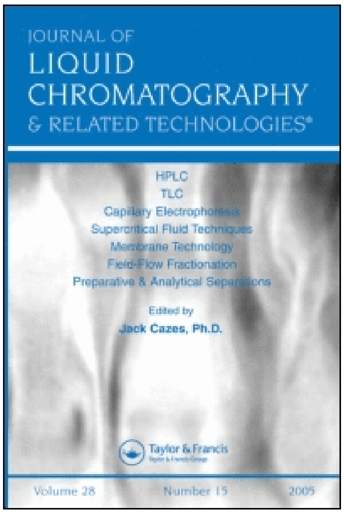

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High Performance Liquid Chromatography in Environmental Analysis: Present and Future Applications

Badar I. Afghan[a]; Aaron W. Wolkoff[b]
[a] Analytical Chemistry Research Section, Analytical Methods Division, National Waters Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, Canada [b] Waters Scientific Ltd., Mississauga, Ontario, Canada

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY IN ENVIRONMENTAL ANALYSIS: PRESENT AND FUTURE APPLICATIONS

Badar K. Afghan*,

Analytical Chemistry Research Section,
Analytical Methods Division
National Waters Research Institute
Canada Centre for Inland Waters
867 Lakeshore Road, Box 5050
Burlington, Ontario L7R 4A6 Canada

and

Aaron W. Wolkoff

Waters Scientific Ltd.,
6840 Viscount Road
Mississauga, Ontario L3T 3H7 Canada

ABSTRACT

This review is intended to present the authors' views on the present and future applications of high performance liquid chromatography (HPLC) to environmental analysis. It is chiefly concerned with publications in the period 1977 - 1980 and is not meant to be an all-inclusive review. The authors have selected only those publications which either deal with compounds of enviromental interest or methods of future potential to enviromental analysis. For full inventory-type reviews the reader is directed to summaries presented in various journals, e.g. the annual review issue in Analytical Chemistry & Journal of Chromatography.

INTRODUCTION

As a result of efforts to upgrade living standards through increased productivity and food supplies, the dependence of mankind upon synthetic and naturally occuring chemicals has increased rapidly since World War II. To date, over six million chemicals are known to exist, many of which find their way into our environment. Many synthetic compounds tend to accumulate in the components of the environment, including segments of the food chain. In addition, numerous compounds are also transformed via chemical, microbiological or photolytic pathways to other products which in some cases may pose a more serious hazard then the original compound.

In 1978, the Implementation Committee of the Great Lakes Water Quality Board of the International Joint Commission presented a report covering available data on the distribution and bioaccumulation of "toxic materials" in the basins of Lake Erie, Huron, Superior and Michigan (1). This report identified over 350 contaminants detected in water, sediment, air, discharges, sludge, plankton, fish and wildlife of the basins. In addition, US EPA and the Canadian Environmental Agencies have also developed priority pollutant lists with the ultimate aim of controlling and regulating the input of these and other hazardous materials into the environment. These pollutants include pesticides, PCB's and related compounds, halogenated aliphatics, ethers, phenols and cresols, phthalate esters, aromatic and polyaromatic hydrocarbons, nitrosamines and other nitrogen-containing compounds as well as metals and inorganics.

Thus, there is a need to develop appropriate analytical techniques for detecting, quantifying and confirming a wide variety of chemicals at ultra-trace levels in sample matrices ranging from original products to wastes as well as various components of the enviornment (e.g. air, water, soil, sediment, suspended material, biota and plants). HPLC offers a great potential for environmental analysis for several reasons. A wide range of compounds ranging from volatile to non-volatile with molecular weights differing as much as 3 - 4 orders of magnitude from each other. Because the mobile phase is a liquid and is thus often similar in nature to the sample matrix, a larger variety of samples can be handled compared to gas chromatography (GC). The separating power of HPLC is potentially greater than that of GC in that two parameters affecting separation, the stationary and mobile phases, can be varied over a wide range of polarities and chemical functionalities. In GC only the stationary phase can be varied since the mobile phase serves only as a carrier. Since the mobile phase is a liquid other techniques may be interfaced, both before and after the separation has been performed, allowing a wide variety of materials and matrices to be analyzed. These, amongst other factors, have made HPLC the fastest growing technique in analytical chemistry (2-4).

COLUMNS AND INSTRUMENTATION

Columns and Packings

Kowlaczyk (5) studied the effect of the porous structure of packings on selectivity of HPLC systems and concluded that the mass transport may be affected by only a portion of the particle material if their porous structure is adequately heterogeneous. The heterogeneity of the particle structure leads to reduced selectivity; however it may be possible to increase the selectivity by raising the temperature. This observation is of importance particularly where home-made wider bore columns, with larger particle diameter, are used for cleanup of environmental samples.

Afghan (6) reported varying selectivity of C-18 columns prepared by various manufacturers. In this work, various C-18 columns were investigated for their ability to separate carbamates and polynuclear aromatic hydrocarbons. Zorbax ODS did not exhibit any separation for metacil, permicarb and zectran. These carbamates were not even eluted when the mobile phase composition was changed from 20% to 70% acetronitrile - water. uBondapak C-18 gave varying retention times for metacil. Chromegabond M-C-18 and M-C-18-2 also exhibited varying selectivity ratios. This phenomena has been reported by other workers.

Colmsjo (7) has reported that C-18 columns manufactured by various manufacturers showed different ability to separate a polynuclear aromatic hydrocarbons (PAH).

Evans (8) proposed a new method for the preparation of high quality bonded phases for use in reverse-phase HPLC. This involved the reaction of silica gel with a trichlorosilane, methanolysis of the product and subsequent capping with trimethylchlorosilane. Chlorinated solvents were found to yield superior bonded phases and the use of elevated temperatures was shown to be unnecessary. Resolution of various substances such as hydrocarbons, ketones and nitro-imidazole was found to be superior compared to bonded phases prepared by other methods.

Van de Venne (9) proposed a method to obtain non-polar chemically-bonded stationary phases with low residual hydroxyl group content which tend to affect the performance, resolution and efficiency of columns. To achieve this lower hydroxyl group content, a partial condensation of surface silanol groups at temperatures greater than 200°C was performed. Commercially available packing materials were compared with materials prepared by this method.

Baum (10) described the preparation of high efficiency columns of micro-particulate Amberlite XAD-2. Columns, slurry-packed with 3.6 - 8.4 μ XAD-2, were found to yield efficiences greater than 20,000 plates per metre. Because of its hydrophobic characteristics, low cost, wide pH range (pH 0 -14), strong adsorbent properties and compatability with virtually all solvents, this packing material offers excellent potential for the separation of the wide variety of compounds in environmental samples. One of us (BKA) is presently evaluating the use of these packings for the separation of trace organics in environmental samples.

Rotsch (11) obtained increased retention and improved peak shapes and improved resolution using Amberlite XAD-2 columns with added tetralkyl ammonium salts added to the mobile phase.

A number of new chemically bonded stationary phases have been reported (12 - 16) to obtain improved separation of aromatics, amines, phenols and inorganic salts.

Recently capillary columns have played a significant role in gas chromatography providing increased resolution and selectivity for various isomers and complex mixtures. A number of workers have attempted to prepare capillary columns for liquid chromatography. Tesarik (17) proposed a procedure for the preparation of HPLC capillary columns involving the reaction between a solution of ammonia and tetramethyl ammonium hydroxide. Scott (18,19) discussed the performance characteristics and advantages of microbore columns in terms of high efficiency, speed and high mass sensitivity separations using biological samples. Krejci (20) demonstrated the possibility of using capillary columns with commercial LC instrumentation. It was possible to obtain high plate counts (up to 1,250,000) using open tubular columns.

A number of authors have reported alumina or silica support-coated open tubular columns to achieve high efficiences (21,22). It was possible to obtain improved resolution for aromatic amines and other organics. Aromatic amines and phthalates were also separated using soda-lime glass treated with alkalai (23). The best column for micro-capillary liquid chromatography was made by treatment with 1N sodium hydroxide solution at 25 - 54°C for two days.

