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A Field Screening Method for Polychlorinated Biphenyl Compounds in Water

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A FIELD SCREENING METHOD FOR POLYCHLORINATED BIPHENYL COMPOUNDS IN WATER

by

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) is continuing in the pursuit of innovative methods of detection of polychlorinated biphenyls (PCBs) in the environment. The objective of this study was to develop a simple, inexpensive, and rapid procedure for determination of PCBs in water. Based on previous testing of real-world samples by General Electric Corporate Research and Development, a co-sponsor of this project, there was a special interest in developing a field-screening procedure of PCB aqueous extracts performed from a current soil remediation procedure in which the extractant contained 1-3% surfactant by weight to enhance solubility of PCBs. A test was therefore developed based on forming complexes of PCBs with Ag^+ followed by UV irradiation to form Ag metal. The appearance of color (gray to brown depending on the PCB concentration) was used to signal the presence of PCB. This method allows the test color to be directly compared with standard color charts to estimate the PCB concentration level without the need for instrumentation. In addition to soil remediation monitoring, potential applications include well monitoring, wellhead protection monitoring, post-closure monitoring, and rapid laboratory screening. For applications related to soil remediation, it was found that filter papers or SPE membranes could be used in a dipstick mode by spraying with methanolic $AgNO_3$ and irradiation with 254 nm light from a hand portable UV light. The detection range was 1.0-500 ppm (or higher) in the presence of 3% Renex KB or Neodol (R) 1-7 surfactants which are currently being used for PCB soil remediation.

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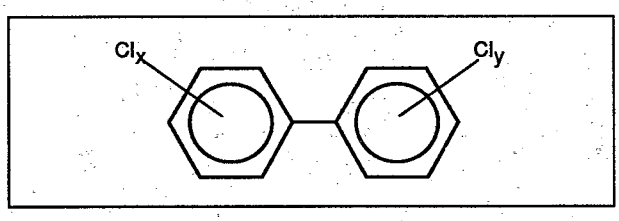
SECTION 1
INTRODUCTION

OVERVIEW

The U.S. Environmental Protection Agency (EPA) continues to examine methods for detection of polychlorinated biphenyl (PCB) compounds in the environment. The research described in this report relates to a search for new concepts of field screening methods applicable to hazardous waste sites with emphasis on in situ ground water monitoring. Polychlorinated biphenyls (PCBs) have been utilized as plasticizers, flame retardants and components in a variety of formulations such as paints, inks, waxes, pesticides, water proofing, and sealers to mention several (1). The largest single use of PCBs has been as coolants and insulation fluid in transformers and capacitors. PCBs can eventually biodegrade in the natural environment. However, when they are taken up and accumulated by living organisms, they cause toxicity problems at low concentrations. PCBs were first discovered in environmental samples in 1966 (2). Early concerns about the ecological impact of PCBs and their toxicities were summarized by Fishbein (1).

A co-sponsor of this work was General Electric Corporate Research and Development. They were interested in a simple PCB test to follow progress of soil remediation.

A PCB compound can have any one of 209 structures depending on the number and positions of the chlorine atoms. The general formula is $C_{12}H_{10-n}Cl_n$, where n=1-10; Mullin and co-workers (3) have reported the synthesis and characterization of each of the 209 PCB congeners. The generic PCB structure is illustrated below.



Commercial PCB products are mixtures of chlorinated biphenyl compounds. Monsanto's Arochlor™ PCB products are classified by four-digit code numbers, e.g., 1260. The first two digits indicate the type of molecule (i.e., 12 indicates biphenyl) and the last two digits indicate the percentage of chlorine in the mixture by weight, i.e., 60.

PCBs are very stable and inert, have low vapor pressures, low flammabilities, high heat capacities, and low electrical conductivities. Most PCBs are oily liquids. Their colors and viscosities vary depending on chlorine content. Less chlorinated congeners are essentially colorless, while the more chlorinated ones are darker and more viscous. In general, PCBs with fewer chlorine atoms are more soluble, more flammable, and less persistent in the environment (4). PCBs are very resistant to hydrolysis, chemical oxidation, and heat. Many descriptions of PCBs and their properties are available (1, 4-9).

Field screening involves the use of rapid, low-cost test methods to determine whether a compound of interest is present or absent, above or below a predetermined threshold at a given site, or at a concentration within a predetermined range of interest (10). There is a need for rapid, simple, inexpensive field screening methods for a variety of semivolatile organic compounds, including PCBs. Most of the analytical procedures used for PCB determination are not attractive for field use because they typically require laborious extractions, chromatographic separations, and considerable training. Descriptions of the current procedures of analysis for PCBs are available (4-6, 9). Common analytical methods for PCBs involve gas chromatography (GC) (e.g., EPA method 608 and NIOSH method 5503) and GC/MS (mass spectrometry) (e.g., EPA method 680). A complication for development of PCB field screening methods is that the compounds are not very soluble, ranging from 0.59 to 0.08 ppm for Arochlor™ 1221 to Arochlor™ 1260, respectively (5). This poses a problem for lower detection limits.

The approach described in this report involves using solid-phase extraction (SPE) membranes to concentrate PCBs from aqueous solution, using filter papers as dipsticks, or placing drops of the test

solutions onto the papers. This is followed by visualization directly of the substrates without further extraction or manipulation. Visualization is accomplished by spraying the substrates with a silver nitrate ($AgNO_3$) solution followed by exposure to ultraviolet (UV) light. The appearance of gray-to-brown stains relative to controls signals the presence of PCBs. Potential screening applications include well monitoring, wellhead protection monitoring, remediation monitoring, post-closure monitoring, and rapid laboratory screening. A specific application addressed in this report is to test for PCBs in 1-3% aqueous surfactant solution; such a method would have direct applications to soil remediation.

Surfactants are currently being used in soil remediation processes.

SILVER ION CHEMISTRY

Silver is considered one of the noble metals and exhibits positive oxidation states of 1, 2, and 3. The +1 state is the most common. The +2 state can be present as silver oxide, and also in certain complexes. Silver +3 compounds are few in number. Most silver compounds are insoluble in water. $AgNO_3$ is one of the few soluble ones. It is colorless and readily reduced. Many organic compounds such as alcohol, sugar, starch, etc., react with it to form finely divided silver. Both light and heat promote the reduction (11).

The solubility of aromatic hydrocarbons (Ar)

$$Ag^+ + Ar \rightleftharpoons AgAr^+ \qquad (1)$$

$$Ag^+ + AgAr^+ \rightleftharpoons Ag_2Ar^{++} \qquad (2)$$

increases in $AgNO_3$ solutions. Andrews and Keefer (12) reported that complexes are formed.

In the above equilibria, the aromatic nucleus acts as an electron donor. In $AgAr^+$, silver ion is pictured as being bonded to the aromatic nucleus from a position above the ring and on the six-fold symmetry axis of the ring. In the case of Ag_2Ar^{++}, it is presumed that the two silver ions are bonded to opposite sides of the plane of the ring (12-14).

Silver chloride (AgCl) is insoluble in water and is very stable in the dark. It is sensitive to light, which causes its decompositions to silver metal and chlorine:

$$AgCl \xrightarrow{h\nu} Ag + Cl_2 \qquad (3)$$

This reaction is a fundamental one in photography. The darkening of a precipitate of silver chloride when exposed to light is due to the photodegradation reaction. The dark coloration results from the finely divided silver that is formed (11).

PCB PHOTODEGRADATION

One route of PCB degradation is through photochemical reactions (15-17). Figure 1 shows several paths of PCB photodegradation reactions under different conditions (15). In the present study, complexation of the PCBs with silver ion may increase the PCB susceptibility to photodegradation, but this was not investigated in any detail. The mechanism of the visualization reaction utilized in the present research most likely involves complexation of the PCB molecules with silver ion, dechlorination under the influence of ultraviolet light giving AgCl, and photodegradation of the AgCl to silver metal. This will be discussed in more detail in a later section.

The ultraviolet absorption spectra of PCBs show major absorption peaks between 240 and 260 nm, depending on the chlorine substitution (17). The UV spectra of PCBs have also been recorded by Brinkman and co-workers (18-19). Femia and co-workers (20) reported fluorescence excitation and emission characteristics of several PCB isomers in α and β-cyclodextrin (CD). The range of emission peaks was 325-387 nm depending on both excitation wavelength (272-300 nm) and the α or β-CD reagent. It was found that the positions of the chlorine atom(s) on the rings drastically affected the fluorescence intensity of a particular PCB isomer. Complexation into the CD cavity resulted in increased emission.

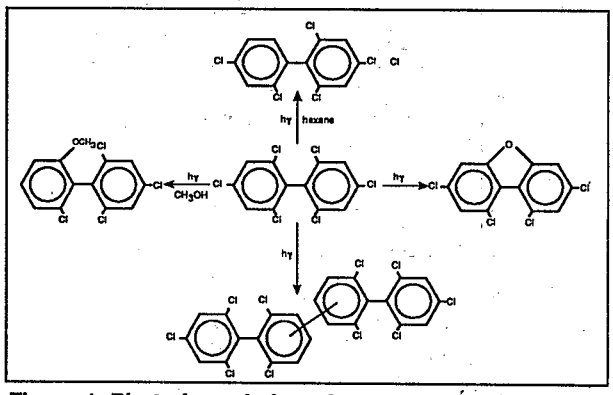


Figure 1. Photodegradation of 2, 2', 4, 4', 6, 6'- Hexachlorobiphenyl.

