

Evaluation of Liquid–Solid Extraction with a New Sorbent and Liquid–Liquid Extraction for Multiresidue Pesticides. Determination in Raw and Finished Drinking Waters

Manuel J. Fernandez, César Garcia, Rafael J. Garcia-Villanova,* and Juan A. Gomez

Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Farmacia, Universidad de Salamanca, Avda. Campo Charro s/n, E-37007 Salamanca, Spain

A comparative study is made of the application of liquid–liquid (LLE) and liquid–solid (LSE) extraction techniques with a new sorbent with trifunctional bonding chemistry (tC_{18}) for environmental sampling and trace enrichment. The experimental conditions of the LLE and LSE methods were evaluated for the determination of 22 organochlorine and 2 organophosphorus pesticides, 2 triazines, and 7 polychlorinated biphenyls (PCBs), which were analyzed by gas chromatography with a capillary column and electron-capture detector (ECD). Mean recovery yields were found to be higher with the LLE method, although LSE for most of the 33 analytes assayed surpassed 70%. The detection limits for both techniques were lower than 5 ng L^{-1} , except for the pesticides parathion (7 ng L^{-1}), methoxychlor (8 ng L^{-1}), atrazine (35 ng L^{-1}), and simazine (95 ng L^{-1}). The absolute standard deviations and the variation coefficients of both techniques were slightly higher in LSE and ranged from 0.5 to 2.6 ng L^{-1} and 7 to 24%, respectively. The method was applied to the analysis of raw and finished drinking water from four towns with different water sources and qualities.

Keywords: *Liquid–solid extraction; GC/ECD of pesticides in water; pesticide enrichment; tC_{18} cartridges*

INTRODUCTION

The determination of organic micropollutants in water samples is often performed by application of the gas chromatography technique (GC). However, only in certain determinations is it possible to inject the aqueous sample directly into the column (Gurka et al., 1992). Generally, organic analytes are isolated and, sometimes, preconcentrated prior to injection into the chromatograph (Namiesnik et al., 1990).

Many applications of the following general methods for the extraction of organic compounds from water can be found in literature: liquid–liquid extraction using either *n*-pentane (Oliver and Dothen, 1980; Stachel et al., 1981; García et al., 1992), methylene chloride (Goldberg and Weiner, 1980; Peters, 1982; López-Avila et al., 1990; Gregory et al., 1991; Kenneth et al., 1992), *n*-hexane (Melcher and Morabito, 1990; Potter et al., 1991), or ethyl acetate (Ballesteros et al., 1990; Kim et al., 1991); gas extraction for volatile organic compounds using either the head-space (Croll et al., 1986; Freiria-Gándara et al., 1990) or the purge-and-trap techniques (Caron and Kramer, 1989; Tomkins et al., 1989; Lépine and Archambault, 1992; Philippaerts et al., 1992; Lin and Falkenberg, 1993); the new hollow fiber membrane technique (LaPack and Tou, 1991; Pratt and Pawliszyn, 1992; Yang and Pawliszyn, 1993); and liquid–solid extraction, generally using cartridges containing prepacked reverse-phase octadecyl (C_{18})-bonded silica materials, either only for organochlorine pesticides (López-Avila et al., 1989; Bruce et al., 1992; Guan, 1992; Tan, 1992) and polychlorinated biphenyl compounds (Moltó et al., 1992) or for several groups of pesticides together (the former and organophosphorus, phthalates, and triazines) (Johnson et al., 1991; Donald et al., 1990; López-Avila and Milanes, 1991; Huang, 1989; Matthew et al., 1989; Nash, 1990; Warren et al., 1991), as well as for other groups of micropollutants (polycyclic aromatic hydrocarbons and phenols).

Finally, two official methods were established several years ago: the liquid–liquid extraction recommended by APHA-AWWA-WPCF (1989) and the liquid–solid extraction EPA method 525, Revision 2.1 (1988).

The present work reports on a comparative study of the application of LLE and LSE procedures for the determination of 33 analytes (organochlorine and organophosphorus pesticides, triazines, and PCBs) in surface raw and finished drinking waters. These 33 compounds have been selected as a group commonly searched and found in these samples, usually in very low levels and for which the ECD method reaches lower detection limits as compared to that using MS quantitation.

The aim of this paper was to assess the validity of a new sorbent, slightly different from the C_{18} , with trifunctional bonding chemistry (tC_{18}), and a smaller particle size, however, with similar pore size. This sorbent, according to the manufacturer's specifications, can be submitted to prolonged exposures of acidic solutions without the risk of releasing the C_{18} functional group; this might be particularly interesting when there is a need to process large volumes of water for measuring parts per trillion levels of contaminants and/or when the extracts are due to be kept for a certain time before eluting them.

As indicated above, many studies have been performed for the C_{18} cartridges; however, nothing has been found in the literature about the tC_{18} .

EXPERIMENTAL PROCEDURES

Apparatus. A Zymark Turbopap concentrator was used for concentrating the sample extracts.

