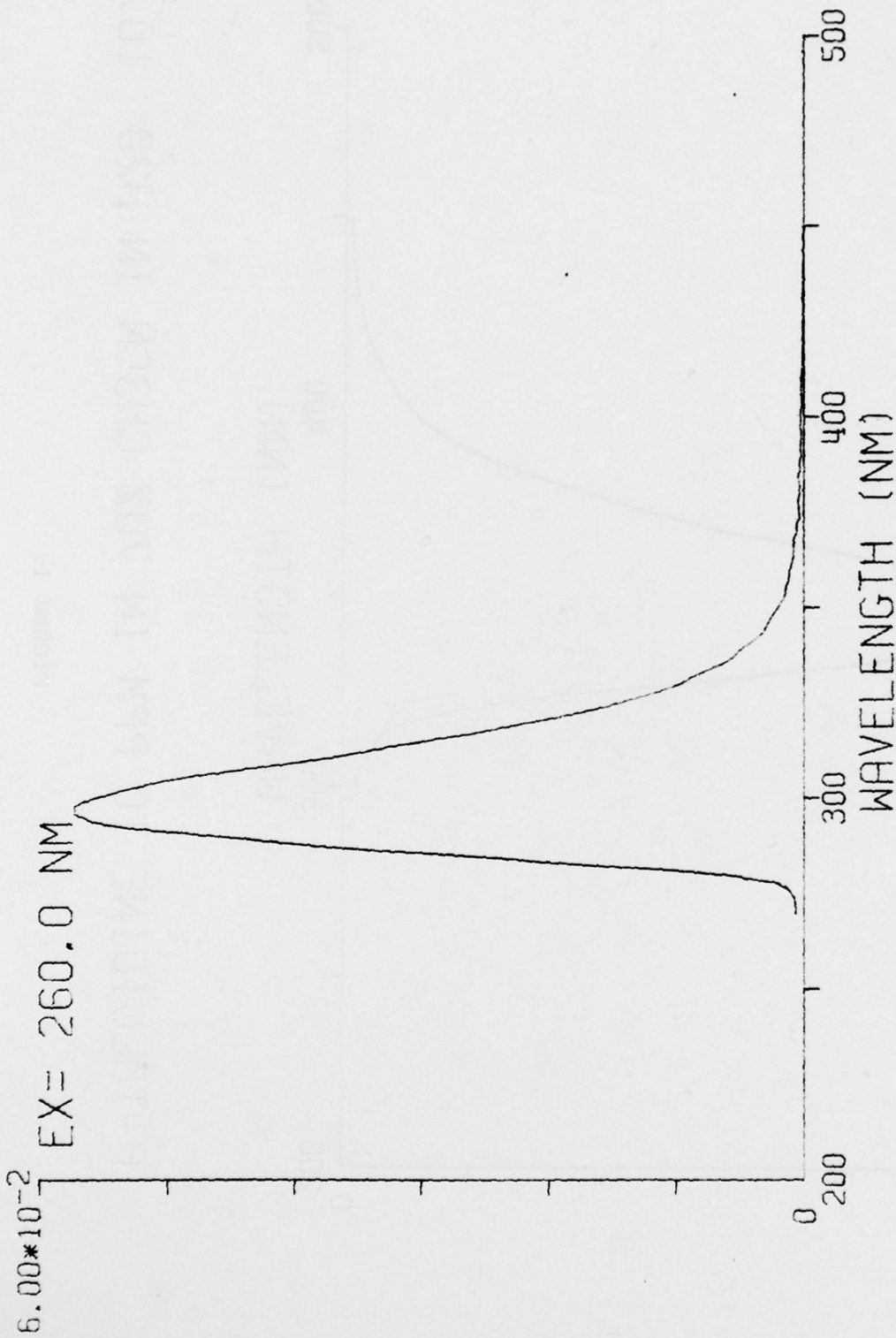


FIGURE 11. P-TERT BUTYLPHENOL 10. PPM IN CH 10,10/2,2 NM SLIT

FIGURE 14

1 / 24 / 79

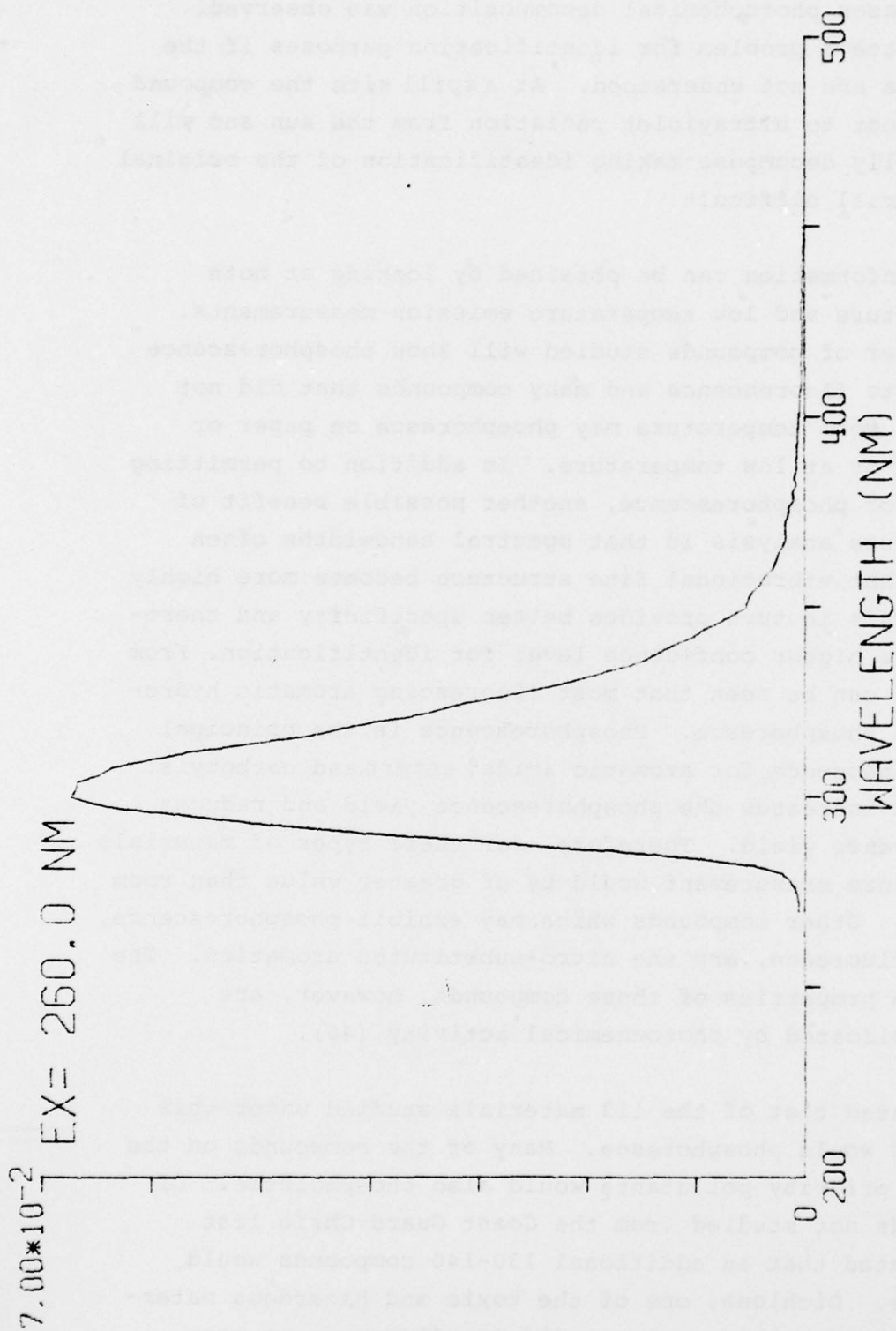


FIGURE 12. P-TERT BUTYLPHENOL 10. PPM IN ETØH 10,10/2,2 NM SL

FIGURE 15

In several cases photochemical decomposition was observed. This may create a problem for identification purposes if the photoproducts are not understood. At a spill site the compound will be subject to ultraviolet radiation from the sun and will photochemically decompose making identification of the original spilled material difficult.

Additional information can be obtained by looking at both room temperature and low temperature emission measurements. A large number of compounds studied will show phosphorescence in addition to fluorescence and many compounds that did not fluoresce at room temperature may phosphoresce on paper or other matrix or at low temperature. In addition to permitting observation of phosphorescence, another possible benefit of low temperature analysis is that spectral bandwidths often narrow, so that vibrational fine structure becomes more highly resolved. This in turn provides better specificity and therefore yields a higher confidence level for identification. From Table 15, it can be seen that most fluorescing aromatic hydrocarbons also phosphoresce. Phosphorescence is the principal form of luminescence for aromatic acids, esters and carbonyls. Halogenation increases the phosphorescence yield and reduces the fluorescence yield. Therefore, for these types of materials, low temperature measurement would be of greater value than room temperature. Other compounds which may exhibit phosphorescence, but rarely fluoresce, are the nitro-substituted aromatics. The luminescence properties of these compounds, however, are usually complicated by photochemical activity (46).

It is estimated that of the 113 materials studied under this contract 100 would phosphoresce. Many of the compounds on the EPA list of priority pollutants would also phosphoresce. Of the compounds not studied from the Coast Guard Chris list it is estimated that an additional 130-140 compounds would phosphoresce. Dichlone, one of the toxic and hazardous materials studied under this contract did not fluoresce at room temperature. However, it did phosphoresce quite strongly at

TABLE 15. EXPECTED INFLUENCE OF SUBSTITUENTS ON THE LUMINESCENCE OF AROMATIC HYDROCARBONS

<u>Substituent</u>	<u>Effect On Fluorescence Wavelength (a)</u>	<u>Effect On Fluorescence Intensity (a)</u>	<u>Phosphorescence</u>	<u>Comments (b)</u>
Alkyl	None	Slight Increase	Yes	For benzene derivatives, $\phi_F \approx \phi_P$ at L.T.
-OH, -OR	Increase	Increase	Yes	$\phi_P > \phi_F$ at L.T. Strong pH dependence of R.T. fluorescence
-CO ₂ H, CO ₂ R, -CO ₂ NH	Increase	Large Decrease	Yes	$\phi_P \gg \phi_F$ at L.T. Hydroxy and amino groups increase ϕ_F
o o -C-H, -C-R	Increase	Large Decrease	Yes	Behavior similar to acids, esters, etc.
-NO, -NO ₂	---	Usually total quenching	Variable	ϕ_P Usually small $\phi_P > \phi_F$ in H-bonding solvents at L.T. (Often photochemically unstable)
-CN	None	Decrease	Yes	
-F, -Cl, -Br, -I	Increase	Increase	Yes	$\phi_P > \phi_F$ at L.T.
-SO ₃ H	None	None	?	

a. From Table 3-1. of Ref. 3

b. ϕ_F , ϕ_P represent fluorescence and phosphorescence quantum yields respectively

low temperature. The phosphorescence spectrum of Dichlone at two different excitation wavelengths are shown in Figures 16 and 17.

Further work in the above areas, along with quantum yield measurements, absorption and excitation spectra measurements, and analysis of photoproducts, will help establish luminescence techniques as a useful means for studying toxic and hazardous materials.

FIGURE 16
Dichlone
54 ppm/MCH (77°K)
Ex. 370 nm

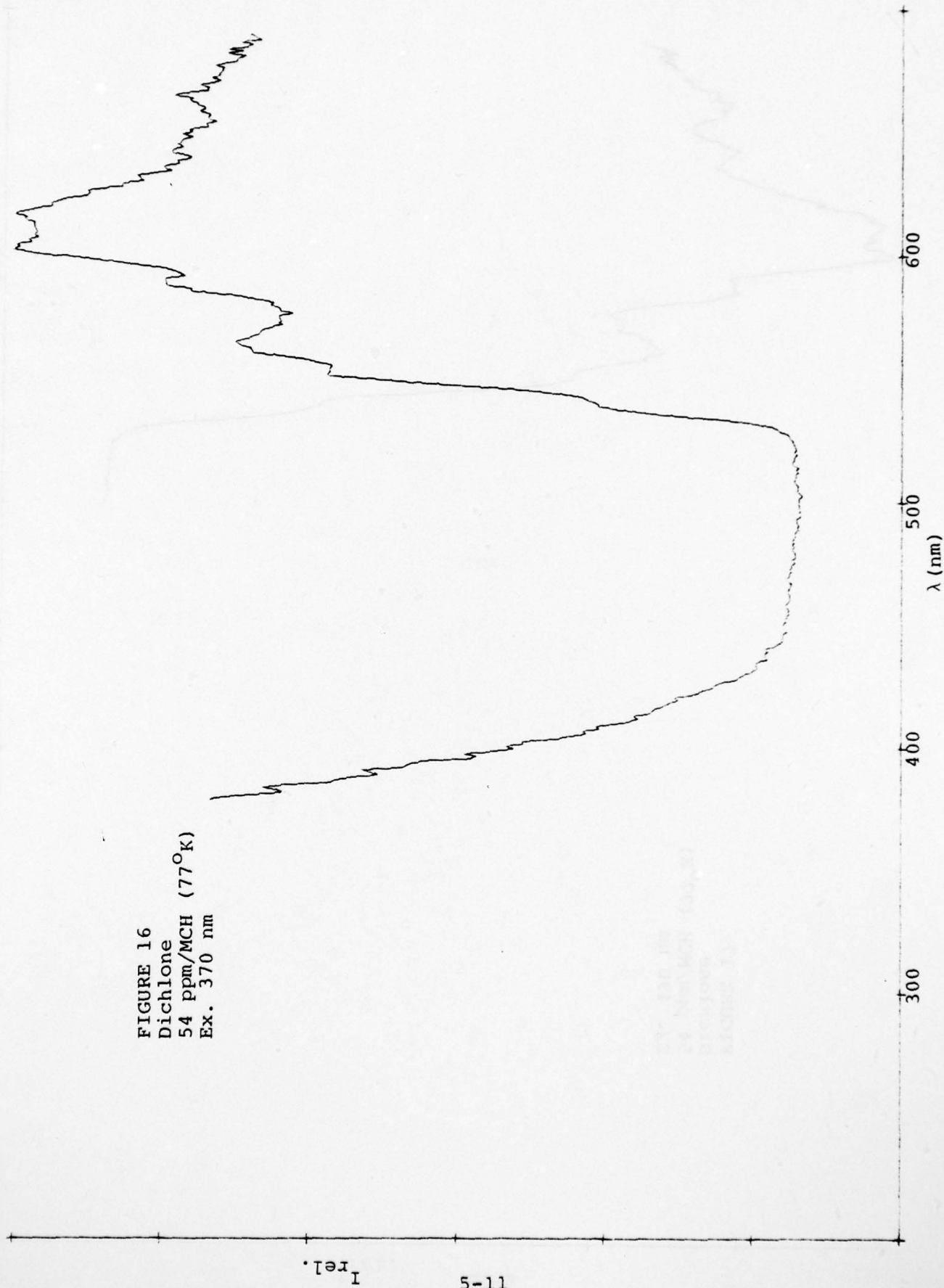
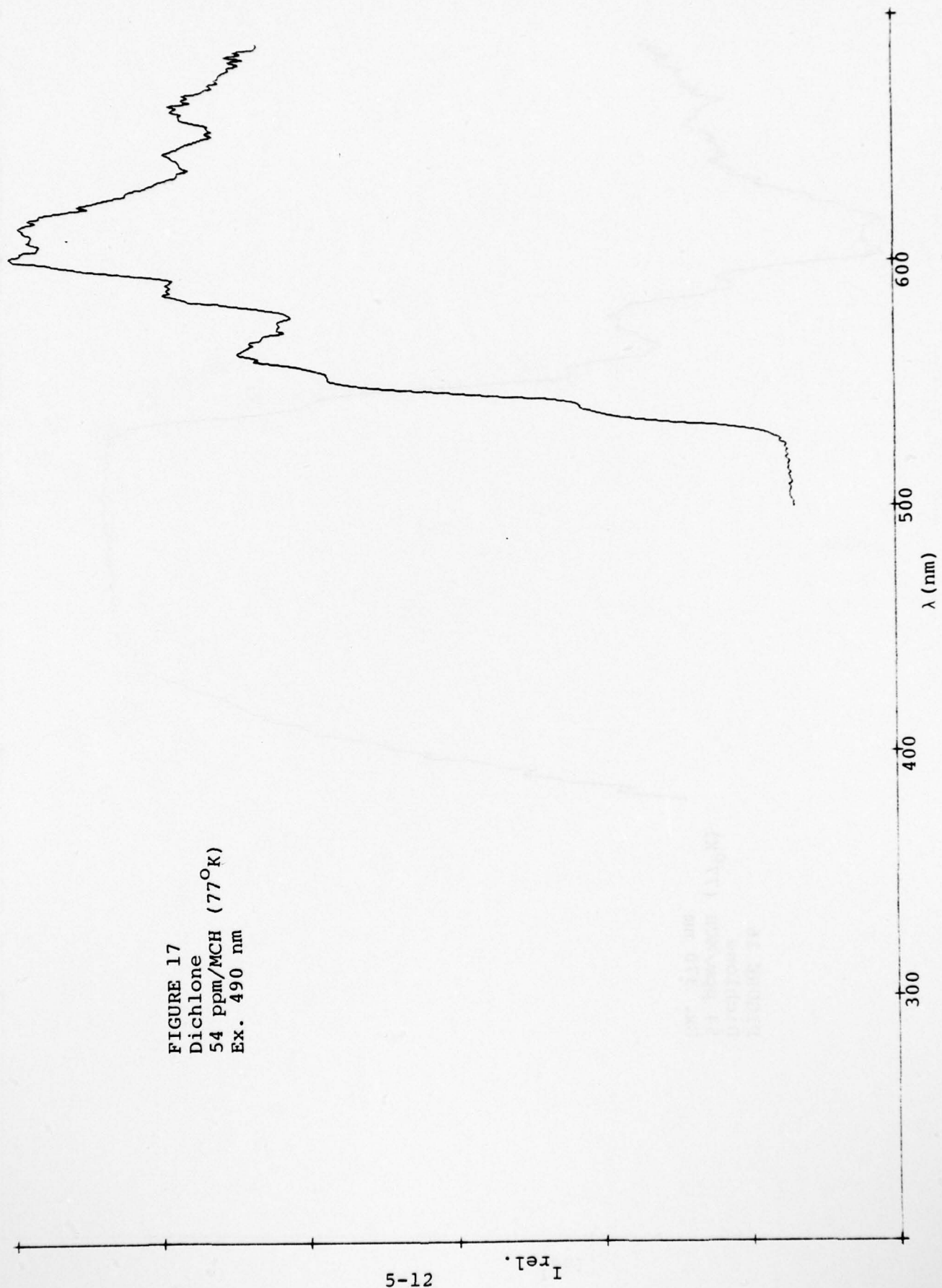


FIGURE 17
Dichlone
54 ppm/MCH (77°K)
Ex. 490 nm



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A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS, (U)
MAY 79 J T BROWNRIGG, D A BUSCH, L P GIERING

F/G 7/2

DOT-CG-81-78-1888

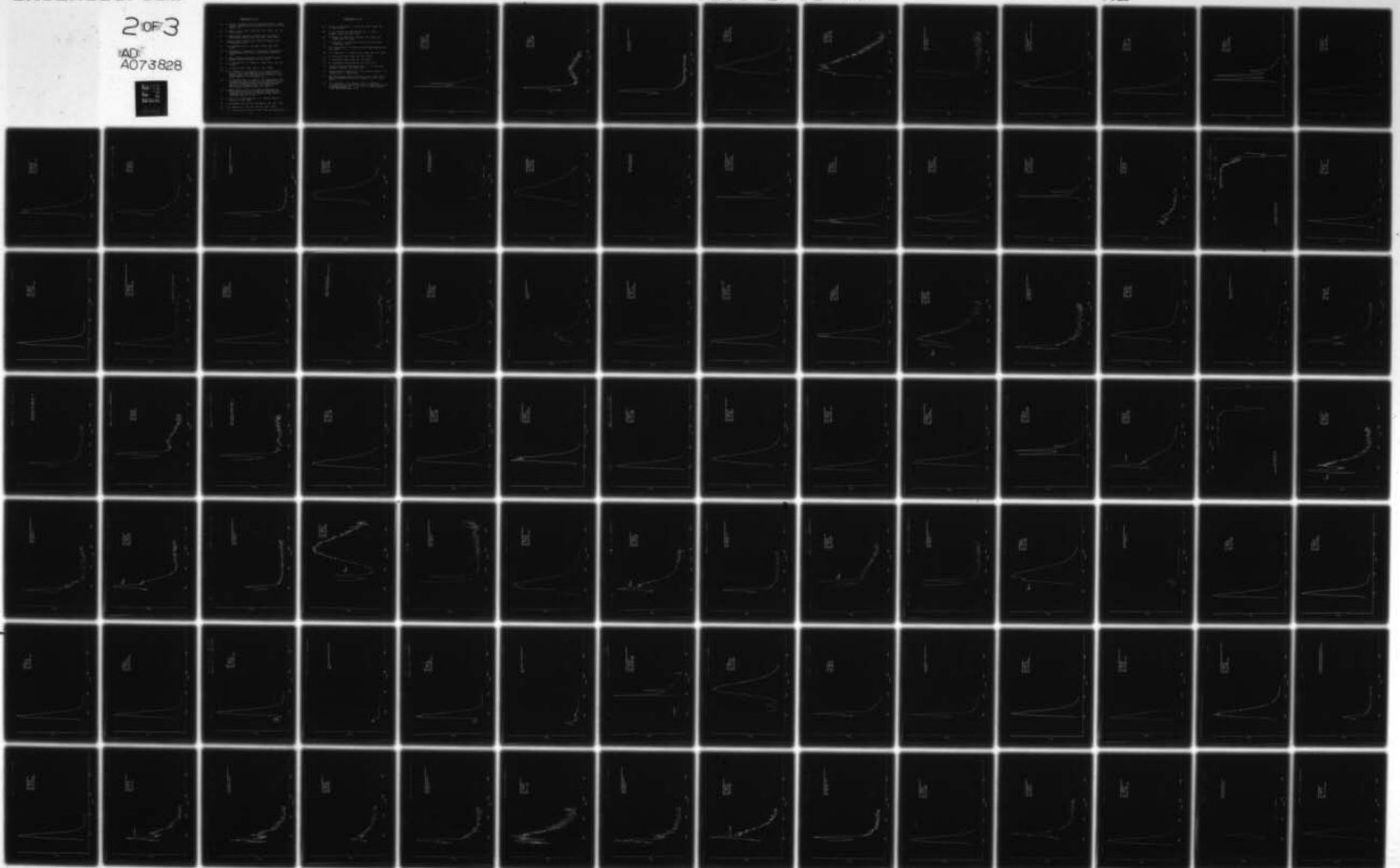
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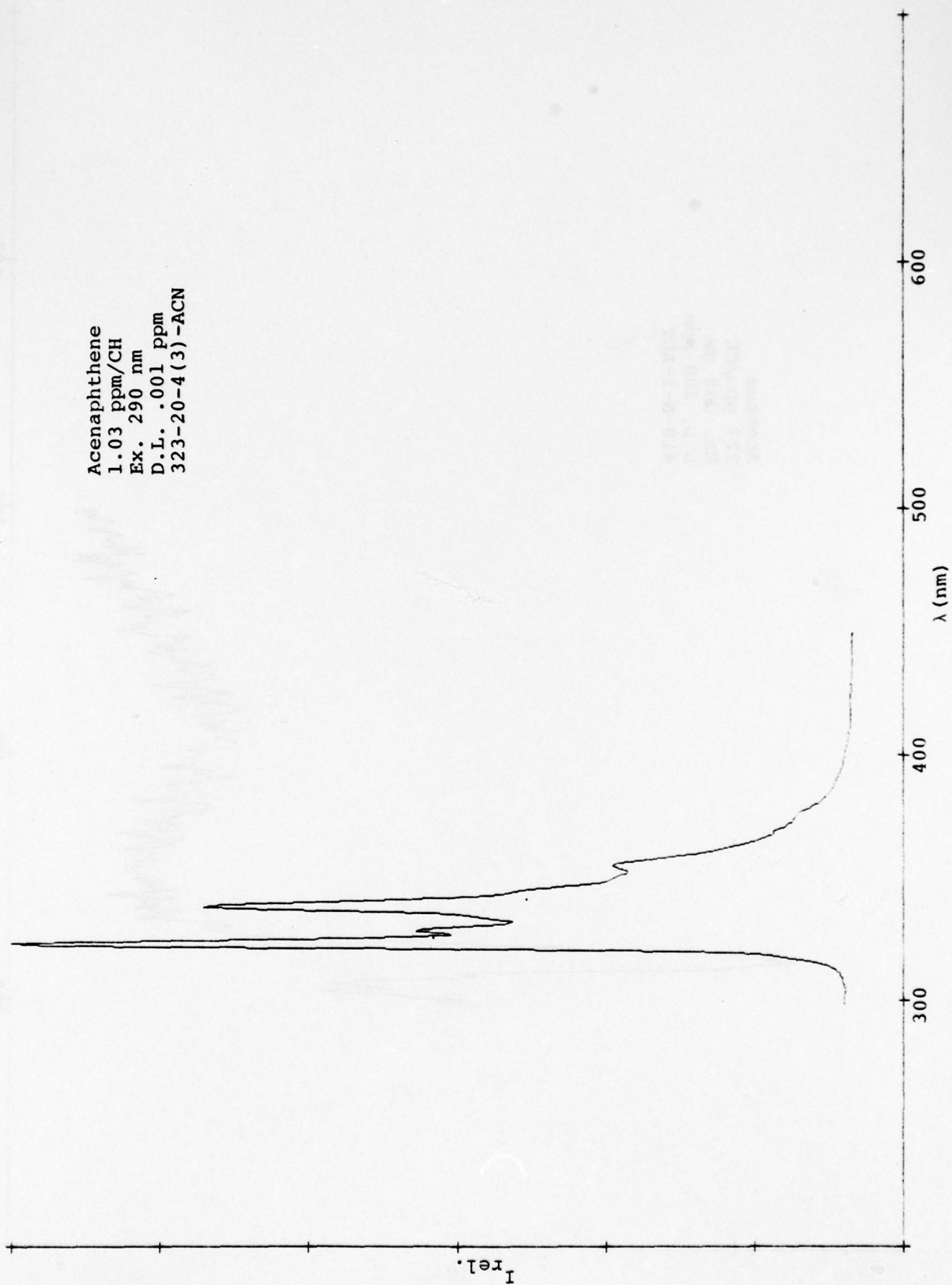
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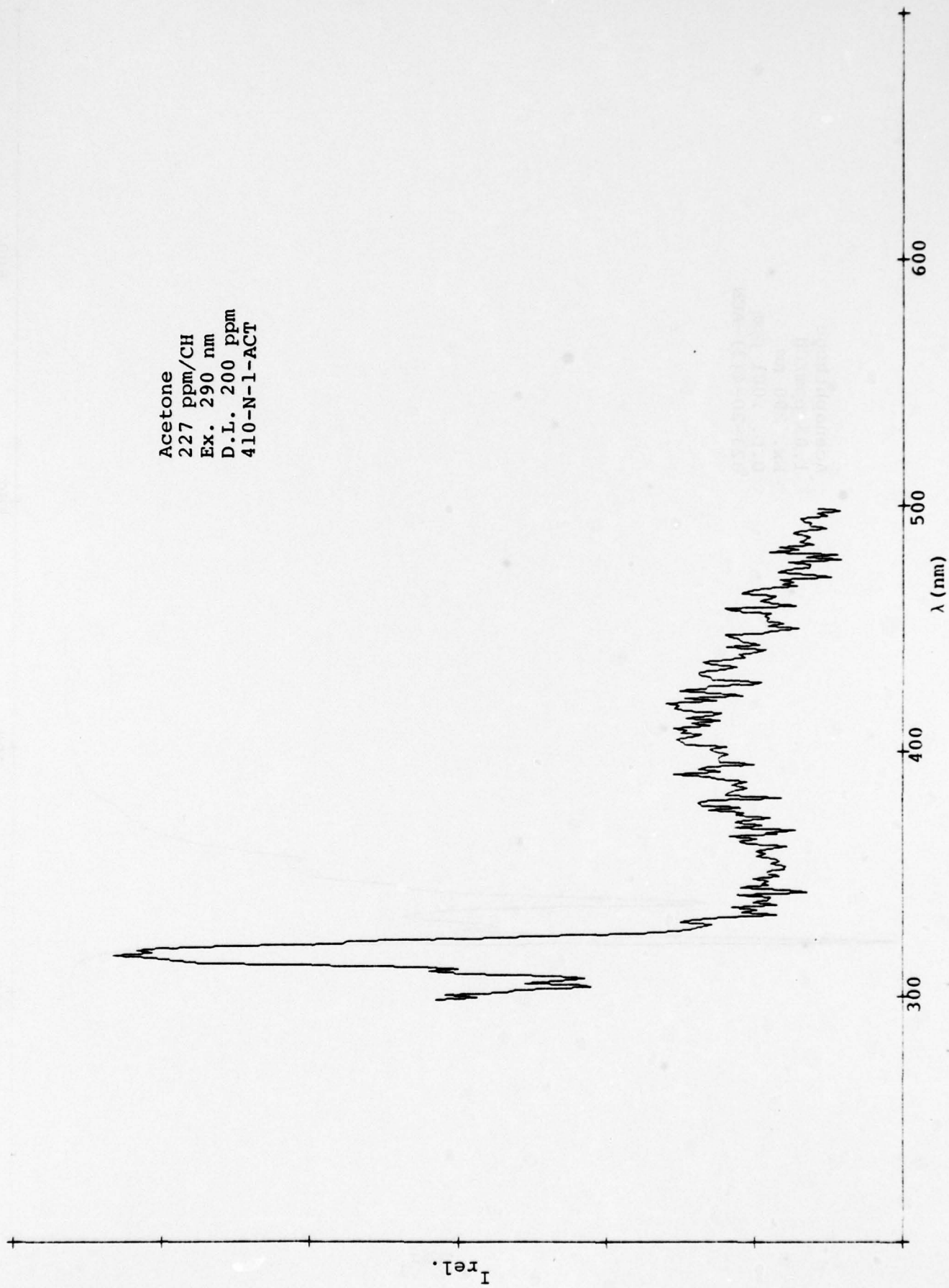
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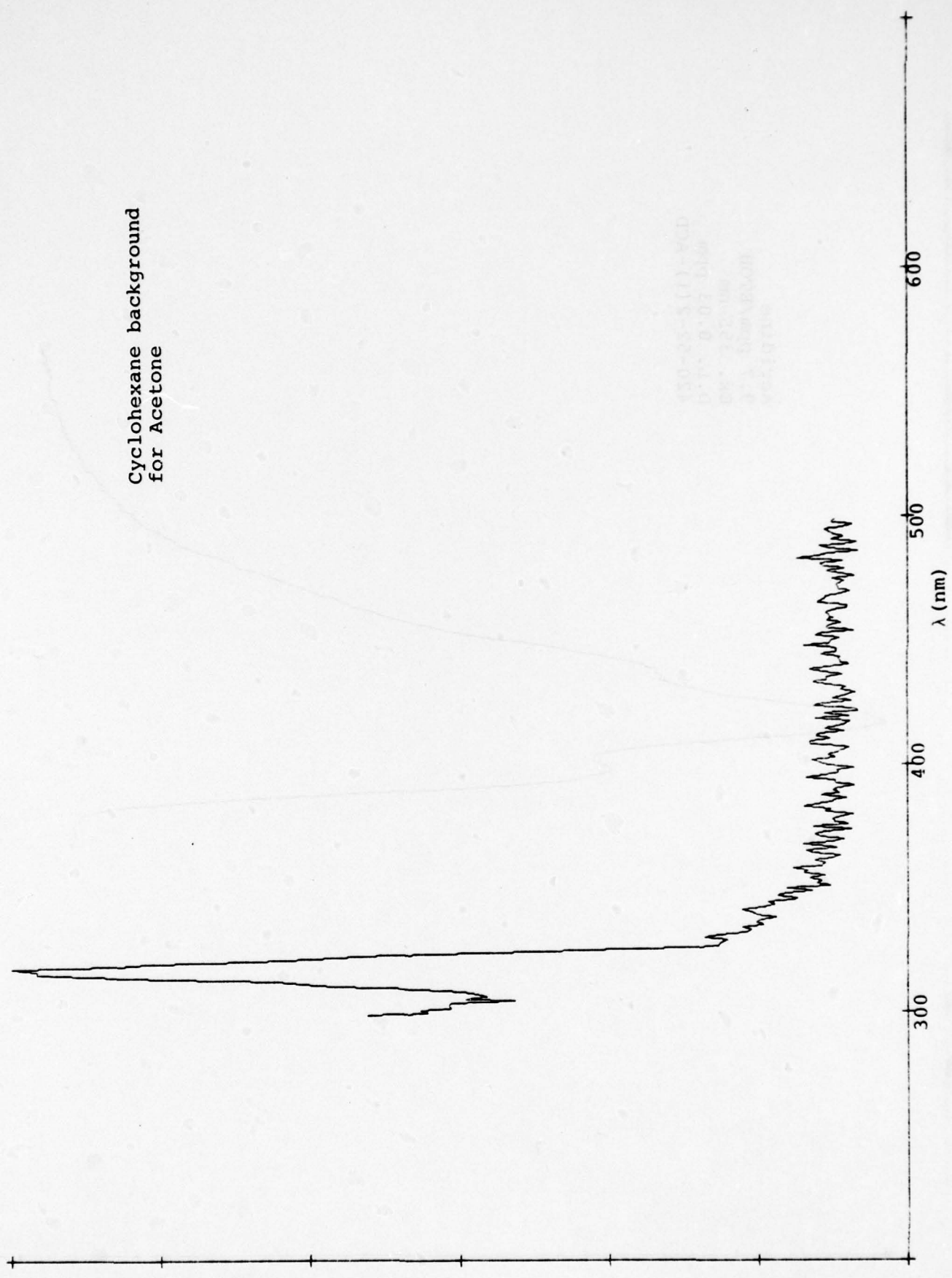
Acenaphthene
1.03 ppm/CH
Ex. 290 nm
D.L. .001 ppm
323-20-4(3)-ACN



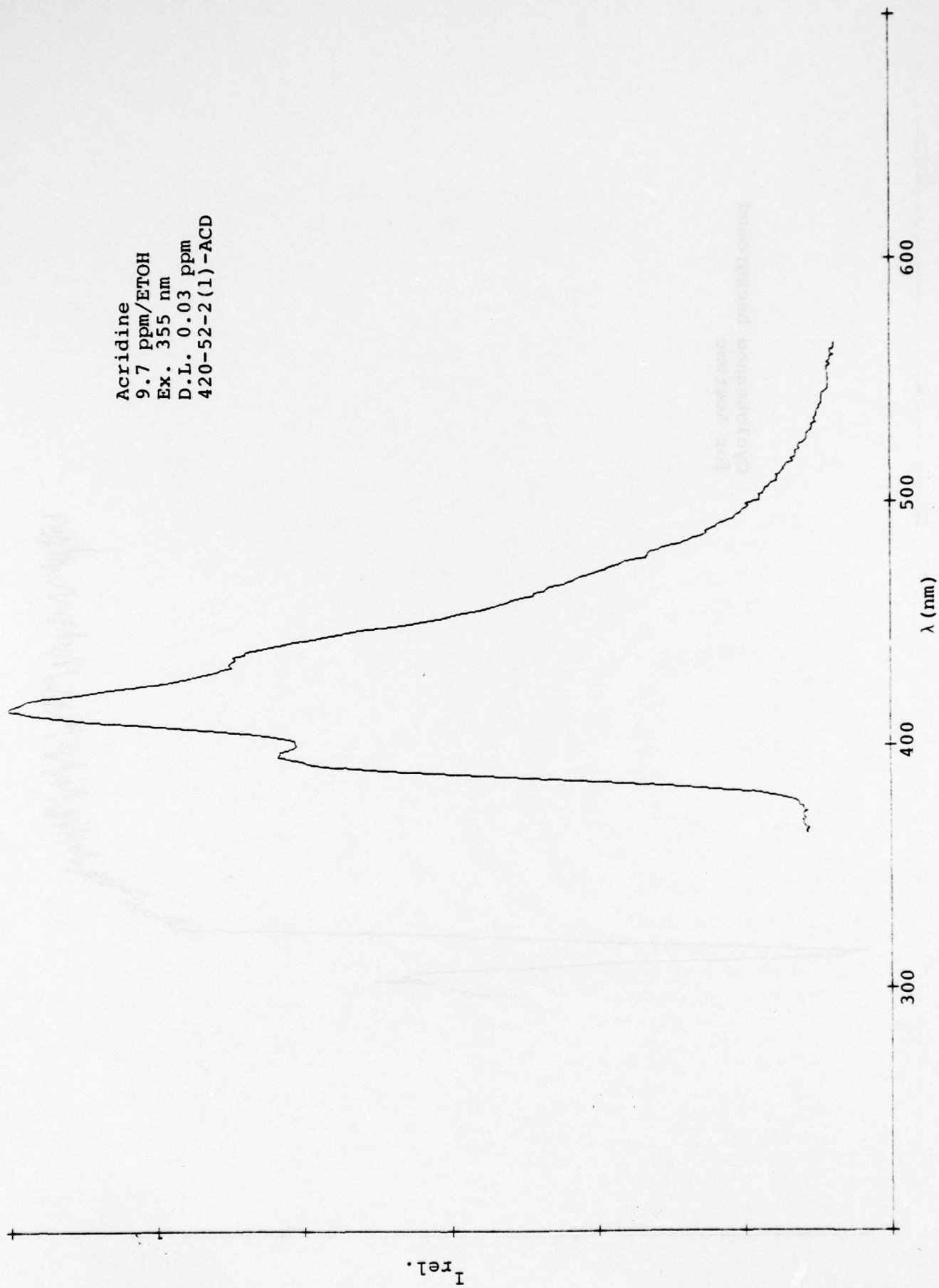
Acetone
227 ppm/CH
Ex. 290 nm
D.L. 200 ppm
410-N-1-ACT



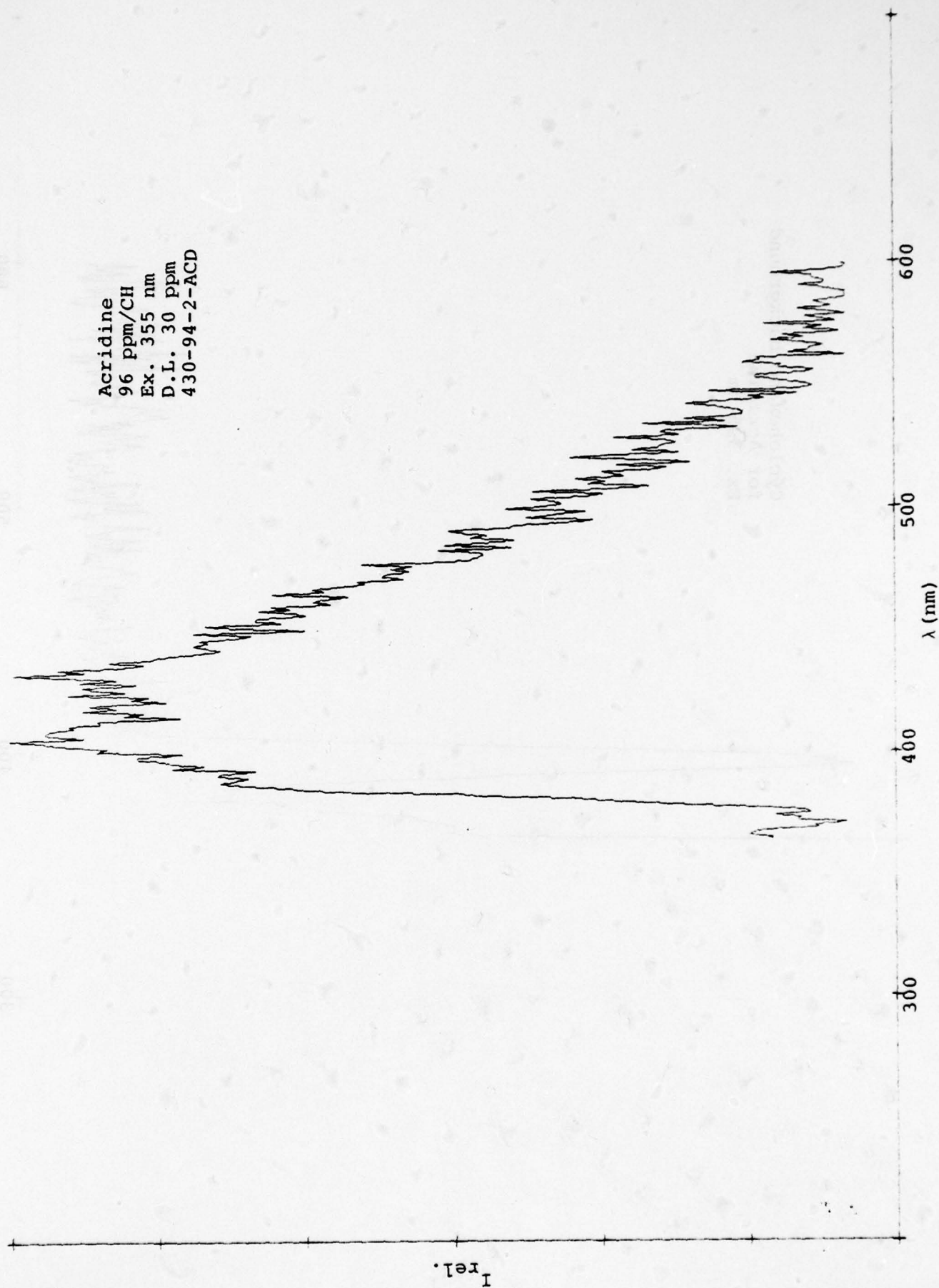
Cyclohexane background
for Acetone



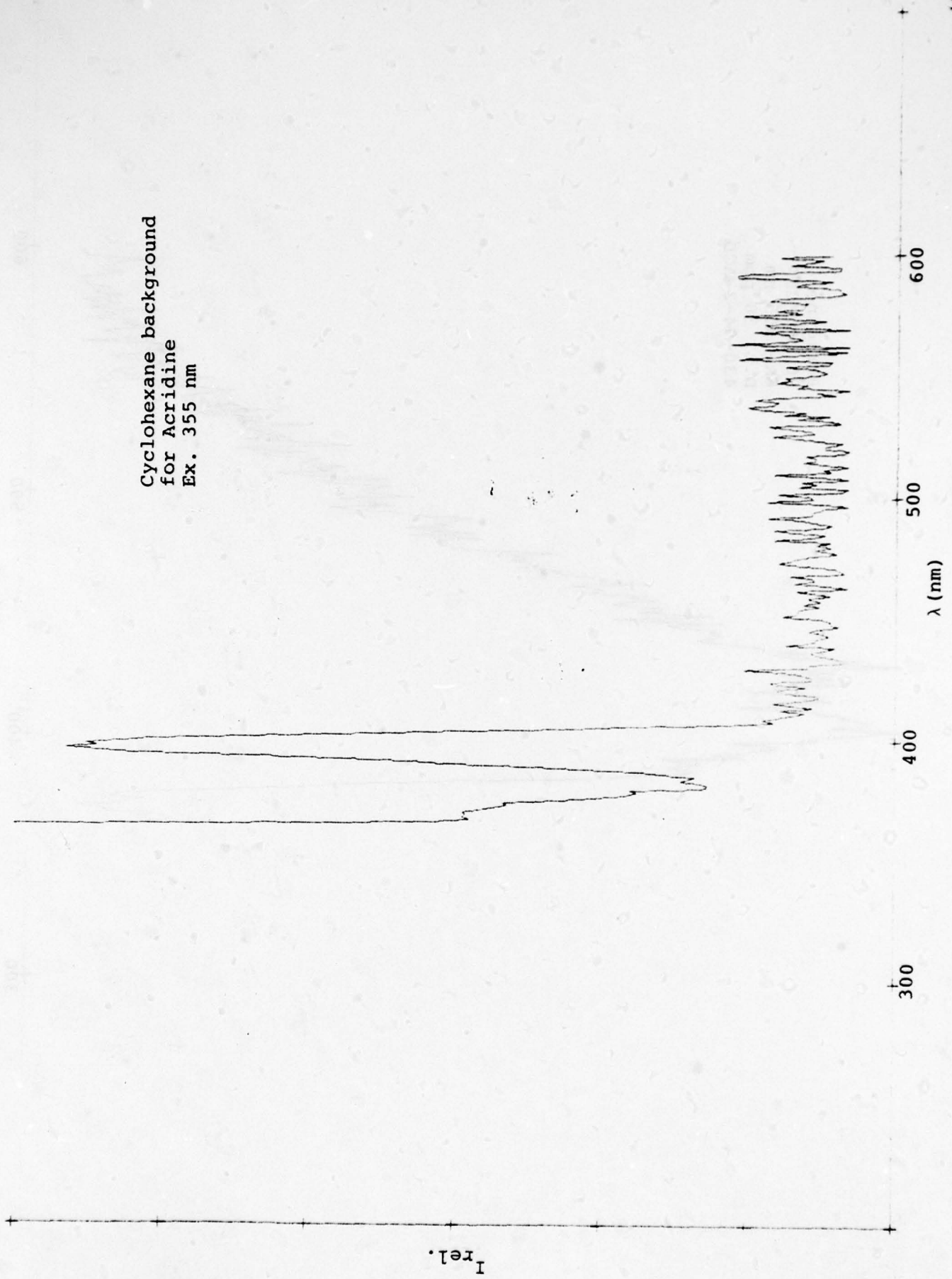
Acridine
9.7 ppm/ETOH
Ex. 355 nm
D.L. 0.03 ppm
420-52-2(1)-ACD



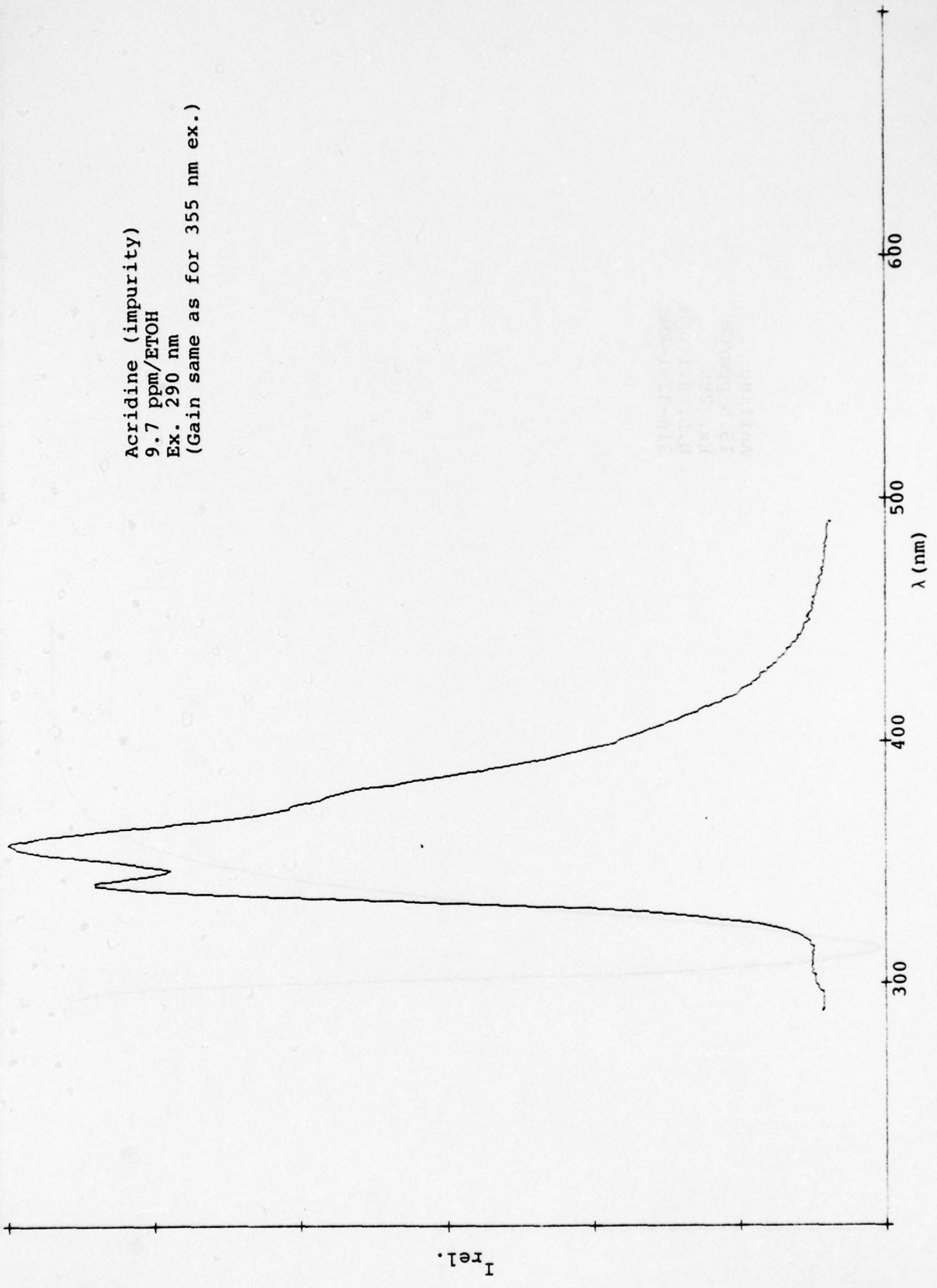
Acridine
96 ppm/CH
Ex. 355 nm
D.L. 30 ppm
430-94-2-ACD



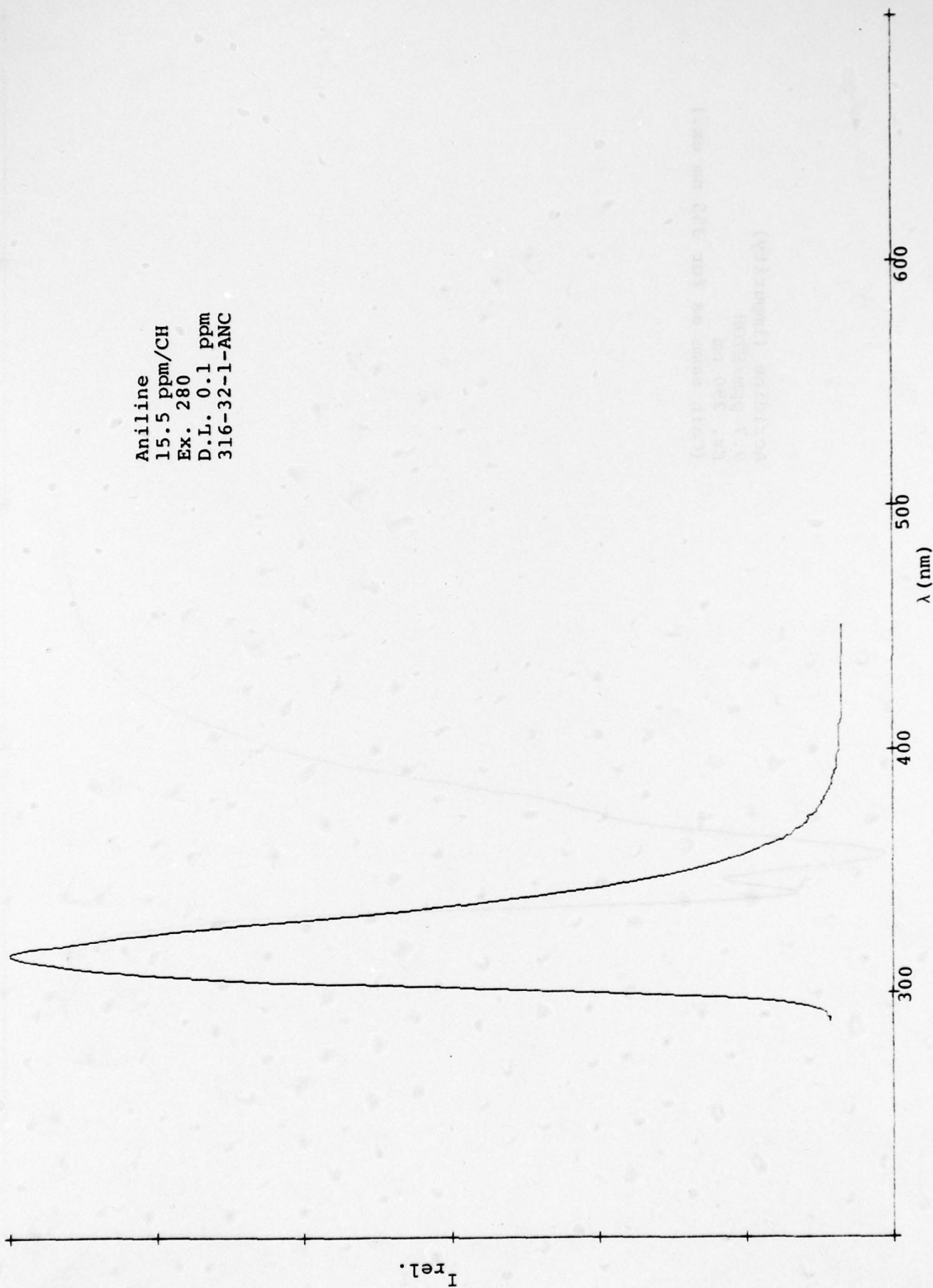
Cyclohexane background
for Acridine
Ex. 355 nm



Acridine (impurity)
9.7 ppm/ETOH
Ex. 290 nm
(Gain same as for 355 nm ex.)

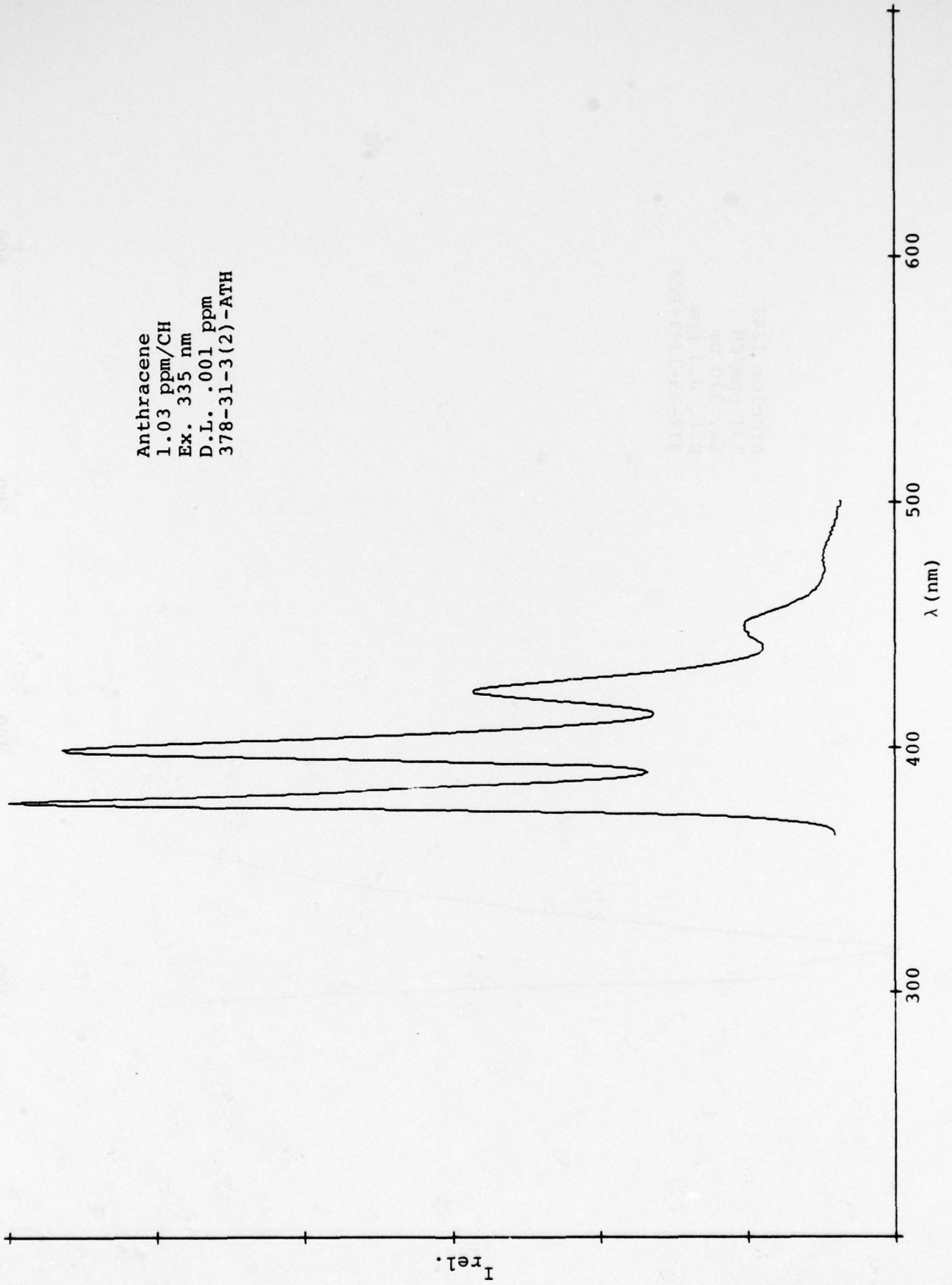


Aniline
15.5 ppm/CH
Ex. 280
D.L. 0.1 ppm
316-32-1-ANC

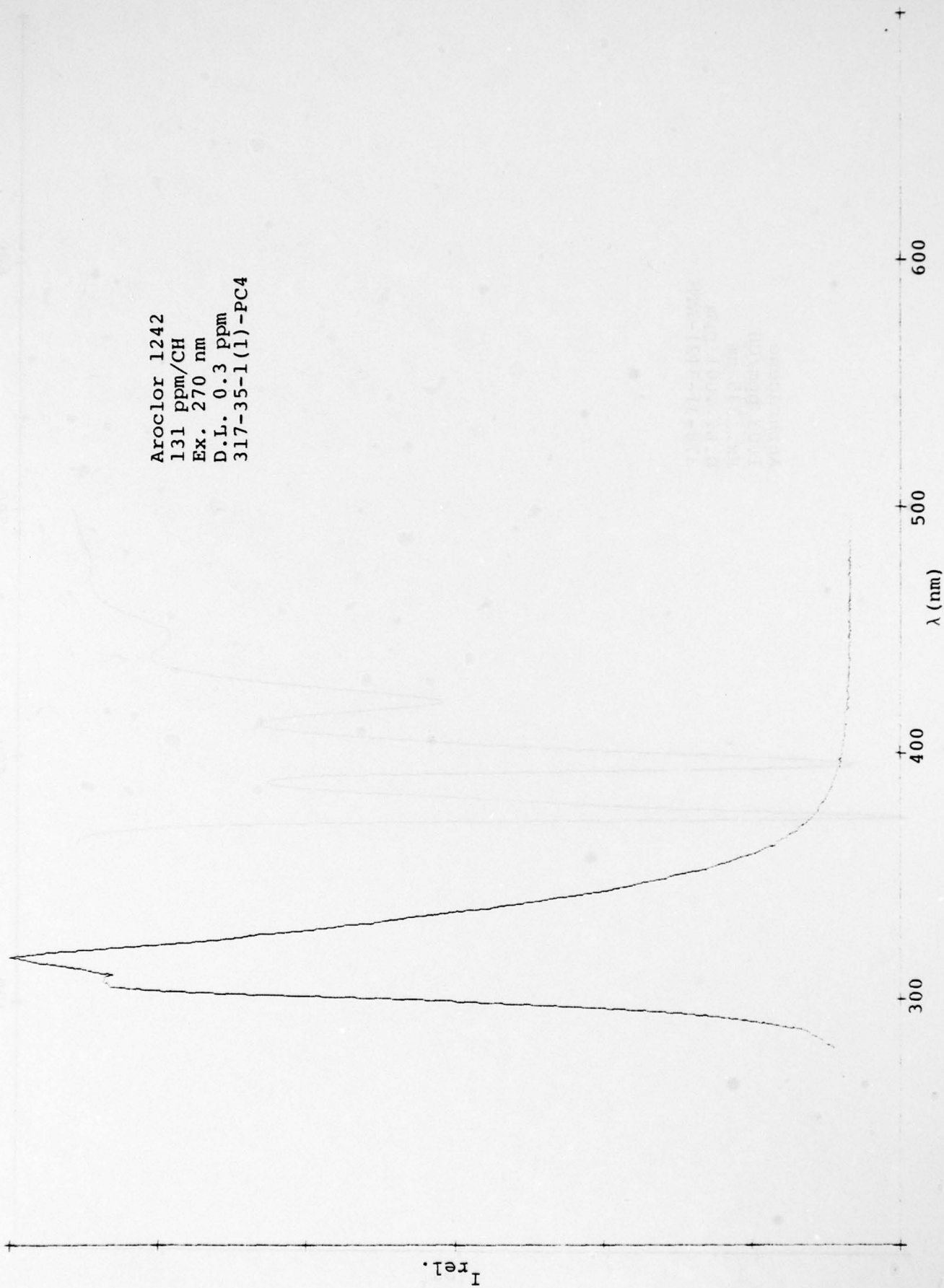


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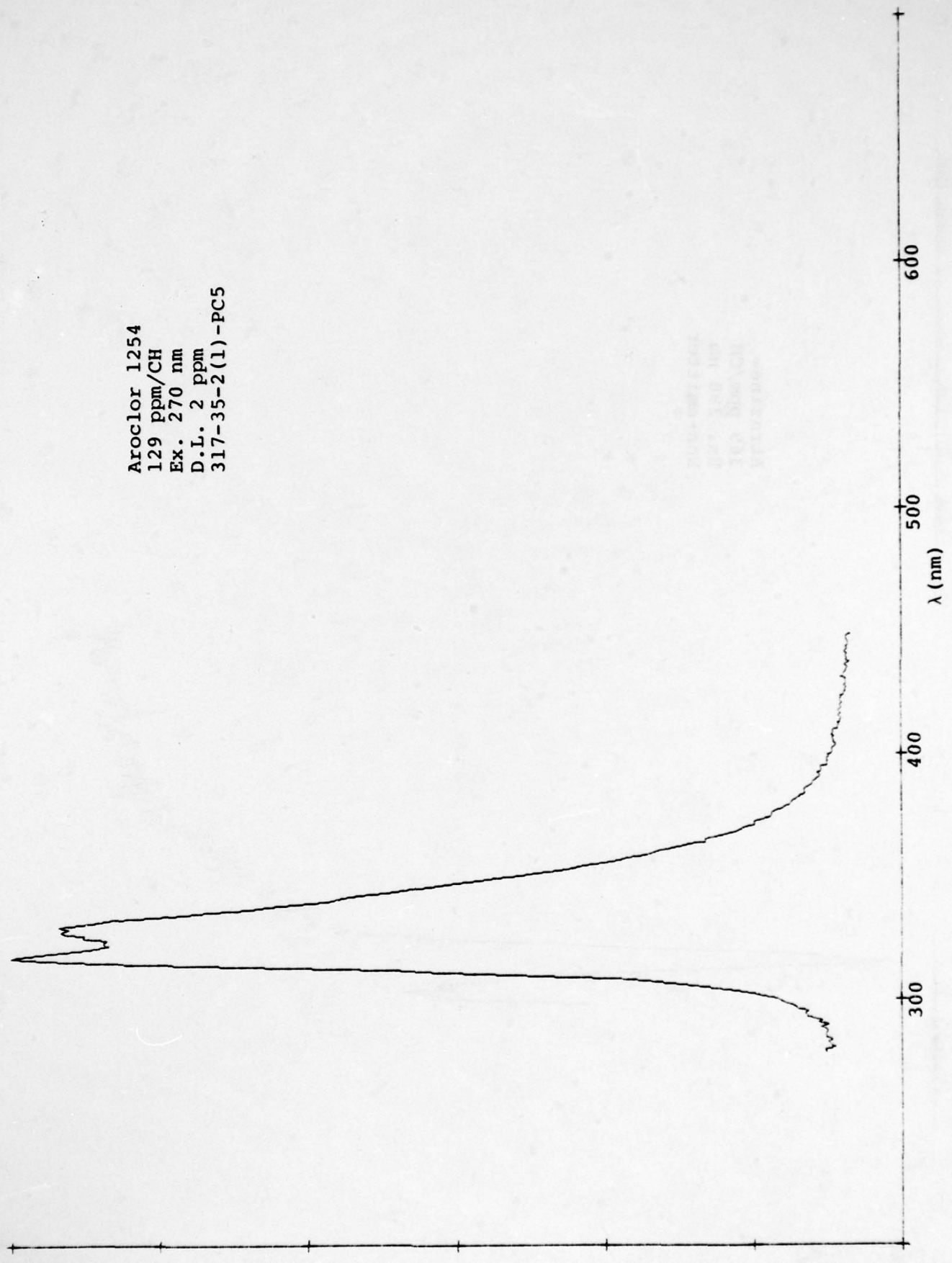
Anthracene
1.03 ppm/CH
Ex. 335 nm
D.L. .001 ppm
378-31-3(2)-ATH



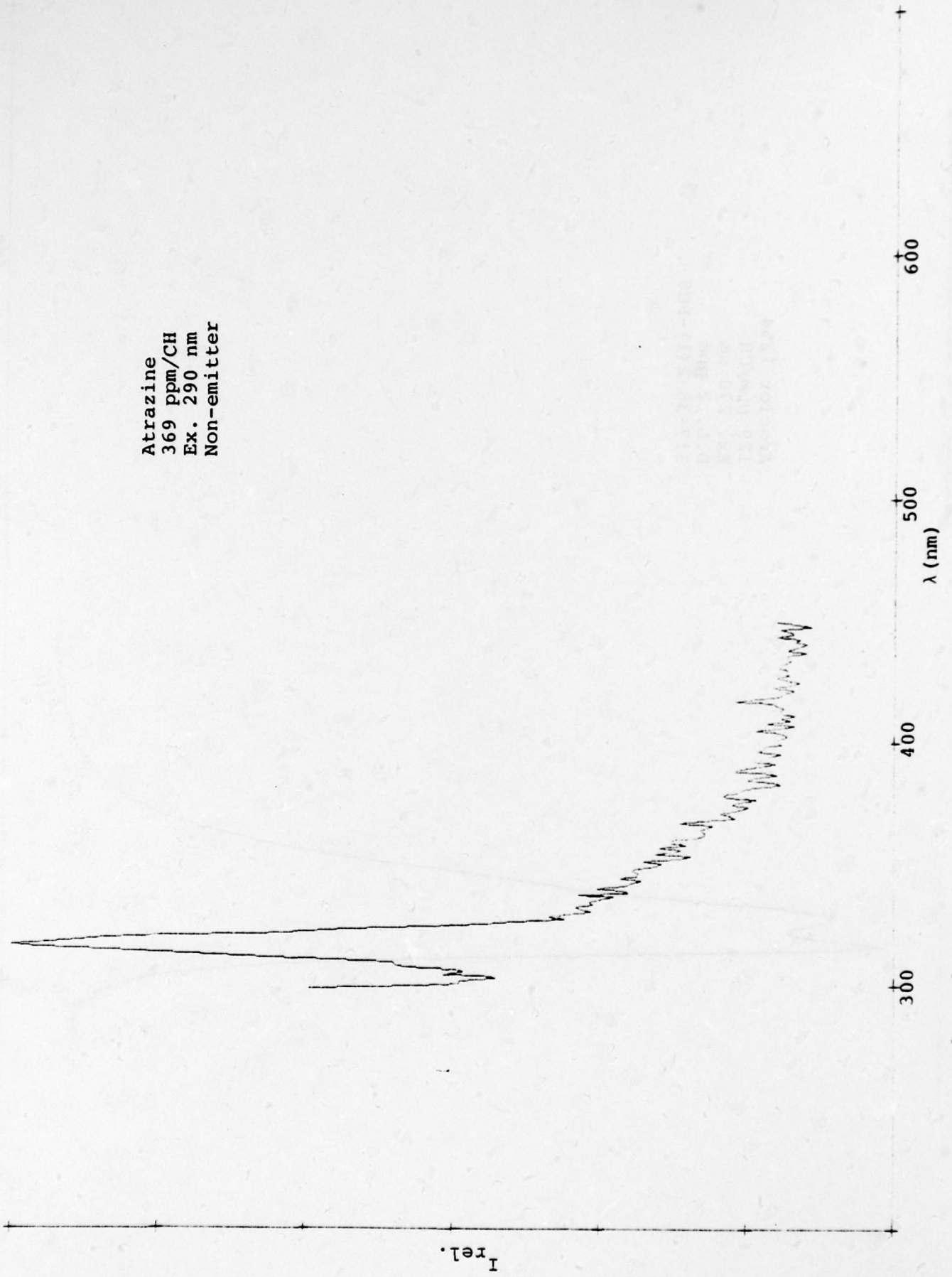
Aroclor 1242
131 ppm/CH
Ex. 270 nm
D.L. 0.3 ppm
317-35-1(1)-PC4



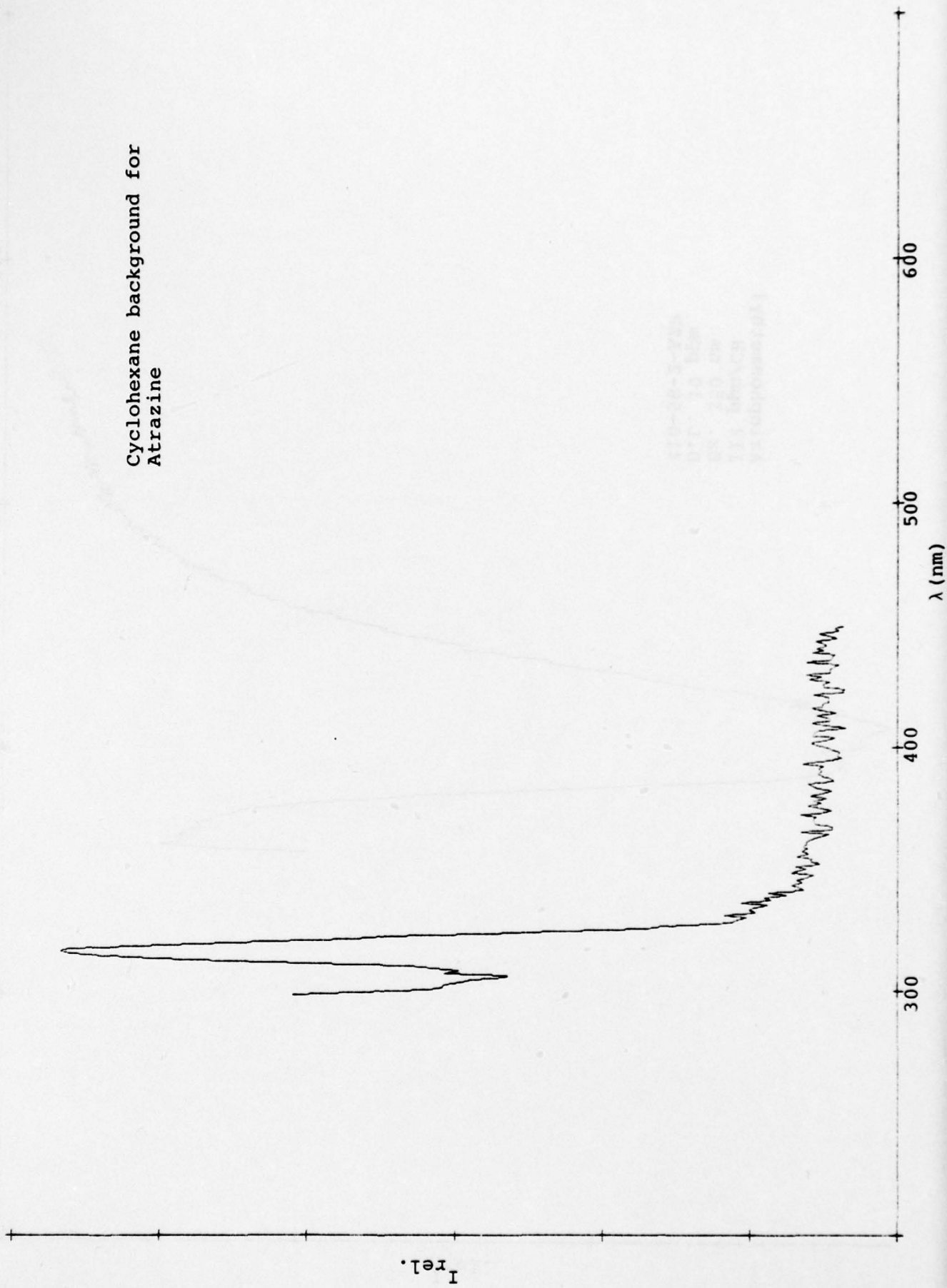
Aroclor 1254
129 ppm/CH
Ex. 270 nm
D.L. 2 ppm
317-35-2(1)-PC5



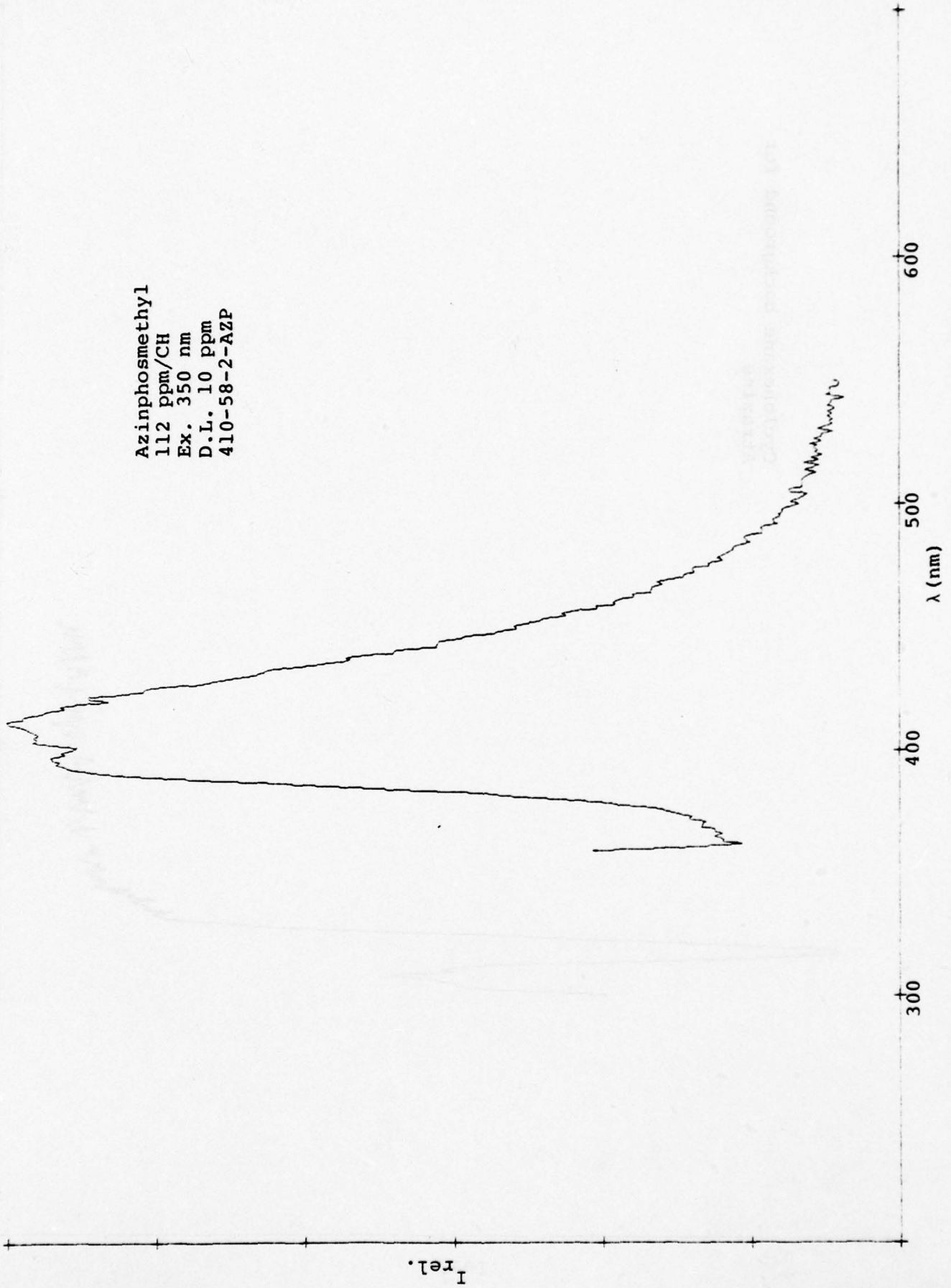
Atrazine
369 ppm/CH
Ex. 290 nm
Non-emitter



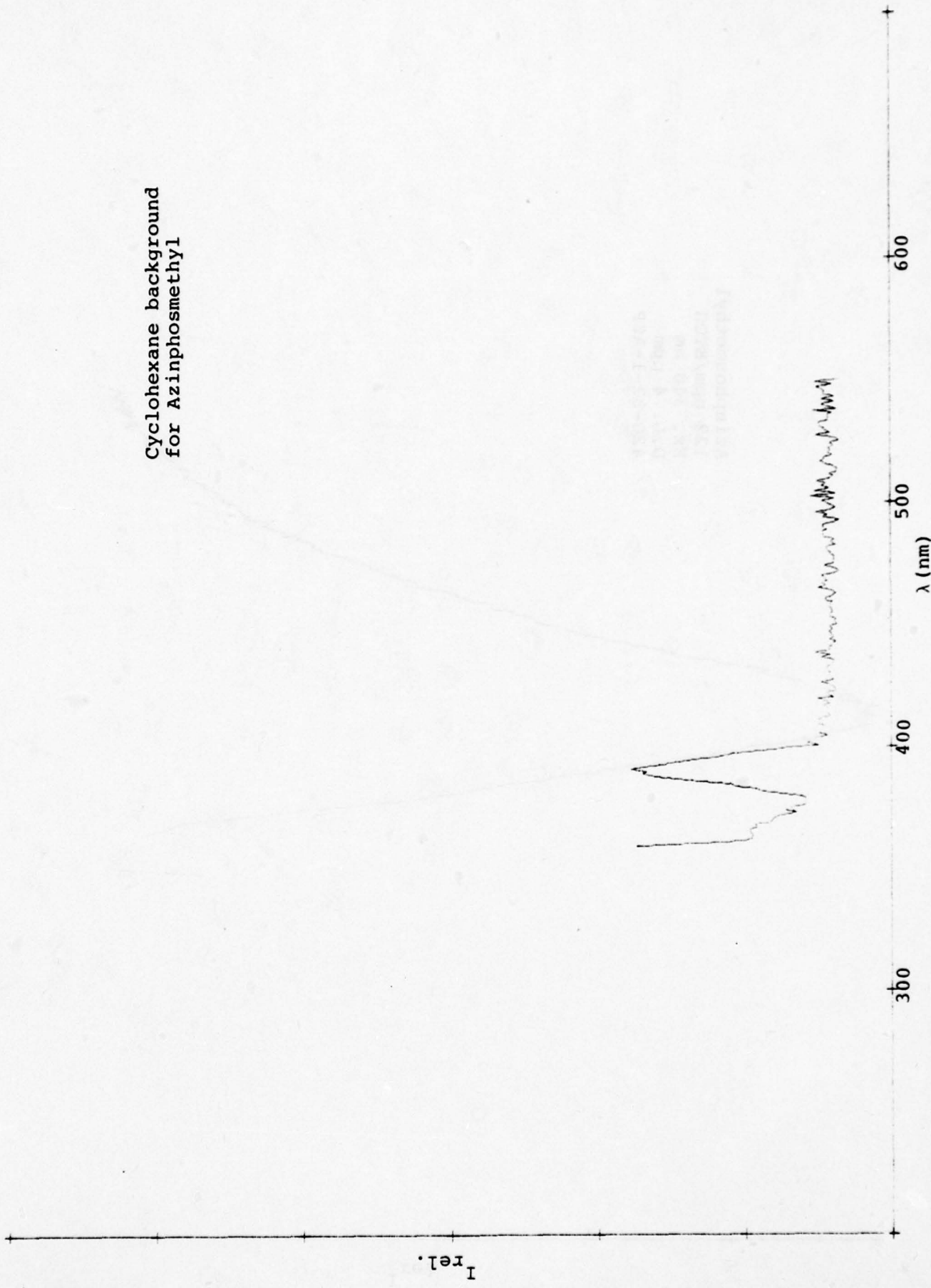
Cyclohexane background for
Atrazine



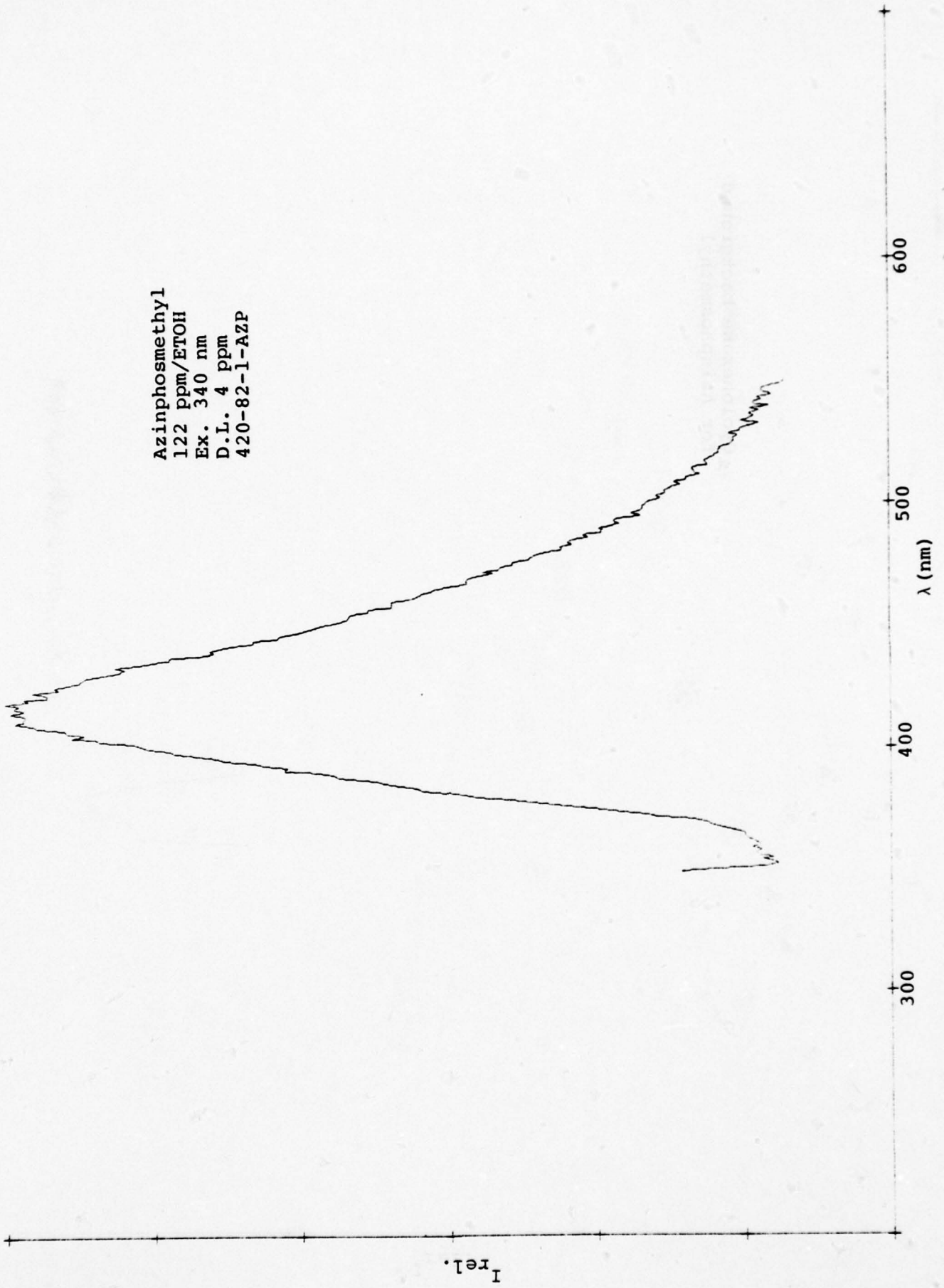
Azinphosmethyl
112 ppm/CH
Ex. 350 nm
D.L. 10 ppm
410-58-2-AZP



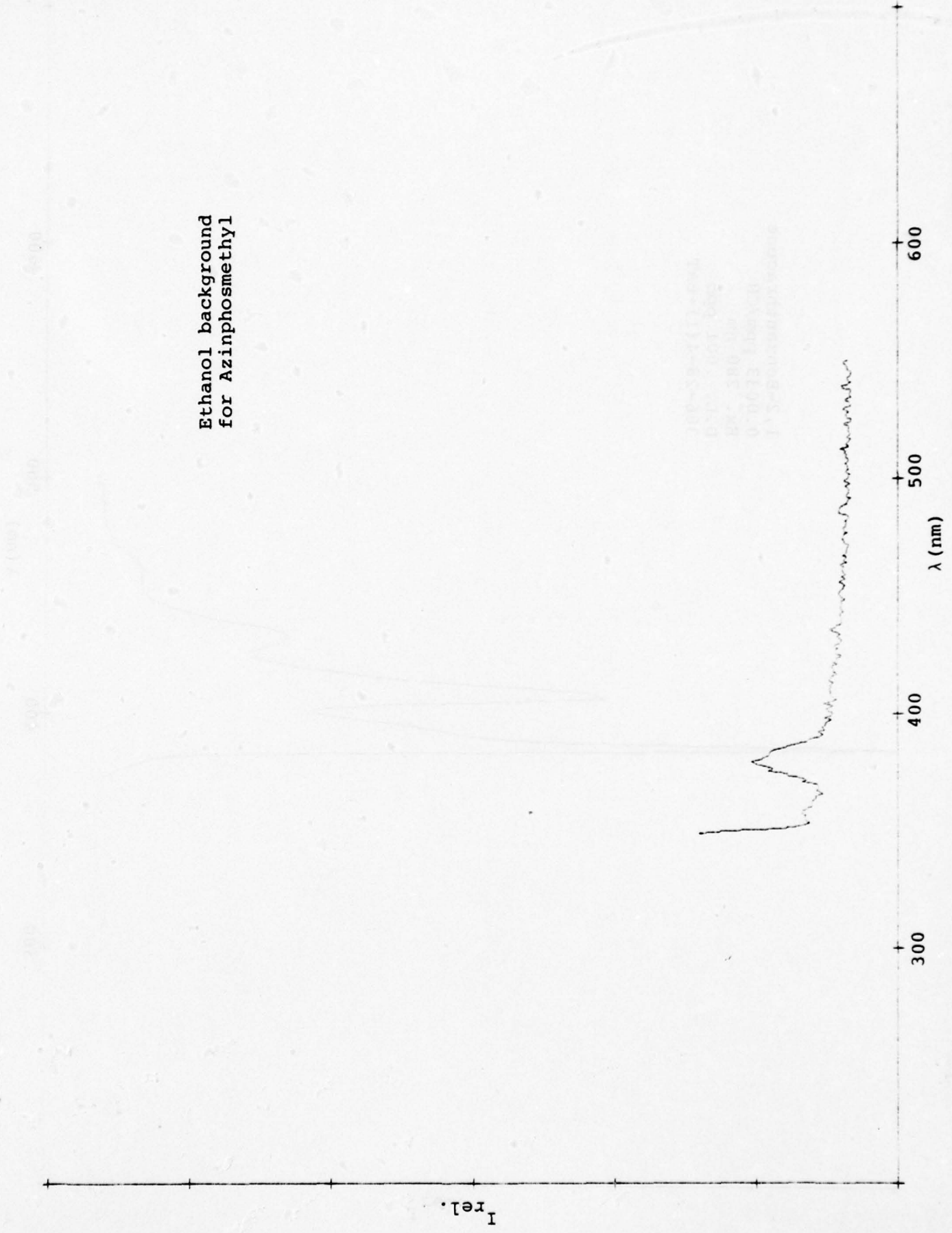
Cyclohexane background
for Azinphosmethyl



