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Ozone Complexes with Substituted Aromatic Compounds

by

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III

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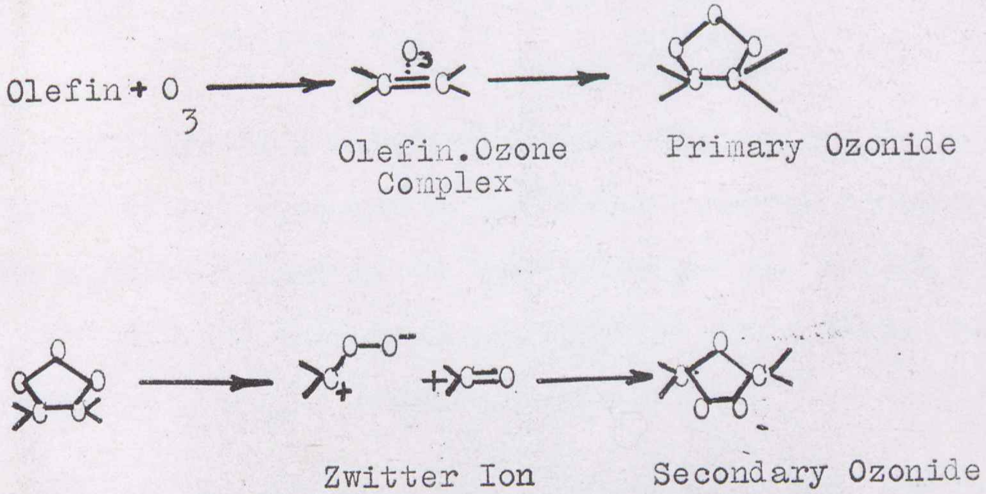
Abstract

Ozone has been observed to complex with aromatic compounds at low temperatures. The ability of an aromatic system to complex with ozone appears to be due to the inductive effect of the substituent on the pi system. The experimental work was done in the solid phase at temperatures of -175°C to -185°C. Under these conditions all the substituted aromatics with electron releasing groups complexed (with the exception of p-dimethyl benzene), and all the substituted aromatics with electron withdrawing groups did not complex including benzene. The complexes are highly colored. To insure the reversibility of the pi complex, infrared spectra were taken of some of the aromatic species before and after complexing. These spectra proved to be identical. Our findings were limited by the vapor pressures of the materials being studied. Pi complexing of ozone, as an electrophile, and an electron donor has long been assumed but only recently has any concrete information been available.

Introduction

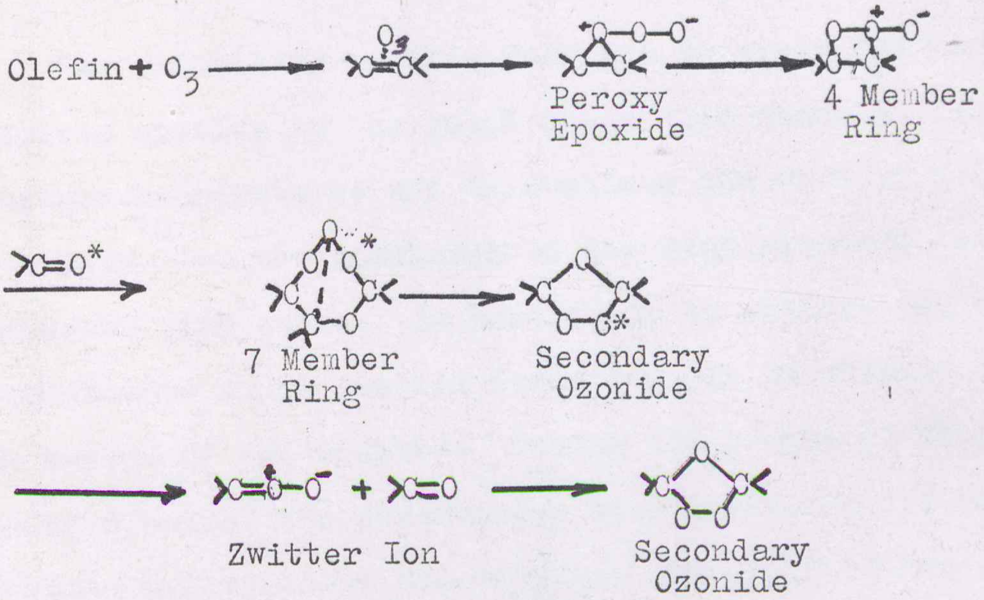
The reaction of ozone with an olefin has been used for many years to produce aldehydes and/or ketones,[1] yet the mechanism governing this reaction has long been a topic of research and debate. Several different pathways are envisioned for the reaction, two of which are discussed. In all the reaction schemes ozone acts as an electrophile attacking the electron rich olefin.[2-14]

A great deal of attention has been given to the nature of primary ozonide and its conversion to secondary ozonide. Currently, there are two mechanism, which have some support. Mechanism I is offered by Criegee and is subscribed to by many researchers in the field.[6, 11, 12, 15]



There has been a substantial amount of proof for the primary ozonide presented by Greenwood,[6, 11, 15] Bailey,[12] and Fliszar.[16] The existence of the zwitter ion, which is the principal intermediate of the Criegee mechanism, has been infered by the experimental work of Criegee,[2] Fliszar,[5, 17, 19, 20] and Bailey.[18]

Mechanism II was proposed by Story to explain some inconsistencies in the Criegee Mechansim.



This mechanism is considerably more complex and involves several types of intermediates, including a peroxy epoxide (to explain epoxide formation in some ozonolysis), a four member ring (to explain reductive ozonolysis) and a seven member ring (to explain isotopic labeling results).

One notes, however, the similarity between the two mechanisms is the pi complex. There has been a great deal of work done on conversion from primary to secondary ozonide and relatively little on the formation of primary ozonide from the pi complex. When we started this work only two studies reported complex formation. Bailey reacted ozone with 1,1-phenylmesitylethylene and noted a colored complex.[9] Hull reacted olefins at liquid nitrogen temperatures with ozone and studied the subsequent pi complexes by infrared spectroscopy.[10] A reversible complex was also observed in the case of ozone and toluene.

The objectives of this work are to study the complexes of aromatic species in the solid phase with ozone at near liquid nitrogen temperatures and to continue the work of Hull and coworkers[10] on the complexes of the high electron density substituents with ozone. In particular to explore the effect of substituents on pi complex formation, in an attempt to infer the nature of the complex. During the course of this work, Bailey reported the observation of pi complexes of several aromatic hydrocarbons and ozone at low temperatures and recorded their visible spectra.[8]

Experimental

Apparatus

A detailed schematic of the vacuum line used is protrayed in **Figure 1.** On the upper portion of the vacuum line there is an oil diffusion pump, liquid nitrogen trap, U tube, two female fittings with stopcocks, flexible coils with stopcocks, another female fitting and another U tube. The arrangement of stopcocks in this portion of the vacuum line allows oil diffusion pump to be omitted from the line, usage of upper or lower portion of vacuum line independently of one another, and isolation of any portion of the vacuum line. The first U tube is used mainly for distillation of material for purification and expansion of the gaseous material contained in the cell. The second U tube is used for ozone formation. The U tube for ozone formation uses a high frequency, high voltage electrical discharge to form ozone. (See Figure 2) The liquid nitrogen traps are used to protect the oil diffusion pump and mechanical pump from volatile, corrosive material. The first two female fittings are used for sample introduction into the line, while the final fitting is used for an NRC 801 vacuum gauge. The flexible coils are used to give flexibility to the system for attachment of the vacuum cell.

The lower portion of the vacuum line contains a liquid nitrogen trap, two liter bulb with cold finger, a mercury manometer and a female fitting. The two liter bulb is used to store oxygen for ozone preparation. The mercury column is used to determine the pressure of oxygen in the line.

The Cell

The cell is of standard design[24] composed of a male and female 91/60 joint. The male joint (Figure 3) has two take-offs with stopcocks and ground ball fittings adapted to the flexible coils of the above vacuum line. There are two potassium chloride windows opposite each other for infrared and ultraviolet work and a third glass window for UV-visible irradiation studies. These windows are attached to the cell by Apiezon Q.

The female joint (Figure 4) had a cold finger which was attached to a copper window frame assembly by a copper to glass seal. The window frame contained a CsBr window. The choice of CsBr as an internal window was made because CsBr is a soft crystal and will not shatter when subjected to the stresses of heating and cooling.

A Cu-Constantine thermocouple was attached to the lower portion of the copper window frame to obtain a cooling curve. The thermocouple was sealed with Apiezon W.

During all the experiments there was no visible decomposition by ozone of the copper window frame. This was probably due to the low temperatures.

The windows were supplied by Harshaw Optical Crystals (Cleveland, Ohio). They were polished by hand on a felt cloth with rouge (aluminum oxide) and ethanol. During warm weather cells had to be frequently polished due to the humidity in the air.

The line and cell is capable of obtaining a temperature of -187°C. This temperature was determined by using a Leads and Northrup potentiometer and galvanometer, a standard cell of 1.0193v, a power source of two 1.5v dry cell batteries, and ice-water bath as a zero reference. The optimum temperature was obtained by pumping on the cold finger, which contains liquid nitrogen, with a mechanical vacuum pump for an additional half hour after solid crystals of nitrogen formed (melting point of nitrogen is -209.95)[25].

The vacuum obtained was determined by an NRC 801 vacuum gauge which measured in microns. We were able to reach a zero reading on the gauge itself, which corresponds to less than one micron. When a discharge coil was placed next to the glass there was no neon effect which indicates a very good vacuum ($\sim$1 μ).[29]

The technique of a normal run involves an initial pump down, cooling, preparation, and deposition of the sample and ozone, and removal of the sample.

The initial pump down is done to eliminate any residual material on the cell window or vacuum line. First, the liquid nitrogen traps are filled to obtain good vacuum and collect any material which might be hazardous to the operator. The mechanical vacuum pump is then started to evacuate the total system including the ozone formation trap. When the vacuum gauge reading is less than 100 microns, the oil diffusion pump (prewarmed) is opened to the system. The pump down continues until the vacuum gauge reads less than 10 microns for one half hour, the normal pressure for a run.

The cold finger of the cell is then cooled by the introduction of liquid nitrogen to the cold finger. When no more large bubbles appear in the liquid nitrogen (about -100°C) an auxiliary mechanical vacuum pump is used to evacuate the cold finger above the liquid nitrogen. After 10 to 20 minutes solid crystals of nitrogen appear (-209.95°C).[25] The vacuum on the cold finger is periodically released to maintain a solid-liquid nitrogen mixture and to refill the cold finger. Once the solid-liquid mixture has been held for thirty minutes the window is ready for deposit. A temperature taken with a Cu-Constantine thermocouple is about -187°C.

The sample is then degassed to remove any air or other soluble gasses which may be dissolved in the sample. To do this the sample is placed in the line, frozen with liquid nitrogen, and pumped on by the mechanical pump for 5 minutes. This can be done during the cooling period for the cell but the stopcock to the cell and oil diffusion pump must be closed. The stopcock for the sample is closed after five minutes and the others again opened. The sample is allowed to warm to room temperature and one notes the evolution of gasses from the liquid. The freezing process is repeated again except that the oil diffusion pump is kept in the system. The sample stopcock is closed again and the others are opened and the sample is allowed to warm to room temperature.

The sample is ready to be deposited on the window. To do so, the stopcocks are closed to the vacuum pump, oil diffusion pump, and cell. The stopcock to the sample is opened until the NRC 801 vacuum gauge reads 3000 microns plus. The stopcock to the sample is then closed and, for short intervals, the lower stopcock of the cell is opened until a definite diffraction pattern can be seen on the CsBr window (one to ten millimoles is an estimation of the amount of material deposited on the window). The stopcock to the oil diffusion pump is then opened and the cell and line are evacuated to less than ten microns.

The ozone can be prepared while the cell is being cooled. The U tube has previously been prepared during the initial pump down. It is then closed to the line before the cell is cooled. Oxygen is drawn into the U tube by opening the stopcock to the rear of the line, which contains only oxygen. The approximate pressure of the line is 3 to 5 mu. A full dewar of liquid nitrogen is raised so the liquid nitrogen level is at the lower most loop of the discharge coil. The electric discharge coil is activated until there is a neon effect in the U tube. At the beginning of the electric discharge a blue ring of ozone is noted on the inside wall of the U tube. The discharge is continued until there is a blueish red neon effect throughout the U tube, which is estimated to be at a pressure of 10 μ.[29] The dewar is then raised to the top of the U tube, all stopcocks are closed, and the stopcock to the mechanical pump, U tube and line are opened. This removes all the excess oxygen due to the fact that the boiling point of oxygen is -182.97°C and ozone is -112°C,[26] and hence the oxygen has a vapor pressure far greater than the ozone. All stopcocks are again closed after a pressure of less than ten microns is reached for ten minutes. The stopcock to the vacuum pump is closed and the stopcocks to the cell are left closed. The liquid nitrogen dewar is lowered from the U tube and the ozone is allowed to expand into the line. The pressure in the line builds to approximately 2000 microns (.3 to 1 millimole).

The stopcock is opened to the cell and the ozone is allowed to distill onto the window. (Noted by drop in pressure on vacuum gauge.) The stopcock to the mechanical vacuum pump is then opened to remove any excess ozone in the line or cell. At this point the U tube for ozone formation was closed off by the stopcock. In most cases the complex formed immediately. In other cases the liquid nitrogen was removed from the cold finger making the window the coldest part of the cell. The ozone can then be observed distilling from the copper cold finger onto the window. Once the complex is formed, it is recorded by the methods detailed in the next section.

To remove the ozone, the cell was opened to the line and the liquid nitrogen blown out of the cold finger. One could actually see the complex decompose and disappear. If a complex did not occur, one could see the blue color of the ozone distill from the window as the temperature of the cell warmed. Also one notes that the vacuum gauge starts falling rapidly. The line is then opened to the mechanical vacuum pump and the cell is warmed to prepare the cell and line for the next compound to be run.

The vacuum pump is run overnight to be sure all material is removed from the cell and line. The line is then ready for the next experiment.

The techniques used for proving a complex were infrared, ultraviolet, and photographic. Infrared was used initially to extend work done by Hull[10]. They note bands at 2100 and 1030 Cm^{-1} corresponding to pi complexes. It turns out that aromatic species give more complex spectra in the infrared than olefins and we, therefore, were unable to ootain any pertinent data of pi complexes. However, we were able to show reversibility of the ozone-aromatic species. The spectra before complex and after complex formation were the same except for a slight loss in intensity--due to loss of material during removal of ozone. The disadvantages of the infrared technique are that complex bands are weak, and there are aromatic absorptions near the region of interest.

On some samples UV-vis spectra were taken. This proved to be extremely difficult to do. The limitations of the technique were due to the fact that only a small amount of material can be on the window to give interpretable results. If the amounts of material were too large, the complex when formed, would give spectra that were off scale. Our ability to control the amount of ozone and how well it came in contact with the window was very poor. Also, if the material crystallized on the window, scattering prevented any significant amount of light passing through the sample. Often the very process of complex formation caused crystallization.

Since all the complexes were colored, photographic slides were the easiest, most convenient method of reporting and recording data. We used a Cannon single lens reflex camera, shutter speed 1/8 second, Kodak high speed color film, f_s 11, ASA - 125, 50 mm lens with two closeup attachments and a ringstand as a tripod. The photographs were taken before the ozone was added, after complex was formed, and after the ozone was removed. Many of the slides show a white crystaline material after ozone was removed, which was just the crystalized substituent being studied.

Results

Some of the general difficulties with this method are as follows. One is restricted to studying compounds, which are volatile at room temperature. This eliminates many substituents due to their high molecular weight or very polar nature and consequently low volatility. For our studies only liquids seemed to work well, with the exception of phenol.

In our use of the infrared and UV-visible spectra there were a number of problems. In the UV-visible there were difficulties caused from too much material on the CsBr window, which caused light scattering and broad absorptions. This was difficult to interpret. The orientation of the window in consecutive spectra also caused problems, since this would change the amount of light scattering. Also on a humid day, the cell would "sweat" causing the KCL windows to fog. In the infrared the major difficulties were orientation of the sample, too little or too much material on the cell window, overlapping spectra, and some light scattering.

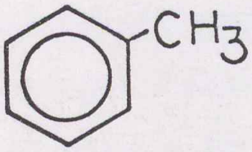
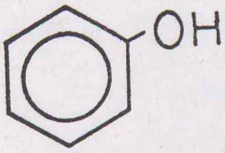
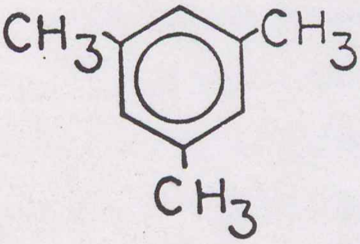
Data was difficult to obtain due to not only the substituent materials parquelauties but also the inability to control the amount of ozone being placed on the window. In addition quite frequently ozone would distill directly to the copper window holder and not to the cell window. When this occured, the liquid nitrogen had to be dumped from the cold finger until the copper warmed sufficiently for the ozone to distill to the window.

For a limited number of compounds we have shown that ozone complexes reversibly with aromatic pi systems. This was shown by the infrared spectra taken before and after the complex. The spectra were identical with the exception of intensity. The loss was presumably due to the vapor pressure of the material at the temperature used for removal of the ozone (up to -100°C). Reversibility is also demonstrated in that after the colored complex is formed ozone may be distilled from the window to the U tube. If the cold finger is again cooled and the U tube warmed, complex reappears. If the ozone is carefully removed, one can again observe the diffraction pattern on the window.

For toluene, mesitylene, and phenol good enough UV*vis spectrum were obtained to determine absorption maximum. Table I summarizes these results.

As an illustration of the clearest result Figure 5 shows the UV-vis spectrum of the complex of ozone and phenol. The spectra shown are difference spectra between actual spectrum and the specrtum after the removal of ozone. This compensates somewhat for the enhanced scattering that occurs because of crystallization of the phenol when the complex forms. The

ABLE I - UV-vis maxima of some ozone•• aromatic compound complexes.

Comp.	λmax (nm)
	385
	400
	450

negative absorbances beyond 600 nm are then due to slightly more scattering of the spectrum of the phenol after removal of the ozone (additional crystallization). The -180°C spectrum shows the initial complex spectrum, with a clear maximum about 400 nm. On warming the sample, while pumping on it, to -150°C some of the ozone is removed and there is less complex. Upon recooling and recording the spectrum, the -150°C spectrum is obtained. It has the same maximum but is of lower absorbance due to there being less complex.

For the rest of the compounds where UV-vis and IR proved difficult, photographs recorded the colors of the complex or the absence of the complex. It was assumed that the visible behavior of these compounds, namely forming a colored species on being exposed to ozone, and on warming going back to colorless state, was indicative of complex formation. In Figure 6 one notes the A photograph of the uncomplexed material, the B photograph of the complexed material, and the C photograph of the material after complex. This behavior was associated with those compounds for which more objective evidence (namely spectra) were obtained. This tendancy of a complex to be colored is not necessarily a prerequisite for complex formation as shown by Dewar.[34] The results of these experiments are summarized in Table II.

