

Simultaneous determination of 42 organic chemicals in bottled water by combining C18 extraction disk with GC-MS and LC/MS/MS technique

Bao-hui Jin, Feng Xiao, Bo Chen, Pei-jin Chen and Li-qi Xie

ABSTRACT

A method for the determination of 42 hazard residues required by 'Japan Positive List System' in bottled water was described. Hazard compounds in bottled water were extracted with a solid phase extraction step using C18 disks. Determination was carried out by gas chromatography/mass spectrometry (GC/MS) and liquid chromatography-tandem mass spectrometry (LC/MS/MS). The disk extraction has high throughput which is well adapted to isolate and enrich these compounds from large volumes of water. For the water sample spiked at three concentration levels (LOQ, 4 times LOQ and 8 times LOQ), the recoveries of all analytes ranged between 65% and 120% with a relative standard deviation < 24% ($n = 8$).

Key words | bottled water, GC/MS, LC/MS/MS, solid-phase extraction disk

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INTRODUCTION

It is very important to human health to ensure the safety of drinking water. The increasing application of chemical compounds has caused the pollution of air, soil, ground and surface water which involves a serious risk to human health due to either direct exposure or through residues in food and drinking water. With microanalysis technology development, recognition that the trace amount of hazardous residues in drinking water could affect human health has been developed constantly. As they are persistent in water for a long period of time, the chronic toxic effects of contaminants through long-term exposure to humans is worth noting. In recent years, pollutant residues in beverages have been found frequently. In 2003, a lab in India reported the presence of pesticides, greatly exceeding European standards, in a dozen popular beverages (Vedwan 2007). In Thailand, the herbicide atrazine was detected in drinking water. This proves that the present treatment steps are not sufficient for removal of such pollutants (Kruawal *et al.* 2005).

Owing to health concerns, strict regulations have been set for the concentrations of organic compounds in drinking

water both in America and in the European Union. In 2006, Japan implemented the 'Positive List System' which has greatly increased the testing requirements for maximum residue limits (MRLs) of agricultural chemicals in food, including water (The Japan Food Chemical Research Foundation 2005). MRL standards for hazard residues in water were established (Tables 1 and 2). For the determination of multiple residues in water, it is a key procedure to concentrate the trace amount compounds. For example, the MRL of aldrin in bottled water is $0.03 \mu\text{g l}^{-1}$ as a requirement of the 'Positive List System'. Traditional liquid-liquid extraction and solid phase extraction (SPE) cartridges which have been applied to determine the levels of pesticides in water, are labour-intensive procedures (Pichon *et al.* 1993), and are unable to achieve the desired high degree of enrichment (Chlron *et al.* 1993). Membrane extraction disk is an alternative trace-enrichment technique, which is also based on the SPE principle. Its main advantage over SPE cartridges is increased productivity permitted by the relatively high flow rates. In general, the time required for the extraction of various hazard residues

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Table 1 | SIM programme and retention time used to analyse compounds in bottled water

