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Multiresidue method for the simultaneous determination of four groups of pesticides in ground and drinking waters, using solid-phase microextraction–gas chromatography with electron-capture and thermionic specific detection

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Abstract

A common sample preparation procedure capable of efficiently concentrating various groups of pesticides, taking advantage of universal detectors like the mass spectrometer or combined techniques of group selective detectors like gas chromatography–electron capture detection (ECD)/thermionic specific detection (TSD), is desirable in environmental analysis. Six solid-phase microextraction fibres available for analysis of semi-volatiles (7, 30 and 100 μm poly(dimethylsiloxane) (PDMS), 85 μm polyacrylate, 60 μm PDMS–divinylbenzene (PDMS–DVB) and 65 μm Carbowax–DVB) were evaluated and the 60 μm PDMS–DVB was selected for the simultaneous extraction of 34 compounds, included in the organochlorine (OCPs), organophosphorous (OPPs), pyrethroid and triazine pesticide groups. All parameters affecting the extraction efficiency from water samples, namely fibre coating, sample agitation, pH and ionic strength, extraction temperature and time, were optimised. The analytical procedure involves solid-phase microextraction extraction, gas chromatographic separation and subsequent ECD and TSD via a post-column splitter adjusted to a split ratio of 1:10, respectively. Detection limits in the range of 1–10 ng l^{-1} for OCPs, 1–30 ng l^{-1} for OPPs, 20–30 ng l^{-1} for pyrethroids and 8–50 ng l^{-1} for triazines are easily attainable with the optimised procedure. The method validated for ground and drinking waters has low cost of implementation and operation although it requires careful maintenance.

Keywords: Solid-phase microextraction; Water analysis; Pesticides; Organochlorine compounds; Organophosphorus compounds; Triazines; Pyrethroids

1. Introduction

Chlorinated pesticides are very toxic and persistent compounds in the environment. Although most of them have been banished from use, they are still detected. The organophosphorous insecticides and triazine herbicides, namely atrazine, are among the most commonly used and detected pesticides in water streams around the world [1,2]. Pyrethroids are pesticides of the last generation, very stable to light

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and temperature although they may suffer rapid biological degradation in the environment [3].

The need for simple methods for screening water samples for environmental contaminants is well known. Due to the large number of active ingredients used, trace analyses of these substances require techniques for the detection of the greatest number of compounds possible, with the fewest number of extraction and clean-up steps [3,4].

Pesticides are generally found in waters at ppt levels, mixed with other contaminants at higher concentrations. To monitor sources of water intended for human consumption in compliance with the EU legislation, analytical methods with detection limits well below 0.1 $\mu g\ l^{-1}$ are needed.

Solid-phase microextraction (SPME) represents a further advance as a solvent-free alternative to the extraction of organic compounds [3,5–9]. Furthermore, SPME overcomes problems related to matrix effects and elution of impurities generated by extraction materials.

Nowadays, in addition to the former general purpose poly(dimethylsiloxane) (PDMS) and polyacrylate (PA)-coated fibres, a large number of fibre coatings based on solid sorbents are available, namely the PDMS–divinylbenzene (PDMS–DVB), Carbowax–DVB (CW–DVB), CW–templated resin (CW–TR), Carboxen–PDMS and DVB–Carboxen–PDMS coated fibres [10]. Some of these porous polymer SPME fibres with bipolar characteristics can be very useful for the simultaneous analysis of pesticides presenting a wide range of polarities. In a previous work by the same authors, the PDMS–DVB coating was compared in its three different commercial types, regarding pesticide analysis, and a structure–efficiency relationship was established [11].

In recent years, many studies can be found using SPME as a sample preparation method for the analysis of organochlorine (OCPs) [12–14], organophosphorous (OPPs) [15–19], and triazine pesticides [20–23] using separate or restrict methods.

The aim of the present work was to develop an SPME multiresidue method, including OCPs, OPPs, triazines and pyrethroid pesticides, in combination with an instrumental set-up of two highly sensitive and selective gas chromatography detection systems, electron-capture detection (ECD) and thermionic specific detection (TSD). Preferably this method should present similar or better sensitivity than the available solid-phase extraction (SPE) methods, when applied to ground and drinking waters. The main reason for developing this method was the need for a methodology able to determine pesticides with different biological activities, some of which can be found together in intensive culture areas.

Not many SPME methods have been developed for the analysis of more than 25 analytes from more than two of the main classes of pesticides [24,25], which is especially true considering the new possibilities of bipolar SPME fibres in trace multiresidue analysis. Effects on extraction efficiency of parameters such as: polarity and thickness of the coating on the fibre, sample agitation, pH and ionic strength of the sample, extraction temperature and extraction time will be discussed. Validation parameters of the optimised procedure will be given.

2. Experimental

2.1. Chemicals and reagents

The various pesticides were supplied by Riedel-de Häen (Seelze, Germany). Individual stock standard solutions of OCPs: hexachlorobenzene (HCB), lindane, heptachlor, aldrin, isodrin, heptachlor epoxide, γ-chlordane, endosulfan I, 4,4′-DDE, dieldrin, endrin, endosulfan II, 4,4′-DDD, endosulfan sulfate and 4,4′-DDT were prepared in *n*-hexane, whereas pyrethroid insecticides: λ-cyhalothrin and α-cypermethrin were prepared in ethyl acetate, and the OPPs: dichlorvos, dimethoate, fonofos, diazinon, parathion-methyl, fenitrothion, malathion, parathion-ethyl, chlorfenvinphos, tetrachlorvinphos, fenamiphos and azinphos-methyl, and triazines: desethylatrazine (DEA), simazine, atrazine, propazine, terbuthylazine and simetryn were dissolved in methanol. Four separate group mixtures were then prepared in methanol containing 2 $mg\ l^{-1}$ of each individual pesticide.

All solvents used were of LiChrosolv gradient grade purchased from Merck (Darmstadt, Germany). Ultrapure Milli-Q water (Millipore, Molsheim, France) was used to daily prepare the working aqueous solutions in the range of 0.01 to 10 $\mu g\ l^{-1}$. When convenient, 0.01 $\mu g\ l^{-1}$ γ-chlordane and 0.04

μg l^{-1} tetrachlorvinphos were used as internal standards (I.S.), respectively for ECD and TSD chromatograms. These compounds are not allowed as pesticides in Portugal since 1986. The organic solvent content in a 0.1 μg l^{-1} standard and real samples was always below 0.5% in methanol, with a major contribution from the internal standard.

