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Comparison of three different poly(dimethylsiloxane)–divinylbenzene fibres for the analysis of pesticide multiresidues in water samples: structure and efficiency

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Abstract

Despite the continuing development of SPME (solid-phase microextraction) fibre coatings, their selection presents some difficulties for analysts in choosing the appropriate fibre for a certain application. There are two distinct types of SPME coatings available commercially. The most widely used are poly(dimethylsiloxane) (PDMS) and poly(acrylate) (PA). Supelco has developed new mixed phases consisting of porous polymer particles, either poly(divinylbenzene) (DVB) or Carboxen suspended in a matrix of PDMS or Carbowax for extracting analytes via adsorption. In addition to the nature of the extracting phase, the thickness of the polymeric film must be taken into account and, surprisingly, the construction of the fibres when apparently they bear the same coating, as it is the case of the three PDMS–DVB fibres available. Other fibre structure properties not well explored were identified and must be taken into consideration. To elucidate their extraction efficiency, three PDMS–DVB fibres, namely 60 μm for HPLC use, 65 μm for GC use and 65 μm StableFlex for GC use, were compared with regard to the extraction of 36 compounds included in four pesticide groups. The first was particularly suited for the extraction of organophosphorus pesticides and triazines whereas the StableFlex exhibited advantages in the analysis of organochlorine pesticides and pyrethroids. An explanation for the extraction differences is suggested based on the different structure of the fibres. Detection limits in the range of 1–10 ng/l for organochlorine pesticides, 1–30 ng/l for organophosphorus pesticides, 8–50 ng/l for triazines and 10–20 ng/l for pyrethroids were attained in a method using the 60 μm PDMS–DVB fibre. The fibre maintains its performance at well above 100 extractions with between-day precision below 10%.

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

1. Introduction

Solid-phase microextraction (SPME) was first developed in 1989 at the University of Waterloo (Ontario, Canada) by Pawliszyn and co-workers and has been marketed since 1993 by Supelco. Since then the technique has grown enormously [1].

It can integrate sampling, extraction, concentration and sample introduction into a single uninterrupted process, resulting in high sample throughput. Its important features are its simplicity, low cost, rapidity, selectivity and sensitivity when combined with appropriate detection modes [1–3]. SPME has been applied to analyses in various fields, such as en-

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vironmental chemistry, forensic chemistry, pharmaceutical, food, beverage, and flavour [4–7].

SPME has been introduced as a modern alternative to traditional sample preparation technology. It eliminates the use of organic solvents, and substantially shortens the time of analysis and allows convenient automation of the sample preparation step [1,2,4,8,9].

Nowadays, in addition to the former general purpose poly(dimethylsiloxane) (PDMS) and poly(acrylate) (PA) coated fibres, a large number of fibre coatings based on solid sorbents are available, namely PDMS–divinylbenzene (DVB), Carbowax–DVB, Carbowax–templated resin (TR), Carboxen–PDMS and DVB–Carboxen–PDMS coated fibres. Extraction of analytes by the new porous polymer SPME fibres with mixed coatings is primarily based on adsorption rather than absorption [10,11]. The surface has a limited number of adsorption sites that can be occupied by the sorbate that, by definition, upholds in an immobile state, whereas when absorption is considered, diffusion into the bulk of the coating takes place and the properties of the coating remain unchanged until a significant amount of analyte is absorbed [10].

Diffusion coefficients of organic molecules into the bulk of DVB and Carboxen are so small that within the time interval of an SPME analysis, all the molecules probably remain attached to its surface. Otherwise, persistent carryover would be observed. Adsorption is therefore considered the only extraction mechanism for those coatings [10]. Furthermore, while absorption is a noncompetitive process, adsorption is by definition competitive [1]. The presence of matrix interfering compounds can affect both the amount extracted and the linear range of the method for porous polymer fibres [8,10].