SECTION 2
OBJECTIVES

The major objective was to develop a simple, inexpensive, and rapid procedure that can be used for screening PCBs in water. The research was meant to advance the state of the technology in providing an attractive alternative to existing field screening methods for PCBs. There is a special interest based on previous testing in developing a test for PCBs in the presence of 1-3% by weight of surfactants. Some soil remediation is currently using these concentrations of surfactants.

As described in this report, the procedure involves forming complexes of the PCBs with silver followed by UV irradiation to form silver metal. A secondary objective was to exploit the results by suggesting guidelines for the development of new field screening methods for organohalogen compounds and other pollutants. The detection limit sought was at 1 ppm.

SECTION 3
FIELD SCREENING METHODS FOR PCBs

Several field screening techniques for PCBs already have been described. A technology that has matured dramatically in the past several years involves the use of immunoassays, all using different formats. An appreciation of the evolution of the technology can be obtained by reading relevant papers that have been presented at recent EPA field screening symposia describing PCB immunoassays (21-22).

Another PCB screening approach involves the use of room temperature phosphorescence (RTP) (23). The application is for screening soils. While the detection limit of the RTP tests is low (7.5 ppb for PCB-1221 to 620 ppb for PCB-1254 (23)), a substantial amount of manipulation is required; also, the screening methods developed to date require sophisticated laboratory instrumentation and trained operators. For example, a second-derivative method and synchronous scanning techniques have been proposed to improve RTP screening of PCBs (24).

There are also field screening techniques based on chloride ion determination. For example, PCBs are extracted from a soil sample using an organic solvent. Sodium is used to strip the chlorine atoms from the PCBs. The chloride ion content of the sample is then measured using either a colorimetric technique or an ion-selective electrode. The chloride ion concentration is used to calculate the PCB content of the original sample. The detection limit for PCBs in soil using commercially available kits is near 10 ppm (4).

Sutcliffe and co-workers (25) have compared colorimetric field kits (sodium reagent) (two kits by determination for total chlorine with sensitivity levels greater than 50 ppm and 500 ppm, respectively) to laboratory instrumental thermal neutron activation analysis as screening tools in a variety of oil matrices. The colorimetric tests were shown to be less reliable and more prone to interferences than instrumental thermal neutron activation analysis. The latter used thermal neutrons to irradiate the PCB contaminated oil samples and γ–rays for quantitative determination of total elemental halogen content of the oil. Several limitations in using the kits were pointed out, as well as cautions against attempts to screen water samples. This brings out the need to seek improvements for existing colorimetric field kits.

As mentioned earlier, the present research is meant to advance the state-of-the-technology in providing an attractive alternative to existing field screening methods for PCBs.

SECTION 4
APPROACH

OVERALL STRATEGY

Preliminary work toward development of a field screening method for PCBs based on the reduction of silver ion to silver metal was performed at the Harry Reid Center (26). The present research is meant to extend the early results toward a simple method for practitioners faced with problems of screening for PCBs in water and in following the course of PCB soil remediation efforts.

One of the key elements of the research involved extraction and concentration of PCBs from water onto solid matrices suitable for visualization reactions. The next step was to choose a chemical reaction or a molecular association effect which would give the operator a visual signal that PCBs are present. The approach, outlined in Figure 2, involved the use of SPE dipsticks to extract and concentrate the PCBs.

The sections to follow outline the rationale that was used to select in choosing the sample collection and visualization methodologies.

CHOICE OF THE PCB SAMPLE COLLECTION TECHNIQUE

Liquid-liquid extraction (LLE) is often used as the method of choice to isolate various organic pollutants, including PCBs, from water. LLE, however, can be time consuming and labor intensive and uses large volumes of solvents which subsequently produce disposal problems. Therefore, interest in replacing LLE with SPE is increasing.

SPE utilizes either columns containing solid sorbents or extraction membranes. Analytes are sorbed onto the SPE matrix, extracted, then analyzed using GC, thin-layer chromatography (TLC), or other techniques. The use of SPE membranes provides advantages not found in columns. Their use can reduce manual labor, speed sample processing, and reduce the volume of solvent needed for extraction (27-28). Several examples of utilizing membranes for the extraction and concentration of analytes from water exist in the literature. For example, PCB-contaminated water has been allowed to pass through SPE membranes, thus concentrating the PCBs (28). The PCBs were subsequently eluted from the membranes using small

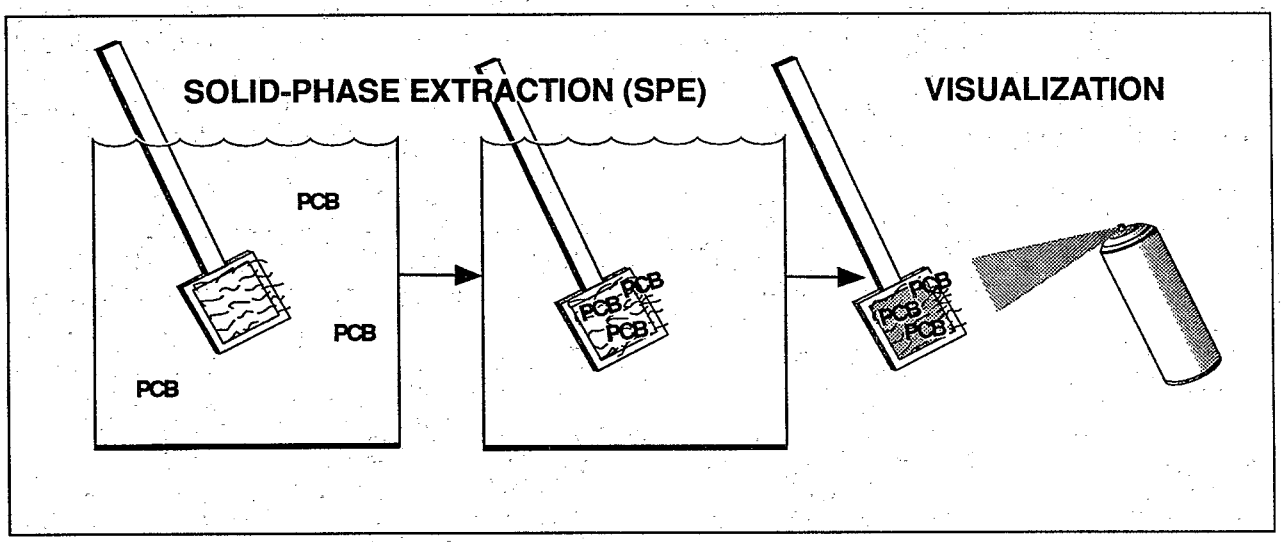


Figure 2. An Approach in the Development of a Field Screening Method for PCBs in Water.

volumes of organic solvent and analyzed using GC. In another study, SPE membranes were utilized in a dipstick mode (rather than filtration) for the extraction of phthalates from water (29). The phthalates were allowed to sorb onto the membranes from contaminated water and were subsequently thermally desorbed and characterized using ion mobility spectrometry (IMS).

In another study, direct solid-state fluorescence was used to analyze anthracene sorbed from water onto SPE membranes (30). One concept explored in the present research involves sampling for PCBs in water utilizing SPE membranes in a dipstick mode with visualization of the sorbed PCBs using a $AgNO_3$ spray and UV light (Figure 2).

Another possibility applicable to higher concentrations of PCBs (as would be found in surfactant solutions used for remediation of PCB contaminated soil) would be to use filter papers in a dipstick mode, not to extract the PCBs but simply to wet the paper with the test solution. Alternatively, drops of the surfactant wash solutions could be placed onto the substrates in preparation for the visualization step. Use of both SPE membranes and filter papers was examined in the present work. Emphasis was placed on the dipstick mode.

CHOICE OF VISUALIZATION REAGENTS

A number of reports appeared in the 1970s on the use of TLC for identification and, in some cases, quantification of PCBs. The most often cited visualization reagent was $AgNO_3$, which was used in combination with UV irradiation (Table 1). Although sample processing and extraction were normally required, sensitivities of 0.5-1.0 ppm of PCBs in wildlife specimens, muscle tissue, egg, and fat were easily attained (31-32). The visualization effect is the appearance of a gray color.

