Development of a Portable Field Monitor for PCBs

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Research Project 1263-5

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Prepared by

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Oak Ridge National Laboratory
Oak Ridge, Tennessee

ABSTRACT

With the advent of recent regulations and those yet pending concerning allowable concentrations of polychlorinated biphenyls (PCBs), personnel in all aspects of the electric power industry, analytical support personnel, and those in the regulatory functions themselves have realized that the PCB problem, as well as these associated regulations, has far surpassed available monitoring capability. In short, detailed, stringent regulations are being set for contamination levels where no accepted ASTM procedure or instrumentation exists. The largest PCB problems occur in the form of PCB-contaminated oil in field transformers and storage containers, and pure askarel in transformers and capacitors. The most immediate need for a portable field instrument would be for use under PCB spill conditions. Portable monitors based on the principles of photoionization detection (PID) and infrared spectroscopy (IR) have been adapted and evaluated for this purpose. The latter includes both flow cell and horizontal multiple internal reflectance (HMIR) sampling configurations. Extensive work has also been performed on solvent-solvent and solvent-soil extractions, as well as PCB adsorption on packings, for use under spill conditions.

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EPRI PERSPECTIVE

PROJECT DESCRIPTION

Utilities must clean up uncontrolled discharges of polychlorinated biphenyls (PCBs) in compliance with federal regulations. A problem in the field is determining whether or not the cleanup is complete, i.e., concentrations in soil or elsewhere after cleanup are below 50 ppm. This final report for RP1263-5 summarizes efforts to develop a portable field instrument for measuring PCBs; it will be followed by another report when additional developmental work is complete.

This project represents one facet of the research being conducted by the EPRI Coal Combustion Systems Division on PCB disposal, spill cleanup, and associated analytic techniques. Previously published PCB reports have addressed disposal options (EPRI Final Report FP-1207, Volume 1), spill plans (EPRI Final Report FP-1207, Volumes 2 and 3), and the ENSCO incinerator test burn (EPRI Final Report FP-1207, Volume 4). Reports were recently published on chemical treatment of PCB capacitors (EPRI Final Report CS-2477) and photodecomposition of PCB spills (EPRI Final Report CS-2513).

PROJECT OBJECTIVE

The objective was to adopt photoionization detection (PID) technology into an instrument and procedure for rapid, easy field analysis of PCBs in soil.

PROJECT RESULTS

The study showed that PID, although promising in the laboratory, is not adequately selective and sensitive to PCBs when they are mixed with mineral oil. Without a linear and consistent response based solely on the concentration of PCBs, the PID approach is impractical. Attempts at selectively ionizing PCBs or concentrating them after removal from interfering substances were not successful.

A more positive note, however, is that infrared spectrometry combined with a horizontal multiple internal reflectance cell can be used for PCB analysis when coupled with solvent extraction. A future project, RP1263-10, will develop a protocol for field analysis of PCBs in soil that uses this analytic technique.

A variety of PCB data have been collected into this report, and the data may prove useful to anyone involved in the physical or chemical separations and analyses of PCBs. In addition, the problems with the development of a PID instrument are described as are the positive and negative aspects of the infrared approach.

Ralph Y. Komai, Project Manager
Coal Combustion Systems Division

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SUMMARY

Polychlorinated biphenyl (PCB) mixtures were manufactured in the United States under the trade name of Aroclor by the Monsanto Chemical Company during the years 1932 to 1971. Askarel is the generic name for the fire-resistant liquid electrical insulation material containing Aroclor (primarily Aroclor 1260) in a solvent comprised principally of trichlorobenzene. Due to the suspected toxicity of these substances, the actual manufacture and commercial use of PCBs have been banned in the United States since 1976 (Toxic Substances Control Act, Public Law 94-469, and Title 40, Code of Federal Regulations, Part 761).

Among the requirements stemming from the PCB regulations are disposal restrictions for PCB-contaminated materials. Many mineral oil-filled transformers have been inadvertently contaminated with PCBs. Transformers containing PCB concentrations of 500 $\mu\text{g/g}$ or greater are classified as PCB transformers; their fluids can only be disposed of in a high-temperature, EPA-approved incinerator (so-called Annex I incinerators). PCB-contaminated transformers are classified as those containing between 50 and 500 $\mu\text{g/g}$. Currently, their fluids may be disposed of in an approved chemical waste landfill, high efficiency boilers, Annex I incinerators, or treated by a number of approved chemical processes.

The owner of a PCB transformer may continue to use it until the end of its service life. Restrictions are encountered when transformers or capacitors have an accidental spill. Under those conditions, cleanup of "soil, gravel, sludge, fill, rubble, or other land-based substances" must be complete to a residual concentration of $\text{PCB} \leq 50 \mu\text{g/g}$. However, no rapid method of determining PCB in soil is currently available. The electric power and manufacturing industries recognize the need for a portable instrument capable of the rapid on-site analysis of PCB from oil and soil samples. The quantitative and qualitative information provided by such an instrument would aid the utility in complying with federal regulations. Ideally, this instrument should be selective, sturdy, relatively inexpensive, and capable of operation by personnel without technical training.

In the present report, we investigated the utility of two different analytical

instrumental approaches for the rapid determination of PCB, namely Photoionization Detection (PID) (Model PI-101 Photoionization Analyzer, HNU Systems, Inc.) and infrared (IR) spectroscopic detection (MiranTM Series Instruments, Foxboro Analytical). Also, as a critical adjuvant to the application of these techniques, we investigated various procedures for the isolation of PCB from complex matrices. These isolation techniques can be used to decrease background interference (hence, increase selectivity) in the analytical measurement of PCB.

Selectivity with the use of PIDs depends upon the energy (usually expressed in the units of electron-volts, eV) provided by the ionization lamp. Lamps with high energy can ionize most organic compounds to produce a relatively nonselective detector response. A lower energy lamp ionizes fewer compounds, and thus it is more selective for these compounds.

PIDs are most applicable to vapor-phase analysis, and we found them to be useful detectors for PCBs separated by gas chromatography. The standard 10.2-eV PID lamp showed good sensitivity for gas chromatographically separated PCBs; relative to the conventional flame ionization detector, sensitivity for PCBs and polycyclic aromatic hydrocarbons (PAHs) was enhanced by a factor of nearly 40-fold. However, the selectivity for the detection of PCB in an askarel-substitute mineral oil (10-C oil, Texaco 11-AC-1, Code AE) was not improved, since PCB and background interference responses were equally enhanced. An experimental lamp with a nominal energy of 8.3 eV was more selective for PCB in this matrix by a factor of nearly 20-fold, relative to the standard 10.2-eV lamp; it was also somewhat less sensitive than the standard lamp.

Although gas chromatography is excellent for laboratory-based assay for PCB, such a procedure is not well suited for the rapid testing of transformer oils or contaminated soils for PCB content in the field. The latter applications require a simple, rugged, and easily transportable analytical instrument.

We therefore examined the utility of the portable PID instrument for the headspace analysis of askarel in contaminated oil. We obtained an authentic used transformer oil containing a PCB content of 490 $\mu\text{g/g}$, as assayed by ASTM method D3534. This askarel-contaminated oil was diluted with noncontaminated oil. A sample (1 mL) of diluted oil was placed in a 1-L, stoppered flask and allowed to equilibrate before a measurement was taken. The detector gave a monotonic response in proportion to the askarel content in the diluted oil.

In order to give a headspace response, the component of interest must have an appreciable volatility. Subsequent testing using the principal components of askarel, namely Aroclor 1260 and trichlorobenzene, indicated that the detector was in fact responding to the trichlorobenzene component, which is more volatile than PCB by a factor of $\sim 10,000$ fold.

Matrix isolation techniques potentially offer a means to separate a component of interest from a complex matrix. These techniques may be used to decontaminate the matrix by the removal of a selected solute, or to isolate the solute from matrix components that would otherwise interfere in its analytical detection. Another application is to isolate the solute of interest into a volatile solvent; the solvent is easily removed in order to concentrate the solute and thus enhance its subsequent detectability.

Matrix isolation techniques may be used to remove PCB from contaminated transformer oil. PCB has a high affinity for oil, and we were unable to find an effective oil-insoluble solid affinity matrix to remove the PCB by batch adsorption. However, PCB can be extracted from oil with use of selected solvents. In general, the oil-immiscible solvents had distribution coefficients [$D = (\text{concentration of PCB in solvent phase}) / (\text{concentration of PCB in oil phase})$] of less than unity, emphasizing the great affinity between PCB and the oil matrix. For example, acetonitrile had a value of $D \sim 0.3$. Yet, on the bases of low solvent toxicity and high solvent volatility (hence easy recovery of solvent), acetonitrile may be the most suitable of the solvents examined for the selective removal of PCB from contaminated oil.

Solvent extraction is also used to recover PCB from soil following a transformer spill. Again, acetonitrile is an effective solvent, especially for the recovery of askarel from soil with low moisture content. Water is soluble in acetonitrile and decreases the cosolubility (hence, recovery) of PCB. Water-immiscible solvents such as hexane, oil, and carbon tetrachloride are found to be effective solvents for the recovery of PCB-contaminated oil or askarel from either dry or moist soil (typical recoveries were 90 to 95%, as estimated with use of radiolabeled PCB tracers).

Lastly, we investigated IR absorption spectroscopy for the determination of PCB in oil. Mineral oil is relatively transparent in the IR spectral region where PCB mixtures strongly absorb light. We found that absorbance measurements made at either the 8.5 or 9.2 μm (μ) wavelength are selective for Aroclor 1260 in the presence of mineral oil (an askarel substitute) or trichlorobenzene (the solvent in askarel fluids). The chief limitation of conventional IR analysis is the modest sensitivity

afforded by the technique; we found it difficult to measure accurately the PCB in oil at concentrations lower than 500 to 1000 $\mu\text{g/g}$.

