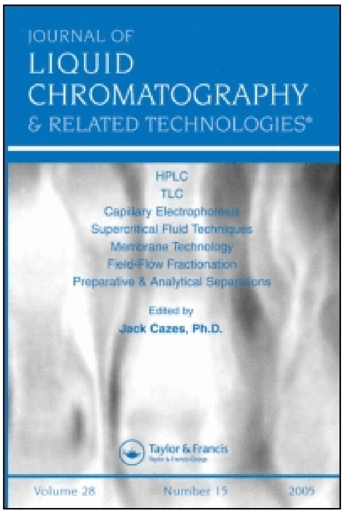

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Analysis of Polychlorinated Biphenyl Residues in Waste Oils by High-Performance Liquid Chromatography

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ANALYSIS OF POLYCHLORINATED BIPHENYL RESIDUES IN WASTE OILS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

The qualitative analysis of polychlorinated biphenyl residues (PCBs) in waste mineral oils can be rapidly and accurately carried out by high-performance reverse phase liquid chromatography (HPLC) using a 25 cm HC-ODS Sil-X (Perkin-Elmer) column and a gradient elution system consisting of water-acetonitrile where the latter increases with linear program from 50 to 77% over 9 minutes.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of compounds possessing a variety of industrial applications related to their electrical,thermal and chemical properties.

Fishbein (1) has written an extensive review on the PCBs encompassing their environmental occurrence,toxicological problems and analytical aspects.

Several methods for quali-quantitative analyses of PCBs in biological and non-biological materials by TLC,GLC-EC or combined GC-MS techniques was reported in excellent review articles (2-5).

Recently,the HPLC analysis of PCBs was described (6-8).

The purpose of the present note is to establish the chromatographic conditions that can be used during the analysis of PCB residues in waste industrial oils by HPLC and to illustrate the advantages of this method over the GLC-EC techniques as concerns the final step in trace residue analysis.

MATERIALS AND METHODS

The samples under investigation are a mixture of waste oils (lubricating oils,machine tool cutting oils,high pressure hydraulic fluids and heat transfer agents,the last two in small percentages) discharged from mechanical industries.

PCBs standards were obtained from commercial suppliers (Fenclor-Caffaro S.p.A.-Milano-Italy).The samples used were mixtures of tri-chloro to hepta-chlorobiphenyl isomeres with a chlorine content ranging from 42 to 64%.

The waste oil samples (2 g) were dissolved in 5 ml of n-hexane (pesticide grade) then transferred to a glass chromatograph column (35 x 0.8 cm I.D.) packed with Kieselgel 60 Merck (70-230 mesh, ASTM) dried at 120 °C for 2 h,cooled in a desiccator,partially deactivated by shaking with 3% by weight of distilled water for 30 minutes and stored in a closed vessel.The column was pre-wetted with n-hexane and then eluted with 45 ml of the same solvent.The eluate contained PCB residues and less-polar components e.g. paraffins,was evaporated to dryness and then the residue extracted three times with 15 ml portions of acetonitrile.The acetonitrile extracts were combined and evaporated just to dryness.The residue was redissolved in 1 ml of acetonitrile.Standard solutions of PCB were prepared in acetonitrile,at the following concentrations:Fenclor 42,2.7 mg/ml; Fenclor 54,2.2 mg/ml;Fenclor 64,0.8 mg/ml.Injections of 0.2 μl of each standard solutions were made for identification.

HPLC chromatograms were run on a Perkin-Elmer Series 3 Liquid Chromatograph.Component elution was monitored with a LC-65T variable wavelength detector (190-800 nm) equipped with a tiny flow through a cell 8 μl in volume.A stainless steel column was used (25 x 0.26 cm I.D.) packed with HC-ODS Sil-X 13 μm (Perkin-Elmer). The separations reported were achieved under the following conditions:the gradient elution system consisted of 50% water and 50% acetonitrile programmed,with linear scan,to 77% acetonitrile at 1.0 ml per minute flow rate over 9 minutes;temperature 60 °C; wavelength 210 nm;chart speed 0.5 cm per minute.Graphs were generally obtained with an attenuation setting corresponding to 0.64 AUFS (absorbance units full scale) on a 10 mV recorder.