The gas chromatograph used was a Hewlett-Packard 5890 Series II fitted with a ^{63}Ni ECD and connected to a Hewlett-Packard 3395 integrator for peak-area determination. A $5 \mu\text{L}$ manual glass syringe was used to inject $1 \mu\text{L}$ samples into a PAS-5 fused-silica capillary column ($25 \text{ m} \times 0.32 \text{ mm}$ inside diameter, $0.52 \mu\text{m}$ film thickness). The confirmation column

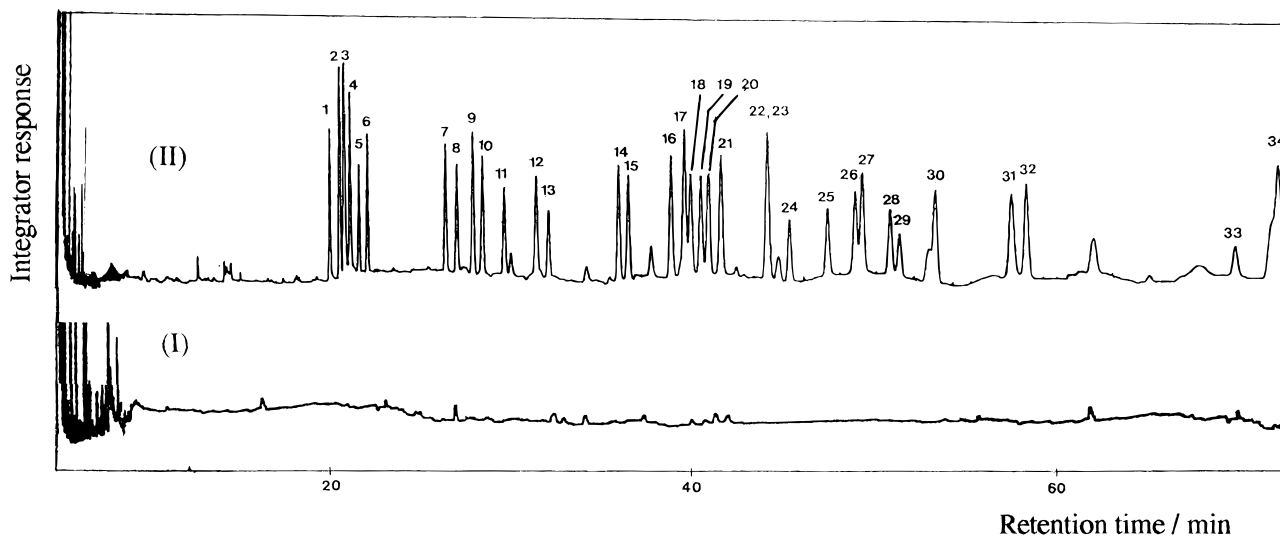


Figure 1. (I) Gas chromatograph of methylene chloride. (II) Gas chromatograph of 33 pesticide standards at $25 \mu\text{g L}^{-1}$ each, except methyl-parathion, parathion ($50 \mu\text{g L}^{-1}$), atrazine ($250 \mu\text{g L}^{-1}$), and simazine ($600 \mu\text{g L}^{-1}$): (1) α -HCH, (2) HCB, (3) simazine, (4) atrazine, (5) β -HCH, (6) γ -HCH, (7) PCB 28, (8) methyl-parathion, (9) heptachlor, (10) α -chlordane, (11) PCB 52, (12) aldrin, (13) parathion, (14) *cis*-heptachlor epoxide, (15) *trans*-heptachlor epoxide, (16) γ -chlordane, (17) *o,p'*-DDE, (18) PCB 101, (19) α -endosulfan, (20) α -chlordane, (21) *trans*-nonachlor, (22) *p,p'*-DDE, (23) dieldrin, (24) *o,p'*-DDD, (25) endrin, (26) β -endosulfan, (27) PCB 118, (28) *p,p'*-DDD, (29) *o,p'*-DDT, (30) PCB 153, (31) *p,p'*-DDT, (32) PCB 138, (33) methoxychlor, and (34) PCB 180.

was a PAS-1701 fused-silica capillary column (25 m \times 0.32 mm inside diameter, 0.25 μm film thickness). The gas chromatographic conditions were as follows: N-55 flow rate, 1 mL min^{-1} ; "make-up" N-55 flow rate, 60 mL min^{-1} ; detector temperature, 300 $^{\circ}\text{C}$; injector temperature, 250 $^{\circ}\text{C}$; oven program temperature, 80 $^{\circ}\text{C}$ for 1 min, increased at 8 $^{\circ}\text{C min}^{-1}$ to 190 $^{\circ}\text{C}$, held for 2 min, then increased at 0.8 $^{\circ}\text{C min}^{-1}$ to 210 $^{\circ}\text{C}$, held for 1 min, then increased at 0.6 $^{\circ}\text{C min}^{-1}$ to 230 $^{\circ}\text{C}$, and held for 10 min; and sample size, 1 μL (splitless).

Liquid-solid extraction was performed with a Sep-pak cartridge, with trifunctional bonding chemistry tC_{18} (1000 mg of C_{18} -bonded porous silica), obtained from Waters.