Table 1. Citations on Using Thin Layer Chromatography and $AgNO_3$-UV Light for the Detection of PCBs

Source	Sensitivity
Collins, 1972 (31)	0.05 µg; 1 ppm
Bush, 1973 (32)	1 µg; 0.5 ppm
Kawabata, 1974 (33)	8 - 17 µg
Ismail, 1974 (34)	1 µg
Mulhern, 1971 (35)	0.2 µd
Abbot, 1969 (36)	10 ng; 0.01 ppm
Anderson, 1984 (37)	1 mg (no $AgNO_3$)

Several papers have been published on the use of diphenylamine as a visualization reagent. An aluminum oxide chromatography substrate containing 1% diphenylamine exposed to 254 nm radiation resulted in a fluorescence signal in the presence of PCBs; this was measured by scanning with a densitometer (38-39). Another report described the use of diphenylamine and zinc chloride to give a light violet color with PCBs (40).

Based on a review of the available literature, it was judged that the use of $AgNO_3$ as a visualization reagent afforded the best opportunity of meeting the objectives of the report research.

DESIGN OF EXPERIMENTS

The design of experiments for the development and optimization of a field screening test for PCBs in water involved making certain decisions as well as identification of the parameters to be investigated. Two test formats were chosen for sample collection. One involved dipping SPE membrane or filter paper tabs into the test solution. In the other format, drops of the test solution were placed onto the filter paper tabs. Emphasis was placed on the dipstick format. Other formats such as filtering the test solution through SPE membranes could have been used as well; however, discussions with the sponsor and the proposed application of screening effectiveness of soil remediation by washing with aqueous surfactant led to the decision to keep the procedure as simple as possible with little training of the operator being necessary.

A co-sponsor of this report research (General Electric Corporate Research and Development) has developed a proprietary process for remediation of PCB-contaminated soil. Details are not available, however, it was indicated that adding surfactants (Neodol (R) 1-7 and Renex) to water increases the solubility of PCBs to the 500 ppm level. In such cases, sample concentration using SPE would not seem necessary. However, experiments using SPE to concentrate the PCBs were included to increase the applicability of the test to other screening scenarios.

An early decision, which drove the design of experiments for test development, was the choice of the visualization reaction. As mentioned above, a $AgNO_3$ spray was chosen which led to color changes as the result of silver ion reduction. This decision was based on a review of the literature on color reactions of PCBs, especially use of sprays for TLC.

Seven PCB analytes (as described in the Experimental section) were chosen for testing. The research experiments were divided into three major areas dealing with interferences, sensitivity, and optimization of procedures. A major interference expected was chloride ion. This was confirmed and will be described later. Experiments were designed to eliminate the interference. Humic acid was expected in organic soils and was also examined for any deleterious effects. Eleven semivolatile and volatile organic compounds, most containing chlorine or bromine atoms, were also tested as interferences.

Effects on sensitivity focused on the nature of the reaction matrices (i.e., ten different filter papers, one TLC gel plate and one SPE membrane were screened), the presence or absence of surfactants, and the nature of added surfactants.

Experiments were also designed in an attempt to optimize the test procedures. Effects of long and short wavelength UV light on the silver ion reduction were examined. The use of TiO_2 (a known photocatalyst) was checked for sensitivity enhancement purposes.

Fluorescence emission spectra of $AgNO_3$-PCB mixtures were also checked to see if there was any fluorescence enhancement. This might be an attractive alternative to the use of color change in applications where fluorescence instruments are available.

The various parameters, discussed above and utilized in the design of experiments, are summarized in Table 2. Not every parameter was checked against every other parameter to the fullest extent in the test plan. For example, not every one of the seven PCBs was checked against each of the different filter papers with each of the six surfactants.

Table 2. Parameters Utilized in the Design of Experiments for the Development of a Screening Test for PCBs in Water

Test analytes	Seven PCBs
Sample collection	SPE membrane Filter paper Dipstick mode Placing test solution drops onto the test matrices
Choice of visualization	$AgNO_3$ spray followed by UV light irradiation reaction
Interferences	Chloride ion Humic acid sodium salt Seven semivolatile organic compounds Four volatile organic compounds
Sensitivity	SPE membrane Ten different filter papers Present/absence of surfactants Nature of added surfactants
Optimization of test procedures	Short vs. long wavelength UV light Potential use of TiO_2 for sensitivity enhancement Fluorescence enhancement vs. color change

However, it has been judged that the tests chosen were more than sufficient to establish the sensitivity range, to appreciate what interferences to expect, to understand how the test might be utilized, and to form a base of information for test improvements.

SECTION 5
EXPERIMENTAL

REAGENTS AND MATERIALS

Silver nitrate ($AgNO_3$), humic acid (sodium salt, reagent grade, technical), Triton X-100 ($CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4(OCH_2CH_2)XOH$, X = 10 (avg)), Triton X-100 (reduced) ($CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_8(OCH_2CH_2)_XOH$, X = 10 (avg)), and Triton X-405 (reduced) ($CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_XOH$, X = 40 (avg)) were obtained from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. Dow Corning Z-6020 silane (aminoethylaminopropyltrimethoxysilane) was a sample from Dow Corning, Midland, Michigan. Sodium chloride was obtained from Mallinckrodt, Paris, Kentucky. Methanol (high purity solvent) was purchased from Burdick & Jackson, Muskegon, Michigan. PCBs (Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260) were gifts of the U.S. EPA Environmental Monitoring System Laboratory, Las Vegas, Nevada. These are authentic PCB samples of quality assurance purity drawn from the U.S. EPA Quality Assurance Materials Bank. Anion exchange resin and membrane were brought from Bio-Rad Laboratory, Richmond, California. 4-Bromobiphenyl, 1-bromohexane, 1-bromododecane, 1-chlorobenzene, 1-chlorohexane, and 1-chloronaphthalene were from Eastman Kodak Company, Rochester, New York. Deionized water, $CHCl_3$, CCl_4, $Cl_2CHCHCl_2$, CH_2Cl_2, TiO_2, and biphenyl, were obtained from the Chemistry Department, UNLV.

Neodol (R) 1-7 (a C_{11} alcohol ethoxylate with an average of 7 moles of ethylene oxide per mole of alcohol) and Renex KB (a polyoxyethylene alkyl alcohol) are products of the Shell Chemical Co., Houston, Texas, and ICI Americas Inc., Wilmington, Delaware, respectively. Samples were obtained from General Electric Corporate Research and Development, General Electric Co., Schenectady, NY. The composition of all of the surfactants used is given in Table 3.

Table 3. Composition of Surfactants

Surfactant	Composition
Neodol R 1-7	a C_{11} alcohol ethoxylate with an average of 7 moles of ethylene oxide per mole of alcohol
Renex KB	a polyoxyethylene alkyl alcohol
Triton X-100	$CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4$-$(OCH_2CH_2)XOH$, X = 10 (avg)
Triton X-100 (reduced)	$CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_8$-$(OCH_2CH_2)XOH$, X = 10 (avg)
Triton X-405 (reduced)	$CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4$-$(OCH_2CH_2)XOH$, X = 40 (avg)
Dow Corning Z-6020	aminoethylaminopropyl-trimethoxysilane

The SPE membranes, C-18 Empore™, were obtained as disks from Analytichem International, Harbor City, California, with a composition of 90% (by weight) of octadecyl (C18)-bonded silica particles and 10% polytetrafluoroethylene (PTFE). Filter papers (Whatman 1, 40, 42, 541, 542) and silica gel plates for TLC (Whatman) were from W & R Balston Limited, Maidstone, England; S&S 604 and S & S 2043A filter papers were from Carl Schleicher & Schuell Co.; S/P filter paper (F2406-125) was from American Hospital Supply Corporation, Evanston, Illinois; VWR filter paper (catalog number 28320-143, grade 615) was from VWR Scientific Inc., Mt. Holly Springs, Pennsylvania; printing paper (Matrix, Xerographic D.P. Hi-Speed White 434236) was from Zellerbach. All filter papers were available from the HRC, UNLV.

EQUIPMENT

The UV portable light source utilized in the visualization experiments (Mineralight Lamp-

Model UVG-11, 254 nm) was obtained from Ultra-Violet Products, Inc., San Gabriel, California. A viewing box containing both 254 and 365 nm light sources (9818 Series Darkroom) was from Cole-Parmer Instrument Co., Chicago, Illinois. The spectrofluorometer (Spex Fluorolog-model 1680) was from Spex Industries, Inc., Edison, New Jersey; the light sources were 450 W xenon lamps.

TEST PROCEDURES

Tabs (1 x 1 cm) were cut from the filter papers or SPE membrane disks. Solutions of the PCBs were prepared in methanol and diluted to different concentrations with deionized water with and without surfactant. The control solutions also contained surfactants if used in the tests. The surfactant concentrations are given by weight percent.

The SPE tabs were conditioned by dipping into methanol immediately before use. This allowed them to be wet easily by the aqueous test solutions. The SPE tabs were either suspended in the various PCB test solutions for 30 minutes or dipped into them and quickly removed. The tabs were sprayed with 0.059 M $AgNO_3$ in methanol and irradiated with UV light (254 nm) for 1-3 minutes. The development of color relative to a control tab after 1 minute served to indicate the presence of PCBs.

The filter paper tabs (1 x 1 cm) were dipped into the PCB test solutions, removed, sprayed with 0.059 M $AgNO_3$ methanolic solution, and exposed to UV light (254 nm) for 3 minutes in the same manner as mentioned above. The distance between the lamp and filter paper tabs was 1.5 cm.