2.2. Equipment and SPME fibres

Chromatographic analyses were carried out in a Varian 3400 CX (Walnut Creek, CA) gas chromatograph. The injector and detector temperatures were set at 250 and 310 °C isothermal, respectively. The split/splitless injector was maintained in splitless mode during 5 min of SPME fibre desorption. All compounds were resolved in an MDN-5 column (5% diphenyl–95% dimethylsiloxane) (30 m×0.32 mm I.D×0.25 μm film) (Supelco, Bellefonte, PA) using helium as carrier gas and detected either by ECD or TSD operating at 3.2 A intensity, as more convenient. The oven temperature programme was as follows: initial temperature 80 °C (held 2 min), increased by 15 °C/min to 190 °C (held 2 min), increased by 10 °C/min to 220 °C (held 5 min) and finally, increased by 10 °C/min to 260 °C and held at this temperature for 7 min. At the column exit an adjustable splitter (SGE Europe, Milton Keynes, UK) was inserted and later fine-tuned to give about a tenth of the effluent flow to ECD and the remaining to TSD. A supplementary make-up gas (N_2) at a flow-rate of 10 ml/min was also delivered to the splitter. This instrumental configuration allowed complete separation of the pesticides in a single 30-min chromatographic run (with two channels) following a single extraction procedure. OCPs and pyrethroids were detected using ECD whereas OPPs and triazines were analysed by TSD, although ECD can also give a measurable signal for a few of them.

Six SPME fibres with different coating phase or thickness, 7 μm PDMS, 30 μm PDMS, 100 μm PDMS, 85 μm PA, 60 μm PDMS–DVB and 65 μm CW–DVB, were tested for their suitability for the combined pesticide analysis. All SPME fibres (Supelco) were new at the beginning of the study and were conditioned according to the supplier's instructions.

3. Results and discussion

3.1. Method development

3.1.1. Fibre type selection

The sensitivity of an SPME method greatly depends on a correct selection of the fibre coating and thickness, regarding the compounds of interest. In relation to SPME fibres used, the vast majority of work has been done using the PDMS and PA fibres [12,16,26–28]. As they were the first commercially available, their performance for certain types of applications is already well established and still are unsurpassed well-performing and rugged fibres, able to withstand aggressive extraction conditions. Recently, new fibres appeared in order to solve the limitations of the former, when dealing with more polar analytes or multiresidue analysis [8,26,29,30]. In a recent review on solid-phase microextraction of pesticide residues, among 34 references, Beltran et al. reported only one citation where the weakly polar CW–DVB fibre was used in SPME of OCPs, two citations of this fibre for SPME of triazines and one citation each of the CW–DVB and PDMS–DVB fibres for extraction of OPPs. Most papers refer to using the PDMS fibres for the determination of OCPs, the PA fibre for the analysis of triazines and PA or PDMS fibres, indistinctly, for the analysis of OPPs [26]. Several other pesticides were successfully analysed using SPME but no pyrethroid was referenced. Further, Sabik et al. recently reviewed 32 references of multiresidue methods mainly for the determination of triazines and degradation products where only four of them can be found dealing with SPME [4].

In our study, six SPME fibres (7, 30 and 100 μm PDMS, 85 μm PA, 60 μm PDMS–DVB and 65 μm CW–DVB) were evaluated for the simultaneous extraction of OCPs, OPPs and triazine pesticides in water samples. It should be noted that the pyrethroid pesticides were included in the method later, and considering their low representativity it is not likely that they would affect the decisions to be taken. At this point of the discussion, it should also be mentioned that in a previous work developed by the same authors, comparing the extraction efficiency of three available PDMS–DVB fibre coatings (65 μm for GC-use, 60 μm for HPLC-use and 65 μm

StableFlex for GC-use) regarding the analysis of the same target pesticides, it was observed that the 60 μm PDMS–DVB fibre gave the most equilibrated results for the totality of analytes. Further details are described elsewhere [11].

Figs. 1–3 present the results obtained in a study comparing the six selected SPME fibres, respectively, for OCPs, OPPs and triazine pesticides. Significantly different extraction capacities were found for the fibres tested. The OCPs were equally well extracted by the 100 μm PDMS and PA fibres whereas the OPPs and triazines were better extracted with the PDMS–DVB fibre. The latter showed very good response for all 34 compounds, thus, was considered to be the more adequate for the simultaneous analysis of OCPs, OPPs and triazines. Recently some authors have also reported this fibre for the analysis of OCPs in different matrices [14,31].

The PDMS–DVB fibre obtained the best global performance due to its intermediate polarity properties. Using this fibre in a multiresidue method has the advantage of improving the extraction efficiency for those compounds that require enhanced sensitivity, i.e. triazines and some polar OPPs. Especially for fenamiphos, atrazine and dichlorvos, Dugay et al. agree that the PDMS–DVB fibre is the best to use [5]. Lambropoulou et al. demonstrated, also, the benefits of this fibre on the analysis of triazines [22]. In a recent paper, Valor et al. discussed the issue of fibre type selection for the analysis of 52 pesticides based on the determination of the fibre–water partition coefficients [24]. The remarks that were made are fully comparable with our findings, highlighting the benefits of mixed phases like PDMS–DVB in trace analysis of pesticides. From now on the 60 μm PDMS–DVB fibre will be used.

3.1.2. Sample agitation

Concerning SPME, the speed of extraction and the time to reach equilibrium are primarily dependent on the rate of mass transport in the bulk of the sample. In this sense, for optimum performance of the technique it is essential that constant rapid stirring is employed [6,22]. We used magnetic stirring as

