SP

Aroclor Refs.

EPA-R2-72-004
October 1972

Environmental Protection Technology Series

Identification of Polychlorinated Biphenyls in the Presence of DDT-Type Compounds

Office of Research and Monitoring
U.S. Environmental Protection Agency
Washington, D.C. 20460

DSW 037410

STLCOPCB4021234

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

DSW 037411

STLCOPCB4021235

EPA-R2-72-004
October 1972

IDENTIFICATION OF POLYCHLORINATED BIPHENYLS IN THE PRESENCE OF DDT-TYPE COMPOUNDS

Contract No. 68-01-0082
Project 16020 GIY

Project Officer

Dwight G. Ballinger
Analytical Quality Control Lab.
NERC - EPA
Cincinnati, Ohio 45268

Prepared for

OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price $1.25

DSW 037412

STLCOPCB4021236

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

DSW 037413

STLCOPCB4021237

ABSTRACT

Polychlorinated biphenyls (PCB's) interfere with gas chromatographic analyses of DDT and related compounds, necessitating a simple independent method for PCB determination. The purpose of the present study was to determine the applicability of low temperature (77° K) luminescence methods to this problem. Basic studies included documentation of excitation/emission spectra of 6 pesticides (p,p'- and o,p'-DDE, DDD, and DDT), 7 PCB isomers, and 5 PCB mixtures (Aroclors). Although phosphorescence spectra of the DDD and DDT compounds are very similar, possible differences in lifetime and polarization measurements may aid in differentiation. Emission from DDE is at least 100X less intense than that of DDD or DDT, and is therefore more difficult to determine with adequate sensitivity. Spectral differences among various Aroclors are sufficient to allow those studied to be differentiated. Emission from solvent impurities presently limit detection sensitivities to about 1.0 ppm for DDT/DDD and about .01 ppm for Aroclors. By removing interference, detection sensitivities should be improved by two orders of magnitude.

Low temperature luminescence studies in various binary mixtures of Aroclor 1254 and p,p'-DDT indicate Aroclor 1254 may be identified and quantitated in the presence of DDT concentrations 100X greater.

DSW 037414

STLCOPCB4021238

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	3
III	Introduction	5
IV	Experimental Methods	7
V	Pesticides	11
	DDE	11
	DDD and DDT	12
VI	Polychlorinated Biphenyls (PCB's)	19
	PCB Isomers	19
	PCB Mixtures (Aroclors)	30
	Photolysis of Aroclor 1254	42
	Determination of Aroclor 1254 in Water	44
VII	Analysis of Mixtures: Aroclor 1254 and p,p'-DDT	45
	Standard Low Temperature Measurements	45
	Phosphoroscopic Measurements	49
	Photoselection (Polarization) Measurements	49
VIII	Summary	53
	PCB Isomers and Mixtures (Aroclors)	53
	Pesticides	54
	Aroclor/Pesticide Mixtures	54
IX	Acknowledgments	57
X	References	59
XI	Appendix	61

DSW 037415

STLCOPCB4021239

TABLES

No.		Page
1	Average Number of Chlorine Atoms per Isomer in Aroclors, n, and Possible Number of Isomers Having n Chlorine Atoms, $N^{(n)}$	20
2	Major PCB Constituents of Aroclors	22

DSW 037416

STLCOPCB4021240

FIGURES

No.		Page
1	Structural diagrams for biphenyl, p,p'-DDE, p,p'-DDT, and p,p'-DDD	7
2	Numbering system for biphenyl substituents	8
3	Excitation/emission spectra of p,p'-DDE (100 ppm) in methylcyclohexane (MCH) glass at 77° K	11
4	Excitation/emission spectra of p,p'-DDT (100 ppm) in MCH glass at 77° K	13
5	Excitation/emission spectra of o,p'-DDT (100 ppm) in MCH glass at 77° K	13
6	Excitation/emission spectra of p,p'-DDD (100 ppm) in MCH glass at 77° K	14
7	Excitation/emission spectra of o,p'-DDD (100 ppm) in MCH glass at 77° K	14
8	Excitation/emission spectra of p,p'-DDT (10 ppm) in MCH glass at 77° K	15
9	Excitation/emission spectra of o,p'-DDT (10 ppm) in MCH glass at 77° K	15
10	Excitation/emission spectra of p,p'-DDD (10 ppm) in MCH glass at 77° K	16
11	Excitation/emission spectra of o,p'-DDD (10 ppm) in MCH glass at 77° K	16
12	Excitation/emission spectra of biphenyl, 2-chlorobiphenyl, and 4-chlorobiphenyl (all 100 ppm) in MCH glass at 77° K	24
13	Excitation/emission spectra of 4,4'-dichlorobiphenyl (100 ppm) in MCH glass at 77° K	24

DSW 037417

STLCOPCB4021241

FIGURES (Continued)

No.		Page
14	Excitation/emission spectra of biphenyl, 2, 5, 2', 5'-tetrachlorobiphenyl and 2, 4, 5, 2', 5'-pentachlorobiphenyl (all 100 ppm) in MCH glass at 77° K	25
15	Excitation/emission spectra of 2, 5, 2', 5'-tetrachlorobiphenyl and 2, 4, 5, 2', 4', 5'-hexachlorobiphenyl (Hutzinger samples, 100 ppm) in MCH at 77° K	25
16	Excitation/emission spectra of biphenyl (100 ppm) in heptane at 77° K	26
17	Excitation/emission spectra of 2-chlorobiphenyl (100 ppm) in heptane at 77° K	26
18	Excitation/emission spectra of 4-chlorobiphenyl (100 ppm) in heptane at 77° K	27
19	Excitation/emission spectra of 4, 4'-dichlorobiphenyl (100 ppm) in heptane at 77° K	27
20	Excitation/emission spectra of 2, 5, 2', 5'-tetrachlorobiphenyl (100 ppm) in heptane at 77° K	28
21	Excitation/emission spectra of 2, 4, 5, 2', 5'-pentachlorobiphenyl (100 ppm) in heptane at 77° K	28
22	Excitation/emission spectra of biphenyl and 2, 5, 2', 5'-tetrachlorobiphenyl (both 100 ppm) in octane at 77° K	29
23	Excitation/emission spectra of biphenyl and 2, 5, 2', 5'-tetrachlorobiphenyl (both 100 ppm) in nonane at 77° K	29
24	Excitation/emission spectra of Aroclors 1221 and 1248 (both 100 ppm) in MCH glass at 77° K	31
25	Excitation/emission spectra of Aroclor 1248 (100 ppm) in heptane at 77° K	31
26	Excitation/emission spectra of Aroclor 1221 (100 ppm) in heptane at 77° K	32

DSW 037418

STLCOPCB4021242

FIGURES (Continued)

No.		Page
27	Emission spectrum of a mixture of biphenyl (50 ppm) and 4-chlorobiphenyl (50 ppm) in heptane at 77° K	32
28	Excitation/emission spectra of Aroclor 1254 (100 ppm) in MCH glass at 77° K	33
29	Excitation/emission spectra of Aroclor 1221 (N, 100 ppm) in MCH at 77° K	35
30	Excitation/emission spectra of Aroclor 1221 (N, 10 ppm) in MCH at 77° K	35
31	Excitation/emission spectra of Aroclor 1242 (N, 100 ppm) in MCH at 77° K	36
32	Excitation/emission spectra of Aroclor 1242 (N, 10 ppm) in MCH at 77° K	36
33	Excitation/emission spectra of Aroclor 1248 (N, 100 ppm) in MCH at 77° K	37
34	Excitation/emission spectra of Aroclor 1248 (N, 10 ppm) in MCH at 77° K	37
35	Excitation/emission spectra of Aroclor 1248 (N, 1 ppm) in MCH at 77° K	38
36	Excitation/emission spectra of Aroclor 1248 (N, 0.1 ppm) in MCH at 77° K	38
37	Excitation/emission spectra of Aroclor 1254 (N, 100 ppm) in MCH at 77° K	39
38	Excitation/emission spectra of Aroclor 1254 (N, 10 ppm) in MCH at 77° K	39
39	Excitation/emission spectra of Aroclor 1260 (N, 100 ppm) in MCH at 77° K	40
40	Excitation/emission spectra of Aroclor 1260 (N, 10 ppm) in MCH at 77° K	40

DSW 037419

STLCOPCB4021243

FIGURES (Continued)

No.		Page
41	Excitation/emission spectra of Aroclor 1260 (N, 1 ppm) in MCH at 77° K	41
42	Excitation/emission spectra of Aroclor 1260 (N, 0.1 ppm) in MCH at 77° K	41
43	Excitation/emission spectra of 4,4'-dichlorobiphenyl (100 ppm) photolyzed Aroclor 1254 (originally 100 ppm) in ethanol at 77° K	43
44	Excitation/emission spectra of a mixture of p,p'-DDT (50 ppm) and Aroclor 1254 (50 ppm) in MCH glass at 77° K	46
45	Excitation/emission spectra of a mixture of p,p'-DDT (50 ppm) and Aroclor 1254 (5 ppm) in MCH glass at 77° K	46
46	Excitation/emission spectra of a mixture of p,p'-DDT (50 ppm) and Aroclor 1254 (0.5 ppm) in MCH glass at 77° K	47
47	Excitation/emission spectra of a mixture of p,p'-DDT (5 ppm) and Aroclor 1254 (5 ppm) in MCH glass at 77° K	47
48	Excitation/emission spectra of a mixture of p,p'-DDT (5 ppm) and Aroclor 1254 (N, 0.5 ppm) in MCH glass at 77° K	48
49	Excitation/emission spectra of a mixture of p,p'-DDT (5 ppm) and Aroclor 1254 (N, 0.05 ppm) in MCH glass at 77° K	48
50	Polarized excitation spectra of a mixture of Aroclor 1254 (5 ppm) and p,p'-DDT (50 ppm) in MCH glass at 77° K	50

DSW 037420

STLCOPCB4021244

SECTION I

CONCLUSIONS

1. A six month exploratory study has demonstrated that, using low temperature luminescence methods, polychlorinated biphenyls (PCB's) can be determined in the presence of much higher concentrations of DDT-type compounds.

2. The results obtained indicate that a simple, sensitive analytical method for PCB's can be based on these methods.

3. Such a method would be fairly rapid and might be used either independently or as an adjunct to standard methods employing gas chromatography.

DSW 037421

STLCOPCB4021245

SECTION II

RECOMMENDATIONS

1. It is recommended that this exploratory study be followed by a program which will both continue basic studies and establish a simple method for the estimation of PCB's in natural waters. Additional PCB isomers should be studied in order to define sources of Aroclor emission and to establish extent of energy transfer among PCB isomers. Energy-transfer studies involving PCB mixtures and pesticides should be continued.

2. More study should be devoted to adjunct methods which may prove valuable in an analytical methodology for PCB's/DDT's by selectively enhancing certain components. Such studies would involve photochemical experiments, phosphoroscopic methods (differentiation based upon phosphorescence lifetimes), and photoselection methods (differentiation based upon behavior with respect to polarized light).

3. A greater variety of Aroclor/pesticide mixtures covering a wide range of concentrations, should be studied in order to establish detection limits and analytical curves.

4. It is recommended that an independent analytical method for PCB's in the presence of pesticides based on low temperature luminescence methods be developed.

5. The utility of low temperature luminescence methods as an adjunct to gas chromatography for analysis of PCB's/pesticides should be explored.

STLCOPCB4021246

SECTION III

INTRODUCTION

It has been known for some time that polychlorinated biphenyls (PCB's) interfere with the determination of DDT and similar pesticides in standard methods utilizing gas chromatography.[1,2] These groups, pesticides and PCB's, must be separated prior to quantification by GC, the usual methods being column or thin-layer chromatography.[3]

PCB's have been widely used as plasticizers, solvents, and insulators, and have, themselves, become ubiquitous environmental contaminants.[4] These compounds are highly toxic to some species: exposure for 48 hours to .1 ppm Aroclor 1254 (a commercial PCB mixture) in sea water causes 100% mortality in juvenile pink shrimp.[5] Zitko and Choi,[6] Reynolds,[3] and Risebrough[7] have reviewed PCB levels in fish and fish-eating birds. These levels typically range from approximately .01 ppm to 10 ppm in fish, 1 ppm to 100 ppm in birds, and in fact are comparable to levels of DDE found in the same animals. PCB levels in the range 100 to 200 ppm may be responsible for deformities found in terns on Great Gull Island in Long Island Sound.[8] Thus, the related problem of detecting pesticides in the presence of equal or greater concentrations of PCB's may become important. Low temperature molecular luminescence appeared to offer a potentially useful method for the determination of PCB's in the presence of DDT-type compounds, and a six month exploratory study was initiated in order to assess this approach. The results obtained are highly encouraging and dramatically demonstrate the potential utility of this technique for PCB's, DDT analogues, and PCB-DDT mixtures. The technique is of greater applicability, and could in principle be applied to a wide variety of compounds such as chlorinated naphthalenes (Halowaxes), herbicides such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), polybrominated biphenyls (PBB's) and the highly toxic chlorinated dibenzofurans and dibenzo-p-dioxins.[6] Luminescence methods are inherently insensitive to saturated compounds such as endrin and dieldrin, so that interferences which might exist in other methods such as GC are eliminated.

STLCOPCB4021247

SECTION IV

EXPERIMENTAL METHODS

Figure 1 gives the structures of biphenyl, p, p'-DDT, p, p'-DDD, and p, p'-DDE.

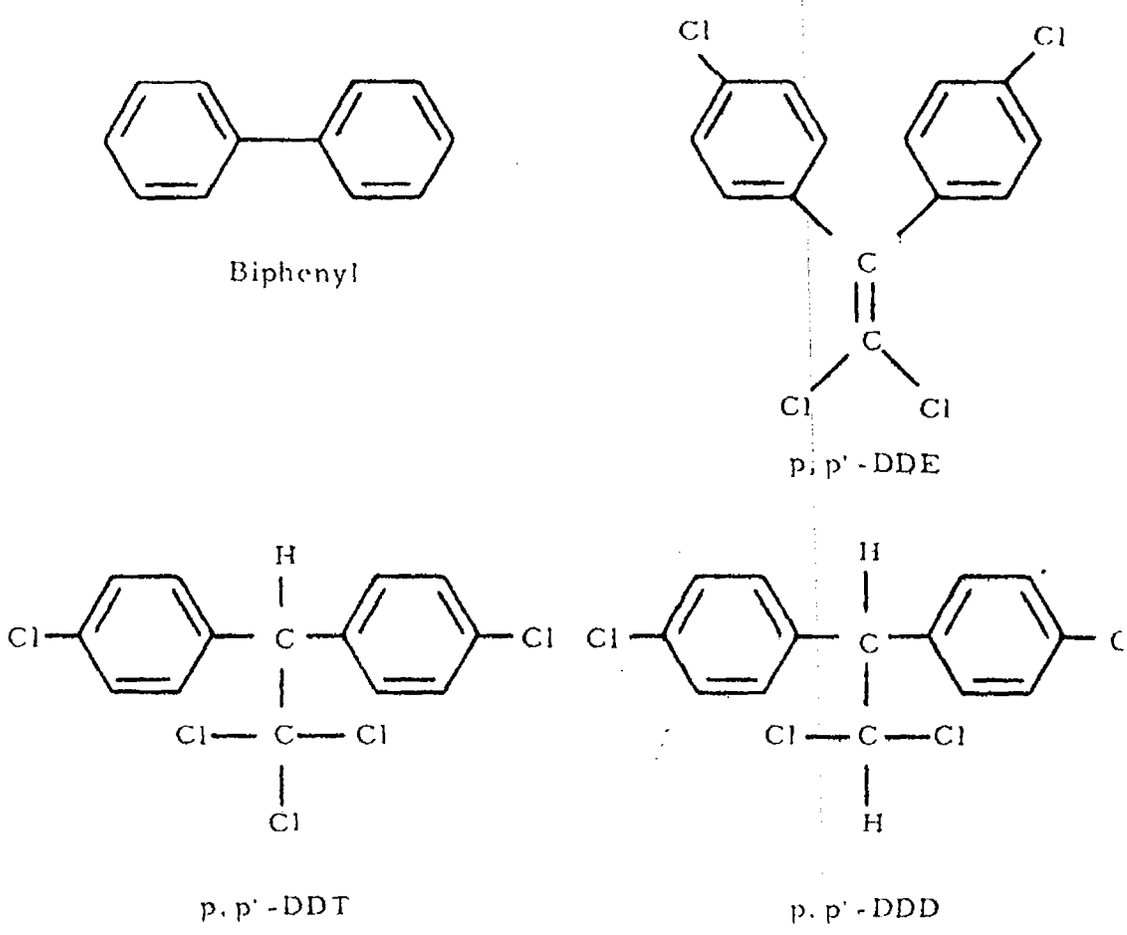


Figure 1. Structural diagrams for biphenyl, p, p'-DDE, p, p'-DDT, and p, p'-DDD

DSW 037424

STLCOPCB4021248

Figure 2 shows the numbering system defining the location of substituents in biphenyl; this will become important in SECTION VI where luminescence spectra of some chlorinated biphenyl isomers are discussed.

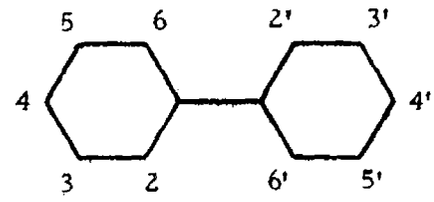


Figure 2. Numbering system for biphenyl substituents

Both p,p'- and o,p'-isomers of DDD, DDT, and DDE have been studied to date. All of these compounds were obtained from the EPA Perrine Primate Research Branch, Perrine, Florida.

PCB isomers studied initially were biphenyl, 2-chlorobiphenyl, 4,4'-dichloro-, 2,5,2',5'-tetrachloro-, and 2,4,5,2',5'-pentachlorobiphenyl. All of these isomer samples (except biphenyl) were generously donated by Dr. R. G. Webb of the EPA Laboratory, Athens, Georgia. Biphenyl was obtained from the Aldrich Chemical Company. More recently, Dr. O. Hutzinger provided us with samples of 2,5,2',5'-tetrachloro- and 2,4,5,2',4',5'-hexachlorobiphenyl, and the luminescence signatures of these isomers have been included in this report.

Aroclor samples studied initially were 1221, 1248, and 1254. The first two samples were provided by the Monsanto Chemical Company, and the last was supplied by Dr. Webb. Dr. E. S. Tucker of Monsanto recently (27 October 1971) provided new samples of the following Aroclors: 1221, 1242, 1248, 1254, and 1260.

Benzene, hexane, heptane, and methylcyclohexane were Matheson, Coleman, and Bell Spectroquality Grade solvents. Octane, Chromatoquality Grade, was obtained from Analabs, Inc. Nonane was obtained from Eastman Chemical Co. Ethylene glycol was Matheson, Coleman, and Bell Chromatography Grade. Ethanol was obtained from Graves Distilling Company and was the Extra Fine Grade.

DSW 037425

STLCOPCB4021249

All solvents were used as received, although attempts were made to purify methylcyclohexane (MCH) using column chromatography (CC). Initial studies employed a 24 in. long, 1 in. diameter glass column packed with Woelm silica gel (Activity Grade 1) as the upper layer and Woelm basic alumina (Activity Grade 1) as the lower layer. Passage of Matheson Spectroquality methylcyclohexane through this column revealed unidentified fluorescent contaminants which were not present prior to the chromatographic operation. Further studies are necessary with each packing material separately to determine the source of contamination. Other purification schemes, such as distillation, are under consideration should problems associated with CC prove difficult to correct.

As discussed in the original proposal, the room temperature fluorescence/excitation spectra of PCB's and DDT-type compounds overlap and thus result in interference. At low temperature (77° K), however, phosphorescence appears and spectral overlap is much reduced, allowing PCB's and DDT's to be selectively determined. For this reason, our efforts have largely focused on low-temperature measurement.

Sample tubes used for low-temperature measurements were 3 mm (inside diameter) Suprasil quartz tubes capped to prevent solvent evaporation or contamination. Sample volumes of .3 - .5 mls were transferred into the quartz tubes with disposable pipettes. Samples were then frozen by direct immersion into a quartz dewar filled with liquid nitrogen (boiling point 77° K) positioned in the Fluorispec.

If samples are cooled to 77° K slowly enough (in approximately 2 minutes or more), a clear glass will usually result for both ethanol and methylcyclohexane, provided that these solvents (and the quartz tube) are adequately dry. In general, no special drying procedures were necessary for these solvents in order to achieve the glassy state. Residual distilled water remaining in tubes after cleaning could be quickly removed by purging the tube with dry nitrogen gas. This residual water, if not removed, usually results in cracked glasses, particularly for methylcyclohexane.

All other solvents formed either cracked glasses or "snows," the latter condition being more characteristic of the n-alkane matrices. These matrices are highly scattering and thus may be less satisfactory for quantitative determinations than the clear glasses. However, these matrices often produce line-like ("quasilinear") spectral bands at low temperatures (see APPENDIX) and thus may prove useful for qualitative studies.

DSW 037426

STLCOPCB4021250

Many other solvent systems have been found to result in clear low temperature glasses, and the interested reader is referred to the literature[9,10] for details. Methylcyclohexane (and ethanol) were chosen for our studies primarily because they form glasses themselves.

Luminescence measurements were made on either the Baird-Atomic SF-1 or SF-100 Fluorispec instruments. These instruments are identical in their optical systems, the SF-100 having more modern and versatile electronics. Most of the spectral data were obtained with analyzing slits set at their smallest values to obtain the maximum spectral resolution (2 nm). The standard source for these instruments is a Hanovia 150 Watt (D. C.) Xenon lamp, and the standard detector is an RCA 1P28 photomultiplier tube.

Data obtained on the SF-1 instrument have been designated as such on the appropriate figures; where no such designation appears, the SF-100 instrument has been used.

DSW 037427

STLCOPCB4021251

SECTION V

PESTICIDES

Excitation and emission spectra have been obtained for p, p' - and o, p' - DDE, DDD, and DDT in methylcyclohexane (MCH) glass at 77° K. Concentrations ranged from 1 to 100 ppm. Near 1 ppm, interference from emitting solvent impurities becomes significant and solvents of higher purity must be used in order to exceed this limit.

DDE

A freshly prepared solution of p, p' -DDE at a concentration of 100 ppm in MCH at 77° K shows a very weak, broad emission band in the region 310 - 440 nm with a maximum at approximately 370 nm (Figure 3).

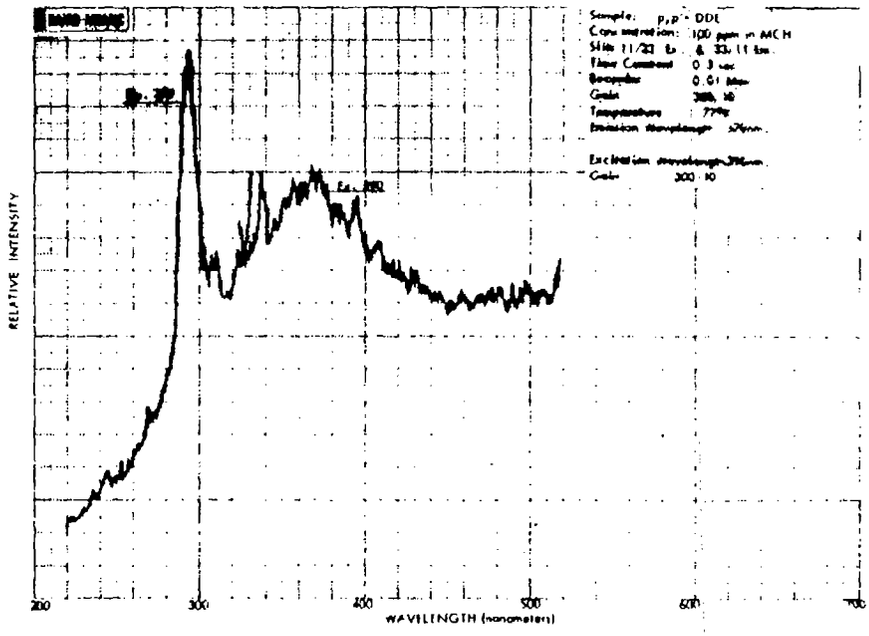


Figure 3. Excitation/emission spectra of p, p' -DDE (100 ppm) in methylcyclohexane (MCH) glass at 77° K

The corresponding excitation occurs in the 300 - 280 nm region with a maximum at 294 nm. A similar solution of o, p' -DDE studied at the same approximate wavelengths shows no evidence of emission. The observed p, p' -DDE emission is roughly 400X less intense than that of the DDD or DDT phosphorescence.