Other stationary phases such as β,β' - oxydipropionitrile and ethylene glycols have been used to separate aromatic-amines and phthalates in normal-phase systems (24). Chemical bonding of an octadecysilane stationary phase was successfully achieved on the inner glass surface of a micro-capillary tube of 60μm I.D. (25). Using methanol-water or acetonitrile-water mobile phases, improved separations of several aromatic hydrocarbons were obtained. Flow rates in the range of 0.3 - 1.3 cm/sec were used without sacrificing efficiency, on columns of 507 cm in length.

A new separation technique utilizing coated open-tubular capillary liquid chromatography with flow segmentation was reported by Snyder and Dolan (26, 27). Segmented-flow liquid chromatography was described as a useful size-exclusion technique for sample treatment prior to HPLC. This technique may serve as an improved clean-up technique for high molecular weight compounds such as humic and fulvic acid materials, proteins, and lipids prior to analysis of environmental samples.

Another new development(28,29) in column technology utilized plastic cartridges containing a packing material. When the cartridges are placed in a chamber and radially-compressed they form a highly-efficient column which generates low back pressures making it useful for fast anlysis times and flow programming. The cartridges are relatively inexpensive and disposable.

Mobile Phase

A promising new field employing aqueous solutions of surfactant aggregates (or micelles) has been sugested (30) as a novel and highly effective mobile phase for HPLC. An aqueous solution of sodium dodecyl sulphate was used for the separation of positional isomers of a wide variety of phenols. PAH's were also separated using flow and concentration gradients. It was also claimed that the reverse-phase column did not show and deleterious effects with this mobile phase for up to four months use.

The influence of organic modifiers and composition of the mobile phase on retention behaviours of various compounds has been studied (31 - 33). It is reported (31), by extensive studies using thirty-two aromatic compounds, that the optimum gradient shape may be convex rather than linear as presently assumed by many workers.

Flow programming has also been evaluated as an alternative to gradient elution in reverse-phase chromatography. Afghan (34) found that the practical application of flow programming during separation of carbamates is limited by pressure increases which in turn could result in damage and subsequent loss in efficienty of analytical columns. However, flow programming was found to be useful for late eluting PAH's (35). Flow programming has also been used to reduce analysis times and retention volumes in paired-ion chromatography and gel permeation chromatography (36, 37).

Gilpin (38) has studied the effect of temperature on the precision of retention times in HPLC. The study covered a series of both normal and reverse phase packing materials as well as varying mobile phase compositions. It was concluded that for reverse-phase systems, the precision of retention measurements was good to excellent. However, normal-phase systems were effected dramatically by changing thermal conditions and the largest errors were observed when a polar stationary phase was used in combination with polar mobile phase modifiers.

Gant (39) has developed a general model for the easy optimization of separations in reverse-phase LC systems. It was found that temperature plays an important role and can be optimised simultaneously with mobile phase composition to obtain increased resolution. Generally, resolution was improved at higher temperature with accompanying lower concentrations of organic in the mobile phase.

Afghan (34) studied the effect of temperature on the separation of carbamates over the range 20 - 40°C, finding that increased temperature reduced retention times and produced undersirable reduction in selectivity. Simultaneous change of temperature and mobile phase composition did not offer any significant improvement over isocratic separations.

Peak broadening induced by the nature of the sample solvent and volume injected have been reported by Williams (40). It was demonstrated that peak heights are affected by changing sample solvent composition. This may produce errors in quantitation particularly when complex mixtures are analyzed. Afghan (34,35) investigated the effect of volume and solvent composition of final aliquots prior to injection. It was found that sample size and solvent composition of final aliquots did not pose significant errors if proper conditions were selected. Sample size was varied from 10μl to 1 ml without loss of separation and reproducibility.

Detectors

Versatility of an analytical technique to cover the wide spectrum of compounds found in environmental samples depends upon a number of factors: (a) it should respond to all compounds of interest; (b) it should be able to provide quantitative data in the nanogram or picogram ranges; (c) it should be able to provide positive identification and confirmation on a cost effective basis; (d) it should not involve extensive and complex derivitization steps. Obviously, the detector plays a significant role in the total analytical scheme. As noted before, the ability to interface a wide variety of detection systems potentially makes HPLC an extremely useful tool in environmental analysis.

During the past 8 - 10 years the area of HPLC detectors has received increasing attention. McKinley (41) has reviewed HPLC detector technology. Detectors utilize properties such as refractive index, absorbance, infrared, fluorescence, conductivity, thermal energy and electro chemistry. Transport detector technology is also discussed as well as derivitization to further enhance detector selectivity and sensitivity.

Ultraviolet absorption (UV) detectors for HPLC are the most frequently employed. Most are of a fixed wavelength but the use of tunable wavelength detectors is receiving increasing attention because of the increased sensitivity and selectivity obtained. Micro-processor control has increased the versatility of variable wavelength detectors and it is now possible to purchase detectors where attenuation and wavelength are changed during a run. One may also scan a peak during a run, using a stopped flow, to obtain a full spectrum to aid in identification and confirmation of compounds. A potentially more useful system, although the costs are presently quite high, is a detector that scans the whole wavelength range very quickly (approx. 1 sec) to give spectra without stopping the flow. Afghan (34,35) utilized a scanning capability to obtain the desired sensitivity and selectivity for carbamates, PAH's and other trace organics.

Fluorescence detectors are also extensively used by a number of workers. Afghan (6) compared commercially available fluorescence detectors with conventional fluorometers and spectrofluorometers using standard flow cells. It was possible to obtain comparable, or, in some cases, increased sensitivity using standard equipment available in most laboratories. Ogan (42) compared the use of cut-off filters with monochromators for HPLC and concluded that cut-off filters provide increased sensitivity for PAH's provided sufficient separation of compounds is achieved.

Derivatization techniques have further enhanced detection sensitivity and selectivity of various compounds such as alcohols, carboxylic acids and amino acids. Derivatization has been employed in conjunction with UV and fluorescence detectors. Lawrence (43) reviewed recent advances in the use of fluorimetric derivatization techniques. Formation of derivatives both prior to HPLC separation (pre-column) and on-line post-column derivatization is discussed. Nanogram quantities of phenols, amines, carboxylic acids and carboxyl compounds can be detected. Specific applications of pre- and post-column derivatization of sterically unhindered primary amines, carbamate insecticides and acidic herbicides such as 2,4-D have also been reported (44-46).

Atomic spectroscopy has been successfully interfaced with HPLC to determine various heavy metals and organometallics. After HPLC separation of arsenite, arsenate, methylarsonic acid and dimethylarsonic acid in soil extracts and drinking water, a graphite furnace atomic absorption spectrometer was used as a selective detector (47). Other high temperature furnace-atomic absorption systems and on-line inductively coupled argon plasma systems have also been used with HPLC (48-50).

A microcomputer-controlled interface between HPLC and a diffuse reflectance infrared fourier transform spectrophotometer (HPLC/FT-IR) was described by Kuehl (51). The technique is capable of achieving detection limits down to submicrogram quantities for low-volatile compounds.

A new naphelometric detector has been developed for HPLC (52) to detect low concentrations of non-polar lipids. The detector utilized a helium neon laser beam as a light source and the scatttered light is detected at right angles to the incident beam. A special light scattering detection cell is also described which exhibits a wide linearity range (0.5 to 100ug).

Although the above detectors (HPLC/FT-IR and naphelometric) have not been evaluated extensively for the types of compounds usually found in environmental samples, we are of the opinion that they offer an excellent means for anlysis of lipids, non-volatiles and other high molecular weight substances such as humic and fulvic acids.

During the past 3 - 5 years, the use of electro-analytical instrumentation as sensitive and selective detectors for HPLC has grown rapidly. These include voltametry and amperometry (53 -58), titration techniques (59), current semi-integral electro-analysis (60), coulometry (61,62) and conductivity (63,64). These detectors offer an excellent means of detecting and confirming a wide variety of inorganic, organic and organo metallic compounds. The systems are capable of covering a wide dynamic range of concentrations ranging from ultra-trace levels to macro amounts. Sensitivities as low as 10^{-11}g for certain electroactive substances can be achieved, making these detectors very suitable for environmental applications.