Some of these porous polymer SPME fibres with bipolar characteristics can be very useful for the simultaneous analysis of pesticides enlarging the spectrum of the SPME applications [11]. One of the critical aspects on SPME optimisation is the selection of the appropriate fibre. Many aspects of the extraction mechanism and properties of the new polymeric coatings have not been completely described [11].

The aim of the present paper was to elucidate the different behaviour noted for the PDMS–DVB fibres proposed for GC use, HPLC use and StableFlex for GC use, in the analysis of 36 compounds included in four groups of pesticides: organochlorine, organophosphorus, pyrethroid and triazine pesticides, in water samples.

2. Experimental

2.1. Chemicals, reagents and equipment

The various pesticides were supplied by Riedel-de Häen (Seelze, Germany). Individual stock standard solutions of organochlorine pesticides [(1) hexachlorobutadiene (HCBD), (2) hexachlorobenzene (HCB), (3) lindane (LIN), (4) heptachlor (HEP), (5) aldrin (ALD), (6) isodrin (ISO), (7) heptachlor epoxide (HEE), (8) γ-chlordane (CLD), (9) endosulfan I (ENS I), (10) 4,4′-DDE, (11) dieldrin (DIE), (12) endrin (END), (13) endosulfan II (ENS II), (14) 4,4′-DDD, (15) endosulfan sulfate (ENSS), (16) 4,4′-DDT] were prepared in *n*-hexane, pyrethroids [(17) λ-cyhalothrin (CYH), (18) α-cypermethrin (CYP)] in ethyl acetate, and the organophosphorus pesticides [(19) dichlorvos (DIC), (20) dimethoate (DIM), (25) fonofos (FON), (26) diazinon (DIA), (27) parathion-methyl (PARM), (29) fenitrothion (FET), (30) malathion (MAL), (31) parathion (PAR), (32) chlorfenvinphos E (CLF E), (33) chlorfenvinphos Z (CLF Z), (34) tetrachlorvinphos (TET), (35) fenamiphos (FEM), (36) azinphos-methyl (AZI)] and triazine pesticides [(21) simazine (SIM), (22) atrazine (ATR), (23) propazine (PRO), (24) terbuthylazine (TER), (28) simetryn (SYN)] were dissolved in methanol. Four separate group mixtures were then prepared in methanol containing 2 mg/l 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 prepare the working aqueous solutions. The aqueous pesticide solution used for SPME experiments contained the following concentrations: 0.1 μg/l of organochlorine pesticides (OCPs), organophosphorous pesticides (OPPs) and pyrethroids, 1 μg/l of triazines and DIM and 0.01 μg/l of TET and CLD (used as internal standards). The analyte concentrations and SPME extraction

conditions were such as to give a regular peak height profile.

Chromatographic analyses were carried out in a Varian 3400 CX (Walnut Creek, CA, USA) gas chromatograph. The injector and detector temperatures were set at 250 and 310 °C, respectively. All compounds were resolved in a MDN-5 column (30 m×0.32 mm I.D.×0.25 μm film) (Supelco, Bellefonte, PA, USA) using helium as carrier gas and detected either by electron-capture detection (ECD) or thermoionic-specific detection (TSD) operating at 3.2 A intensity, as more convenient.

At the column exit an adjustable splitter (SGE Europe, Milton Keynes, UK) was interposed in order to give about a tenth of the effluent flow to the ECD system and the remainder to the TSD system. This instrumental configuration allowed quantitating all 36 pesticides in a single 30-min chromatographic run following a single extraction procedure.

2.2. SPME fibres and extraction conditions

The PDMS–DVB coating was selected in its three commercially available fibre types: 65 μm PDMS–DVB for GC, 60 μm PMDS–DVB for HPLC and 65 μm PDMS–DVB StableFlex for GC use. All SPME fibres (Supelco) used for manual sampling were new at the beginning of the study and were conditioned according to the suppliers' instructions.

