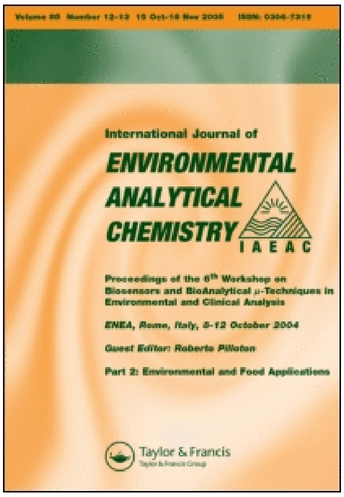

**International Journal of Environmental Analytical Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Multiresidue Analysis of Organic Pollutants in Water by SPE with a C8 and SDVB Combined Cartridge

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**To cite this Article** Davì, M. Letizia , Liboni, Michelina and Malfatto, M. Grazia(1999) 'Multiresidue Analysis of Organic Pollutants in Water by SPE with a C8 and SDVB Combined Cartridge', International Journal of Environmental Analytical Chemistry, 74: 1, 155 — 166

**To link to this Article: DOI:** 10.1080/03067319908031422

**URL:** http://dx.doi.org/10.1080/03067319908031422

*Intern. J. Environ. Anal. Chem.*, Vol. 74(1-4), pp. 155-166
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# MULTIRESIDUE ANALYSIS OF ORGANIC POLLUTANTS IN WATER BY SPE WITH A C8 AND SDVB COMBINED CARTRIDGE

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*(Received 6 April 1998 ; In final form 18 June 1998)*

A multi-component target method for screening purposes to determine organic pollutants of different polarities in water is reported. The following classes of chemicals were tested: base-neutral and acidic herbicides, phenolic compounds, polycyclic aromatic hydrocarbons and phthalic acid esters.

Data was initially obtained from the extraction of one liter of water sample, using separate octyl bonded porous silica (C8) and highly crosslinked polystyrene based polymer columns (SDVB) cartridges. A second set of data was obtained using for the extraction a combined cartridge containing both phases. The analysis was carried out directly by GC-MS in SIM mode, without any derivatisation, with the exception of acidic herbicides, derivatised with pentafluorobenzylbromide. The obtained results showed recoveries between 75% and 98% at two different spiking levels, with relative standard deviations below 15%.

*Keywords:* Organic pollutants; water; C8 SPE extraction; SDVB SPE extraction; GC-MS

## INTRODUCTION

In accordance with the EEC directive 80/778 concerning the quality of drinking water, and the EEC directive 75/440 concerning the quality of surface water intended for human consumption, the monitoring of organic pollutants in water matrices is becoming more important[1–4]. Laboratories must assure that maximum acceptable concentrations of undesirable or toxic and noxious compounds are not exceeded.

Ideally, the development of some inexpensive multiresidue analytical method should facilitate the rapid extraction of a wide range of organic pollutants at the required sensitivity limit[5,6]. For identification and quantification gas chromatography-mass spectrometry (GC-MS) using selected ion monitoring is the more widely used technique[7].

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The traditional approach for the preparation of the water sample has been the use of liquid-liquid extraction (LLE), but the well known problems of this technique have led to the use of solid-phase extraction with different chemically bonded silica particles. However, for polar compounds in water, the extraction efficiency of C8 and C18 cartridges is very low[8].

On the other hand, the proposed methods for polar compounds determination do not seem suitable to analyze routinely a wide range of target analytes having different physical-chemical properties. For this reason, we developed a method for SPE of water samples using highly crosslinked polystyrene based polymer columns capable of retaining analytes of a wide range of polarities. The high surface area of this non-polar sorbent can provide the retention of very polar and water soluble analytes which have been difficult to extract using non-polar silica based sorbents.

The goal of this work was to optimize a method for determining a wide variety of polar and non polar organic compounds in water samples, by using cartridges filled with layers of C8 and SDVB sorbent materials. For this purpose, classes of chemicals with a large range of polarity were selected.