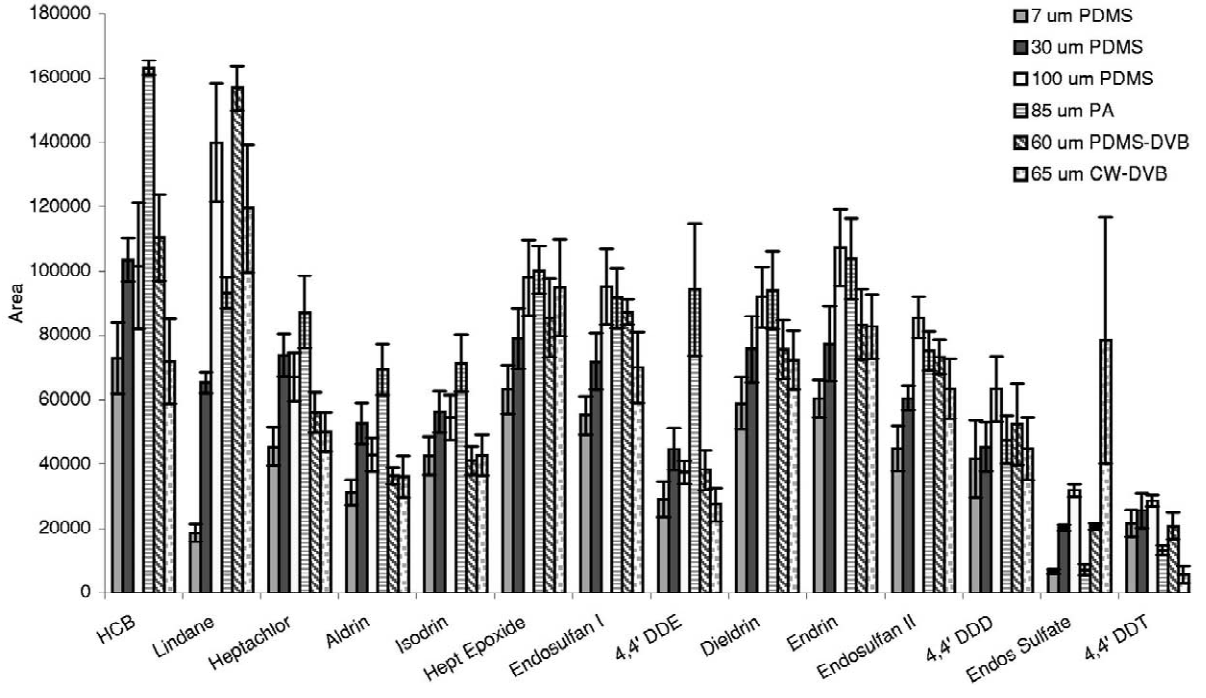

Fig. 1. Extraction efficiency of six SPME fibres, graphically represented as average peak areas obtained for each organochlorine pesticide. Error bars represent the standard deviation of five replicates. SPME conditions were as follows: 1.5-ml sample containing 1.0 μg l^{-1} each OCP, 30 min extraction at ambient temperature without agitation.

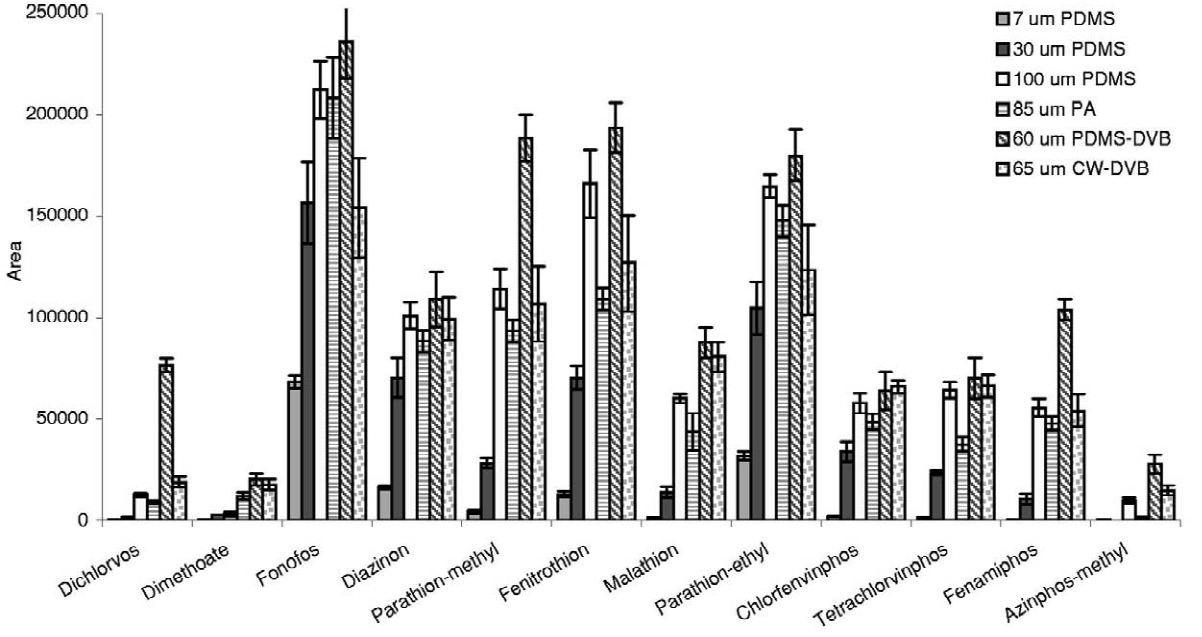

Fig. 2. Extraction efficiency of the six SPME fibres tested, graphically represented as average peak areas obtained for each organophosphorous pesticide. Error bars represent the standard deviation of five replicates. Extraction conditions were the same as in Fig. 1, but using a 10 $\mu g\ l^{-1}$ pesticide solution.

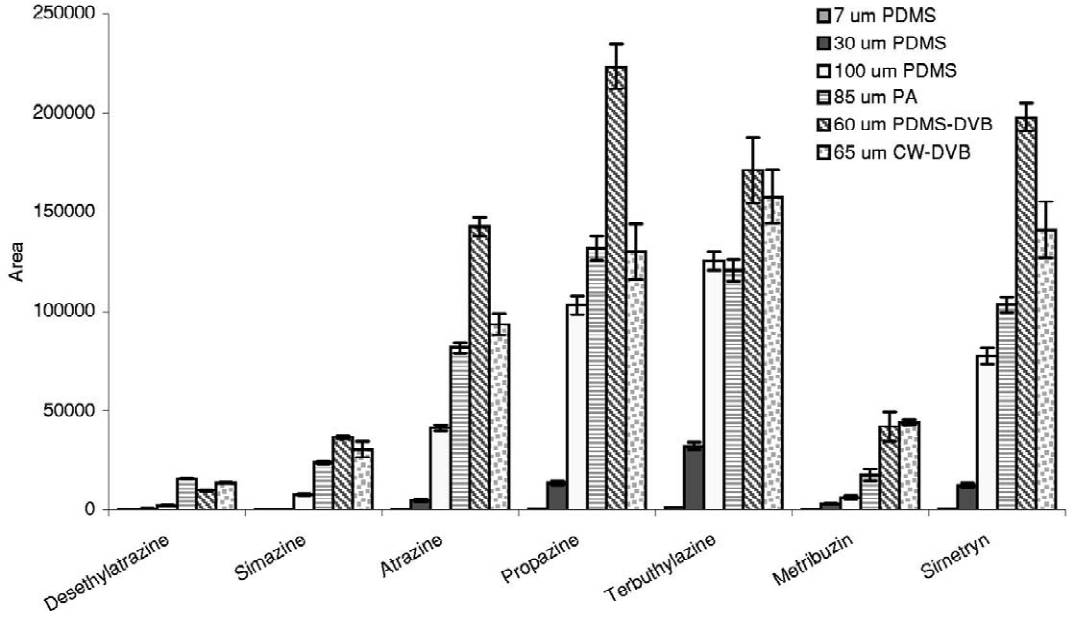

Fig. 3. Extraction efficiency of six SPME fibres towards triazines, graphically represented as average peak areas obtained for each compound. Error bars represent the standard deviation of five replicates. Extraction conditions were the same as in Fig. 2.