DSW 037428

STLCOPCB4021252

These results differ from those presented in the fourth monthly report, and the earlier results may have been influenced by photo-products formed upon standing in the presence of room lights for several months. The present results again differ from those of Moye and Winefordner,[11] who report a phosphorescence maximum at 425 nm and corresponding excitation maxima at 270 and 245 nm for p, p'-DDE in ethanol at 77° K. The results quoted by these authors for p, p'-DDE are very similar to their values for p, p'-DDD and p, p'-DDT: excitation maxima at 265 and 275 nm and phosphorescence maxima at 415 and 420 nm respectively in ethanol at 77° K. In addition, the phosphorescence detection limits given by Moye and Winefordner for all these compounds are roughly the same (within a factor of 5) and imply that the DDE emission should be much stronger than we observe.

At the present time, we believe that the low temperature DDE emission is intrinsically much weaker than that of DDD or DDT. It is not certain, however, if the emission shown in Figure 3 is actually that of p, p'-DDE or is in fact due to an impurity in DDE.

DDD and DDT

Excitation and emission spectra of the four DDD and DDT compounds (100 ppm in MCH) are very similar as shown in Figures 4 through 7. The phosphorescence origins are in the region 355 - 366 nm. The band systems are slightly structured to the short-wavelength side of the maximum but become stronger and more diffuse at longer wavelengths. No evidence of fluorescence was observed in these compounds. The excitation spectra show prominent, narrow (3 - 4 nm half-widths) origin bands at 275 - 277 nm followed by several other weaker and slightly broader bands. A second system, presumably due to a different electronic transition, appears at 240 - 246 nm. Our results on p, p'-DDD and p, p'-DDT are in general consistent with the data of reference 11, and the excitation spectra resemble the absorption spectrum of the parent hydrocarbon, diphenyl methane as given by Berlman.[12]

Spectra of these same compounds at a concentration of 10 ppm in MCH appear in Figures 8 through 11. The additional emission which appears, particularly in the DDD spectra, is due to impurities present in the pesticide samples. The reason that the impurity emission becomes relatively more intense at lower concentrations is due to the phenomenon of energy transfer. At high solute concentrations, impurities can efficiently transfer their excitation energy to the major emitting component (the pesticide). At reduced concentrations energy transfer becomes less favorable and it is more likely that the impurities will emit rather than transfer excitation energy.

DSW 037429

STLCOPCB4021253

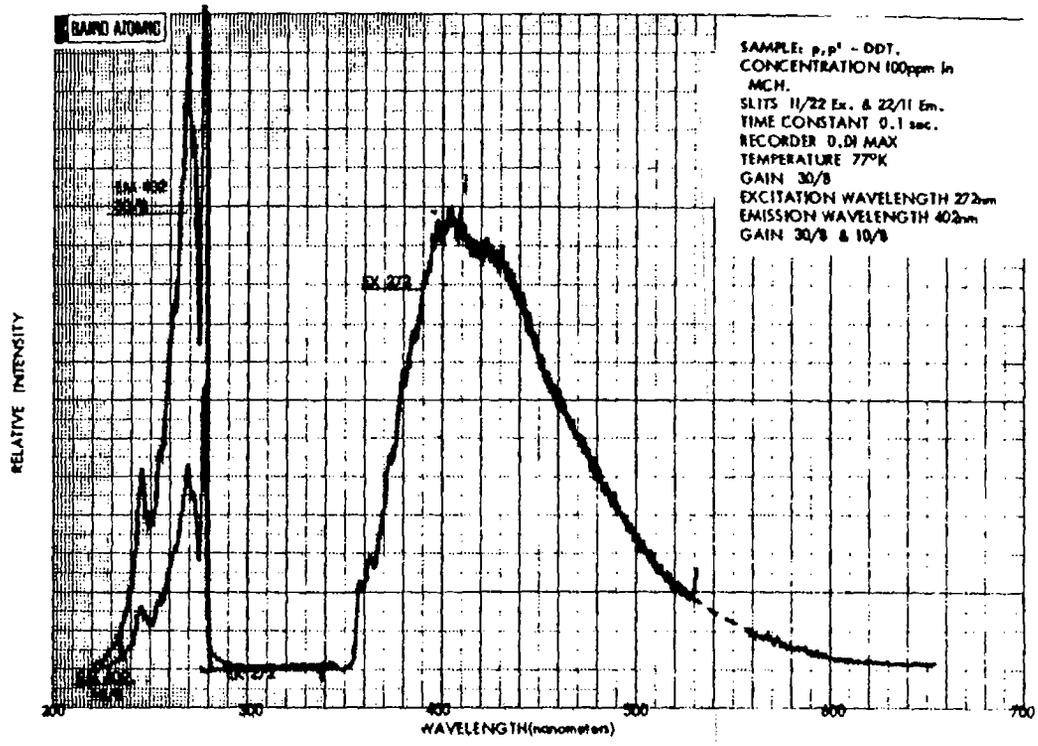


Figure 4. Excitation/emission spectra of p, p' - DDT (100 ppm) in MCH glass at 77° K

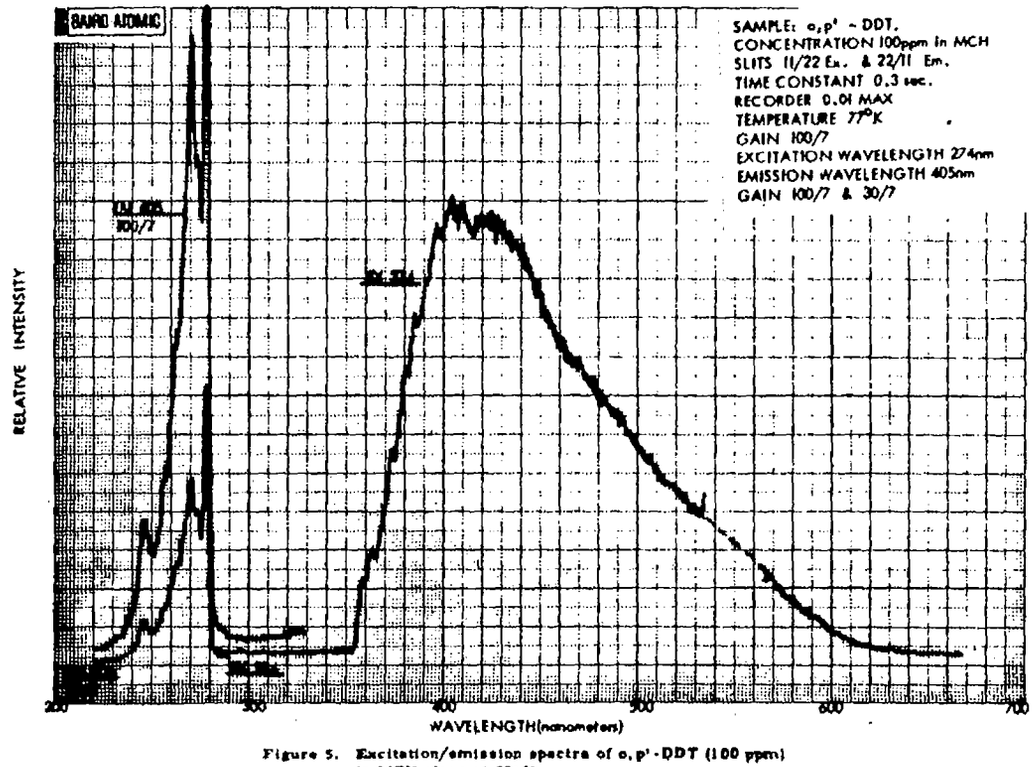


Figure 5. Excitation/emission spectra of o, p' - DDT (100 ppm) in MCH glass at 77° K

DSW 037430

STLCOPCB4021254

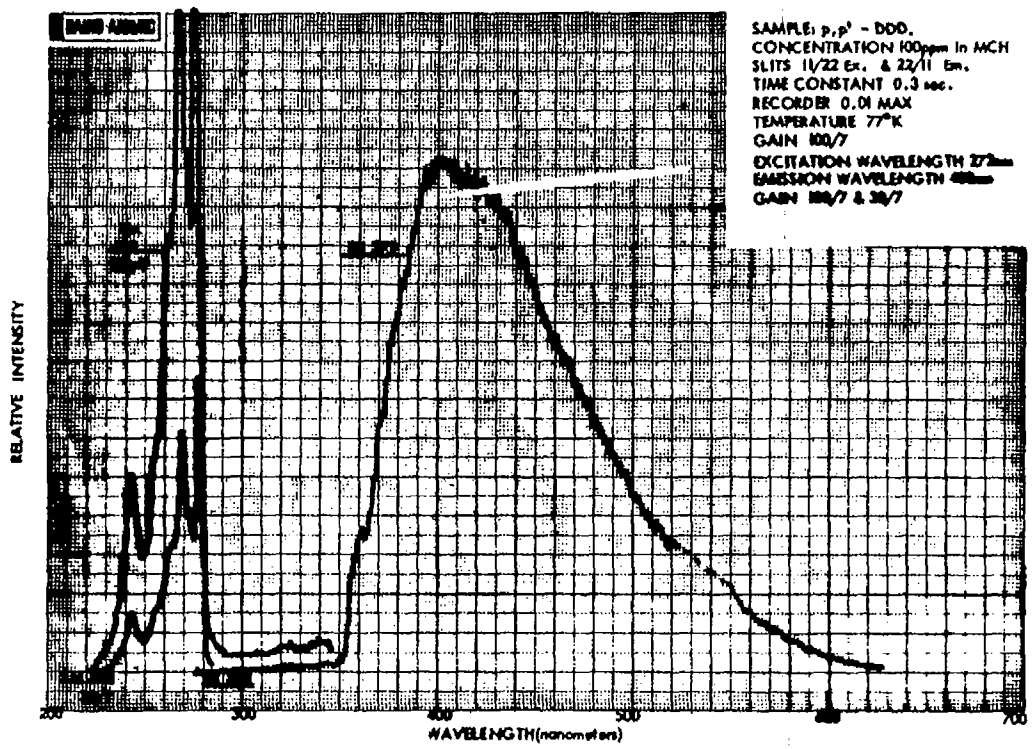


Figure 6. Excitation/emission spectra of p,p'-DDD (100 ppm) in MCH glass at 77° K

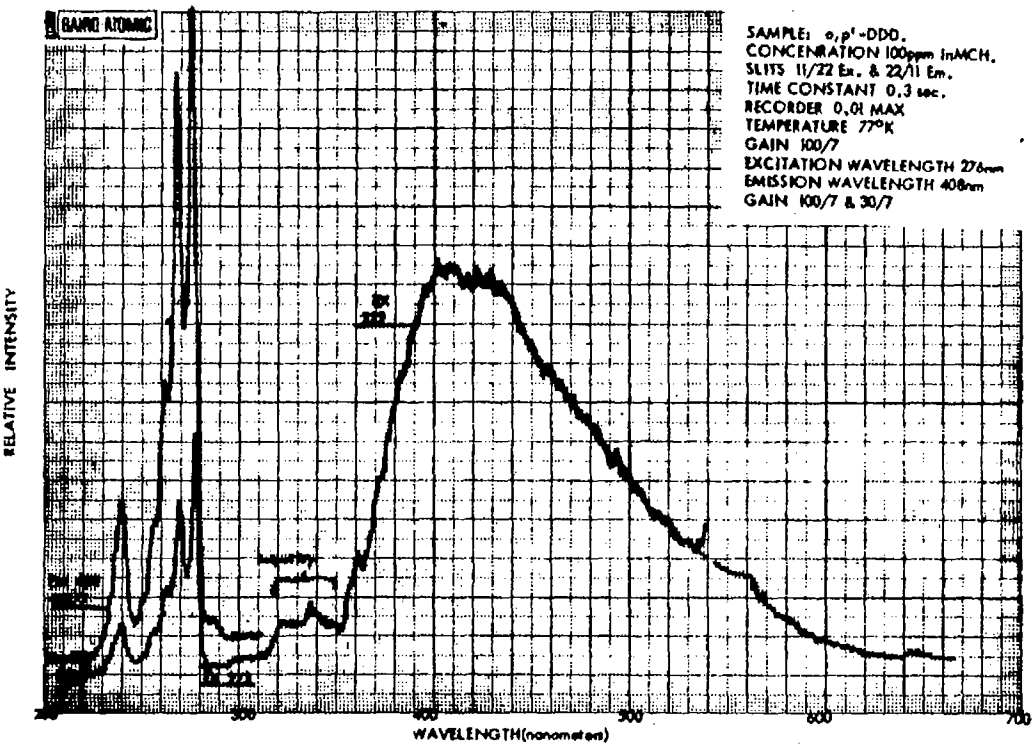


Figure 7. Excitation/emission spectra of o,p'-DDD (100 ppm) in MCH glass at 77° K

DSW 037431

STLCOPCB4021255

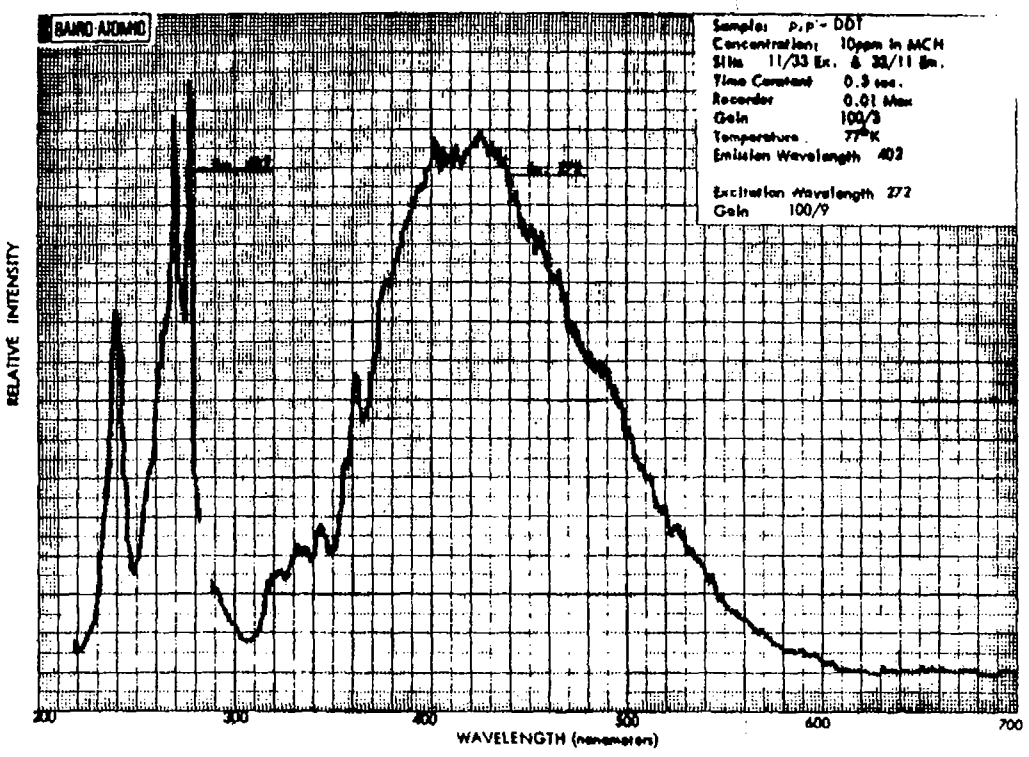


Figure 8. Excitation/emission spectra of p,p'-DDT (10 ppm) in MCH glass at 77° K

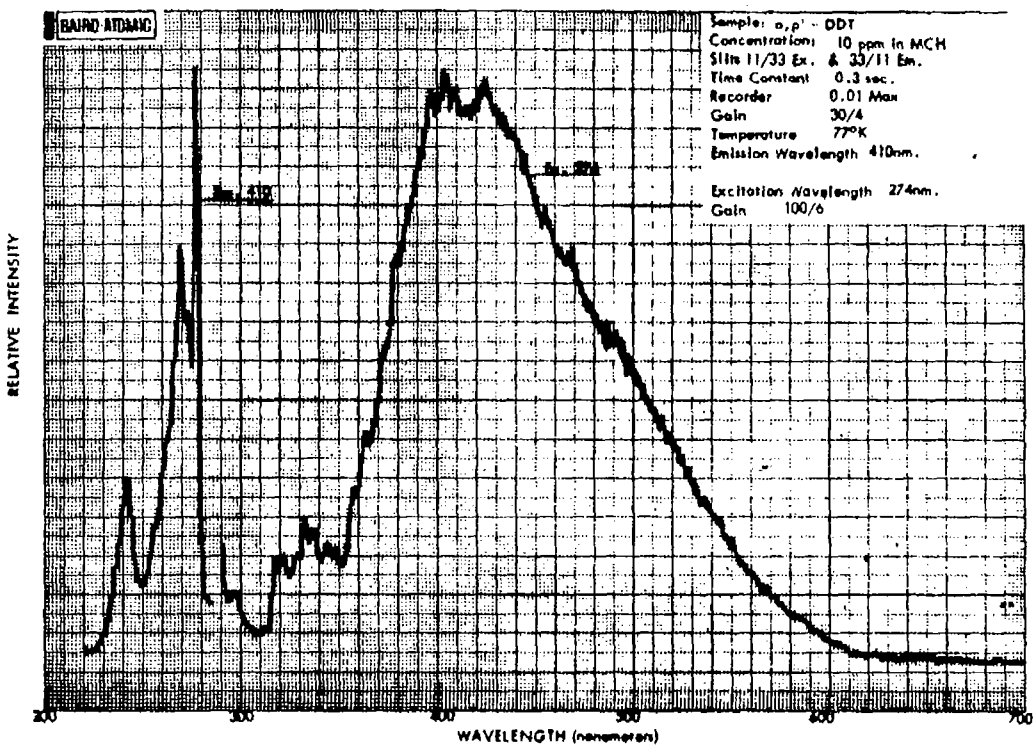


Figure 9. Excitation/emission spectra of o,p'-DDT (10 ppm) in MCH glass at 77° K

DSW 037432

STLCOPCB4021256

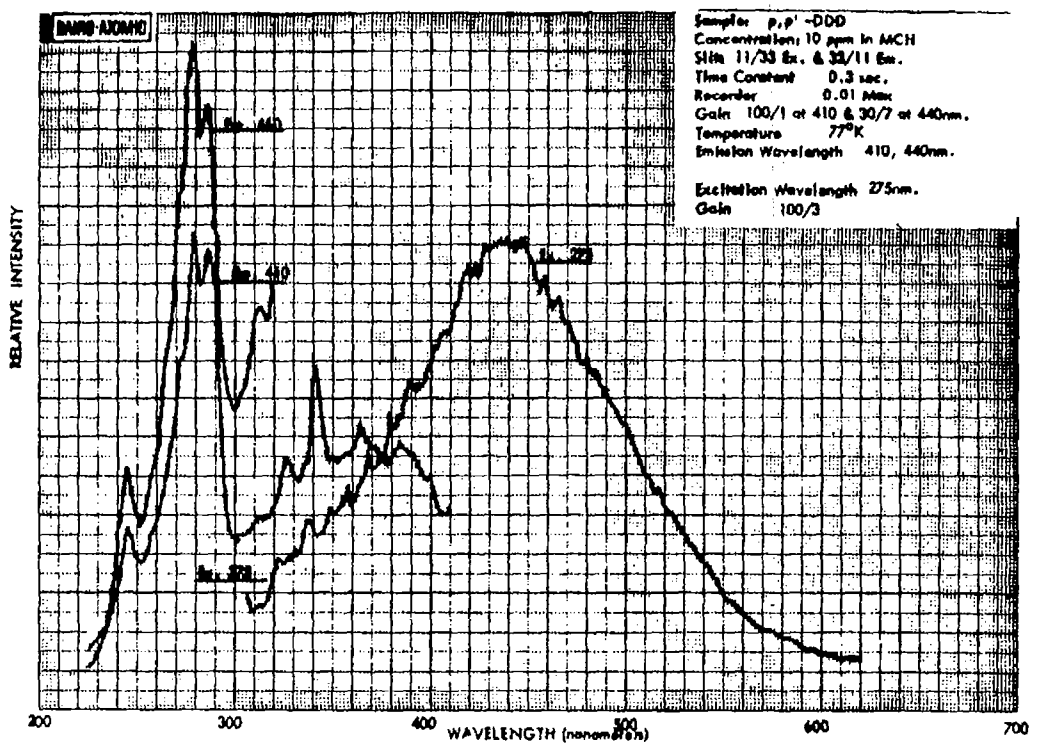


Figure 10. Excitation/emission spectra of p, p'-DDD (10 ppm) in MCH glass at 77° K.

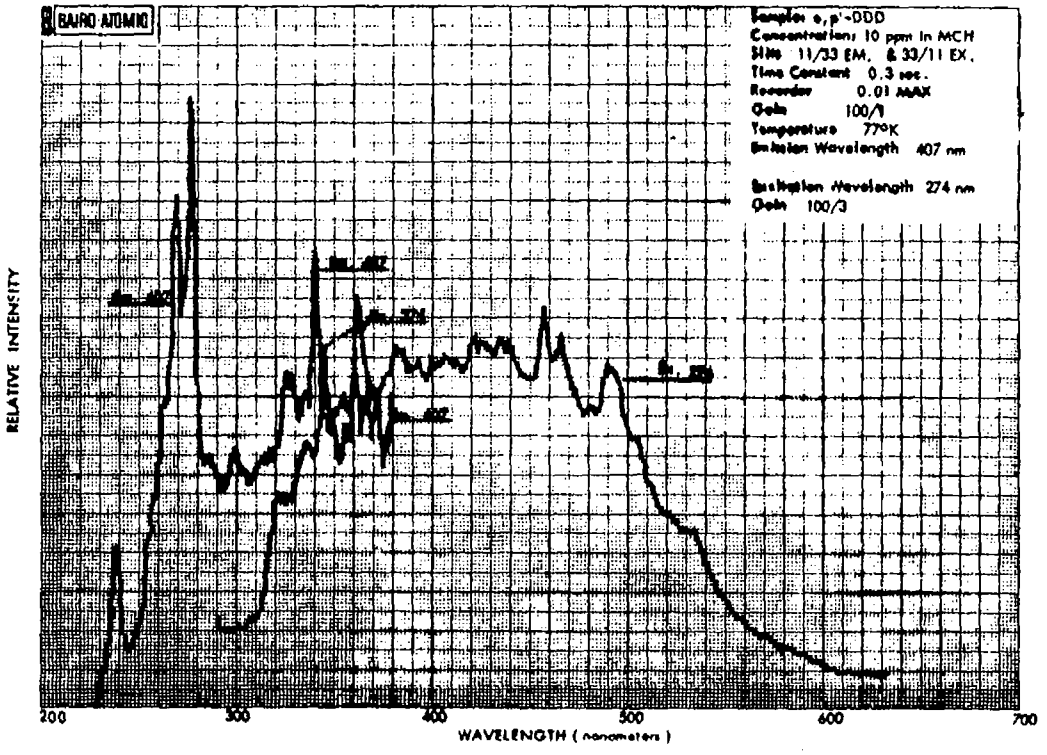


Figure 11. Excitation/emission spectra of o, p'-DDD (10 ppm) in MCH glass at 77° K

DSW 037433

STLCOPCB4021257

Experiments were performed to determine the effect of dissolved oxygen on the phosphorescence yield of p, p'-DDD and p, p'-DDT. Solutions having concentrations of 10 ppm in MCH were studied at 77° K before and after bubbling dry, pure nitrogen gas through the samples for about 5 minutes. No appreciable enhancement (greater than 30%) was observed in the phosphorescence intensity after purging the solutions. It is possible, however, that this method is inadequate for the complete removal of oxygen, and a vacuum system is being constructed in order to achieve better degassing (by allowing pump-freeze-thaw cycles).

