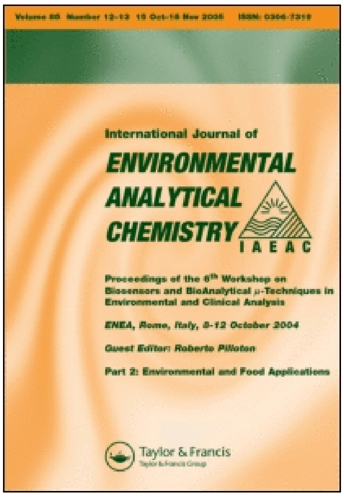

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Chromatographic Separation and Analysis of Chlorinated Hydrocarbons and Phthalic Acid Esters from Ambient Air Samples

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The elution of a series of common atmospheric organic pollutants was tested on a 1.25%-deactivated Florisil column. It was found that phthalate esters and dieldrin could be eluted from the column with 50% (v/v) diethyl ether in petroleum ether. Other chlorinated hydrocarbons, aliphatic hydrocarbons, and polyaromatic hydrocarbons are eluted first with petroleum ether followed by 5% (v/v) diethyl ether in petroleum ether. This procedure was used to successfully separate a mixture of chlorinated hydrocarbons and phthalate esters found in ambient air along the Texas Gulf Coast.

The world-wide distribution of synthetic organic pollutants, such as polychlorinated biphenyls (PCB) and DDT compounds, has been attributed to long-range transport and deposition from the atmosphere.[1–4] In fact, the atmosphere carries an extraordinarily complex mixture of natural and synthetic organic compounds. Analysis of such complex mixtures typically requires the combined use of high-resolution gas chromatography (GC), sensitive and

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selective chromatographic detectors, and efficient separation of compound classes prior to GC analysis. In ambient air samples from the Texas Gulf Coast, pollutants which have been measured include DDT compounds, components of technical chlordane, PCB, toxaphene, hexachlorocyclohexane isomers, and phthalic acid esters. Several of these compound classes, e.g., PCB and toxaphene, contain hundreds of individual isomers which are not totally resolved even by high resolution, fused-silica capillary GC. Thus, in order to avoid potential interferences between compound classes, it is necessary to perform an initial separation step prior to quantitation by GC. This paper reports a chromatographic procedure which successfully resolves toxaphene, PCB, and phthalate esters into separate fractions for GC analysis. Individual chlorinated hydrocarbon pesticides such as chlordane and DDT compounds are fractionated between the three separate fractions. In addition, the separation of some common aliphatic and aromatic hydrocarbons was tested using the procedure.

Procedures have been described which separate some of the compound classes of interest here. For example, Giam *et al.*[5] report the use of 3%-deactivated Florisil to separate phthalate esters from PCB and DDT. Jansson *et al.*[6] and Bidleman *et al.*[7] have reported the separation of PCB and toxaphene components using different silica gel column techniques. Zell and Ballschmitter[8] described the use of 1.25%-deactivated Florisil to separate PCB, toxaphene and other chlorinated hydrocarbons in biota and sediment samples. However, their work did not include phthalate esters, chlorinated hydrocarbons such as dieldrin, and aliphatic and aromatic hydrocarbons. The method described below extends and modifies the procedure of Zell and Ballschmiter[8] to include phthalate esters. Tests with other organic compounds are also reported here.

MATERIALS AND METHODS

A Hewlett-Packard 5880A model GC equipped with a ^{63}Ni electron capture detector and a DB-1 fused silica capillary column (30 m) was used for determination of chlorinated hydrocarbons and phthalate esters. Hydrogen was used as carrier gas at 25 psi; 95% argon/5% methane was used as make-up gas at a flow rate of 30 ml/min. The oven temperature program was: 100°C for 1 min; 100 to 130°C at

10°C/min; 3 min hold at 130°C; 130–270°C at 5°C/min; and a final 5 min hold at 270°C. Detector and injector temperatures were 320°C and 260°C, respectively, with splitless-mode injection. A Varian model 3700 GC with flame ionization detector and DB-1 fused-silica capillary column (15 m) was used for the analysis of aliphatic and aromatic hydrocarbons. Hydrogen was carrier gas at 14 psi. The oven temperature program was 70–270°C at 10°C/min. Injector and detector temperatures were 220°C and 300°C, respectively.