Figure V - UV-vis difference spectrum of the ozone • phenol pi complex.

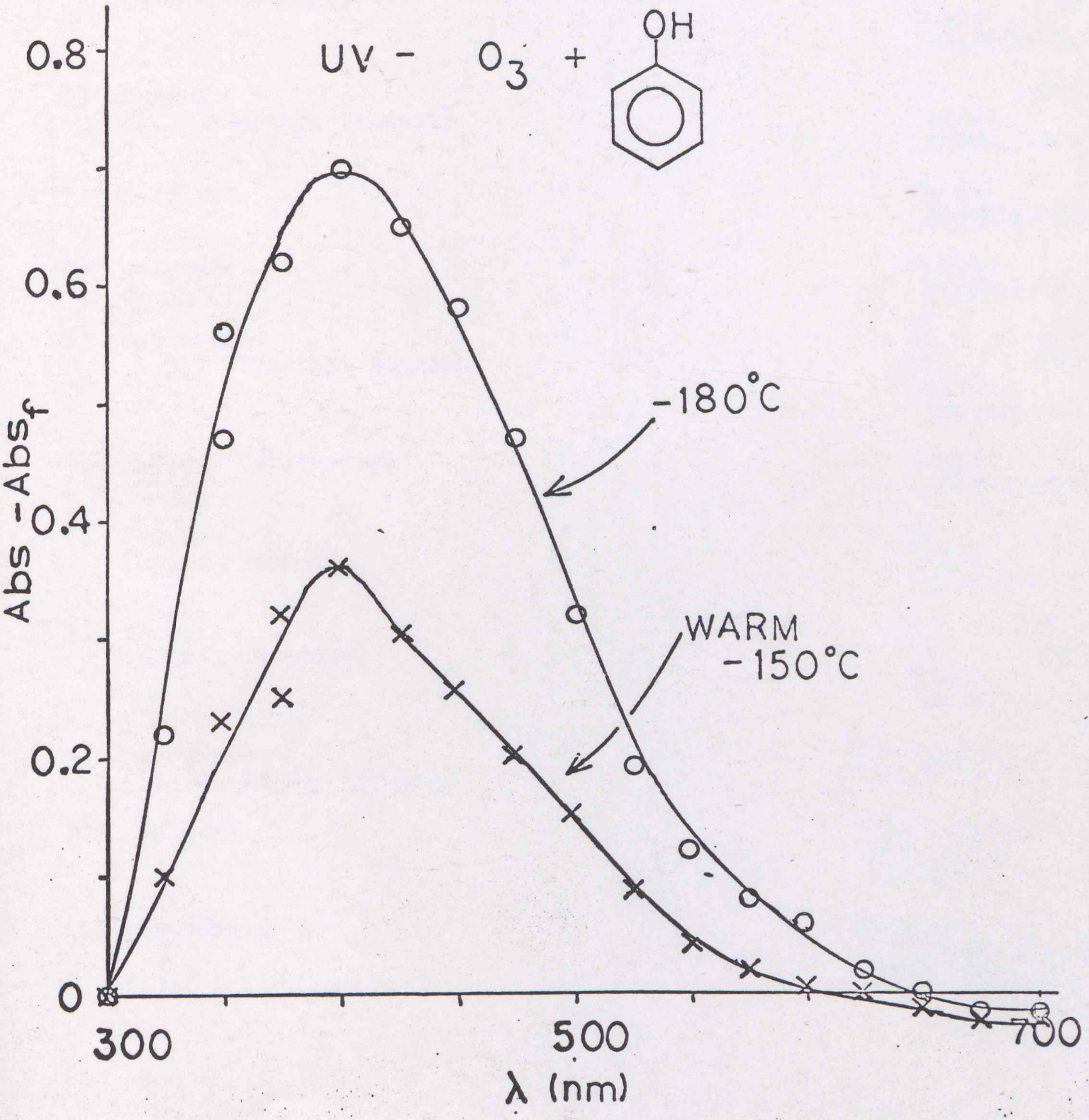


TABLE II - Results of complexing experiments.

Substituent	Type	Complex
1) Toluene (Methyl benzene)	Electron Releasing	Pos IR -Pos UV -Pos Photographic-Pos
2) O-Xylene (1, 2 dimethyl benzene)	"	UV -Pos Photographic-Pos
3) M-Xylene	"	Photographic-Pos
4) p-Xylene	"	Photographic-Neg
5) Mesitylene (1,3,5 trimethyl benzene)	"	IR -Pos UV -Pos Photographic-Pos
6) 1,2,4,5 tetramethyl	"	Photographic-Neg
7) Phenol (Hydroxy benzene)	"	IR -Pos Photographic-Pos
8) Anisole (methoxy benzene)	"	IR -Pos UV -Pos Photographic-Pos
9) Pyrochatchol (1,2 dihydroxy benzene)	"	Photographic questionable
10) Aniline	"	Forms complex; decomposes violently
11) Napthalene	"	Photographic - possible; complex color very faint

TABLE II - Results of Complexing experiments.
Continued

Substituent	Type	Complex
12) Anthracene	Electron Releasing	Photographic questionable
13) Benzene	"	IR - No complex observed UV - No complex observed Ozone on cell window
14) Benzaldehyde	Electron withdrawing	Photographic - no complex
15) Chlorobenzene	"	Photographic - no complex Could see blue color of ozone on cell window

The trend, which seems to be adhered to for the most part, is for electron releasing groups to enhance the ability of substituted aromatic systems to complex with ozone. This trend is demonstrated by the inability of benzene to complex with ozone, while methyl benzene, 1,2 and 1,3-dimethyl benzene, and 1,3,5 trimethyl benzene all complexed. Other aromatic compounds with electron releasing groups that formed complexes were phenol (-OH), Anisole ($-OCH_3$) and aniline ($-NH_2$).

The electron withdrawing groups seemed to impede the ability of a substituted aromatic pi system to complex with ozone. The aromatic compounds with electron withdrawing groups tried were chlorobenzene (-CL), benzaldehyde ($-\overset{O}{\overset{\|}{C}}-H$), and if hydrogen is considered electron withdrawing, benzene.

Other substituents done were difficult to interpret within these general trends. Two compounds notable for their not complexing were 1,2,4,5 tetramethyl benzene and 1,4-dimethyl benzene. Napthalene and anthracene were not easily studied due to their high molecular weight and consequently low volatility, which made them difficult to distill onto the window. Aniline was observed to give a redish brown complex, which decomposed destructively and, hence, its complex does not appear to be reversible.

Discussion

A pi complex of an electrophile with aromatic compounds is a well known phenomenon.[28] These pi complexes are of the charge transfer variety consisting of a donor and acceptor molecule. The donor can be any compound that is electron rich (this includes aromatic compounds, olefins, or a molecule with an unshared pair of electrons). The acceptor can be any molecule, ion or metal that can accept an electron. Many of the charge transfer complexes can be characterized by the appearance of a UV absorption at longer wavelengths. This band is called a charge transfer band.[35] Table III shows relative stabilities of other complexes compared with p-Xylene of various alkylbenzenes along with whether an ozone complex was observed.

Our results generally point to a complex with electron rich aromatic species. Each compound that we observed a color change showed a new band in the UV-vis and, therefore, we conclude we are dealing with a charge transfer pi complex. This pi complex occurs with the aromatic species being the electron donor and the ozone being the electron acceptor.

In a recent paper Bailey[8] corrolates the complex band position in the UV-vis with the ionization potential. With decreasing ionization potential of substituents he found bands at longer wavelengths. Although Bailey noted colors which were not in agreement with ours, he worked at a lower temperature (freon 12-liquid nitrogen and isopentane--liquid nitrogen) and on

TABLE III - Comparison of relative stabilities of alkylbenzene complexes.[27] with p-Xylene.

Benzene Sub.	Ag^+	Br_2	I_2	ICl	SO_2	Picric Acid	HCl	O^3 This Work	Bailey[8]
Benzene	.98	.46	.48	.36	.35	.70	.60	-	Pos.
Toluene	1.04	.64	.52	.57	.59	.84	.92	Pos.	Pos. Spectra
O-Xylene	1.26	1.01	.87	.82	1.23	1.03	1.13	Pos.	Pos. Spectra
M-Xylene	1.19	.96	1.00	.92	1.11	.98	1.26	Pos.	
P-Xylene	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-	
Mesitylene	.70		2.65	3.04	1.57	1.12	1.59	Pos.	Pos. Spectra

cooling he noted color changes. Other inconsistencies could be due to solvent or crystal interactions, since he worked in glasses and solution.[34]

The inconsistencies in our own data, primarily 1,4 dimethylbenzene and 1,2,4,5-tetramethylbenzene, could possibly be due to steric hindrance of the ozone approach to the molecule, crystal forces being greater than complex formation causing the complex to be thermodynamically disfavored, or electronic forces of the molecule at this low temperature could cause the complex to not be formed. The fact that not every substituent we checked gave a complex, might also be due to the fact that a charge transfer bond is lacking.[35]

In conclusion aromatic species and ozone form a pi complex. This complex seems to be related to the electron releasing ability of the attached substituents and shows a long wavelength UV-vis band. The complex is probably of the charge transfer type from the aromatic compound to the ozone. Presumably the electron donation is from the highest occupied molecular orbital of the donor to the lowest unoccupied antibonding molecular ortibal of the ozone. The stability of the ozone may be decreased and, therefore, more reactive by the aromatic pi electrons in the antibonding orbitals.

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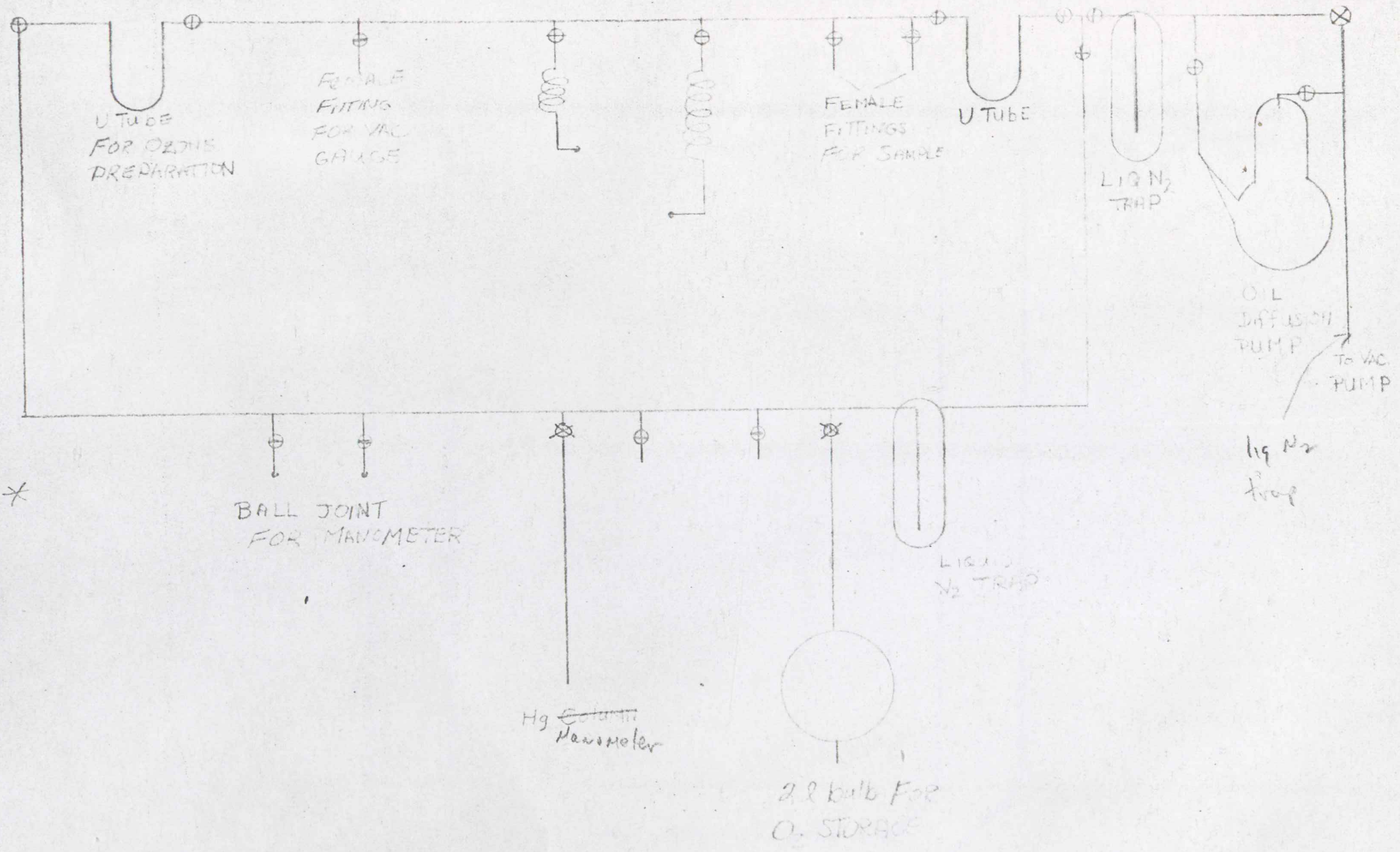
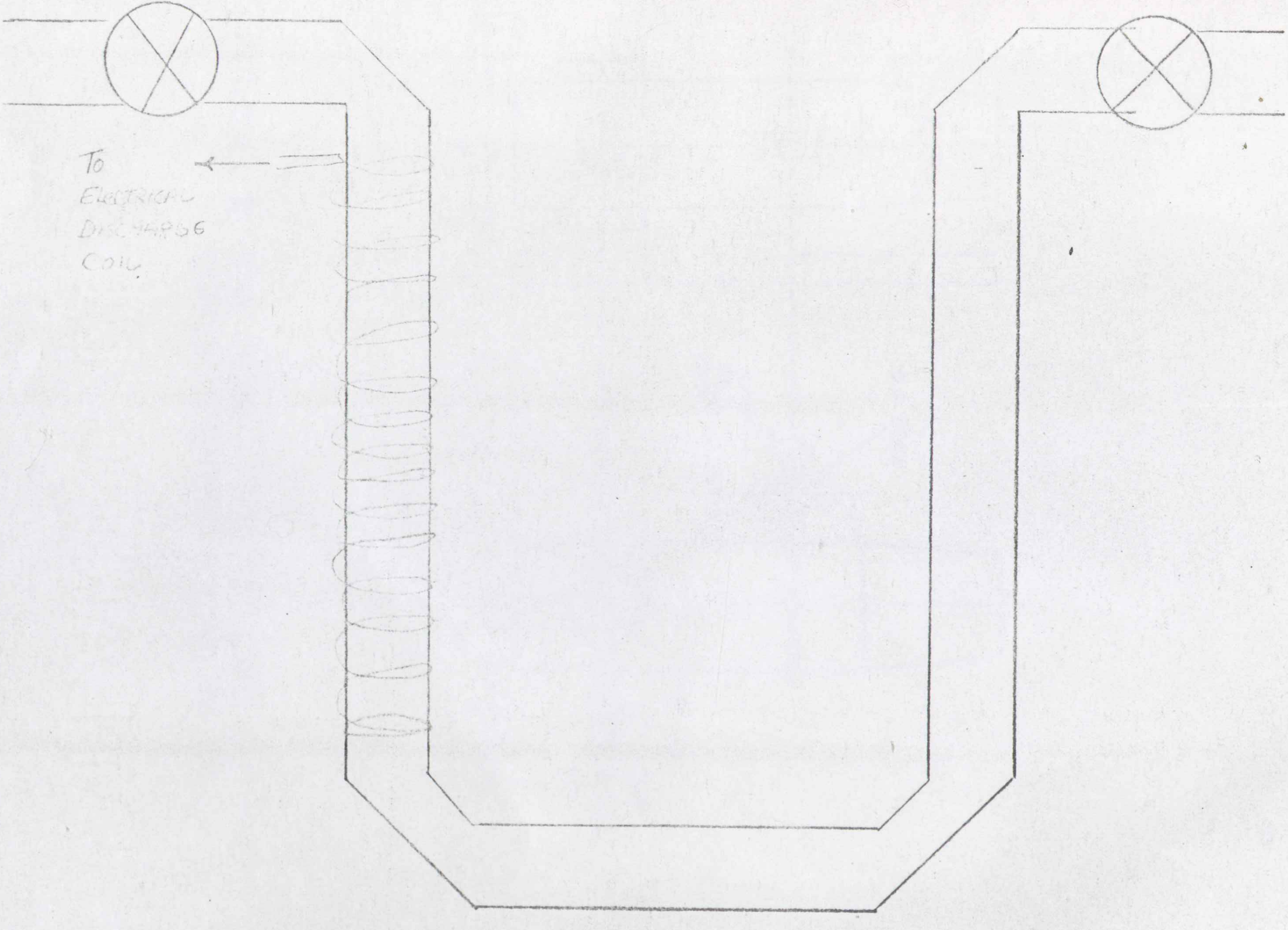


FIGURE 1: SCHEMATIC OF VACUUM LINE

FIGURE 2 U tube USED FOR OZONE FORMATION



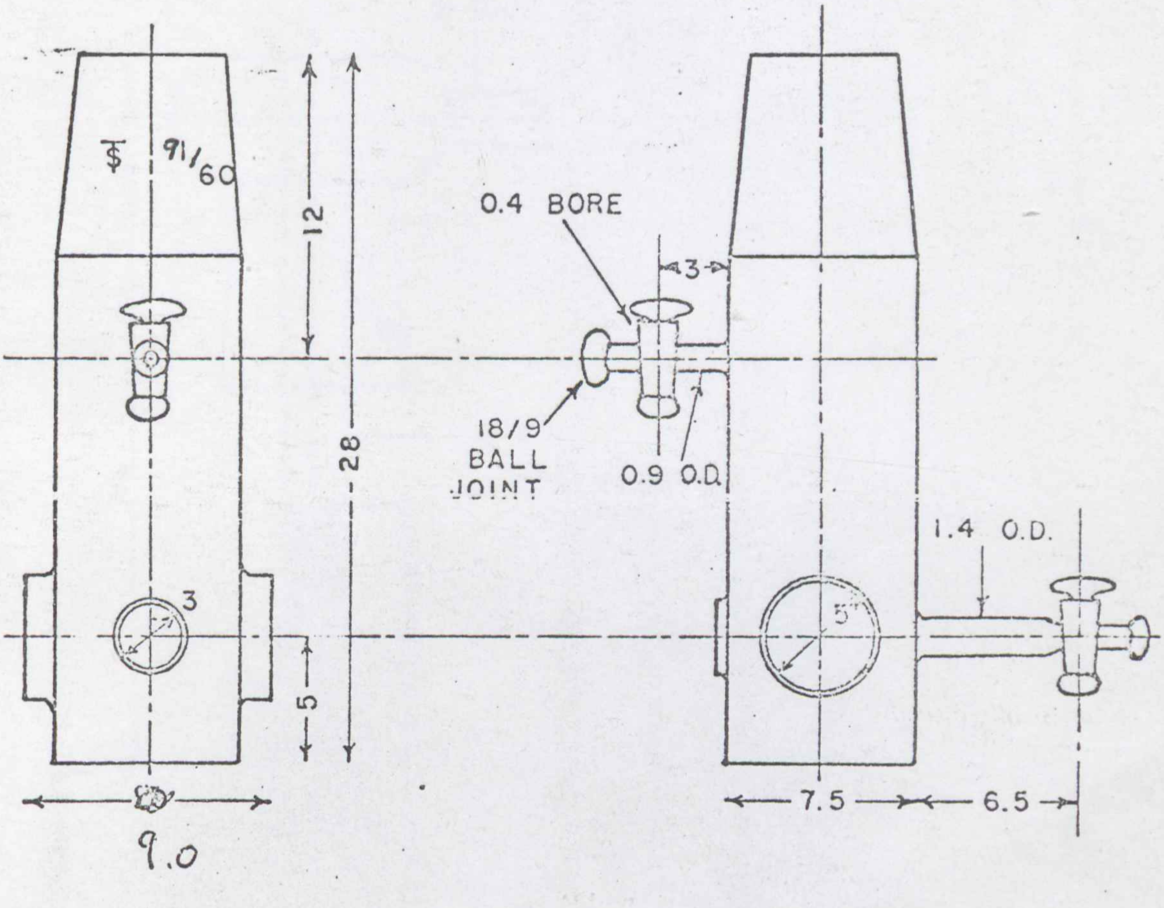


FIGURE 3. THE LOW TEMPERATURE CELL OUTER JACKET (UNITS IN CM).

