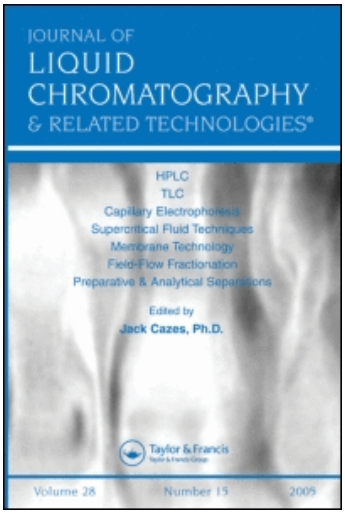

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Analysis of PCB's by Thin-Layer Chromatography

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ANALYSIS OF PCB'S BY THIN-LAYER CHROMATOGRAPHY

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ABSTRACT

A screening thin layer chromatography (TLC) technique has been developed that can be done in the field. Quantitative analysis by TLC densitometry can be done in a laboratory (or field van). A densitometer is needed for quantitative work by TLC. An Apple computer may be added to use as a computational device. Semi-quantitative results may be obtained by visual comparisons. Confirmations may be made by silver halide visualization on TLC. Dehalogenation with sodium biphenyl, chlorination with antimony pentachloride, or mass spectral confirmation may be used. Quantitative analysis is possible of the derivatized positive samples.

INTRODUCTION

EPA's concern has prompted a rash of analyses for PCB's. PCB's may be analyzed by sophisticated and expensive instrumentation or by simple TLC analysis. PCB's (polychlorinated biphenyls) are very commonly encountered organic chemicals; the chlorine content varies from <20% to 70% or more. Commercial trade

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names are Arochlor® or Pyranol®. They have been used as transformer oils, capacitor dielectric fluids, paint vehicles, pesticide extenders, and plasticizers for resins. They end up in solid foods, milk and chewing gum by indirect and direct routes.

Gas chromatographic (GC) analyses have been used to analyze PCB's since 1956.[1] Methods have been improved[2-10] as they were used and applied to new matrices.[11-13] Reviews of methods and instrumentation[14,15] have been published. EPA funded a study on method standardization.[16]

Levine[17] et al, compared cleanup methods and found that sulfuric acid extraction was the optimum cleanup for transformer oils. In this work acid cleanup was compared to SEP PAK® C^{18} cleanup and GLC compared with TLC quantitation.

EXPERIMENTAL REAGENTS AND APPARATUS

Thin layer plates - Whatman C^{18} reverse phase with fluorescent indicator (Excitation 254 nm), Whatman, Inc., Clifton, NJ; thin layer plates - Merck silica normal phase with fluorescent indicator (Excitation 254 nm), Brinkmann Instruments, Des Plaines, Illinois; 8% $AgNO_3$ in silica gel plates, Analtech Inc., Wilmington, Delaware; separatory funnels (250

ml); calibrated tubes, 1-15 ml with Teflon® stopcocks, Kimball Glass Company, Vineland, New Jersey; disposable pipettes, Fisher Scientific Company, Pittsburgh, Pennsylvania; PCB standards, EPA Research Triangle North Carolina; microliter syringes, Hamilton, Las Vegas, Nevada; concentrator tubes, Research Specialty, Los Angeles, California; dimethylformamide, acetonitrile, pet ether,and methanol were redistilled in glass; Milli Q water, Millipore Systems, Downers Grove, Illinois; sodium chloride reagent, Fisher Scientific Company, Pittsburgh, Pennsylvania, short wave length UV light (254 mm), UV Products, San Gabriel, California; $AgNO_3$ spray, $AgNO_3$, Fisher Scientific Company; sprayer, Kontes Glass Company, Vineland, New Jersey; TLC 800 Scanner, Kontes Glass Company; gas chromatograph with Ni63 detector, model 270, Packard Instrument Company, Downer's Grove, Illinois; recorders, Linear Instrument - P. J. Coberit Associates, St. Louis, Missouri. GLC columns used were 50% 3% OV-17 and 50% 3% OV-1; on Gas Chrom Q 100-120 mesh, six foot glass columns, 3 mm I.D. were used. Column temperature used was 200°C or 225°C; SEP PAK® (C^{18}) cartridges, Waters Associates, Milford, Massachusetts.

