

- (8) L. R. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes", *Spec. Publ. No. 17*, The Chemical Society, London, 1964.
(9) R. Cecil and J. R. McPhee, *Adv. Protein Chem.*, **14**, 293 (1959).
(10) L. Michaelis and E. S. G. Barron, *J. Biol. Chem.*, **81**, 29 (1929).
(11) C. Voegtlin, J. M. Johnson, and S. M. Rosenthal, *J. Biol. Chem.*, **93**, 435 (1931).
(12) J. S. Fruton and H. T. Clarke, *J. Biol. Chem.*, **106**, 667 (1934).
(13) E. S. G. Barron, *Arch. Biochem. Biophys.*, **59**, 502 (1955).
(14) E. S. G. Barron, Z. B. Miller, and G. Kalinsky, *Biochem. J.*, **41**, 62 (1947).

- (15) R. Wade, M. Winitz, and M. P. Greenstein, *J. Am. Chem. Soc.*, **78**, 371 (1956).
(16) "The Sadtler Standard Spectra", Sadtler Research Laboratories, *N.M.R.*, **1**, 286 (1966).
(17) M. Cefola, Sr., Simon Peter, P. S. Gentile, and Rev. A. V. Celiana, *Talanta*, **9**, 537 (1962).

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AIDS FOR ANALYTICAL CHEMISTS

Rapid and Inexpensive Method for Detection of Polychlorinated Biphenyls and Phthalates in Air

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The total production of phthalic acid esters is about ten times larger than that of polychlorinated biphenyls (PCBs), which are recognized as environmental pollutants. In recent years, scientists have been concerned with the release of phthalate plasticizers into the environment (1), but previously reported methods are often insufficiently sensitive, elaborate, or multistep procedures which introduce contaminants to the sample. Thomas (2), using ethylene glycol as a trapping solvent, detected 300 ng/m³ of di(2-ethylhexyl)phthalate (DEHP), 750 ng/m³ butylphthalyl butyl glycolate, and 700 ng/m³ di-*n*-butyl phthalate (DBP) in air samples taken at the water works of the Municipality of Hamilton in Canada. Recently, gas chromatographic column packings or solid supports have been used to trap organics from air (3-10) and have proved to be more advantageous than other methods. Mieux and Dietrich (7) used 5% Dexsil 300 on 80-100 mesh HP Chromosorb W to determine trace organics in air; the particular phthalate esters present could not be identified because of GC interferences. It is well established that environmental analytical chemistry needs simple, inexpensive, and sensitive analytical methods for routine monitoring.

This paper describes a simple, inexpensive, and sensitive method for the determination at low levels (ng/m³) of not only specific phthalate esters but also PCBs and DDT in air; Florisil was used for both sampling and separation of the mixture of pollutants.

EXPERIMENTAL

Apparatus. A Tracor Model MT-220 gas chromatograph (GC) equipped with a Nickel-63 (10 mCi) electron capture (EC) detector in a dc mode was used for analyses. It was fitted with a 6-ft × ¼-in. o.d. borosilicate glass column packed with 3% SE-30 on Gas Chrom Q (100-120 mesh); nitrogen was used as the carrier gas at a flow rate of 60 cm³/min. The injector, detector, and column temperatures were 250, 275, and 200 °C, respectively.

A Hewlett-Packard Model 5700A GC equipped with a ⁶³Ni (15 mCi) EC detector and a 6-ft × ¼-in. o.d. borosilicate glass column packed with 3% SE-30 on Chromosorb WHP (100-120 mesh) was also used for analyses. Methane 10%/argon 90% was used as the carrier gas at a flow rate of 60 cm³/min. The injector, detector, and oven temperatures were 200, 300, and 200 °C, respectively. The EC detector responses were linear up to 100 ng DEHP per injection.

Second-column confirmation was performed on a Barber-Colman Model 5360 GC with a Tritium (300 mCi) EC detector in a pulse mode, equipped with a 6-ft × ¼-in. o.d. borosilicate glass column packed with 1.5% SP-2250 and 1.95% SP-2401 on Supelcon AW-DMCS (100-120 mesh). The injector, detector, and column temperatures were 210, 210, and 195 °C, respectively. The operating sensitivity for the detectors was about 5 ng DEHP giving 50% full scale deflection (fsd).

Reagents. Petroleum ether (Mallinckrodt Nanograde) was used as received. Anhydrous ether (Mallinckrodt) was freshly distilled immediately before use.

Anhydrous sodium sulfate (granular, Mallinckrodt) and Florisil (60/100 PR grade, Floridin Chemical Co.) were heated at 320 °C for at least 24 hr prior to use. All solvents and reagents were checked for contamination before use by GC analysis of a concentrate of the solvent or solvent rinse of solid reagents.

Procedure. A Pasteur disposable capillary pipet or a short section of conventional GC column (¼-in. o.d.) was used as the collection column. Each column was packed with 0.3 g of deactivated Florisil (3% water W/W), followed by 1 g of granular anhydrous sodium sulfate and a small plug of glass wool. The column was connected to an oil-less vacuum pump with Teflon tubing. For example, we used a flow rate of about 2-4 l./min with the free air capacity of the pump being 90 l./min. Sampling times varied but as long as 60 hr were used.

The Florisil was eluted with 4 ml of petroleum ether followed by 4 ml of diethyl ether. The two fractions were collected in graduated centrifuge tubes, concentrated or diluted as needed, and analyzed by gas chromatography. The petroleum ether fraction contains the chlorinated hydrocarbons while the ether eluate contains the phthalate esters. Excellent blanks were obtained with background levels of 1 ng for DEHP, 0.1 ng for PCBs, and 0.1 ng for DDT.

