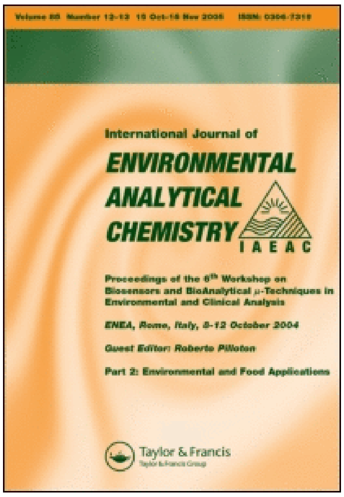

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SOLID PHASE EXTRACTION (SPE) IN TWO LAYERS CARTRIDGE FOR SIMULTANEOUS ANALYSIS OF MEDIUM AND HIGHLY POLAR PESTICIDES IN WATERS

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HPLC-DAD and GC-NPD methods were developed to measure medium and highly polar pesticide concentrations in ground and surface waters. To analyse these pesticides in relation with the European Directives, a comparison of different "off-line" solid phase extraction sorbents was carried out. The use of a home-made (SPE) two layers poly(divinylbenzene-co-N-vinylpyrrolidone) – octadecyl-bonded silica (Oasis-C18) cartridge allows to analyse simultaneously medium and highly polar pesticides in natural waters, with quantification limits between 0.03 and 0.05 µg/l according to each pesticide. The recoveries on this sorbent vary between 90 and 105 % with R.S.D. below 7 % in MilliQ water and between 88 and 115 % with R.S.D. below 20 %, except for bentazone (26 %), in surface water.

Keywords: HPLC-DAD; GC-NPD; pesticides; waters; solid phase extraction

INTRODUCTION

All the monitoring surveys that have been carried out for many years, pointed out that the agriculture and non-agriculture pesticides use has led to residues in superficial and ground waters[1–4]. To tackle this problem and to reduce this process of water contamination, different measures were decided legally by competent European authorities. In drinking water, they led to the promulgation of the 80/778/EEC directive[5] adapted in the 98/83/CE[6] that specifies the maximal admitted concentration of 0.1 µg/l for each pesticide and 0.5 µg/l for the whole in drinking water. These measures were consistent with the promulgation

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of the 97/57/CE directive[7], that states the VI annex of the 91/414 directive concerning the setting on the market of pesticides.

To be able to measure pesticide concentrations below the legal norm, HPLC-DAD, GC-NPD, GC-MS or LC-MS methods were developed by many laboratories[8–17]. To concentrate the water samples, different techniques are still used as liquid-liquid extraction (LLE)[17]. The use of solid phase extraction (SPE) presents a lot of advantages, such as the decrease of solvent consumption or an easier handling. For many pesticides, the SPE recovery data correspond to European guidelines set up in the "91/414/EEC Directive on residue analytical method"[18]. It imposes that the recoveries have to be set between 70 and 110 % with relative standard deviation (R.S.D.) below or equal to 20 %, with different exceptions.

According to the good results obtained on C18 phases, the concentration by "on or off-line" SPE is commonly applied for medium polar pesticides[11,12,18–23]. Nevertheless, the SPE concentration of polar pesticides did not allow to assure recovery data that respect the legal norms[10].

Since a couple of years, polymeric sorbents such styrene divinylbenzene (SDB) or copolymers with hydrophilic-lipophylic balance (Oasis HLB)[20] were elaborated to improve the results achieved with Sep-Pak C18 sorbents. However, the problem of simultaneous extraction of medium and most polar compounds was still encountered.

Upon the request of Belgian authorities[24], and following preliminary studies[25], a monitoring of Belgian ground and surface waters[26] was carried out for eight pesticides (atrazine, simazine, diuron, isoproturon, lenacil, bentazone, chloridazon, metolachlor) during four years. In this context, we developed HPLC-DAD and GC-NPD methods, based on an "off-line" SPE. This method had to be able to measure medium (atrazine, simazine, diuron, isoproturon, lenacil and metolachlor) and highly polar pesticide (bentazone and chloridazon) concentrations with recovery data respecting the admitted norms. Although cartridges filled with different adsorbents are available, we realized in our laboratory a special two-layers cartridge with some commercial phases. It is composed with two superposed different phase layers, Oasis HLB and C 18.

