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Development of a gas chromatography–mass spectrometry method for the determination of household insecticides in indoor air

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Abstract

This work presents a GC–MS method for the determination of 17 household insecticides and acaricides in indoor air. Air samples were collected with a sampling train which consisted of a glass fibre filter and two polyurethane foam plugs, followed by a high-volume air pump. Filters and plugs were analysed separately. The overall recoveries ranged from 85 to 109% (4–11% RSD). Minimum method detection limits between 0.1 and 5 ng/m^3 were determined.

Keywords: Air analysis; Environmental analysis; Calibration; Pesticides; Organophosphorus compounds; Pyrethroids; Carbamates

1. Introduction

Insecticides and acaricides are commonly used to kill insects and for pest control operations. A wide variety of products for professional and private use are available on the market. In order to assess the possible health hazards to humans, multi-component analytical methods for determining these active substances in the indoor environment are urgently required.

The selection of investigated compounds was based on the ''Promulgation of Tested and Certified Disinfectants and Procedures for Pest Control'' according to §10c of the German Epidemic Law (Bundes-Seuchengesetz) [1].

An analytical method was developed for monitoring 17 insecticides and acaricides that were selected from the most important classes of pest control agents for indoor use in Germany. These included the following active substances: cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, fenvalerate, permethrin (pyrethroids); chlorpyrifos, dichlorvos, diazinon, fenitrothion, fenthion, malathion (organophosphates); diflubenzuron, propoxur (carbamates); chlorodecone, lindane (chlorinated pesticides) and piperonyl butoxide (insecticide synergist).

Several methods for sampling pesticides in air have been described previously in which the following sampling media were used: silica gel [2], Tenax [3–8], Chromosorb [3], XAD [9,10], extraction disks [11], polyurethane foam (PUF) plugs [3,5,12–16], air bags [17], impingers [18], impactors [18], glass fibre filters [9–12,15,18], and activated carbon or carbon fibre filters [19,20]. Common techniques like gas chromatography with electron capture (ECD), nitrogen–phosphorus (NPD), and mass spectrometry

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(MS) detection and HPLC with UV detection were used for identification and quantification.

In the studies cited above, methods for single compounds or compound classes (mainly organophosphates and chlorinated pesticides) were developed and validated. The objective of the present study was to develop a new method for the detection of important insecticides used indoors in Germany, particularly including the pyrethroids in addition to the different compound classes mentioned above, with sufficient sensitivity to detect these compounds at typical concentrations.

To achieve low detection limits, large volumes of air had to be collected. From the sampling media mentioned above, PUF plugs are particularly suitable for this purpose [12,13,15]. Therefore, a combination of glass fibre filters and PUF plugs as sampling media was chosen to collect both particle-bound and gaseous compounds. Investigations on the distribution characteristics of each compound between these two sampling media were made. GC–MS was applied as the detection method, providing good sensitivity and selectivity in multi-component analysis.

2. Material and methods

2.1. Chemicals

The following chemicals were obtained from Riedel-de-Haen, Seelze, Germany: chlorodecone (98%), chlorpyrifos (99%), cyfluthrin (98.2%), cypermethrin (95.8%), diazinon (98.8%), deltamethrin (99.8%), diflubenzuron (99.9%), dichlorvos (98.8%), ethyl acetate (Pestanal grade), fenitrothion (97.6%), fenthion (97%), lindane (99.9%), malathion (98.1%), permethrin (95.4%), piperonyl butoxide (98.8%) and propoxur (99.9%).

Cyhalothrin (98.5%) and fenvalerate (96%) were purchased from Dr Ehrenstorfer GmbH, Augsburg, Germany.

2.2. Equipment

2.2.1. Laboratory equipment

The following equipment was used: a Sonorex RK100H ultrasonic bath (Bandelin Electronic, Berlin, Germany), microliter pipettes and pipette tips (Eppendorf, Hamburg, Germany), silanized glass wool (Macherey-Nagel, Düren, Germany), glass beakers and Pasteur pipettes (Omnilab, Gehrden, Germany), 1- and 10-ml volumetric flasks from Omnilab and a Turbovap II Sample Concentration Workstation with 200-ml tubes (0.5 ml stem) (Zymark, Rüsselsheim, Germany).

2.2.2. Sampling equipment

The following equipment was used: a GS 050 sampling unit, consisting of a SPM-G sampling head (carrying a glass fibre filter and two PUF plugs) and a high-volume air pump (ca. 50 l/min) (Derenda, Berlin, Germany) (according to the German VDI-Norm 2463/7 [21]), glass fibre filters GF10, diameter 50 mm (Schleicher & Schüll, Dassel, Germany), PUF plugs, diameter 60 mm×5 cm (Klaus Ziemer, Mannheim, Germany). Plugs were pre-cleaned before use in a one liter Soxhlet extractor with acetone (16 h) and ethyl acetate (16 h) subsequently.