The examined compounds with their retention time, minimum detection limit (MDL) and monitored ions are reported in Table I. The MDL was calculated by using a statistical procedure for the minimum concentration that can be measured with a 99% confidence that the concentration is greater than zero[9]. The MDL concentrations listed in Table I were obtained using reagent water, spiked with the standard mixture solutions, to have a concentration near to the lower level of instrumental detection. Seven one liter aliquots of this solution were analysed and the standard deviation (*s*) calculated. The desidered MDL was obtained from the product t times s, where the value of *t* for (7 −1) = 6 degrees of freedom, at the 99% confidence level, in the one-tailed distribution, is 3.14.

TABLE I Retention times, method detection limits (MDL) and characteristic masses for the examined compounds of environmental interest

| *Classes of chemicals* | *Compounds* | *Retention time (min)* | *Primary ions* | *Secondary ions* | | *MDL µg/L* |
|---|---|---|---|---|---|---|
| **Base-neutral herbicides:** | metribuzin | 20.12 | 198 | 144 | | 0.02 |
| (triazine): | atrazine | 17.28 | 200 | 202 | 215 | 0.01 |
| | desethylatrazine | 10.24 | 158 | 160 | 145 | 0.50 |
| | ametrine | 20.77 | 227 | 212 | | 0.02 |
| | deisopropylatrazine | 9.12 | 173 | 175 | 158 | 0.50 |
| | terbutylazine | 17.61 | 173 | 175 | 158 | 0.01 |
| (N-subst amide): | alachlor | 20.92 | 146 | 188 | | 0.03 |
| | metolachlor | 22.03 | 162 | 238 | 146 | 0.02 |

| *Classes of chemicals* | *Compounds* | *Retention time (min)* | *Primary ions* | *Secondary ions* | | *MDL µg/L* |
|---|---|---|---|---|---|---|
| | propachlor | 15.11 | 120 | 176 | | 0.03 |
| (carbamate): | molinate | 13.24 | 126 | 187 | 83 | 0.01 |
| (propioanilide): | propanil | 19.27 | 161 | 163 | | 0.03 |
| (oxadiazol): | oxadiazon | 25.54 | 174 | 177 | 147 | 0.02 |
| (thiocarbamate): | tiobencarb | 21.45 | 72 | 100 | | 0.04 |
| **Acidic herbicides** | | | | | | |
| (phenoxy acids): | 2,4 D | 25.77 | 181 | | | 0.04 |
| | MCPA | 23.79 | 181 | | | 0.01 |
| | | 24.32 | 181 | | | |
| | MCPB | 28.91 | 181 | | | 0.01 |
| | MCPP (Mecoprop) | 23.25 | 181 | | | 0.02 |
| (thiadiazinone): | bentazone | 28.59 | 181 | | | 0.03 |
| **Phenolic Compouds :** | phenol | 14.55 | 94 | 66 | 65 | 0.48 |
| | 2-chlorophenol | 14.97 | 128 | 130 | 64 | 0.20 |
| | 2- methylphenol | 16.88 | 108 | 107 | 79 | 0.10 |
| | 3-methylphenol | 17.41 | 108 | 107 | 79 | 0.10 |
| | 4-methylphenol | 18.52 | 108 | 107 | 79 | 0.40 |
| | 2-nitrophenol | 19.01 | 139 | 65 | 109 | 0.30 |
| | 2,4-dimethylphenol | 19.64 | 122 | 107 | 121 | 0.10 |
| | 2,4-dichlorophenol | 20.03 | 162 | 164 | 98 | 0.50 |
| | 2,6-dichlorophenol | 20.61 | 162 | 164 | 98 | 0.50 |
| | 4-chloro3-methylphenol | 22.03 | 142 | 144 | 107 | 0.10 |
| | 2,4,6-trichlorophenol | 23.34 | 196 | 198 | 200 | 0.30 |
| | 2,4-dinitrophenol | 25.75 | 184 | 63 | 154 | 0.50 |
| | 4-nitrophenol | 25.86 | 65 | 139 | 109 | 0.50 |
| | 4,6-dinitro2-methylphenol | 27.10 | 198 | 182 | 77 | 0.50 |
| | pentachlorophenol | 29.02 | 266 | 264 | 268 | 0.50 |
| **Polycyclic Aromatic Hydrocarbons :** | naphthalene | 9.78 | 128 | 129 | 127 | 0.10 |
| | acenaphthylene | 14.09 | 152 | 151 | 153 | 0.20 |
| | acenaphthene | 14.53 | 154 | 153 | 152 | 0.10 |
| | fluorene | 15.88 | 166 | 165 | 167 | 0.02 |
| | phenanthrene | 18.63 | 178 | 179 | 176 | 0.01 |
| | anthracene | 18.85 | 178 | 179 | 176 | 0.01 |
| | fluoranthene | 21.68 | 202 | 101 | 100 | 0.02 |
| | pyrene | 22.24 | 202 | 101 | 100 | 0.01 |
| | benzo(a)anthracene | 25.76 | 228 | 229 | 226 | 0.01 |
| | chrysene | 25.82 | 228 | 226 | 229 | 0.01 |
| | benzo(b)fluoranthene | 30.74 | 252 | 253 | 125 | 0.02 |
| | benzo(k)fluoranthene | 30.80 | 252 | 253 | 125 | 0.01 |
| | benzo(a)pyrene | 32.54 | 252 | 253 | 125 | 0.01 |
| | indeno(1,2,3 cd) pyrene | 40.12 | 276 | 138 | 277 | 0.01 |

