Active Sampling Followed by Solid-Phase Microextraction for the Determination of Pyrethroids in Indoor Air

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Abstract

A method based on solid-phase enrichment followed by headspace (HS)–solid-phase microextraction (SPME) is optimized to determine pyrethroids in air. By active sampling, pyrethroids present in air are retained in 25 mg of activated florisil and then transferred from the solid sorbent to an SPME fiber in the HS mode. A small volume of solvent is added to the adsorbent to favor this process. The selection of the adsorbent, as well as the optimization of certain parameters affecting the SPME, is performed using an experimental design strategy. Linearity is studied by external calibration in a wide range of concentrations using gas chromatography coupled to three different detection systems: electron capture detection, micro-electron capture detection, and mass spectrometry. An analysis of variance with a lack-of-fit test is run to validate the calibration data. Breakthrough of the adsorbent was studied sampling from 0.5 to 10 m^3 air, demonstrating that 1 m^3 air could be sampled without losses of pyrethroids. Quantitative recoveries are obtained at three concentration levels, with adequate repeatability. Limits of detection of the method are estimated at the sub-ng/m^3 level in most cases, well below the regulatory limits. Finally, several real indoor samples are collected and analyzed by the proposed method. Identification and quantitation of all target analytes present in the room air are possible.

Introduction

Pyrethroids are synthetic insecticides, derivatives of the chrysanthemic acid, that have been produced based upon the structure of natural pyrethrins. They have been developed to enhance the biological activity of pyrethrins, being more stable in the environment. They have been increasingly used in the place of more toxic pesticides, such as organophosphate and organochlorine insecticides. Pyrethroids are widely spread throughout the environment to control pest insects in agriculture (e.g., cypermethrin, λ-cyhalothrin, cyfluthrin, permethrin, and deltamethrin), homes (allethrin, phenothrin, tetramethrin, and cyphenothrin), and as a topical head lice treatment (permethrin). Inhalation is an important route of exposure to these chemicals, especially indoors in poorly ventilated areas just after spraying or in closed agricultural areas. Overexposure to pyrethroids in humans could affect the central nervous system, causing seizures and paresthesias. The U.S. Environmental Protection Agency has classified some pyrethroids as possible human carcinogens and some of them are suspected to act as endocrine disruptors (1). The Occupational Safety and Health Administration has established a permissible exposure limit of 5 mg/m^3 in workplace air (2). Commercial insecticides available for use in today's market are often formulated with oils or petroleum distillates and are combined with other compounds known as synergists (like piperonyl butoxide) to enhance their insecticidal activity, or they are mixed with fungicides, such as 2-phenylphenol, or with other pesticides, like propoxur (a carbamate pesticide).

Currently, developing fast and simple methods to analyze the low concentrations of pollutants in air is a continuous challenge for the scientific community. Calibration of methods is also a hard and expensive task because of the difficulty of generating standard mixed gaseous matrixes or vapor-saturated air samples.

Some pyrethroids have been determined in air before, mainly together with other pesticides, taking part in multicomponent methods (3–5). In these methods, pesticides are usually collected from air into solid sorbents and then extracted using large volumes of solvents, meaning that long, tedious clean-up and concentration stages of the resulting extracts are required later .

Solid-phase microextraction (SPME) is a solvent-free preparation technique developed by Pawliszyn et al. (6). A partition between the fiber coating and the analytes from the sample is established in an equilibrium process. Working in nonequilibrium conditions under the same experimental conditions allows shorter extraction times because the analytes are not quantitatively extracted. Direct exposition of the SPME fiber to air has been applied for the sampling and analysis of some volatile organic compounds in indoor air (7).

Until now, several pyrethroids have been analyzed using SPME

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in matrices like water (8–13), fruits, or vegetables (8,14), but as far as the authors know, only Ferrari et al. (15) have proposed a method based on the SPME technique for the monitoring of a pyrethroid (bioallethrin), among other kinds of pesticides, in confined atmospheres.

Saba et al. (16,17) have proposed a sorbent-enrichment step followed by headspace (HS)–SPME to determine benzene and toluene in air using Tenax as the adsorbent. Recently, the authors have optimized the combination of solid-phase extraction (SPE)–SPME to analyze volatile and semivolatile polychlorobenzenes and polychlorinated biphenyls in indoor air (18,19).

The aim of this paper is to demonstrate that the combination of both SPE and SPME techniques can be useful to develop a method rapid and sensitive enough for the determination of several common pyrethroids, as well as other compounds that can be currently found in commercial formulations, such as piperonyl butoxide, propoxur, and 2-phenylphenol, in air. The selection of the adsorbent and some parameters affecting the SPME step has been carried out using an experimental design strategy, allowing the simultaneous optimization of factors and the study of possible factor interactions. Performance of the proposed method is studied in terms of linearity, precision, and recovery. Limits of detection were found at the sub-ng/m^3 level for all the target analytes using gas chromatography (GC) with micro-electron capture detection (μECD). The method was applied to some contaminated indoor air samples in which some of the target compounds could be determined.