METHODS

Dimethyl formamide (DMF) was compared with acetonitrile (ACN) as an extraction solvent in terms of the amount of PCB recovered and cleanliness of sample extracts. A modification of the Mills[18] method for pesticide analysis was used. One half ml of oil, 50 ml of pet ether, 50 ml of DMF or ACN were mixed and pet ether separated and discarded. Fifty milliliter of salt water was added to the residual solvent used in the extraction and the PCB's partitioned into pet ether. Concentration was done under nitrogen on a steam bath at approximately 40°C. The samples were analyzed by thin layer chromatography (TLC) on normal and reverse phase, using 1% acetone in 99% Heptane and 95/5/1 + 1/2% NaCl, methanol water and ammonium hydroxide, respectively as developing solvents. TLC on normal phase TLC plates with $AgNO_3$ in the solid phase allows direct visualization on the plate by short wave UV irradiation.

Gas chromatography was done by injecting aliquots of concentrated extracts on the mixed phase columns with the Packard Ni^{63} electron capture detector. The column temperature was 225°C, injector, 250°C and detector, 280°C. The columns usually lasted 6 months

or more. Difficult samples required lowering column temperatures to 200°C. The analysis schemes are shown in figure two.

Antimony Pentachloride Chlorination[19]

An extract which was cleaned up by extraction, partition, (the cleanup by SEP PAK® is shown in figure one) or sulfuric acid reaction, is placed in a Teflon® lined screw-capped test tube (Bakelite plastic cap). 100 µl $SbCl_5$ is added carefully to test tube (10 ml) and the cap screwed on. Teflon tape is wrapped around the tube to seal it. The tube is heated to 150°C for two hours. The contents are removed to concentrated HCL in a separatory funnel. The acid layer when clear is extracted two times with Benzene. The Benzene is washed with $NaHCO_3$ to remove excess HCL and $SbOCl_3$. The benzene extract was concentrated and analyzed by TLC or GC as above. Temperatures of 240°C - 250°C were used to increase the analysis rate of derivatized samples.

Comparison of Sulfuric Acid[17] and SEP Pak® Cleanups

Concentrated acid was used to contact the extracts and removed by aqueous washing and dehydration with Na_2SO_4. SEP PAK® C^{18} columns were washed with methanol

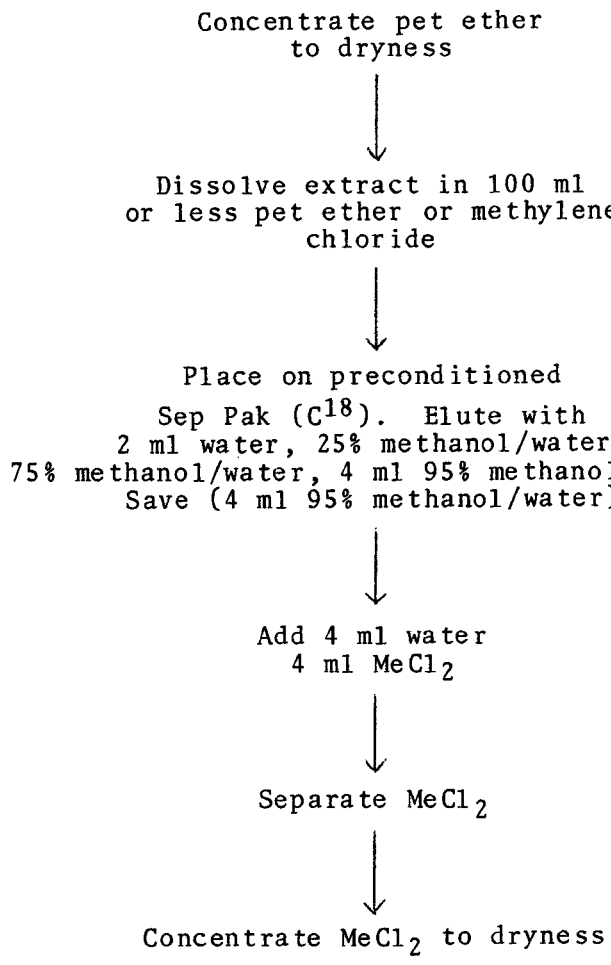

FIGURE 1
Sep Pak® Cleanup

(MeOH) and water and vacuum dried. Extracts after concentration and redissolving were placed on the SEP PAK® column in 100 µl of methylene chloride or pet ether and eluted with 2 ml 25% MeOH/HOH, 2 ml 50% MeOH/HOH water, 4 ml MeOH/HOH (95-5). The last eluate