We investigated several techniques for the quantitative IR analysis of PCB from soil. The simplest procedure is to apply the contaminated soil directly to the window of a multiple internal reflectance (MIR) cell. This technique is useful only for the assay of fresh spills onto naturally moist soil. When lipophilic PCB or askarel is applied to moist soil, it is repelled to the outer portions of the soil pores and thus it is amenable to detection with use of a surface measurement technique, such as IR on a MIR window. However, when the soil dries out, the PCB can penetrate the pores of the soil where it is not easily detected with a surface technique; the PCB must then be extracted from the soil in order for it to be detected. Extraction of PCB from soil is a reliable technique, especially when a water-immiscible solvent is used. Mineral oil is itself an excellent solvent for the extraction of PCB from soil, but unfortunately results in a dilution of PCB.

The most promising technique is the extraction of PCB into a volatile solvent such as acetonitrile, hexane, or carbon tetrachloride. The PCB solute is easily concentrated by evaporation of the solvent. If an aliquot of volatile solvent is applied to the window of a horizontal MIR cell and allowed to evaporate, a thin film of PCB solute is deposited. Quantitative measurements on this solvent-free film are much more sensitive than solution-phase measurements. We were able to detect and quantify Aroclor 1260 at the level of a few dozen micrograms after the evaporation of extractant. Extractions from noncontaminated soil samples showed no intrinsic background interference at the wavelengths of interest.

The inherent selectivity of IR analysis coupled to the exploitation of the unique features of the horizontal MIR for quantitative analysis of nonvolatile films yield an instrumental approach with a great deal of promise as a portable monitor for the rapid measurement of PCB from askarel spills.

Section 1

INTRODUCTION

STATEMENT OF PROBLEM

Polychlorinated biphenyl (PCB) mixtures were manufactured in the United States under the trade name of Aroclor by the Monsanto Chemical Company during the years 1932 to 1971. Askarel is the generic name for the fire-resistant liquid electrical insulation material containing Aroclor (primarily Aroclor 1260) in a solvent comprised principally of trichlorobenzene. The widespread use of PCBs as dielectric and heat-exchange fluids, coupled with their resistance to decomposition, has made them ubiquitous and persistent environmental pollutants (worldwide production of PCB since 1929 is estimated at $>2 \times 10^9$ kg). During the 1960s, evidence accumulated in regard to the toxicity and potential carcinogenicity of these compounds, and since 1976, the actual manufacture and commercial use of PCBs have been banned in the United States (Toxic Substances Control Act, Public Law 94,469, and Title 40, Code of Federal Regulations, Part 761.

Among the requirements stemming from the PCB regulations are disposal restrictions for PCB-contaminated materials. Transformers containing PCB concentrations of 500 ppm or greater are classified as PCB transformers. Their fluids can only be disposed of in a high-temperature EPA-approved incinerator. PCB-contaminated transformers are classified as those containing between 50 and 500 ppm. Currently, their fluids may be disposed of in an approved chemical waste landfill if the fluids meet certain criteria specified in the regulations, in Annex I incinerators, in high-efficiency boilers, or by certain approved chemical processes.

The owner of a PCB transformer may continue to use it until the end of its service life (1). Restrictions are encountered when transformers or capacitors have an accidental spill. Under the latter conditions, cleanup of "soil, gravel, sludge, fill, rubble, or other land-based substances" must be to the 50-ppm level; however, no rapid method of determining concentration levels in the soil is available.

Measurement of PCBs at the ppm level has thus far been restricted to the use of

expensive and time-consuming laboratory-based procedures such as gas chromatography with electron capture detection. The electric power and manufacturing industries recognize the need for a portable instrument capable of the rapid on-site analysis of PCB from soil samples. The quantitative and qualitative information provided by such an instrument would aid the utility in complying with federal regulations. Ideally, this instrument should be selective, sturdy, relatively inexpensive, and capable of operation by personnel without technical training.

CHARACTERIZATION OF PCB

Commercial PCB mixtures are prepared by the chlorination of biphenyl with anhydrous chlorine, using iron filings or ferric chloride as the catalyst (2). The product is purified by treatment with alkali and by distillation. Thus, the various technical grades of PCB represent different distillation ranges and contain correspondingly different average chlorine contents. Aroclor 1260, used in electrical transformers, is characterized by a distillation range of 385 to 420°C, an average chlorine content of 60% (w/w), and an average molecular weight of 372. These commercial mixtures of PCB are very complex mixtures of isomers, containing close to 100 components each (3).

CHARACTERIZATION OF ASKAREL

With its beginning in 1932, the use of askarels has been incredibly widespread. Askarel liquid insulation is made by thinning Aroclor 1260 with trichlorobenzene or tri-, tetrachlorobenzene mix (possible interferences for PCB monitors). General Electric Company introduced Pyranol 1499 in 1932 followed by Westinghouse's Inerteen in 1936. As shown in Table 1-1, several alterations of formulations were made in the 1940s. Tin tetraphenyl, phenoxy propene oxide, and a diepoxide were added as hydrogen chloride scavengers. The two modern commercial types of formulations are General Electric's Transformer Pyranol A13B3B type and Westinghouse Inerteen PPO (7336-9) type. Because of an overall failure rate of less than 0.5%, a number of units remain in service, dating back to 1933 with askarels of somewhat different composition.

Table 1-1
COMPOSITION OF TRANSFORMER MATERIALS

	<u>Pyranol</u>				<u>Inerteen</u>	<u>Inerteen PPO (7336-9)</u>
	<u>1488</u>	<u>1467</u>	<u>1470</u>	<u>A13B3B</u>		
Year introduced	1932	1944	1952	1963	1936	1945
<u>Ingredients (wt %)</u>						
Aroclor 1260	60	60	45	45	60	60
Trichlorobenzene	40	40	40	40	40	40
Tetrachlorobenzene			15	15		
Tin tetraphenyl		0.125	0.125			
Phenoxy propene oxide						0.20
Diepoxide				0.125		

Section 2

PHOTOIONIZATION DETECTION OF PCB AND ASKAREL

BACKGROUND

Our objective in this phase of the project is to evaluate the potential application of photoionization detectors (PIDs) for detecting and measuring PCBs under spill conditions. The principle of operation with this detector is the ionization of a molecule upon absorption of sufficiently energetic (far-ultraviolet) light:

where RH is an ionizable molecule and $h\nu$ is a photon with an energy greater than or equal to the ionization potential (IP) of the molecule. A positively biased high-voltage electrode accelerates the resulting ions to a collection electrode, and the resultant current flow is proportional to concentration of ionizable species.

Different molecules require different photon energies for ionization, thus permitting a degree of selectivity by proper lamp selection. Table 2-1 lists selected gases that may be used to fill discharge lamps to produce various ionization energies. Thus a hydrogen-filled lamp emits at 121.6 nm, equivalent to an energy of 10.2 eV. Photoionization lamps are commercially available from HNU Systems, Inc. (Newton, MA 02164) at nominal energies of 11.7, 10.9, 10.2, and 9.5 eV. The photon intensity produced by the 10.2-eV PID lamp is 10- to 20-fold greater than that produced by the commercially available lamps, and correspondingly it is more sensitive for the detection of many organic solutes.

Molecules with ionization potentials up to 0.3 eV higher than a given lamp energy can be ionized and detected, but with less efficiency than a molecule with ionization potentials lower than the lamp energy. Although the IP can be used to determine whether a molecule will or will not respond to a given PID, it cannot be used to predict relative sensitivities for a series of ionizable compounds. In general, however, lamps with lower energies (i.e., ≤ 10.2 eV) have a higher molar response to aromatic compounds (π -electrons) than to alkanes (σ electrons). Most saturated hydrocarbons ionize in the range of 11 to 12 eV, whereas PCBs ionize at energies

Table 2-1
POSSIBLE GASES FOR USE IN GASEOUS DISCHARGE LAMPS FOR A PID

<u>Gas</u>	<u>Energy (eV)</u>	<u>Wavelength (nm)</u>	<u>Window</u>	<u>Highest Energy Window Transmittance (eV)</u>	<u>% Transmittance</u>
Xe	8.43	146.96	MgF ₂	10.9 (113 nm)	
O ₂	9.5	130.0	MgF ₂	10.9 (113 nm)	50% at 10.2 eV
Kr	10.0	123.58	MgF ₂	10.9 (113 nm)	
H ₂	10.2	121.6	MgF ₂	10.9 (113 nm)	
N ₂	10.9	113.0	LiF	11.9 (104 nm)	25% at 11.4 eV
He	11.4	108.0	LiF	11.9 (104 nm)	
Ar	11.8	105.0	LiF	11.9 (104 nm)	

nearer 8 eV. Thus detection of PCB in a hydrocarbon matrix (e.g., mineral oil) should be more selective using a lower energy lamp.

THE PHOTOIONIZATION DETECTOR COUPLED TO GAS CHROMATOGRAPHY

PIDs are most applicable to vapor-phase analysis and are useful detectors for components separated by gas chromatography (4,5). The 10.2-eV lamp is most frequently used by virtue of its sensitivity. Langhorst (6) has evaluated this detector in regard to its response toward select groups of organic molecules. As classes, PCBs and polycyclic aromatic hydrocarbons (PAHs) have the highest molar sensitivities. The PID gas chromatographic detector is reported to be 10 to 40 times more sensitive toward PAHs than is the conventional flame ionization detector (FID) (7), and chlorobenzenes can be determined in environmental and biological samples at low parts-per-billion levels (8). In the latter application, the relative molar responses for mono- to hexachlorobenzenes were within 10 to 15% of each other, demonstrating that the PID (in contrast to the electron capture detector) responds to π electrons, not the degree of halogenation.