Preliminary studies on p, p'-DDT in heptane at 77° K reveal no additional sharpening of the phosphorescence, in contrast with some of the PCB isomers (SECTION VI). In addition, the phosphorescence maximum of p, p'-DDT was found to shift from approximately 405 nm in MCH to approximately 455 nm in heptane. Similarly, the excitation band at 277 nm in MCH shifts to 290 nm in heptane. These spectral differences may reflect changes in the DDT geometry in the two matrices, and in particular may suggest that the relative orientation of the DDT phenyl groups in the two matrices are rather different.

DSW 037434

STLCOPCB4021258

SECTION VI

POLYCHLORINATED BIPHENYLS (PCB's)

PCB Isomers

Commercial mixtures of polychlorinated biphenyls and terphenyls are manufactured in the United States by the Monsanto Company under the tradename "Aroclor." Foreign manufacturers of similar products include Prodelee in France ("Phenoclor"), Bayer in Germany ("Clophen"), with additional production in the USSR and Japan.

Monsanto uses a four digit code to specify Aroclors. The first two digits of the code designate the parent hydrocarbon type as follows:

12: Chlorinated biphenyls

25: Mixture of chlorinated biphenyls and chlorinated terphenyls (75:25)

44: Mixture of chlorinated biphenyls and chlorinated terphenyls (60:40)

54: Chlorinated terphenyls

The last two digits of the code designate the weight percentage of organically bound chlorine. For example, Aroclor 1254 is a mixture of chlorinated biphenyls having 54% chlorine.

A weight percentage of 54% chlorine implies that an "average" isomer in this Aroclor has five chlorine substituents. For five chlorine atoms per biphenyl a total of 46 isomers are statistically possible assuming that conformations differing only by a possible angle of twist (0° to 180°) between phenyl groups are equivalent. Of course, this figure does not represent the actual isomer content of this Aroclor, since certain isomers are favored by the chlorination reaction, and the occurrence of isomers having more or less than five chlorine atoms is also possible. Table 1 summarizes the average number of chlorines per biphenyl, n_{av}, in various Aroclors, the closest whole number value of n_{av}, n, and the statistically possible number of isomers, N, having n chlorine atoms, $N^{(n)}$. The statistical calculation is subject to the restraint noted previously. Aroclors in parentheses denote hypothetical mixtures.

DSW 037435

STLCOPCB4021259

Table 1. Average Number of Chlorine Atoms per Isomer in Aroclors, n, and Possible Number of Isomers Having n Chlorine Atoms, $N^{(n)}$

Aroclor	n_{av}	n	$N^{(n)}$
(1200)	0.0	0	1
1221	1.2	1	3
1232	2.0	2	12
1242	3.1	3	24
1248	3.9	4	42
1254	4.9	5	46
1260	6.3	6	42
1262	6.8	7	24
(1266)	8.0	8	12
1268	8.7	9	3
(1271)	10.0	10	1

From Table 1, there is a total of 210 PCB isomers possible statistically having from zero to ten chlorine atoms. Hence the problem of establishing the isomer distribution in a given Aroclor is very difficult, and only recently has progress been made.

Webb and McCall[13] have identified 30 PCB isomers in Aroclors 1221, 1232, 1242, 1248 and 1254 by comparison of GC retention times and IR spectra with those of isomers prepared by the Gomberg or Ullmann reactions. Sissons and Welti[14] have performed a similar study on Aroclor 1254 utilizing NMR and mass spectroscopy data obtained on 40 isomers; GC retention indices were used to predict the isomer components of Aroclor 1242 and 1260. Tas and deVos[15] have established four major components of Phenoclor DP6 (a mixture similar to Aroclor 1260) using NMR and IR spectra of these isomers prepared by the Ullmann reaction. Hutzinger, et al.,[16] have reported the synthesis of many PCB isomers so that further work on identification of isomers in Aroclors may be forthcoming from these and other laboratories.

Table 2 summarizes the major components of Aroclors and Phenoclor DP6 as determined by Webb and McCall, Sissons and Welti, and Tas and deVos.

DSW 037436

STLCOPCB4021260

Important isomers available to us and thus chosen for study were: biphenyl; 2- and 4-chlorobiphenyl; 4,4'-dichlorobiphenyl; 2,5,2',5'-tetrachlorobiphenyl; 2,4,5,2',5'-pentachlorobiphenyl; and 2,4,5,2',4',5'-hexachlorobiphenyl. These compounds appear underlined in Table 2.

Figures 12 through 15 show spectra of the isomers in MCH at 77° K. Spectra of the isomers in heptane at 77° K appear in Figures 16 through 21. Figures 22 and 23 show spectra of biphenyl and 2,5,2',5'-tetrachlorobiphenyl in octane and nonane respectively. Where composites have been used, the spectrum of one isomer has been vertically displaced for clarity.

Part of the isomer study included an investigation of several solvents to determine possible solvent effects upon spectral bandwidths. Excitation and emission spectra of biphenyl were obtained in the following matrices at 77° K: hexane, heptane, octane, nonane, benzene, MCH, and ethylene glycol: water (2:1 by volume). Only MCH formed a clear glass upon cooling rapidly (approximately two minutes) to 77° K. Ethylene glycol: water formed a cracked glass and some of the biphenyl remained insoluble, but this presented no special difficulty. The other solvents used, particularly the alkanes, formed "snows" and hence the scatter was greatly increased.

As expected from the early work of Shpolskii,[17] the biphenyl emission at 77° K was found to be sharpest in the n-alkane matrices. A brief account of the conditions favoring this so-called "Shpolskii" effect appears in the APPENDIX. In particular, the biphenyl emission was extremely sharp (half width of 2 - 4 nm) and highly detailed in heptane (Figure 16) and hexane. Band widths may in fact be slit limited in these matrices. Heptane was found to produce a barely perceptible narrowing over hexane. Spectra obtained in the remaining solvents were broader (half widths approximately 20 nm) and typically resembled those observed in MCH (Figure 12).

The spectra in octane and nonane (Figures 22 and 23) were broader, the biphenyl origin band having an approximate half widths of 6 and 10 nm respectively. The spectrum of biphenyl in octane reveals a broad emission at about 390 nm which may be due to biphenyl aggregates (see APPENDIX).

Isomer spectra were obtained in several solvents, leading to the following conclusions:

a) The ratio of fluorescence to phosphorescence is reduced upon chlorination: for biphenyl, the uncorrected ratio of fluorescence to

DSW 037437

STLCOPCB4021261

Table 2. Major PCB Constituents of Aroclors†

	1221	1232	1242	1248	1254	1260 (DP6)
Biphenyl	W	W				
2-	W	W	W			
4-	W	W				
2,2'-	W	W	W, S			
2,3'-		W	W, S			
2,4'-	W	W	W, S			
4,4'-		W				
2,3,2'-		W	W, S*			
2,3,3'-			S*			
2,4,2'-			W, S			
2,4,3'-			S			
2,4,4'-			W, S*	W		
2,5,2'-		W	W, S	W		
2,5,3'-			S*			
2,5,4'-			W			
2,6,4'-			S			
3,4,2'-			W, S	W		
2,3,2',5'-			W	W	W, S*	
2,4,2',5'-			S*	W		
2,4,3',4'-			W	W		
2,5,2',5'-			W, S*	W	W, S*	
2,5,3',4'-			W, S	W	S	
2,3,4,3'-			S*			
2,3,4,2',5'-					S	
2,3,4,3',4'-					S	
2,3,6,2',3'-				W	W, S	
2,3,6,2',5'-			S*		W, S*	S*

DSW 037438

STLCOPCB4021262

Table 2. Major PCB Constituents of Aroclors† (cont.)

	1221	1232	1242	1248	1254	1260 (DP6)
2,3,6,2',6'-				W		
2,3,6,3',4'-					S*	
2,4,5,2',3'-					W,S	
2,4,5,2',4'-					W,S*	
2,4,5,2',5'-				W	W,S*	S*
2,4,5,3',4'-					W,S	
2,3,4,2',3',4'-						S
2,3,4,2',3',6'-					S	S*
2,3,4,2',4',5'-					S*	S*,(T)
2,3,5,2',4',6'-						S*
2,3,6,2',3',6'-						S
2,3,6,2',4',5'-					W,S*	S*
2,4,5,2',4',5'-					W,S*	S*,(T)
2,3,4,5,2',3',4'-						S*,(T)
2,3,4,5,2',4',5'-						S,(T)
2,3,4,5,2',4',6'-						S*
2,3,4,6,2',3',5'-						S*
2,3,5,6,2',3',4'-						S*

† Data from References 13 (W), 14 (S), and 15 (T).

* Denotes alternative assignments are possible.

DSW 037439

STLCOPCB4021263

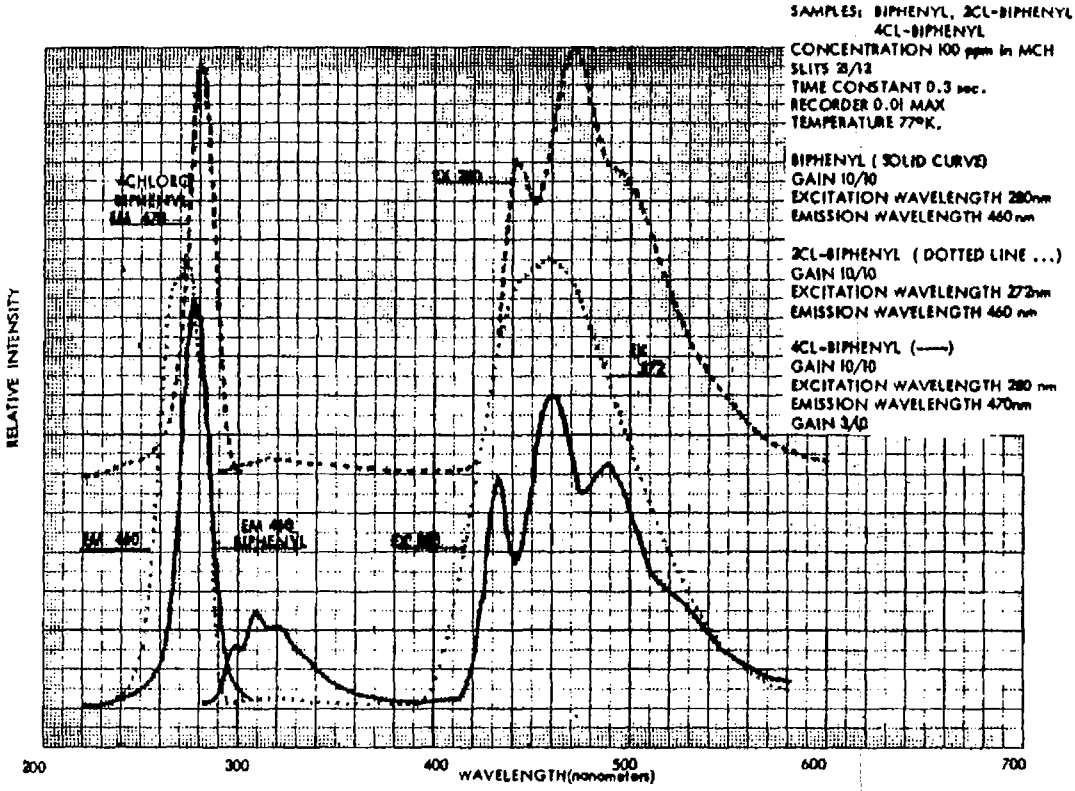


Figure 12. Excitation/emission spectra of biphenyl, 2-chlorobiphenyl, and 4-chlorobiphenyl (all 100 ppm) in MCH glass at 77° K

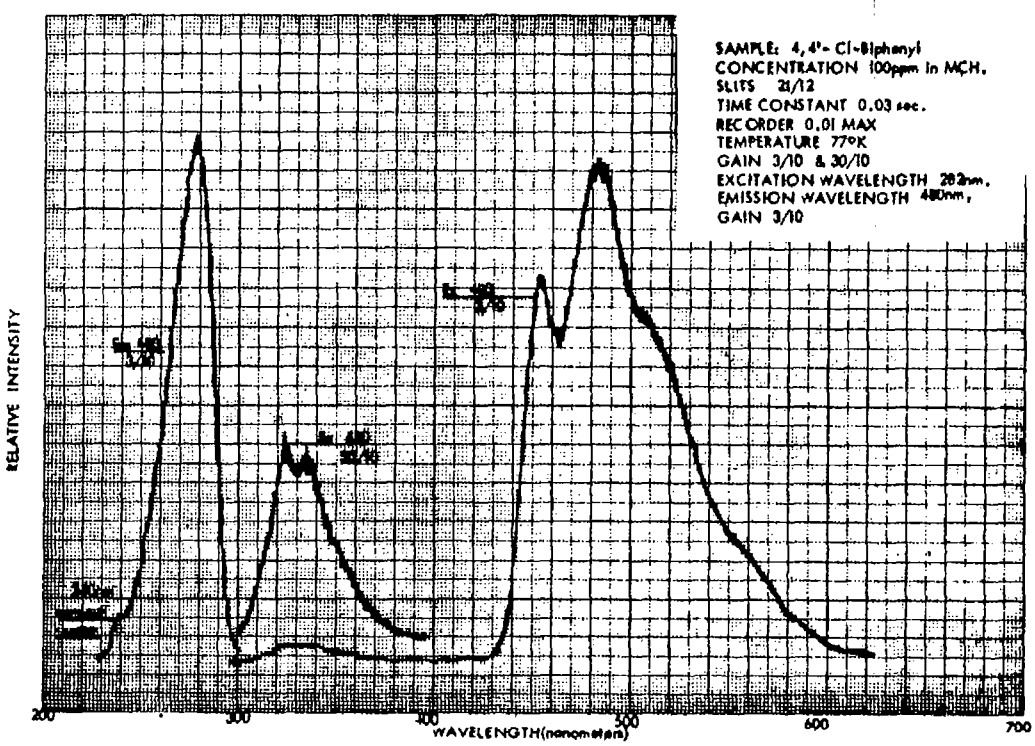


Figure 13. Excitation/emission spectra of 4,4'-dichlorobiphenyl (100 ppm) in MCH glass at 77° K

DSW 037440

STLCOPCB4021264

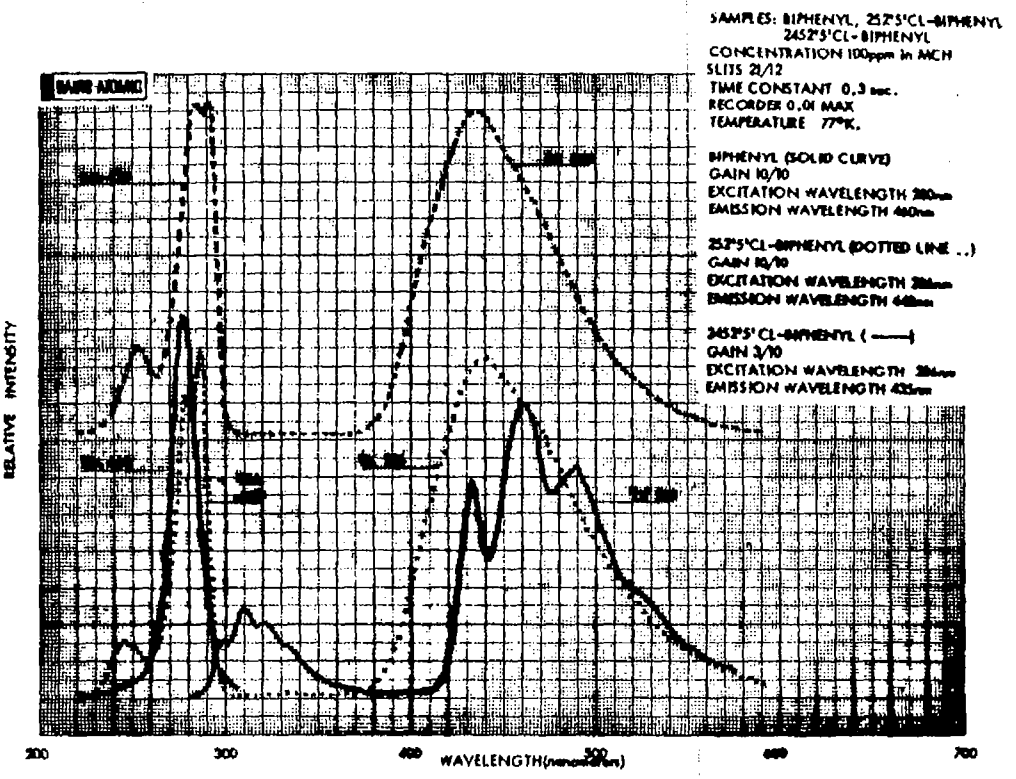


Figure 14. Excitation/emission spectra of biphenyl, 2, 5, 2', 5'-tetrachlorobiphenyl and 2, 4, 5, 2', 5'-pentachlorobiphenyl (all 100 ppm) in MCH glass at 77° K

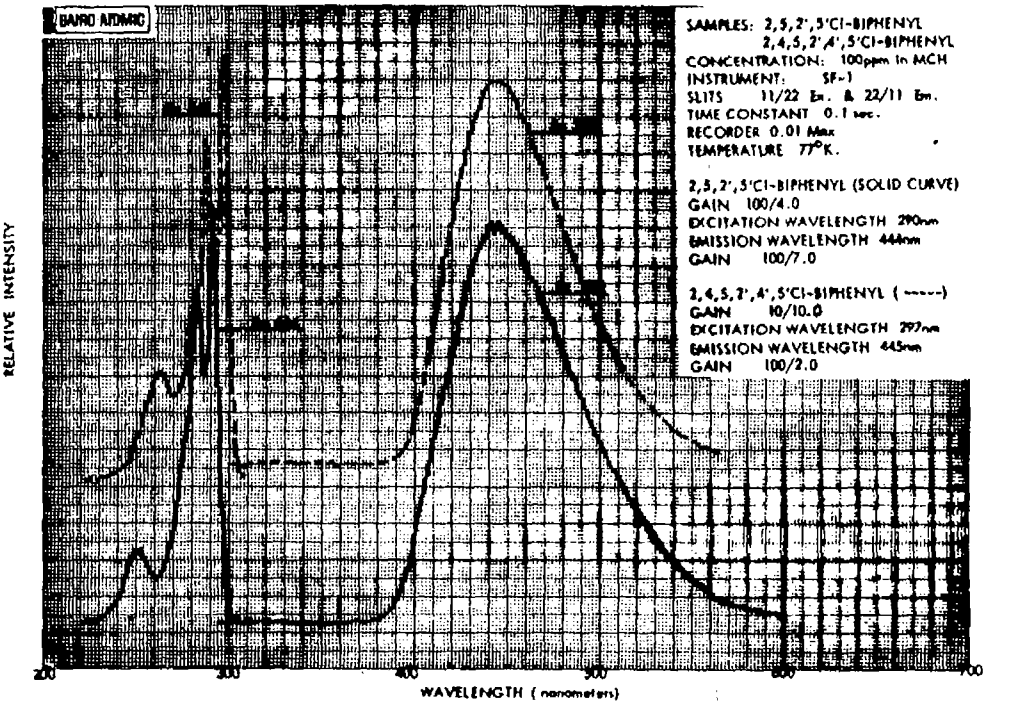


Figure 15. Excitation/emission spectra of 2, 5, 2', 5'-tetrachlorobiphenyl and 2, 4, 5, 2', 4', 5'-hexachlorobiphenyl (Hutzinger samples, 100 ppm) in MCH at 77°K

DSW 037441

STLCOPCB4021265

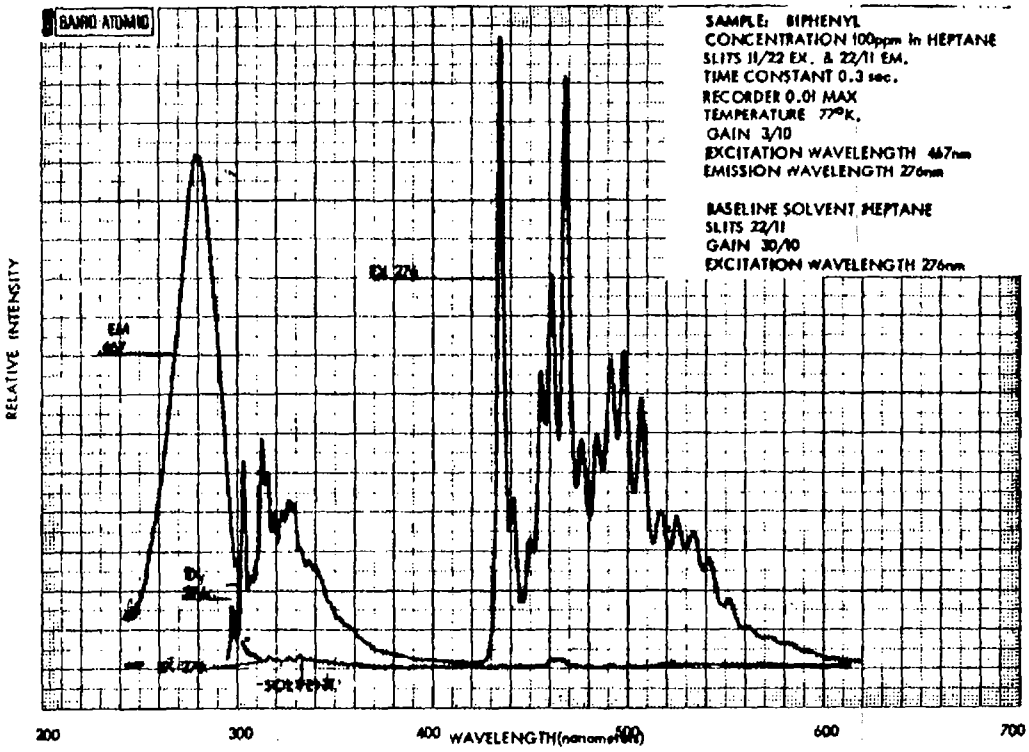


Figure 16. Excitation/emission spectra of biphenyl (100 ppm) in heptane at 77° K

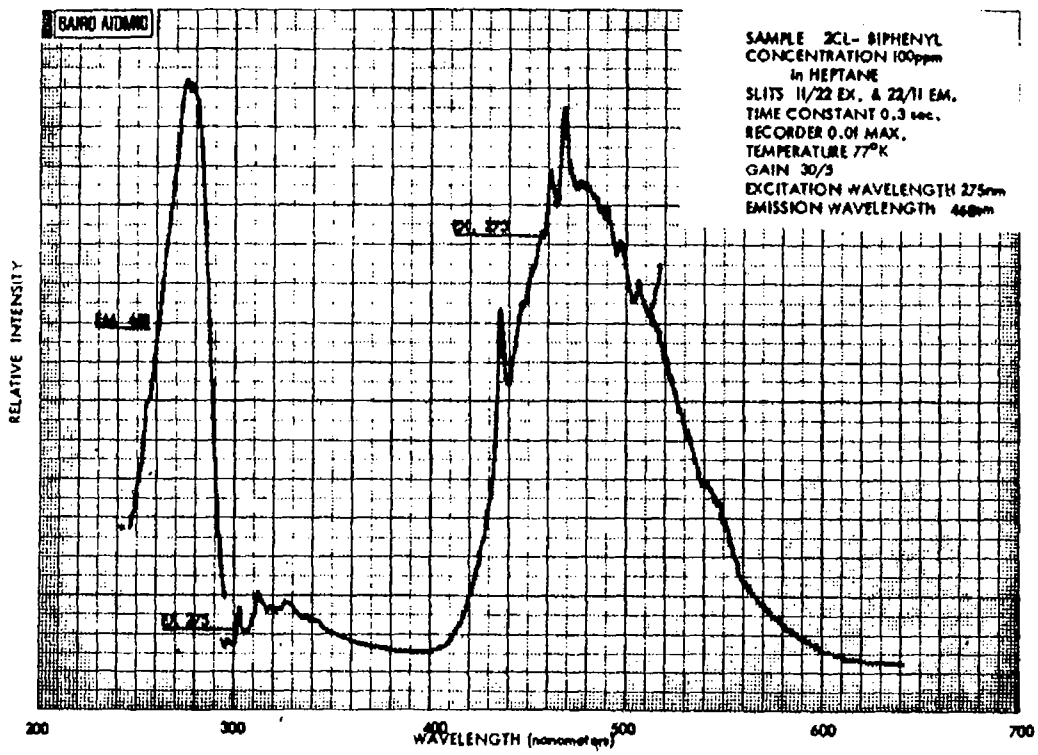


Figure 17. Excitation/emission spectra of 2-chlorobiphenyl (100 ppm) in heptane at 77° K