Experimental

Reagents

2-Hydroxybiphenyl (2-phenylphenol), cyphenothrin (mixture of *cis* and *trans* isomers), allethrin (mixture of stereo isomers), transfluthrin, empenthrin, cyfluthrin (mixture of isomers), piperonyl butoxide, tetramethrin, permethrin (mixture of *cis* and *trans* isomers), phenothrin (mixture of isomers), propoxur, and λ-cyhalothrin were of pestanal grade and were supplied by Riedel-de-Haën (Seelze, Germany). Cypermethrin (mixture of isomers) and deltamethrin were purchased from Supelco (Bellefonte, PA). All organic solvents (acetone and *n*-hexane) were of pesticide grade and were provided by Merck (Mollet del Vallés, Barcelona, Spain).

Standard stock solutions of 9000–11000 μg/mL of individual samples were prepared in acetone, and a stock mixture solution of all reagents at a concentration of 100 μg/mL was obtained by appropriate dilution of standard solutions of individual samples in acetone. Working solutions were prepared by appropriate dilution in hexane. All solutions were stored in amber-colored vials at –20°C.

Air sampling and extraction of pyrethroids

To collect pyrethroids from air, a known volume of air was forced to pass through a glass tube containing a small amount (25 mg) of activated florisil adsorbent of 60–100-μm mesh (Aldrich, Steinheim, Germany), using a model S-8 vacuum pump (Telstar, Tarrasa, Spain). Florisil is activated overnight in an oven at 105°C. Some experiments were performed using 25 mg of Tenax TA of 60–80-μm mesh (Supelco) as adsorbent instead of florisil. To avoid external contaminations, only Teflon (PTFE) tubing was used for the connections. The adsorbent, enriched with the target analytes, was then transferred to a 10-mL glass vial and sealed with an aluminium cap furnished with PTFE-faced septum. The vial was placed into a water bath at 100°C. Vials should be immersed up to the neck in the thermostated water bath to achieve good repeatability. Then, the compounds retained by the adsorbent were extracted by exposing an SPME fiber to the HS of the vial (HS–SPME) for a fixed period of time. To favor desorption of the analytes from the adsorbtion to the HS of the vial, a small volume of an organic solvent (100 μL of acetone) is generally added to the adsorbent before the SPME fiber. As soon as SPME was completed, the fiber was inserted into the injector port, and pyrethroids were desorbed in to the GC for 5 min.

To study the retention efficiency of pyrethroids on the adsorbent, as well as the optimization of the experimental extraction conditions, 100 μL of standard mixtures of the analytes in hexane were directly spiked onto the adsorbent. The sample was then left to homogenize at 5°C for 4 h. The spiked adsorbent was treated as described previously. If necessary, those vials containing spiked adsorbent could be stored without losses at –20°C during a period of a few days.

To detect a possible breakthrough, some experiments required the coupling of a second glass tube filled with 25 mg of adsorbent (acting as a blank) after the first spiked one. Both portions of adsorbent were individually extracted following the experimental procedure described in this section. If breakthrough occurred, analytes should also be collected in the second tube.

SPME manual holder and fibers were obtained from Supelco. Five different SPME fiber coatings were used in this work: 65 μm carbowax (CW)–divinylbenzene (DVB), 75 μm carboxen (CAR)–polydimethylsiloxane (PDMS), 65 μm PDMS–DVB, 100 μm PDMS, and 85 μm polyacrylate (PA).

GC analysis

Several pieces of equipment were used, mainly depending on the sensitivity required to carry out the analysis by GC.

GC with conventional electron capture detection (ECD) analysis was performed in a Hewlett Packard 5890 Series II-Plus GC system (Hewlett Packard, Palo Alto, CA) equipped with a split/splitless injector and operated by Hewlett Packard Chemstation software. A Factor-Four capillary column VF-5MS (30 m × 0.25-mm i.d., 0.25-μm film thickness) (Varian, Walnut Creek, CA) was used for the separation of pyrethroids. Nitrogen was employed as the carrier and make-up gas with a constant flow of 1.1 mL/min (12 psi at 60°C) and 40 mL/min, respectively. The detector temperature was maintained at 280°C.

GC–μECD analysis was performed using an Agilent 6890N Network GC System (Agilent Technologies, Palo Alto, CA), operated by GC Chemstation software (Agilent) and equipped with a split/splitless injector. An HP-5 column (30 m × 0.32-mm i.d., 0.25-μm film thickness) was used to separate the pyrethroids. Helium was employed as the carrier gas at a constant pressure of 12 psi (flow of 2.5 mL/min at 60°C) and nitrogen as make-up gas at a constant flow of 60 mL/min.

GC–mass spectrometry (MS) was performed using a Varian

3800 GC equipped with a Varian Saturn 2000 ion trap mass detector, operated by Saturn GC–MS WorkStation V 5.4 software. Also, a Varian 3400 GC equipped with a Saturn 3 ion trap mass detector was used, operated by Saturn version 5.4 software. Analytes were separated on a HP-5MS column (30 m × 0.32-mm i.d., 0.25 µm film thickness). Helium was employed as the carrier gas at a constant flow of 1.0 mL/min (8 psi at 60°C). Trap and transfer line temperatures were fixed at 220°C and 280°C, respectively. The MS was operated in the electron ionization mode at 70 eV. The mass range was scanned from *m/z* 70 to 270 in the full-scan mode with a delay time of 8 min.