Azinphosmethyl
122 ppm/ETOH
Ex. 340 nm
D.L. 4 ppm
420-82-1-AZP

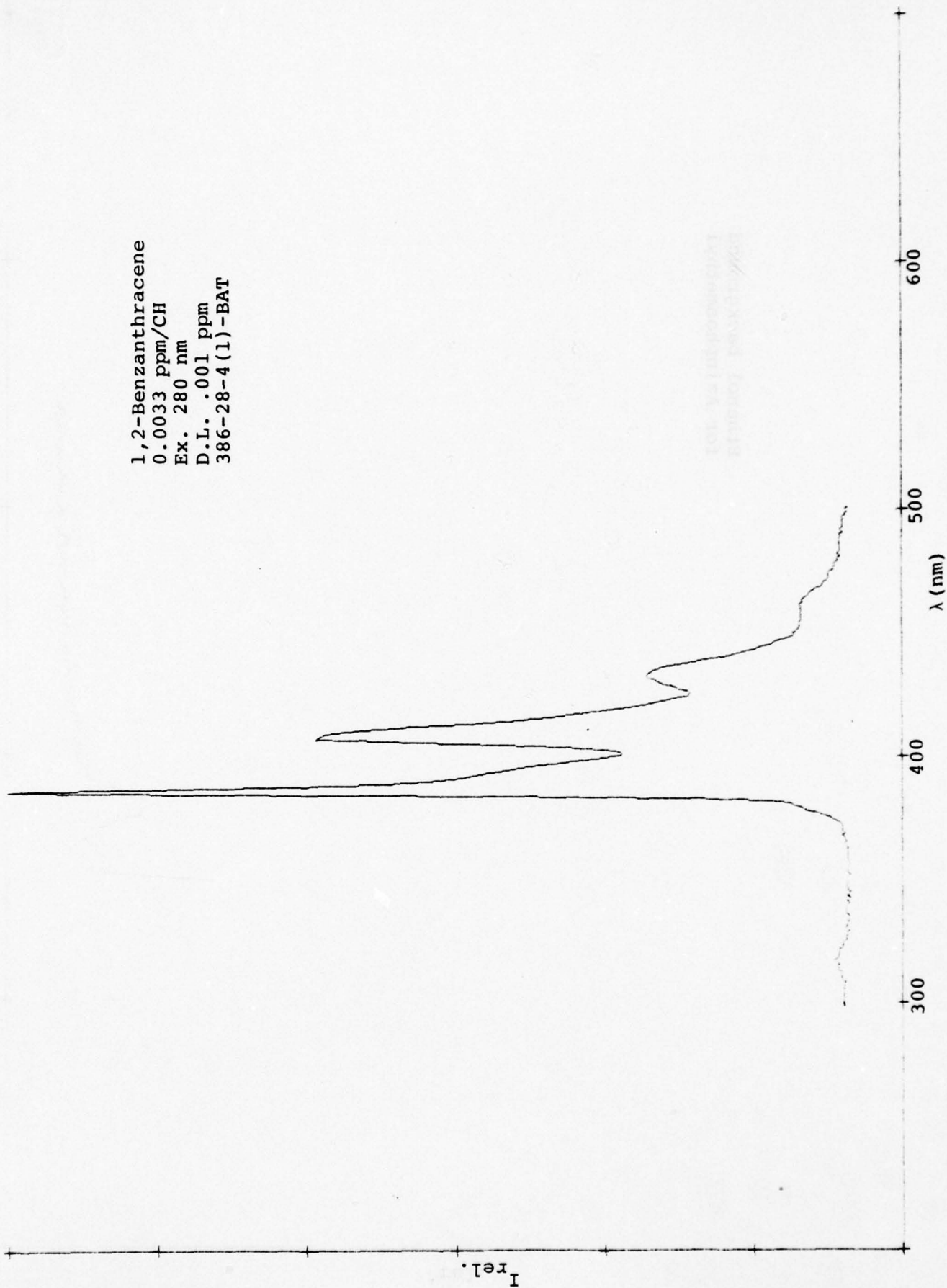


Ethanol background
for Azinphosmethyl

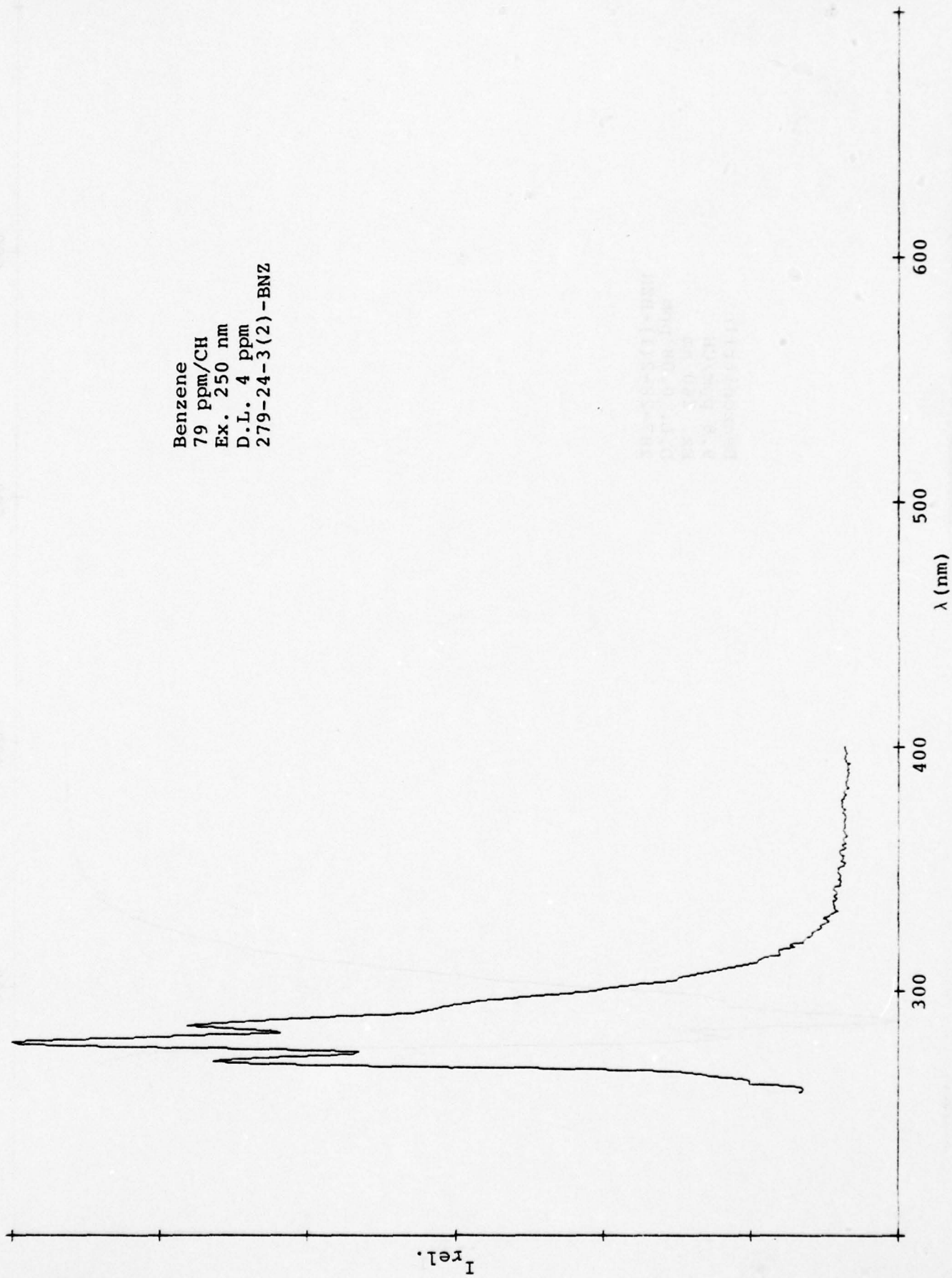


100-50-4111-1000
0.1% (w/v) soln
100% EtOH
0.1673 absorbance
1.5-8000000000000000

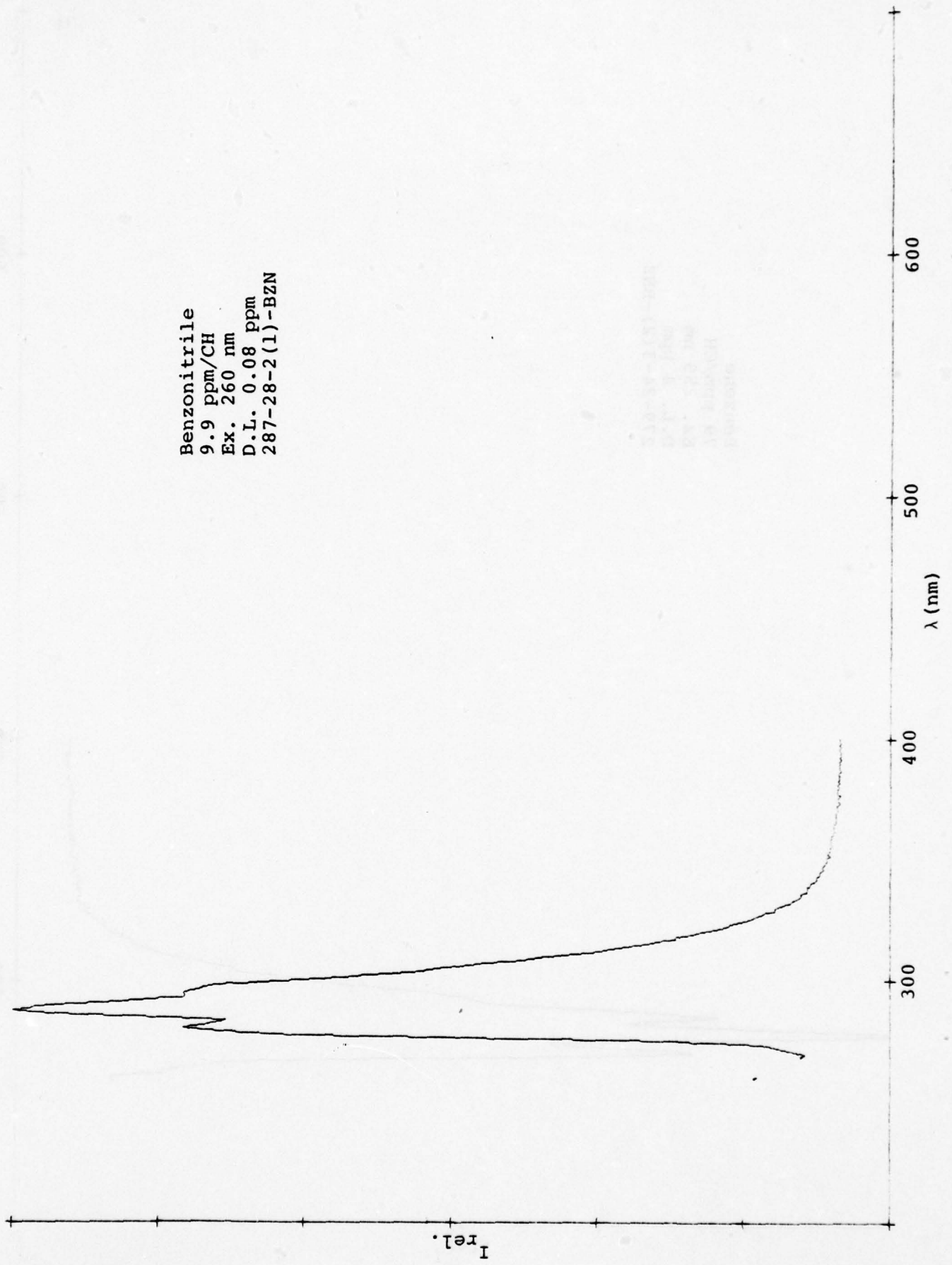
1,2-Benzanthracene
0.0033 ppm/CH
Ex. 280 nm
D.L. .001 ppm
386-28-4(1)-BAT



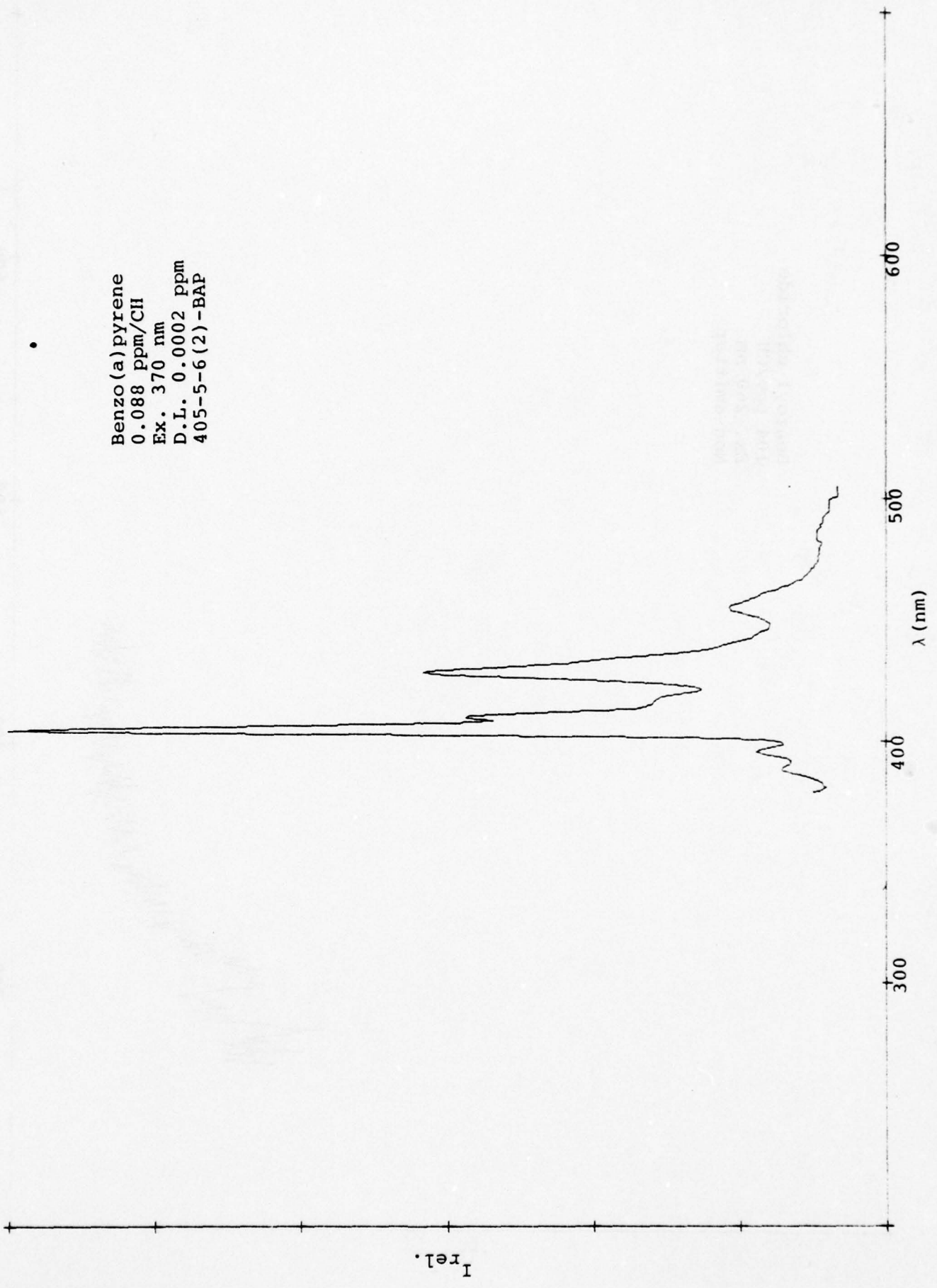
Benzene
79 ppm/CH
Ex. 250 nm
D.L. 4 ppm
279-24-3(2)-BNZ



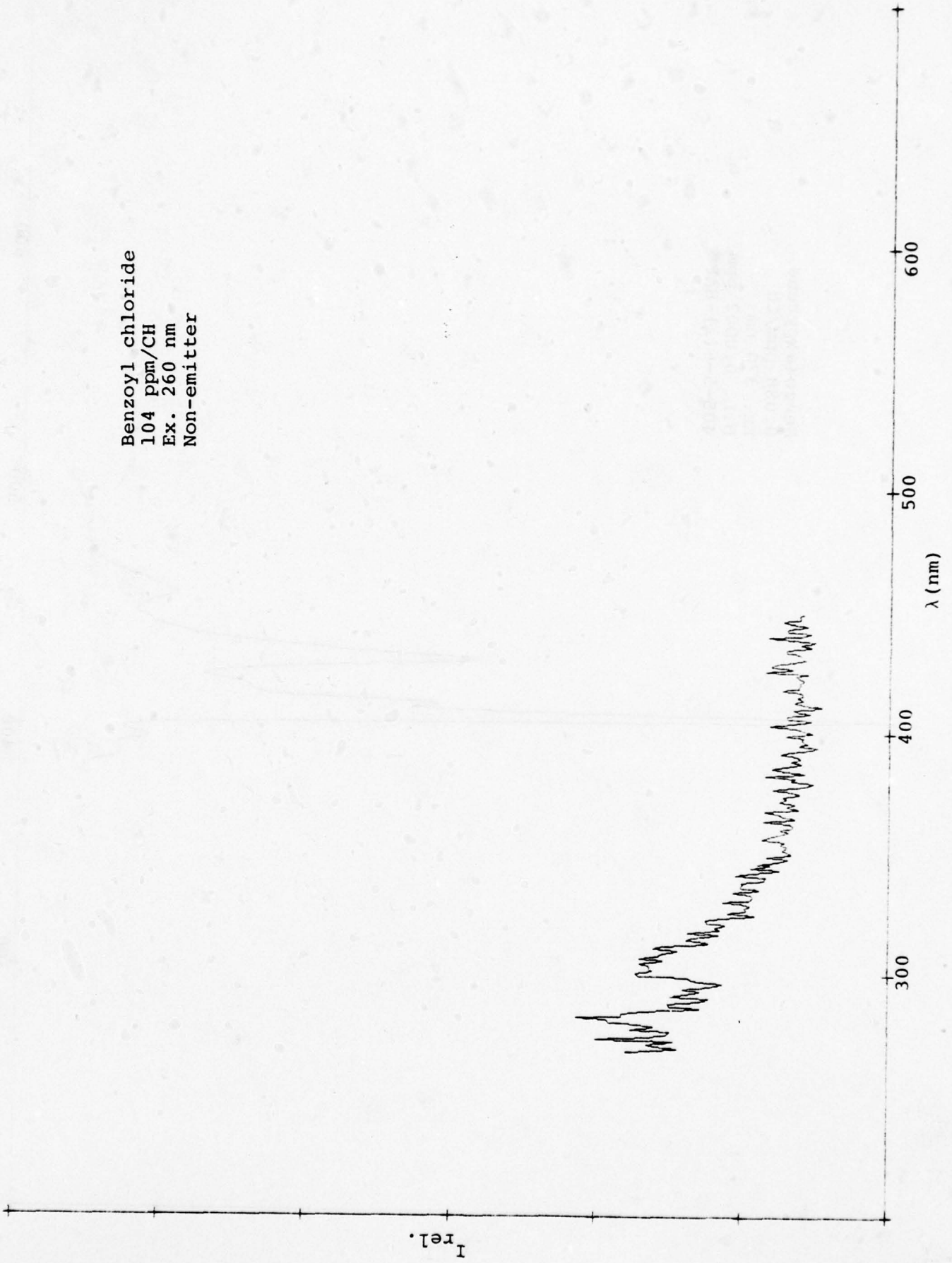
Benzonitrile
9.9 ppm/CH
Ex. 260 nm
D.L. 0.08 ppm
287-28-2(1)-BZN



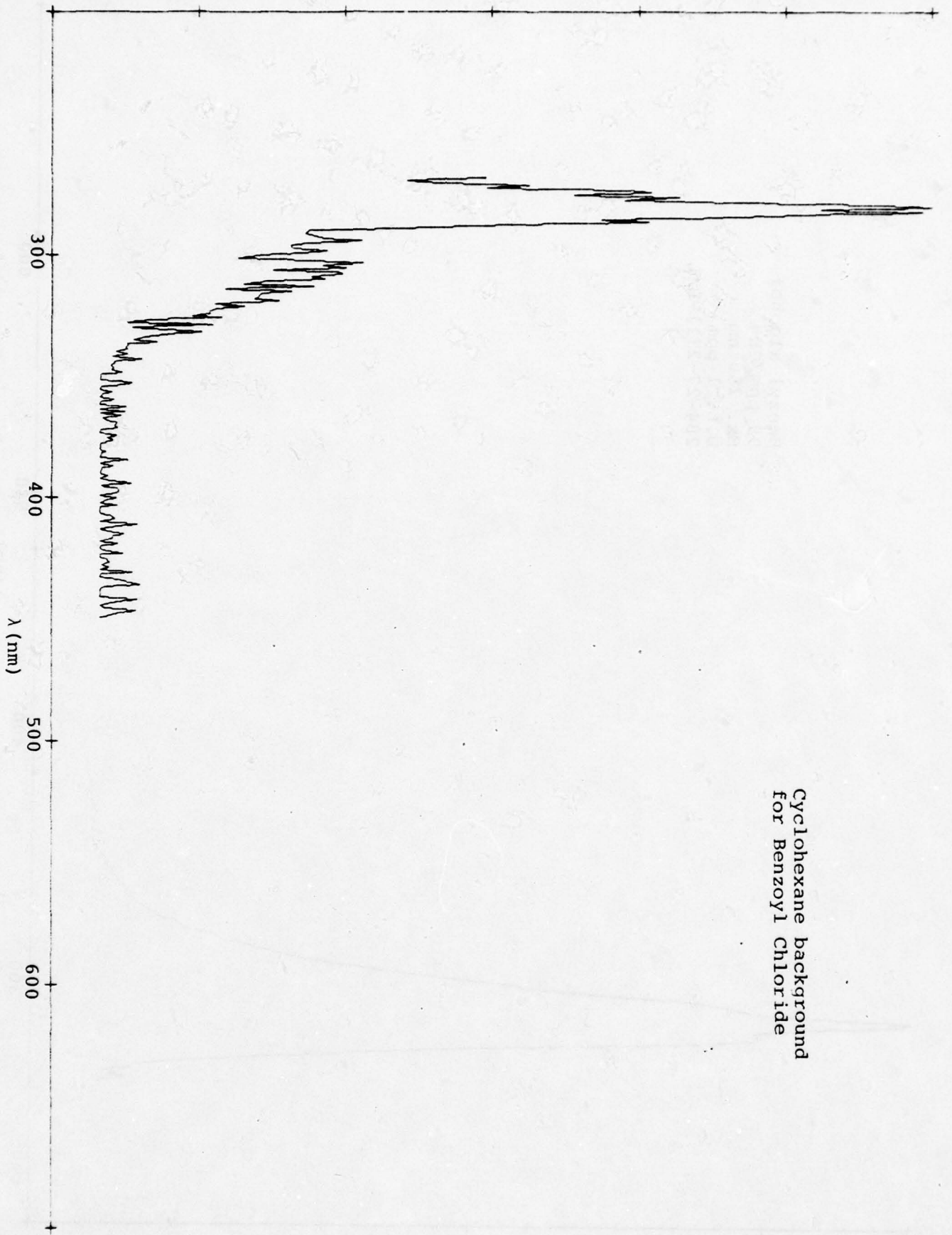
Benzo (a) pyrene
0.088 ppm/CH
Ex. 370 nm
D.L. 0.0002 ppm
405-5-6(2)-BAP



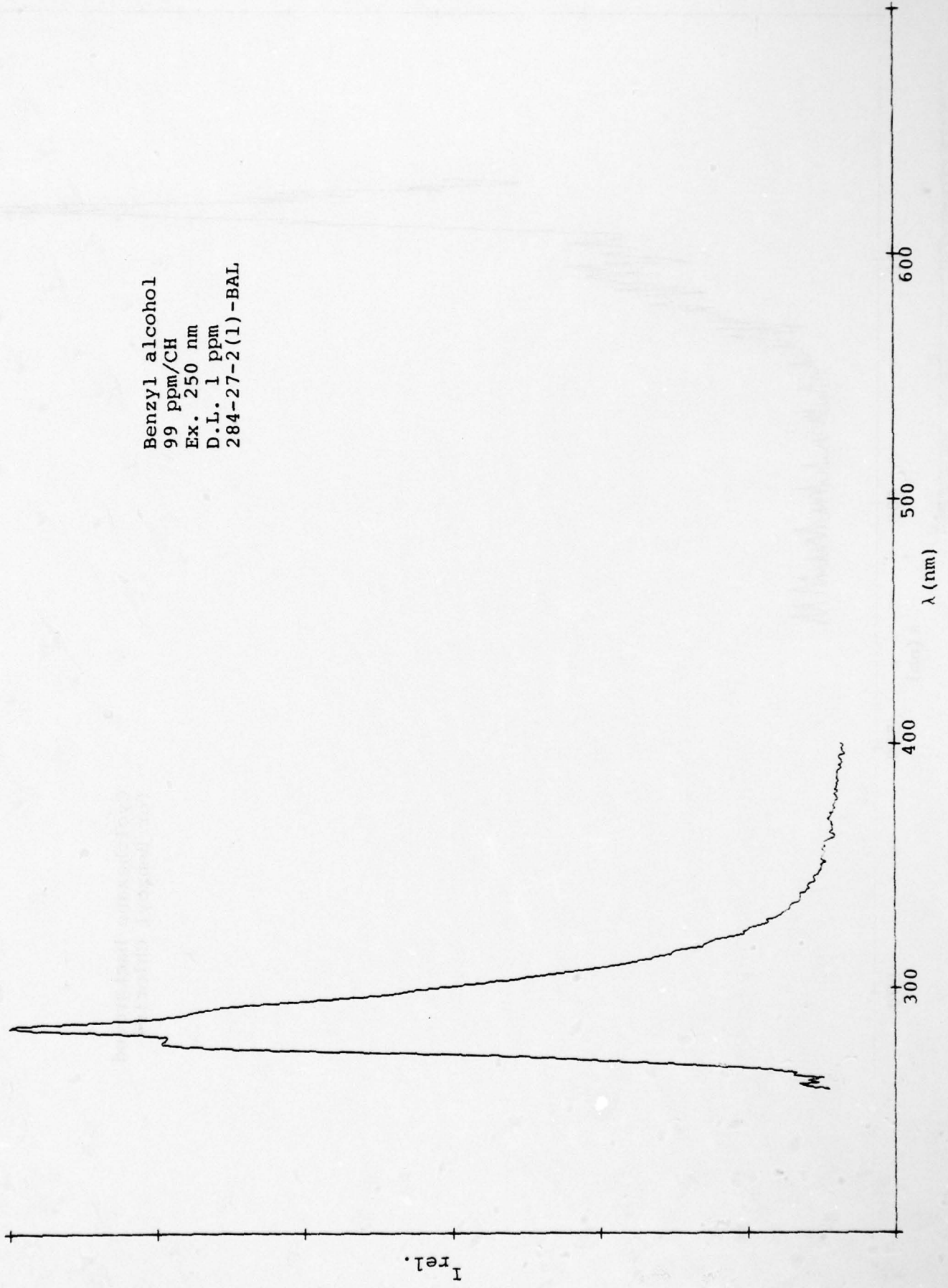
Benzoyl chloride
104 ppm/CH
Ex. 260 nm
Non-emitter



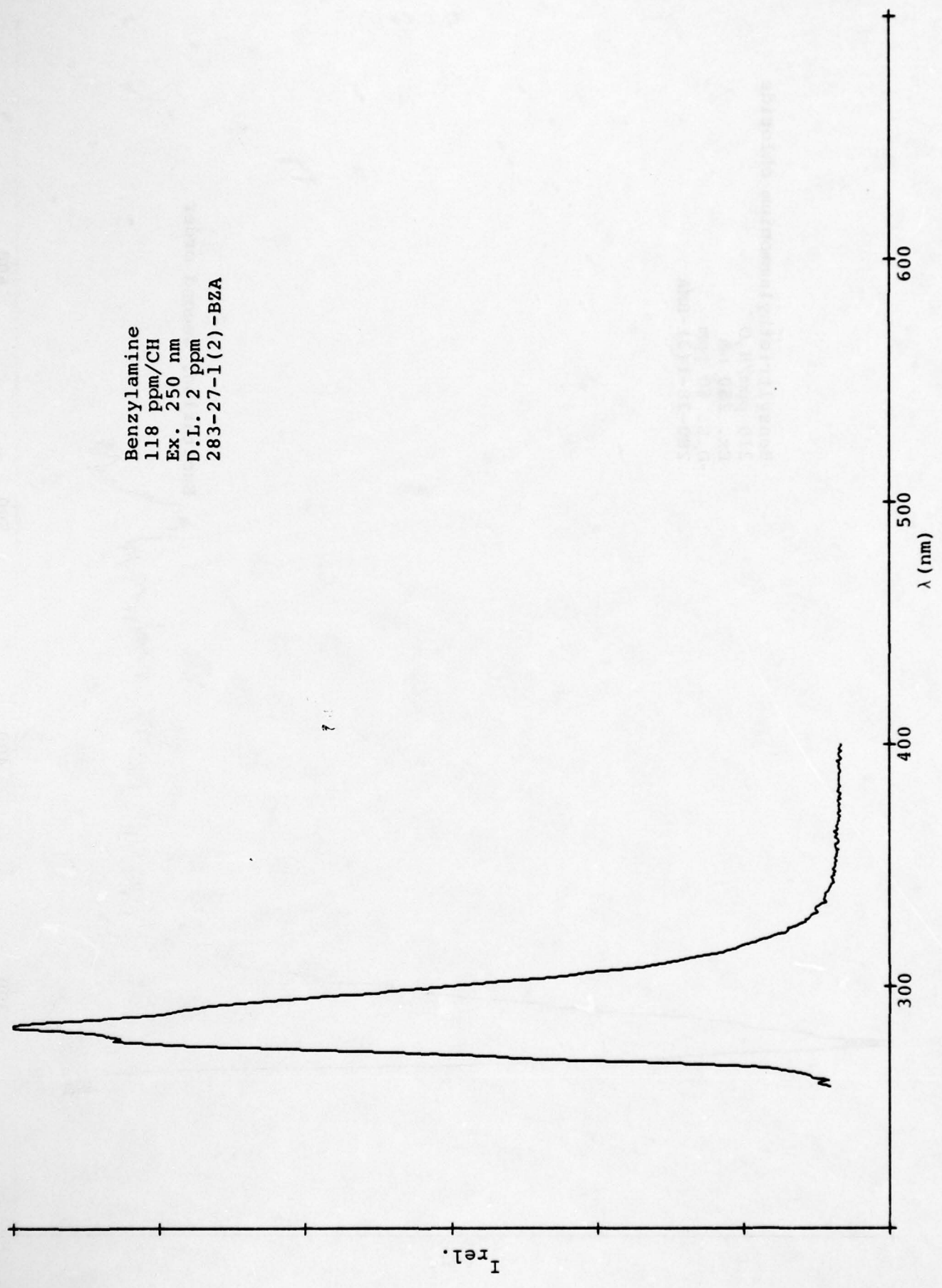
Cyclohexane background
for Benzoyl Chloride



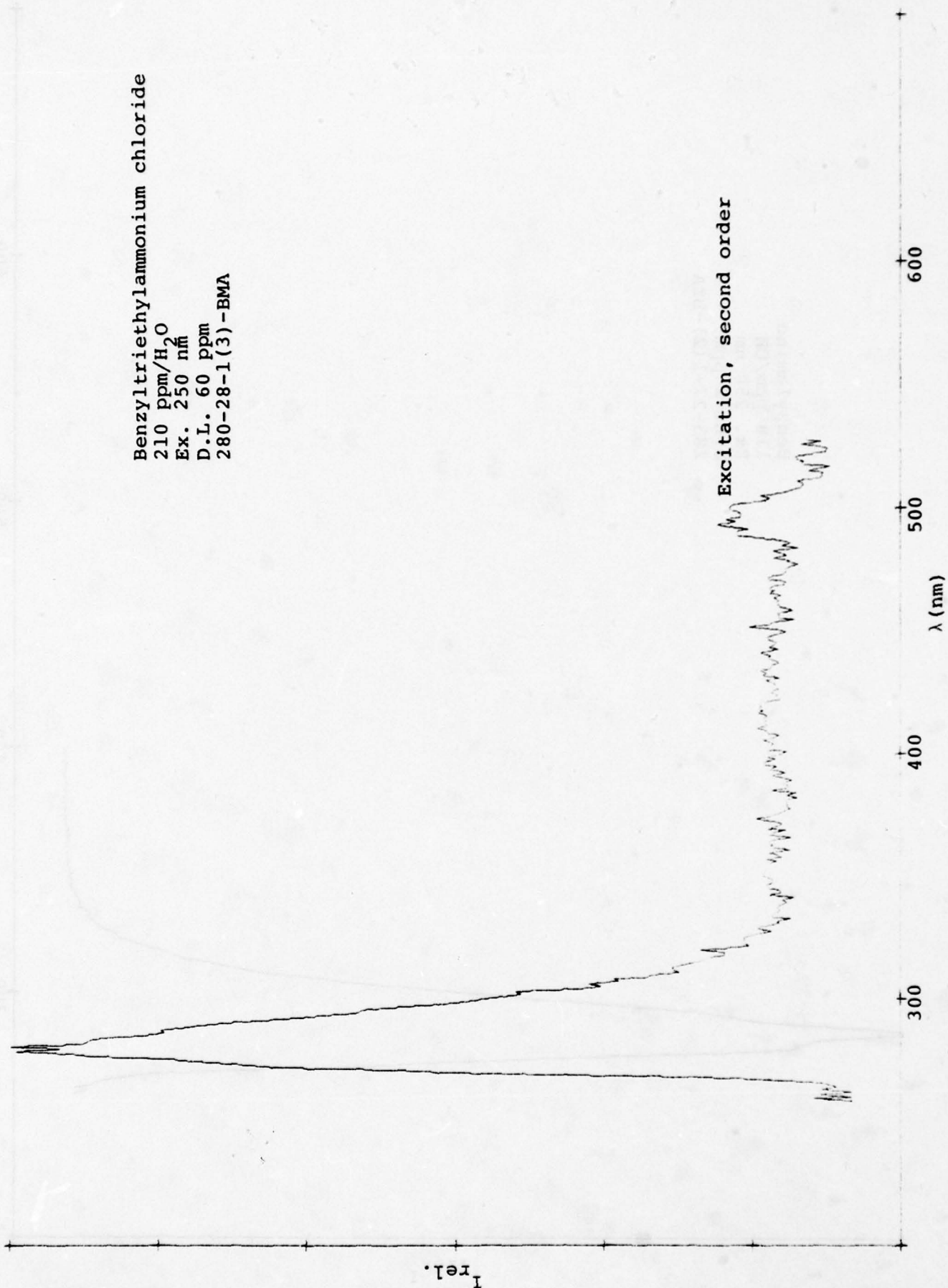
Benzyl alcohol
99 ppm/CH
Ex. 250 nm
D.L. 1 ppm
284-27-2(1)-BAL



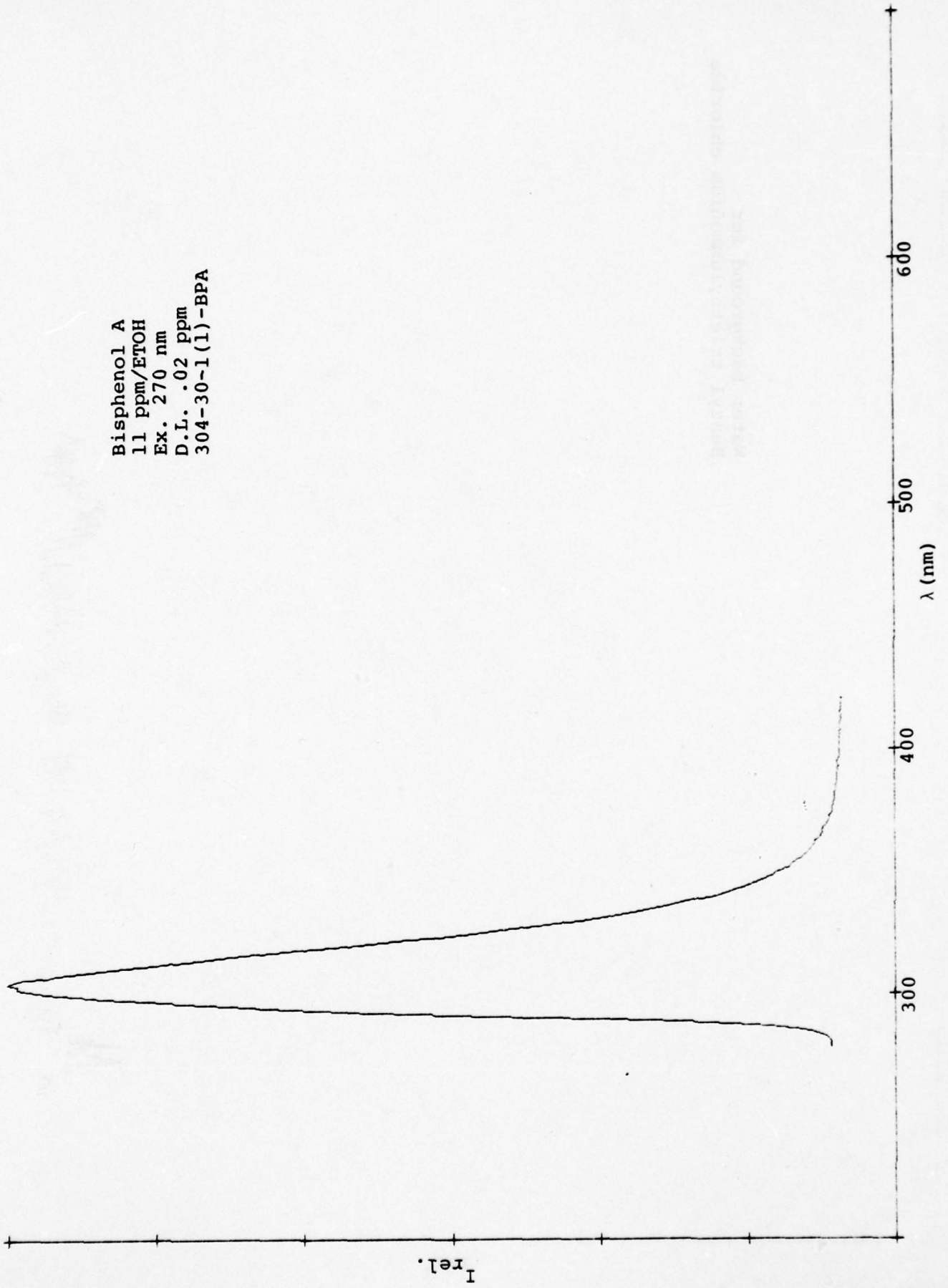
Benzylamine
118 ppm/CH
Ex. 250 nm
D.L. 2 ppm
283-27-1(2) -BZA



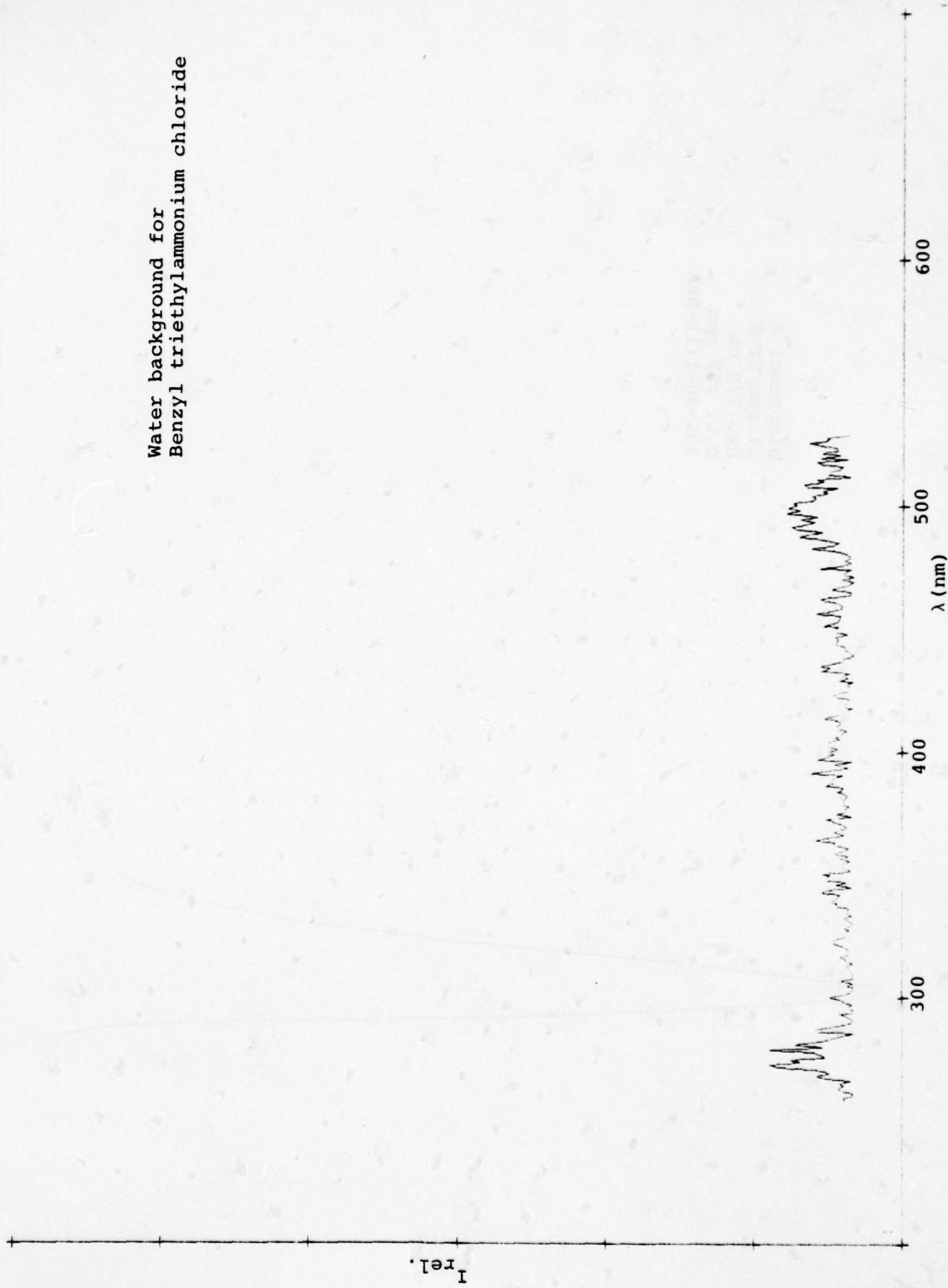
Benzyltriethylammonium chloride
210 ppm/H₂O
Ex. 250 nm
D.L. 60 ppm
280-28-1(3)-BMA



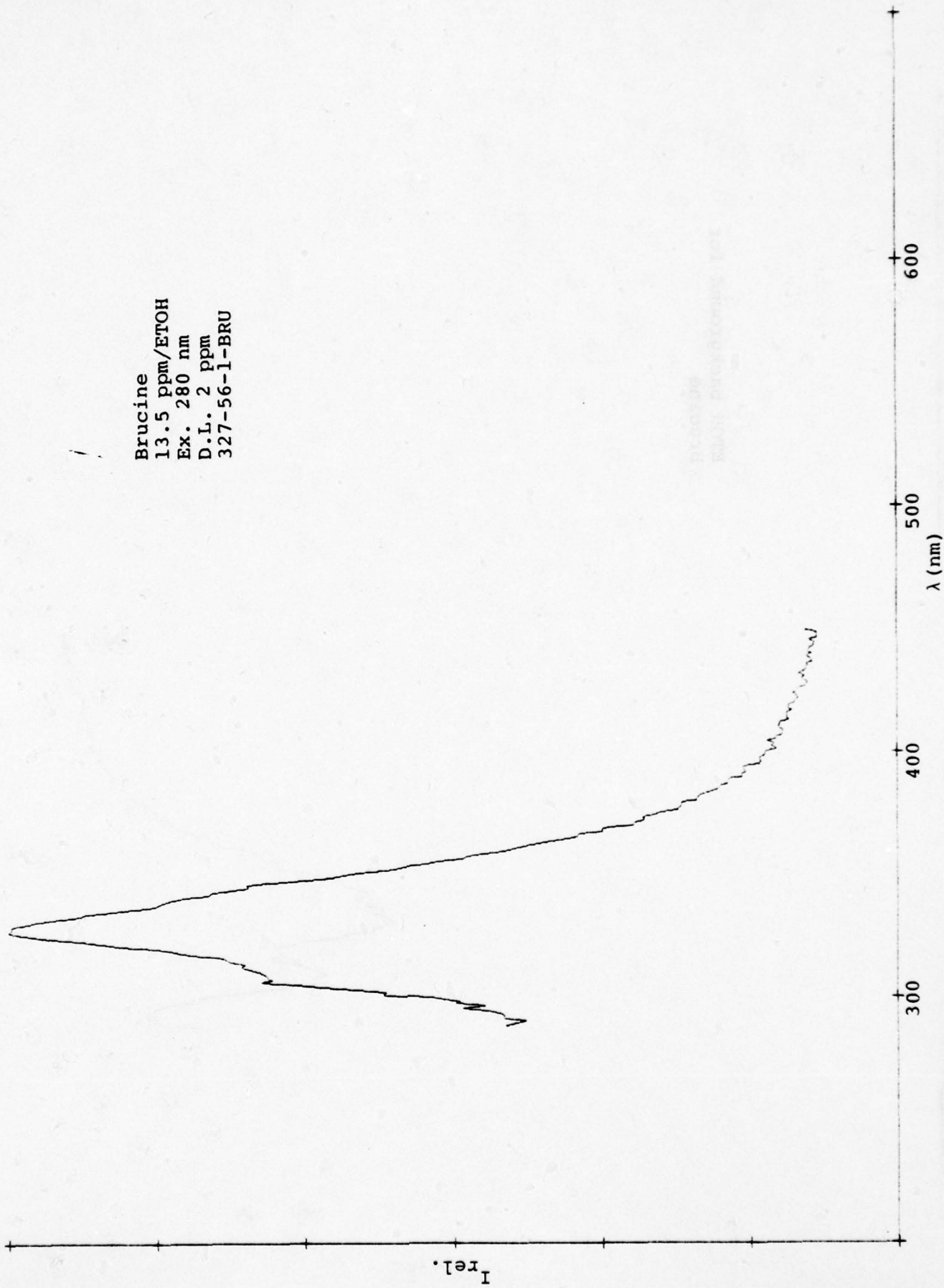
Bisphenol A
11 ppm/ETOH
Ex. 270 nm
D.L. .02 ppm
304-30-1(1)-BPA



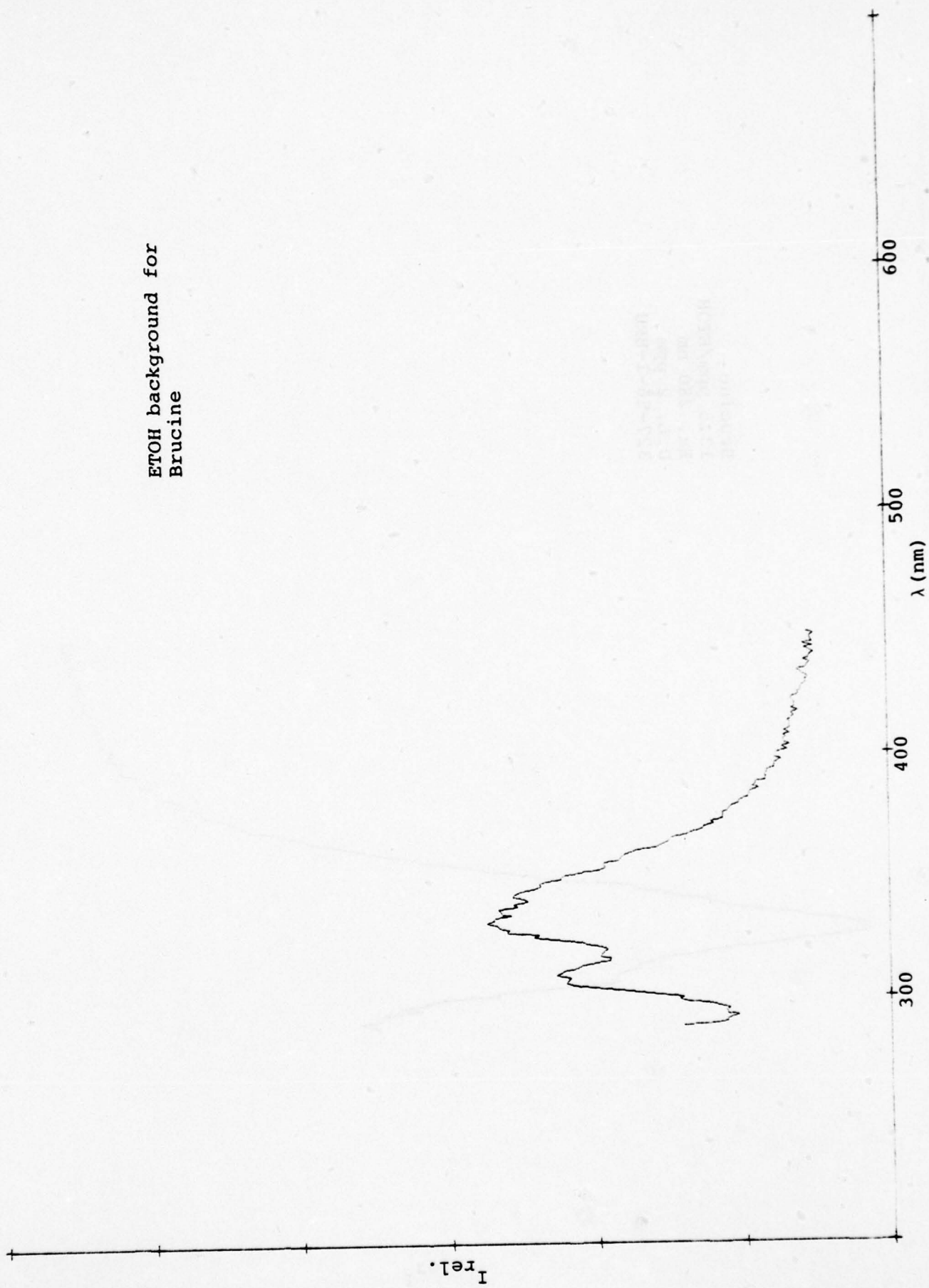
Water background for
Benzyl triethylammonium chloride



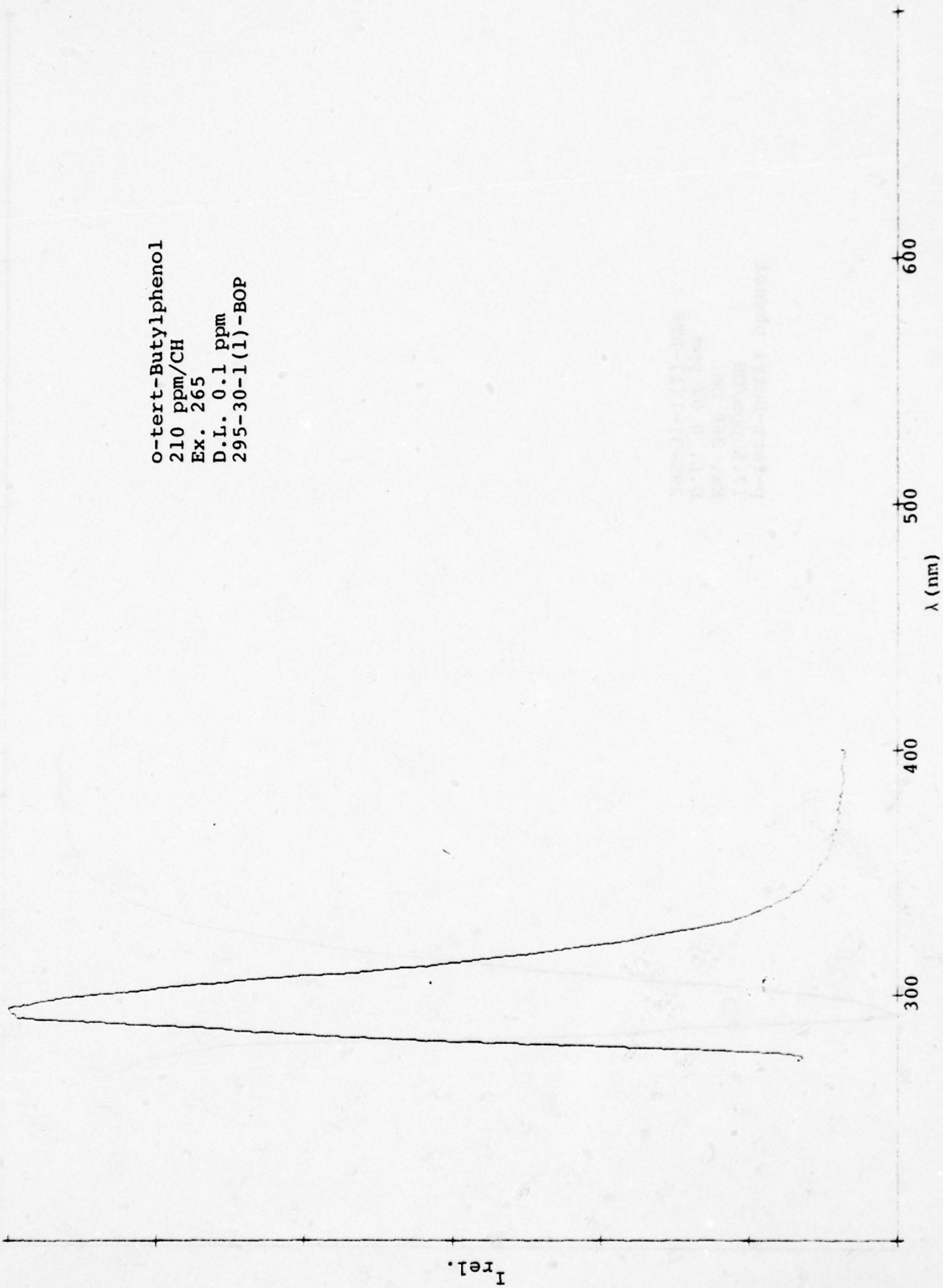
Brucine
13.5 ppm/ETOH
Ex. 280 nm
D.L. 2 ppm
327-56-1-BRU



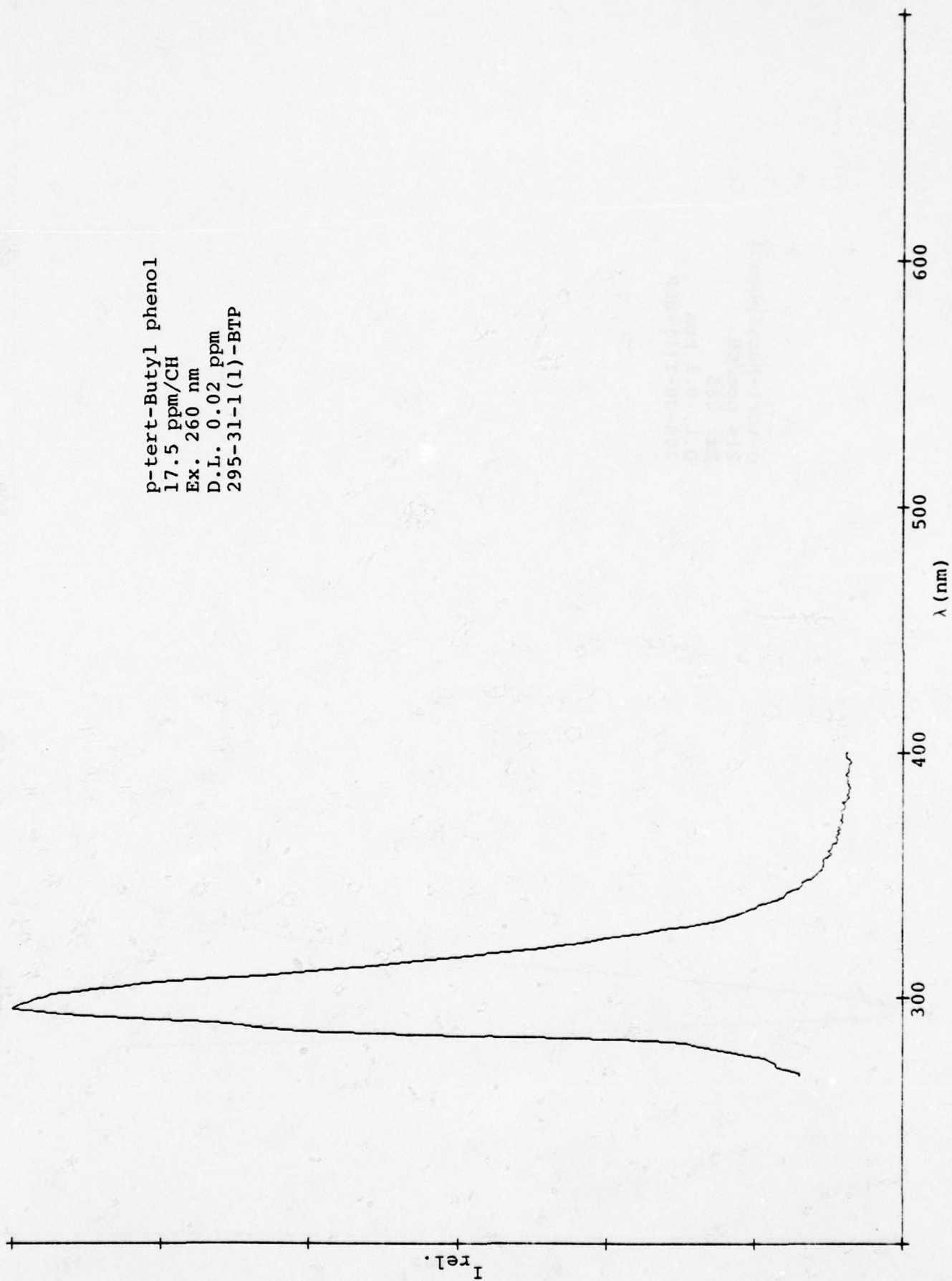
EtOH background for
Brucine



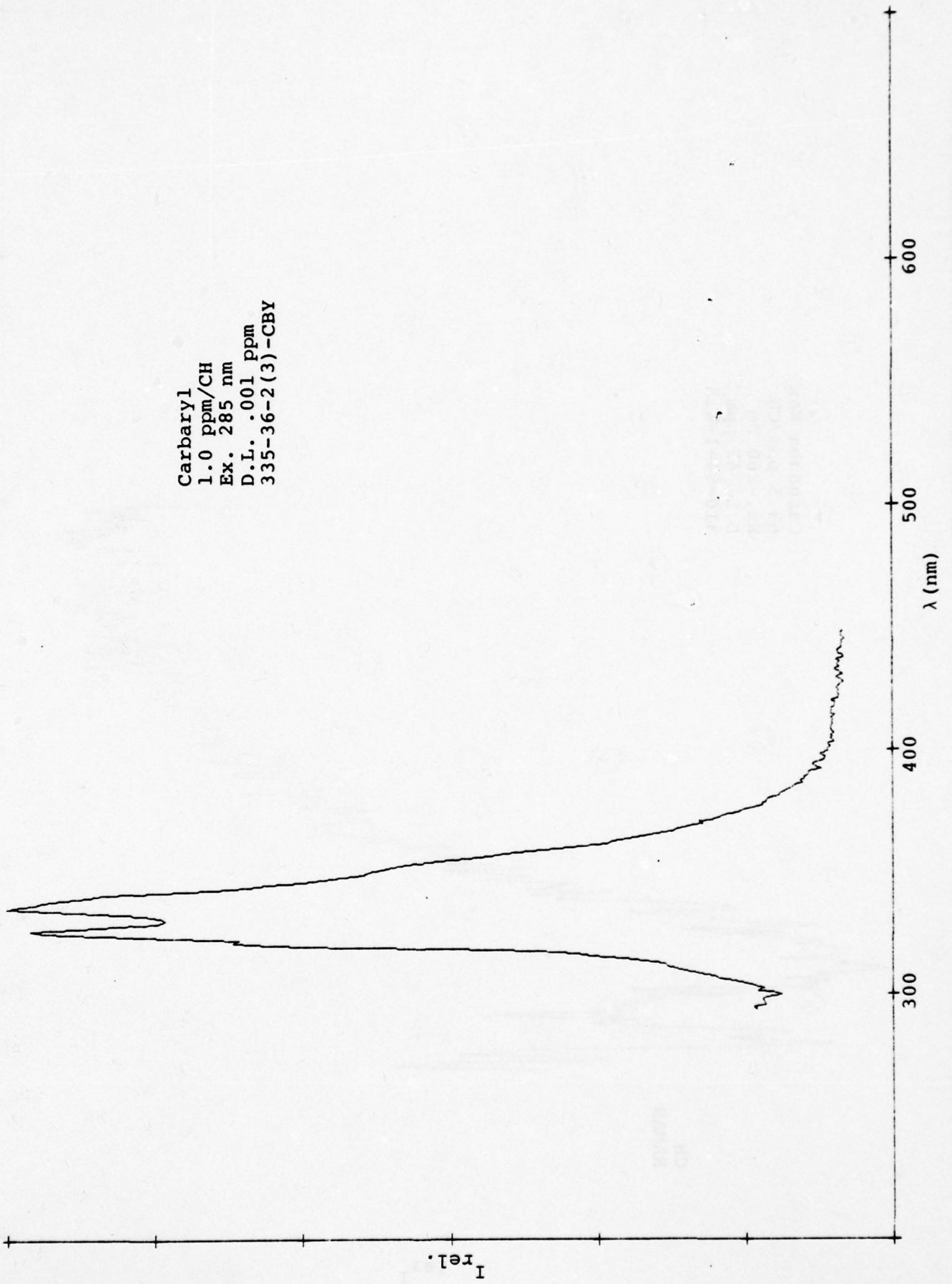
O-tert-Butylphenol
210 ppm/CH
Ex. 265
D.L. 0.1 ppm
295-30-1(1)-BOP



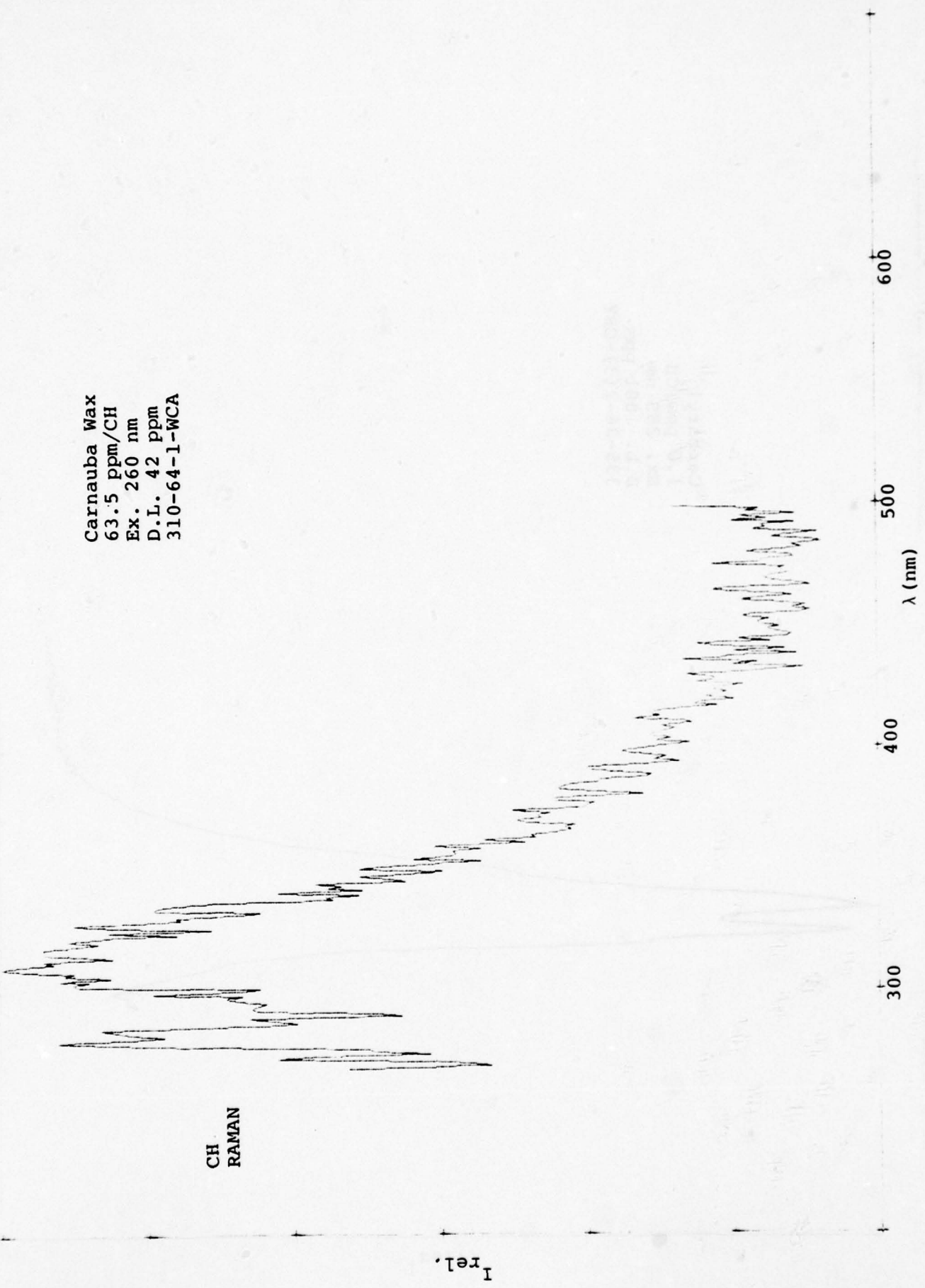
p-tert-Butyl phenol
17.5 ppm/CH
Ex. 260 nm
D.L. 0.02 ppm
295-31-1(1)-BTP



Carbaryl
1.0 ppm/CH
Ex. 285 nm
D.L. .001 ppm
335-36-2(3)-CBY

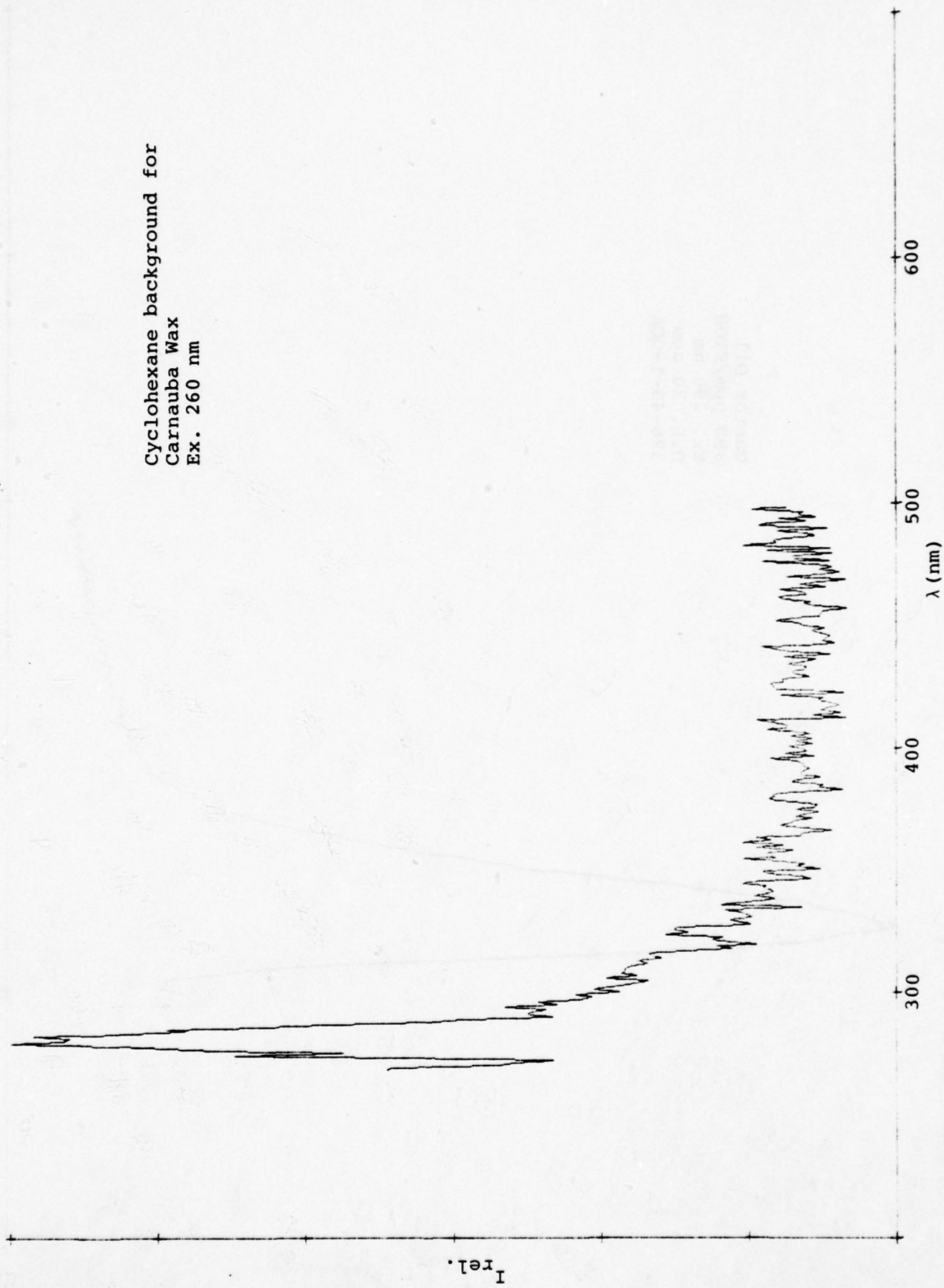


Carnauba Wax
63.5 ppm/CH
Ex. 260 nm
D.L. 42 ppm
310-64-1-WCA

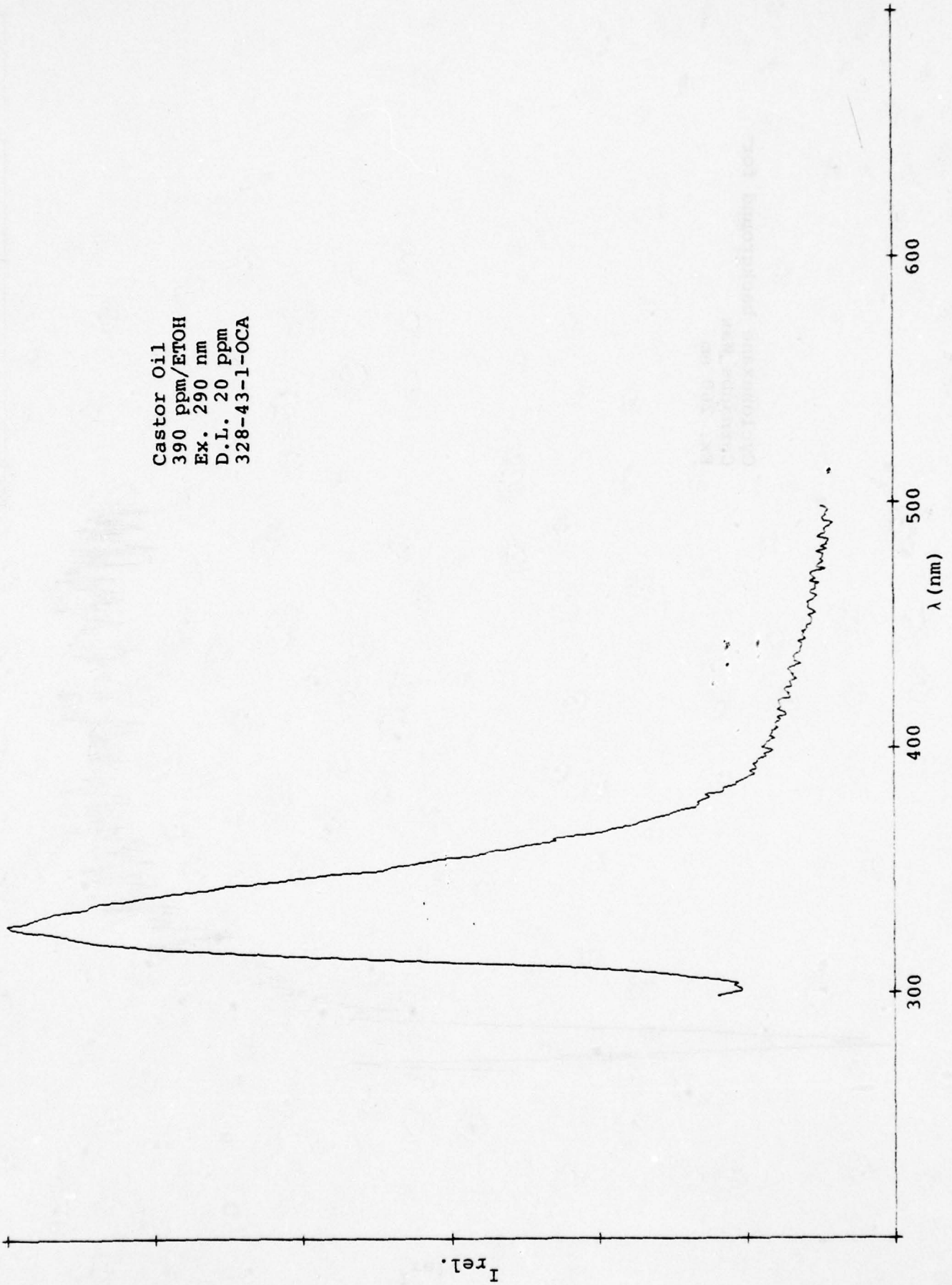


CH
RAMAN

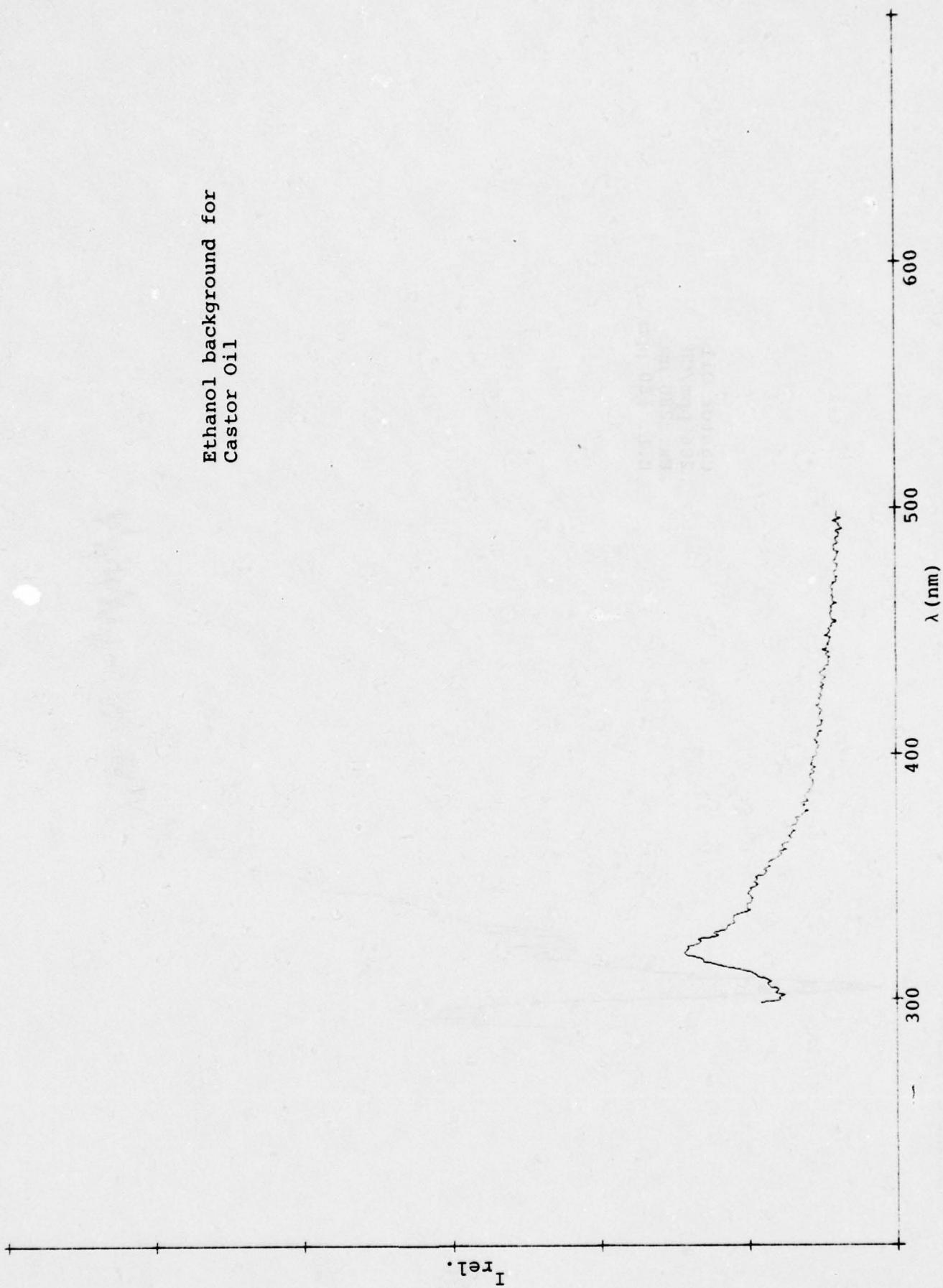
Cyclohexane background for
Carnauba Wax
Ex. 260 nm



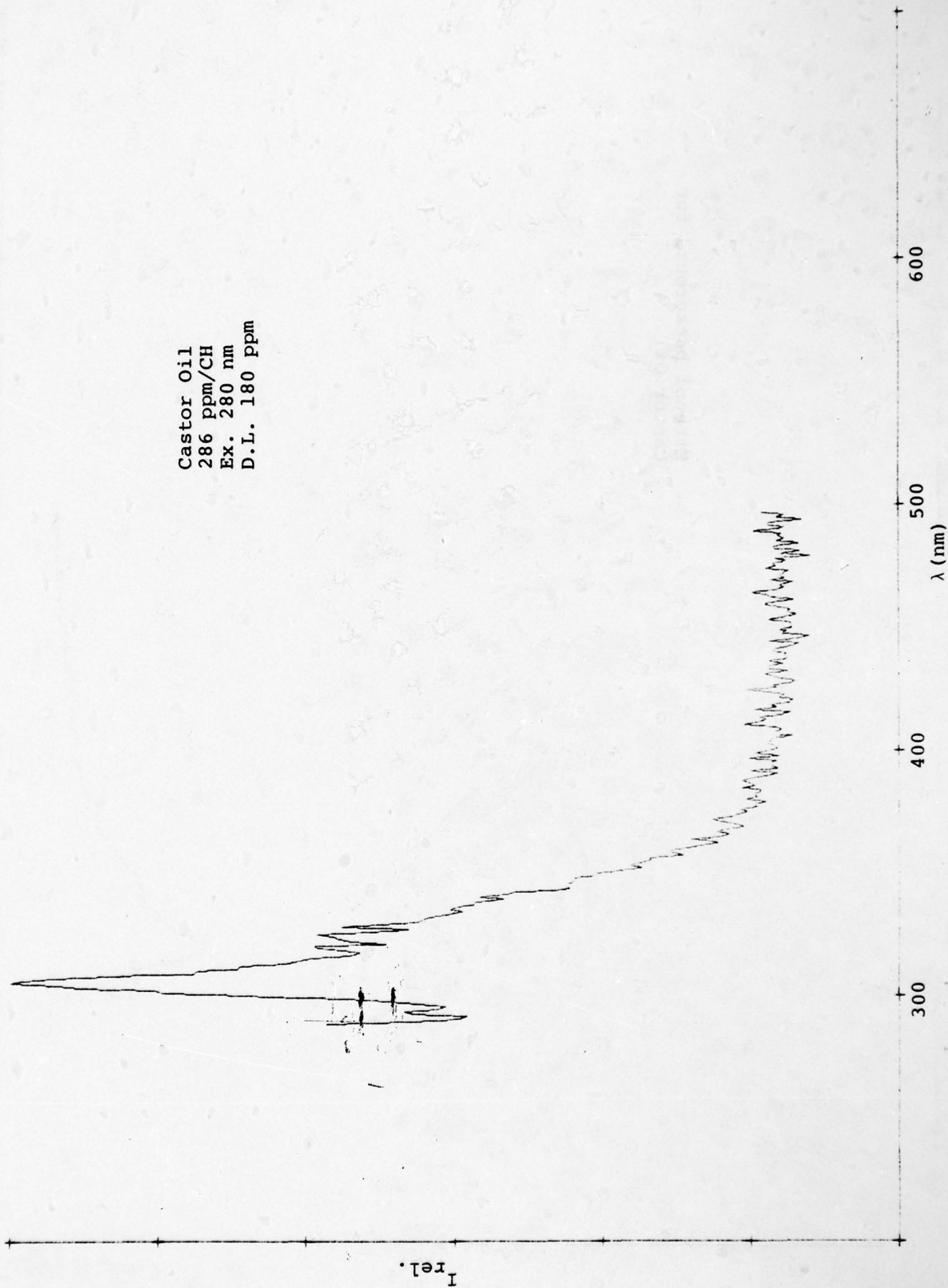
Castor Oil
390 ppm/ETOH
Ex. 290 nm
D.L. 20 ppm
328-43-1-OCA



