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Journal of Chromatography B, 706 (1998) 231–244

JOURNAL OF CHROMATOGRAPHY B

Quantitative analysis of polychlorinated biphenyls, organochlorine insecticides, polycyclic aromatic hydrocarbons, polychlorinated hydrocarbons and polynitrohydrocarbons in spiked samples of soil, water and plasma by selected-ion monitoring gas chromatography–mass spectrometry

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Received 17 June 1997; received in revised form 28 October 1997; accepted 10 November 1997

Abstract

A broad range of pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated hydrocarbons (PCHs), polynitrohydrocarbons (PNHs), polychlorinated biphenyls (PCBs) and organochlorine (OCs) insecticides were simultaneously analyzed in spiked soil, water or plasma samples by using gas chromatography–mass spectrometry (GC–MS). Water and plasma samples containing the pollutants were extracted by a solid-phase extraction (SPE) method using florisil columns. The soil samples, fortified with the toxicants, were extracted with water, methanol or dichloromethane (DCM). The water extract was processed by the SPE method. The methanol and DCM samples were dried, dissolved in acetonitrile and subjected to the SPE extraction. The extracted samples were analyzed by GC–MS programmed to monitor selected ions. The deuterium labelled compounds were used as the internal standards. The chromatographic profile of total ions indicated complete separation of some compounds such as isophorone, naphthalene, all PCBs, most OC insecticides and PNHs; high M_r PAHs and some PCHs were partially or incompletely separated. The chromatographic profile of individual ion indicated good separation of each ion. The minimum detection limit ranged from 1 to 4 pg injected when 1 or 2 ions were monitored or from 20 to 200 pg injected when 20 ions were monitored. The SPE method that provided 60–105% recovery of pollutants from water samples, provided only 2–60% recovery from plasma samples. This may be due to the binding of pollutants to plasma proteins. Water recovered 1–30%, while methanol or DCM recovered 65–100% of the pollutants added to the soil samples. The use of internal standards corrected for the loss of pollutants from plasma or soil. © 1998 Elsevier Science B.V.

Keywords: Polychlorinated biphenyls; Organochlorine insecticides; Polycyclic nuclear hydrocarbons; Polychlorinated hydrocarbons; Polynitrohydrocarbons

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PII S0378-4347(97)00560-4

1. Introduction

Many of the industrial and agricultural pollutants, such as organochlorine (OC) pesticides, polychlorinated biphenyls (PCBs), polychlorinated hydrocarbons (PCHs), polynitrohydrocarbons (PNHs) and polycyclic aromatic hydrocarbons (PAHs) cause cancer, liver damage, conception abnormalities, fetal death and other chronic abnormalities [1–6]. These pollutants enter the environment as a result of indiscriminate spraying of OCs for insect control, oil spillage, fossil fuel consumption, automobile exhaust and waste discharge [7–9]. Migration of chemicals from soil to water and vice versa may cause an accumulation of multiple residues in water and agricultural produce designed for animal or human consumption. A significant number of these chemicals have been reported in drinking water, soil and biological samples [10–12]. Therefore, to ensure public safety, a simple and sensitive analytical method is needed for the multi-residue analysis of OC insecticides, PCBs, PCHs, PAHs and PNHs in water and biological samples.

The analysis of OC insecticides, PCBs, PCHs, PAHs and PNHs in the environmental and biological samples is a multi-step process [13,14]. The samples are extracted by dichloromethane (DCM) and then fractionated by a solid-phase column (charcoal, silica, florisil or C_{18} columns) [14], or a gel-permeation column [15]. The different fractions are analyzed by using a gas chromatograph with flame-ionization detector (GC–FID), electron-capture detector (GC–ECD) or mass-selective detector (GC–MS); or by using high-performance liquid chromatograph (HPLC) with UV or fluorescence detection [14,16–19]. These methods, however, have many disadvantages. (1) The liquid–liquid extraction causes incomplete recovery of high-molecular-mass (M_r) PAHs from environmental samples [14]. (2) GC and HPLC both provided incomplete separation of many pollutants [14]. (3) Quantitative analysis of the pollutants may be difficult due to the lack of pure standards and suitable internal standards (I.S.s). Recently, a supercritical fluid extraction (SFE) method has been described [20] that improved the extraction efficiency of pollutants from soil samples. The SFE method, however, is not suitable for water or plasma samples since it requires a solid matrix.

The present study, therefore, describes a simple and sensitive method for the simultaneous quantitative analysis of a broad range of pollutants such as OC insecticides, PCBs, PCHs, PAHs and PNHs in spiked samples of water, soil or plasma using GC–MS and selected ion monitoring (SIM).

2. Experimental

2.1. Materials

Acenaphthene, acenaphthylene, anthracene, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*k*]fluoranthene, chrysene, 2-chlorobiphenyl, 2-chloronaphthalene, dibenz[*a,h*]anthracene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 2,3-dichlorobiphenyl, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,2′,3,3′,4,4′,6-heptachlorobiphenyl, hexachlorobenzene, 2,2′,4,4′,5,6′-hexachlorobiphenyl, hexachlorobutadiene, hexachlorocyclopentadiene, hexachloroethane, fluoranthene, fluorene, indeno[1,2,3,-*c,d*]pyrene, isophorone, naphthalene, nitrobenzene, 2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl, 2,2′,3′,4,6-pentachlorobiphenyl, phenanthrene, pyrene, 2,2′,4,4′-tetrachlorobiphenyl, 1,2,4-trichlorobenzene and 2,4,5-trichlorobiphenyl were obtained from Protocol (Middlesex, NJ, USA). γ-BCH, β-BCH, α-BCH, d-BCH, c-chlordane, t-chlordane, DDD, DDE, DDT, dieldrin, endosulfan-I, endosulfan-II, endrin, endrin aldehyde, endrin ketone and heptachlor in DCM were obtained from Alltech (Chicago, IL, USA). Deuterium (d) labelled acenephthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, perylene-d_{12} and phenanthrene-d_{10} were obtained from Alltech and were used as I.S. Partition coefficient of each compound was calculated by using the OASIS program developed at the University of Technology, Bulgaria [21,22].