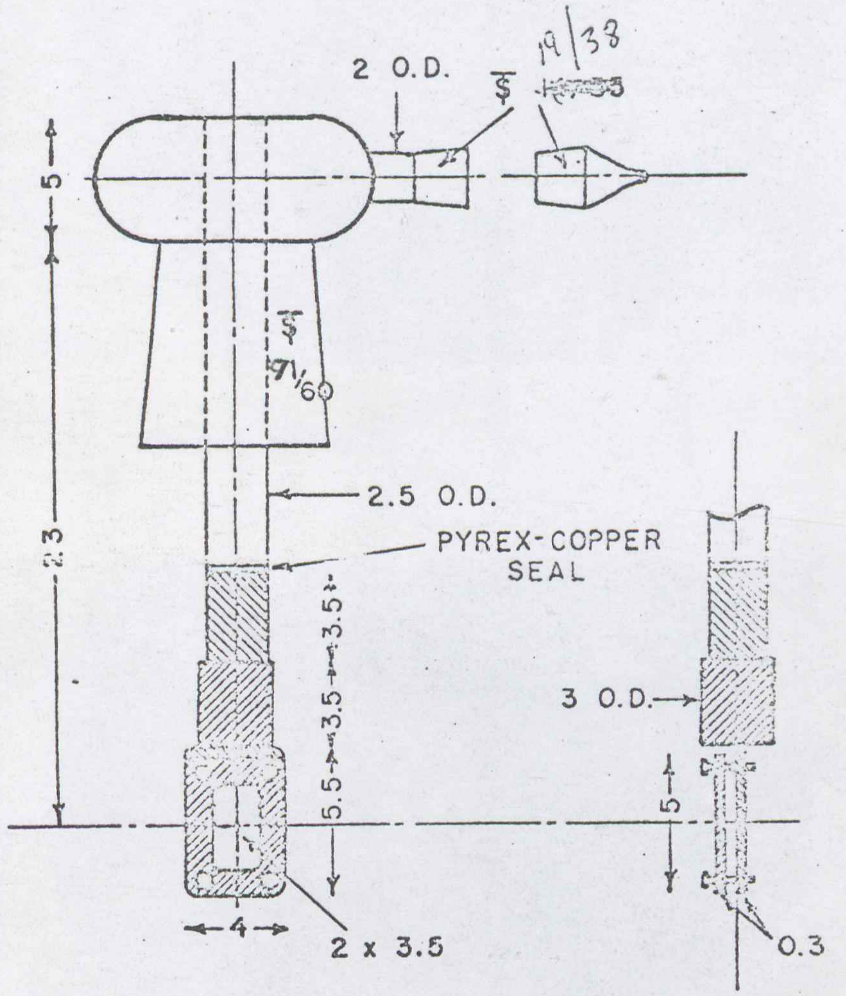
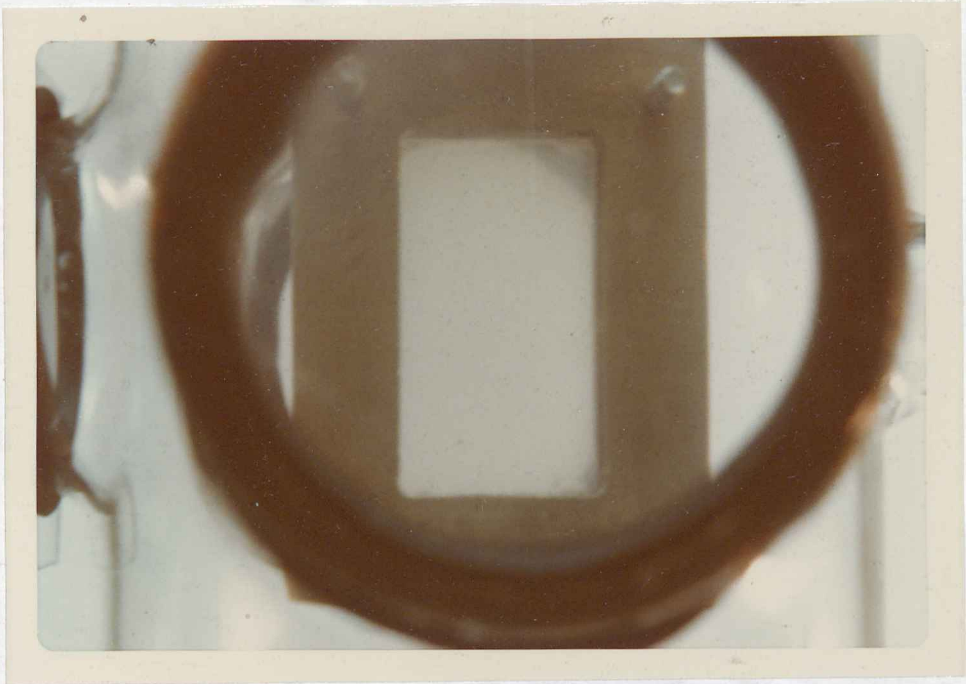
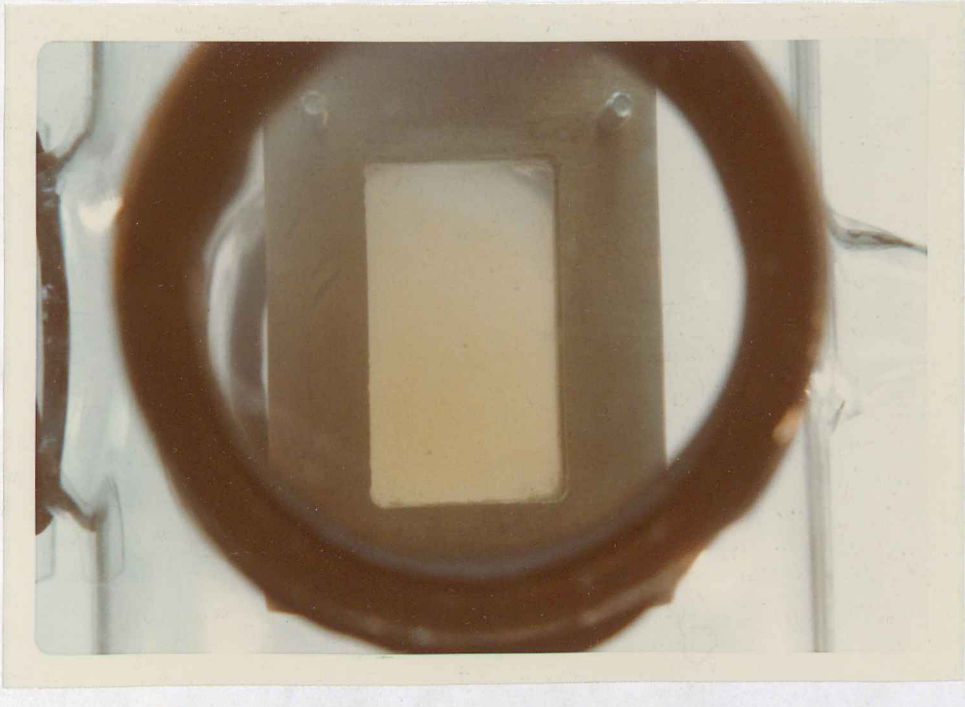


FIGURE 3. THE LOW TEMPERATURE CELL COLD-FINGER (UNITS IN CM).

Figure 6: Photographic reporting of O-Xylene.

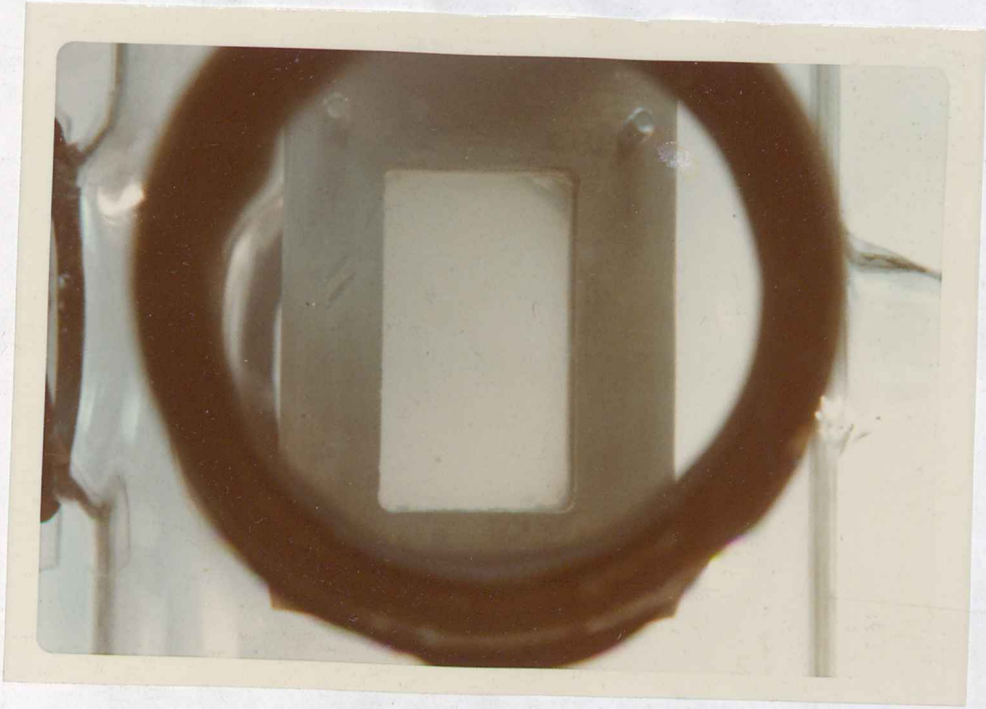


A) Before complex

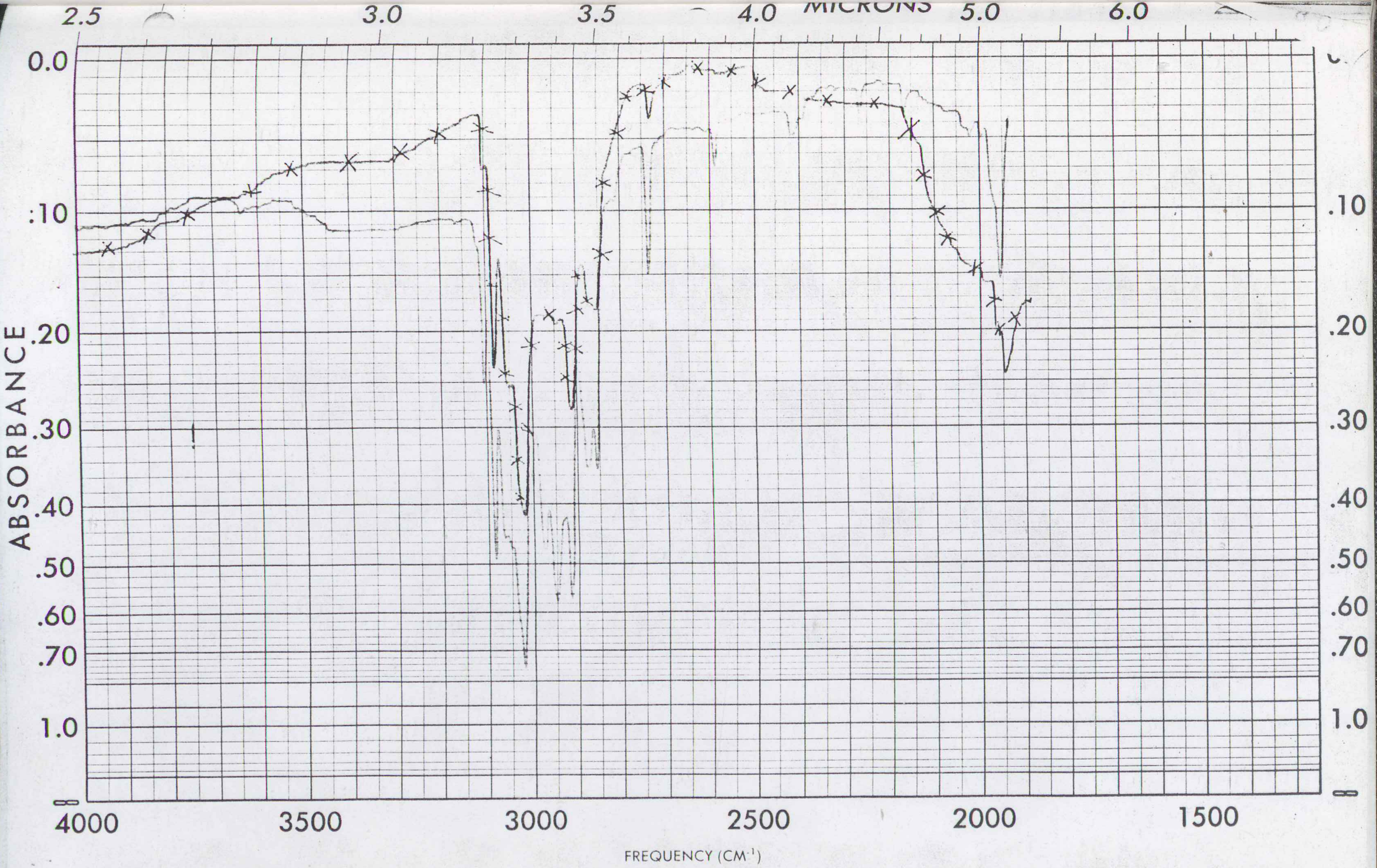


B) Complex

Figure 6
Continued



C) After complex



SAMPLE TOLUENE (-185°C) red y

ORIGIN Regular - Toluene
"X" - Complex

SOLVENT [illegible]