| *Classes of chemicals* | *Compounds* | *Retention time (min)* | *Primary ions* | *Secondary ions* | | *MDL µg/L* |
|---|---|---|---|---|---|---|
| | dibenzo(a,h)anthracene | 40.43 | 278 | 139 | 279 | 0.02 |
| | benzo(ghi)perylene | 42.62 | 276 | 138 | 277 | 0.02 |
| **Phthalic acid esters :** | dimethyl phthalate (DMP) | 12.21 | 163 | 194 | 164 | 0.01 |
| | diethyl phthalate (DEP) | 18.10 | 149 | 177 | 150 | 0.01 |
| | dibutyl phthalate (DBP) | 19.93 | 149 | 150 | 104 | 0.01 |
| | benzylbutyl phthalate (BBP) | 21.70 | 149 | 91 | 206 | 0.01 |
| | diethylhexyl phthalate (DEHP) | 32.13 | 149 | 167 | 279 | 0.01 |
| | dioctyl phthalate (DOP) | 35.57 | 149 | | | 0.01 |

## EXPERIMENTAL SECTION

### Materials

The compounds used in this work were the highest purity materials available from commercial sources. The mixed solutions of PAHs and of phenolic compounds in dichloromethane at 2000 µg/L for each compound, were from ULTRAscientific. Individual herbicides and phthalic acid esters were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Solvents were of analytical grade (Carlo Erba, Milan, Italy).

Solid phase extraction was carried out with chemically bonded (C8) silica cartridge (ISOLUTE$^R$, IST, UK, 200 mg/6 mL), highly crosslinked polystyrene -divinylbenzene (SDVB) based polymer cartridges (ISOLUTE ENV+$^R$, IST, UK, 200 mg / 6 mL and C8 and SDVB layered cartridges (ISOLUTE$^R$, IST, UK, 200 mg + 500 mg / 6 mL).

For the filtration of surface water before the extraction glass fiber (3M Empore Filter Aid 400$^R$, 40 microns diameter) was used to inhibit the migration of suspended solids to the sorbent bed. Organic free water was used, obtained with purification system Milli Q (Millipore).

### Sample treatment

Aqueous samples were spiked at two concentration levels with known volumes of each class of working standard solution to perform recovery tests.

The stock standard solutions were prepared by dissolving a precise quantity (10 – 30 mg) of chemically pure compounds in 100 mL of an appropriate water-miscible organic solvent (acetone or alcohol). The standard solutions were diluted with water-miscible solvent and added to one liter of the sample, to obtain concentrations of 1.0 and 5.0 µg/L for each of the chemicals tested.