A Gilson Minipuls 3 peristaltic pump was used to assist in passing the water samples.

Reagents. The use of high-purity reagents and solvents helped to minimize interference problems. The solvents used, methylene chloride, *n*-hexane, and isooctane, were obtained from Carlo Erba and were of RS grade for the analysis of pesticide residues.

Anhydrous sodium sulfate, sodium thiosulfate, and hydrochloric acid were of RPE grade and were supplied by Carlo Erba.

Ultra High Quality water from Elgastat was used as reagent water.

Standard solutions of organochlorine pesticides and polychlorinated biphenyl compounds were from the laboratory of Dr. Ehrenstorfer, supplied by Delta Cientifica at a concentration of 10 mg L^{-1} in isooctane. Atrazine, simazine, parathion, and methyl-parathion were more than 97% pure and were supplied by Riedel-de-Häen. Working solutions used for qualitative and quantitative analyses were prepared by suitable dilution of standards with isooctane.

Procedure. Water samples were collected in 2500 mL amber glass bottles, previously washed with Mucosol (Merz + Co) and rinsed with methylene chloride. Raw water samples were filtered through glass wool, and 75 mg L^{-1} $\text{Na}_2\text{S}_2\text{O}_3$ was added to the treated water samples as a dechlorinating agent. Raw and treated water samples were acidified to pH 2 with HCl before the extraction procedure.

Liquid-Liquid Extraction. It was performed according to the method recommended by APHA-AWWA-WPCF (1989).

All glassware in this procedure was washed with the extraction solvent.

A sample of 1000 mL was extracted successively with 3 volumes of 60 mL of a solution containing 15% hexane in methylene chloride. The extract was collected, passed through anhydrous Na_2SO_4 , and concentrated in the Turbovap concentrator to 0.5 mL.

Table 1. Recovery of Pesticide Standards in Reagent Water

compound	LLE (%)	LSE (%)
HCB	108 \pm 8 ^a	90 \pm 7
α -HCH	104 \pm 12	91 \pm 11
β -HCH	95 \pm 13	73 \pm 8
γ -HCH	101 \pm 8	94 \pm 12
heptachlor	106 \pm 15	86 \pm 11
α -chlordane	116 \pm 11	83 \pm 10
aldrin	98 \pm 12	85 \pm 11
<i>cis</i> -heptachlor epoxide	95 \pm 6	78 \pm 8
γ -chlordane	97 \pm 21	83 \pm 14
<i>o,p'</i> -DDE	92 \pm 5	84 \pm 9
α -endosulfan	94 \pm 10	76 \pm 8
α -chlordane	96 \pm 8	86 \pm 16
<i>trans</i> -nonachlor	92 \pm 10	84 \pm 12
<i>p,p'</i> -DDE	95 \pm 14	82 \pm 13
dieldrin	92 \pm 9	84 \pm 10
<i>o,p'</i> -DDD	94 \pm 11	75 \pm 8
endrin	96 \pm 14	80 \pm 14
β -endosulfan	93 \pm 16	75 \pm 9
<i>p,p'</i> -DDD	89 \pm 7	74 \pm 11
<i>o,p'</i> -DDT	88 \pm 11	77 \pm 10
<i>p,p'</i> -DDT	114 \pm 19	82 \pm 12
methoxychlor	111 \pm 15	67 \pm 8
methyl-parathion	105 \pm 14	78 \pm 11
parathion	96 \pm 10	83 \pm 15
atrazine	91 \pm 9	79 \pm 8
simazine	85 \pm 14	81 \pm 10
PCB 28	92 \pm 8	87 \pm 18
PCB 52	94 \pm 14	83 \pm 11
PCB 101	91 \pm 13	76 \pm 8
PCB 118	104 \pm 11	73 \pm 9
PCB 153	93 \pm 8	74 \pm 14
PCB 138	98 \pm 15	78 \pm 10
PCB 180	87 \pm 10	69 \pm 12

^a $n = 3$. Mean recovery \pm SD (%).

Liquid-Solid Extraction. Sep-pak tC_{18} cartridges were preactivated with methylene chloride, methanol, and reagent water at pH 2. The sample, 1000 mL, was passed with the help of a peristaltic pump at a flow rate of 6–8 mL min^{-1} . Analytes were then eluted with 15 mL of methylene chloride, and the extract was passed through anhydrous Na_2SO_4 and concentrated to 0.5 mL with the Turbovap concentrator.

Extraction efficiency in LLE and LSE was calculated by comparison of the areas of the analyte peaks in the chromatogram of the extract with those in the chromatogram of a standard solution.