All reference standards were obtained from EPA-Research, Triangle Park, NC, USA. Organic solvents used for extraction and clean-up of glassware were pesticide analysis grade (Omnisolve) from MCB Manufacturing Chemists, Inc. Anhydrous diethyl ether (MCB) was freshly distilled immediately before use. Florisil (60/100 P.R. grade) was obtained from Floridin Chemical Co. Glassware used in this experiment, such as Soxhlet extractor, separating column, K-D concentrator, and glass vials were cleaned up and checked using previously reported procedures!

Florisil (60–100 mesh) was heated at 450–500°C for at least 2 h to combust organic contaminants. After heating, it was stored in an oven at 200°C until use. Florisil was deactivated by adding (1.25% w/w) organic-free water dropwise to clean deactivated Florisil and then rotating the Florisil in a flask for at least 3 h. 1.25% H_2O-deactivated Florisil was packed in a 32 cm-long bed in a 0.7 cm i.d. glass column for group separation. 1 ml of sample extract or spiked sample was transferred onto the top of the Florisil column. Sixty ml of petroleum ether or pentane were used for elution of the first fraction; 60 ml of 5% diethyl ether in petroleum ether were used for eluting the second fraction; 60 ml of 50% diethyl ether in petroleum ether eluted the final fraction. The flow rate was 1.0–1.5 ml/min. Each eluant was concentrated to 1 ml for GC analysis.

Fifty to sixty g of Florisil (16–30 mesh) were used for trapping organic compounds in ambient air using procedures described elsewhere.[9] After sampling, the Florisil was extracted with pentane for 16 h in a Soxhlet extractor followed by extraction with methylene chloride. The pentane extract was concentrated to 1 ml in a K-D concentrator. The methylene chloride extract was concentrated to about 5 ml in a K-D apparatus; 150 ml of pentane were added and the extract was reconcentrated. After initial GC examination of each fraction, both concentrates were combined and concentrated to 1 ml for separation on deactivated Florisil.

RESULTS AND DISCUSSION

The fractionation and recovery of chlorinated hydrocarbon pesticides and phthalate esters from 1.25%-deactivated Florisil is presented in Table I. With the single exception of p,p′-DDT, there is excellent separation of different and potentially interfering compounds into

TABLE I

Fractionation and percent recovery of chlorinated hydrocarbons on 1.25%-deactivated Florisil columns.

Chlorinated hydrocarbons	Amount added (ng)	Recovery (%) Fraction I	Recovery (%) Fraction II	Recovery (%) Fraction III	No. of analyses
Pentachlorobenzene	30	106	1	0	8
Hexachlorobenzene	37	90	0	0	8
γ-chlordene	32	95	1	0	7
α-chlordene	29	96	0	0	7
2,4′ DDE	30	97	0	0	7
trans-Nonachlor	27	116	2	0	6
p,p′-DDE	30	112	0	0	7
o,p′-DDT	38	89	0	0	6
p,p′-DDT	30	51	48	0	6
PCB (Aroclor 1254)	354	93	0	0	5
PCB (Aroclor 1260)	400	113	0	0	5
α-Hexachlorocyclohexane	25	9	85	0	8
γ-Hexachlorocyclohexane	17	0	95	0	8
γ-chlordane	24	0	84	0	8
α-chlordane	17	2	90	0	8
o,p′-DDD	70	0	86	0	6
p,p′-DDD	39	0	88	0	6
Toxaphene	801	0	76	0	5
Dieldrin	24	0	6	101	4
Phthalate esters					
Dimethyl phthalate	494	0	0	8	3
Diethyl phthalate	456	0	0	33	3
Dipropyl phthalate	322	0	0	76	3
Diisobutyl phthalate	526	0	0	83	3
Di-*n*-butyl phthalate	872	0	0	88	3
Butylbenzyl phthalate	27	0	0	74	3
Di-ethylhexyl phthalate	1099	0	0	81	3