DSW 037442

STLCOPCB4021266

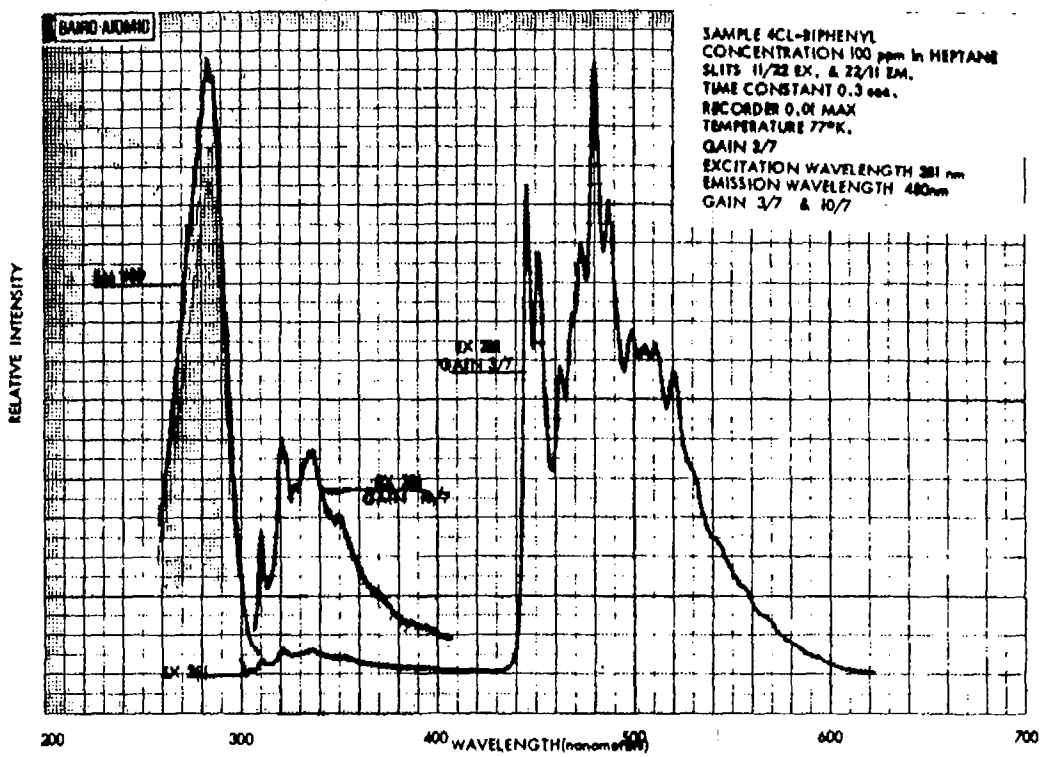


Figure 18. Excitation/emission spectra of 4-chlorobiphenyl (100 ppm) in heptane at 77° K

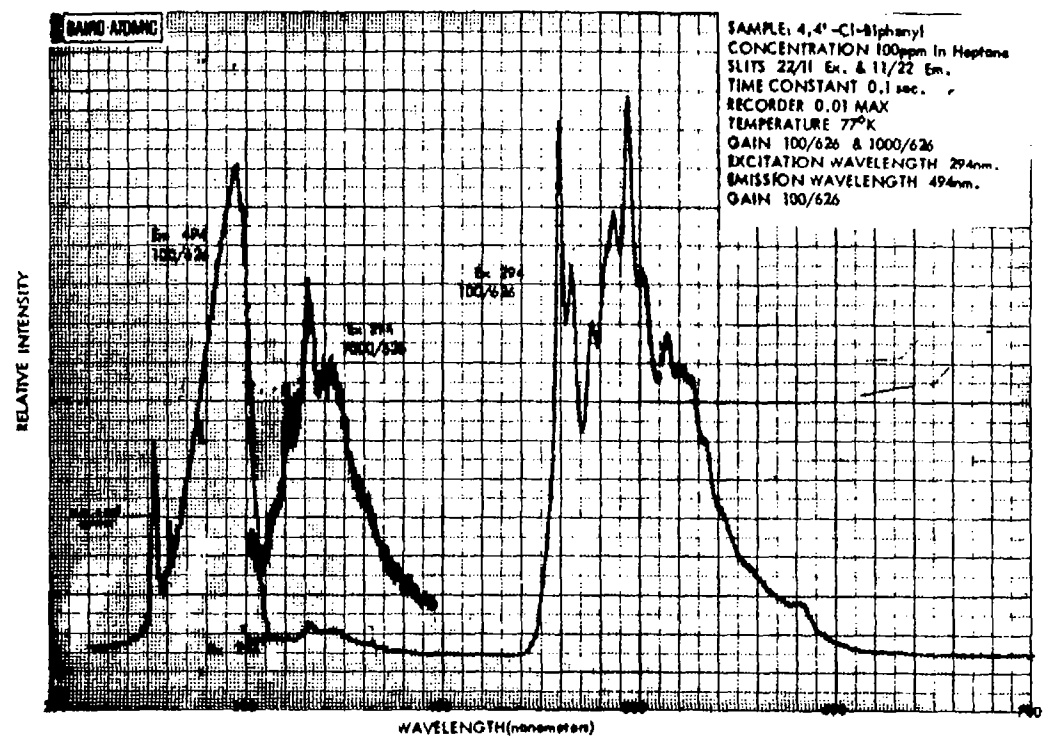


Figure 19. Excitation/emission spectra of 4, 4'-dichlorobiphenyl (100 ppm) in heptane at 77° K

DSW 037443

STLCOPCB4021267

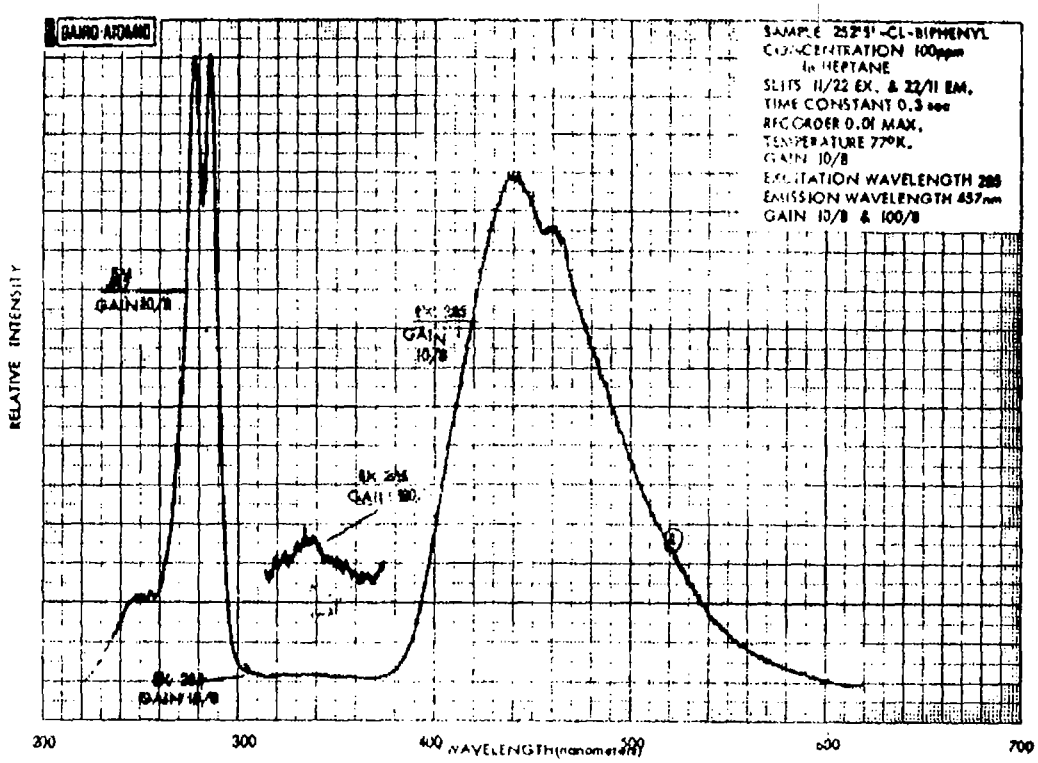


Figure 20. Excitation/emission spectra of 2, 5, 2', 5'-tetrachloro-biphenyl (100 ppm) in heptane at 77°K

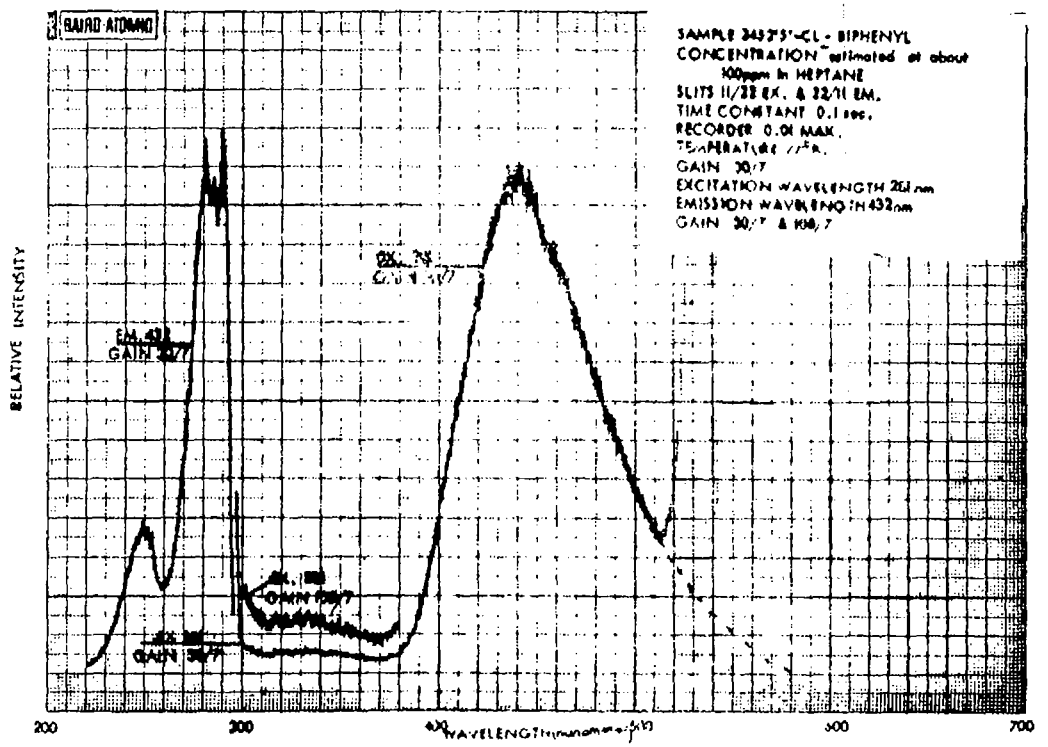


Figure 21. Excitation/emission spectra of 2, 4, 5, 2', 5'-pentachloro-biphenyl (100 ppm) in heptane at 77°K

DSW 037444

STLCOPCB4021268

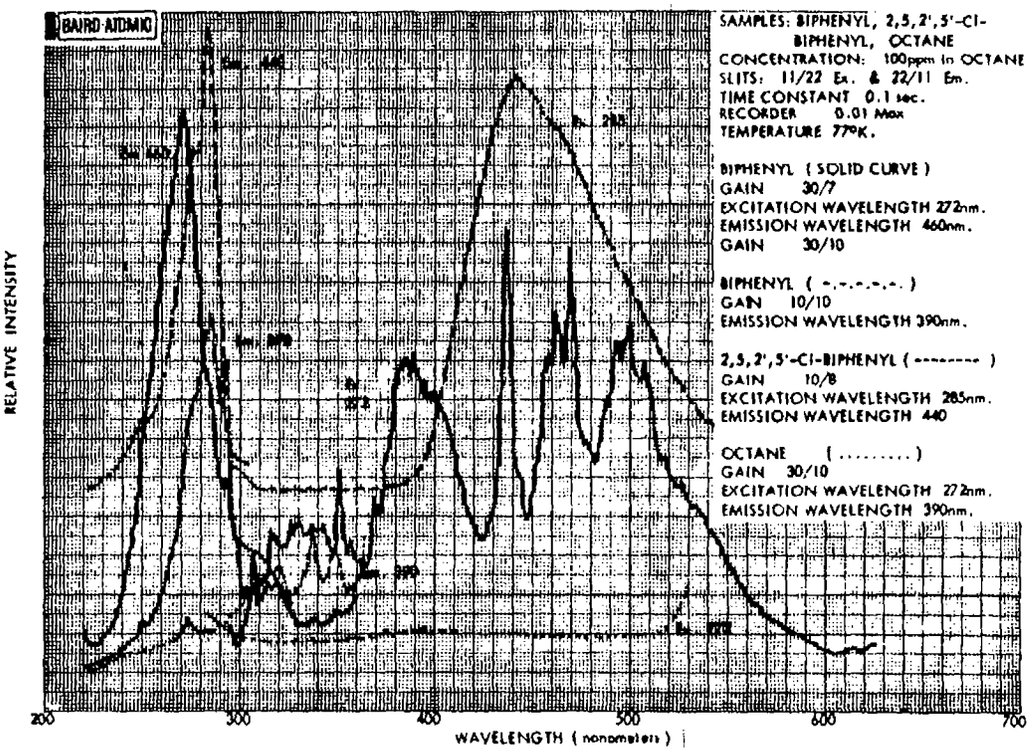


Figure 22. Excitation/emission spectra of biphenyl and 2, 5, 2', 5'-tetrachlorobiphenyl (both 100 ppm) in octane at 77° K

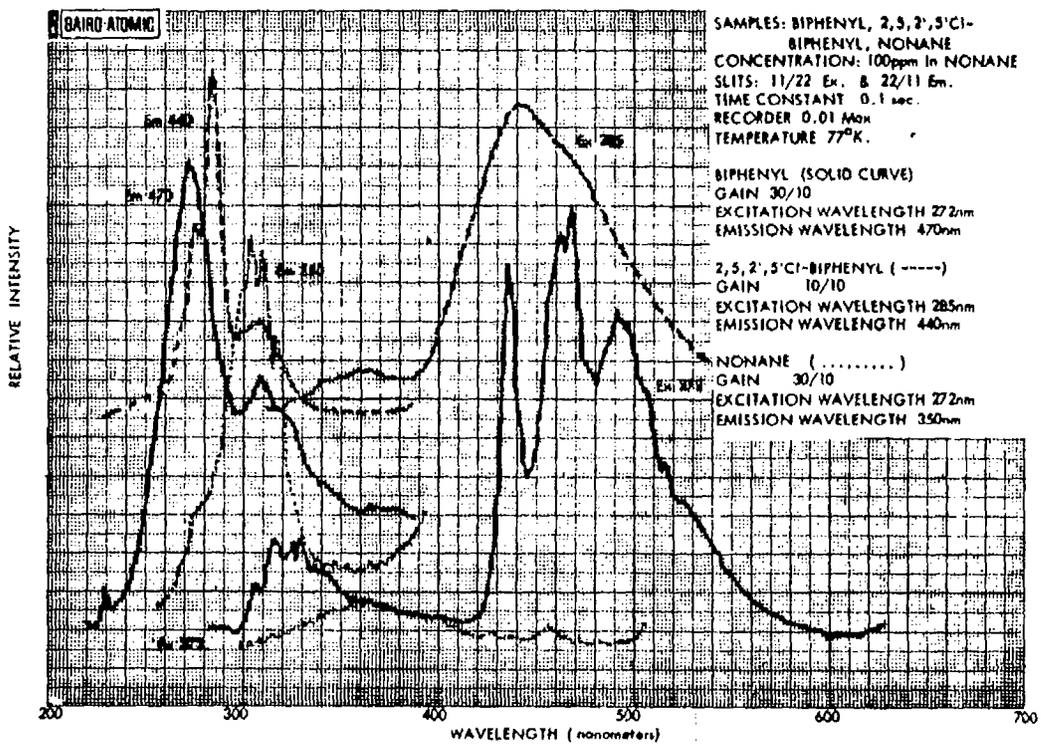


Figure 23. Excitation/emission spectra of biphenyl and 2, 5, 2', 5'-tetrachlorobiphenyl (both 100 ppm) in nonane at 77° K

DSW 037445

STLCOPCB4021269

phosphorescence is about 1:3, while in the chlorinated compounds this is reduced by factors of 10 - 100. This phenomenon is possibly due to an enhancement of intersystem crossing rates by the chlorine substituents, favoring the formation of phosphorescent triplet states.[18,19]

b) In MCH, the emission intensity for the two isomers having a chlorine substituent at the 4-position is stronger by a factor of three or four than for the other compounds, and may reflect the higher oscillator strengths expected theoretically.[20]

c) In heptane, the emission of biphenyl, 4-chlorobiphenyl and 4,4'-dichlorobiphenyl show the greatest amount of structure (Figures 16, 18, and 19). The 2-chlorobiphenyl isomer (Figure 17) shows some structure overlapping a diffuse background. The sharper system was subsequently identified as being due to biphenyl impurity in the 2-isomer; we estimate its relative abundance at about 1%. The tetra- and pentachloro-compounds show rather diffuse emission in heptane (Figures 20 and 21). The same general trends are also observed in MCH, but in this solvent the sharp structure of the lower-chlorinated isomers is largely obliterated (Figures 12 and 13).

d) In order to determine whether an n-alkane of longer chain length would sharpen the spectra of a more highly chlorinated isomer, spectra of 2,5,2',5'-tetrachlorobiphenyl (Hutzinger sample) were studied in octane and nonane (Figures 22 and 23). Neither solvent noticeably sharpened the emission, and suggests that the emission of this compound and perhaps others of high chlorine content may be intrinsically diffuse.

e) Both in heptane and in MCH, the excitation spectra of 2,5,2',5'-tetrachloro- and 2,4,5,2',5'-pentachlorobiphenyl show two rather narrow bands at 280 - 290 nm, followed by a second system at 245-255 nm (Figures 14, 15, 20, 21). The spectrum of 2,4,5,2',4',5'-hexachlorobiphenyl in MCH is similar, except that the shorter wavelength system has shifted to about 263 nm (Figure 15). These features are much less evident in the spectra of isomers having fewer chlorine substituents; these compounds generally show only a single diffuse band (Figures 12, 13, 16 through 19).

PCB Mixtures (Aroclors)

Initially, two Aroclors, 1221 and 1248, were studied in MCH and heptane. Spectra are shown in Figures 24 through 27. The 1248 emission showed only very slight evidence of sharpening in the heptane matrix (Figure 25). This is not unexpected since the components are

DSW 037446

STLCOPCB4021270

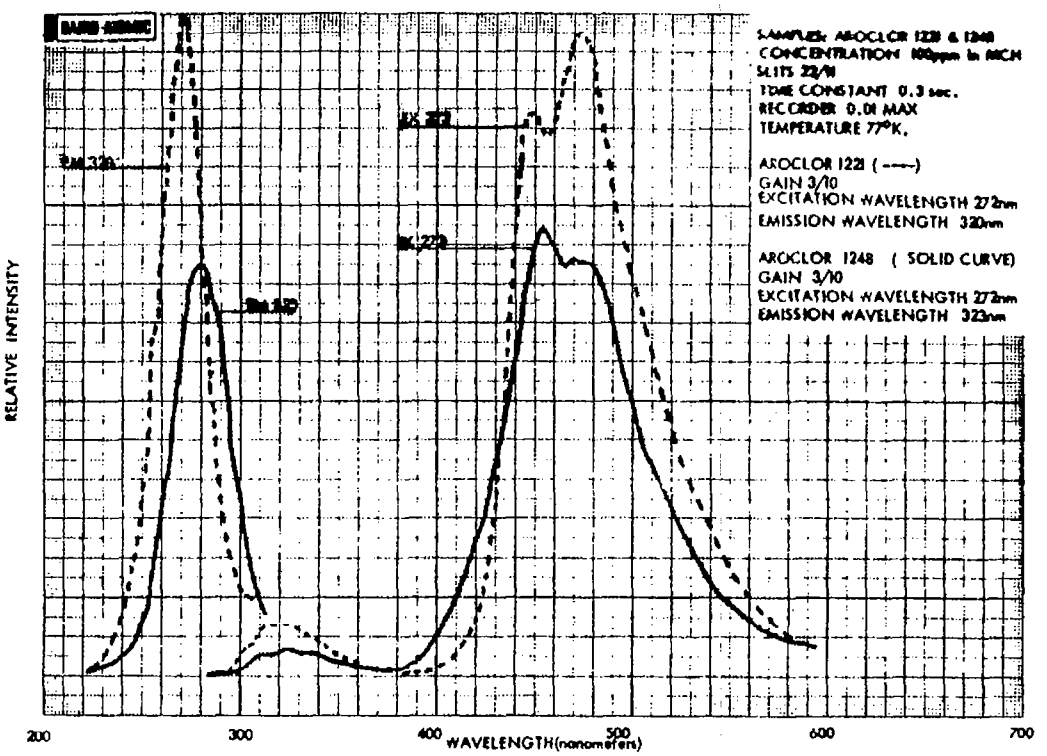


Figure 24. Excitation/emission spectra of Aroclors 1221 and 1248 (both 100 ppm) in MCH glass at 77° K