Table 2. Detection Limits of Pesticide Analyzed

compound	detection limits (ng L ⁻¹)	
	LLE	LSE
HCB	1.6	2.6
α-HCH	2.5	2.3
β-HCH	3.2	4.4
γ-HCH	2.1	2.3
heptachlor	3.6	3.2
α-chlordene	2.4	3.4
aldrin	3.0	3.6
cis-heptachlor epoxide	2.8	4.4
γ-chlordane	3.1	2.1
o,p'-DDE	1.8	3.1
α-endosulfan	2.5	2.8
α-chlordane	1.8	3.2
trans-nonachlor	2.5	2.0
p,p'-DDE	3.2	3.4
dieldrin	1.9	2.6
o,p'-DDD	2.6	4.1
endrin	3.6	4.5
β-endosulfan	3.5	4.2
p,p'-DDD	3.1	3.8
o,p'-DDT	4.1	5.3
p,p'-DDT	4.4	3.9
methoxychlor	7.7	9.2
methyl-parathion	5.1	6.6
parathion	6.5	7.3
atrazine	33.2	36.0
simazine	104.1	89.0
PCB 28	2.8	3.3
PCB 52	2.4	2.9
PCB 101	2.6	2.8
PCB 118	2.8	4.1
PCB 153	2.5	3.6
PCB 138	2.3	3.8
PCB 180	3.5	4.7

Quantification. Analyte concentrations were determined by the addition to samples of *trans*-heptachlor epoxide as internal standard before LLE or LSE at a concentration at which the

height of the peak was similar to that of the analytes present in the samples.

To 4 volumes of 1 L of reagent water were added amounts of a concentrated multicomponent solution of the 33 analytes to be investigated so as to reach concentrations of 6.25, 12.5, 25.0, and 50.0 ng L⁻¹, with the exception of the compounds methoxychlor, methyl-parathion, and parathion (12.5, 25.0, 50.0, and 100.0 ng L⁻¹), atrazine (62.5, 125.0, 250.0, and 500.0 ng L⁻¹), and simazine (150.0, 300.0, 600.0, and 1200.0 ng L⁻¹). Each of these four volumes was added to 25.0 ng L⁻¹ internal standard. To these solutions was applied the above-indicated LLE technique.

The same procedure was performed for the LSE technique to be tested.

One microliter of each extract was injected in the chromatograph in order to build up the calibration curves for each extraction technique.

For control of the results, periodic calibration graphs were obtained of the compounds identified in the samples within the working concentration range.

RESULTS AND DISCUSSION

The gas chromatogram of a mixture of 33 pesticide standards is shown in Figure 1. All 33 compounds could be resolved and eluted in a reasonable time by employing the GC conditions stipulated above. Also shown is the gas chromatogram of the solvent, methylene chloride, concentrated to the same level as that used in the sample analysis; it may be seen that no response to the ECD is remarkable during the time of elution of the analytes.

Extraction Efficiency. *Liquid-Liquid Extraction.* Extraction efficiency was determined by the addition to 1000 mL of reagent water, acidified to pH 2 with HCl, of the 33 analytes at three different concentrations, 12.5, 25.0, and 50.0 ng L⁻¹, with the exception of the compounds methoxychlor, methyl-parathion, and par-

Table 3. Recovery of Pesticide Standards Added to Raw Water Using Liquid-Liquid Extraction

compound	added (ng L ⁻¹)	present (ng L ⁻¹)	found (ng L ⁻¹)	recovery ^a (%)	mean recovery ^b (%)
HCB	12.0	—	11.6	97	102 ± 13
α-HCH	12.0	5.1	16.3	95	98 ± 8
β-HCH	12.0	—	10.2	85	92 ± 11
γ-HCH	12.0	4.5	16.8	102	105 ± 12
heptachlor	12.0	—	14.0	117	111 ± 18
α-chlordene	12.0	6.2	18.4	101	94 ± 10
aldrin	12.0	—	10.6	88	87 ± 11
cis-heptachlor epoxide	12.0	—	10.7	89	92 ± 9
γ-chlordane	12.0	7.8	19.0	96	90 ± 12
o,p'-DDE	12.0	—	10.3	86	92 ± 9
α-endosulfan	12.0	—	10.6	88	94 ± 12
α-chlordane	12.0	—	11.9	99	97 ± 7
trans-nonachlor	12.0	—	11.4	95	94 ± 12
p,p'-DDE	12.0	5.8	16.0	90	94 ± 10
dieldrin	12.0	—	11.0	92	95 ± 11
o,p'-DDD	12.0	—	11.3	94	89 ± 13
endrin	12.0	—	10.2	85	90 ± 9
β-endosulfan	12.0	—	11.5	96	94 ± 15
p,p'-DDD	12.0	—	9.9	83	86 ± 14
o,p'-DDT	12.0	—	10.4	87	91 ± 16
p,p'-DDT	12.0	—	14.3	119	108 ± 21
methoxychlor	25.0	—	22.7	91	87 ± 10
methyl-parathion	25.0	—	22.0	88	92 ± 10
parathion	25.0	—	22.8	91	86 ± 14
atrazine	125.0	51	167.0	95	92 ± 11
simazine	300.0	—	273.0	91	94 ± 10
PCB 28	12.0	—	11.0	92	96 ± 9
PCB 52	12.0	—	10.3	86	93 ± 12
PCB 101	12.0	—	9.6	80	91 ± 13
PCB 118	12.0	—	11.3	94	92 ± 9
PCB 153	12.0	—	10.9	91	94 ± 10
PCB 138	12.0	—	11.0	92	86 ± 11
PCB 180	12.0	—	10.1	84	88 ± 13

^a Recovery of intermediate concentration level. ^b Mean recovery (%) ± SD of the three concentration levels of added pesticides.