separate chromatographic fractions. The first fraction contains essentially all the chlorobenzenes, polychlorobiphenyls, DDE, and o,p′-DDT. As noted, in this series of tests, p,p′-DDT is split between the first two fractions. However, subsequent testing of different batches of Florisil showed that with some Florisil samples p,p′-DDT eluted exclusively in the second fraction. Thus, each batch of Florisil must be tested prior to use to ensure the correct elution behavior. Of the chlorodane group, the chlordenes and *trans*-nonachlor are separated into the first fraction, while α- and γ-chlordane are present solely in the second fraction. Toxaphene, DDD, and the hexachlorocyclohexanes are also all present in the second fraction.

No phthalate esters are eluted in the fractions containing chlorinated hydrocarbons, and the only chlorinated hydrocarbon appearing in the "phthalate" fraction is dieldrin. From the observed elution pattern, we expect that compounds such as endrin and endosulfan as well as various organophosphate pesticides will also appear in the third fraction, but this was not tested here. Other studies of organochlorine contamination using a 1.25%-deactivated Florisil column cleanup step may have missed the presence of dieldrin and similar contaminants by not obtaining a more polar eluate from the column. The more polar phthalates, dimethyl and diethyl phthalate, are only incompletely recovered using this column procedure. However, good recovery of other phthalates was obtained. Other solvent combinations were tested to obtain more complete recovery of phthalates, but the only other combination which eluted phthalates from the column was 5% acetone in hexane. Other solvents tested were 20% diethyl ether in petroleum ether, 2% acetone in hexane, and methylene chloride.

Because it is often of interest to examine ambient air for other general classes of atmospheric organics, we tested the behavior of various aliphatic and aromatic hydrocarbons on the 1.25%-deactivated Florisil column (Table II). As expected, all aliphatic compounds eluted in the first fraction. Aromatic compounds were distributed between the first and second fraction. With some exceptions, alkyl-substituted benzenes and two-ring aromatics were observed primarily in the first fraction, while three-ring and larger compounds were found in the second fraction.

The chromatographic procedure was used on extracts of air samples from the Texas Gulf Coast. In this area we found that occasional pulses of toxaphene-contaminated air can be mixed with

TABLE II

Fractionation and recovery of aliphatic and aromatic hydrocarbons on 1.25%-deactivated Florisil.

Compounds	Recovery (%) Fraction I	Fraction II	Fraction III	No. of analyses
Aliphatic hydrocarbons				
Tridecane	87	0	0	3
Tetradecane	91	0	0	3
Pentadecane	90	0	0	3
Hexadecane	90	0	0	3
Pristane	84	0	0	3
Phytane	84	0	0	3
Hexacosane	96	0	0	3
Triacontane	90	0	0	3
Aromatic hydrocarbons				
1,2,3,5-Tetramethylbenzene	91	0	0	2
1,2,3,4-Tetramethylbenzene	90	0	0	2
Naphthalene	88	0	0	2
2-Methylnapthalene	92	0	0	2
1-Methylnaphthalene	92	0	0	2
Biphenyl	93	0	0	2
2,6-Dimethylnaphthalene	90	0	0	2
1,3-Dimethylnaphthalene	92	0	0	2
Acenaphthene	91	0	0	2
4-Phenyltoluene	21	68	0	2
Fluorene	0	100	0	2
3,3′-Dimethylbiphenyl	17	68	0	2
4,4′-Dimethylbiphenyl	0	96	0	2
9,10-Dihydrophenanthrene	0	97	0	2
1-Methylfluorene	0	99	0	2
Phenanthrene	0	105	0	2
Anthracene	0	90	0	2
9-Methylanthracene	0	62	0	2
Fluoranthene	0	106	0	2
Pyrene	0	108	0	2

relatively clean coastal marine air. Thus, efficient separation of toxaphene and other componenets was necessary. Figures 1a–c illustrate representative chromatograms obtained from ambient air at Sabine Pass, Texas during late summer, 1982. It should be noted that these chromatograms represent compounds present in the gas, rather than the particulate, phase of ambient air. Average concentrations of some of the identified components are given in Table III. Additional detail and discussion of these results are presented elsewhere.[9]