RESULTS AND DISCUSSION

Since the electron capture detector is sensitive to the presence of phthalates (11) as well as to the chlorinated hydrocarbons, we have been investigating electron-capture gas chromatographic methods for the trace analysis of these two groups of compounds in environmental samples. In developing these procedures, we found that airborne contamination in the laboratory would be a significant problem. Since "clean-rooms" are expensive and often not available in many laboratories, we sought a way to rapidly analyze and monitor the air in various working areas in order to select those areas that were optimal for our work. The solid sampling systems, such as the gas chromatographic packings or other adsorbents, appeared to offer the

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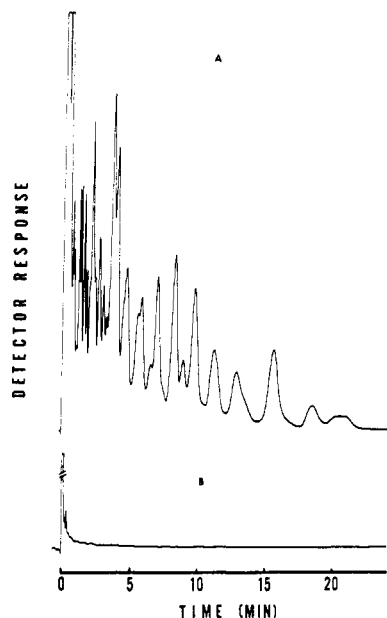


Figure 1. Gas chromatograms of petroleum ether eluates from Florisil

(A) Air sample; (B) procedure blank

best route to a simple, convenient, and rapid method for air analyses. However, many of the previously utilized systems involved elaborate, sometimes expensive and fragile apparatuses or were very time consuming. We had observed that Florisil adsorbed organic chemicals on exposure to contaminated air. Since Florisil could also provide a preliminary chemisorption separation of the pollutants of interest, we undertook a study of its use as an air-sampling adsorbant.

DEHP is one of our more persistent contaminants and preliminary experiments were conducted using it as the test compound. A series of five 1-cm columns of Florisil prepared in Pasteur pipets were connected in sequence. Air was then drawn through 25 ml of DEHP into the columns at 750 cm³/min for 6 days. After this period, only the first column adjacent to the DEHP source contained detectable DEHP. Thus, the Florisil was demonstrated to be very efficient for trapping this compound from air. Similarly, columns spiked with DDT and PCBs were shown to retain virtually all of the added sample on the first column even after 5 days of air flow at 2–3 l./min.

A series of test samples was then obtained in various working areas of the building. The gas chromatograms obtained from the petroleum ether eluates resembled those from the PCBs, as shown in Figure 1. DEHP was a major component of the ether eluate, along with a number of unidentified compounds, as in Figure 2. The analysis of these samples yielded 35–90 ng/m³ of PCB and 30 to 70 ng/m³ of DEHP with the highest values found near the heating vents and in the hoods.

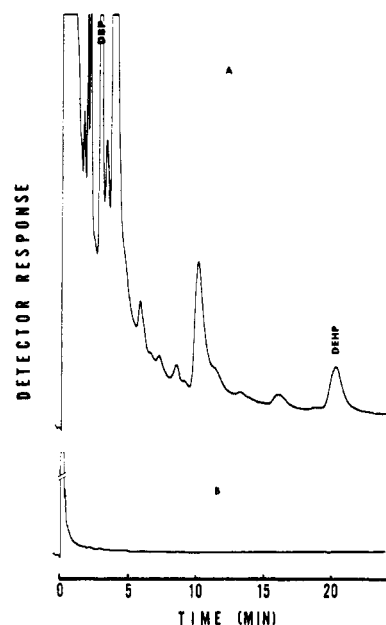


Figure 2. Gas chromatograms of ethyl ether eluates from Florisil

(A) Air sample; (B) procedure blank

The above method has been used successfully for assessing our laboratory and office air, and is useful for the frequently encountered chlorinated hydrocarbons (DDT, PCBs) and phthalate esters. It is apparent that this system can be used for monitoring air in industrial plants or other working areas and that its scope can be expanded. For example, other organic compounds can be adsorbed and separated by different adsorbants or eluant combinations. Also, larger columns can be used for shorter sampling times or for detecting lower concentrations of contaminants. An important feature of this procedure is the very low blanks obtained (1 ng or less).

LITERATURE CITED

- (1) *Environ. Health Perspect.*, **3**, (1973).
- (2) G. H. Thomas, *Environ. Health Perspect.*, **3**, 23 (1973).
- (3) F. R. Cropper and S. Kaminsky, *Anal. Chem.*, **35**, 737 (1963).
- (4) F. W. Williams and M. E. Umstead, *Anal. Chem.*, **40**, 2232 (1968).
- (5) A. Dravnieks, B. K. Krotoszynski, J. Whitefield, A. O'Donnell and T. Burgwald, *Environ. Sci. Technol.*, **5**, 1220 (1971).
- (6) W. A. Aue and P. M. Teli, *J. Chromatogr.*, **62**, 15 (1971).
- (7) J. P. Mieure and M. W. Dietrich, *J. Chromatogr. Sci.*, **11**, 559 (1973).
- (8) T. C. Thomas and J. N. Seiber, *Bull. Environ. Contam. Toxicol.*, **12**, 17 (1974).
- (9) T. F. Bidleman and C. E. Olney, *Bull. Environ. Contam. Toxicol.*, **11**, 442 (1974).
- (10) W. Bertsch, R. C. Chang, and S. Zlatkis, *J. Chromatogr. Sci.*, **12**, 175 (1974).
- (11) W. Bunting and E. A. Walker, *Analyst*, **92**, 575 (1967).

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