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Phthalate Esters as Potential Contaminants during GC Analysis of Environmental Samples Using Electron Capture and Mass Spectrometric Detectors

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The electron-capture detector (ECD) has been extensively used for the analysis of organochlorine pesticides and polychlorinated biphenyls for health and environmental protection (Aue and Kapila 1973; Grob 1985; Hachenberg 1973; Pellizzari 1974; Sencik 1975). The sensitivity of the ECD towards polyhalogenated compounds is exceptional. The ECD is also useful for the detection of many other classes of compounds. For example, EPA methods 604, 606, and 609 for the analysis of phenolic compounds, phthalate esters, and nitroaromatics, respectively, recommend the use of the ECD as the gas chromatographic (GC) detector. The ability of the ECD to respond sensitively to many different classes of organic compounds has meant that it lacks selectivity toward any of these classes.

Gas chromatography using a mass spectrometer as the detector (GC/MS) has established itself as a reliable technique for the analysis of trace pollutants in environmental samples (Sherma 1991). GC/MS is commonly operated in either scan mode, where the mass spectrometer scans over a specified mass range, or in selective ion monitoring (SIM) mode, where the mass spectrometer is preset to detect only one or a few mass ions (McFadden 1973). GC/MS is often used to verify the findings of other conventional GC detectors, such as the ECD.

Phthalate esters have long been recognized as a class of contaminants found in the aquatic environment (Sherma 1991). They are also ubiquitous in the analytical laboratory due to the use of plasticware or tubing that often contains phthalate esters as plasticizers (Simonds and Church 1963). As mentioned earlier, phthalate esters can be analyzed by GC/ECD. They are also listed among the compounds to be analyzed by EPA GC/MS method 625. Reported herein are the ECD response factors relative to lindane of 14 phthalate esters using capillary GC. Lindane was chosen for this comparison because of its strong response to the ECD and its availability in pure form. Also reported herein are the mass ions that are present in the electron impact (EI)-mass spectra of these phthalate esters. These ions can often be useful in (1) recognizing the presence of these compounds in a mixture and (2) for quantitation of these compounds.

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MATERIALS AND METHODS

A Finnigan-MAT model 9600 gas chromatograph attached to a Finnigan-MAT model 4021 computerized mass spectrometer was used.

A 20 m x 0.25 mm (i.d.) fused-silica, capillary column chemically bonded with a 1-µm thickness of Durabond-5, a 5% phenyl methyl silicone (DB-5), obtained from J & W Scientific (Folsom, CA) was used. The injection-port and transfer-line temperatures were 230° and 260° C, respectively. The column-oven temperature was held at 40°C for 1 min and then increased to 290° C at a rate of 8° C/min. A 1-µL volume was injected in the splitless mode. The MS was operated in the electron impact mode using an electron energy of 70 eV. The mass range that was scanned was 40 to 450 daltons.

A Hewlett-Packard model 5880A equipped with a capillary injection port and an ECD was used. A 30 m x 0.25 mm (i.d.) fused-silica, capillary column chemically bonded with a 0.25-µm thickness of DB-5 obtained from J & W Scientific was used. The injection-port and detector temperatures were 220° and 280°C, respectively. The column-oven temperature was held at 110°C for 0.5 min, then increased to 250°C at a rate of 20°C/min, and held at 250°C for 8 min. Finally it was increased to 280°C at a rate of 15°C/min and held at 280°C for 10 min. The helium carrier gas flow rate was 0.8 mL/min. The ECD makeup-gas (5% methane in argon) flow rate was 24 mL/min. A 1-µL volume was injected in the splitless mode. Quantitation was performed using a Hewlett-Packard 3350 on-line data acquisition system. The height response integration method was used.

Fourteen phthalate esters were used in this study. Listed in the order of their increasing molecular weights were dimethyl isophthalate (compound 1), dimethyl phthalate (2), diethyl phthalate (3), diethyl terephthalate (4), dimethyl 4-nitrophthalate (5), dimethyl nitroterephthalate (6), diallyl phthalate (7), dipropyl phthalate (8), diisobutyl phthalate (9), dibutyl phthalate (10), benzylbutyl phthalate (11), diphenyl phthalate (12), dicyclohexyl phthalate (13), and bis[2-ethylhexyl] phthalate (14). Dioctyl adipate (compound 15) was added for the comparison between the ECD responses for the di-substituted ester of an aliphatic diacid and the dioctyl ester of phthalic acid (compound 14). Lindane (compound 16), gamma-1,2,3,4,5,6-hexachlorocyclohexane, was included as a reference standard for ECD responses. Compounds 3, 5, 6 and 10 were obtained from Eastman Kodak Chemical Company. All other phthalate esters were obtained from Aldrich Chemical Company. Dioctyl adipate was obtained from Hewlett-Packard Company. Lindane (100%) was obtained from PolyScience Corp. (Evanston, IL). All sixteen standard compounds were used as received without additional purification.