Our initial evaluations of the applicability of PIDs for the detection of PCBs in gas chromatograph effluent were performed with the aid and cooperation of Dr. Jack Driscoll of HNU Systems, Inc. (9). The performance characteristics of both a standard 10.2-eV lamp and an experimental 8.3-eV discharge lamp were compared to those of the conventional FID detector for the detection of PCB in transformer oil. These preliminary results are illustrated qualitatively in Figure 2-1. The response for the 10.2-eV PID was judged to be approximately 40-fold more sensitive than the FID (cf. Figure 2-2); however, use of this detector did not improve the selectivity for PCB since PCB and background interference response were equally enhanced. The results of these preliminary investigations may be summarized as follows:

1. Compared to the FID, the PID with a 10.2-eV lamp does not improve selectivity for PCBs.
2. The PID with a 10.2-eV lamp does provide a fairly uniform response for chlorinated compounds regardless of degree of chlorination — useful for quantitation of individual PCBs.
3. The PID with a 8.3-eV lamp has sufficient sensitivity to determine PCBs to less than 1 ppm in oil.
4. The PID with a 8.3-eV lamp demonstrates a 15- to 20-fold improvement in the selectivity for PCB in oil, as compared to the 10.2-eV PID or the FID. This capability appears to be sufficient for the analysis of many different oil samples.

Figure 2-1. Gas chromatographic separation of transformer oil (dashed lines) and oil supplemented with 60 $\mu\text{g/g}$ PCB (as Aroclor 1260). Effluent is monitored with use of PID (10.2-eV and 8.3-eV lamps) and FID at similar recorder response level. A methyl silicone stationary phase is used. (Source: HNU, Inc.)

5. PermaBond columns appear ideal for rapid gas chromatographic analysis of PCBs in oil.

These studies demonstrate the utility of the PID for the determination of PCB eluted in a gas chromatographic effluent. In terms of sensitivity, but not selectivity, the PID (10.2 eV) appears to perform comparably with the electron capture detector specified in the ASTM procedure (method D3534) for the gas chromatographic detection of PCB. PID selectivity for PCB in an oil matrix is enhanced with use of an experimental 8.3-eV lamp, but sensitivity is somewhat decreased. Some chemicals that are potential interferences (by virtue of their relatively low ionization potentials) in the detection of PCB with the 8.3-eV PID lamp are listed in Table 2-2. To further enhance the selectivity for PCB, it may be necessary to use physical or chemical

Figure 2-2. Glass capillary gas chromatographic separation of Aroclor 1254, as monitored with PID (10.2-eV lamp) and FID.

separation of PCB from oil (e.g., by selective adsorption or extraction) prior to chromatographic analysis.

HEADSPACE ANALYSIS WITH USE OF PID

Although gas chromatography is excellent for laboratory-based assay for PCB, such a procedure is not well suited for the rapid testing of transformer oils or contaminated soils for PCB content in the field. The latter applications require a simple, rugged, and easily transportable analytical instrument.

A portable PID detector is commercially available from HNU Systems, Inc. The HNU Model PI-101 Photoionization Analyzer is the portable "offspring" of the PI-51-02 PID designed as a GC detector. In a recent report, "Evaluation of Portable, Direct-Reading Hydrocarbon Meters" (10), NIOSH reports favorably on the portable PID as an organic vapor analyzer. It has several specific advantages over its competitors. It does not require a hydrogen gas fuel source or flame (the PID meets the safety requirements of Class I, Division 2 of the National Electrical Code) and it does not respond to many hydrocarbons, in contrast to total carbon analyzers such as

Table 2-2
POSSIBLE INTERFERENCES FOR 8.3-eV LAMP

<u>Molecule</u>	<u>IP (eV)</u>
<u>Sulfur Compounds</u>	
methyl disulfide	8.46
dimethyl sulfide	8.69
ethyl disulfide	8.27
benzenethiol	8.33
ethylmethyl sulfide	8.55
diethyl sulfide	8.43
di- <u>n</u> -propyl sulfide	8.30
<u>Amines</u>	
aniline	7.70
methylamine	8.97
ethylamine	8.86
<u>n</u> -propylamine	8.78
<u>i</u> -propylamine	8.72
<u>n</u> -butylamine	8.71
<u>i</u> -butylamine and <u>s</u> -butylamine	8.70
dimethylamine	8.24
diethylamine	8.01
di- <u>n</u> -propylamine	7.84
di- <u>i</u> -propylamine	7.73
di- <u>n</u> -butylamine	7.69
trimethylamine	7.82
triethylamine	7.50
tri- <u>n</u> -propylamine	7.23
<u>Cl-Benzene</u>	
<u>p</u> -dichlorobenzene	8.94
<u>o</u> -dichlorobenzene	9.07
<u>m</u> -dichlorobenzene	9.12
<u>p</u> -chlorotoluene	8.70
<u>o</u> -chlorotoluene	8.83
<u>m</u> -chlorotoluene	8.83

Table 2-2 (continued)

<u>Molecule</u>	<u>IP (eV)</u>
<u>Heterocyclics</u>	
furan	8.89
2-methyl furan	8.39
thiophene	8.86
2-chlorothiophene	8.68
pyrrole	8.20
<u>Miscellaneous</u>	
toluene	8.82
ethyl benzene	8.76
<i>i</i> -propylbenzene	8.69
<i>n</i> -butylbenzene	8.69
<i>o</i> -xylene	8.56
<i>m</i> -xylene	8.56
<i>p</i> -xylene	8.45
styrene	8.47
α -methylstyrene	8.35
cyclohexene	8.95
naphthalene	8.12
1-methylnaphthalene	7.96
biphenyl	8.27
phenol	8.50
anisole	8.22

flame ionization detectors. The readout meter of the PID is linear (linear range 0.1 to 600 ppm; useful range 0.1 to 2000 ppm for benzene) and is capable of reading directly in ppm. For NIOSH tests of vinyl chloride, instrument readings were 96% of actual concentrations, lag time was <5 s. Furthermore, the monitor requires only a 2-min warmup time, has excellent zero and calibration stability, operates for 8 to 10 h on rechargeable batteries, and weighs <17.6 kg (8 lb).

A block diagram of this instrument is given in Figure 2-3. A small DC fan is used to pull air (and organic vapors) through the sensor at a flow rate of 300 to 700 cm/min.

Figure 2-3. Block diagram of portable photoionization analyzer.
(Source: HNU, Inc., PI-101 Operations Manual.)

In order to test the potential applicability of this type of instrument for the assay of askarel-contaminated oil, we obtained an authentic used transformer oil containing a PCB content of 490 ppm ($\mu\text{g/g}$), as assayed by the ASTM method. This contaminated oil was diluted with varying amounts of noncontaminated 10-C oil (Texaco 11-AC-1, Code AE). The experimental setup is illustrated in Figure 2-4. One milliliter of each standard was placed in individual 1- $\frac{1}{2}$, stoppered flasks and allowed to equilibrate (~ 5 min). The 8-in. probe was then placed just off the bottom of each flask and a measurement taken with the use of the standard 10.2-eV PID lamp. Ambient temperature was $\sim 25^\circ\text{C}$.

The results from this preliminary study are shown in Figure 2-5. A monotonic detector response is obtained with increasing PCB content from askarel-contaminated

Figure 2-4. Experimental setup for the headspace analysis (PID detection) of contaminated oil or selected chemicals.

Figure 2-5. Headspace analysis (10.2-eV PID lamp) of askarel-contaminated oil.

oil (note: noncontaminated oil was used to set the detector null signal). From this, we anticipated that it could be feasible to detect askarel-contaminated transformer oil, rapidly and sensitively, directly on the headspace of an operating transformer. Factors that may affect this mode of measurement include variable headspace volume, temperature (actual transformer operating temperature is frequently close to 50°C), and pressure (some transformers are under positive pressure).

It remained necessary to demonstrate the selectivity of the simple headspace analyzer, using both the standard 10.2-eV PID lamp and the experimental 8.3-eV lamp. Early versions of the experimental lamp produced by HNU Systems, Inc., were found to have very short operational lifetimes (e.g., as short as a week or less). At present, the 8.3-eV lamp is not available commercially. In order to prepare an 8.3-eV discharge lamp for evaluation, we found it necessary to refill an experimental lamp with 1.7 Torr of highly purified Xenon (see Table 2-1) and to develop a high-vacuum seal between the MgF_2 window and the electrode metal. The spectral outputs of an experimental 8.3-eV discharge lamp (prepared in-house) and a standard 10.2-eV discharge lamp were measured by connecting the lamps to the entrance slit of a Seya-Namioka vacuum spectrophotometer. The spectral distribution of the emitted light is shown in Figure 2-6. As expected, the output of the 10.2-eV lamp is centered at 121.6 nm. The output of the experimental lamp is centered at 145.2 nm (corresponding to an energy of 8.5 eV). The maximum intensity of the experimental lamp appears to be of the order of a third that of the 10.2-eV lamp.

These same lamps were tested against a menu of chemicals with varying ionization potentials, using the experimental setup depicted in Figure 2-4. The results are summarized in Table 2-3. In order to produce a high response in headspace analysis with the PID, the compound must have an appropriate ionization potential (i.e., comparable to or below that of the PID lamp energy), have a high molar sensitivity factor, and finally it must have sufficient vapor pressure to reach the detector at an appreciable concentration. In general, Table 2-3 confirms the selectivity of the PID lamps while emphasizing the importance of the requirement for sample volatility in headspace analysis. In contrast to the gas chromatographic (high-temperature) data, increasing concentrations of PCB in oil did not produce an incremental detector response (10.2-eV lamp) in ambient temperature headspace analysis. In this study, PCB in oil was prepared from a commercial source of Aroclor 1260 (obtained from Nanogen International, Freedom, CA 95019, as part of batches originally manufactured by the Monsanto Chemical Co.) rather than from dilutions of an askarel material (cf. Figure 2-5).

Figure 2-6. Spectral distribution of light produced by the discharge of photoionization lamps.

The vapor pressure of askarel and its principal components (PCB and trichlorobenzene) are presented in Table 2-4. PCB has very low volatility. The vapor pressure of Aroclor mixtures of PCB is greater than that of the individual component isomers, yet the vapor pressure of Aroclor mixtures is some 10,000-fold less than that of trichlorobenzene. Thus, the reported vapor pressure of transformer askarels is effectively due to the solvent. This explains the disparity between the data shown in Figure 2-5 (PID headspace response to askarel in oil) and Table 2-3 (PID headspace response to PCB in oil). At ambient temperature, insufficient PCB would reach the detector to permit a selective response. This is, of course, different than is the case for the detection of PCB in a gas chromatographic effluent (i.e., a high-temperature vapor).