agitation method and demonstrated that static extraction could only achieve 10–30% in extraction efficiency of that at 600 rev./min, so the latter was selected.

3.1.3. Sample pH effect

The affinity of target analytes for an adsorbent acting primarily by hydrophobic interactions can be enhanced keeping the molecules in a non-ionized form. The pesticides selected for this study are predominantly apolar and non-charged compounds thus, the sample pH does not seem to have a drastic impact in analyte extraction. The same conclusion could be drawn by experimentally analysing the pH effect between 4, 7 and 10. Although the results were not significantly different, keeping the sample pH unchanged seems to be advantageous and it prevents analyte breakdown detected for malathion and endosulfan at pH 10.

3.1.4. Extraction temperature

Extraction temperatures between 25 and 70 °C were tested in order to compare the effect of this parameter on extraction yields. Regarding the results presented in Fig. 4, it is recommended to increase the sample temperature to around 60 °C to improve the simultaneous extraction of different OCPs, OPPs and triazine pesticides. This figure was constructed converting the peak area values in the following manner: peak area values for individual pesticides, over the range of the variable, were normalized considering the highest area obtained as 1. The plot for each pesticide group, intended to show the particular behaviour of a relatively homogeneous chemical family, was then obtained by adding the plots of the

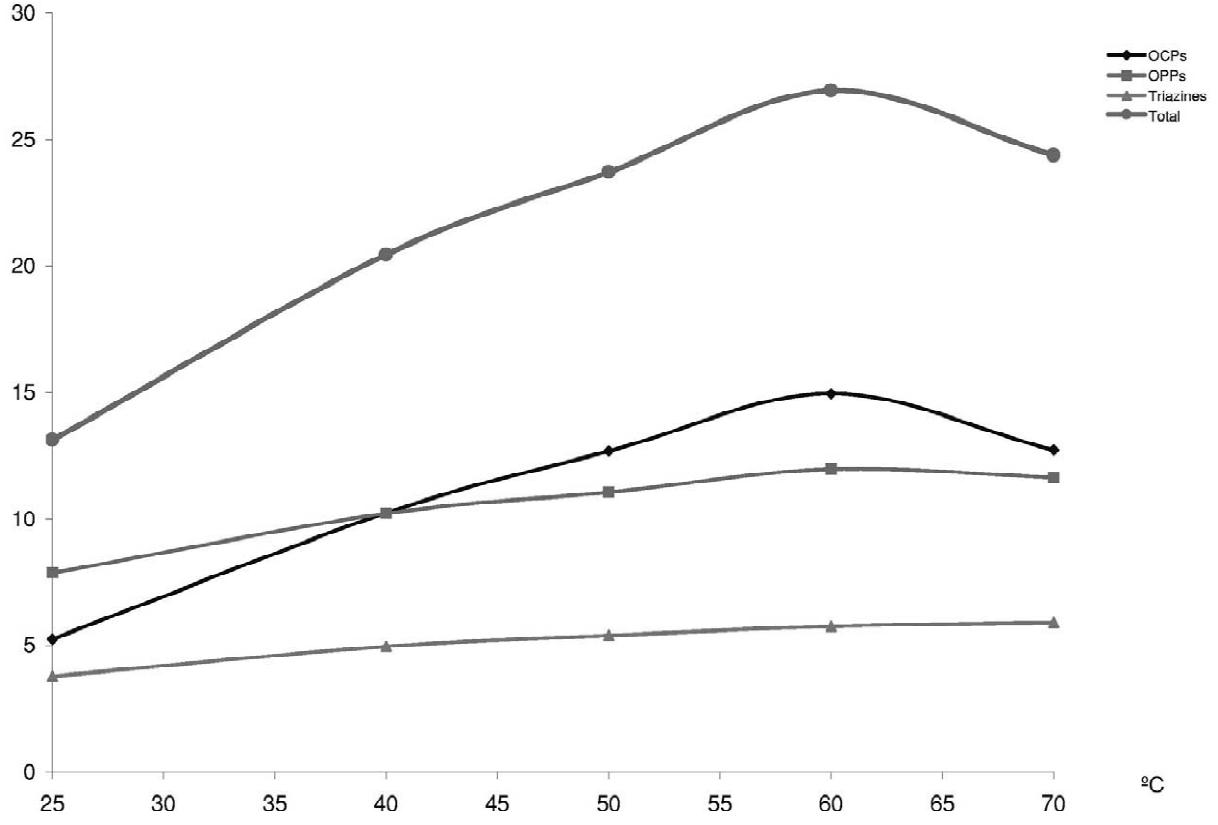

Fig. 4. Optimisation of the extraction temperature regarding the analysis of three groups of pesticides. Four replicate analyses were performed at the following levels: 25, 40, 50, 60 and 70 °C. SPME conditions, 3 ml pesticide solution at 0.1 μg l^{-1}, extraction with a 60 μm PDMS–DVB fibre during 30 min, rapid agitation applied and neutral pH. *y*-Axis, arbitrary scale.

respective members. To obtain a trace of the total behaviour of the pesticides in order to extract less subjective conclusions about the optimum variable level, another plot was created as the arithmetic sum of pesticide group plots. The same procedure applies to Figs. 5 and 6.