Interference testing followed the same procedure except for very volatile analytes, in which cases, quartz plates were used to cover the test tabs during the UV irradiation and color development stages. The interferences which were tested in this research were chloride ion, humic acid, biphenyl, 1-chloronaphthalene, 1-chlorobenzene, 4-bromobiphenyl, 1-bromohexane, 1-chlorohexane, 1-bromododecane, $CHCl_3$, CCl_4, $Cl_2CHCHCl_2$, and CH_2Cl_2.

Ameritone paint color sheets were employed as standards for defining the exact color and intensity. All results were based on at least duplicate runs, but mostly triplicate.

FLUORESCENCE MEASUREMENTS

Emission spectra were measured with excitation at either 254 or 290 nm, depending on the experiment. Tabs (1 x 2 cm) were examined on their front surfaces with excitation and emission bandpasses at 4.25 and 2.13 nm, respectively. S & S 2043A filter paper was chosen based on reports that it gave high RTP yields with PCBs (23-24). Whatman 541 filter paper was examined as well. Various concentrations of PCB-1232 (0, 1, 10, 100 ppm) in aqueous solution containing 3% by weight Renex KB surfactant were examined.

A 5.0 µL aliquot of the PCB solution was spotted onto the center of a filter paper tab. The tab was placed onto a glass slide, dried under an infrared heat lamp for 5 minutes and its emission spectrum measured. A 5.0 µL aliquot of $AgNO_3$ solution was then spotted onto the center of the tab, followed by heat lamp drying, and spectral measurement. This procedure was reversed in some experiments wherein the $AgNO_3$ solution was spotted first.

SECTION 6
RESULTS AND DISCUSSION

USE OF SOLID PHASE EXTRACTION (SPE) MEMBRANES

Initial results indicated that the use of SPE membranes in combination with the $AgNO_3$ visualization reaction leads to detection of PCBs in water (not containing surfactants) at the 0.5-1.0 ppm level. This was when the SPE tabs were allowed to remain in the test solutions for one hour in a passive mode. Allowing the SPE tabs to remain in the solutions for 22-24 hours did not improve the sensitivity. Decreasing the tab exposure time to 30 minutes raised the detection limit to 5 ppm.

Methanol was used to initially dissolve the PCB samples as part of the test solution preparations. However, it is suspected that adsorptive losses occurred on the surfaces of the glass containers used for the experiments, irrespective of the presence of methanol, since the PCB concentrations were near or over their solubility limits in water. Absorptive losses of PCBs on glassware are well documented (4). Due to this loss, the detection limits observed in the initial experiments in the absence of surfactant are undoubtedly high. However, if wall loss was significant, longer exposure of the tabs should have made a difference; this was not noted.

SPE membranes were also employed to extract PCBs from aqueous solution containing surfactant by suspending tabs in the test solutions for 30 minutes (Table 4). The detection limit was found to vary between 0.5-5 ppm depending on the PCB. This compares well to the preliminary results without surfactant.

EXAMPLES OF FINDINGS USING FILTER PAPERS

Examples of experimental results for PCB determination in aqueous surfactant solutions are given in Tables 5-6. The results were obtained by dipping Whatman 541 tabs into aqueous solutions containing various PCBs and either Renex KB or Neodol (R) (1-7) surfactants, removing the tabs quickly, adding $AgNO_3$, and irradiating the tabs with UV light. These particular surfactants were emphasized throughout the research because of the interest of the co-sponsor (General Electric Corporate Research and Development) in their use in remediation of PCB-contaminated soil. The numbers and tones (e.g., 2H56G Lustre Beige) refer to Ameritone™ paint color sheets as mentioned in the Experimental section.

The results given in Tables 5 and 6 show that PCBs can be detected on Whatman 541 filter paper in the presence of relatively high concentrations of the surfactants Renex KB or Neodol (R) 1-7. The colors differed somewhat depending on the PCB and the surfactant. There does not appear to be a trend showing that the PCBs containing either a higher or lower percentage of chlorine are more easily detectable. At 500 ppm PCB concentrations the test colors were basically brown with some gray being evident. It was interesting to find that the control tabs showed very little color even though the solutions contained 3% surfactant.

The sensitivity limit in detecting various PCBs in solutions containing either Renex KB or Neodol (R) 1-7 was 1.0 ppm (Tables 7 and 8).

It is also interesting to note that dipping the filter paper Whatman 541 tabs and quickly removing them is about as sensitive as the technique in which SPE tabs (in the presence of surfactant) were allowed to stand for 30 minutes. The surfactant may be competing with the PCBs for sorption onto the SPE medium.

An experiment was performed to determine whether the presence of surfactant had an effect on the test sensitivity. Using PCB-1232 and Whatman 541 tabs in the presence and absence of Neodol (R) 1-7, no difference was found. PCB-1232 was detected at 1 ppm in both cases.

EFFECT OF INTERFERENCES

Chloride Ion. It was expected that Cl^- would interfere in the visualization reaction since AgCl

Table 4. Results with PCBs Using SPE Tabs Suspended for 30 Minutes in Test Solutions Containing 3% Surfactant

	0 ppm	0.1 ppm	0.5 ppm	1 ppm	5 ppm	10 ppm	Sensitivity
PCB-1232 (R) 1-7 Neodol	Negative	Negative	Negative	Negative	Light gray, lighter than 1H50F Shagbark	Light gray, similar to 1H50F Shagbark	5 ppm
PCB-1254 Neodol (R) 1-7	Negative	Negative	Very light gray, similar to 2H45G	Light gray, similar to 1H49F Taupe	Gray, similar to 2M41D Dawn Phantom	Dark gray, lighter than 2M42D Coffee Tint	0.5 ppm
PCB-1221 Renex KB	Negative	Negative	Negative	Negative	Very light gray, similar to 1H49F Taupe	Very light gray, similar to 1H50F Shagbark	5 ppm
PCB-1232 Renex KB	Negative	Negative	Negative	Light gray, a little lighter than 2H45G Water	Light gray, similar to 1H49F Taupe	Light gray, similar to 1H50F Shagbark	1 ppm

Table 5. Test Results with PCBs Using Whatman 541 Tabs and 3% Renex KB

	0 ppm	1 ppm	10 ppm	100 ppm	500 ppm
PCB-1016	Negative	Negative	Light gray	Gray	Brown, some gray
PCB-1221	Negative	Negative	Light gray	Light gray	Brown, some gray
PCB-1232	Negative, lighter than 2H56G Lustre	Very light gray, lighter than 2M40E Liquorice Tint	Light gray, similar to 2M40E Liquorice Tint	Light gray, similar to 1M50E Dolphin	
PCB-1242	Beige, Negative, lighter than 2H56G Lustre Beige	Light gray, lighter than Phantom	Light gray, similar to 2M41D Fawn Phantom	Gray, a little darker than 2M39D Meteor	
PCB-1248	Negative	Negative	Very light gray	Gray	Brown, some gray

Table 6. Test Results with PCBs Using Whatman 541 Tabs and 3% Neodol (R) 1-7

	0 ppm	1 ppm	10 ppm	100 ppm	500 ppm
PCB-1232	Negative	Very light gray	Light gray	Light gray	Brown, some gray
PCB-1242	Negative, lighter than 2H45F Warm Beige	Very light gray, lighter than 2M43E Gobi	Light gray, a little lighter than 2M41D Fawn Phantom	Gray, a little grayer than 2M42D Fawn Phantom	
PCB-1248	Negative, lighter than 2H45F Warm Beige	Very light gray, a little grayer than 2M43E Gobi	Light gray, a little lighter than 2M41D Fawn Phantom	Gray, lighter than 2D40C Drake, darker than 2M39D Meteor	
PCB-1254	Negative	Light gray	Light gray	Gray	Brown, some gray

Table 7. Results of Sensitivity Experiments Using Whatman 541 Tabs and 3% Renex KB

	0 ppm	0.5 ppm	1 ppm	Sensitivity
PCB-1232	Negative	Negative	Very light gray	1 ppm
PCB-1242	Negative, lighter than 2H45F Warm Beige	Very light gray, lighter than 2M45F Warm Beige	Very light gray, a little grayer than 2M43E Gobi	1 ppm
PCB-1248	Negative, lighter than 2H45F Warm Beige	Negative, lighter than 2H45F Warm Beige	Very light gray, a littler grayer than 2M43E Gobi	1 ppm
PCB-1254	Negative	Negative	Light gray	1 ppm

Table 8. Results of Sensitivity Experiments Using Whatman 541 Tabs and 3% Neodol (R) 1-7

	0 ppm	0.5 ppm	1 ppm	Sensitivity
PCB-1232	Negative	Negative	Very light gray	1 ppm
PCB-1242	Negative, lighter than 2H45F Warm Beige	Negative, lighter than 2M45F Warm Beige	Very light gray, a little grayer than 2M43E Gobi	1 ppm
PCB-1248	Negative	Negative, lighter than 2H45F Warm Beige	Very light gray	1 ppm
PCB-1254	Negative	Negative	Light gray	1 ppm

would be formed and is sensitive to light. The interference of Cl^- was confirmed using Whatman 541 tabs in the absence of surfactants.