CURVE NO. 3

CONC. deposit

CELL PATH 10cm

REFERENCE air

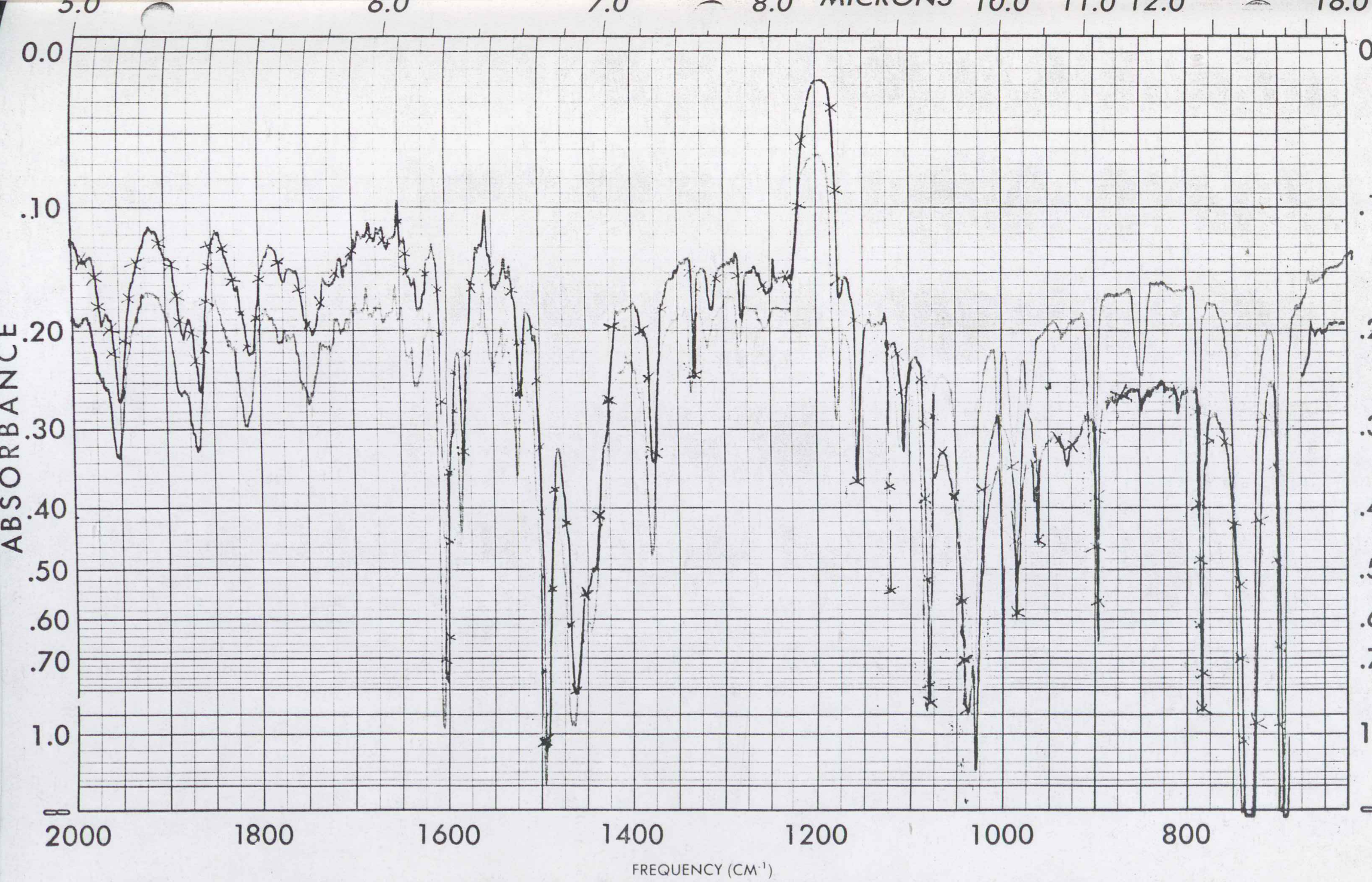
SCAN SPEED fast

SLIT 40

OPERATOR DC

DATE 2/23/74

REMARKS

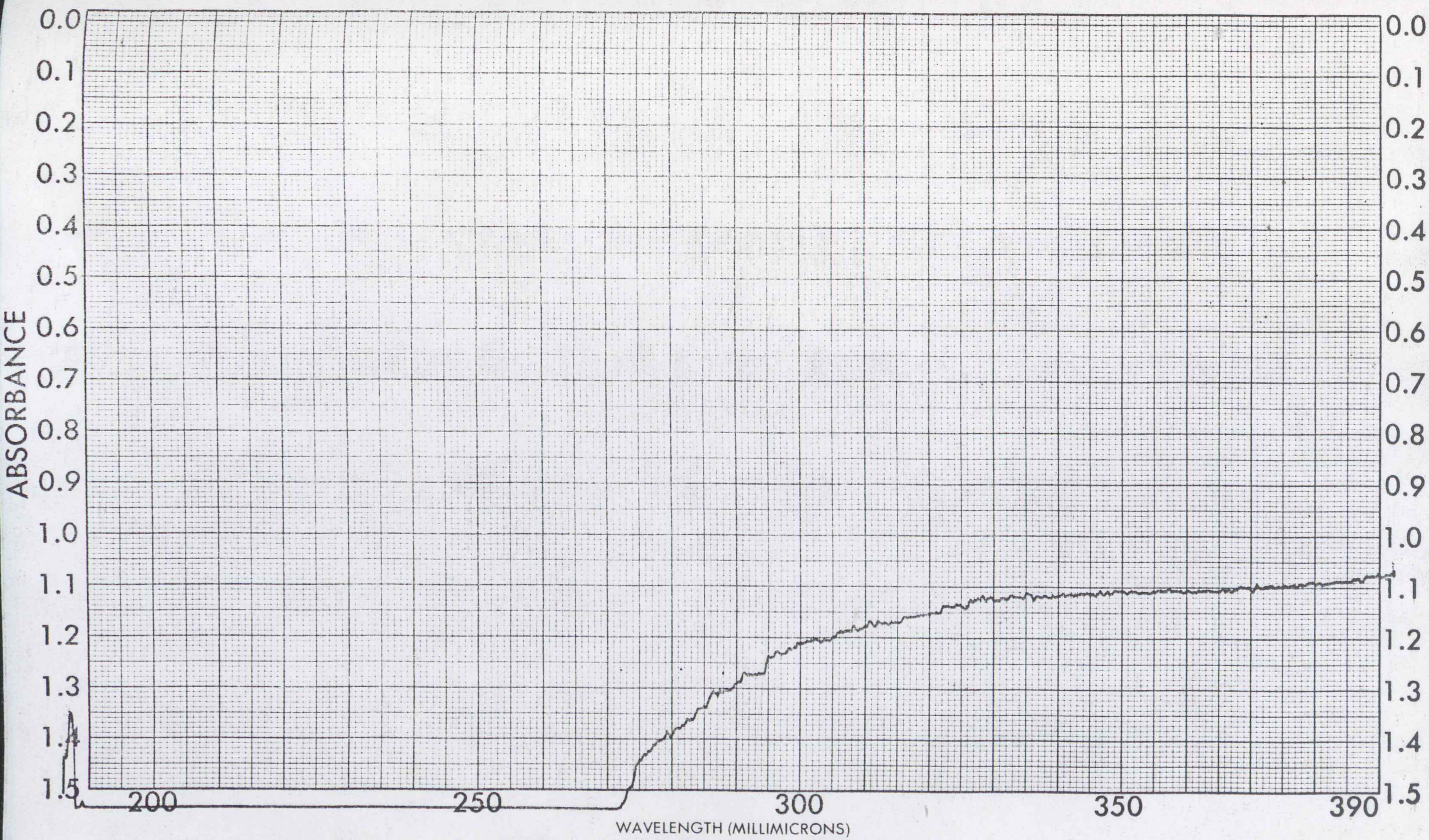


SAMPLE TOLUENE (-185°C)
red: Regular - Toluene
"X" - Complex
ORIGIN
SOLVENT none

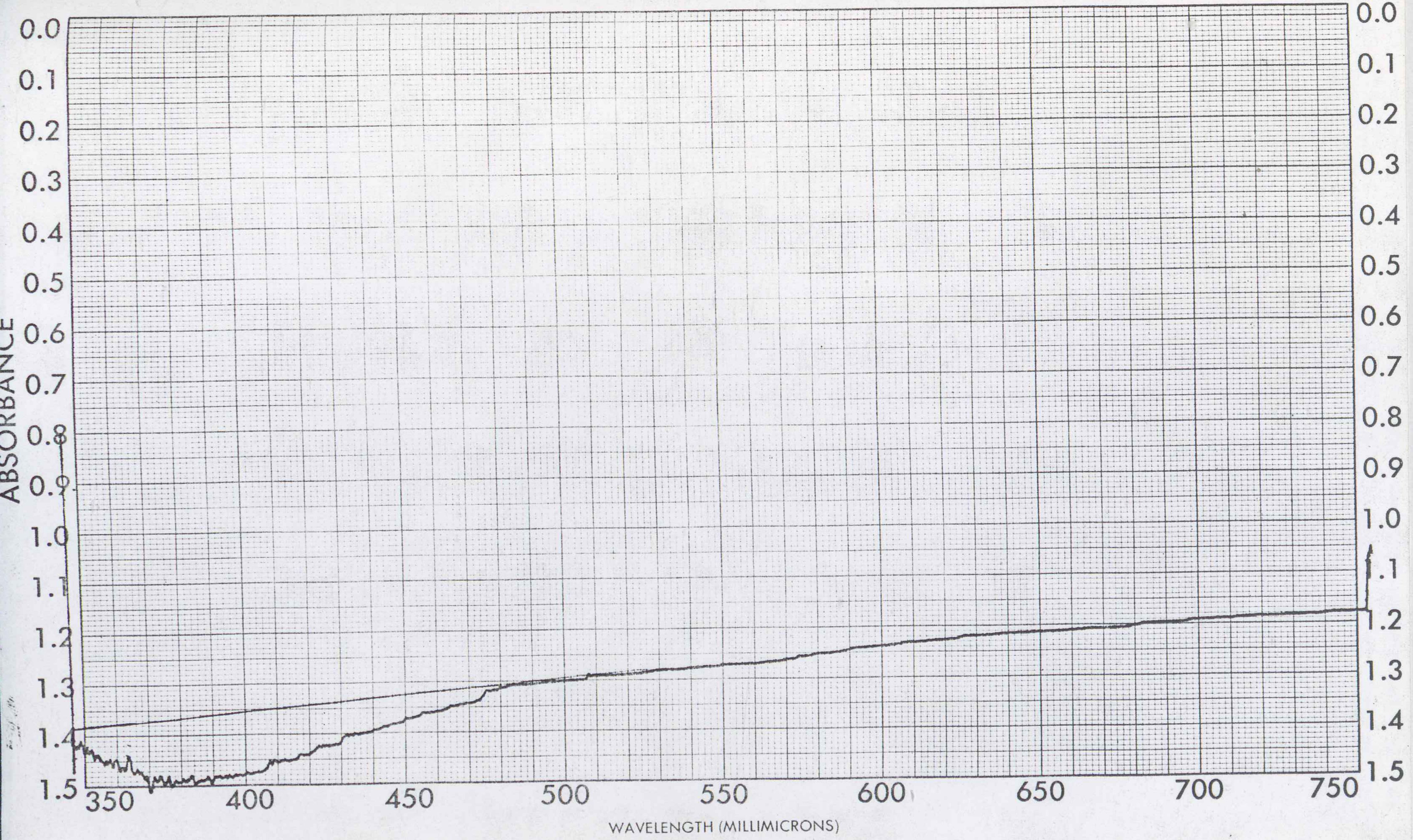
CURVE NO. 3
complex CONC. deposit
CELL PATH 10 cm
REFERENCE air

SCAN SPEED fast
SLIT 40
REMARKS

OPERATOR DCL
DATE 2/23/74



SAMP	TOLUENE·OZONE COMPLEX (−185°C)	CURVE NO.	1	SCAN SPEED	fast	OPERATOR	DCE
		CONC.		SLIT	30	DATE	5/4/71
ORIGI		CELL PATH	10	REMARKS			
SOLVENT		REFERENCE					

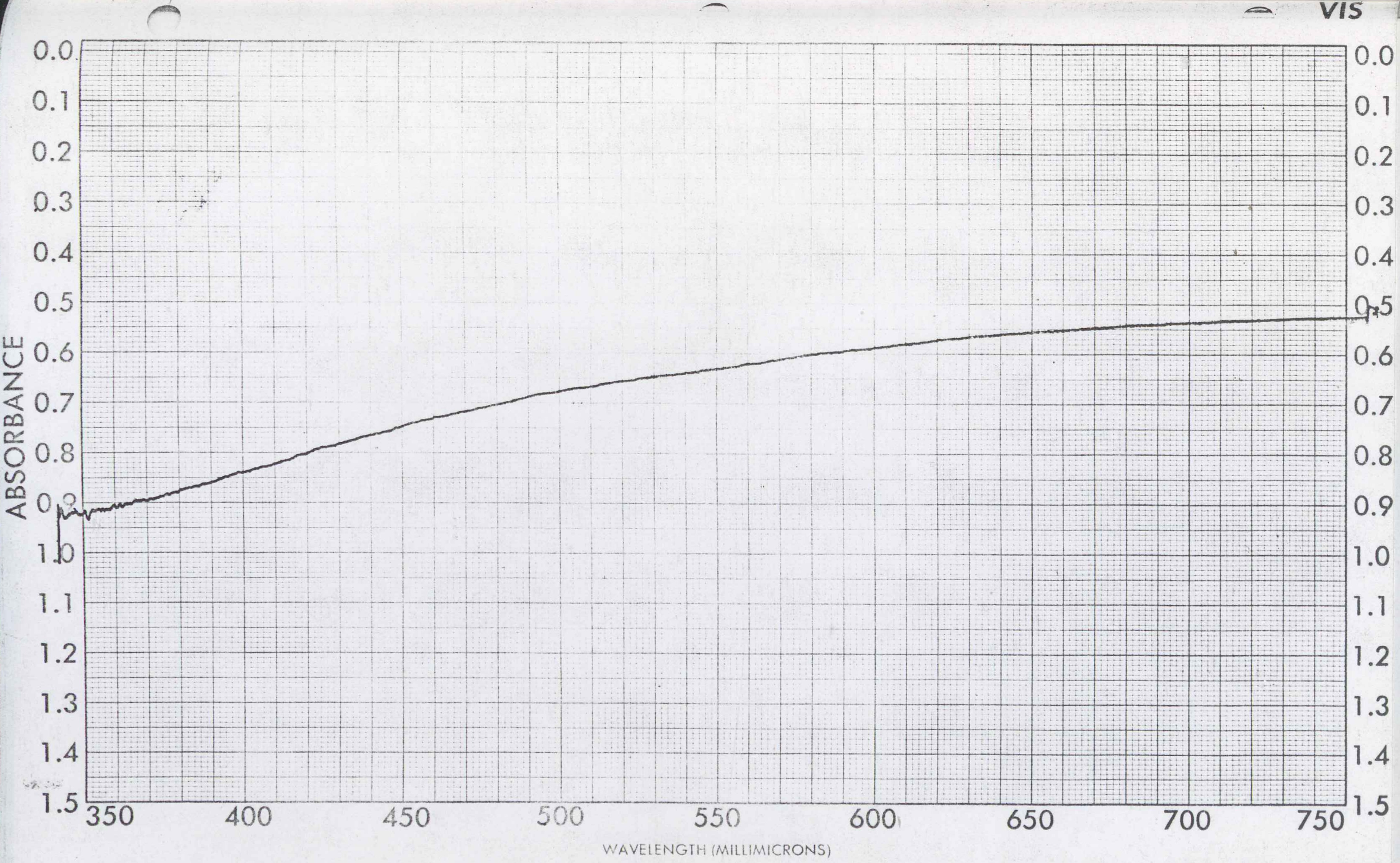


SAMPL TOLUENE•OZONE
COMPLEX
(-185°C)
ORIGI
SOLVENT

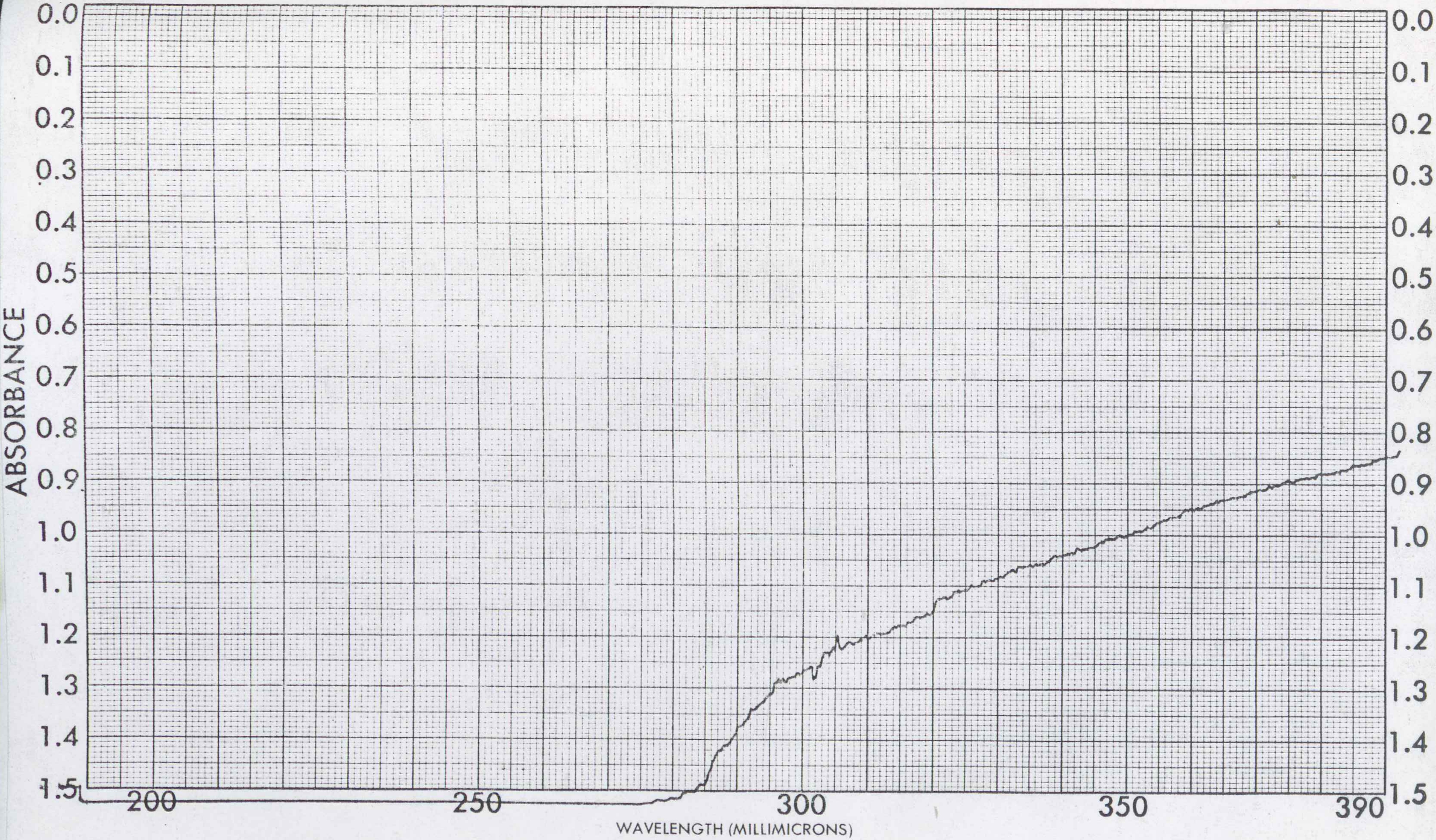
CURVE NO. 1
CONC.
CELL PATH
REFERENCE

SCAN SPEED fast
SLIT 30
OPERATOR DCE
DATE 5/4/74
REMARKS

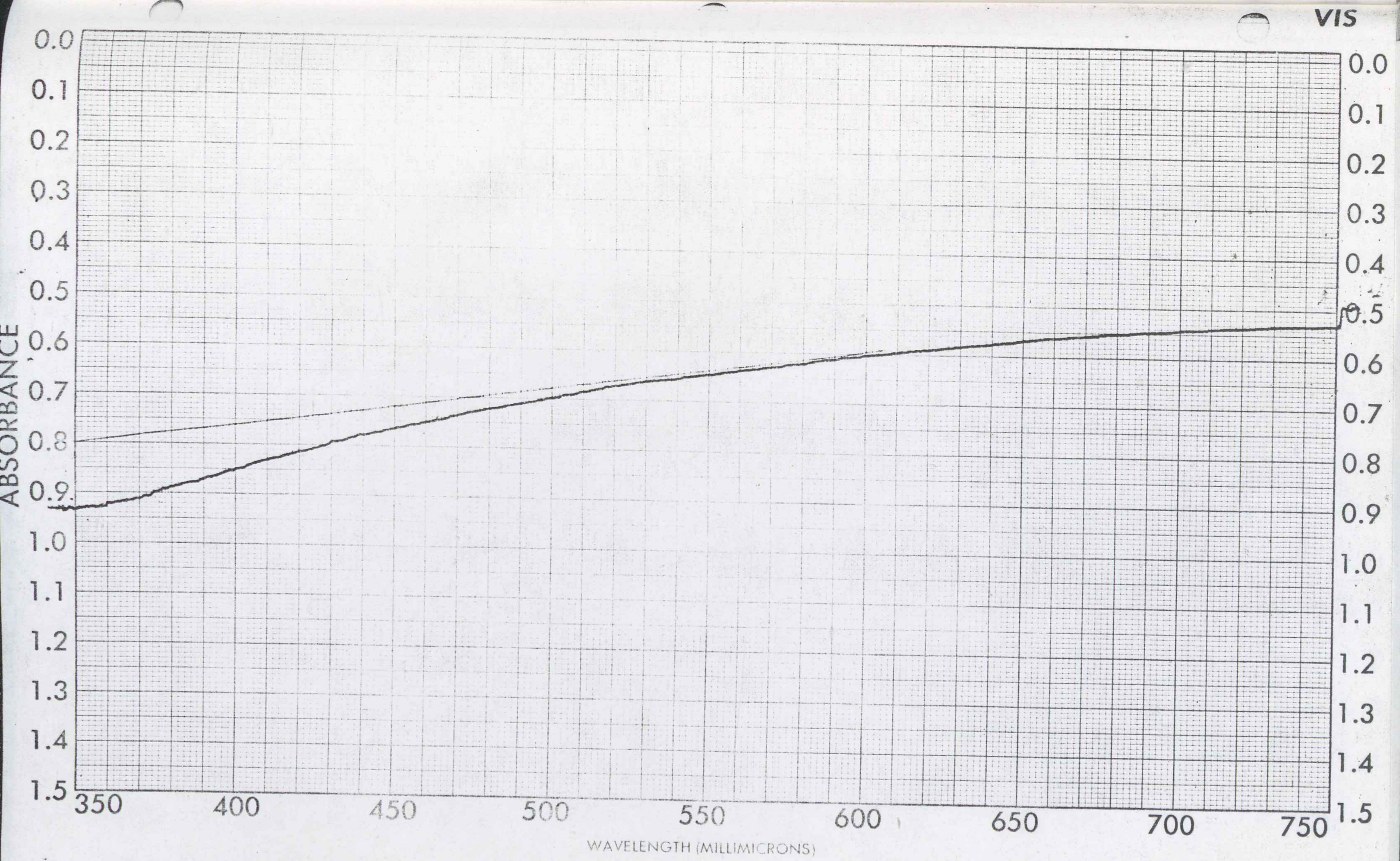
SAMPLE Toluene After Ozone Removed	CURVE NO. 2	SCAN SPEED fast	OPERATOR DCe
	CONC.	SLIT 30	DATE 5/4/74
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		