Early in our consideration of the potential application of the PID for the headspace analysis of PCB in oil, we recognized that it would be necessary to heat the sample in order to enhance its volatility. Figure 2-7 is a schematic of a proposed sample vaporization chamber for use with the portable PID instrument. To test the

Table 2-3

PID RESPONSE FOR SELECTED COMPOUNDS AND MIXTURES

Compound	IP (eV)	Vapor Pressure ^a (Torr) at 25°C	Literature Relative Molar Sensitivity (10.2 eV Lamp) ^b	Portable PID Response (Headspace Analysis at 25°C)	
				10.2 eV Lamp ^c	8.3 eV Lamp ^d
Acetonitrile	12.22	105	NA ^e	1	-0.2
Carbon tetrachloride	11.47	128	NA	0	0
Chloroform	11.42	218	NA	3	0
Methylene chloride	11.35	529	NA	1	0
Methanol	10.85	137	<0.02	14	0
Hexane	10.18	168	<0.03	8	0
Acetone	9.69	261	0.35	9	0
Benzene	9.25	140	≅1.00	138	0.1
Toluene	8.82	29	1.09	54	0.2
Phenol	8.50	0.3	1.05	118	0.5
Aniline	7.70	0.5	1.13	126	2.8
Silicone oil	NA	NA	NA	6	0
1,2,4-Trichlorobenzene	NA	0.4	1.20	33	NA
PCB	NA	(10 ⁻⁴ to 10 ⁻⁵) ^f	~2.53	NA	NA
10-C oil	NA	NA	NA	0.4	0
10-C oil + Aroclor 1260:					
444 ppm	NA	NA	NA	0.6	0
296 ppm	NA	NA	NA	0.6	0
222 ppm	NA	NA	NA	0.6	0

^aR. H. Perry, C. H. Chilton, and S. D. Kirkpatrick. Chemical Engineers Handbook, 4th ed., New York: McGraw-Hill, 1963, pp. 3-47 to 3-58 (extrapolated values).

^bM. L. Langhorst, J. Chromatogr. Sci., **19**, 98 (1981). (Gas chromatographic data.)

^cSensitivity = span 9.8.

^dSensitivity = span 1.

^eInformation not available.

^fD. W. MacKay and A. W. Wolkhoff, Environ. Sci. Technol., **7**, 611 (1973).

Table 2-4
VAPOR PRESSURE OF SELECTED COMPOUNDS AND MIXTURES

	Vapor Pressure (Torr) at 25°C	Reference
<u>PCB Isomers</u>		
		<i>a</i>
2,2',5,5'-Tetrachlorobiphenyl	6×10^{-5}	
2,2',4,5,5'-Pentachlorobiphenyl	9×10^{-6}	
2,2',4,4',6,6'-Hexachlorobiphenyl	1×10^{-5}	
<u>Aroclor Mixtures</u>		
		<i>b</i>
1242	4×10^{-4}	
1248	5×10^{-4}	
1254	8×10^{-5}	
1260	4×10^{-5}	
<u>Transformer Askarels</u>		
		<i>c</i>
Pyranol (45% Aroclor 1260, 40% Trichlorobenzene)	4×10^{-1}	
Inerteen PPO (60% Aroclor 1260, 40% Trichlorobenzene)	4×10^{-1}	
<u>Solvent</u>		
1,2,4-Trichlorobenzene	4×10^{-1}	<i>d</i>

^aJ. W. Westcott and T. F. Bidleman, J. Chromatogr. **210**, 331 (1981).

^bD. W. MacKay and A. W. Wolkoff, Environ. Sci. Technol. **7**, 611 (1973).

^cMonsanto Askeral Inspection and Maintenance Guide, Monsanto Functional Fluids Dept., St. Louis, MO.

^dR. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, Chemical Engineers' Handbook, 4th ed., New York:McGraw-Hill, 1963.

Figure 2-7. Schematic of a proposed sample vaporization chamber for use with the portable PID instrument.

applicability of this concept, we tested the menu of substances listed in Table 2-3 after preheating the flask and contents to 50°C. Unfortunately, the warm vapors condensed in the cool probe, precluding accurate measurement. If preheating of the sample is required to enhance volatility, it will also be necessary to heat the probe unit and detector chamber as well (such as is done for gas chromatographic detection).

SUMMARY AND CONCLUSIONS

PIDs are most applicable to vapor-phase analysis, and we found them to be useful detectors for PCBs separated by gas chromatography. The 10.2-eV PID lamp showed good sensitivity for gas chromatographically separated PCBs. However, selectivity for PCBs in an oil matrix was relatively poor. In contrast, an experimental 8.3-eV lamp showed enhanced selectivity, but reduced sensitivity.

We examined the utility of the portable PID instrument for the headspace analysis of askarel in contaminated oil. The 10.2-eV lamp gave a monotonic response with respect to askarel content in oil, but subsequent testing suggests that this response is due to the solvent (trichlorobenzene) component of askarel rather than to PCB. This is a consequence of the fact that the vapor pressure of trichlorobenzene is approximately 10,000-fold higher than that of PCB mixtures.

Section 3

MATRIX ISOLATION TECHNIQUES

INTRODUCTION

Matrix isolation techniques are important adjuvants in the selective detection and measurement of PCB after a spill has occurred. An example is the recovery of PCB from soil, usually achieved with use of solvent extraction. The solvent selected must have a high affinity for PCB and must not interfere with the subsequent measurement of the recovered PCB. For measurement using the PID, this implies use of a solvent with a high ionization potential (hence low background response). If infrared (IR) detection is used (see Section 4), the solvent must have high transparency in the spectral region of interest. An alternative approach is to use a volatile solvent which is easily removed from the isolated PCB.

Matrix isolation is also used to enhance detection specificity. For example, the sensitive, commercially available 10.2-eV PID does not have a great deal of inherent selectivity for PCB over a hydrocarbon (i.e., mineral oil) background. In this example, preliminary isolation of PCB from oil (e.g., by selective adsorption or extraction) into a solvent with decreased background response would effect an enhanced selectivity in a subsequent measurement of the isolated PCB.

THE USE OF RADIOLABELED (^{14}C) PCB IN MATRIX ISOLATION STUDIES

Initially, the distribution of PCB following matrix isolation experiments was quantitatively estimated with use of packed-column gas chromatography with electron capture detection (ASTM method D3534), as performed by the Service Section of the ORNL Analytical Chemistry Division. The assay procedure, although sensitive, was labor-intensive and costly (~\$50/assay) and required a week or more before assay results were available. Cheaper, more timely assays were clearly needed.

The use of radiolabeled tracer would be a simple and convenient means to monitor PCB distribution. Seidl and Ballschmiter (11) prepared a labeled PCB mixture for use in studying the isolation of PCB from soil. We prepared similarly "spiked" materials by the addition of minute quantities of uniformly labeled (^{14}C) PCB isomeric mixture (~54 wt % chlorine, Cat. No. NEC-690, New England Nuclear Corporation)

to an appropriate unlabeled carrier (askarel or PCB-contaminated oil). Five to ten microliters of the unlabeled material (cost ~\$4) is added to 50 ml of solution containing unlabeled PCB; 0.1 ml of the resultant "spiked" material yields 2000 to 3000 disintegrations per minute (DPM) for liquid scintillation counting. This activity is such that good counting statistics (<1% standard deviation) are obtained in less than 10 min counting time, with correspondingly rapid sample turnaround time. Appropriate standards and blanks are included in each batch of assays.

BATCH ADSORPTION STUDIES

We briefly examined the feasibility of the batch adsorption of PCB from contaminated oil. The objective was to find an oil-insoluble matrix with a sufficient affinity for PCB such that PCB could be stripped from oil. This approach, if successful, could be used to decontaminated oil. Alternately, the adsorbed PCB could subsequently be eluted as a concentrated solution in a solvent more amenable to selective detection of PCB.

We examined a number of potential adsorbent materials, including alumina, open-pore polyurethane, silica, silica coated with C₁₈-hydrocarbon (part No. 51910, Waters Associates, Inc.), neoprene, carbonaceous resins (XE-340 and XE-347, Rohm and Haas, Inc.), and Columbia activated charcoal (Union Carbide Corp.). In preliminary studies, we used PCB (Aroclor 1260) in ethanol solvent and elution from sorbant with use of ethanol, thus permitting us to quantitate PCB in the column effluent by gas chromatography without interference by oil matrix. The data are given in Table 3-1; Columbia ACC and XE-347 effectively removed PCB from the polar solvent (i.e., minimal recovery of PCB in the column effluent).

However, none of these materials was particularly effective in removing PCB from the oil matrix (Table 3-2). The most effective sorbants were XE-347 and Columbia activated charcoal, removing 5 and 9%, respectively, of PCB from an authentic transformer oil originally containing 320 µg/g of Aroclor 1260. Flow characteristics as well as sorbent wetting capabilities were far superior for the XE-347 material.

EXTRACTION OF PCB FROM MINERAL OIL

As indicated in Table 3-3, relatively few solvents are immiscible with 10-C oil and are thus potentially useful as extraction media. Table 3-4 lists several candidate extraction media which were tested for their effectiveness in removing PCB from oil, together with their estimated apparent distribution coefficient, D:

Table 3-1

REMOVAL OF PCB FROM ETHANOL BY ADSORPTION CHROMATOGRAPHY^a

Sorbant	Cumulative % PCB Recovered in Column Effluent Column Volume Eluted (Ethanol Solvent)			
	1	2	3	4
Columbia ACC	0	1.5	3.5	6.5
XE-347	2.5	5.8	9.8	11.8
Neoprene	25	80	87.5	ND ^b
Alumina	32	84	ND	ND
Silica	51	94	ND	ND
RPC ^c	85	96	ND	ND
OPP ^d	93	96	ND	ND

^a1 mg of Aroclor 1260 in 1 ml ethanol is applied to 4 g of pre-wetted sorbant and eluted with successive column volumes of ethanol.

^bNot determined.

^c μ Bondapak C₁₈ (Waters Associates, Inc.).