Several SPME analyses of the aqueous pesticide solution were carried out with each of the fibres in order to collect the peak area data for each individual pesticide. Extractions were performed by immersion of the fibre in 3 ml of sample, with permanent stirring and temperature control at 60 °C. Neither pH adjustment nor ionic strength correction was needed. Analytes were allowed to adsorb onto the fibre at this fixed conditions for 30 min, and afterwards desorbed in the hot injection port of the gas chromatograph, for 5 min. Fibre blanks were also obtained in order to elucidate the contribution of the fibre to the interfering peaks appearing in the chromatogram.

3. Results and discussion

For a better understanding of the sorption mechanism and where it takes place in an adsorption type SPME fibre, especially the PDMS–DVB coated fibre, it would be worthwhile to know its configuration. Table 1 contains information related to the PDMS–DVB fibre structure in terms of different layers and thickness.

The PDMS–DVB coating volume and fibre surface area were calculated based on the data of the different layers and considering its cylindrical geometry.

As can be realised from the data presented, the PDMS–DVB coating is not directly attached to the fused-silica fibre. Instead, two layers of polymeric film acting as a support for the PDMS–DVB coating are inserted just below the thick porous polymer sorbent. The DVB polymer is suspended in a liquid phase, which promotes the adhesion of the sorbent to the fibre.

With the aim of comparing the extraction efficiency of the three apparently similar PDMS–DVB fibre types (differing only 5 μm in the coating thickness), six replicate extractions of the aqueous pesticide solution were made with each of the fibres.

Table 1
Structure composition of the three different PDMS–DVB porous polymer fibres available

	SPME fibre		
	PDMS–DVB 65 μm	PDMS–DVB, 60 μm	PDMS–DVB, StableFlex 65 μm
Fused silica core diameter (μm)	110	80	80
Polymer of core (μm)	0	40	20
PDMS precoat (μm)	5	0	5
PDMS–DVB coating thickness (μm)	65	60	65
Total diameter of fibre (μm)	250–260	280–290	260–270
PDMS–DVB coating volume (μl)	0.378	0.415	0.398
Fibre surface area (mm^2)	7.85	8.80	8.17

The entire experiment was conducted on the same day to avoid additional variation due to samples and equipment bias. With this procedure different results can only be attributed to different extraction efficiency of the fibres.

Figs. 1 and 2 display the results obtained, by representing the mean peak area for each of the pesticides and each of the fibres tested. Fig. 1 presents the results for the pesticides detected by ECD i.e. OCPs and pyrethroids, whereas Fig. 2 presents the results for the pesticides detected by TSD i.e. OPPs and triazines. Compounds were grouped by chemical family and detection system, which allows for easier comprehension of the general behaviour towards the different fibres.

Among the OCPs and pyrethroid pesticides, the StableFlex fibre gives significantly better results for 11 compounds. The fibre proposed for HPLC achieves the second best results for most of compounds, with the exception of LIN, which have a special affinity for this fibre resulting in a significantly better extraction. Considering the HCB and LIN molecular formulas it should be noted that they have a reversed extraction intensity when using a PDMS fibre (results not shown) or the present PDMS–DVB fibres, which highlights the advantage of using a different extraction mechanism.

When analysing OPPs and triazines using the three PDMS–DVB fibres, the chromatographic pattern completely changed. The PDMS–DVB fibre indicated for HPLC use is the chosen one, achieving significantly better results for eleven pesticides. This group contains the most problematic compounds so further considerations must be made. The triazine pesticides lack sensitivity when detected via TSD. Accordingly, the HPLC-indicated fibre should be used. The PDMS–DVB coating was demonstrated to be well suited for extracting many nitrogen containing analytes [12] particularly in the 60 μm form. Furthermore, the OPPs DIC and AZI require enhanced sensitivity, which can only be obtained using the HPLC-indicated fibre. In fact, AZI cannot be