SAMPLE 7, Toluene After Ozone Removed	CURVE NO. 2	SCAN SPEED Fast	OPERATOR DCE
	CONC.	SLIT 30	DATE 5/4/74
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		



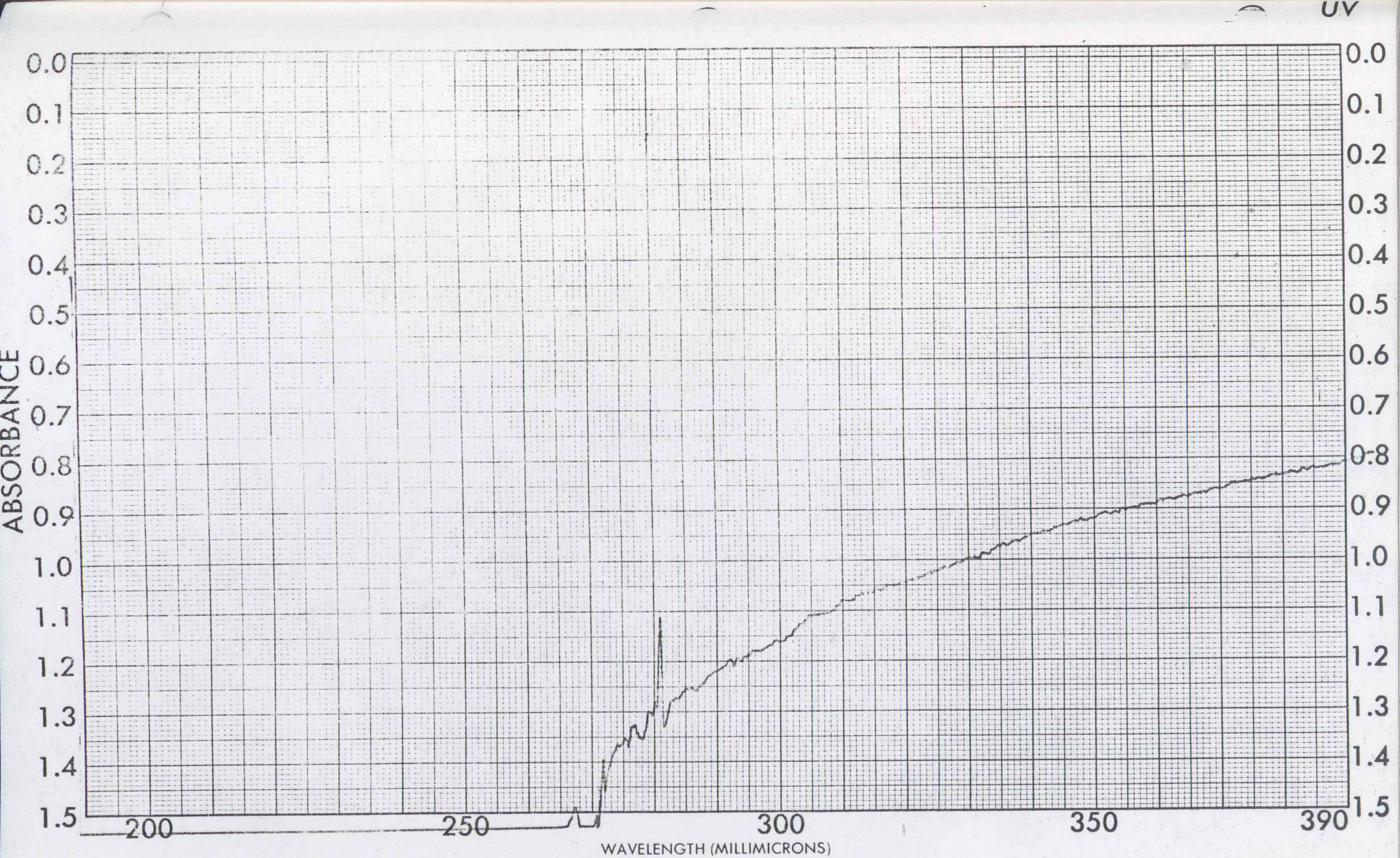
SAMPLE O-XYLENE (-185°C)	CURVE NO.	SCAN SPEED fast
	CONC.	SLIT 30
		OPERATOR DCE
		DATE 5/9/74
ORIGIN	CELL PATH 10cm	REMARKS @ -175°C
SOLVENT none	REFERENCE	



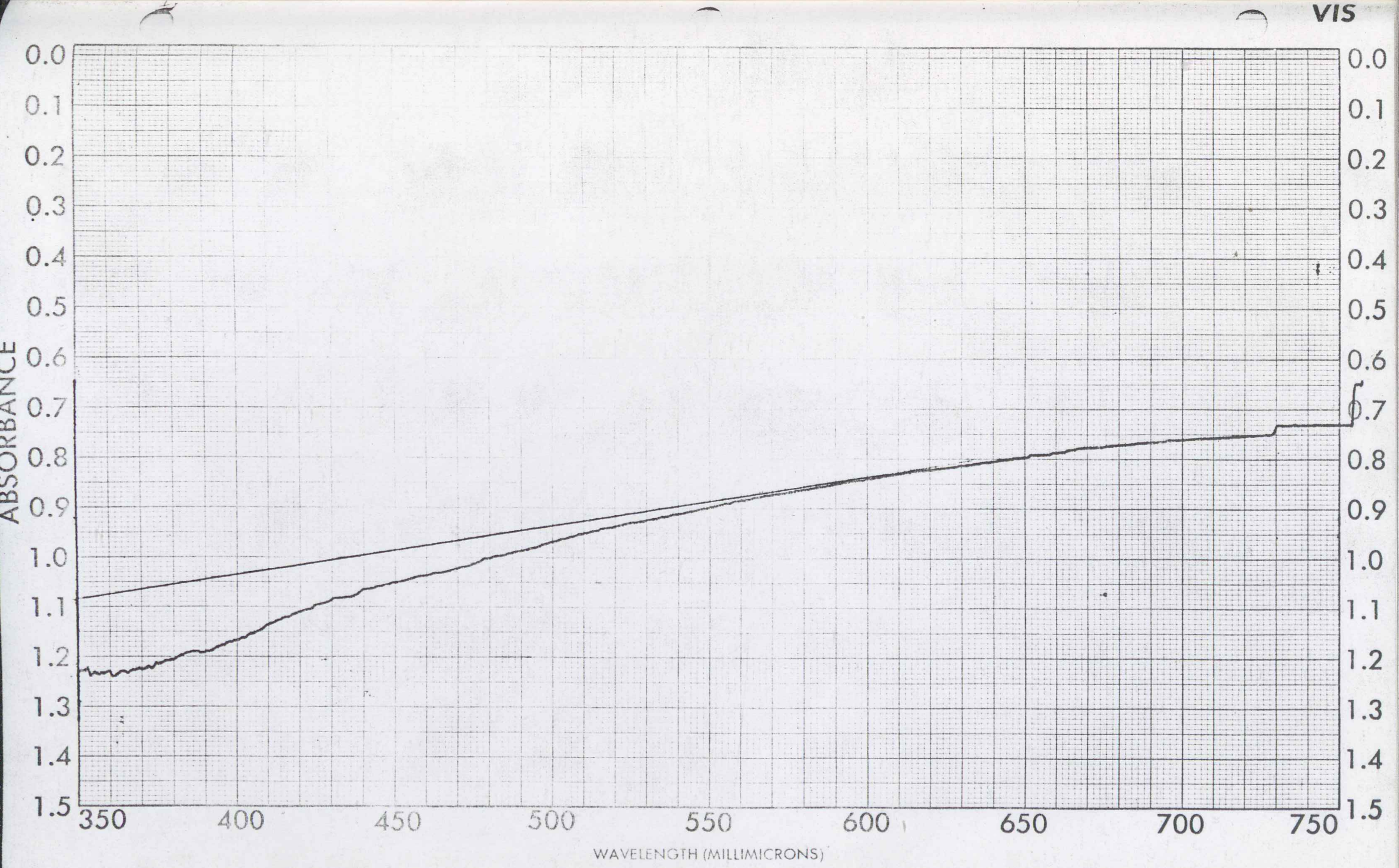
SAMPI O-XYLENE (-185°C)
ORIGII
SOLVE neat

CURVE NO.
CONC.
CELL PATH 10
REFERENCE

SCAN SPEED fast
SLIT 30
OPERATOR DCC
DATE 5/7/74
REMARKS @ -174°



SAMPLE	O-XYLENE•OZONE COMPLEX (-185°C)	CURVE NO.	SCAN SPEED fast
		CONC.	SLIT 30
ORIGIN		CELL PATH 10cm	OPERATOR DCE
SOLVENT		REFERENCE	DATE 5/7/74
			REMARKS



SAMPL O-XYLENE·OZONE COMPLEX (-185°C)

ORIGII

SOLVENT

CURVE NC

CONC.