Standards and spiked samples were prepared by adding different concentrations of each pollutant (100 ng/ml to 10 μg/ml) and the I.S. mixture (500 ng) in DCM, water or plasma samples. The final pollutant concentration ranged from 1 ng/ml to 1 μg/ml. The soil sample (10 g) was soaked into 50 ml methanol containing 0.2 ng/ml to 0.2 μg/ml of the toxicants with or without the internal standards. The methanol layer was evaporated at 45°C and

reduced pressure and then the soil sample was dried in a ventilated hood.

Florisil columns were prepared in plastic syringes (6 ml) fitted with porous membranes. The syringes were layered with 0.5 g of florisil followed by 2 g of aluminum oxide. The columns were prewashed with 4 ml of methanol, 4 ml of water and then 4 ml of acetonitrile.

2.2. Extraction of water and plasma samples by the florisil column

A 1-ml volume of the fortified water or plasma sample was mixed with 4 ml of acetonitrile. The samples were centrifuged and the supernatant was collected. The remaining plasma precipitate was further extracted with 4 ml of acetonitrile and the combined supernatant was poured onto the column. The sample was allowed to pass through the column. The column was washed with 4 ml of acetonitrile. The combined acetonitrile extract was dried at 45°C in nitrogen. The dried residue was dissolved in 10 μl DCM, a 1-μl volume of which was injected into the GC–MS.

2.3. Extraction of soil samples

The soil samples were mixed with 50 ml each of water, methanol or DCM. The mixture was shaken at room temperature for 15 min and then centrifuged at 2000 *g* for 30 min. The supernatant was collected. The water extract was concentrated at 45°C and reduced pressure to 10 ml. The sample was then analyzed as described above. Methanol and DCM samples were dried at 45°C under nitrogen and dissolved in 10 ml of acetonitrile. The acetonitrile layer was subjected to SPE as described above.

2.4. GC–MS conditions

A HP-5890 gas chromatograph with 5970 mass selective detector and HP-5 (crosslinked 5% phenylmethyl silicone, 30 m×0.25 mm) column was used in this study. The column temperature was programmed as follows: 75°C for 2 min, 3°C/min to 150°C, 5 min hold at 150°C, 5°C/min to 200°C, 5 min hold at 200°C, 3°C/min to 300°C and 10 min hold at 300°C. The helium flow was 20 ml/min. The injector temperature was 200°C and sample injection was made in splitless mode (30 s splitless time). The column head pressure was 7.5 p.s.i. The transfer line and the source temperatures were 280°C. The source pressure was 5×10^{-5} Torr. The mass-spectrum of individual compounds were determined by injecting 1 μl of each standard (10 μg/ml in DCM) into the GC–MS programmed to scan ions from m/z 50 to 500. Then, a specific ion was selected for each compound. A SIM program was constructed in which the pollutants were screened in four groups each having specific ions for each compound and a specific group start time (Table 1).

2.5. Quantitation

Individual ions were retrieved from the total-ion chromatogram. The ion peak was integrated and area under the curve (AUC) was determined. AUC for different concentrations of each ion was divided with the AUC of the I.S. (1,4-dichlorobenzene-d_4 for group 1, acenephthene-d_{10} or phenanthrene-d_{10} for group 2, chrysene-d_{12} for group 3 and perylene-d_{12} for group 4). A graph was drawn by plotting concentration on the x-axis and $AUC_{st}/AUC_{I.S.}$ on the y-axis. The concentration of the pollutants in

Table 1
SIM program for monitoring various toxicants in water or plasma

Group	Start (min)	Ions monitored (m/z)
1	3	77, 82, 86 (I.S.$_1$), 128, 136 (I.S.$_2$), 146, 150, 180, 201, 225, 284
2	11	152, 153, 163, 165, 178, 180, 181, 188 (I.S.$_3$), 254, 256, 272, 284, 292
3	44	82, 166, 174, 195, 202, 207, 209, 224, 228, 235, 240 (I.S.$_4$), 263, 272, 276, 290, 293, 324, 353, 358, 375
4	65	253, 264 (I.S.$_5$), 276, 278, 290

I.S.$_1$=1,4-dichlorobenzene-d_4, I.S.$_2$=naphthalene-d_8, I.S.$_3$=phenanthrene-d_{10}, I.S.$_4$=chrysene-d_{12} and I.S.$_5$perylene-d_{12}.

water, soil or plasma samples was determined from the standard curve by using a linear regression analysis.

2.6. Recovery

Pollutant standards were dissolved in DCM and analyzed directly by the GC–MS. Pollutant concentrations in soil (water, methanol and DCM extracts), water and plasma were analyzed as described above. AUC was determined for each ion. Recovery was calculated by using the following methods:

(1) AUC for a pollutant's ion was plotted against the pollutant concentration in DCM. Pollutant concentration in water or plasma sample was determined from the standard curve. Percentage recovery was determined by comparing the amount added with the amount recovered. This method determined true recovery.

(2) AUC for a pollutant's ion was divided by the AUC for the internal standard's ion. The ratio was plotted against the pollutant concentration in DCM. Pollutant concentrations were determined from the standard curve. This method determined recovery corrected by the I.S.

2.7. Minimum detection limit (MDL)

Blank or spiked water, soil and plasma samples were analyzed as described above. The mean and the standard deviation (S.D.) for the blank baseline were determined. A graph was drawn by plotting the pollutant concentration at the *x*-axis and peak area at the *y*-axis. The slope of the curve was determined. The S.D. of blank baseline was divided with the slope of the standard curve. The linearity of the detection was determined by plotting [(AUC_{st}/$AUC_{I.S.}$)/amount added] against [(AUC_{st}/$AUC_{I.S.}$)/amount observed]. In another experiment, MDL was determined for each compound individually by measuring 1 or 2 ions.

3. Results and discussion

3.1. Electron impact ionization of the pollutants

EI ionization of PAHs produced the molecular ion (M^+) in highest abundance (Table 2). PCHs and PNHs produced M^+ and $M^{-[Cl\ or\ nitro]}$ ions (Table 2). The ionization of PCBs produced M^+ and several dechlorinated biphenyl ions ($M^{-Cl(n)}$) in high abundance (Table 3). Some of the important ions formed by the EI ionization of OC insecticides are listed in Table 4. The positive ($M^{+(1\ to\ 3)}$) or negative ($M^{-(1\ to\ 3)}$) molecular ions and the dechlorinated molecular ions (M^{-Cl}) were the predominant ions produced by OC insecticides. Heptachlor (*m*/*z* 373 and 374) produced molecular ions in highest abundance. Methoxychlor exhibited the ion at *m*/*z* 227 in highest abundance due of the loss of the $-CCl_3$ group from the molecule. Ion at *m*/*z* 337 of chlordane was formed by the loss of one Cl group from the molecule. Dechlorination was also responsible for the ionization of aldrin, lindane, endrin and endosulfan. The ion at *m*/*z* 235 and 237 from DDT and DDD was formed as a result of the loss of the $-CCl_n$ (n=2 for DDD or 3 for DDT) group.