The most important benefit of this special SPE two layers cartridge is to reduce significantly the experimental work, time and costs.

EXPERIMENTAL

Apparatus

LC analyses were performed with a HPLC Beckman with GOLD System, including a Programmable Solvent Module 126 and a Diode Array Module 168 Detector. The loop injection was 50 μl.

GC analyses were performed with a GC Carlo Erba Top 8000 including a NPD Detector and an On column Injector

Stationary phases columns and SPE cartridges

The HPLC analytical column was 25 cm 4 mm I.D. packed with 5-μm Nucleosil 100–5 C18 HD (Machery-Nagel). The GC was equiped with a WCOT column (30 m; 0.32 mm I.D.; 0.25 μm CP-Sil 8 CB (Chrompack)).

Two kinds of SPE cartridges were used for water extraction. The first ones were trade mark, namely C 18 kind [tC18 6cc (1 g) lot W 8175 B1 (Waters), Chromabond C 18 (1 g) lot 67.297], and copolymers [Oasis 3cc (60 mg) lot T8115 B1 (Waters) and SDB 2 6cc (200 mg) lot L24138 (Baker)]. The second one was a home made cartridge that consisted of adding 500 mg bulk C18 (Waters) to a cartridge Oasis 3cc (60 mg) lot W 8190 J1.

Chemicals

All organic solvents were purchased "chromatographic grade"(Sigma-Aldrich, Belgium). LC-quality water was prepared by purifying distilled water in a Milli-Q filtration system (Millipore, Belgium). Other chemicals were obtained from Merck. The various pesticides were supplied by Dr. Ehrenstorfer (Filter Service and Alltec Europe, Belgium).

Stock standard solutions of 100 mg/l of each pesticide were prepared by weighing and dissolving them in methanol. These standard solutions were stored at 4°C and were used for the preparation of dilute working standard solutions and for spiking water samples. No change in the chromatograms of the standard solutions was observed during the 3 months of the study.

Procedures

Extraction procedure

The extraction procedure was based on a SPE off-line. When it is needed, the pH of water samples is adjusted to 2.5 adding phosphoric acid. The cartridges are conditioned with: (a) 6 ml acetonitrile-methanol (70 : 30 v/v), (b) 12 ml MilliQ water. The sample volume (1000 ml) was extracted by percolating at 9 ml/min. Afterwards, the cartridges were dried with a N_2flow. The samples desorption was carried out with 3 ml acetonitrile-methanol (70 : 30 v/v) and diluted until 5 ml with the same mixture. The sample separation was performed for HPLC-DAD (4 ml) and GC-NPD (1 ml) analyses. The samples were evaporated to dryness and