The fortified samples were taken from drinking water, from the surface water of the River Po and from organic free water Milli Q to establish if water matrix affects the analytical results. The surface water samples were filtered before extraction using a glass fibre filter, to avoid cartridge obstruction. Because phthalate esters are nearly always present as background contamination in all chromatographic analyses, a laboratory reagent blank was analysed to ensure accurate values from spiked samples analyses.

Sample extraction with C8 cartridges was performed as described elsewhere for the C8 disk[10]:

- a rinse of ethyl acetate (10 mL) was performed to eliminate possible organic interferences from sorbent bed;
- air was allowed to pass through the cartridges to eliminate solvent traces;
- methanol (10 mL) was added to solvate the sorbent bed, followed by organic free water (10 mL);
- the sample (1 L) was passed through the cartridges under vacuum;
- after filtration, air was allowed to pass through the cartridges, for some minutes;
- elution was carried out with ethyl acetate (10 mL) under moderate vacuum.

With SDVB cartridges, the extraction efficiency was enhanced by suppressing ionisation of the analytes by pH control of the sample. For this reason conc. HCl (500 µL) was added to the sample before the filtration.

The cartridge was:

- washed with a solution of acetone – ethyl acetate 1:1 (10 mL);
- dried by air under vacuum;
- conditioned with methanol (10 mL), followed by organic free water at the same pH as the sample (10 mL);
- dried by air allowed to pass through the cartridges, for some minutes after sample filtration;
- eluted with a solution of acetone – ethyl acetate 1:1 (10 mL).

The cartridge with two layers of different absorbent materials was treated as the SDVB one, but the sample was passed through it by two steps: the first at normal water pH condition (5.6 – 8 pH unit), the second after acidification with conc. HCl (500 µL) of the sample previously passed through the same cartridge. For this procedure, an apparatus for water collection after filtration was needed. In all three cases, the same step lengths and vacuum conditions of about 10 mm Hg, corresponding to a sample flow rate of about 60 mL/minute were used. Methanol (10 ml) was added to the samples, to preserve sorbent solvation during filtration in each kind of cartridge. The extracts were concentrated under dry nitrogen flow and the residue was redissolved with 0.5 μL of n-hexane-acetone 1:1.

The extraction conditions are summarized in Table II.

TABLE II Extraction conditions

| *Sorbent bed* | *Sorbent washing* | *Cartridge conditioning* | *Elution* | *pH Sample* |
|---|---|---|---|---|
| C8 | Ehyl acetate | methanol | Ehyl acetate | 5.6 – 8 |
| SDVB | Acetone – Ehyl acetate 1:1 | methanol | Acetone – Ehyl acetate 1: 1 | 2 |
| C8 + SDVB | Acetone – Ehyl acetate 1: 1 | methanol | Acetone – Ehyl acetate 1: 1 | 5.6 – 8<br>then 2 |

After three injections of few microliters of the extract for PAHs, phenols, base-neutral herbicides and phthalic acid esters determination, the extract was dried under dry nitrogen flow and adjusted with anhydrous acetone (4 mL) to derivatize acidic herbicides by adding 200 μL of pentafluorobenzylbromide (10% solution in anhydrous acetone) and a few cristals of potassium carbonate as catalyst. After 24 hours at ambient temperature the solution was concentrated under vacuum to eliminate the solvent and the extra derivatizing agent. Under dry nitrogen flow the residue was dried and then redissolved with 0.5 μL of n-hexane-acetone 1:1.

## INSTRUMENTAL SECTION

A Hewlett Packard 5890 gas chromatograph with 5971A Hewlett Packard mass selective detector and Vectra 386/25 HP Chemstation data system was used. Splitless injection into a Ultra 2 (HP) capillary column (25 m × 0.2 mm, 0.33 um film) was used. Helium was used as carrier gas at a flow-rate of 1.2 mL/min. The mass spectrometer HP5971A was scanned from 35 to 350 amu at approximately 1 scan/s. For PAH analysis the injector and detector temperatures were both 280 °C. The initial temperature was 90 °C for 3 min, increasing at 10 °C/min to a final temperature of 290 °C for 25 min.