The sensitivity for Cl^- was found to be 1 ppm. No color was observed at the 0.5 ppm level. Positive tests were found with PCBs at the 0.5 ppm level but this is understandable since the equivalent Cl content in the PCBs would be at a higher concentration. The colors matched closely those obtained using PCBs, i.e., very light gray at 1 ppm and brown at highest concentrations (in this case, 1000 ppm Cl^-).

The Cl^- interference was eliminated by adding a few granules of an anion exchange resin (AG 1-X2) to the test solution, lightly agitating, and performing the test in the usual manner. The results were negative up to 1000 ppm Cl^-.

The anion exchange resin (0.1 g) was also added to 1 mL solution containing 3% Neodol (R) 1-7 and various concentrations of PCB-1232 (1-500 ppm) in the absence of Cl^-. The detection limit for PCB-1232 in the presence of the Neodol was found to be 1 ppm as mentioned earlier (Table 6). However, in the presence of the anion exchange resin, the limit was raised to 10 ppm implying sorption of the PCB by the resin. It is judged that the detection limit could be lowered to 1 ppm with optimization of the amount of resin used; however, this was not pursued. It was important to find that Cl^- interference could easily be removed by using an anion exchange resin.

It was also found that Cl^- interference could be removed by simply washing the filter paper tabs with distilled water. Unfortunately, PCBs were also removed easily from the paper. This was also true for SPE tabs that were dipped into PCB solutions and quickly withdrawn. However, PCBs are not removed to any extent from SPE tabs that have been exposed to PCB solutions for a period of time or from SPE membranes through which the PCB solutions have been allowed to filter. An organic solvent is required to remove the PCBs. Therefore, in cases of high contamination by Cl^-, the use of SPE tabs for PCB sorption for a period of time followed by a water wash may be very attractive.

Organic Compounds. Seven volatile and semi-volatile compounds and one nonvolatile organic compound were tested initially as interferences (Table 9). They are listed by order of reactivity to $AgNO_3$-UV visualization with the least reactive being shown first. One of the major interferences that might be expected in ground water in the vicinity of high organic content soil is humic acid. However, this posed the least interference among the compounds tested, even at 1000 ppm. Humic acid was also added to PCB test solutions but was not found to interfere up to 500 ppm. A pink background became evident at 1000 ppm.

Several of the compounds, including biphenyl, showed light pink colors at 100 ppm. With the PCBs, pink colors were not found. Therefore, these would not be considered as serious interferences. However, it is clear that most aromatic and aliphatic compounds containing halogen (either Cl or Br) should be expected to interfere. In field screening scenarios, the sites have already been characterized and the pollutants are known. In remediation processes, the target compounds are known as well. If there are a number of organohalogen pollutants, the $AgNO_3$-UV procedure can serve as a class test. However, not all organochlorine compounds will necessarily react readily. Four volatile compounds ($CHCl_3$, CCl_4, $Cl_2CHCHCl_2$, and CH_2Cl_2) were investigated as neat liquids on Whatman 541 tabs. A drop of methanolic $AgNO_3$ was placed on the tab containing the neat liquid; the tab was covered with a quartz plate and irradiated for 30 seconds using 254 nm light. Carbon tetrachloride developed the most color (Table 10). Tests were also performed with CCl_4 diluted in methanol. However, no differences were observed in comparison with the blanks up to 3000 ppm, i.e., the test is much more sensitive for PCBs than for CCl_4.

EFFECT OF MATRIX

Ten filter papers, one SPE membrane, and one TLC silica gel plate were examined as matrices for the $AgNO_3$-UV visualization test using PCB-1232 in solutions containing 3% Neodol (R) 1-7. Most

Table 9. Interference Test Results Using Whatman 541 Tabs and Neodol (R) 1-7

Interferant	0 ppm	1 ppm	10 ppm	100 ppm	500 ppm	1000 ppm
Humic Acid, Sodium Salt	Negative	Negative	Negative	Negative	Very light pink	Light pink
Biphenyl	Negative	Negative	Negative	Very light pink		
1-Chloronaphthalene	Negative	Negative	Almost blank	Light pink		
1-Chlorobenzene	Negative	Negative	Very light gray	Light gray		
4-Bromobiphenyl	Negative	Negative	Light gray	Light gray		
1-Bromohexane	Negative	Very light gray	Some gray, some pink	Some brown, Some pink		
1-Chlorohexane	Negative	Marginal	Light gray	Gray	Unstable color	
1-Bromododecane	Negative	Negative	Light brown	Some brown	Unstable color	

Table 10. Test Results with Neat Organochloro Liquids Using Whatman 541 Tabs

	Control	$CHCl_3$	CCl_4	$Cl_2CHCHCl_2$	CH_2Cl_2
Coloration	Negative	Very light brown, some gray similar to 2M56E County Garden	Gray, a little little darker than 1M49D Sandal Grove	Light brown, some yellow browner than 2M56E County Garden	None

of the papers and the TLC plate gave colors in the absence of PCB. These ranged from grays to browns of different shades and intensities (Table 11). As shown in the Table 11, the background interfered with no differences in color being detectable between the blanks and the tests up to 100 ppm of the PCB.

Whatman 541 filter paper gave a negative blank. The blank for Whatman 542 was a very light gray, but the background did not interfere with the PCB test and did not raise the detection limit. The blank with the C-18 Empore™ SPE membrane was also negative. Whatman 541 appears to be the best choice among the filter papers examined and was used in most of the experiments, many of which were described earlier.

Whatman filter papers 541 and 542 are hardened ashless papers manufactured for use under strong acid or alkaline conditions. Filter paper 541 is for large or gelatinous precipitates. Filter paper 542 is for high retention of fine particles. Whatman 1 is a classic general purpose filter paper. Whatman 40 and 42 are ashless papers. Paper 40 is a general purpose gravimetric one, while paper 42 is for extremely fine precipitates. No information was found on chemical composition or any additives which might be present.

It is clear that many matrices may be expected to increase the sensitivity of Ag^+ to photodegradation. In continued development of the visualization test, it seems worthwhile to screen a large number of different types of TLC plates, membranes, and papers. It is expected that improvement might be made in test sensitivity by finding an optimum balance of matrix properties between acceptable blanks and enhancement of photosensitization. Possible candidates are glass fiber paper and hydrophilic polypropylene membrane which do not give responses in preliminary blank determinations.

EFFECT OF SURFACTANT

Table 12 gives test results with PCB-1232 solutions containing different surfactants. Triton X-100 gave a blank response which masked the PCB test results at 1 and 10 ppm. The Dow Corning Z-6020 blank response completely masked the test results. This is not surprising. Triton X-100 contains an aromatic ring which would be expected to complex with Ag^+. The Dow Corning material contains amino groups which should complex readily with Ag+ and facilitate photodegradation.

Triton X-100 (reduced) and Triton X-405 (reduced) contain cyclohexyl rings. These compounds seem to inhibit the photodegradation with an overall effect of raising the detection limit for the PCB to 10 ppm and 100 ppm, respectively.

The Neodol (R) 1-7 and Renex KB gave acceptable blank responses with the latter giving a slight coloration. It was interesting to find that use of a mixture of surfactants (Neodol (R) 1-7 and Triton X-100 (reduced), each 1.5% by weight in the solutions), led to a decrease of the detection limit for PCB-1232 to 0.5 ppm using either Whatman 541 or C-18 Empore™ SPE tabs; the UV exposed time was three minutes (Table 13). Whatman 42 tabs, which were previously found to cause high blanks, continued to do so but the colors differed somewhat.

The choice of surfactant will undoubtedly be driven more by effectiveness in remediation of PCB contaminated soil rather than by impact on a field screening test. It was fortunate to find that Neodol (R) 1-7 and Renex KB did not adversely affect the $AgNO_3$-UV visualization test since these compounds are currently being used for soil remediation.

REACTION MECHANISM

The mechanism of the visualization reaction most likely involves complexation of the PCBs with silver ion followed by reduction to Ag metal (Figure 3). Various studies have led to the conclusion that Ag^+ forms complexes with aromatic rings (12-14). Crystals of a $AgClO_4$ complex with benzene have been isolated (41). Complexes of PCBs with Ag^+ undoubtedly occur as well, though stability may vary depending on the PCB isomer and the number of Cl atoms. If Ag^+ complexes of PCBs involve π electron bonding (as with benzene), then PCBs with greater numbers of Cl atoms should yield less stable complexes. The photodegradation of silver salts to silver metal has been known for many years. It is clear from the results of the current research that the presence of PCBs accelerates the photodegradation.