Similar GC oven and injector temperatures were established for all equipment. The oven was initially set at 60°C and held for 2 min. Three rates of temperature increase were used: the first increase rate was 20°C/min to 230°C; second rate was 5°C/min to 270°C, with a 5-min hold; and the third rate was 5°C/min to 290°C. The total acquisition time was 27.5 min. The injector was set at different temperatures depending on the fiber used: 260°C (CW–DVB), 270°C (PDMS and PDMS–DVB) or 300°C (PA), and programmed to return to the splitless mode 2 min after the beginning of a run.

Chromatographic conditions were optimized to get a good separation of peaks. Figures 1 and 2 show the chromatograms of a standard mixture of the target analytes using GC–MS and GC–µECD, respectively. As can be seen, some of the compounds gave isomeric peak clusters.

Results and Discussion

First, studies were carried out to investigate the second part of the process, which is the transfer of analytes from the SPE adsorbent to the SPME fiber, in order to achieve maximum chromatographic response. To favor analyte sorbent desorption, the experiments were carried out at 100°C, and the extraction time was set at 30 min.

The influence of the factors involved in the SPME step was studied by means of a multifactor design; however, previously, five different fiber coatings (CW–DVB, CAR–PDMS, PDMS–DVB, PDMS, and PA) were tested. For all compounds, poor responses were obtained using CAR–PDMS. The CW–DVB fiber provided lower or similar results to PDMS–DVB, PDMS, or PA. Based on our experience, the CW–DVB fiber was discarded because of the low stability of its coating. Therefore, PA, PDMS–DVB, and PDMS fibers were included in an experimental design approach for further optimization together with other experimental factors.

A multifactor categorical design, which allows the simultaneous optimization of factors that could affect the SPME step, was selected. Table I summarizes the three factors involved in the design. As was mentioned previously, PDMS–DVB, PDMS, and PA were the fibers selected. Other factor included in the experimental design was the type of adsorbent used to retain analytes. Tenax TA was included in the study because of its ability to retain volatile and semivolatile compounds from air (18,19) and its fast desorption kinetics (20). In addition, some authors have reported that some pyrethroids were efficiently retained on activated florisil columns (21), and, thus, activated florisil has also been included. The third factor studied was the addition of solvent. The addition of a small amount of solvent have previously demonstrated to favor the transfer of compounds, such as polychlorobenzenes and polychlorinated biphenyls, to the SPME fiber (18,19). Taking this fact into account, the addition of a small volume of acetone (100 µL) to the adsorbent prior to SPME was also considered.

The design was performed in a single block of 12 runs, providing 2 error degrees of freedom (22). This design makes possible the study of main factors and second order interactions.

Table II shows the analysis of variance (ANOVA) for factors and interactions. A factor is significant when its *p*-value is lower than

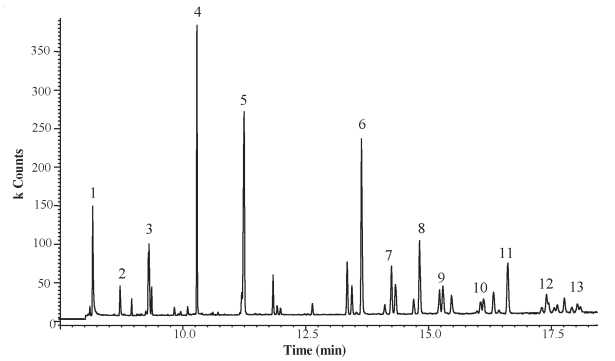

Figure 1. Total ion current chromatogram of a standard solution of the target analytes at 1 µg/mL. Peak identification: 2-phenylphenol, 1; propoxur, 2; empenthrin, 3; transfluthrin, 4; allethrin, 5; piperonyl butoxide, 6; tetramethrin (2 peaks), 7; phenothrin, 8; lambda-cyhalothrin (2 peaks), 9; cyphenothrin (3 peaks), 10; permethrin, 11; cyfluthrin (4 peaks), 12; and cypermethrin (4 peaks), 13.

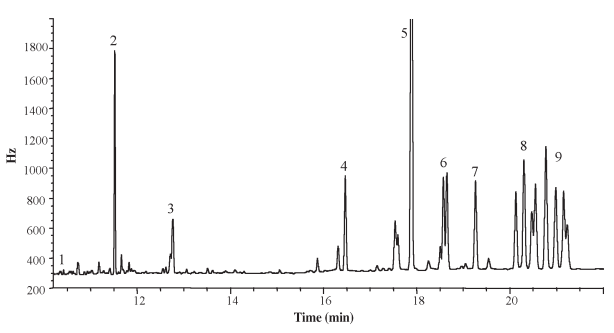

Figure 2. µECD chromatogram of a standard solution of the target analytes at 50 ng/mL (transfluthrin and allethrin at 5 ng/mL). Peak identification: empenthrin, 1; transfluthrin, 2; allethrin, 3; tetramethrin (2 peaks), 4; lambda-cyhalothrin, 5; cyphenothrin (3 peaks), 6; permethrin, 7; cyfluthrin (4 peaks), 8; and cypermethrin (4 peaks), 9.