Blaedell (65) has proposed an improved flow cell with a rotating glassy carbon disc electrode for voltammetric and amperometric techniques. High analytical currents are obtained due to efficient mass-transport and new hydrodynamic modulation techniques reduce the major background currents during voltammetry.

Frie (66) proposed an efficient electro-chemical scrubber containing a porous silver electrode that permits the cleanup of mobile phase for oxygen, trace metals and other reducible organic impurities in the eluent. In conjunction with a mercury dropping electrode, background currents and noise were significantly reduced.

For further discussion of these detection systems, the reader is referred to recent reviews (67,68). The reader is also referred to a review by Kissinger (69) whereinhe discusses the combination of pre- and post-column derivatization and electro-chemical detectors for non-electroactive compounds. This is an area which will offer a useful approach to obtain selectivity and sensitivity for various environmental samples.

Phenolic compounds in water have been determined (70) using electro-chemical detection employing a unique carbon-polyetheylene tubular anode. Trace levels (ppb) could be determined by this method. Picloram, a herbicide, was detected at 15ng/ml (71) using differential pulse polarography. The system exhibited good linearity up to 5 x 10^{-4}M.

Afghan (6) reported the potential of voltametric detection in the determination of a wide range of environmental samples such as phenols, amines, heterocyclics carbonyls and organometallics. Compounds presently under investigation (72) using electro-chemical detection include triazines, amines, phenols, carbamates and carboxyl containing compounds.

Probably the utimate in detection systems is the mass spectrometer. Although relatively expensive, and at present relatively insensitive, it offers one of the few techniques where positive identifications of chromatographic peaks is possible. GC-MS has proven to be an extremely useful tool but is limited to volatile compounds or derivatives of non-volatiles. Because LC can cover a range from non-volatile to volatile compounds, LC-MS may offer a greater potential then GC-MS. Direct coulping of LC with the mass spectrometer has been reported (73,74). A new approach (75) has been laser vaporization of the LC effluent and a molecular beam technique to transport and ionize the sample. Volatile aromatics and other compounds were employed in this study. LC-MS has also been reported (76 - 80) for the separation and detection of aromatic compounds, PCB isomers, herbicide photolysis products and other priority pollutants. Finally McFadden (80) has extensively reviewed continuous on-line LC-MS systems.

Numerous other techniques have also been interfaced with HPLC to obtain quantitative and qualitative data. These include: hydrogen nuclear magnetic resonance (81) for the determination of alkanes, alkylbenzenes and substituted naphthalenes; an electron capture detector (6,82) for organo-chlorine pesticides whereby 10-100 times more sensitivity compared to UV or fluorescence was obtained. Flame aerosol detectors (83) and a thermal energy analyzers (84) are also proposed.

SPECIAL TECHNIQUES

Separation of a complex mixture can be achieved using coupled column chromatography (85) for sample preparation prior to analysis. Using sequential analysis two techniques can be combined. For example, exclusion chromatography can be employed as a preliminary cleanup of malathion in vegetable matter with subsequent analysis by reverse-phase HPLC. (86). Carbamate pesticides have also been analyzed (87) by an on-line coupled-column technique. This method has also been described (88) as two-dimensional column liquid chromatography. The authors described a system consisting of two columns in series utilizing two different separation mechanisms for the analysis of plant extracts.

HPLC is a powerful tool and can be used for trace enrichment, cleanup and separation. A number of authors (89 - 92) have employed pre-column and/or guard columns for on-line trace enrichment of phthalate esters, PCB isomers, choranilines and metal ions prior to separation by HPLC.

Offline techniques involving the use of short columns packed with chromatographic support (Amberlite XAD-2 resin and C-18 Sep-

Paks^R) have also been used for trace enrichment and sample cleanup. (91,92).

On line column switching has been employed for sample cleanup (93) for trace analysis of complex mixtures. An automated cleanup for 2,3,7,8 - tetrachlorodibenzo-p-dioxin was described by Ramstad (94). This low cost cleanup procedure utilizes a silica column for repetitive usage. Up to 400 runs were processed on a single column without loss of cleanup efficiency. Wolkoff (95), Larose (96) and Thruston (97) optimized HPLC systems for cleanup of environmental samples prior to GC or GC-MS analysis of organochlorine pesticides and PCB's.

High molecular weight compounds have been removed from complex matrices using gel permeation chromatography (GPC) as a preliminary separation technique (98 - 100). Tessari (101) evaluated an automated GPC cleanup procedure and found that it proved to be a cost-effective technique for the separation of various organochlorine pesticides and PCB's. Afghan(34, 35) utilized GPC for the removal of high molecular weight species prior to HPLC separation of PAH's and carbamates in natural waters, suspended solids, road run-offs, soils, sediments and fish.

Ion-pair, ligand exchange and ion exchange chromatography has also been explored to obtain improved separation of organic compounds (102 - 104). Tomlinson (105) has reviewed ion pair HPLC in terms of its use, separation efficiency and future prospectives. Davanakov (106) reviewed ligand-exchange chromatography for the separation of various compounds such as phenols, carboxylic acids, amines, sulphur-containing compounds as well as unsaturated and aromatic compounds.

Finally, the reader is referred to some pertinent articles published in the last 3 - 4 years giving general reviews or methodologies: Fielding (107) proposed an analytical scheme for the isolation, separation and identification of trace levels of non-volatile organic compounds from drinking water; separation was carried out both on preparative and analytical scale; and

Lawrence (108) reviewed and tabulated HPLC separations and systems which have beem employed for pesticide analysis; data is given for 116 pesticides.

SPECIFIC APPLICATIONS

Organochlorine Compounds

Collaborative studies were conducted by Grorud (109) for chlorinated phenoxy acids (MCPA and 2,4,5-T) formulations. The study concluded that HPLC can provide accurate and reproducible results.

Brinkman reported separation and analysis of PCB's (110, 111) and chlorinated naphthalenes (112, 113) by normal phase HPLC. Analysis of chlorinated dibenzo-p-dioxins on alumina has also been reported (114 - 116).

Organophosphorous Insecticides

Otsuki (117) described the determination of abate in water at the ppb level using a diphenylsilane column. Szalontac (118) reported behaviour of 23 organophosphorous insecticides on silica. For the analysis of vinyl phosphate isomers, he concluded that HPLC offers certain advantages compared to GC.

Carbamate Insecticides

Cook (119) proposed a method for the determination of carbofuran residues in soil and water. The method is based on an initial extraction of the parent compound with methanol/water and subsequent hydrolysis of carbofuran to its phenol. The resultant phenol was separated and determined using HPLC and UV detection at 280nm. The sensitivity of the above method could probably be further improved if the phenol is determined by fluorescence detection as proposed by Wolkoff (120).

Pieper (121) developed an improved method for determination of carbamates in forest foliage and stream water using liquid chromatography. Sparacino (122) studied the HPLC behavior of some 30 carbamates using both normal and reverse-phase modes. Multiple wavelengths (190-220nm) were selected for the absorptiometric detection of various carbamates.

Afghan proposed an improved HPLC-Multidetection system for simultaneous determination of a number of carbamates in the sub-ppb range. The method has been applied to natural waters, soils and sediments (34).

Triazines

Dufek (123) studied the separation and HPLC behaviour of twenty two S-triazine derivatives on an NH_2-chemically bonded phase. It was found that the NH_2 phase provided better separation of triazines compared to other stationary phases.

An HPLC method for determination of atrazine residue in soils was compared with a colorimetric method (124). HPLC was capable of detection as low as 5ng using UV at 254nm.