Temperatures higher than 60 °C have a detrimental effect on the extraction of OCPs. Above this point the temperature effect favouring the transfer rate of analytes to the fibre coating is overcome by its negative effect on the analyte's partition coefficient between the fibre and the sample matrix. The plot for OPPs shows that between 60 and 70 °C there is equilibrium between positive and negative effects of temperature (except for dichlorvos). In the case of triazines the situation is different and extraction yields would benefit with higher temperatures than 60 °C. This result is not surprising as these compounds generally have a lower fibre–water partition coefficient, even using a bipolar SPME fibre, which results in a proportionally lower negative interference of temperature on the fibre–water partition coefficient comparatively with the favourable effect on mass transfer rate. Considering the different profiles obtained there is evidence that whenever various families are being analysed a medium value should be encountered. Most authors agree on the importance of extraction temperature optimisation on SPME of pesticides and recommend employing temperatures up to 100 °C depending on the target pesticides and on the matrix type [9,26,32].

3.1.5. Ionic strength adjustments

Most authors report beneficial effects of the addition of NaCl to the sample over extraction efficiency of many compounds. Nevertheless many

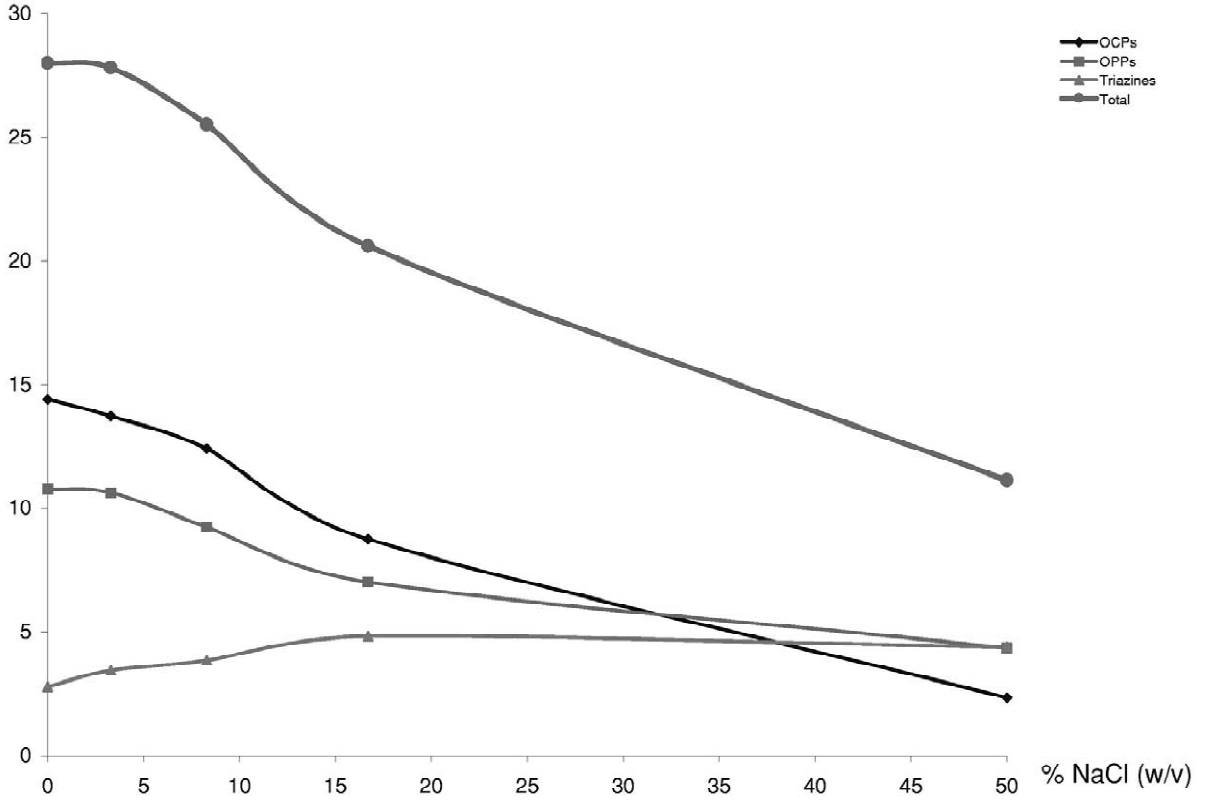

Fig. 5. Influence of the ionic strength of the sample on SPME of pesticides using a PDMS–DVB coated fibre. Effects on extraction efficiency were evaluated at the following salt contents: 0, 3.3, 8.3, 16.7% NaCl and at saturation. SPME conditions, the same as in Fig. 4, at controlled temperature of 60 °C, four replicates. *y*-Axis, arbitrary scale.