Compound	CAS number	Molecular formula	Molecular weight	MRL (mg l ⁻¹)	Time in SIM (min)	Observed ion (m/z)	Retention times (min)
Molinate	2212-67-1	C ₉ H ₁₇ NOS	187	0.006	17.00	83, 126*, 187	18.43
Trifluralin	1582-09-8	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	335.3	0.02		264, 290, 306*	18.56
α-BHC	319-84-6	C ₆ H ₆ Cl ₆	290.8	0.002	21.00	181, 183*, 219	21.93
Atrazine	1912-24-9	C ₈ H ₁₄ ClN ₅	215.7	0.002		173, 200*, 215	23.20
Terbutylazine	5915-41-3	C ₉ H ₁₆ ClN ₅	229.7	0.007	23.25	173, 214*, 229	23.51
Lindane	55963-79-6	C ₆ H ₆ Cl ₆	290.8	0.002		109, 181*, 219	24.02
Dimethoate	60-51-5	C ₅ H ₁₂ NO ₃ PS ₂	229	0.006	24.20	87*, 93, 125	24.47
β-BHC	319-85-7	C ₆ H ₆ Cl ₆	290.8	0.002		109, 181, 219*	25.82
Alachlor	15972-60-8	C ₁₄ H ₂₀ ClNO ₂	269.8	0.02	26.50	146, 160*, 188	27.08
δ-BHC	319-86-8	C ₆ H ₆ Cl ₆	290.8	0.002		109, 181*, 219	27.67
Aldrin	309-00-2	C ₁₂ H ₈ Cl ₆	365	0.00003	28.00	66, 91, 263*	28.32
Metolachlor	51218-45-2	C ₁₅ H ₂₂ ClNO ₂	284	0.01		146, 162*, 238	29.61
Chlorpyrifos	2921-88-2	C ₉ H ₁₁ Cl ₃ NO ₃ PS	350.6	0.03	29.90	97, 193*, 314	30.29
Pendimethalin	40487-42-1	C ₁₃ H ₁₉ N ₅ O ₄	281	0.02	32.00	162, 252*, 281	33.15
Cyanazine	21725-46-2	C ₉ H ₁₃ ClN ₆	240.7	0.0006	34.00	212, 225*, 240	34.56
Trans chlordane	12789-03-6	C ₁₀ H ₆ Cl ₈	409.8	0.0002		237, 272, 373*	35.03
Cis chlordane	5103-71-9	C ₁₀ H ₆ Cl ₈	409.8	0.0002	35.60	237, 272, 373*	35.97
Endosulfan I	959-98-8	C ₉ H ₆ Cl ₆ O ₃ S	406.9	0.01		195, 241*, 339	36.18
p,p'-DDE	72-55-9	C ₁₄ H ₈ Cl ₄	318	0.001	38.00	176, 246*, 318	38.73
Dieldrin	60-57-1	C ₁₂ H ₈ Cl ₆ O	381	0.00003		79, 108, 263*	38.99
Endrin	72-20-8	C ₁₂ H ₈ Cl ₆ O	381	0.006	41.00	81, 263*, 265	41.94
o,p-DDT	789-02-6	C ₁₄ H ₉ Cl ₅	354.5	0.001	43.00	165, 199, 235*	43.35
p,p'-DDD	72-54-8	C ₁₄ H ₁₀ Cl ₄	320	0.001	44.00	165, 199, 235*	44.84
Endosulfan II	33213-65-9	C ₉ H ₆ Cl ₆ O ₃ S	406.9	0.01		195*, 241, 339	45.11
p,p'-DDT	50-29-3	C ₁₄ H ₉ Cl ₅	354.5	0.001	46.00	165, 235*, 237	46.74
Methoxychlor	72-43-5	C ₁₆ H ₁₅ Cl ₃ O ₂	345.6	0.02	49.00	227*, 238, 308	49.40
Pyriproxyfen	95737-68-1	C ₂₀ H ₁₉ NO ₃	321	0.3		96, 136*, 226	50.12

Note: Quantitation ions are marked with an asterisk.

using disks is half of that using cartridges (Barceló *et al.* 1994). Therefore, with the technique of membrane extraction disks it is easy to increase the sample volume in order to enhance the sensitivity of detection. At present, the membrane extraction disks have been used widely to analyse chemical compounds in water (Brouwer *et al.* 1992; Hodgson 1992; Tříska 1995; Chee *et al.* 1996; Martín *et al.* 1996; Munch & Bashe 1997).

In this work, we utilize the techniques of membrane extraction disk, GC/MS and LC/MS/MS to develop a simultaneous determination method of 42 hazard residues

in bottled water. The limit of quantitation of the method satisfies the requirement of the 'Japan Positive List System' and recoveries, precisions and other indexes are suitable for residue determination.

METHODS

Reagents and standards

Unless otherwise specified, all reagents should be of analytical grade. Chemical compounds given in Tables 1 and 2

Table 2 | Multiple reaction monitoring (MRM) settings for positive and negative ion LC/MS/MS analysis of hazard residues in bottled water