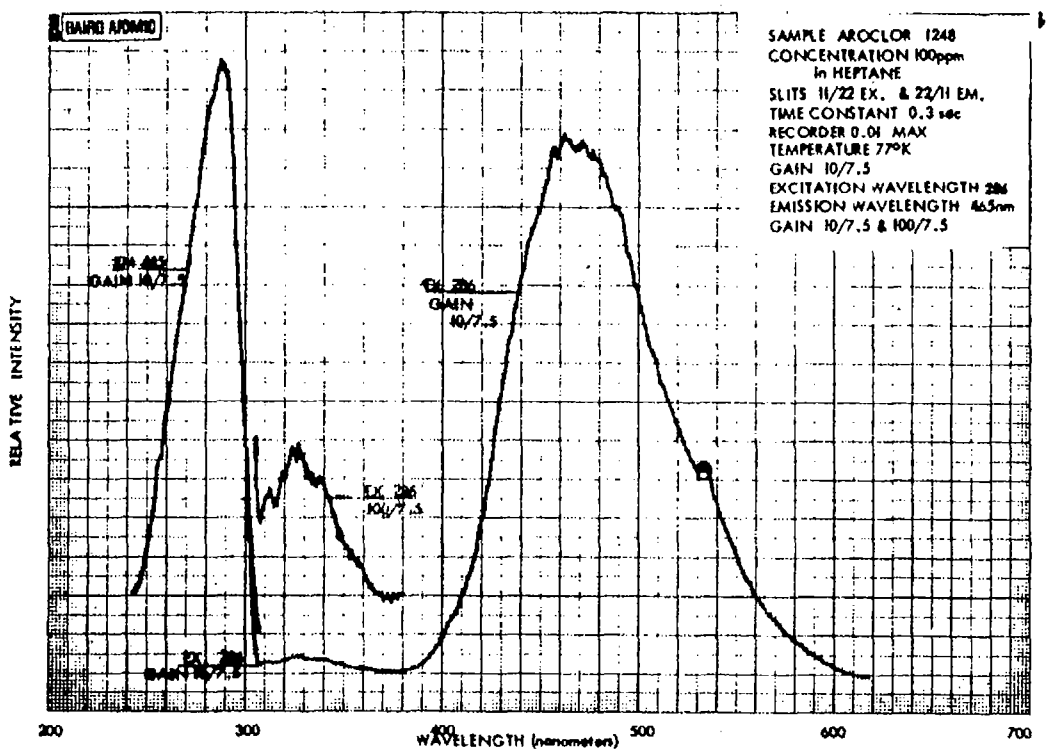


Figure 25. Excitation/emission spectra of Aroclor 1248 (100 ppm) in heptane at 77° K

DSW 037447

STLCOPCB4021271

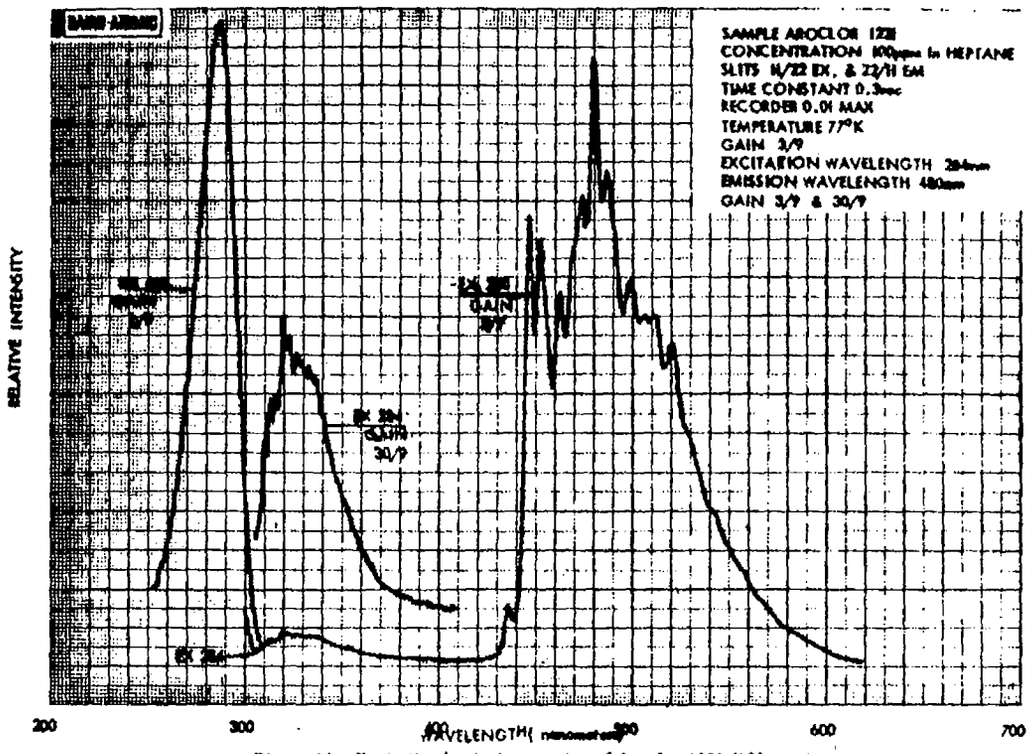


Figure 26. Excitation/emission spectra of Aroclor 1221 (100 ppm) in heptane at 77° K

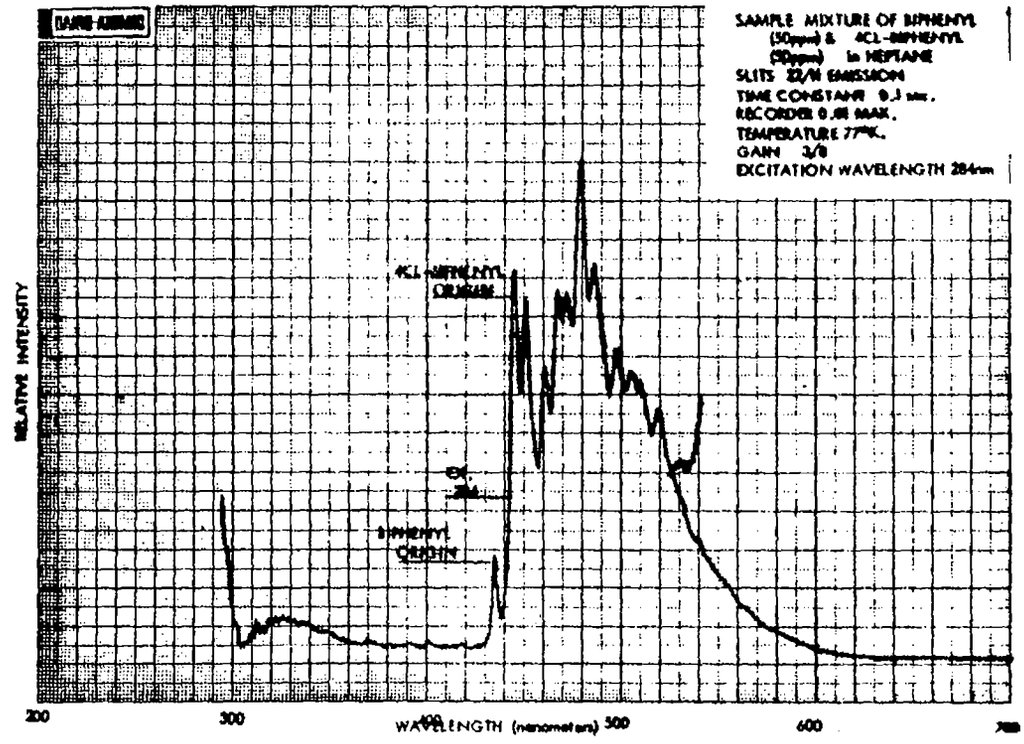


Figure 27. Emission spectrum of a mixture of biphenyl (50 ppm) and 4-chlorobiphenyl (50 ppm) in heptane at 77° K

DSW 037448

STLCOPCB4021272

more highly chlorinated, and the isomer emission spectra of two such components are diffuse. The 1221 emission, however, revealed considerable sharpening in heptane as opposed to MCH (Figures 24 and 26), again reflecting the predominance of the lower-chlorinated species. In fact, both biphenyl and 4-chlorobiphenyl could be identified in Aroclor 1221 by comparison with the isomer spectra. Figure 27 shows the emission of a mixture of these isomers (each 50 ppm) in heptane at 77° K; from the spectrum of the Aroclor excited at the same wavelength (Figure 26), one can estimate the relative amount of the 4-chloro-isomer as being at least 50% and perhaps more. (More quantitative estimates will be possible pending a better understanding of possible energy transfer among isomers. Such studies are planned for the continuation of this program.)

Figure 28 shows spectra of Aroclor 1254 in MCH at 77° K. The excitation spectrum monitored at 405 nm resembles that of either 2, 5, 2', 5'-tetrachloro- or 2, 4, 5, 2', 5'-pentachlorobiphenyl (Figures 14 and 15). Both of these isomers have been identified in Aroclor 1254 using GC (Table 2).

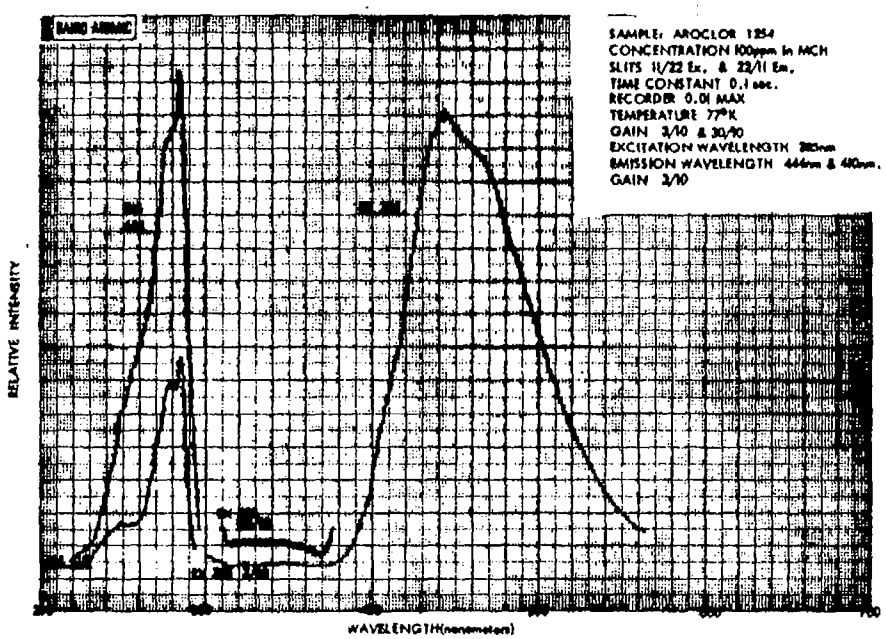


Figure 28. Excitation/emission spectra of Aroclor 1254 (100 ppm) in MCH glass at 77° K

DSW 037449

STLCOPCB4021273

Recently, excitation and emission spectra of Aroclors 1221, 1242, 1248, 1254, and 1260 (obtained 27 October 1971 from Dr. E. S. Tucker of Monsanto) have been documented. All Aroclors were studied at 100 and 10 ppm in MCH at 77° K. Aroclors 1248 and 1260 were also studied in the same solvent at concentrations of 1 and 0.1 ppm. Spectra of these "new" samples have been designated with an (N) in Figures 29 through 42. The spectra obtained are sufficiently different (particularly the excitation spectra) and could be used to distinguish the various Aroclors. It is of interest to note the resemblance of the Aroclor 1260 excitation spectrum (Figure 39) to that of 2,4,5,2',4',5'-hexachlorobiphenyl (Figure 15).

The spectra of the "new" Aroclors do not differ greatly from those of the samples obtained earlier, although some differences are apparent. These differences are due either to somewhat different isomer content among different batches, or in the case of Figure 24, are due to the fact that in some earlier traces the fluorescence region was monitored in excitation and in the latter cases the phosphorescence region. Since the contributing isomers will be different for these two regions (lower chlorinated species dominate in fluorescence), so will the excitation spectra differ.

Another effect is apparent in the Aroclors, namely the change in structure of the excitation spectra upon dilution. Usually, the shorter wavelength region intensifies and the apparent excitation maximum shifts to shorter wavelengths. The first effect is largely a geometrical effect; since the Aroclor is about 20 times more dense optically (strongly absorbent) at 230 nm than at 290 nm, the shorter wavelength radiation is absorbed much closer to the surface of the sample than is the longer wavelength radiation. As a result, emission due to short wavelength excitation originates at the surface while that due to longer wavelengths originates throughout the sample. The normal geometry of the instrument is such that emission occurring at or near the sample surface is not collected as efficiently as is emission occurring near the center of the sample, so that the apparent emission intensity produced by radiation of shorter wavelength is less. As the sample is diluted, penetration by the excitation beam becomes deeper at all wavelengths and the geometrical factor becomes less apparent.

The second effect, viz., the apparent shift in the excitation maximum to shorter wavelength upon dilution, is probably largely a geometric effect, but may also reflect energy transfer among PCB isomers. Energy transfer phenomena are expected to increase at higher solute concentrations, and should favor emission from those isomers having the lowest energy (longest wavelength) electronic transitions. As the

DSW 037450

STLCOPCB4021274

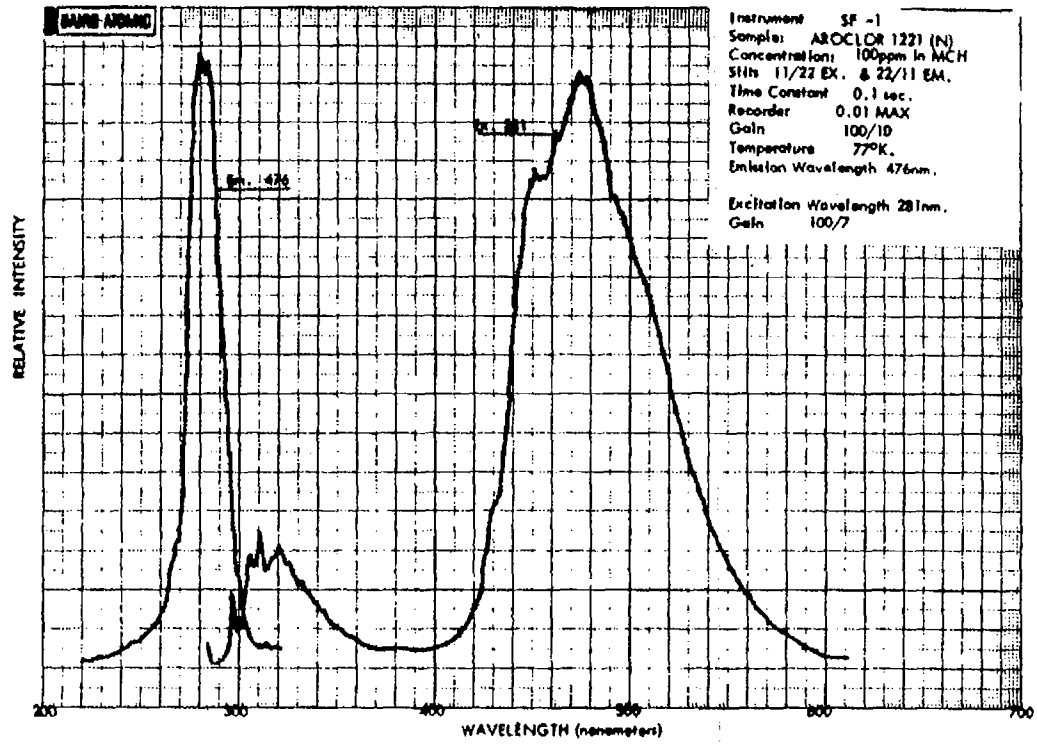


Figure 29. Excitation/emission spectra of Aroclor 1221 (N, 100 ppm) in MCH at 77° K

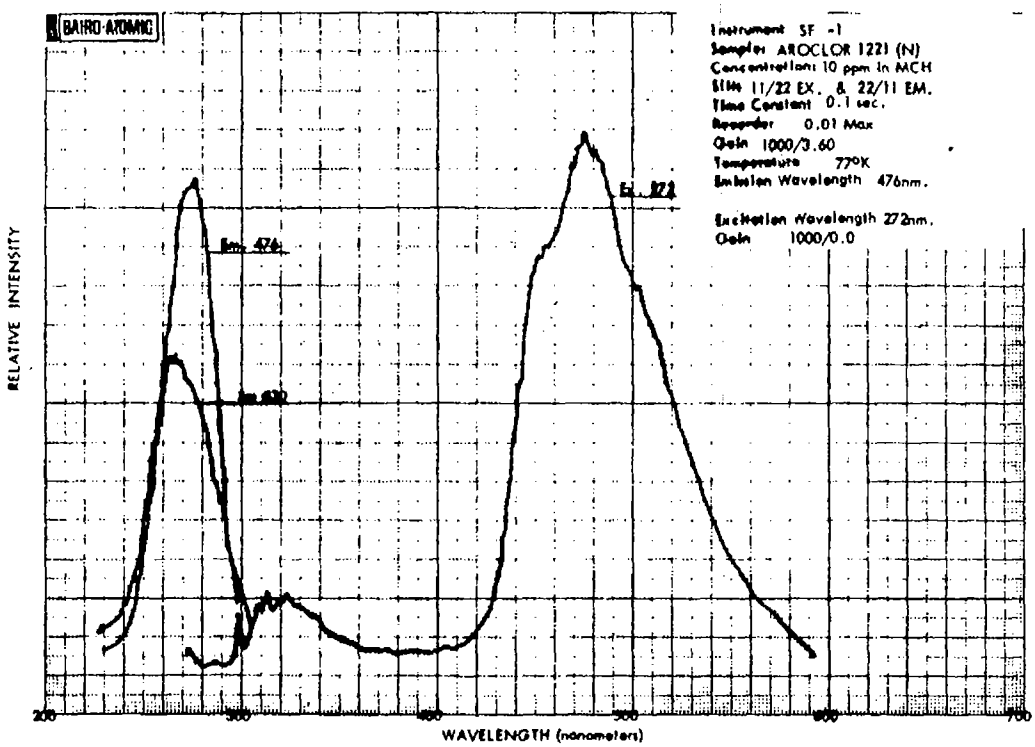


Figure 30. Excitation/emission spectra of Aroclor 1221 (N, 10 ppm) in MCH at 77° K

DSW 037451

STLCOPCB4021275

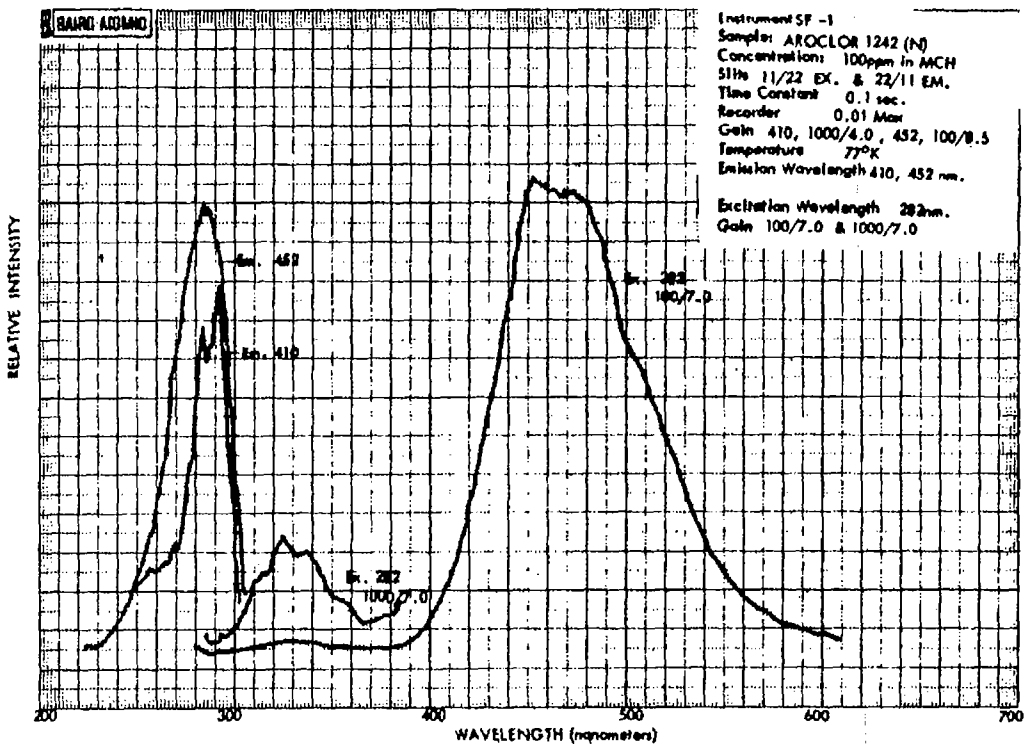


Figure 31. Excitation/emission spectra of Aroclor 1242 (N, 100 ppm) in MCH at 77° K

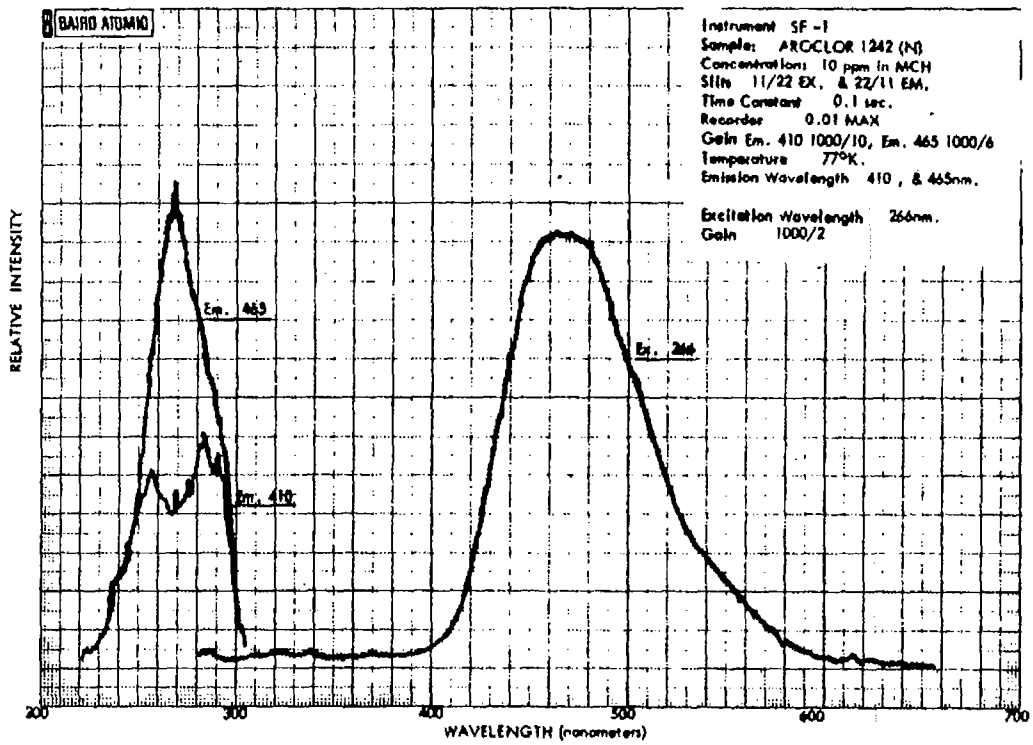


Figure 32. Excitation/emission spectra of Aroclor 1242 (N, 10 ppm) in MCH at 77° K