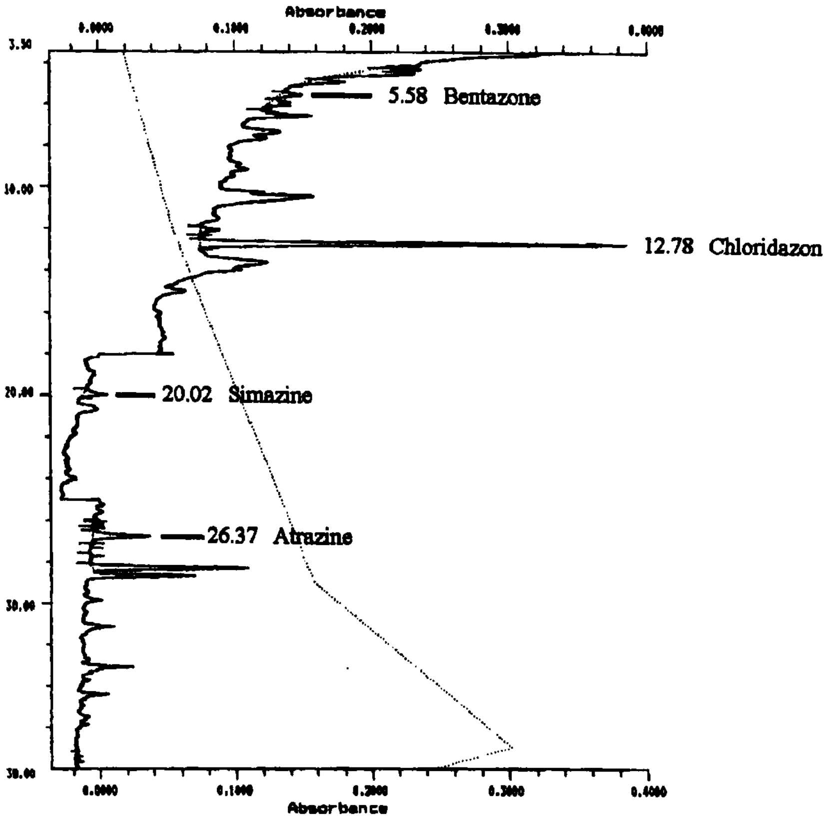
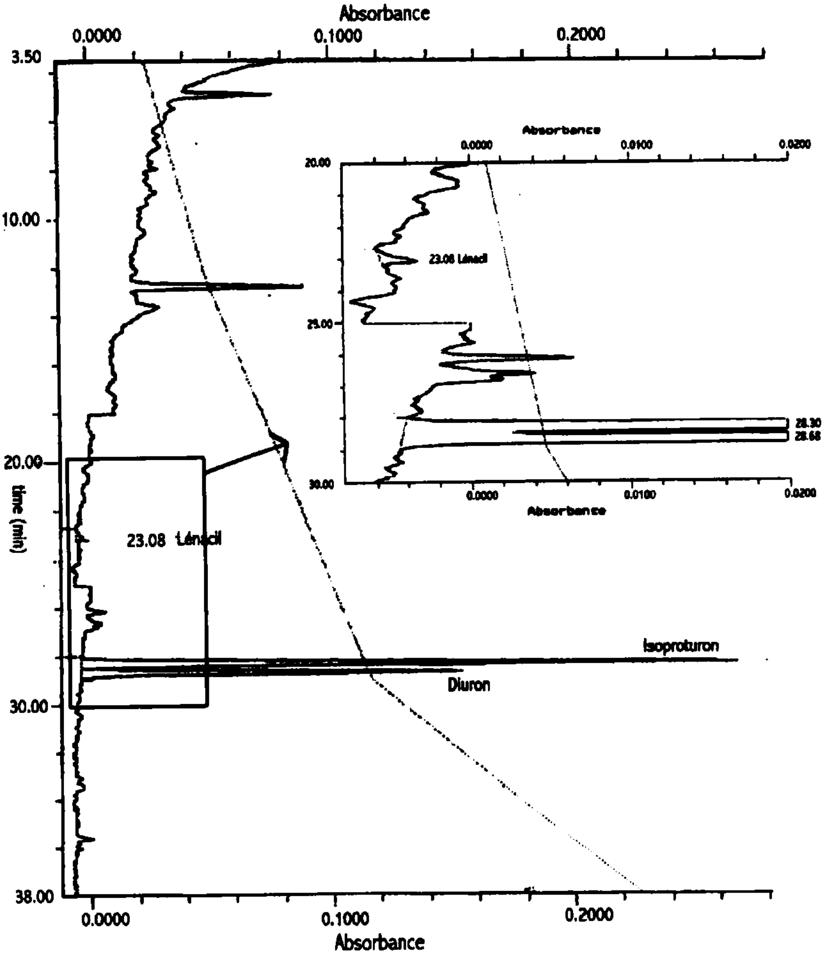


FIGURE 1 HPLC-DAD Chromatogram (channel A: from minute 0 to minute 18, λ: 231 nm and from minute 18 to minute 42 : λ : 225 nm) of Bentazone (0.18 μg/l), Chloridazon (4.97 μg/l) and Simazine (0.16 μg/l), Atrazine (0.50 μg/l) in surface water (Dyle river) in April 1999

diluted in 400 μl ammonium acetate 1mM-acetonitrile (80–20 v/v) for HLPC-DAD analyses and in 100 μl 2,2,4 trimethylpentane-acetone (95/5 v/v) with internal standard (ametryne-1,08 μg/ml) for the GC-NPD analyses. Ametryne belongs to the triazines group of pesticides and has a fine GC-NPD response. It is not sold anymore in Belgium for several years and it has been never found in Belgian ground and surface waters monitoring. Its retention time is close to those of the products of interest.