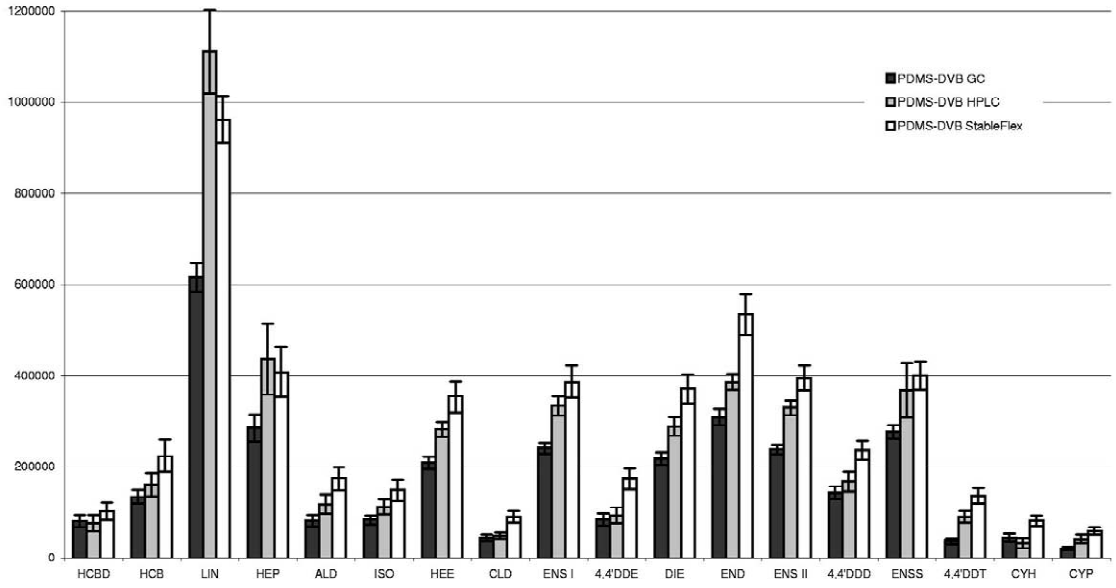

Fig. 1. Graphical display of mean peak areas ($n=6$) obtained for OCPs and pyrethroid pesticides (ECD) in a comparative study involving the three PDMS–DVB type fibres described in the experimental section. Error bars represent the confidence interval for the mean at 95% confidence level.