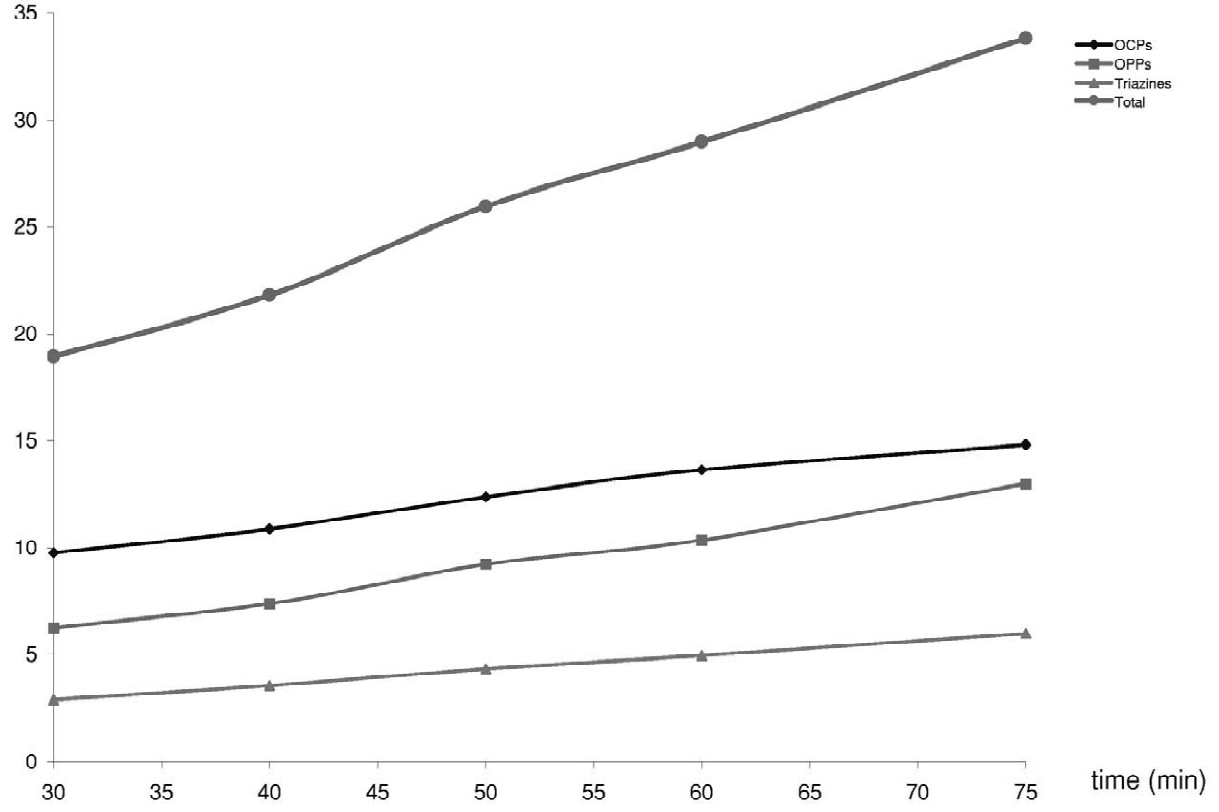

Fig. 6. Extraction time profile for target pesticide groups using the PDMS–DVB fibre. Extracted amounts over different extraction times: 30, 40, 50, 60 and 75 min, were determined. SPME conditions, 3 ml pesticide solution at 0.1 μg l^{-1}, extraction using a 60 μm PDMS–DVB fibre at 60 °C, rapid agitation of the sample without pH and ionic strength correction, five replicates. *y*-Axis, arbitrary scale.

exceptions have been noted [26]. The influence of this parameter over the extraction of several pesticides using the PDMS–DVB fibre, was experimentally verified testing pesticide solutions containing 3.3, 8.3, 16.7% and saturation of NaCl, in comparison with a solution in ultrapure water. The results are shown in Fig. 5.

The extraction yield of all triazines and some polar OPPs (i.e. dichlorvos, dimethoate and fenamiphos) was improved by 1.2 to 3 times until the concentration of 16.7% NaCl. At saturation conditions it was possible to obtain improvements of 13.7, 4.3, 4.7 and 9.9 times, respectively for DEA, simazine, dichlorvos and dimethoate. Unfortunately, for the rest and the majority of the pesticides the extraction yield was greatly reduced, even at low NaCl concentrations. Particularly for apolar compounds, with very low water solubility, the presence of other species in solution may reduce the molecules' movement towards the fibre coating, negatively affecting recoveries and precision. Additionally, high salt contents can affect the fibre stability, particularly in the case of CW–DVB fibre [26]. By observation of Fig. 5, it can be seen that the salinity condition most appropriate would be between 0 and 3.3% NaCl. Considering that real samples naturally have an ionic strength higher than ultrapure water it was considered better not to make any ionic strength adjustments.

3.1.6. Extraction time

The speed and efficiency of SPME extractions are determined by the parameters previously discussed in this paper, as well as by intrinsic properties of the analytes. Once the extraction parameters were set-up at the most favourable conditions, the extraction time

profile was studied. As a general rule, the quantities extracted by the fibre are initially proportional to time and as equilibrium is approached a further increase in the extraction time will not produce substantial sensitivity gains. Fig. 6 displays the extraction time profile for the pesticide groups being studied. The extraction of OCPs shows a tendency to the equilibrium state around 60 min. On the other hand, at this point the extraction of OPPs and triazines maintains an increasing pathway until 75 min extraction time. Some authors referred to equilibrium extraction times for these analytes, although using other extraction conditions, of the order of 90–120 min [6,24,32].

Larger extraction times than 60 min are not reasonable on method implementation since analysis output is greatly reduced. For practical reasons, a 60-min extraction was selected and proved to be sufficient to attain the desired sensitivity.

3.1.7. Splitter adjustment

Considering the relative sensitivities of both detection methods, ECD and TSD, the splitter included in the chromatographic system was adjusted in order to give about a tenth of the column effluent flow to ECD and the remaining flow to TSD. The flow ratio was established like this as a result of the extremely high sensitivity of the ECD for OCPs and pyrethroids, whereas the TSD requires as much analyte as possible entering the detector. Under these conditions the best performance of both detectors working simultaneously can be obtained. The split ratio has minor changes during the oven temperature programme. Since the splitter is a crucial element in method calibration, careful maintenance and regular confirmation of its performance should be undertaken.

3.2. Method validation

Method validation is an important part in method development that consists in the process of defining analytical requirements, and confirming that the method under consideration has performance capabilities consistent with those requirements. The method being discussed was optimised and validated at the following operational conditions: 3 ml of sample are extracted by immersion of a 60 μm PDMS–DVB fibre during 60 min; sample agitation is employed at 600 rev./min and temperature control at 60 °C; neither pH adjustment nor ionic strength correction are applied.

Table 1 presents the validation parameters of the developed method, consisting of SPME extraction using a bipolar PDMS–DVB coated fibre and subsequent chromatographic analysis using two selective detectors functioning simultaneously. Linear calibration curves for all pesticides over five calibration levels, from 0.01 to 1.0 μg l^{-1}, were constructed using 0.01 μg l^{-1} γ-chlordane as internal standard for OCPs and pyrethroids, and 0.04 μg l^{-1} tetrachlorvinphos as internal standard for OPPs and triazines. Linear regression coefficients are present in Table 1.

Typical chromatograms for a 0.1 μg l^{-1} aqueous pesticide solution can be seen in Figs. 7 and 8. Clear chromatograms can be observed where target peaks are easily identified.

Limits of detection (LODs) were calculated by the analysis of pesticide solutions at a low concentration (0.002 μg l^{-1} OCPs and OPPs, 0.02 μg l^{-1} triazines and pyrethroids) to obtain the respective peak areas and afterwards applying the formula:

$$\mathrm{LOD} = \frac{3.3\sigma}{S}$$

where σ is the standard deviation of the response and S is the slope of the calibration curve.

These were later confirmed by extraction of aqueous pesticide solutions at the same levels. The LODs obtained applying an S/N ratio of 3 to the analytical signal are in good agreement with the ones resulting from theoretical calculation. The method described showed very good sensitivity with detection limits in the low ng l^{-1} range for almost all of the target analytes, well below the regulatory limit of 0.1 μg l^{-1} for individual pesticides in drinking water. These were equivalent or better than the ones obtained by other authors, despite using a flow splitter to ECD and TSD [16,18,21,22]. Likewise, the quantitation limits calculated applying a factor of 10 in the formula above, comply with the referred limit. DEA and dimethoate cannot be analysed with this method at the required limits.