HPLC-DAD procedure

The analytical separation was carried out by reversed-phase chromatography using a C_{18} analytical column and an elution gradient acetonitrile – ammonium



<ql : below the quantification limit = 0.04 µg/l

FIGURE 2 HPLC-DAD Chromatogram (channel B: from minute 0 to minute 18, λ : 285 nm; from minute 18 to minute 25, λ : 270 nm and from minute 25 to minute 42 : λ : 250 nm) of Lenacil (<ql), Isoproturon (5.41 µg/l) and Diuron (2.78 µg/l) in surface water (Dyle river) in April 1999

acetate buffer 1 mM. The gradient was respectively 90–10 (2 min) to 80–20 in 10 min, to 55–45 in 17 min, to 20–80 in 8 min and to 90–10 in 5 min. The flowrate was 1.1 ml/min. The analysed herbicides were bentazone, chloridazon, simazine, atrazine, lenacil, isoproturon and diuron. The quantification of every herbicide was carried out by external standardization (calibration line).

GC-NPD procedure

The analytical separation was performed with a CB SIL 8 analytical column, with helium carrier gas. The flowrate was 3 ml/min. The on-column injector temperature was maintained at 30°C. The temperature program followed a linear increasing from 80°C to 300°C in 18 minutes. The analysed herbicides were metolachlor, simazine, atrazine and lenacil.

Experiment principle

The experiment principle was to determine the accuracy, the reliability, the determination limit and the selectivity of the extraction procedure. The recoveries were determined by "off line"-SPE with 5 different phases of cartridges at 2 pH (2.5 and 7) for eight pesticides. These were metolachlor, bentazone, chloridazon, lenacil, diuron, isoproturon, atrazine and simazine.

The spiking concentration of the water samples was 0.30 µg/L, a concentration near the limit set up by European Guidelines.

TABLE I Quantification and detection limits in HPLC-DAD and GC-NPD

Pesticide	*Quantification Limit (µg/l)*		*Detection Limit (µg/l)*	
	HPLC-DAD	GC-NPD	HPLC-DAD	GC-NPD
Bentazone	0.05	–	0.02	–
Chloridazon	0.05	–	0.02	–
Lenacil	0.04	0.02	0.01	0.01
Metolachlor	–	0.03	–	0.01
Atrazine	0.05	–	0.02	–
Simazine	0.05	–	0.02	–
Diuron	0.04	–	0.01	–
Isoproturon	0.04	–	0.01	–

– : not analysed by this technique

RESULTS AND DISCUSSION

Analytical LC separation

The HPLC-DAD method in reversed phase chromatography was developed in the context of a monitoring of Belgian ground and surface waters. The gradient was defined to take into account the influence of the dissolved natural organic matter in relation with the separation and the quantification of the pesticides of interest. It allows to analyse bentazone, chloridazon, simazine, atrazine, lenacil, isoproturon and diuron, with the detection and quantification limits mentioned in Table I. Chromatogram examples are shown in Figures 1 and 2.

Analytical GC separation

The GC-NPD method was firstly developed to quantify metolachlor out of the scope of HPLC analysis. But this GC method allows to analyse lenacil and to detect simazine and atrazine as well. Their detection and quantification limits are described hereunder. A chromatogram example is shown in Figure 3