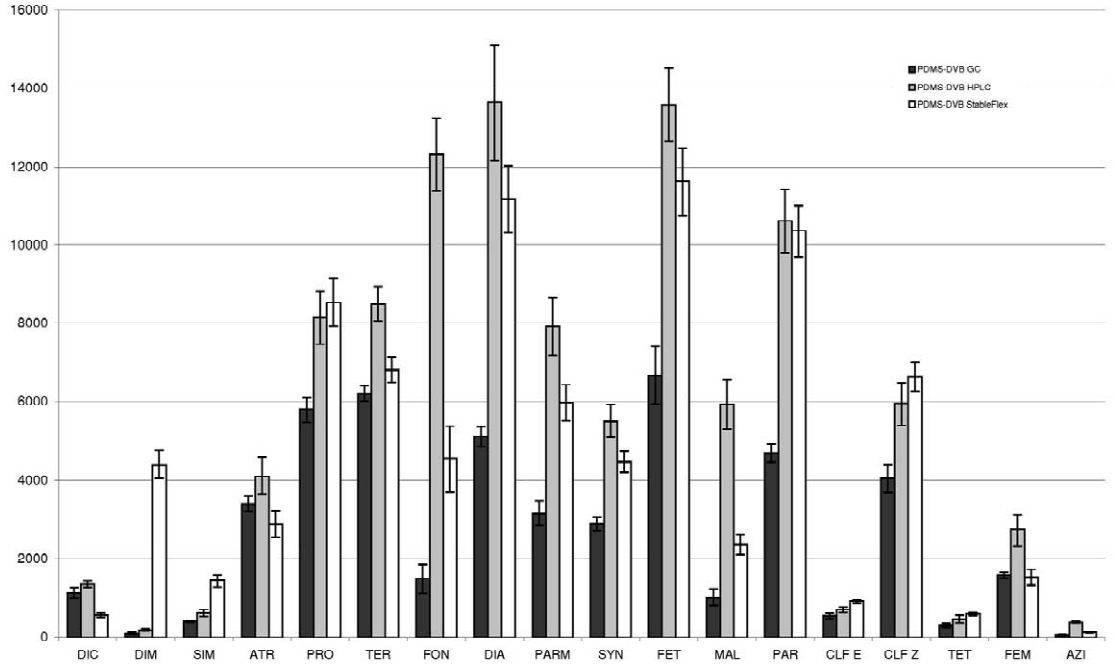

Fig. 2. Graphical display of mean peak areas ($n=6$) obtained for OPPs and triazine pesticides (TSD) in a comparative study involving three PDMS–DVB type fibres. Error bars represent the confidence interval for the mean at 95% confidence level.

detected at all using the GC-indicated fibre and is poorly extracted by the StableFlex fibre. Two more compounds require particular attention, namely FON and MAL. In these cases, the GC use and StableFlex fibres exhibit less than half analyte recovery when compared to the HPLC use fibre, as well as much variation between fibres of the same batch.

The overall mean variation between fibres of the same batch was determined to be 12.6; 25.5 and 39.1%, respectively, for the HPLC use, StableFlex and GC use fibres, with a great contribution for last two from the phenomenon mentioned above.

For some of the pesticides in Fig. 2, the StableFlex fibre would be acceptable, however it introduced several interfering peaks in the chromatogram, both in empty zones and co-eluting with target analytes. The qualitative and quantitative analysis of DIM and SIM is drastically disturbed.

The presence of interfering peaks, including the major 2,4-diisocyanate-1-methylbenzene (confirmed by MS) in the StableFlex chromatograms, even after repeated conditioning and runs, does not have any detrimental effect on the ECD chromatogram, unlike the TSD chromatogram. All fibres gave chromatograms which were easy to interpret, both in ECD and TSD detection, except for the StableFlex fibre which made TSD chromatograms more unreadable (see Figs. 3 and 4).

Using the PDMS–DVB HPLC fibre allows the simultaneous extraction of the 36 pesticides, with a single SPME procedure and analysed in a single chromatographic run with an instrumental configuration of coupled ECD–TSD. The advantages are obvious for the analysis of OPPs and triazines, while the analysis of OCPs and pyrethroids is not so demanding.

Despite the similarities between the fibres studied, namely fibre coating nature and thickness usually used as criterion for fibre selection [9], the information in Table 1 shows that great differences can be found which can explain their different extraction selectivities and efficiencies.

The PDMS–DVB HPLC use fibre is the one containing the larger volume of PDMS–DVB stationary phase. This fact may explain its improved adsorption capacity in the extraction of OPPs and triazine pesticides. Furthermore, this fibre has a thick polymer film directly attached to the silica core. This