^dOpen-pore polyurethane.

Table 3-2

REMOVAL OF PCB FROM 10-C OIL BY ADSORPTION CHROMATOGRAPHY

Sorbant	PCB in Oil (μ g/g) ^a		PCB Removal (%)
	Feed	Effluent	
Columbia ACC (25°C)	320	291	9.1
XE-347 (25°C)	320	304	5.0
XE-347 (35°C)	368	365	0.8
Fly Ash (25°C)	368	366	0.5

^aPCB in oil as determined by ASTM method D3534.

^bMeasured in first column volume eluted.

Table 3-3
MISCIBILITY OF SELECTED SOLVENTS

	Acetonitrile	Aniline	Benzene	Carbon Tetrachloride	Chloroform	Cyclohexane	Dimethyl Sulfoxide	p-Dioxane	Dodecane	Ethyl Acetate	Ethyl Alcohol	Ethyl Benzene	Ethyl Ether	Hexadecane	Hexane	Isooctane	Methyl Alcohol	Methylene Chloride	Mineral Oil ^a	Nitrobenzene	Nitromethane	Pentane	Tetralin	Tetrahydrofuran	Toluene	1,2,4-Trichlorobenzene	Trichlorotrifluoroethane	Xylenes
Acetonitrile	/	M	M	M	M	I	M	M	I	M	M	M	M	S	I	I	M	M	I ^b	M	M	S	M	M	M	M	M	M
Aniline	M	/	M	M	M	SR	MR	M	I	M	M	M	M	I	I	I	M	M	I	MR	M	M	I	M	M	M	M	I
Benzene	M	M	/	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Carbon Tetrachloride	M	M	M	/	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Chloroform	M	M	M	M	/	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Cyclohexane	I	SR	M	M	M	/	I	M	M	M	M	M	M	M	M	M	SR	M	M	M	M	I	M	M	M	M	M	M
Dimethyl Sulfoxide	M	MR	M	M	M	I	/	M	I	M	M	M	S	I	I	I	M	M	I ^b	M	M	I	M	M	M	M	S	M
p-Dioxane	M	M	M	M	M	M	/	M	M	M	M	M	S	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Dodecane	I	I	M	M	M	M	I	M	/	M	M	M	M	M	M	M	I	M	M	S	I	M	M	M	M	M	M	M
Ethyl Acetate	M	M	M	M	M	M	M	M	M	/	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Ethyl Alcohol	M	M	M	M	M	M	M	M	M	M	/	M	M	I	M	M	M	M	S	M	M	M	M	M	M	M	M	M
Ethyl Benzene	M	M	M	M	M	M	M	M	M	M	M	/	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Ethyl Ether	M	M	M	M	M	M	S	M	M	M	M	M	/	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Hexadecane	S	I	M	M	M	M	I	S	M	M	I	M	M	/	M	M	S	M	M	I	M	M	M	M	M	M	M	M
Hexane	I	I	M	M	M	M	I	M	M	M	M	M	M	/	M	S	M	M	M	M	M	M	M	M	M	M	M	M
Isooctane	I	I	M	M	M	M	I	M	M	M	M	M	M	/	S	M	M	M	S	M	M	M	M	M	M	M	M	M
Methyl Alcohol	M	M	M	M	SR	M	M	I	M	M	M	M	S	S	S	/	M	I ^b	M	M	M	M	M	M	M	M	M	M
Methylene Chloride	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	/	M	M	M	M	M	M	M	M	M	M	M
Mineral Oil ^a	I ^b	I	M	M	M	M	I ^b	M	M	M	S	M	M	M	M	M	I ^b	M	/	M	I ^b	M	M	M	M	M	M	M
Nitrobenzene	M	MR	M	M	M	M	M	S	M	M	M	M	M	M	M	S	M	M	/	M	S	M	M	M	M	M	M	M
Nitromethane	M	M	M	M	M	I	M	M	M	M	M	M	I	I	I	M	M	I ^b	M	/	M	M	M	M	M	S	M	M
Pentane	S	I	M	M	M	M	I	M	M	M	M	M	M	M	M	M	M	S	M	/	M	M	M	M	M	M	M	M
Tetralin	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	/	M	M	M	M	M	M
Tetrahydrofuran	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	/	M	M	M	M	M
Toluene	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	/	M	M	M	M
1,2,4-Trichlorobenzene	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	/	M	M	M
Trichlorotrifluoroethane	M	I	M	M	M	M	S	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	/	M	M
Xylenes	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	/	M

^aTransformer oil, 11-AC-1 Code AE.

^bShows slight miscibility of these organic solvent pairs when viewed with 365-nm uv lamp.

Table 3-4
EXTRACTION OF PCB FROM 10-C OIL

<u>Extraction Medium</u>	$D = \frac{\text{Conc. PCB in Extraction Medium}}{\text{Conc. PCB in 10-C Oil}}$
Acetonitrile	0.30; 0.28
Acetonitrile + 0.2% tributylphosphate	0.28
Aniline	1.15; 1.07
Nitromethane	0.23
DMSO	0.93; 1.03
Methanol	0.15
Perfluorotributylamine (FC-43)	0.12
Perfluorooctane (FC-104)	0.05

$$D = \frac{\text{Concentration in extractant phase}}{\text{Concentration in oil phase}},$$

$$= \frac{\text{Weight \%, extractant}}{\text{Weight \%, oil}} \times \frac{\text{Volume, oil}}{\text{Volume, extractant}}.$$

Aniline and methanol were partially soluble in 10-C oil. With the exception of dimethylsulfoxide (DMSO), the oil-immiscible solvents were not particularly efficient in removing PCB from mineral oil.

A contaminated oil cleanup procedure could be envisioned whereby an extraction solvent is used to strip PCB from oil. If the extractant phase is removed after each equilibration and is replaced with fresh solvent each time, and the oil phase is thus re-extracted n times, the percentage of the original mass of PCB remaining in the oil phase will be given by the expression:

$$\% \text{ remaining in oil phase} = 100\% \left[\frac{1}{1 + D \left(\frac{\text{Volume extractant}}{\text{Volume oil}} \right)} \right]^n.$$

Thus, three repetitive extractions of oil, each with a volume of DMSO solvent equal to the volume of oil, would remove ~87% of PCB; in contrast, three such extractions with acetonitrile would remove ~53% of PCB. Three repetitive extractions using two volumes of extractant to each volume of oil would remove ~96 and ~75% of PCB, using acetonitrile, respectively.

Although DMSO is the more effective extractant, it may be undesirable to use this solvent in an oil cleanup process, due to the fact that PCB in DMSO would be a substantial health hazard to operating personnel; accidental exposure to this solution would result in rapid uptake of PCB through biological membranes. Again, DMSO has a relatively high boiling point (189°C), making it more difficult to recover solvent by distillation. Contaminated DMSO could be stripped of PCB by back-extraction with a more volatile (hence, recoverable) solvent, but this would further complicate such a process.

At any rate, DMSO was judged to be an inappropriate solvent for use in subsequent quantitation of PCB since it would contribute to the nonselective background response for the envisioned modes of PCB detection. Acetonitrile emerges as the most practical of the extractants for the removal of PCB in oil. As indicated in Table 2-3, CH₃CN has a high ionization potential (12.22 eV) and thus a low background response using the PID. It also has a relatively low boiling point (82°C), making it easy to concentrate PCB solute (by solvent evaporation) in order to enhance analytical detectability. Likewise, it is an easily recoverable solvent for use in the cleanup of contaminated oil.

We sought to enhance the effectiveness of acetonitrile for the extraction of PCB from oil by the addition of selected compounds (in stoichiometric excess over the concentration of PCB in oil). We hoped to enhance PCB recovery by forming a charge transfer complex or by the addition of an emulsifier. The compounds tested (and their concentration in acetonitrile extractant) were: AgNO₃ (0.05 w/w), Tween 80 (a nonionic detergent; 0.05 w/w), sodium dodecylsulfate (0.05 w/w), sodium dodecylbenzene sulfates (saturated solution), potassium myristate (saturated solution), and tributylphosphate (0.2 w/w). None of these preparations produced a distribution coefficient that was significantly different from acetonitrile alone (cf. Table 3-4).

EXTRACTION OF PCB AND ASKAREL FROM SOIL

Seidl and Ballschmiter (11) have reported on the recovery of PCB isomers from soil using different solvent systems, including hexane, acetonitrile, and acetone. Soil was extracted with these solvents using a Soxhlet extractor (10-h contact time) or cold extraction using an ultrasonic bath. Their results are summarized in Table 3-5. These authors demonstrate that PCB can be recovered from soil in high yield by extraction with suitable solvents.

We further investigated the recovery of PCB (both as contaminated oil and as askarel) from soil. Since we propose that the extraction be performed in the field, we

Table 3-5
RECOVERY OF PCB FROM SOIL (LITERATURE VALUES)

Solvent	Extraction Procedure	PCB Recovered from Soil	
		Dried Soil	Soil + 0.07 (w/w) H ₂ O
Hexane	Soxhlet extraction (hot solvent)	~70%	~85%
CH ₃ CN	Soxhlet extraction (hot solvent)	>95%	ND ^a
or Acetone	Ultrasonic extraction (cold solvent)	~80%	ND

Source: G. Seidl and K. Ballschmiter, Chemosphere 5, 373 (1976).

^aNot determined.

evaluated the PCB removal efficiency from naturally moist as well as dried soil. Also, a simplified extraction procedure (i.e., shaking soil with solvent in a sealed container) is preferred over Soxhlet extraction or sonication.

In the first series of experiments, we examined the recovery of PCB-contaminated oil from soil. Mineral oil supplemented with Aroclor 1260 (~500 ppm) was spiked with radiolabeled PCB and added in variable quantities to a fixed weight of soil sample. The soil is used "as is" (i.e., without drying to reduce its natural moisture content). "Extraction" (actually, dilution) of the contaminated soil with an aliquot of hexane recovered greater than 90% of the PCB. This value is similar to that reported by Seidl and Ballschmiter (Table 3-5), using exhaustive Soxhlet extraction of moist soil with hexane solvent.