Preliminary investigations were carried out to establish the best chromatographic conditions for testing the materials under study.

RESULTS AND DISCUSSION

The efficiency of the single stage cleanup procedure employed was examined by applying known weigths of PCBs standards in 1 g of a mixture of mineral oils (PCB free) to the Kieselgel column,and eluting with 40 ml of n-hexane,the results being compared on HPLC analysis with those obtained from the original standard solutions.

The optimum resolution of the PCB residues were obtained using a water-acetonitrile gradient elution system in which the acetonitrile concentration increased with linear program from 50 to 77% over 15 minutes;however a time of 9 minutes is an acceptable compromise between speed and resolution.Separation of standard solutions of Fenclor 42,54 and 64 are illustrated in Fig. 1.In agreement with published data (9-10) the HPLC retention time increases with increasing substitution of chlorine atoms into biphenyl nucleus.HPLC graph of PCB residues in a sample of waste oil is reported in Fig. 2.In order to investigate the validity of the HPLC method the waste oil samples were also analysed by GLC-EC.A Perkin-Elmer 990 gas-chromatograph fitted with EC detector was used.

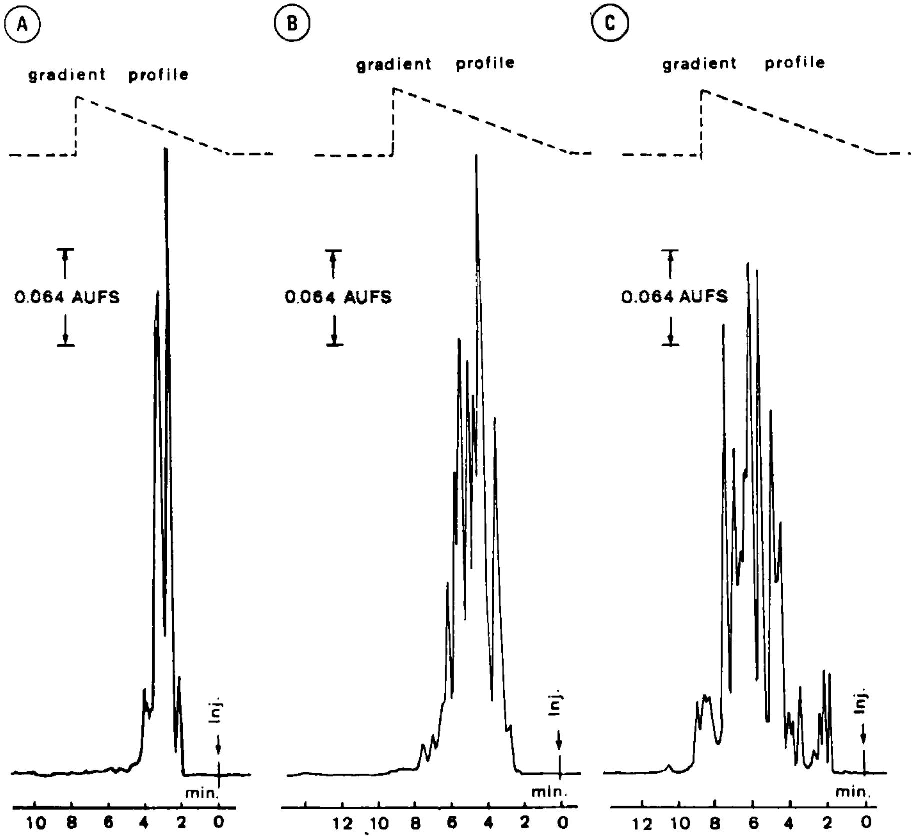

FIGURE 1

HPLC of (A) Fenclor 64,(B) Fenclor 54,(C) Fenclor 42. Conditions : column,25 x 0.26 cm I.D. filled with 13 μm HC-ODS Sil-X;gradient elution system,water-acetonitrile where the latter increase with linear program from 50 to 77% over 9 minutes;flow rate,1 ml/min; temperature,60 °C;chart speed,0.5 cm/min;wavelength 210 nm.