Ethanol background for
Castor Oil



Castor Oil
286 ppm/CH
Ex. 280 nm
D.L. 180 ppm

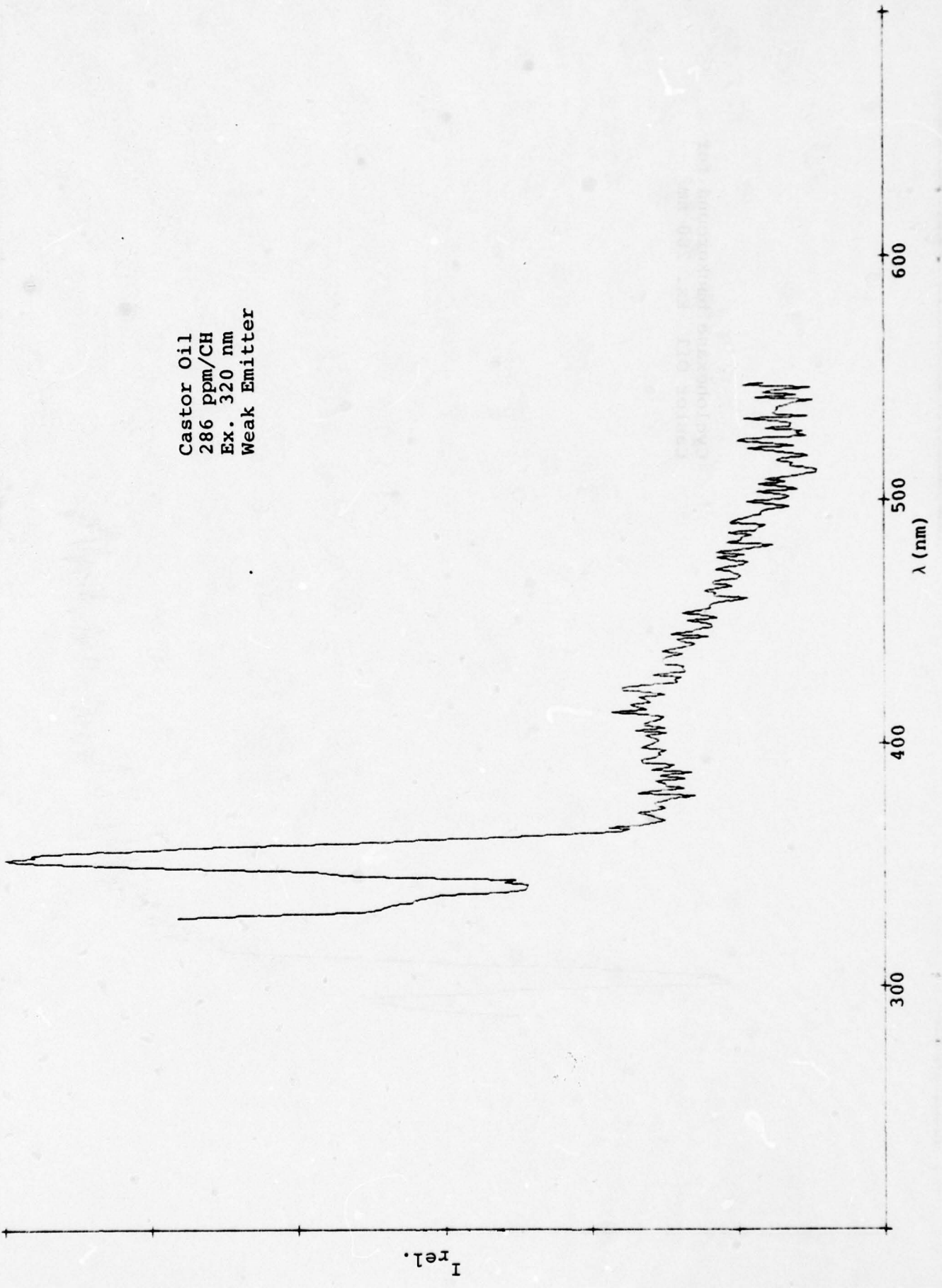


Cyclohexane background for
Castor Oil Ex. 280 nm

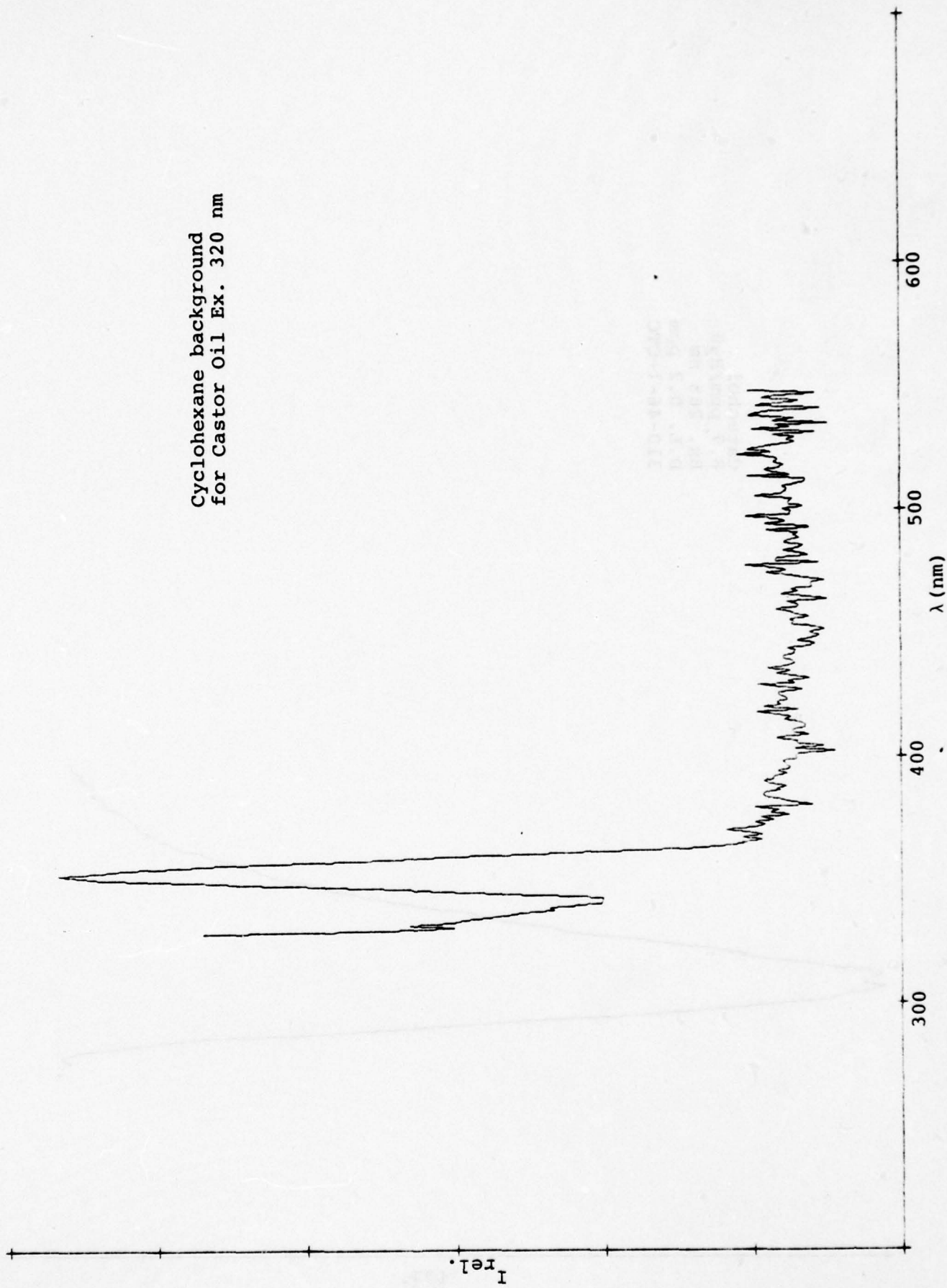


Model 8000
SPE 730 100
SPE 100000
C-1000 001

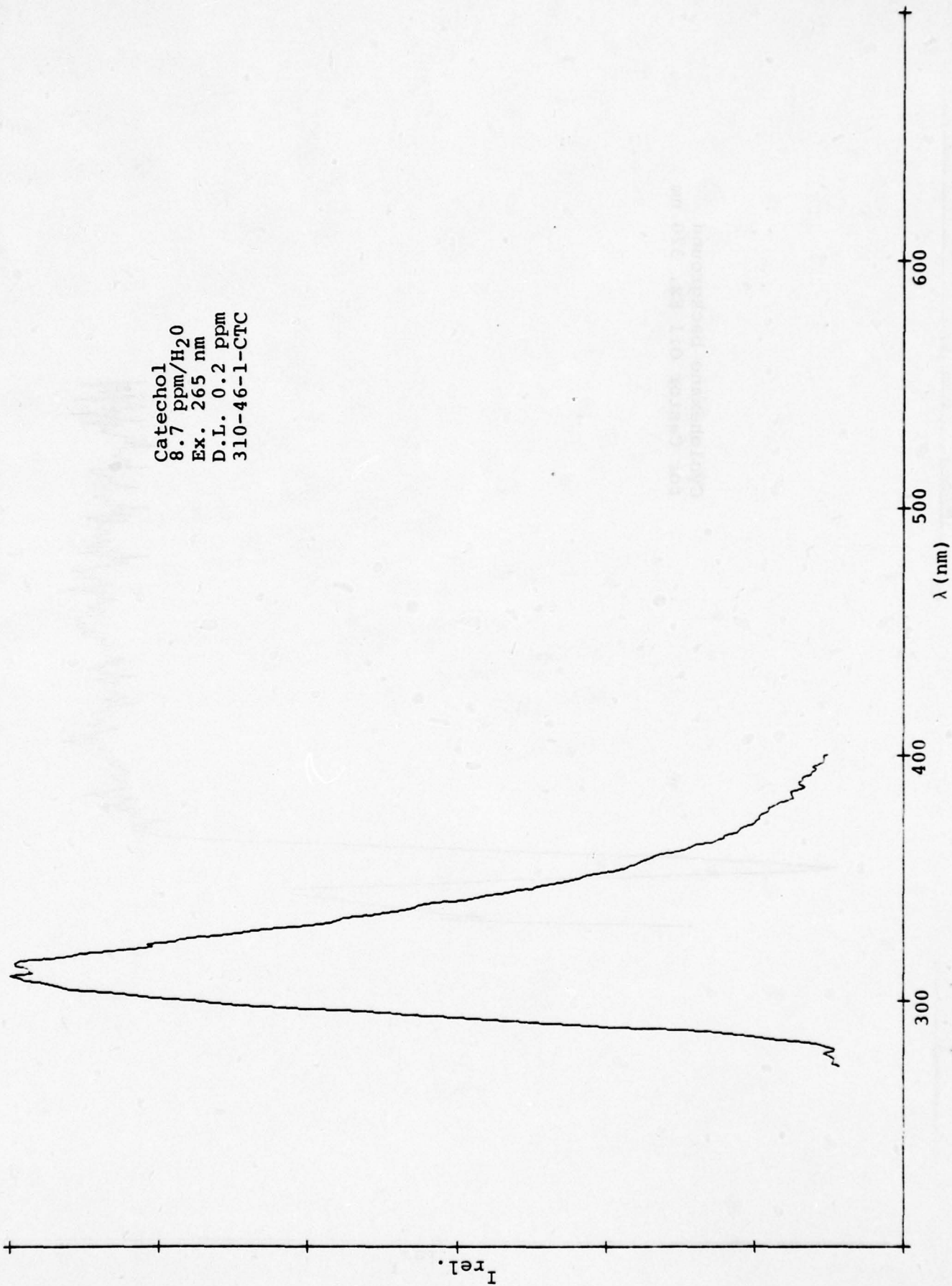
Castor Oil
286 ppm/CH
Ex. 320 nm
Weak Emitter



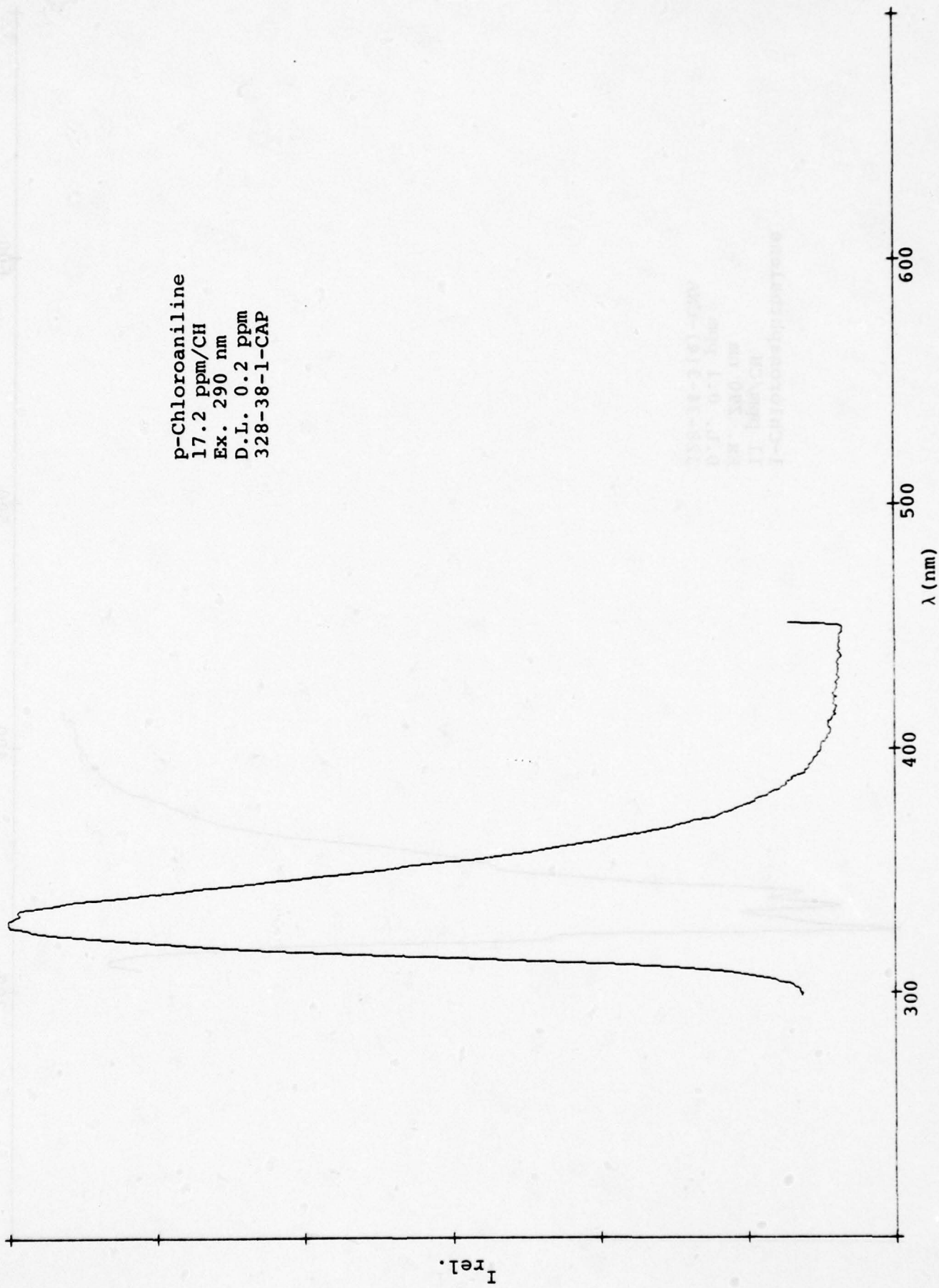
Cyclohexane background
for Castor Oil Ex. 320 nm



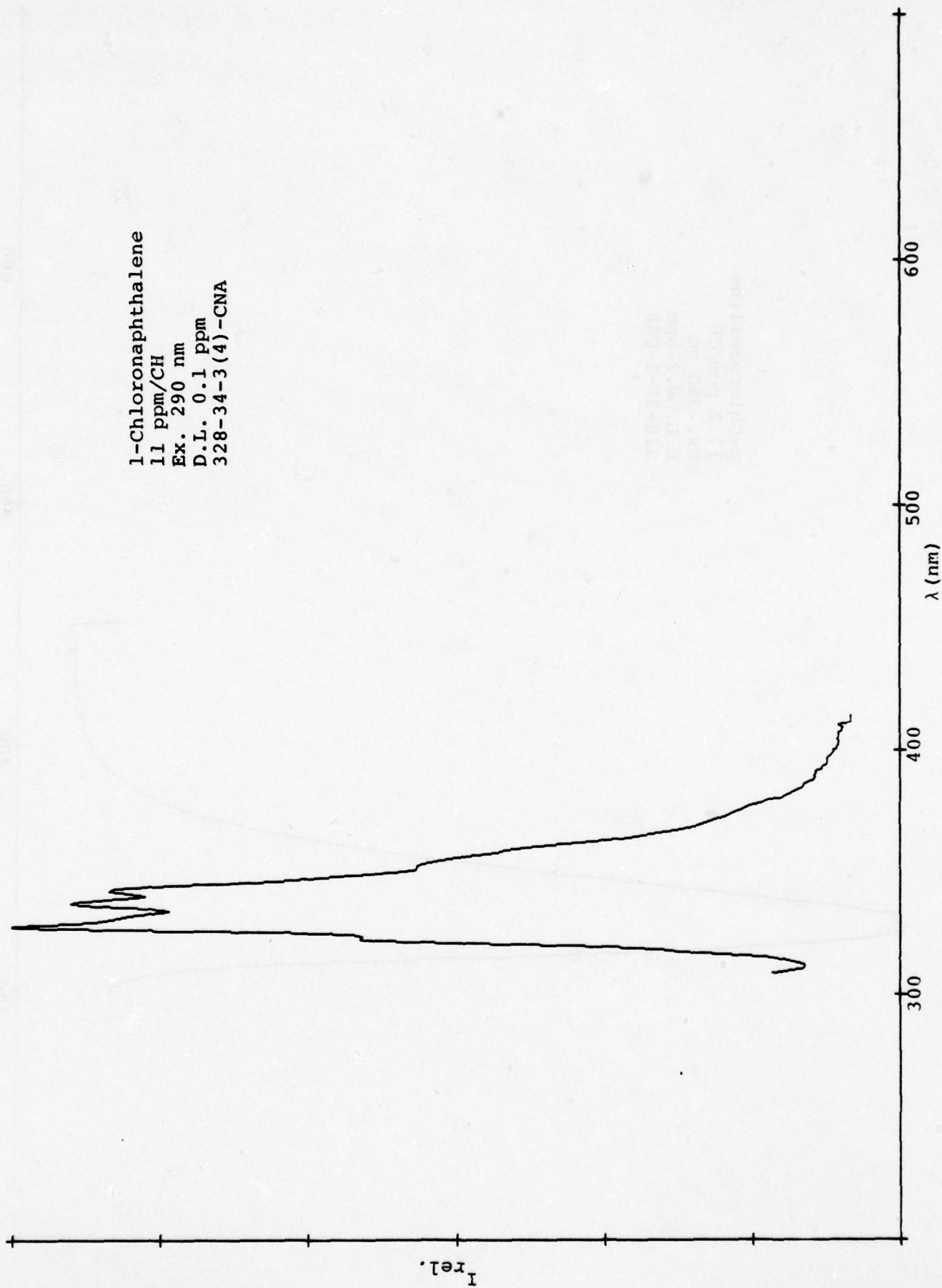
Catechol
8.7 ppm/H₂O
Ex. 265 nm
D.L. 0.2 ppm
310-46-1-CTC



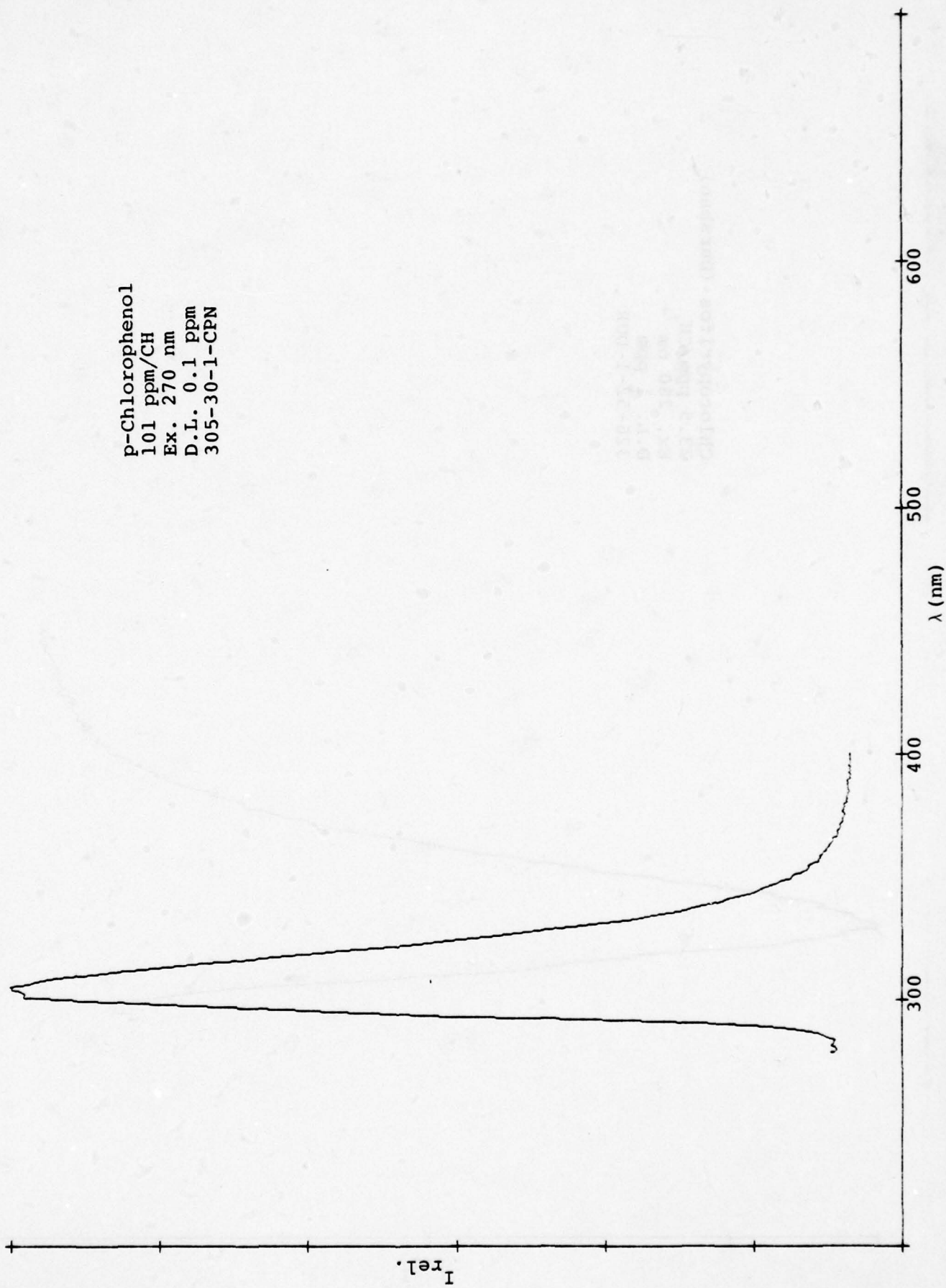
p-Chloroaniline
17.2 ppm/CH
Ex. 290 nm
D.L. 0.2 ppm
328-38-1-CAP



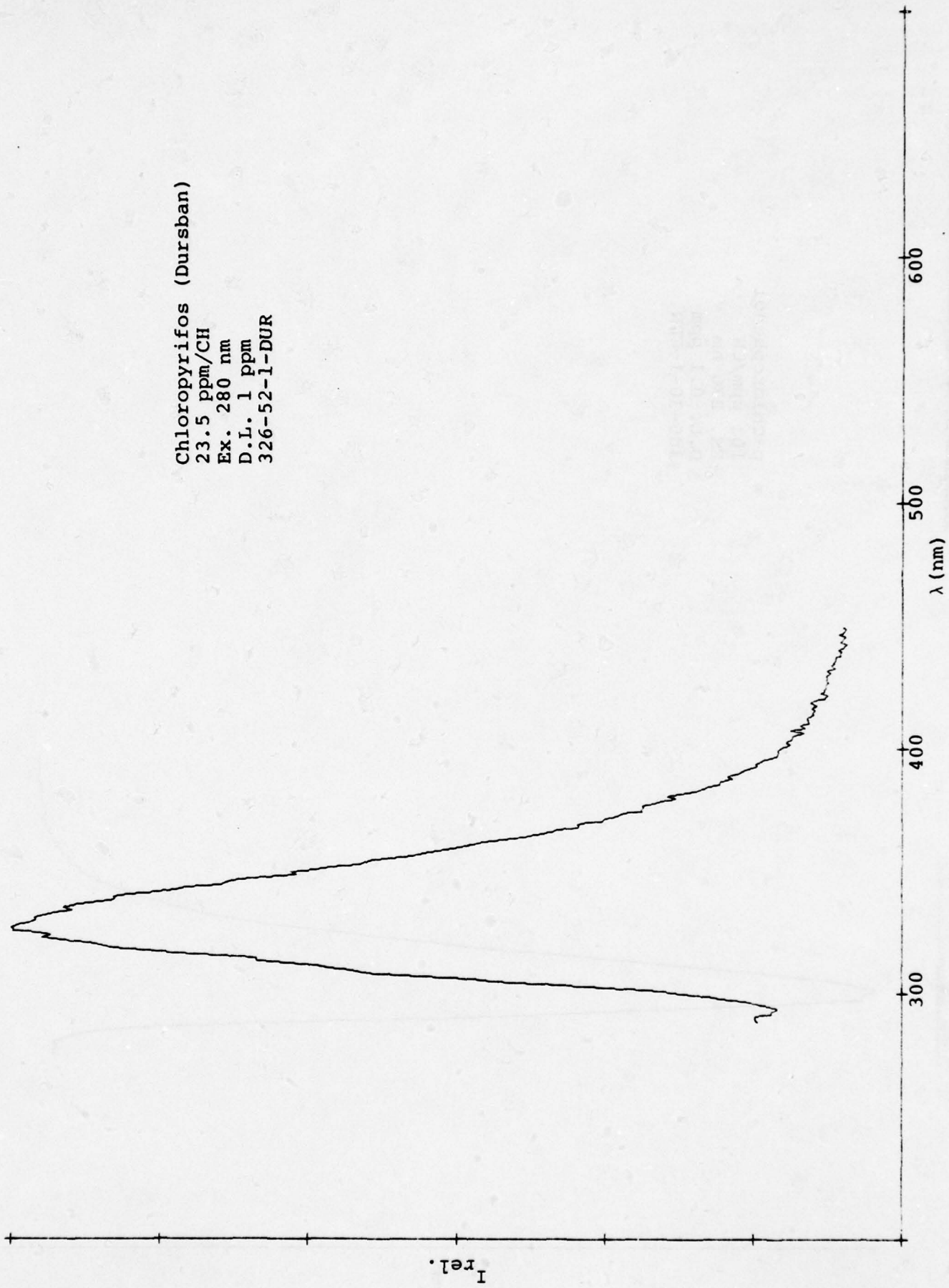
1-Chloronaphthalene
11 ppm/CH
Ex. 290 nm
D.L. 0.1 ppm
328-34-3(4)-CNA



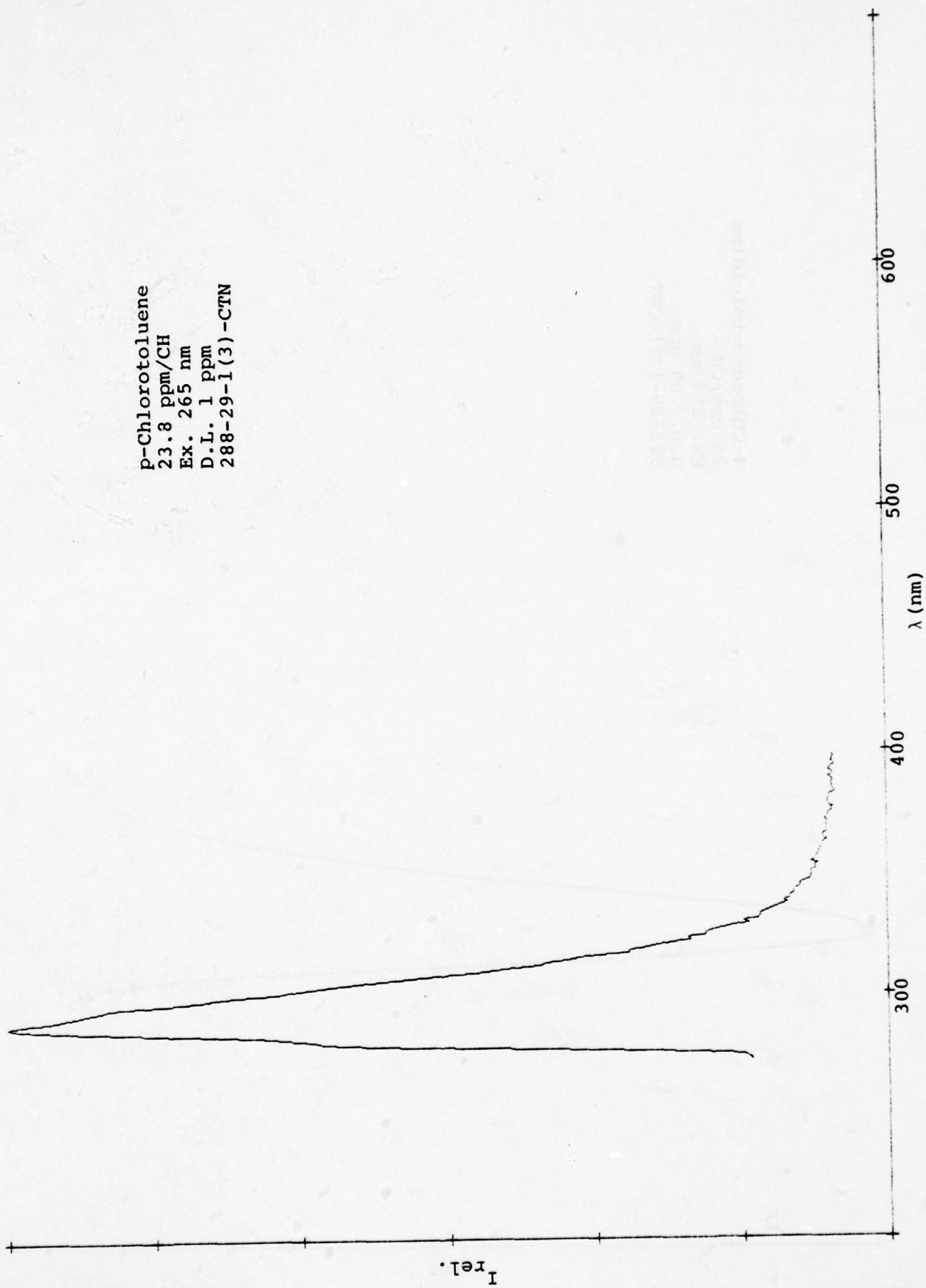
p-Chlorophenol
101 ppm/CH
Ex. 270 nm
D.L. 0.1 ppm
305-30-1-CPN



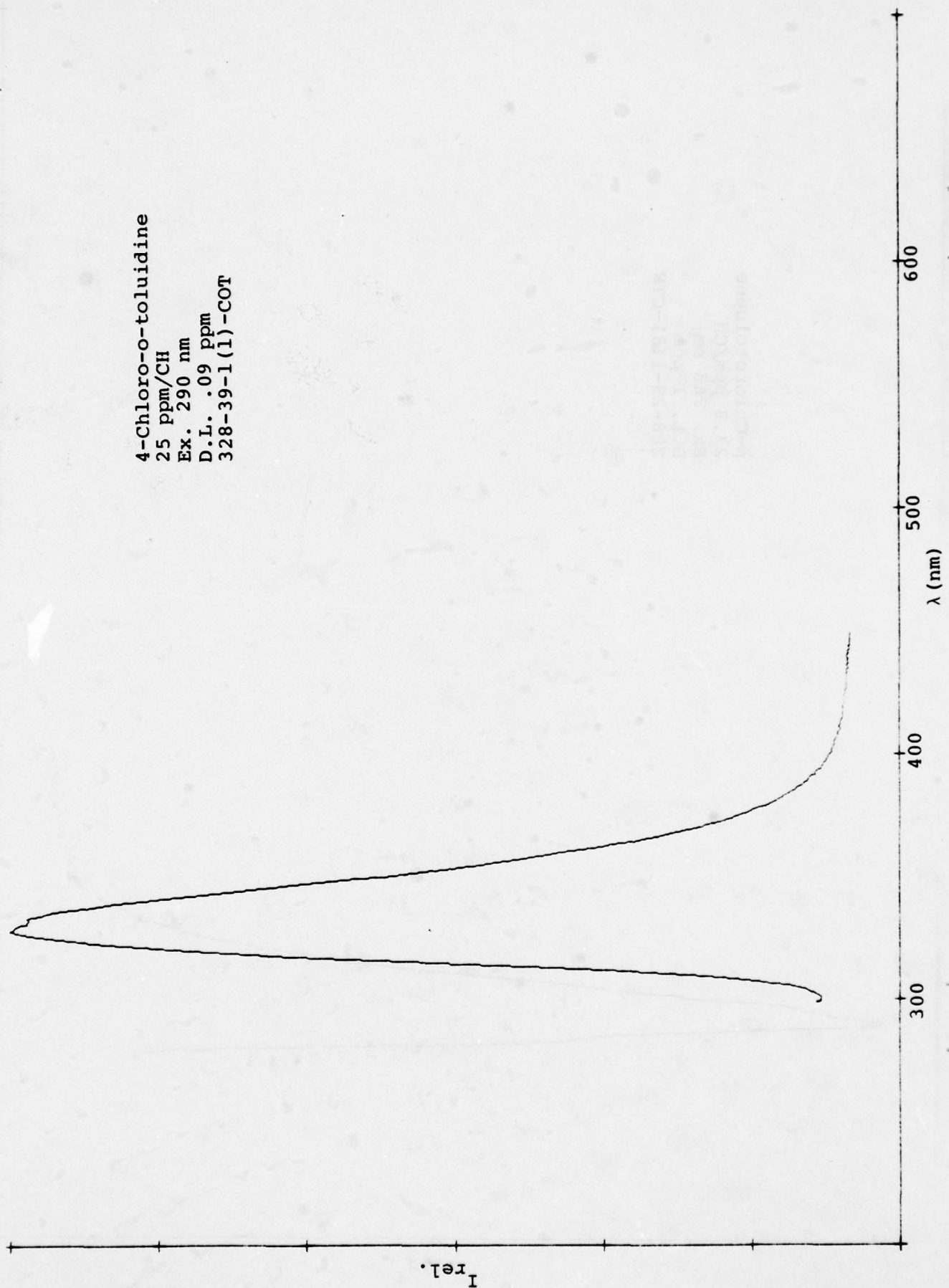
Chloropyrifos (Dursban)
23.5 ppm/CH
Ex. 280 nm
D.L. 1 ppm
326-52-1-DUR



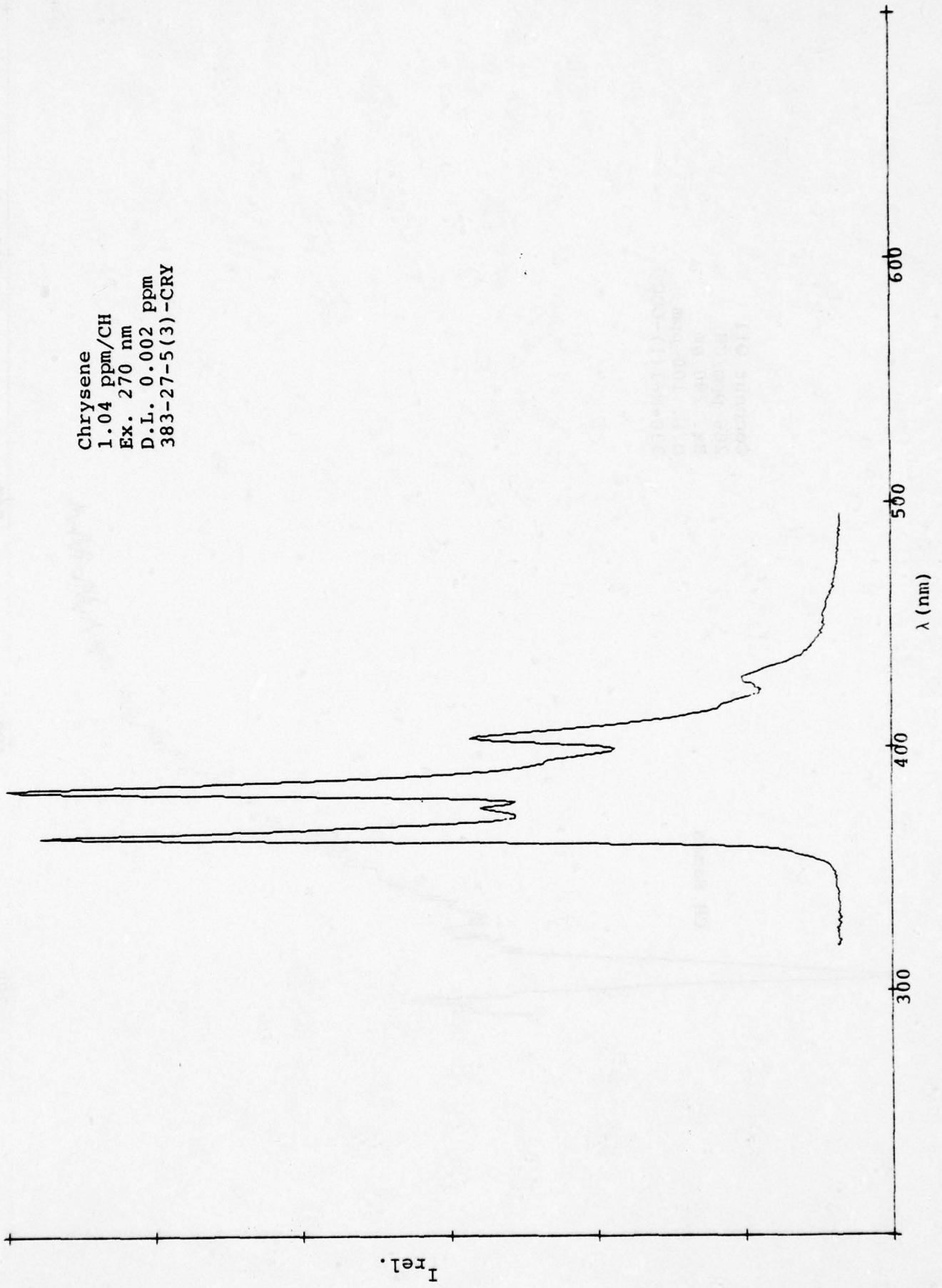
p-Chlorotoluene
23.8 ppm/CH
Ex. 265 nm
D.L. 1 ppm
288-29-1(3)-CTN



4-Chloro-o-toluidine
25 ppm/CH
Ex. 290 nm
D.L. .09 ppm
328-39-1(1)-COT

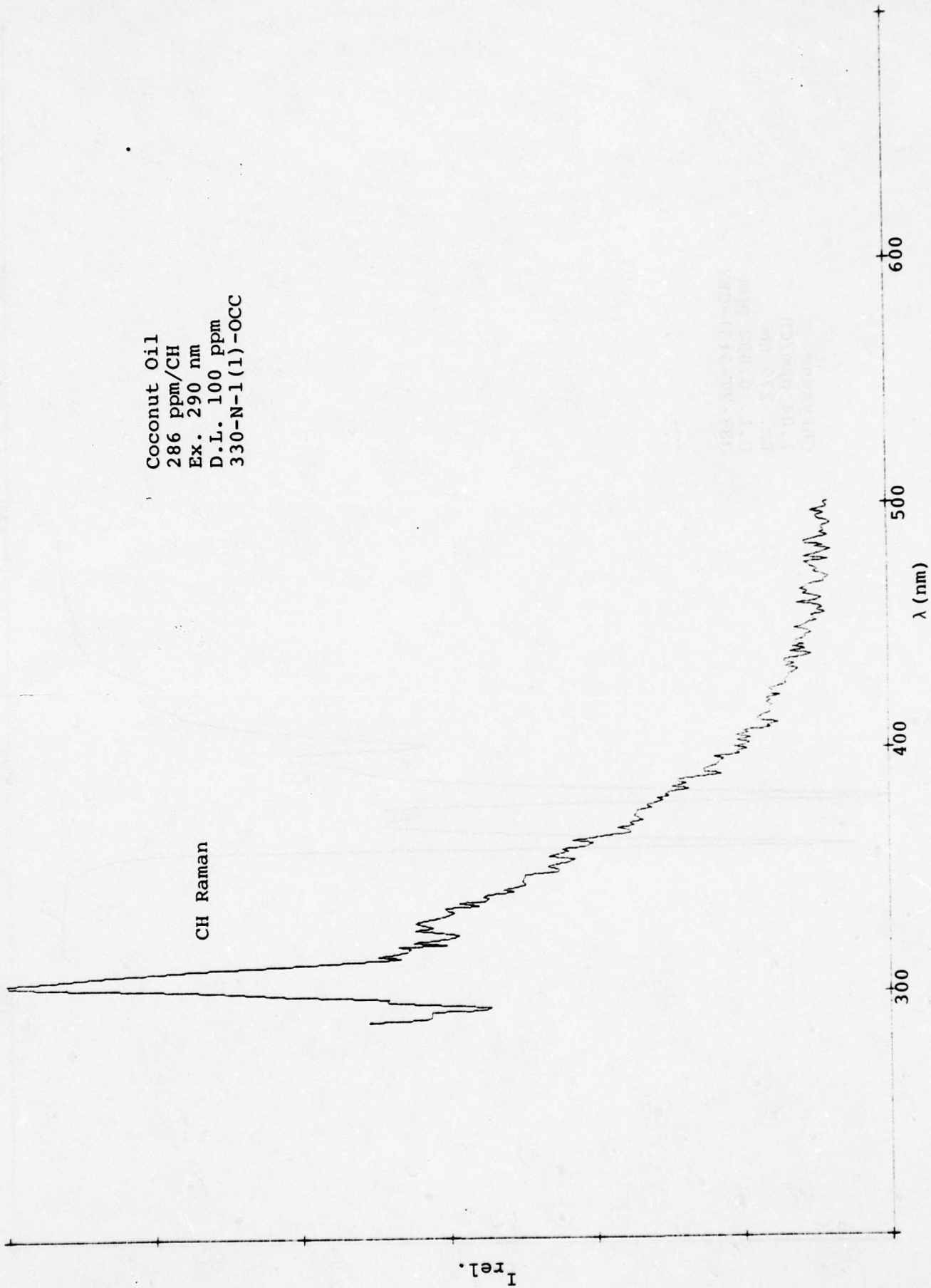


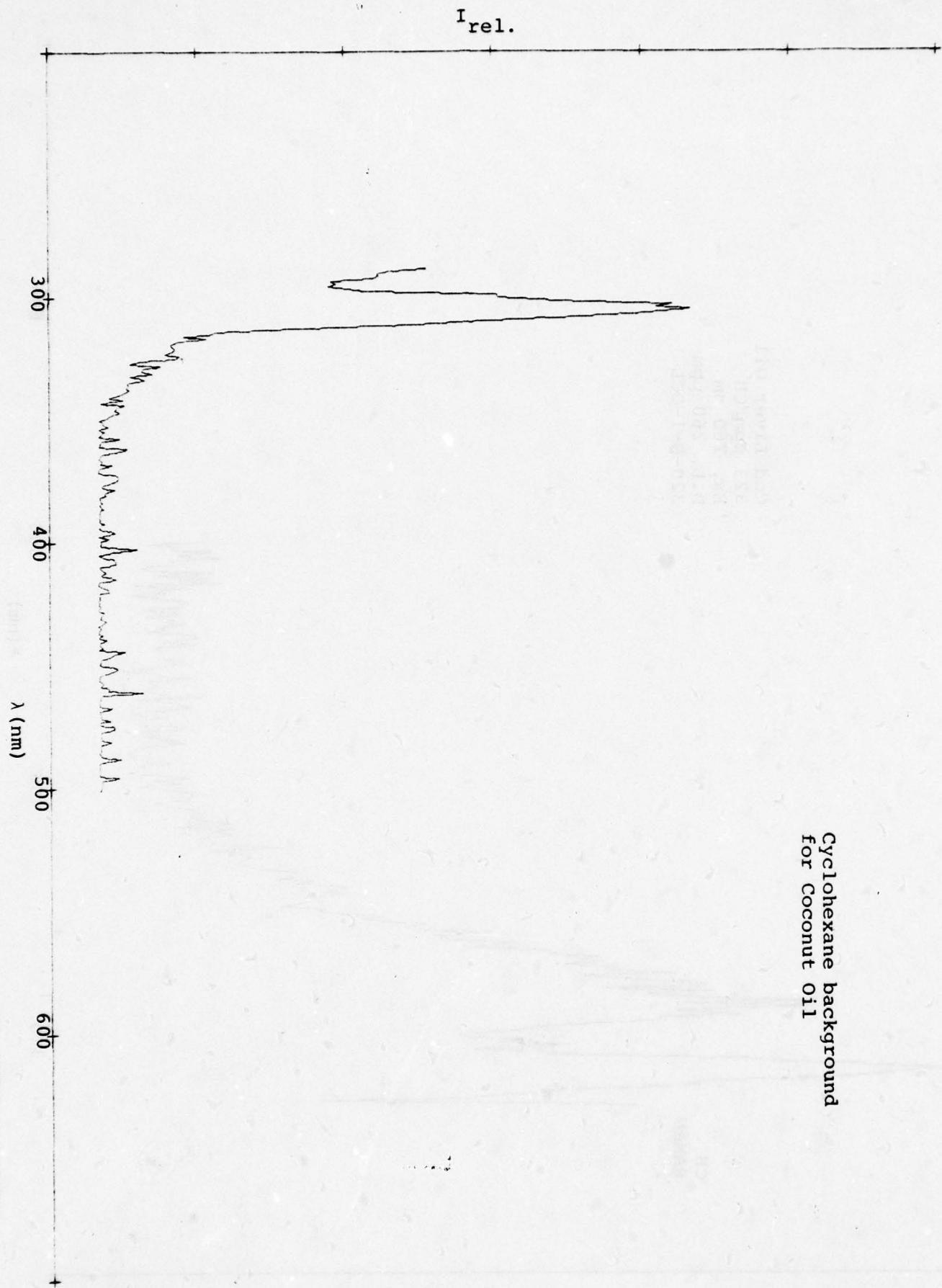
Chrysene
1.04 ppm/CH
Ex. 270 nm
D.L. 0.002 ppm
383-27-5(3)-CRY



Coconut Oil
286 ppm/CH
Ex. 290 nm
D.L. 100 ppm
330-N-1(1)-OCC

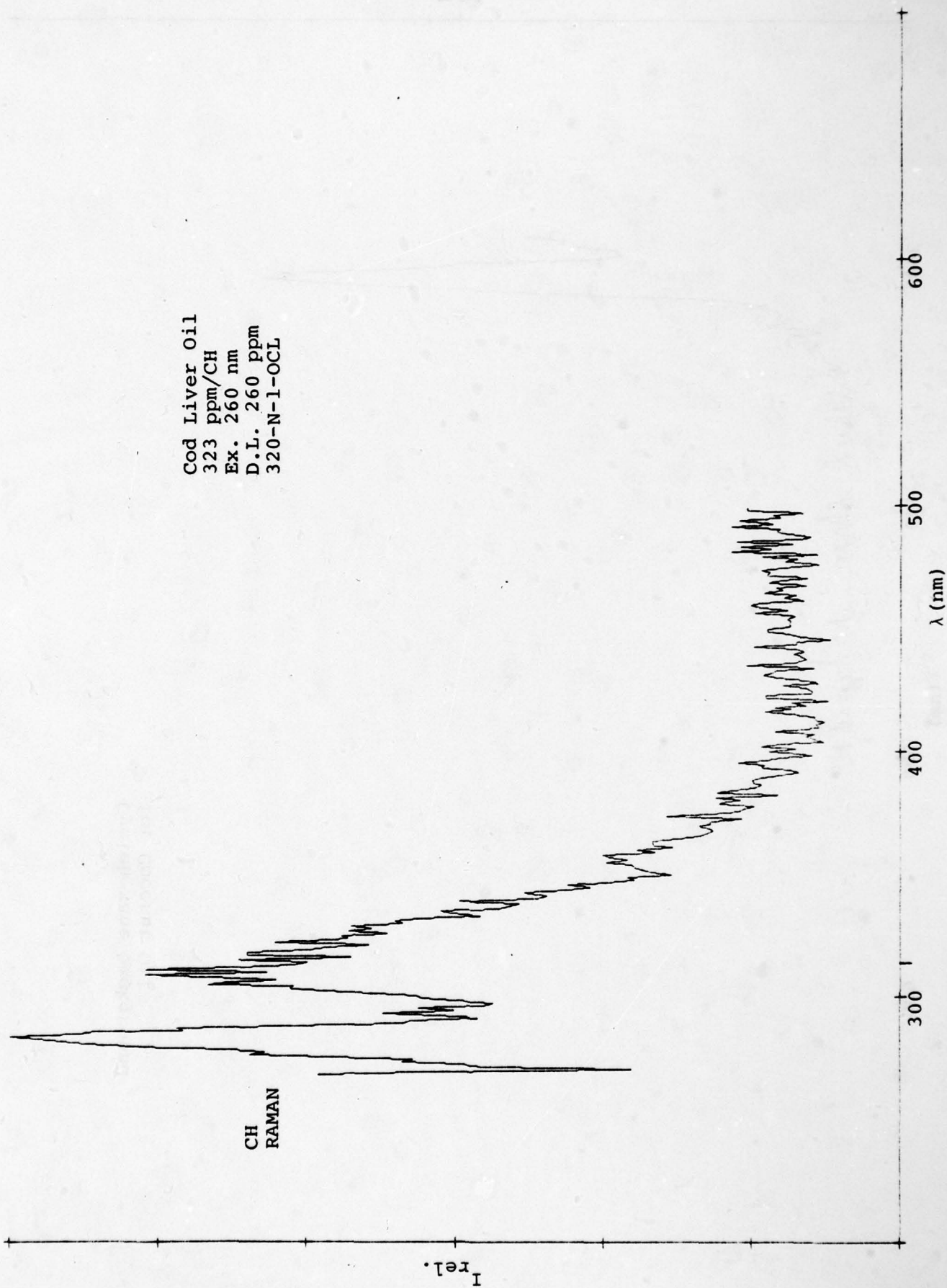
CH Raman



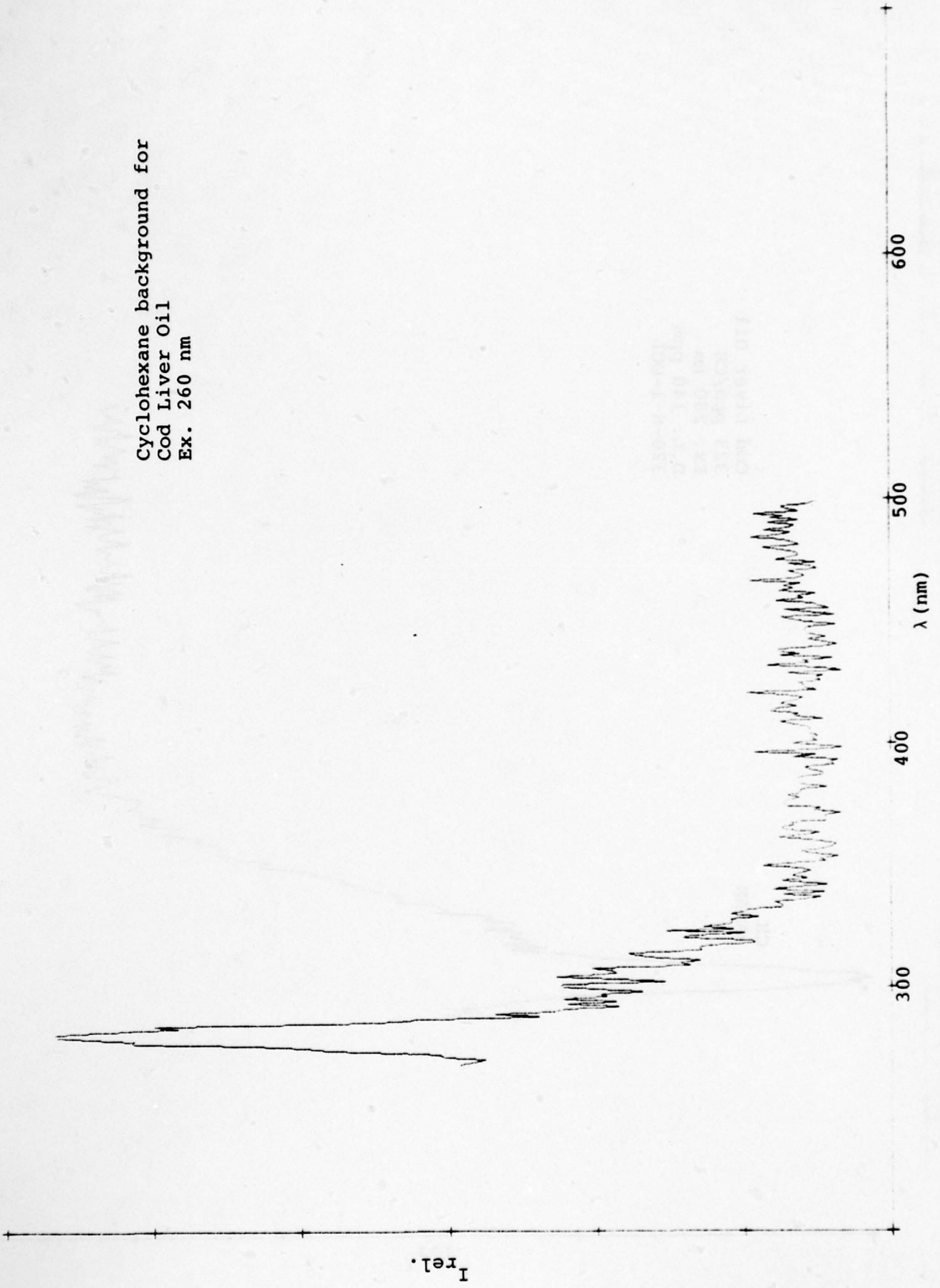


Cyclohexane background
for Coconut Oil

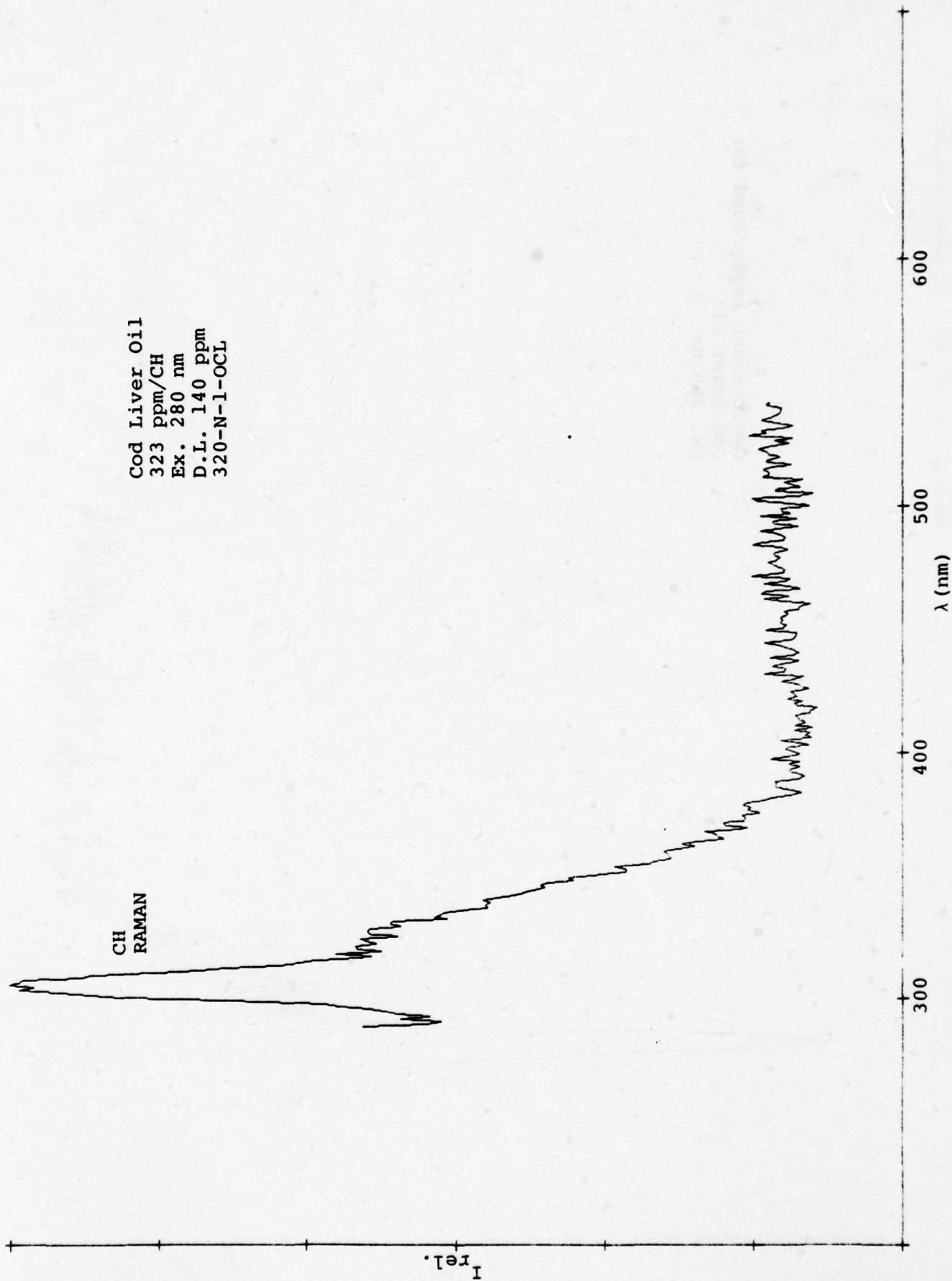
Cod Liver Oil
323 ppm/CH
Ex. 260 nm
D.L. 260 ppm
320-N-1-OCL



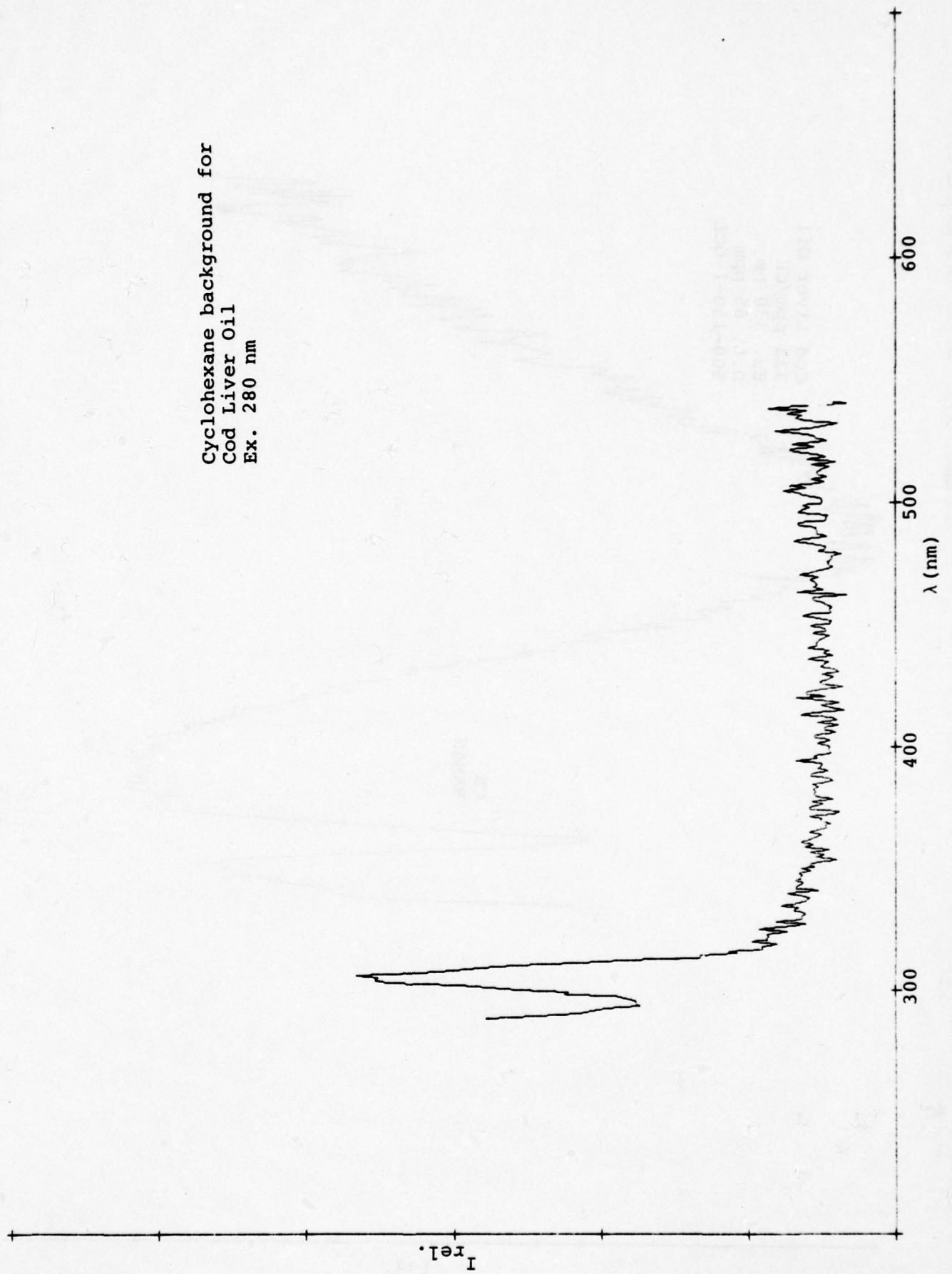
Cyclohexane background for
Cod Liver Oil
Ex. 260 nm



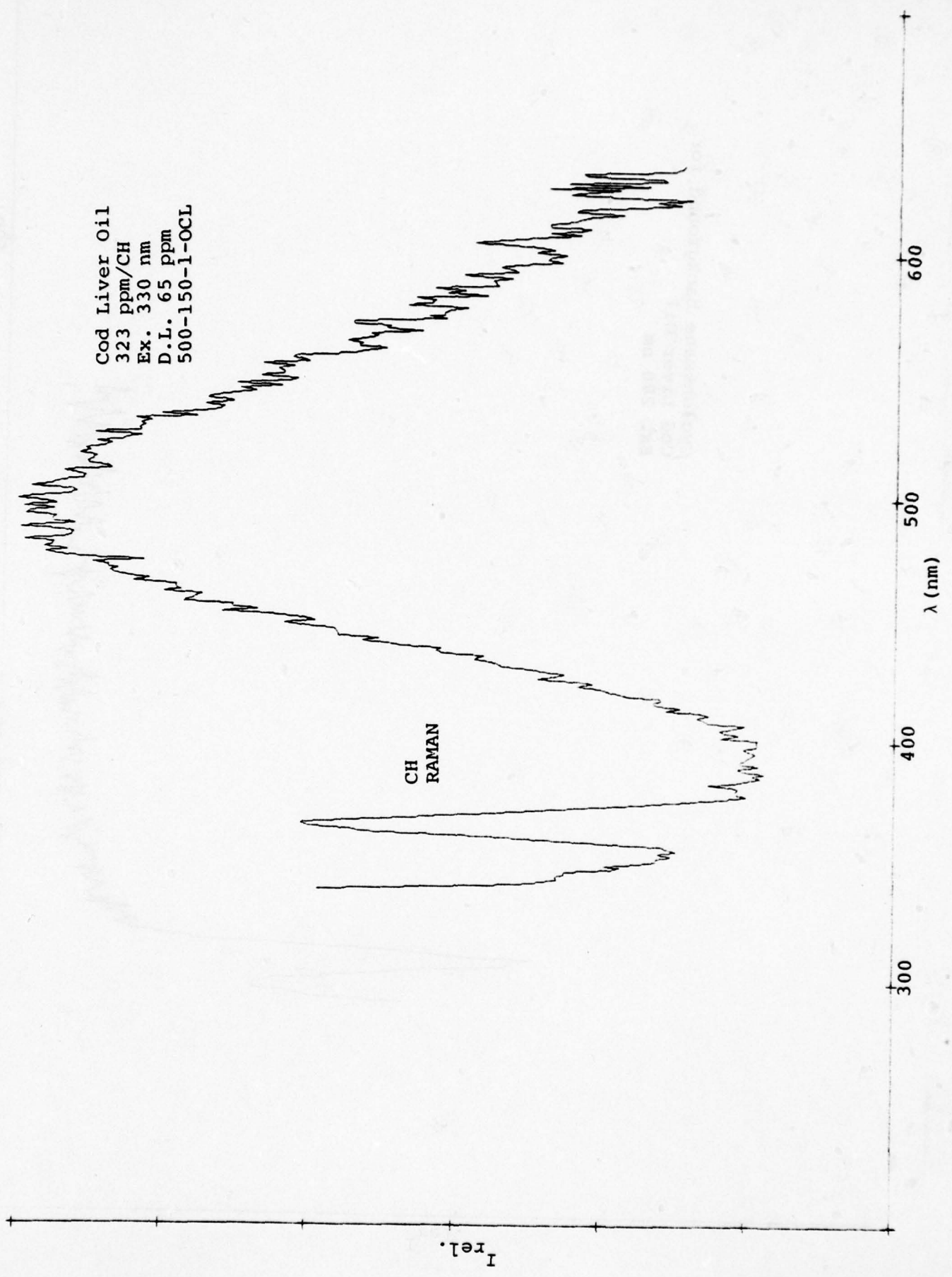
Cod Liver Oil
323 ppm/CH
Ex. 280 nm
D.L. 140 ppm
320-N-1-OCL



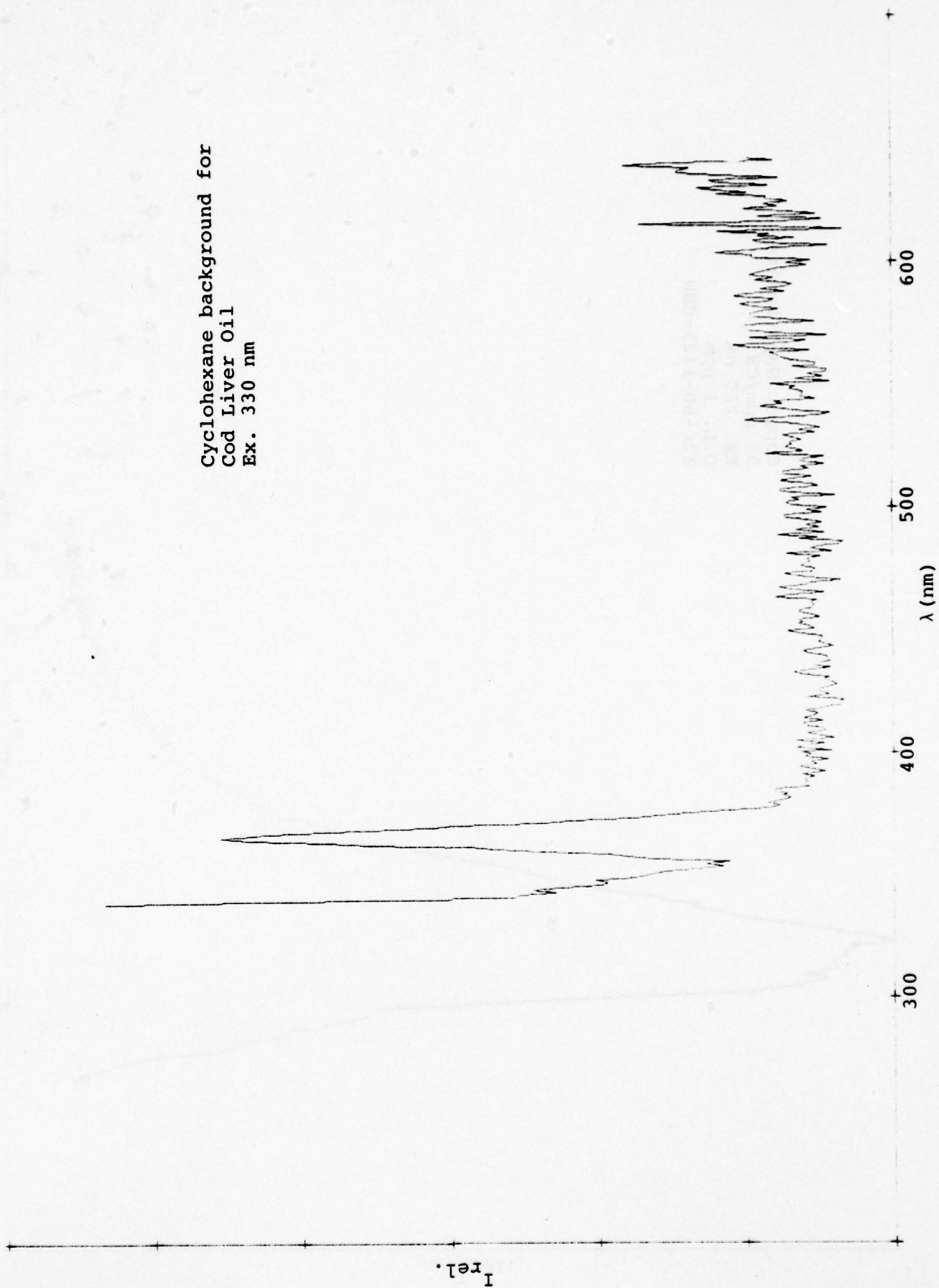
Cyclohexane background for
Cod Liver Oil
Ex. 280 nm



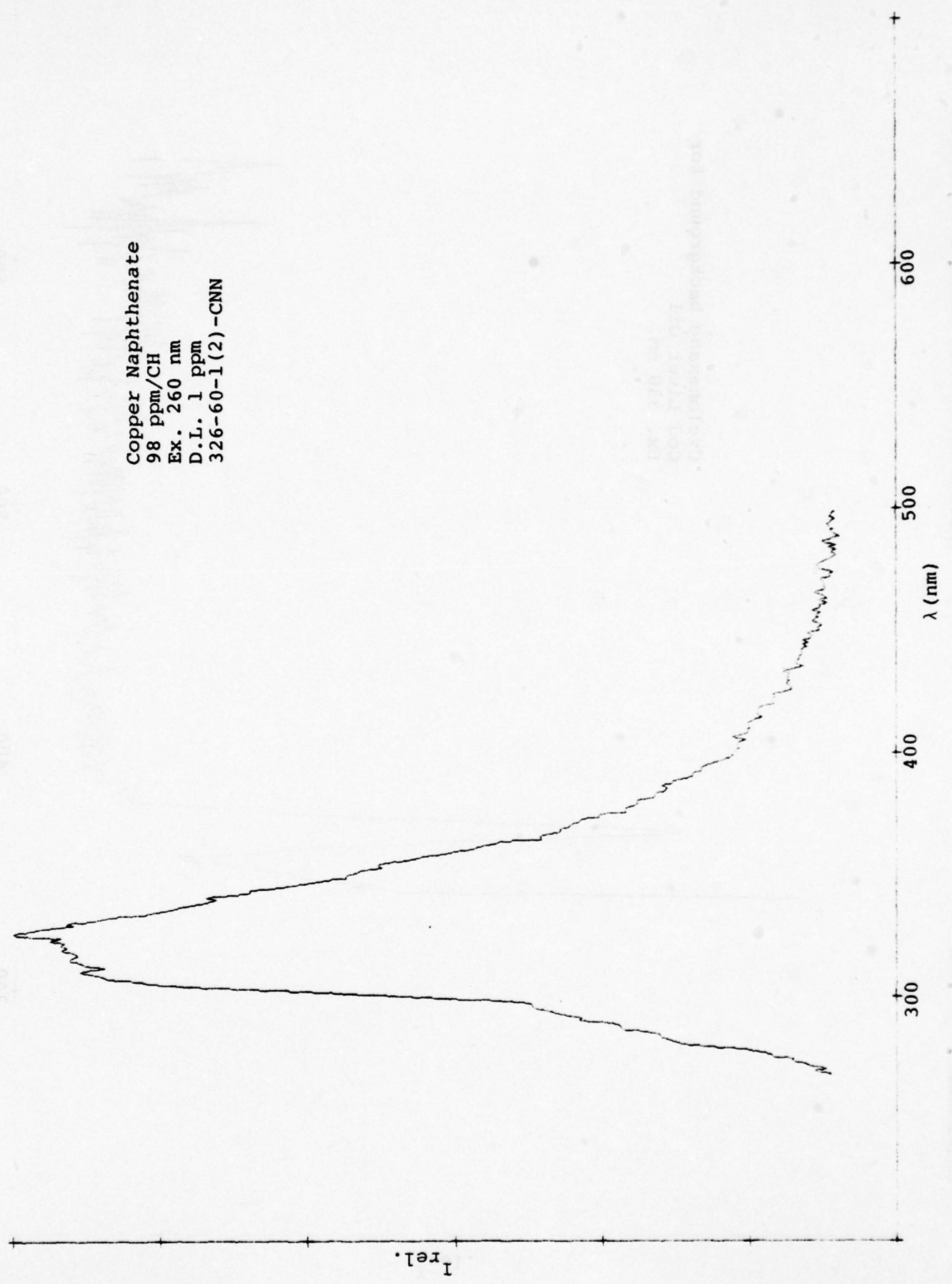
Cod Liver Oil
323 ppm/CH
Ex. 330 nm
D.L. 65 ppm
500-150-1-OCL



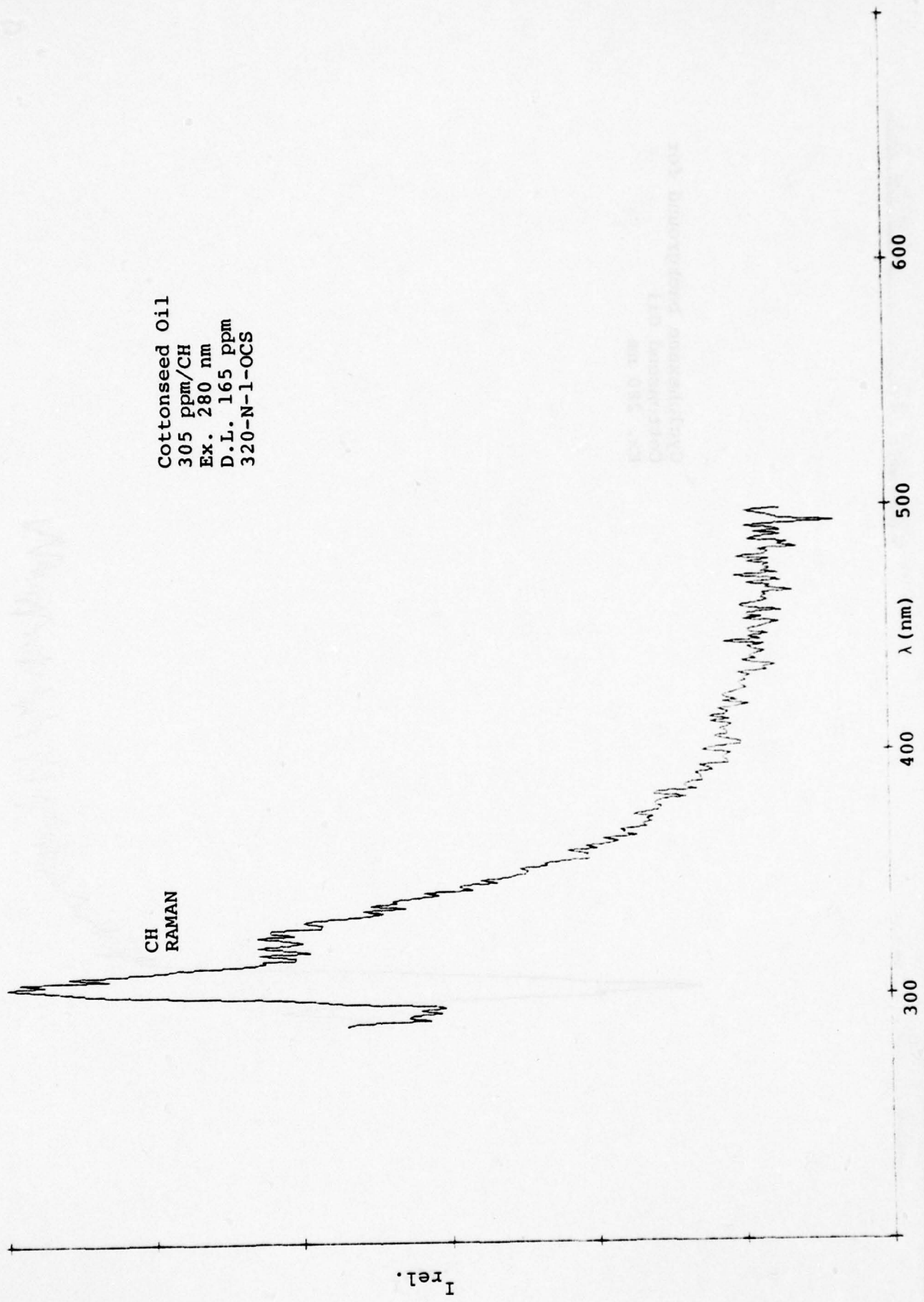
Cyclohexane background for
Cod Liver Oil
Ex. 330 nm



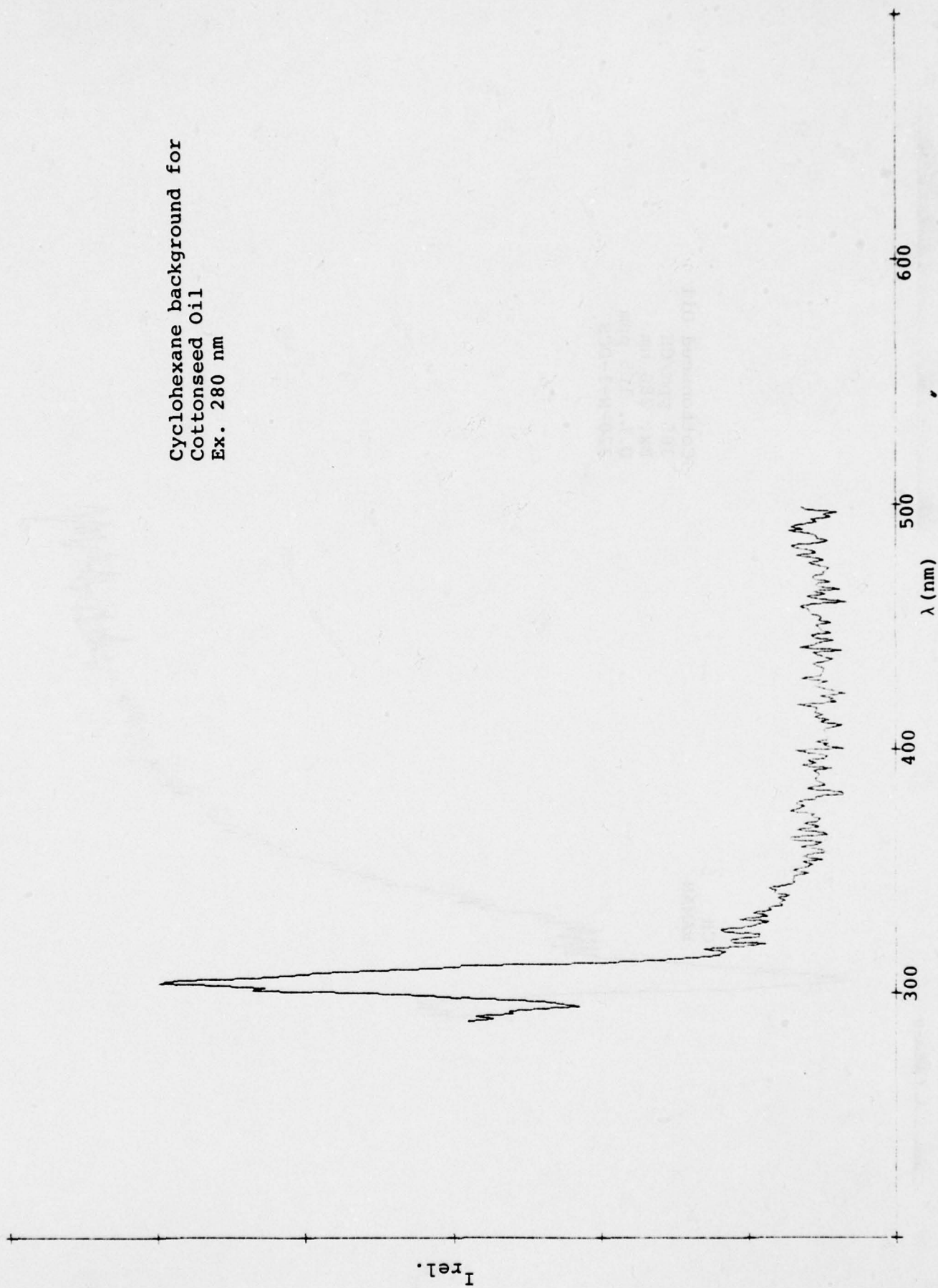
Copper Naphthenate
98 ppm/CH
Ex. 260 nm
D.L. 1 ppm
326-60-1(2)-CNN



Cottonseed Oil
305 ppm/CH
Ex. 280 nm
D.L. 165 ppm
320-N-1-OCS

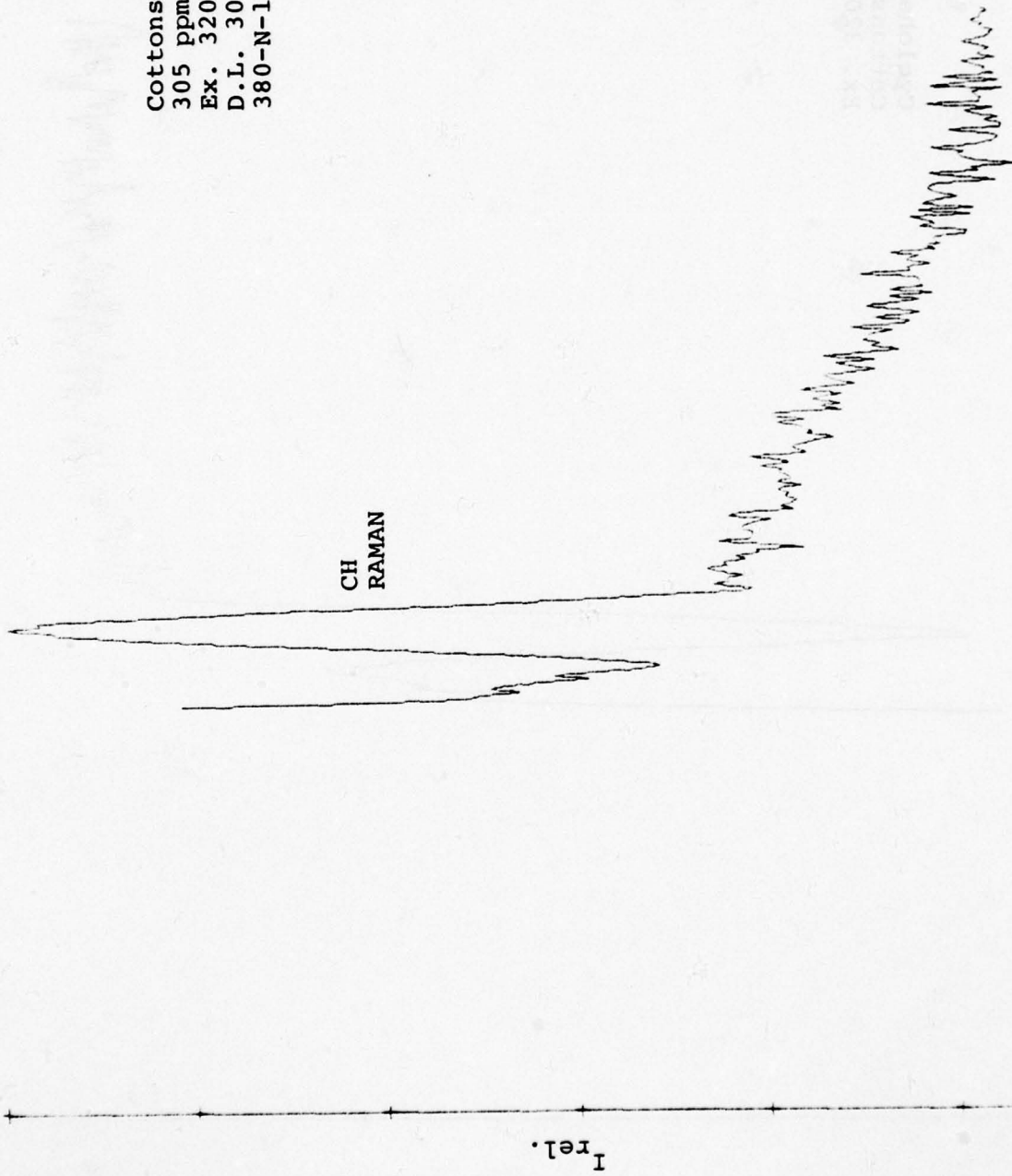


Cyclohexane background for
Cottonseed Oil
Ex. 280 nm

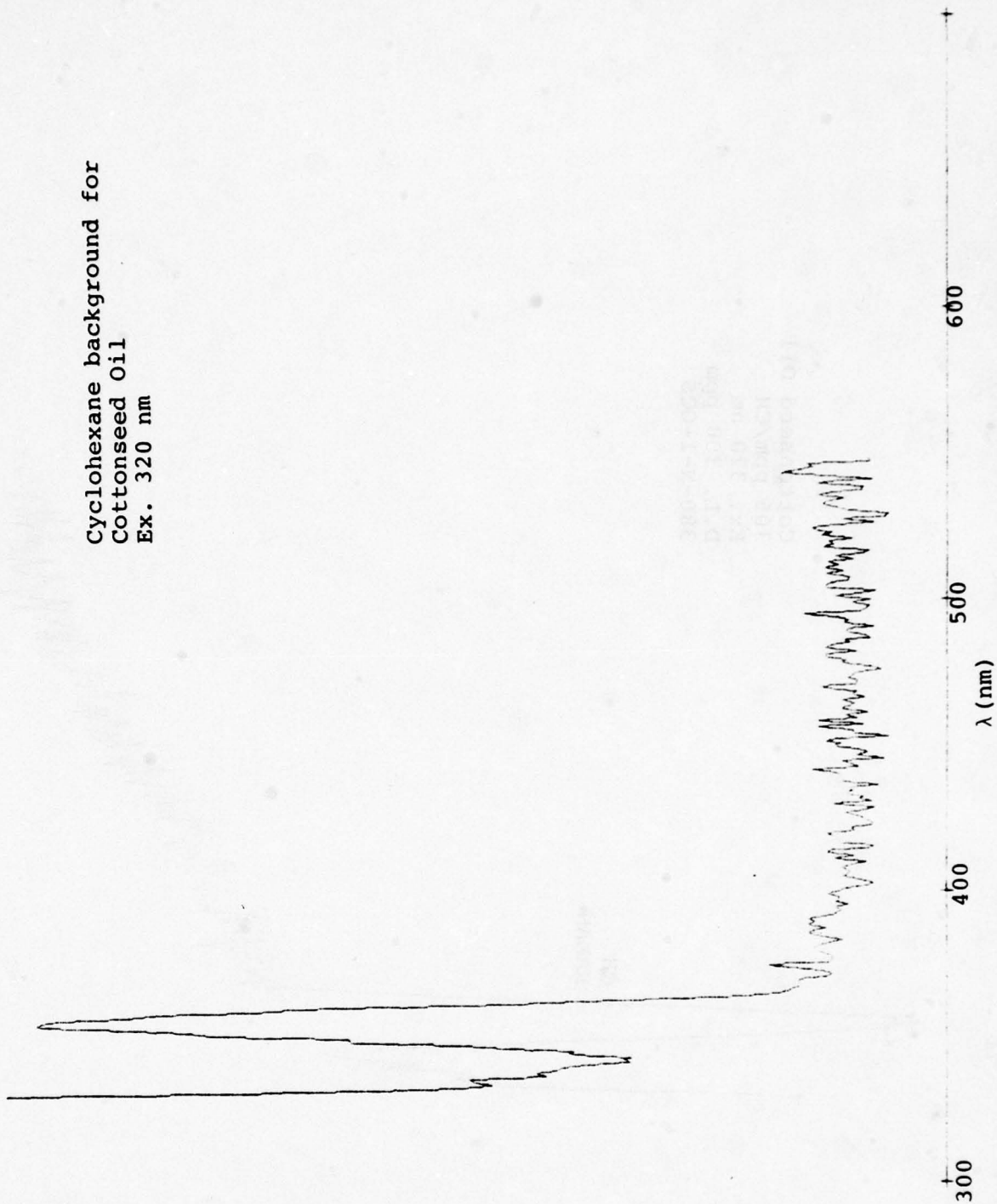


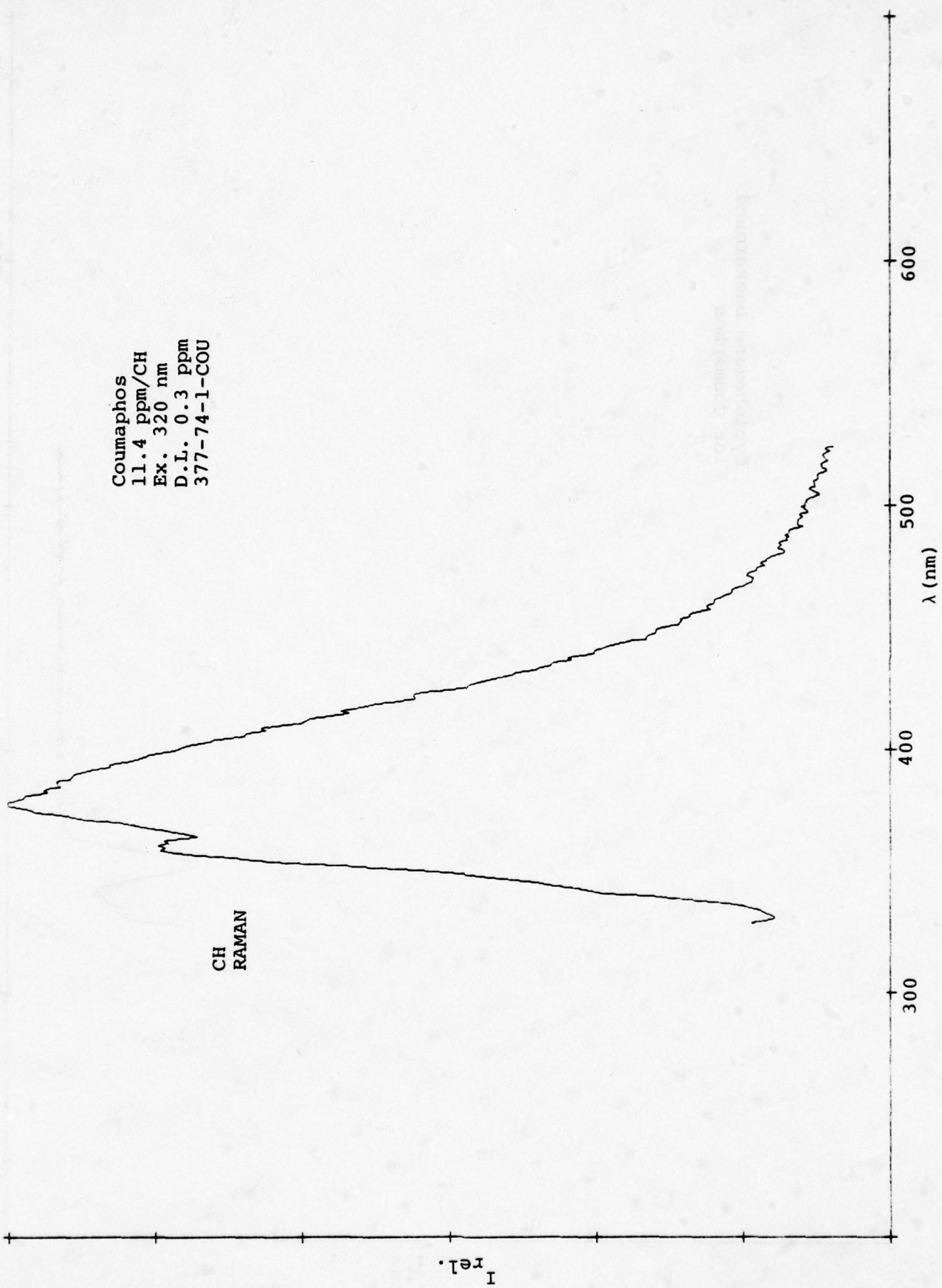
Cottonseed Oil
305 ppm/CH
Ex. 320 nm
D.L. 300 ppm
380-N-1-OCS