Extraction of contaminated oil from soil using oil-immiscible acetonitrile solvent represents a partitioning of PCB between the oil and solvent. A single extraction from naturally moist soil using acetonitrile solvent yielded an apparent distribution coefficient (D) of 0.11, in contrast to a coefficient of 0.28 (Table 3-4) for the extraction from oil alone. The decrease in apparent distribution coefficient may be due to the moisture content of the soil (water is miscible with acetonitrile and would be expected to decrease the co-solubility of PCB) or to the affinity of PCB for soil.

In order to eliminate the effects of oil/solvent partitioning, we investigated the recovery of Pyranol (askarel) from soil; Pyranol is miscible with acetonitrile

as well as other, more lipophilic, solvents. In order to investigate the effect of soil moisture on PCB recovery, we first prepared a desiccated soil by drying the soil (68E Collegedale) in a vacuum oven (-80 kPa, 120°C) for approximately 4 h, then storing the crumbled soil overnight in a vacuum desiccator. The soil was then pulverized into fine dust and passed through a No. 30 (0.6-mm) sieve. Varying amounts (0 to 1 g) of water were added to 5-g samples of desiccated soil, with mixing, and the soil allowed to equilibrate in a sealed tube for at least 2 h. Next, 0.5 mL (0.8 g) of Pyranol spiked with radiolabeled PCB was added to the soil samples, with mixing, and allowed to equilibrate prior to the addition of solvent (5 mL). Soil and solvent were contacted with use of a vortex mixer for 5 min, and then the phases were allowed to separate. The extractant phase was assayed to estimate the PCB removal efficiency. The data are summarized in Table 3-6 for the removal of askarel from soil using 10-C oil, carbon tetrachloride, and acetonitrile solvents. As expected, the PCB removed from the soil by a single equilibration with acetonitrile solvent decreases in proportion to increasing soil moisture content. In contrast, the removal of PCB from soil with use of water-immiscible solvent appears to be slightly enhanced by increasing soil moisture.

Table 3-6
REMOVAL OF ASKAREL FROM SOIL: EFFECT OF MOISTURE

Water (w/w) Added to Dried Soil	% PCB Removed		
	10-C Oil	CCl ₄	CH ₃ CN
0.00	83	87	96
0.09	94	97	60
0.17	84	ND ^a	42

^aNot determined.

SUMMARY AND CONCLUSIONS

Matrix isolation techniques may be used to remove PCB from contaminated transformer oil. PCB has a high affinity for oil, and we were unable to find an effective affinity matrix to remove the PCB by batch adsorption. However, PCB can be extracted from oil with use of selected solvents. From the viewpoints of solvent toxicity, volatility (hence, easy recovery of solvent) and PCB removal efficiency, acetonitrile

appears to be the most promising of the solvents tested.

Solvent extraction is also used to recover PCB from soil following a transformer spill. Again, acetonitrile is an effective solvent, especially for the recovery of askarel from soil with low moisture content. Water is soluble in acetonitrile and decreases the cosolubility of PCB. Water-immiscible solvents such as hexane, oil, and carbon tetrachloride are effective solvents for the recovery of PCB-contaminated oil or askarel from dry or moist soil.

Section 4

INFRARED SPECTROPHOTOMETRIC DETECTION OF PCB AND ASKAREL

INTRODUCTION

The infrared (IR) absorption spectrum of an organic compound is virtually a unique property. As witness to this fact, the spectral region from 6.7 to 14 μm is often referred to as being the "fingerprint region." The complexity of IR spectra provides many relatively sharp absorption bands for the differentiation and comparison of compounds and thus can provide a degree of specificity exceeded by few other analytical methods. Infrared spectroscopy has potential application as a portable field monitor for the selective determination of PCB. In contrast to the PID monitor, IR spectroscopy should not be adversely affected by a mineral oil matrix. Indeed, mineral oils such as Nujol (a high-boiling petroleum fraction) are the most frequently used solvents for the preparation of a solution for a spectral scan.

INSTRUMENTATION

Fourier Transform Infrared (FTIR) Spectroscopy

Our initial approach to achieving the project objective was to establish analytical conditions for the selective measurement of PCB in the presence of solvents such as mineral oil or trichlorobenzene, and to define the range of PCB concentration for which quantitative analysis is feasible.

In some of our initial investigations, we used the technique of Fourier transform infrared (FTIR) spectroscopy (Digilabs FTS-20C instrumentation). The chief advantage of this technique over conventional dispersive instruments is that it offers a superior signal-to-noise ratio in energy-limited situations (such as in IR spectroscopy) while presenting high spectral resolution. Figure 4-1 illustrates the FTIR absorption spectrum for Pyranol, an askarel containing Aroclor 1260 in a solvent comprised chiefly of trichlorobenzene (cf. Table 1-1). The high-resolution spectrum indicates numerous absorption bands that may be selected for quantitative analysis.

Upon filling an electrical transformer with mineral oil, the oil may become contaminated with PCB due to common lines. Figure 4-2 illustrates the FTIR spectrum

Figure 4-1. FTIR spectrum of Pyranol.

for 10-C oil, a frequently-used dielectric fluid for transformers. The spectrum is that of a simple hydrocarbon, and offers many excellent absorption windows in the region of absorbance by askarel. This is shown clearly in Figure 4-3, which superimposes a segment of the absorption spectrum of 10-C oil and 10-C oil containing 10%, by volume, of Pyranol.

Although the Fourier transform technique has advantages for qualitative and quantitative IR analysis, the instrumentation is judged to be delicate and expensive to have much utility as a field monitor.

MiranTM 1A

For the next stage in our investigations, we used conventional single beam IR photometers, namely the MiranTM series of instruments from Foxboro Analytical. Specifications for the simplest of these instruments (series 1) are given in Table

Figure 4-2. FTIR spectrum of 10-C oil (Texaco 11-AC-1, code AE).

4-1. The Miran 1A instrument is shown in Figure 4-4. Wavelength selection with this instrument is made with a circular interference-wedge filter, which does not give as much spectral resolution as a grating instrument but does provide greater sensitivity (due to more radiant energy reaching the detector). These instruments have the advantages of low cost, ruggedness, and portability.

The instrument illustrated in Figure 4-4 is mounted with a standard flow cell (0.2 mm pathlength, ZnSe windows, 9 μ l cell volume). The zinc selenide (ZnSe) window material is durable and resistant to water. For high-sensitivity detection in the "fingerprint" region for PCB, a barium fluoride (BaF_2) flow cell provides more light throughput (i.e., approximately 70% vs 40% transmission for ZnSe). The instrument may also be used with a multiple internal reflectance (MIR; q.v.) cell.

Table 4-1
SPECIFICATIONS FOR MIRAN™ SERIES 1 IR SPECTROPHOTOMETERS

	MIRAN-1A Spectrometer	MIRAN-1 Interchangeable Filter Analyzer	MIRAN-1 Fixed Filter Analyzer
Part No.	063-5681	063-5650	063-5651
Principle	Single-beam infrared spectrometer — direct meter readout in absorbance units or % T.		
Source	Nichrome-wire wound ceramic rod, energy peak at 3.5 microns.		
Wavelength Selection	Variable filter 2.5 to 14.5 microns.	Slide-mounted interchangeable single wavelength filter, 2.5 to 14.5 microns.	Factory installed single wavelength filter 2.5 to 14.5 microns.
Scan Time	9 minutes	N/A	N/A
Resolution	0.05 microns at 3 microns 0.12 microns at 6 microns 0.25 microns at 11 microns	Depends upon filter selected	Depends upon filter selected
Noise Level	Less than 1×10^{-4} absorbance units, without cell, 1 mm slit, 1 second time constant, 3.5 microns, 23°C.		
Drift	Less than 0.004 absorbance units at 3.5 microns, 23°C (8 hours, no sample cell).		
Photometric Accuracy	Better than $\pm 0.5\%$ full scale (± 0.000125 absorbance units with 0.025 absorbance units full scale range.		
Slit Settings	0.5, 1, 2 mm, and closed	Fixed slit	Fixed slit
Response Time	1, 4, 10 and 40 seconds		
Full Scale Ranges	0-0.025, 0-0.1, 0-0.25, 0-1, 1-2 absorbance units and 0-100% transmission		
Recorder Output	0-1 volt DC full scale	0-1 volt DC full scale	0-1 volt DC full scale
Power Requirements	115/230 volts, 50/60 Hz, 25 watts	115/230 volts, 50/60 Hz, 25 watts.	115/230 volts, 50/60 Hz, 25 watts.
Weight	12.5 pounds	12 pounds	11.5 pounds
Dimensions	5.5" x 5.5" x 10" plus 8 x 5 inch sample platform	5.5" x 5.5" x 10" plus 8 x 5 inch sample platform	5.5" x 5.5" x 10" plus 5 x 5 inch sample platform

Source: Foxboro Analytical, Co.

Figure 4-3. FTIR spectrum (segment) for 10-C oil and oil supplemented with askarel.

Miran-980

The majority of our development work on monitoring PCB spills was actually performed with the use of a Miran-980 programmable IR spectrophotometer (see Figure 4-5). This spectrometer is as rugged as the Miran-1A instrument, has similar optics (and thus similar resolution and sensitivity), and can also be fitted with either a flow cell or MIR. What sets this instrument apart, however, is the fact that it is microcomputer controlled and is capable of automated background-corrected spectral scanning. Thus the black body curve, and/or solvent matrix, can be subtracted from a spectral scan. The Miran-980 also provides automatic analysis of mixtures with complete data reduction. As can be seen from Figure 4-5, the Miran-980 provides (1) a keyboard for operating and data reduction functions, (2) a printer for "peak picking" and absorbance, transmittance or concentration readout, and (3) a cassette for methods storage.

Figure 4-4. Miran 1A portable IR spectrophotometer.