The precision of the entire analytical procedure was determined as repeatability and intermediate

Table 1
Validation parameters of the SPME method at optimum extraction conditions. Compounds numbered from 1 to 17 were detected using ECD whereas compounds numbered from 18 to 36 were detected by TSD

Peak no.	Pesticides	t_R (min)	LOD[a] ($\mu g\ l^{-1}$) ($n=14$)	LOD[b] ($\mu g\ l^{-1}$)	Precision (RSD) ($n=20$)	Extraction yield (%) ($n=8$)	Recovery (%) ($n=10$)	Carryover (%) ($n=5$)	Calibration curve r^2
1	HCB	11.49	0.003	0.003	11.6	16.7	102.1	2.3	0.996
2	Lindane	12.03	0.0009	0.0005	9.7	25.1	99.1	n.d.	0.994
3	Heptachlor	13.74	Invalid	0.007	12.3	16.8	78.3[d]	n.d.	0.989
4	Aldrin	14.60	0.003	0.007	10.0	14.1	93.8	0.2	0.992
5	Isodrin	15.34	0.003	0.001	9.8	15.5	97.5	0.8	0.991
6	Hept. epoxide	15.62	0.002	0.002	5.8	21.4	103.4	n.d.	0.992
7 I.S.	γ-Chlordane	16.28	–	~0.001	–	26.6	–	n.d.	–
8	Endosulfan I	16.70	0.002	0.001	3.7	24.5	103.6	0.4	0.993
9	4,4′-DDE	17.43	0.006	0.007	10.0	15.0	99.8	1.5	0.992
10	Dieldrin	17.62	0.002	0.0008	13.6	21.3	102.4	0.4	0.994
11	Endrin	18.44	0.003	0.001	6.8	24.2	103.1	0.2	0.995
12	Endosulfan II	18.80	0.003	0.002	6.1	26.0	102.4	0.9	0.996
13	4,4′-DDD	19.08	0.004	0.002	8.6	19.1	102.0	1.6	0.993
14	Endos. sulfate	20.56	0.012	0.005	12.2	34.0	104.1	n.d.	0.992
15	4,4′-DDT	20.69	0.007	0.005	9.6	20.4	102.5	1.6	0.993
16	λ-Cyhalothrin	24.44	0.015	0.020	9.8	–	–	n.d.	0.992
17	α-Cypermethrin	28.72	0.027	0.030	12.3	–	–	n.d.	0.977
18	Dichlorvos	6.75	0.008	0.010	10.6	3.9	117.3[d]	n.d.	0.994
19	DEA	10.85	Invalid	0.800	56.2[c]	0.4	96.8	n.d.	0.969
20	Dimethoate	11.54	Invalid	0.400	23.7[c]	1.3	94.4	n.d.	0.982
21	Simazine	11.61	0.031	0.050	39.1[c]	–	131.7[d]	n.d.	0.956
22	Atrazine	11.71	0.001	0.030	9.4	16.1	103.4	n.d.	0.996
23	Propazine	11.78	0.003	0.025	12.3	22.1	100.5	n.d.	0.994
24	Terbutylazine	12.04	0.005	0.008	8.5	25.4	104.5	n.d.	0.992
25	Fonofos	12.16	0.001	0.001	8.5	43.4	96.2	n.d.	0.992
26	Diazinon	12.27	0.003	0.003	7.9	37.1	98.8	n.d.	0.995
27	Parathion-methyl	13.47	0.002	0.001	7.0	37.7	96.6	n.d.	0.998
28	Simetryn	13.55	0.027	0.030	8.8	16.5	94.7	n.d.	0.989
29	Fenitrothion	14.09	0.004	0.010	6.4	46.5	96.0	n.d.	0.991
30	Malathion	14.30	0.004	0.005	8.7	36.2	102.7	n.d.	0.987
31	Parathion-ethyl	14.59	0.004	0.004	8.0	43.2	95.7	n.d.	0.993
32	Chlorfenvinphos E	15.33	0.001	0.005	13.9	49.0	104.5	n.d.	0.948
33	Chlorfenvinphos Z	15.65	0.014	0.005	16.4	46.4	97.3	n.d.	0.966
34 I.S.	Tetrachlorvinphos	16.50	–	~0.003	–	51.9	–	n.d.	–
35	Fenamiphos	16.84	0.002	0.006	13.2	27.4	103.5	n.d.	0.961
36	Azinphos-methyl	23.67	0.002	0.020	9.2	33.9	77.4[d]	n.d.	0.997

t_R, retention time; n.d., not detected.
[a] Detection limits theoretically calculated on the basis of the background noise.
[b] Detection limits confirmed with standard solutions applying an $S/N = 3$.
[c] The concentration tested was close to the detection limit resulting in higher RSDs.
[d] Matrix effect is statistically significant at 95% confidence level.

precision of retention times, peaks areas and calculated concentrations for a 0.1 $\mu g\ l^{-1}$ aqueous pesticide mixture. The precision of retention times was excellent at 0.07% relative standard deviation (RSD). The intermediate precision of concentrations, expressed by the RSD of 20 replicate analyses spread over 3 days, was generally below 15% with many cases below 10%, see Table 1. The precision of the method benefits from using internal standards.