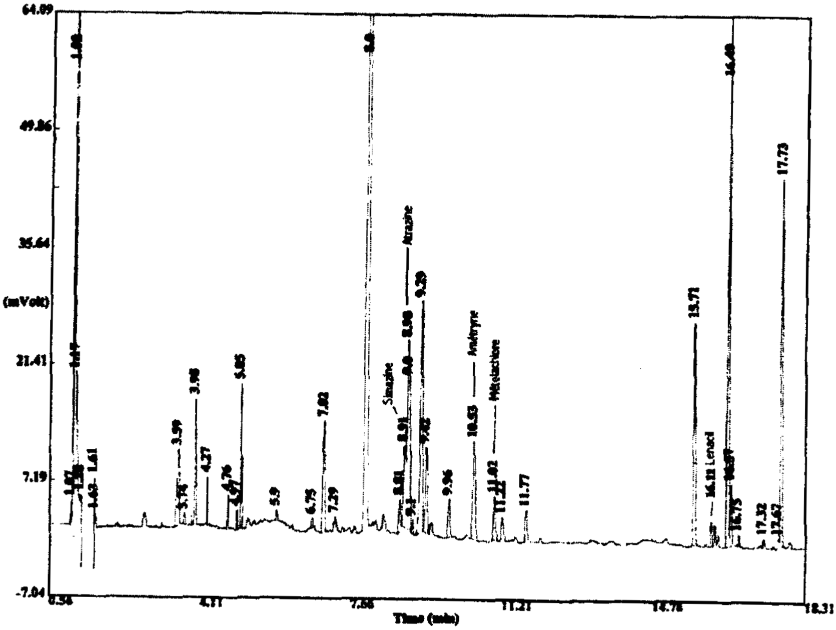


FIGURE 3 GC-NPD Chromatogram of Metolachlor (0.48 µg/l), Simazine (0.11 µg/l), Atrazine (0.46 µg/l) and lenacil (0.04 µg/l), internal standard : ametryne (1.18 µg/ml), in surface water (Dyle river) in April 1999

Quantification and detection limits

Taking into account the concentration factor with SPE off-line, these analytical methods allow to reach the quantification limits (signal to noise ratio : 6/1) and detection limits (signal to noise ratio: 3/1), which are indicated in Table I.

TABLE II Rentazone, Chloridazon, Lenacil and Metolachlor recoveries and Relative Standard Deviation in MilliQ water

Phase	*pH*	*Bentazone*		*Chloridazon*		*Lenacil*		*Metolachlor*	
		Recovery (%)	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*	*Recovery (%)*	*R.S.D (%)*
tC18 (Waters)	2.5	87.6	8.42	39.3	3.66	103.8	13.6	90.0	10.2
C18 (Chromabond)	2.5	67.1	25.3	25.8	29.4	72.5	22.3	75.5	9.7
Oasis HLB (Waters)	2.5	72.3	9.52	96.4	5.73	99.9	14.5	65.2	9.9
SDB2	2.5	30.9	6.70	102.5	5.95	95.4	1.43	75.3	2.75
Oasis HLB +C18 (Waters)	2.5	93.7	3.36	101.3	6.20	92.3	3.46	104.6	4.42
tC18 (Waters)	7.0	–	–	41.6	11.0	100.2	13.3	91.6	8.10
C18 (Chromabond)	7.0	–	–	35.0	10.9	92.5	7.08	64.6	10.7
Oasis HLB (Waters)	7.0	65.2	13.1	92.5	8.54	87.7	6.08	54.1	23.0
SDB2	7.0	28.7	7.78	96.2	9.73	86.4	6.50	70.7	5.32
Oasis HLB +C18 (Waters)	7.0	70.7	16.6	94.8	11.2	83.3	8.09	93.7	4.39

-: data below the quantification limit

TABLE III Atrazine, Simazine, Diuron and Isoproturon recoveries and Relative Standard Deviation in MilliQ water

Phase	*pH*	*Atrazine*		*Simazine*		*Diuron*		*Isoproturon*	
		Recovery (%)	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*
tC18 (Waters)	2.5	80.9	21.9	74.0	12.9	98.7	8.80	93.6	6.67
C18 (Chromabond)	2.5	69.5	20.2	68.1	25.0	67.0	17.8	70.4	19.6
Oasis HLB (Waters)	2.5	84.3	3.17	86.9	6.20	77.8	8.45	80.8	6.70
SDB2	2.5	102.2	8.58	101.5	1.41	87.0	3.45	92.6	3.46
Oasis HLB +C18 (Waters)	2.5	93.0	2.93	102.2	6.72	95.0	3.69	93.8	1.57
tC18 (Waters)	7.0	91.3	16.9	89.7	11.6	95.2	7.62	98.0	7.42
C18 (Chromabond)	7.0	91.9	1.73	96.1	8.40	81.3	12.2	89.7	8.88
Oasis HLB (Waters)	7.0	88.6	13.8	87.9	6.78	78.3	4.45	86.6	9.88
SDB2	7.0	87.3	8.95	91.6	9.47	80.5	6.07	84.8	5.62
Oasis HLB +C18 (Waters)	7.0	104.6	16.5	91.3	5.96	89.6	8.78	90.3	8.35