Multiple Internal Reflection Spectroscopy

In addition to conventional, short-pathlength flow cell operation, we adapted a multiple internal reflection (MIR) cell to a Miran-980. The principle of operation of MIR, also referred to as attenuated total reflection (ATR), is based on the fact that infrared energy being totally, internally reflected within an optical material (e.g., ZnSe) with a high refractive index will actually penetrate a short distance into the applied sample. If the sample absorbs energy from specific wavelengths, this attenuation of the beam, usually expressed as an absorbance, is related to concentration. Such MIR spectra closely resemble absorption spectra using a transmission cell.

The two common configurations of MIR cells are illustrated in Figures 4-6A and 4-6B. The former shows a so-called vertical multiple internal reflection (VMIR) cell; the latter illustrates a horizontal multiple internal reflection (HMIR) window. In VMIR, a nonviscous sample is placed on both sides of the window material, thus the

MIRAN-980

Figure 4-5. Miran-980 IR spectrophotometer.

Figure 4-6. Multiple internal reflectance (MIR):
A. Vertical MIR (sample on both sides of crystal);
B. Horizontal MIR (sample on surface); and C. Light path and typical dimensions of MIR crystals.

sample receives twice as many reflections of light as in a HMIR cell (sample on one side only). The HMIR configuration, however, was used for all of our MIR studies because of its convenience and simplicity in handling viscous samples (e.g., askarel, PCB/oil, or contaminated soil). A sample can be simply applied, scanned, and wiped off (with an organic solvent) with no carryover contamination or flow-cell clogging. For reasons of inertness, durability, and wide spectral range, our Miran-980 work was done with a HMIR with a ZnSe window. Table 4-2 lists the properties of available MIR crystals; Figure 4-6C illustrates the light path, typical angle of incidence,

Table 4-2
PROPERTIES OF MIR CRYSTALS

Material	Transmission Range	Index of Refraction	Remarks
TlBr - TlI Thallium Bromiodide (KRS-5)	0.5-35 μm	1.76	Do not use with aqueous solution. Good for solid samples but will cold flow with sustained pressure
Ge Germanium	2-11.5 μm	4.0	Ideal for liquid sampling at room temperature. Do not use where high-pressure contact with solid sample is required
Si Silicon	0.2-6.2 μm	3.5	Excellent for the near IR region
ZnSe Zinc selenide	1-18 μm	2.4	Best for aqueous samples. ZnSe is brittle and must be used with care for solid sampling
Sapphire	1-6.5 μm	1.8	High chemical resistance. Best for the near IR
Diamond	6-50 μm	2.4	High chemical resistance

and typical dimensions of such a crystal. Figure 4-7 schematically represents an MIR optical diagram from source to detector, which would apply to VMIR or HMIR. Finally, the advantages of MIR for field analysis are outlined in Table 4-3.

Figure 4-7. Typical MIR optical diagram. (Source: Foxboro Analytical Co., Miran 1A Operating Manual.)

SPECTRAL SCANS WITH THE MIRAN-980

Our primary interest in developing an infrared detector for PCBs was in quantitative analysis; however, IR does lend itself also to qualitative identification. While it does not exhibit the characterization capabilities of gas chromatography (GC), the particular region we were dealing with is commonly referred to as the fingerprint region. Figure 4-8 is the transmission spectrum of 10-C oil (Texaco 11-AC-1, Code AE), as recorded with use of the Miran-980. It has the spectrum of a typical paraffin oil. Indeed, mineral oils from different sources did not have significantly

Table 4-3

ADVANTAGES OF MULTIPLE INTERNAL REFLECTION

- Useful for strong IR absorbers
- Aqueous samples or those containing some water (ZnSe window)
- Horizontal MIR is best suited for nonvolatile, viscous, gummy, or semisolid samples
- Vertical MIR cells are available for volatile or low-viscosity samples
- Can be used for liquids containing suspended solids (eliminates scattering problems common in transmission cells due to particulate matter)
- Eliminates dilution errors
- Eliminates cell alignment
- Rapid sampling with no carryover contamination
- Eliminates interference patterns found in short pathlength transmission IR cells

different spectra or absorbances, and the oil matrix background is not one that would vary a great deal from sample to sample or utility to utility. Thus, aged 10-C oil (yellow colored), 10-C oil decolorized with use of Florisil® adsorption, Nujol, and various medicinal-grade paraffin oils appear the same by low-resolution IR analysis.

As we had done previously by PID/GC, we examined several different PCB mixtures commonly found in cutting, cooling, and transformer oils by HMIR. Figure 4-8 represents the scan of Aroclor 1242 (Thermino Fr-Lo, Monsanto). Subtle differences can be seen between the scan of this PCB (42 wt % chlorine on biphenyl) and that of Aroclor 1248 (48 wt % chlorine), shown in Figure 4-9. The spectral differences become more apparent when compared further with a scan of Aroclor 1260 (Figure 4-10). It is this latter PCB that is of primary concern in transformer contamination and spills. Unlike the lower-molecular-weight PCBs that have a liquid-to-syrup consistency, 1260 is a wax-like material. To scan this type of material by HMIR required dissolution in a volatile organic solvent such as hexane, carbon tetrachloride, acetonitrile, etc. As this solvent vaporized from the horizontal MIR stage, a thin film was deposited.

Figure 4-8. Low-resolution IR spectrum of Monsanto Thermino Fr-Lo (Aroclor 1242)

Figure 4-9. Low-resolution IR spectrum of Aroclor 1248.

Figure 4-10. Low-resolution IR spectrum of Aroclor 1260 (film).

A potential interferent in PCB measurement in askarel is the typical thinning agent trichlorobenzene (TCB). The scan of TCB is shown in Figure 4-11. Although both PCB and TCB scans exhibit similarities, significant differences in spectra are also apparent. TCB solvent can represent from 40 to 60 wt % of an askarel (cf. Table 1-1). Figure 4-12 is the spectral scan for Pyranol, comprised of 45% (w/w) Aroclor 1260 and 40% (w/w) TCB (see Table 1-1).

In order to determine the analytical wavelengths that are most selective for Aroclor 1260 in the presence of TCB, we ran HMIR scans of Aroclor 1260 diluted (volume: volume) with varying amounts of TCB versus a neat TCB blank (see Figure 4-13). The observed peaks (i.e., transmittance <1.0) represent wavelengths selective for Aroclor 1260 over TCB. Conversely, the regions at the top of the figure, where transmittance apparently exceeds 1.0, represent wavelengths of selectivity for TCB over Aroclor 1260 (due to the subtraction of the very large peaks in the TCB blank). From these data, a plot of Aroclor 1260 weight/weight (w/w) versus absorbance at various wavelengths (λ) was made. The linear least-squares regression analysis of this plot is given in Table 4-4. The correlation coefficients and relative standard errors are quite good for such a method. Looking at these factors and the fact that

Figure 4-11. Low-resolution IR spectrum of trichlorobenzene.

Figure 4-12. Low-resolution IR spectrum of used Pyranol (45% Aroclor 1260).

Figure 4-13. Scan of mixtures of Aroclor 1260 and trichlorobenzene vs a trichlorobenzene reference.

Table 4-4

AROCLOR 1260 IN TRICHLOROBENZENE VS TRICHLOROBENZENE:
LINEAR LEAST-SQUARES REGRESSION ANALYSIS (PCB VS ABSORBANCE)

Selectivity	λ_1 7.17 μ	λ_2 7.5 μ	λ_3 8.5 μ^a
Slope	1.687 $\pm$ 0.110	1.697 $\pm$ 0.187	0.922 $\pm$ 0.085
γ -Intercept	-0.198 $\pm$ 0.042	-0.153 $\pm$ 0.072	-0.109 $\pm$ 0.033
Corr. Coeff.	0.9979	0.9940	0.9958
Rel. Std. Error	5.35%	8.05%	7.56%

^aBest selectivity (distinct peak).

the 8.5 μm absorbance is the most distinctive peak for Aroclor 1260, this wavelength was concluded to be the most selective for PCB over TCB.

The IR absorptivity of Pyranol, Aroclor 1260, TCB, and 10-C oil at selected wavelengths is summarized in Table 4-5.

Table 4-5
RELATIVE IR ABSORBANCE OF SOME TRANSFORMER FLUID COMPONENTS
AT SELECTED WAVELENGTHS^a

$\lambda(\mu)$	Aroclor 1260	Pyranol	TCB ^b	10-C Oil
7.0	++	++	++	+++
7.2	++	++	$\pm$	-
7.4	++	++	$\pm$	$\pm$
7.5	++	++	-	-
8.5	++	++	$\pm$	-
9.2	+++	++	$\pm$	-
12.3	+++	+++	+++	$\pm$

^aRelative absorbance: +++ strong absorbance; ++ moderate absorbance; $\pm$ weak absorbance; and - very weak absorbance or window.

^bTCB = 1,2,4-trichlorobenzene.

ANALYSIS OF PCB IN OIL

A series of dilutions of Pyranol in 10-C oil was scanned on the Miran-980 instrument, with automatic subtraction of a once-run background scan of 10-C oil (thus approximating a dual-beam spectral scan). This series of scans is illustrated in Figure 4-14, and the computed absorbance data are plotted in Figures 4-15 and 4-16 for selected wavelengths. The linear least-squares regression analysis of the data is summarized in Table 4-6 suggests that absorbance measurements at either 8.5 or 9.2 μm offer the best compromise between sensitivity and selectivity.

Conventional solution phase IR spectroscopy typically has modest sensitivity as a result of both low radiant source intensity and the inherent low energy of IR radiation (hence, poor detection efficiency). Also, since many solvents absorb IR

Figure 4-14. Scan of mixtures of askarel and 10-C oil vs a 10-C oil reference.

Figure 4-15. Used Pyranol in 10-C oil: absorbance at selected wavelengths (12.3, 7.0, 9.2, and 7.4 μ) vs PCB content.