Compound	CAS number	Molecular formula	Molecular weight	MRL (mg l ⁻¹)	Identity	Parent ion (Da)	Daughter ion (Da)	Collision energy (V)	Cone voltage (V)	Dwell time (ms)	Retention times (min)
Aldicarb	116-06-3	C ₇ H ₁₄ N ₂ O ₂ S	190	0.01	MNH ₄ ⁺	208.1	116.0 88.9	11 20	11	50	8.41
Carbofuran	1563-66-2	C ₁₂ H ₁₅ NO ₃	221	0.007	MNH ₄ ⁺	222.1	165.2 123.0	17 29	30	50	8.79
Malathion	121-75-5	C ₁₀ H ₁₉ O ₆ PS ₂	330	0.01	MNH ₄ ⁺	331.1	127.1 285.0	17 10	57	50	9.95
Isoproturon	34123-59-6	C ₁₂ H ₁₈ N ₂ O	206.3	0.009	MNH ₄ ⁺	207.4	72.1 165.3	30 22	57	50	9.39
Chlorotoluron	15545-48-9	C ₁₀ H ₁₃ ClN ₂ O	212.7	0.03	MNH ₄ ⁺	213.3 215.3	72.1	34 34	54	50	9.30
Simazine	122-34-9	C ₇ H ₁₂ ClN ₅	201.6	0.002	MNH ₄ ⁺	202.2	132.2 124.2	28 28	52	50	8.87
2,4,5-T	93-76-5	C ₈ H ₅ Cl ₃ O ₃	255.5	0.009	(M-H) ⁻	252.9 254.9	195.0 197.0	-20 -20	-20	35	8.01
Fenoprop	93-72-1	C ₉ H ₇ Cl ₃ O ₃	269.5	0.009	(M-H) ⁻	266.9 268.9	195.0 197.0	-22 -22	-20	35	8.37
2,4-D	94-75-7	C ₈ H ₆ Cl ₂ O ₃	221	0.03	(M-H) ⁻	218.9 220.9	161.0 163.0	-20 -20	-25	35	7.66
2,4-DB	94-82-6	C ₁₀ H ₁₀ Cl ₂ O ₃	249	0.09	(M-H) ⁻	247.0 249.0	161.0 163.0	-22 -22	-15	35	8.29
Pentachlorophenol	87-86-5	C ₆ HCl ₅ O	266.3	0.009	(M-H) ⁻	262.9 264.8	35.1	-42 -42	-50	35	9.62
MCPA	94-74-6	C ₉ H ₉ ClO ₃	200.6	0.002	(M-H) ⁻	199.0 201.0	141.0 143.0	-20 -20	-25	35	7.72
Mecoprop (MCP)	93-65-2	C ₁₀ H ₁₁ ClO ₃	214.6	0.01	(M-H) ⁻	213.0	141.0 71.0	-22 -14	-25	35	8.05
Dichlorprop	120-36-5	C ₉ H ₈ Cl ₂ O ₃	235	0.1	(M-H) ⁻	233.0	161.0 125.0	-22 -38	-20	35	8.00
Fenitrothion	122-14-5	C ₉ H ₁₂ NO ₅ PS	277	0.01	(M-H) ⁻	262.0	152.1 126.1	-24 -19	-42	50	10.16

were purchased from Dr Ehrenstorfer Laboratory (Promochem, Wesel, Germany), with purities between 95 and 99.5%. Stock solutions of solutes were prepared by weighing and dissolving them in methanol or acetone and these were stored at 4°C. Stock solutions were used for the preparation of diluted standard solutions and for spiking water samples. Acetone, ethyl acetate, methanol, *n*-hexane and acetonitrile were HPLC grade (Merck, Darmstadt, Germany). Anhydrous sodium sulphate was heated at 400°C for at least 4 h and pre-rinsed before use. Hydrochloric acid was used to adjust the pH value of the water sample. Bottled water (natural mineral water) was purchased from a market.

Apparatus

A solid phase extraction disk, ENVI-18 DSK or ENVI -8 DSK (47-mm diameter, Supelco, Sigma–Aldrich), was placed on the filtration support according to the instructions (Eichelberger *et al.* 1991), wrinkled side up. The vacuum source was a MZ 2C vacuum pump (Vacuubrand, Wertheim). GC/MS analyses were performed with an Agilent 6890-5973 GC/MS system. A DB-35ms column (J&W Scientific, 30 m × 0.25 mm × 0.25 μm) was used with temperature programmed control. LC/MS/MS analysis was performed using an Agilent 1100 LC system and an API 3000 triple quadrupole mass spectrometer with electrospray ionization (ESI), operating in the positive or negative ion mode. Centrifuge (Hettich), mechanical Shaker (Minishaker MS1, IKA), nitrogen evaporator (Zymark LV) and Rotary evaporator (Heidolph, Laborota 4003) were used to pretreat the water samples. A pH meter (Cyber Scan pH510) was used to adjust the pH value of water samples.

Sample preparation and extraction

One litre of bottled drinking water was allowed to equilibrate to room temperature in a narrow mouth amber glass bottle. The pH value of the water sample was adjusted to 2.5 with 1 mol l⁻¹ hydrochloric acid. Analyte standards were spiked into water samples.

Ten millilitres ethyl acetate and 10 ml acetone were poured onto the disk for cleaning and drawn through the disk immediately by moderate vacuum (15 mm Hg/50 kPa).