2.2.3. Instrument configuration and measurement parameters

An Agilent 6890 gas chromatograph, equipped with split/splitless-injector, Agilent 7683 autosampler and HP-5MS column (60 m length, 250 μm I.D., 0.25 μm d_f bonded phase of 5% diphenyl-/95% dimethylpolysiloxane on fused silica), was used with an Agilent 5973N mass-selective detector. Ionization mode was positive electron impact (EI), 70 eV at 230 °C. The injection port temperature was set to 250 °C, the transfer line temperature to 280 °C and the quadrupole temperature to 150 °C. Carrier gas flow was 1.4 ml/min helium (constant flow mode). The oven temperature programme was ramped from 60 °C (1 min holdup time) to 170 °C (10 °C/min) and finally to 280 °C (4 °C/min), with a holdup time of 25 min. The injection volume was 1 μl.

The MS system was run in the selected ion monitoring (SIM) mode. The following target and qualifier ions (m/z) were monitored: chlorodecone (272/237), chlorpyrifos (197/314), cyfluthrin (163/215), cyhalothrin (181/141), cypermethrin (163/127), diazinon (179/137), deltamethrin (181/93), dichlorvos (109/185), fenitrothion (277/125), fenthion (278/125), fenvalerate (167/125), lindane (181/219), malathion (173/125), permethrin (183/127), piperonyl butoxide (176/119), propoxur (110/152).

Under the given conditions, a reproducible decomposition of diflubenzuron in the injection port was observed that resulted in two thermal degradation products, i.e. *para*-chlorobenzene-isocyanate (153/90) and 2,6-difluorobenzene amide (141/157), which were also monitored. The underlined masses (m/z) in parentheses were used for quantification (target ions), and the other masses (m/z) were used for the confirmation of a specific compound (qualifier ions). Every compound was identified by retention time and target/qualifier-ion response ratio (with a maximum acceptable error of ±20%).

2.3. Preparation of standards and external calibration

The individual standard solutions (approx. 2 mg/ml) were prepared by weighing approximately 20 mg of a substance into a 10-ml volumetric flask and adding ethyl acetate up to the index mark. The standard mix solution (approx. 100 μg/ml) was made by transferring approx. 500 μl of an individual standard solution into a 10-ml volumetric flask and adding ethyl acetate up to the index mark. Stock standard solutions were obtained by diluting the standard mix solution with ethyl acetate. For the *matrix-matched calibration*, a volume of 10 m^3 of pesticide-free air from an indoor environment was drawn through the glass fibre filters and PUF plugs, respectively, and their ethyl acetate extracts were used for the dilution of the mixed standard solution. Calibration was carried out with standard stock solutions ranging from 0.1 to 2.0 μg/ml.

2.4. Sample preparation

2.4.1. Extraction of glass fibre filters

The filter was cut into pieces with a pair of scissors, transferred to a glass beaker and extracted three times with approx. 10 ml ethyl acetate for 5 min in an ultrasonic bath. The combined extracts were reduced to 0.5 ml with a gentle flow of nitrogen (Turbovap) and filtered through a 1-ml pipette tip plugged with silanized glass wool. After washing the tip with approximately 0.4 ml of ethyl acetate, the final volume was adjusted to 1 ml.

2.4.2. Extraction of PUF plugs

Each plug was placed in a 600-ml glass beaker, allowed to soak in approx. 50 ml of ethyl acetate and squeezed periodically with a 300-ml glass beaker during a 2-min extraction in an ultrasonic bath. This procedure was repeated three times. The combined extracts were treated in the same way as the filter extracts.

2.4.3. Recovery studies

First, the recovery rates of the analytes on filters and PUF plugs were investigated separately, both with and without the throughput of air (10 m^3). Fortification of the filters was made by pipetting a 100-μl volume of standard solution onto the center of the filter, allowing the solvent to soak into the filter and evaporate prior to analysis. PUF plugs were fortified by injecting the standard solution into the plugs with a 100-μl syringe.

Then, the overall recoveries on the complete sampling unit (filter and two PUF plugs) were determined by spiking the filter and drawing 10 m^3 of pesticide-free air, as confirmed by analysis of blank samples, through the sample head. Spiking level was 1 μg absolute. Filter and PUF plugs were extracted and analysed separately.