A stock solution containing 1 µg of compound per µL of high-purity toluene was prepared for each of the sixteen standards. Working solutions of 10 picomole/µL (pmole/µL) were prepared by transferring appropriate volume of each of the stock solutions and dissolving in 10.0 mL of toluene in a 1-oz narrow-mouthed bottle fitted with a sealable cap. Table 1 lists the amount of each of the compounds in nanogram/µL (ng/µL) for these working solutions. Other working solutions of mixtures of two or more compounds were similarly prepared as needed.

Table 1. Amount of compounds in 10 pmole/μL working solutions.

No.	Compound	Amt. expressed in ng/μL in the working solutions
1	Dimethyl isophthalate	1.94
2	Dimethyl phthalate	1.94
3	Diethyl phthalate	2.22
4	Diethyl terephthalate	2.22
5	Dimethyl 4-nitrophthalate	2.39
6	Dimethyl nitroterephthalate	2.39
7	Diallyl phthalate	2.46
8	Dipropyl phthalate	2.50
9	Diisobutyl phthalate	2.78
10	Dibutyl phthalate	2.78
11	Benzylbutyl phthalate	3.12
12	Diphenyl phthalate	3.18
13	Dicyclohexyl phthalate	3.30
14	Bis(2-ethylhexyl) phthalate	3.90
15	Dioctyl adipate	3.70
16	Lindane	2.88

RESULTS AND DISCUSSION

Table 2 summarizes the data generated from GC/EI-MS and GC/ECD analyses using two separate DB-5 capillary GC-columns. The first data column (I) lists for each compound the identity number as given in the Materials and Methods section. The second column (II) lists compound names. The third column (III) lists the retention time of each GC peak in minutes. The fourth column (IV) shows the relative retention time as compared to dimethyl phthalate (Compound 2) using the formula: relative retention time = (retention time of compound N/ retention time of dimethyl phthalate). Similar relative retention data were obtained from the GC/ECD runs; therefore, they are not listed in the table. The fifth column (V) lists for each compound the mass peaks from its mass spectrum that are above 70 daltons. The basepeak in each spectrum is indicated with (100%) in intensity. The molecular ion is labeled with (M+); when it is absent, the major peak with the highest mass is identified. The last column (VI) lists the GC/ECD response relative to lindane (RRL) for each of the phthalate and adipate esters. The RRL of a compound is calculated according to this equation: RRL of compound N = (peak height of compound N/ peak height of lindane) x 100. Lindane, which yields a strong ECD response, is defined to be 100 in RRL. When the retention time of a compound was very similar to that of lindane, each was injected separately. Otherwise, lindane was injected with one or more of the esters as an internal standard.

The RRL data in column VI show the effects of the substituent groups on the ECD response. For the dialkyl substituted phthalates, the RRL increased from around 4 for dimethyl phthalates to 16.7 for bis[2-ethylhexyl] phthalate. The presence of two cyclic groups in dicyclohexyl phthalate and two alkenyl groups in diallyl phthalate increased their RRL to 21. An aryl group increased the relative response to about 60 for benzylbutyl phthalate. Dimethyl nitrophthalates were

Table 2. GC retention data, mass spectral data, and the ECD relative peak area using lindane as reference standard for the phthalate and adipate esters.