Many reports are available on the dechlorination of PCBs under the influence of light (e.g., 15-17, 42-44). There have been various studies on enhancing the photodechlorination. For example, surfactants and sodium borohydride have been found to be useful (43). Silver ion may enhance the photodechlorination and form AgCl. Direct

Table 11. Test Results with PCB-1232 Using Different Matrices with 3% Neodol (R) 1-7

	0 ppm	1 ppm	10 ppm	100 ppm
Whatman 1	A little gray, brown (little browner than 1D47C King Bird)	A little gray, brown (little browner than 1D47C King Bird)	A little gray, brown (little browner than 1D47C King Bird)	A little gray, brown (litle browner than 1D47C King Bird)
Whatman 40	Brown, similar to 2M42Z Silver Mushroom	Brown, similar to 2M42Z Silver Mushroom	Brown, similar to 2M42Z Silver Mushroom	Brown, similar to 2M42Z Silver Mushroom
Whatman 42	Very light gray, lighter than 2M42D Fawn Phantom	Very light gray, lighter than 2M42D Fawn Phantom	Very light gray, lighter than 2M42D Fawn Phantom	Light gray, similar to 2M41D Fawn Phantom
Whatman 541	Negative	Very light gray	Light gray	Light gray, similar to 2M41D Fawn Phantom
Whatman 542	Very light gray, similar to 2M45E Gobi	Light gray, a little lighter than 2M41D Fawn Phantom	Light gray, similar to 2M41D Fawn Phantom	Gray, some brown similar to 2M45D Sand Stream
S & S 604	Pink, similar to 2M46D Solomon Sand	Pink, similar to 2M46D Solomon Sand	Pink, similar to 2M46D Solomon Sand	Pink, similar to 2M46D Solomon Sand
S & S 2043A	Dark gray, darker than 2Y34A Tara	Dark gray, darker than 2Y34A Tara	Dark gray, darker than 2Y34A Tara	Dark gray, darker than 2Y34A Tara
S/P	Gray, some brown, a little browner than 2D40C Drake	Gray, some brown, a little browner 2D40C Drake	Gray, some brown, a little browner 2D40C Drake	Gray, some brown, a little browner than 2D40C Drake
VWR	Dark gray, darker than 2M40C Drake	Dark gray, darker than 2M40C Drake	Dark gray, darker than 2M40C Drake	Dark gray, darker than 2M40C Drake
C-18 Empore™	Negative, similar to 1H50G Autumn Acorn	Very light gray, similar to 1H50F Shagbark	Light gray, similar to 2M40E Liquorice Tint	Gray, similar to 2M42E Silver Mushroom
Matrix printing paper	Brown, lighter than 2U48B Rocket	Brown, lighter than 2U48B Rocket	Brown, lighter than 2U48B Rocket	Brown, lighter than 2U48B Rocket
Plate for TLC (silica gel)	Dark brown, similar to 2UM25A Brigadoo	Dark brown, similar to 2UM25A Brigadoo	Dark brown, similar to 2UM25A Brigadoo	Dark brown, similar to 2UM25A Brigadoo

Table 12. Test Results with PCB-1232 Using Whatman 541 Tabs and Different Surfactants (3%)

	0 ppm	1 ppm	10 ppm	100 ppm
Triton X-100	Some yellow, some black	Some yellow, some black	Some yellow, some black	Gray
Triton X-100, reduced	Negative, darker than 2H30P Airy	Negative, similar to 2H30P Airy	Light gray, lighter than 6M41D Fawn Phantom	Gray, similar to 2M40E Liquorice Tint
Triton X-405, reduced	Negative, almost white	Negative, almost white	Negative, almost white	Gray
Dow Corning Z-6020, Silane	Brown, darker than 2U41B Brown Benedictine	Brown, darker than 2U41B Brown Benedictine	Brown, darker than 2U41B Brown Benedictine	Brown, darker than 2U41B Brown Benedictine
Neodol (R) 1-7	Negative	Very light gray	Light gray	Light gray
Renex KB	Negative, lighter than 2H56G Lustre Beige	Very light gray, lighter than 2M40E Liquorice Tint	Light gray, similar to 2M40E Liquorice Tint	Light gray, similar to 1M50E Dolphin

Table 13. Test Results with PCB-1232 on Different Matrices Using a Mixture of 1.5% wt Triton X-100 (reduced) and 1.5% wt Neodol (R) 1-7

	0 ppm	0.5 ppm	5 ppm	50 ppm
Whatman 541	Negative, similar to 1H50G Autumn Acorn	Light gray, lighter than 1H50F Shagbark	Light gray, similar to 1H50F Shagbark	Gray, similar to 2M40E Liquorice Tint
C-18 Empore™	Negative, lighter than 2H40G	Light gray, similar to 1H59F Taupe	Light gray, a little darker than 1H59F Taupe	Gray, some brown similar to 2M41D Fawn Phantom
Whatman 42	Light brown, similar to 2M43E Gobi	Light brown, similar to 2M43E Gobi	Light brown, similar to 2M43E Gobi	Gray, similar to 2M41D Fawn Phantom

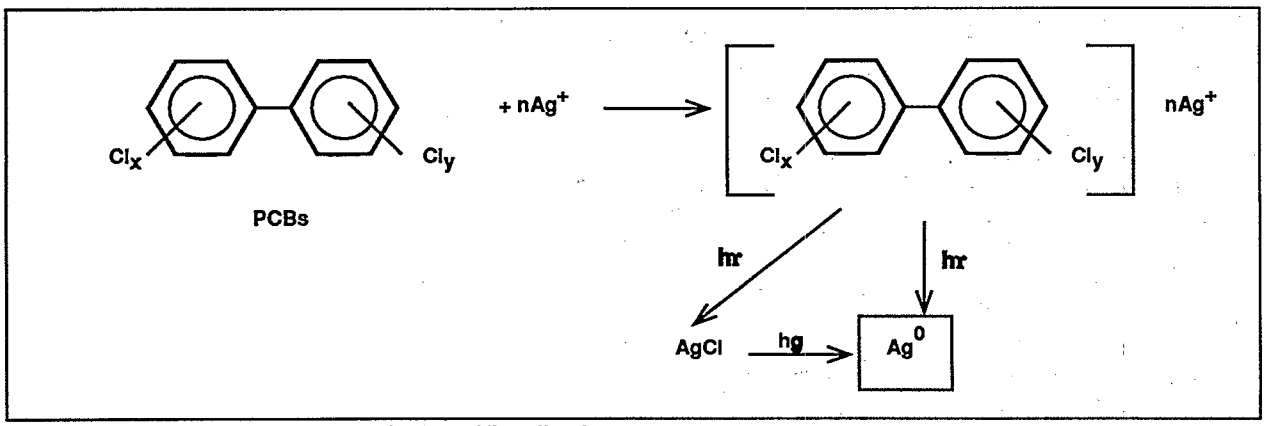


Figure 3. Possible Mechanism of the PCB Visualization.

reduction of Ag^+ by the PCB under influence of light is possible but a less likely mechanism in view of what has been reported on PCB photodegradation giving Cl^-.

Humic acid also has aromatic rings; however, it did not sensitize the photodegradation of Ag^+. Humic acid is a large and complicated molecule. The benzene rings may not be readily available. Biphenyl gave a weak response at 100 ppm (Table 9). It is also clear from the interference testing that an aromatic ring is not necessary. Several aliphatic bromo and chloro compounds also gave the color. However, the lowest detection limits were obtained with PCBs.

EFFECT OF LIGHT WAVELENGTH

A UV viewing box, equipped with 254 and 365 nm light sources, was used to check the effect of wavelength on the visualization of sodium chloride on Whatman 541 tabs. The use of 365 nm light gave a response, but it took three times longer than with the 254 nm source. There is no particular advantage in using the longer wavelength light. Sunlight through a window is also effective, but the intensity was very high on the particular day the experiment was run, and the control tabs changed color upon being exposed to sunlight after 1 minute.

Choice of light intensity is a consideration. The 254 nm lamp in the UV box was less intense than the portable lamp normally used. Irradiation for 3 minutes of Whatman 541 tabs containing sodium chloride gave a detection limit of 10 ppm, whereas a limit of 1 ppm was found with the portable lamp.

EFFECT OF TITANIUM DIOXIDE

A possible approach to sensitivity enhancement is to utilize a photocatalyst to facilitate dechlorination of the PCBs. A photocatalyst which has been investigated for both oxidation and reduction reactions is TiO_2 (47-48). Several experiments were performed with TiO_2 using PCB-1232. For example, TiO_2 was deposited on Whatman 541 paper by filtering a suspension of TiO_2 in $AgNO_3$ solution through it. A drop of the PCB test solution was placed on the paper followed by UV irradiation. The amount of TiO_2 and $AgNO_3$, pH and the techniques were varied. Unfortunately, high blanks were observed. Colors were obtained in as little as 6 seconds with 365 nm irradiation. The TiO_2 was found to be an exceptionally good photocatalyst for the reduction of Ag^+. Use of TiO_2 in the absence of Ag+ showed no color with PCB-1232 on irradiation with 254 nm light for 30 seconds. The use of a catalyst for the dechlorination of PCB as part of a field screening test is still judged to be a good idea but requires additional experimentation.