DSW 037452

STLCOPCB4021276

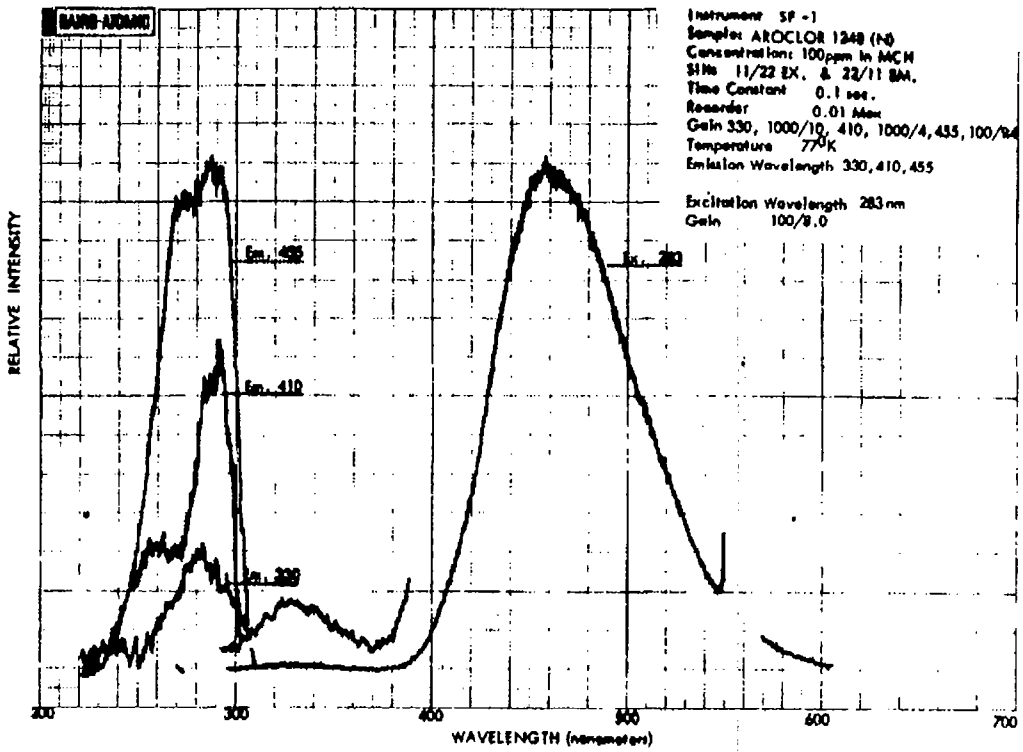


Figure 33. Excitation/emission spectra of Aroclor 1248 (N, 100 ppm) in MCH at 77° K

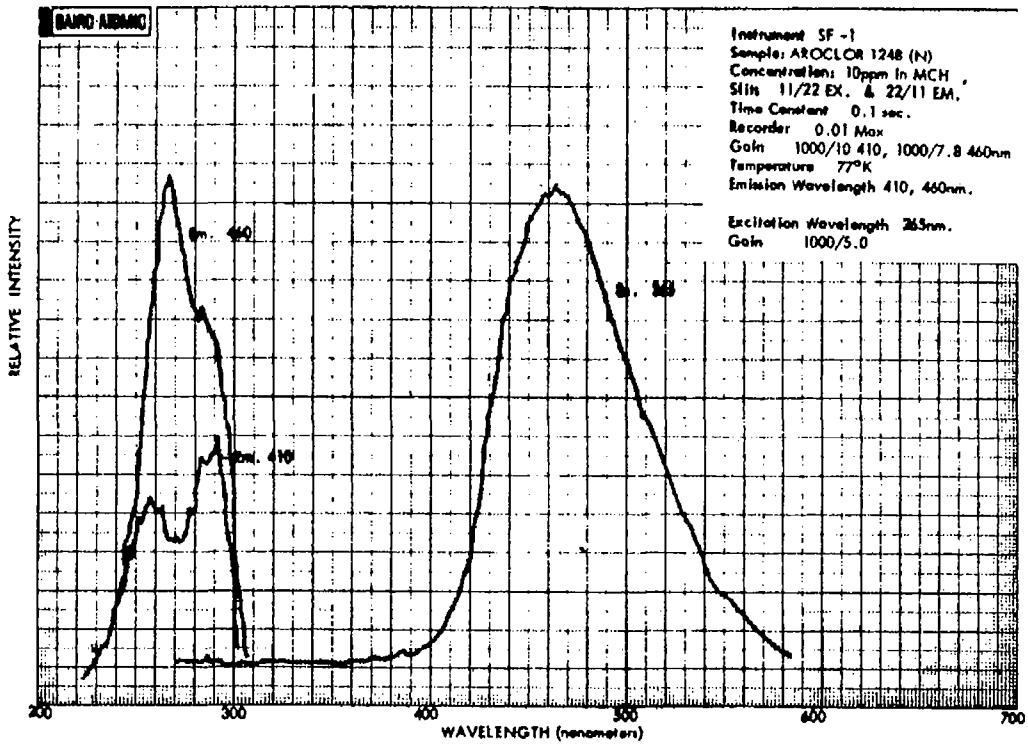


Figure 34. Excitation/emission spectra of Aroclor 1248 (N, 10 ppm) in MCH at 77° K

DSW 037453

STLCOPCB4021277

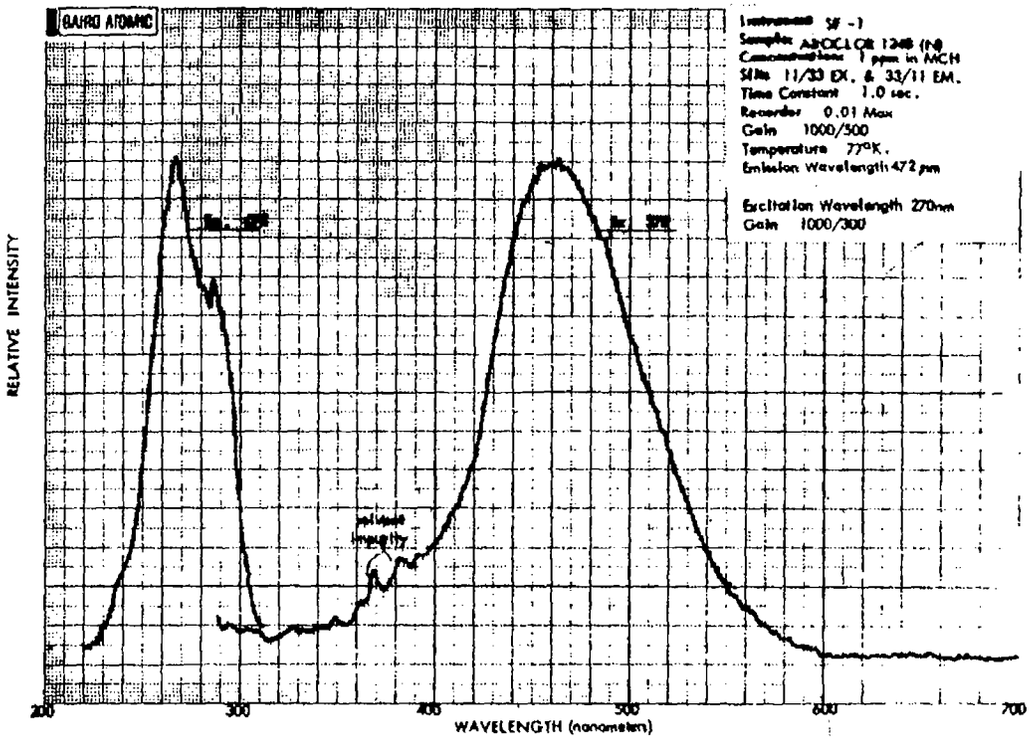


Figure 35. Excitation/emission spectra of Aroclor 1248 (N, 1 ppm) in MCH at 77° K

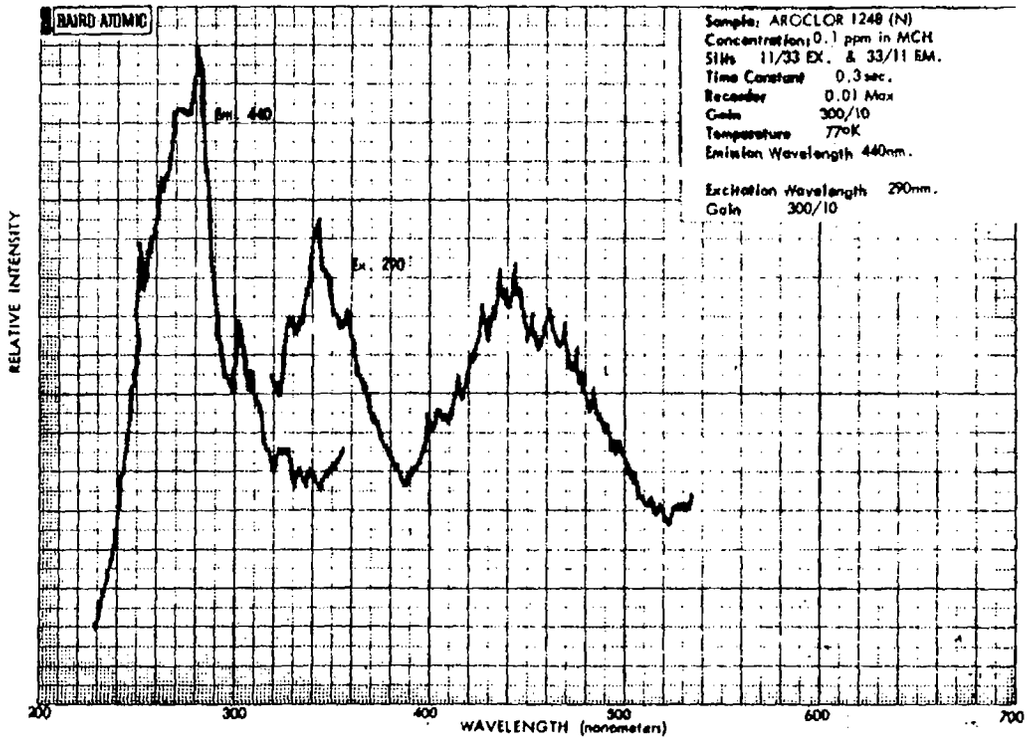


Figure 36. Excitation/emission spectra of Aroclor 1248 (N, 0.1 ppm) in MCH at 77° K

DSW 037454

STLCOPCB4021278

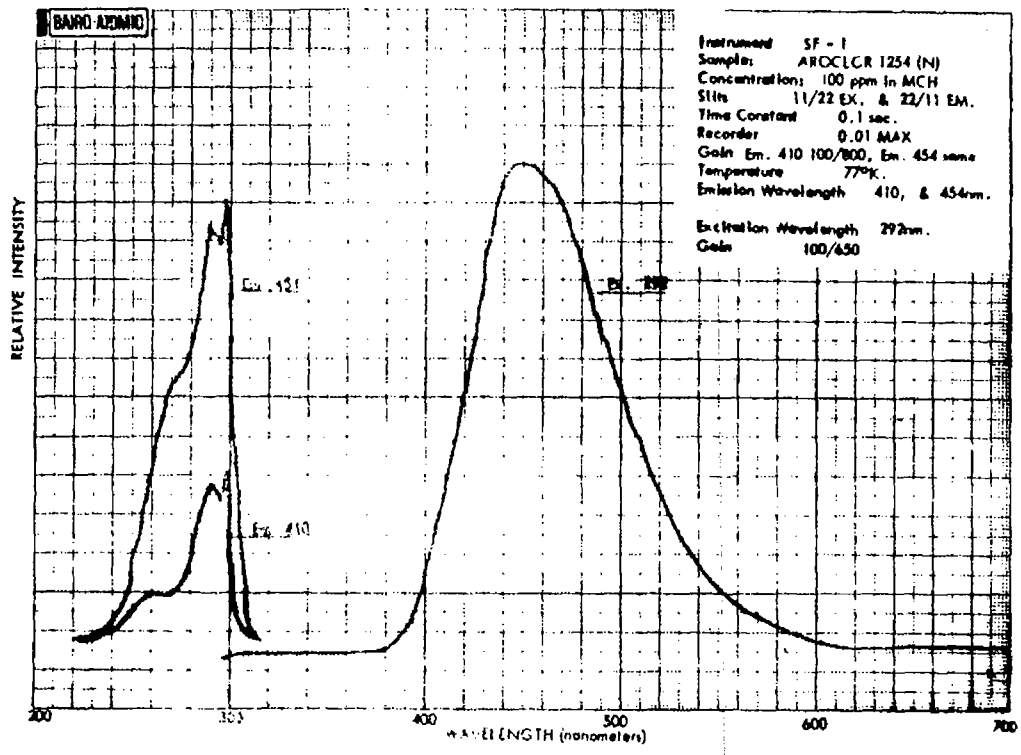


Figure 37 Excitation/emission spectra of Aroclor 1254
[illegible] ppm in MCH at 77° K

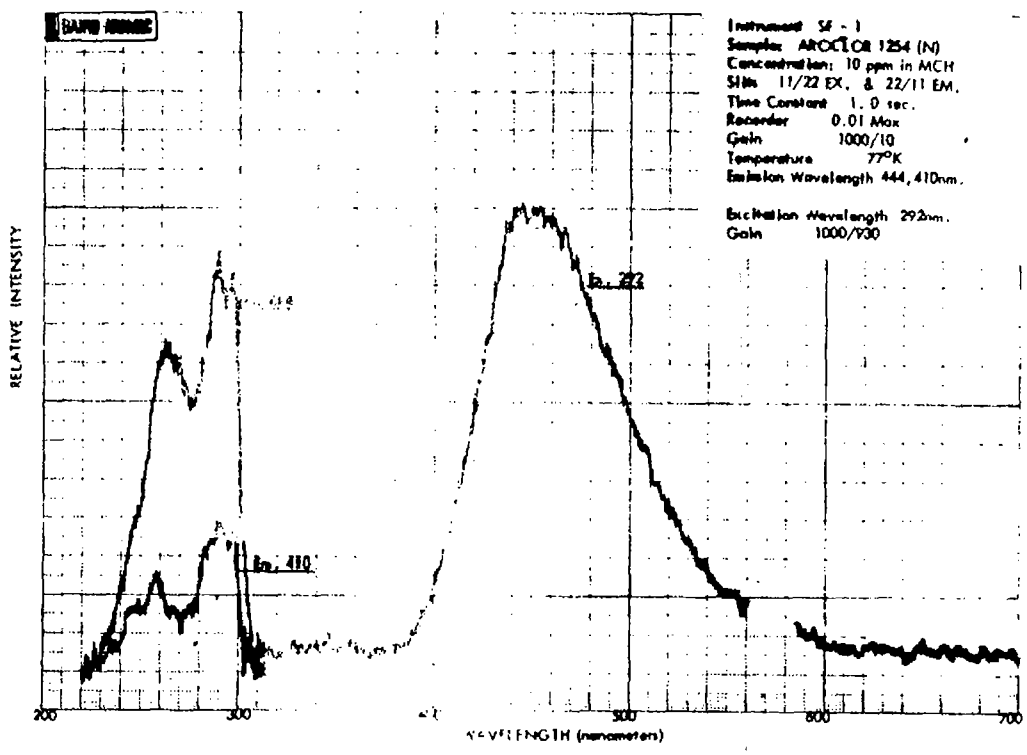


Figure [illegible] Excitation/emission spectra of Aroclor 1254
[illegible] MCH at 77° K

DSW 037455

STLCOPCB4021279

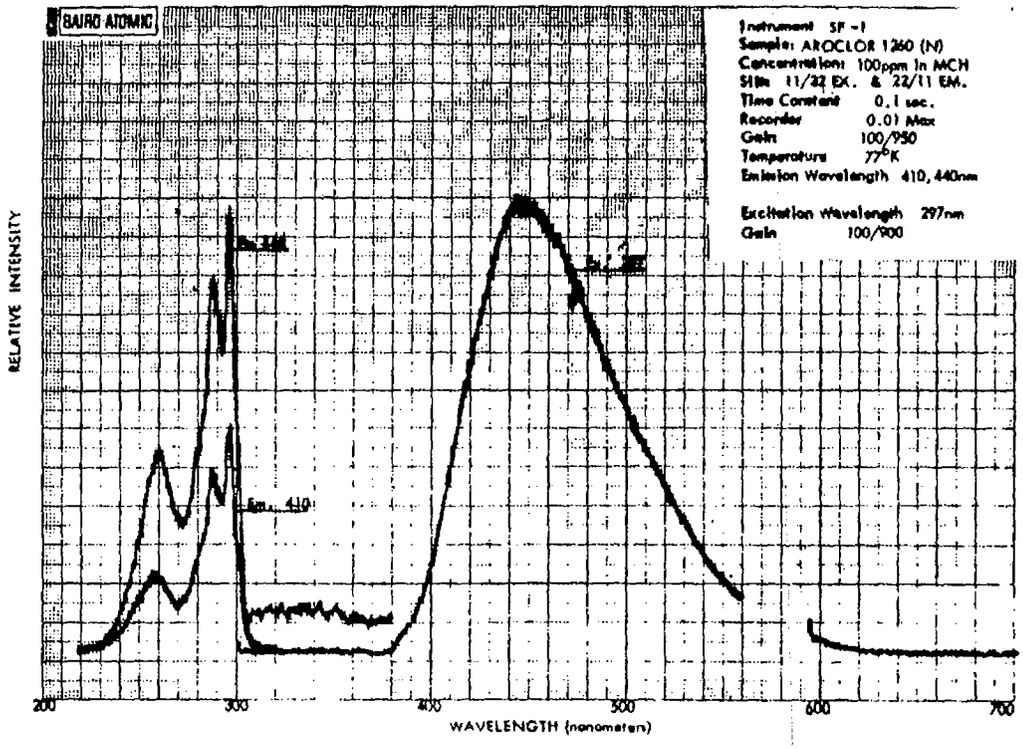


Figure 39. Excitation/emission spectra of Aroclor 1260 (N, 100 ppm) in MCH at 77° K

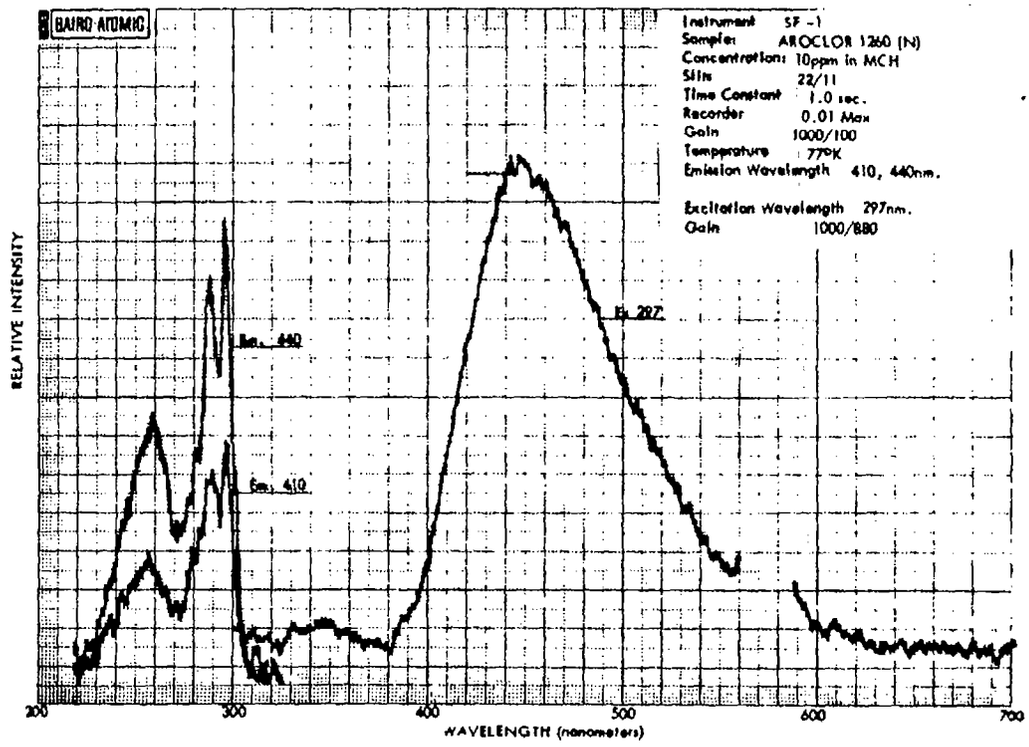


Figure 40. Excitation/emission spectra of Aroclor 1260 (N, 10 ppm) in MCH at 77° K

DSW 037456

STLCOPCB4021280

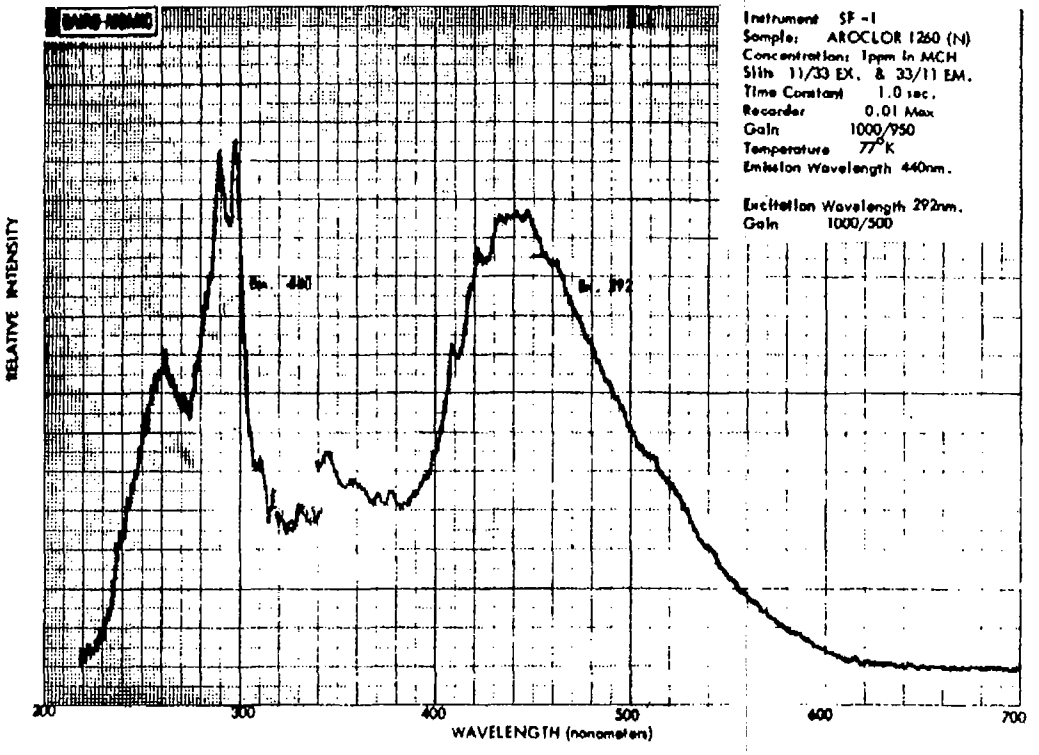


Figure 41. Excitation/emission spectra of Aroclor 1260 (N, 1 ppm) in MCH at 77° K

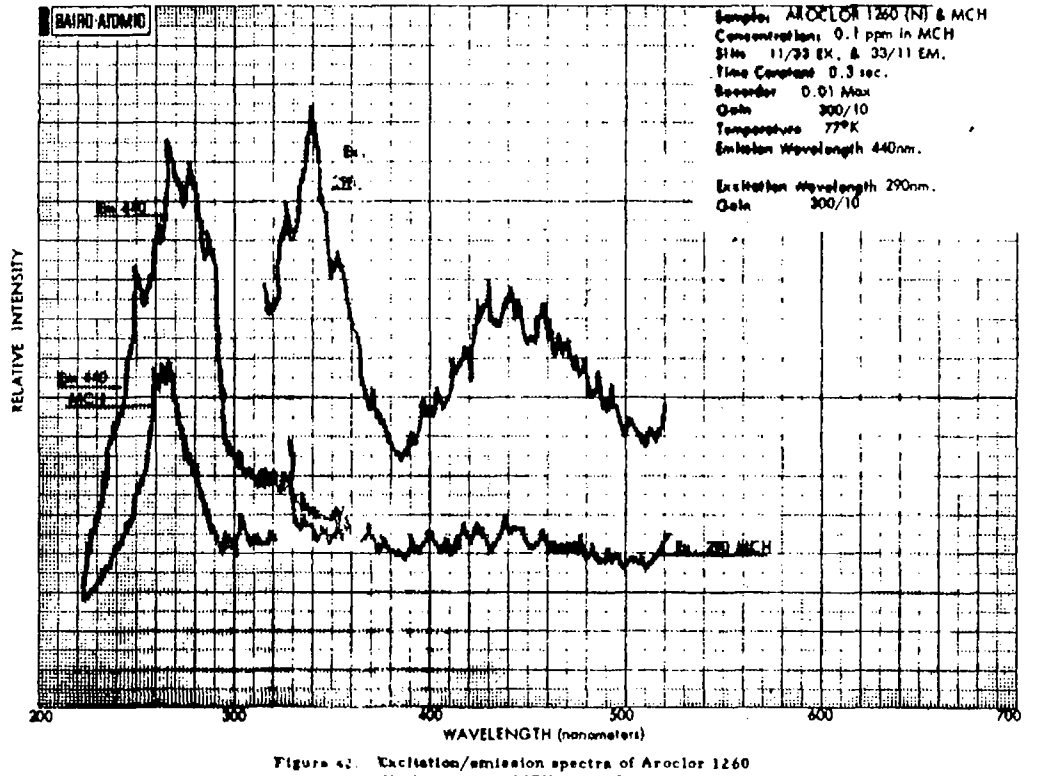


Figure 42. Excitation/emission spectra of Aroclor 1260 (N, 0.1 ppm) in MCH at 77° K

DSW 037457

STLCOPCB4021281

concentration decreases, energy transfer processes become less probable, and the excitation structure appears to shift to shorter wavelengths. Since the observed excitation changes are probably a complex combination of both geometric and energy transfer effects, it would appear that in an analytical method these effects would have to be determined empirically for a given Aroclor.