Sample Information		*GC Retention Data* (From GC/MS)		*Mass Spectral Data*	*GC/ECD Data*
Compound No. (I)	Compound (II)	RT (Min) (III)	Rel RT (IV)	Mass Peaks Above 70 Dalton (V)	Rel Peak Height (Against Lindane) (VI)
1	Dimethyl isophthalate	6.43	1.09	76,92,103,120,135,163(100%),164,194(M+)	3.47
2	Dimethyl phthalate	5.90	1.00	77,92,104,120,135,163(100%),164,194(M+)	4.40
3	Diethyl phthalate	7.25	1.23	76,104,105,121,149(100%),176,177,178,222(M+)	5.49
4	Diethyl terephthalate	7.67	1.30	76,103,104,121,149,150,166,177(100%),178,193,194,222(M+)	4.64
5	Dimethyl 4-nitrophthalate	8.90	1.51	74,75,76,103,104,119,134,147,150,162,178,208(100%), 209,239(M+)	99.95
6	Dimethyl nitroterephthalate	8.95	1.52	74,75,103,104,119,132,135,147,150,162,179,193,208(100%), 209,239(M+)	99.87
7	Diallyl phthalate	8.62	1.46	76,93,98,104,121,132,149(100%),150,172,188,189 (M- C3H5O),190	21.15
8	Dipropyl phthalate	9.02	1.53	76,93,104,105,121,122,149(100%),150,191,209,250(M+)	7.39
9	Diisobutyl phthalate	9.82	1.66	76,93,104,105,121,132,149(100%),150,167,223(M- C4H7)	11.34
10	Dibutyl phthalate	10.73	1.82	76,93,104,121,149(100%),205,223,278(M+)	11.47
11	Benzylbutyl phthalate	15.87	2.69	76,91,104,105,123,132,135,149(100%),150,178,206,207, 238,312(M+)	60.78
12	Diphenyl phthalate	17.85	3.03	77,104,115,141,152,153,225(100%;M- C6H5O),226	23.30
13	Dicyclohexyl phthalate	17.08	2.90	76,82,83,104,121,122,149(100%),150,167,168,249(M- C6H9)	21.72
14	Bis[2-ethylhexyl] phthalate	17.80	3.02	71,83,84,104,112,113,149(100%),150,167,168,270(M- C8H15)	16.70
15	Dioctyl adipate	16.17	2.74	70,71,83,84,100,101,111,112,113,128,129(100%),130,147, 259(M- C8H15)	0.01
16	Lindane	8.68	1.47	73,74,75,83,85,87,96,99,109,111,121,123,135,145,146,147, 156,158,181,183(100%),185,208,217,219,221,252,254, 254,256,288(M+),290,292	100.0

found to be equivalent in response to lindane. In contrast, dioctyl adipate which contains only linear alkyl chains and carboxy groups yielded no response.

The first GC peak appeared when the oven temperature was approximately 195° C; it belonged to dimethyl phthalate (compound 2). Nine phthalates (compounds 1,3,4,5,6,7,8,9,10) and lindane followed within five minutes; each was separated from its neighbors by less than 50 seconds. The last of these eluted when the oven temperature reached 250°C. Two closely eluting compounds (11 and 15) appeared after a 5-minute gap. The last three peaks (compounds 13, 14, and 12) eluted closely together after the oven temperature reached 290°C. The temperature range mentioned is that which is commonly used for the analysis of semi-volatile compounds. Since a large number of phthalate esters have been in use as plasticizers (Simonds and Church 1963) and all would generate ECD signals, they may contribute to "noisy" chromatograms when they somehow find their way into the samples.

The mass spectral data of the phthalates and the adipate exhibited 62 mass peaks between 70 and 250 daltons. In addition to the familiar m/z 149 which is the base peak for many dialkyl phthalate esters, m/z 163, 177, 208, and 225 can also be present as base peaks for certain phthalate esters. One should be aware of the possibility that these mass peaks may generate responses when they are selected for selective ion monitoring (SIM). This could create confusion when this technique is used for the analysis of trace level samples that had been exposed to plasticizers. We suggest that with careful techniques and better understanding of their properties, the effects of phthalate esters in GC/ECD and GC/MS analysis may be kept at a minimum.

REFERENCES

Aue WA, Kapila S (1973) The electron capture detector - controversies, comments, and chromatograms. J Chrom Sci 11:255-263

Grob RL (1985) Modern Practice of Gas Chromatography. J. Wiley & Sons, N.Y., N.Y., p 255

Hachenberg H (1973) Industrial Gas Chromatographic Trace Analysis. Heyden & Son Ltd., London, England, p 10

McFadden W (1973) Techniques of Combined Gas Chromatography/Mass Spectrometry: Applications in Organic Analysis. Wiley-Interscience, N.Y., N.Y., p 4

Niimi AJ (1987) Biological half-lives of chemicals in fishes. In: Ware GW (ed) Reviews of Environmental Contamination and Toxicology, vol 99. Springer-Verlag, N.Y., N.Y., p 1

Pellizzari ED (1974) Electron capture detector in gas chromatography. J of Chrom 98:323-361

Sevcik J (1975) Detectors of Gas Chromatography. Elsevier Scientific Publishing Co., Amsterdam, The Netherlands, p 72

Sherma J (1991) Pesticides. Anal Chem 63:118-130R

Simonds HR, Church JM (1963) A Concise Guide to Plastics. Reinhold Publishing Co., N.Y., N.Y., 2nd ed., p 153

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