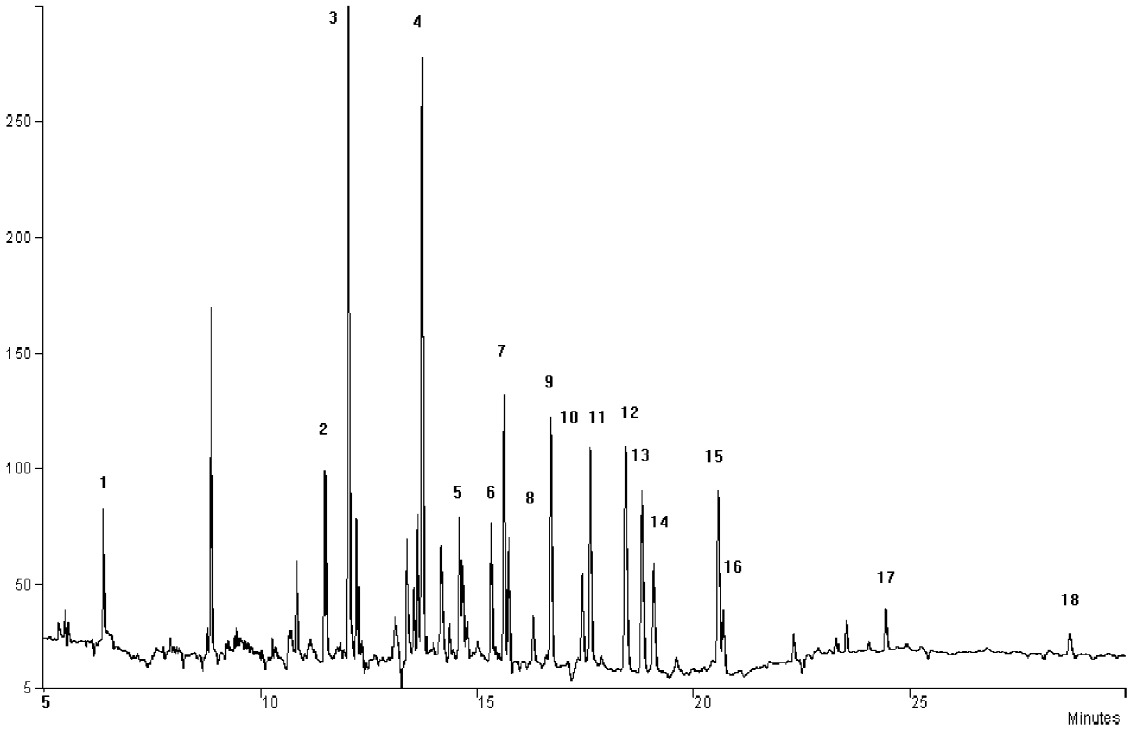

Fig. 3. Chromatogram acquired by ECD after SPME of an aqueous pesticide solution according to the procedure adopted in the Experimental section. The 60 μm PDMS–DVB fibre was used. For peak assignment refer to Section 2.

is a moderately polar polymer that may interact with analytes of close related polarity. Analytes with a certain degree of polarity like some OPPs and triazines can benefit from the existence of the polymer of core.

The 60 μm PDMS–DVB fibre is especially recommended for HPLC use due to its resistance to organic solvents because of the absence of the epoxy glue. However, it can also be used for GC analysis with thermal desorption and no damage was detected over a long usage period.

The organochlorine and pyrethroid pesticides are generally better extracted using the new PDMS–DVB StableFlex fibre. This fibre was the last of this type to be introduced, as an expanding improvement to all adsorbent type fibres. The thin coating of plastic on the fused silica makes the StableFlex fibre more flexible. The phase coating partially binds to the flexible core, which results in a more stable coating and less breakable fibre [12]. This fibre also contains a thinner moderately polar polymer of core together with 5 μm of PDMS precoat. This fact can be favourable to the extraction of nonpolar analytes but does not seem to be sufficient to justify the improved affinity of the StableFlex fibre for OCPs and pyrethroid pesticides. In any case, it was previously shown that the selectivity of StableFlex fibres may be slightly different to the same coating on a standard fused-silica core [12].

The PDMS–DVB fibre proposed for GC use has the lowest extraction ability for all the pesticides studied. It does not have a polymer of core and has the smallest PDMS–DVB coating volume and fibre surface area. As a bipolar adsorbent fibre, it maintains the extractions characteristics of the others but in a lower profile.

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 [11]. The benefits of mixed phases like PDMS–DVB in multiresidue pesticide analysis were noted [11,13].