2.4.4. Indoor spraying experiment

An indoor spraying experiment was made to check the method and generate application samples. A model room was sprayed with 10 ml of a standard mix solution (100 μg/ml) in light petroleum–acetone (90:10, v/v) during a 10-s period. The total air volume of the model room was approximately 41 m^3. Thus, the initial concentration of each compound immediately after spraying was 244 μg/m^3 assuming a homogeneous distribution. The room was furnished with a sofa, two tables, three chairs, a bookshelf and a cupboard and had a window for daylight and ventilation purposes. The room was equipped with linoleum type flooring. The walls and ceiling were made of plaster coated with white paint. Air sampling was started 30 min after spraying (sample a), collecting a volume of about 4.1 m^3. A second air sample was drawn after 1 week, without intermediate venting of the room. This time, approximately 10 m^3 of air was collected (sample b).

Temperature and humidity were 25 °C and 45% in both cases.

3. Results and discussion

3.1. Validation of the GC–MS method

The total ion current (TIC) chromatogram (SIM mode) of the mixed standard solution is shown in Fig. 1. All components are baseline-separated. Analytes that showed two or more isomers in the chromatogram were integrated by peak summing.

Reproducibility was checked by injecting a mixed standard solution (1 μg/ml) 20 times. Relative standard deviations were found to be ≤0.1% for retention times and ≤10% for the concentration values.

For monitoring the investigated compounds in the SIM mode, the two most intensive mass peaks of each compound's mass spectrum, obtained in the scan mode, were usually used. In the case of piperonyl butoxide, the qualifier mass of m/z 149 was replaced because of interferences with phthalate-type plasticizers. The qualifier masses of cyfluthrin (m/z 206) and deltamethrin (m/z 253) were also replaced, because they were characteristic of the bleeding of the GC column. Ions with m/z 119 (piperonyl butoxide), 215 (cyfluthrin) and 93 (deltamethrin) were used instead. The calibration curves exhibited a very small linear range at low levels. Correlation coefficients ranged from 0.980 to 0.998 for levels from 0.1 to 1.0 and 1.0 to 2.0 μg/ml, respectively. For reasons of convenience, calibration was carried out with quadratic calibration functions for levels from 0.1 to 2.0 μg/ml, yielding correlation coefficients greater than 0.997.

3.2. Recovery studies

In the beginning, quantitative analysis was carried out using calibration curves obtained from pure

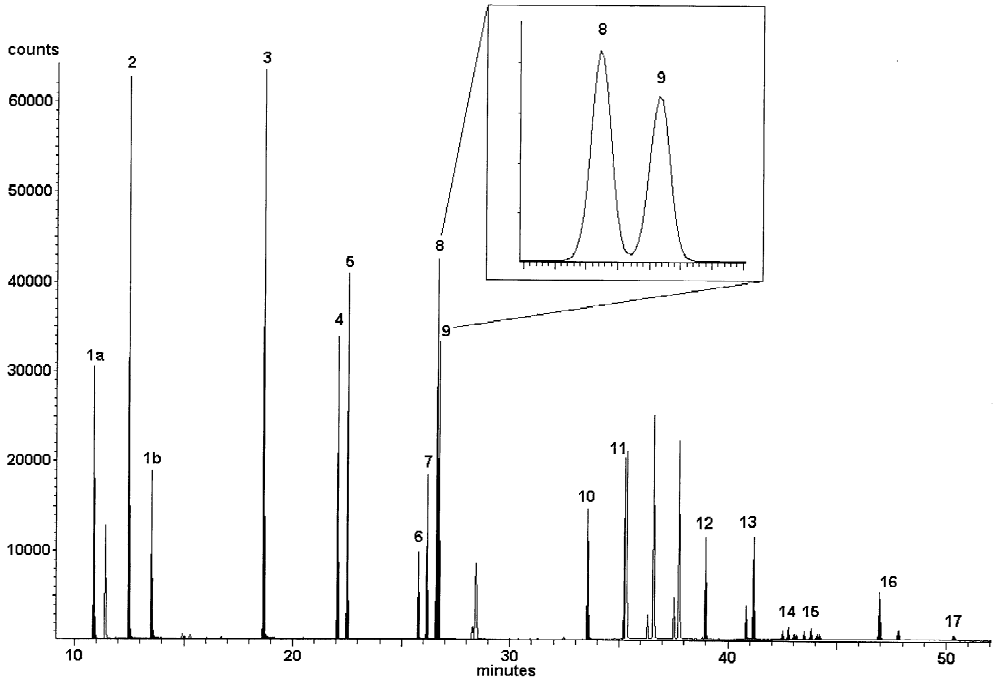

Fig. 1. TIC chromatogram (SIM mode) of the mixed standard solution (1 μg/ml) in ethyl acetate; *p*-chlorobenzene-isocyanate (1a), 2,6-difluorobenzene amide (1b), dichlorvos (2), propoxur (3), lindane (4), diazinon (5), fenitrothion (6), malathion (7), fenthion (8), chlorpyrifos (9), chlorodecone (10), piperonyl butoxide (11), cyhalothrin (12), permethrin (13, two peaks), cyfluthrin (14, four peaks), cypermethrin (15, four peaks), fenvalerate (16, two peaks), deltamethrin (17); non-assigned peaks are not discussed in this publication.