Hormann (125) has described a method for the determination of hydroxy metabolites of S-triazines using silica and UV detection at 240nm. Recoveries range from 70 - 113% with detection limits as low as 0.05 mg/kg

Organo-metallic Herbicides

Iadevaia and Woolson (129) described HPLC separation of arsenical pesticide residues and their detection by graphite furnace atomic absorption. The compounds were separated on an ion exchange column with gradient elution. The detection limit for various arsenic compounds was about 5ng per injected volume (20μl). Calibration curves were linear up to 200ng.

Polynuclear Aromatic Hydrocarbon (PAH)

Black (128) described an isocratic separation of PAH's on octadecylsilane. The method is applied to sediment and involves an alkaline digestion and partitioning step prior to final analysis. Using UV and fluorescence detection, PAH's could be determined (129, 130) in natural and drinking water at the low parts per trillion level. Locke (131, 132) determined PAH's in suspended matter employing first extraction with cyclohexane followed by pre-fractionation by TLC. The resultant PAH fraction was separated on octadecylsilane using UV and fluorescence detection.

Afghan (35) has developed an improved method for PAH's in environmental samples using a multidetection system. A critical comparison of various concentration, cleanup and separation procedures was carried out. Cleanup procedures include GPC and chromatography on alumina. UV and fluorescence detection is employed and the method is applicable to natural waters, suspended solids, sediments, fish, road run-offs, precipitation and coal leachets.

Kesiske (133) applied HPLC to the analysis of PAH's and amino acids in water samples, included ground water, drinking water and surface water.

Phenols

Kuwata (134) proposed a method for the determination of phenols in air. Derivitization of the parent phenol was carried out with p-nitrobenzenediammonium tetrefluroborate prior to analysis by HPLC.

Pentachlorophenol in waste waters, sea water and marine biota has been reported (135, 136). Separation from other contaminants such as dioxins and other chlorinated phenols was achieved using cyclohexane-acetic acid as a mobile phase. Because the method did not involve derivitization or extensive cleanup, it was concluded that HPLC methods would be rapid and cost-effective.

HPLC has also been reported to determine isomers of aminophenol (137) and other naturally cocuring phenols (138).

Phthalate Esters

Schouten (139) compared HPLC and GC for the analysis of phthalate esters in river water and found good agreement between the two methods. HPLC was found to be less time consuming. A number of other workers have also reported the use of HPLC for the separation and identification of phthalate esters (6, 14, 141).

Amines

Young (142) reported optimum conditions for the separation of over fifty amines used in industry research. The separations were carried out on various silica gels using chloroform and/or cyclohexane mobile phases. Lin (143) proposed HPLC determination of naturally occuring primary and secondary amines in fish and shrimp samples. Pre-column derivitization was employed to separate aliphatic amines. The procedure was tested on dried fish and shrimp, fresh fish and canned fish samples. A thermal energy analyzer was used in conjunction with HPLC to determine nitrosamines in agricultural and home-use pesticides (144). The latter article does not deal with the analysis of environmental samples; however, it is significant and may have a potential for environmental analysis of nitrosamines.

Amino acids at picogram and subpicogram levels can be detected using pre-column derivitization prior to HPLC - fluorescence detection. The use of o-phthaldialdehyde has been recommended for a derivitizing agent to improve selectivity and sensitivity (145 - 151). The above approach is used to analyse sea water and biological fluids with good precision and accuracy.

Miscellaneous Compounds

The combinationa of HPLC and infrared detection was used for the analysis and characterization of polyethylene fatty acid surfactants and their decomposition products in industrial process waters (152). Trace amounts of non-ionic surfactants of the alkylphenol type have been measured in waste waters using HPLC with UV and IR detection systems(149). Trace enrichment was carried out using a pre-column packed with Porapak Q and subsequent elution with n-hexane.

HPLC has also received increasing attention in the separation and analysis of naturally occuring organics. Nagel (150) developed a separation scheme for the analysis of plant phenolic acids and their esters using HPLC. A number of stationary phases were evaluated for obtaining optimum separation. Reverse and normal phase chromatography on a weakly polar diol column was used to achieve optimum separation.

Separation of quinones and anthroquinones and their derivatives is also reported using HPLC (151, 152). The evaluation of several packings and solvent mixtures to optimize separation is also discussed.

High pressure liquid chromatography is also used for quantitative determination of esters of porphyrins and humic acid substances. Horchner and Riefveld (153) have developed an alternate method for obtaining improved separation of porphyrin esters. Saito and Hayno (154) proposed aqueous gel permeation chromatography for separation and characterization of humic substances.

Octanol - Water Partition Coefficients

The use of high performance liquid chromatography for measurement of octanol-water partition coefficient was described by Nahum (155). The technique was found to be rapid, accurate and has the further advantage that small samples are sufficient to determine the partition coeffients. Octanol water partition coefficients are used to predict the bioconcentration potential of organic compounds.

HPLC can also serve as a fast and cost effective technique for determination of aqueous solubility of organic compounds. Aqueous solubility is an important parameter that affects persistance, fate and transport of pollutants. May et al (156) determined the solubility of PAH's using dynamically coupled column liquid chromatography. The precision of the solubility measurements was ±3% or better.

SUMMARY

This review is intended to guide the reader to new and useful techniques in the HPLC analysis of environmental pollutants.

High performance liquid chromatography will prove to be a unique tool for clean-up of samples. With the development of the newer and more sensitive detection systems along with its ability to be interfaced with a wide variety of detection systems, will make HPLC as common in the environmental laboratory as GC is today.

REFERENCES

1. Konaswewich, D., Traversy, W. and Zar, H., International Joint Commission, Great Lakes Water Quality Board - Appendix E, Status Report on Organic and Heavy Metal Contaminants in the Lakes Erie, Michigan, Huron & Superior Basins, Windsor, 1978.

2. Lynch, M., and Weiner, E., HPLC: High Performance Liquid Chromatography, Environ. Sci. & Technol., 13, 666, 1979.

3. Grafteo, A.P., and Cooke, N.H.C., Summary of the U.S./Japan Seminar of Advanced Techniques of Liquid Chromatography, J. Chromatogry. Sc., 17,202,1979.

4. Veening, H., High Resolution Liquid Chromatography, CRC Critical Reviews in Analytical Chemistry, 5, 163, 1975.

5. Kowalczyk, J.S., Gazda, K., and Herbut, G., Effects of the Porous Structure of Particles on Selectivity in Liquid Chromatographic Systems, J. High Resolution Chromatogr. & Chromatogr. Comm., 2, 654,1979.

6. Afghan, B.K., Analytical Potential of HPLC and Associated Technicques for the Analysis of Pest-

icide Residues & Carcinogenic Compounds, 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, U.S.A.

7. Colmosjo, A.L., and MacDonald, J.C., Column Induced Selectivity in Separation of Polynuclear Aromatic Hydrocarbons by Reversed-Phase, High Performance Liquid Chromatography, Chromatographia, 13, 350, 1980.

8. Evans, M.B., Dale, A.D., and Little, C.S., The Preparation and Evaluation of Superior Bonded Phases for Reversed-Phased, High Performance Liquid Chromatography., Chromatographia. 13, 5, 1980.

9. Van de Venne, J.L.M., Rindt, J.P.M., Coenen, G.J.M.M. and Cramers, C.A.M.G., Synthesis of a Nonpolar, Chemically Bonded Stationary Phase with Low Residual Hydroxyl Group Content, Chromagraphic, 13,11, 1980.

10. Baum, R.G., Saetre, R., and Cantwell, F.F., Liquid Chromatography Columns of Microparticulate Amberlite XAD-2, Anal. Chem., 52, 15, 1980.

11. Rotsch, T.D., and Pietrzyk, D.J., Ion-Interaction in High Performance Liquid Chromatography of Benzenesulfonic Acids on Amerlite XAD-2, Anal. Chem., 52, 1323, 1980.

12. Matlin, S.A., Lough, W.J., and Bryan, O.G., HPLC with Chemically Bonded Stationary Phases, J. High Resolut. Chromatogr. and Chromatog. Comm., 2, 507 1979.