CELL PATH 10cm

REFERENCE

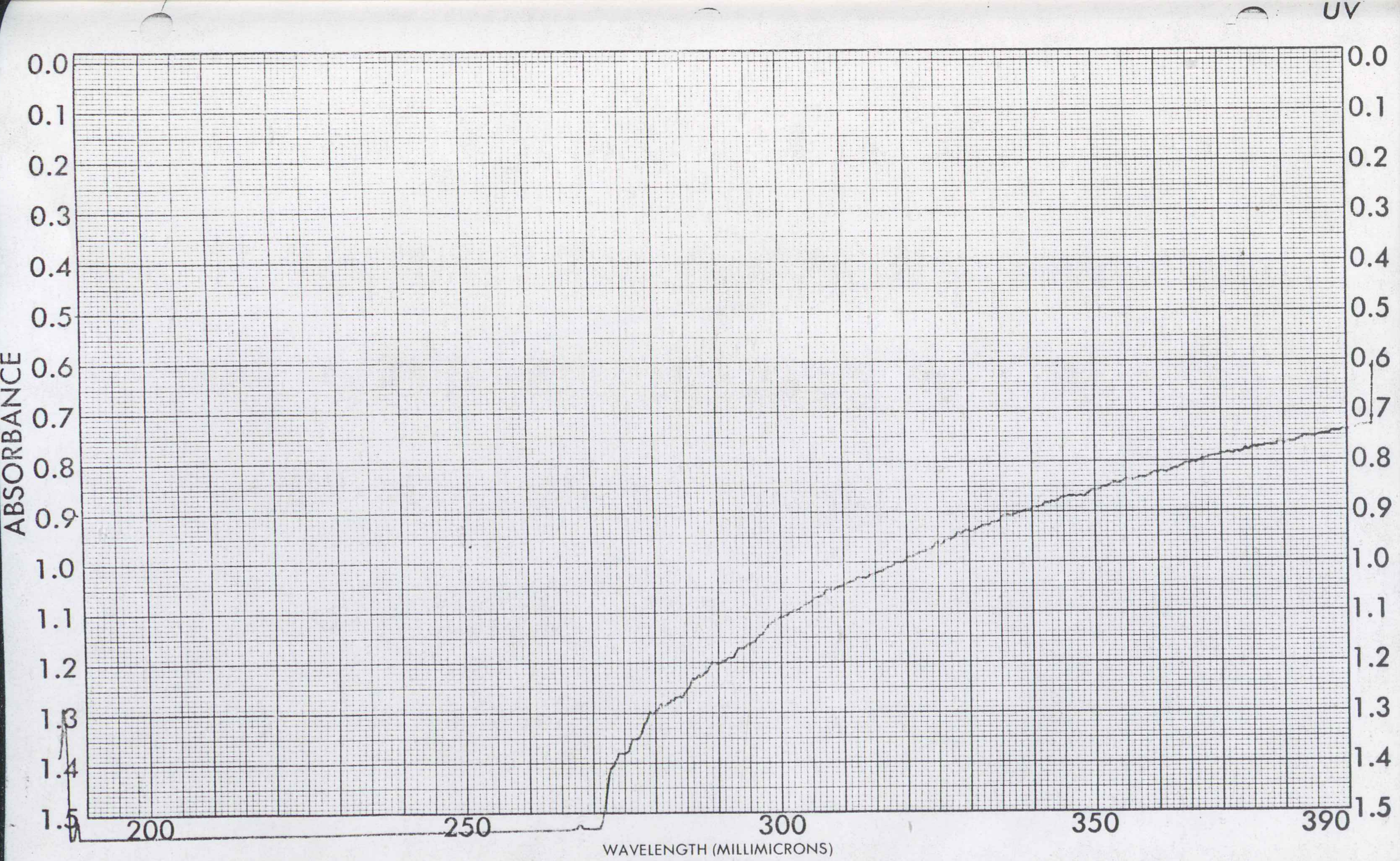
SCAN SPEED fast

SLIT 30

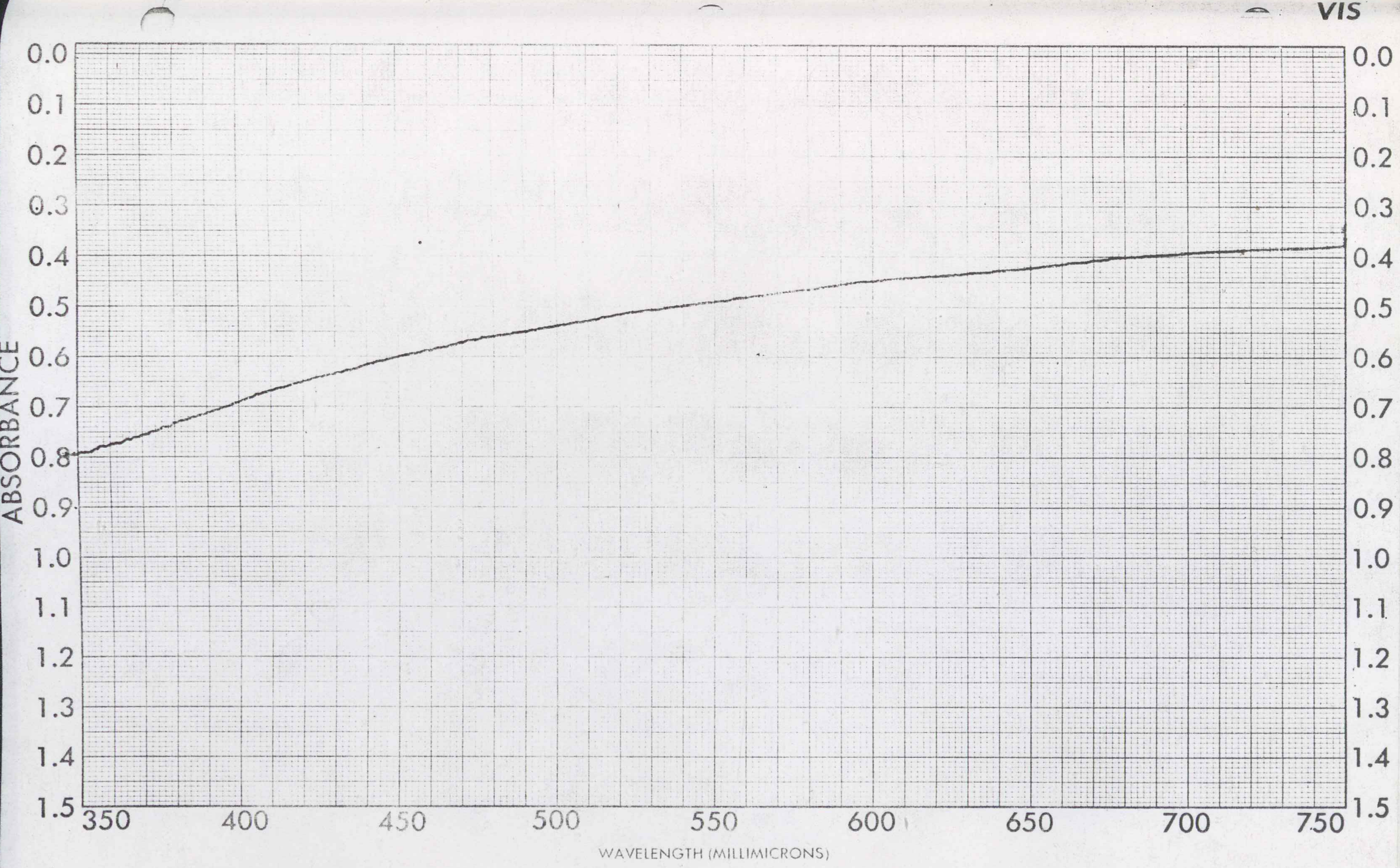
OPERATOR DCE

DATE 5/7/74

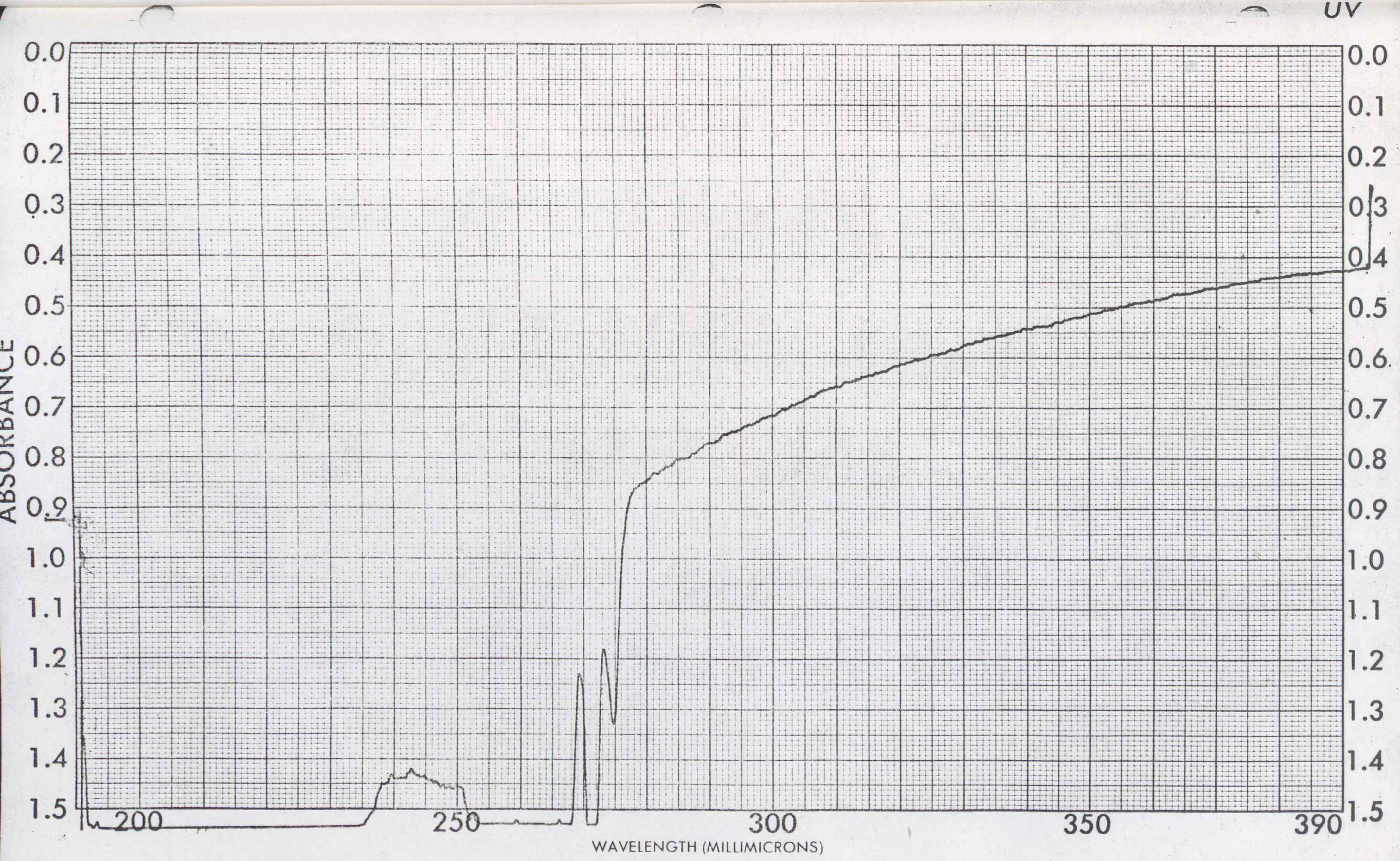
REMARKS Dark reddish-yellow



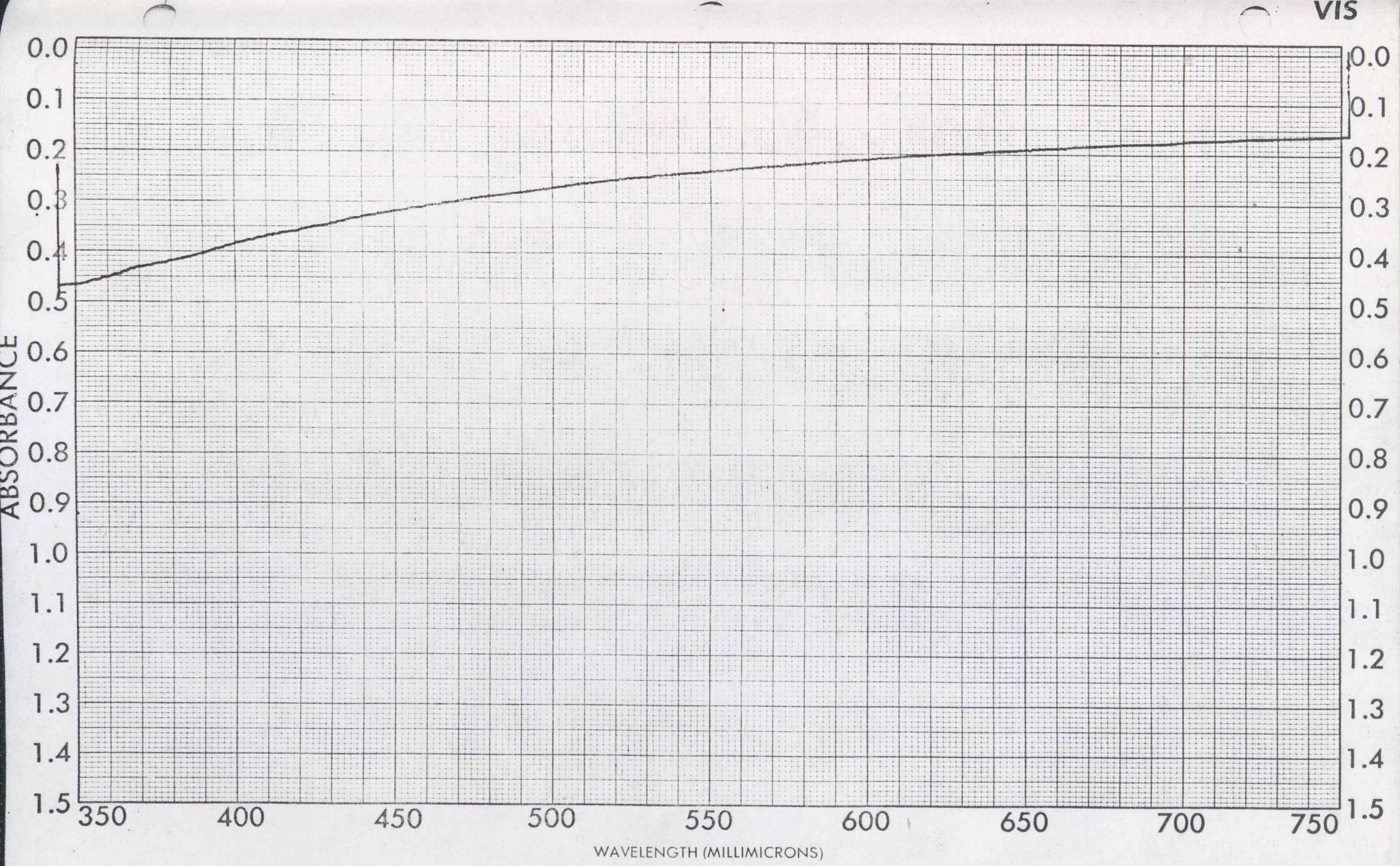
SAMPLE O aft ORIGIN SOLVENT	ch. O-XYLENE AFTER COMPLEX	CURVE NO. CONC. CELL PATH 10 REFERENCE air	SCAN SPEED fast SLIT 30 REMARKS
			OPERATOR DCE DATE 5/7/74



SAMPLE (O-XYLENE AFTER COMPLEX	CURVE NO	SCAN SPEED *fast*	OPERATOR *JCE*
	CONC.	SLIT *30*	DATE *5/7/74*
ORIGIN	CELL PATH *10 cm*	REMARKS	
SOLVENT	REFERENCE		



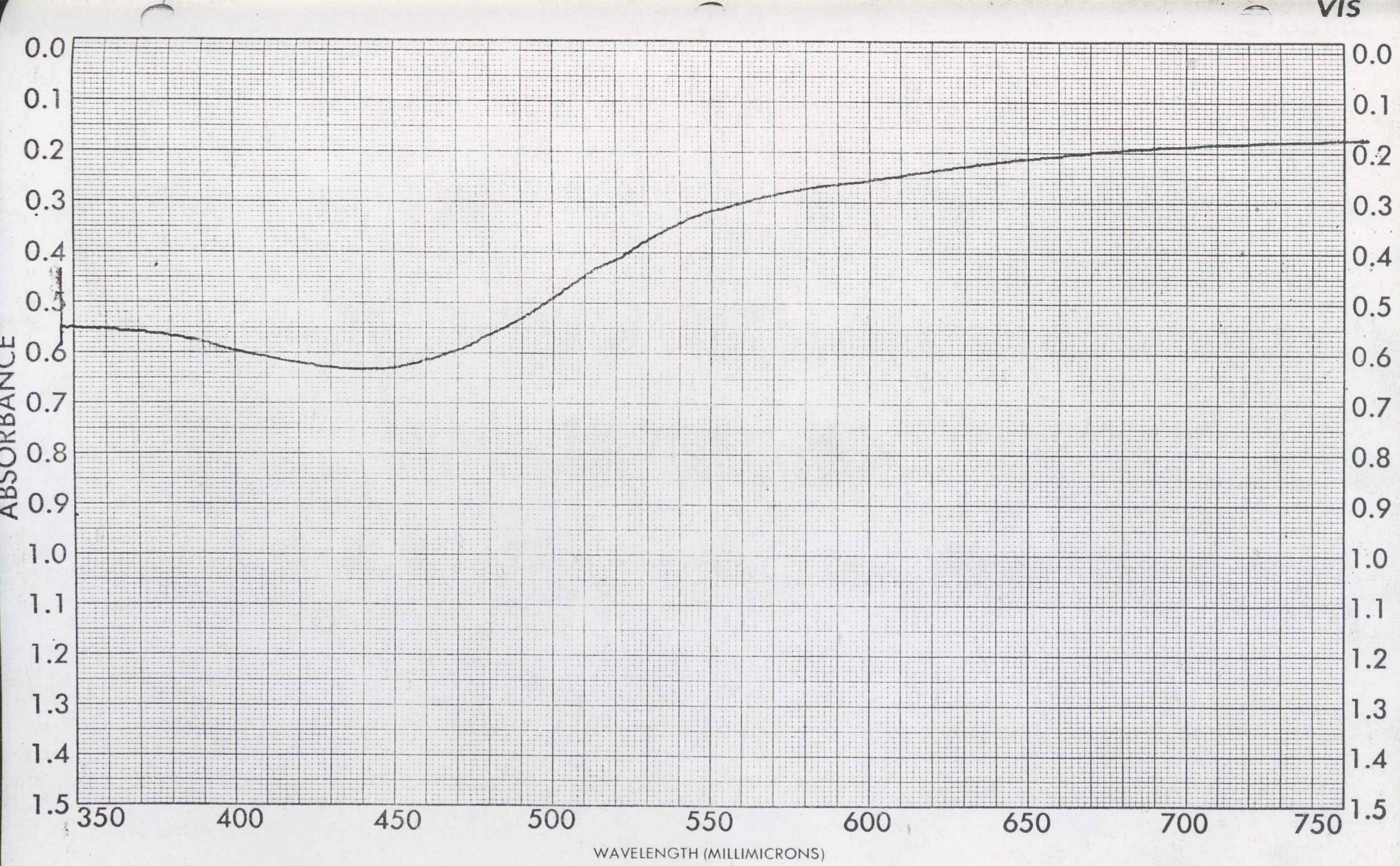
SAMPLE before MESITYLENE (-185°C)	CURVE NO. 10a, (see 10a$_2$)	SCAN SPEED	OPERATOR J.H.
	CONC.	SLIT	DATE 4/20
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE Air		



SAMP MESITYLENE (-185°C)	CURVE NO. $10a_2$ (See $10a_1$)	SCAN SPEED	OPERATOR L.H
	CONC.	SLIT	DATE 9/20
ORIGI	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

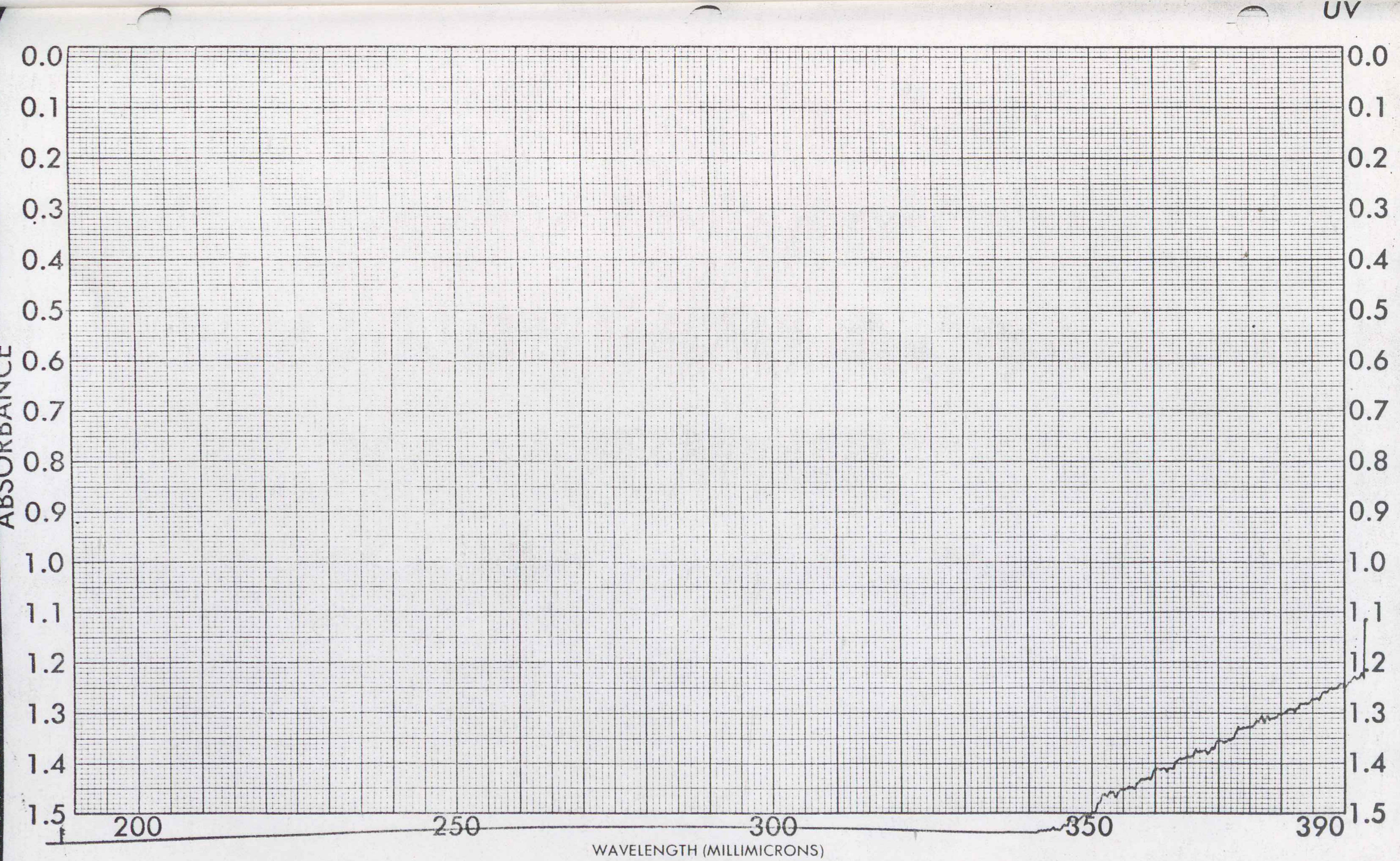
UV

SAMPLE MESITYLENE·OZONE COMPLEX (−185°C)
ORIGIN
SOLVENT
CURVE NO. 10 b_1 (See 10 b_2)
CONC.
CELL PATH
REFERENCE
SCAN SPEED
SLIT
OPERATOR J.H.
DATE 4/20
REMARKS O_3 just let in cell onto face (complex 445 nm)

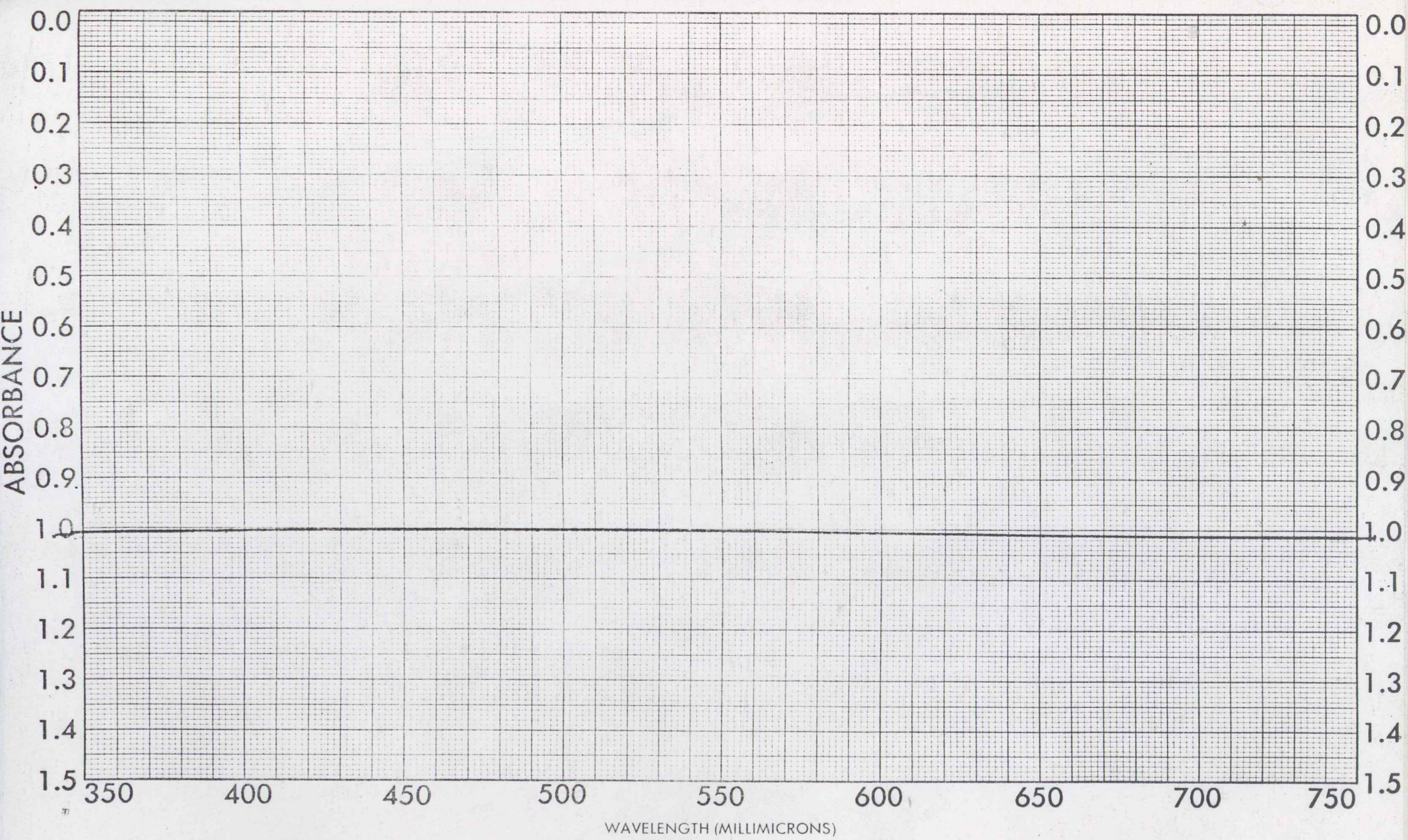


SAMPLE MESITYLENE·OZONE COMPLEX (-185°C)	CURVE NO. 10b$_2$ (See 10b$_1$)	SCAN SPEED	OPERATOR Sl
	CONC.	SLIT	DATE 4/20
ORIGIN	CELL PATH	REMARKS O$_3$ just let into cell ~ (complex 445 nm)	
SOLVENT	REFERENCE		