standard solutions (ethyl acetate only). In fact, some components showed excessive recovery rates of up to 150%. Since no blank values of the investigated compounds were found, this can only be caused by a ''matrix enhancement effect'', more precisely described as ''matrix-induced chromatographic response enhancement'', which was reported previously [11,22,23]. It is explained by the blocking of active sites in the injection port due to sample matrix, resulting in reduced analyte loss during injection and higher response values of the measured components.

3.2.1. Recovery rates on glass fibre filters

Recovery rates of spiked filters ranged from 76 to 133% (5–10% RSD, $n=9$) when using pure standard solutions. The following analytes tended to give high recoveries on filters: the diflubenzuron fragment molecules, propoxur, piperonyl butoxide, diazinon, malathion, fenvalerate and permethrin (115–133%).

Using matrix-matched calibration, recoveries between 87 and 118% (3–9% RSD, $n=9$) were achieved. Exception: dichlorvos is a relatively volatile compound (vapour pressure 1.6 Pa at 20 °C) with a poor recovery rate of 42%. Furthermore, it was determined which analytes remained trapped when a volume of 10 m^3 of air was drawn through the filter. Chlorpyrifos, diazinon, dichlorvos, lindane and propoxur could not be retained at all, whereas fenitrothion, malathion and fenthion were partially retained. This is in good agreement with previously published data using quartz fibre disks [11]. The other compounds showed good recoveries (93–106%, 4–6% RSD, $n=6$, matrix-matched calibration). The results are listed in Table 1.

3.2.2. Recovery rates on PUF plugs

Recovery rates of spiked plugs ranged from 65 to 124% (6–12% RSD, $n=6$), when using pure standard solutions. After air had been drawn through the plugs, the recoveries even increased by 82–150%. This result shows that both PUF and air matrix enhance response levels. In particular, fenitrothion, malathion, piperonyl butoxide, cyhalothrin, fenvalerate and permethrin tended to give high recoveries (126–150%) on PUF plugs.

Using matrix-matched calibration, recoveries between 89 and 107% (5–9% RSD, $n=4$) were achieved. Exception: dichlorvos (65% without air throughput). This is due to its relatively high volatility as mentioned above. Once again, it was determined which analytes remained trapped when a

Table 1
Mean recoveries (R_m) and relative standard deviations (RSD) in percent on glass fibre filters

Peak no.	Compound	R_m (A)	(RSD, %)	R_m (B)	(RSD, %)
1a	*p*-Chlorobenzene-isocyanate	87	(9.3)	93	(4.4)
1b	2,6-Difluorobenzene amide	118	(9.6)	104	(3.7)
2	Dichlorvos	42	(5.8)	n.d.	–
3	Propoxur	107	(3.2)	n.d.	–
4	Lindane	102	(2.9)	1	(0.0)
5	Diazinon	103	(3.1)	n.d.	–
6	Fenitrothion	109	(2.8)	50	(8.9)
7	Malathion	112	(3.1)	60	(7.5)
8	Fenthion	106	(8.8)	19	(12.9)
9	Chlorpyriphos	101	(3.5)	n.d.	–
10	Chlorodecone	109	(2.5)	106	(3.7)
11	Piperonyl butoxide	111	(3.3)	95	(5.5)
12	Cyhalothrin	110	(3.3)	104	(4.1)
13	Permethrin	107	(2.9)	105	(5.0)
14	Cyfluthrin	104	(3.5)	102	(5.3)
15	Cypermethrin	107	(2.9)	102	(4.9)
16	Fenvalerate	108	(3.1)	104	(4.9)
17	Deltamethrin	107	(4.9)	104	(5.3)

(A) No air was drawn through the filter ($n=9$); (B) 10 m^3 of air was drawn through the filter ($n=6$); n.d. not detected (matrix-matched calibration).

volume of 10 m^3 of air was passed through the plug. All compounds except dichlorvos were retained well, with recoveries from 73 to 116% (5–11% RSD, $n=4$, matrix-matched calibration). The results are listed in Table 2.

Dichlorvos was not trapped efficiently. Due to its high volatility, it evaporated during the spiking procedure, causing a loss of 35%, and after air had been drawn through the sampling unit, the remaining amount was reduced by 50% (33% recovery). Similar results for dichlorvos were found using a glass fibre filter followed by a tube filled with Tenax TA (40.2% recovery at a flow-rate of approx. 4.2 l/min, total air volume 1 m^3 [4]).