3.2. Chromatography

A typical total-ion (TI) chromatogram of a mixture containing PCBs, OC insecticides, PCHs, PNHs and PAHs is shown in Fig. 1. The low M_r PCHs and PAHs appeared in group 1 (t_R 4–11 min); hexachlorobenzene, PNHs and mono- or di- chlorinated PCBs appeared in group 2 (t_R 15–30 min); OCs, tri- to octachlorinated PCBs and some PAHs appeared in group 3 (t_R 30–70 min); and the high M_r PAHs appeared in group 4 (t_R >70 min). The GC profile indicated complete separation of some compounds such as isophorone, naphthalene, all PCBs, most OC insecticides and PNHs; but partial to incomplete separation of others such as high M_r PAHs and some PCHs. The chromatographic profile of individual ions (Fig. 2 for PAHs, Fig. 3 for OCs, Fig. 4 for PCBs and Fig. 5 for PCHs and PNHs) indicated good separation of each ion. The individual ion was retrieved from the TI profile and the peak was integrated. The peak height (PH) and the area under-the-curve (AUC) were determined. The d-labelled and the unlabelled compounds produced different ions. AUC was determined for both ions.

GC–ECD [23] or GC–MS [24,25] have been previously used for the analysis of pollutants in environmental and biological samples. GC–ECD is more sensitive than GC–MS for pollutant analysis. GC–ECD, however, has many disadvantages: (1)

Table 2
Tabulation of important ions (m/z) with their abundances (%) produced by polychlorinated hydrocarbons, polynitrohydrocarbons and polycyclic aromatic hydrocarbons

Compound (partition coefficient)	Ion (m/z)
2-Chloronaphthalene (3.7)	*162*(100), 127(50), 166(24), 126(20)
1,2-Dichlorobenzene (3.15)	*146*(100), 148(60), 111(50), 75(50), 50(50)
1,3-Dichlorobenzene (3.15)	*146*(100), 148(50), 111(40), 75(60), 50(40)
1,4-Dichlorobenzene (3.15)	*146*(100), 148(60), 111(30), 75(30), I.S.: *150*(100)
2,4-Dinitrotoluene	*165*(100), 89(70), 63(65), 182(15)
2,6-Dinitrotoluene	*165*(100), 63(90), 89(50), 182(10)
Hexachlorobenzene (5.4)	*284*(100), 286(70), 282(50), 288(30), 249(25)
Hexachlorobutadiene (2.7)	*225*(100), 223(60), 227(50), 190(50), 141(25), 143(25)
Hexachlorocyclopentadiene (1.7)	*237*(100), 239(60), 235(50), 272(20), 95(20)
Hexachloroethane (3.7)	118(100), 119(90), *201*(50), 166(30), 168(15)
Isophrone	*82*(100), 138(20), 81(5)
Nitrobenzene	*77*(100), 51(80), 50(50), 123(40), 93(20)
1,2,4-Trichlorobenzene (3.7)	*180*(100), 183(90), 145(30), 109(20)
Acenaphthene (3.6)	*154*(100), 153(90), 152(50), 76(30)
Acenaphthylene (4)	*152*(100), 154(10), 150(10), 76(10)
Anthracene/phenanthrene (4.9)	*178*(100), 152(20), 179(15);I.S.: *188*(100)
Benzo[*a*]anthracene (5.5)	*223*(100), 221(20), 202(5), 200(4)
Benzo[*a*]pyrene (5.6)	*252*(100), 126(25), 254(20), 225(15)
Benzo[*b*]fluoranthene (5.5)	*253*(100), 126(10), 224(5)
Benzo[*g,h,i*]perylene (6)	*276*(100), 138(30), 137(27), 278(10)
Benzo[*k*]fluoranthene (5.5)	*253*(100), 126(20), 250(10)
Chrysene (5.3)	*228*(100), 113(20), 115(17), 226(10); I.S.: *240*(100)
Dibenz[*a,h*]anthracene (6.5)	*278*(100), 139(30), 138(25), 125(10)
Fluoranthene (4.4)	*202*(100), 200(20), 101(15), 100(10)
Fluorene (3.5)	*166*(100), 164(70), 139(10)
Indeno[123-*c,d*]pyrene (6)	*276*(100), 138(30), 137(25), 248(10)
Naphthalene (3.1)	*128*(100), 102(20), 101(15), 129(5)
Perylene	252(100), 132(25), 131(15), I.S. 264(100)
Pyrene (4.6)	202(100), 101(30), 100(25)

Italics: Ions monitored.
Underlined: Ions common for 2 or more compounds.
I.S.=deuterium (d) labelled analog.

Table 3
Tabulation of important ions (m/z) with their abundances (%) produced by polychlorinated biphenyls

Compound (partition coefficient)	Ion (m/z)
2-Chlorobiphenyl (4.27)	*188*(100), 152(75), 76(50), 154(40), 150(5)
2,3-Dichlorobiphenyl (4.8)	152(100), *222*(90), 224(50), 93(25)
2,4,5-Trichlorobiphenyl (5.38)	*186*(100), 256(98), 258(90), 150(30), 75(25)
2,2′,4,4′-Tetrachlorobiphenyl (5.94)	220(100), *292*(98), 290(80), 294(40)
2,2′,3′,4,6-Pentachlorobiphenyl (6.5)	254(100), 256(98), *326*(98), 184(70), 291(40)
2,2′,4,4′,5,6′-Hexachlorobiphenyl (7.06)	*360*(100), 290(90), 362(70), 145(60), 218(50), 289(50)
2,2′,3,3′,4,4′,6-Heptachlorobiphenyl (7.6)	*324*(100), 394(98), 396(90), 162(80), 252(60)
2,2′,3,3′,4,5,6,6′-Octachlorobiphenyl (8.2)	*430*(100), 358(80), 429(80), 360(70), 179(70)

Italics: ions monitored.