The condition of vacuum was maintained for 5 minutes to remove all solvent. A volume of 1 l of spiked water sample was passed through a C18 or C8 preconditioned membrane disk (all types of disk were activated by passing 10 ml of methanol and 10 ml of distilled water through them). The vacuum level was adjusted to provide a flow rate of approximately 50 ml/minute. The disk must not go dry until the entire sample has been processed. The adsorbed chemical compounds were then slowly eluted with the 20 ml solution of acetone + *n*-hexane. After dehydration with anhydrous sodium sulfate, the organic phase was evaporated to 2 ~ 3 ml on a rotary evaporator using a water bath at 40°C. The remaining organic phase was transferred to a 15 ml graduated test tube. The flask was rinsed with 6 ml acetone three times. Each rinse was transferred to the same test tube. The solution in test tube was evaporated to less than 0.5 ml in a water bath at 40°C under a gentle stream of nitrogen, diluted exactly to 1 ml with acetone and injected into GC/MS and LC/MS/MS system.

GC/MS conditions

Injection port temperature was 230°C and injection mode was splitless. For GC separation, the column temperature programme used was as follows: 35°C (hold 1 min) and 1°C/min to 40°C, then 20°C/min to 180°C (hold 1 min), 1.5°C/min to 220°C (hold 2 min), and finally, 15°C/min to a final temperature of 300°C (hold 5 min). The carrier gas was helium of more than 99.999% purity and a flow rate of 1.0 ml min⁻¹. The temperature for the transfer line and the ion source were set at 280 and 230°C, respectively. The injection volume was 1 μl. Mass spectrometric detector was operated in electron impact ionization mode with an ionizing energy of 70 eV. The solvent delay of 5.0 min was employed. Analysis was performed in the SIM mode based on the use of one target and two qualifier ions. Chemical compounds were identified according to retention times, target and qualifier ions. Table 1 summarizes some of the chemical compounds studied with their target and qualifier ions used in SIM mode.

LC/MS/MS conditions

Chromatographic separations were achieved using a Zorbax Edipse XDB-C18 HPLC column (150 × 2.1 mm,

3.5 μm , Angilent) maintained at a constant temperature of 20°C. The mobile phase consisted of 5 m mol l^{-1} ammonium acetate (eluent A) and methanol (eluent B), delivered at a flow rate of 0.3 ml min^{-1} . The chromatographic gradient used was: from 0 to 5 min the percentage of eluent B linearly increases from 5% to 90% and is maintained at 90% to 11 min; from 11 to 11.5 min, the percentage of eluent B linearly decreases from 90% to 5% and is maintained at 5% to 16 min.

The mass spectrometer was operated in the positive or negative mode. Nitrogen was used as nebulizer gas (5.01 min^{-1}), auxiliary gas (7.01 min^{-1} heated to 500°C), curtain gas (9.01 min^{-1}) and as CAD gas (5.01 min^{-1}). Ion spray voltage was set to 4,500 V for positive EI and -4,500 V for negative EI. Multiple reaction monitoring (MRM) experiments were conducted for all chemical compounds. Optimization of the collision energy (CE) for each individual compound was done by infusion of the compound directly into the LC effluent using a syringe pump (Harvard, Kent). Parent and daughter ions monitored, dwell time and collision energies used, are shown in Table 2, for ESI positive and negative modes.

RESULTS AND DISCUSSION

The selection of solid extraction disks and eluents

Octyl- and octadecylsilane SPE membrane (C8 and C18, respectively) were used to compare the extraction capability for the residues in water. *n*-Hexane and acetone were considered to elute the analytes from disks. Consistently with the hydrophobic character of octyl- and octadecylsilane SPE membrane, *n*-hexane seemed appropriate for eluting. Acetone is a strong solvent which is suitable for dissolving different polar compounds. The results showed that when either *n*-hexane or acetone was used to elute disks, C18 all provided better recoveries than C8. When C18 disks were used, the elution efficiency of acetone was better than that of *n*-hexane for determining 27 compounds by GC/MS. For determining 15 compounds by LC/MS/MS, the elution efficiency of *n*-hexane was better than that of acetone. Therefore, the C18 disk was selected for the enrichment of analytes in the water sample and the solution

of acetone + *n*-hexane (1:1, V/V) was used to elute analytes in the disk.

Effect of pH value of the water sample

The recovery efficiencies of each analyte were investigated in the pH range of 2.0 ~ 10.0 by using 1 mol l^{-1} HCl and NaOH to adjust the pH value of the water sample. The results showed that better quantitative recoveries of analytes were achieved under acidic conditions compared with neutral or alkaline conditions. In particular, the quantitative recoveries of analytes determined by LC/MS/MS were best at a pH value of 2.5. For the compounds determined by GC/MS, The recoveries at pH 2.0 were consistent with pH 2.5, except that the recoveries of molinate and trifluralin were slightly higher. Judging from these results, pH 2.5 was selected as the pH of the sample for the simultaneous preconcentration of multi-residues.