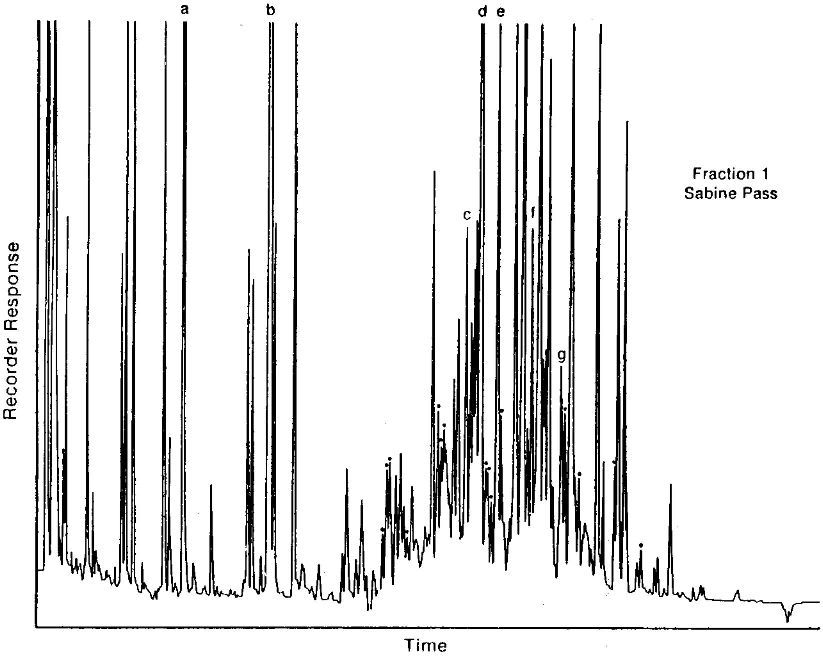

FIGURE 1a Electron capture gas chromatogram of ambient air from Sabine Pass, Texas; Florisil Fraction I. Compound identities: a = pentachlorobenzene, b = hexachlorobenzene, c = o,p′-DDE, d = *trans*-nonachlor, e = p,p′-DDE, f = o,p′-DDT, g = p,p′-DDT, • = polychlorinated biphenyl biomass.

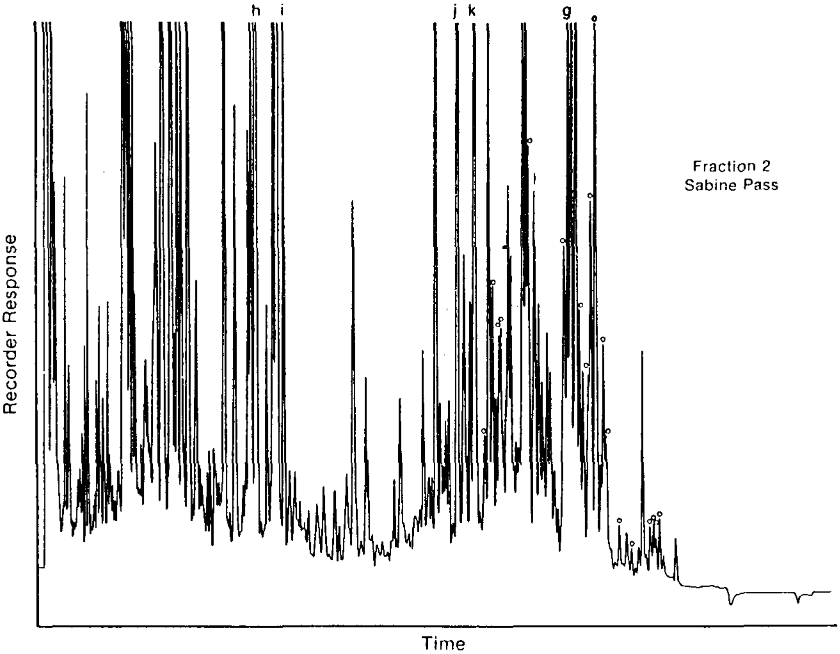

FIGURE 1b Electron capture gas chromatogram of ambient air from Sabine Pass, Texas: Florisil Fraction II. Compound identities: h = α-hexachlorocyclohexane, i = γ-hexachlorocyclohexane (lindane), j = γ-chlordane, k = α-chlordane, l = p,p′-DDD, g = p,p′-DDT, o = components of toxaphene.

