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Chemical characteristics of aerosol insecticide deposition in indoor surfaces

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Abstract We investigated the deposition rate of aerosol insecticide on through woollen surfaces inside a test chamber. Compared to floor surface, the deposition rate of aerosol insecticide active ingredient on table of 1 m high was up to 2.07 times for piperonyl butoxide, 1.64 times for tetramethrin and 2.95 times for permethrin represented by 0.51, 0.37 and 0.23 $\mu\text{g cm}^{-2}$ for the three molecules, respectively. Application of the household used cleaning to the woollen table surface decrease these concentrations by 61.32%, 45.01% and 59.80% for the three pesticides respectively, this cleaning procedure still not efficient for the floor surfaces. Moreover, indoor conditions permit the removal of 46.42%, 21.92% and 14.35% of the table surface deposition rate after one week, for the three pesticides, respectively. These conditions ensure the removal of only 28.72%, 20.69% and 24.05% of the three deposit molecules respectively on floor surface.

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1. Introduction

Pesticides have been linked to a wide spectrum of human health hazards, ranging from short-term impacts such as head-

aches and nausea to chronic impacts like cancer, reproductive harm and endocrine disruption. Chronic health effects may occur years after even minimal exposure to them in the environment (Berrada et al., 2009). Synthetic pyrethroids are widely used as the broad-spectrum pest control agents in agricultural production (Fanggui et al., 2006; Francesc et al., 2005; Pang et al., 2006). In urban areas, pyrethroids are used for structural pest control, landscape maintenance, public health pest control and rights of way and their major transport pathway into surface waters is generally by storm water drainage (Abhilash and Singh, 2009; López et al., 2001; Muccio et al., 1997). Some studies have demonstrated that these products show neurotoxic effects on the mammalian central nervous system (Khayamian et al., 2009; Nasuti et al., 2008; Wanga et al., 2009; Moros et al., 2007; Brown et al., 1996; Oepkemeiera et al., 1999). The Occupational Safety and Health Administration (OSHA) has established the occupational exposure

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limit for an 8 h workday, 40 h workweek, at 5 mg of pyrethrins and pyrethroids per cubic meter of workplace air (Barro et al., 2006; Elflein et al., 2003).

Almost all the analytical methods for the determination of pyrethroids are based on the use of chromatographic techniques. GC-ECD is the most popular method (Alvarez et al., 2008), while GC-MS is used for pyrethroids residues confirmation (Huang et al., 2007; Schettgen et al., 2002; Stajnbaher and Kralj, 2003; Woudneh and Oros, 2006; Vonderheide et al., 2009; Pizzutti et al., 2009; Olejnik et al., 2009; Leng and Gries, 2005; Lesueur et al., 2008). Some applications of LC-MS to the analysis of pyrethroids residues have also been reported (Liang et al., 2009; Cheng et al., 2009).

Pyrethroids on aerosol insecticides form are mainly used for household insects. Therefore, the mean purpose of this study has been the development of fast chromatographic methods for the simultaneous determination of all pyrethroids in indoor area surfaces for the estimation of aerosol insecticide deposition rates.

2. Experimental

2.1. Chemicals and solvents

The following chemicals were obtained from Dr. Ehrenstorfer GmbH, Augsburg, Germany: permethrin (94.0%) and tetramethrin (99.0%). Technical piperonyl butoxide (93.0%) was sourced from Endura Spa, Italy. Acetone was of highest analytical grade available.

2.2. Analytical conditions

GC-MS was performed using a Hewlett-Packard system (GC 6890; MSD 5973). Samples (injected volume, 1 μ L) were introduced into the gas chromatograph injector held at 250 °C. The

temperature program used was the following: 260–280 °C at 10 °C min⁻¹, 280 °C for 3 min for the quantitative analysis. Helium was used as carrier gas with a constant flow of 1 mL min⁻¹.

Mass spectrometric data were obtained under the following conditions: electron ionization, 70 eV; source temperature, 230 °C; transfer line, 280 °C. Mass spectra were first obtained in full scan mode (range of acquisition, 45–450 m/z) in order to define analytes retention times and to identify qualifying ions that had to be used in selected ion monitoring mode. Following analyses were performed in SIM mode; two characteristic ions related to each substance were acquired. The following quantifier ions (m/z) were monitored: permethrin (183), tetramethrin (164) and piperonyl butoxide (176).

Table 2 Results of the indoor spraying experiment on table and on floor ($n = 5$).