CH
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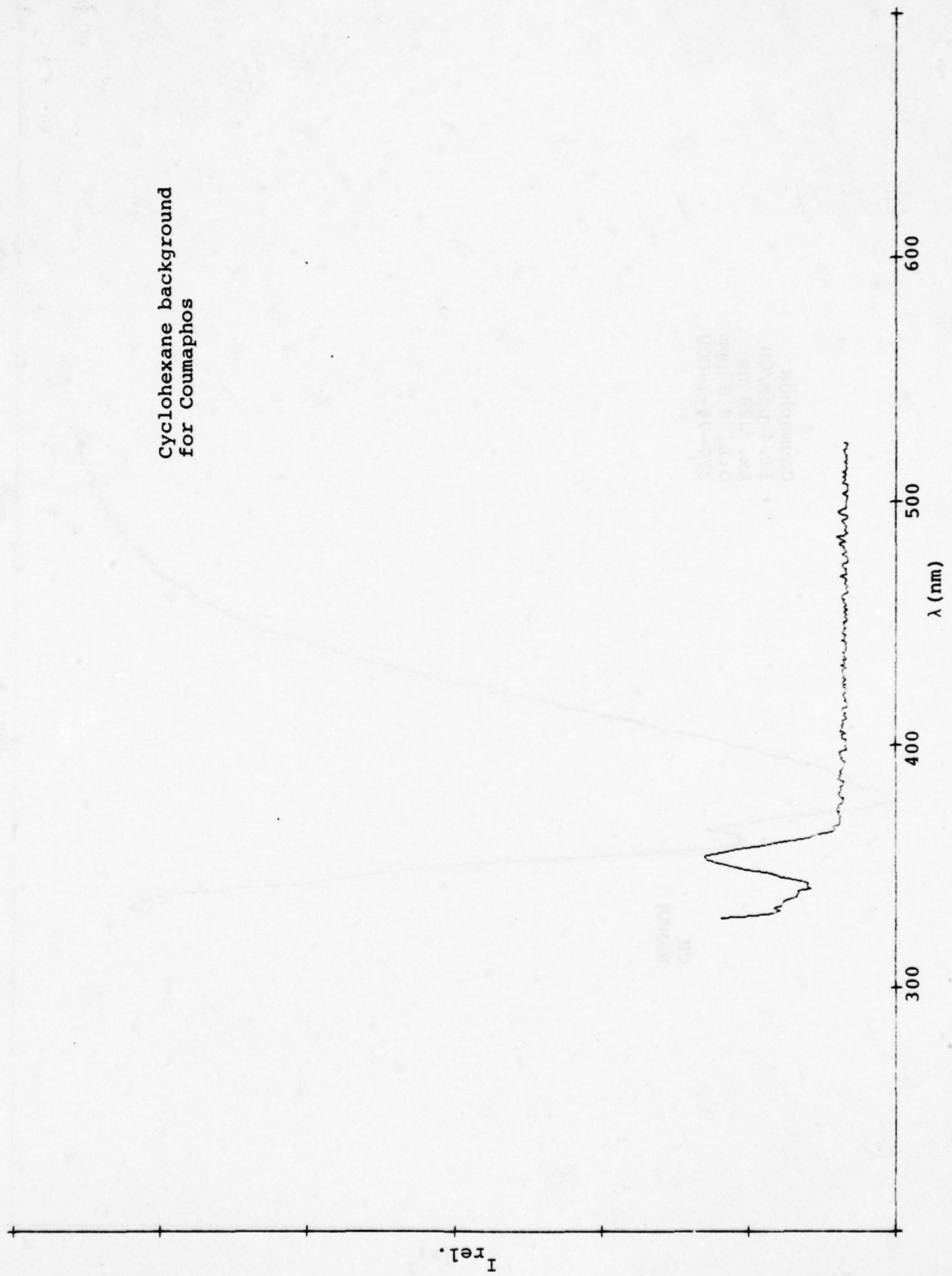


Cyclohexane background for
Cottonseed Oil
Ex. 320 nm

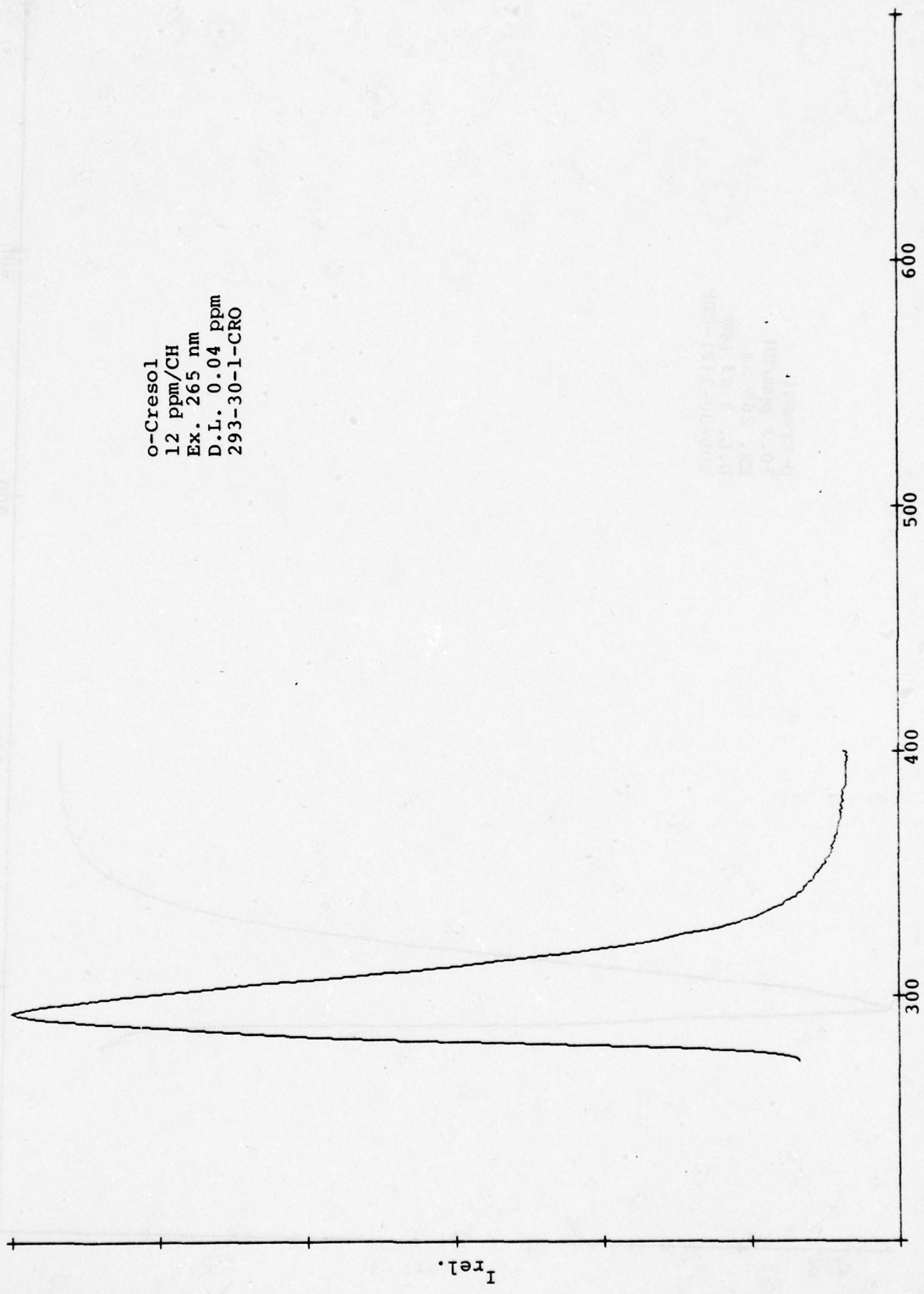




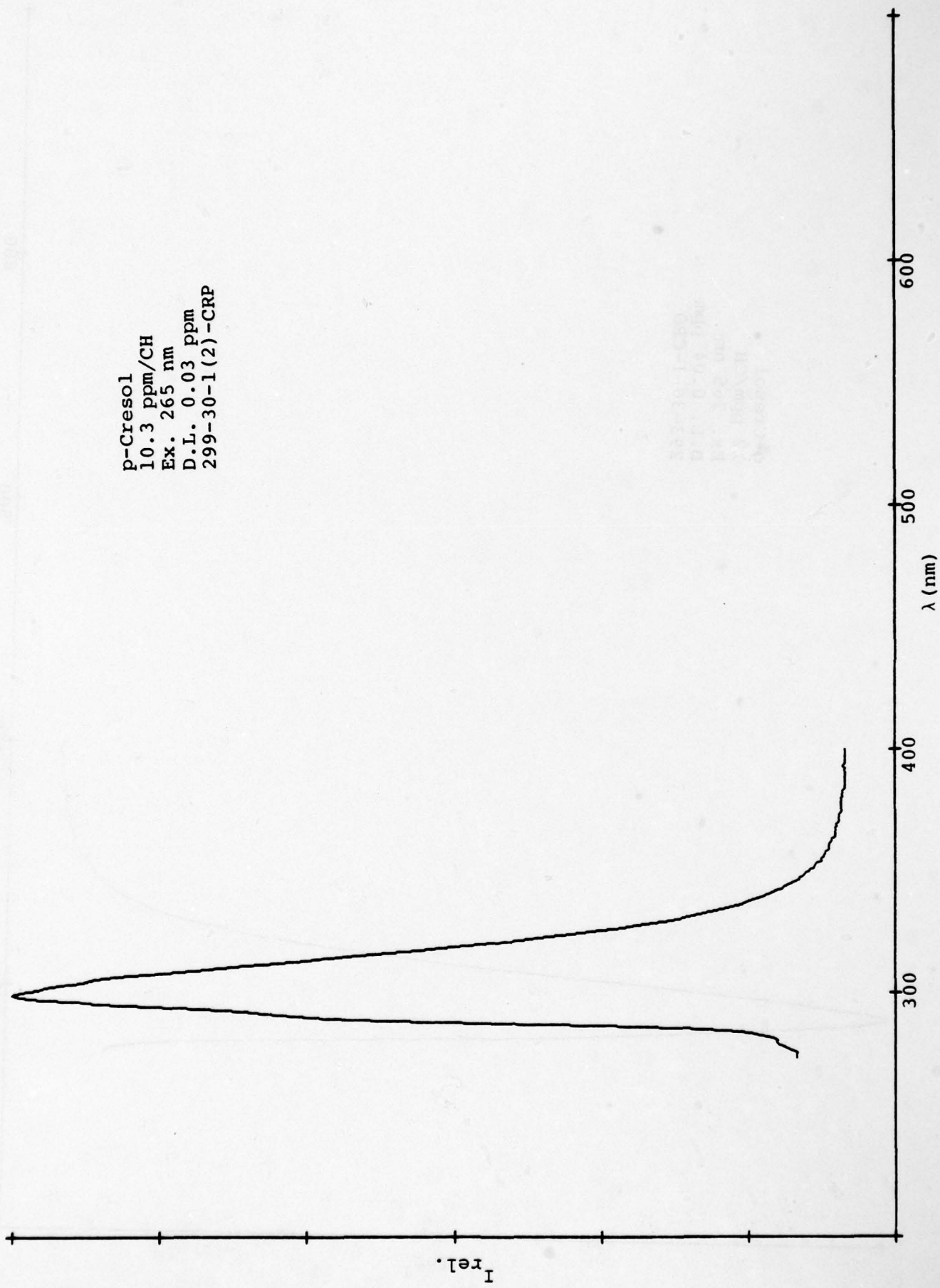
Cyclohexane background
for Coumaphos



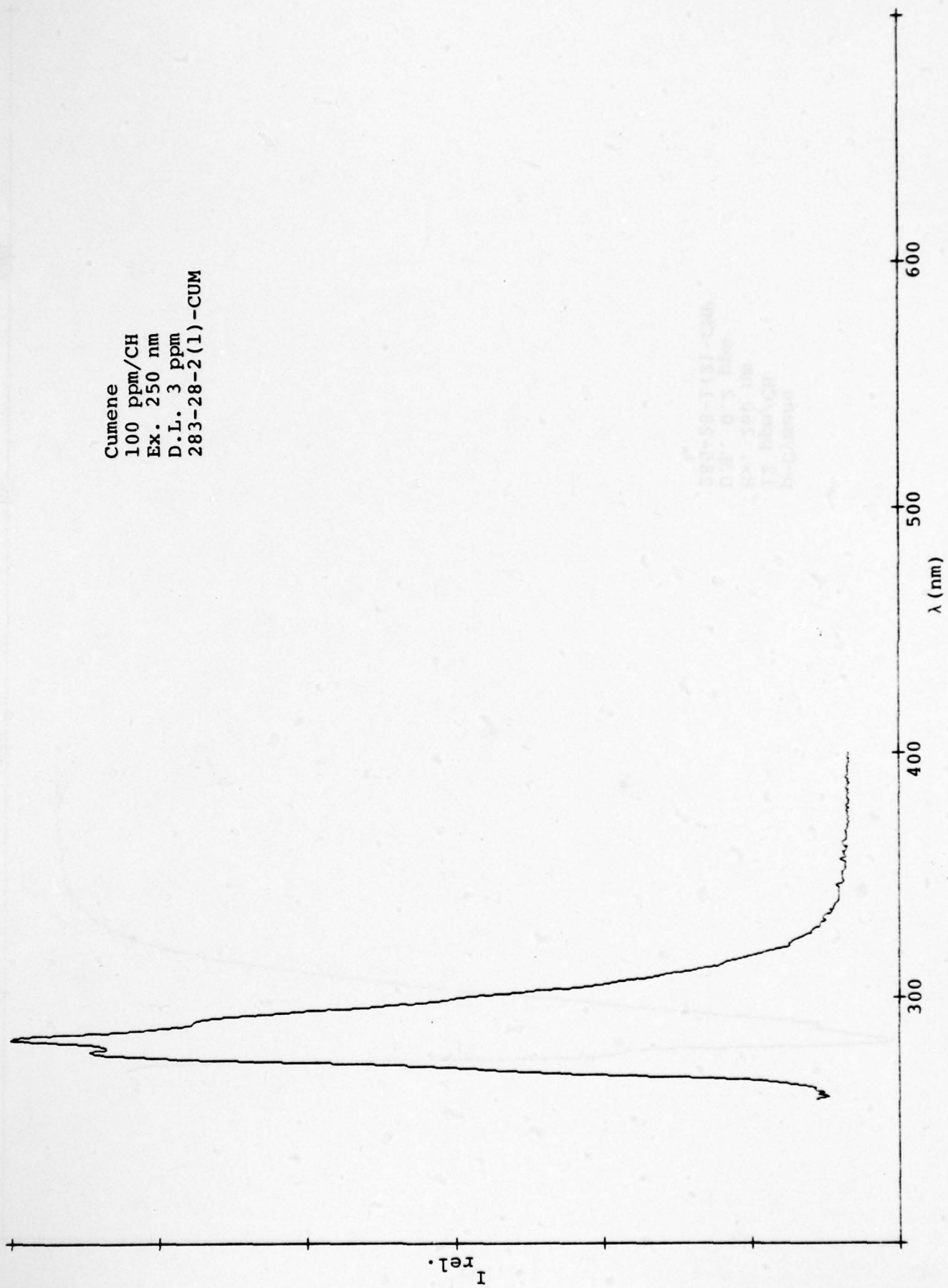
o-Cresol
12 ppm/CH
Ex. 265 nm
D.L. 0.04 ppm
293-30-1-CRO



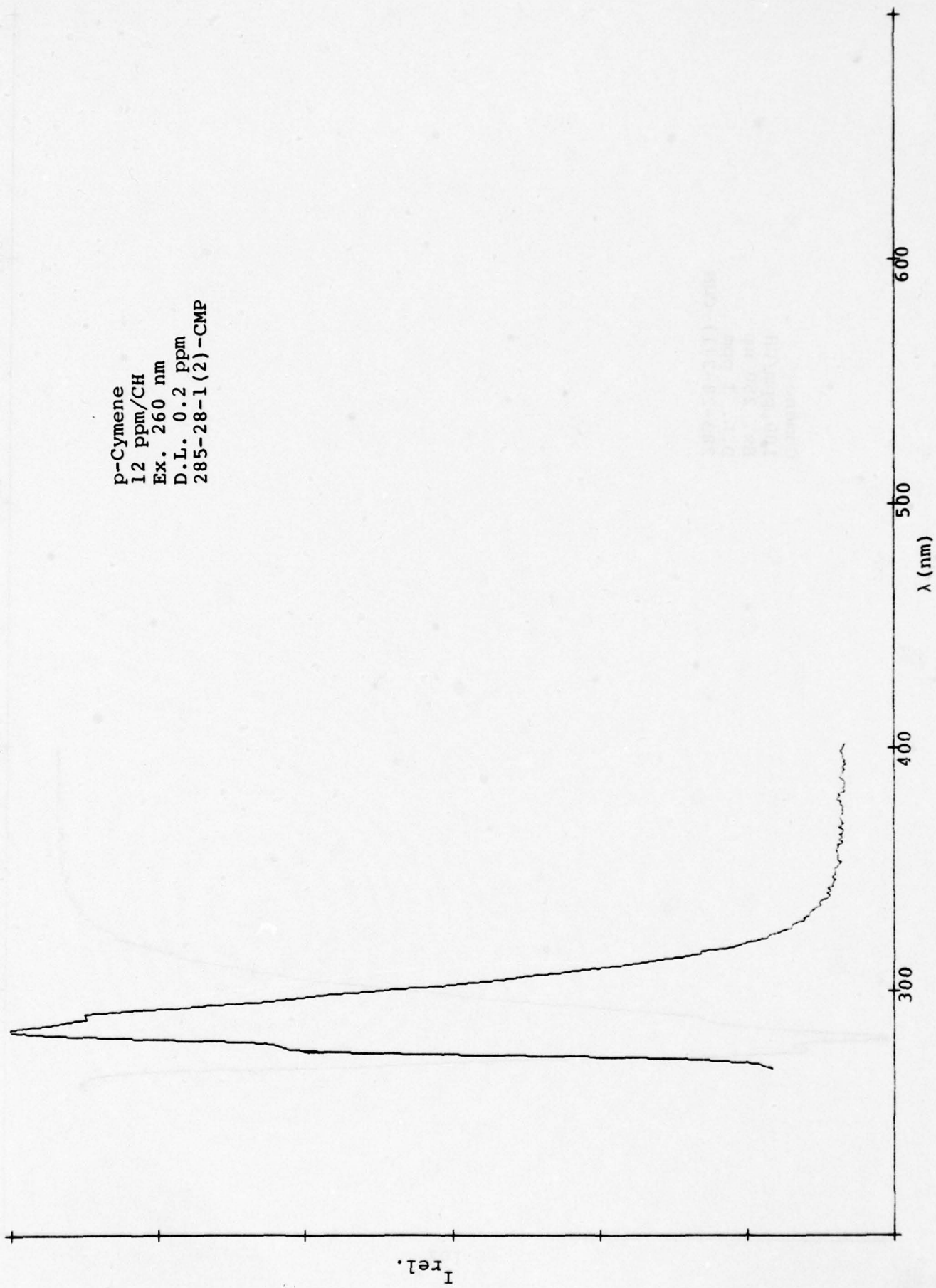
p-Cresol
10.3 ppm/CH
Ex. 265 nm
D.L. 0.03 ppm
299-30-1(2)-CRP



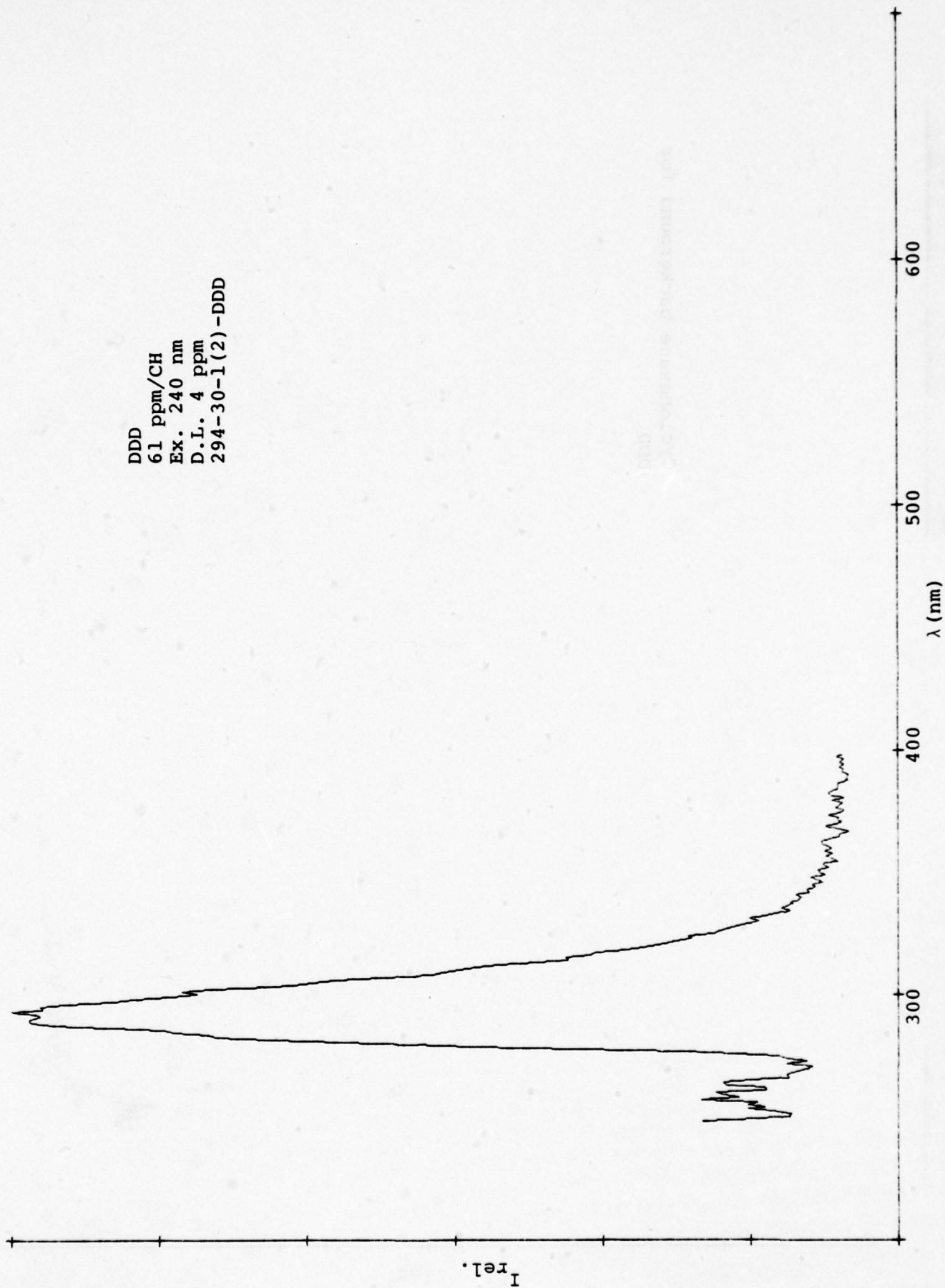
Cumene
100 ppm/CH
Ex. 250 nm
D.L. 3 ppm
283-28-2(1)-CUM



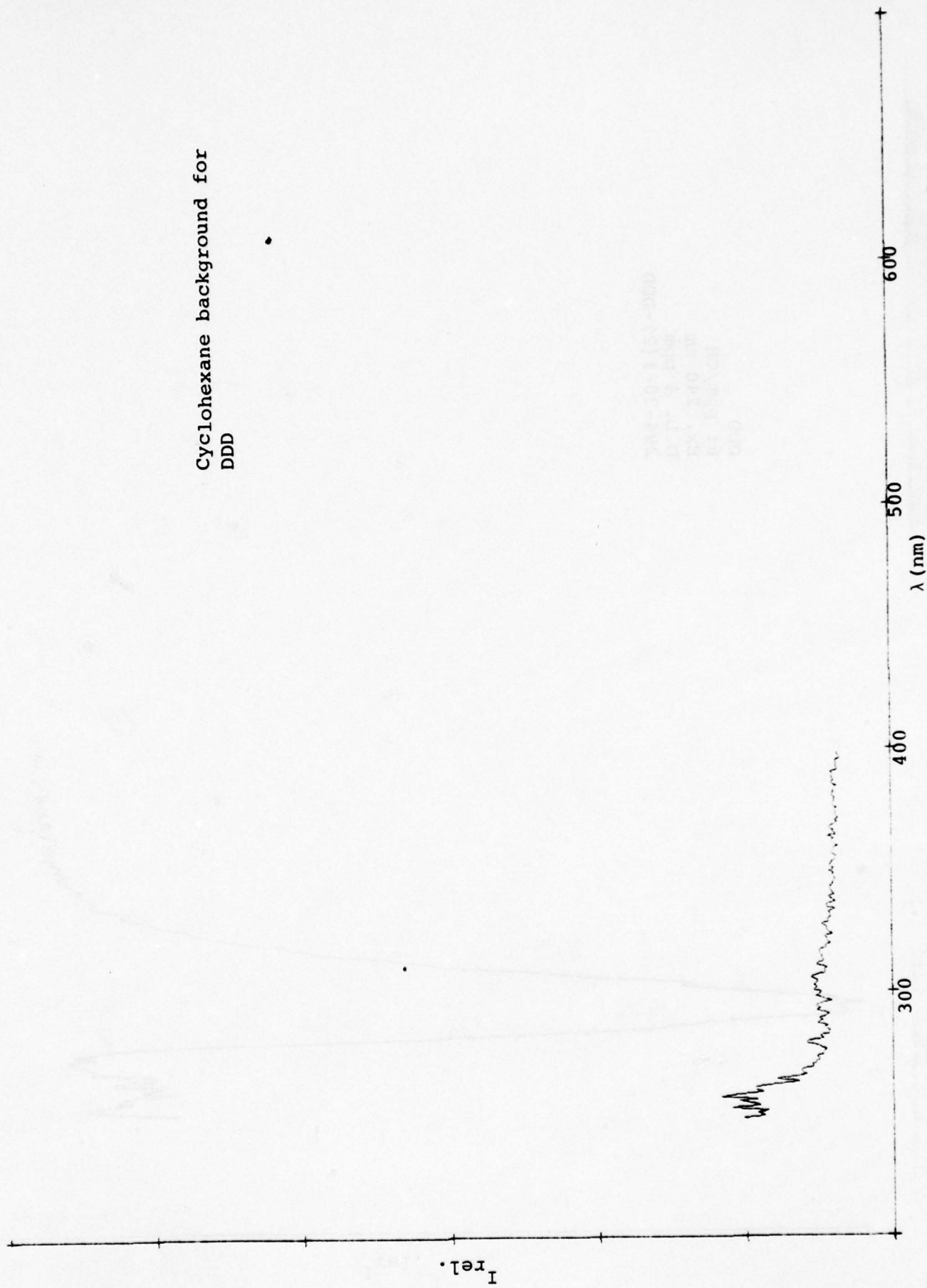
p-Cymene
12 ppm/CH
Ex. 260 nm
D.L. 0.2 ppm
285-28-1(2)-CMP



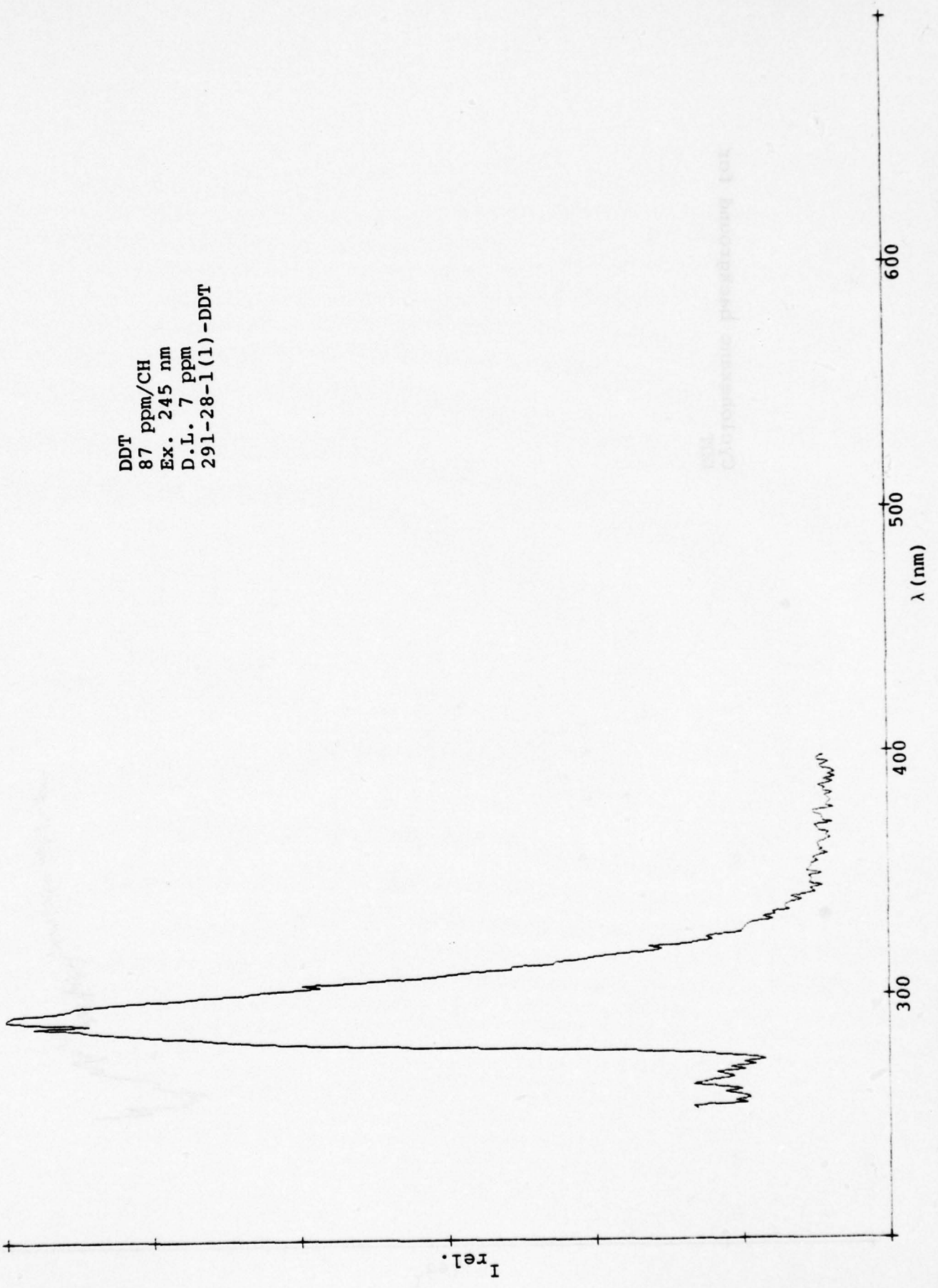
DDD
61 ppm/CH
Ex. 240 nm
D.L. 4 ppm
294-30-1(2)-DDD



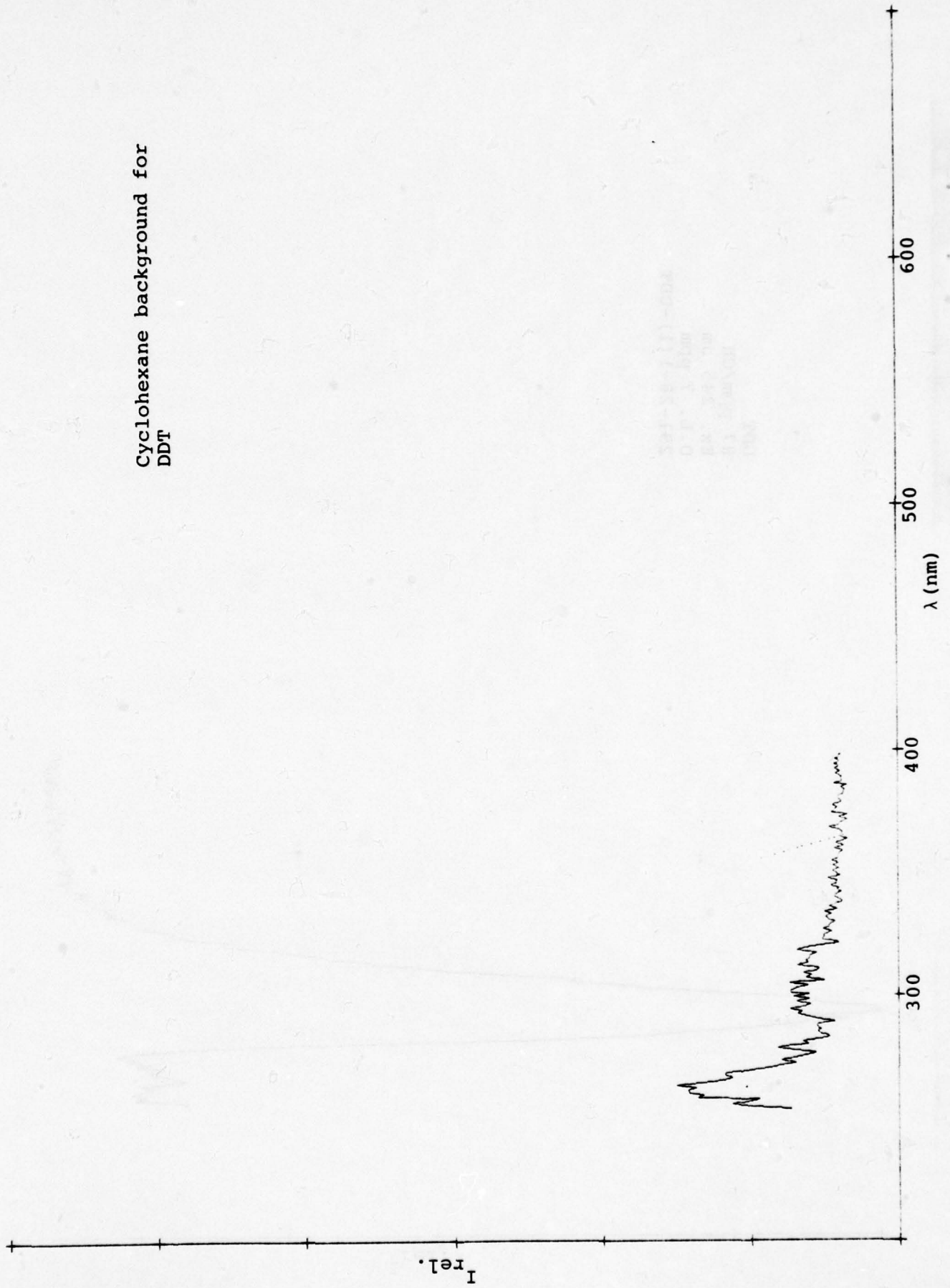
Cyclohexane background for
DDD



DDT
87 ppm/CH
Ex. 245 nm
D.L. 7 ppm
291-28-1(1)-DDT

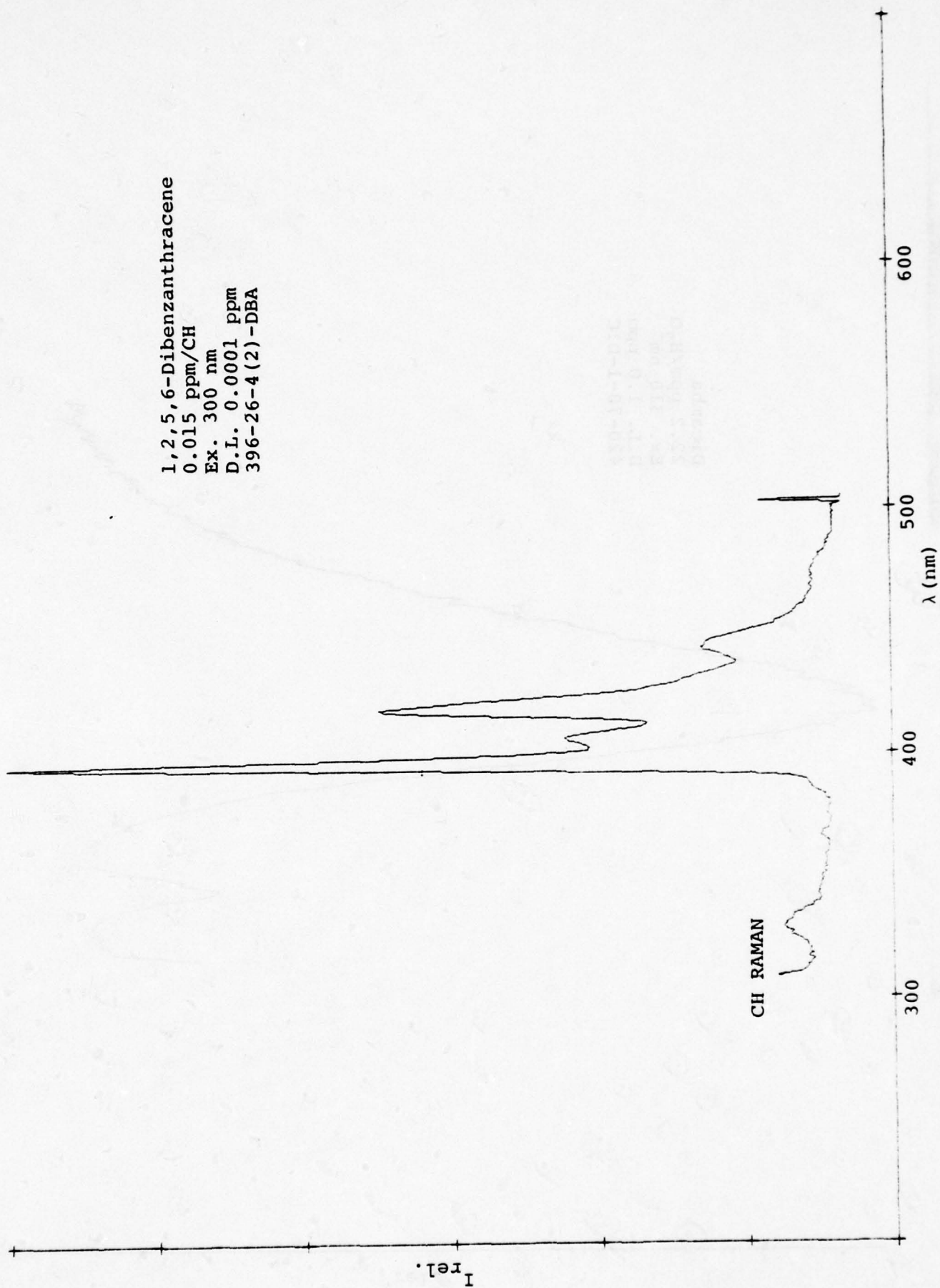


Cyclohexane background for
DDT

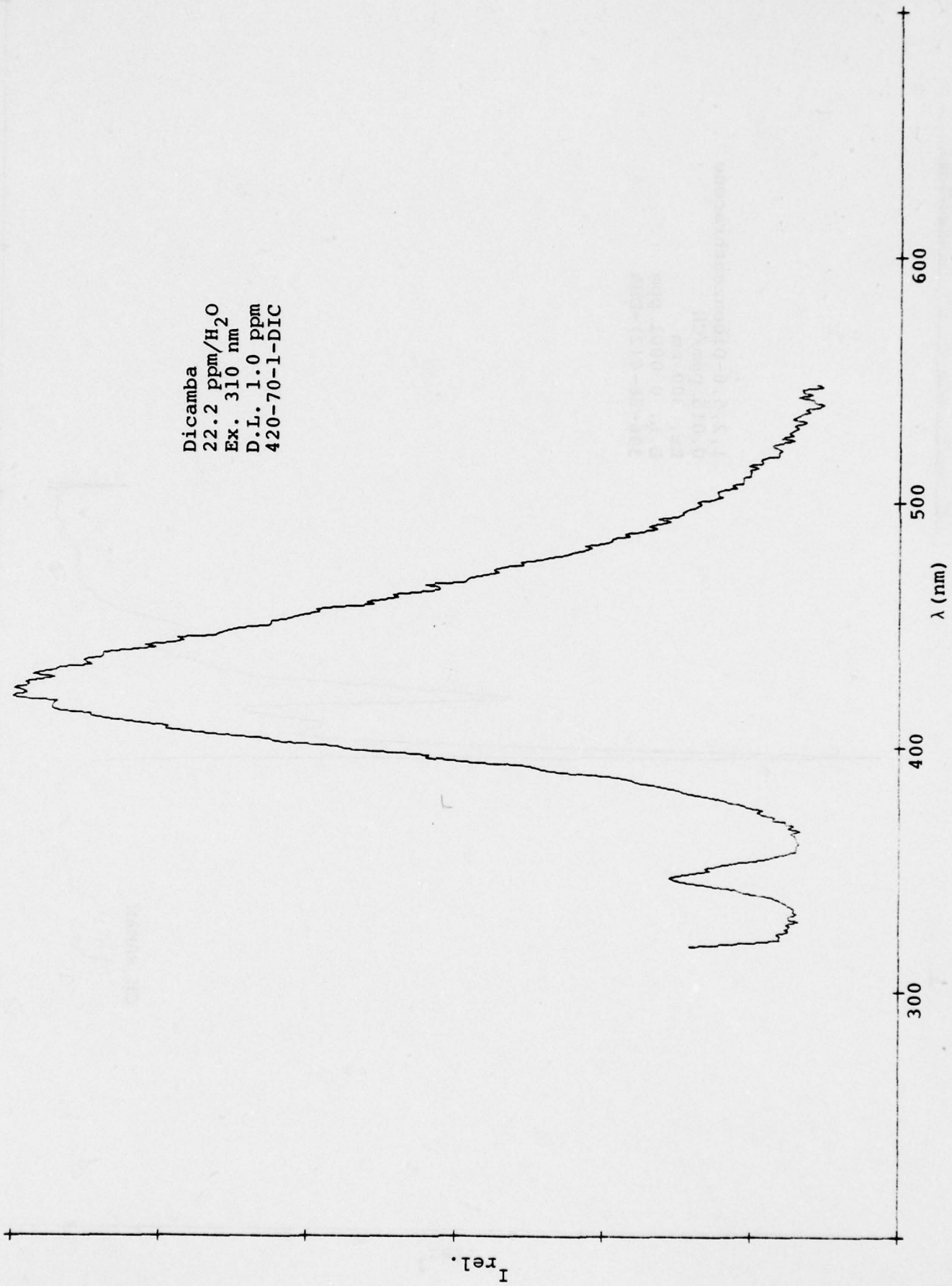


300-350 (17) - 2004
O.P. J. 10/10
EX. 340, 710
P. 10/10/10
10/10

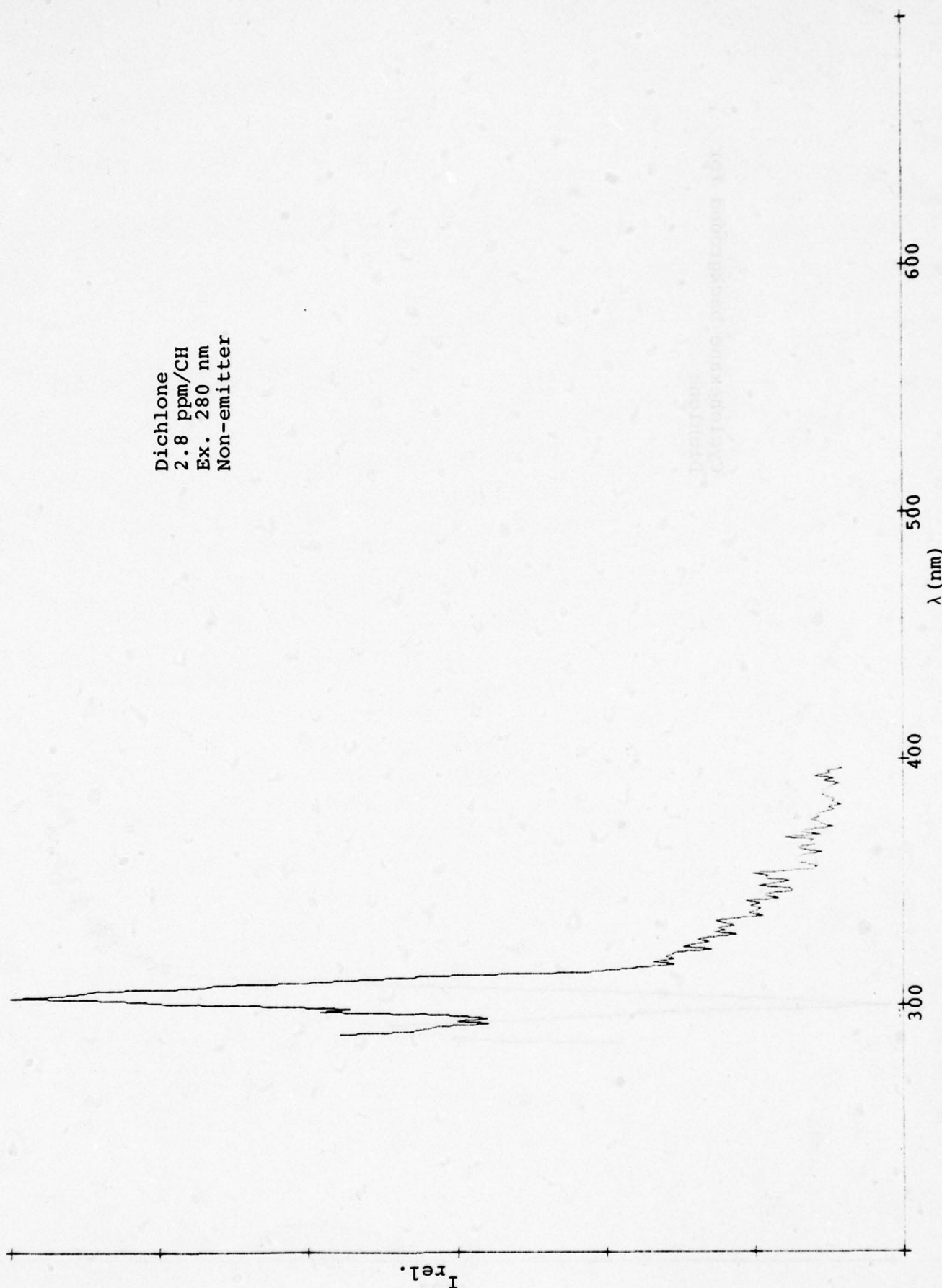
1,2,5,6-Dibenzanthracene
0.015 ppm/CH
Ex. 300 nm
D.L. 0.0001 ppm
396-26-4(2)-DBA



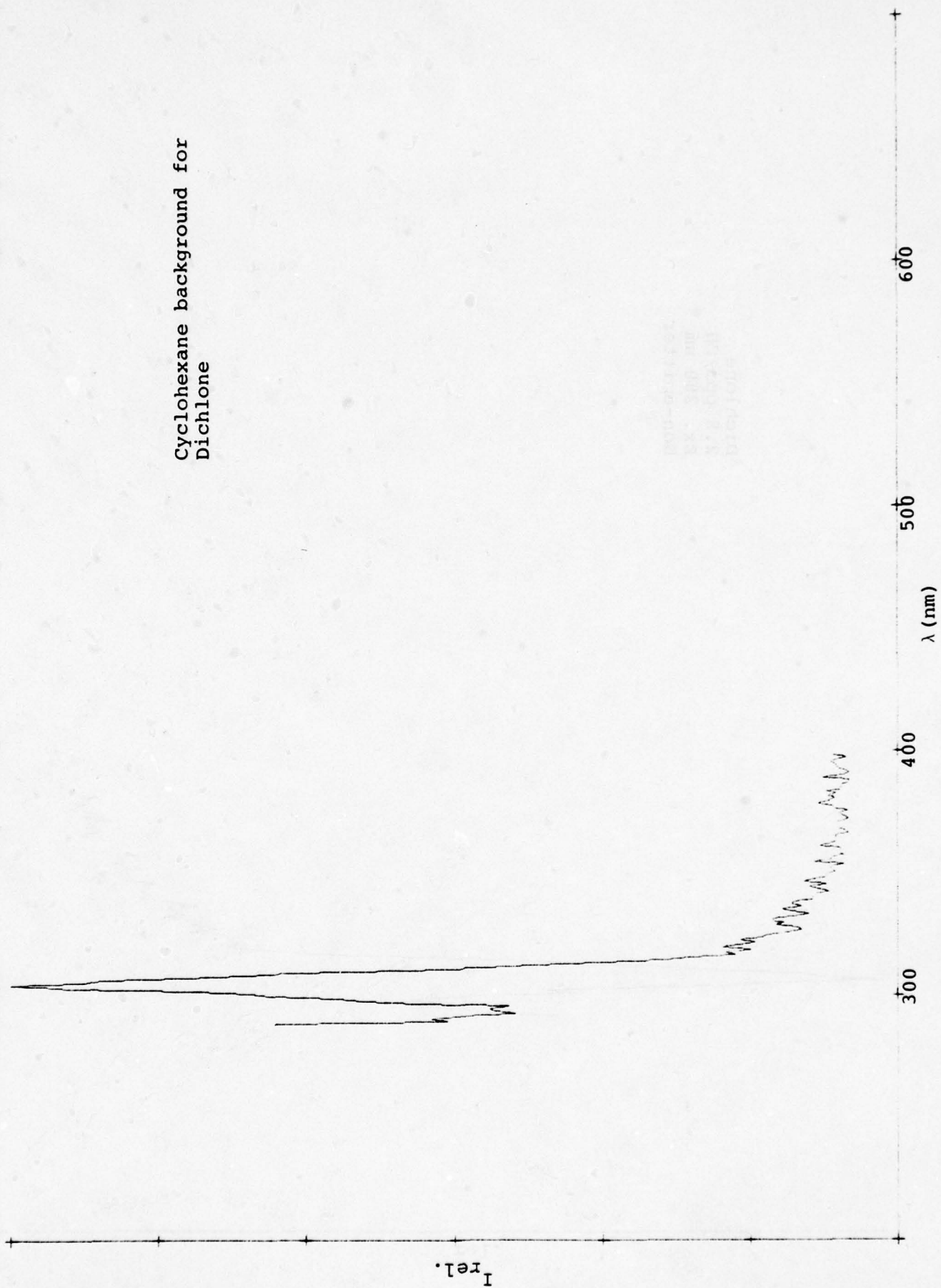
Dicamba
22.2 ppm/H₂O
Ex. 310 nm
D.L. 1.0 ppm
420-70-1-DIC



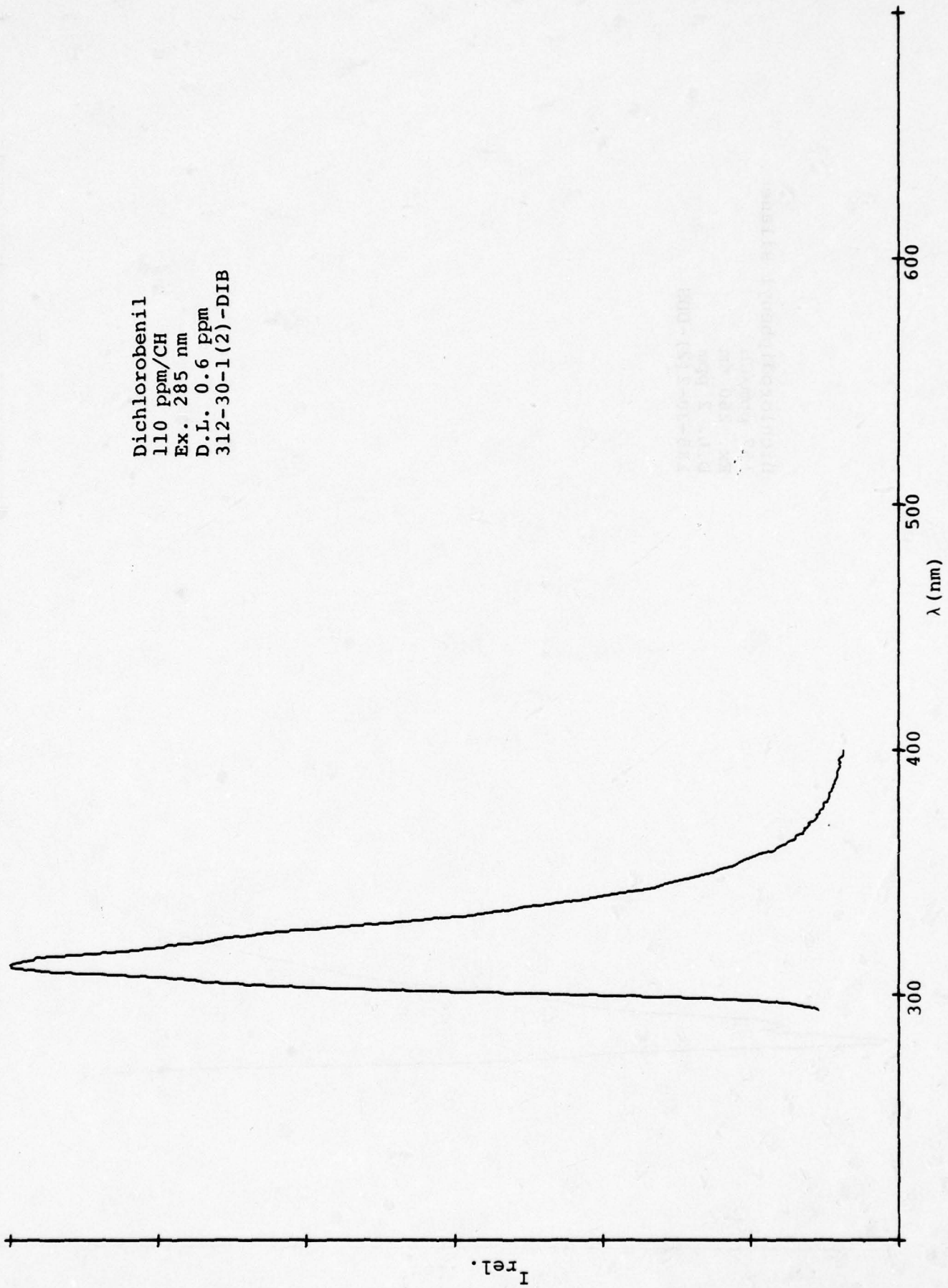
Dichlone
2.8 ppm/CH
Ex. 280 nm
Non-emitter



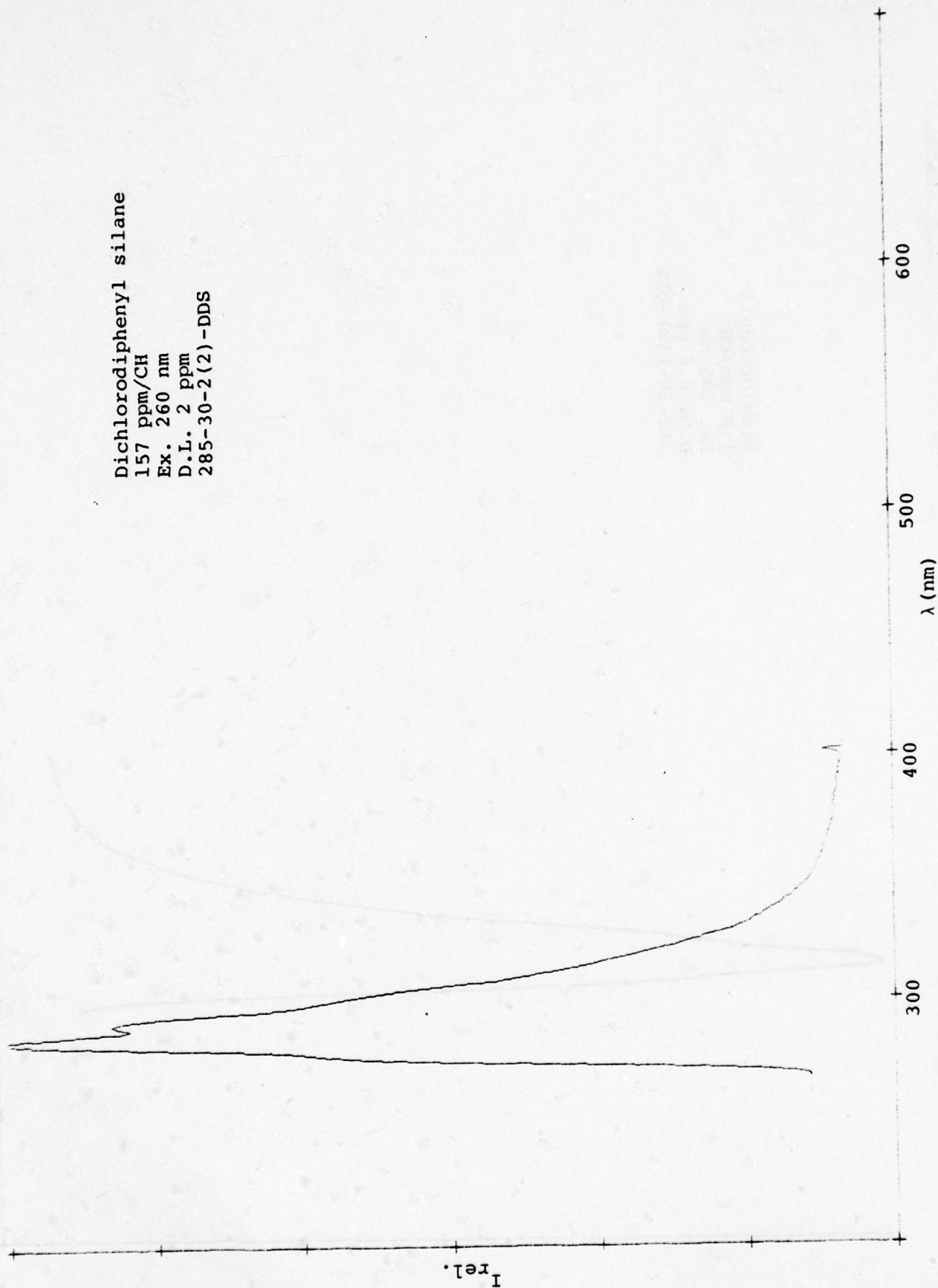
Cyclohexane background for
Dichlone



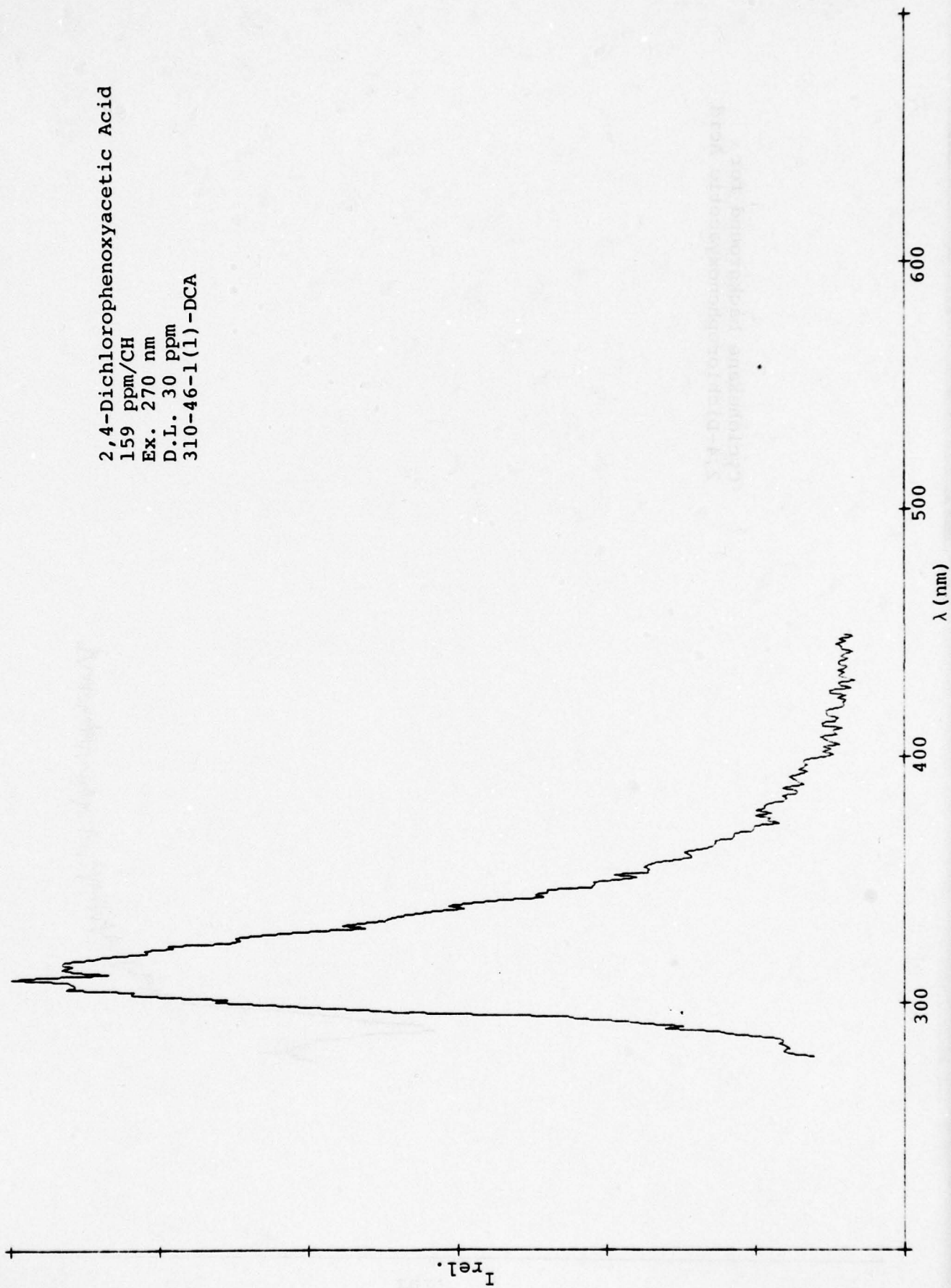
Dichlorobenil
110 ppm/CH
Ex. 285 nm
D.L. 0.6 ppm
312-30-1 (2) -DIB



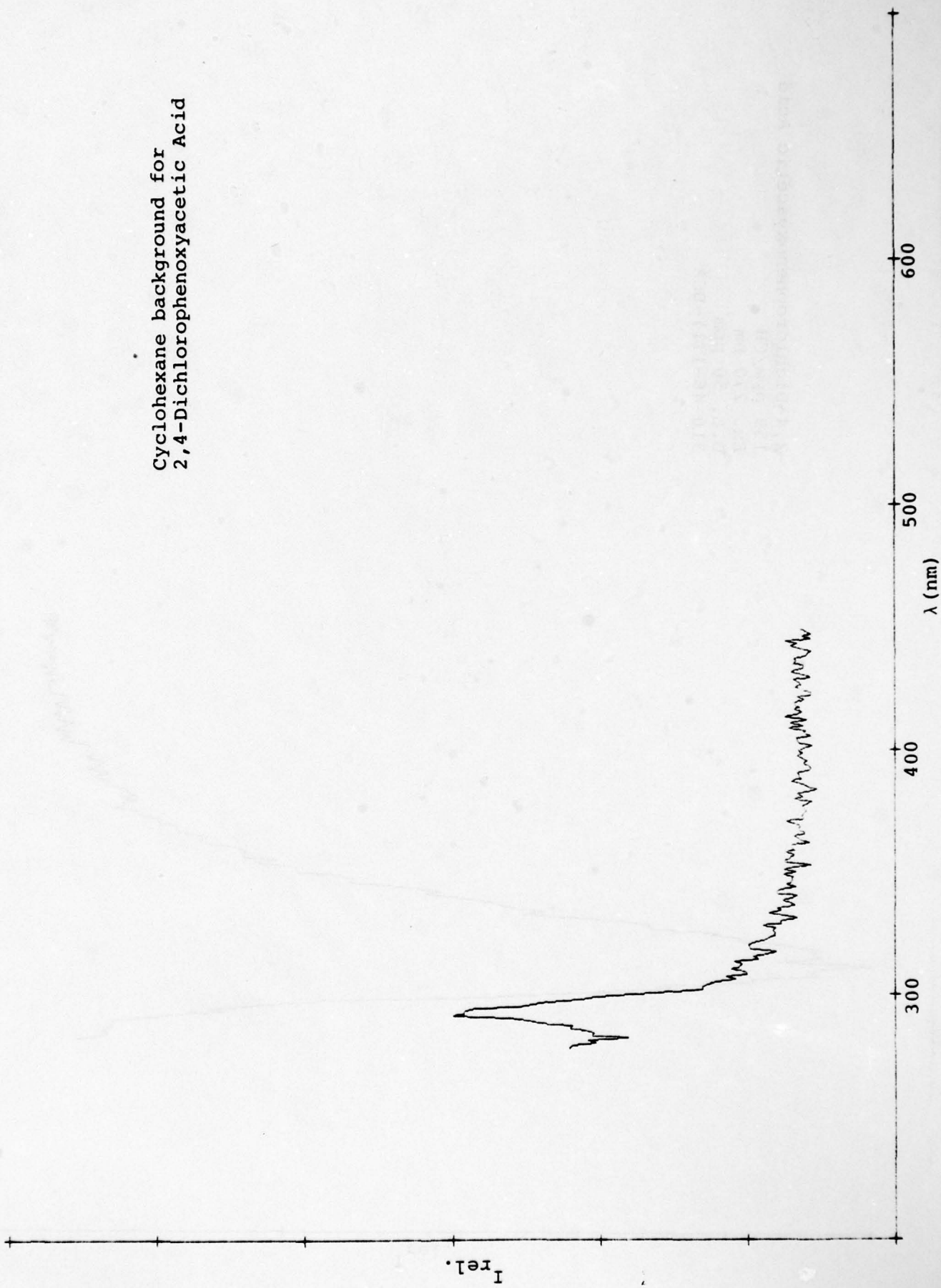
Dichlorodiphenyl silane
157 ppm/CH
Ex. 260 nm
D.L. 2 ppm
285-30-2(2)-DDS



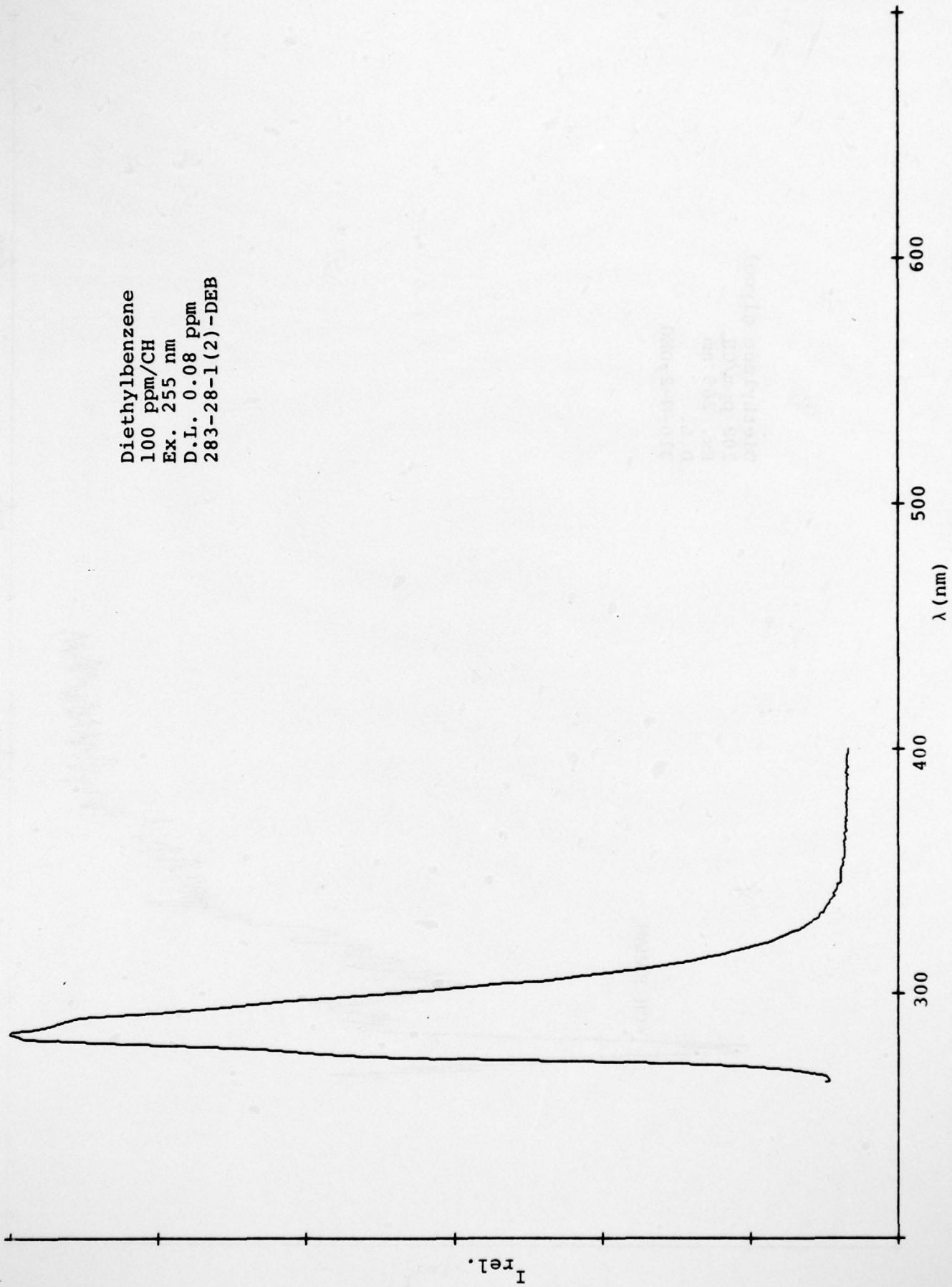
2,4-Dichlorophenoxyacetic Acid
159 ppm/CH
Ex. 270 nm
D.L. 30 ppm
310-46-1(1)-DCA



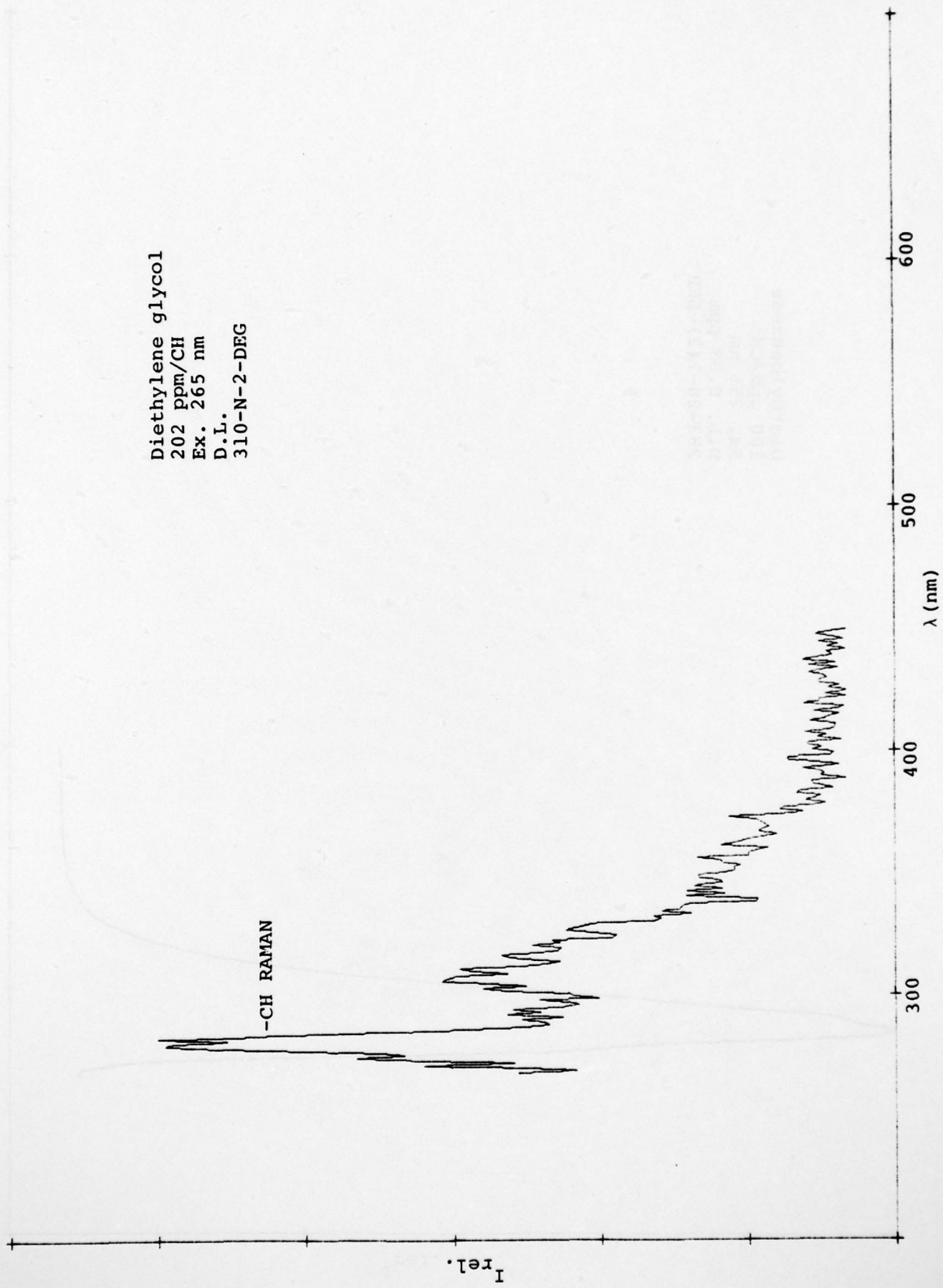
Cyclohexane background for
2,4-Dichlorophenoxyacetic Acid



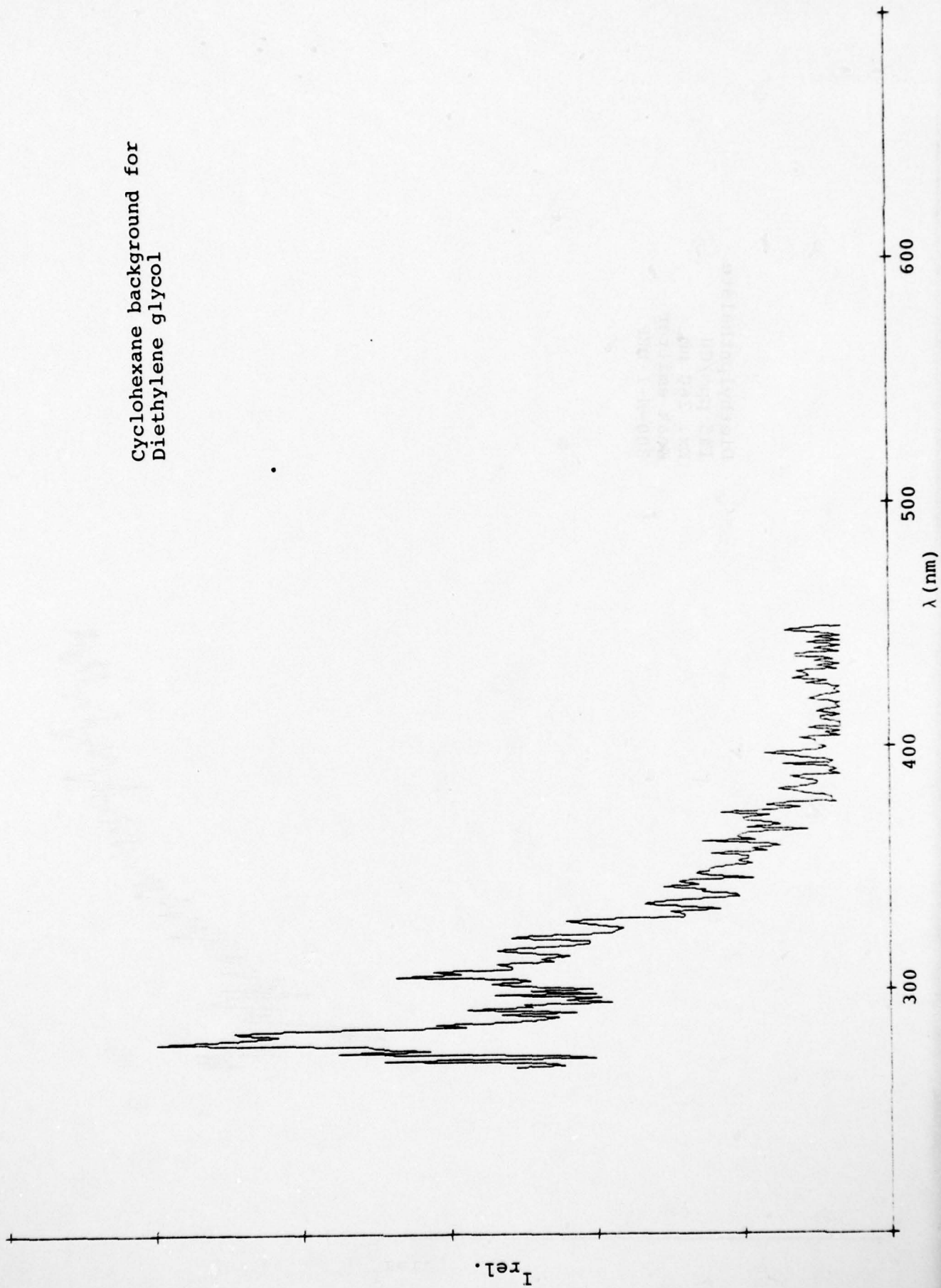
Diethylbenzene
100 ppm/CH
Ex. 255 nm
D.L. 0.08 ppm
283-28-1(2)-DEB



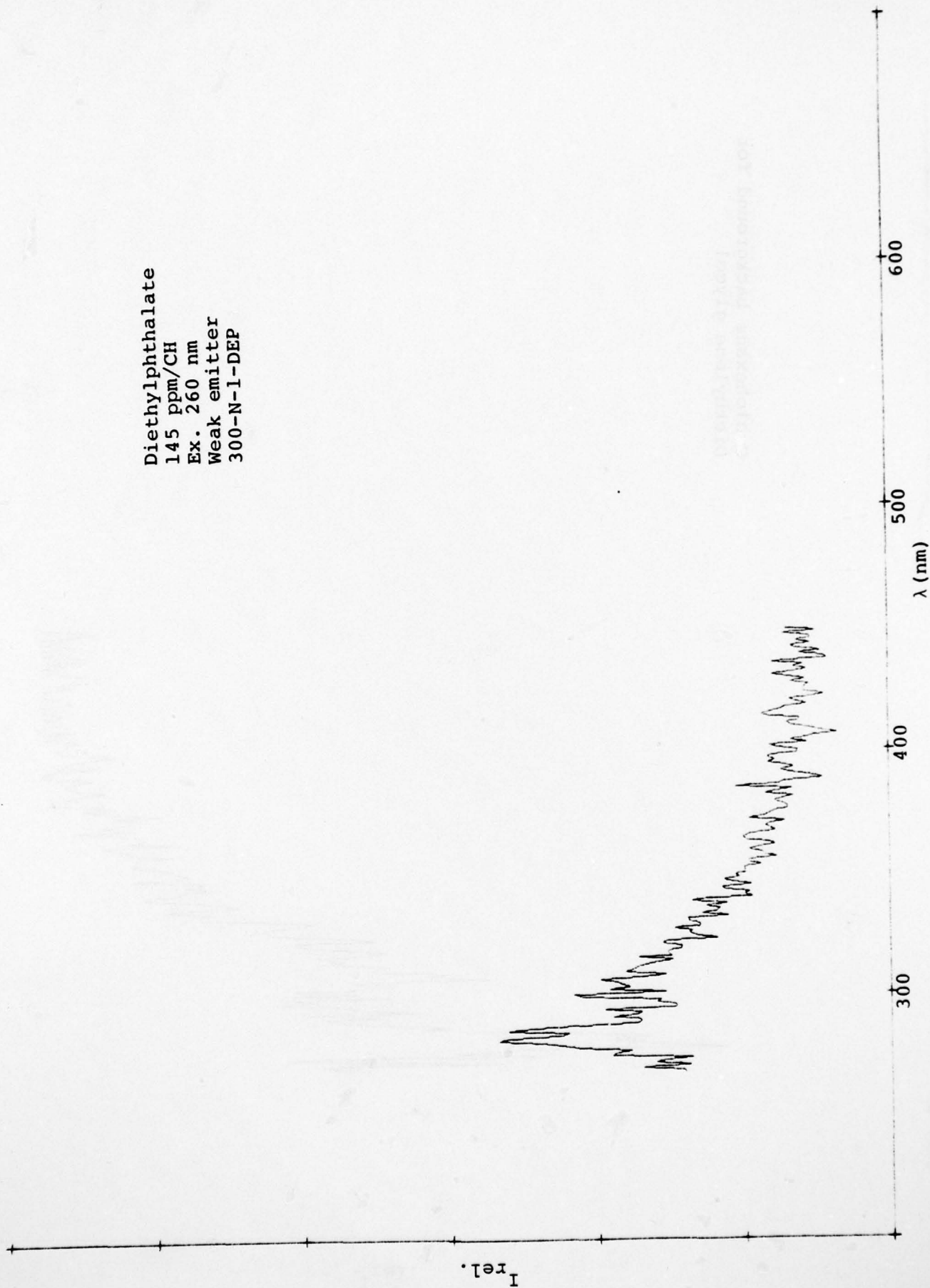
Diethylene glycol
202 ppm/CH
Ex. 265 nm
D.L.
310-N-2-DEG



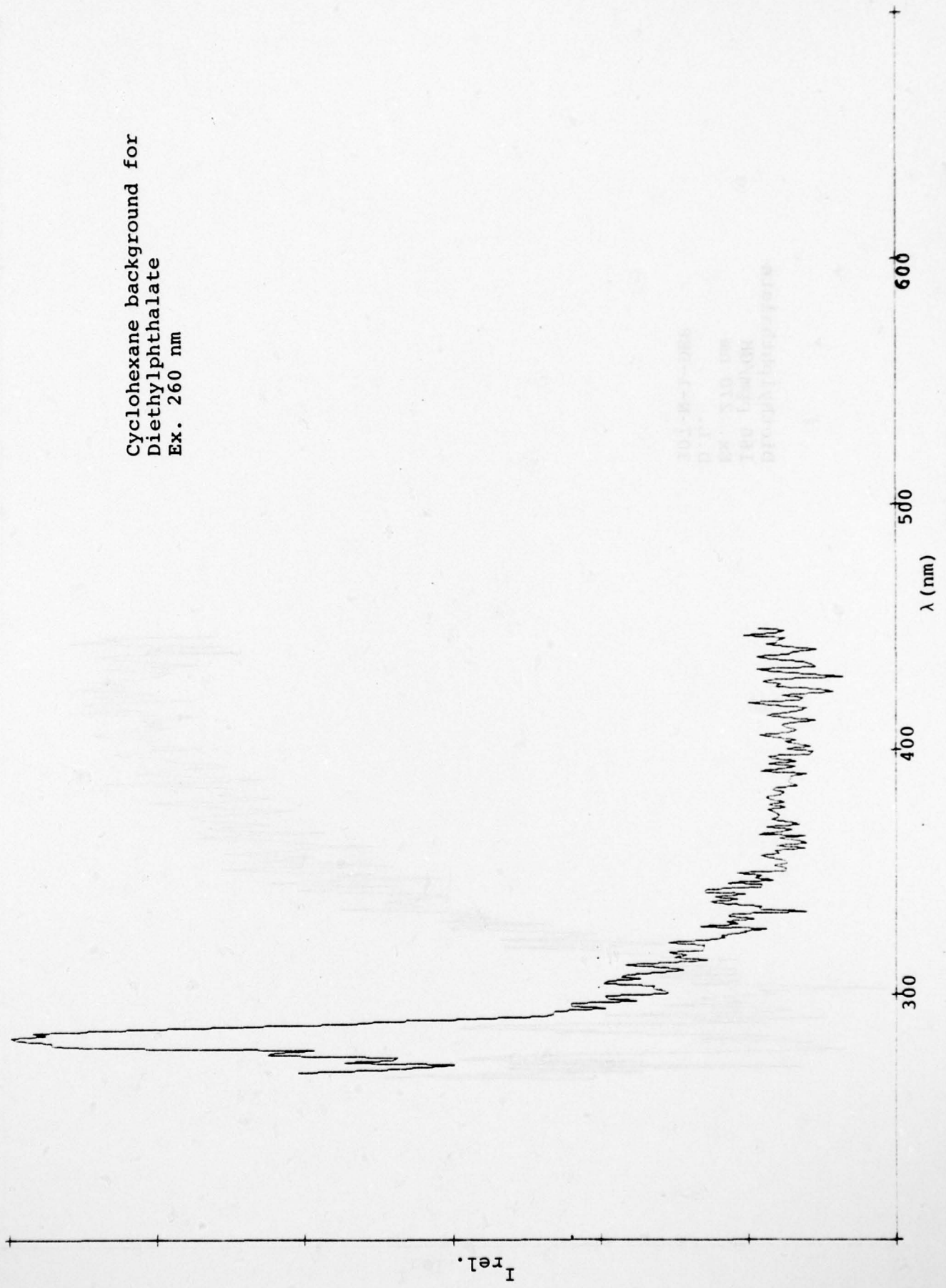
Cyclohexane background for
Diethylene glycol