Table I. Factors and Levels Considered in the Experimental Design

Factor	Code	Low level	Medium level	High level
Fiber	A	PDMS–DVB	PDMS	PA
Adsorbent	B	Tenax		Florisil
Solvent	C	Dry		Acetone

0.05 (at a 95% confidence level) or 0.10 (at 90%). As can be seen in Table II, taking into account the high *F*-ratios and low *p*-values, the addition of acetone was significant for the extraction of most of the pyrethroids as well as the type of adsorbent and the interaction type of adsorbent addition of solvent (interaction BC, Table II) at a 90% confidence level. The type of adsorbent used to retain the target analytes and the addition of solvent before SPME, as well as their interaction, should be studied in more detail because they seriously affect the microextraction procedure. The type of fiber coating and those factor interactions in which this factor takes place do not appear to be significant for the extracting process, with the exception of empenthrin and transfluthrin.

Figure 3 shows the type of adsorbent addition of solvent (interaction BC) graphs for two selected pyrethroids. Transfluthrin behavior represents the most volatile pyrethroids (empenthrin, transfluthrin, and allethrin). These compounds were poorly extracted from the dry adsorbent and the extraction was not dependent on the type of adsorbent used. Nevertheless, the remaining pyrethroids exhibited the behavior shown in Figure 3 for tetramethrin. This means that the best extraction conditions (highest responses) were achieved by adding acetone to florisil. However, poor responses were attained using both dry adsorbents or wet Tenax. Additionally, for most of these compounds, the type of adsorbent is a significant factor.

The effect of the addition of solvent and the fiber coating is represented in Figure 4 for transfluthrin and tetramethrin. For all pyrethroids, the best responses were attained when acetone was added to the adsorbent, and it was independent of the fiber used. Allethrin and transfluthrin show similar behavior. For these two compounds, PDMS had the lowest responses, whereas PA or PDMS–DVB conducted to similar results. However, for tetramethrin, the results are different, obtaining the highest responses with the PA fiber. The remaining pyrethroids present

Table II. ANOVA Showing the Significance of Main Effects and the Second Order Interactions

	A: fiber		B: adsorbent		C: solvent	
Compound	***F*-ratio**	***p*-value**	***F*-ratio**	***p*-value**	***F*-ratio**	***p*-value**
Factors						
Empenthrin	71.2	0.014	6.00	0.134	260	0.004
Transfluthrin	126	0.008	3.08	0.221	3311	0.000
Allethrin	3.01	0.249	0.80	0.466	24.5	0.039
Tetramethrin	1.14	0.468	10.0	0.087	12.3	0.073
λ-Cyhalothrin	1.04	0.491	18.1	0.051	19.8	0.047
Cyphenothrin	1.28	0.439	11.6	0.076	15.1	0.060
Permethrin	1.15	0.465	15.9	0.058	15.7	0.058
Cyfluthrin	1.62	0.382	6.73	0.122	7.76	0.108
Cypermethrin	1.81	0.356	8.19	0.104	9.70	0.090
	AB		**AC**		**BC**	
Compound	***F*-ratio**	***p*-value**	***F*-ratio**	***p*-value**	***F*-ratio**	***p*-value**
Interactions						
Empenthrin	0.54	0.647	66.5	0.015	23.2	0.041
Transfluthrin	1.10	0.476	117	0.008	7.80	0.108
Allethrin	0.99	0.503	3.07	0.246	0.78	0.470
Tetramethrin	1.02	0.496	1.07	0.484	9.99	0.087
λ-Cyhalothrin	1.01	0.498	1.02	0.495	18.0	0.051
Cyphenothrin	1.01	0.498	1.24	0.447	10.6	0.083
Permethrin	0.98	0.506	0.91	0.523	15.1	0.060
Cyfluthrin	1.18	0.460	1.23	0.448	6.46	0.126
Cypermethrin	1.13	0.469	1.46	0.406	7.64	0.110

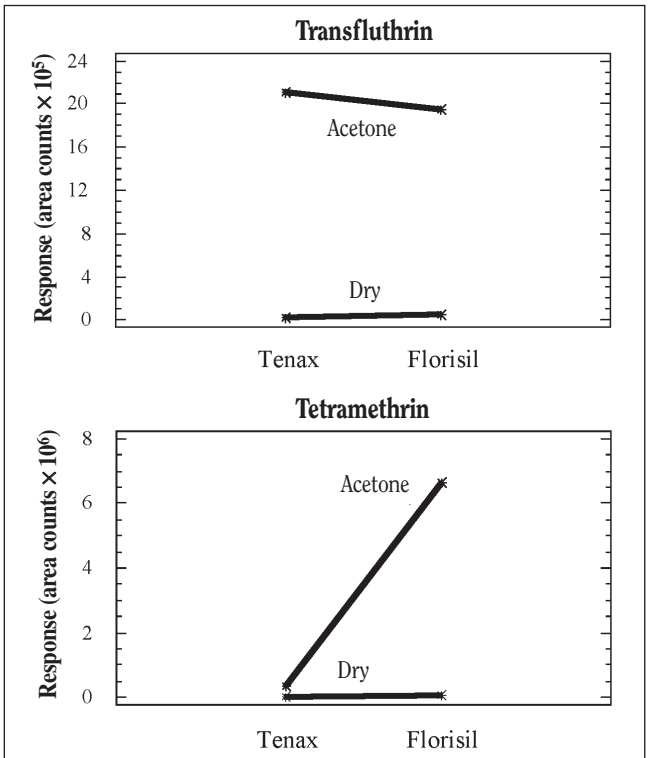

Figure 3. Influence of the factors type of adsorbent and addition of solvent for transfluthrin and tetramethrin.