13. Matlin, S.A., Lough, W.J., and Bryan, O.G., HPLC with Chemically Bonded Stationary Phases, J. High Resolut. Chromatogr. and Chromatogr. Comm., 3, 33, 1980.

14. Mourey, T.H., Siggia, S., Uden, P.C., and Crowley., High Performance Liquid Chromatographic Separation of Polycyclic Aromatic Hydrocarbons on Microparticulate Pyrrolidone and Application to the Analysis of Shale Oil, Anal. Chem., 52, 885, 1980.

15. Kimura, K., Nakajima, M., and Shono, T., Poly (Crown Ether) - Modified Silica for Stationary Phase of Liquid Chromatography, Anal. Lett., 13, 741, 1980.

16. Taylor, P.J., and Sherman, P.L., Liquid Crystals as Stationary Phases for High Performance Liquid Chromatography, J. Liq. Chromatogr., 3, 21, 1980.

17. Tesarik, K., Preparation of Glass Capillary Columns for Liquid Chromatography, J. Chromatogr., 191, 25, 1980.

18. Scott, R.P.W. Microbore Columns in Liquid Chromatography, J., Chromatogr. Sci., 18, 49, 1980.

19. Scott, R.P.W., and Kucera, P., Mode of Operation and Performance Characteristics of Microbore Columns for use in Liquid Chromatography, J. Chromatogr., 169, 51, 1979.

20. Krejci, M., Tesarik, K., and Pajurek, J., Open Tubular Columns in Liquid Chromatography, J. Chromatogr., 191, 17, 1980

21. Hirata, F., Novotny, M., Tsuda, T., and Ishu, D., Packed Microcapillary Columns with Different Selectivities for Liquid Chromatography, Anal. Chem., 51, 1807, 1979.

22. Hibi, K., Ishii, D., and Tsuda, T., Alumina and Support-Coated Open Tubular Columns in Open-Tubular Micro-Capillary Liquid Chromatography, J. Chromatogr., 189, 179, 1980.

23. Ishii, D., Tsuda, T., and Takeuchi, T., Studies of Open-Tubular Micro-Capillary Liquid Chromatography, IV. Soda-Lime Glass Columns Treated with Alkaline Solution, S. Chromatogr., 185, 73, 1979.

24. Hibi, K., Tsuda, T., Toyohide, T., Nakanishi, T., and Ishu, D., Studies of Open-Tubular Microcapillary Liquid Chromatograph III. β,β' - Oxydipropionitrile & Ethylene Glycol Stationary Phases, J. Chromatogr., 175, 105, 1979.

25. Tsuda, T., Hibi, K., Nakanishi, T., Takeuchi, T., and Ishii, D., Studies of Open-Tubular Micro-Capillary Liquid Chromatography, II. Chemically Bonded Octadecylsilane Stationary Phase, J. Chromatogr., 158, 227, 1978.

26. Snyder, L.R., and Dolan, J.W., Coated-Open-Tubular Chromatography with Flow Segmentation, I. Theory, J. Chromatogr., 185, 43, 1979.

27. Dolan, J.W., and Snyder, L.R., Coated-Open-Tubular Chromatography with Flow Segmentation, II. Experi-

mental Study & Optimization for Size-Exclusion Separation, J. Chromatogr., 185, 57, 1979.

28. Fallick, G.J. and Rausch, C.W. New HPLC column technology, a revolution in resolution, Paper presented at the 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 5-9, 1979.

29. Assenza, S.P., Brown, P.R., Evaluation of Reversed-Phase, Radially-Compressed, Flexible-Walled Columns for the Separation of Low Molecular Weight, UV-Absorbing Compounds in Serum. J. Liquid Chromatogr., 3, 41, 1980.

30. Armstrong, D.W., and Henry, S.J., Use of an Aqueous Micellar Mobile Phase for Separation of Phenols & Polymuclear Aromatic Hydrocarbons via HPLC, J. Chromatogr., 3, 657, 1980.

31. Schoenmakers, P.J., Billret, H.A.H., and DeGalen, L., Influence of Organic Modifiers on the Retention Behaviour in Reversed-Phase Liquid Chromatography and its Consequences for Gradient Elution, J. Chromatogr., 185, 179, 1979.

32. Tanaka, N., Goodell, H., and Karger, B.L., The Role of Organic Modifiers on Polar Group Selectivity in Reversed-Phase Liquid Chromatography, J. Chromatogr., 158, 233, 1978.

33. Puncocharova, J., Kriz, J., Vodicka, L. Prusova, D., Influence of Mobile Phase Composition and Nature of Sample on Retention Data from High-

Performance Liquid Chromatography, J. Chromatogr., 191, 81, 1980.

34. Afghan, B.K., Ryan, J.F., and Wilkinson, R.J., Analysis of Carbamates in Natural Waters, Soils and Sediments using HPLC - Multidetection System, in preparation for publication.

35. Afghan, B.K., Wilkinson, R.J., and Ryan, J.F., An Improved Method for Analysis of Polynuclear Aromatic Hydrocarbons in Environmental Samples, in preparation for publication.

36. Block, J.H., Ayres, J.W., Henry, D.R., and Levine, H.L., Use of Flow Programming in Paired-Ion High-Performance Liquid Chromatographic Analysis of Dosage Dorms Containing Dyphylline, J. Chromatogr. 193, 111, 1980.

37. Aubert, J.H., Tirrell, M., On the Origins of Flow-Rate Dependence of Elution Volume in Gel Permeation Chromatography, Separation Sci., And Technol., 15, 123, 1980.

38. Gilpin, R.K., and Sisco, W.R., Effect of Temperature on Precision of Retention Measurements in Liquid Chromatography, J. Chromatogr., 194, 285, 1980.

39. Gant, J.R., Dolan, J.W., and Snyder, L.R., Systematic Approach to Optimizing Resolution in Reversed-Phase Liquid Chromatography, with emphasis on the Role of Temperature, J. Chromatogr. 185, 153, 1979.

40. Williams, K.J., Le Wan Po, A., and Irwin, W.J.,

Sample-Solvent-Induced Peak Broadening in the Reversed-Phase High-Performance Liquid Chromatography of Aspirin and Related Analgesics, J. Chromatogr. 194, 217, 1980.

41. McKinely, W.A., Popovich, E.J. and Layne, T., A Review of HPLC Detectors, American Lab., 37, 1980.

42. Ogan, K., Katz, E., Porro, T.J., The Role of Spectral Selectivity in Fluorescence Detection for Liquid Chromatography. J. Chromatogr. Sci., 17, 597, 1979.

43. Lawrence, J.F., Fluorimetric Derivatization in High Performance Liquid Chromatography, J. Chromatogr., Sci., 17, 147,1979.

44. Krause, R.T., Resolution, Sensitivity and Selectivity of a High-Performance Liquid Chromatographic Post-Column Fluorometric Labeling Technique for Determination of Carbamate Insecticides, J. Chromatogr. 185, 615, 1979.

45. Tomkins, B.A., Ostrum, W.H., and Ho, C.H. Derivatization of Primary Aromatic Amines with Fluroreseamine, Anal. Lett., 13, 589, 1980.

46. Dunges, W., Fluorescence Labelling of Picomole Amounts of Acidic Herbicides for Toxicologial Analysis, Chromatographic, 9, 624, 1976

47. Brinckman, F.E., Jewett, K.L., and Iversen, W.P., Irgolic, K.J., Ehrhardt, K.C. and Stockton, R.A., Graphite Furnace Atomic Absorption Spectrophotometers As Automated Element-Specific Detectors for High-Pressure Liquid Chromatography. The Determination of

Arsenite, Arsenate, Methylarsonic Acid and Dimethylarsinic Acid, J. Chrometogr. 191, 31, 1980.

48. Stockton, R.A., and Irgolic, K.J., The Hitachi Graphite Furnace-Zeeman Atomic Absorption Spectrometer as an Automated, Element-Specific Detector for High Pressure Liquid Chromatography: The separation of Arsenobetaine, Arsenocholine and Arsenite/Arsenate, Int. J. Environ. and Chem., 6, 313, 1979.