-: data below the quantification limit

TABLE IV Ground and surface waters characteristics

Water	*T.O.C. mg C / l*	*Humic acids concentration mg/l*[a]	*Fulvic acids concentration mg/l*[a]	*pH*	*Conductivity (μS/cm)*
Ground water	0.77	0.14	0.55	7.32	815
Surface water (Tailfer)	2.18	0.39	1.57	8.14	441

a. following Legube[27]

Extraction recoveries with different SPE sorbents

In MilliQ water

Recovery data for each pesticide are shown in Tables II and III. Each value corresponds to a mean of 4 replicates. These data demonstrate that the pesticide recoveries vary largely regarding to the kind of phases.

(a) It appears that medium polar pesticides, as triazines or phenylurea, follow a similar pattern. In fact, at pH 7, the recoveries spread between 90 and 105 % with a R.S.D < 17 % on tC18 and Oasis+C18. At pH 2.5 they lied between 87 and 103 % with a R.S.D < 7 % on Oasis+C18 and SDB2. According to the phase specificities, the pH value influences the recoveries. For instance, they are above 87 % at low pH on phases adapted to acid conditions as SDB2. At pH 7, the results demanded by "91/414/EEC Directive-guideline on residue analytical method" can be reached with more different sorbents.

(b) For lenacil, (an uracil pesticide) admitted recoveries were performed with the five different sorbents at both pH values. For metolachlor, admitted recoveries were performed with the different sorbents at both pH values, except on Oasis at pH 2.5 and 7.0 and chromabond at pH 7.0. It appears that for this medium polar pesticide, tC18 phase was the most adapted sorbent at both pH values.

For these two medium polar pesticides, the recoveries on tC 18 phases at pH 7 were set in according to "91/414/EEC Directive-guideline on residue analytical method". The copolymers do not bring necessary improvements.

(c) For chloridazon, admitted results were reached at the two pH values on Oasis, Oasis+C18 and SDB2. The copolymer sorbents seem to remove the chromatographic effect obtained with C18 phases. They improve clearly recoveries of this pesticide.

(d) For the acid pesticide, bentazone, admitted results were achieved at pH 2.5 on tC18, Oasis, and Oasis+C18, on which the highest recovery (94 %) was obtained. At pH 7, only Oasis+C18 allowed to perform admitted results. At pH 2.5, bentazone (pKa: 3.3) is not ionized and can be better sorbed by the immobile phase. Nevertheless, a few phases are able to achieve admitted recoveries for this polar pesticide.

From these results, we bring to the conclusion that only Oasis-C18 (Waters) phase at pH 2.5 allows to reach recoveries set between 90 and 110 % with R.S.D. below 7 % for the medium and most polar pesticides.

The accuracy and the reliability of the extraction process with these pesticides are assured with recoveries between 70 and 110 %, and relative standard deviation below 20 %.

The additional effects of Oasis and C18 sorbents, put in two superposed layers, permit to extract simultaneously medium and highly polar pesticides, and more particularly bentazone with the other pesticides. With SDB2, other copolymer, according to the pH value the recoveries correspond to "91/414/EEC Directive-guideline on residue analytical method", except for bentazone.

Determination in different matrices

Before integrating the Oasis-C18 (Waters) two layer cartridges in a routine analysis method of pesticides in water, the recoveries have to be investigated taking into account the influence of the dissolved natural organic matter.