Diethylphthalate
145 ppm/CH
Ex. 260 nm
Weak emitter
300-N-1-DEP

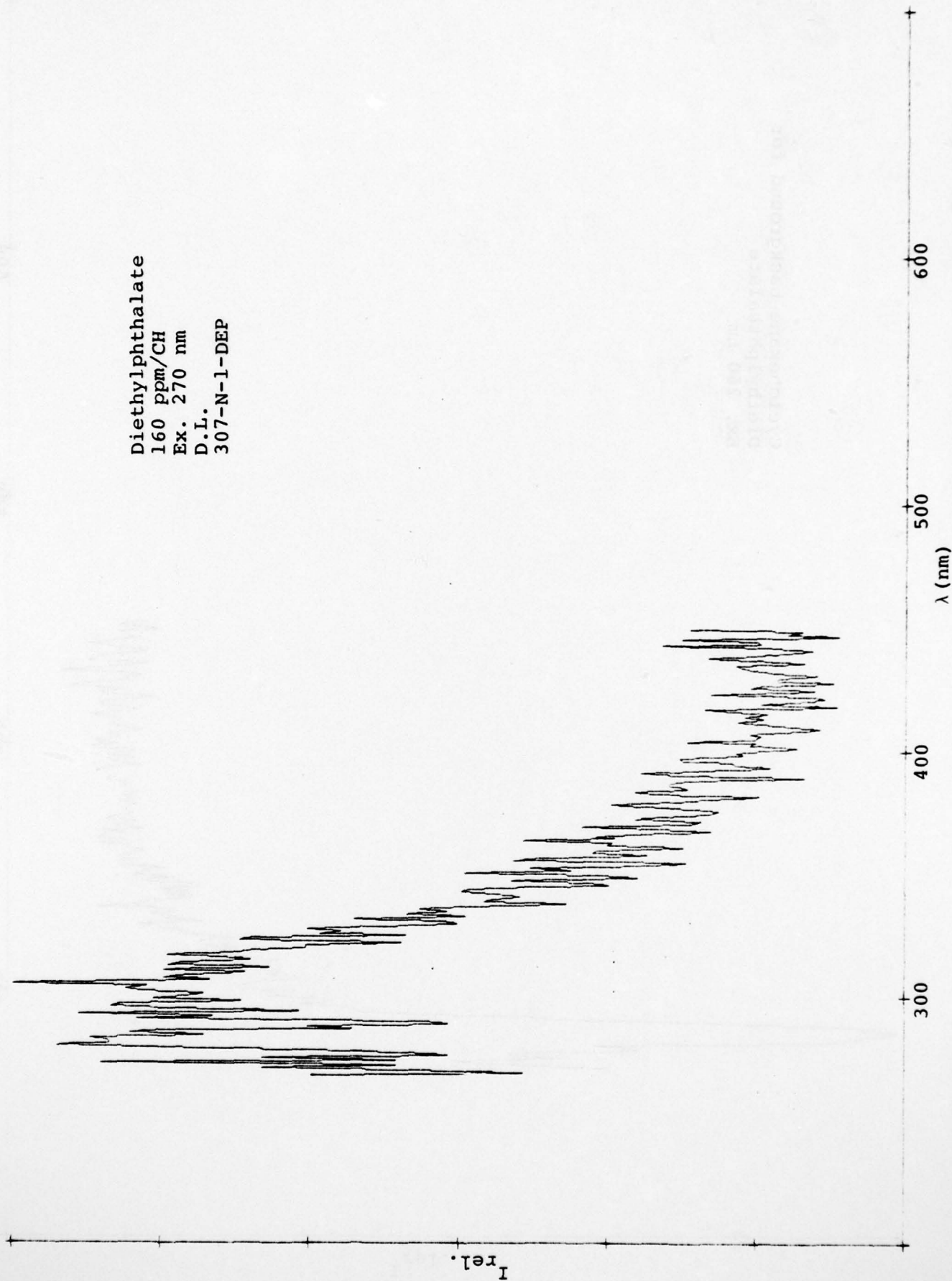


Cyclohexane background for
Diethylphthalate
Ex. 260 nm

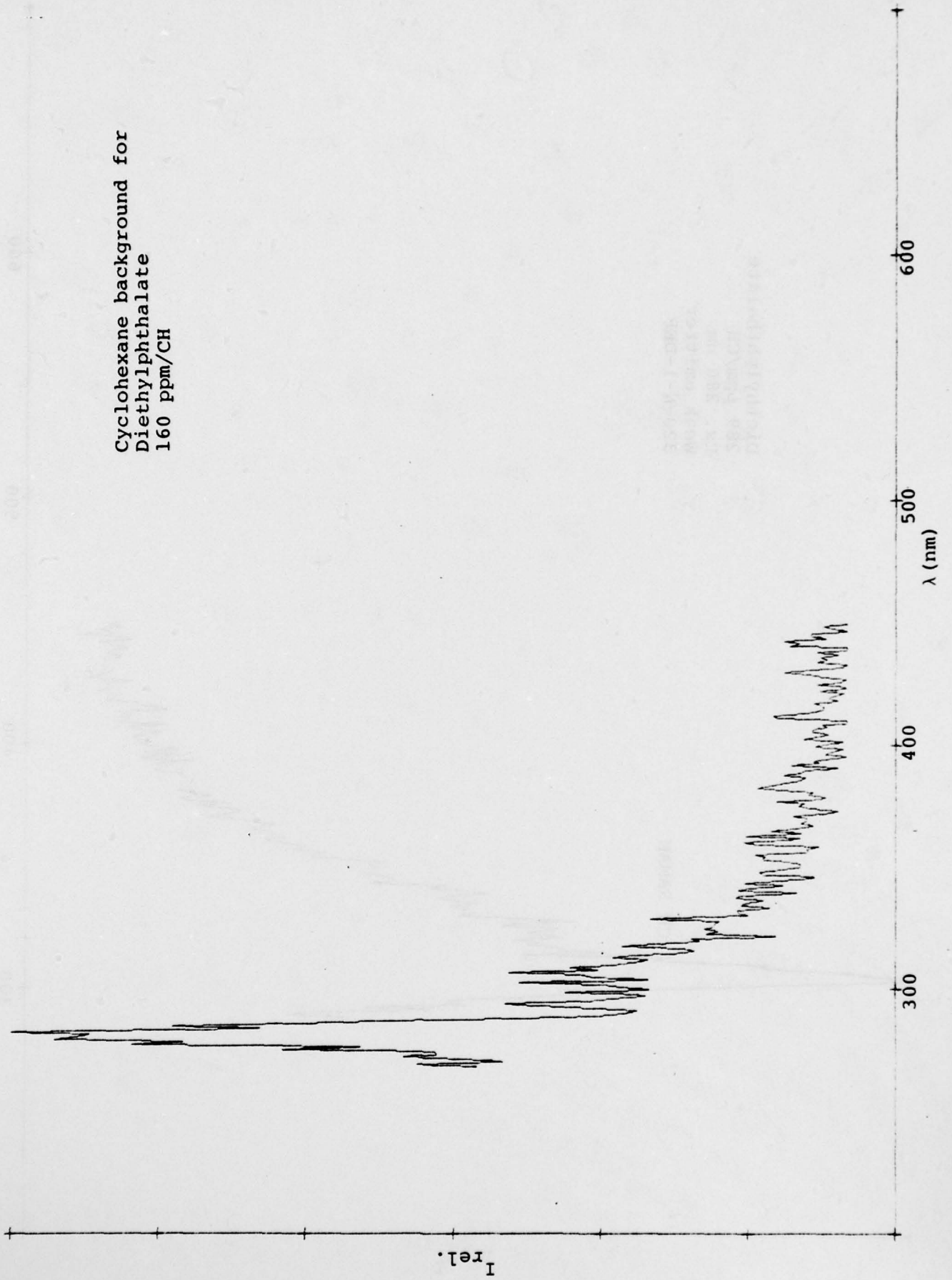


301-6-7-086
D.E.
Ex. 260 nm
780 L/min
Diethylphthalate

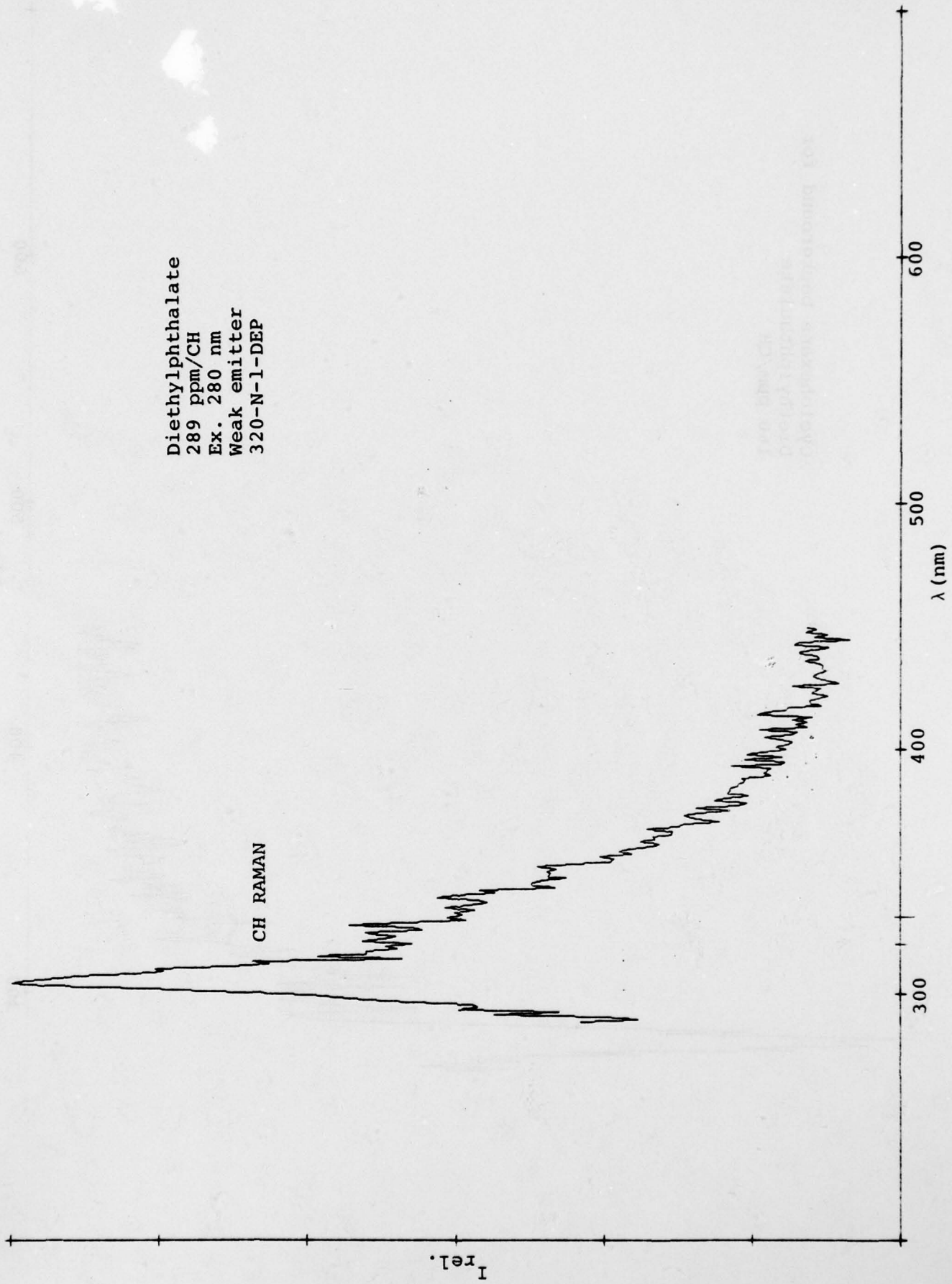
Diethylphthalate
160 ppm/CH
Ex. 270 nm
D.L.
307-N-1-DEP



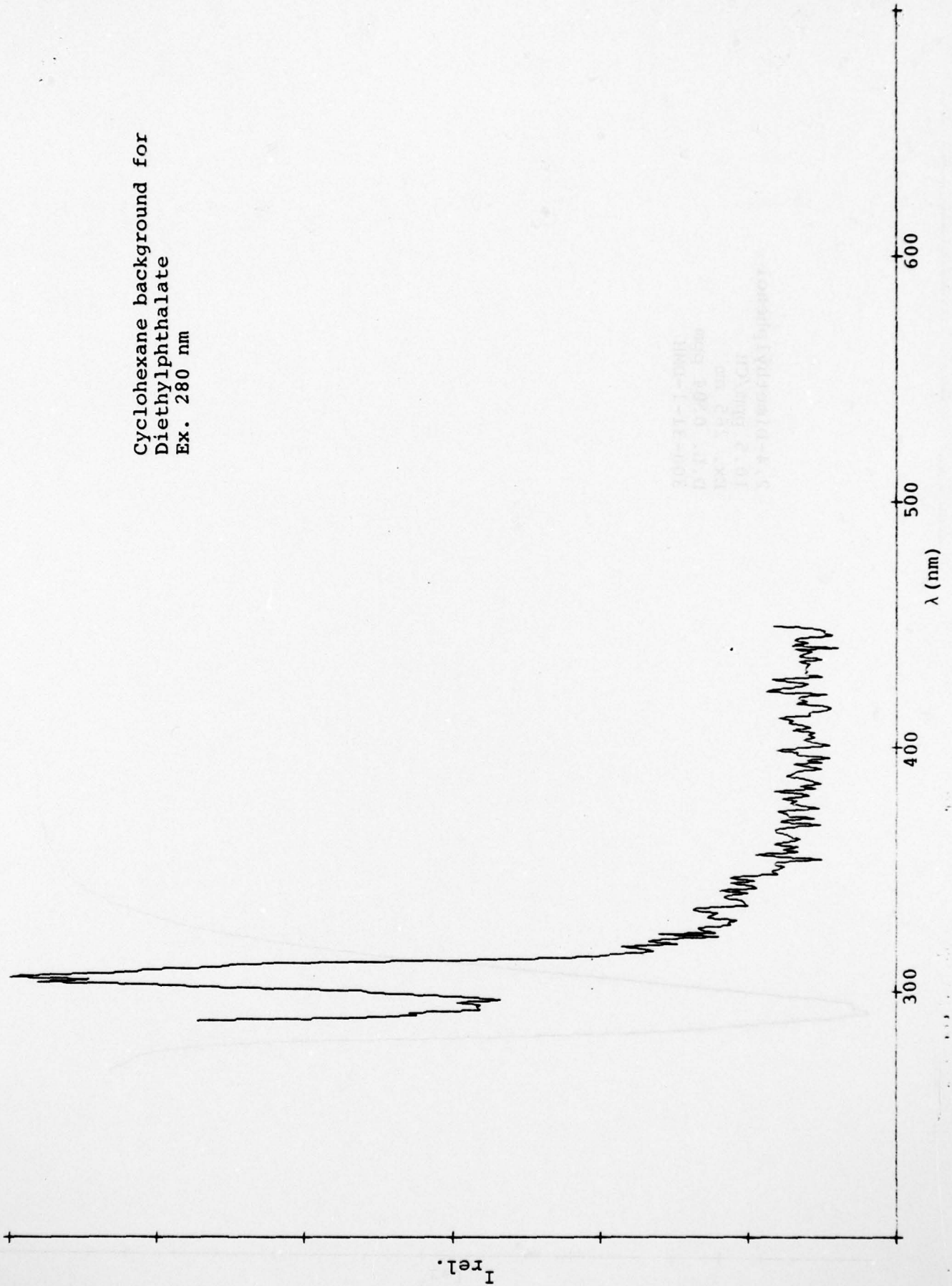
Cyclohexane background for
Diethylphthalate
160 ppm/CH



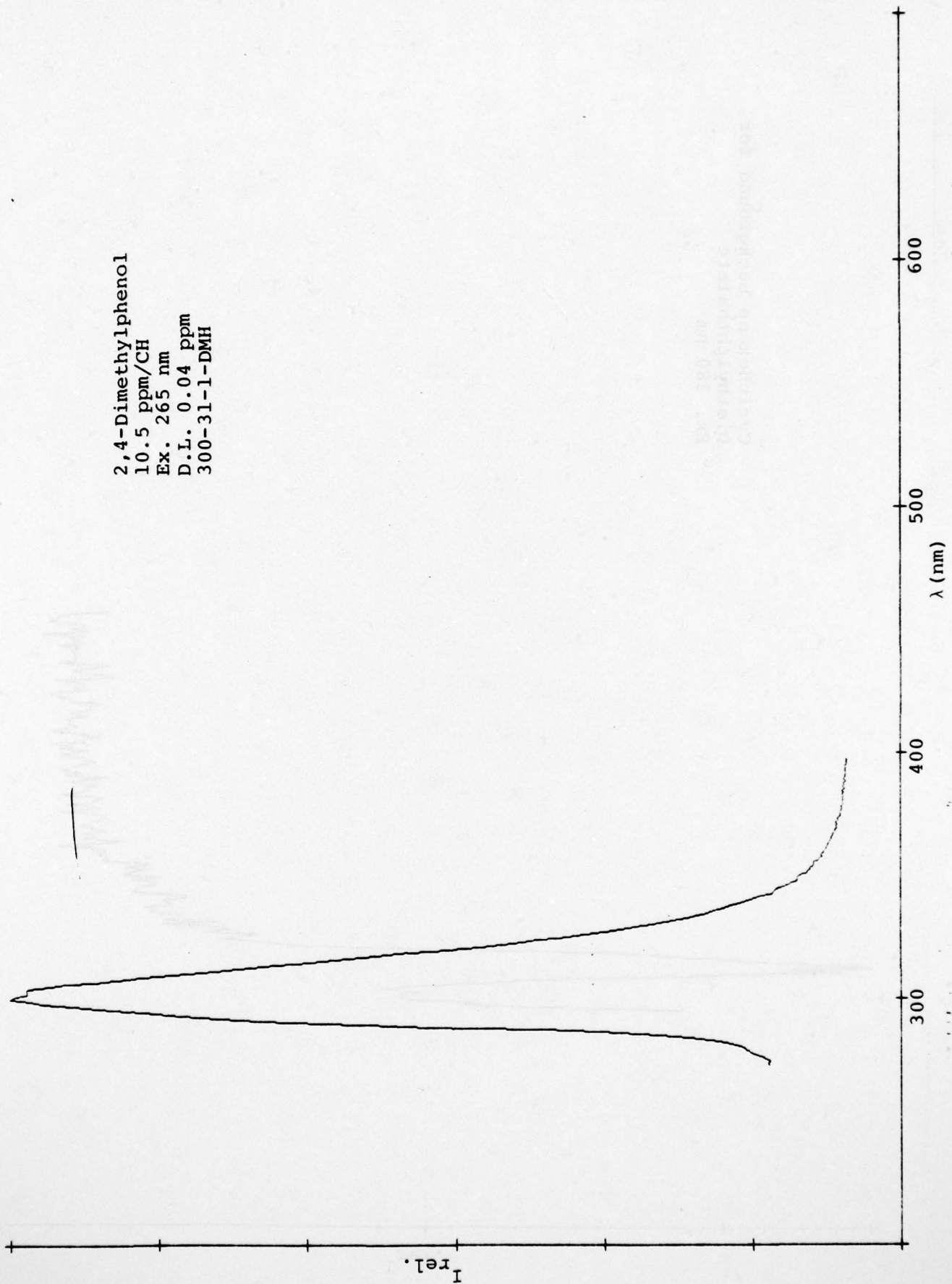
Diethylphthalate
289 ppm/CH
Ex. 280 nm
Weak emitter
320-N-1-DEP



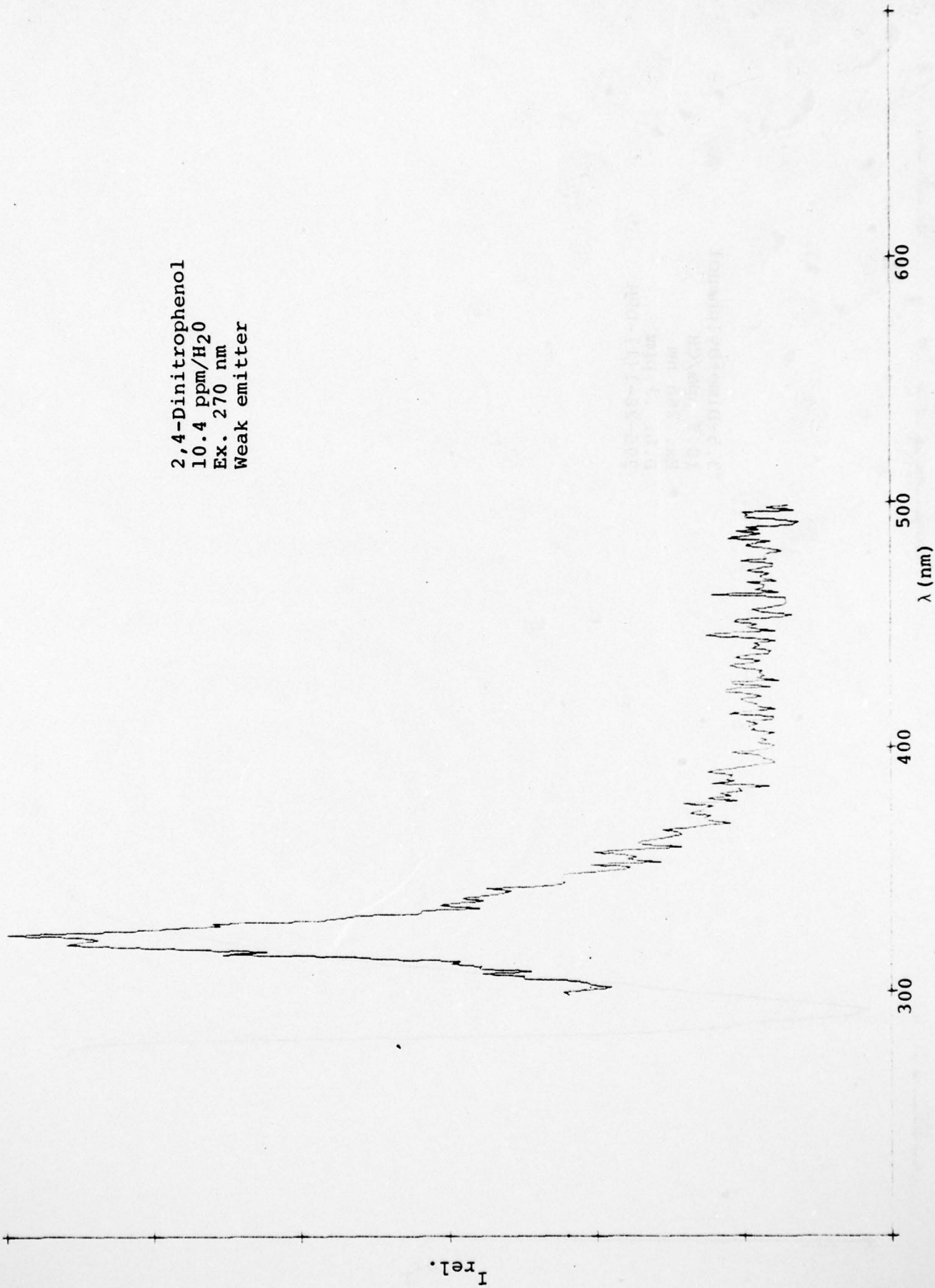
Cyclohexane background for
Diethylphthalate
Ex. 280 nm



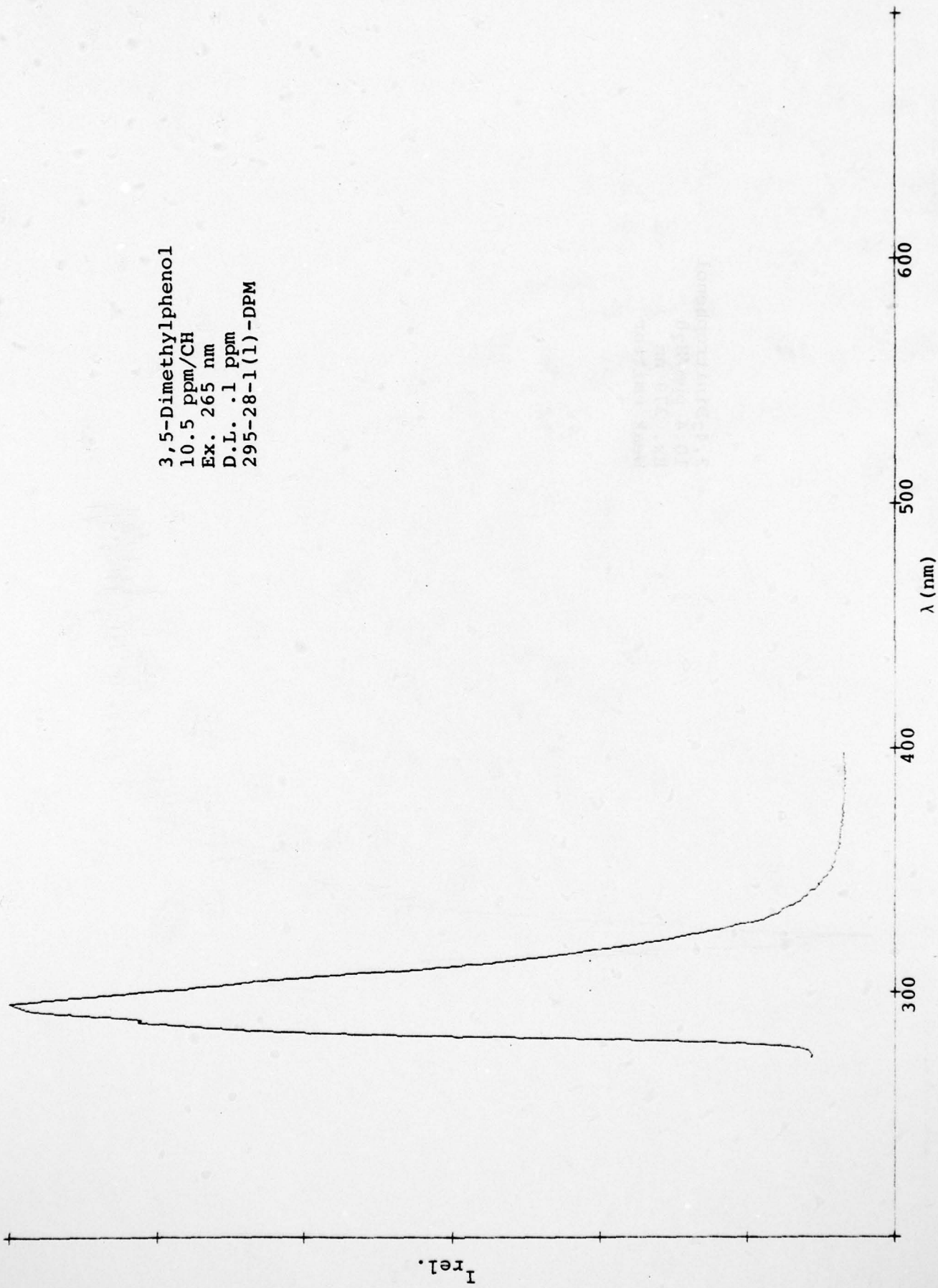
2,4-Dimethylphenol
10.5 ppm/CH
Ex. 265 nm
D.L. 0.04 ppm
300-31-1-DMH



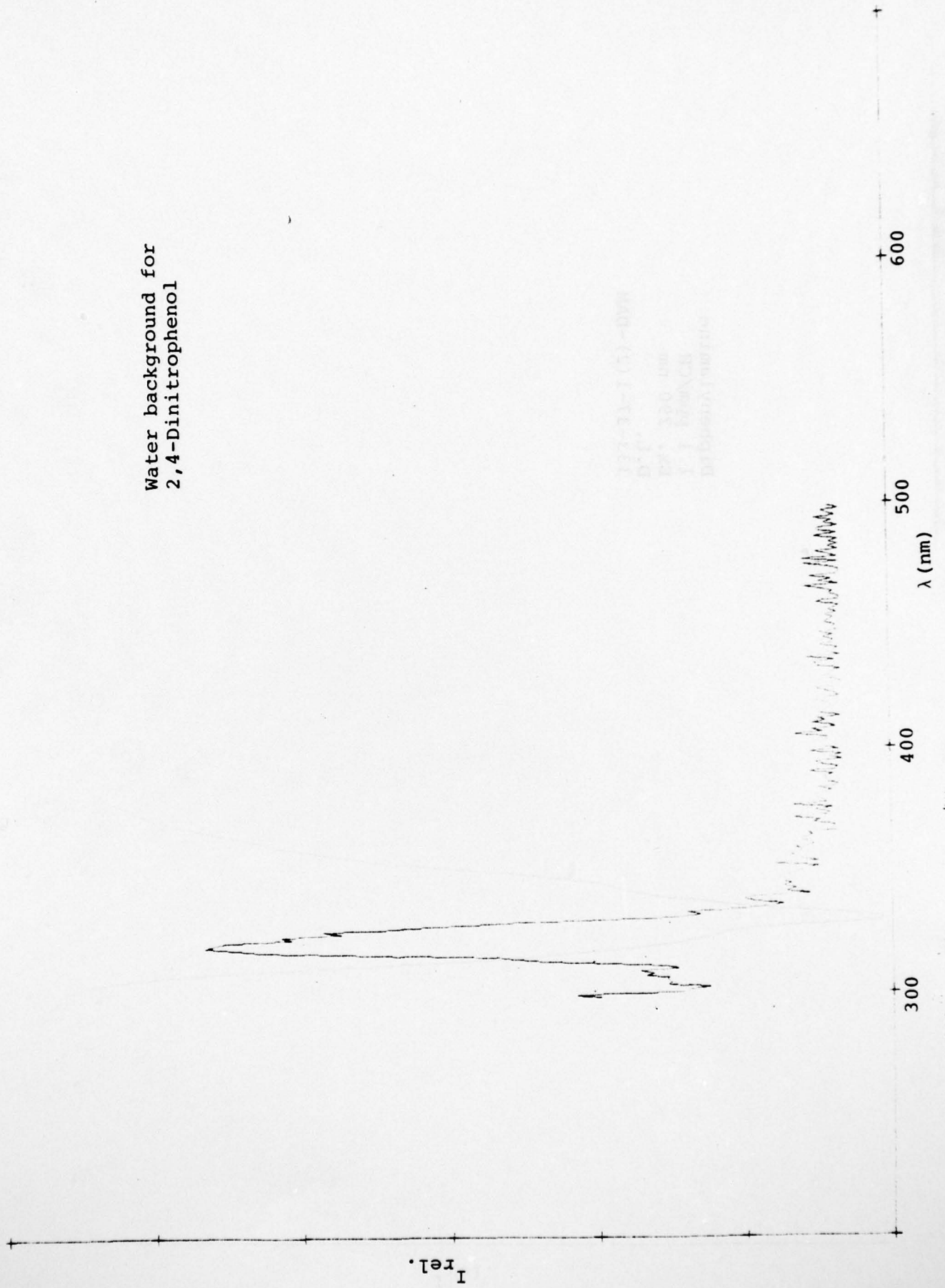
2,4-Dinitrophenol
10.4 ppm/H₂O
Ex. 270 nm
Weak emitter



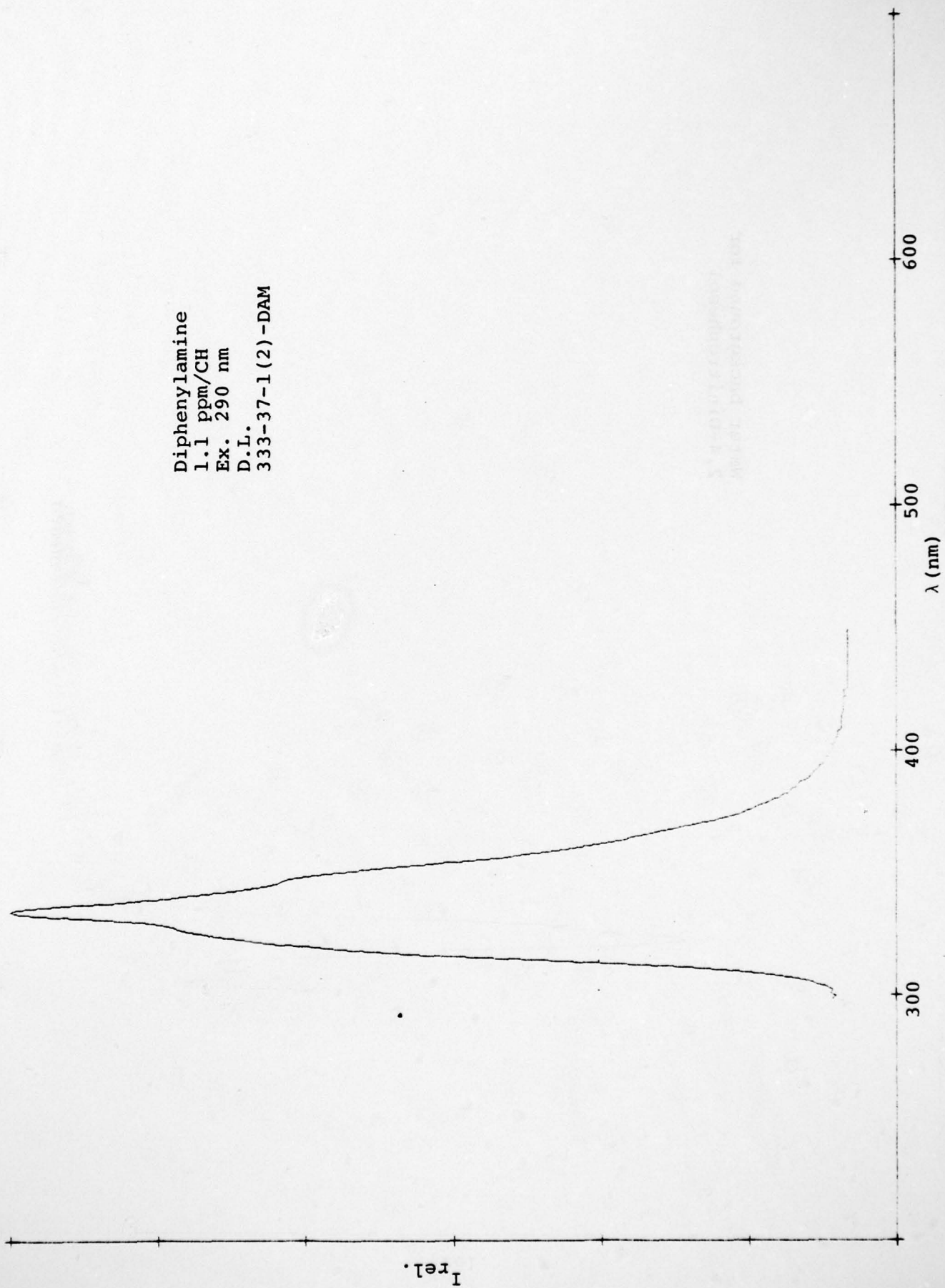
3,5-Dimethylphenol
10.5 ppm/CH
Ex. 265 nm
D.L. .1 ppm
295-28-1(1)-DPM



Water background for
2,4-Dinitrophenol



Diphenylamine
1.1 ppm/CH
Ex. 290 nm
D.L.
333-37-1 (2) -DAM



AD-A073 828

BAIRD CORP BEDFORD MA GOVERNMENT SYSTEMS DIV
A LUMINESCENCE SURVEY OF HAZARDOUS MATERIALS, (U)
MAY 79 J T BROWNRIGG, D A BUSCH, L P GIERING
USCG-D-53-79

F/G 7/2

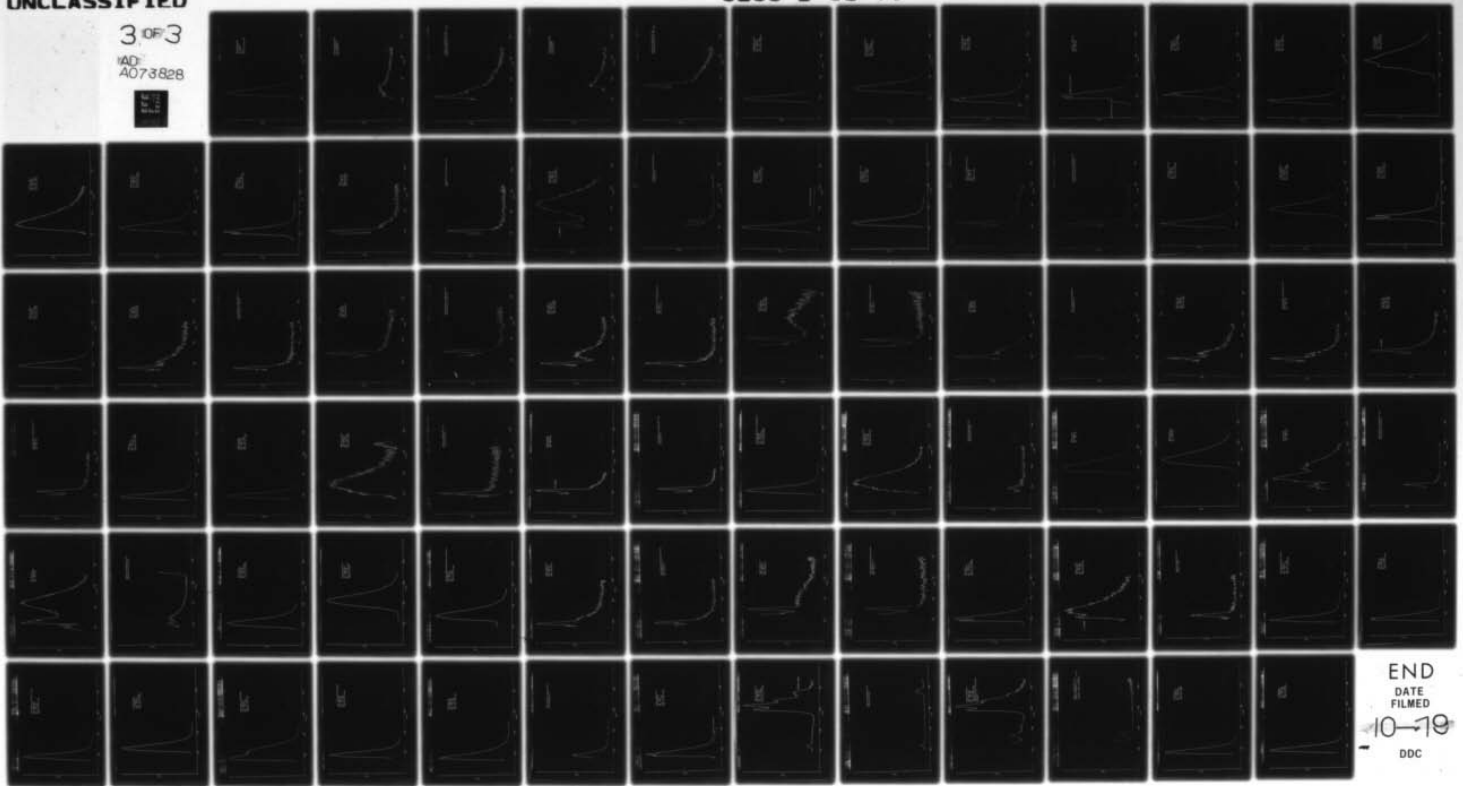
DOT-CG-81-78-1888

NL

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3 OF 3

AD-A073828

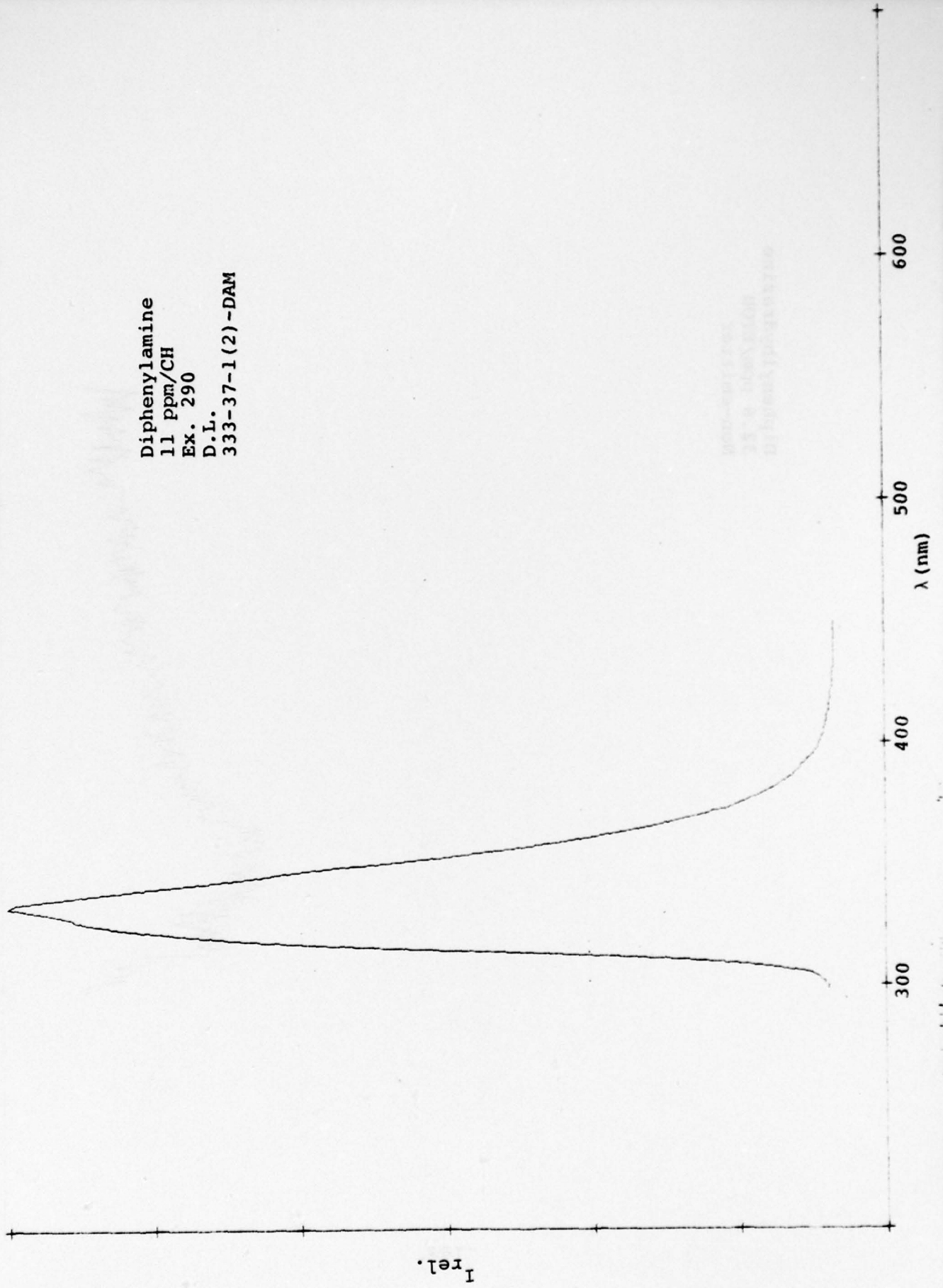


END
DATE
FILMED

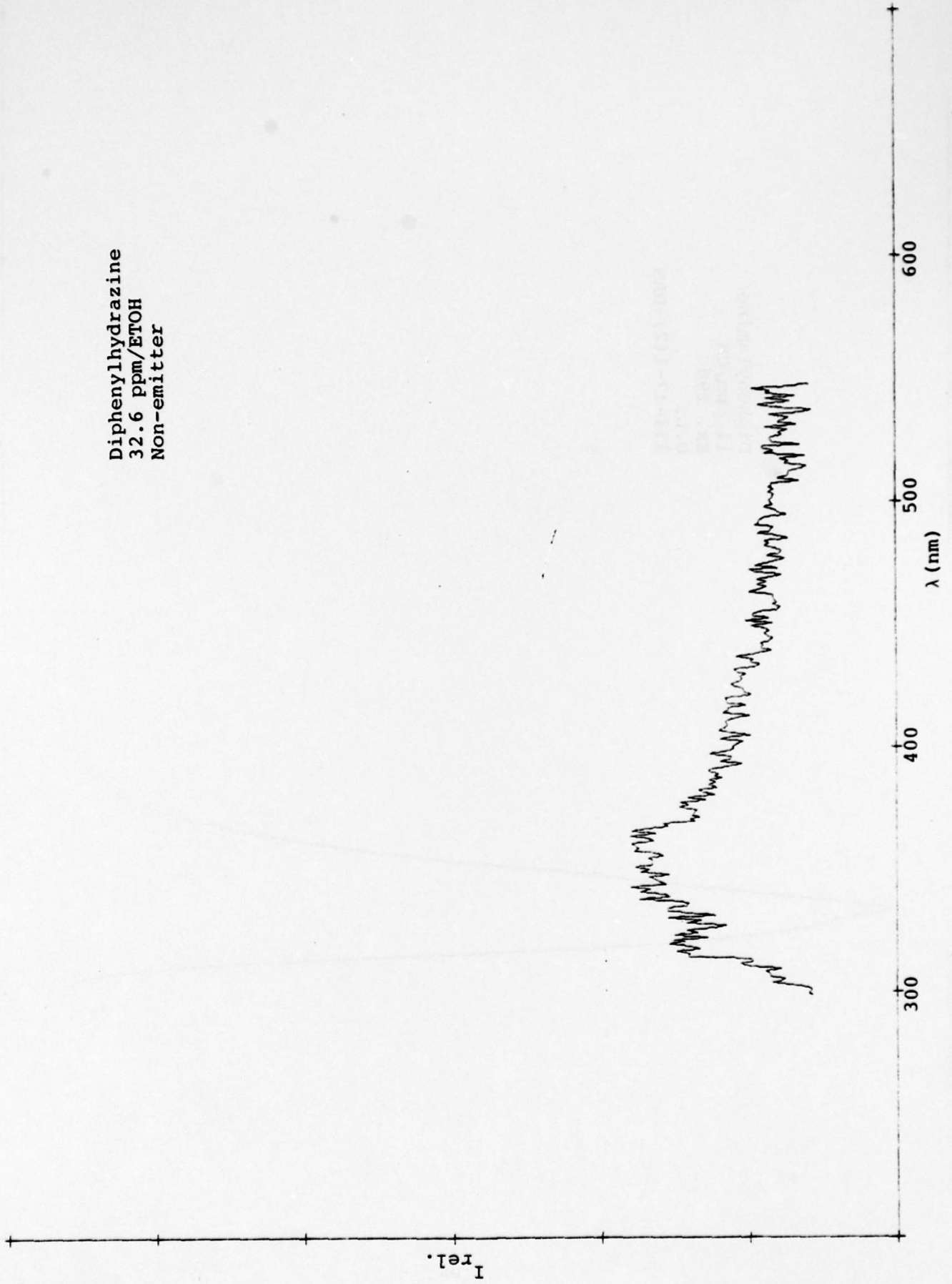
10-19

DDC

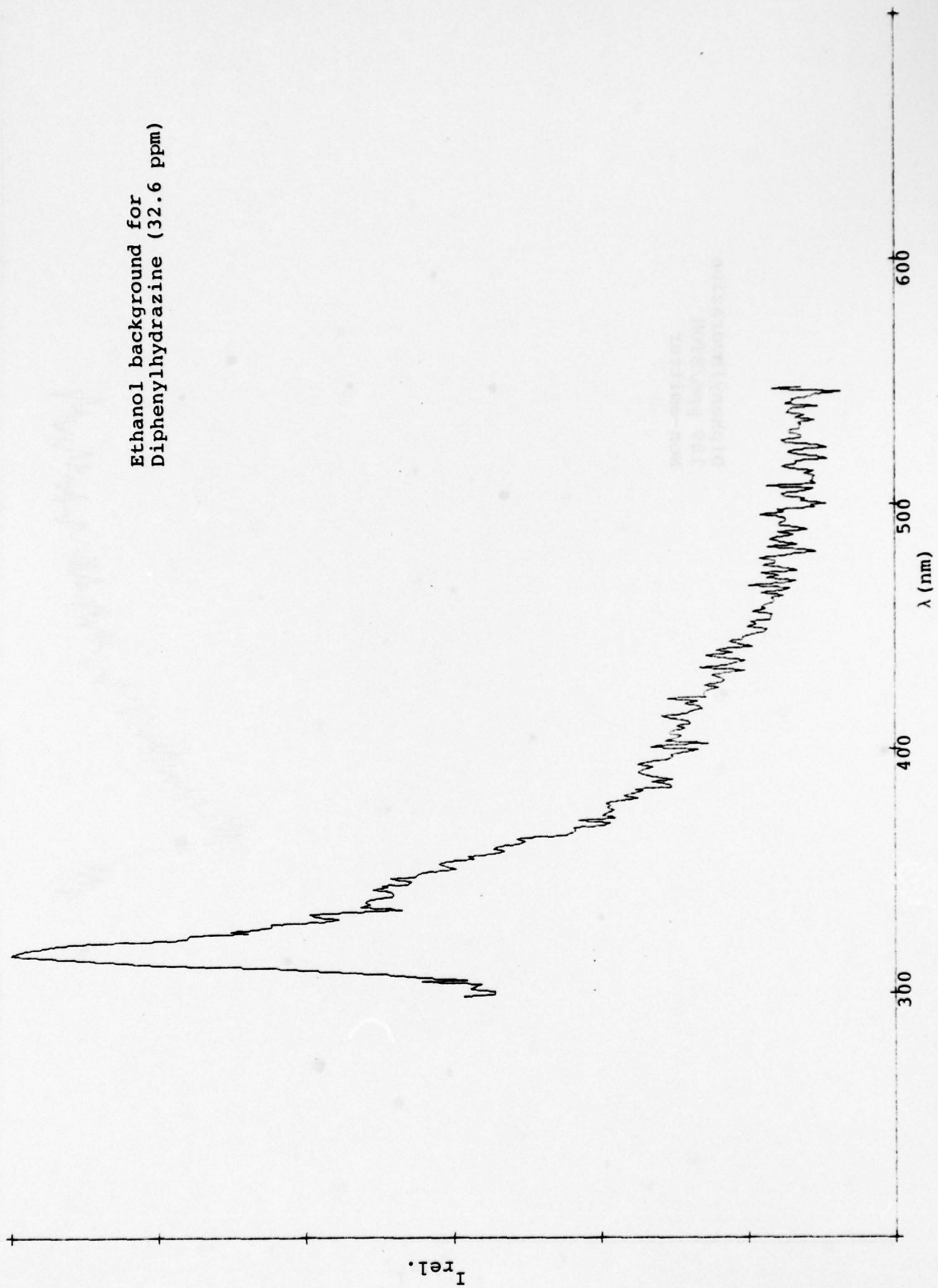
Diphenylamine
11 ppm/CH
Ex. 290
D.L.
333-37-1(2)-DAM



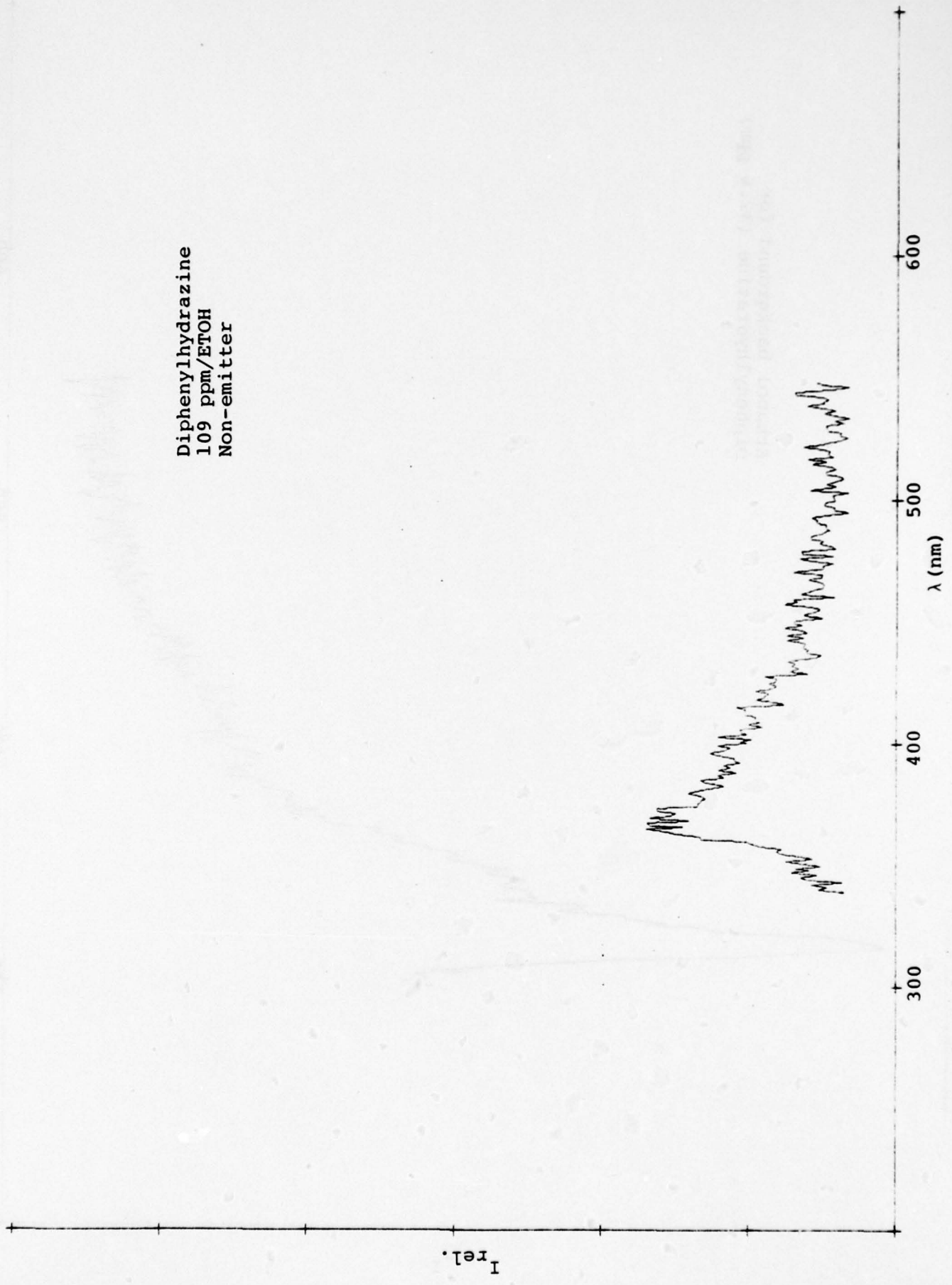
Diphenylhydrazine
32.6 ppm/ETOH
Non-emitter



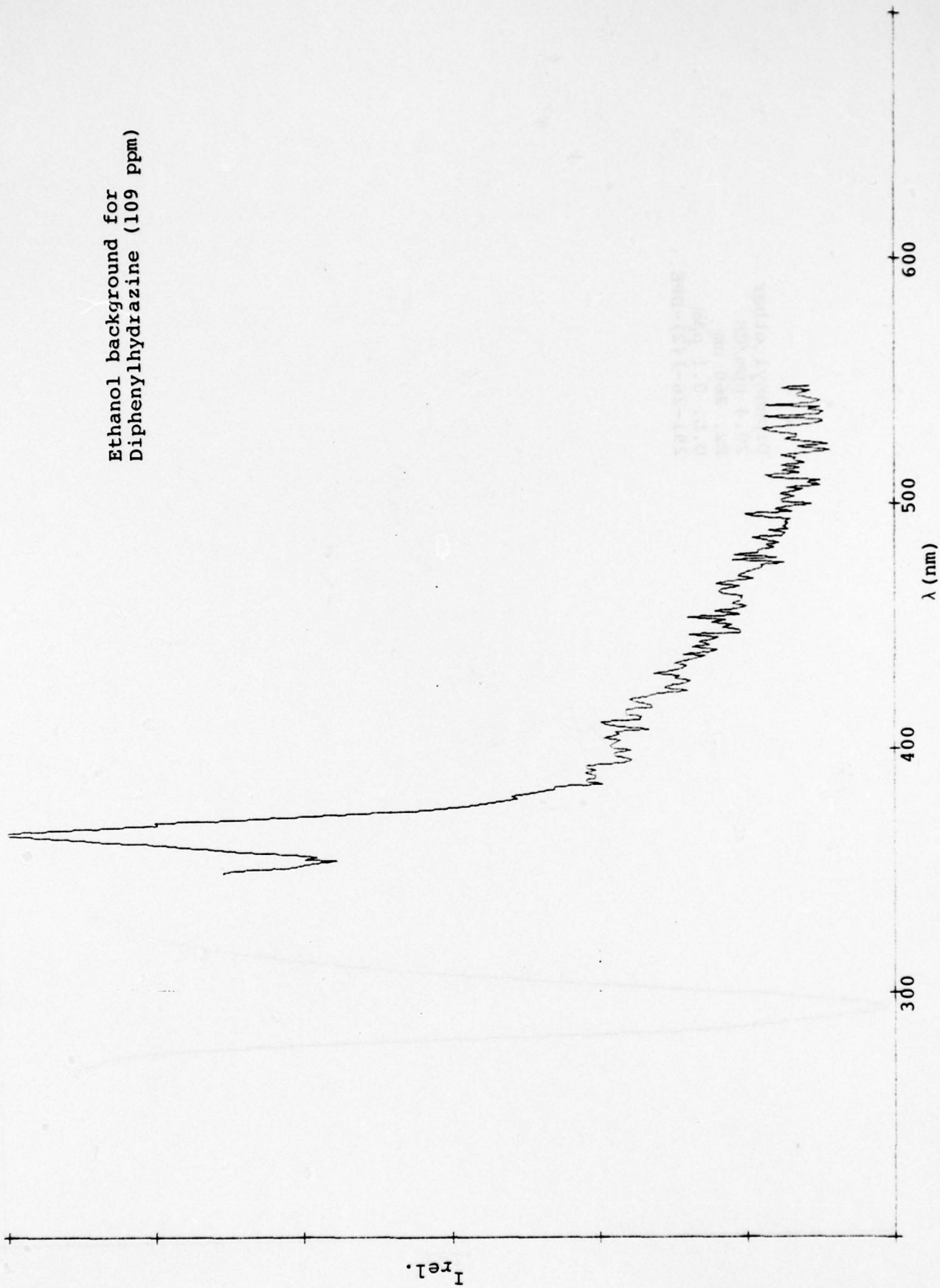
Ethanol background for
Diphenylhydrazine (32.6 ppm)



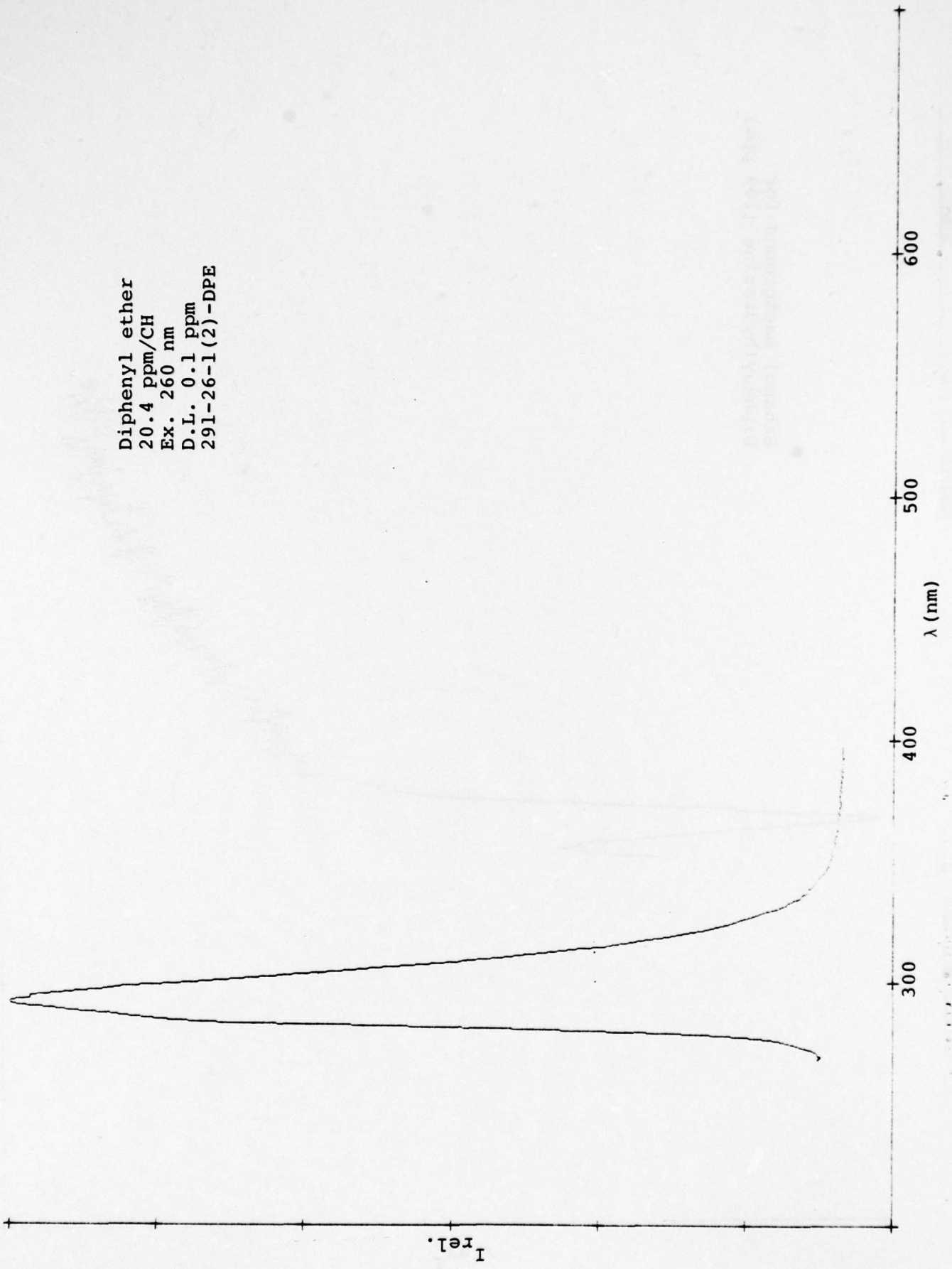
Diphenylhydrazine
109 ppm/ETOH
Non-emitter



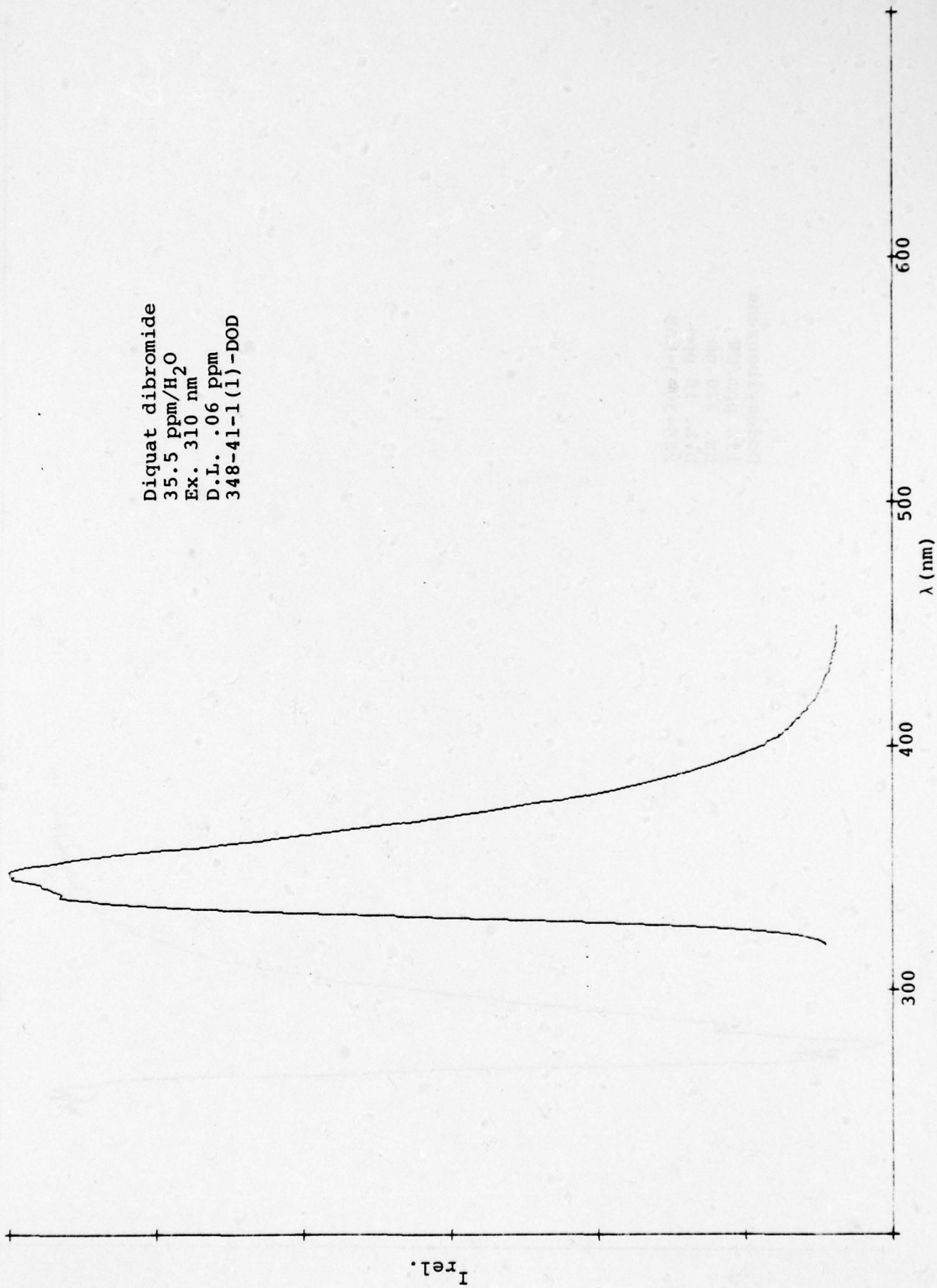
Ethanol background for
Diphenylhydrazine (109 ppm)



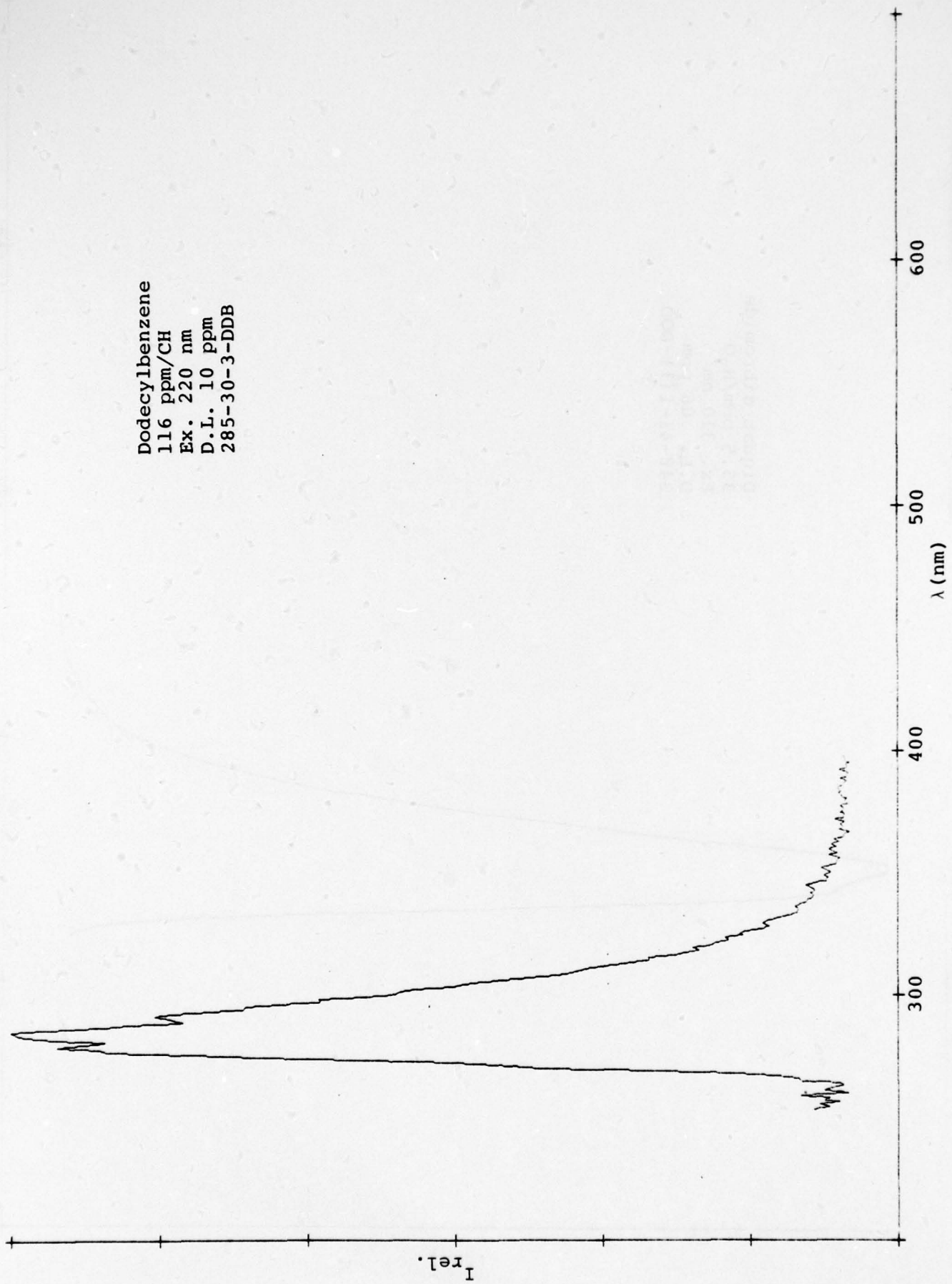
Diphenyl ether
20.4 ppm/CH
Ex. 260 nm
D.L. 0.1 ppm
291-26-1(2)-DPE

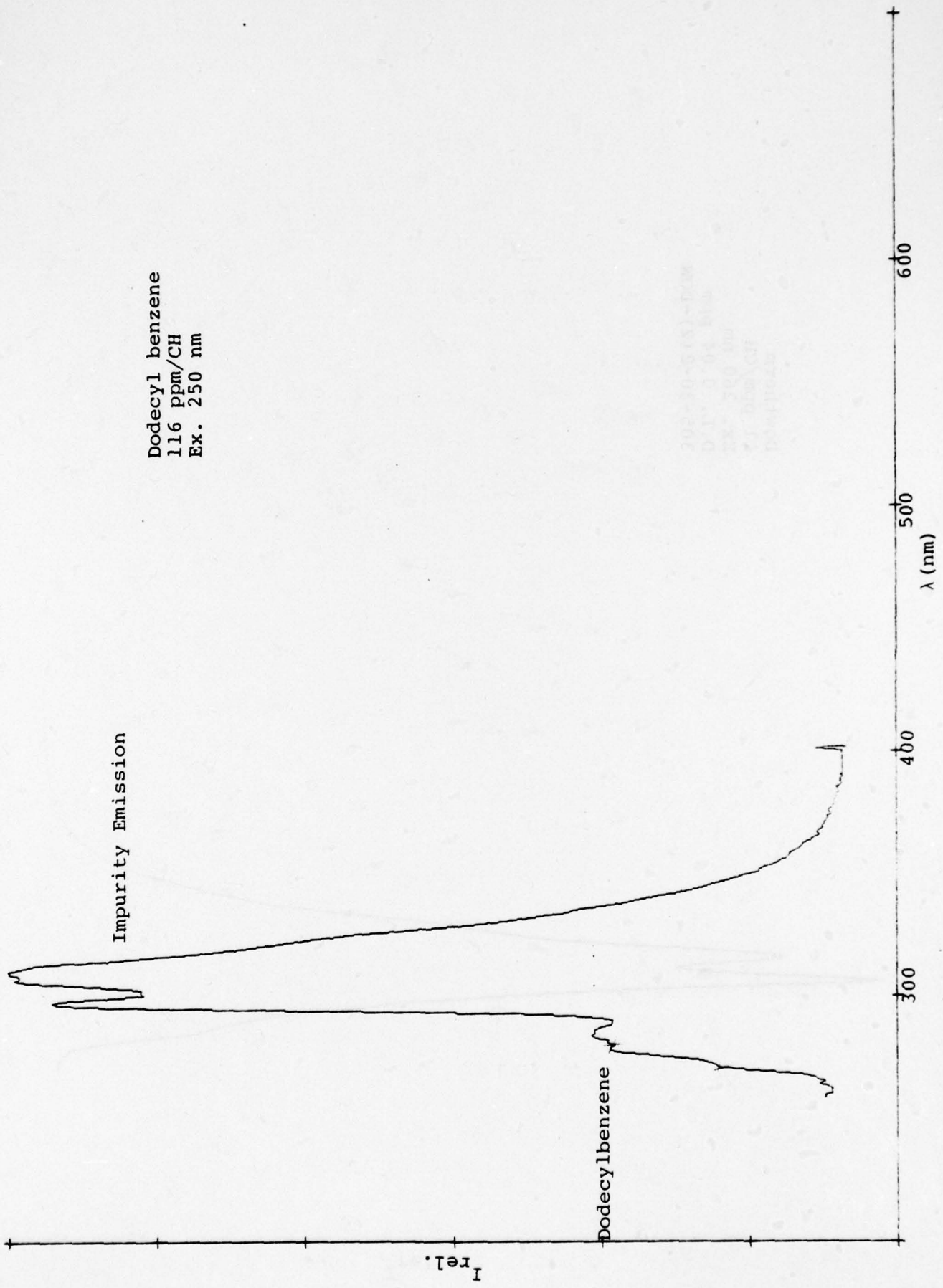


Diquat dibromide
35.5 ppm/H₂O
Ex. 310 nm
D.L. .06 ppm
348-41-1(1)-DOD

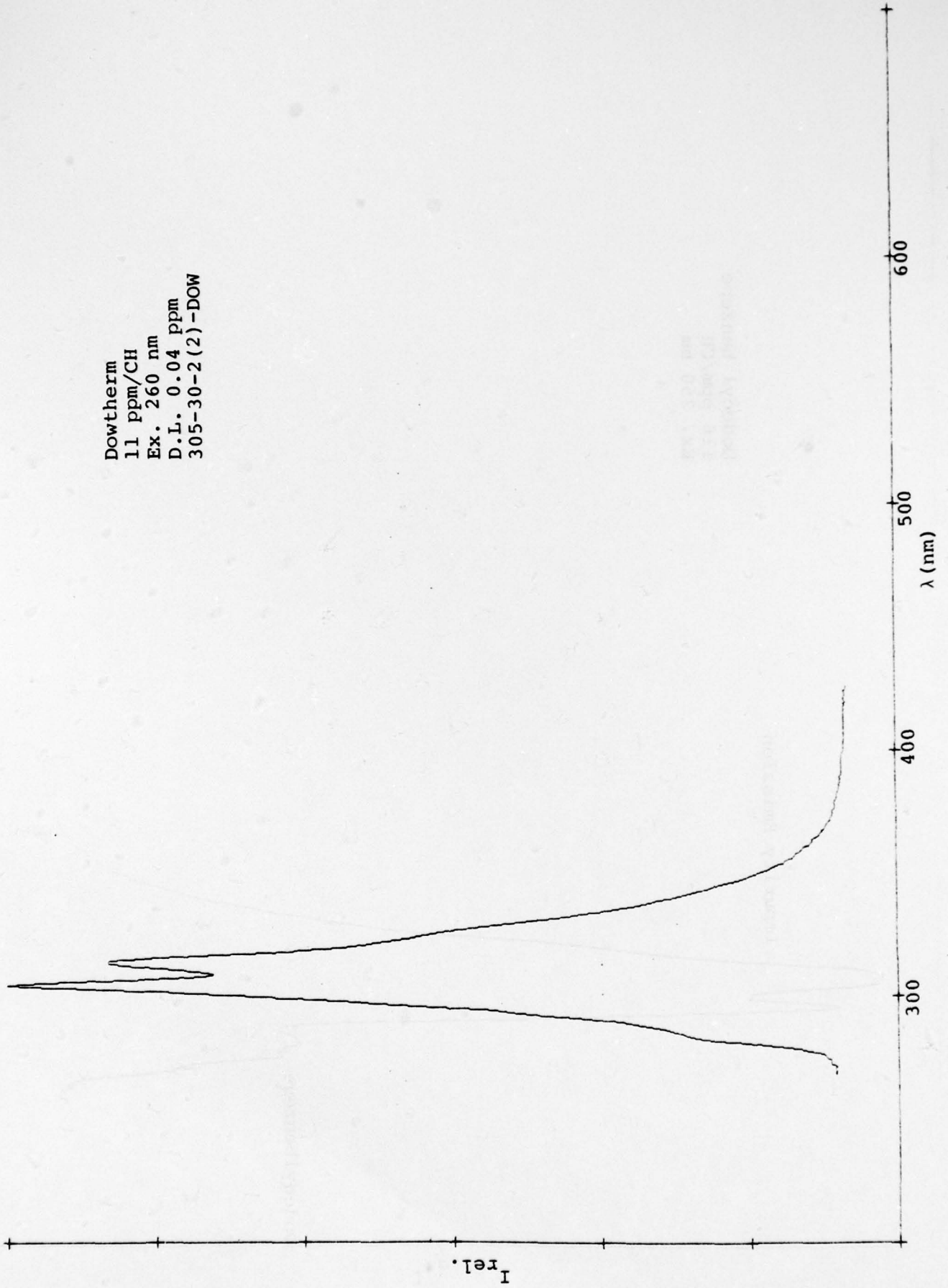


Dodecylbenzene
116 ppm/CH
Ex. 220 nm
D.L. 10 ppm
285-30-3-DDB

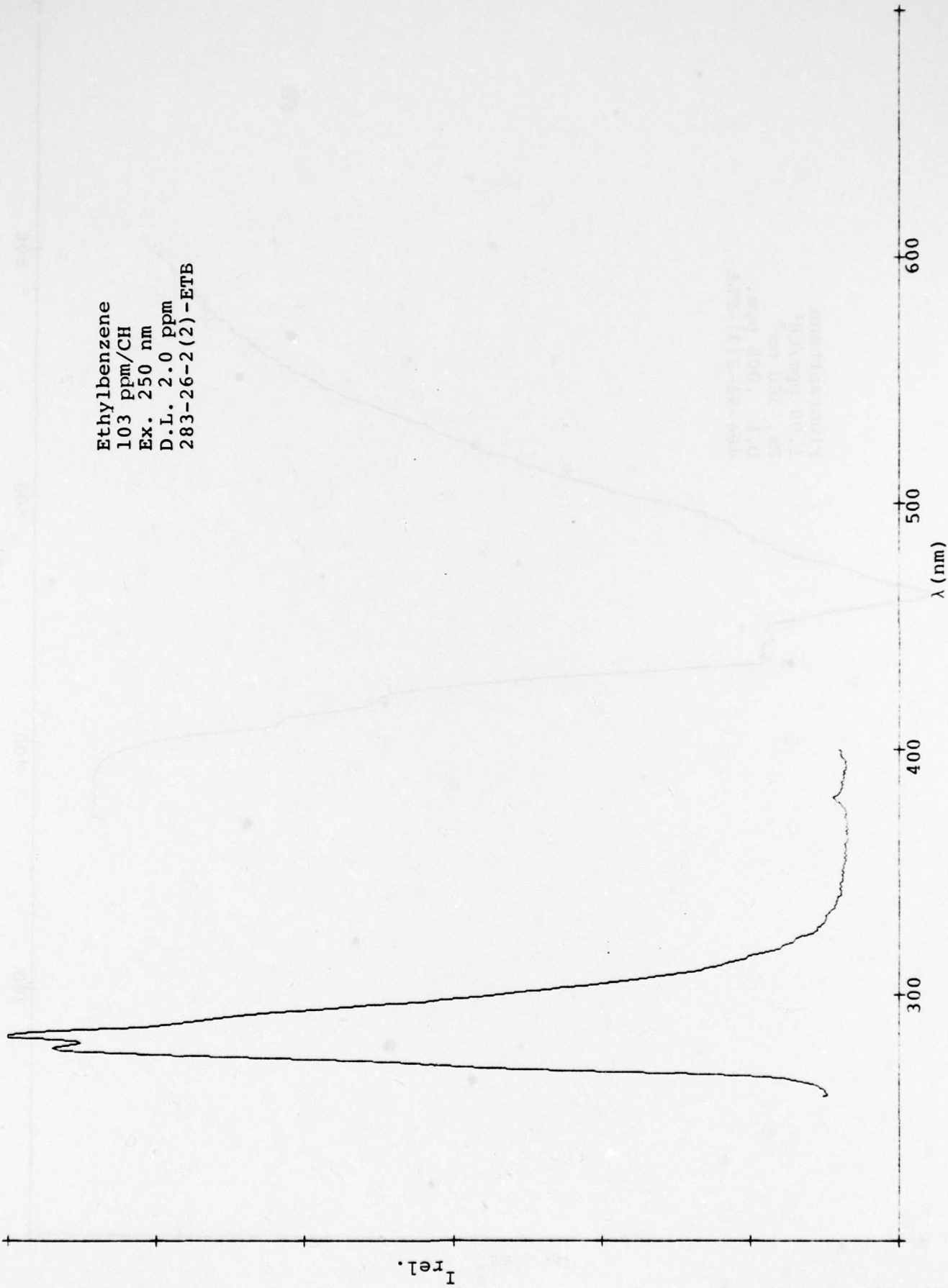




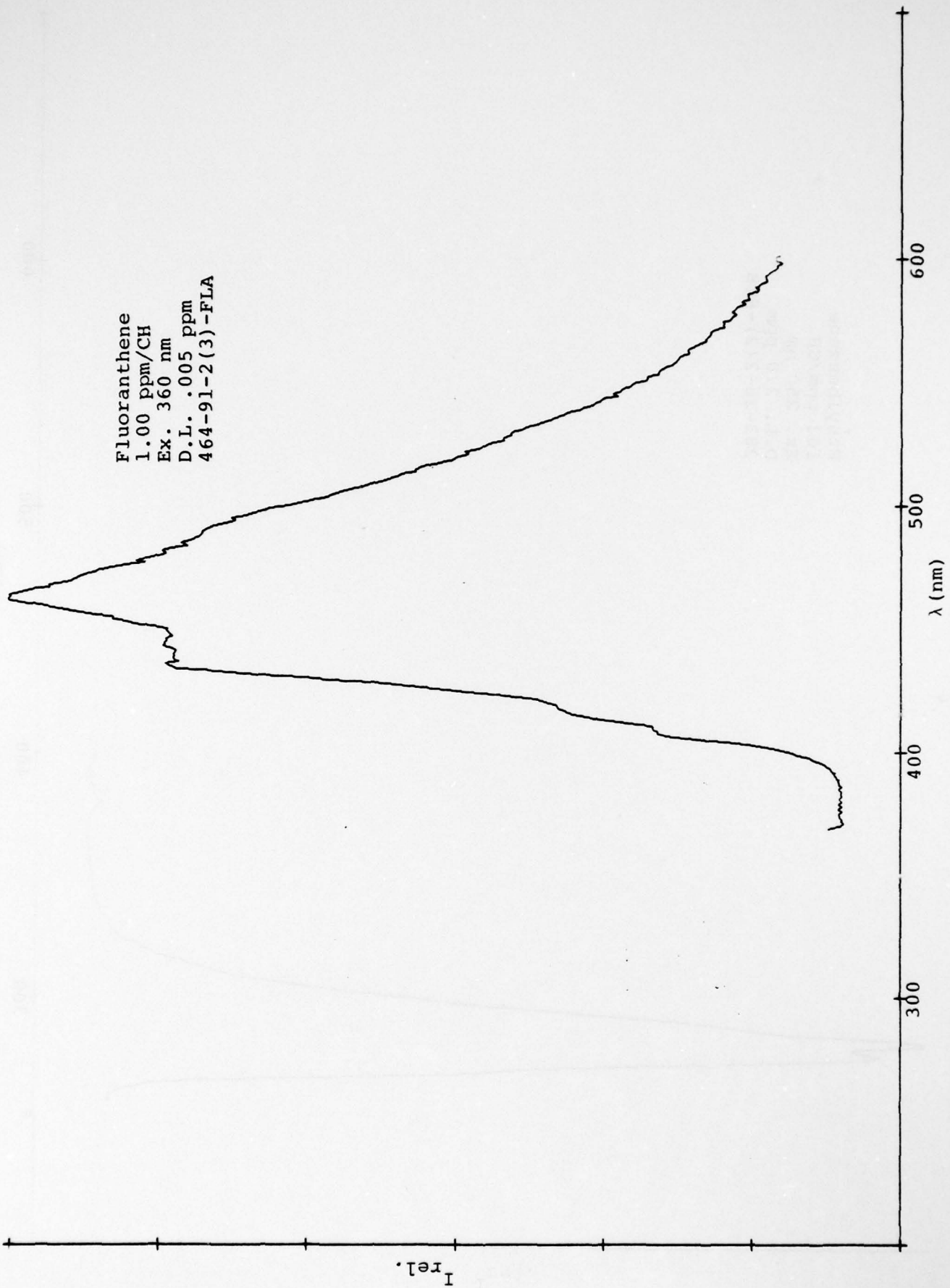
Dowtherm
11 ppm/CH
Ex. 260 nm
D.L. 0.04 ppm
305-30-2(2)-DOW



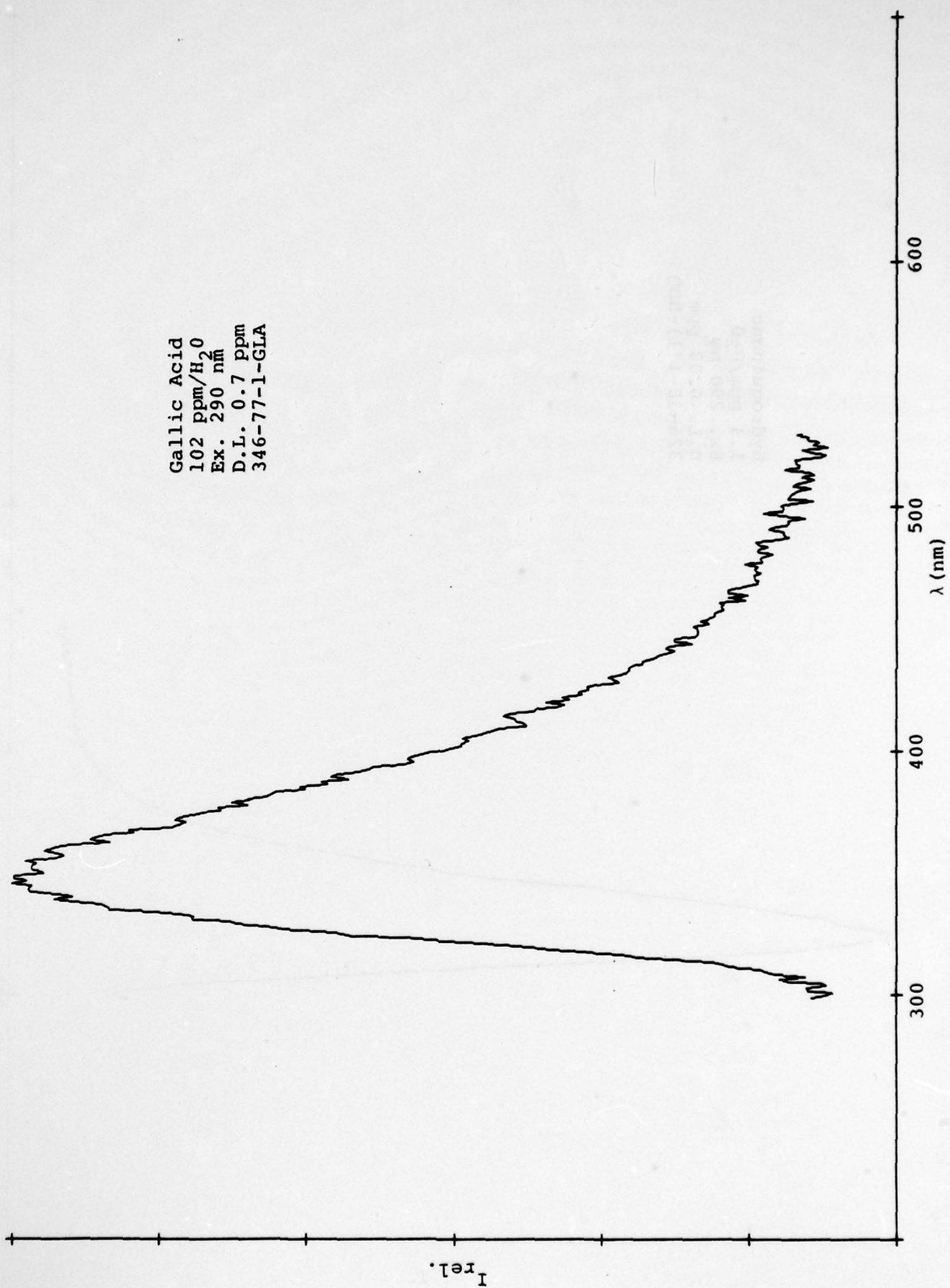
Ethylbenzene
103 ppm/CH
Ex. 250 nm
D.L. 2.0 ppm
283-26-2 (2)-ETB