ECD provides a nonselective detection of compounds, thus, resulting in several interfering peaks in the GC–ECD traces. (2) The method requires rigorous extraction and bromide derivatization of samples before analysis. (3) Samples tested positive by the GC–ECD method may require further confirmation

Table 4
Tabulation of important ions produced by the EI fragmentation of OC insecticides

OC (PC)	Ions (m/z)
γ-HCH (4.1)	183(100), 181(86), 111(69),219(67), 146–148(20)
β-HCH (4.1)	109(100), 111(72), 181(55), 193(55), 219(47), 217(46)
α-HCH (4.1)	183(100), 181(94), 111(87), 109(81), 51(66), 219(80)
δ-HCH (4.1)	181(100), 183(99), 109(95), 111(95), 219(80), 216(74)
Heptachlor (4)	272(100), 274(96), 65(49), 237(32), 339(30), 374(18)
Aldrin (3.6)	66(100), 91(48), 263(48), 101(29), 265(27), 293(18), 298(16)
Heptachlor-epx.	81(100), 353(98), 355(79), 351(53), 357(47), 235(21), 237(21)
t-Chlordane (4.3)	373(100), 375(98), 377(54), 371(47), 272(20), 237(16)
Endosulfan I	237(100), 239(93), 241(85), 195(74), 235(70), 272(42), 339(54)
c-Chlordane (4.3)	375(100), 373(93), 377(80), 371(45)
DDE (5.8)	246(100), 248(61), 318(60), 316(52), 316(56), 176(37), 320(36)
Dieldrin (2.7)	79(100), 81(36), 82(34), 263(21), 265(20), 279(13), 281(8)
Endrin ketone	67(100), 263(70), 316(60), 261(59), 243(58), 245(58)
Endosulfan II	195(100), 159(72), 237(87), 239(64), 85(60), 269(50)
DDD (5.8)	235(100), 237(66), 165(56), 236(16), 199(16)
Endrin aldehyde	67(100), 345(62), 343(40), 347(39), 250(35), 243(23)
DDT (6.8)	235(100), 237(71), 165(51), 272(21), 387(15), 422(6)
Endrin (2.7)	67(100), 317(80), 315(65), 319(63), 139(31), 279(29), 149(25)
Methoxychlor (5.4)	227(100), 228(2), 252(1.5), 114(1.5)

OC: Organochlorine insecticides, PC: partition coefficient.
Underlined: Ions common in two or more compounds.

by GC–MS [23,26]. Recently, Pastor et al. [25] have described a rigorous extraction protocol for the purification of biological samples for analysis by GC–ECD or GC–FID. Although the method separated PCBs, OCs and other pollutants, it was time consuming and required 5–100 g of tissue samples. Unlike the GC–ECD method, the GC–MS method provided selective detection of each compound and, thus, allowed simultaneous identification and quantitation of pollutants. Coeluted compounds were identified based on their specific ions. This suggests that GC–MS, in SIM mode, provides a simple, sensitive and confirmatory analysis of targeted toxicants in environmental and biological samples.

3.3. Recovery

The SPE procedure used in this study was simpler and relatively less time consuming than that using multi-step extraction [25], gel permeation [14] or supercritical fluid extraction [20]. Recovery was determined by using two different methods: one that included the internal standards and measured corrected recovery, and the other that did not include the internal standards and determined true recovery. The extraction used in this study provided 65–110% recovery of each pollutant from water samples in the presence or absence of the internal standards (Table 5). Thus, almost all the pollutants present in water were extracted by the SPE procedure. Extraction of spiked plasma samples without the I.S. provided 2–60% recoveries (Table 5). This may be due to the binding of pollutants to plasma proteins in a non-recoverable form. In the presence of the I.S.s, 65–110% recovery from plasma was observed. Thus, the I.S.s may be essential when analyzing plasma samples.

The recovery of pollutants from soil was dependent upon the type of solvent used. Water, in the absence of the I.S.s, recovered approximately 1–30% of the compounds added to soil samples. However, when the I.S.s were used, the recovery values increased to approximately 60–100% (Table 5). The recovery of pollutants by water from soil was inversely proportional to their partition coefficient values (Fig. 6). Methanol and DCM provided 60–100% recovery both in the presence or the absence of the I.S.s. Thus, the lower recovery of pollutants from soil in water may be due to the lipophilic binding of the pollutants to soil particles.

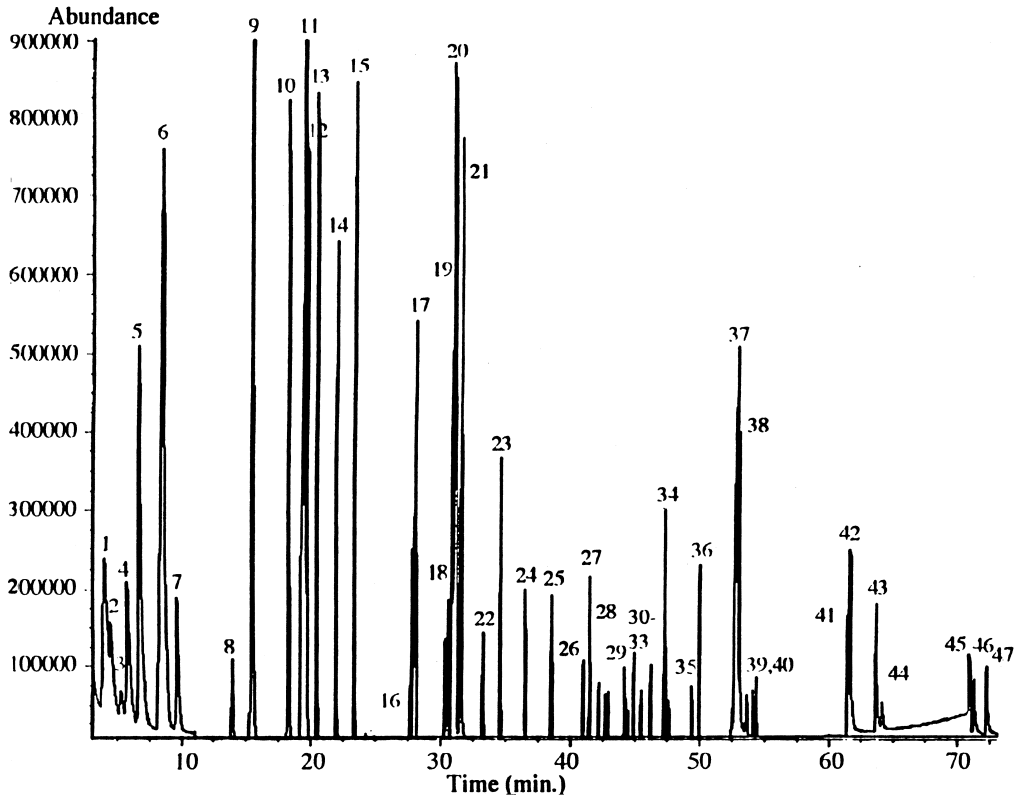

Fig. 1. Total-ion chromatogram of polycyclic aromatic hydrocarbons, polychlorinated hydrocarbons, polychlorinated biphenyls, polynitrohydrocarbons and organochlorine insecticides extracted from water samples