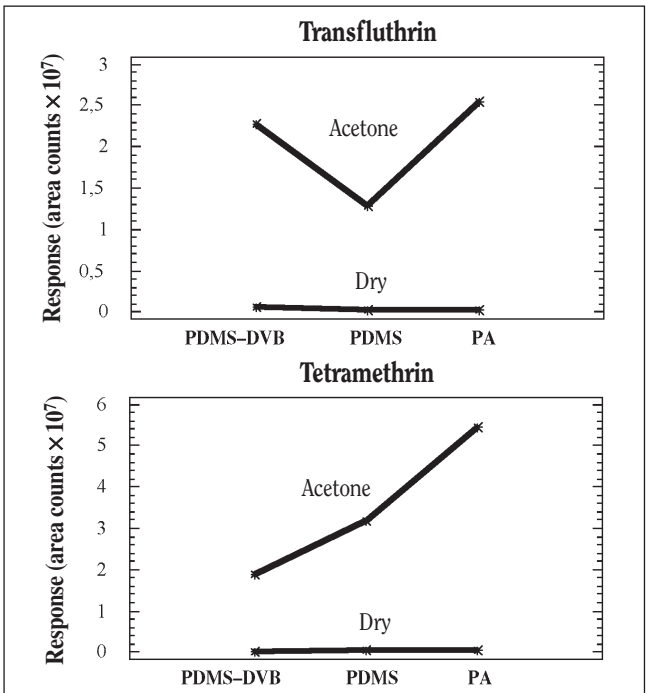

Figure 4. Influence of the type of fiber and addition of solvent for transfluthrin and tetramethrin.

similar behavior to that shown in the graph obtained for tetramethrin.

Figures 3 and 4 clearly confirm that the addition of a small volume of acetone to the adsorbent favor the pyrethroids extraction. Thus, after this study, optimal conditions can be summarized for further experiments as follows: the addition of acetone (100 µL) to florisil and the use of PA fiber.

A kinetic study was performed exposing the PA fiber to the HS of the vial in a range between 5 and 120 min. For transfluthrin and allethrin, equilibrium has been reached within a time of 15 min, but the remaining compounds have not reached equilibrium even after 120 min of extraction. Thus, analytical response for these compounds could be improved by exposing the fiber for longer extraction times. However, according to the total chromatographic run time (27.5 min), a short practical extraction time of 30 min was selected to extract pyrethroids quickly and with adequate responses to achieve good detection limits (see later in this paper).

After demonstrating that pyrethroids can be transfered to an SPME fiber and optimizing the SPME step, the sampling step using florisil as adsorbent was studied.

To evaluate if breakthrough occurred for the target analytes, preliminary experiments were performed by sampling 0.5 m^3 air through a tube containing florisil enriched with 100 ng of each of the target analytes to give an equivalent air concentration of 1000 ng/m^3. In these experiments, a second tube with clean florisil was placed consecutively acting as a blank. Both tubes were individually extracted by SPME in the optimal conditions and analyzed. The analytes were not found in the second tube, which demonstrated that breakthrough volume had not been reached. Next, experiments were focused on determining whether breakthrough of the adsorbent could take place by sampling volumes of air up to 10 m^3. The obtained results are shown in Figure 5. Responses were normalized to that obtained after sampling 0.5 m^3 air. This figure shows that a detriment in response was only observed for empenthrin, allethrin, tetramethrin, and cyphenothrin after sampling larger volumes than 1 m^3 air. It can also be seen that no breakthrough occurred for transfluthrin, λ-cyhalothrin, permethrin, cyfluthrin, and cypermethrin, even after sampling 10 m^3 air. Hence, a volume of 1 m^3 air was selected for a general method, although large volumes of air could be sampled for the remaining compounds, which would allow improving sensitivity for pyrethroids that did not show breakthrough.

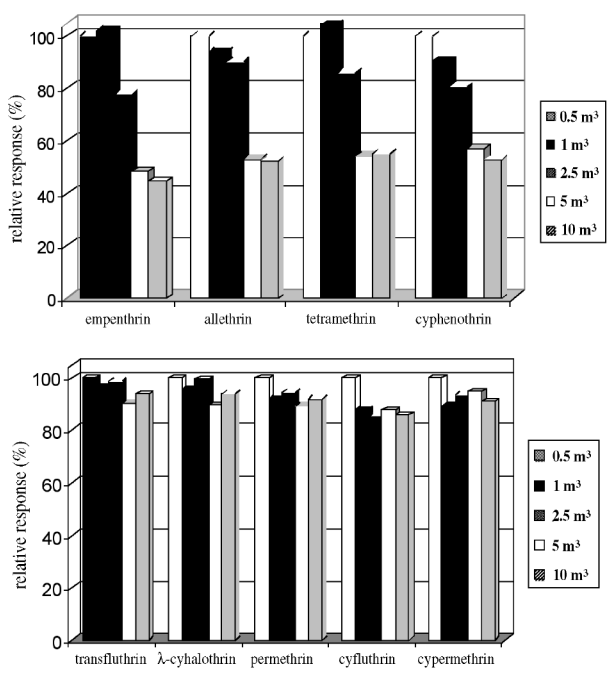

Figure 5. Variation of the chromatographic response with the volume of air sampled for the studied pyrethroids.