49. Koizumi, H., McLaughlin, R.D., and Hadeishi, T., High Gas Temperature Furnace for Species Determination of Organometallic Compounds with a High Pressure Liquid Chromatograph and a Zeeman Atomic Absorption Spectrometer, Anal. Chem., 51, 387, 1979.

50. Gast, C.H., Kraak, J.C., Poppe, H., and Maessen, F.J. M.J., Capabilities of On-Line Element-Specific Detection in High-Performance Liquid Chromatography Using an Inductively Coupled Argon Plasma Emmission Source Detector, J. Chromatogr. 185, 549, 1979.

51. Kuehl, T., and Griffiths, P.R., Microcomputer-Controlled Interface between a High Performance Liquid Chromatograph and a Diffuse Reflectance Infrared Fourier Transform Spectrometer, Anal., Chem., 52, 1394, 1980.

52. Smith, S.L., Jorgenson, J.W., and Novotny, M., Analysis of Neutral Lipids by High-Performance Liquid Chromatography and Nephelometric Detection, in "Trace Organic Analysis: A New Frontier in Analytical Chemicals," National Bureau of Standards, Spec., Pub., N.B.S., Gaithersburg, Maryland, 1979, pp 429.

53. Stulik, K., and Pacakova, V., Electrochemical Detector for High-Performance Liquid Chromatography, J. Chrometogr. 192, 135, 1980.

54. Kutner, W., Debowski, J., and Kemula, W., Polarographic Detection for High-Performance Liquid Chromatography Using a Flow-Through Detector, J. Chromatogr. 191, 47, 1980.

55. Hanekamp, H.B., Voogt, W.H., and Bos, P., Application of Pulse Techniques in a Polarographic Flow-Through Detector with Potential-Controlled Drop Synchronization, Anal. Chem., Acta, 118, 73, 1980.

56. Blaedel, W.J. and Yim, Z., Rapid Pulsed Flow Voltammetry, Anal., Chem., 52, 564, 1980.

57. Blank, C.L., Dual Electrochemical Detector for Liquid Chromatography, J. Chromatogr., 117, 35, 1976.

58. Lown, J.A., Koile, R., and Johnson, D.C., Amperometric Flow-Through Wire Detector: A Practical Design with High Sensitivity, Anal. Chim. Acta, 116, 33, 1980.

59. Toth, K., Nagy, G., Feher, Z., Horvia, G., and Pungor, E., The Application of Electroanalytical Detectors in Continuous Flow Analysis, Anal. Chim., Acta, 114, 45, 1980.

60. Brilmyer, G.H., Lamey, S.C. and Maloy, J.T., Liquid Chromatography Detection by Current Semintegral Electroanalysis in Flowing Streams, Anal., Chem., 47, 2304, 1975.

61. Takata, Y., and Muto, G., Flow Coulometric Detector for Liquid Chromatography, Anal. Chem., 45, 1864, 1973.

62. Tjaden, R., Lankelma, J., Poppe, H., Muusze, G., Anodic Coulometric Detection with a Glassy Carbon Electrode in Combination with Reversed-Phase High-Performancy Liquid Chromatography: Determination of Blood Levels of Perphenazine and Flu-Phenazine, J. Chromatogr. 125, 275, 1976.

63. Dolan, W.J., and Seiber, J.N., Chlorine-Selective Detection for Liquid Chromatography with a Coulson Electrolytic Conductivity Detector, Anal. Chem., 49, 326, 1977.

64. Small, H., Stevens, T.S., and Baikam, W.C., Novel Ion Exchange Chromatographic Method Using Conductimetric Detection, Anal. Chem., 47, 1801, 1975.

65. Blaedel, W.J., and Wang, J., Pulsed Rotation Voltammetry in a Flow-Through Cell, Anal. Chimica Acta, 116, 315, 1980.

66. Hanekamp, H.B., Voogt, W.H., Bos, P., and Frei, R.W., An Electrochemical Scrubber for the Elimination of Eluent Background Effects in Polarographic Flow-Through Detection, Amal, Chimica, Acta, 118, 81, 1980.

67. Rucki, R.J., Electrochemical Detectors for Flowing Liquid Systems, Talanta, 27, 147, 1980.

68. Fujinaga, T., and Kihara, S., Electrolytic Chromatograph and Coulopotentiography - A Rapid Electrolysis at the Column Electrode Used for the Preparation,

Separation, Concentration, and Estimation of Trace and/ or Unstable Substances, C.R.C. Crit. Rev. in Anal. Chem. 233, 1977.

69. Kissinger, P.T., Bratin, K., Davis, G.C. and Pachia, L.A., The Potential Utility of Pre-and Post-Column Chemical Reactions with Electrochemical Detection in Liquid Chromatography, J. Chromatogr. Sci. 17, 137, 1979

70. Armentrout, D.N., McLean, J.D., and Long, M.W., Trace Determination of Phenolic Compounds in Water by Reversed Phase Liquid Chromatography with Electrochemical Detection Using a Carbon-Polyethylene Tubular Anode, Anal. Chem., 51, 1039, 1979.

71. Whittaker, J.W., and Osteryoung, J., Determination of Picloram and Dowco 290 by Pulse Polarography, J. Agric. Food Chem., 28, 89, 1980.

72. Afghan, B.K. and Bately, G., Analytical Potential of Voltammetry Detection for Pesticide Residue and Industrial Contaminants in Enviromental Samples - unpublished results.

73. Stalling, D.L., Petty, J.D., Dubay, GR., and Smith, R.A., Application of LC/MS to Chromatographic Separation of Aromatics Using Carbon as the Station Phase, J. Chromatogr. Sci., 18, 107, 1980.

74. Takeuchi, T., On-Line Coupling of a Micro Liquid Chromatograph and Mass Spectrometer through a Jet Separator, Anal. Chem., 50, 659, 1978.

75. Blakley, C.R., McAdams, M.R., Vestal, M.L., Crossed-Beam Liquid Chromatograph-Mass Spectrometer Combination, J. Chromatogr. 158, 261, 1978.

76. McFadden, W.H., Liquid Chromatography/Mass Spectrometry Systems and Applications, J. Chromatogr. Sci., 18, 97 1980.

77. Skinner, R.F., Thomas, Q., Giles, J., and Crosby, D.G., The Determination of Herbicide Photolysis Products by LC/MS, J. Chromatogr. Sci., 18, 108, 1980.

78. McAdams, M.J., and Vestal, M.L., Analysis of Priority Pollutants by Crossed-Beam LC/MS, J. Chromatogr. Sci., 18, 110, 1980.

79. Games, D.E. and Weerasinghe, N.C.A., Analysis of the Metabolites of CIPC (Chloropropham), J. Chromatogr. Sci., 18, 106, 1980.

80. Kenyon, C.N., Melera, A., Erni, F., Use of the Direct Liquid Inlet LC/MS System for the Analysis of Complex Mixtures of Biological Origin, J. Chromatogr., Sci., 18, 103, 1980.

81. Haw, J.F., Glass, T.E. Hausler, D.W., Motell, E., and Dorn, H.C., Direct Coupling of a Liquid Chromatograph to a Continuous Flow Hydrogen Nuclear Magnetic Resonance Detector for Analysis of Petroleum and Synthetic Fuels, Anal. Chem., 52, 1135, 1980.

82. Chamberlain, A.T., and Marlow, J.W., Solvent Systems and Applications of the Liquid Chromatograph Electron Capture Detector, J. Chromatogr. Sci., 15, 29, 1977.

83. Wise, S.A., Mowery, Jr., R.A., and Juvet, Jr. R.S., A Universal Detector for Liquid Chromatography: The Flame Aerosol Detector, J. Chromatogr., Sci., 17, 601, 1979.

84. Ross, R.D., Morrison, J., Rounbehler, D.P., Fan, S., and Fine, D.H., N-Nitroso Compound Impurities in Herbicide Formulations, J. Agric. Food Chem., 25, 1416, 1977.