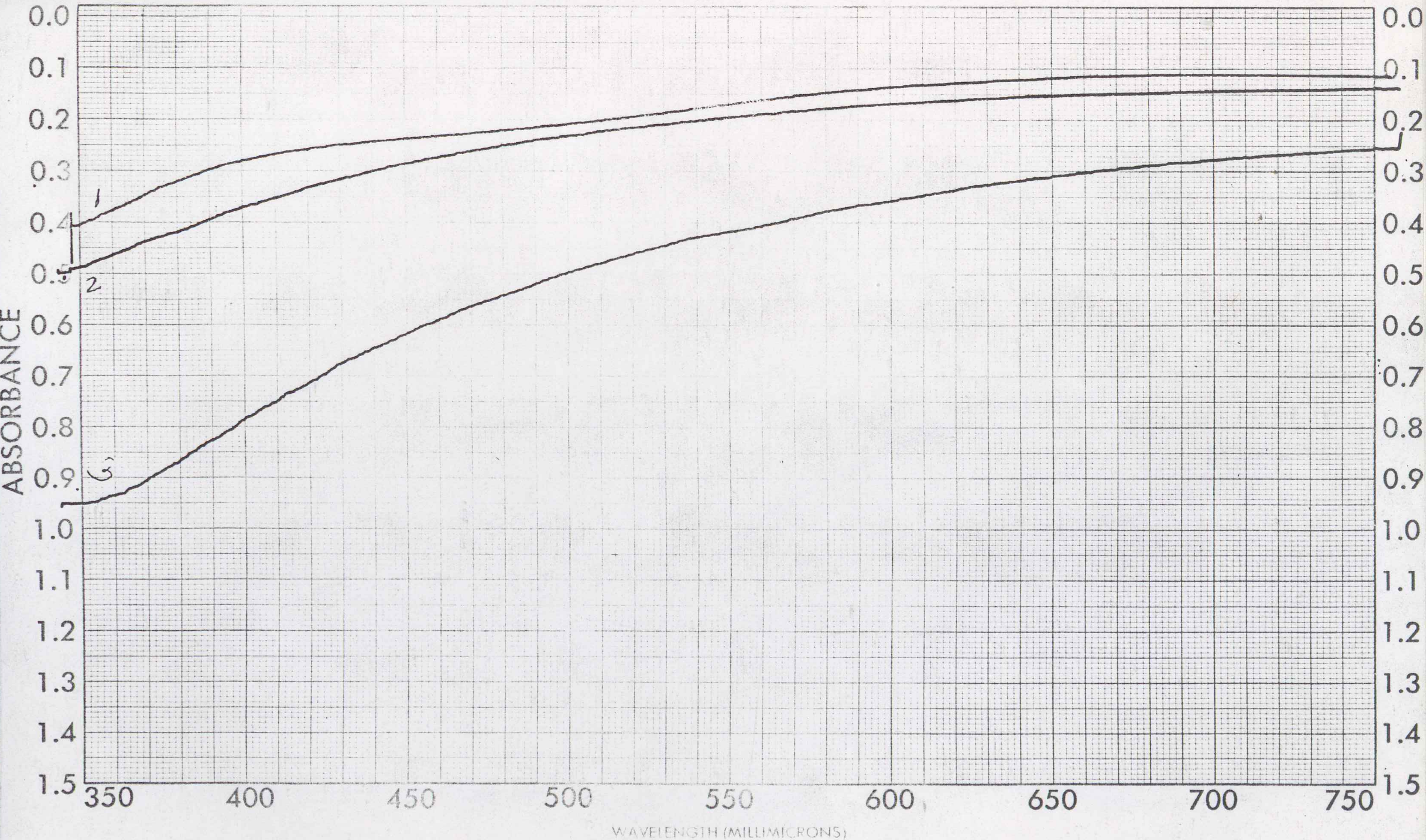
PR 11 (202 1512)



SAMPLE MESITYLENE AFTER COMPLEX	CURVE NO. 10c,	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE
ORIGIN	CELL PATH	REMARKS Crystalized - lots of scattering.	
SOLVENT	REFERENCE		

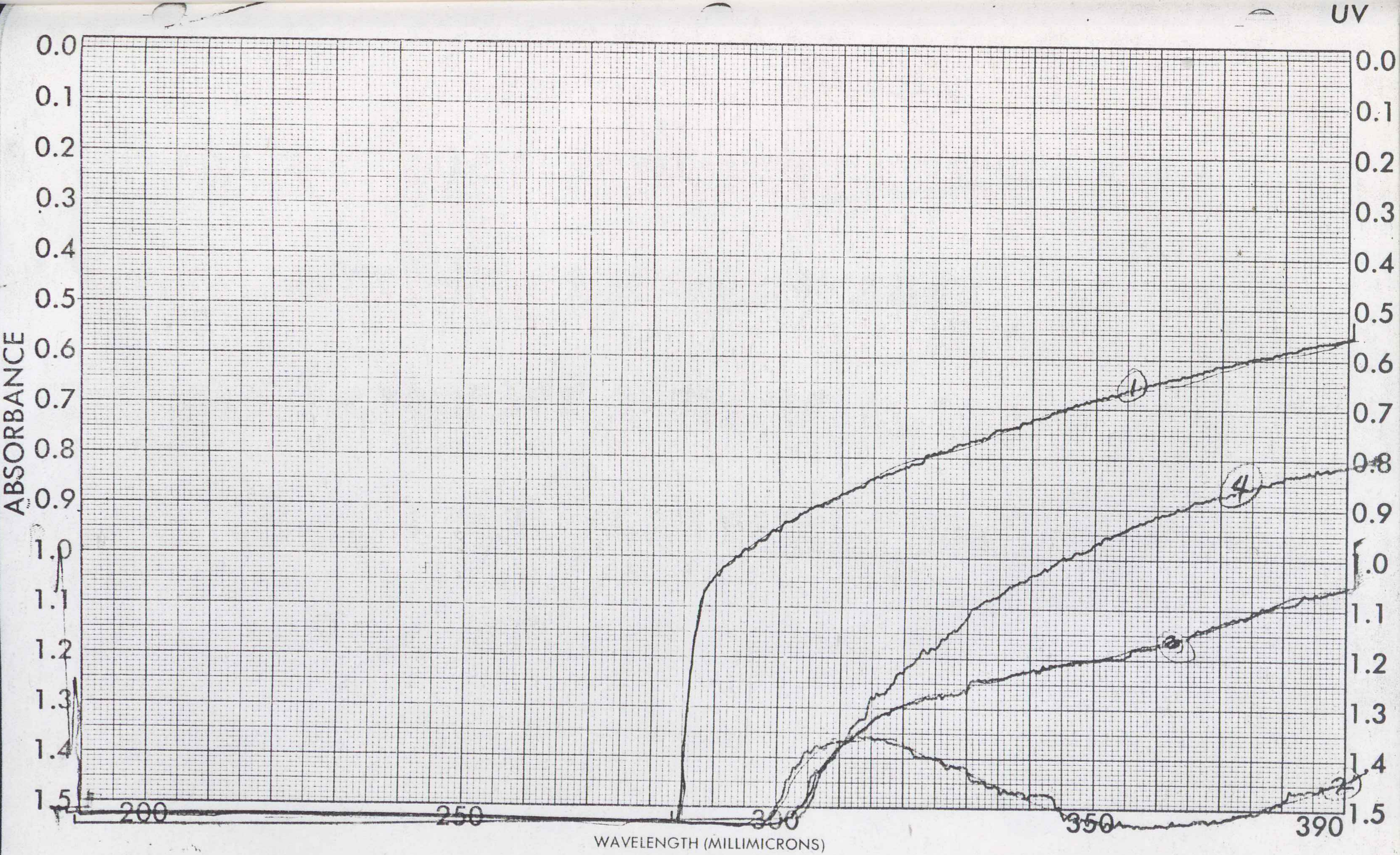


SAMPLE MESITYLENE AFTER COMPLEX	CURVE NO. 10cc	SCAN SPEED
	CONC.	OPERATOR
		SLIT
		DATE
ORIGIN	CELL PATH	REMARKS ?
SOLVENT	REFERENCE	

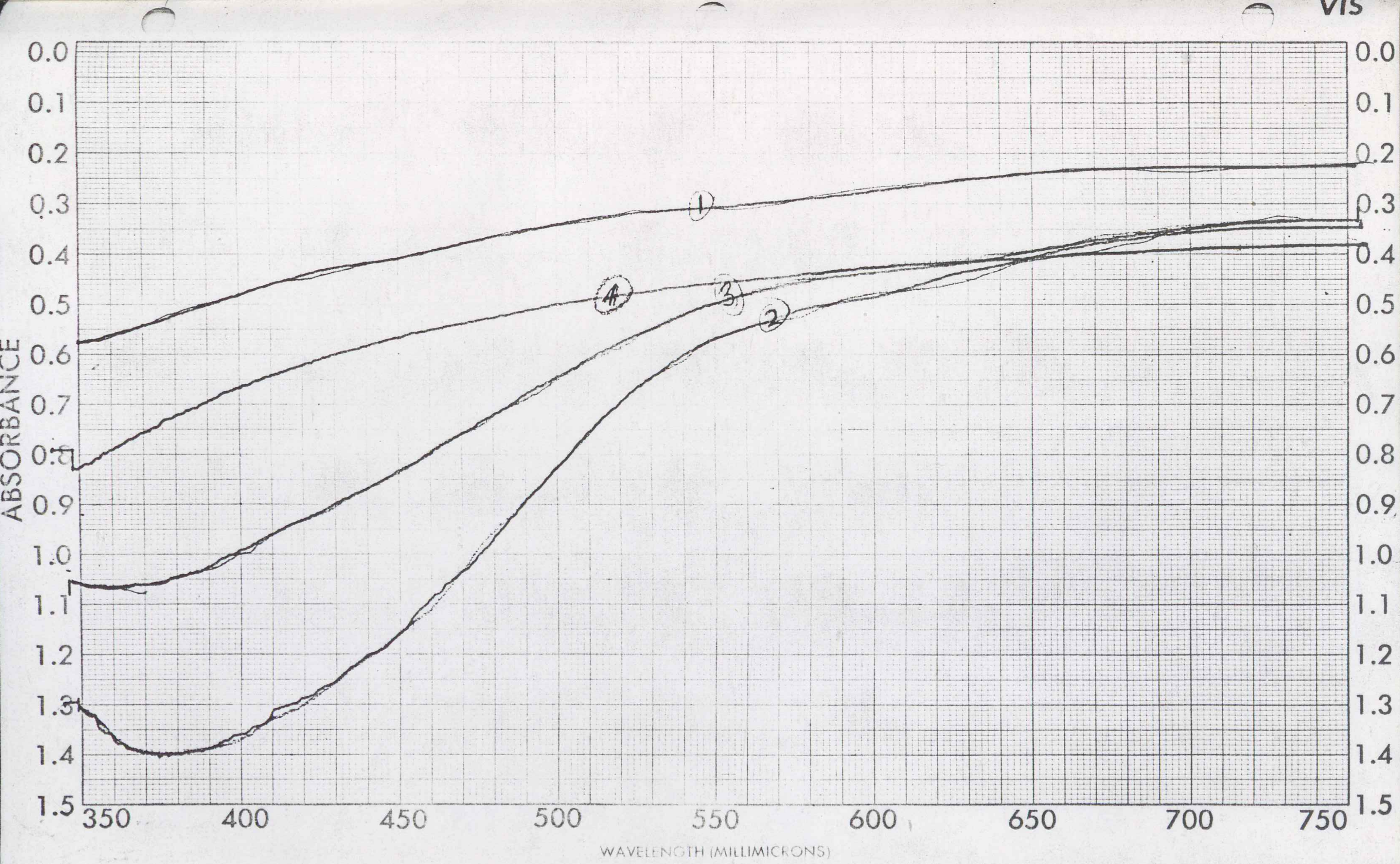


SAMPLE CH_3 CH MESITYLENE·OZONE COMPLEX (-185^{0}C)	CURVE 1-Origional material 2-After complex 3-Complex	SCAN SPEED fast	OPERATOR DCE
	CONC.	SLIT 100	DATE 6/11/74
ORIGIN	CELL PA	REMARKS ① origional material ② total after complex ③ complex. · O_3 CH	
SOLVENT	REFEREN		

PR 11

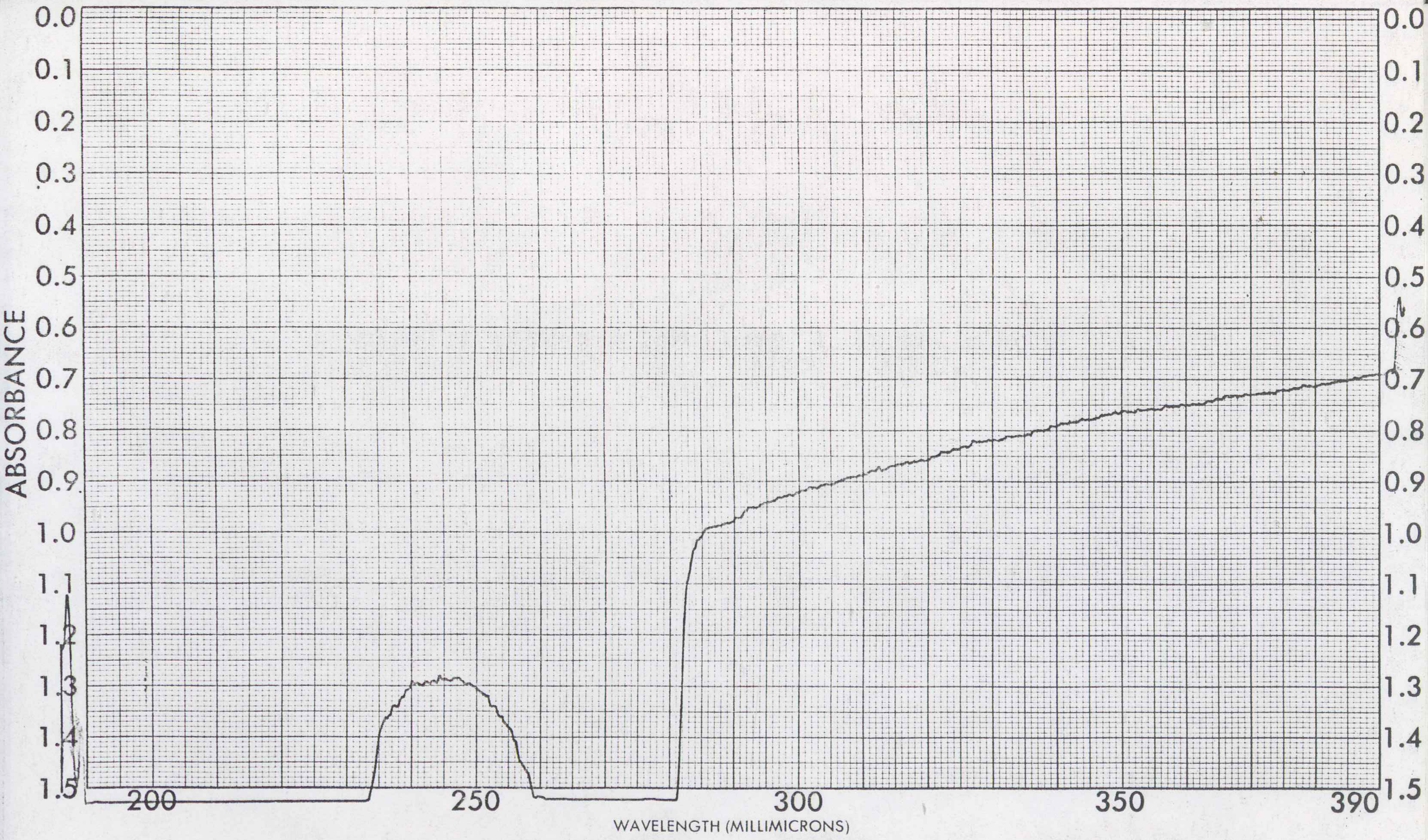


SAMPLE	Phenol(-135°C)	CURVE N	1-Origional Material 2-Complex 3-Some complex removed 4-All complex removed	SCAN SPEED	OPERATOR S.A.
		CONC.		SLIT	DATE 5/31/74
ORIGIN		CELL PAT		REMARKS pg 99-100 notebook 1) ϕ-OH 2) ϕ-OH + O_3 3) some O_3 removed 4) all O_3 removed	
SOLVENT		REFERENC.			