In summary, the proposed SPE–SPME method for the determination of pyrethroids in air involves pumping 1 m^3 air through 25 mg of florisil (SPE step). Then, after transferring the adsorbent to a glass vial, SPME of the wet adsorbent is carried out at 100°C for 30 min using PA fibers.

Performance of the method

In all the validation experiments, the results are referred to the sampling of 1 m^3 air. To assure blank samples, air blanks as well as adsorbent blanks were obtained in a clean room provided with a laminar flow system and analyzed before every set of experiments.

Some compounds other than pyrethroids are commonly present in commercial insecticide formulations. They can be found at high concentrations in air, so their determination together with pyrethroids could be of interest. Therefore, theperformance of the method developed for pyrethroid was also studied for 2-phenylphenol (fungicide), propoxur (carbamate pesticide), and piperonyl butoxide (pyrethroid synergist). It should be noted that MS detection was required for the study of these compounds, as well as for phenothrin, because these compounds showed negligible response by ECD.

Linearity of the method was evaluated by external calibration spiking of the adsorbent with known amounts of analytes and performing the determination using three different detection systems. This type of calibration proved to be valid for the quantitation of other pollutants, (18,19) and, as will be demon-

Table III. Linearity of the Method Using MS Detection

Compound	Quantitation ions	Correlation coefficient (*r*)	LOF test	
			F-ratio	*P*-value
2-Phenylphenol	169+170	0.9952	0.08	0.994
Propoxur	110+152	0.9954	0.58	0.716
Empenthrin	123	0.9966	0.41	0.831
Transfluthrin	163	0.9963	1.14	0.404
Allethrin	123	0.9978	1.46	0.300
Piperonyl butoxide	176	0.9954	2.15	1.174
Tetramethrin	164	0.9989	1.66	0.249
Phenothrin	123+183	0.9929	0.27	0.918
λ-Cyhalothrin	181+197	0.9900	3.31	0.075
Cyphenothrin	123	0.9926	1.65	0.264
Permethrin	183	0.9993	1.40	0.327
Cyfluthrin	163	0.9903	11.8	0.078
Cypermethrin	163	0.9910	0.78	0.564

strated later, it is also suitable for pyrethroid quantitation in air samples. For GC–MS determination, linearity was evaluated in a concentration range from 2 to 1000 ng/m^3 (20–1000 ng/m^3 for cyfluthrin and cypermethrin). The correlation coefficients (*r*) were higher than 0.99 (Table III). Linearity of the method using ECD detection was studied between 5 and 500 ng/m^3, except for transfluthrin and allethrin, which had high responses, allowing an estimation of linearity in a wide range between 0.5 and 500 ng/m^3. The lowest concentrations of pyrethroids were determined using a µECD detector. Linearity was estimated between 0.5 and 50 ng/m^3, except for transfluthrin, allethrin (from 0.05 to 50 ng/m^3), and empenthrin (from 5 to 50 ng/m^3). Correlation coefficients (*r*) were higher than 0.99 for all pyrethroids using both ECD and µECD detectors (Table IV). ANOVA was performed to validate all calibration models. The lack-of-fit (LOF) test indicates whether the model is adequate to describe the observed data or a more complicated model should be used. The test is performed by comparing the variability of the proposed model residuals to the variability between observations (chromatographic response) at replicate values of the independent variable (known concentration of compounds in the florisil samples). Tables III and IV show that *P*-values of the LOF test are greater than 0.05 for all compounds in the calibration range considered, which indicates that linear regression models were adequate for the obtained data at a confidence level of 95%.

Table IV. Linearity of the Method Using ECD and µECD Detection Systems

	ECD detection			µECD detection		
		LOF test			LOF test	
Compound	Correlation coefficient (*r*)	*F*-ratio	*P*-value	Correlation coefficient (*r*)	*F*-ratio	*P*-value
Empenthrin	0.9967	1.27	0.359	0.9998	0.06	0.943
Transfluthrin	0.9990	1.57	0.272	0.9907	0.01	0.999
Allethrin	0.9988	1.04	0.445	0.9945	0.15	0.924
Tetramethrin	0.9973	2.14	0.168	0.9957	0.05	0.948
λ-Cyhalothrin	0.9991	0.53	0.718	0.9989	0.08	0.928
Cyphenothrin	0.9969	1.94	0.197	0.9932	0.04	0.962
Permethrin	0.9977	4.45	0.067	0.9947	0.12	0.885
Cyfluthrin	0.9969	0.14	0.964	0.9950	0.06	0.946
Cypermethrin	0.9963	0.20	0.934	0.9977	0.34	0.723

Repeatability of the SPME process was studied at various concentration levels. Table V shows the RSD values (expressed as a percentage) obtained using GC–MS determination for samples containing 50 and 500 ng/m^3. The higher sensitivity of the µECD detection allows studying repeatability of the SPME process at lower concentrations. In Table V, the repeatability results at 5 ng/m^3 are also presented. Repeatability was considered satisfactory in all these cases because RSD values were, in general, lower than 15%.