Table 4. Recovery of Pesticide Standards Added to Raw Water Using Liquid-Solid Extraction

compound	added (ng L ⁻¹)	present (ng L ⁻¹)	found (ng L ⁻¹)	recovery ^a (%)	mean recovery ^b (%)
HCB	12.0	—	9.8	82	87 ± 10
α-HCH	12.0	5.2	14.8	86	94 ± 12
β-HCH	12.0	—	8.5	71	78 ± 13
γ-HCH	12.0	3.6	14.4	92	96 ± 15
heptachlor	12.0	—	10.4	87	84 ± 11
α-chlordane	12.0	5.4	14.1	81	85 ± 9
aldrin	12.0	—	9.1	76	82 ± 15
cis-heptachlor epoxide	12.0	—	9.5	79	76 ± 12
γ-chlordane	12.0	7.0	15.4	81	83 ± 13
o,p'-DDE	12.0	—	8.9	74	80 ± 12
α-endosulfan	12.0	—	9.8	82	78 ± 10
α-chlordane	12.0	—	9.4	78	81 ± 11
trans-nonachlor	12.0	—	9.1	76	83 ± 17
p,p'-DDE	12.0	5.1	14.4	84	80 ± 10
dieldrin	12.0	—	10.6	88	84 ± 22
o,p'-DDD	12.0	—	9.8	82	76 ± 8
endrin	12.0	—	9.6	80	77 ± 12
β-endosulfan	12.0	—	9.2	77	73 ± 10
p,p'-DDD	12.0	—	8.2	68	76 ± 9
o,p'-DDT	12.0	—	8.5	71	72 ± 12
p,p'-DDT	12.0	—	9.3	78	83 ± 17
methoxychlor	25.0	—	16.1	64	68 ± 8
methyl-parathion	25.0	—	20.3	81	84 ± 15
parathion	25.0	—	19.1	76	73 ± 11
atrazine	125.0	59.0	158.0	86	89 ± 13
simazine	300.0	—	249.0	83	78 ± 11
PCB 28	12.0	—	9.1	76	84 ± 12
PCB 52	12.0	—	9.7	81	76 ± 14
PCB 101	12.0	—	9.0	75	82 ± 11
PCB 118	12.0	—	8.6	72	77 ± 13
PCB 153	12.0	—	9.1	76	72 ± 10
PCB 138	12.0	—	8.6	72	75 ± 8
PCB 180	12.0	—	8.0	67	73 ± 11

^a Recovery of intermediate concentration level. ^b Mean recovery (%) ± SD of the three concentration levels of added pesticides.

athion (25.0, 50.0, and 100.0 ng L⁻¹), atrazine (125.0, 250.0, and 500.0 ng L⁻¹), and simazine (300.0, 600.0, and 1200.0 ng L⁻¹). The extraction solvent was 15% hexane in methylene chloride, and the successive extractions were made with a volume of 60 mL of solvent for each. Shaking time was 120 s and standing time 10 min. The extract, 180 mL, was passed through anhydrous Na₂SO₄ and concentrated to 0.5 mL in the Turbovap concentrator. The extraction process was repeated three times for each of the three concentration levels.

Table 1 shows the results obtained on the efficiency of extraction of the 33 compounds analyzed for the intermediate concentration level. The results obtained for the lower and upper limits of each compound studied do not differ significantly from those observed for the intermediate level.

Mean recovery yields were above 80%, and standard deviations ranged from 5 to 21%, which are acceptable values to obtain reproducible results in quantitative analysis.

Liquid-Solid Extraction. Extraction efficiency with the liquid-solid method was determined by passing through conditioned Sep-pak tC₁₈ cartridges 1000 mL of reagent water, to pH 2, containing the 33 analytes at the same concentration levels as those used in LLE. The analytes were eluted with 15 mL of methylene chloride and the extracts concentrated to 0.5 mL with the Turbovap concentrator. The extraction process was repeated three times for each of the concentration levels.

The results obtained regarding the extraction efficiency of the 33 analytes for the intermediate concentration level are shown in Table 1. The results obtained for the other two levels do not differ significantly from those obtained for the intermediate concentration level.

The mean recovery yields by LSE are lower than those obtained with the LLE method, although the standard deviations (between 7 and 18%) are similar to those obtained with the LLE method.

The mean yields of the LSE method are above 70% with the exception of the pesticides methoxychlor and PCB 180, for which yield was about 60%. Accordingly, these are also acceptable values for obtaining reproducible results in application to quantitative analysis.