	Deposition rate (%)	Concentration ($\mu\text{g cm}^{-2}$)
<i>On table</i>		
20 min after treatment without cleaning		
PBO	3.18 \pm 0.17	0.507 \pm 0.027
Tetramethrin	5.82 \pm 0.27	0.371 \pm 0.017
Permethrin	2.04 \pm 0.07	0.229 \pm 0.080
20 min after treatment with ordinary cleaning		
PBO	1.23 \pm 0.06	0.196 \pm 0.009
Tetramethrin	3.20 \pm 0.28	0.204 \pm 0.017
Permethrin	0.82 \pm 0.32	0.092 \pm 0.036
7 days after treatment without cleaning		
PBO	1.23 \pm 0.13	0.196 \pm 0.021
Tetramethrin	3.30 \pm 0.33	0.199 \pm 0.021
Permethrin	1.66 \pm 0.07	0.186 \pm 0.008
<i>On floor</i>		
20 min after treatment without cleaning		
PBO	1.53 \pm 0.04	0.244 \pm 0.006
Tetramethrin	3.54 \pm 0.12	0.226 \pm 0.007
Permethrin	0.69 \pm 0.13	0.077 \pm 0.014
20 min after treatment with ordinary cleaning		
PBO	1.39 \pm 0.09	0.221 \pm 0.013
Tetramethrin	3.69 \pm 0.08	0.235 \pm 0.005
Permethrin	1.01 \pm 0.16	0.113 \pm 0.017
7 days after treatment without cleaning		
PBO	1.09 \pm 0.15	0.173 \pm 0.024
Tetramethrin	2.81 \pm 0.61	0.179 \pm 0.104
Permethrin	0.52 \pm 0.10	0.058 \pm 0.005

Table 1 Active ingredient concentration and quantities present in two second aerosol insecticide pulverisation ($n = 10$).

Active ingredient	Concentration (%)	Quantity (μg)
Piperonyl butoxide	0.39 \pm 0.04	3525.62 \pm 385.41
Tetramethrin	0.18 \pm 0.06	1627.21 \pm 177.88
Permethrin	0.14 \pm 0.06	1265.61 \pm 138.35

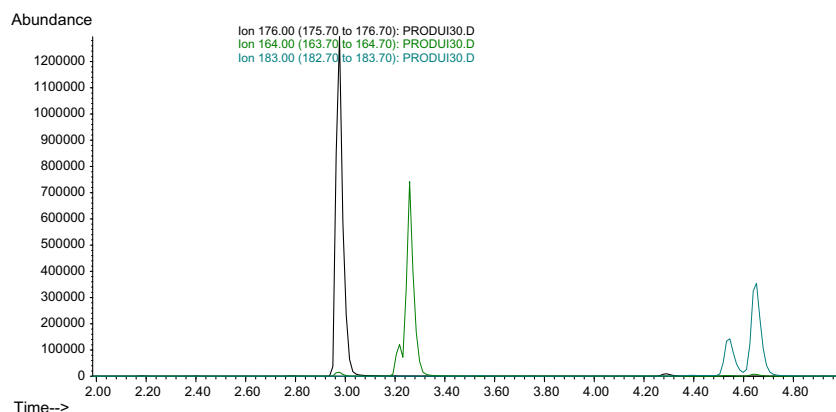


Figure 1 Chromatogram obtained for two second pulverisation solution of the aqueous formulation insecticide aerosol S3AW.

2.3. Preparation of standards and external calibration

The individual standard stock solutions of pesticides (10 mg mL^{-1}) and the standard mix solutions at 1 and 0.1 mg mL^{-1} were prepared in acetone and stored at 6°C in the dark.

Calibration samples were prepared at concentrations of 10, 20, 30, 40, 50 and 60 ng mL^{-1} and quality control samples were prepared at 100, 200, 300, 400, 500 and 600 ng mL^{-1} .

2.4. Sample and contamination preparation

2.4.1. Sample preparation

Samples of the most used aerosol insecticide on Algerian household were purchased from market and codified S3AW (aqueous formulation insecticide aerosol). Two second pulverization was immediately weighted for the aerosol insecticide sample. The volume was diluted to 10 mL with acetone. Preparation was replicated ten times.