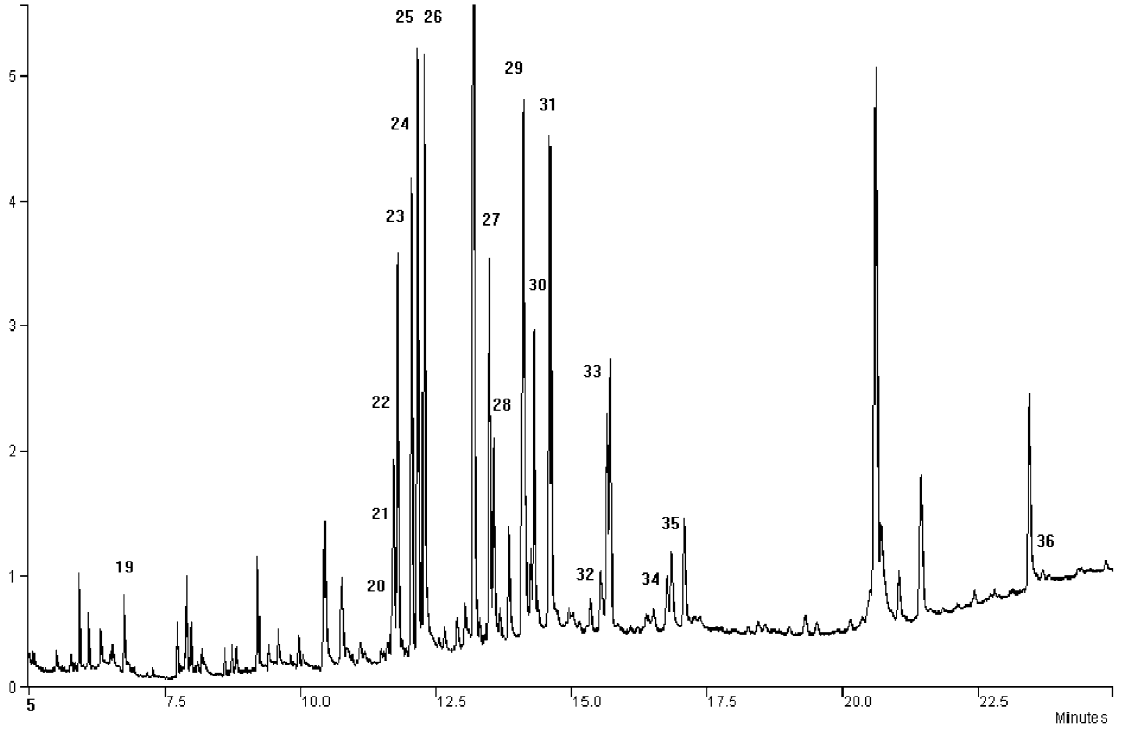

Fig. 4. Chromatogram acquired by TSD after SPME of an aqueous pesticide solution according to the procedure adopted in the Experimental section. The 60 μm PDMS–DVB fibre was used. For peak assignment refer to Section 2.

By extending the extraction time to 60 min, detection limits in the range of 1–10 ng/l for OCPs, 1–30 ng/l for OPPs, 8–50 ng/l for triazines and 10–20 ng/l for pyrethroid pesticides were attained using the reported 60 μm PDMS–DVB fibre. The fibre maintains its performance well for >100 extractions with between-day precision below 10%, using internal standard calibration.

4. Conclusions

Usually the process of fibre type selection is made based on the nature and thickness of the polymeric coating. In our study, involving three different PDMS–DVB coated fibres, we wanted to demonstrate that they do not have equal extraction efficiencies and there are other fibre structure properties that must be taken into consideration. Internal sublayers that exist in PDMS–DVB fibres can have an important role in the selectivity of the fibre towards small differences in the polarity of analytes.

The process of SPME fibre selection for a particular application cannot be entirely dependent on product information but based on a deep knowledge of inherent properties of the fibre. In our opinion this is another aspect be taken into account.

In our target group of 36 pesticides the 60 μm PDMS–DVB fibre gives the best combination of sensitivity fulfilling the requirements of the method for drinking and surface water analysis, according to EU Directives.

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