Effect of the eluent volume on the recoveries of the analytes

The effect of eluent volume on the recoveries of the analytes was studied by using the solution of acetone + *n*-hexane (1:1, v/v). For several analytes of terbuthylazine, chlorpyrifos, methoxychlor, carbofuran and 2,4-D chosen at random, the relationship of their mean recoveries ($n = 5$) and the eluent volume is shown in Figure 1. By increasing the volume from 5 ml to 20 ml, their recoveries increased significantly. Moreover, compared with 20 ml, the

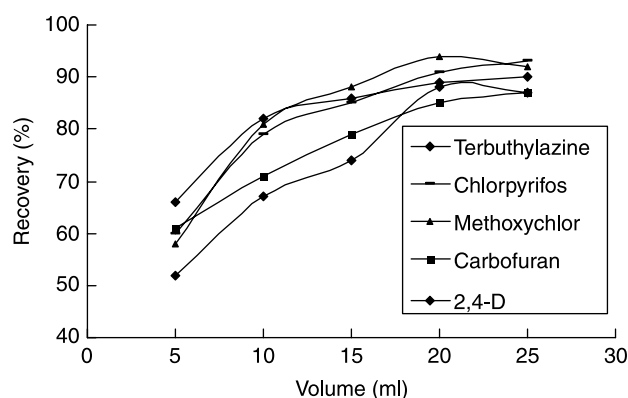


Figure 1 | Effect of eluent volume in the recoveries of terbuthylazine, chlorpyrifos, methoxychlor, carbofuran and 2,4-D.

Table 3 | MDLs, LOQs and recoveries of studied compounds in bottled water

Compound	Detection technique	MDL (mg l ⁻¹)	LOQ (µg/kg)	Mean recovery and precision, % (n = 8)					
				Spiking level 1		Spiking level 2		Spiking level 3	
				Recovery	RSD	Recovery	RSD	Recovery	RSD
Molinate	GC/MS	0.004	1.00	89.0	21.0	93.1	15.9	88.5	11.3
Trifluralin	GC/MS	0.005	1.00	85.9	23.0	87.6	16.2	84.7	12.0
α-BHC	GC/MS	0.008	1.00	89.6	20.5	81.2	15.6	84.5	12.9
Atrazine	GC/MS	0.006	1.00	78.3	19.5	79.0	14.7	85.8	11.3
Terbuthylazine	GC/MS	0.006	1.00	80.2	18.5	83.4	15.6	86.3	12.7
Lindane	GC/MS	0.010	1.00	87.6	21.3	77.9	14.8	84.6	12.2
Dimethoate	GC/MS	0.008	1.00	72.9	13.5	83.5	17.7	87.1	13.0
β-BHC	GC/MS	0.007	1.00	93.3	18.8	80.3	18.8	87.8	12.3
Alachlor	GC/MS	0.005	1.00	76.6	14.7	82.8	16.8	82.5	12.2
δ-BHC	GC/MS	0.008	1.00	82.4	20.2	80.9	16.2	78.2	10.9
Aldrin	GC/MS	0.010	0.02	77.5	19.8	80.3	18.5	79.5	11.6
Metolachlor	GC/MS	0.004	1.00	78.7	21.2	80.9	17.6	86.3	12.6
Chlorpyrifos	GC/MS	0.004	1.00	77.1	18.1	83.5	16.6	86.1	10.6
Pendimethalin	GC/MS	0.007	1.00	78.1	13.3	78.1	12.3	86.0	12.4
Cyanazine	GC/MS	0.009	0.50	87.4	19.2	80.5	17.9	81.5	9.9
Trans chlordane	GC/MS	0.010	0.10	83.0	23.6	79.6	18.6	84.8	12.8
Cis chlordane	GC/MS	0.010	0.10	83.8	20.3	86.7	15.8	82.3	13.8
Endosulfan I	GC/MS	0.012	1.00	90.6	21.3	83.2	16.7	83.3	13.2
p,p'-DDE	GC/MS	0.006	1.00	87.7	21.0	83.2	12.9	79.1	12.3
Dieldrin	GC/MS	0.011	0.02	86.3	14.1	82.8	16.8	89.8	12.7
Endrin	GC/MS	0.012	0.50	90.6	18.6	81.3	16.4	85.0	12.8
o,p-DDT	GC/MS	0.007	1.00	86.6	19.8	82.5	16.2	84.1	12.9
p,p'-DDD	GC/MS	0.007	1.00	79.4	11.7	82.3	18.8	80.2	12.9
Endosulfan II	GC/MS	0.012	1.00	83.1	20.7	81.2	16.8	86.1	13.5
p,p'-DDT	GC/MS	0.008	1.00	82.8	21.7	77.5	16.0	79.9	11.3
Methoxychlor	GC/MS	0.006	1.00	91.9	18.1	81.3	16.5	81.7	13.9
Pyriproxyfen	GC/MS	0.004	1.00	85.3	15.4	86.7	15.8	80.5	12.0
Aldicarb	LC/MS/MS	0.004	1.00	107.9	15.7	90.3	9.2	80.1	3.4
Carbofuran	LC/MS/MS	0.003	1.00	86.5	15.1	75.6	5.1	86.5	3.5
Malathion	LC/MS/MS	0.002	1.00	65.8	7.5	70.9	10.5	70.3	6.4
Isoproturon	LC/MS/MS	0.011	1.00	70.6	14.4	83.2	11.3	88.6	5.4
Chlorotoluron	LC/MS/MS	0.023	1.00	79.7	14.3	88.1	10.3	99.0	4.4
Simazine	LC/MS/MS	0.023	1.00	119.2	22.9	87.1	12.9	82.5	8.6
2,4,5-T	LC/MS/MS	0.008	1.00	77.1	19.1	83.1	11.1	92.3	4.2
Fenoprop	LC/MS/MS	0.012	1.00	100.8	20.4	107.5	5.3	83.6	6.1
2,4-D	LC/MS/MS	0.024	1.00	116.5	16.6	103.6	4.7	82.2	9.5
2,4-DB	LC/MS/MS	0.041	1.00	91.3	14.8	90.7	9.4	100.8	5.6
Pentachlorophenol	LC/MS/MS	0.057	1.00	66.3	12.2	68.4	8.7	76.4	6.2
MCPA	LC/MS/MS	0.030	1.00	91.4	10.3	77.2	4.5	91.6	8.3