Performance Characteristics of the Method Developed. *Detection Limit.* In order to determine the detection limits (DL) of the 33 analytes studied, the LLE and the SPE methods were applied to reagent solutions whose concentration in each of the analytes was from 2 to 5 times the estimated DL. Seven determinations were performed, and the DL values were calculated according to the expression of Glaser et al. (1981):

$$DL = 3.707S_c$$

where 3.707 is the Student's *t* for 6 degrees of freedom and 99% probability and *S_c* is the standard deviation of the seven determinations.

The values obtained are shown in Table 2. For the same analyte, no significant differences are seen between the DL calculated by the LLE and the LSE methods. With respect to the individual values, the DL values for the LSE technique are below 5.3 ng L⁻¹, except for the pesticides parathion (7.3 ng L⁻¹), methoxychlor (9.2 ng L⁻¹), atrazine (36.0 ng L⁻¹), and simazine (89.0 ng L⁻¹).

Precision. The LLE and the LSE methods were applied to five synthetic samples prepared in an identical way and containing 10.0 ng L⁻¹ of each pesticide with the exception of methoxychlor, methyl-parathion,

Table 5. Concentrations of Pesticides in Raw Water of Four Different Towns^a

compound	raw water 1		raw water 2		raw water 3		raw water 4	
	LLE	LSE	LLE	LSE	LLE	LSE	LLE	LSE
HCB	— ^b	—	3.9	3.1	—	—	—	—
α-HCH	12.2	10.8	6.6	7.2	5.1	5.2	5.7	4.4
γ-HCH	8.2	8.9	3.7	3.2	4.5	3.6	3.4	3.9
heptachlor	13.0	10.5	—	—	—	—	7.3	5.9
α-chlordene	5.7	4.8	5.8	6.6	6.2	5.4	7.1	6.4
γ-chlordane	12.1	12.6	5.4	4.6	7.8	7.0	6.5	5.7
α-endosulfan	9.2	7.4	—	—	—	—	—	—
p,p'-DDE	—	—	—	—	5.8	5.1	—	—
dieldrin	5.7	5.3	—	—	—	—	—	—
atrazine	80.1	72.3	50.8	39.1	51.2	59.4	—	—
PCB 28	8.1	6.5	8.6	7.3	—	—	—	—

parameter	raw water 1	raw water 2	raw water 3	raw water 4
conductivity (μS cm ⁻¹)	454	202	108	166
DQO (KMnO ₄) (mg of O ₂ L ⁻¹)	5.6	4.1	3.4	2.2

^a Values are in nanograms per liter. ^b Nondetected.

and parathion (20.0 ng L⁻¹ of each), atrazine (100.0 ng L⁻¹), simazine (240.0 ng L⁻¹), and, as internal standard, *trans*-heptachlor epoxide (25.0 ng L⁻¹). The standard deviations and variation coefficients (VC) are slightly higher with the SPE technique and range from 0.5 to 1.6 ng L⁻¹ and from 7 to 24%, respectively; these values are acceptable according to the VC criterion predicted by Horwitz (1982).

Recovery. Recovery was studied by applying the LLE and the LSE techniques to surface raw water used by the city of Salamanca (Spain) for later purification for drinking purposes. Six samples were filtered through glass wool and acidified with HCl to pH 2, and the 33 analytes were added to each sample. LLE was applied to three samples and LSE to the other three. Tables 3 and 4 show the results obtained in recovery of the 33 analytes for the intermediate concentration level and the mean recovery values for the three concentration levels.

Recovery yields by LLE and LSE for the intermediate concentration level and the mean yields for the three concentration levels did not differ significantly from those obtained when both techniques were applied in reagent water. The mean recovery yields with LLE surpassed 80%, and the standard deviations ranged from 7 to 21%. The mean recovery yields with LSE surpassed 70% except for the pesticide methoxychlor (68%), and the standard deviations ranged from 8 to 22%.

Application of the Method. The LLE and the LSE methods were applied to the determination of spiked (26 pesticides and 7 PCBs) and nonspiked natural water samples. Both raw and finished drinking waters from four selected towns with different mineralization (conductivity) and organic matter (DQO) values (see Table 5) were assayed. With the exception of methoxychlor, methyl-parathion, and parathion (12.0 ng L⁻¹), atrazine (62.0 ng L⁻¹), and simazine (150.0 ng L⁻¹), 6.0 ng L⁻¹ of each analyte was spiked to eight water samples (both raw and finished waters from four towns). The results showed no significant influence for the efficiency of the LLE and LSE methods regarding the different nature of the waters assayed.

From the results obtained in duplicate analysis of the nonspiked raw water (Table 5), it may be deduced that of the 33 analytes studied only 11 were found: α-HCH, γ-HCH, α-chlordene, and γ-chlordane in all four samples; atrazine in three; heptachlor and PCB 28 in two; and HCB, α-endosulfan, p,p'-DDE, and dieldrin in one sample.

In the nonspiked finished water samples, only four pesticides were found: γ-HCH in three samples and α-HCH, α-chlordene, and γ-chlordane in one sample. The levels were found to be close to the DL of the method.

The levels found when both LLE and LSE methods were applied do not differ to a significant extent.