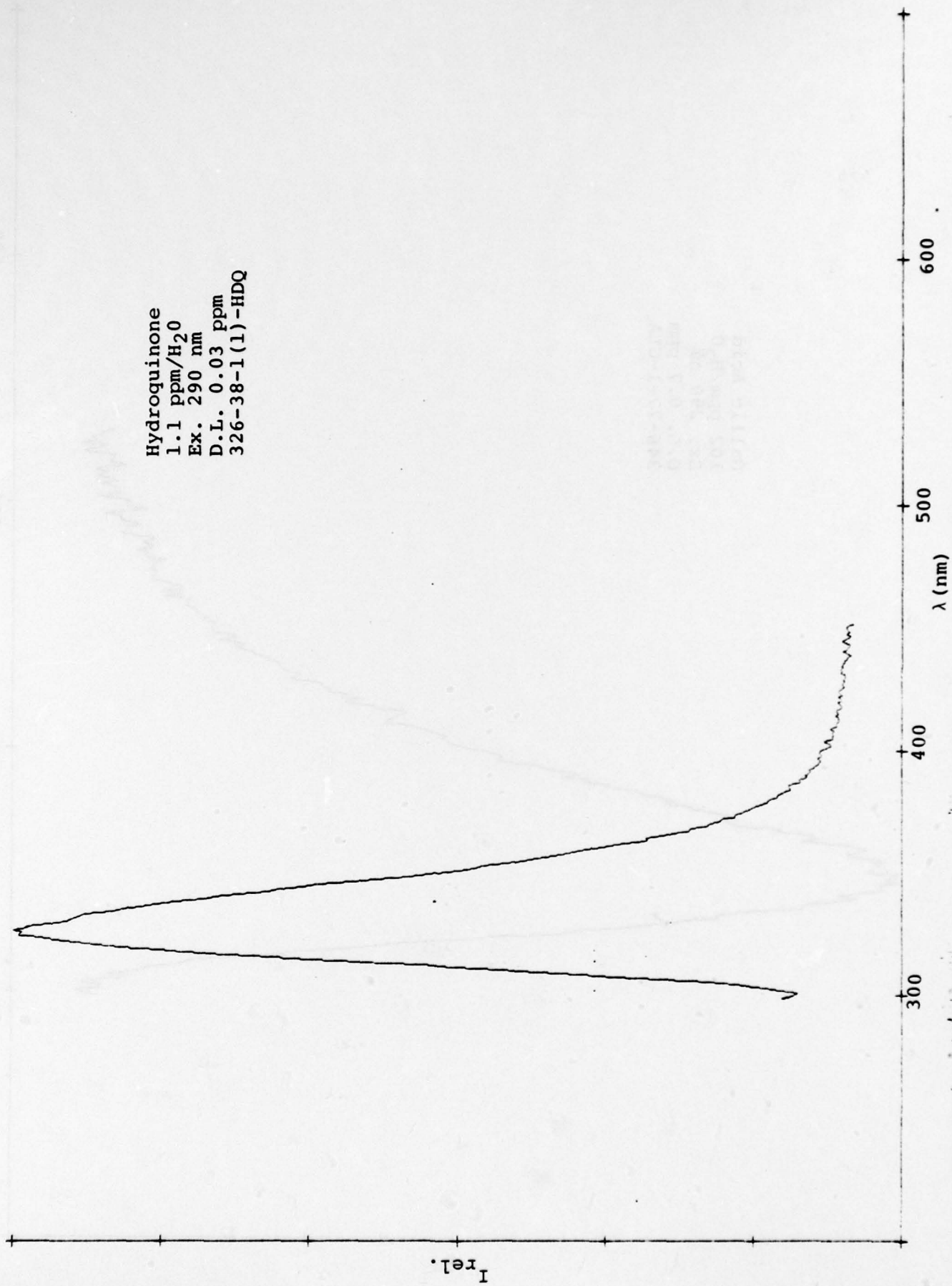
Fluoranthene
1.00 ppm/CH
Ex. 360 nm
D.L. .005 ppm
464-91-2(3)-FLA



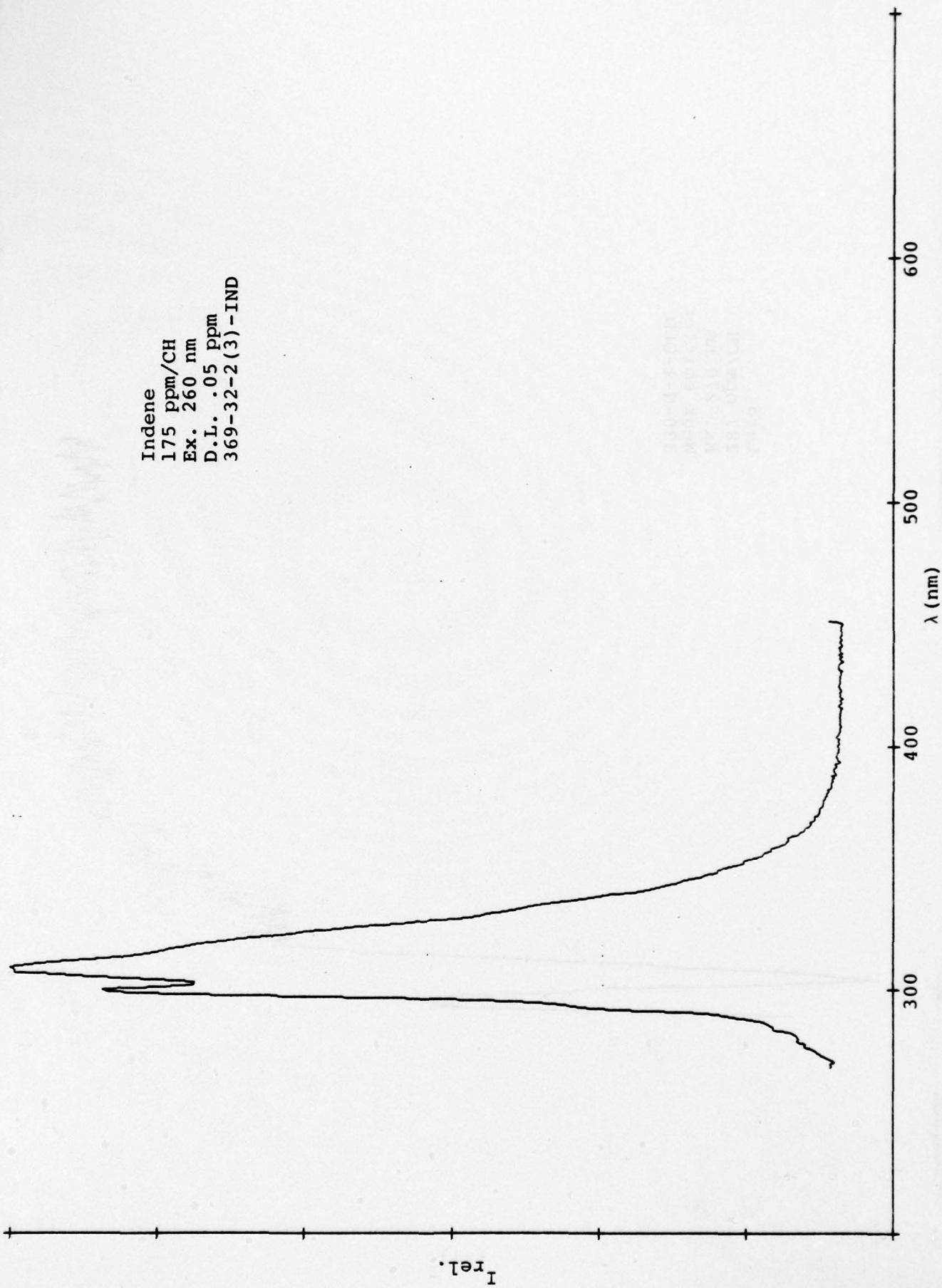
Gallic Acid
102 ppm/H₂O
Ex. 290 nm
D.L. 0.7 ppm
346-77-1-GLA



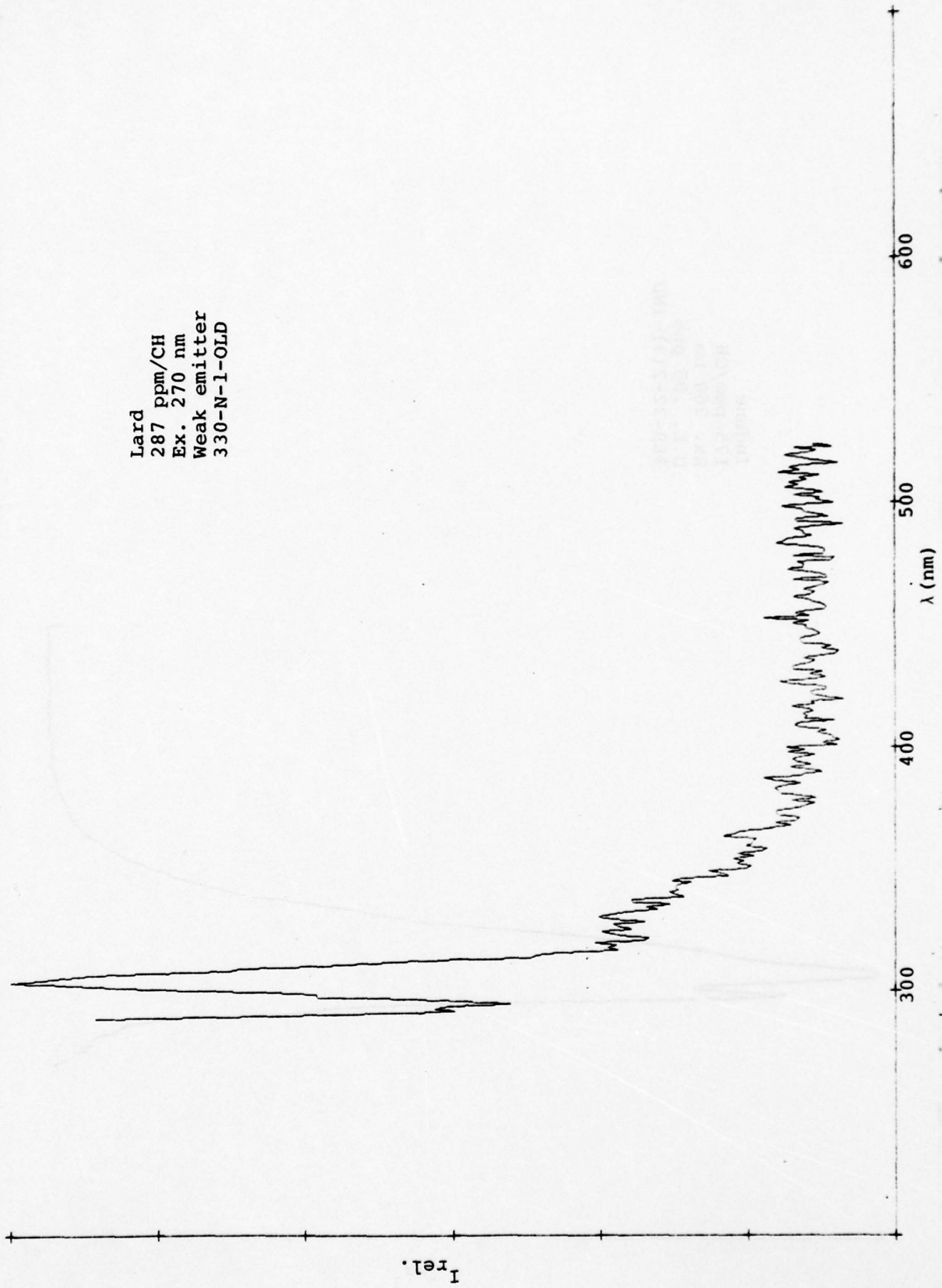
Hydroquinone
1.1 ppm/H₂O
Ex. 290 nm
D.L. 0.03 ppm
326-38-1(1)-HDQ



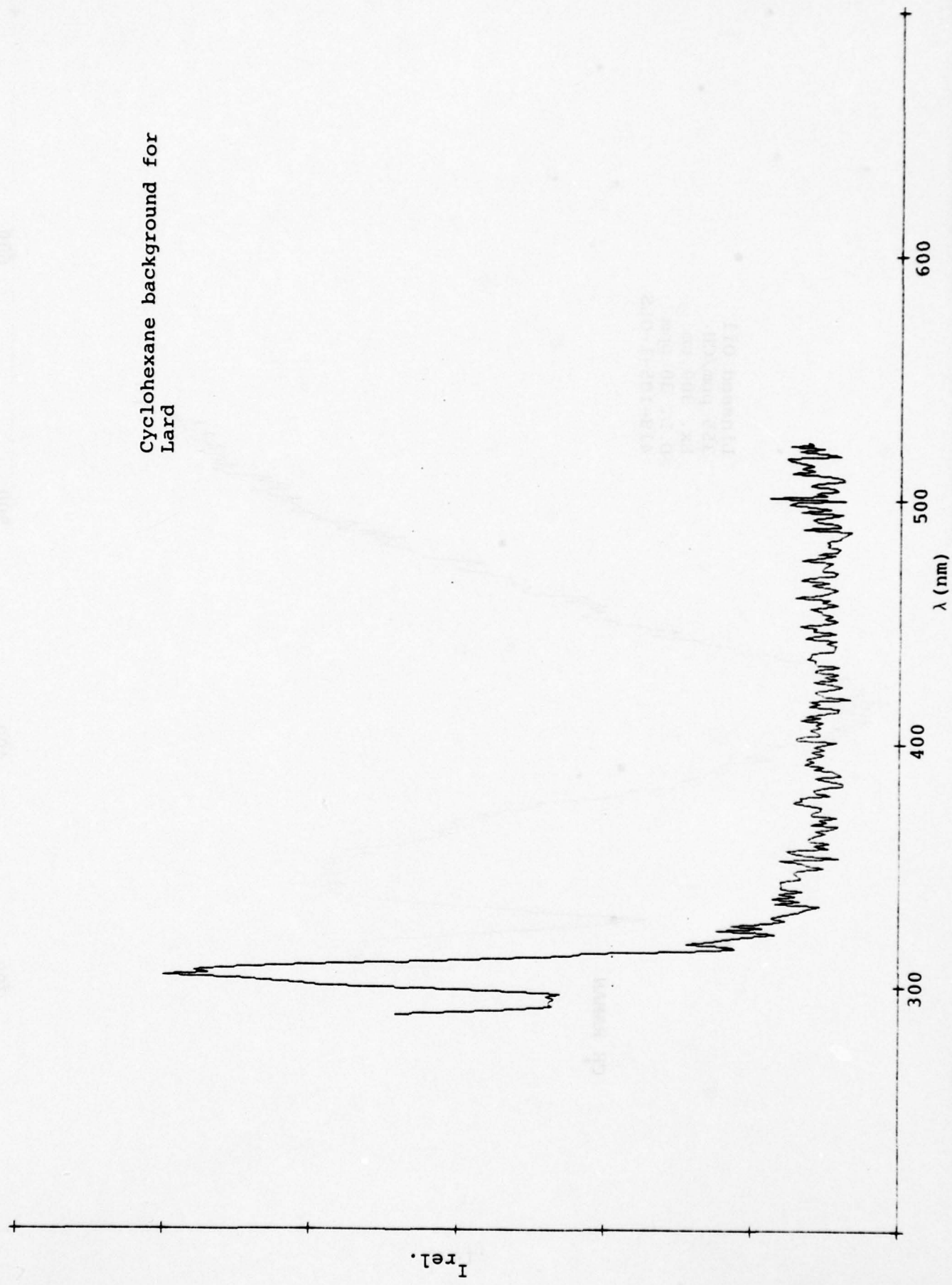
Indene
175 ppm/CH
Ex. 260 nm
D.L. .05 ppm
369-32-2(3)-IND



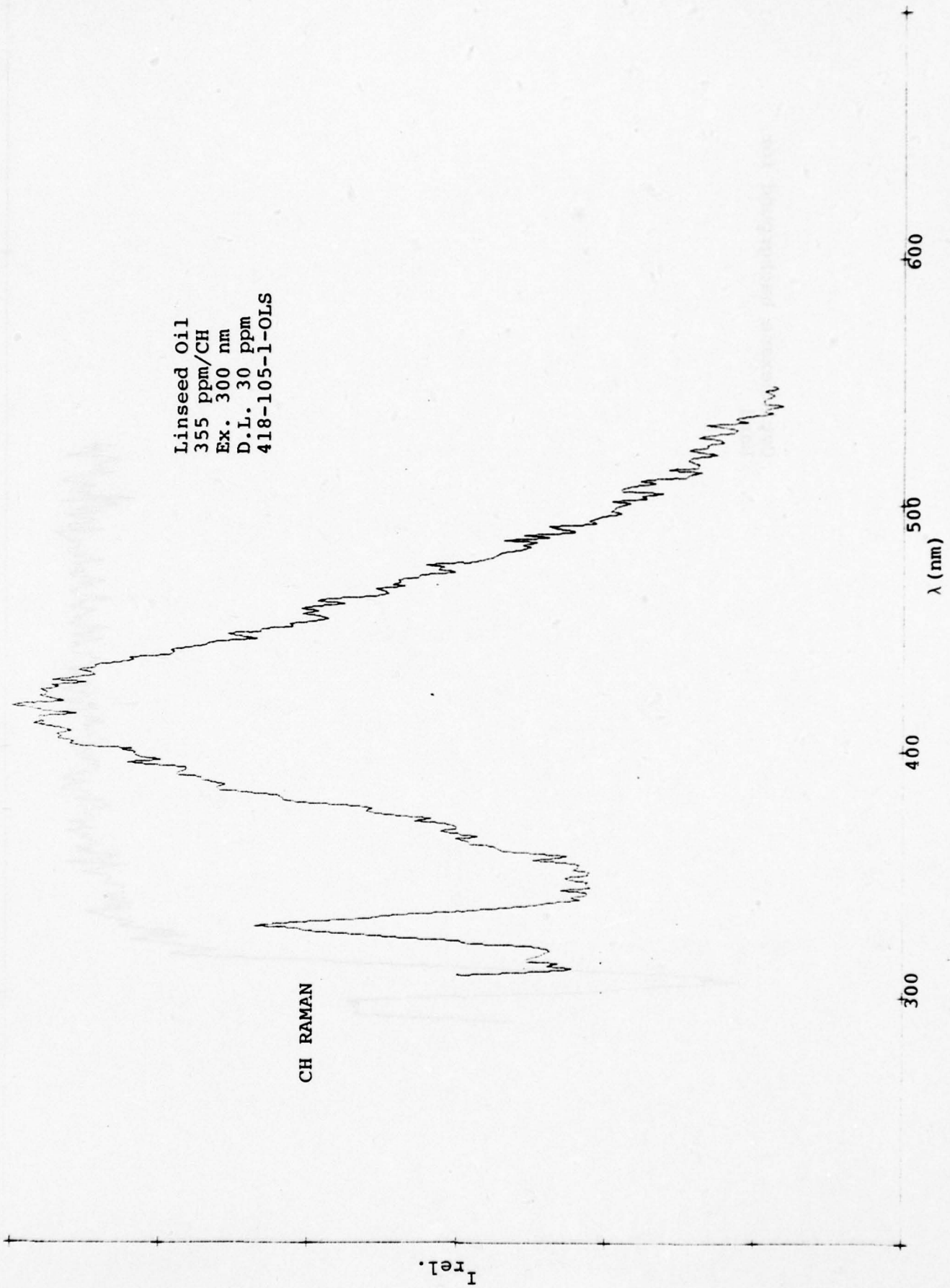
Lard
287 ppm/CH
Ex. 270 nm
Weak emitter
330-N-1-OLD



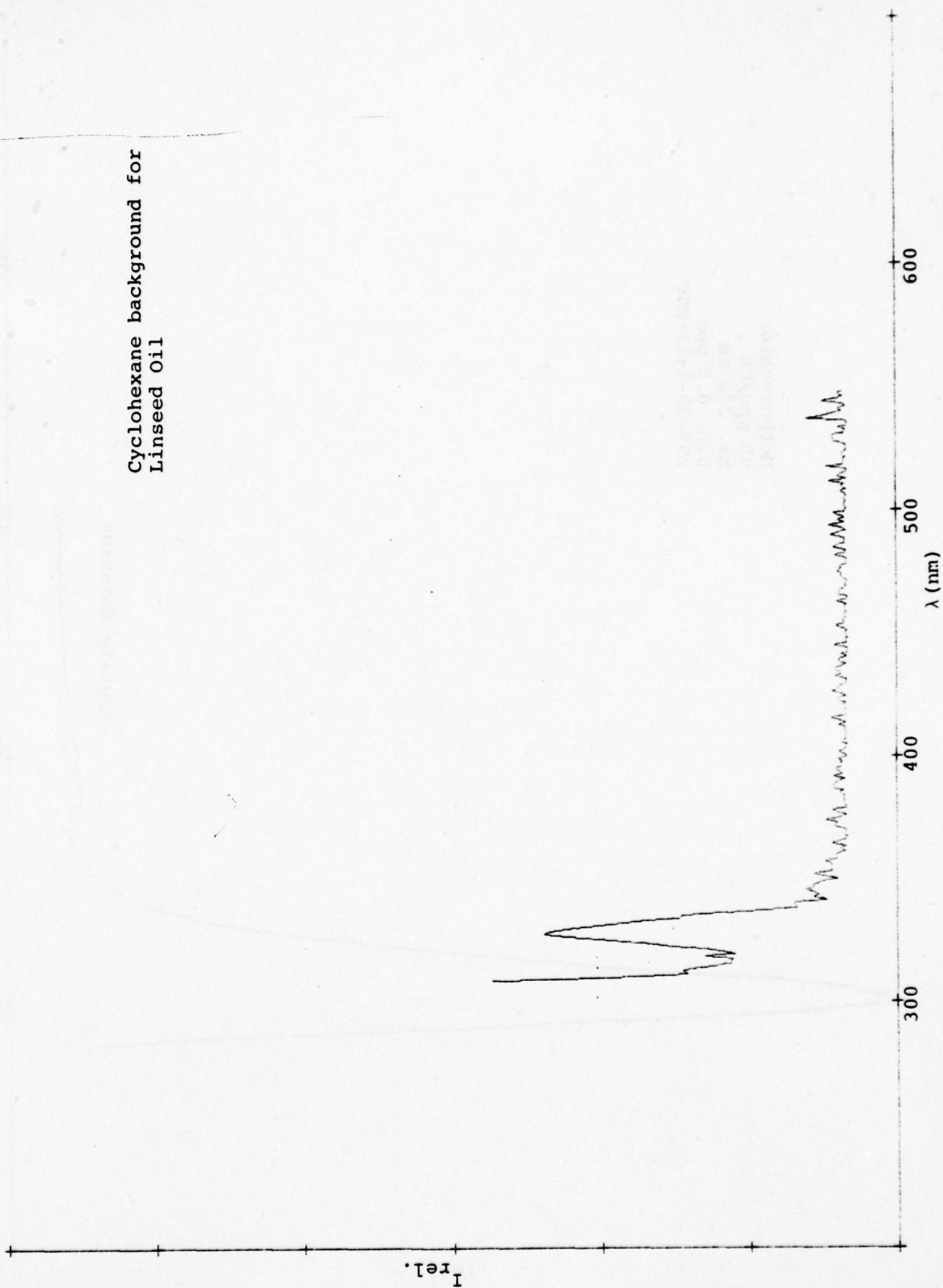
Cyclohexane background for
Lard



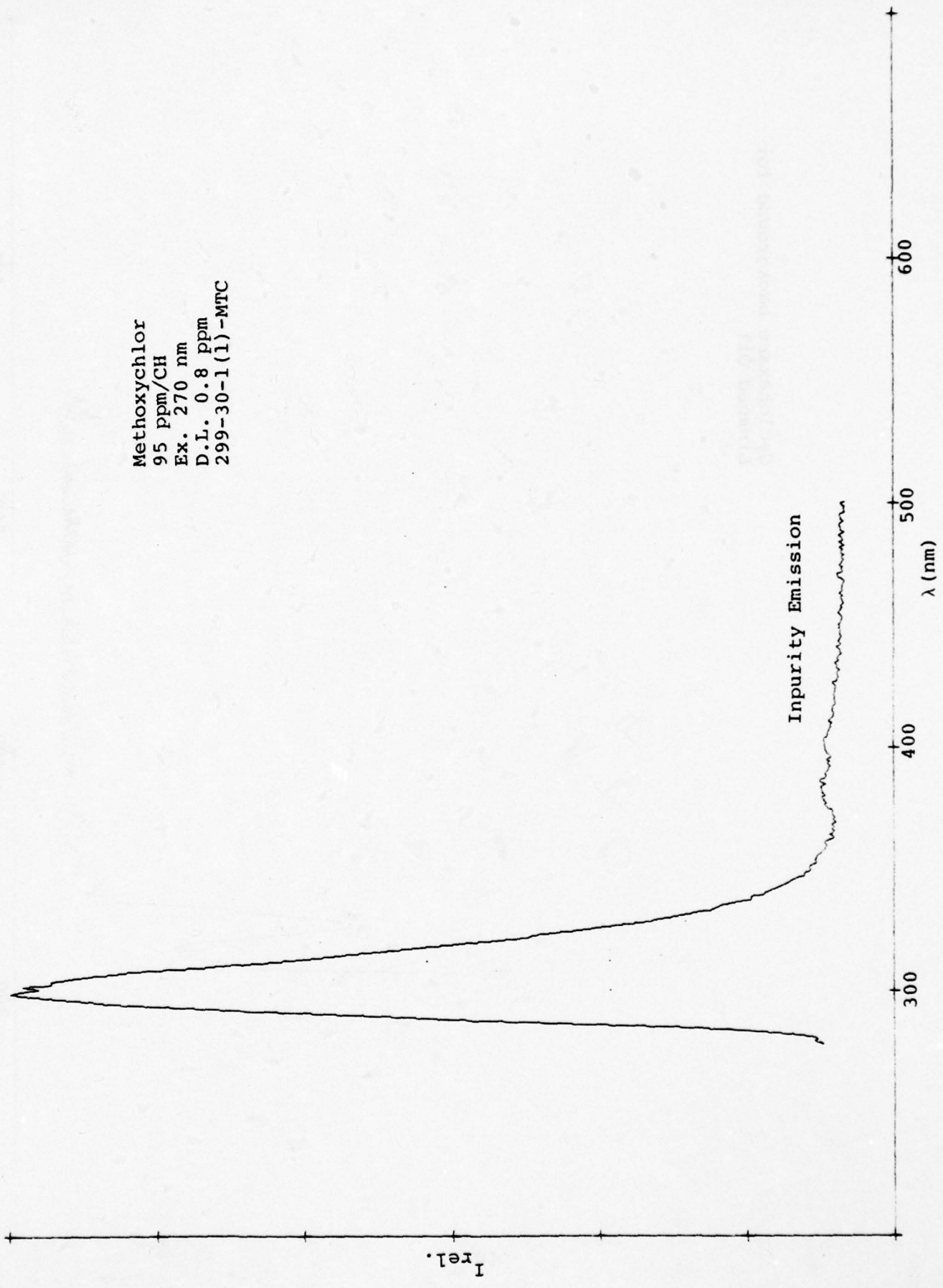
Linseed Oil
355 ppm/CH
Ex. 300 nm
D.L. 30 ppm
418-105-1-OLS



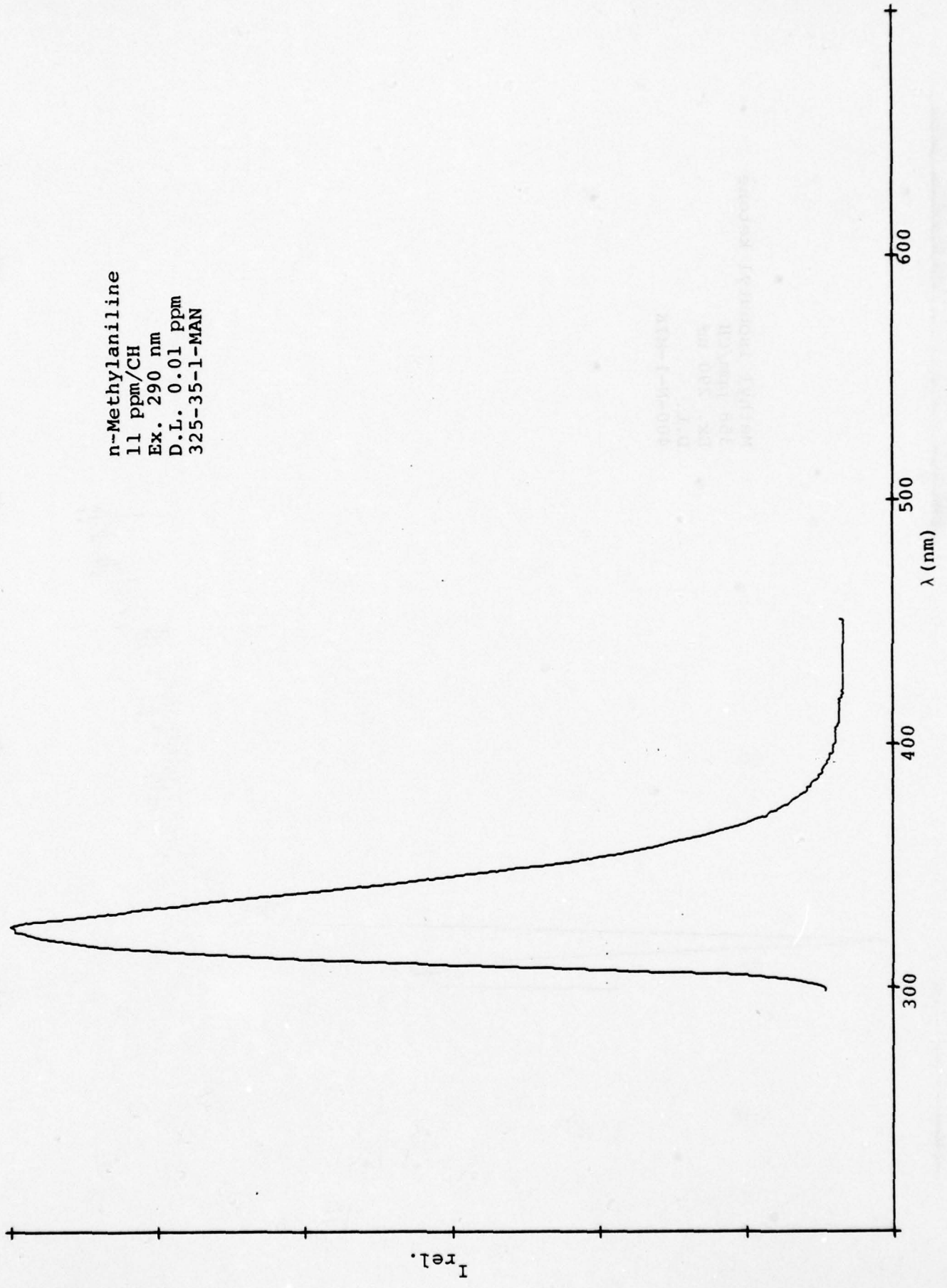
Cyclohexane background for
Linseed Oil



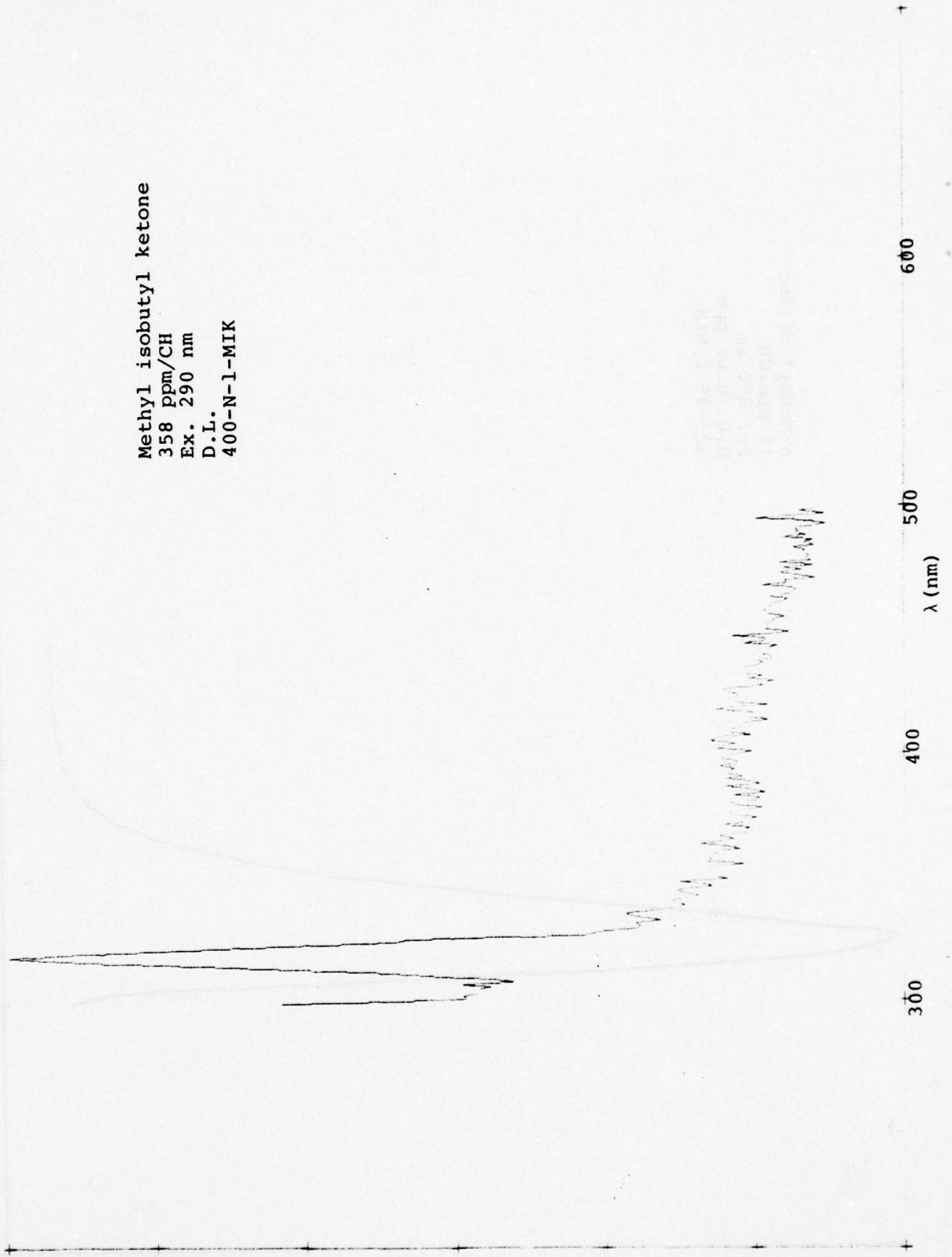
Methoxychlor
95 ppm/CH
Ex. 270 nm
D.L. 0.8 ppm
299-30-1 (1)-MTC



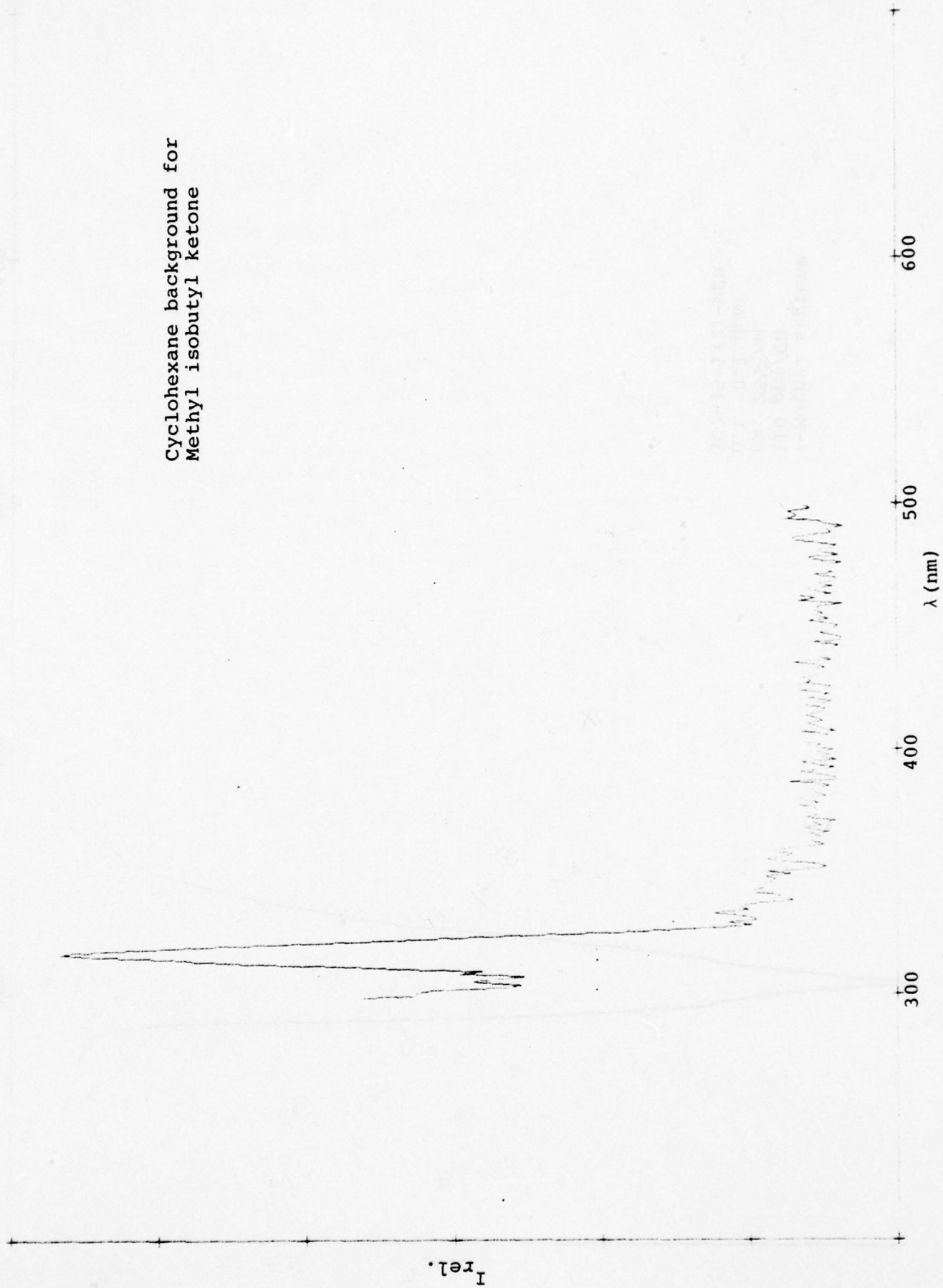
n-Methylaniline
11 ppm/CH
Ex. 290 nm
D.L. 0.01 ppm
325-35-1-MAN



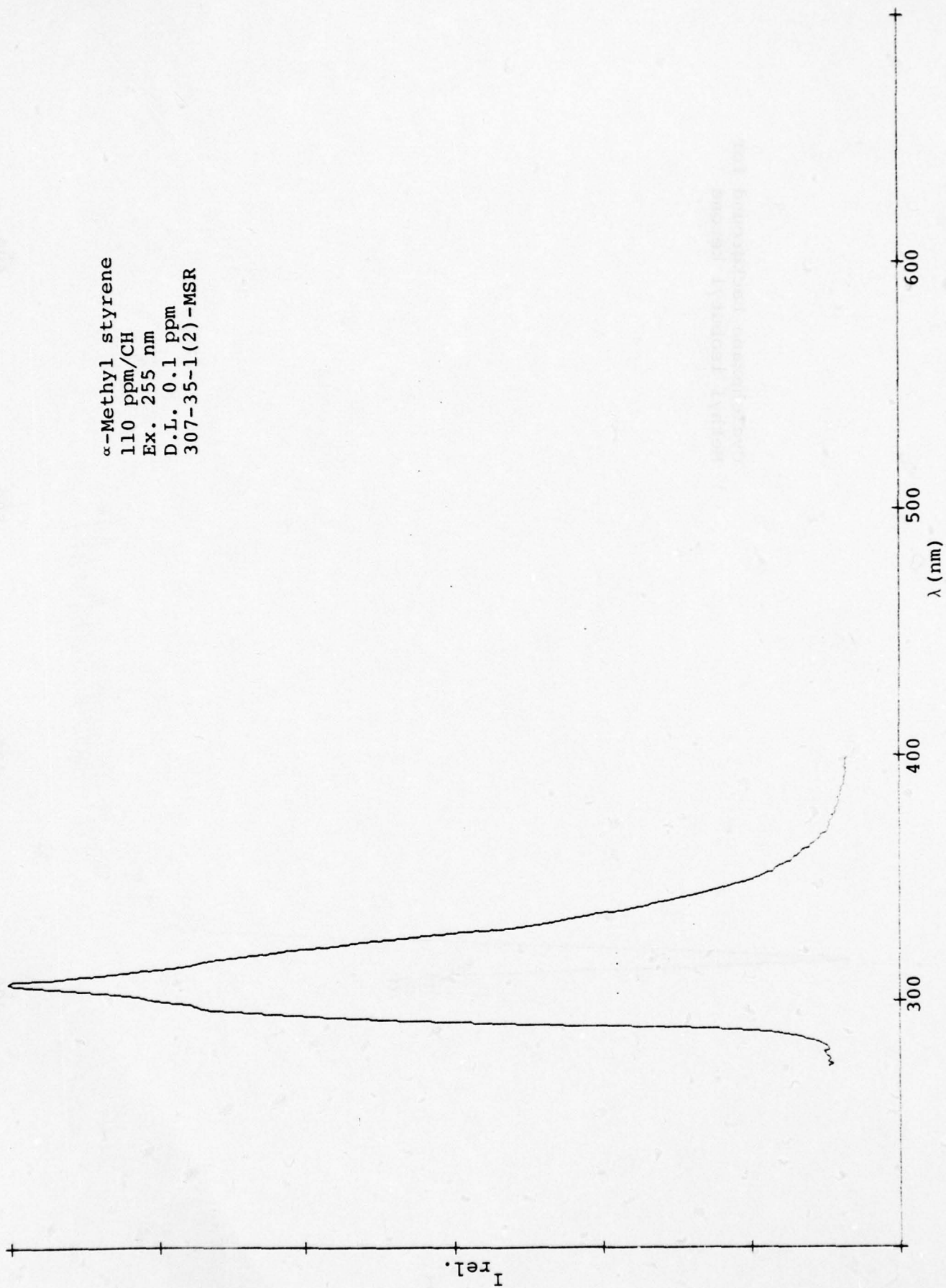
Methyl isobutyl ketone
358 ppm/CH
Ex. 290 nm
D.L.
400-N-1-MIK



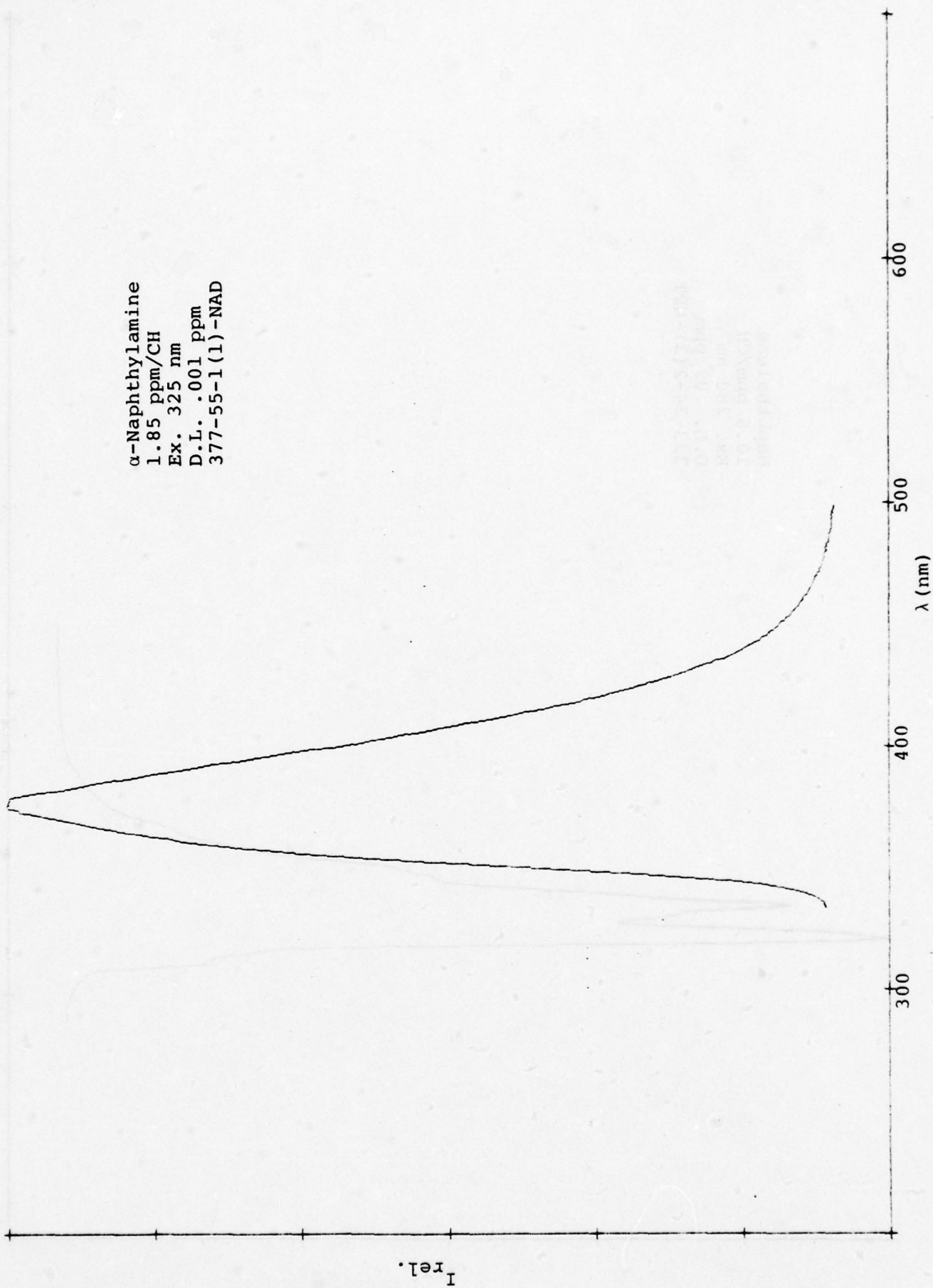
Cyclohexane background for
Methyl isobutyl ketone



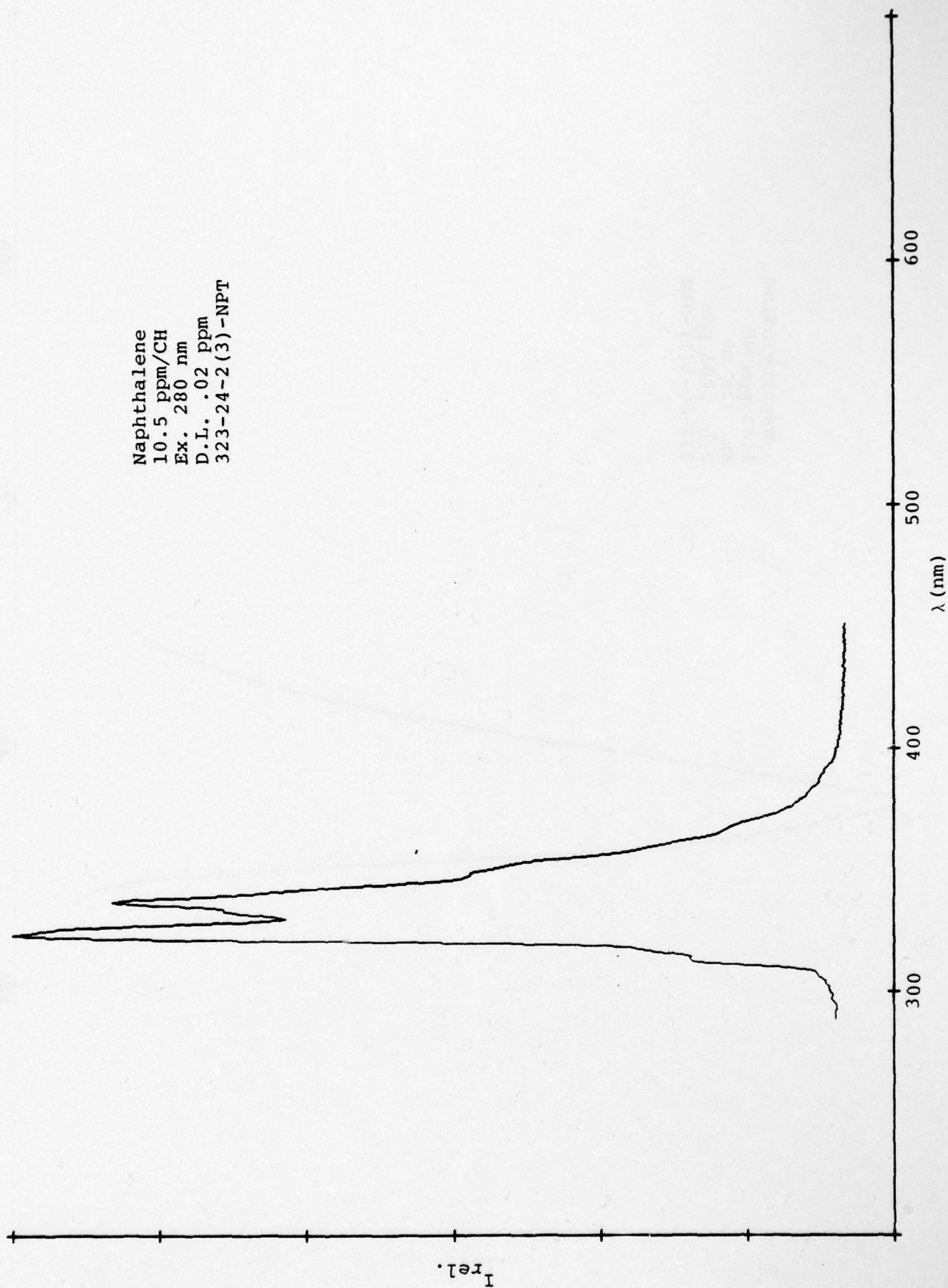
α -Methyl styrene
110 ppm/CH
Ex. 255 nm
D.L. 0.1 ppm
307-35-1(2)-MSR



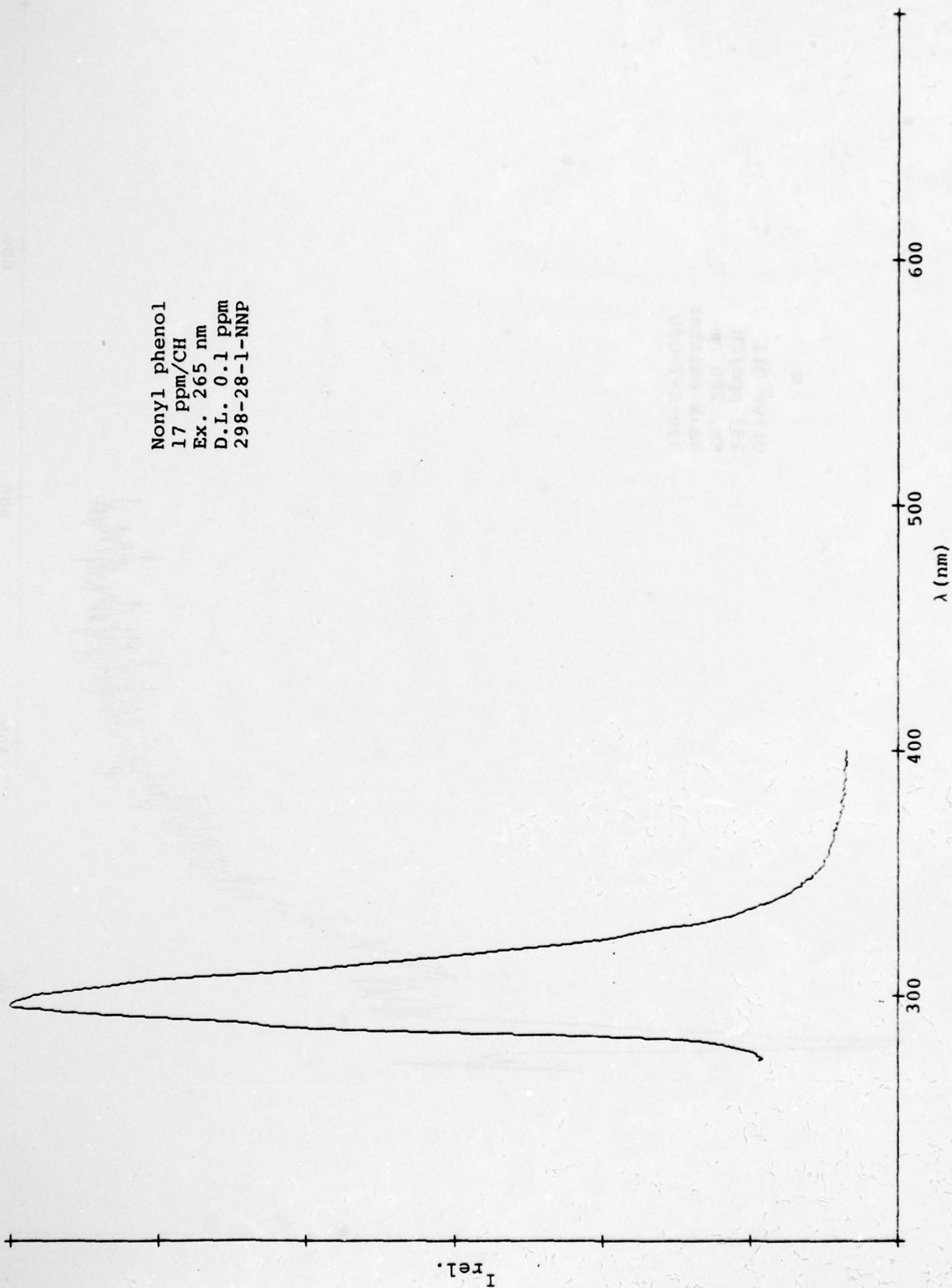
α -Naphthylamine
1.85 ppm/CH
Ex. 325 nm
D.L. .001 ppm
377-55-1(1)-NAD



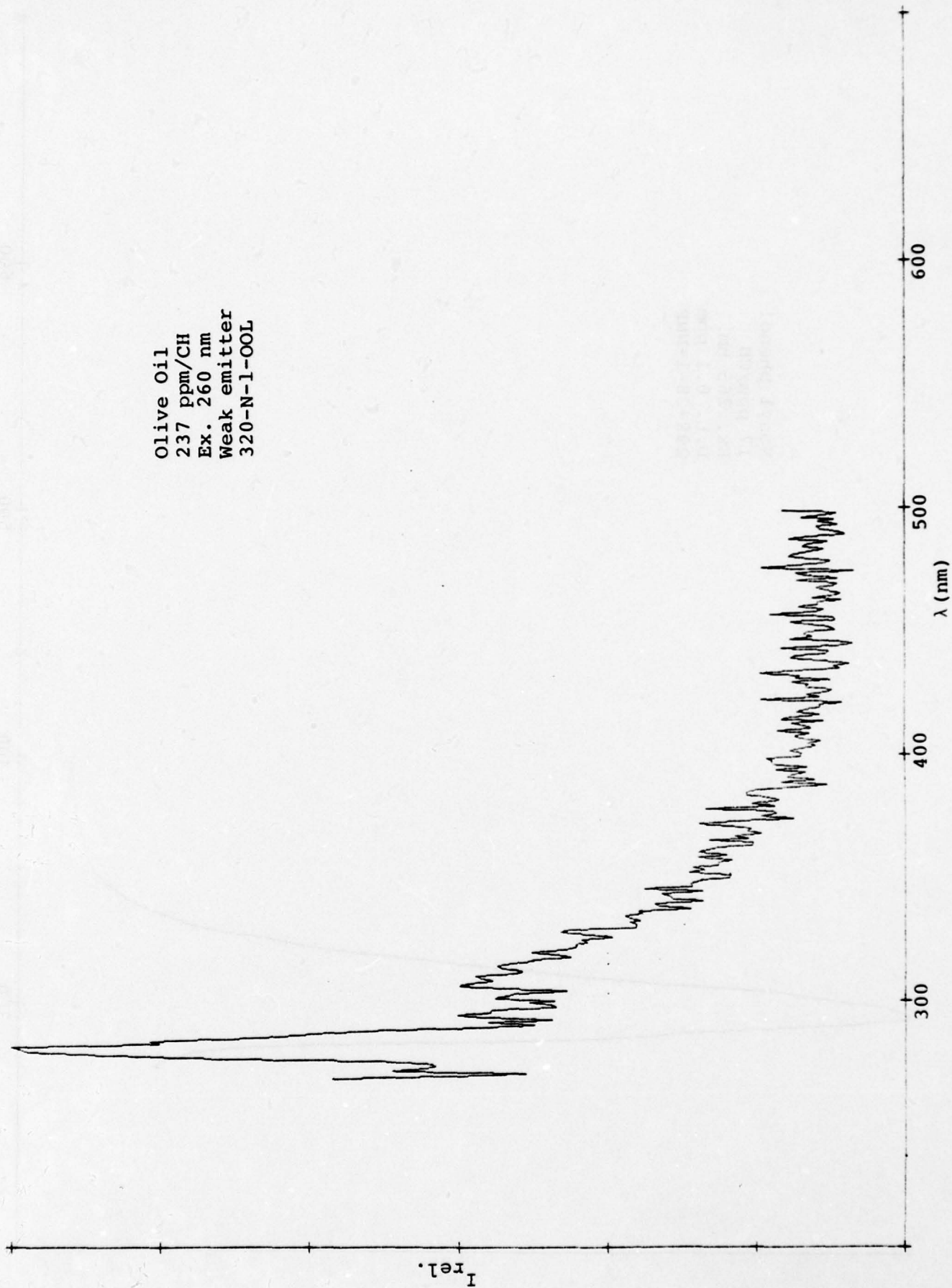
Naphthalene
10.5 ppm/CH
Ex. 280 nm
D.L. .02 ppm
323-24-2 (3) -NPT



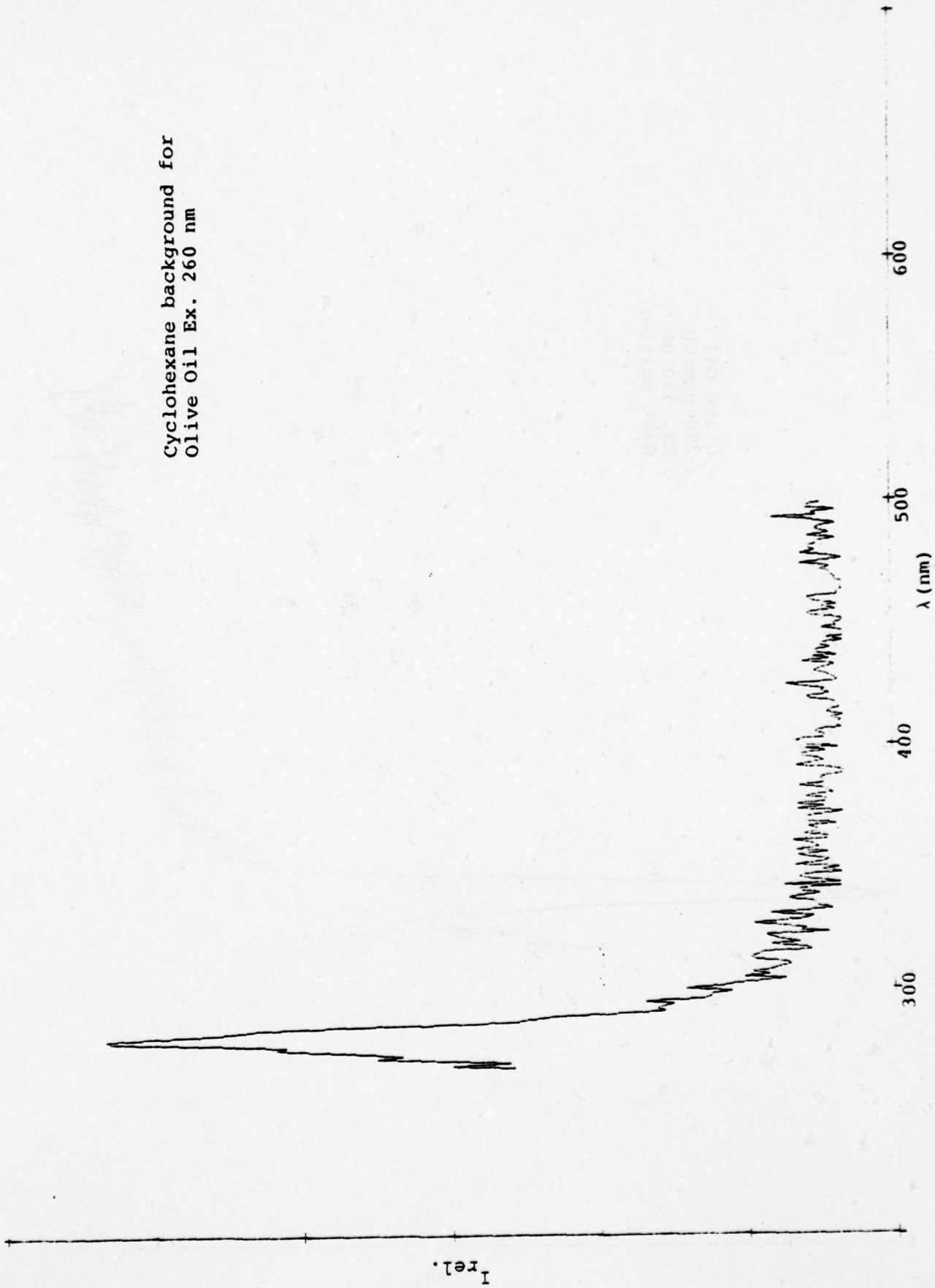
Nonyl phenol
17 ppm/CH
Ex. 265 nm
D.L. 0.1 ppm
298-28-1-NNP



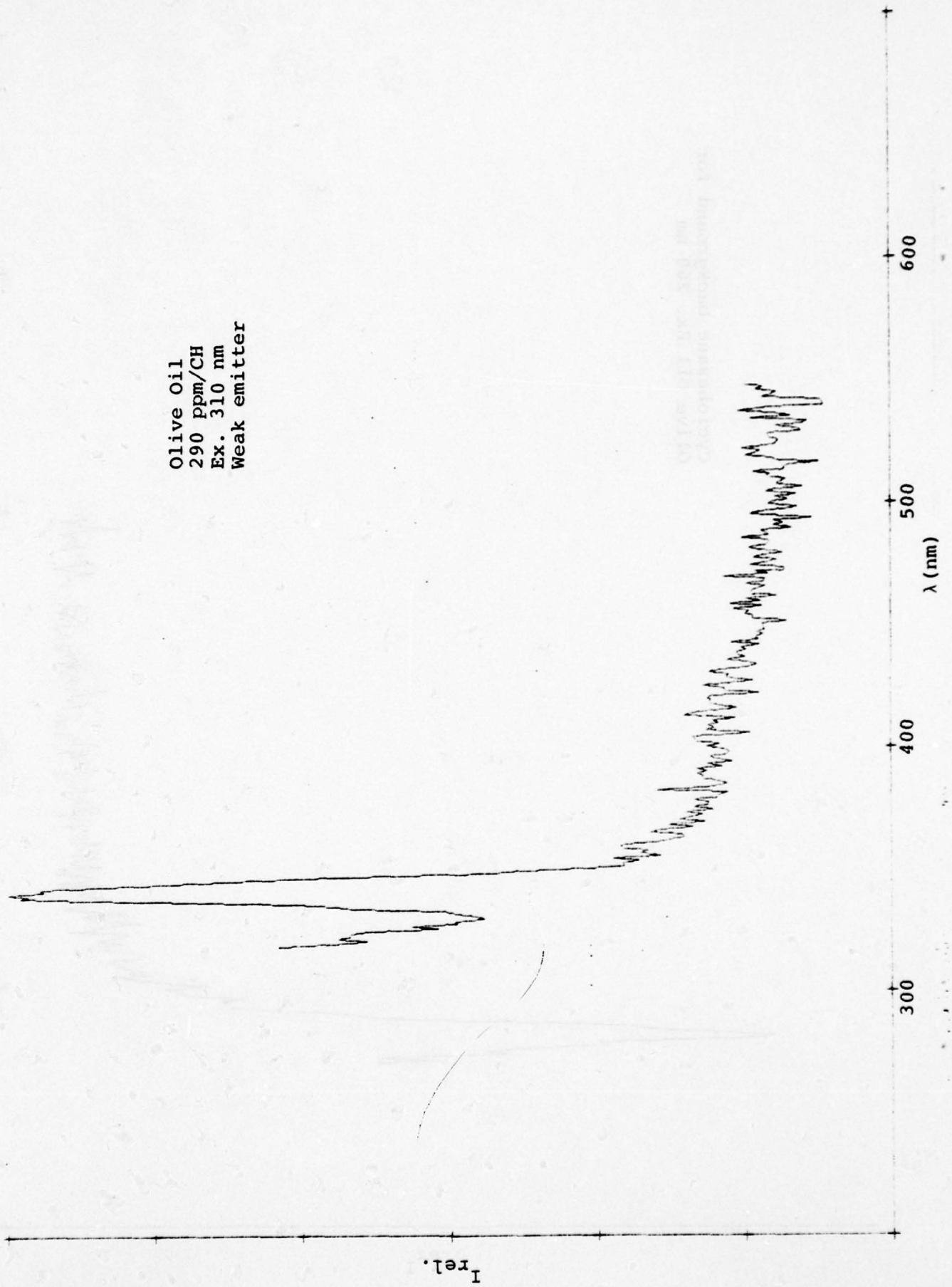
Olive Oil
237 ppm/CH
Ex. 260 nm
Weak emitter
320-N-1-OOL



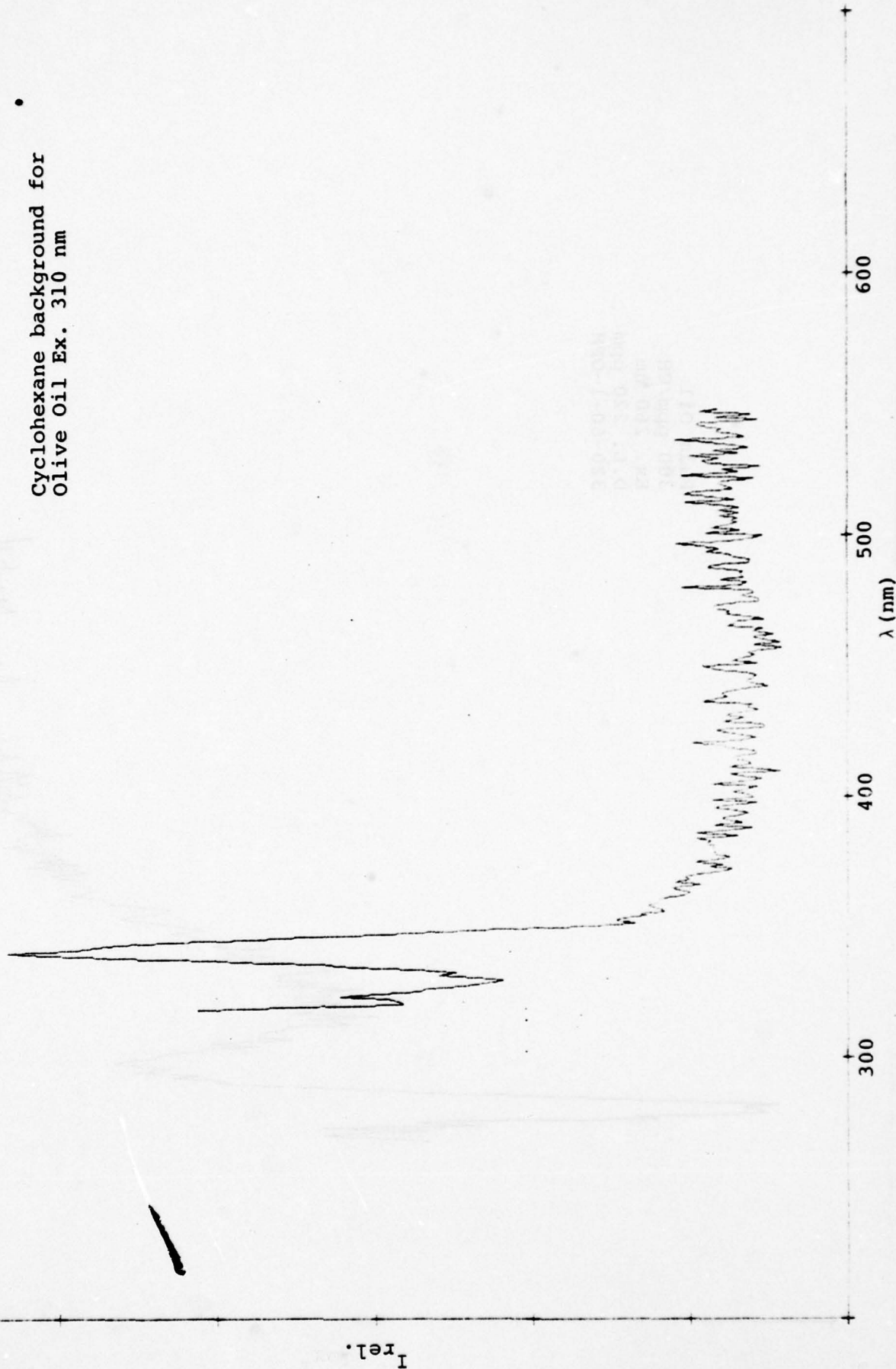
Cyclohexane background for
Olive Oil Ex. 260 nm



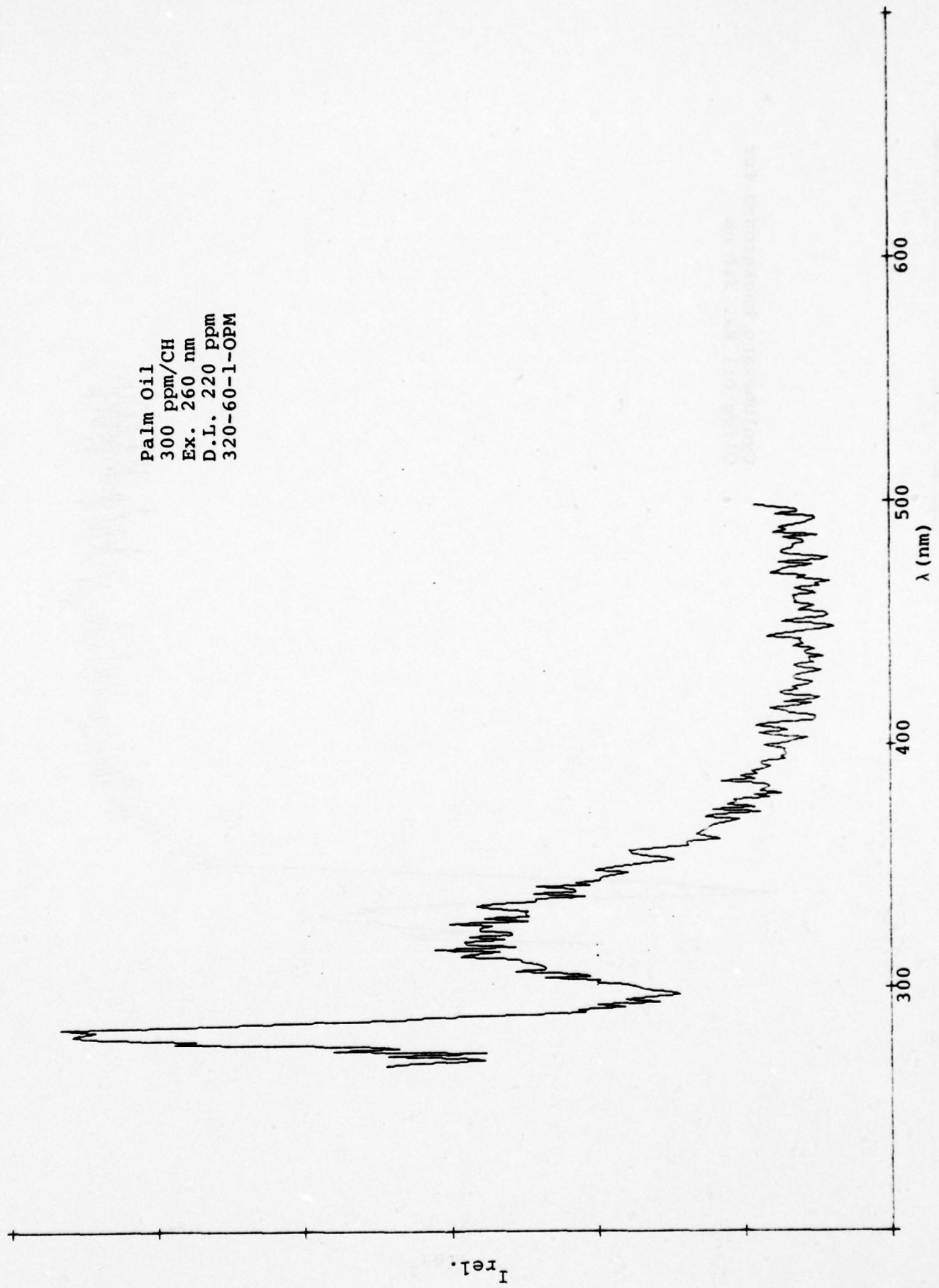
Olive Oil
290 ppm/CH
Ex. 310 nm
Weak emitter



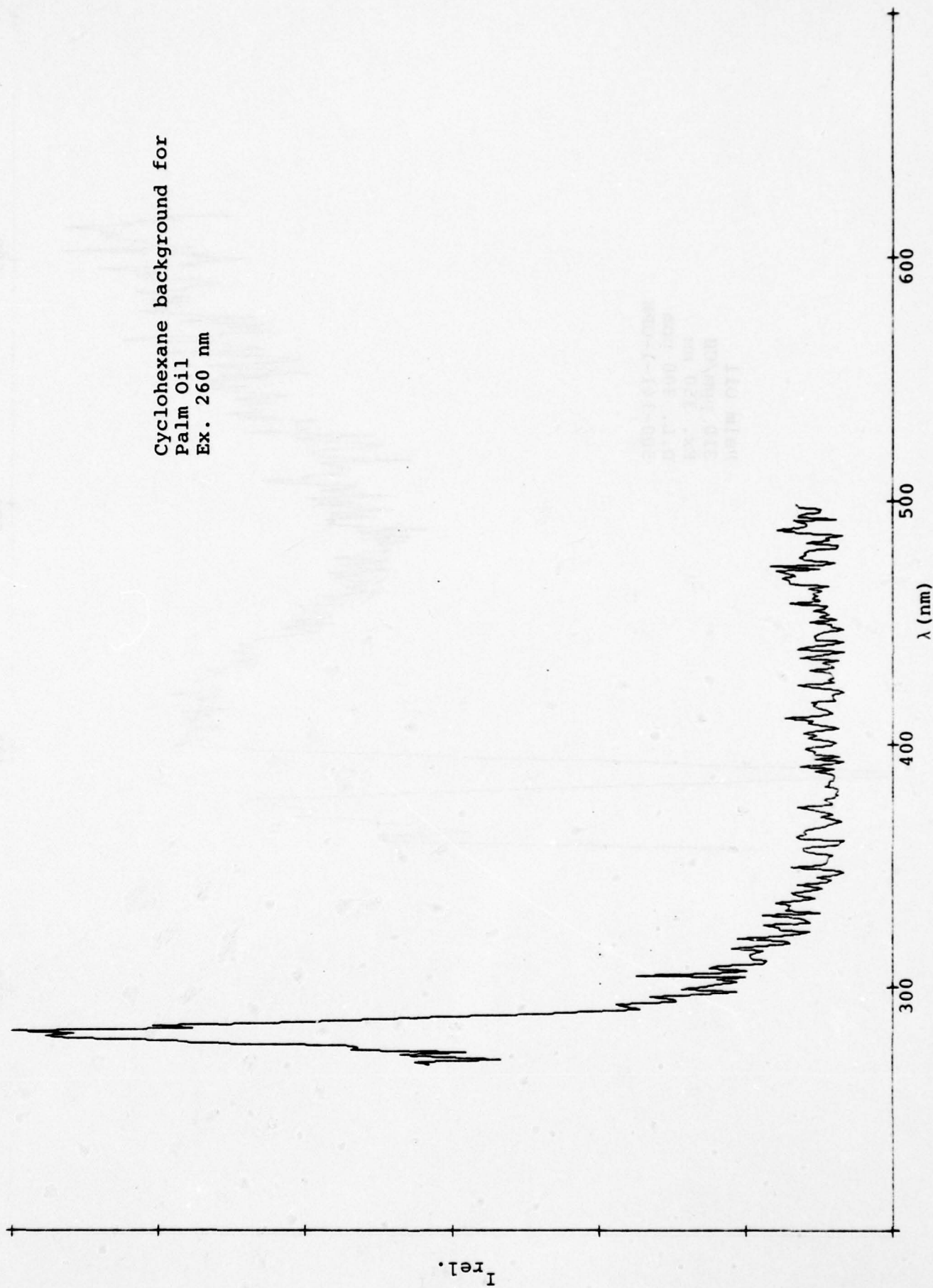
Cyclohexane background for
Olive Oil Ex. 310 nm



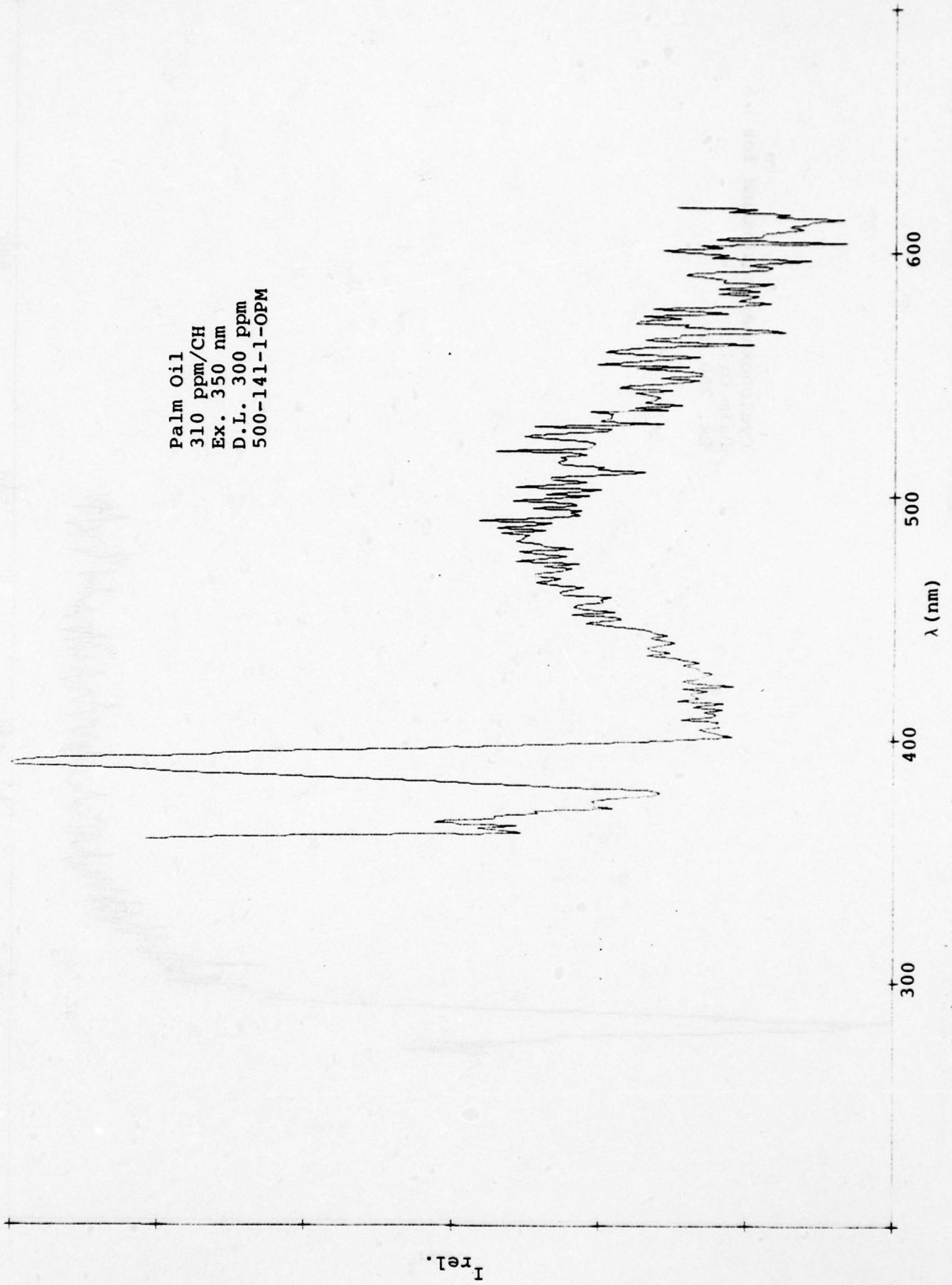
Palm Oil
300 ppm/CH
Ex. 260 nm
D.L. 220 ppm
320-60-1-OPM



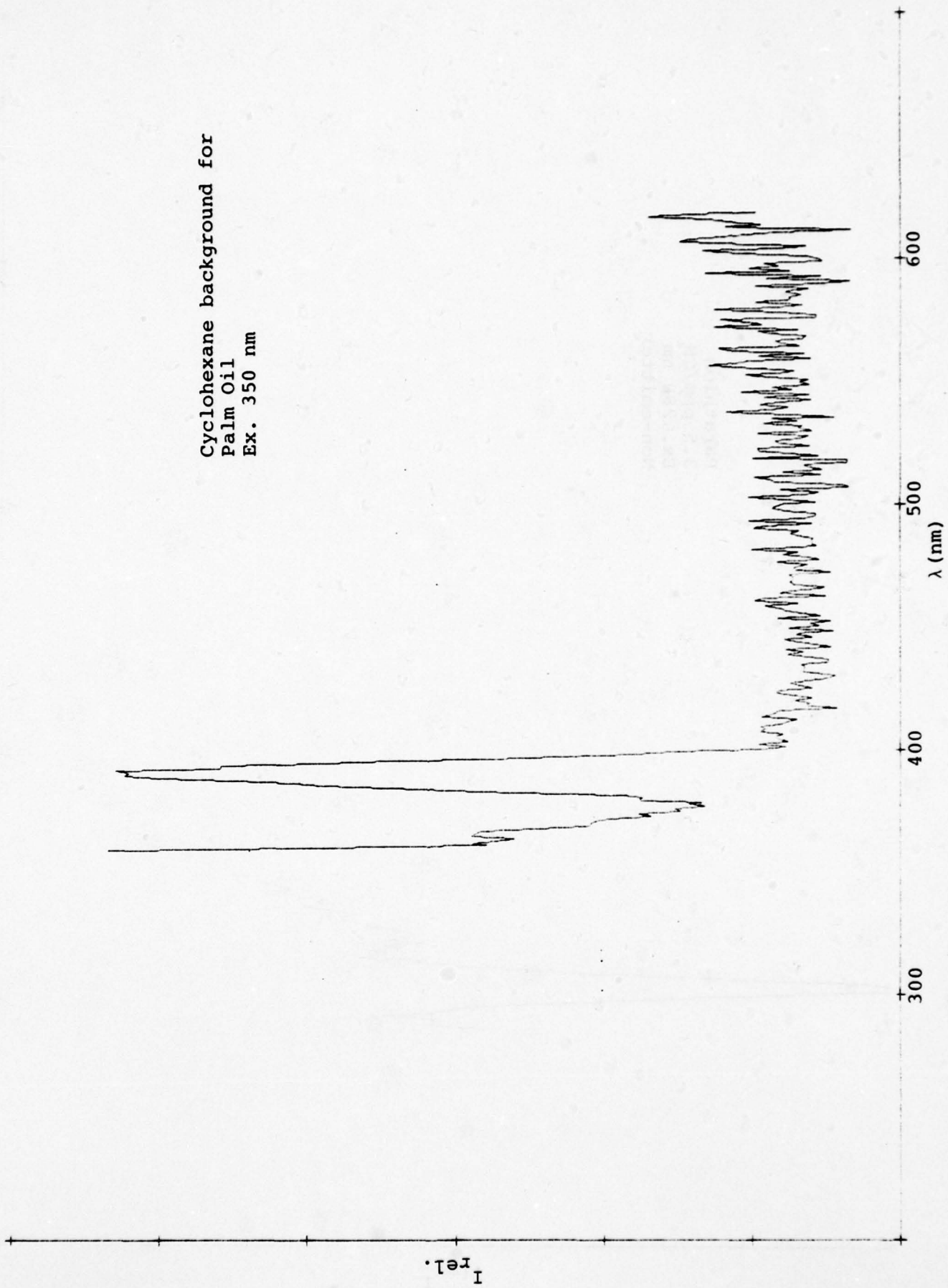
Cyclohexane background for
Palm Oil
Ex. 260 nm