Table 3 | (continued)

Compound	Detection technique	MDL (mg l ⁻¹)	LOQ (µg/kg)	Mean recovery and precision, % (n = 8)					
				Spiking level 1		Spiking level 2		Spiking level 3	
				Recovery	RSD	Recovery	RSD	Recovery	RSD
Mecoprop	LC/MS/MS	0.056	1.00	101.2	13.7	83.0	7.1	87.5	6.6
Dichlorprop	LC/MS/MS	0.150	1.00	85.2	14.1	84.4	6.8	92.3	3.6
Fenitrothion	LC/MS/MS	0.030	1.00	100.6	16.1	84.7	11.7	76.3	11.3

recoveries displayed only minor changes when the eluent volume increased to 25 ml. It was proved that quantitative recoveries (>85%) could be obtained with 20 ml eluent. Therefore, the volume of 20 ml eluent was used in the following experiments.

Validation of the method

Multi-level calibration curves were created for the quantification using standard solutions of the analytes in acetone. Method detection limits (MDL) were determined at a signal-to-noise ratio of 3 and the limits of quantification (LOQ) were determined as the lowest concentration in the linear range of each analyte. MDLs and LOQs are shown in Table 3. Figures 2 and 3 showed the GC/MS (SIM)

chromatogram of standard solution and MRM chromatograms of standard solution, respectively. The concentrations of aldrin, dieldrin, trans-chlordane, cis-chlordane, cyanazine and endrin were 0.02 mg l⁻¹, 0.02 mg l⁻¹, 0.1 mg l⁻¹, 0.1 mg l⁻¹, 0.5 mg l⁻¹ and 0.5 mg l⁻¹. The concentrations of other compounds were 1.0 mg l⁻¹.

The accuracy of the proposed method was evaluated by means of recovery experiments carried out using spiked samples at different analyte concentration levels (spiked level 1, 2 and 3) and a blank constituted by the unspiked sample. The concentrations of all analytes in the spiked level 1, 2 and 3, respectively, were the same, 4 times and 8 times the concentration of the LOQs. In all cases, the recovery percentage values ranged between 65% and 120% with a relative standard deviation <24% (n = 8) (Table 3).