85. Ogan, K., and Katz, E., Coupled-Column Chromatography Used for Sample Preparation for Chromatographic Analyses Of Oil and Coal Samples, Second Symp. Environ. Anal. Chem., Brigham Young U., Ohio, June, 1980.

86. Johnson, E.L., Gloor, R., and Majors, R.E., Coupled Column Chromatography Employing Exclusion and a Reversed Phase: A Potential General Approach to Sequential Analysis, J. Chromatogr., 149, 571, 1978.

87. Huber, J.F.K., and Vodenik, R., Exploitation of Phase-System Selectivity by Two-Column Liquid Chromatography: Separation of Carbamate Pesticides, J. Chromatogr., 122, 331, 1976.

88. Erni, F., and Frei, R.W., Two-Dimensional Column Liquid Chromatographic Technique for Resolution of Complex Mixtures, J. Chromatogr. 149, 561, 1978.

89. Van Vliet, H.P.M., Bootsman, Th.C., Frei, R.W. and Brinkman, U.A.Th., On-Line Trace Enrichment in High-Performance Liquid Chromatography using a Pre-Column, J. Chromatogr., 185, 483, 1979.

90. Frei, R.W., Trace Enrichment and Chemical Derivation in Liquid Chromatography: Problems and Potential in Environmental Analysis, Int. Symp. Anal. Chem. of Pollutants, 5, 143, 1977.

91. Saner, W.A., Jadamec, J.R., Sager, R.W. and Killeen T.J., Trace Enrichment with Hand-Packed CO:PELL ODS Guard Columns and Sep-Pak C_{18} Cartridges, Anal. Chem., 51, 2180, 1979.

92. Cassidy, R.M., and Elchuk, S., Trace Enrichment Methods for the Determination of Metal Ions by High Performance Liquid Chromatography, J. Chromatogr. Sci., 18, 217, 1980.

93. Hulpke, H., Werthmann, U., Chromatogrphia, 13, 395, 1980.

94. Ramstad, T., Mahle, N.H., and Matalon, R., Automated Cleanup of Herbicides by Adsorption Chromatography for the Determination of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin, Anal. Chem., 49, 386, 1977.

95. Wolkoff, A.W. & Larose, R.H., Procedure for the Quantitative Liquid Chromatographic Separation and Clean Up of 18 Organo-Chlorine Pesticides and PCB's in Extracts of Water, Waste-water, Fish or Sediment. CCIW Internal Report 1977.

96. Larose, R.H., High-Speed Liquid Chromatographic Cleanup of Environmental Samples Prior to the Gas Chromatographic Determination of Lindane. J. of A.O.A.C. 57, 1046, 1974.

97. Thruston, Jr., A.D., High Pressure Liquid Chromatography Techniques for the Isolation and Identification of Organics in Drinking Water Extracts, J. Chromatogr. Sci., 16, 254, 1978.

98. Stalling, D.L., Tindle, R.C., and Johnson, J.L., Cleanup of Pesticide and Polychlorinated Biphenyl Residues of Fish Extracts by Gel Permeation Chromatography, J. of AOAC, 55, 32, 1972.

99. Tindle, R.C., and Stalling, D.L., Apparatus for Automated Gel Permeation Cleanup for Pesticide Residue Analysis: Applications to Fish Lipids, Anal. Chem., 44, 1768, 1972.

100. Griffitt, K.R., and Craun, J.C., Gel Permeation Chromatographic System: An Evaluation, J. of AOAC, 57, 168, 1974.

101. Tessari, J.D., Griffin, L., and Aaronson, M.J., Comparison of Two Cleanup Procedures (Mills, Onley, Gaither vs Automated Gel Permeation) for Residues of Organochlorine Pesticides and Polychlorinated Biphenyls in Human Adipose Tissue, Bull. Envirm. Contam. Toxicol, 25, 59, 1980.

102. Taylor, P.W. and Nickless, G., Paired-Ion High-Performance Liquid Chromatography of Partially Biodegraded Linear Alkylbenzenesulphonate, J. Chromatogr., 185, 259, 1979.

103. Riley, C.M., Tomlinson, E., and Jefferies, T.M., Functional Group Behaviour in Ion-Pair Reversed-Phase High-Performance Liquid Chromatography Using Surface-Active Pairing Ions, J. Chromatogr. 185, 197, 1979.

104. Scott, R.P.W. and Kucera, P., Some Aspects of Ion-Exchange Chromatography Employing Adsorbed Ion

Exchangers on Reversed-Phase Columns, J. Chromatogr., 175, 51, 1979.

105. Tomlinson, E., Jefferies, T.M., and Riley, C.M., Ion-Pair High-Performance Liquid Chromatography, J. Chromatogr., (Chromatogr. Rev.) 159, 215, 1978.

106. Davankov, K.A., and Semechkin, A.V., Lingard-Exchange Chromatography, J. Chromatogr., (Chromatogr. Rev.) 141, 313, 1977.

107. Crathorne, B., Watts, C.D. and Fielding, M., Analysis of Non-Volatile Organic Compounds in Water by High-Performance Liquid Chromatography, J. of Chromatogr., 185, 671, 1979.

108. Lawrence, J.F., and Turton, D., High-Performance Liquid Chromatographic Data for Pesticides, J. Chrometogr., (Chromatogr. Rev.) 159, 207, 1978,

109. Grorud, R.B. and Stevens, T.S., Isomer Specific Assay of Ester and Salt Formulations of 2-Methyl-4-Chlorophenoxyacetic Acid and 2,4,5-Trichlorophenoxyacetic Acid by High Pressure Liquid Chromatography; Collaborative Study, J. Assoc. Off. Anal. Chem., 63,873, 1980.

110. Brinkman, U.A.TH., Seetz, J.W.F.L. and Reymer, H.G.M., High-Speed Liquid Chromatography of Polychlorinated Bi-Phenyls and Related Compounds, J. Chrometgr., 116, 353, 1976.

111. Brinkman, U.A.Th., DeKok, A., DeVries, G., and Reymer, H.G.M., High-Speed Liquid and Thin Layer

Chromatography of Poly-Chlorinated Biphenyls, J. Chromatogr., 128, 101, 1976.

112. Brinkman, U.A.Th., and DeKok, A., High-Performance Liquid Chromatographic Analysis of the Heptachloronaphthalenes present in Halowax 1051, J.Chromatogr. 129, 451, 1976.

113. Brinkman, U.A.Th., DeKok, A., Reymer, H.G.M. and DeVries, G., Analysis of Polychlorinated Naphthalenes by High-Performance Liquid and Thin-Layer Chromatography, J. Chrometogr., 129, 193, 1976.

114. Dolphin, R.J. and Willmott, F.W., Separation of Chlorinated DiBenzo-p-Dioxins from Chlorinated Congeners, J. Chromatogr., 149, 161, 1978.

115. Pfeiffer, C.D., Nestrick, T.J., and Kocher, C.W., Determination of Chlorinated Dibonzi-p-Dioxins in Purified Pentachlorophenol by Liquid Chromatography, Anal. Chem. 50, 800, 1978.

116. Pfeiffer, C.D., Determination of Chlorinated Dibenzo-p-Disxins in Pentachlorophenol by Liquid Chromatography, J. Chromatogr., 14, 386, 1976.

117. Otsuki, A., Takaku, T., Determination of an Organophosphorus Insecticide in Water at Parts per Billion by Reversed Phase Adsorption Liquid Chromatography, Anal., Chem., 51, 833, 1979.

118. Szalontai, G., High-Performance Liquid Chromatography of Organophosphorus Insecticides, J. Chromatogr., 124, 9, 1976.

119. Nelson, T.R., and Cook, R.F., A High-Pressure Liquid Chromatogrphic Method for the Determination of Carbofuran Residues in Soil and Water, J. Agric. Food Chem. 27, 1186, 1979.

120. Wolkoff, A.W., Larose, R.H., A Highly Sensitive Technique for the Liquid Chromatographic Analysis of Phenols and other Environmental Pollutants, J. Chromatogr., 99, 731, 1974.