Peak identification

Peak	Compound	Peak	Compound	Peak	Compound
1	1,4-Dichlorobenzene	2	1,3-dichlorobenzene	3	Hexachloroethane
4	Nitrobenzene	5	Isophorone	6	Naphthalene
7	Hexachlorobutadiene	8	Unidentified	9	Chlornephthalene
10	Acenephthylene	11	Acenephthene	12	Acenephthene-d_{10}
13	2-Chlorobiphenyl	14	2,6-Dinitrotoluene	15	2,4-Dinitrotoluene
16	α-HCH	17	Hexachlorobenzene	18	2,3-Dichlorobiphenyl
19	Phenanthrene	20	Phenanthrene-d_{10}	21	Anthracene
22	γ-HCH	23	2,4,5-Trichlorobiphenyl	24	Heptachlor
25	2,2′,4,4′-Tetrachlorobiphenyl	26	Unidentified	27	Unidentified
28	2,2′,3′,4,6-Pentachlorobiphenyl	29	Fluoranthene	30	Endosulfan/chlordane
31	Endrine ketone	32	Unidentified	33	2,2′,4,4′,5,6′-Hexachlorobiphenyl
34	Dieldrin	35	4,4′-DDD	36	4,4′DDT
37	Chrysene	38	Benzo[*a*]anthracene	39	2.2′,3,3′,4,4′,6-Heptachlorobiphenyl
40	2,2′,3,3′,4,5,6,6′-Octachlorobiphenyl	41	Benzo[*b*]fluranthene	42	Benzo[*k*]fluranthene
43	Endrin aldehyde	44	Unidentified	45	Benzo[*a*]pyrene
46	Dibenzo[*a,k*]anthracene	47	Indene[123-*c,d*]pyrene		

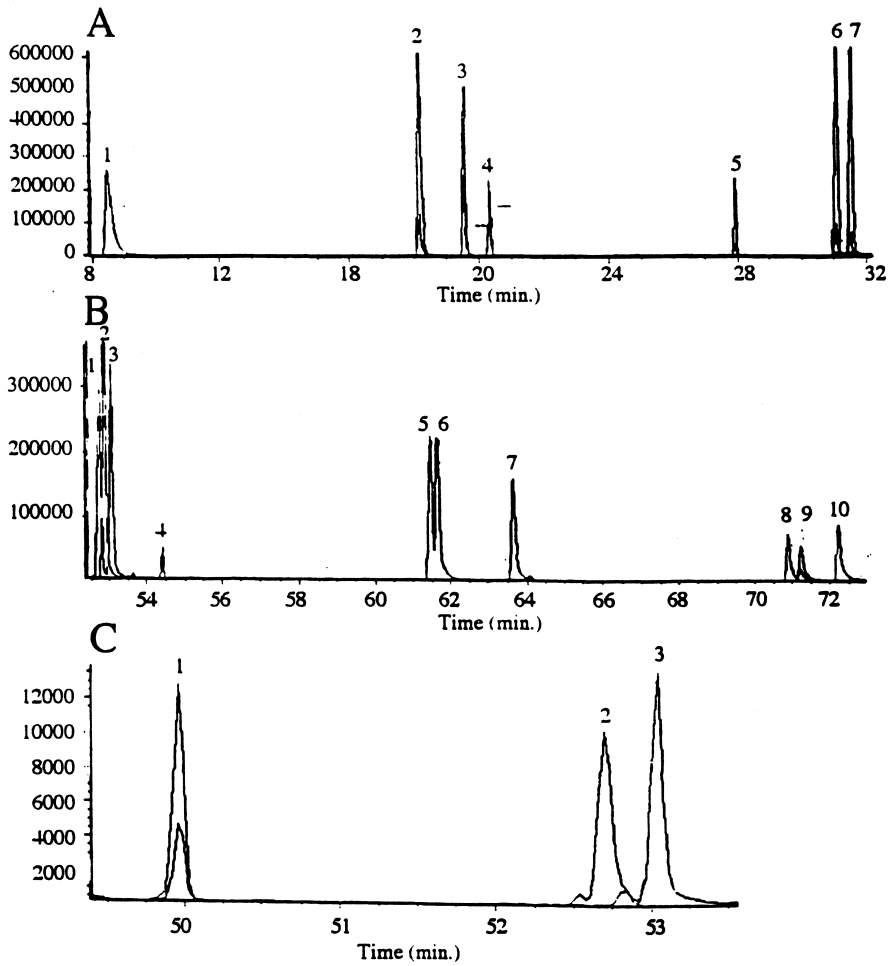

Fig. 2. Chromatographic separation of selected ions (m/z in parenthesis) for polycyclic aromatic hydrocarbons

Peak identification

Peak	Compound	Peak	Compound
(A)			
1	Naphthalene (128)	2	Acenaphthylene (153)
3	Acenaphthene-d_{10} (153)	4	Acenaphthene
5	Unidentified	6	Phenanthrene (178)
7	Anthracene (178)		
(B)			
1	Chrysene (228)	2	Chrysene-d*12* (240)
3	Benzo[*a*]anthracene (223)	4	Unidentified
5	Benzo[*b*]fluranthene ((252)	6	Benzo[*k*]fluaranthene (252)
7	Benzo[*a*]pyrene (252)	8	Benzo[*g,h,i*]perylene (276)
9	Dibenzo[*a,h*]anthracene (278)	10	Indeno[123-*c,d*]pyrene (276)
(C)			
1	Fluorene (166)	2	Pyrene (202)
3	Fluranthene (202)		