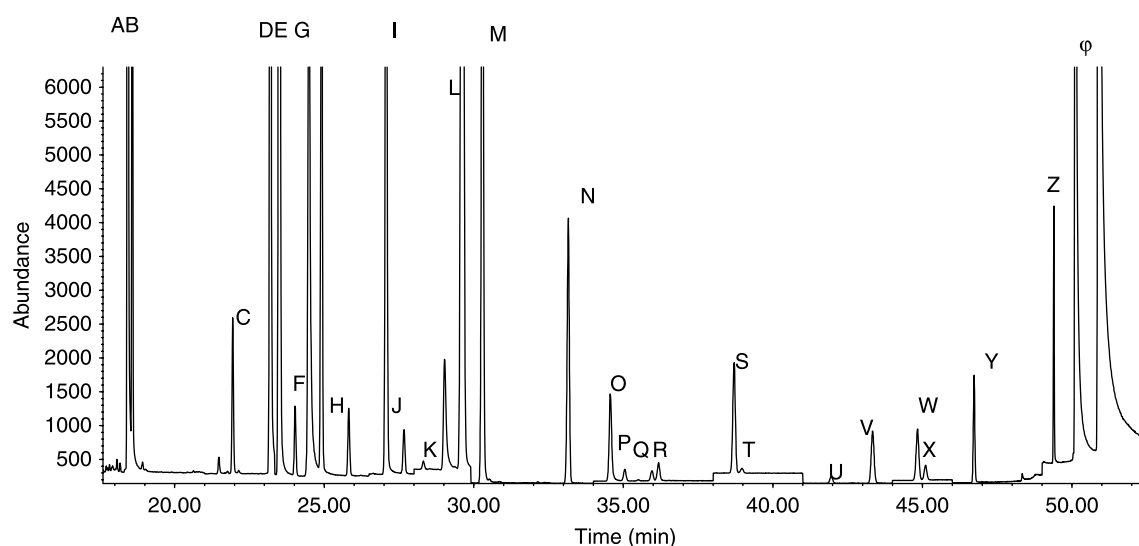


Figure 2 | TIC chromatogram of standard solution; A: molinate; B: trifluralin; C: α-BHC; D: atrazine; E: terbutylazine; F: γ-BHC; G: dimethoate; H: β-BHC; I: alachlor; J: δ-BHC; K: aldrin; L: metolachlor; M: chlorpyrifos; N: pendimethalin; O: cyanazine; P: trans-chlordane; Q: cis-chlordane; R: endosulfan I; S: p,p'-DDE; T: dieldrin; U: endrin; V: o,p'-DDT; W: p,p'-DDD; X: endosulfan II; Y: p,p'-DDT; Z: methoxychlor; φ: pyriproxyfen.