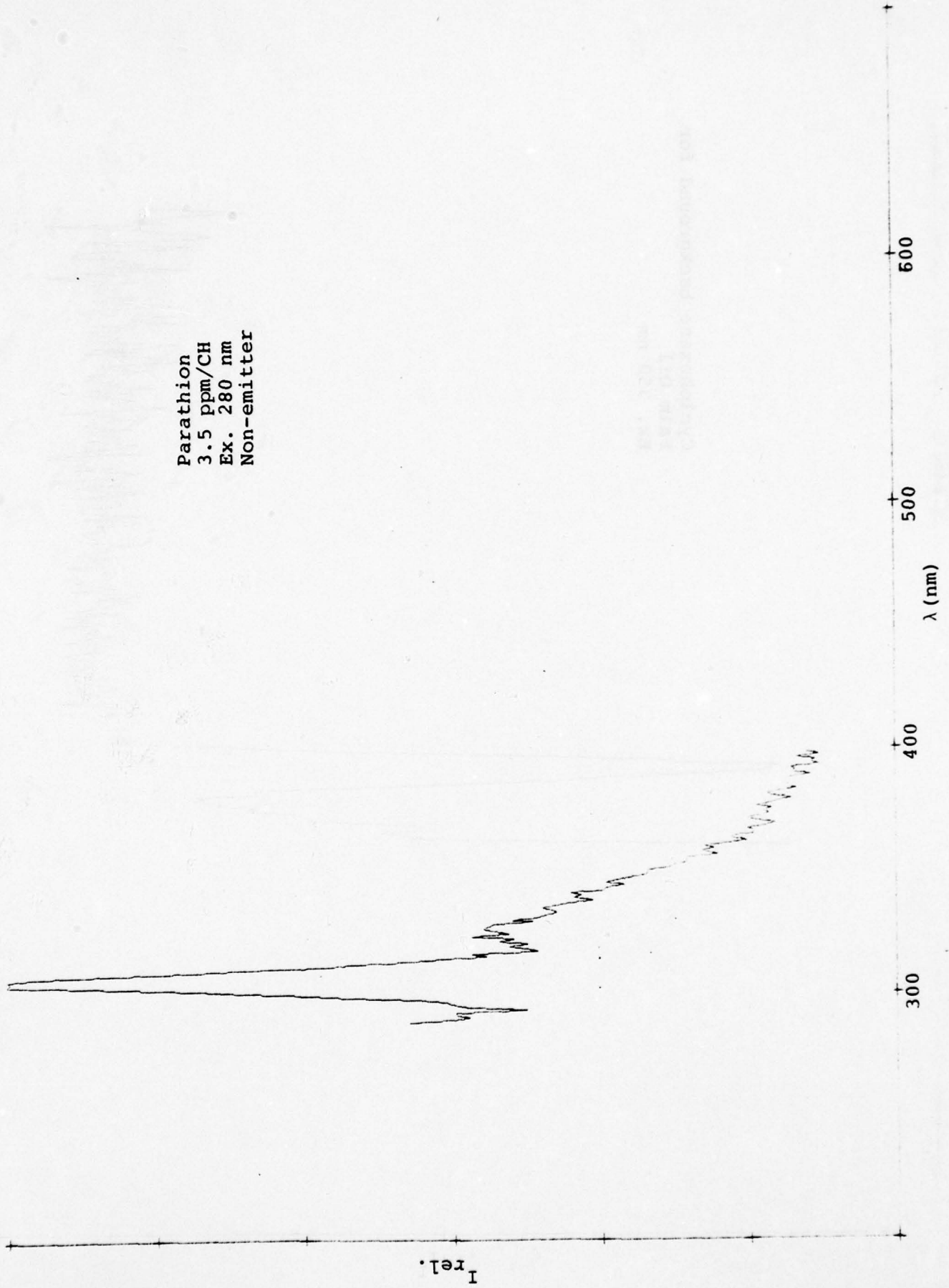
Palm Oil
310 ppm/CH
Ex. 350 nm
D.L. 300 ppm
500-141-1-OPM



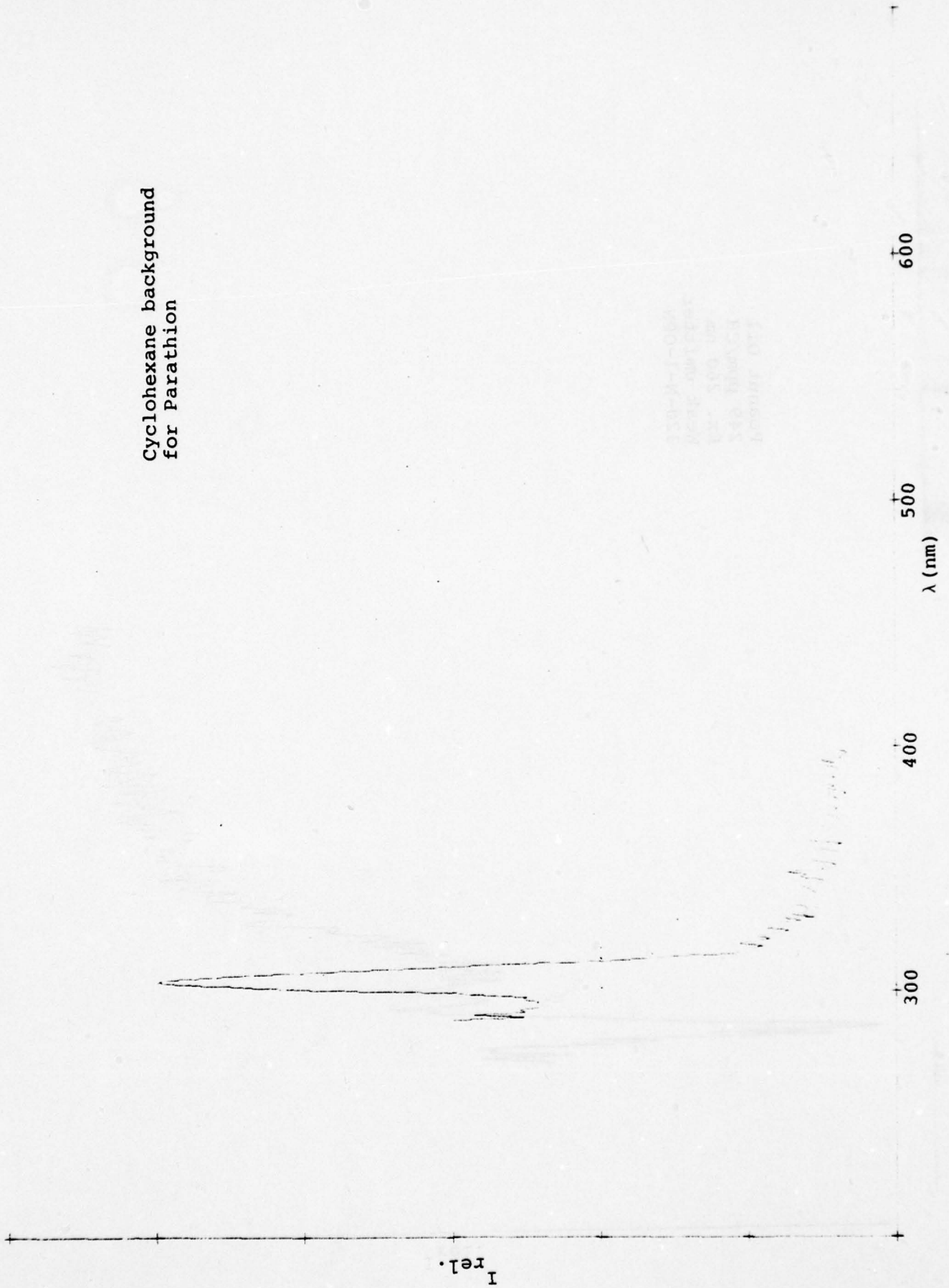
Cyclohexane background for
Palm Oil
Ex. 350 nm



Parathion
3.5 ppm/CH
Ex. 280 nm
Non-emitter

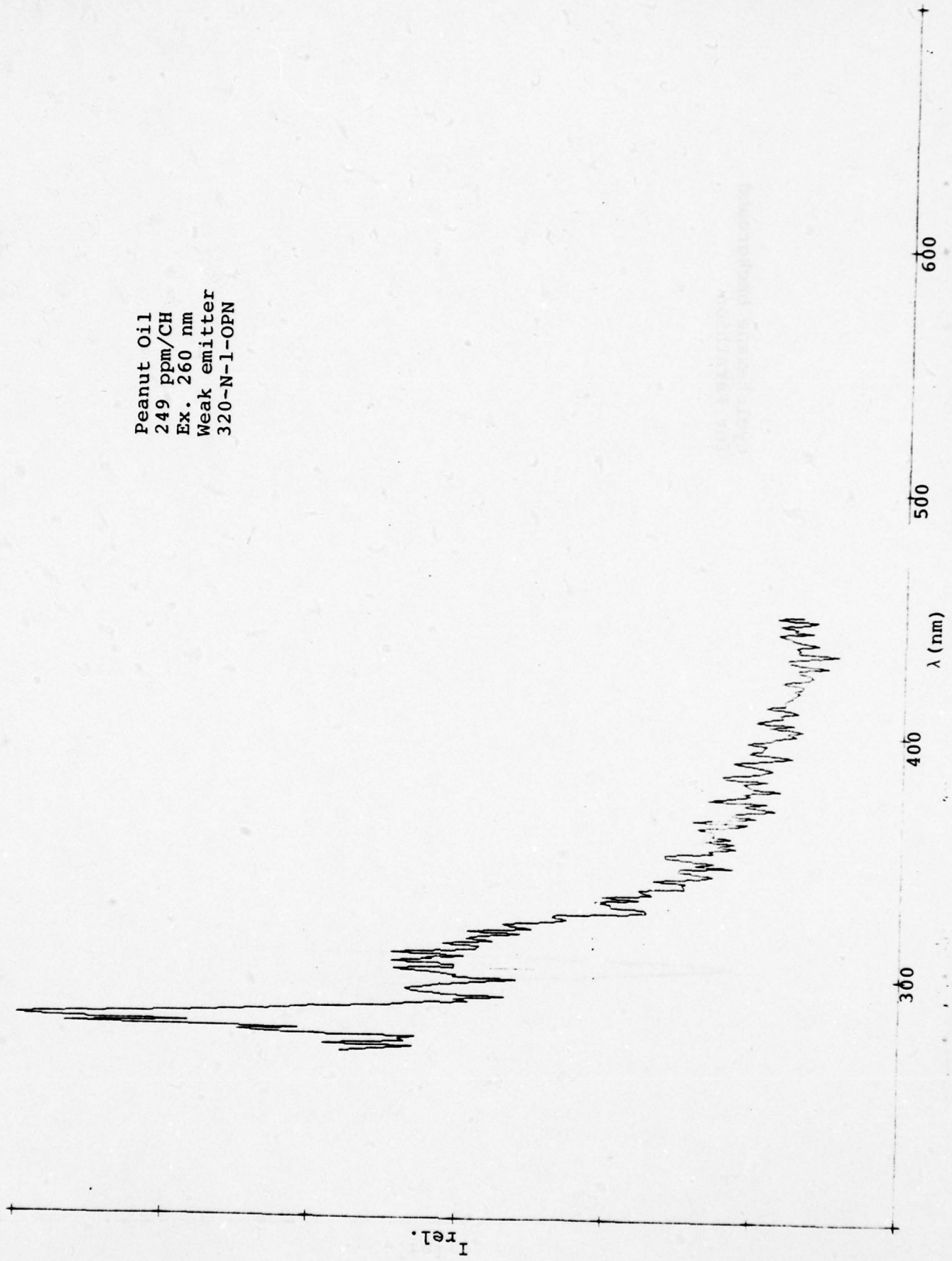


Cyclohexane background
for Parathion

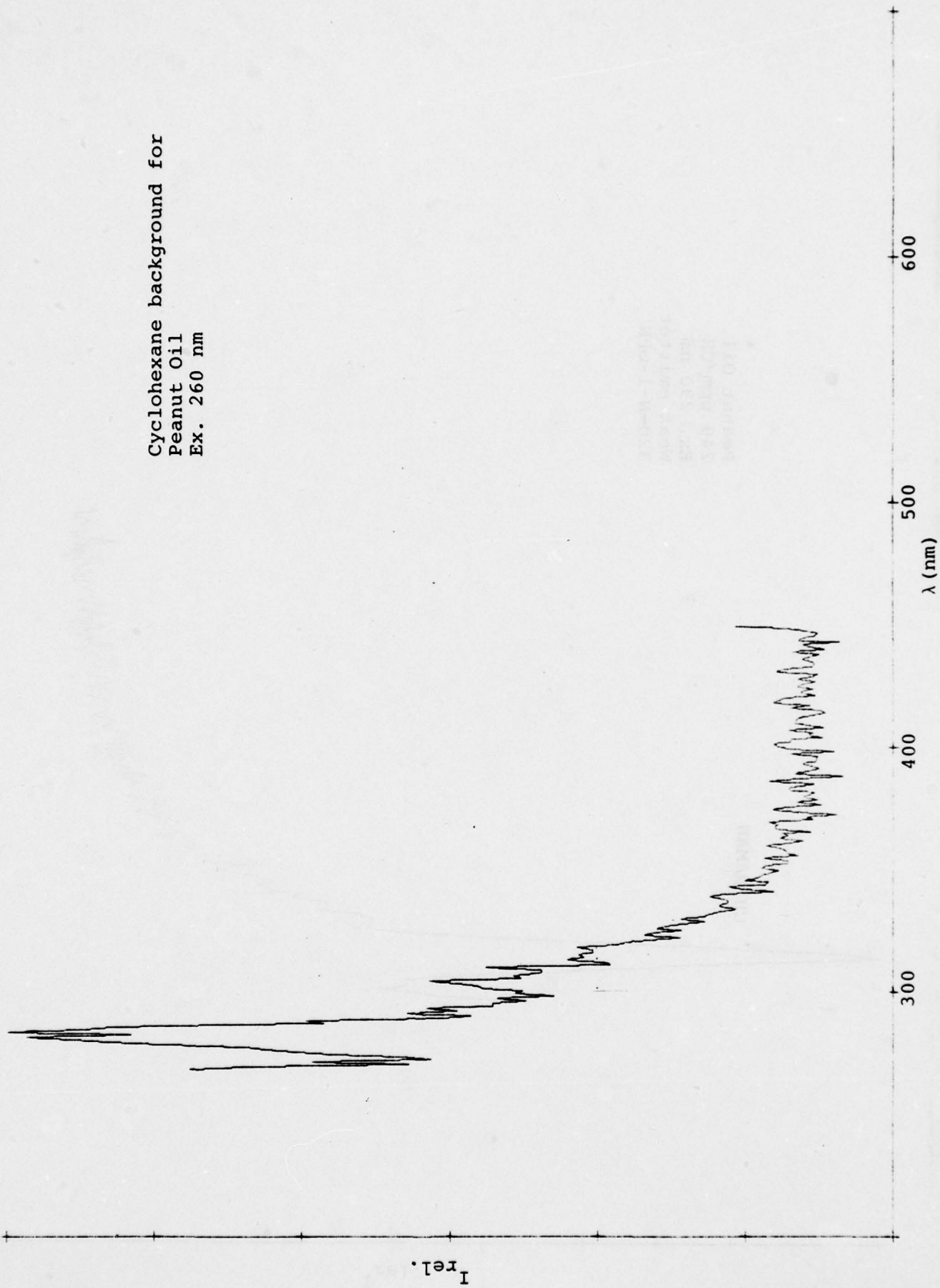


300-400-000
Temp. 20°C
1% 300 mg
300 mg
January 1957

Peanut Oil
249 ppm/CH
Ex. 260 nm
Weak emitter
320-N-1-OPN

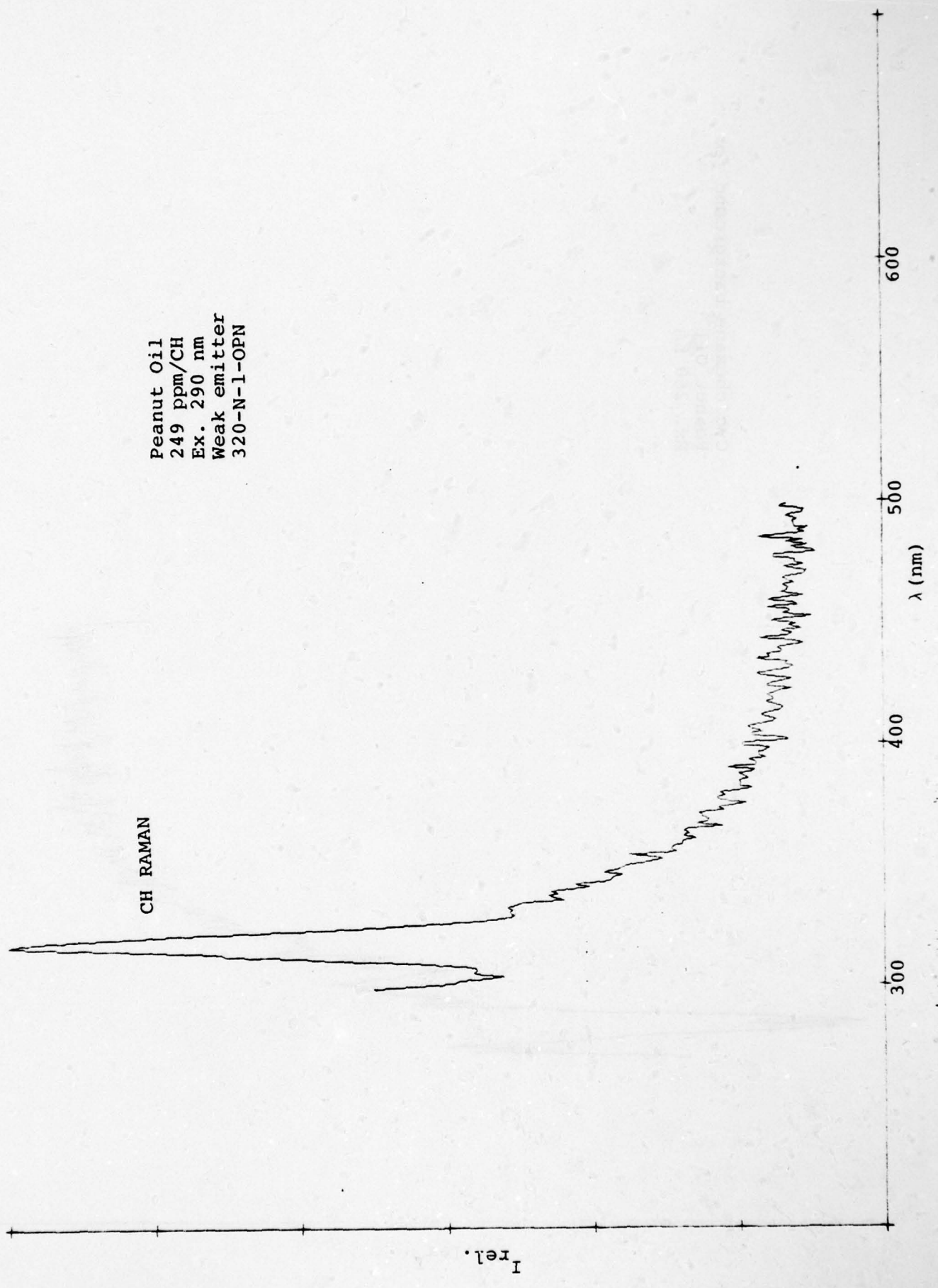


Cyclohexane background for
Peanut Oil
Ex. 260 nm

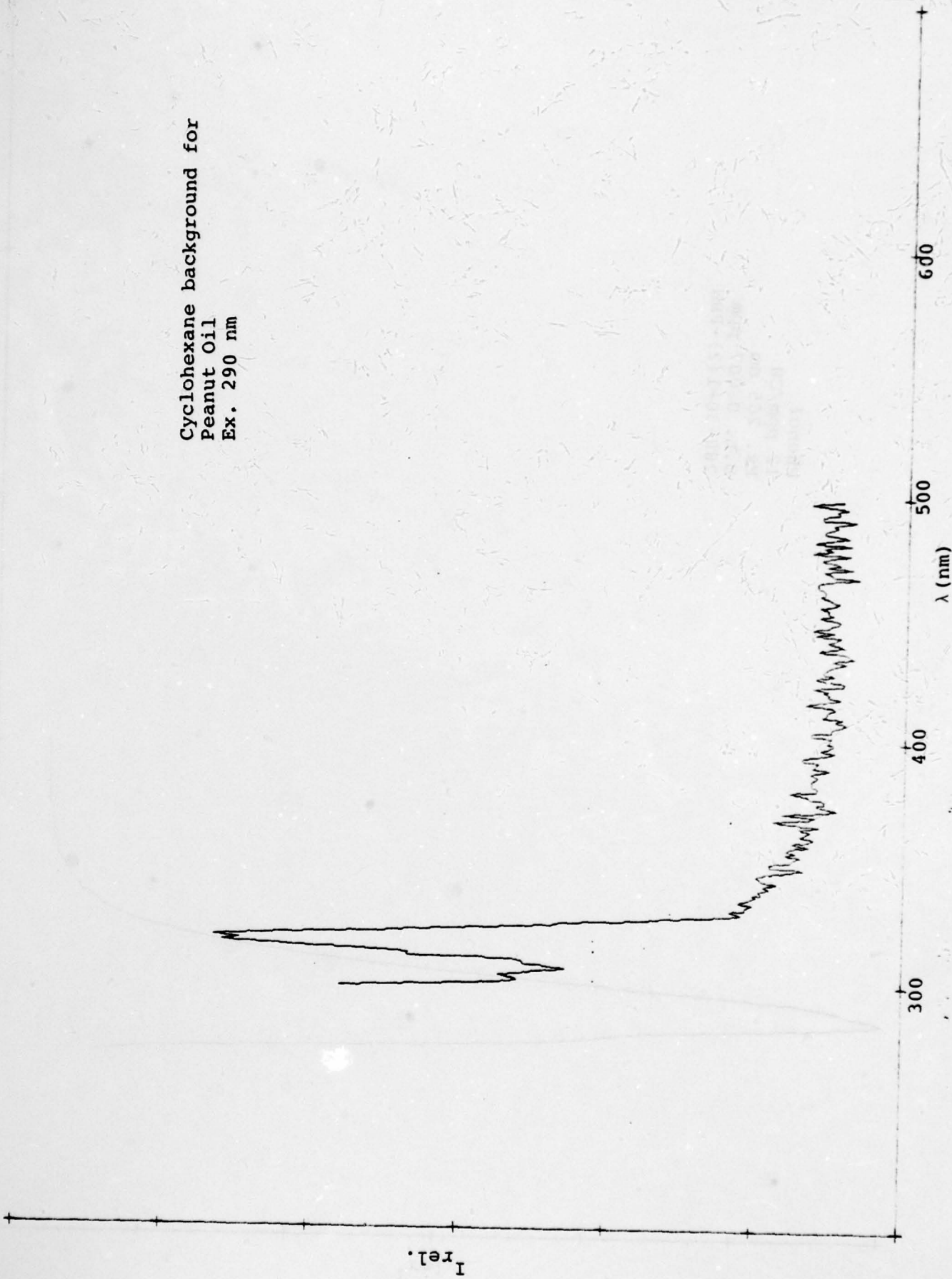


Peanut Oil
249 ppm/CH
Ex. 290 nm
Weak emitter
320-N-1-OPN

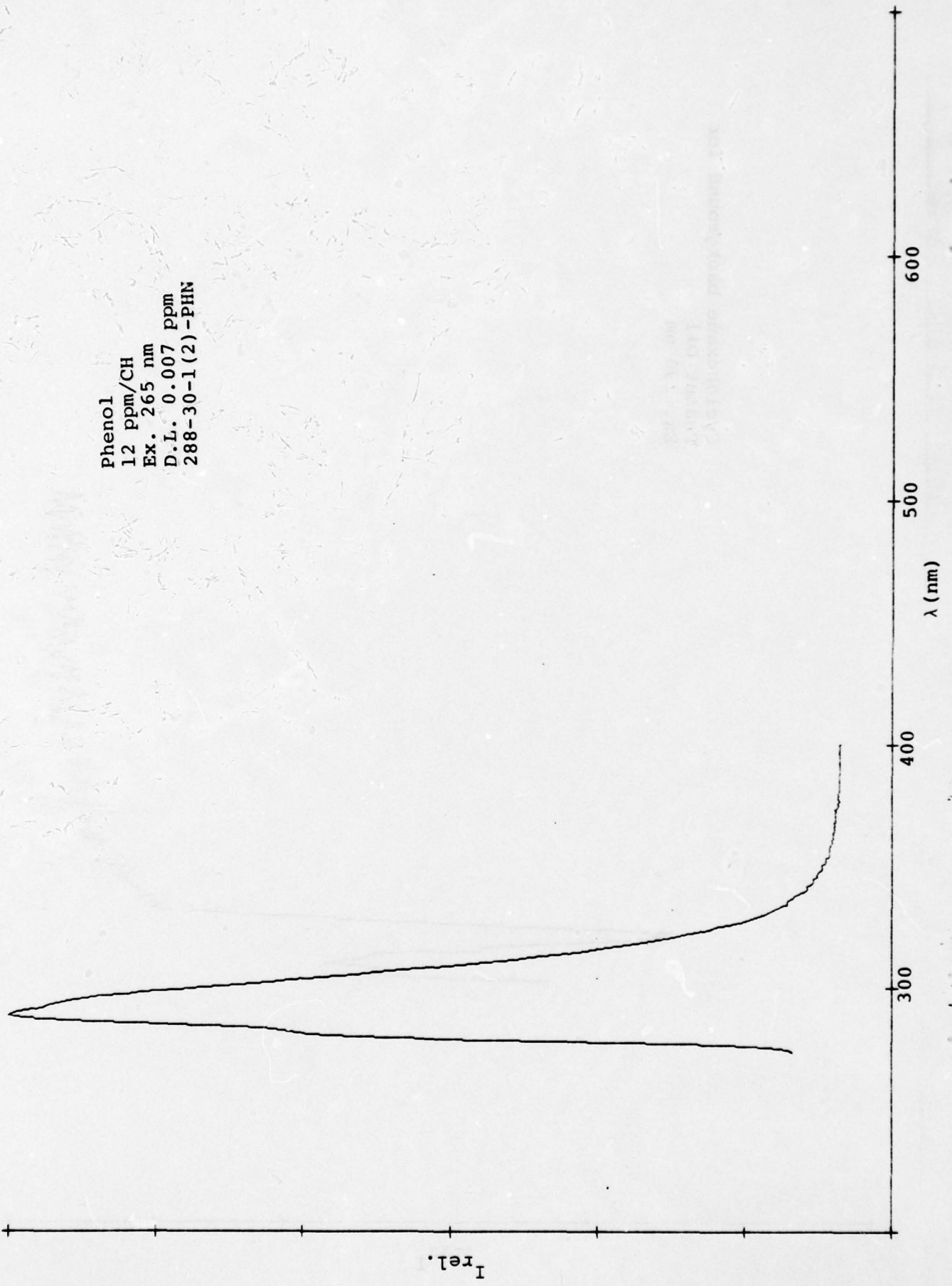
CH RAMAN



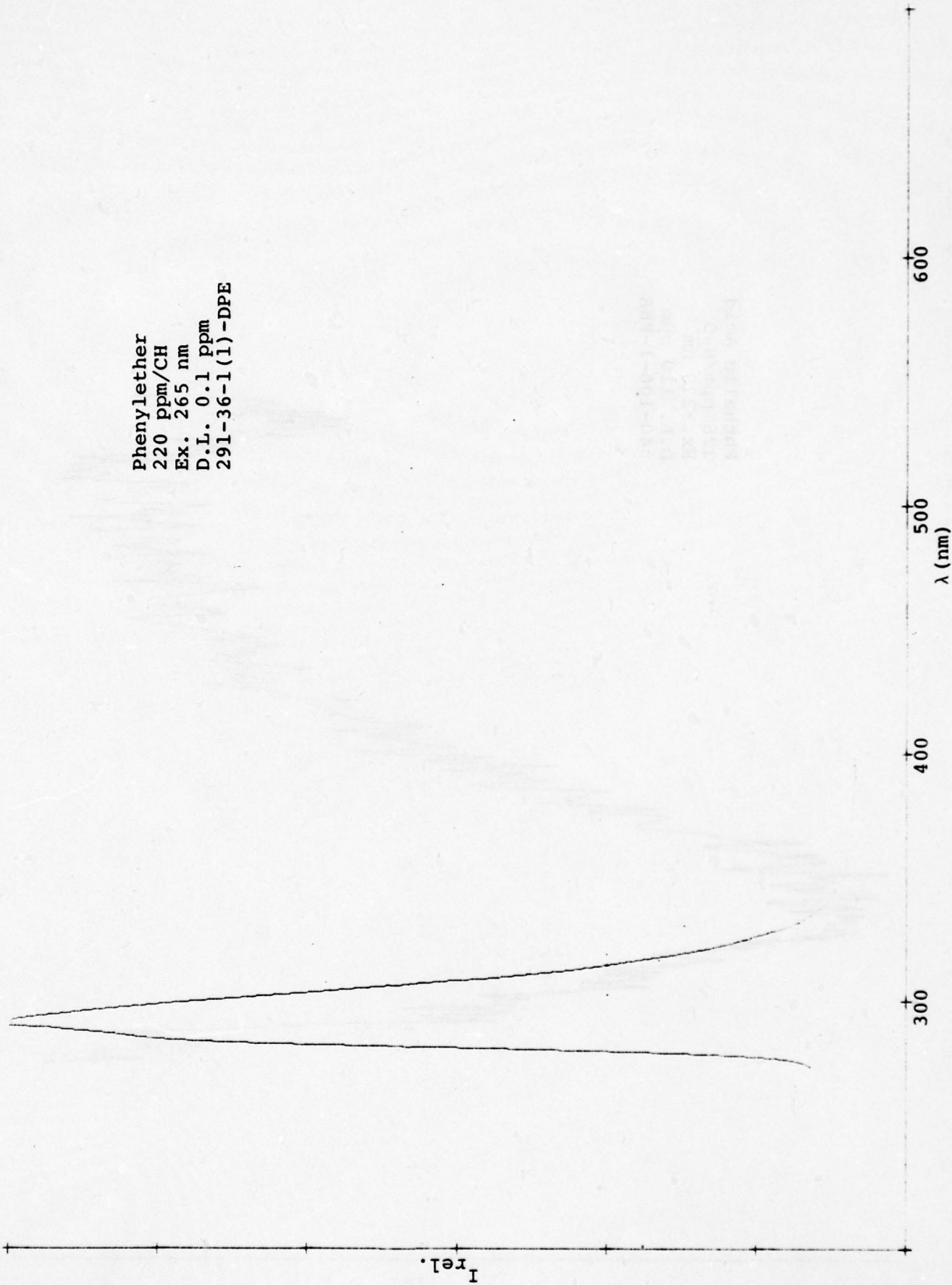
Cyclohexane background for
Peanut Oil
Ex. 290 nm



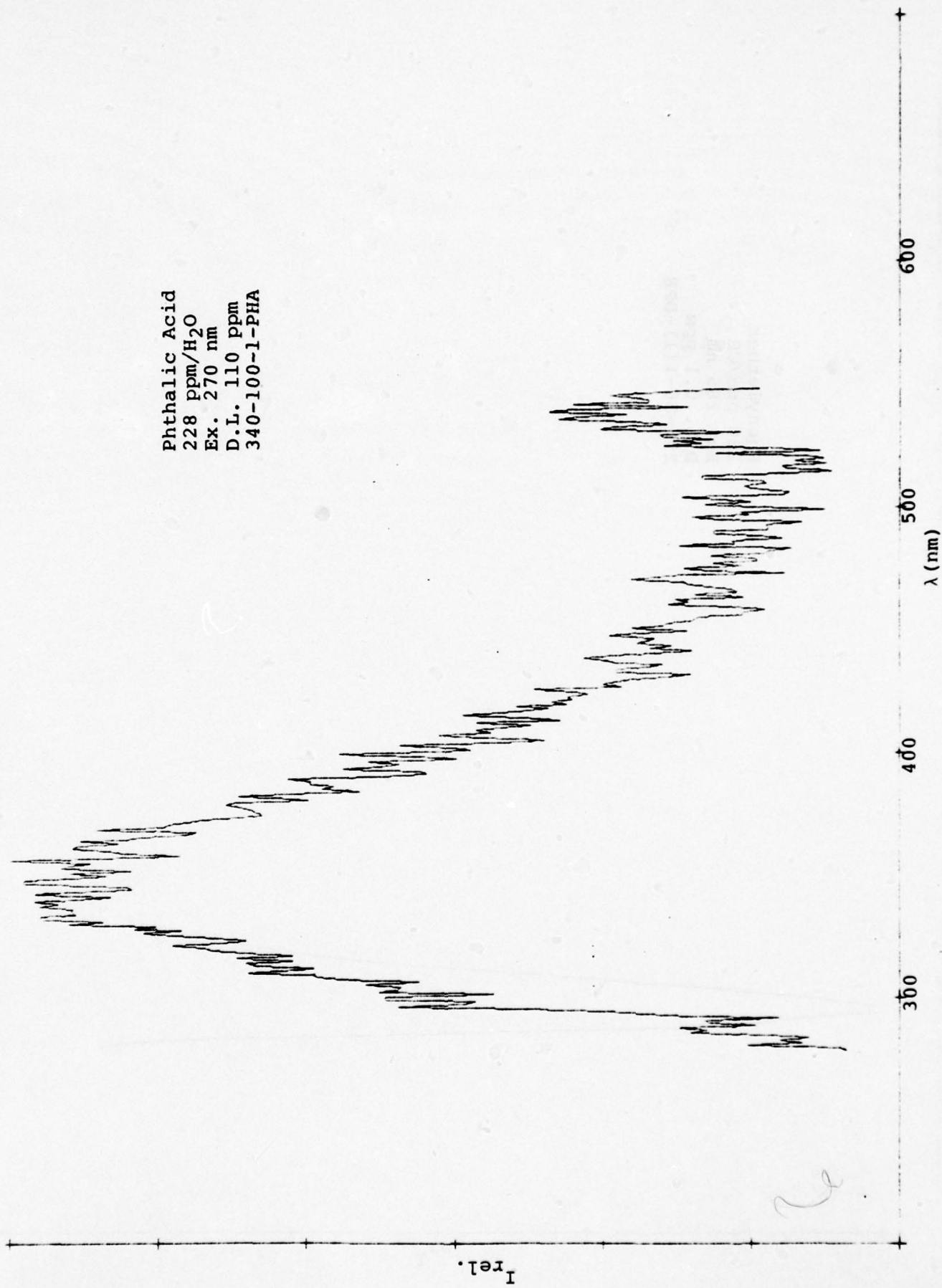
Phenol
12 ppm/CH
Ex. 265 nm
D.L. 0.007 ppm
288-30-1 (2) -PHN



Phenylether
220 ppm/CH
Ex. 265 nm
D.L. 0.1 ppm
291-36-1 (1) -DPE

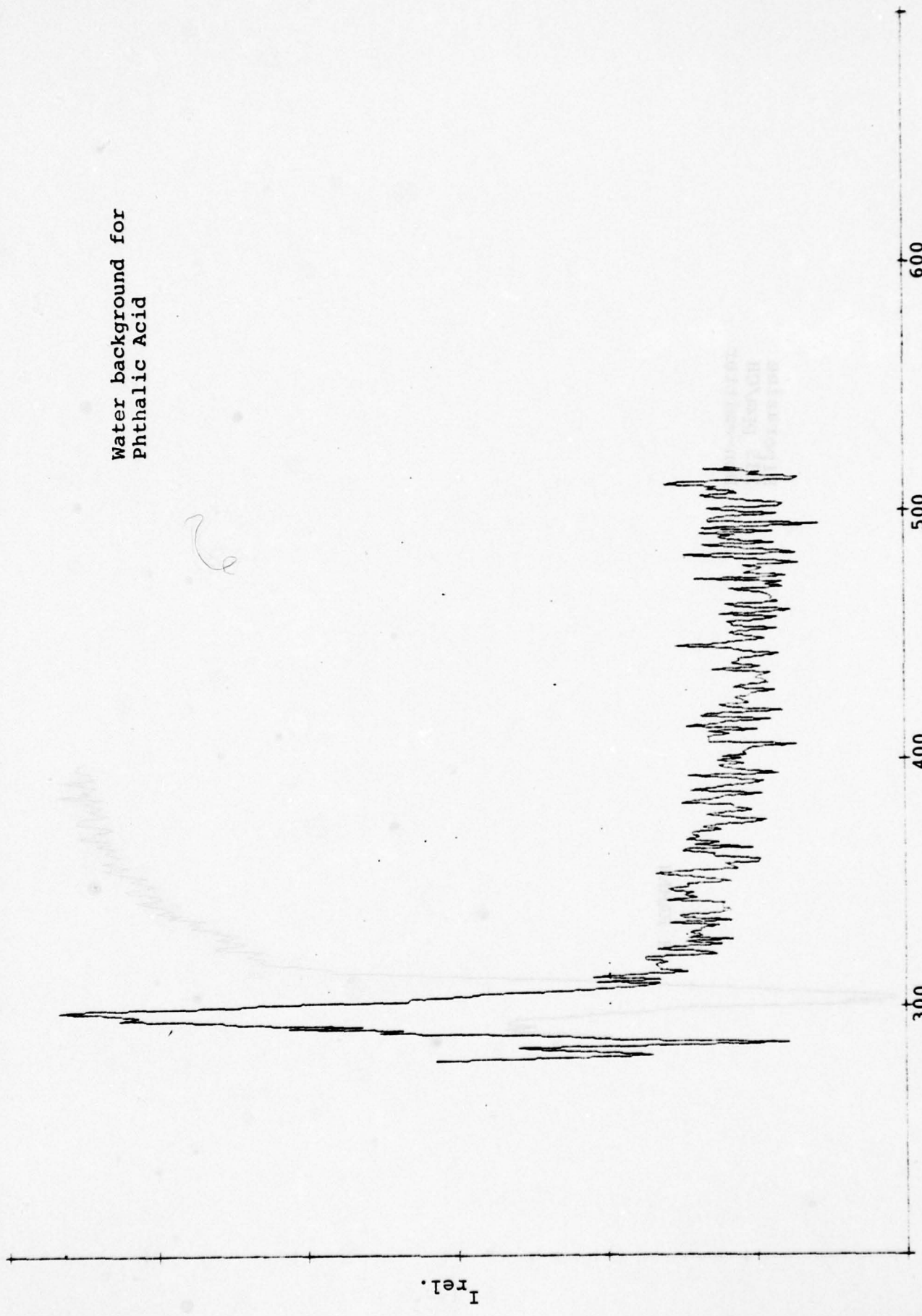


Phthalic Acid
228 ppm/H₂O
Ex. 270 nm
D.L. 110 ppm
340-100-1-PHA



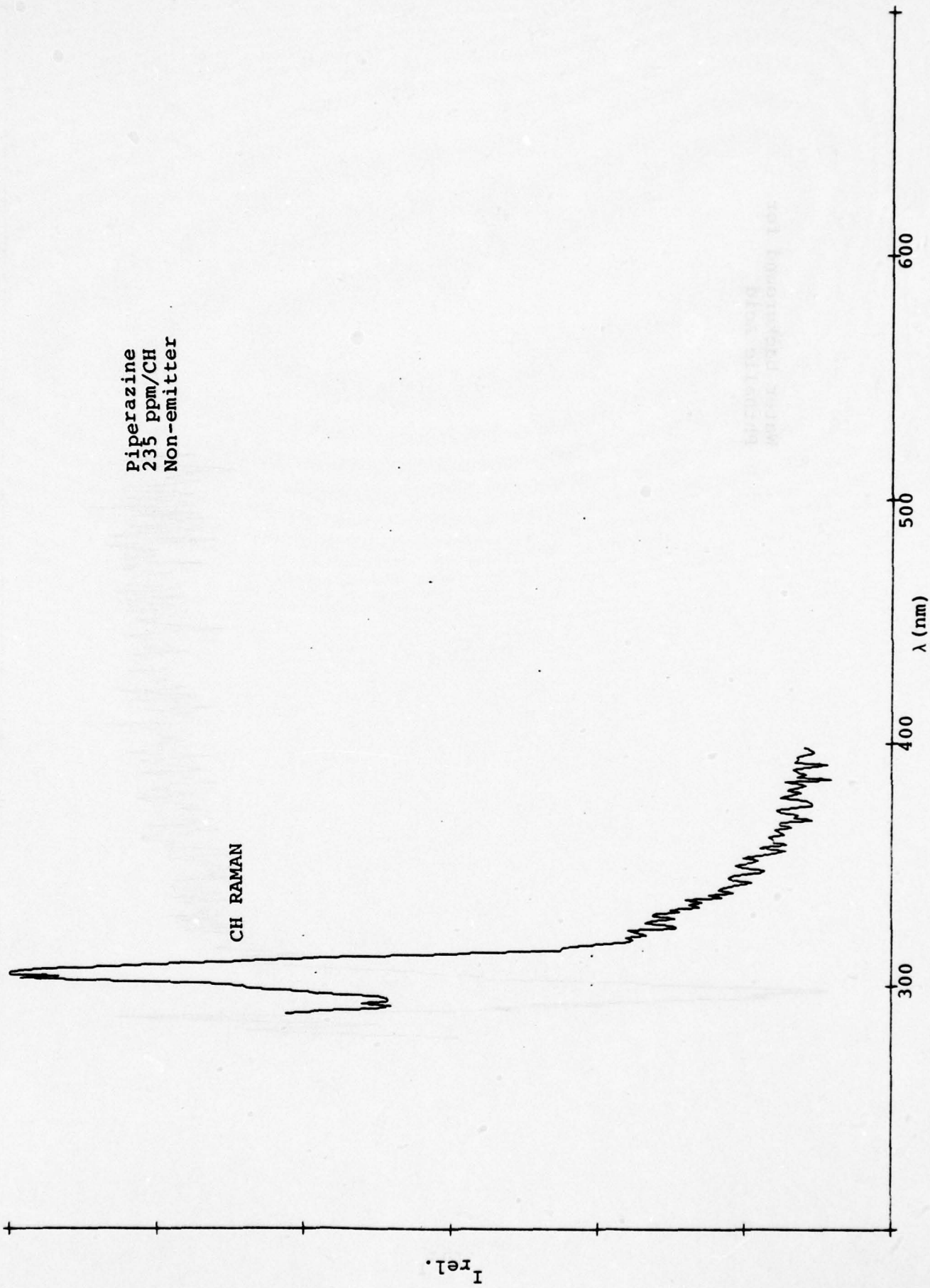
Water background for
Phthalic Acid

300 400 500 600

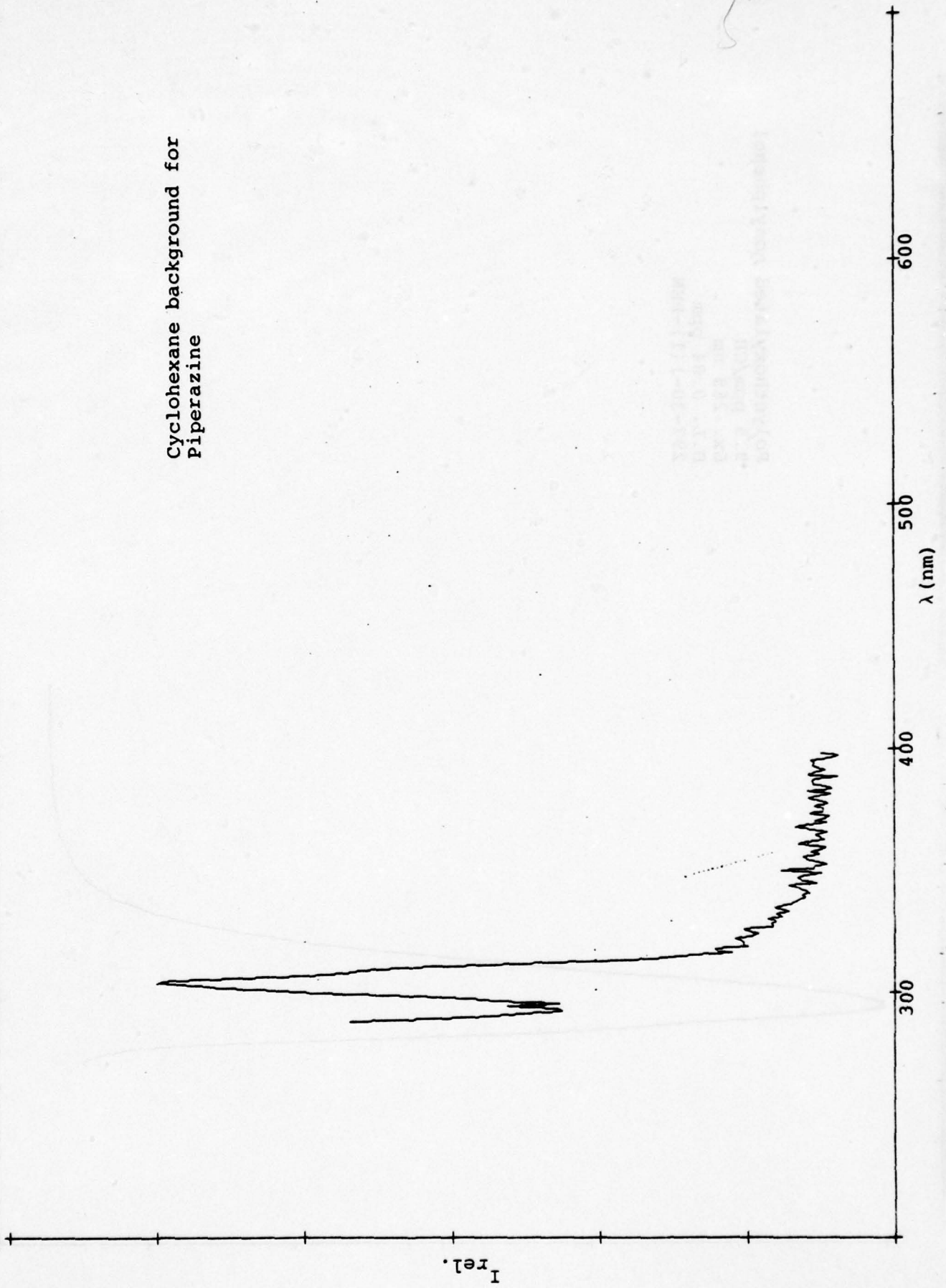


2

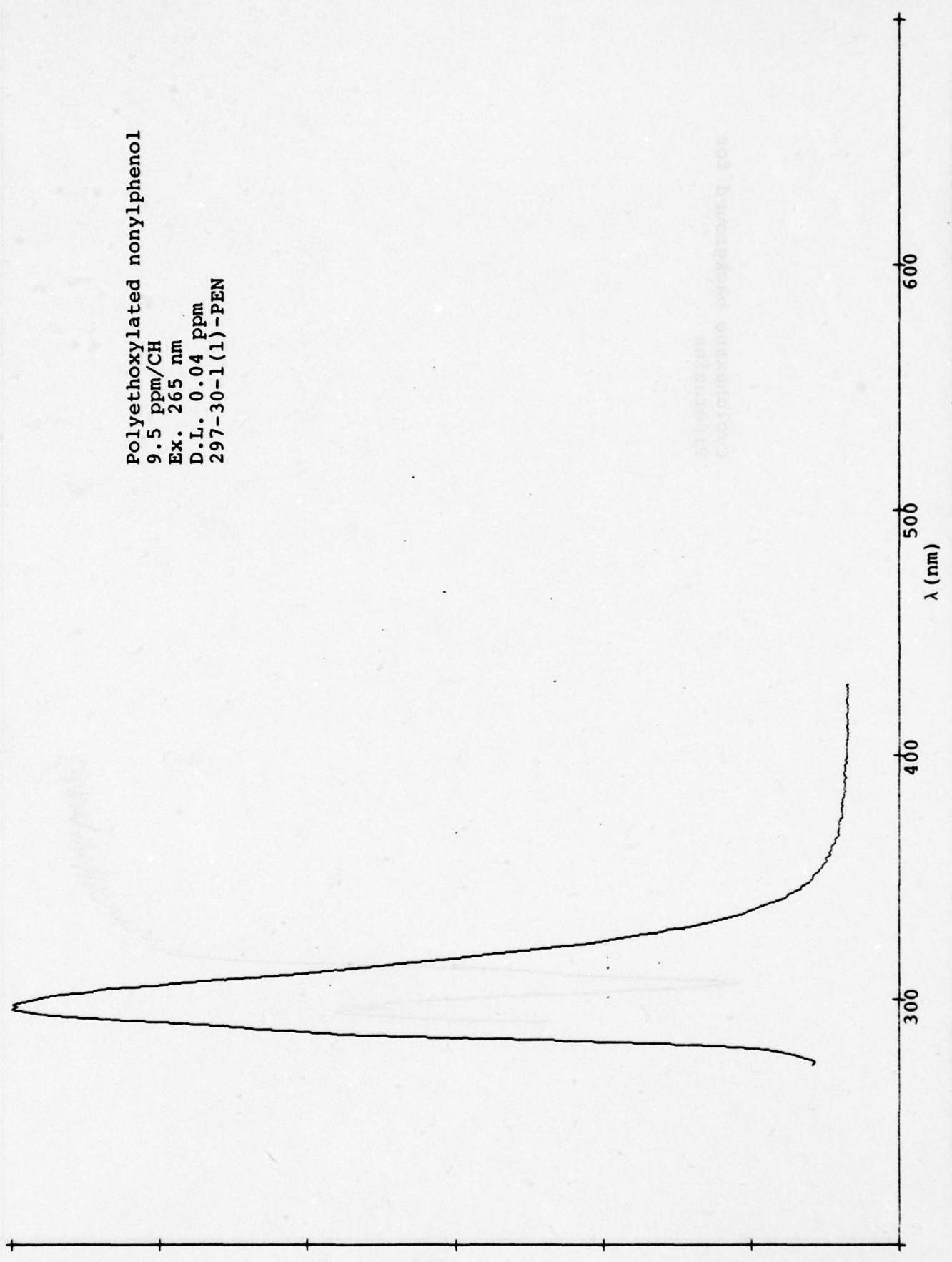
Piperazine
235 ppm/CH
Non-emitter



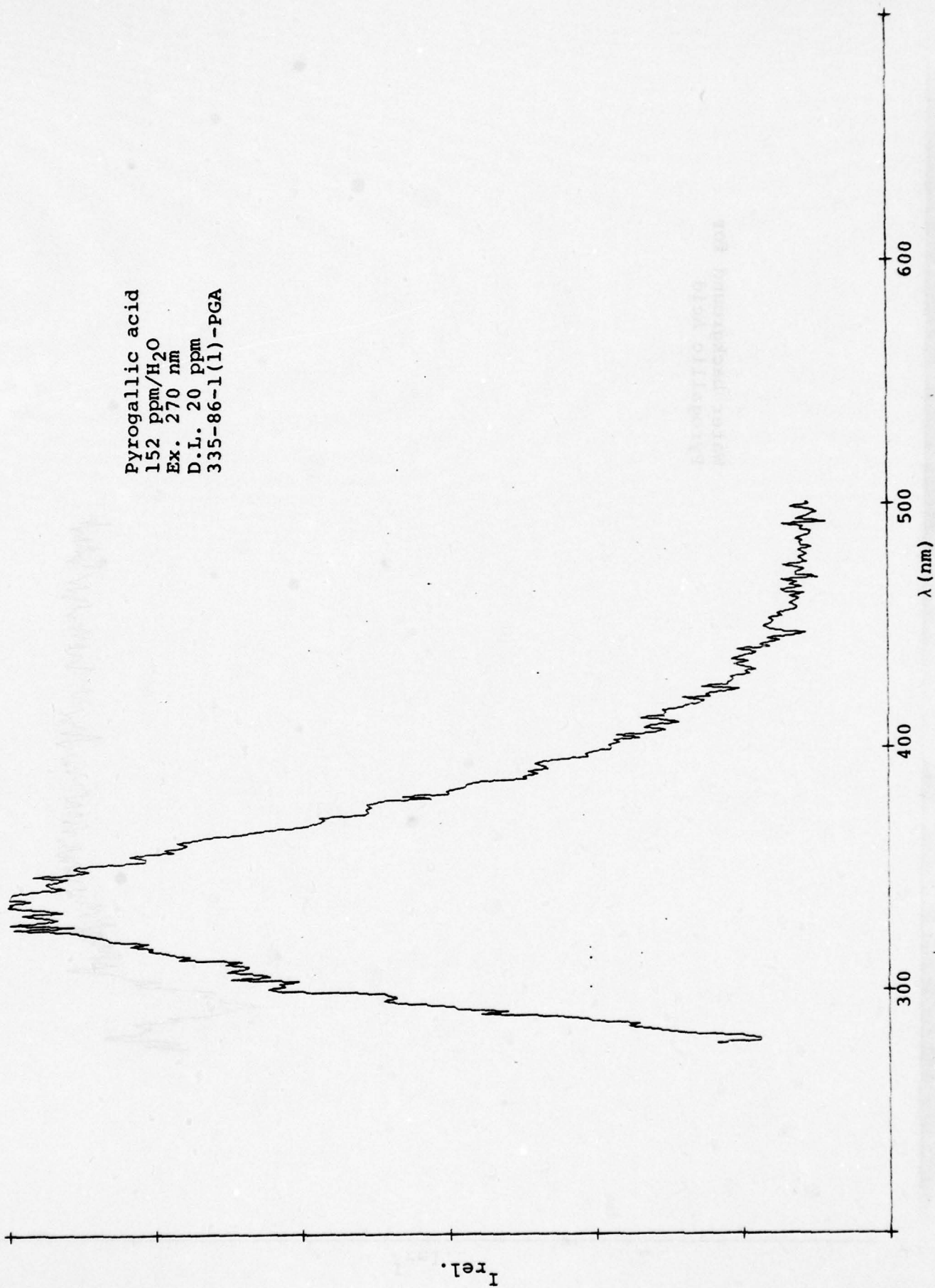
Cyclohexane background for
Piperazine



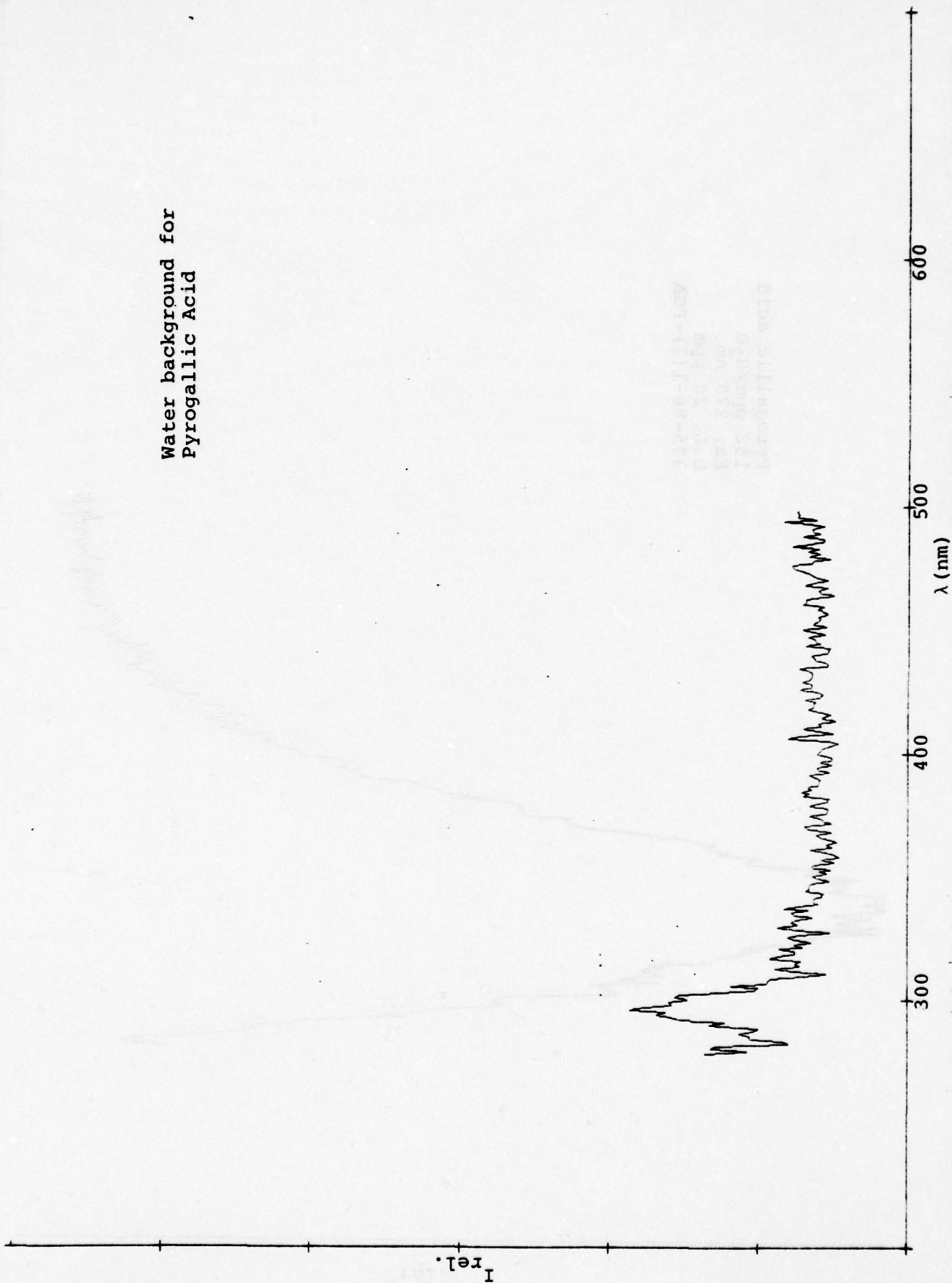
Polyethoxylated nonylphenol
9.5 ppm/CH
Ex. 265 nm
D.L. 0.04 ppm
297-30-1(1)-PEN

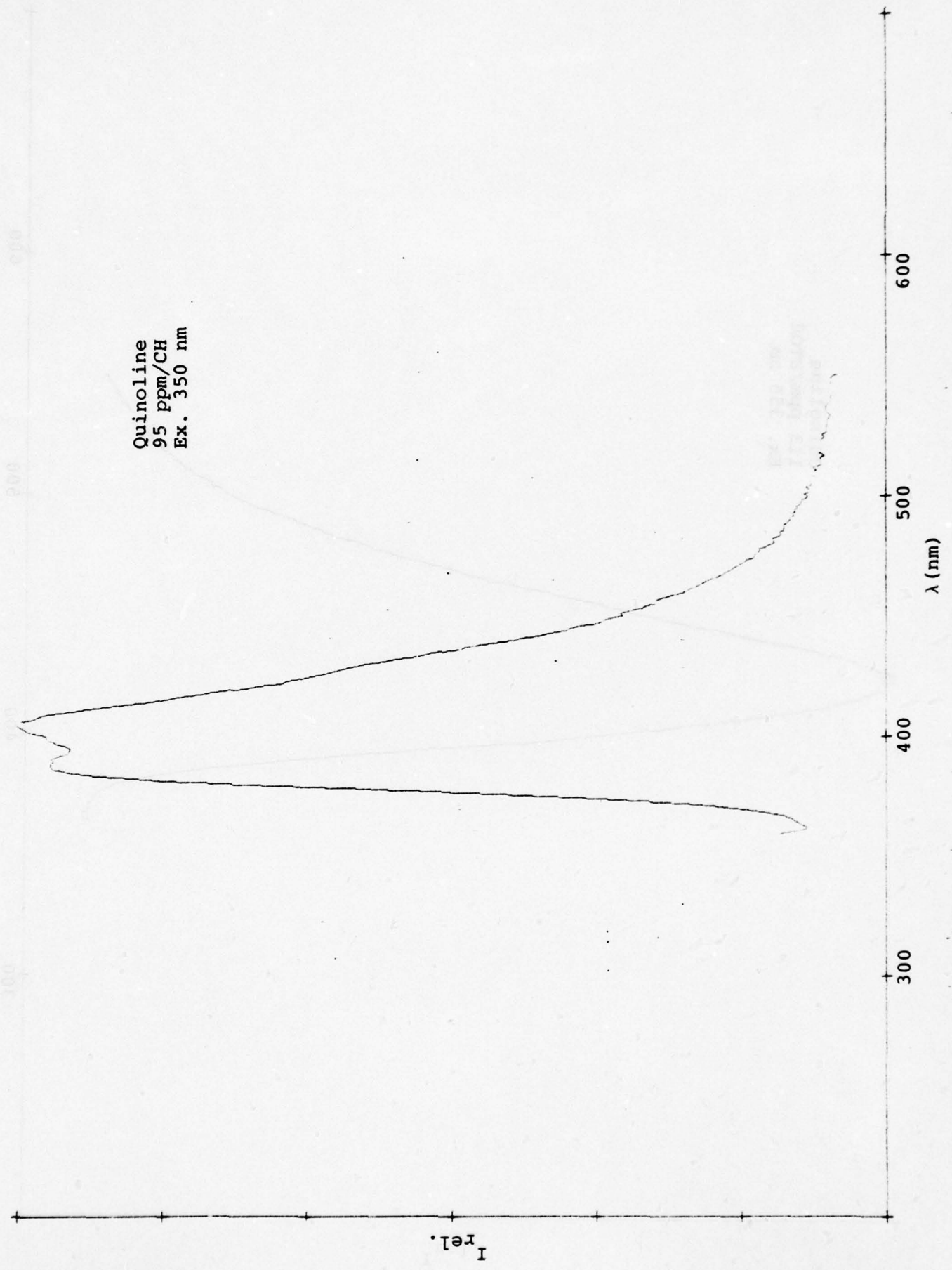


Pyrogallic acid
152 ppm/H₂O
Ex. 270 nm
D.L. 20 ppm
335-86-1(1)-PGA

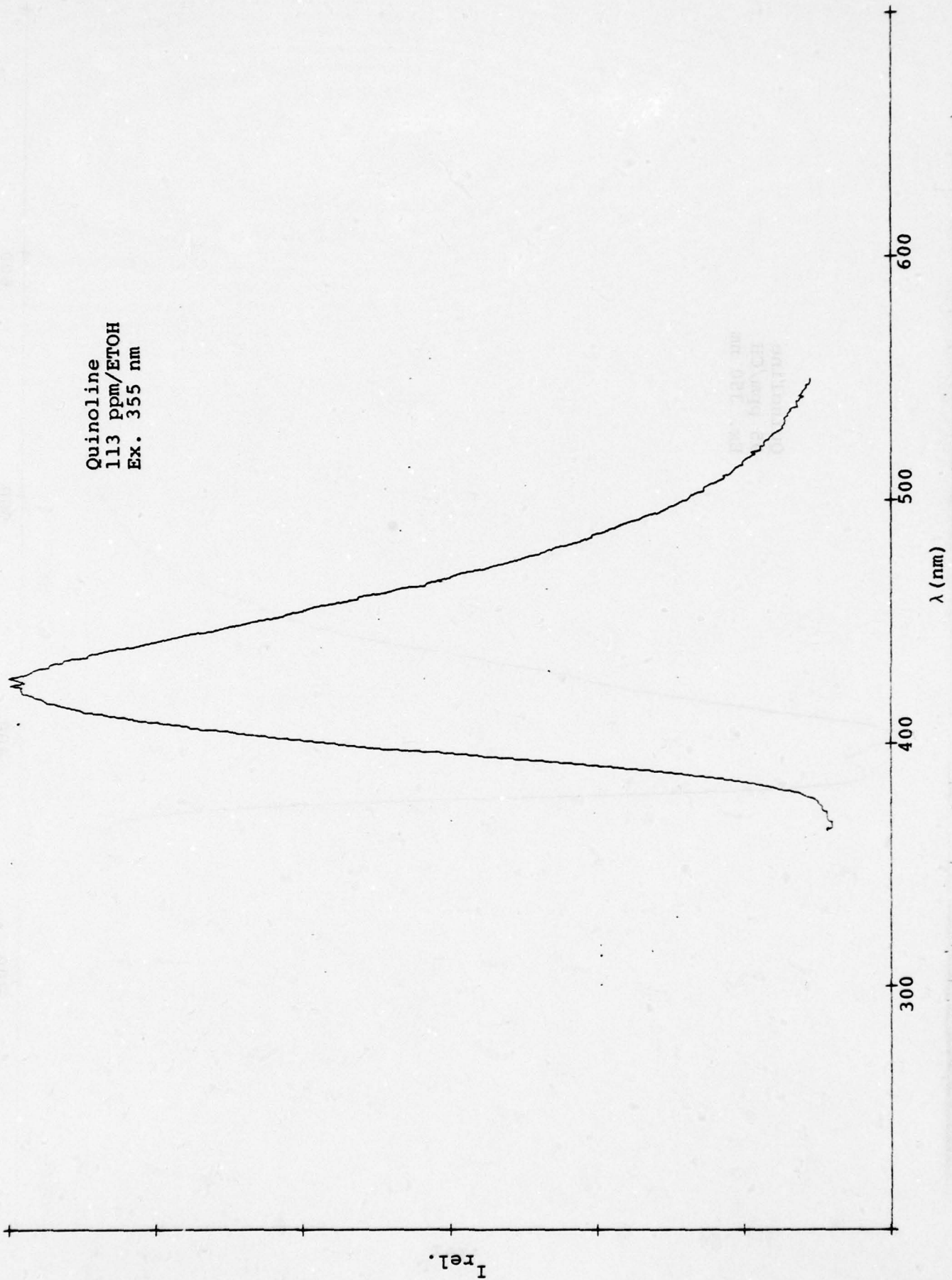


Water background for
Pyrogalllic Acid



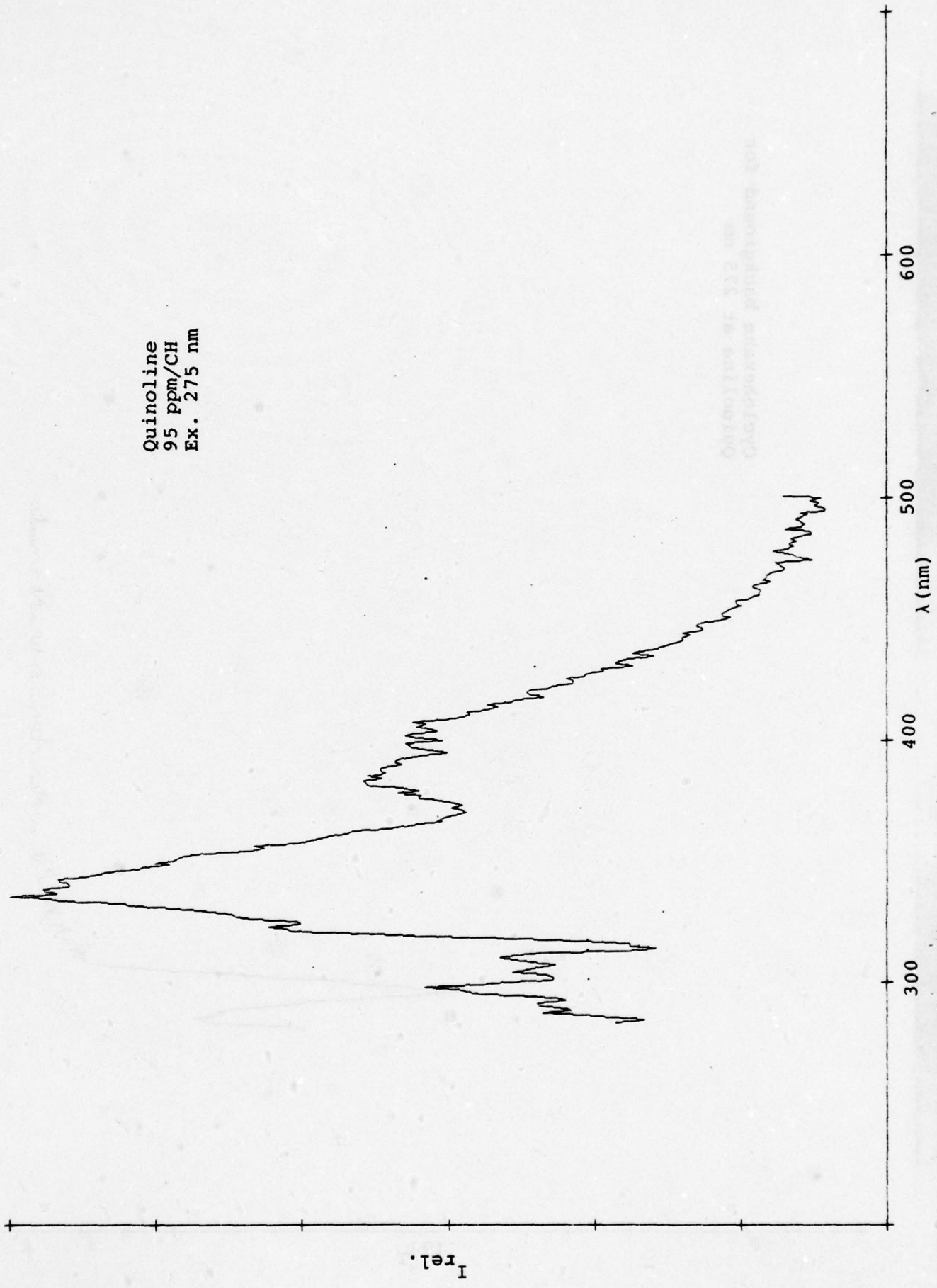


Quinoline
113 ppm/ETOH
Ex. 355 nm

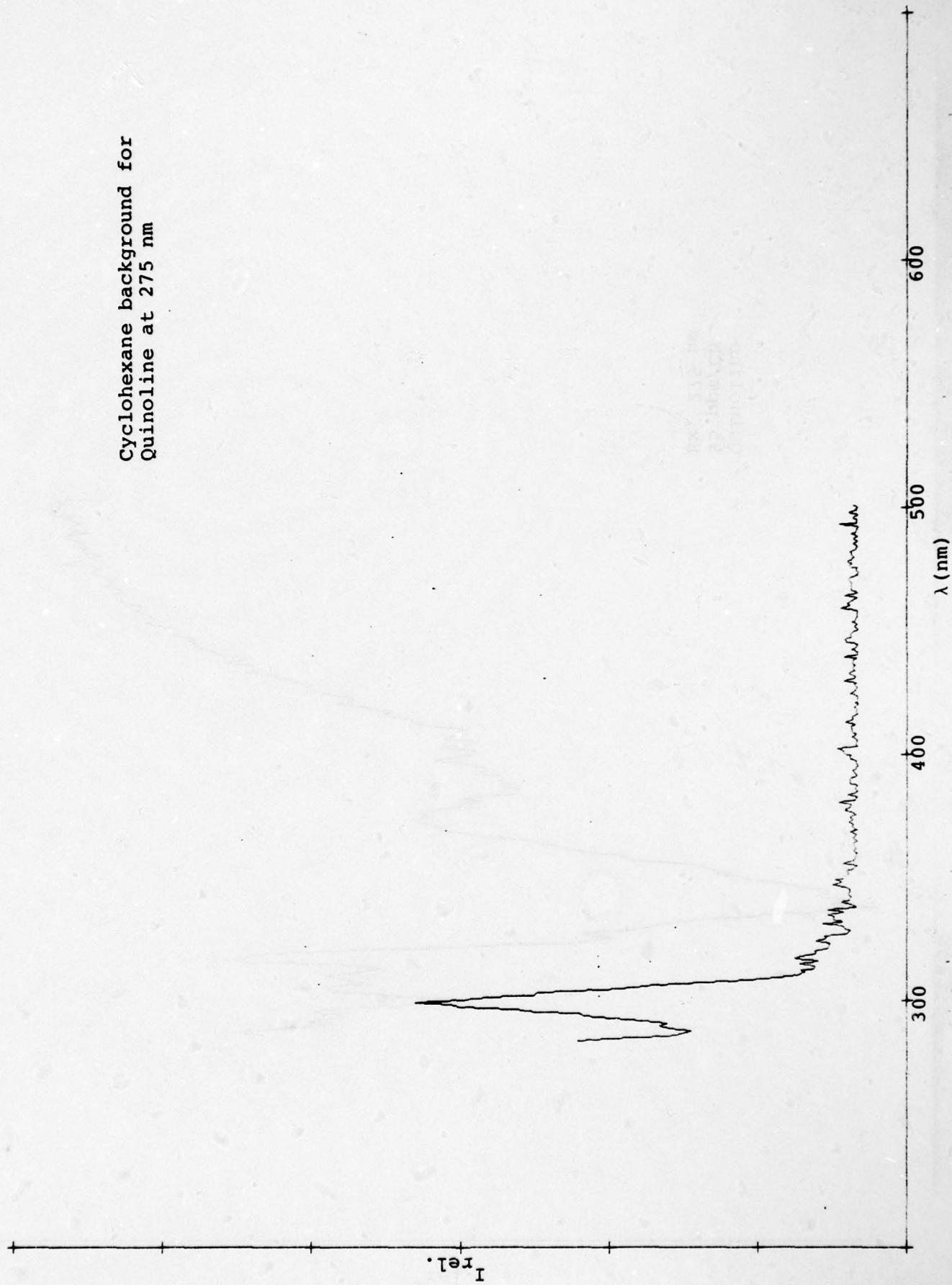


Quinoline
95 ppm/CH
Ex. 275 nm

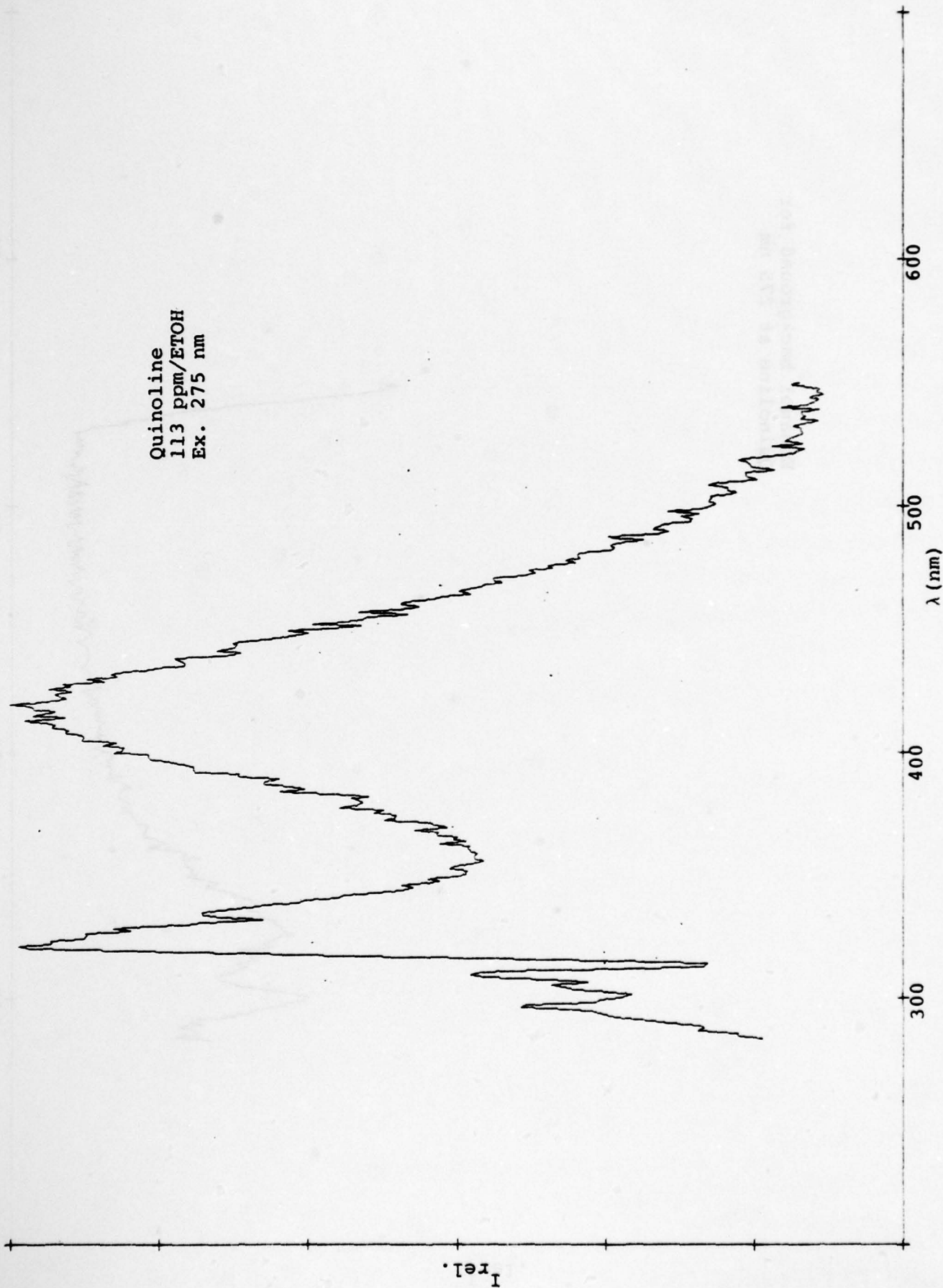
Quinoline of 513 mg
Chloroform polythene cell



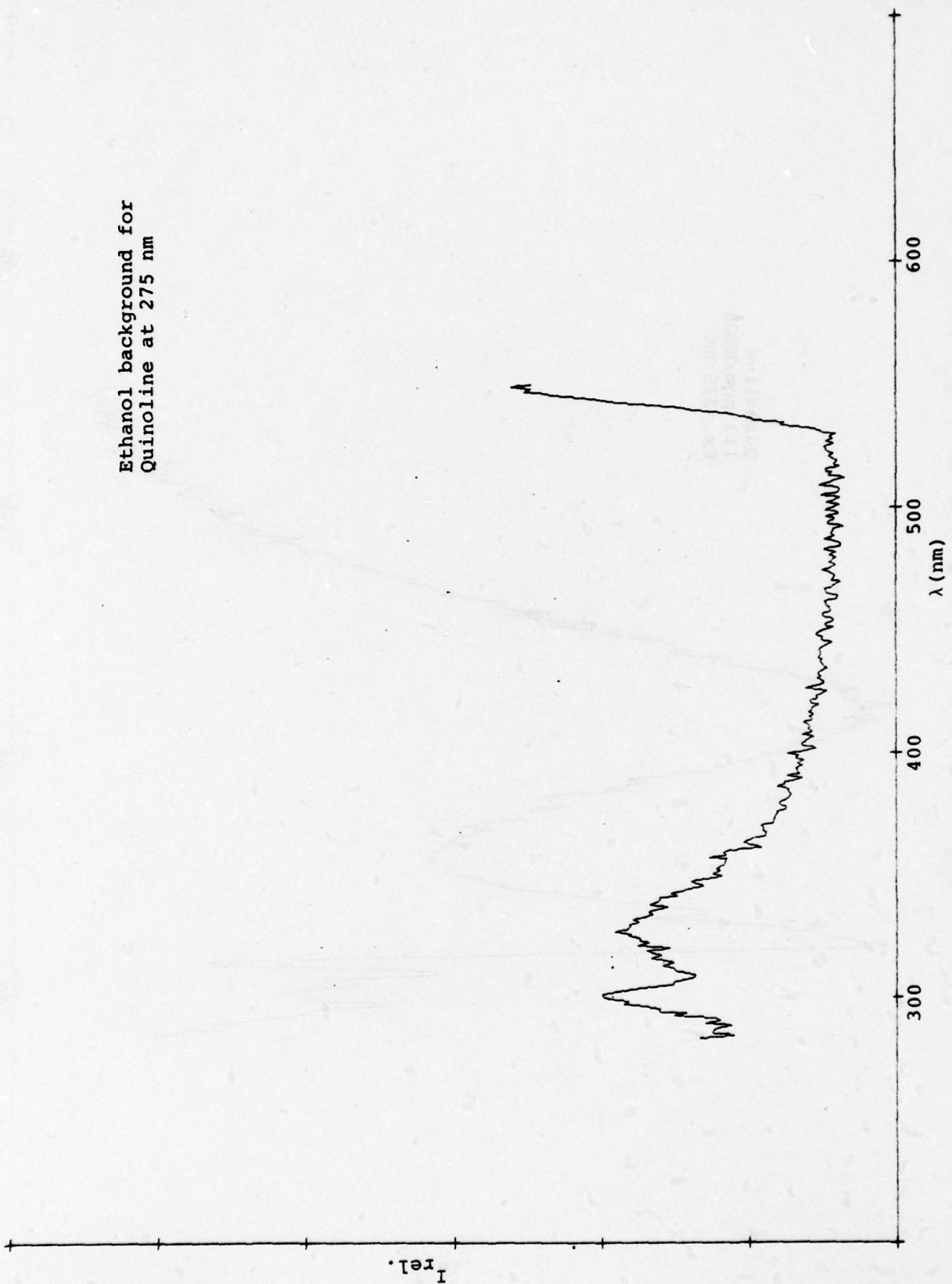
Cyclohexane background for
Quinoline at 275 nm



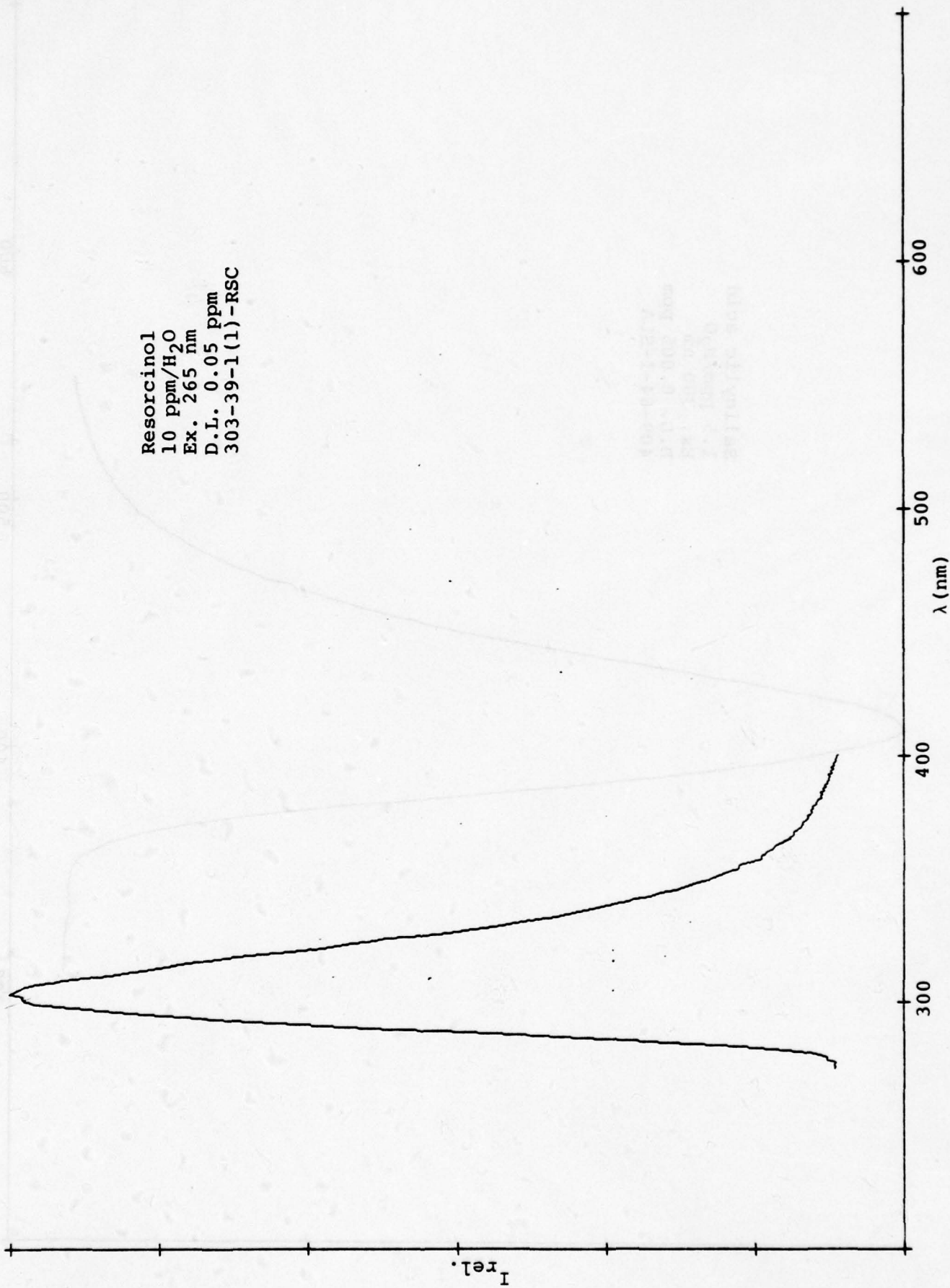
Quinoline
113 ppm/ETOH
Ex. 275 nm



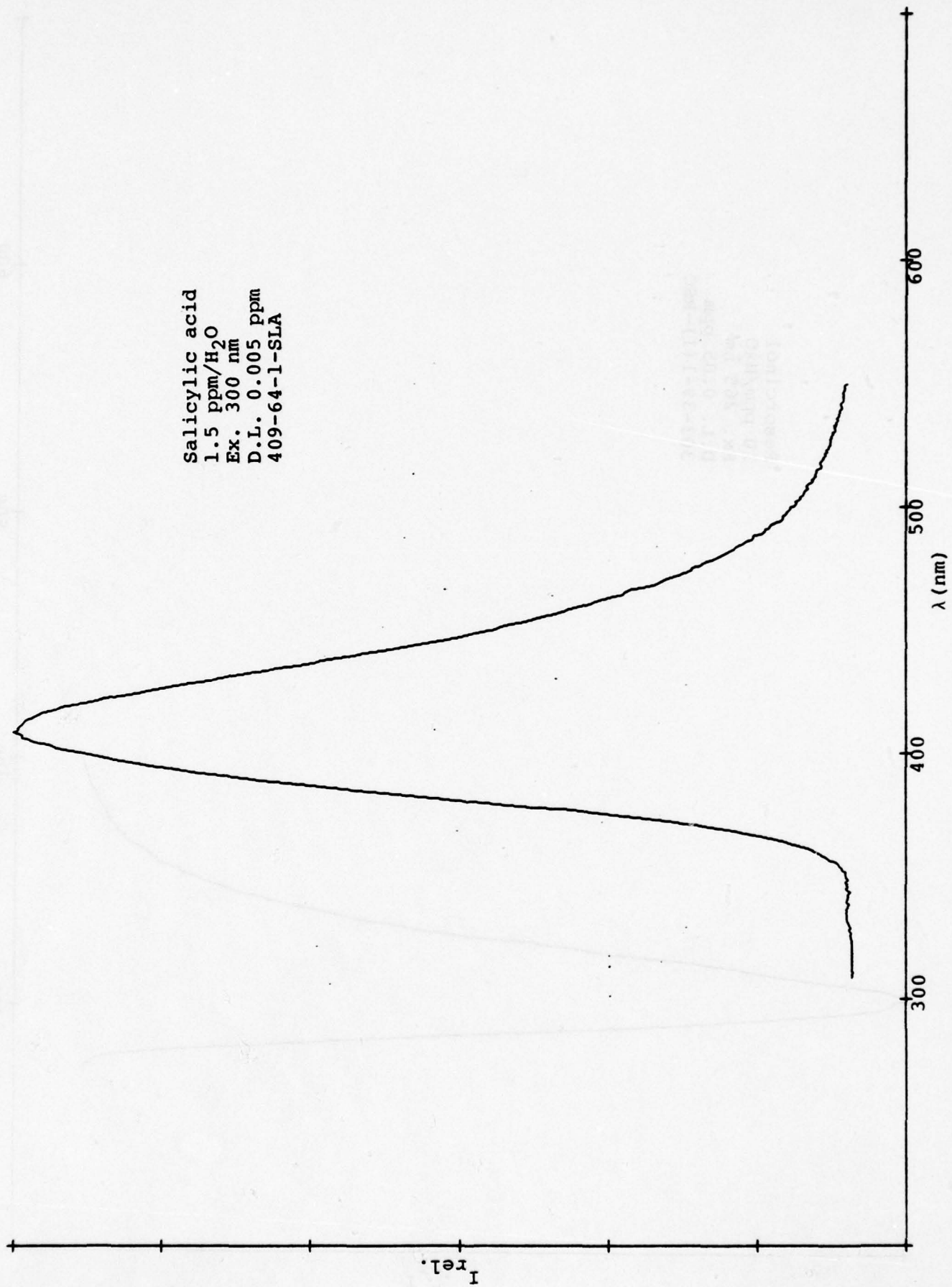
Ethanol background for
Quinoline at 275 nm