3.2.3. Overall recovery rates (filter and two PUF plugs)

As outlined in Section 2.4.3, the fortified filter was spiked with the standard mix solution (1 μg each compound). After evaporation of the solvent at room temperature, the filter and the two PUF plugs were placed in the sample head, through which 10 m^3 of air were drawn.

Using matrix-matched calibration, good recoveries between 85 and 109% (4–11% RSD, $n=5$) were obtained for all analytes except dichlorvos (39% recovery, 16% RSD). The results are listed in Table 3.

P-Chlorobenzene-isocyanate, 2,6-difluorobenzene amide, chlorodecone, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, fenvalerate, piperonyl butoxide and permethrin were completely trapped on the filter, so that no PUF plugs were needed for these agents. If the concentration of these analytes in air is very high (e.g. during spraying) or the sampled air volume exceeds 10 m^3, PUF plugs may become necessary to retain analytes which break through the filter. Dichlorvos cannot be retained efficiently on glass fibre filters or PUF plugs or a combination of both sampling media.

3.3. Instrumental and method detection limits (MDLs)

Instrumental detection limits, defined as a minimum signal-to-noise ratio of 3, ranged between 0.5 and 2.5 pg absolute for most compounds except fenvalerate (12 pg), cyfluthrin (42 pg), cypermethrin (47 pg) and deltamethrin (52 pg). Minimum method detection limits (mMDL) for sampling 10 m^3 of air and 1 ml final sample volume can be extrapolated from the instrumental detection limits assuming 100% recovery and the absence of blanks. The

Table 2
Mean recoveries (R_m) and relative standard deviations (RSD) in percent on PUF plugs

Peak no.	Compound	R_m (A)	(RSD, %)	R_m (B)	(RSD, %)
1a	*p*-Chlorobenzene-isocyanate	98	(4.6)	108	(5.3)
1b	2,6-Difluorobenzene amide	100	(5.0)	102	(5.4)
2	Dichlorvos	65	(19.6)	33	(26.8)
3	Propoxur	98	(5.8)	73	(9.5)
4	Lindane	89	(8.5)	85	(6.0)
5	Diazinon	100	(5.8)	87	(6.4)
6	Fenitrothion	102	(5.8)	90	(8.5)
7	Malathion	100	(5.7)	89	(6.6)
8	Fenthion	106	(8.8)	116	(7.7)
9	Chlorpyriphos	97	(4.8)	93	(6.0)
10	Chlorodecone	99	(5.7)	91	(7.2)
11	Piperonyl butoxide	106	(7.4)	93	(8.0)
12	Cyhalothrin	103	(5.8)	92	(9.6)
13	Permethrin	107	(6.2)	93	(9.4)
14	Cyfluthrin	99	(5.9)	90	(9.7)
15	Cypermethrin	98	(6.1)	92	(9.0)
16	Fenvalerate	104	(6.8)	92	(10.3)
17	Deltamethrin	102	(6.8)	94	(11.3)

(A) No air was drawn through the plug ($n=4$); (B) 10 m^3 of air was drawn through the plug ($n=4$) (matrix-matched calibration).

Table 3
Mean recoveries (R_m) and relative standard deviations (RSD) in percent in the overall recovery experiment

Peak no.	Compound	R_m	(RSD, %)	Filter (%)[a]	PUF1 (%)[a]	PUF2 (%)[a]
1a	*p*-Chlorobenzene-isocyanate	85	(11.4)	100		
1b	2,6-Difluorobenzene amide	109	(7.9)	100		
2	Dichlorvos	39	(15.6)		87	13
3	Propoxur	87	(8.8)	10	90	
4	Lindane	92	(5.1)	1	99	
5	Diazinon	97	(4.2)		100	
6	Fenitrothion	102	(6.2)	43	57	
7	Malathion	98	(4.8)	58	42	
8	Fenthion	88	(5.1)	21	79	
9	Chlorpyriphos	96	(2.8)		100	
10	Chlorodecone	105	(5.9)	100		
11	Piperonyl butoxide	99	(5.8)	100		
12	Cyhalothrin	106	(6.1)	100		
13	Permethrin	107	(5.7)	100		
14	Cyfluthrin	103	(5.4)	100		
15	Cypermethrin	102	(5.0)	100		
16	Fenvalerate	103	(4.7)	100		
17	Deltamethrin	98	(4.9)	100		

Air throughput: 10 m^3; matrix-matched calibration, $n=5$.
[a] Relative analyte distribution between the sampling media in the sampling unit.

corresponding calculated mMDLs are 0.1–0.3 ng/m^3 air for most compounds except fenvalerate (1 ng/m^3) and cyfluthrin, cypermethrin, deltamethrin (4–5 ng/m^3).