The GLC operating conditions were as follows:nitrogen carrier gas flow rate 85 ml per minute at the column outlet;column,injection port and detector temperatures 200 °C;2 m x 3 mm I.D. stainless steel column containing Cromosorb W (80-100 mesh) coated with 3%

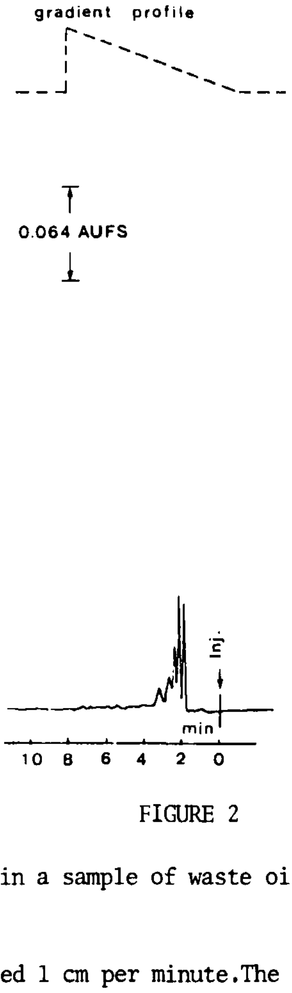

FIGURE 2

HPLC of PCB residues in a sample of waste oil. Conditions as in Fig.1.

(w:w) SE 30;chart speed 1 cm per minute.The EC detector was operated at -50 V.A typical GLC-EC response of PCB residues in a sample of waste oil is shown in Fig. 3.It should be noted that the peaks obtained are due mainly to contaminants (11) which cannot completely be separated by the cleanup technique employed. When present in significant quantity or numbers,these interfering co-extracted compounds can adversely affect the sensitivity of the method being used,thereby casting serious doubts upon the identity of the suspect residues.In our laboratory many tentative approximations of PCBs content of waste oil samples by HPLC have been made.

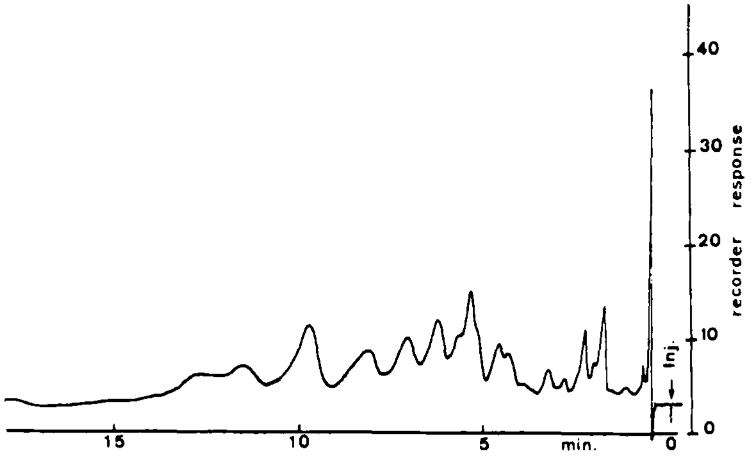

FIGURE 3

GLC-EC of PCB residues in a sample of waste oil. Conditions : column, 2 m x 3 mm I.D. filled with Cromosorb W (80-100 mesh) coated with 3% SE 30;temperature,200 °C;nitrogen carier gas flow 85 ml/min;chart speed 1 cm/min.

It must be emphasized that a suitable method for accurate quantitative analyses of PCBs in biological and non-biological systems is at present non-existent.Within the strict limitations of being able to define all contaminants of a mixture for the family profile of commercial PCBs for a specific type of sample,one may by HPLC approximate,not quantitate,the PCB content.More work is required before we can recommend LC procedures for PCBs quantitation,though sponsoring their expediency as a tool for counterchecking the results yielded by other analytical methods.

CONCLUSIONS

The results of the present experimental investigations confirm that HPLC method has several distinct advantages over the conventional techniques currently in use.It is rapid,convenient and applicable to routine analysis.Furthermore in the case of non-biological samples such as waste mineral oils,in which the qualitative determination of PCB residues is often plagued by interfering co-extracted materials,the use of reverse phase HPLC is an alternative useful technique.

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11. GLC-MS spectre of this fraction showed no other compounds but hydrocarbons.At present,since the exact composition of the employed mixtures is not known,we are not able to identify with certainty these "contaminants".