For phenolic compounds the initial temperature was 40°C for 3 min, then 5°C/min up to 100°C and 10°C/min up to 240°C for 15 min. The injector and detector temperatures were, respectively, 200°C and 280°C.

For base-neutral-acidic herbicides and phthalic acid esters the injector and MS detector temperatures were 250 °C and 280 °C respectively. The initial temperature was 60 °C for 3 min, increasing at 30 °C/min up to 150 °C, and then 5 °C/min to a final temperature of 280 °C for 10 min.

The quantification was carried out by external calibration. A series of injections of the target compounds (0.1 0.5, 1.0, 2.5, 5.0 ng) were used to obtain the calibration graphs and to determine the calibration equations, which were linear over the studied range.

## RESULTS AND DISCUSSION

For this study we selected a limited number of analytes, taking into consideration their different polarity, their toxicity[11], and their potential for entering the aquatic environment. The herbicides examined represent the classes of compounds most widely used in agricultural practice in our region. In the past atrazine was widespread used as a corn herbicide in the Pianura Padana fields, therefore two of its initial degradation products were considered, whose presence had been evidenced in the aquatic environment[12].

Tables III to VII show the results of the quantitative analyses to determine the total method precision and accuracy with the three extraction procedures by spiking samples of surface water at the lower concentration (1 μg/L). The mean total method accuracy, which is expressed as a percentage of the true value, and the RSD are the results of seven replicate determinations.

TABLE III Mean accuracy and precision data for base-neutral herbicides obtained with surface water sample spiked at 1 μg/L. The results are the average of seven independent replicate determinations

| *BASE-NEUTRAL HERBICIDES* | *C8* | | *SDVB* | | *C8 + SDVB* | |
|---|---|---|---|---|---|---|
| | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* |
| metribuzin | 72 | (5) | 88 | (4) | 90 | (4) |
| atrazine | 88 | (4) | 81 | (4) | 92 | (3) |
| desethylatrazine | 80 | (8) | 90 | (6) | 89 | (7) |
| ametrine | 87 | (4) | 82 | (3) | 90 | (2) |
| deisopropylatrazine | 75 | (6) | 87 | (4) | 85 | (5) |
| terbutylazine | 90 | (3) | 85 | (2) | 95 | (2) |
| alachlor | 85 | (3) | 80 | (6) | 82 | (4) |
| metolachlor | 88 | (5) | 90 | (4) | 95 | (3) |
| propachlor | 78 | (6) | 83 | (5) | 80 | (4) |
| molinate | 78 | (8) | 70 | (10) | 75 | (15) |
| propanil | 75 | (5) | 65 | (8) | 75 | (5) |
| oxadiazon | 86 | (4) | 85 | (5) | 85 | (3) |
| tiobencarb | 78 | (4) | 75 | (8) | 75 | (6) |

TABLE IV Mean accuracy and precision data for acidic herbicides obtained with surface water sample spiked at 1 μg/L. The results are the average of seven independent replicate determinations

| *ACIDIC HERBICIDES* | *C8* | | *SDVB* | | *C8 + SDVB* | |
|---|---|---|---|---|---|---|
| | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* |
| 2,4D | 75 | (10) | 88 | (6) | 86 | (8) |
| MCPA | 82 | (7) | 95 | (7) | 95 | (6) |
| MCPB | 78 | (7) | 92 | (5) | 94 | (5) |
| MCPP | 80 | (6) | 90 | (6) | 92 | (5) |
| bentazone | 77 | (8) | 87 | (5) | 88 | (3) |

TABLE V Mean accuracy and precision data for phthalic acid esters obtained with surface water sample spiked at 1 μg/L. The results are the average of seven independent replicate determinations

| *PHTHALIC ACID ESTERS* | *C8* | | *SDVB* | | *C8 + SDVB* | |
|---|---|---|---|---|---|---|
| | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* |
| diethylexyl phthalate | 93 | (4) | 90 | (4) | 92 | (3) |
| dibutyl phthalate | 95 | (3) | 92 | (2) | 95 | (3) |
| benzylbutyl phthalate | 97 | (4) | 93 | (3) | 96 | (2) |
| diethyl phthalate | 98 | (3) | 94 | (2) | 98 | (2) |
| dimethyl phthalate | 98 | (4) | 95 | (4) | 98 | (2) |
| dioctyl phthalate | 92 | (5) | 90 | (6) | 94 | (5) |