Table V. Repeatability of the SPME Step

	RSD (%)		
Compound	5 ng/m^3 (*n* = 3)	50 ng/m^3 (*n* = 5)	500 ng/m^3 (*n* = 3)
2-Phenylphenol	–	6	2
Propoxur	–	8	7
Empenthrin	6	3	6
Transfluthrin	8	6	10
Allethrin	5	5	14
Piperonyl butoxide	–	8	19
Tetramethrin	7	8	15
Phenothrin	–	9	13
λ-Cyhalothrin	16	16	6
Cyphenothrin	14	11	8
Permethrin	7	19	9
Cyfluthrin	11	12	8
Cypermethrin	9	18	15

Recoveries of the target analytes using the complete SPE–SPME procedure were estimated at three concentration levels: 50 and 500 ng/m^3 using GC–MS detection and 5 ng/m^3 using µECD (Table VI). Recoveries (found/added concentration expressed as a percentage) were calculated for each compound sampled in 1 m^3 air. Using GC–MS determination, recoveries of pyrethroids ranged from 76% to 111% (RSD values were below 21%) for the low concentration level (50 ng/m^3) and from 76% to 119% for the high concentration level (500 ng/m^3) with RSD values below 18% (Table VI). Recovery of the proposed method was also evaluated for the nonpyrethroid compounds 2-phenylphenol, propoxur, and piperonyl butoxide, obtaining results ranging between 82% for 2-phenylphenol and 108% for piperonyl butoxide (RSD ≤ 11%) [for the lowest concentration level (50 ng/m^3)] and from 94% for 2-phenylphenol to 121% for propoxur (RSD ≤ 12%) [for the highest concentration level (500 ng/m^3)]. Using µECD detection, recoveries were estimated at 5 ng/m^3 and ranged from 89% to 105% with RSD less than or equal to 19%. Recoveries for transfluthrin and allethrin were calculated at 0.5 ng/m^3 and were 99% and 96%, respectively (RSD = 3%). Therefore, recovery was quantitative for all compounds, and precision of the total sampling-extraction method can be considered adequate. It is important to note that the

Table VI. Recovery of the Proposed SPE–SPME Method

	Recovery, % (%RSD)		
Compound	5 ng/m^3 (*n* = 3)	50 ng/m^3 (*n* = 5)	500 ng/m^3 (*n* = 3)
Empenthrin	99 (8)	77 (10)	76 (6)
Transfluthrin	99 (3)	101 (6)	101 (3)
Allethrin	96 (3)	80 (14)	85 (11)
Tetramethrin	91 (9)	76 (9)	91 (9)
λ-Cyhalothrin	104 (12)	104 (20)	119 (2)
Cyphenothrin	89 (19)	102 (20)	88 (10)
Permethrin	95 (9)	111 (21)	104 (11)
Cyfluthrin	105 (13)	105 (6)	113 (17)
Cypermethrin	96 (13)	92 (9)	114 (18)

sampling step does not introduce more variability to the results.

Limits of detection (LOD) (signal-to-noise ratio of 3) are presented in Table VII. LODs are strongly dependent on the detector used. The limits achieved were low enough to check for levels of pyrethroids established by many countries' regulations. The best LODs (< 0.080 ng/m^3 for most of pyrethroids) were determined by GC–μECD. Using this detector, LODs are well below those reported up to now for the determination of pyrethroids in air (3,4,15,23,24). Excellent detection limits were obtained, especially for transfluthrin and allethrin (≤ 2 pg/m^3). On the other hand, LODs for phenothrin and the non-pyrethroid analytes, which did not exhibit response in ECD, were estimated using GC–MS detection, obtaining an LOD of 0.27 ng/m^3 for phenothrin, but LODs for the nonpyrethroid compounds ranged from 0.042 ng/m^3 for 2-phenylphenol to 0.60 ng/m^3 for propoxur. In summary, GC–MS determination is very useful if a general detection of the compounds studied is required. Additionally, sensitivity could be enhanced by increasing the volume of air sampled, except for those compounds for which losses in the adsorbent were observed (Figure 5).

Table VII. LOD of the Proposed SPE–SPME Method

	LOD (s/n* = 3, ng/m^3)		
Compound	**GC–MS**	**GC–ECD**	**GC–μECD**
Empenthrin	0.046	4.6	2.1
Transfluthrin	0.055	0.083	0.001
Allethrin	0.092	0.20	0.002
Tetramethrin	0.20	0.45	0.027
λ-Cyhalothrin	1.5	0.87	0.076
Cyphenothrin	0.92	0.97	0.068
Permethrin	0.55	0.85	0.043
Cyfluthrin	7.1	4.6	0.24
Cypermethrin	3.7	2.3	0.19

* Signal-to-noise ratio.