Figure 4-16. Used Pyranol in 10-C oil: absorbance at selected wavelengths (7.17, 7.5, or 8.5 μ) vs PCB content.

radiation, cell pathlengths are typically narrow (0.1 to 1 mm). Generally, solute concentrations must exceed 0.1% (1000 ppm) for good detectability. In order to better define the range of PCB concentrations for which IR analysis is applicable, we sought to measure Pyranol in 10-C oil near the limit of detection, using the simple Miran 1A instrument at a fixed wavelength of 9.2 μ m. A flow cell, 0.2 mm pathlength, with BaF₂ windows was used, and the instrument was manually blanked using noncontaminated 10-C oil. The results are shown in Figure 4-17. Reliable solution phase IR measurement of PCB at concentrations below 500 μ g/g will be difficult to obtain with use of conventional instrumentation.

ANALYSIS OF PCB FROM SOIL

Our final studies involved the development of two methods for measuring PCB in soil. In the first method, PCB was "extracted" from the naturally moist soil using 10-C oil as the extractant/diluent. Here, varying amounts of used Pyranol were added to soil (14 to 70 mg of Aroclor 1260 per gram of soil). This contaminated soil was then contacted with 2 ml of 10-C oil. The resulting supernatant was subsequently injected into a flow cell (0.2 mm pathlength, ZnSe windows) on the Miran 1-A and scanned (100% transmittance was set with new 10-C oil). The calibration curves for these scans at several selected wavelengths are illustrated in Figure 4-18. A theoretical removal efficiency of 100% was assumed for calculations, with an actual computed recovery of 95%. It is clear that the IR absorbance is related linearly to the amount of PCB or askarel applied to the soil.

Table 4-6
REGRESSION ANALYSIS FOR THE QUANTITATIVE MEASUREMENT
OF ASKAREL IN 10-C OIL VS 10-C OIL

	Linear Least-Squares Regression Analysis ^a			
	λ_1	λ_2	λ_3	λ_4
	7.0 μ	7.4 μ	9.2 μ^b	12.3 μ
Slope	1.275 $\pm$ 0.049	0.553 $\pm$ 0.074	1.088 $\pm$ 0.024	2.552 $\pm$ 0.076
Y-Intercept	0.032 $\pm$ 0.008	0.021 $\pm$ 0.013	0.009 $\pm$ 0.004	0.017 $\pm$ 0.012
Correlation Coefficient	0.9978	0.9828	0.9995	0.9987
Relative Standard Error	4.85%	10.7%	2.19%	4.30%
	λ_1	λ_2		
	7.17 μ	7.5 or 8.5 μ^c		
Slope	1.274 $\pm$ 0.054	0.948 $\pm$ 0.035		
Y-Intercept	-0.0125 $\pm$ 0.0095	-0.009 $\pm$ 0.006		
Correlation Coefficient	0.9982	0.9986		
Relative Standard Error	4.66%	4.04%		

^a x = Aroclor 1260 (wt %); y = absorbance at given wavelength (λ).

^b9.2 μ best window in 10-c oil.

^c8.5 μ best selectivity for 1260 over TCB.

Figure 4-17. Askarel in oil: absorbance at 9.2 μ vs concentration.

Figure 4-18. Pyranol extracted from soil (absorbance vs amount of PCB applied to soil).

The second quantitative method involved measuring the PCB in soil directly. This is, of course, the simplest possible technique for use in spill conditions, and is applicable to fresh spills on naturally moist soil. In Figure 4-19, varying amounts of Pyranol (0 to 1 g) were applied to 5-g samples of soil (68E Collegedale), mixed well, and scanned (vs blackbody response) directly on the MIR window. The soil blank was negligible (as can be seen in the top scan of Figure 4-19), and the IR absorbance at various wavelengths was directly proportional to the PCB applied to the soil.

Figure 4-19. Contaminated soil applied directly to horizontal MIR crystal (absorbance vs amount of PCB applied to soil).

We then allowed the contaminated soil samples to dry out completely by leaving them exposed in a fume hood for one week. The dried soil was rescanned and did not have the spectrum characteristic of Pyranol. Apparently, as the natural moisture of the soil evaporated, Pyranol was able to penetrate into the pores of the soil. Addition of moisture to the dried, contaminated soil did not appear to drive the askarel back to the surface of the soil particles where it would be amenable to the direct analyses by IR spectroscopy. To be amenable to detection with use of a surface technique, such as MIR, the PCB must be on the surface. When lipophilic PCB is added to moist soil, the water in the interior of the soil pores repels the PCB to the exterior portion of the pores so that it is then detectable. If the soil

dries out, PCB can then penetrate into the interior of the pores where it is not readily detectable by a surface technique. If water is then added, the lipophilic PCB remains in the interior of the pores and repels the water to the exterior.

The effect of soil moisture was further examined. As before, water was added in varying amounts to previously desiccated soil, and finally a fixed amount of Pyranol (~ 0.07 w/w) was applied to the moisture-equilibrated soil. The contaminated soil samples were subsequently scanned on the MIR window, as shown in Figure 4-20. In

Figure 4-20. Contaminated soil (~ 0.07 w/w Pyranol) applied directly to MIR crystal — effect of soil moisture on measured absorbance: A. 0.17 (w/w) water added to dried soil; B. 0.09 (w/w) water added to dried soil; and C. Dried soil.

this figure, curves A, B, and C represent soil with a nominal moisture content (w/w) of 0.17, 0.09, and 0.0, respectively. The spectrum of Pyranol is clearly evident in the contaminated moist soil (curve A) but is completely absent in the desiccated soil sample (curve C).

In conclusion, the simple, direct scanning of a fresh askarel spill on naturally moist soil may be useful in confirming the surface contamination as askarel, but the absence of such a spectrum does not preclude the possibility of a previous spill.

ASSAY OF PCB AS A FILM DEPOSITED ON AN MIR CRYSTAL

The direct measurement of PCB on soil is found to be strongly dependent upon the prior history of the soil sample (i.e., moisture content of the soil at the time of the spill and the storage conditions of the contaminated sample). The extraction of PCB from soil permits a more reliable measure of PCB content, but extraction using a nonvolatile solvent such as oil represents an unwanted further dilution of PCB. The optimum approach may be the extraction of PCB from soil into a volatile solvent, as discussed in Section 3. The solvent is easily removed by evaporation, permitting more sensitive determination of PCB residue.

As indicated in Table 4-3, MIR is well suited for nonvolatile, viscous, or gummy samples such as PCB. The spectrum of gum-like Aroclor 1260 (Figure 4-10) was obtained by applying a solution of the material in carbon tetrachloride to the horizontal MIR and allowing the volatile solvent to evaporate. Since the source light only penetrates the sample a minute depth with each reflection in an MIR window, the technique is ideally suited for optical measurements on a thin film. If askarel from soil is extracted with volatile solvent and deposited as a film on an MIR window, PCB should be more easily detectable than it is in solution phase.

Suitable volatile solvents for the extraction of askarel from soil and subsequent deposition of PCB on the MIR window include acetone, acetonitrile, hexane, and carbon tetrachloride. The recovery of PCB from soil using these solvents is excellent (cf. Tables 3-5 and 3-6).

In preliminary experiments, we prepared a stock solution of Pyranol in CCl_4 (1000 ppm, as Aroclor 1260), and applied various aliquots of this solution to the window of the horizontal MIR mounted on the Miran-980 spectrophotometer. The volatile solvent quickly evaporated, leaving a residual film on the window. A spectral scan of the film was identical to the spectrum of Pyranol. Quantitative data using this simple technique are given in Figure 4-21. The data are a composite for the application of varying aliquots (0.02 to 0.1 mL) of stock or dilute stock (1:10 dilution, or 100 ppm as Aroclor 1260), and for the repetitive application of a fixed volume of standard solution. The window is easily cleaned between samples with use of

Figure 4-21. Absorbance at 9.2 μ (as film on MIR) as a function of PCB applied. Sample is applied as a solution of Pyranol in carbon tetrachloride, and the solvent is allowed to evaporate before absorbance measurements are made.

solvent on a cotton swab. Aroclor 1260 could be measured at the level of tens of micrograms.

Samples of noncontaminated soil were extracted with CCl_4 , and the nonvolatile residue (if any) was scanned; essentially no IR-absorbing material was detectable and thus there was no inherent blank problem. If hexane or CCl_4 is used as an extractant, potential interferents would be lipophilic, nonvolatile compounds. Chlorinated pesticides are one class of potential interferents. Figure 4-22 shows the IR scan of a mixture containing Lindane, Aldrin, and Heptachlor; there is minimal interference at a wavelength of 8.5 μm , the most selective wavelength for the detection of Aroclor 1260.

SUMMARY AND CONCLUSIONS

Inherently, infrared (IR) analysis is a highly selective technique. Absorbance measurements at either 8.5 or 9.2 μm are selective for Aroclor 1260 in the presence of mineral oil (an askarel substitute) or trichlorobenzene (the solvent in askarel fluids). The chief limitation of conventional IR analysis is the modest sensitivity

Figure 4-22. Low-resolution IR spectrum of a mixture of pesticides (Lindane, Aldrin, and Heptachlor) applied as a film on a horizontal MIR).

afforded by the technique. We found it difficult to accurately measure PCB in oil at concentrations lower than 500 to 1000 $\mu\text{g/g}$.

We investigated several techniques for the quantitative IR analysis of PCB from soil. The simplest procedure is to apply the contaminated soil directly to the window of a multiple internal reflectance (MIR) cell. This technique is useful only for the assay of fresh spills onto naturally moist soil. Extraction of PCB from soil is the most reliable technique, especially when a water-immiscible solvent is used. Mineral oil is itself an excellent solvent for the extraction of PCB from soil, but unfortunately results in a dilution of PCB.

The most promising technique is the extraction of PCB into a volatile solvent such as carbon tetrachloride. The PCB solute is easily concentrated by evaporation of the solvent. If an aliquot of volatile solvent is applied to the window of a horizontal MIR cell and allowed to evaporate, a thin film of PCB is deposited. Quantitative measurements on this solvent-free film is much more sensitive than solution phase measurements. Extractions from uncontaminated soil samples show no inherent background interference.

The inherent selectivity of IR analysis coupled to the exploitation of the unique features of the horizontal MIR for quantitative analysis of nonvolatile films yield an instrumental approach with a great deal of promise as a portable monitor for the rapid measurement of PCB from askarel spills.

Section 5

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