TABLE VI Mean accuracy and precision data for phenolic compounds obtained with surface water sample spiked at 1 μg/L. The results are the average of seven independent replicate determinations

| *PHENOLIC COMPONDS* | *C8* | | *SDVB* | | *C8 + SDVB* | |
|---|---|---|---|---|---|---|
| | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* |
| phenol | 75 | (10) | 86 | (6) | 84 | (10) |
| 2-chlorophenol | 84 | (6) | 90 | (5) | 90 | (8) |
| 2-methylphenol | 88 | (5) | 95 | (4) | 96 | (5) |
| 3-methylphenol | 86 | (5) | 96 | (4) | 96 | (4) |
| 4-methylphenol | 86 | (4) | 98 | (4) | 96 | (6) |
| 2-nitrophenol | 78 | (8) | 88 | (3) | 87 | (7) |
| 2,4-dimethylphenol | 88 | (5) | 97 | (4) | 95 | (6) |
| 2,4-dichlorophenol | 82 | (11) | 93 | (3) | 90 | (10) |
| 2,6-dichlorophenol | 82 | (8) | 94 | (3) | 90 | (8) |
| 4-chloro3-methylphenol | 80 | (8) | 90 | (5) | 86 | (7) |
| 2,4,6-trichlorophenol | 78 | (9) | 90 | (6) | 85 | (11) |
| 2,4-dinitrophenol | 76 | (10) | 88 | (5) | 87 | (10) |
| 4-nitrophenol | 79 | (6) | 90 | (4) | 90 | (7) |
| 4,6-dinitro2-methylphenol | 82 | (7) | 94 | (3) | 90 | (6) |
| pentachlorophenol | 80 | (8) | 86 | (5) | 85 | (10) |

TABLE VII Mean accuracy and precision data for PAHs obtained with surface water sample spiked at 1 μg/L. The results are the average of seven independent replicate determinations

| *PAHs* | *C8* | | *SDVB* | | *C8 + SDVB* | |
|---|---|---|---|---|---|---|
| | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* | *Rec%* | *(RSD%)* |
| naphthalene | 87 | (3) | 86 | (4) | 87 | (4) |
| acenaphthylene | 90 | (4) | 88 | (4) | 90 | (3) |
| acenaphthene | 90 | (5) | 90 | (4) | 90 | (4) |
| fluorene | 98 | (2) | 90 | (4) | 92 | (4) |
| phenanthrene | 98 | (3) | 92 | (5) | 94 | (4) |
| anthracene | 94 | (3) | 95 | (4) | 95 | (3) |
| fluoranthene | 95 | (5) | 96 | (5) | 95 | (2) |
| pyrene | 98 | (2) | 90 | (6) | 96 | (2) |
| benzo(a)anthracene | 96 | (2) | 87 | (5) | 96 | (3) |
| chrysene | 98 | (5) | 95 | (6) | 96 | (5) |
| benzo(b)fluoranthene | 97 | (4) | 98 | (4) | 98 | (3) |
| benzo(k)fluoranthene | 96 | (3) | 96 | (2) | 95 | (3) |
| benzo(a)pyrene | 95 | (4) | 94 | (4) | 95 | (2) |
| indeno(1,2,3 cd) pyrene | 93 | (2) | 95 | (2) | 93 | (3) |
| dibenzo(a,h)anthracene | 95 | (3) | 94 | (3) | 95 | (4) |
| benzo(ghi)perylene | 96 | (4) | 98 | (5) | 96 | (4) |

An examination of the results obtained by using the three different cartridges showed that the overall mean accuracy and the mean RSD for PAHs, base-neutral herbicides and phthalic acid esters are comparable in all three kinds of extraction. Only some herbicides (propanil, tiobencarb and alachlor) and some PAHs (fluorene, phenanthrene, pyrene and benzo(a)anthracene) showed higher recoveries with the C8 cartridge, with lower RSD.