3.4. Indoor spraying experiment

An indoor spraying experiment, as described in Section 2.4.4, was carried out in order obtain indoor air samples containing all compounds of the multi-component method. The results are listed in Table 4. Approximately 13% of each analyte sprayed was found in the air 30 min after application (sample a). The remainder had already been deposited on surfaces and house dust. Sample b was collected 1 week later. Only small amounts of some components in the lower ng/m^3 levels were found in the air, presumably due to resuspended particles and thermal desorption from surfaces. Piperonyl butoxide was the only analyte that showed a higher concentration in the indoor air.

The relative analyte distribution in the sample unit of sample a was slightly different from the distribution obtained in the overall recovery studies, because 30 min after spraying, the analytes were still incorporated in aerosol droplets. These droplets were readily collected by the glass fibre filter, resulting in a distribution shift towards the filter. Fenitrothion, malathion and fenthion were now collected solely on the filter.

The chromatograms of sample a and sample b are shown in Figs. 2–3 and 4–5, respectively.

3.5. Additional components

The pyrethroids allethrin, phenothrin, resmethrin and tetramethrin were also investigated in our experiments. Although recovery rates on filters and PUF plugs were good without the throughput of air, they could not be recovered quantitatively in the overall recovery studies (Section 3.2.3) by spiking the filter and drawing air through the sampling unit. The reasons are unclear. Nevertheless, in the aerosol spraying experiments, these compounds were recovered exclusively on the filters, which was confirmed by comparing the results obtained with: (1) a sampling unit containing a filter and two PUF plugs, (2) a sampling unit containing just a filter and (3) a sampling unit containing two PUF plugs. Furthermore, the amounts found in the aerosol spraying experiment (sample a) were about the same as those

Table 4
Results of the indoor spraying experiment

Peak no.	Compound	Sample a ($\mu g/m^3$)	Sample b ($\mu g/m^3$)
1a	*p*-Chlorobenzene-isocyanate	3.6	n.d.
1b	2,6-Difluorobenzene amide	3.7	n.d.
2	Dichlorvos	2.8 (0.1/97.5/2.4)	n.d.
3	Propoxur	2.6 (21.8/78.2/–)	0.010 (9.2/90.8/–)
4	Lindane	2.3 (11.0/89.0/–)	0.012 (6.7/93.3/–)
5	Diazinon	2.5 (3.6/96.4/–)	n.d.
6	Fenitrothion	2.4	0.003
7	Malathion	2.6	0.003
8	Fenthion	1.2	n.d.
9	Chlorpyriphos	2.2 (69.5/30.5/–)	0.006 (14.3/85.7/–)
10	Chlorodecone	3.6	n.d.
11	Piperonyl butoxide	4.1	0.118
12	Cyhalothrin	3.9	n.d.
13	Permethrin	4.0	0.001
14	Cyfluthrin	4.4	n.d.
15	Cypermethrin	4.2	n.d.
16	Fenvalerate	4.2	n.d.
17	Deltamethrin	4.5	n.d.

Sample a was collected 30 min after spraying, sample b was collected 1 week later. All concentrations are listed in $\mu g/m^3$. n.d., not detected. Components 1, 6–8 and 10–17 were completely retained on the filter. For the other components, the relative distribution in the sample unit is given in parentheses (filter/PUF1/PUF2) in %.

of the other compounds. Consequently, aerosol sampling of these compounds is possible. Therefore, we assume a decomposition mechanism for allethrin, phenothrin, resmethrin and tetramethrin on the filter during the spiking experiment. Further investigations will be made on this topic.