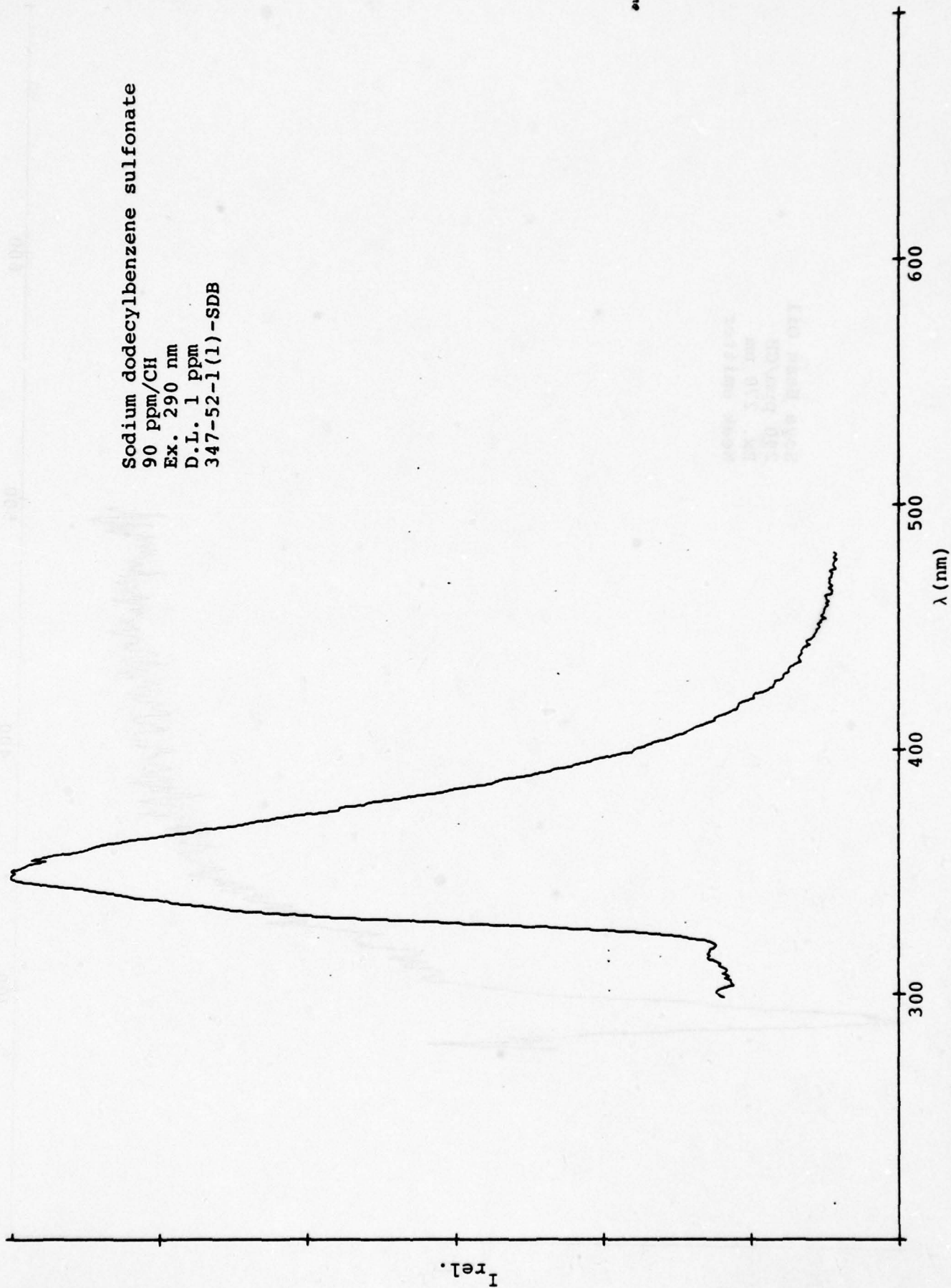
Resorcinol
10 ppm/H₂O
Ex. 265 nm
D.L. 0.05 ppm
303-39-1(1)-RSC



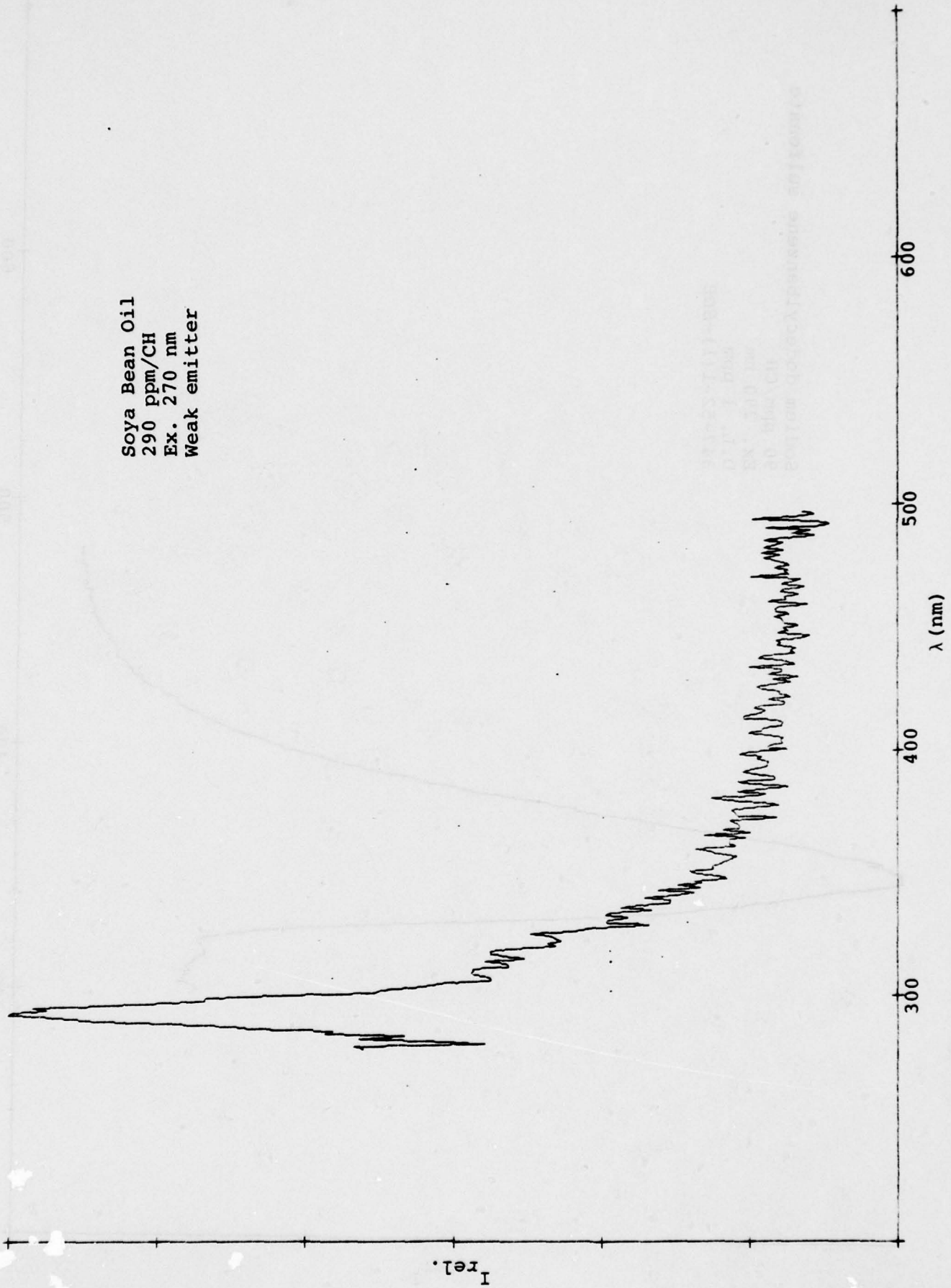
Salicylic acid
1.5 ppm/H₂O
Ex. 300 nm
D.L. 0.005 ppm
409-64-1-SLA



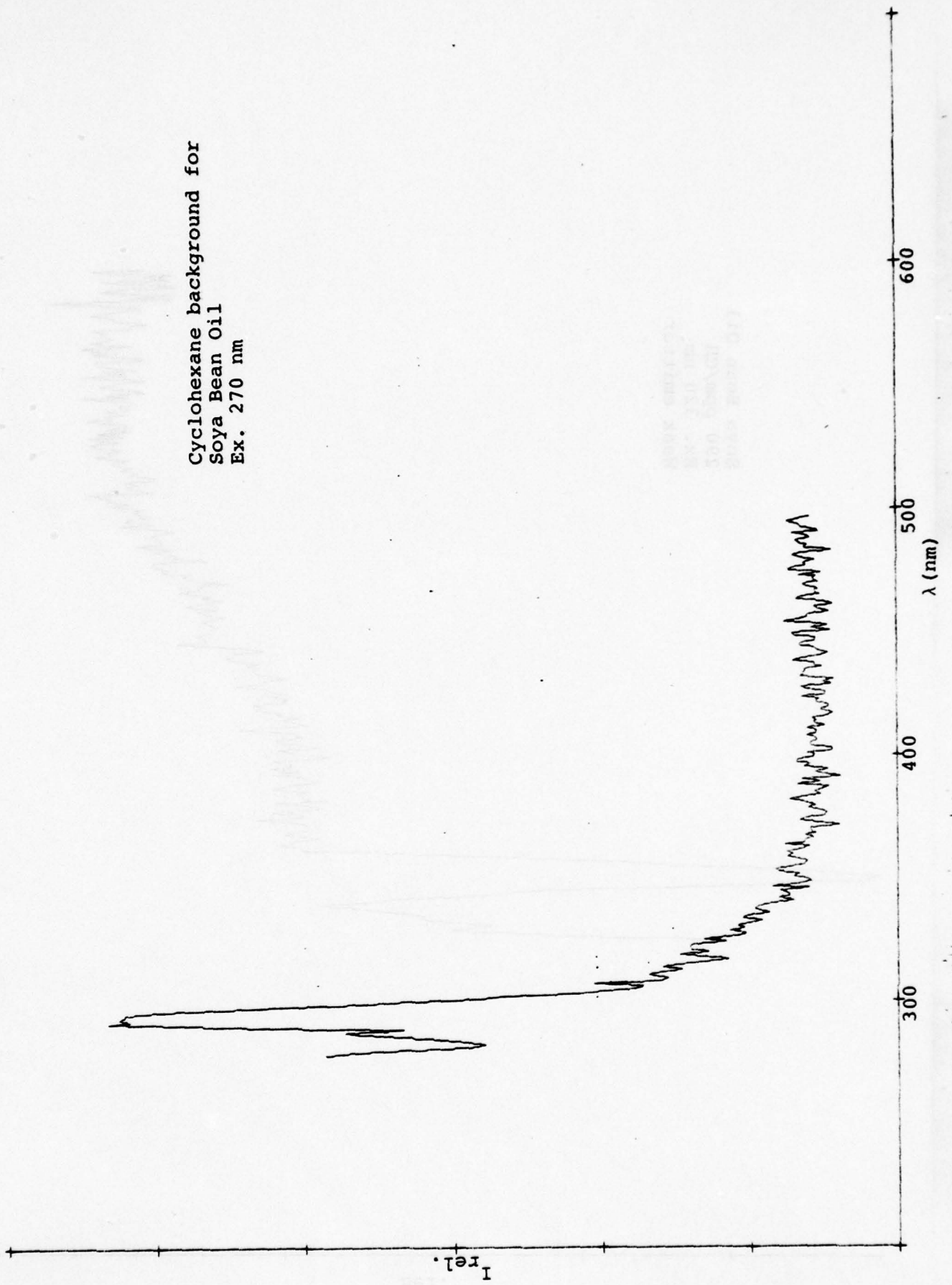
Sodium dodecylbenzene sulfonate
90 ppm/CH
Ex. 290 nm
D.L. 1 ppm
347-52-1(1)-SDB



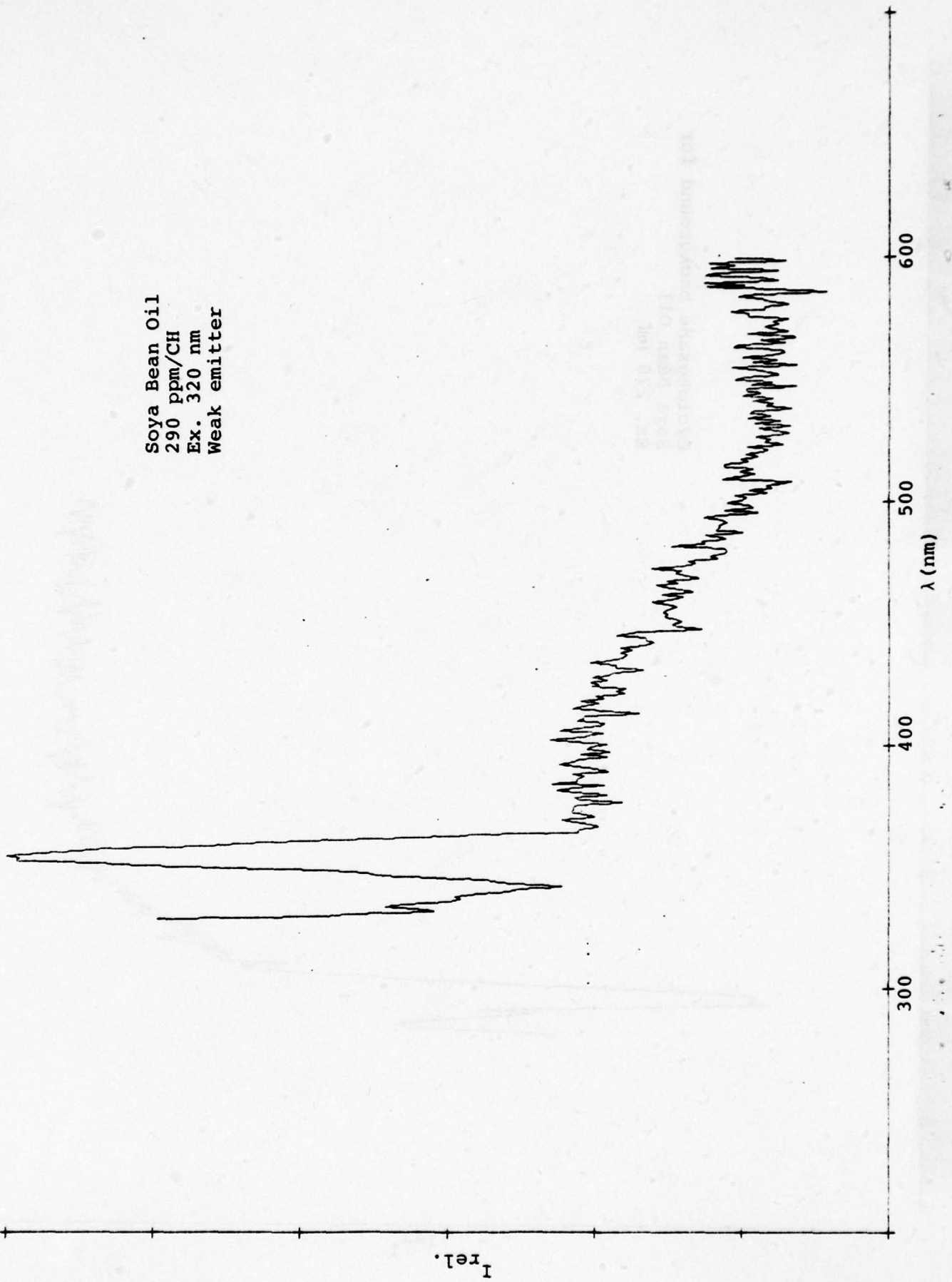
Soya Bean Oil
290 ppm/CH
Ex. 270 nm
Weak emitter



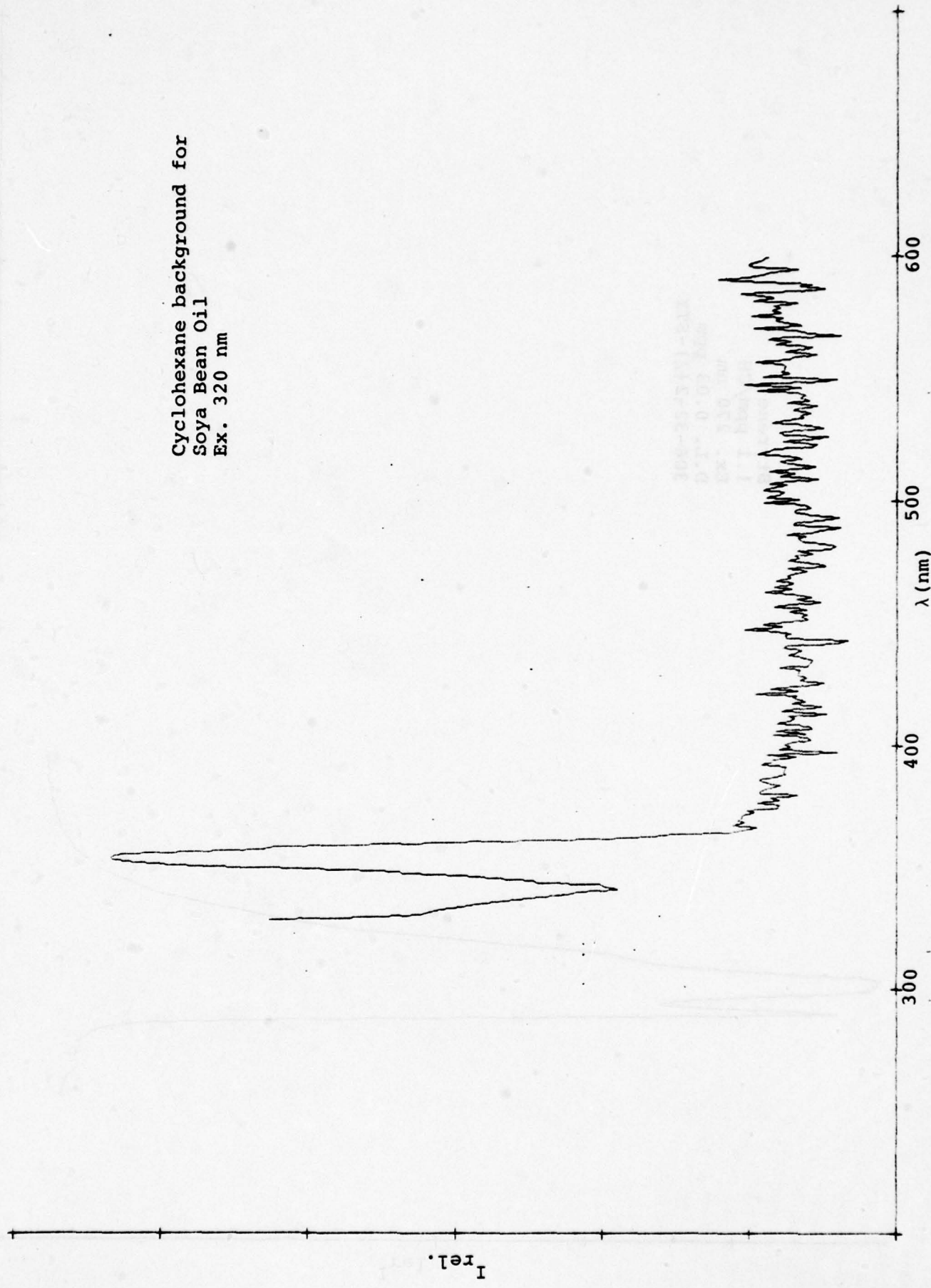
Cyclohexane background for
Soya Bean Oil
Ex. 270 nm



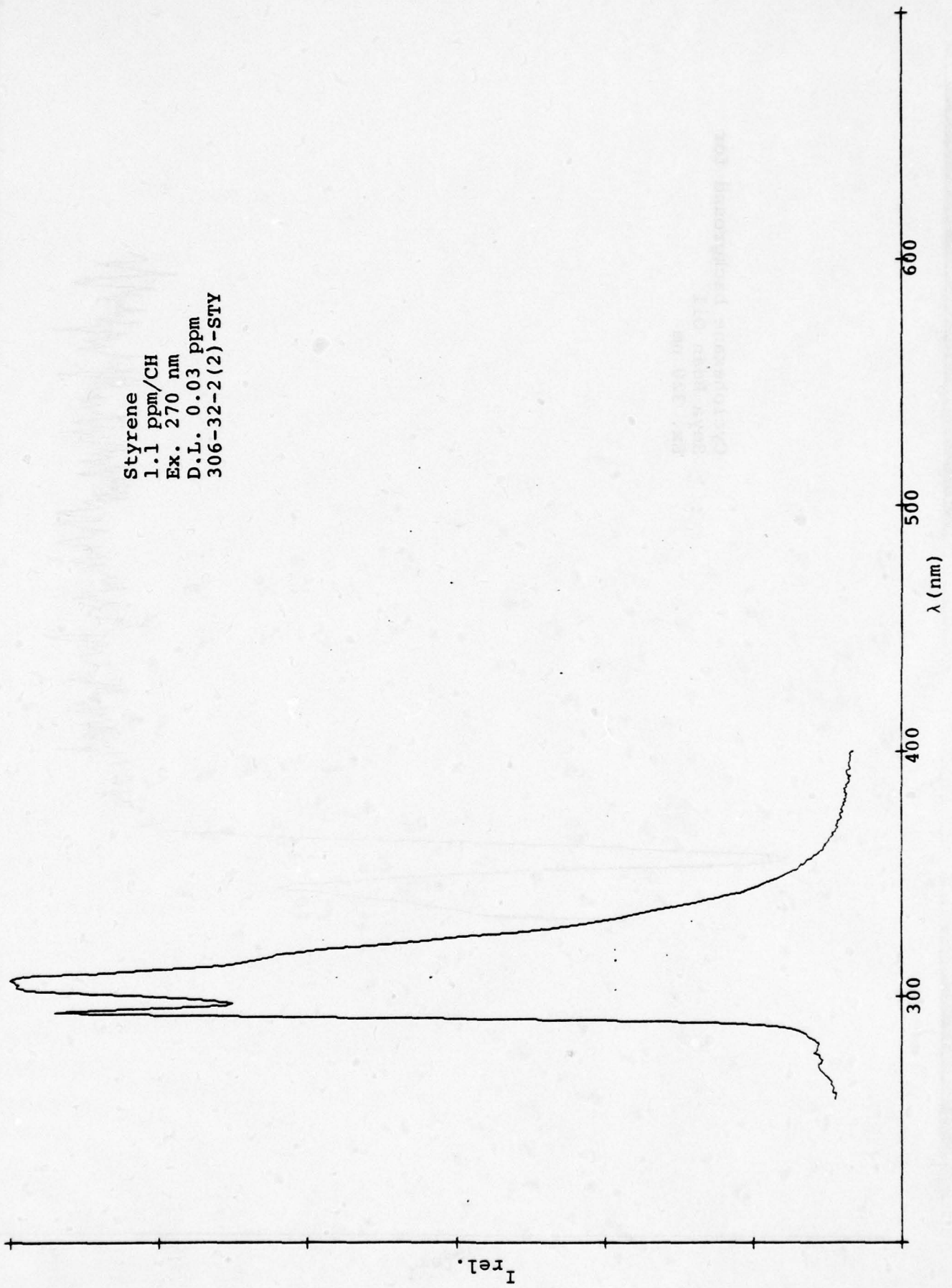
Soya Bean Oil
290 ppm/CH
Ex. 320 nm
Weak emitter



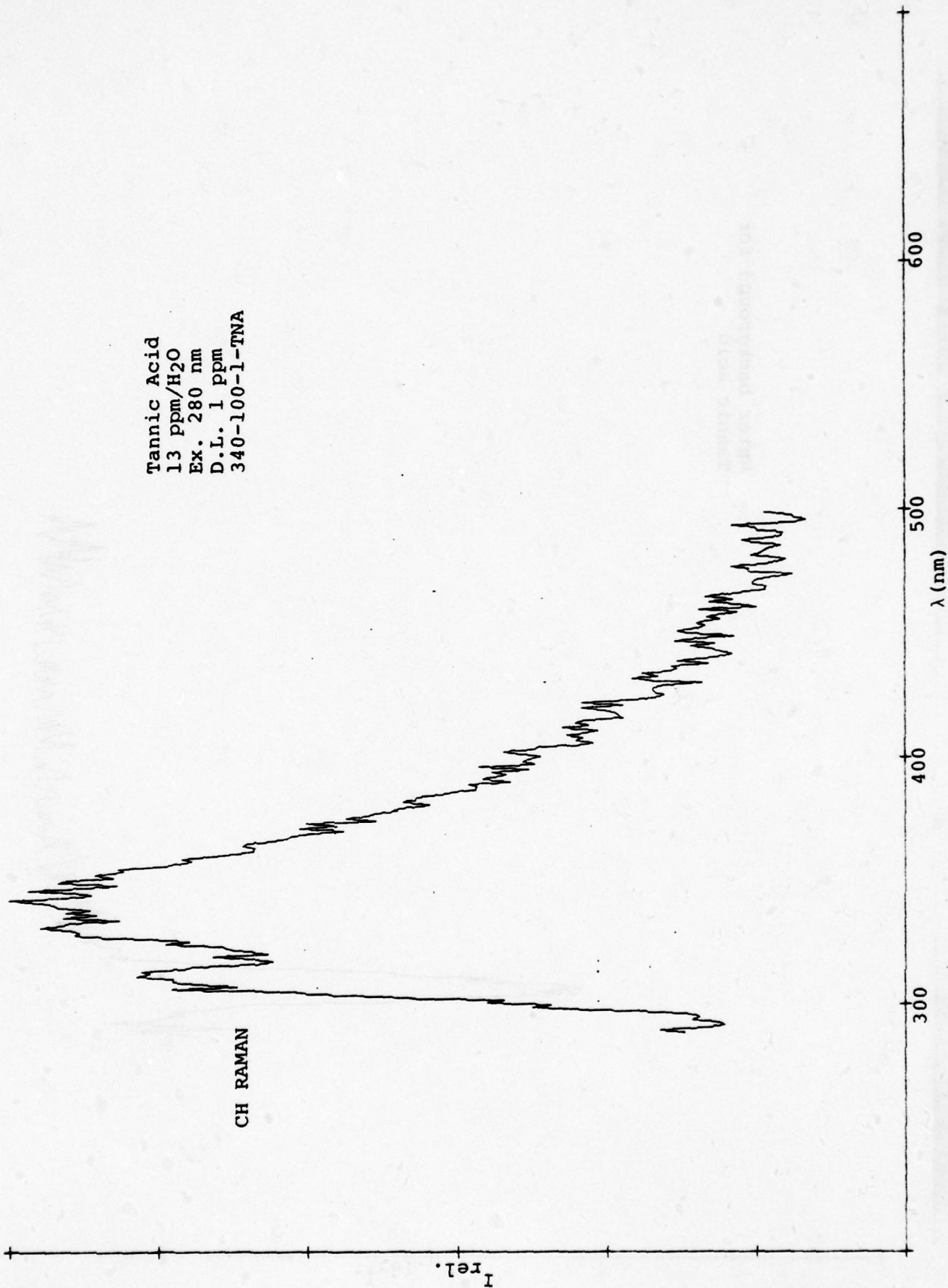
Cyclohexane background for
Soya Bean Oil
Ex. 320 nm



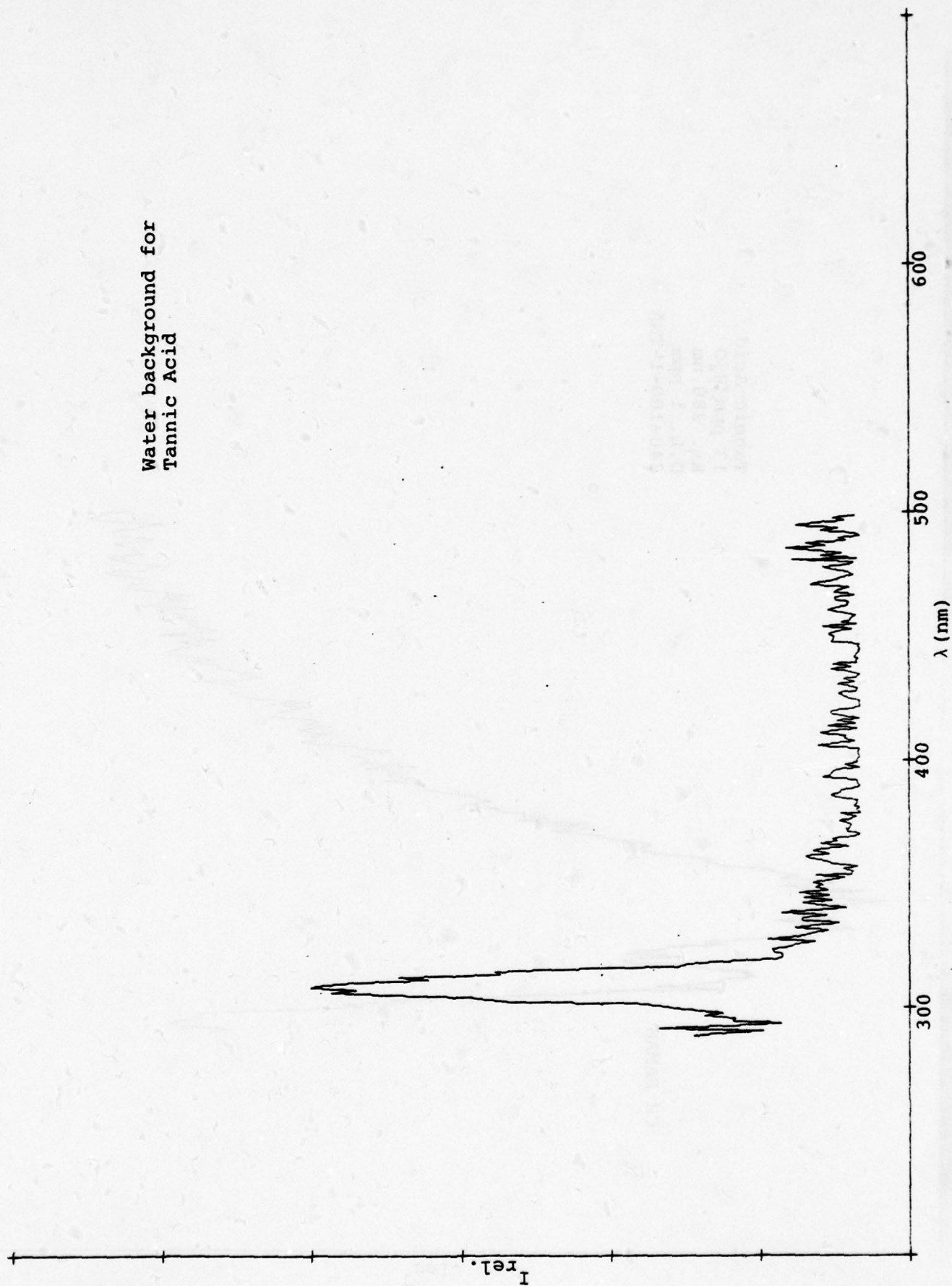
Styrene
1.1 ppm/CH
Ex. 270 nm
D.L. 0.03 ppm
306-32-2(2)-STY



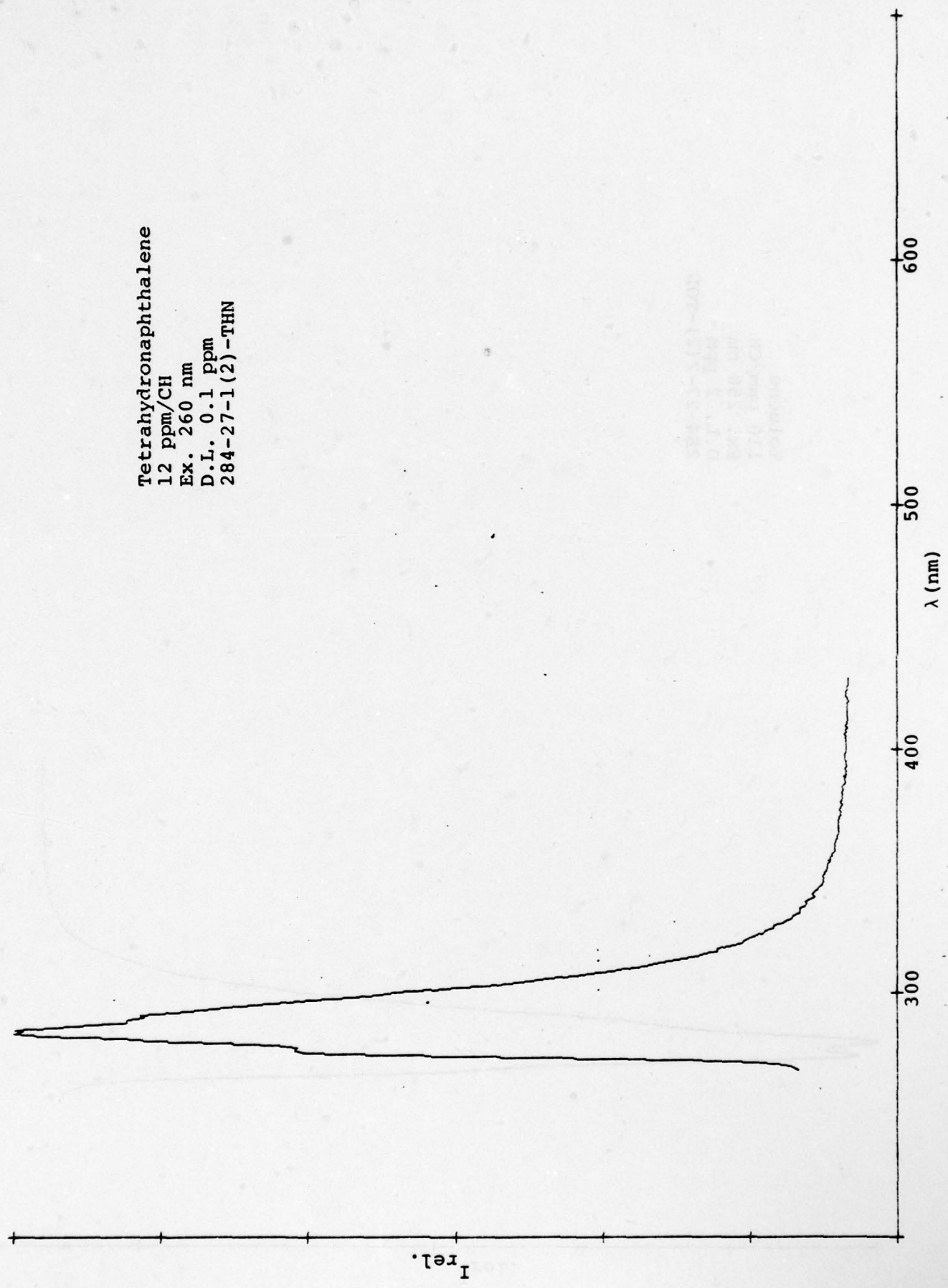
Tannic Acid
13 ppm/H₂O
Ex. 280 nm
D.L. 1 ppm
340-100-1-TNA



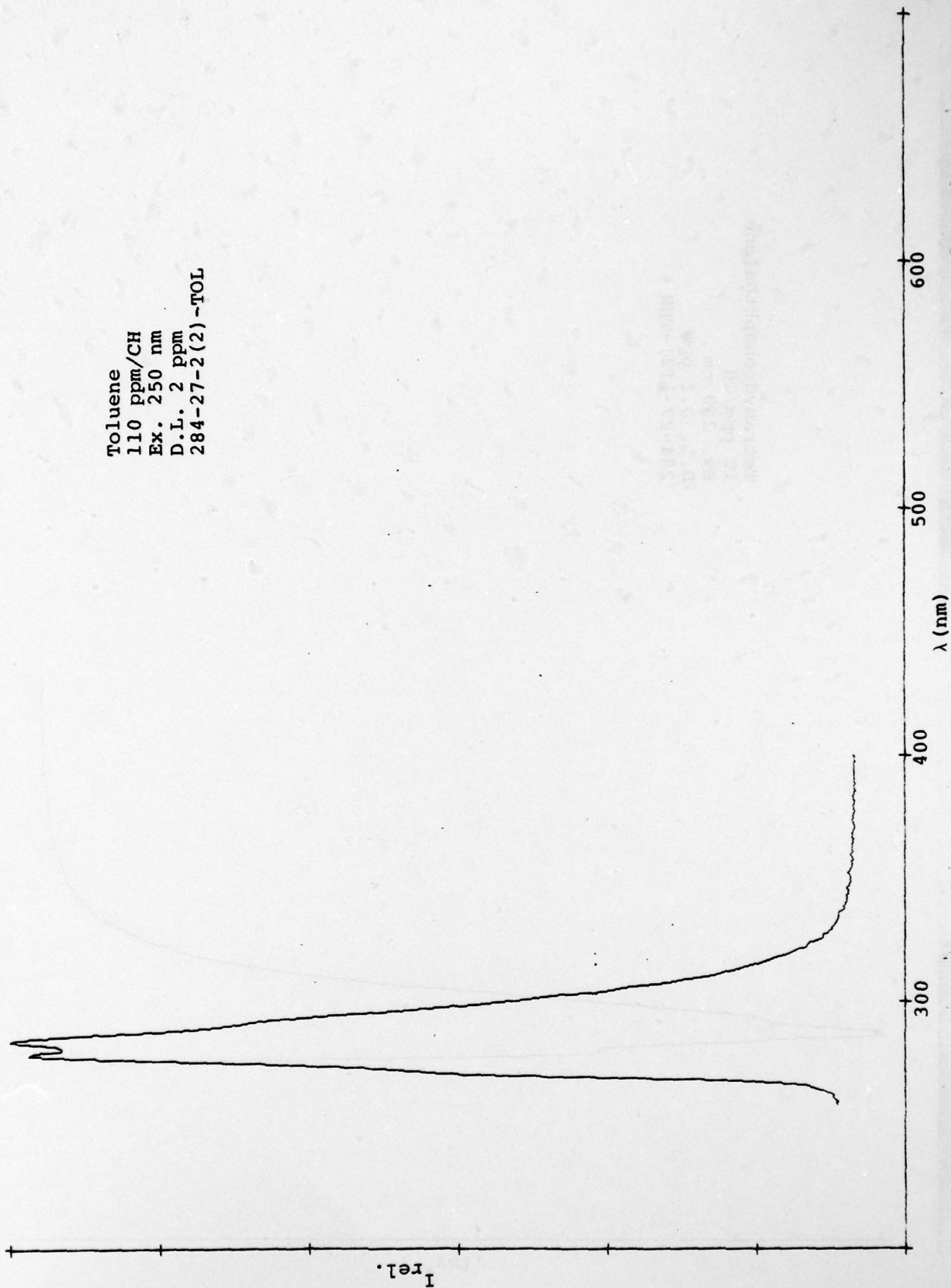
Water background for
Tannic Acid



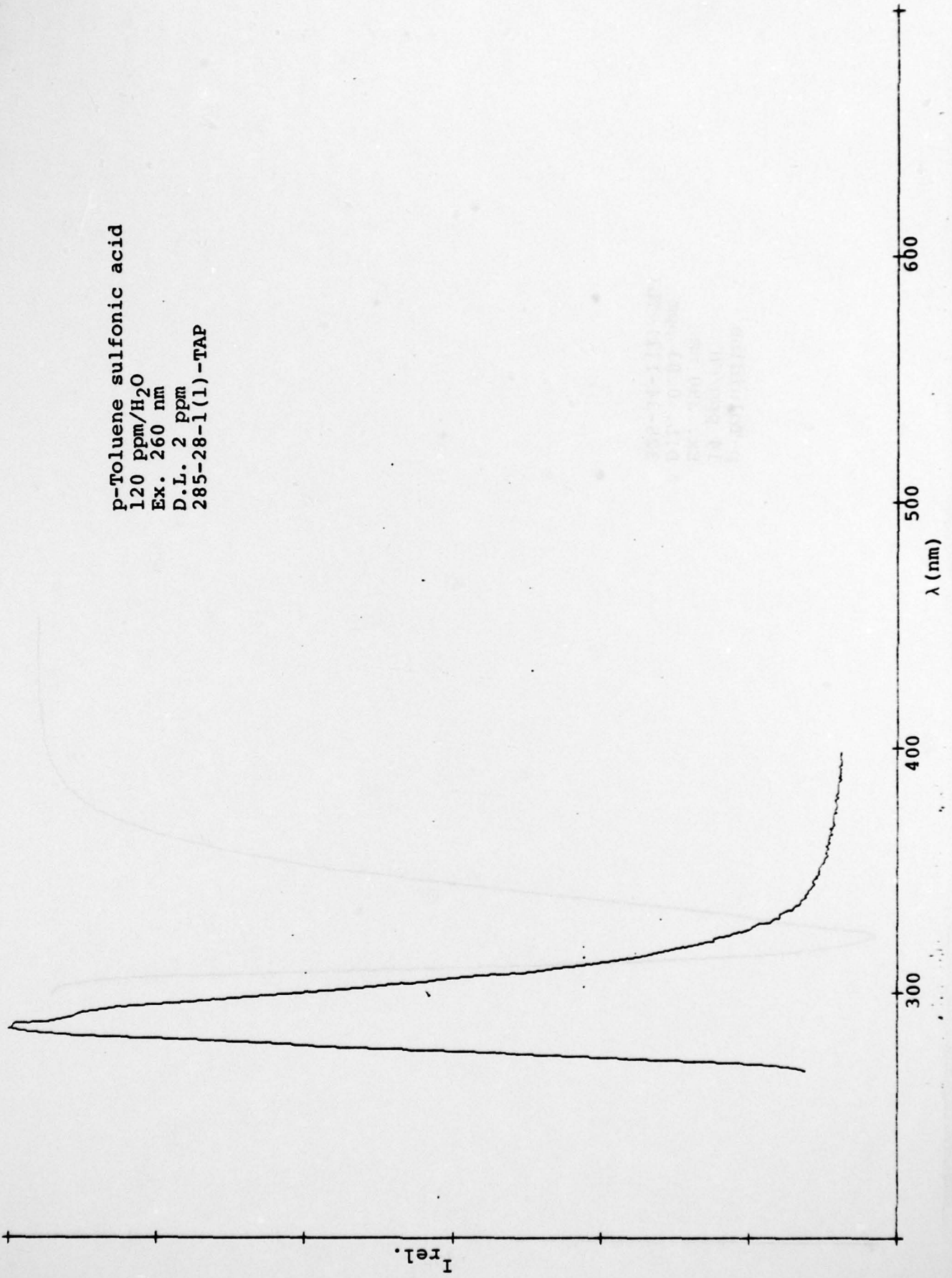
Tetrahydronaphthalene
12 ppm/CH
Ex. 260 nm
D.L. 0.1 ppm
284-27-1 (2) - THN



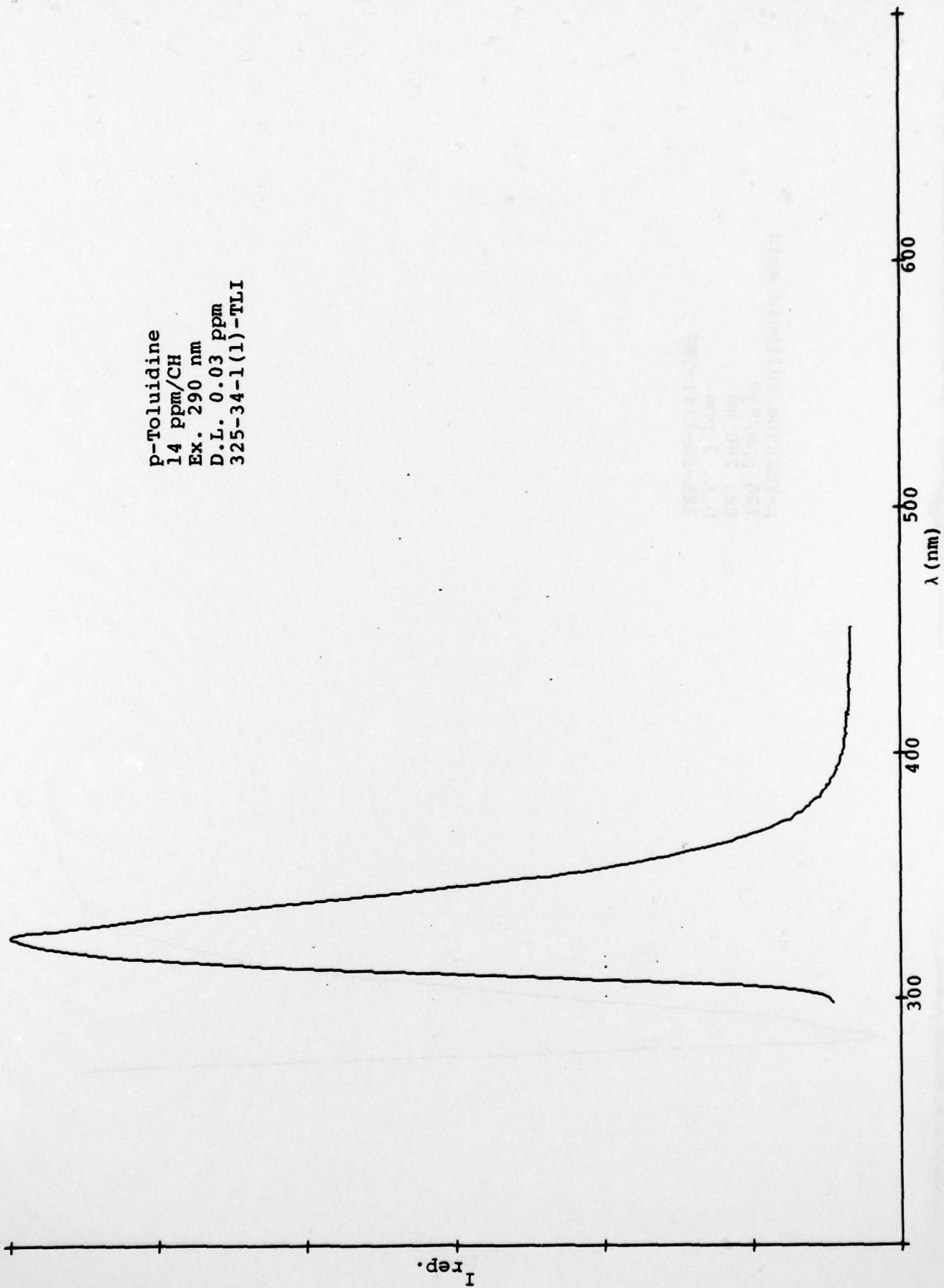
Toluene
110 ppm/CH
Ex. 250 nm
D.L. 2 ppm
284-27-2(2)-TOL



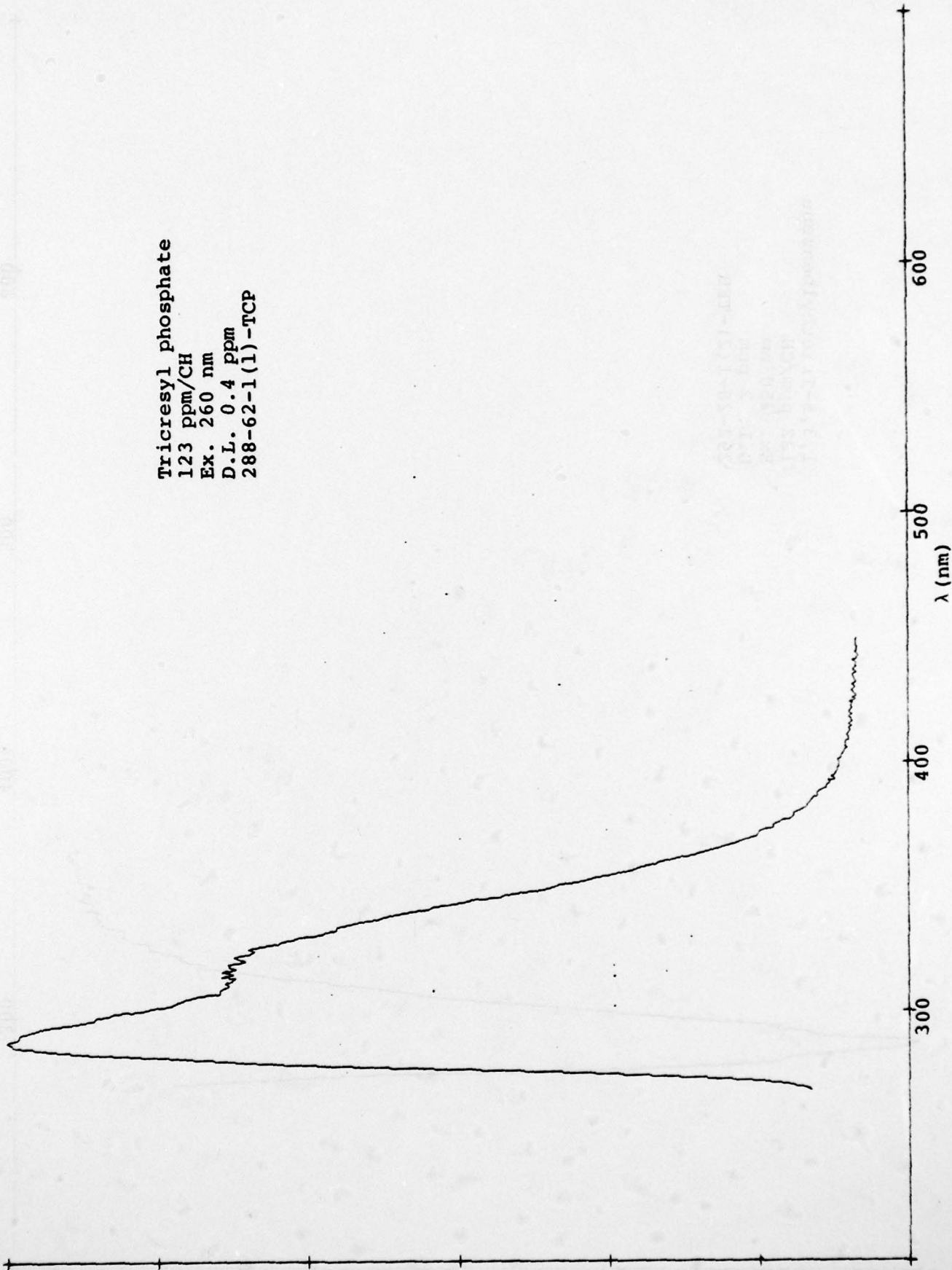
p-Toluene sulfonic acid
120 ppm/H₂O
Ex. 260 nm
D.L. 2 ppm
285-28-1(1)-TAP



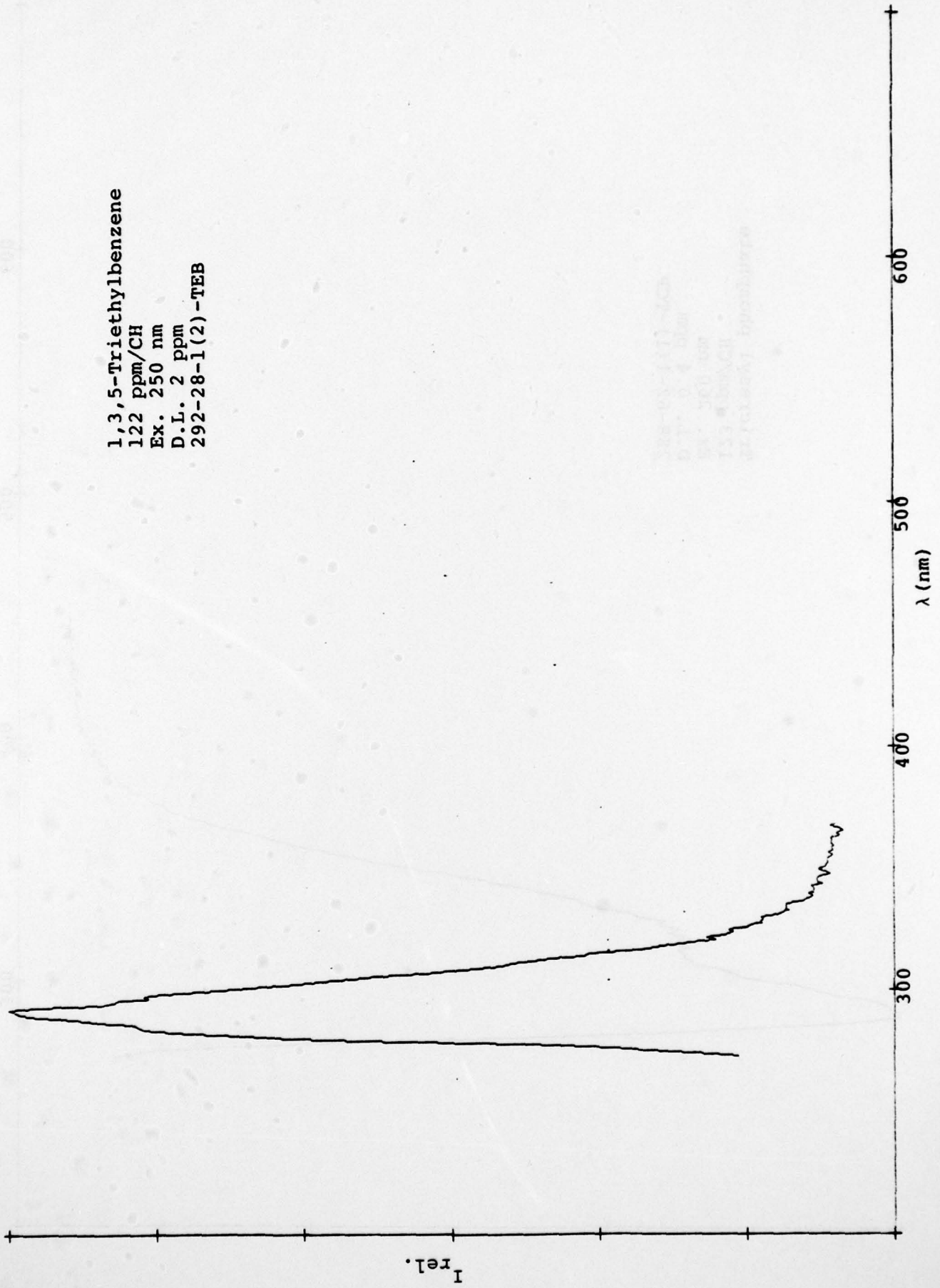
p-Toluidine
14 ppm/CH
Ex. 290 nm
D.L. 0.03 ppm
325-34-1(1)-TLI



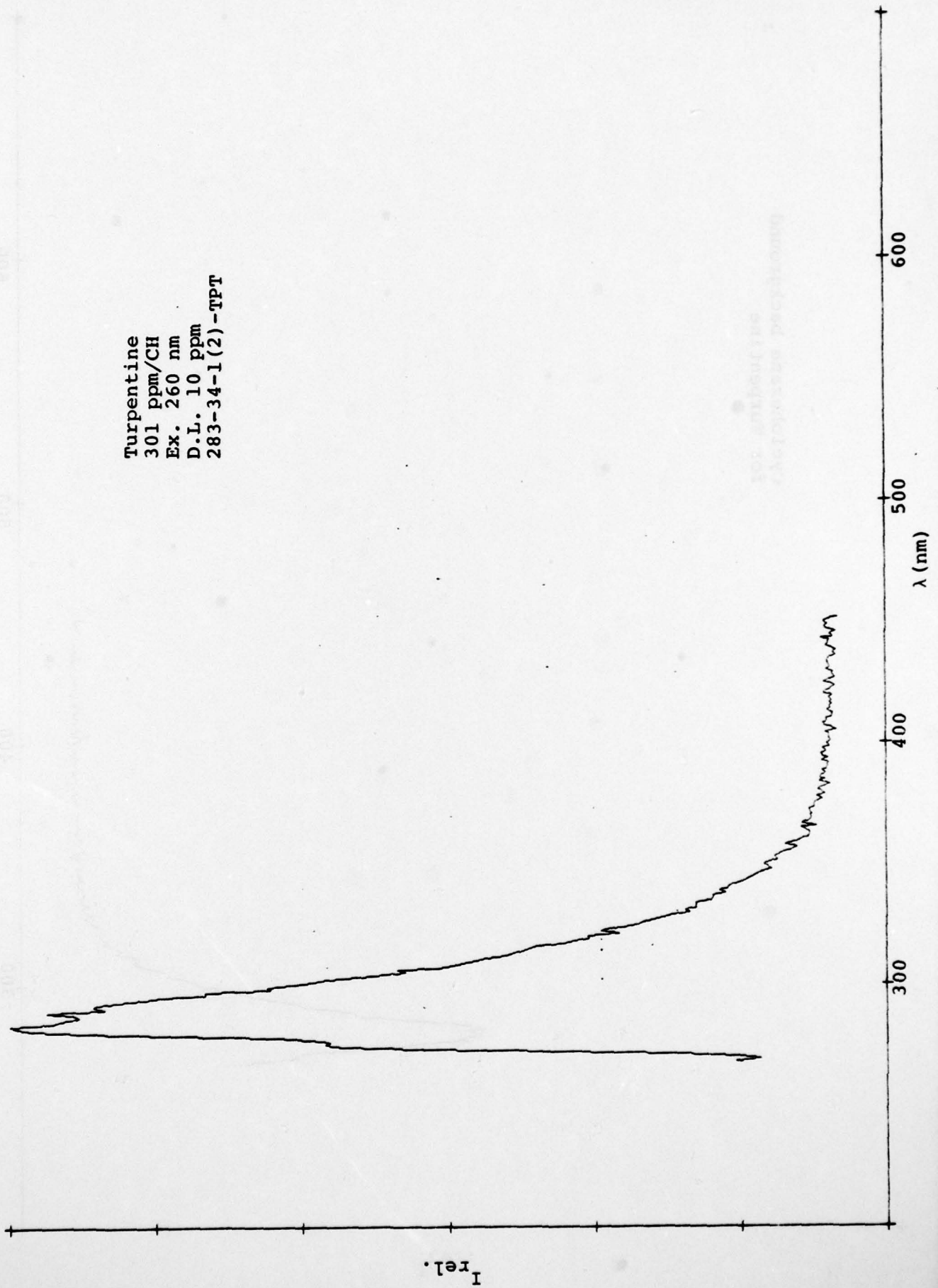
Tricresyl phosphate
123 ppm/CH
Ex. 260 nm
D.L. 0.4 ppm
288-62-1(1)-TCP



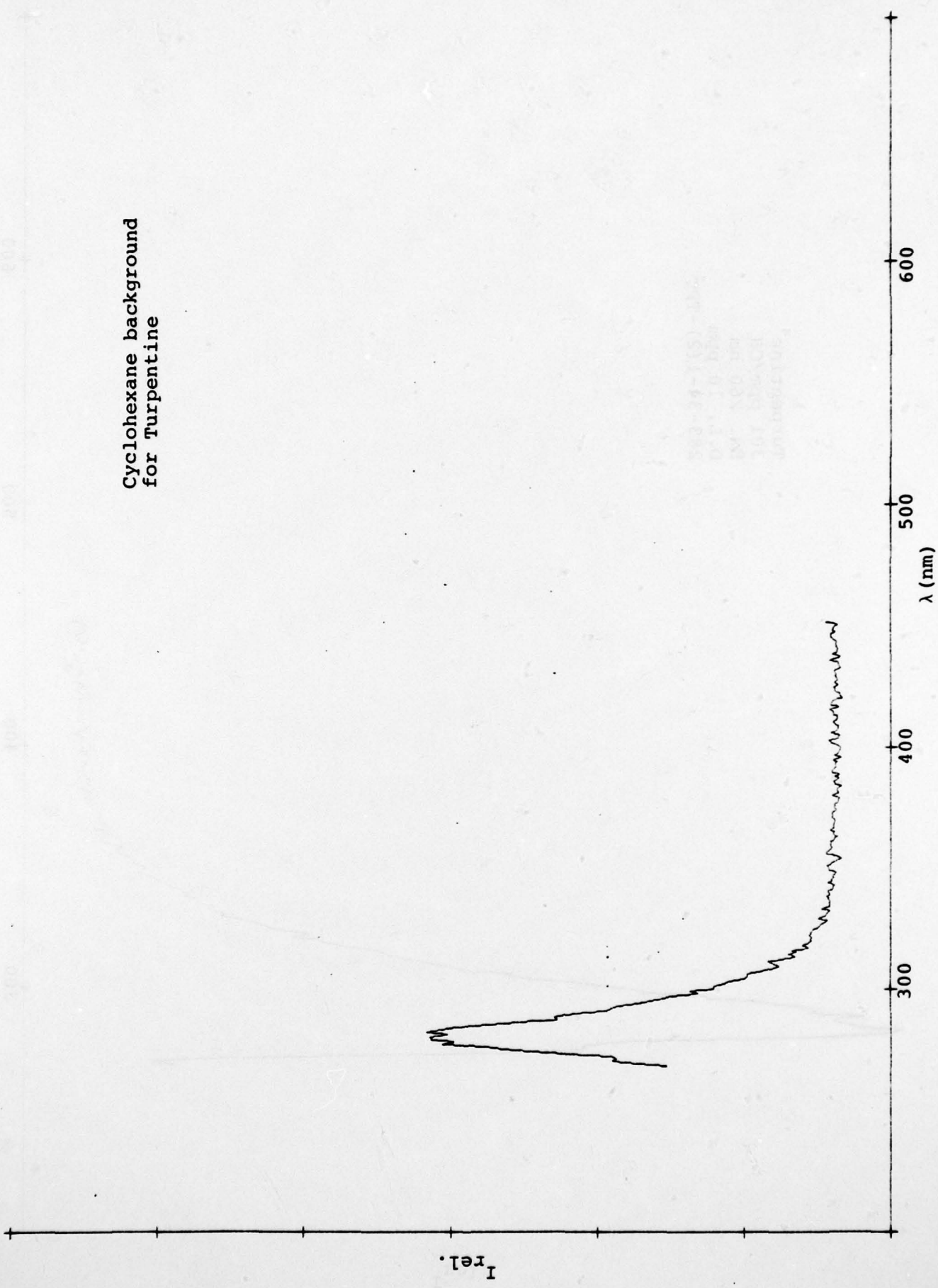
1,3,5-Triethylbenzene
122 ppm/CH
Ex. 250 nm
D.L. 2 ppm
292-28-1(2)-TEB



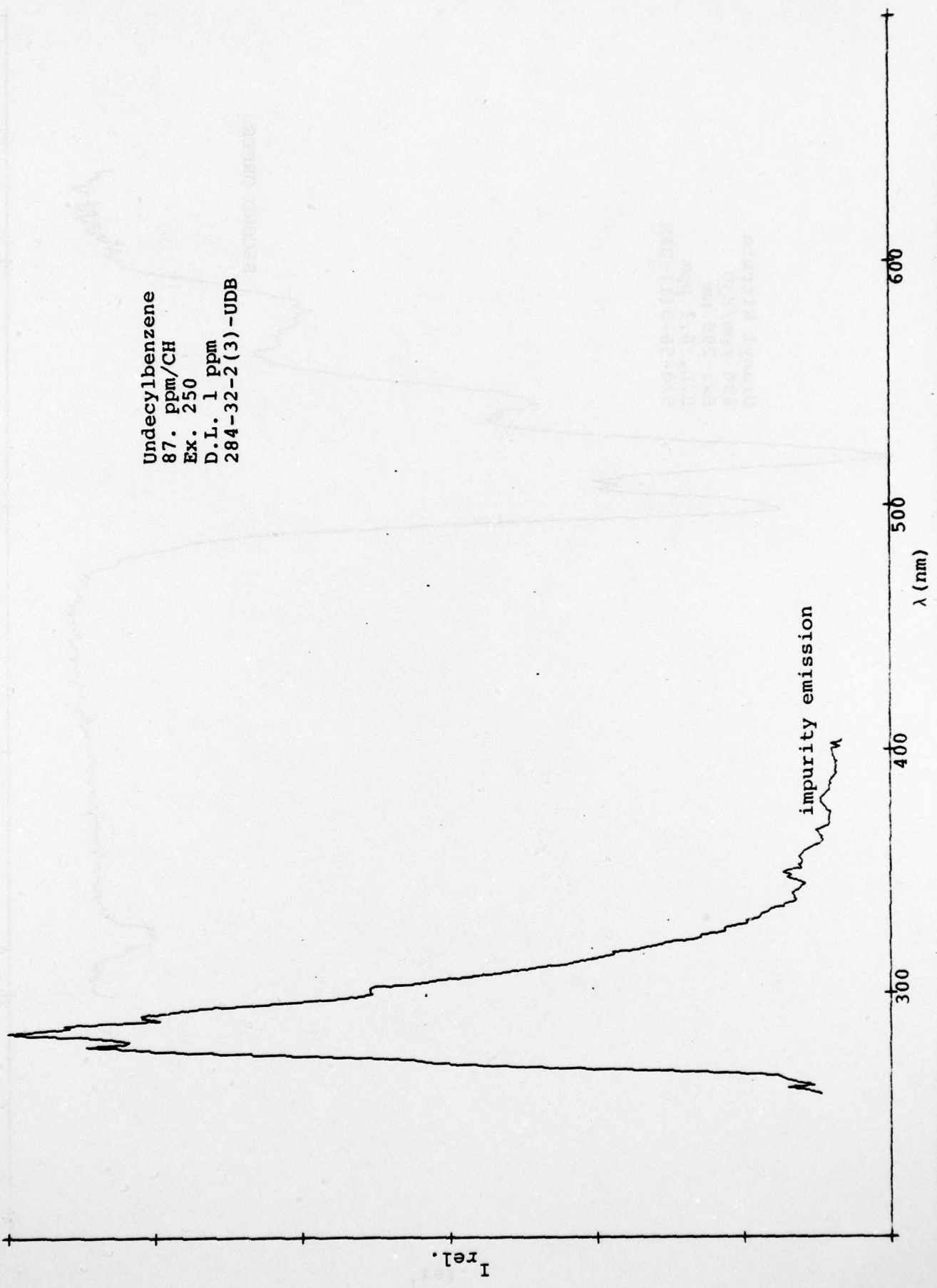
Turpentine
301 ppm/CH
Ex. 260 nm
D.L. 10 ppm
283-34-1(2)-TPT



Cyclohexane background
for Turpentine

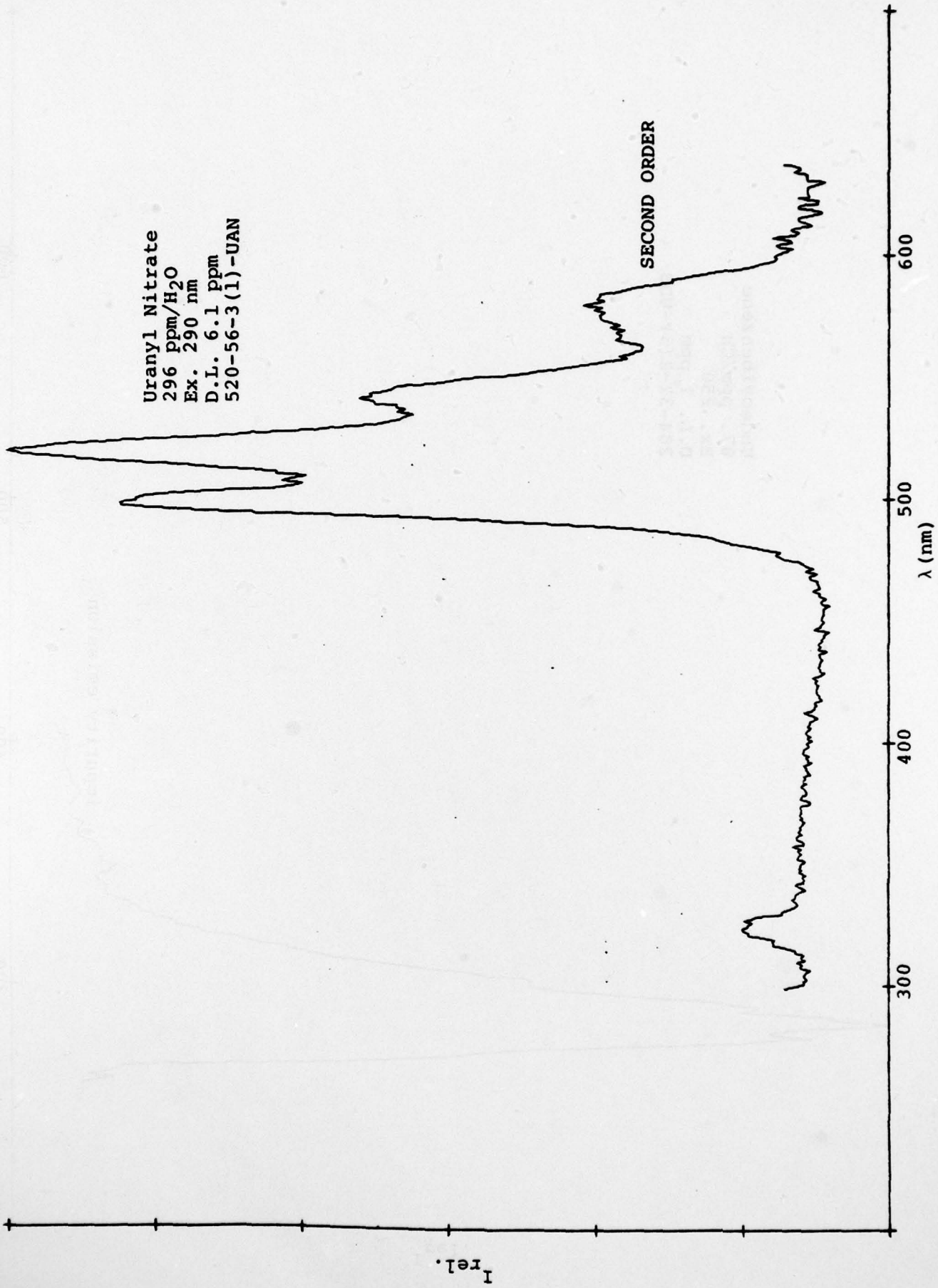


Undecylbenzene
87. ppm/CH
Ex. 250
D.L. 1 ppm
284-32-2(3)-UDB

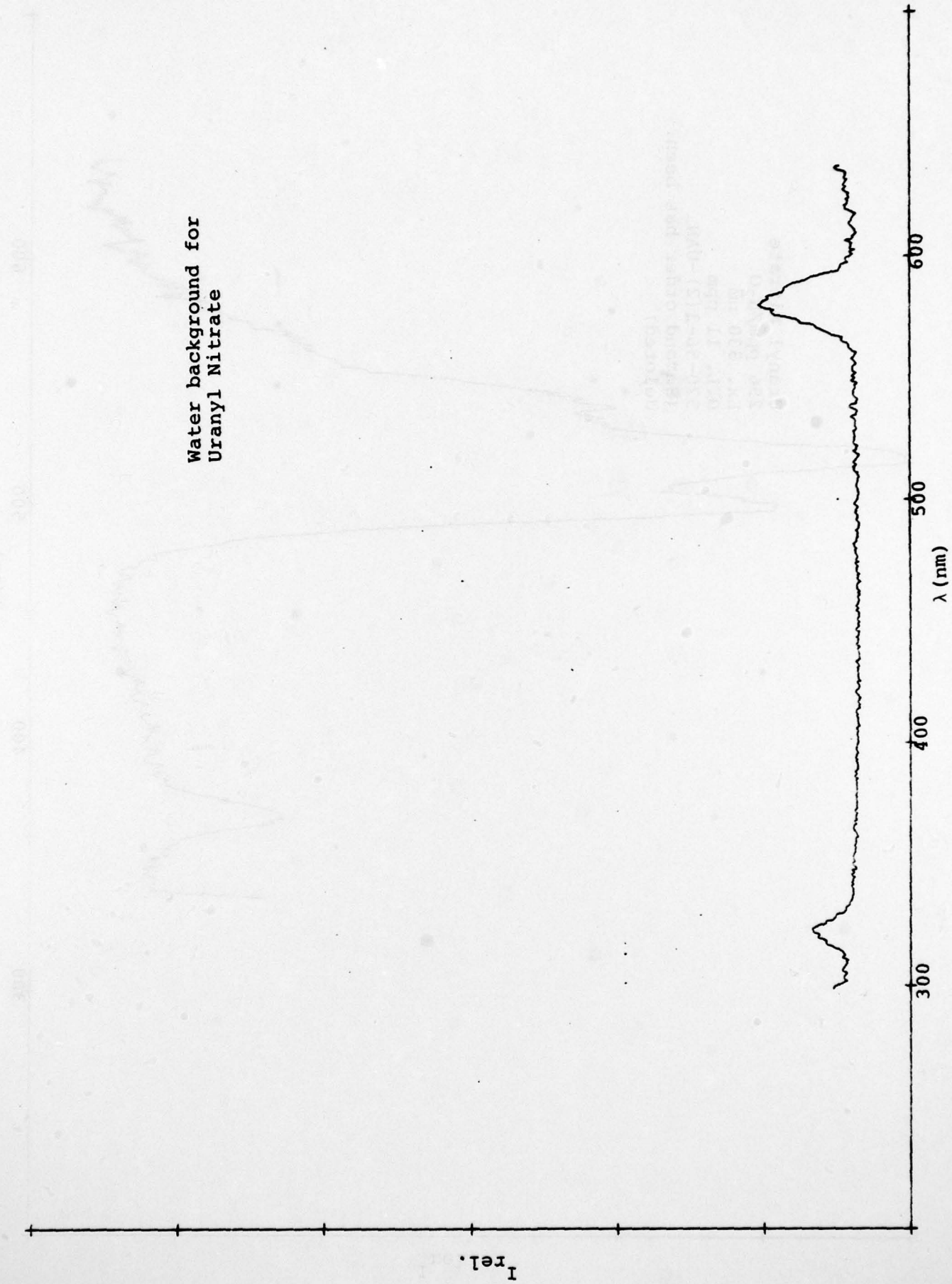


Uranyl Nitrate
296 ppm/H₂O
Ex. 290 nm
D.L. 6.1 ppm
520-56-3(1)-UAN

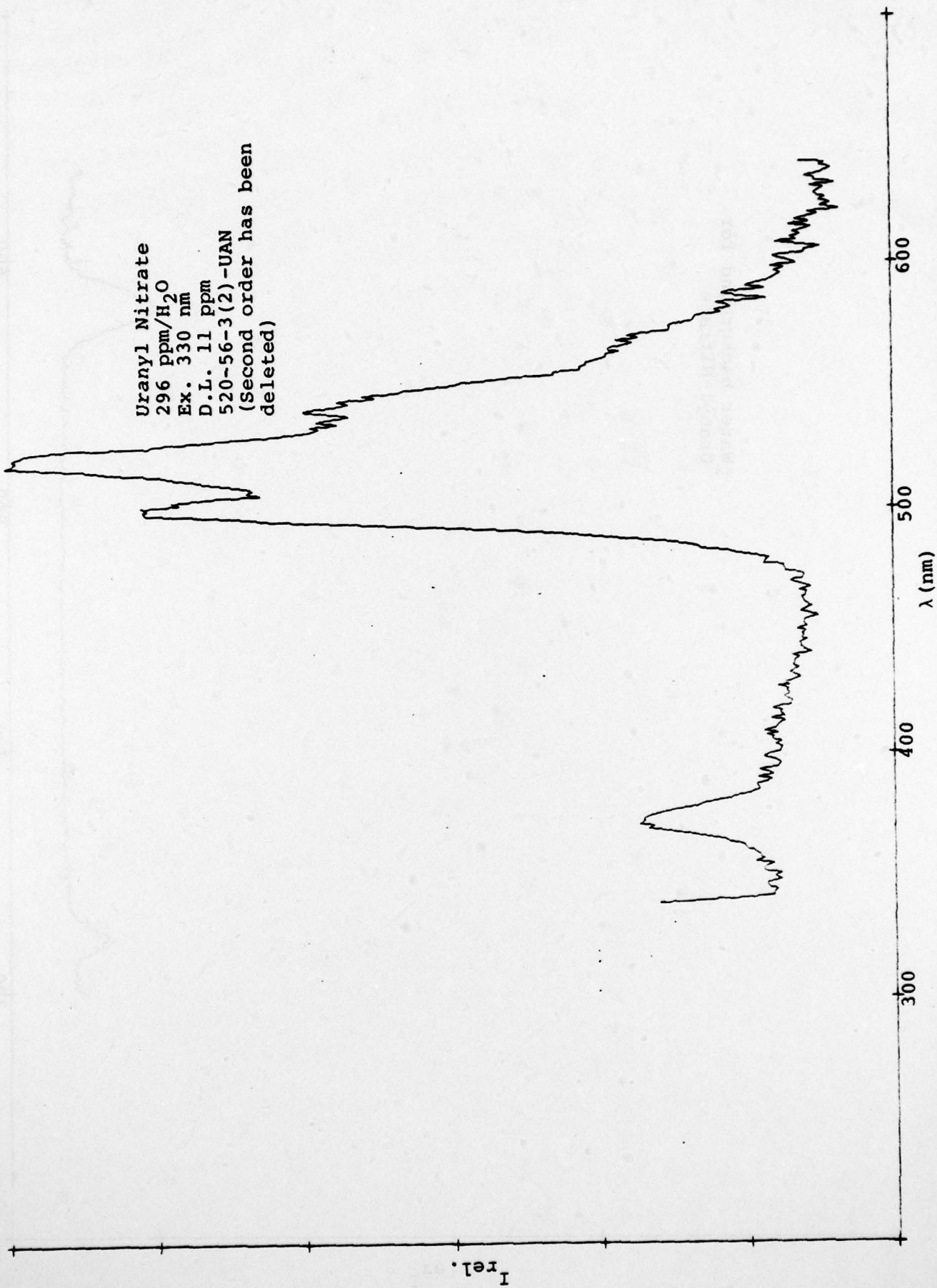
SECOND ORDER



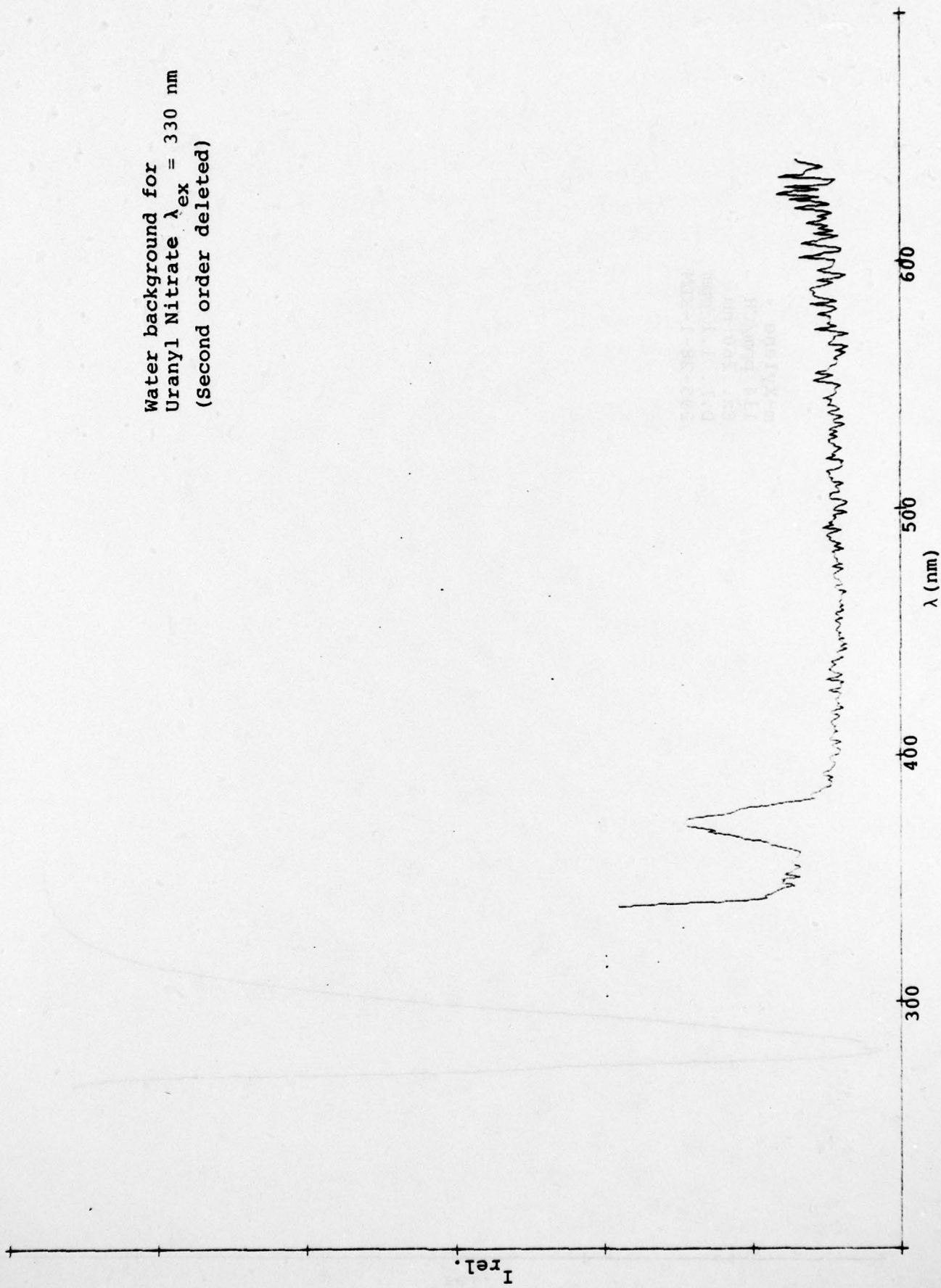
Water background for
Uranyl Nitrate



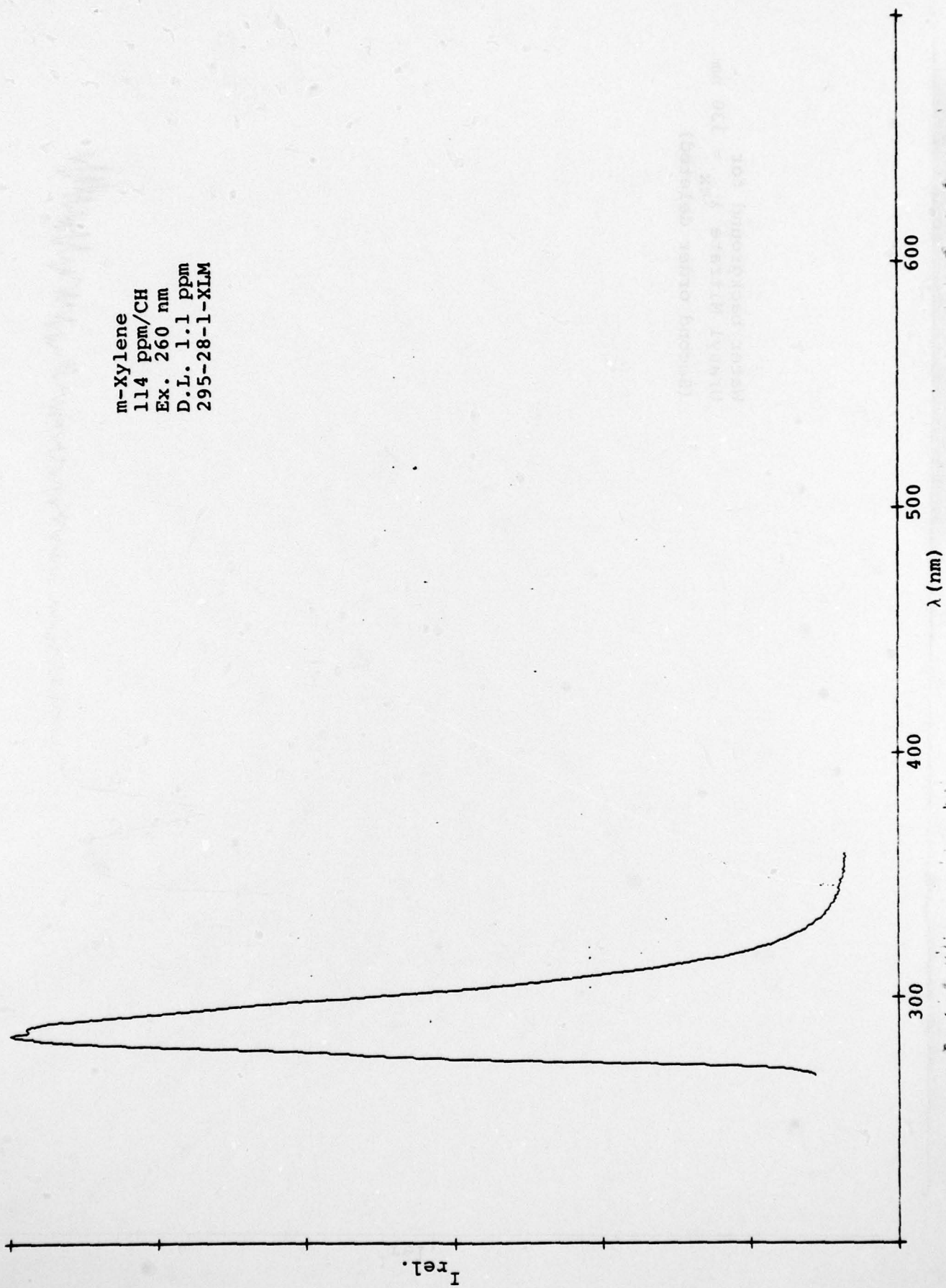
Uranyl Nitrate
296 ppm/H₂O
Ex. 330 nm
D.L. 11 ppm
520-56-3(2)-UAN
(Second order has been
deleted)



Water background for
Uranyl Nitrate $\lambda_{ex} = 330 \text{ nm}$
(Second order deleted)



m-Xylene
114 ppm/CH
Ex. 260 nm
D.L. 1.1 ppm
295-28-1-XLM



o-Xylene
92 ppm/CH
Ex. 260 nm
D.L. 1 ppm
285-30-1-XLO