On the contrary SDVB and C8-SDVB combined cartridges gave an overall mean accuracy higher than the C8 cartridge, with a mean RSD lower for acidic herbicides, phenols and atrazine metabolites, whose polar characteristics were already known[13,14]. The very accessible high surface area of the non-polar, highly cross linked polystyrene-divinylbenzene sorbent can provide retention of very polar and water soluble analytes which have traditionally been difficult to extract using non polar silica based sorbents.

The range of the obtained mean recovery percentages with the two layer column was from 75% to 98%. All RSD remained below 15%. The recoveries obtained with samples spiked at the higher concentration level (5 μg/L) were comparable with these, but with lower RSD (below 11%).

Surprisingly, in some cases, the mean recovery with the C8-SDVB sorbent was lower than those obtained with the two sorbents separately. It was not possible to determine the reason for the different behaviours of some chemicals with the two layer cartridge. However, it is important to take into account that the passage through the two kinds of sorbent could change the physico chemical properties of the sample.

The recoveries obtained with two layers were satisfactory, and the advantage of using these combined absorbents is that with only two sample passages through the cartridge, it is possible to extract a wide range of compounds with good accuracy and precision.

Systematic studies were done to determine the factors that affect the optimum C8-SDVB sampling/elution conditions for all target compounds: i.e. sample pH, elution solvent, solvent evaporation, sample volume.

The control of sample pH allows to maximise recoveries by suppressing the ionisation of the polar analytes. At neutral condition with C8 sorbent, the acidic herbicides and the phenols were not recovered at all.

The choice of a water miscible mixed solvent such as acetone-ethyl acetate (1:1 v/v) for analyte elution from the SDVB cartridges was due to the better reproducibility obtained with this system. In fact, bad precision was obtained when attempting to elute analytes from the column with water immiscible solvents without completely drying the sorbent bed.

The evaporation step needed to be optimized, due to the high volatility of some of the target compounds (e. g. phenol, molinate, naphthalene), wich would lower their recoveries. The more wide RSD for these compounds could be attributed to the weakness of the evaporation step[15].

This extraction method was applied for the analyses of drinking water, natural water and waste water. Accuracy and precision of the method were compared with the different matrices through the determination of the method detection limit (MDL). MDL is one of the important factors to decide the adequacy of methods for testing drinking water which requires determinations below µg/L levels of analytes. MDLs with C8-SDVB sorbent of the target compounds extracted from waste water are higher than those obtained from natural water or drinking water as expected[16]: MDLs vary from 0.01 µg/L to 1.00 µg/L for natural water by filtration of one liter of sample. For waste water, after filtration of 100 mL of sample, the MDLs vary from 0.1 to 5.0 µg/L.

MDLs for drinking water and organic free water are reported in Table I, and vary from 0.01 to 0.50 µg/L. The phenols showed poor MDL in comparing to the other studied compounds. This is due to the direct analysis in GC of these chemicals without any derivatisation and to the apolar character of the gas chromatographic column used. In Figure 1 is reported a gas chromatographic trace of a surface water sample spiked with a standard solution of the examined base-neutral herbicides and phthalic acid esters at concentration of 0.1 μg/L, with the exception of atrazine metabolites at 1 μg/L. Figure 2 shows a chromatographic trace of the same surface water sample spiked with a standard solution of phenolic compounds at 1 μg/L.