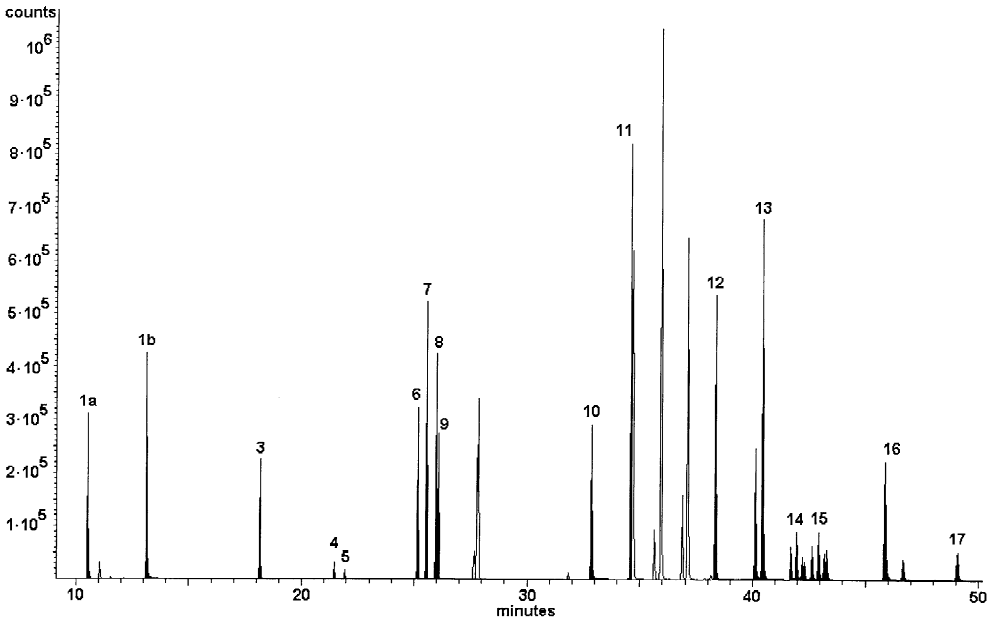

Fig. 2. Indoor spraying experiment. TIC chromatogram (SIM mode) of the glass fibre extract (sample a); peak labelling, see Fig. 1.

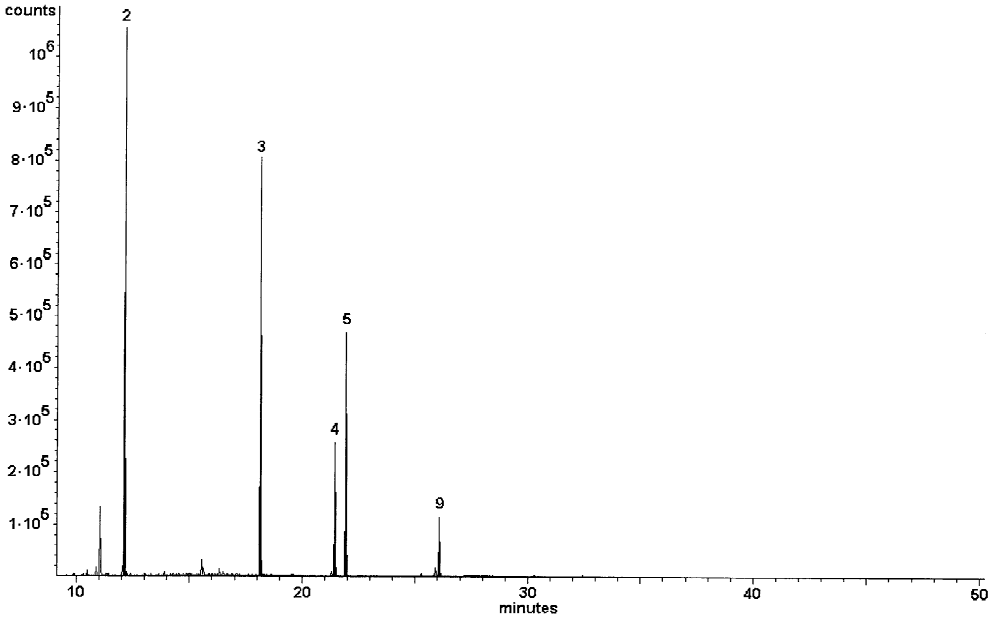

Fig. 3. Indoor spraying experiment. TIC chromatogram (SIM mode) of the extract of the first PUF plug (sample a); peak labelling, see Fig. 1.