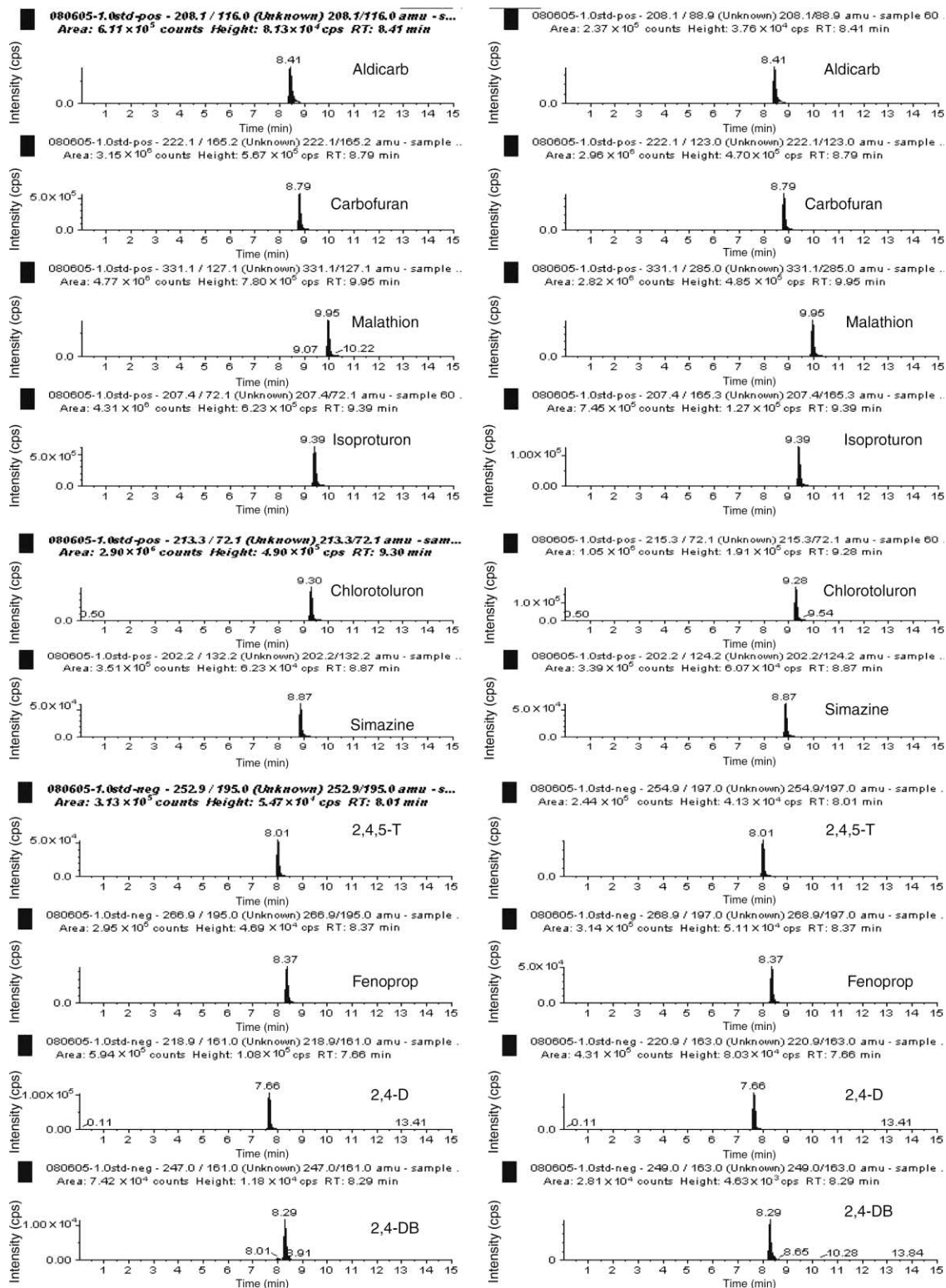


Figure 3 (continued)

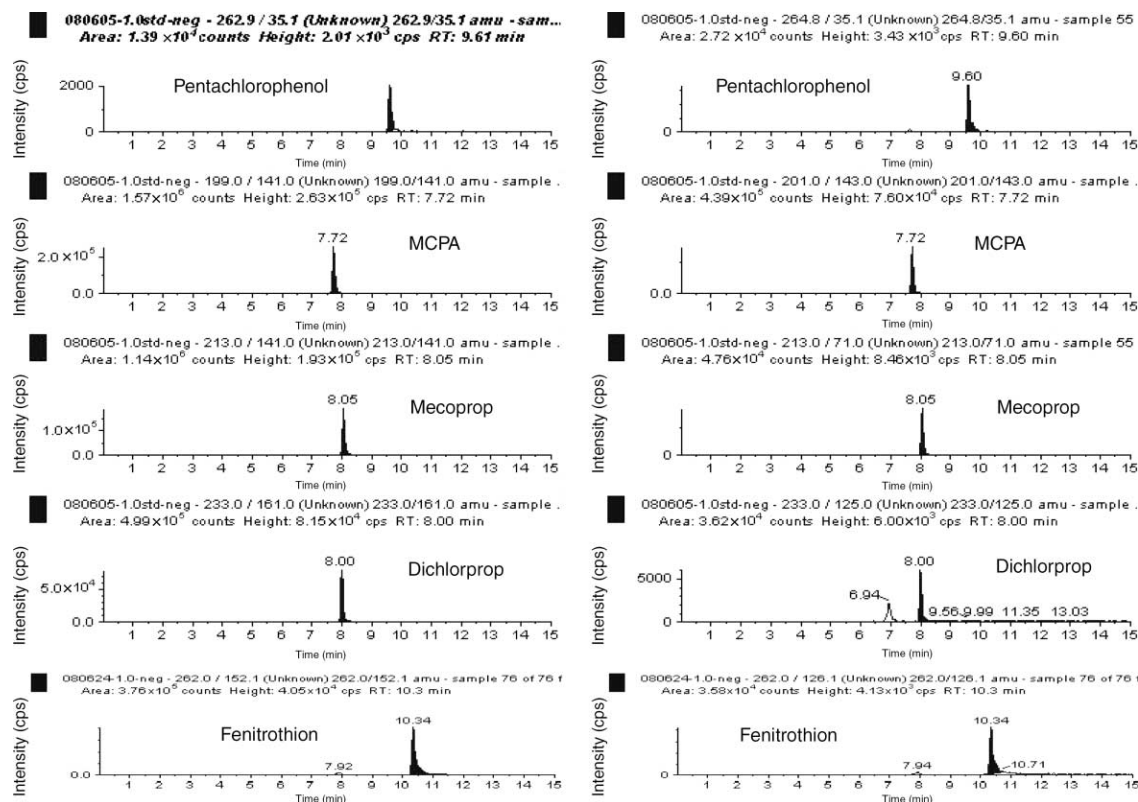


Figure 3 | MRM chromatograms of standard solution.

CONCLUSIONS

This work demonstrated that the C18 SPE disk was well suited as a sample preparation procedure for the extraction of hazardous compounds in bottled water. C18 disks enable larger sample volumes to be treated and hence enable much a lower level of hazardous compounds to be detected in bottled water. The recovery values ranged between 65% and 120% with a relative standard deviation $<24\%$ ($n = 8$).

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