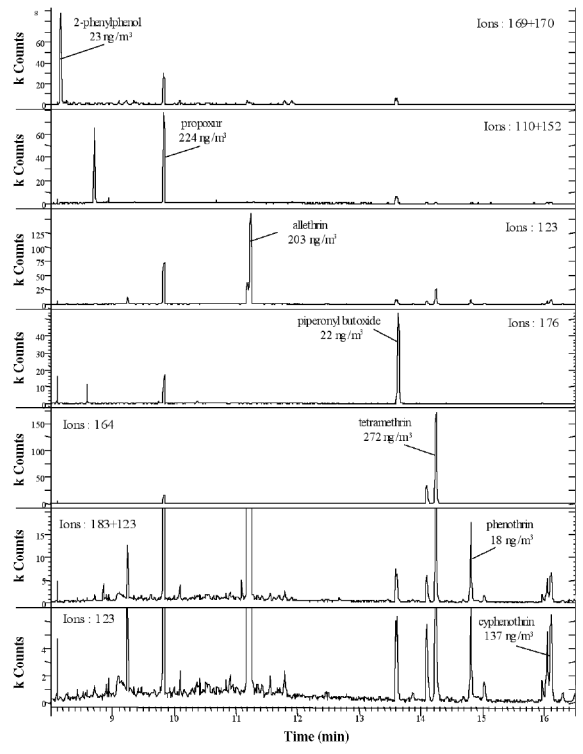

Figure 6. Extracted ion current chromatograms of a contaminated indoor air sample.

Finally, several real samples were collected in closed rooms treated with aerosols and electro-evaporators containing household insecticides commonly used in Spain. The proposed method allowed the determination of all the target compounds present in the contaminated room air. Three samples were taken at different times after spraying aerosols and activating an electro-evaporator containing allethrin. One sample was collected just at the moment of the application, and the two other samples were 60 and 150 min after application. Analysis was carried out by GC–MS, and the chromatogram, including the quantitation for one of these samples, is shown in Figure 6. An exponential detriment in the concentration of pyrethroids and nonpyrethroid compounds with the time from the application was observed. Nevertheless, the concentration of allethrin was maintained constant, probably because of a compensation between two different effects [i.e., dilution or deposition (or both) of the amount sprayed from aerosols and the concentration of the compound progressively diffused by the electro-evaporator]. A rapid reduction in the concentrations of allethrin and deltamethrin in ambient room air after an aerosol application was also reported by other authors (23). Some samples were also analyzed by GC–μECD. Because of the high sensitivity of this detector (Table VII), sample volumes of air as large as 1 m^3 are, in this case, not necessary. Thus, samples from 50 to 250 L were collected in a room polluted with allethrin, tetramethrin, cyphenothrin, permethrin, cyfluthrin, and cypermethrin and analyzed. Results showed a linear increase in the chromatographic response with the volume of air sampled ($r \geq 0.995$) for all compounds tested. Therefore, the analysis of these samples is also possible using the developed SPE–SPME method. In Figure 7, the chromatogram and the quantitation results obtained for one of these samples are shown. Other components of the household insecticides, such as fragrances (galaxolide and tonalide), pyriproxifen (an insect growth regulator), and butylated hidroxytoluene (BH) (a phenolic compound used as antioxidant) were also identified by GC–MS in the air samples analyzed by the proposed method.

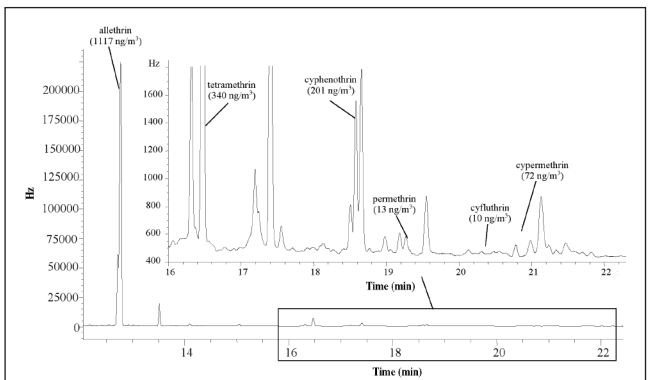

Figure 7. μECD chromatogram of a contaminated indoor air sample.

Conclusion

A method based on the combination of SPE and SPME for the analysis of pyrethroids in indoor air is proposed. Air is pumped through a very small amount of florisil to retain the target analytes. Then, SPME of the adsorbent is performed, followed by GC analysis. The optimization of some parameters affecting the microextraction process included an experimental design strategy. An important advantage of the method is that external calibration can be performed by direct spiking of the adsorbent with the analytes. Performance of the method was evaluated using different GC detection systems. Good sensitivity was achieved, especially when the determination is performed by GC–μECD. Additionally, the method was applied to real samples, and all of the insecticides present in air could be identified and quantitated. The proposed method is cheap, simple, environmentally friendly, and fast because active sampling is completed in 10 min, but extraction and determination of the pyrethroids takes 30 min each.

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