Degassing experiments performed on 10 ppm solutions of Aroclor 1254 in MCH using the technique described previously (SECTION V) showed that the Aroclor phosphorescence intensity remained unaffected within 10%. Again, however, we must emphasize that the method used for oxygen removal may not be highly efficient, a vacuum system being preferred for this operation.

In the fifth monthly report it was stated that an impurity emission associated with Aroclor 1254 appears at Aroclor concentrations less than about 1 ppm. The structured emission consists of fluorescence in the 300 - 370 nm region (maximum at approximately 310 nm) and phosphorescence in the region 400 - 500 nm. The phosphorescence and fluorescence systems appear to be associated with separate emitting species. More recently, these emissions have been observed in non-Aroclor samples as well. We presently believe that the source of these emissions are in fact from plasticizers used in the polyethylene stoppers for our sample containers.

Photolysis of Aroclor 1254

Preliminary photolysis experiments were performed on Aroclor 1254 both in MCH and ethanol at 77° K and at room temperature. The methods employed were simple, but were probably adequate to reveal gross effects. The sample was irradiated while in the quartz optical dewar at its normal position in the Baird-Atomic SF-1 Fluorispec instrument, using the standard instrument source (SECTION IV). Excitation slits were at their full width (spectral band pass about 24 nm) and the excitation monochromator set at 285 nm.

Irradiation for two hours with the sample at 77° K in either solvent produced no significant spectral changes. (Since the average data-acquisition time on our instruments rarely exceeds 15 minutes, it seems unlikely that normal low-temperature measurements could induce serious photochemical changes in the Aroclor.)

Room-temperature irradiation was done in the same manner for periods of 15 - 18 hours. In MCH, some photochemical changes were observed, but these were found to be much more pronounced in ethanol, wherein

DSW 037458

STLCOPCB4021282

additional structure appeared in the Aroclor phosphorescence system. This new structure bore a resemblance to the phosphorescence spectra of some of the lower-chlorinated biphenyl isomers as discussed previously (SECTION VI). In particular, the principal peaks of this system were found to agree rather well both in energy and relative intensity with those appearing in the phosphorescence spectrum of 4,4'-dichlorobiphenyl; spectra of the photolyzed Aroclor are compared with those of this isomer (in ethanol) in Figure 43.

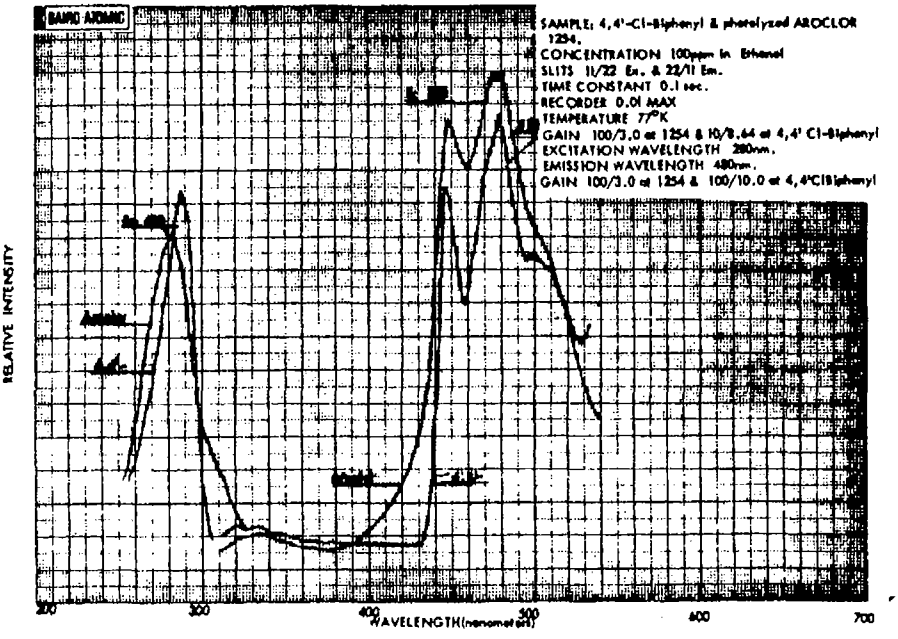


Figure 43. Excitation/emission spectra of 4,4'-dichlorobiphenyl (100 ppm) photolyzed Aroclor 1254 (originally 100 ppm) in ethanol at 77° K

Although this identification is only tentative, it is interesting to note in this connection some recent photochemical studies of toxic chlorinated dibenzo-p-dioxins.[21] Photolysis of these compounds in alcoholic media apparently results in homologs of diminished chlorine content, suggesting reductive dechlorination as a primary mechanism.

Similar photochemical effects in PCB isomers and mixtures have very recently been reported by Hutzinger and Safe.[22] Sample irradiation was performed in the vapor phase, in aqueous suspension, in thin films of pure material, and in hexane, methanol, and aqueous dioxane solutions.

DSW 037459

STLCOPCB4021283

In all experiments, large amounts of dechlorinated compounds were found among the decomposition products. In addition, new "polar" compounds, which probably included hydroxychlorobiphenyls, were formed when air and water were present during photolysis. The authors suggest that the hydroxy compounds may act as intermediates in the formation of toxic chlorinated dibenzofurans.

Determination of Aroclor 1254 in Water

Several experiments, in order of increasing technical difficulty, were performed relating to the determination of Aroclor 1254 in water. Water saturated with this Aroclor was examined at room temperature in a 1 cm path cuvette. Excitation at wavelengths known to produce emission at 77° K in organic solvents revealed no clear evidence of Aroclor fluorescence (phosphorescence is not observed at room temperature). This is probably a consequence of both the low Aroclor solubility in water (.3 - 1 mg/l[23] or perhaps less[24]) and the low fluorescence yields found for more highly chlorinated PCB isomers.

In order to enhance the solubility of the Aroclor in water and allow examination at low temperatures, ethylene glycol was added to an Aroclor 1254/water sample in the ratio two parts ethylene glycol to one part water, and the solution examined at 77° K. Aroclor phosphorescence was not apparent in this sample, but was probably obscured by emitting impurities present in the ethylene glycol. An attempt to substitute ethanol for ethylene glycol proved unsuccessful for the same reason. These experiments were therefore inconclusive and should be repeated with solvents of higher purity. If successful, this method would be important in that possible extraction steps might be eliminated.

Finally, Aroclor 1254 was extracted from water with methylcyclohexane. The organic layer was dried with sodium sulfate[2] and examined at 77° K. Aroclor phosphorescence was observed, and comparison of the intensity with that of a 1 ppm standard solution indicated an Aroclor solubility in water of approximately 0.01 mg/l. This value must be regarded as tentative, since a UV absorption of the same extract showed differences presumably due to altered isomer composition.

DSW 037460

STLCOPCB4021284

SECTION VII

ANALYSIS OF MIXTURES: AROCLOR 1254 AND p,p'-DDT

Standard Low Temperature Measurements

The phosphorescence of Aroclor 1254 is approximately 10X stronger than that of DDT in MCH at 77° K. Detection limits (also in MCH at 77° K) for the DDT/DDD compounds and for Aroclors are presently limited by solvent impurity emission and are on the order of 1 ppm and .01 ppm respectively. These limits could be reduced by two orders of magnitude by suitable solvent purification and such experiments are planned for the continuation program.

Excitation and emission spectra of three mixtures containing 50 ppm p,p'-DDT (all samples) and 50, 5, and 0.5 ppm Aroclor 1254 are shown in Figures 44 - 46. The solvent used was MCH glass at 77° K.

Since DDT has virtually no absorption at wavelengths greater than 280 nm, excitation of the mixture in the 290 nm region allows the Aroclor phosphorescence to be observed relatively free of DDT emission. Also, since the Aroclor phosphorescence at 380 nm is negligible, an excitation spectrum monitored in this region produces largely the spectrum of DDT with little interference from Aroclor. Energy-transfer processes are probably not strongly operative in this system since the DDT phosphorescence spectrum is always evident.

Similar results were obtained in mixtures of 5 ppm p,p'-DDT with 5, 0.5, and 0.05 ppm Aroclor 1254. In these mixtures the Aroclor phosphorescence is clearly visible as shown in Figures 47 through 49.

These results imply that at the concentrations used, Aroclor 1254 can be observed in the presence of at least 100X higher levels of p,p'-DDT. Similar results are expected at lower absolute concentrations.

Of interest too is that 5 and 50 ppm DDT can be detected in the presence of an equal amount of Aroclor. This suggests that it may be possible to detect smaller quantities of DDT-type pesticides in the presence of larger quantities of Aroclors; this determination would of course be less sensitive than the reverse situation due to the smaller phosphorescence yields of the pesticides.

Results similar to those obtained for the above Aroclor/DDT mixtures are expected to obtain for other Aroclors and pesticides, provided the

DSW 037461

STLCOPCB4021285

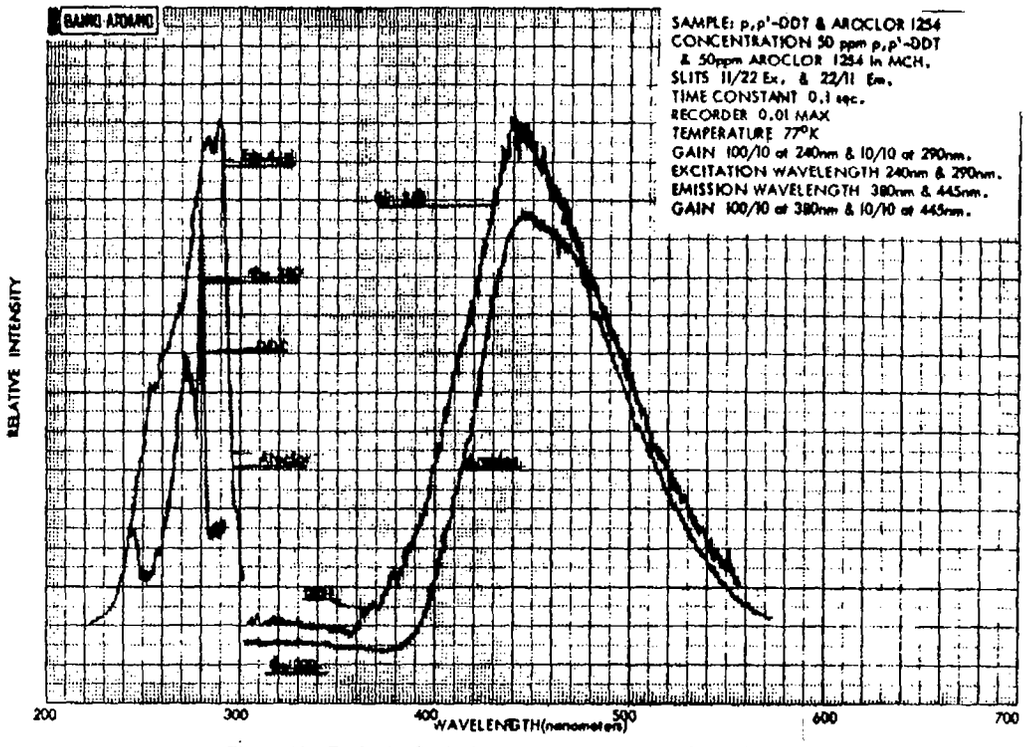


Figure 44. Excitation/emission spectra of a mixture of p, p'-DDT (50 ppm) and Aroclor 1254 (50 ppm) in MCH glass at 77° K

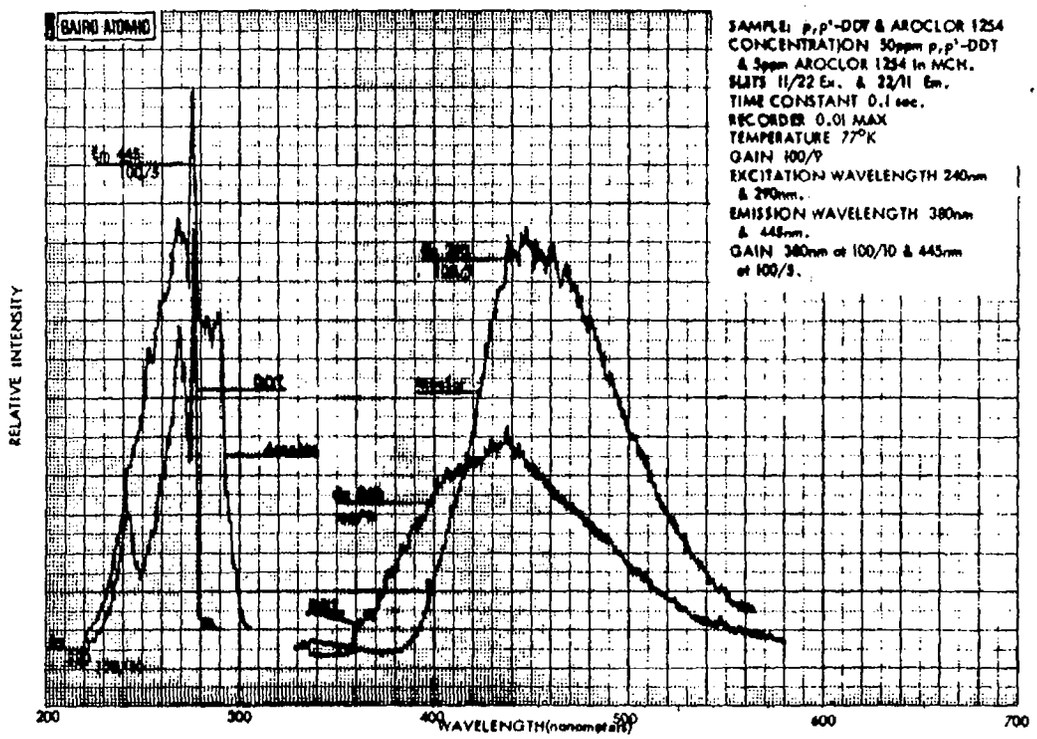


Figure 45. Excitation/emission spectra of a mixture of p, p'-DDT (50 ppm) and Aroclor 1254 (5 ppm) in MCH glass at 77° K

DSW 037462

STLCOPCB4021286

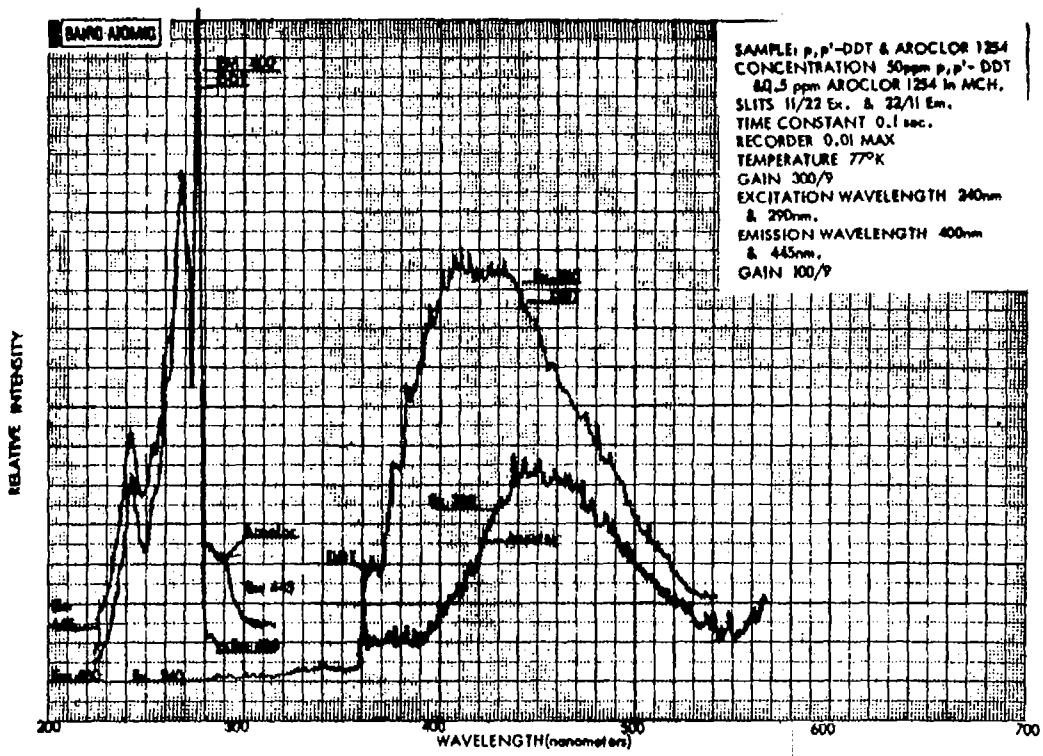


Figure 46. Excitation/emission spectra of a mixture of p, p'-DDT (50 ppm) and Aroclor 1254 (0.5 ppm) in MCH glass at 77° K

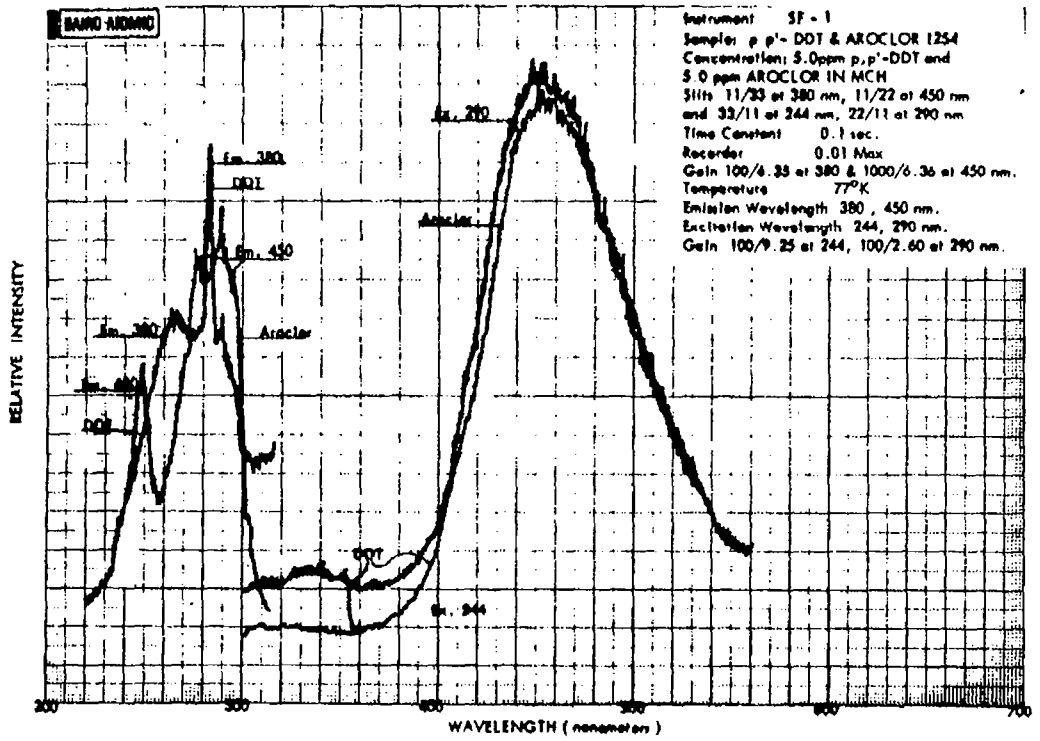


Figure 47. Excitation/emission spectra of a mixture of p, p'-DDT (5 ppm) and Aroclor 1254 (5 ppm) in MCH glass at 77° K

DSW 037463

STLCOPCB4021287

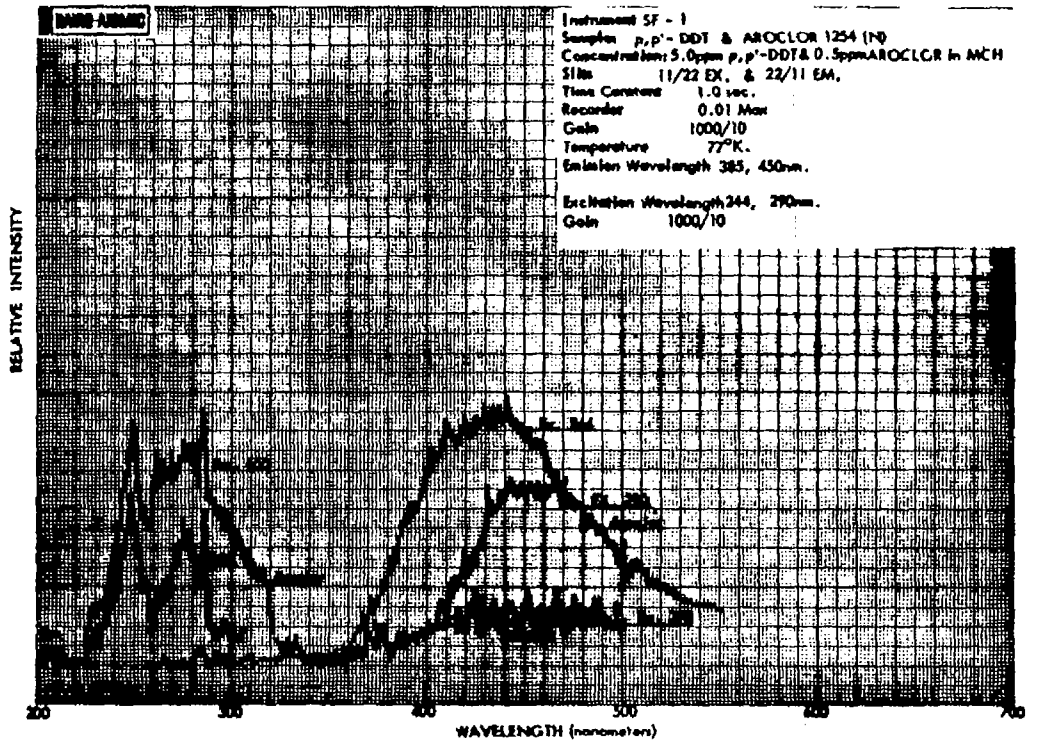


Figure 48. Excitation/emission spectra of a mixture of p, p'-DDT (5 ppm) and Arocler 1254 (N, 0.5 ppm) in MCH glass at 77° K

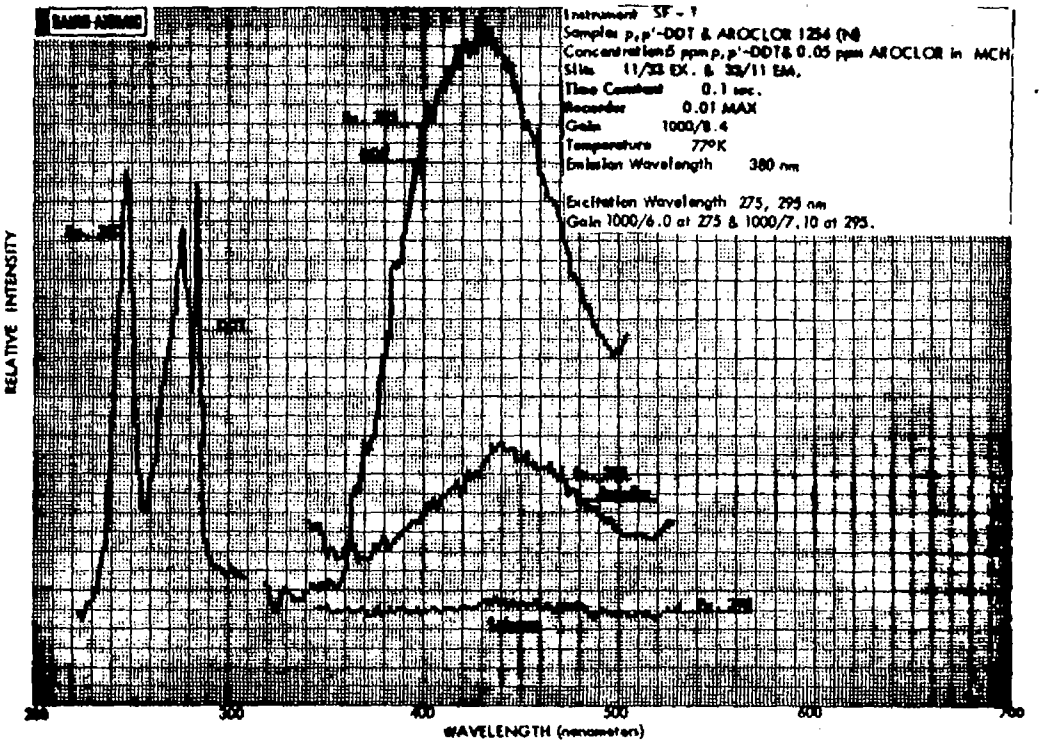


Figure 49. Excitation/emission spectra of a mixture of p, p'-DDT (5 ppm) and Arocler 1254 (N, 0.05 ppm) in MCH glass at 77° K

DSW 037464

STLCOPCB4021288

pesticide were either DDT or DDD. The very weak emission observed for DDE (SECTION V) makes it difficult to determine with high sensitivity by molecular emission methods. On the other hand, DDE should produce little if any interference for PCB's with which it might occur. Further, PCB's do not interfere with analysis of DDE in gas chromatographic analyses.[25]

Phosphoroscopic Measurements

Exploratory phosphoroscopic and polarization measurements were performed on a mixture of Aroclor 1254 (5 ppm) and p,p'-DDT (50 ppm) in MCH at 77° K in order to determine whether they could provide additional discrimination in the analysis of Aroclor/pesticide mixtures.