RESULTS WITH SAMPLES FROM SOIL REMEDIATION

One of the co-sponsors of this work, General Electric Corporate Research and Development, has developed a proprietary process for remediation of soils contaminated with PCBs by washing with surfactants. Details of the process are not available, but two of the surfactants being used are known since samples were supplied for this investigation. The use of surfactants in solution above their critical micelle concentrations to increase the solubility of hydrophobic compounds is known. It was mentioned by the sponsor that the soil washings could contain PCBs at the 500 ppm level. A recent paper on use of surfactants to remediation soil mentioned that PCB-1260 has shown an increase in solubilization of 660,000 times relative to that in water alone (49).

Ten samples of surfactant solutions of PCB-1260 from soil washing operations using 2% Renex KB surfactant were received from General Electric Corporate Research and Development. The samples contained some sediment which was allowed to settle. Test samples were withdrawn from the top. Half of the samples had a PCB concentration of approximately 10 ppm and the other half approximately 40 ppm. These were not based on analyses but on differences between analyses of soil samples before and after a wash. All contained Renex KB surfactant at the 2% level.

The procedure described previously was followed except that pieces of anion exchange membranes were added to the test solutions to eliminate any Cl^- interference. Solutions of PCB 1260 at 10 ppm and 40 ppm, containing 2% Renex KB, were used as controls. There was no difficulty in differentiating the test samples by level of concentration. However, the colors obtained with the General Electric samples were darker than expected when compared to the controls. The colors from the General Electric 10 ppm and 40 ppm samples were closer to colors expected from 40 ppm and 400 ppm, respectively. A control soil wash, i.e., the surfactant wash from an equivalent clean soil was not available. Therefore, it is not known whether

an interference might have been caused by a component from the soil. Also, it is not known whether other ingredients were present in the soil wash.

Though the test results were high, they were promising. Of course, the possibility exists that they were higher concentrations than labeled, but the solutions were not analyzed. If the tabs had been performed on site, more information would have been available, and appropriate changes to the test and/or the color interpretation most likely could have been made on the spot.

BLIND SAMPLE TEST

Five blind samples were prepared by co-worker Robert L. Curiale. At low concentrations, the results (Table 14) were very good. Two samples that were reported at concentrations of 5 ppm and 30 ppm were actually 3 ppm and 25 ppm, respectively. The three remaining samples were reported at best between 100 and 500 ppm; their colors were indistinguishable amongst one another. In actuality, they were 175, 325, and 450 ppm.

Table 14. Results of Blind Sample Test

Actually Con.	3 ppm	25 ppm	175 ppm	325 ppm	450 ppm
Estimated Con.	5 ppm	30 ppm	100-500 ppm	100-500 ppm	100-500 ppm

FLUORESCENCE MEASUREMENTS

Fluorescence measurements were performed with PCB-1232 solutions containing 3% Renex KB on Whatman 541 and S&S 2043A filter papers to see if spraying with $AgNO_3$ would enhance the PCB fluorescence. If so, it might offer the opportunity to decrease the detection limit.

The S & S 2043A paper prepared from 1, 10, and 100 ppm solutions of PCB-1232 gave emission peaks at 326 nm using 290 nm excitation. Excitation at 254 nm gave a peak at 316 nm. Spectra obtained using control solutions without PCBs confirmed that the emission peaks were from the PCB.

Whatman 541 filter paper was one of the best for the visualization experiments but did not serve as a useful matrix for fluorescence measurements. No emission was found for papers prepared from 10 ppm solutions of PCB-1232. Spotting $AgNO_3$ solution onto the PCB tabs did not lead to the appearance of any peaks above the background of the paper.

Spotting the S & S 2043A filter paper containing PCBs with methanolic $AgNO_3$ led to complete quenching of the emission (Figure 4). This may not be surprising since the paper itself photosensitizes the reduction of Ag^+. Silver metal may be serving to mask the PCB fluorescence. S & S 2043A is one of the best paper substrates for measurement of solid state PCB emission and RTP but interferes in the visualization test. Several modifications were made in the procedure such as spotting the $AgNO_3$ first, followed by the PCB. However, this was not successful.

The fluorescence experiments were not pursued further.

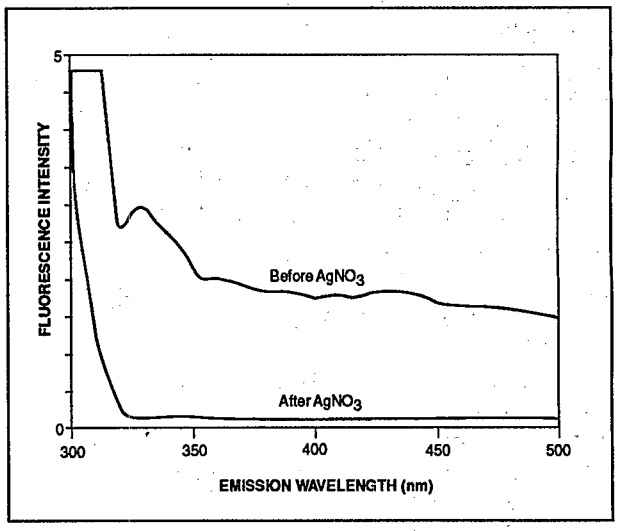


Figure 4. Solid State Emission Curves of 10 ppm PCB-1232 with 3% Renex KB on Tabs of S & S 2043A Filter Paper Before and After Adding 0.059 M $AgNO_3$ in Methanol Solution.

IMPLICATIONS FOR FIELD SCREENING

The basic idea of using simple sample handling methods in combination with visualization techniques to detect PCBs in water is attractive for field screening applications based on results of the present research. The method developed in this research is rapid, simple, and of low cost. It appears adaptable in detecting from 0.5 to 500 ppm or more of PCBs in soil remediation scenarios where relatively high concentration of surfactant are present. Use of simple color charts can be used to determine whether PCBs are present or absent above or below a predetermined threshold at a particular site.

If ppm contamination of PCBs is suspected, the sample can be collected by using a filter paper dipstick or by placing drops of the test solution onto paper tabs. If ppb concentration are suspected, SPE techniques will have to be utilized. SPE dipsticks can be placed into the solution and allowed to stand for a period of time or the solution filtered through the SPE membranes. The sample handling is summarized in Figure 5 as a decision tree.

One potential barrier to the utility of this procedure for PCBs is the interference of other organohalogen compounds. However, the method could be expanded to field screening for organohalogen compounds in general if they were suspected to be present.

There are many tradeoffs in choosing methods for field screening and measurements, including cost, response time, sensitivity, selectivity, size, and weight. Figure 6 gives a comparison of GC/MS, immunoassay, and $AgNO_3$/UV methods for several of the major tradeoffs in screening for PCBs. GC/MS and immunoassay stand out in selectivity and sensitivity, whereas the $AgNO_3$/UV procedure appears attractive relative to factors of cost, time, and simplicity. It would be very useful in the next development stage to perform the test in the field in a soil remediation scenario and compare the procedures and results to commercially available PCB immunoassay kits.

The results of the work brought out several areas of opportunity for test improvement. An obvious one would be to expand the search for matrices (TLC plates, membranes, and filter papers) which give an optimum balance between acceptable blanks and enhancement of photosensitization. Another opportunity is to search for photocatalysts which speed up dechlorination of PCBs but do not sensitize reduction of Ag^+. Also, a detailed examination of photographic chemistry including color photography may identify opportunities for enhanced sensitivity and selectivity. The PCB visualization relates to photography. The presence of PCB in a solution may drastically alter the rate of image development using commercially available film or photographic paper.

The use of SPE membranes can be expanded by incorporating indicator molecules in the matrix. The membrane could serve to both extract and detect pollutants either in water or in air (Figure 7). Preliminary experiments with tetracyanoethylene (an electron acceptor) in C-18 Empore™, SPE membranes, led to the appearance of color with toluene. PCBs were not tested.

As with all field screening methods, laboratory analyses need to be performed to confirm test results consistent with previously set data quality objectives.