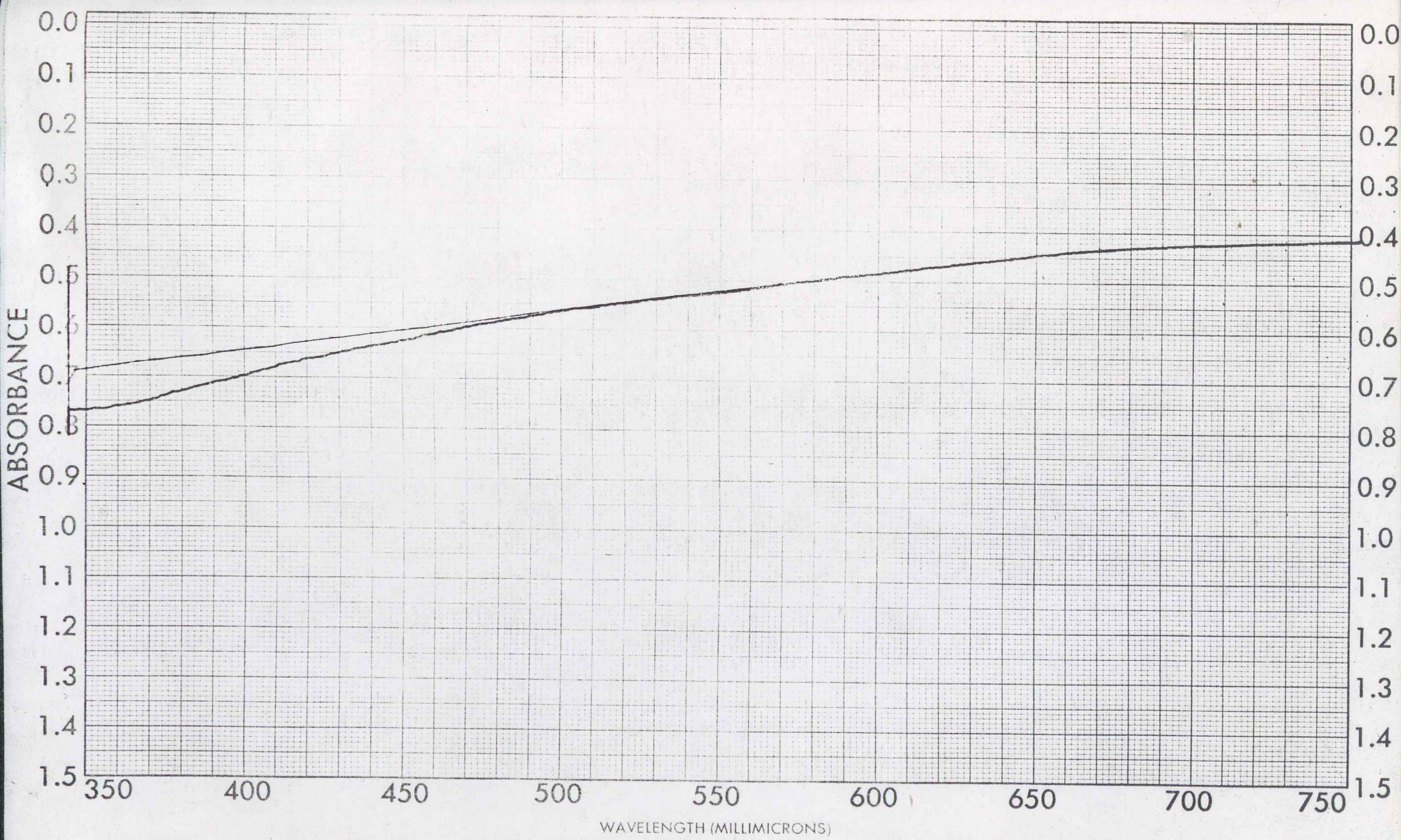
SAMPI	Phenol(-185°C)	CURVE	1-Origional material	SCAN SPEED	OPERATOR S.H.
ORIGI		CONC.	2-Complex	SLIT	DATE 5/30/74
		CELL P	3-Some complex removed	REMARKS See pg 100 note book for legend 1) ϕ-OH 2) ϕ-OH O_3 3) Some O_3 removed	
SOLVE...		REFERE...	4-All complex removed		

UV



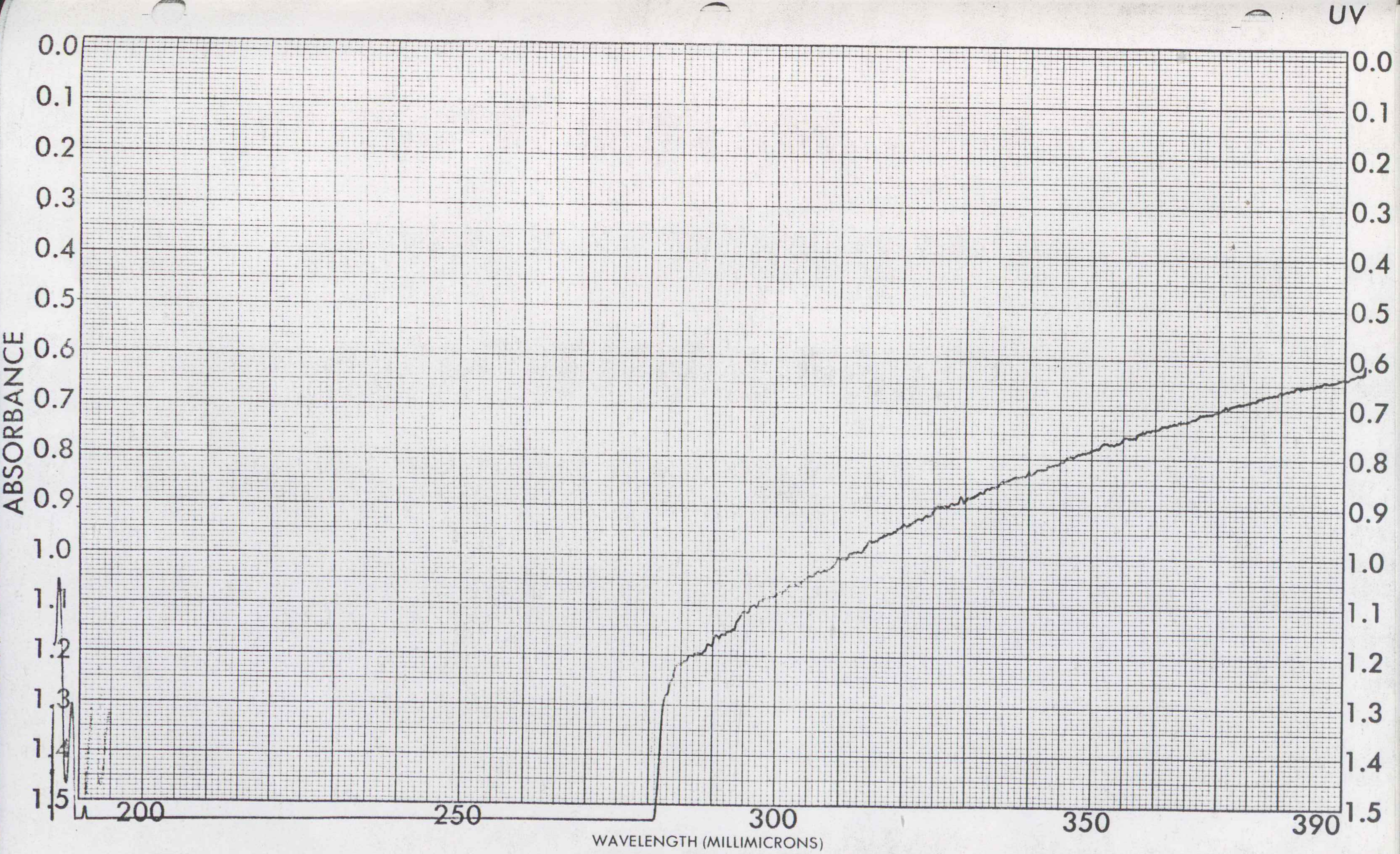
SAMPL Anisole	CURVE NO.	SCAN SPEED fast	OPERATOR DCE
	CONC.	SLIT 30 nm	DATE 5/9/74
ORIGI	CELL PATH	REMARKS	
SOLVE.	REFERENCE air		

VIS



SAMPL Anisole	CURVE NO.	SCAN SPEED fast	OPERATOR DCE
	CONC.	SLIT 30mm	DATE 5/9/74
ORIGII	CELL PATH	REMARKS	
SOLVE... [illegible]	REFERENCE air		

PR 11



SAMPLE Anisole•Ozone Complex (-185°C)

ORIGIN

SOLVENT

CURVE NO.

CONC.

CELL PATH

REFERENCE

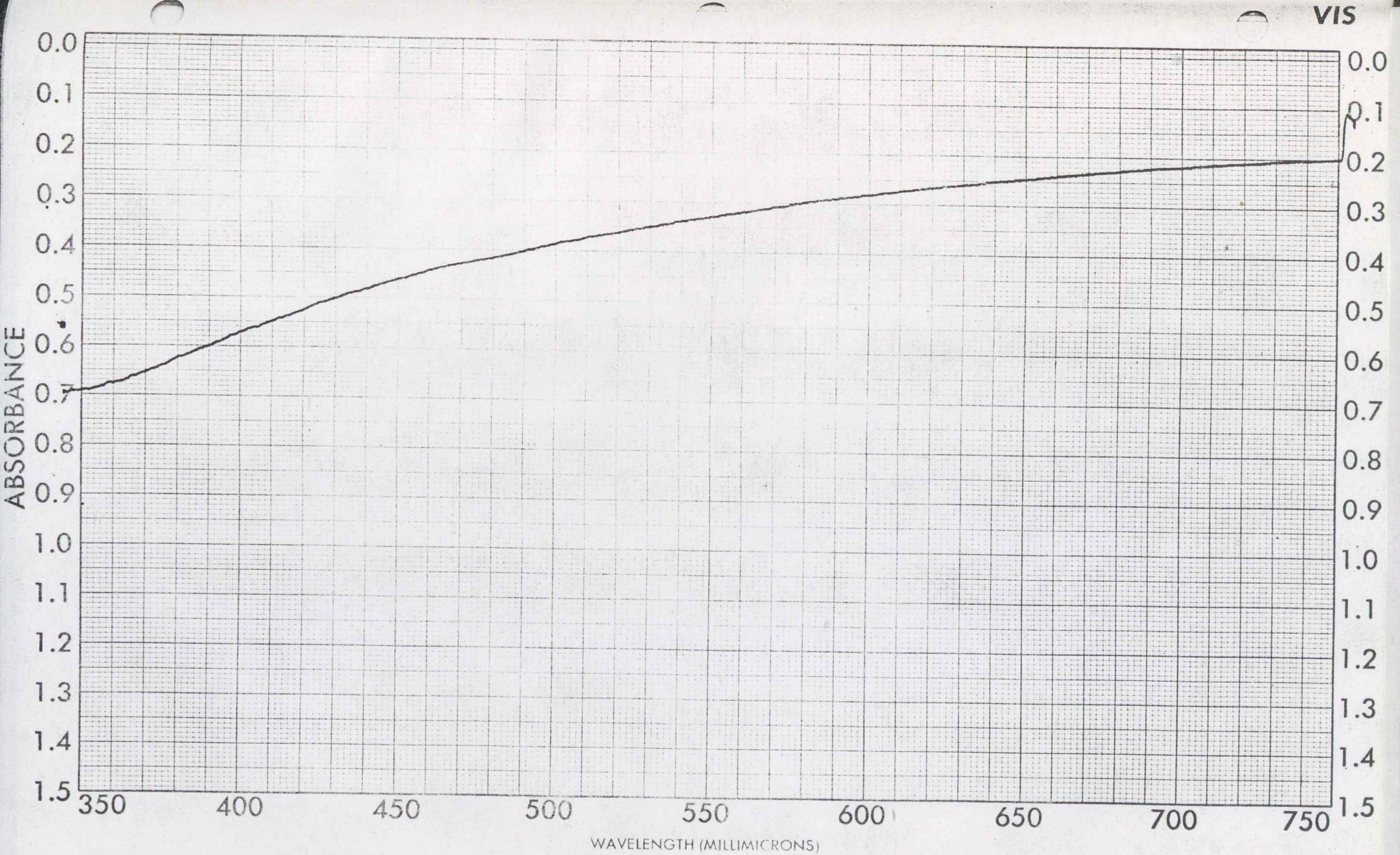
SCAN SPEED fast

SLIT 30

OPERATOR WCE

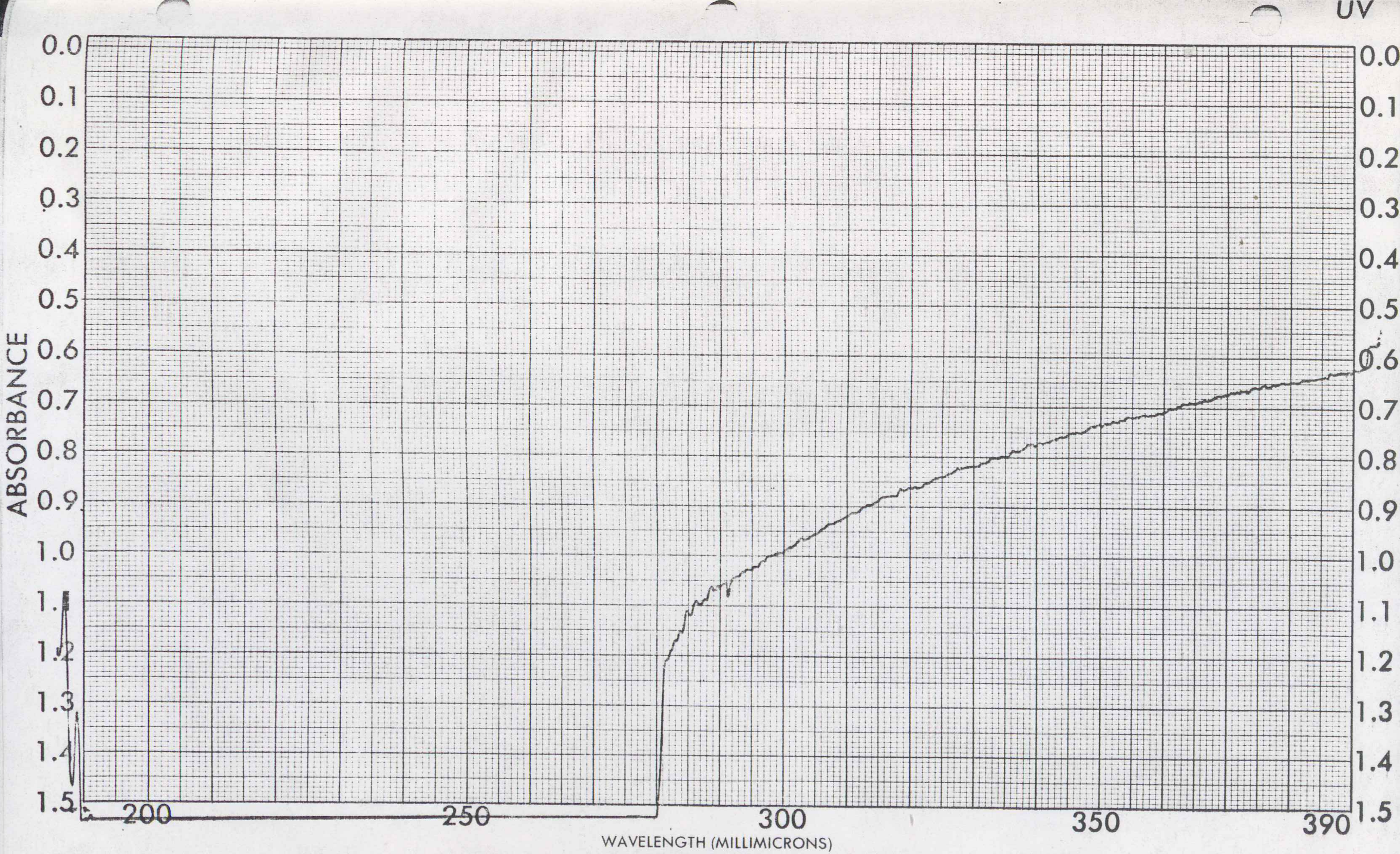
DATE 5/9/74

REMARKS

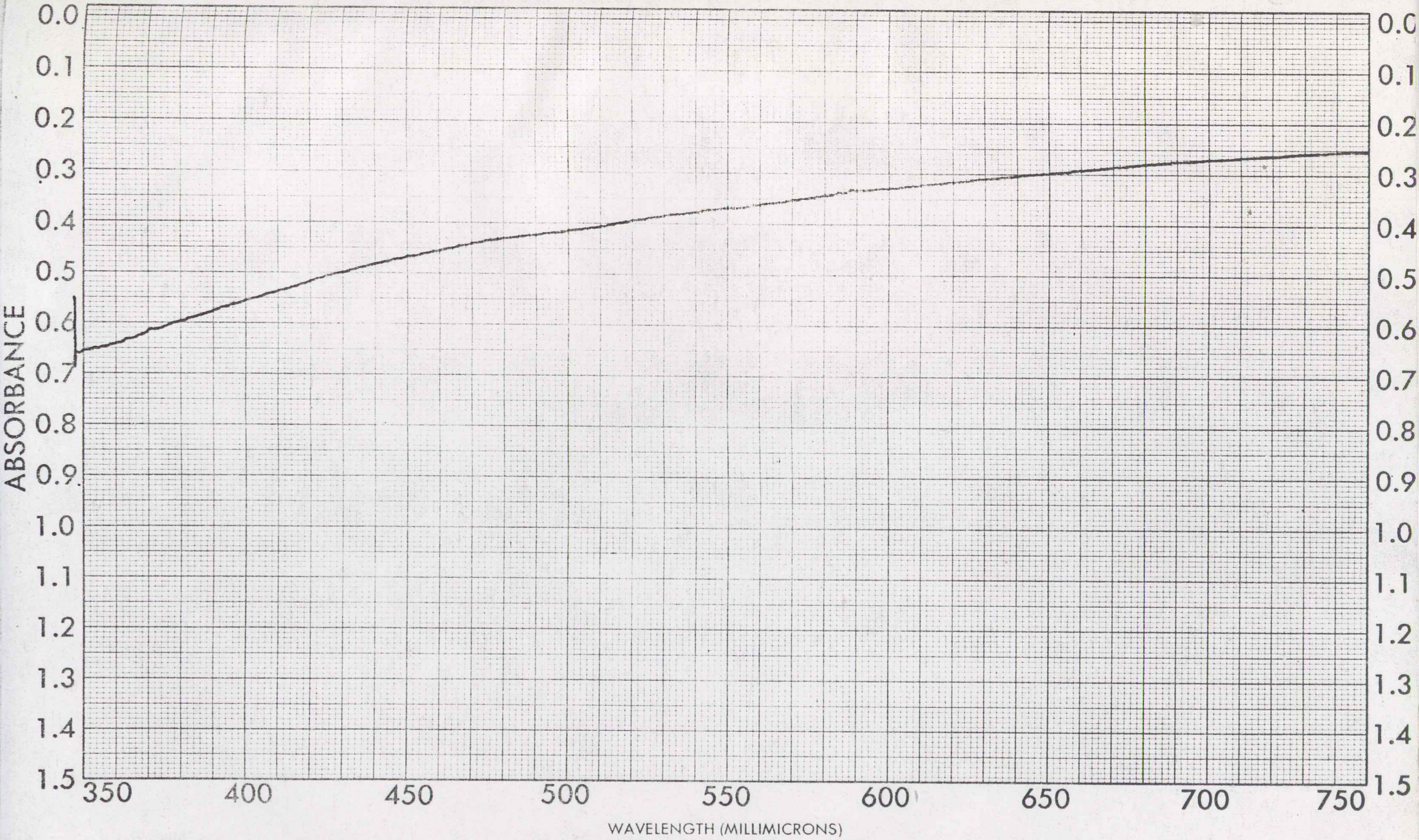


SAMPLE ANISOLE·OZONE COMPLEX (-185°C)	CURVE NO.	SCAN SPEED fast	OPERATOR DC
ORIGIN	CONC.	SLIT 30	DATE 5/9/74
SOLVENT	CELL PATH	REMARKS	
	REFERENCE		

PR 11



SAMPLE ANISOLE AFTER COMPLEX (-185°C)	CURVE NO.	SCAN SPEED fast	OPERATOR DE
	CONC.	SLIT 30	DATE 5/9/74
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE air		



SAMPLE ANISOLE AFTER COMPLEX (−185°C)
ORIGIN
SOLVENT
CURVE NO.
CONC.
CELL PATH
REFERENCE air
SCAN SPEED 30
SLIT 30
OPERATOR DE
DATE 5/9/74
REMARKS

PR 11