In the samples studied, the number of analytes found and their concentrations are directly related to the values of mineralization and organic matter content of the raw water samples. However, the concentration levels of the pesticides are lower than the limits recommended by the report Revision of the WHO guidelines for drinking water quality (1992).

Conclusion. This study reveals that the new sorbent tC₁₈ tested for LSE as well as the use of the ECD for GC quantitation lowers the DL for the analytes studied as compared to those of the EPA Method 525, Revision 2.1 (1988). The results obtained with this proposed LSE method do not differ significantly from those obtained with the LLE method. In addition, it is suitable for automation and employs much lower amounts of usually toxic organic solvents.

LITERATURE CITED

- APHA-AWWA-WPCF. In *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; Clesceri, L. S., Greenberg, A. E., Trussell, R. R., Eds.; Washington, DC, 1989.
- Ballesteros, E.; Gallego, M.; Valcárcel, M. On-line coupling of a gas chromatograph to a continuous liquid-liquid extractor. *Anal. Chem.* **1990**, *62*, 1587.
- Bruce, A. T.; Roosevelt, M.; Roger, A. J. Determination of eight organochlorine pesticides at low nanogram/liter concentrations in groundwater using filter disk extraction and gas chromatography. *J. Assoc. Off. Anal. Chem.* **1992**, *75* (6), 1091.
- Caron, F.; Kramer, J. R. Gas Chromatographic Determination of volatile sulfides at trace levels in natural freshwaters. *Anal. Chem.* **1989**, *61*, 114.
- Croll, B. T.; Sumner, M.; Leathard, D. Determination of trihalomethanes in water using gas syringe injection of headspace vapours and electron-capture gas chromatography. *Analyst* **1986**, *111*, 73.
- Donald, F. H.; Craig, G. M.; George, A. S.; Dennis, D. B. Membrane approach to solid-phase extractions. *Anal. Chim. Acta* **1990**, *236*, 157.
- Eichelberger, J. W., Behymer, T. D., Budde, W. L., Eds. EPA Method 525. *Determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatography/mass spectrometry*, Revision 2.1; En-