The SPME technique does not produce exhaustive

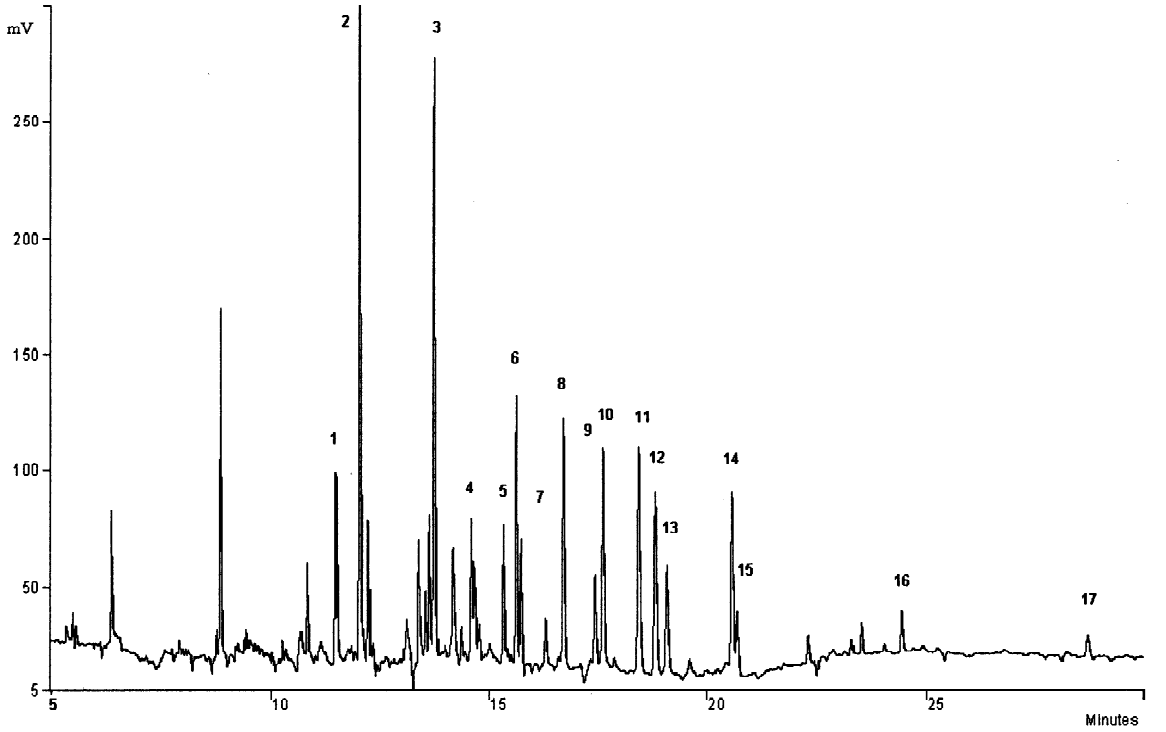

Fig. 7. Chromatographic separation of OCPs and pyrethroids detected by ECD, after SPME extraction of an aqueous pesticide solution containing 0.1 μg l^{-1} (0.01 μg l^{-1} γ-chlordane I.S.), using the optimised conditions. For peak assignment refer to Table 1.

extraction of analytes. The PDMS–DVB fibre's extraction yields were determined as the ratio between the extracted amount (calculated from calibration curves of standards directly injected) and the initial amount added to the vial. The results are displayed in Table 1. As can be seen, mass recoveries between 5.3 and 34% for OCPs, between 27.4 and 51.9% (except dimethoate 1.3%) for OPPs, and between 16.1 and 25.4% (except DEA 0.4%) for triazine pesticides, were obtained. In comparison with a study published by Correia et al. [32], using a 100 μm PDMS fibre, the results obtained by us are fairly higher which positively confirms the suitability of the PDMS–DVB fibre for pesticide residue analysis. The authors reported extraction yields always below 25%. To our knowledge, extraction yields for such an extensive list of pesticides using the PDMS–DVB coating have not been reported so far.

Matrix effects were also investigated comparing the peak areas obtained in the analysis of spiked ultrapure water and groundwater at a concentration of 0.1 μg l^{-1}. Although it is admissible that humic and fulvic acids interfere with pesticide extraction, matrix effects were significantly detected in only seven situations. Since the method uses an internal calibration, those situations were compensated by the internal standard and only four of them remained significant. In this sense, final results do not require correction for the recoveries. It should be stressed that the fibre performance suffers a continuous degradation during usage, which could be responsible for some recovery decrease.

The carryover of the system is a phenomenon that can be a source of false positives in pesticide analysis, which is particularly important for methods capable of trace level detection. In order to investigate its occurrence, five extractions of a 0.1 μg l^{-1} pesticide solution were carried out, each followed by a blank extraction. The results can be found in Table 1. This study revealed some carryover of the system in the analysis of OCPs, which can be understood since they are very apolar pesticides with high

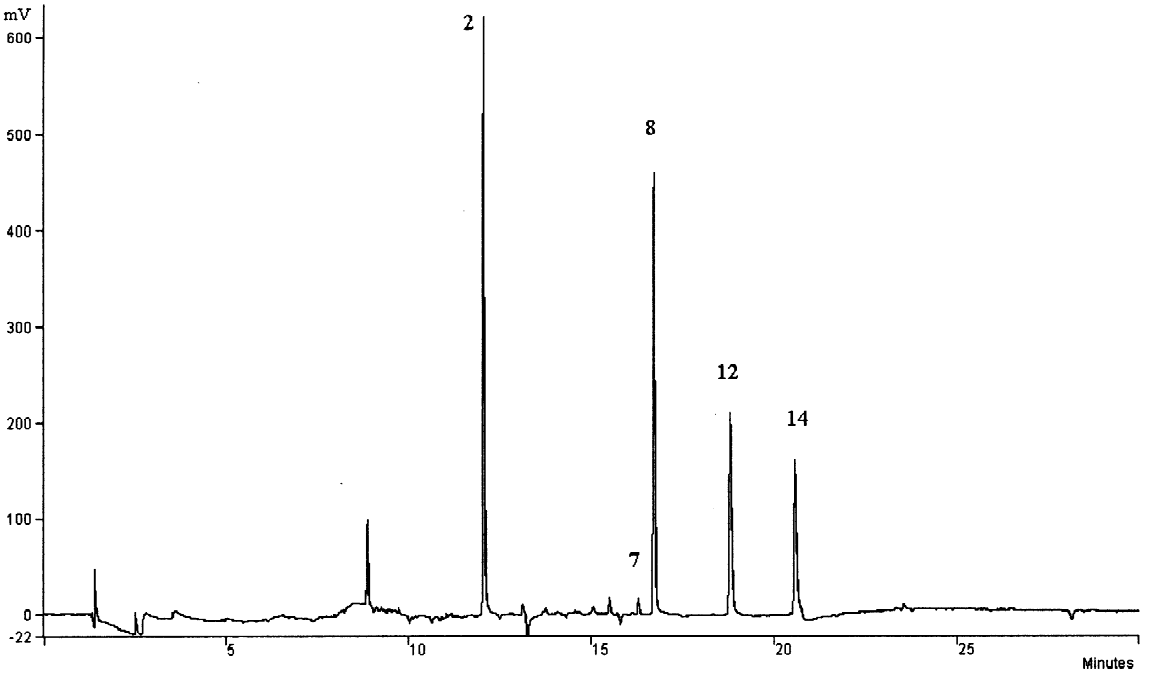

Fig. 9. An ECD chromatogram representative of a real sample contaminated with the following concentrations of pesticides: (2) 0.182 μg l^{-1}, (7) internal standard, (8) 0.340 μg l^{-1}, (12) 0.252 μg l^{-1}, (14) 0.235 μg l^{-1}. For peak assignment refer to Table 1.

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