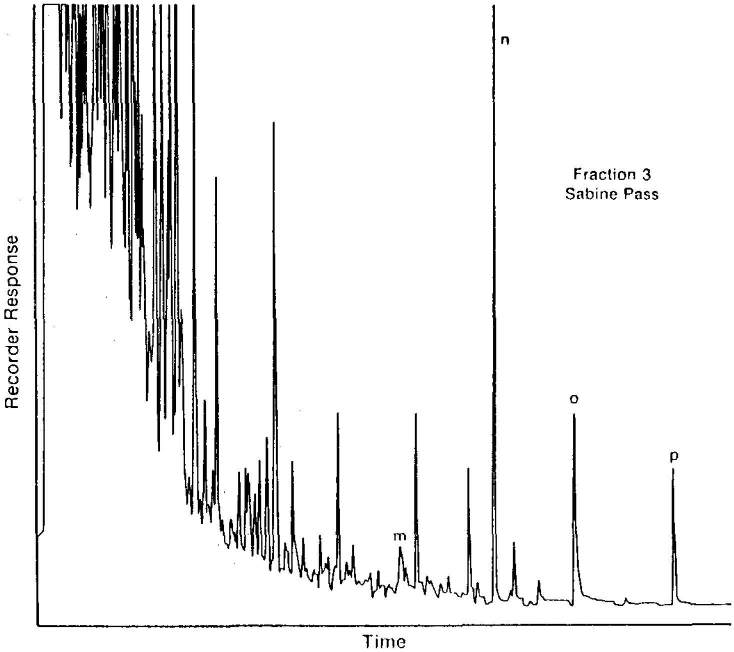

FIGURE 1c Electron capture gas chromatograh of ambient air for Sabine Pass, Texas: Florisil Fraction III. Compound identities: m = dibutyl phthalate, n = dieldrin, o = butylbenzyl phthalate, p = diethylhexyl phthalate.

TABLE III

Average concentration of selected organic pollutants in ambient air along the Texas Gulf Coast.

Compound	Average concentration (bg/m^3)
Pentachlorobenzene	39
Hexachlorobenzene	126
PCB (Aroclor 1254)	58
α-Hexachlorocyclohexane	410
Lindane	29
Chlordane	36
Nonachlor	18
Toxaphene	570
p,p′-DDE	9
p,p′-DDT	19
Dieldrin	17
Di-*n*-butyl phthalate	420
Di-2-ethylhexyl phthalate	620

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References

1. C. S. Giam, E. Atlas, H. S. Chan and G. S. Neff, *Atmos. Environ.* **14,** 65 (1980).
2. E. L. Atlas and C. S. Giam, *Science* **211,** 163 (1981).
3. T. F. Bidleman, E. J. Christensen, W. N. Billings and R. Leonard, *J. Mar. Res.* **39,** 443 (1981).
4. S. Tanabe, M. Kawano and R. Tatsukawa, *Trans. Tokyo Univ. Fisheries* **5,** 97 (1982).
5. C. S. Giam, H. S. Chan and G. S. Neff, *Anal. Chem.* **47(13),** 2225 (1975).
6. B. Jansson, R. Vaz, G. Blumkirst, S. Jensen and M. Olsson, *Chemosphere* **8,** 181 (1979).
7. T. F. Bidleman, J. Matthews, C. E. Olney and C. P. Rice, *J. Assoc. Offic. Analyt. Chem.* **61,** 820 (1978).
8. M. Zell, K. Ballschmiter and Z. Fresenius, *Anal. Chem.* **300,** 387 (1980).
9. E. Atlas, K. Sullivan, L. W. Chang and C. S. Giam, in preparation (1984).