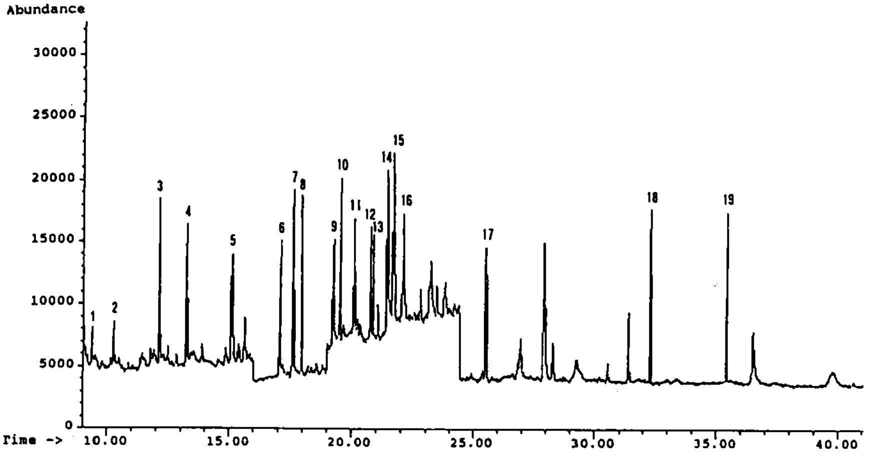

FIGURE 1 Gas chromatographic trace of a surface water sample spiked with: 1. deisopropylatrazine, 2. desethylatrazine at 1 μg/L, 3. dimethyl phthalate (DMP), 4. molinate, 5. propachlor, 6. atrazine, 7. terbutylazine, 8. diethyl phthalate (DEP), 9. propanil, 10. dibutyl phthalate (DBP), 11. metribuzin, 12. ametrine, 13. alachlor, 14. tiobencarb, 15. benzylbutyl phthalate (BBP), 16. metolachlor, 17. oxadiazon, 18. diethylhexyl phthalate (DEHP), 19. dioctyl phthalate (DOP) at 0.1 μg/L

The extracts obtained by using SDVB and C8-SDVB cartridges showed some interferences in Total Ion Chromatography. This problem may be due to the sample pH condition, rather than to contaminants contained in the sorbent material. The only cleanup step used for these cartridges was the initial washing step with a few mL of the eluting solvents. Given the small particle diameter and short distances needed for contaminants to diffuse into the wash solvent, the initial washing step plus the methanol conditioning step may be sufficient to remove any contaminants. The sample filtration at acidic pH condition probably allows to extract natural acidic compounds or products of their degradation, contained in the sample. Nevertheless, the purity of the extract is not a problem with the GC-MS analyses by monitoring single ions of each interested compound. It is important to underline that only for acidic herbicides the GC-MS technique shows a lower selectivity and sensitivity than the GC-ECD.

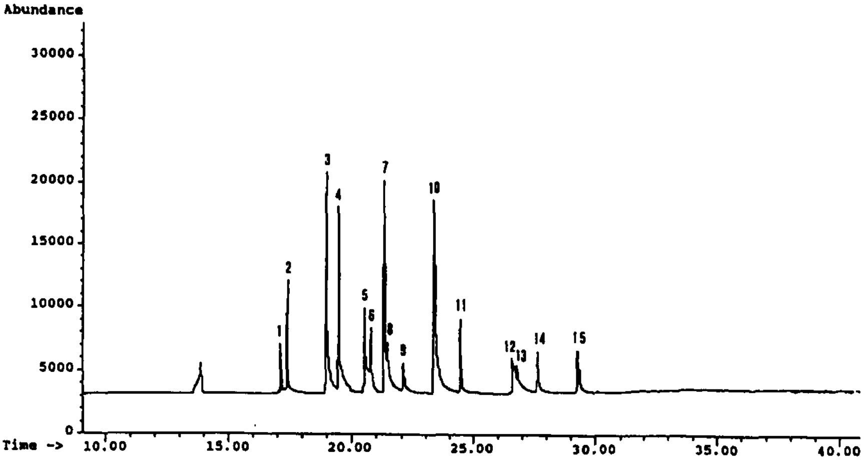

FIGURE 2 Gas chromatographic trace of a surface water sample spiked with: 1. phenol, 2. 2-chlorophenol, 3. 2-methylphenol, 4. 3-methylphenol, 5. 4-methylphenol, 6. 2-nitrophenol, 7. 2,4-dimethylphenol, 8. 2,4-dichlorophenol, 9. 2,6-dichlorophenol, 10. 4-chloro3-methylphenol, 11. 2,4,6-trichlorophenol, 12. 2,4-dinitrophenol, 13. 4-nitrophenol, 14. 4,6-dinitro2-methylphenol, 15. pentachlorophenol at 1 μg/L

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