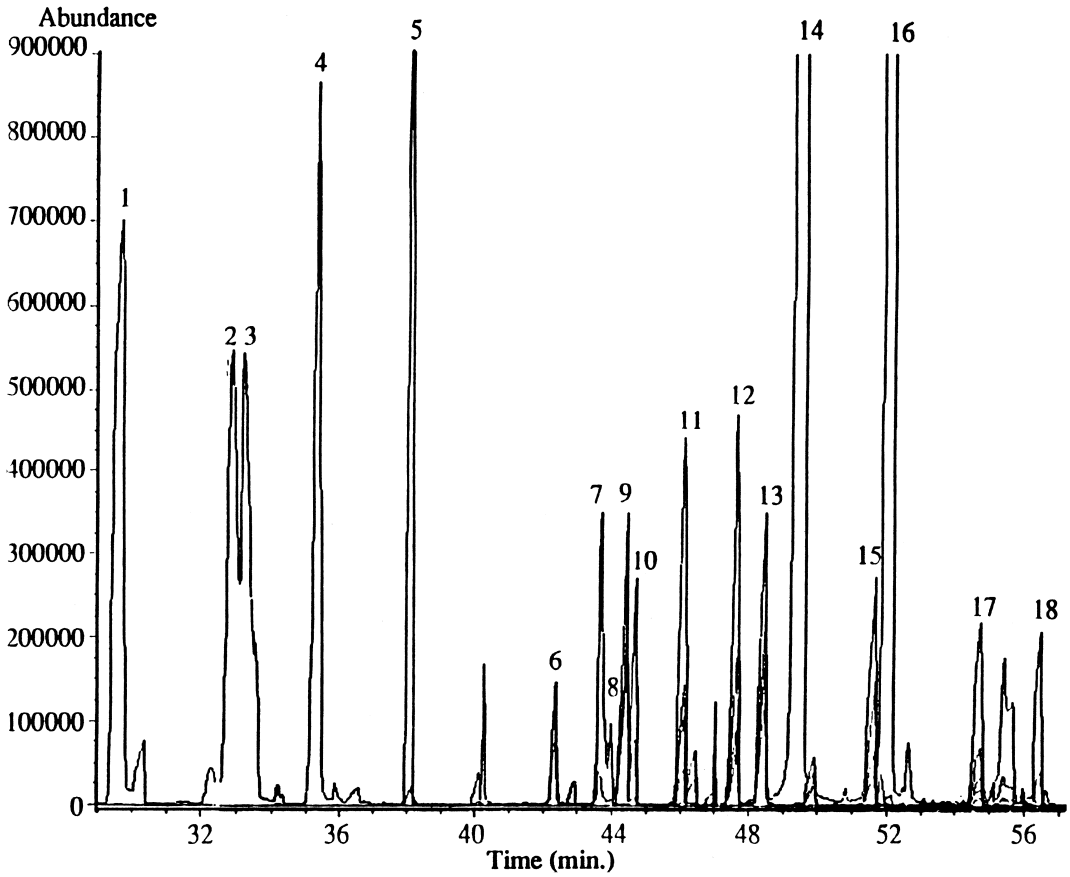

Fig. 3. Chromatographic separation of selected ions (m/z in parentheses) for organochlorine insecticides extracted from water samples

Peak identification

Peak	Compound	Peak	Compound
1	γ-HCH (181)	2	β-HCH (181)
3	α-HCH (181)	4	δ-HCH (181)
5	Heptachlor (272)	6	Aldrin (263)
7	Heptachlor epoxide (353)	8	t-Chloridane (375)
9	Endosulfan I (195)	10	c-Chloridane
11	Dieldrin (263)	12	Endrin ketone (263)
13	Endosulfan II (195)	14	4,4′-DDD (235)
15	Endrin aldehyde (353)	16	4,4′-DDT (235)
17	Endrin (209)	18	Methoxychlor (227)

3.4. Minimum detection limit

Previous studies have shown that GC–MS in SIM mode exhibited MDL levels of 1–4 pg for organophosphates [27] and <1 pg for PCBs [25]. The MDL of GC–MS depends upon the number of ions monitored and the electron multiplier voltage (EMV) at which the analysis is performed [27]. The sensitivity of GC–MS decreases by increasing the number of ions monitored and/or by decreasing the

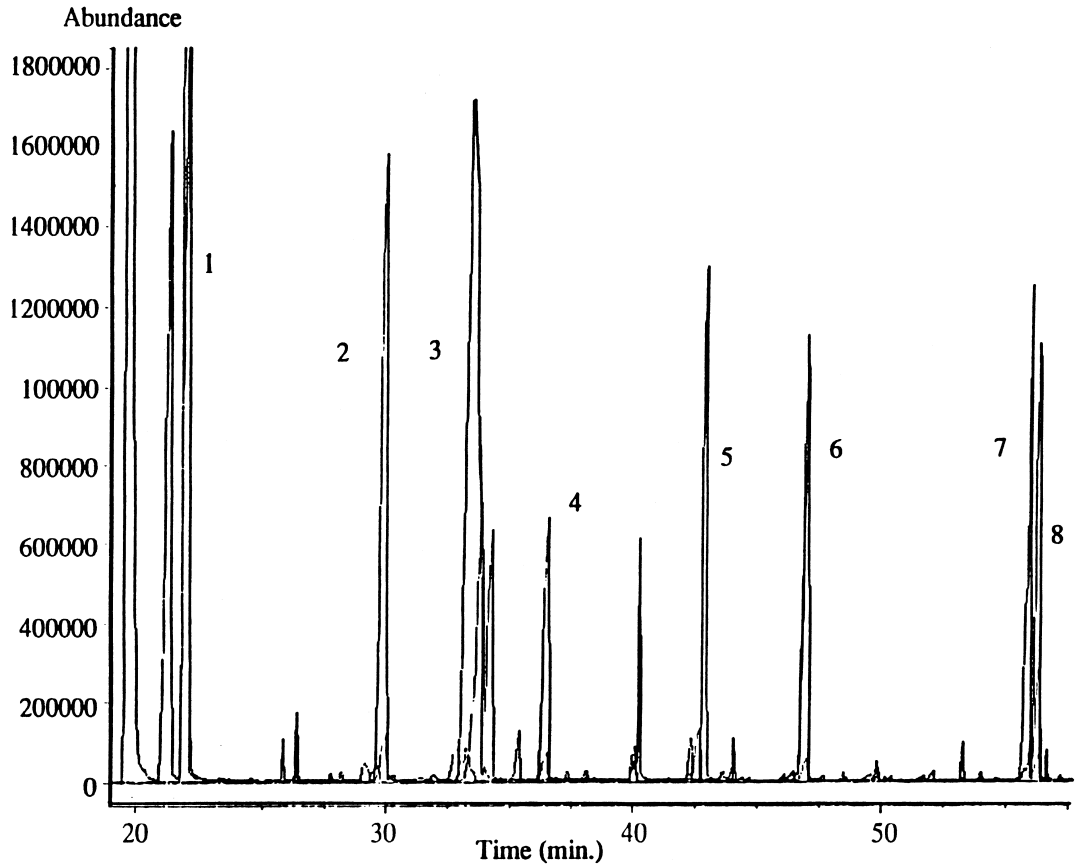

Fig. 4. Chromatographic separation of selected ions (m/z in parentheses) for polychlorinated biphenyls extracted from water samples