The phosphoroscopic method could be of value in separating phosphorescence emissions which are spectrally overlapping but differ in their respective lifetimes. The phosphoroscope, a standard accessory on the Fluorispec, was a rotating-can type which could be operated at continuously variable speed. A good general discussion of this and other types of phosphoroscopes can be found in Reference 9. In this type of experiment, the component having the longer phosphorescence lifetime can be selectively enhanced by operating the phosphoroscope at minimum speed. For the mixture chosen, the enhancement thus obtained was low, presumably due to the similar lifetimes of the components. Aroclors having low chlorine content (e.g., Aroclors 1221, 1232) and thus longer phosphorescence lifetimes are expected to show greater selective intensification using this method.

Photoselection (Polarization) Measurements

Polarized excitation spectra are obtained in a viscous or rigid medium by exciting the sample with vertically polarized light and monitoring the vertically and horizontally polarized components of the emission. The results of such an experiment are usually expressed by the degree of polarization P as given by the equation

$$P = \frac{I_{VV} - GI_{VH}}{I_{VV} + GI_{VH}}$$

I_{VV} represents the emission intensity when both polarizer and analyzer are oriented to pass only vertically polarized light, i.e., light polarized with electric vector normal to the plane containing the excitation and observation beam. Similarly, I_{VH} represents the intensity for vertical orientation of the polarizer and horizontal orientation of the

DSW 037465

STLCOPCB4021289

analyzer. G is an instrumental correction factor whose determination is discussed in detail by Azumi and McGlynn.[26]

The polarization spectrum would ordinarily consist of a plot of P vs excitation wavelength. Theoretically, the value of P can range from +. 50 to −. 33, but these limits are seldom observed experimentally. Wavelength regions having positive values of P indicate that the transition moments responsible for absorption and emission of light are parallel. Conversely, negative values of P result when these moments are orthogonal. Thus, the polarization spectrum gives valuable information on the relative orientation of molecular transition moments. A general discussion of photoselection methods, with recent references, is given in Reference 9.

Polarized excitation spectra were obtained for a mixture of Aroclor 1254 (5 ppm) and p, p'-DDT (50 ppm) in MCH glass at 77° K. Plots of P versus wavelength have not as yet been made due to a possible inaccuracy in the value of the correction factor G. Nevertheless, we have decided to include the unreduced data, namely I_{VV} and I_{VH} in this report for purposes of illustration. These spectra appear in Figure 50.

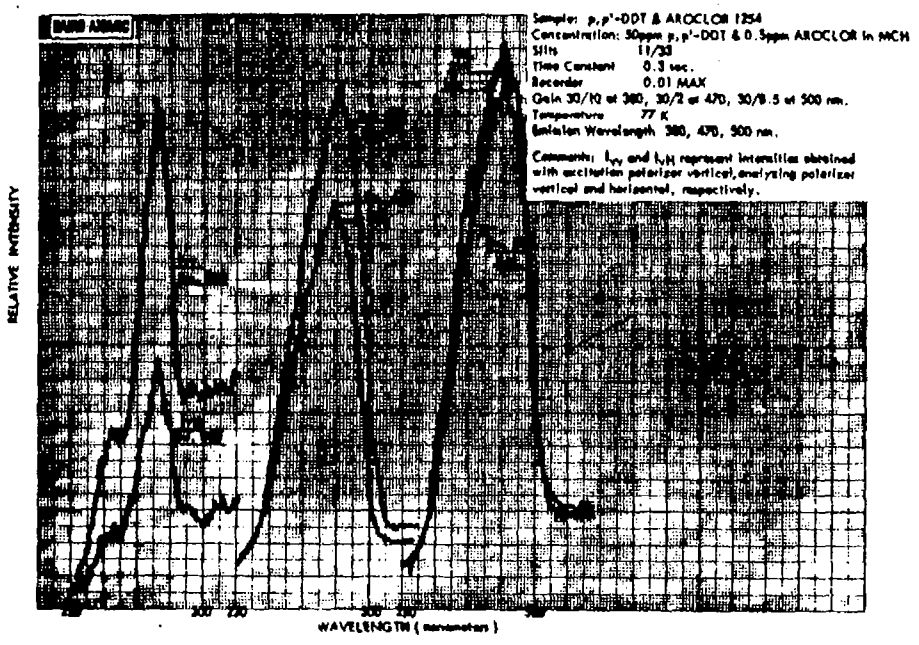


Figure 50. Polarized excitation spectra of a mixture of Aroclor 1254 (5 ppm) and p, p'-DDT (50 ppm) in MCH glass at 77° K

DSW 037466

STLCOPCB4021290

Spectra obtained by monitoring 380, 470, and 500 nm emission contain increasingly larger proportions of Aroclor emission; the 380 nm spectrum is in fact predominantly that of DDT. Clearly, the degree of polarization becomes much less positive ($I_{VV} \geq I_{VH}$) as the excitation spectrum is monitored at successively longer wavelengths, indicating that the values of P for the Aroclor differ significantly from those of DDT. It should be noted that the sharp origin band of p, p'-DDT found at 277 nm in the unpolarized spectra (Figures 4 and 8) was not observed in the polarization spectrum monitored at 380 nm, and we are unable to account for this at the present time. The results reported here are very preliminary and future work must include comprehensive studies on the polarization behavior of the individual components. However, the preliminary results suggest that polarization methods may be of value in enhancing contrast between Aroclors and pesticides.

DSW 037467

STLCOPCB4021291

SECTION VIII

SUMMARY

The purpose of this study was to examine the applicability of low temperature luminescence as a means of detecting polychlorinated biphenyls (PCB's) in the presence of DDT and related pesticides. Basic studies completed during the six month contract period have thus focused upon the documentation of important pesticide and PCB spectra, including various mixtures of these.

PCB Isomers and Mixtures (Aroclors)

Excitation and emission spectra have been obtained for seven PCB isomers at low temperatures. Most measurements were done using methylcyclohexane (MCH) solvent, which forms a clear rigid glass at 77° K. Phosphorescence in these compounds (PCB isomers) is more intense than fluorescence, and increased chlorine substitution increases the relative yield of phosphorescence to fluorescence. Some of the lower-chlorinated isomers exhibit quasilinear spectra in heptane matrix at low temperature; a similar sharpening is observed in the emission spectra of Aroclor 1221 in heptane, reflecting the low chlorine content of the isomer components. Spectra of isomers and Aroclors having relatively high chlorine content are not significantly sharpened in a heptane matrix. This may be a result of intrinsic broadness, or may indicate that aliphatic hydrocarbon solvents having greater chain length (e.g., octane, nonane) are more appropriate Shpolskii matrices. It should be noted, however, that spectra of 2,5,2',5'-tetrachlorobiphenyl in octane and nonane at 77° K showed no evidence of additional sharpening, so that for this isomer, at least, the diffuseness of the phosphorescence is probably intrinsic.

Even in solvents producing relatively broad spectra, spectral differences are sufficient to allow the five Aroclors we have studied (1221, 1242, 1248, 1254, and 1260) to be differentiated. Further work along these directions would include a greater number of important PCB isomers (which had been previously identified in Aroclor mixtures) in order to further define sources of luminescence in Aroclors.

Photochemical changes have been noted in Aroclor 1254, and these studies should be extended to other Aroclors and pesticides to determine whether analytical methods could be based upon prior photolysis. Additional PCB isomer spectral data might prove helpful in this context since the photoproducts include other isomers.[22]

DSW 037468

STLCOPCB4021292

Pesticides

The excitation and emission spectra of the four DDT and DDD compounds are all very similar. It may be possible to distinguish between these by differences in phosphorescence lifetime or polarization. Observed emission from DDE isomers was very much weaker than for the DDD or DDT compounds. Further experiments are needed to determine whether the observed emission is due to DDE itself or to an impurity. The low emission yield of DDE makes it more difficult to determine with sensitivity, but also reduces its interference with PCB measurements. Further, PCB's do not interfere significantly with the GC determination of p,p'-DDE.[25]

Aroclor/Pesticide Mixtures

Mixtures of Aroclor 1254 and p,p'-DDT were studied in MCH at 77° K. Aroclor concentrations ranged from .05 to 50 ppm with DDT concentrations of 5 and 50 ppm. It was found that Aroclor could be detected in the presence of DDT levels at least 100X greater. Conversely, DDT could be detected in the same mixtures in the presence of equal (or lower) levels of Aroclor. Lower concentrations of the components could have been realized. The current practical limit is due to emission from solvent impurities which limit detection sensitivities to approximately 1 ppm and .01 ppm for DDT/DDD and Aroclor respectively. Better solvent purity is therefore essential. Much additional work is needed in this area to establish linear ranges of detectability and also detection limits.

Polarization and phosphoroscopic methods were applied to a mixture of Aroclor 1254 (5 ppm) and p,p'-DDT (50 ppm) in MCH at 77° K in order to enhance, if possible, contrast between these components. The phosphoroscopic method, which exploits differences in phosphorescence lifetimes, did not result in much additional contrast for the mixture chosen, presumably because of similarities in lifetimes. Better contrast should be obtained with Aroclors of lower chlorine content (e.g., 1221, 1232) and thus longer phosphorescent lifetimes. In the polarization method (also known as photoselection) an excitation spectrum is obtained by monitoring horizontally- and vertically-polarized components of emission produced by excitation with polarized light. This method revealed differences in polarization between Aroclor and DDT which might be used to enhance contrast. The experimental results are very preliminary, however, and require much further study.

DSW 037469

STLCOPCB4021293

In conclusion, the basic studies conducted during the initial contract period, while not complete, are very encouraging and clearly demonstrate the applicability of low temperature luminescence to the determination of PCB's in the presence of DDT-type compounds.

DSW 037470

STLCOPCB4021294

SECTION IX

ACKNOWLEDGMENTS

We gratefully acknowledge the support and direction of Mr. D. Ballinger of the EPA Analytical Water Control Laboratory, Cincinnati, Ohio.

Sincere thanks are due to Dr. R. G. Webb of the Athens, Georgia, EPA Laboratory, and Dr. O. Hutzinger of the National Research Council of Canada, Halifax, Nova Scotia for providing samples of PBC Isomers. We are also indebted to Dr. E. S. Tucker of the Monsanto Company for providing us with additional Aroclor samples.

The special contribution of Miss Judith Guilfoyle to the early phases of the project is gratefully acknowledged. Finally, thanks are due Mrs. Geraldine Garnick for considerable assistance with the laboratory studies.

DSW 037471

STLCOPCB4021295

SECTION X

REFERENCES

1. J. Armour and J. Burke, "Polychlorinated Biphenyls as Potential Interference in Pesticide Residue Analysis," FWPCA Laboratory Information Bulletin No. 918, July 1, 1969.

2. "FWPCA Methods for Chlorinated Hydrocarbon Pesticides in Water and Wastewater," U. S. Department of the Interior, Federal Water Pollution Control Administration, April, 1969.

3. L. M. Reynolds, Residue Reviews, 34, 27 (1971).

4. J. Pichirallo, Science, 173, 899 (1971).

5. T. W. Duke, J. I. Lowe, and A. J. Wilson, Jr., Bull. Envir. Contam. and Toxicol., 5, 171 (1970).

6. V. Zitko and P. M. K. Choi, Fisheries Research Board of Canada, Technical Report No. 272, 1971.

7. R. W. Risebrough in Impingement of Man on the Oceans, D. W. Hood, Ed., Wiley-Interscience, New York, 1971.

8. H. Hays and R. W. Risebrough, Natural History, 80, 39 (1971).

9. J. D. Winefordner, P. A. St. John and W. J. McCarthy in Fluorescence Assay in Biology and Medicine, Vol. II, by S. Udenfriend, Academic Press, New York and London, 1969, pp. 85-89.

10. Beat Meyer, Low Temperature Spectroscopy, American Elsevier Publishing Co., Inc., New York, 1971, pp. 203-205.

11. H. A. Moye and J. D. Winefordner, J. Agr. Food Chem., 13, 516 (1965).

12. I. B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York and London, 1965, p. 88.

13. R. A. Webb and A. C. McCall, "Identities of Polychlorinated Biphenyl (PCB) Isomers in Aroclors," presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., 13 September 1971.

DSW 037472

STLCOPCB4021296

14. D. Sissons and D. Welti, J. Chromatogr. 60, 15 (1971).

15. A. C. Tas and R. H. deVos, Environmental Science and Technology, 5, 1213 (1971).

16. O. Hutzinger, S. Safe, and V. Zitko, Bull. Environ. and Toxicol., 6, 209 (1971).

17. E. V. Shpolskii, Soviet Phys. Usp., 3, 372 (1960); 5, 522 (1962); 6, 411 (1963).

18. D. S. McClure, J. Chem. Phys., 17, 905 (1949).

19. M. Bixon and J. Jortner, J. Chem. Phys., 48, 715 (1968).

20. J. Petruska, J. Chem. Phys., 34, 1111 (1961).

21. D. G. Crosby, A. S. Wong, J. R. Plimmer, and E. A. Woolson, Science, 173, 748 (1971).

22. O. Hutzinger and S. Safe, "Photochemical Behavior of Chlorobiphenyls (PCB)", presented at the NIH Conference on Polychlorinated Biphenyls, Quail Roost Conference Center, Durham, N. C., 20 December 1971.

23. V. Zitko, Fisheries Research Board of Canada, Manuscript Report Series No. 1038 (1970).

24. R. G. Webb and A. C. McCall, unpublished results.

25. R. W. Risebrough, P. Reiche, and H. S. Olcott, Bull. Environ. Contam. and Toxicol., 4, 192 (1969).

26. T. Azumi and S. P. McGlynn, J. Chem. Phys., 37, 2413 (1962).

DSW 037473

STLCOPCB4021297

SECTION XI

APPENDIX

When dilute solutions of organic molecules in n-alkane matrices are analyzed at low temperatures, it is often found that the absorption and emission spectra become quite narrow, often resembling atomic lines. A review of this "quasilinear" structure has been given by Shpolskii,[1] who pioneered in this important field.

Usually, it is found that the sharpest spectra are obtained in those n-alkane matrices whose molecular dimensions are nearly the same as those of the solute molecule. Single vibronic bands of the free molecule usually appear as multiplets in the alkane matrix. The energy separation between multiplets is usually the same for all vibronic bands and is probably due to guest substitution in several different crystalline phases of the host. Additional multiplets may arise from energetically different sites within a particular phase.

Bandwidths are strongly temperature dependent, becoming broader as the temperature is raised. Kizel and Sapozhnikov,[2] for example, have found that the origin band of 3,4-benzopyrene varies in half widths from about 5 cm^{-1} at 77° K to 140 cm^{-1} at 140° K, and attribute this broadening to a redistribution of intensity into photon (lattice) vibrational modes.

Diffuse spectra may accompany the quasilinear structure. Grebenshchikov and Personov[3] measured the temperature dependence of the triplet lifetimes and intensities of several molecules, including biphenyl, in various n-alkane matrices from 77° K to the melting point. Oxygen quenching of the phosphorescence was observed above 90° K, but not at 77° K. Biphenyl was found to possess quasilinear structure in heptane, but in decane this structure became much more diffuse. The diffuse system in decane was found to be much more sensitive to oxygen quenching upon warming than was the quasilinear heptane system. The authors thus attributed the sharp system to well-separated guest molecules distributed substitutionally in the alkane matrix and the broad system to molecules adsorbed on the surfaces of microcrystals of the host. Grebenshchikov, et al.[4] also reached the conclusion of two different emitting moieties (one having sharp spectra and the other diffuse) in their studies of luminescence bandwidths of several organic molecules in n-alkane matrices having from 6 to 12 carbon atoms. Finally, Bolotnikova and Gurov[5] found both broad and narrow emission in a 10^{-3} M solution of anthracene in heptane at 77° K. The broad emission was strongest at the surface of the sample, whereas the sharp emission was strongest in the central region of the sample. The authors concluded

DSW 037474

STLCOPCB4021298

that the broad emission was due to the molecular aggregates of anthracene excluded during crystallization. This result suggests that quasilinear spectra should be more favorable at low solute concentrations. In an earlier study, however, Bolotnikova and Naumova[6] found that spectra of naphthalene in heptane at concentrations ranging from 10^{-5} to 10^{-1} M became sharper as the naphthalene concentration was increased, the quasilinear structure appearing at 10^{-2} M. Similarly, the phosphorescence of phenanthrene in n-octane became increasingly sharp at concentrations above 10^{-3} M. In n-hexane however, the phenanthrene phosphorescence was found to be quasilinear, independent of concentration. No reference was made to these apparent anomalies in later work (Bolotnikova and Gurov[5]).

In summary, it is usually found that quasilinear spectra are obtained in n-alkane matrices whose molecules have dimensions similar to that of the guest. For example, naphthalene and anthracene should have sharpest spectra in pentane and heptane, respectively. Invariably, spectra become sharper as the temperature is decreased and usually temperatures of 77° K or lower are preferable. Variables such as rate of crystallization and concentration as these affect bandwidths are less well understood at present, and it would appear advisable to determine the nature of these effects empirically for given combinations of solute and solvent.

1. E. V. Shpolskii, Sov. Phys. Usp., 3, 372 (1960); 5, 522 (1962); 6, 411 (1963).

2. V. A. Kizel and M. N. Sapozhnikov, Phys. Stat. Sol., 41, 207 (1970).

3. D. M. Grebenshchikov and R. I. Personov, Opt. Spectrosc., 26, 142 (1969).

4. D. M. Grebenshchikov, N. A. Kovrizhnykh, and R. I. Personov, Opt. Spectrosc., 30, 32 (1971).

5. T. N. Bolotnikova and F. I. Gurov, Opt. Spectrosc., 28, 94 (1970).

6. T. N. Bolotnikova and T. M. Naumova, Opt. Spectrosc., 25, 253 (1968).

DSW 037475

STLCOPCB4021299

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. | 2. | 3. Accession No. W

4. Title
IDENTIFICATION OF POLYCHLORINATED BIPHENYLS IN THE PRESENCE OF DDT-TYPE COMPOUNDS,

5. Report Date
6.
8. Performing Organization Report No.

7. Author(s)
Brownrigg, J. T., Eastwood, D., and Hornig, A. W.

9. Organization
Baird-Atomic, Incorporated
Bedford, Massachusetts

10. Project No.
16020 GIY

11. Contract/Grant No.
68-01-0082

13. Type of Report and Period Covered

12. Sponsoring Organization

15. Supplementary Notes
Environmental Protection Agency report number EPA-R2-72-004, October 1972.

16. Abstract Polychlorinated biphenyls (PCB's) interfere with gas chromatographic analyses of DDT and related compounds, necessitating a simple independent method for PCB determination. The purpose of the present study was to determine the applicability of low temperature (77°K) luminescence methods to this problem. Basic studies included documentation of excitation/emission spectra of 6 pesticides (p,p'- and o,p'-DDE, DDD, and DDT), 7 PCB isomers, and 5 PCB mixtures (Aroclors). Although phosphorescence spectra of the DDD and DDT compounds are very similar, possible differences in lifetime and polarization measurements may aid in differentiation. Emission from DDE is at least 100X less intense than that of DDD or DDT, and is therefore more difficult to determine with adequate sensitivity. Spectral differences among various Aroclors are sufficient to allow those studied to be differentiated. Emission from solvent impurities presently limit detection sensitivities to about 1.0 ppm for DDT/DDD and about .01 ppm for Aroclors. By removing interference, detection sensitivities should be improved by two orders of magnitude.

Low temperature luminescence studies in various binary mixtures of Aroclor 1254 and p,p'-DDT indicate Aroclor 1254 may be identified and quantitated in the presence of DDT concentrations 100X greater.

17a. Descriptors
*Analytical techniques, *Chemical analysis, *Fluorescence, *Chlorinated hydrocarbon pesticides, *DDT, Spectroscopy, Spectrophotometry, Organic compounds, Aromatic compounds, Pesticides, Organic pesticides.

17b. Identifiers
*Polychlorinated biphenyls, *Aroclors, *Low temperature luminescence, Luminescence.

17c. COWRR Field & Group 05A, 07B

18. Availability	19. Security Class. (Report)	21. No. of Pages	Send To:
	20. Security Class. (Page)	22. Price	WATER RESOURCES SCIENTIFIC INFORMATION CENTER U.S. DEPARTMENT OF THE INTERIOR WASHINGTON, D. C. 20240

Abstractor | Institution

WRSIC 102 (REV JUNE 1971) GPO 913.761

* U. S. GOVERNMENT PRINTING OFFICE : 1972—514-148/65

DSW 037476

STLCOPCB4021300