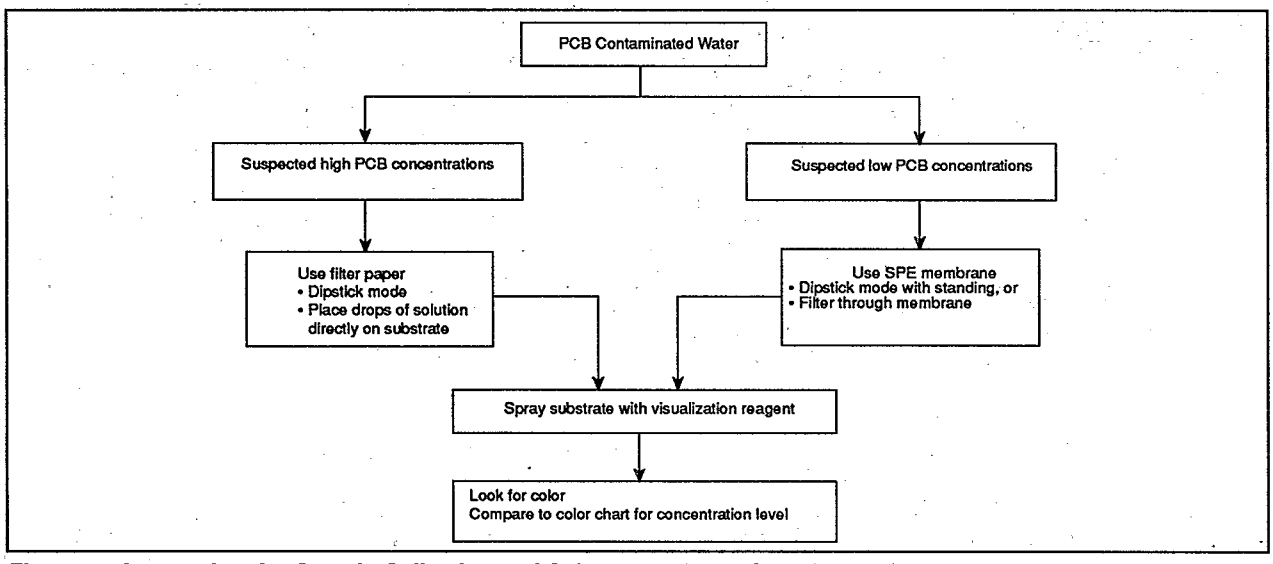


Figure 5. Approaches for Sample Collection and Subsequent Detection of PCBs in Water.

COST	GC/MS > Immunoassay > $AgNO_3$/UV
TIME	GC/MS > Immunoassay ~ $AgNO_3$/UV
SELECTIVITY	GC/MS > Immunoassay > $AgNO_3$/UV
SENSITIVITY	GC/MS ~ Immunoassay > $AgNO_3$/UV
SIMPLICITY	$AgNO_3$/UV > Immunoassay > GC/MS

Figure 6. Comparison of Methods for PCBs.

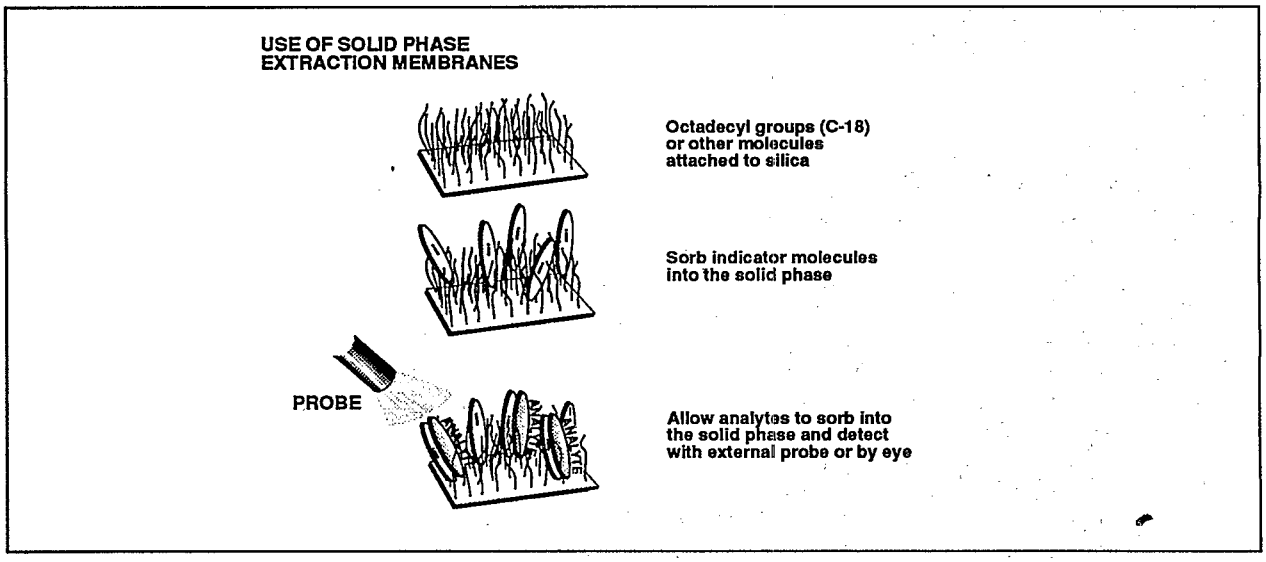


Figure 7. An Approach for Sample Collection and Detection.

The research focused on concept validation and technique optimization. The combination of SPE or filter papers in a dipstick mode followed by visualization of sorbed PCBs on the SPE or filter tabs using $AgNO_3$ does seem very attractive for field screening.

SECTION 7
SUMMARY AND CONCLUSIONS

The objective of this study was to develop a simple, inexpensive, and rapid procedure which could be used in field screening for PCBs in water. There was special interest in developing a test in the presence of 1-3% by weight of surfactants in order to follow the progress of remediating soil contaminated with PCBs by washing the soil with surfactant solution. A test was developed based on forming Ag^+ complexes of PCBs with $AgNO_3$ followed by UV irradiation to form Ag metal. The appearance of color (gray to brown depending on the PCB concentration) was used to signal the presence of PCB. This is a visual test. Instruments are not required. The test color can be compared to standard color charts to give an estimate of the PCB level. In addition to soil remediation monitoring, potential applications include well monitoring, wellhead protection monitoring, post-closure monitoring, and rapid laboratory screening. For applications related to soil remediation, it was found that filter papers or SPE membranes could be used in a dipstick mode by spraying with methanolic $AgNO_3$ and irradiation with 254 nm light from a hand portable UV light. The detection range was 1.0-500 ppm (or higher) in the presence of 3% Renex KB or Neodol (R) 1-7; these are surfactants that are currently being used for PCB soil remediation. A detection limit of 0.5 ppm was found in solutions containing mixtures of Neodol (R) 1-7 and Triton X-100 (reduced) surfactants. Samples of 2% Renex KB soil washings containing 10 and 40 ppm of PCB 1260 were screened. These were from actual operations. The samples could easily be differentiated but for unknown reasons, the test results indicated that higher PCB concentration may have been present. If the tests had been performed on site, more information would have been available and appropriate changes to the test and/or the color interpretation most likely could have been made on the spot.

A number of factors were found to affect the sensitivity of the visualization reaction, including choice of the test matrix, nature of the surfactant light wavelength and intensity, and presence of possible interferences. Whatman 541 and 542 filter papers and C-18 Empore™ SPE membranes were found to be the best matrices out of the 12 tested as surfaces for the visualization reaction. The other materials served to photosensitize Ag^+ reduction in the absence of PCBs. Neodol (R) 1-7 and Renex KB did not adversely affect the $AgNO_3$-UV visualization reaction. However, the four other surfactants examined did, either giving a high blank or increasing the detection limit. Use of 254 and 365 nm light and intense Nevada sunlight did serve to facilitate reduction of Ag^+ in the visualization reaction. However, use of 365 nm increased the time needed for the photodegradation to occur. On the other hand, intense sunlight resulted in the Ag^+ used on the blanks being reduced to Ag metal in a relatively short time.

As expected, Cl^- was found to interfere in the visualization reaction. The sensitivity was found to be 1 ppm in the absence of surfactants. The colors matched closely those obtained using PCBs at equivalent ppm concentration. The interference was eliminated by adding a few granules or a membrane tab of an anion exchange resin to the test solution. However, it appears that the resin also sorbs PCBs to some extent. The PCB detection limit was raised to 10 ppm from 1 ppm. It is judged that the limit can be lowered back to 1 ppm with optimization of the amount of resin used. One of the major interferences that might be expected in ground water in the vicinity of high organic content soil is humic acid. However, the interference is negligible even at 1000 ppm. Also, humic acid did not interfere with the PCB test. Several organic compounds including biphenyl showed a light pink color. However, since pink colors were not observed with PCBs, these are not considered to be serious interferences. Nevertheless, it is clear that many aromatic and aliphatic compounds containing halogen (Cl or Br) may interfere. Volatile

organic compounds such as $CHCl_3$, CCl_4, $Cl_2CHCHCl_2$, and $CHCl_2$ were not found to interfere. In field screening scenarios, the sites have already been characterized and the pollutants are known. In remediation processes, the target compounds are known as well. If there are a number of orgaohalogen pollutants, the $AgNO_3$-UV procedure can serve as a class test.

The potential of exploiting the results for a PCB field screening test is judged to be high. The information which has been gathered can be used as a basis to further improve the PCB test and to develop new field screening methods for other pollutants. A promising area for further research is the use of a catalyst for the dechlorination of PCBs (and other organohalogen compounds) which does not photosensitize Ag^+ reduction. Further test development in the short term could benefit from a search for test matrices (TLC plates, membranes, and filter papers) which give an optimum balance between acceptable blanks and enhancement of photosensitization. Also, a detailed examination of photographic chemistry, including color photography, may identify opportunities for enhanced sensitivity and selectivity. The use of indicators presorbed in SPE membranes that can both extract and detect pollutants in either water or air seems to be a promising area to explore as well.

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