Peak identification

Peak	Compound	Peak	Compound
1	2-Chlorobiphenyl (152)	2	2,3-Dichlorobiphenyl (222)
3	2,4,5-Trichlorobiphenyl (256)	4	2,2′,4,4′-Tetrachlorobiphenyl (292)
5	2,2′,3′,4,6-Pentachlorobiphenyl (254)	6	2,2′,4,4′,5,6-Hexachlorobiphenyl (290)
7	2,2′,3,3′,4,4′,6-Heptachlorobiphenyl (324)	8	2,2′,3,3′,4,5,6,6′-Octachlorobiphenyl (358)

EMV [27]. This study indicated that GC–MS programmed to monitor 1 or 2 ions exhibited MDL of 1–4 pg (1–10 ng/ml in water or soil samples) at 2200 EMV and <1 pg (<1 ng/ml in water or soil samples) at 2800 EMV (data not shown). GC–MS programmed to monitor 20 ions exhibited MDL of 10–100 pg (10–100 ng/ml in water or soil samples) at 2200 EMV (Table 6). MDL values obtained from water were similar to the one reported previously for biota samples [25] or coastal sediments [28]. The observation that PAHs concentration in coastal sediments ranged from 1 to 100 ng/g [28] suggests that the sensitivity level of the present method may be sufficient for measuring pollutant concentrations in water samples. The concentration of free pollutants in plasma may be approximately 10 times lower than those in water samples possibly due to the binding of the pollutants with plasma proteins. Therefore, it

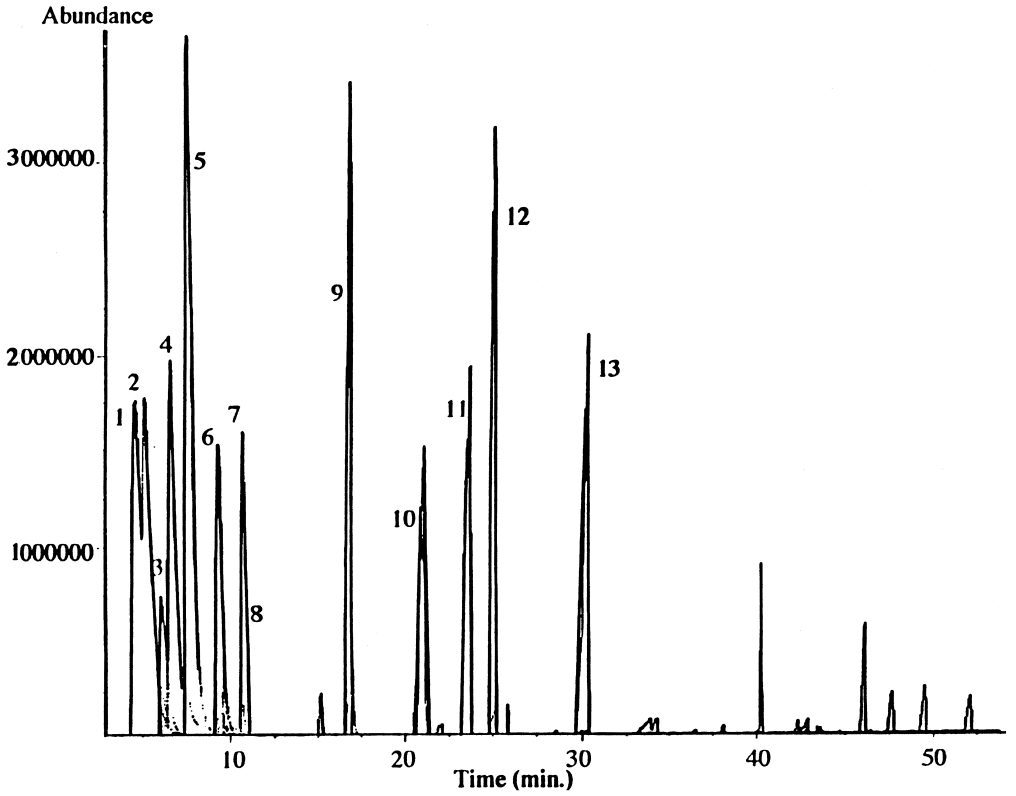

Fig. 5. Chromatographic separation of selected ions (m/z in parentheses) for polychlorinated hydrocarbons and polynitrohydrocarbons extracted from water samples

Peak identification

Peak		Peak	
1	1,2-Dichlorobenzene (146)	2	1,4-dichlorobenzene-d_4 (150)
3	Hexachloroethane (201)	4	Nitrobenzene (77)
5	Isophorone (82)	6	Unidentified
7	Trichlorobenzene (180)	8	Hexachlorobutadiene (225)
9	2-Chloronaphthalene (162)	10	Hexachlorocyclopentadiene (237)
11	2,6-Dinitrotoluene (165)	12	2,4-Dinitrotoluene (165)
13	Hexachlorobenzene (284)		

may be necessary to extract a larger volume of plasma samples for accurate quantitative analysis.