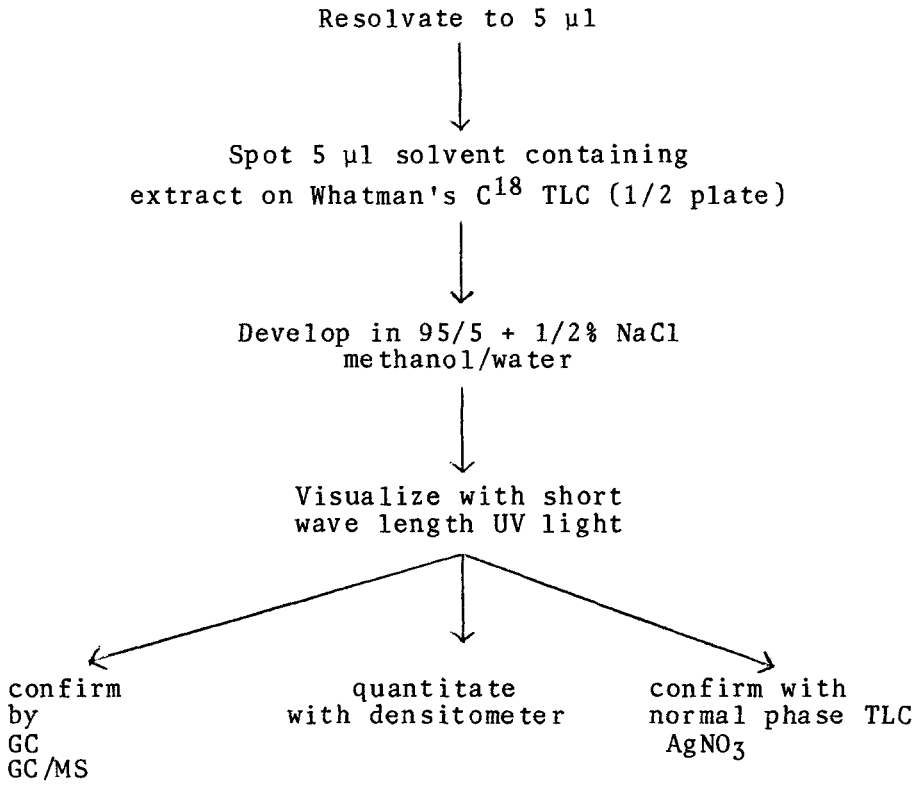

FIGURE 2
PCB Analysis

was mixed with 4 ml water, 4 ml $MeCl_2$, shaken and the $MeCl_2$ layer removed. The extracts desolvated, redissolved in isooctane and analyzed by TLC or GLC. Quantitation by GC was done by triangulation of the area of peaks matching the Arochlor analyte closest in pattern to the analyte. TLC quantitation was done by area measurement of the TLC bands under UV irradiation with a Kontes 800 scanner. Concentrations of 5 samples

TABLE I

Thin Layer Chromatography

Rf's, PCB's and PBB

Compound	Normal Phase RF	Reverse Phase RF
Arochlor 1248	.6	.7
Arochlor 1254	.5	.6
Arochlor 1260	.4	.5
PolyBromo Biphenyl	.3	.4
	Heptane Solvent	95% Ethanol Solvent

Sensitivity 0.1 µg Fluorescent Quenching

Sensitivity 0.5 µg $AgNO_3$ conversion

TABLE II

Analysis PCB's Thin Layer Chromatography

Densitometry with Camag Densitometer

	Band Area		Slope factor Area/ng
1 µg	70 x 10	700	600
2 µg	126 x 10	1260	630
3 µg	170 x 10	1700	560
4 µg	210 x 10	2100	520

Sensitivity less than 10 ng PCB

Repeatability ± 5%

TABLE III

Arochlor Concentrations as Arochlor 1260

TLC Sulfuric Acid Cleanup	TLC Sep Pak Cleanup	GLC Sep Pak Cleanup
11	10	15
4	4	6
41	40	40
54	55	53
17	18	14

of contaminated transformer oil were compared using TLC, GLC analysis with sulfuric acid and SEP PAK C^{18} cleanups.

RESULTS

The Rf's of PCB's are shown in Table I. The densitometric results obtained with the Camag densitometer are shown in Table II. Comparative analysis of transformer oils are shown in Table III.

CONCLUSION

TLC may be used to rapidly and inexpensively screen samples of transformer oils for PCB's. Quantitative analysis may be done by TLC densitometry or GC electron capture analysis. Cleanup steps using SEP PAK® C^{18} or sulfuric acid cleanups are very beneficial for improving the quality of the extracts for chemistry rapid analysis. Confirmation may be made by silver nitrate reaction on normal phase silica TLC, GLC, GC/MS. Antimony pentachloride derivatization converts PCB's to decachlorobiphenyl making confirmation and analysis more simple--one compound to analyze--and more sensitive.

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