121. Pieper, G.R., Residue Analysis of Carbaryl on Forest Foliage and in Stream Water Using HPLC, Bull. Environm. Contam. Toxicol., 22, 167, 1979.

122. Sparacino, C.M., and Hines, J.W., High-Performance Liquid Chromatography of Carbamate Pesticides, J. Chromatogr., Science, 14, 549, 1976.

123. Dufek, P., Pacakova, V., and Tesarova, E., Separation and Behaviour of s-Triazine Derivatives on a NH_2-Chemically Bonded Stationary Phase by High-Performance Liquid Chromatography, J. Chromatogr., 191, 115, 1980.

124. Vickrey, T.M., Karlesky, D.L., and Blackmer, G.L., Colorimetry and High Performance Liquid Chromatography of Atrazine Residues in Soil: Comparison of Methods, J. Assoc. Off. Anal. Chem. 63, 506, 1980.

125. Ramsteiner, K.A., and Hormann, W.D., High-Pressure Liquid Chromatographic Determination of Hydroxy-s-triazine Residues in Plant Material, J. Agric. Food Chem., 27, 934, 1979.

126. Iadevaia, R., Aharonson, N.,and Woolson, E.A., Extraction and Cleanup of Soil Arsenical Residues for Analysis by High Pressure Liquid Chromatographic-Graphite Furnace Atomic Absorption, J. Assoc. Off., Anal. Chem., 63, 742, 1980.

127. Woolson, E.A., and Aharonson, N., Separation and Detection of Arsenical Pesticide Residues and Some of Their Metabolites by High Pressure Liquid Chromatography-Graphite Furnace Atomic Absorption Spectrometry, J. Assoc. Off. Anal. Chem., 63, 523, 1980.

128. Black, J.J., Dymerski, P.P., and Zapisek, W.F., Routine Liquid Chromatographic Method for Assessing Polynuclear Aromatic Hydrocarbon Pollution in Fresh Water Environments, Bull. Environm. Contam. Toxicol, 22, 278, 1979.

129. Sorrell, R.K., and Reding, R., Analysis of Polynuclear Aromatic Hydrocarbons in Environmental Waters by High-Pressure Liquid Chromatography, J.'Chromatogr., 185, 655, 1979.

130. Ogan, K.,Katz, E., Slavin, W., Concentration and Determination of Trace Amounts of Several Polycyclic Aromatic Hydrocarbons in Aqueous Samples, J. Chromatogr. 16, 517, 1978.

131. Dong, M., and Locke, D.C., High Pressure Liquid Chromatographic Method for Routine Analysis of Major Parent Polycyclic Aromatic Hydrocarbons in Suspended Particulate Matter, Anal. Chem., 48, 368, 1976.

132. Dong, M., and Locke, D.C., Separation of Aza-Arenes By High-Pressure Liquid Chromatography, J. Chromatogr., 15, 32, 1977.

133. Kasiske, D., Klinkmuller, K.D., and Sonneborn, M., Application of High-Performance Liquid Chromatography To Water Pollution Analysis, J. Chromatogr., 149, 703, 1978.

134. Kuwata, K., Uebort, M., and Yamazaki, Y., Determination of Phenol in Polluted Air as p-Nitrobenzeneazophenol Derivative by Reversed Phase High Performance Liquid Chromatography., Anal. Chem., 52, 857, 1980.

135. Ervin, H.E., and McGinnis, G.D., Analysis of Pentachlorophenol in Waste Water Using High-Performance Liquid Chromatography, J. Chromatogr., 190, 203, 1980.

136. Fass, L.F., Moore, J.C., Determination of Pentachlorophenol in Marine Biota and Sea Water by Gas-Liquid Chromatography and High-Pressure Liquid Chromatography, J. Agric. Food Chem., 27, 554, 1979.

137. Sakural, H., and Ogawa, S., Determination of Aminophenol Isomers by High-Speed Liquid Chromatography, J. Chromatogr.Sci., 14, 499, 1976.

138. Court, W.A., High-Performance Reversed-Phase Liquid Chromatography of Naturally Occurring Phenolic Compounds, J. Chromatogr., 130, 287, 1977.

139. Schouten, M.J., Copius Peereboom, J.W., and U.A.

Th. Brinkman, Liquid Chromatographic Analysis of Phthalate Esters in Dutch River Water, Intern., J. Environ Anal. Chem., 7, 13, 1979.

140. Mori, S., Identification and Determination of Phthalate Esters in River Water by High-Performance Liquid Chromatography, J. Chromatogr., 129, 53, 1976.

141. Otsuki, A., Reversed-Phase Adsorption of Phthalate Esters from Aqueous Solutions and Their Gradient Elution Using a High-Performance Liquid Chromatography, J. Chromatogr., 133, 402, 1977.

142. Young, P.R., and McNair, H.M., High-Pressure Liquid Chromatography of Aromatic Amines, J. Chromatogr., 119, 569, 1976.

143. Lin, J.K., and Lai, C.C., High Performance Liquid Chromatographic Determination of Naturally Occurring Primary and Secondary Amines with Dabsyl Chloride, Anal. Chem., 52, 630, 1980.

144. Bontoyan, W.R.,Law, M.W., and Wright, Jr., D.P., Nitrosamines in Agricultural and Home-Use Pesticides, J. Agric. Food Chem., 27, 631, 1979.

145. Lindroth, P.,and Mopper, K., High Performance Liquid Chromatographic Determination of Subpicomole Amounts of Amino Acids by Precolumn Fluorescence Derivatization with o-Phthaldialdehyde, Anal. Chem., 51, 1667, 1979.

146. Hill, D.W., Walters, F.H., Wilson, T.D., and Stuart, J.D., High Performance Liquid Chromatographic Determination of Amino Acids in the Picomole Range, Anal. Chem. 51, 1338, 1979.

147. Cronin, J.R., Pizzarello, S., and Gandy, W.E., Amino Acid Analysis with o-Phthalaldehyde Detection; Effects of Reaction Temperature and Thiol on Fluorescence Yields, Anal. Bio. Chem., 93, 174, 1979.

148. Cassidy, R.M., and Niro, C.M., Application of High-Speed Liquid Chromatography to the Analysis of Polyoxyethylene Surfactants and their Decomposition Products in Industrial Process Waters, J. Chromatogr., 126, 787, 1976.

149. Krejci, M., and Roudna, M., Analysis of Non-Ionic Surfactants of the Alkyphenol Type in the Presence of Mineral Oil by means of Liquid Chromatography, J. Chromatogr., 91, 549, 1974.

150. Nagels, L., Van Dongen, W., DeBrucker, J., and DePooter, H., High-Performance Liquid Chromatographic Separation of Naturally Occurring Esters of Phenolic Acids, J. Chromatogr., 187, 181, 1980.

151. Rittich, B., and Krska, M., Separation of Quinones and their Derivatives by High-Performance Liquid Chromatography, J. Chromatogr., 130, 189, 1977.

152. Rai, P.P., Turner, T.D., and Matlin, S.A., High-Pressure Liquid Chromatography of Naturally Occurring Anthraquinones, J. Chromatogr., 110, 401, 1975.

153. Horchner, P., and Rietveld, T., Rapid Method for the Quantitative Determination of Porphyrin Methyl Esters by High-Pressure Liquid Chromatography, J. Chromatogr., 123, 414, 1976.

154. Saito, Y., and Hayano, S., Application of High-Performance Aqueous Gel Permeation Chromatography to Humic Substances from Marine Sediment, J. Chromatogr., 177, 390, 1979.

155. Nahum, A., and Horvath, C., Evaluation of Octanol-Water Partition Coefficients by Using High-Performance Liquid Chromatography, J. Chromatogr., 192, 315, 1980

156. May, W.E., and Wasik, S.P., and Freeman, D.H., Determination of the Solubility Behavior of Some Polycyclic Aromatic Hydrocarbons in Water, Anal. Chem., 50, 997, 1978.