Following the same protocol, the recovery experiments were carried out with Oasis-C18 (Waters) two layer cartridges in ground and surface waters. These waters were kindly supplied by C.I.B.E. (Compagnie Intercommunale Bruxelloise des Eaux, Water Supplier in Belgium). The surface water corresponds to a raw water of Meuse river, drawn from Tailfer Plant (Profondeville, C.I.B.E.)

In order to avoid a too quick clogging of the filters by the suspension particles, the waters samples were filtered through GF/C filters (1.2 μm). Afterwards, they were treated as mentioned at point "Procedures". The water characteristics are shown in Table IV and the results in Table V.

TABLE V Pesticides recoveries on Oasis-C18 Waters two layers cartridges at pH 2,5 in ground and surface waters

Pesticide	*Ground water*		*Surface water*	
	Recovery[a] (%)	*R.S.D. (%)*	*Recovery[a](%)*	*R.S.D. (%)*
Bentazone	100.0	2.37	91.8	26.2
Chloridazon	110.8	5.64	115.1	15.3
Lenacil	92.9	8.80	88.3	16.7
Metolachlor[b]	98.7	3.68	109.3	11.3
Atrazine	109.1	1.71	98.4	20.5
Simazine	96.2	6.72	100.6	13.3
Diuron	91.1	5.65	88.2	16.8
Isoproturon	93.2	9.79	91.4	16.2

a. mean of 4 determinations
b. GC data

In ground water, it appears that recoveries of medium and highly polar pesticides are set between 91 and 111 % with R.S.D. between 2 and 10 %. In surface water, the recoveries of these pesticides are set between 88 and 115 % with R.S.D. between 11 and 20 % and with 26 % in the particular case of bentazone.

These results show that Oasis+C18 two layer cartridges allows to reach recovery values similar to those performed in MilliQ water. In fact, the 500 mg of C18 phase placed above Oasis, retains partly the dissolved natural organic matter, as well as a sorbent. The combined effects deliver such results for medium and highly polar pesticides.

Nevertheless, the influence of the dissolved natural organic matter increases the R.S.D. values. From values below 7 % in MilliQ water, and below 10 % in ground water, R.S.D. values in surface water rise between 11 and 20 %, but reaches 26 % in the case of bentazone.

CONCLUSIONS

The developed HPLC-DAD and GC-NPD analytical methods allow to measure out in MilliQ water, with a quantification limit of 0.05 µg/l: atrazine, simazine, bentazone and chloridazon, of 0.04 µg/l: lenacil, diuron and isoproturon, and of 0.03 µg/l: metolachlor.

The scheme of these methods is based on an "off-line" solid phase extraction step, with a special two layers cartridge : poly(divinylbenzene-co-N-vinylpyrrolidone) – octadecyl-bonded silica (Oasis-C18), that allows at pH 2.5 to reach recoveries for medium and most polar pesticides between 90 % and 105 % with R.S.D. below 7 % in MilliQ water. These recoveries allow to reach the quantification limits mentioned at Table I.

These recoveries are also applicable in ground and surface waters. Actually, the dissolved natural organic matter does not modify significantly the recovery values, but increases in surface water the R.S.D. values then between 11 and 20 % for chloridazon, lenacil, metolachlor, atrazine, simazine, isoproturon and diuron. For bentazone, the R.S.D. value in surface water exceeds the admitted value of 20 %. In that case, according to the influence of the fulvic and humic acids in the beginning of the chromatographic analysis, it would be interesting to consider it as an exception foreseen in the European Directive.

The HPLC-DAD and GC-NPD methods with this "off-line" SPE on Oasis-C18 two layers cartridges allow to carry out monitoring of medium and highly polar pesticides in ground and surface waters according to the admitted concentrations defined in the European Directives.

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References

[1] M. Schiavon, C. Perrin-Ganier, and J.M. Portal. *Agronomie*, **15**, 157–170 (1995).

[2] H. Sabik *Intern. J. Environ. Anal. Chem*, **72 – 2**, 113–128 (1998).

[3] T.A. Albanis and D.G. Hela, *Intern. J. Environ. Anal. Chem*, **70**, 104–120 (1998).