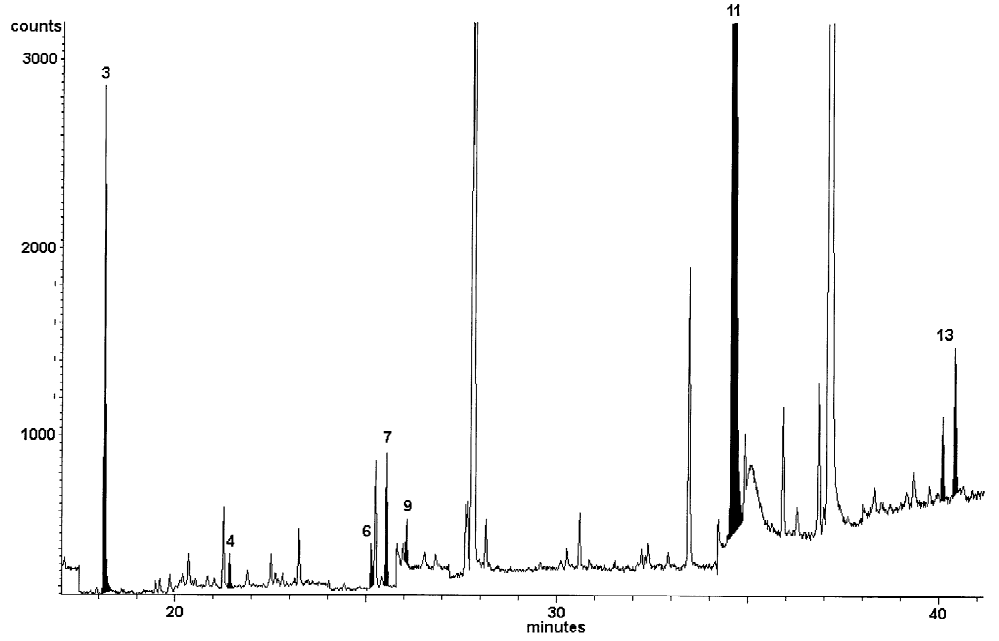

Fig. 4. Indoor spraying experiment. TIC chromatogram (SIM mode) of the glass fibre extract (sample b); peak labelling, see Fig. 1.

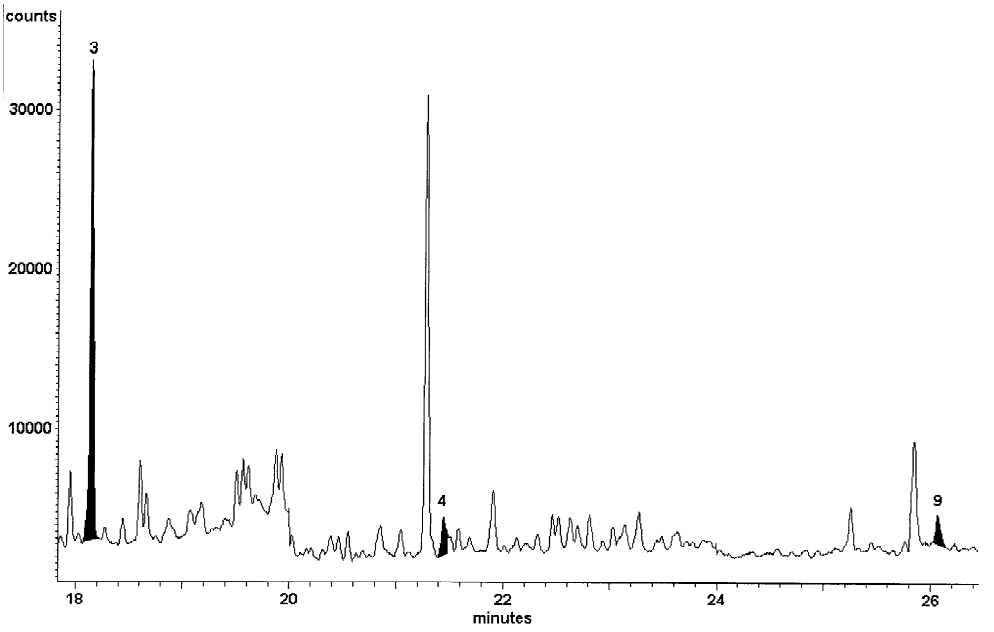

Fig. 5. Indoor spraying experiment. TIC chromatogram (SIM mode) of the extract of the first PUF plug (sample b); peak labelling, see Fig. 1.

4. Conclusion

This work presents a new GC–MS method for monitoring 17 selected insecticides and acaricides, commonly used for indoor spraying or in pest control operations in Germany. Such a multi-component method which includes very different compound classes has not been reported to date. Furthermore, the matrix-induced chromatographic response enhancement effect was investigated in detail. The method uses a combination of glass fibre filter and PUF plugs as sampling media. The distribution of the analytes between these three sampling media was determined, demonstrating that some compounds were completely retained with the filter, some only with an additional PUF plug.

The analyst has to bear in mind that even such a ''simple'' matrix like air can cause analyte response enhancements in gas chromatography leading to excessive recovery rates and increased analyte concentration findings in samples. In addition, filter (to a lesser extent) and PUF matrix contribute to the ''matrix-induced chromatographic response enhancement''. In order to achieve correct quantitative results, a technique has to be applied that takes this fact into account. Since (expensive) internal isotope standards are hardly commercially available and standard addition techniques in multi-analyte methods are time-consuming, quantification with matrix-matched standards provides a good alternative for accurate and reliable results.

The sampling method described is suitable for all compounds except dichlorvos because of its relatively high volatility. In addition, GC is not the appropriate method for the determination of diflubenzuron because of its complete decomposition into two degradation products during injection. In this case, a liquid chromatographic method would be preferred. Nevertheless, the decomposition reproducibility seems to be sufficient for a quantitative analysis. Therefore, the method can be used for diflubenzuron, if there is no other method available, or for screening purposes, provided that the results are subsequently confirmed by a different method.

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