The GC–MS method, although relatively less sensitive than the GC–ECD method, has one major advantage over the GC–ECD method. GC–MS in SIM mode monitors only the selected ions. This provides selective detection of pollutants in water or plasma sample. Thus, the detection limit of GC–MS can be improved by pooling and concentrating a large volume (10–20 ml) of extracted samples without significant contamination problem. Coelution of two or more compounds can be easily distinguished based on their ions. Compounds can be added and deleted from the SIM program by simply adding and deleting specific ions, respectively. For example, if only OC insecticides need to be ana-

Table 5
Percentage recovery of each compound from water, plasma and soil samples

Compound	Water (%)	Plasma (%)	Soil/DCM (%)	Soil/MeOH (%)	Soil/H_2O (%)
2-Chloronaphthalene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-Dichlorobenzene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, Hexachloropentadiene, hexachloroethane, 1,2,4-trichlorobiphenyl, 2-Chlorobiphenyl, 2,3-dichlorobiphenyl, acenaphthene	80–100[a] 70–105[b]	2–9[a] 75–105[b]	75–95[a] 80–95[b]	60–90[a] 65–85[b]	15–30[a] 60–80[b]
Hexachlorobenzene, hexachlorobutadiene, isophorone, nitrobenzene, acenaphthene, acenaphthylene, anthracene, naphthalene, α,β-HCH, δ-HCH, γ-HCH, c- and t-chlordane, dieldrin, endrin aldehyde, endosulfan I and II, endrin, endrin ketone, pyrene	70–100[a] 65–110[b]	10–30[a] 70–110[b]	65–90[a] 70–85[b]	70–100[a] 70–95[b]	6–15[a] 65–90[b]
2,2′,4,4′-Tetrachlorobiphenyl; 2,2′,3′,4,6′-pentachlorobiphenyl, 2,2′,4,4′,5,6′-hexachlorobiphenyl; 2,2′,3,3′,4,4′,6-heptachlorobiphenyl; 2,2′,3,3′,4,5,6,6-octachlorobiphenyl, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*k*]fluoranthene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorene, indeno[123-*c,d*]pyrene, phenanthrene, 4,4′-DDD, 4,4′-DDE, 4,4′-DDT, heptachlor	65–100[a] 70–105[b]	30–60[a] 75–105[b]	60–80[a] 65–85[b]	65–85[a] 65–100[b]	1–5[a] 70–90[b]

[a] Calculated without the internal standard.
[b] Calculated by using the internal standard values.

Table 6
Minimum detection limit of toxicants in water and plasma samples determined at 2200 EMV

OC	Water (ng/ml)	Plasma (ng/ml)	Soil (ng/g)
p,p′DDT, p,p′DDD, *cis*-chlordane, *trans*-chlordane, α-HCH, β-HCH, γ-HCH, d-HCH, heptachlor, p,p′DDE, methoxychlor	35±10[a] 1.7±0.3[b]	250±50[a] 25±5[b]	40±4[a] 5±1[b]
Endrin, dieldrin, endrin ketone, endrin aldehyde	50±15[a] 3±0.5[b]	300±40[a] 40±10[b]	45±4[a] 2±0.3[b]
Endosulfan I, II	100±7[b] 5±1[b]	250±10[a] 30±3[b]	95±8[a] 10±1[b]
Acenaphthene, anthracene, benzo[*b*]fluoranthene benzo[*g,h,i*]perylene, chrysene, dibenzo[(*a,h*]anthracene, hexachlorobutadiene; 2,4,5-trichlorobiphenyl; 2,2′,3,3′,4,4′,6-heptachlorobiphenyl; 2,2′,3,3′,4,5,6,6′-octachlorobiphenyl, indeno[1,2,3-*c,d*]pyrene, naphhthalene, phenanthrene	45±10[a] 2.5±.5[b]	350±110[a] 40±20[b]	50±5[a] 3±0.5[b]
2-Chloronaphthalene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, hexachloropentadiene, nitrobenzene; 2-chlorobiphenyl; 1,2,4-trichlorobenzene; 2,2′,3′,4,6-pentachlorobiphenyl; 2,2′,4,4′,5,6′-hexachlorobiphenyl, benzo[*a*]pyrene	65±15[a] 3±0.6[b]	400±200[a] 50±25[b]	55±6[a] 4±0.5[b]
1,2-Dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachloroethane,2,2′,4,4′-tetrachlorobiphenyl, benzo[*a*]anthracene, fluoranthene, fluorene, pyrene	110±20[a] 5±1[b]	250±50[a] 20±5[b]	90±5[a] 10±1[b]

[a] Minimum detection limit obtained by monitoring 20 ions simultaneously (all toxicants were monitored simultaneously) at 2200 EMV.
[b] Minimum detection limit obtained by monitoring 1 or 2 ions at a time when each compound was analyzed individually at 2200 EMV.

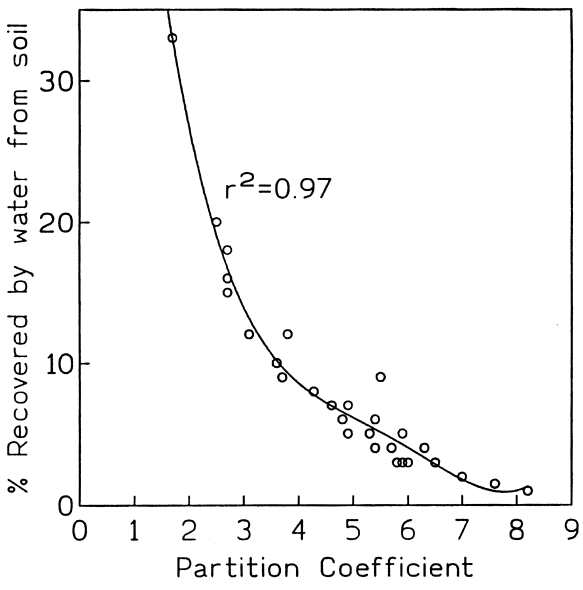

Fig. 6. Correlation between the partition coefficient and the recovery by water of pollutants from soil column

lyzed, the SIM program can be amended to monitor 10–12 OC ions in 3–4 groups, resulting in 3–4 ions/group. The MDL will be approximately 1–4 ng/ml.

4. Conclusions

GC–MS, in SIM mode, provides a simple, sensitive and confirmatory analysis of targeted toxicants in environmental and biological samples. SPE by using florisil columns is suitable for the quantitative, multi-residue (50 compounds) analysis of soil, water or plasma samples. The HP-5 column provided clear separation of some compounds but partial to incomplete separation of others. However, by extracting selected ions from the TI chromatogram, individual pollutant was identified and quantitated. Recovery from water and plasma samples were determined by using d-labelled internal standards. The results obtained with spiked samples indicate that the method

can be used for the rapid screening of pollutants in soil, water and plasma samples.

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