- Environmental Monitoring Systems Laboratory, U.S. EPA: Cincinnati, OH, 1988.
- Freiria-Gandara, M. J.; Álvarez-Devesa, A.; Lorenzo-Ferreira, R. A.; Bermejo-Martínez, F. Identification and determination of halogenated hydrocarbons in water of Galicia (N. W. Spain) by headspace gas-chromatography. *Anal. Lett.* **1990**, *23*, 1939.
- García, C.; Tiedra, P.; Ruano, A.; Gómez, J. A.; García-Villanova, R. J. Evaluation of the liquid-liquid extraction technique and application to the determination of volatile halo-organic compounds in chlorinated water. *J. Chromatogr.* **1992**, *605*, 251.
- Glaser, J. A.; Foerster, D. L.; McKee, G. D.; Quave, S. A.; Budde, W. L. Trace analyses for wastewaters. *Environ. Sci. Technol.* **1981**, *15*, 1426.
- Goldberg, M. C.; Weiner, E. R. Extraction and concentration of phenolic compounds from water and sediment. *Anal. Chim. Acta* **1980**, *115*, 373.
- Gregory, D. F.; William, T. F.; Paul, G. T. Performance of the Goulden large-sample extractor in multiclass pesticide isolation and preconcentration from stream water. *J. Agric. Food Chem.* **1991**, *39*, 1618.
- Guan, H. T. Comparison of solvent extraction and solid-phase extraction for the determination of organochlorine pesticide residues in water. *Analyst* **1992**, *117*, 1129.
- Gurka, D. F.; Pyle, S. M.; Titus, R. Environmental analysis by direct aqueous injection. *Anal. Chem.* **1992**, *64*, 1749.
- Horwitz, W. Evaluation of analytical methods used for regulation. *J.-Assoc. Off. Anal. Chem.* **1982**, *65*, 525.
- Huang, L. Q. Simultaneous determination of alachlor, metolachlor, atrazine and simazine in water and soil by isotope dilution gas chromatography/mass spectrometry. *J.-Assoc. Off. Anal. Chem.* **1989**, *72* (2), 349.
- Johnson, W. E.; Fendinger, N. J.; Plimmer, J. R. Solid-phase extraction of pesticides from water: possible interferences from dissolved organic material. *Anal. Chem.* **1991**, *63*, 1510.
- Kenneth, W. E.; Elizabeth, J. E.; James, E. L.; López-Avila, V. Liquid chromatographic determination of pesticides in finished drinking waters: collaborative study. *J.-Assoc. Off. Anal. Chem.* **1992**, *75* (5), 858.
- Kim, I. S.; Sasinos, F. I.; Stephens, R. D.; Wang, J.; Brown, M. Determination of chlorinated phenoxy acid and ester herbicides in soil and water by liquid chromatography particle beam mass spectrometry and ultraviolet absorption spectrophotometry. *Anal. Chem.* **1991**, *63*, 819.
- LaPack, M. A.; Tou, J. C. Membrane extraction mass spectrometry for the on-line analysis of gas and liquid process streams. *Anal. Chem.* **1991**, *63*, 1631.
- Lépine, L.; Archambault, J.-F. Parts-per-trillion determination of trihalomethanes in water by purge-and-trap gas chromatography with electron capture detection. *Anal. Chem.* **1992**, *64*, 810.
- Lin, D. P.; Falkenberg, C. Kinetics of purging for the priority volatile organic compounds in water. *Anal. Chem.* **1993**, *65*, 999-1002.
- López-Avila, V.; Milanes, J. Single-laboratory evaluation of method 8060 for the determination of phthalates in environmental samples. *J.-Assoc. Off. Anal. Chem.* **1991**, *74* (5), 793.
- López-Avila, V.; Dodhiwala, N. S.; June, W.; Werner, F. B. Evaluation of EPA method 8120 for determination of chlorinated hydrocarbons in environmental samples. *J.-Assoc. Off. Anal. Chem.* **1989**, *72* (4), 593.
- López-Avila, V.; Wesselman, R.; Edgell, K. Gas-chromatographic-electron-capture detection method for determination of 29 organochlorine pesticides in finished drinking water: collaborative study. *J.-Assoc. Off. Anal. Chem.* **1990**, *73*, 276.
- Matthew, W. B.; Jeffrey, J.; Miguel, J.; Theresa, Q.; Marshall, C. Rapid method for the determination of alachlor, atrazine and metolachlor in groundwater by solid-phase extraction. *Analyst* **1989**, *114*, 405.
- Melcher, R. G.; Morabito, P. L. Membrane/gas chromatographic system for automated extraction and determination of trace organics in aqueous samples. *Anal. Chem.* **1990**, *62*, 2183.
- Moltó, J. C.; Picó, Y.; Mañes, J.; Font, G. Analysis of polychlorinated biphenyls in aqueous samples using C₁₈ glass column extraction. *J.-Assoc. Off. Anal. Chem.* **1992**, *75* (4), 720.
- Namiesnik, J.; Govecki, T.; Biziuk, M.; Torres, L. Isolation and preconcentration of volatile organic compounds from water. A review. *Anal. Chim. Acta* **1990**, *237*, 1.
- Nash, R. G. Solid-phase extraction of carbofuran, atrazine, simazine, alachlor and cianazine from shallow well water. *J.-Assoc. Off. Anal. Chem.* **1990**, *73* (3), 438.
- Oliver, B. G.; Dothen, K. D. Determination of chlorobenzenes in water by capillary gas chromatography. *Anal. Chem.* **1980**, *52*, 2066.
- Peters, T. L. Comparison of continuous extractors for the extraction and concentration of trace organics from waters. *Anal. Chem.* **1982**, *54*, 1913.
- Philippaerts, J.; Vanhoof, C.; Vansant, E. F. Waste water analysis by purge and trap capillary GC-FTIR spectrometry. *Talanta* **1992**, *39*, 681.
- Potter, T. L.; Carpenter, T.; Putnam, R.; Reddy, K.; Clark, J. M. Rapid method for analysis of atrazine and acetanilide herbicides in groundwater by micro liquid/liquid extraction. *J. Agric. Food Chem.* **1991**, *39*, 2184.
- Pratt, K. F.; Pawliszyn, J. Gas extraction kinetics of volatile organic species from water with a hollow fiber membrane. *Anal. Chem.* **1992**, *64*, 2107.
- Revision of the WHO guidelines for drinking water quality. In *Report of the final task group meeting*. Geneva (Limited distribution document), 1992.
- Stachel, B.; Baetjer, K.; Cetinkaya, M.; Dueszeln, J.; Lahl, U.; Lierse, K.; Thieman, W. On site continuous liquid-liquid extraction of nonpolar organic compounds in water. *Anal. Chem.* **1981**, *53*, 1469.
- Tan, G. H. Comparison of solvent extraction and solid-phase extraction for the determination of organochlorine pesticide residues in water. *Analyst* **1992**, *117*, 1129.
- Tomkins, B. A.; Caton, J. E.; Edwards, M. D.; Garcia, M. E.; Schenley, R. L.; Wachter, L. I.; Griest, W. H. Determination of regulatory organic compounds in radioactive waste samples volatile organics in aqueous liquids. *Anal. Chem.* **1989**, *61*, 2751.
- Warren, E. J.; Nicholas, J. F.; Jack, R. P. Solid-phase extraction of pesticides from water: possible interference from dissolved organic material. *Anal. Chem.* **1991**, *63*, 1510.
- Yang, M. J.; Pawliszyn, J. Extraction of semivolatile organic compounds from aqueous samples using high-density carbon dioxide and hollow fiber membrane module. *Anal. Chem.* **1993**, *65*, 2538.

Received for review October 13, 1994. Revised manuscript received April 13, 1995. Accepted April 30, 1996.® This study was supported financially by a grant from Consejería de Medio Ambiente de la Junta de Castilla-León (España).

JF9405766

® Abstract published in *Advance ACS Abstracts*, June 15, 1996.