[4] I. Heinz, A. Flessau, N. Zullei-Sebert, B. Kuhlmann, U. Schulte-Ebbert, M. Michels, J. Simbrey and G Fleischer. *Economic Efficiency Calculations in Conjunction with the Drinking Water Directive (Directive 80/778/EEC); Part III: The parameter for pesticides and related products.* (Research Report prepared for European Commission, DGXI Environment – University of Dortmund, Germany, 1996).

[5] x1, (1980). Directive du Conseil relative à la qualité des eaux destinées à la consommation humaine J.O. n° L-229/11 du 30/08/80.

[6] x2, (1998). Directive du Conseil du 3 novembre 1998, relative à la qualité des eaux destinées à la consommation humaine J.O. n° L-330 du 05/12/98.

[7] x3, (1997). Directive 95/57 EC du conseil du 22 septembre 97 établissant l'annexe VI de la directive 91/414/EEC concernant la mise sur le marché des produits phytosanitaires J.O. L 265/87 du 27/09/97.

[8] V. Pichon, L.Chen, N.Durand, F. Le Goffic and M-C Hennion. *J. Chromatogr A*, **725**, 107–119 (1996).

[9] V.Pichon, L.Chen and M-C Hennion, *Anal. Chim. Acta*, **311**, 429–436 (1995).

[10] J. Patsias and E. Papadopoulou-Mourkidou. *J. Chromatogr A*, **740**, 83–98 (1996).

[11] A. Oubina, E. Martinez, J. Gascon, D. Barcelo and I.B. De Alleluia, *Intern. J. Environ. Anal. Chem*, **70**, 75–91 (1998).

[12] E. Papadopoulou-Mourkidou and J.Patsias. J. Patsias. *J. Chromatogr A*, **726**, 99–113(1996).

[13] T. Pihlström, A. Hellström and V. Axelson. *Anal. Chim. Acta*, **356**, 155–163 (1997).

[14] M.C. Gennaro, C. Abrigo, D.Giacosa, L.Rigotti and A. Liberatori *J. Chromatogr A*, **718**, 81–88 (1995).

[15] S.J. Stout, A.R. DA Cunha, G.L. Picard and M.M. Safarpour, *J. of AOAC International*, **81**, 685–6901 (1998).

[16] D. de Almeida Azevedo, S. Lacorte, T. Vinhas, P. Viana and D. Barcelo.. *J. Chromatogr A*, **879**, 13–26 (2000).

[17] J-Y Hu, T. Aizawa and Y. Magara. *Wat. Res.*, **33**, 417–425 (1999).

[18] V. Pichon *Analusis*, **25**, 101–106 (1997).

[19] T. Santos, J. Rocha and D. Barcelo. *Intern J. Environ. Anal. Chem*, **70**, 19–28 (1998).

[20] E. Jaskulké, L.Patty and A. Bruchet., In "*Pesticide Chemistry and Bioscience*" (edited by G.T. Brooks -University of Portsmouth, UK, 1999) pp 368–385.

[21] L. Nitschke and W. Schüssler, *Chemosphere*, **36**, 35–41, (1998).

[22] T. Pihlström, A. Hellström and V. Axelsson, *Anal. Chim. Acta*, **356**, 155–163 (1997).

[23] R. Sasano, T. Hamada, M. Kurano and M. Furuno, *J. Chromatogr A*, **896**, 41–49 (2000).

[24] Green Book, Belgaqua-Phytophar (Editions 1997 and 1999).

[25] S. Beernaerts and L. Pussemier. "*Estimation des pertes en produits phytosanitaires vers les eaux superficielles et souterraines dans les différents bassins hydrographiques belges – Rapport de synthèse*" CERVA, Belgium (1997).

[26] M. Gérard, S. Beernaerts, J-P Barthélemy, L. Pussemier and A. Copin. "*Prévision de la pollution des eaux par les produits phytosanitaires en Belgique et remédiation par traitements sur charbons actifs*" (Research Report – Ministère des Classes Moyennes et de l'Agriculture DG 6 and DG 4 – Phytofar. Belgium 1997–1999).

[27] B. Legube, *B. Analusis*, **19–2**, 15–17 (1991).