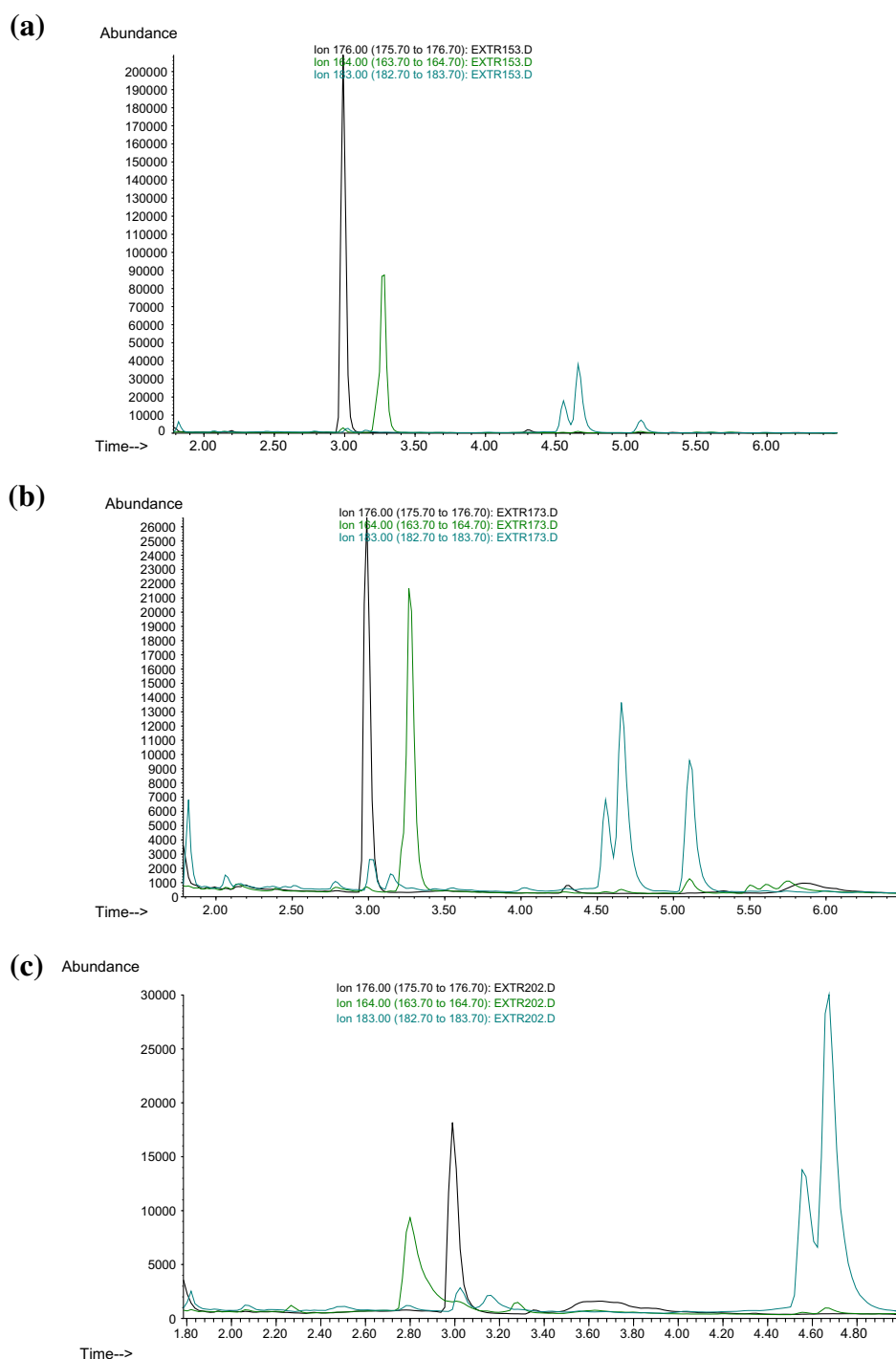


Figure 2 Chromatograms obtained for table deposition residue extracts: 20 min after treatment without cleaning (a) and with ordinary cleaning (b) and seven days after treatment without cleaning (c).

2.4.2. Indoor spraying experiment

An indoor spraying experiment was made to check the contamination rate of floor and table surfaces. A model room was sprayed with two second pulverisation of the tested insecticide aerosol. Two woollen pieces (50 × 50 cm) were deposited

next the wall, the first on the floor (a) and the second on a table of 1 m high (b).

Three groups of samples were collected: group 1 samples (a, b) 20 min after spraying, group 2 samples (a, b) seven days after spraying, group 3 samples (a, b) 20 min after spraying

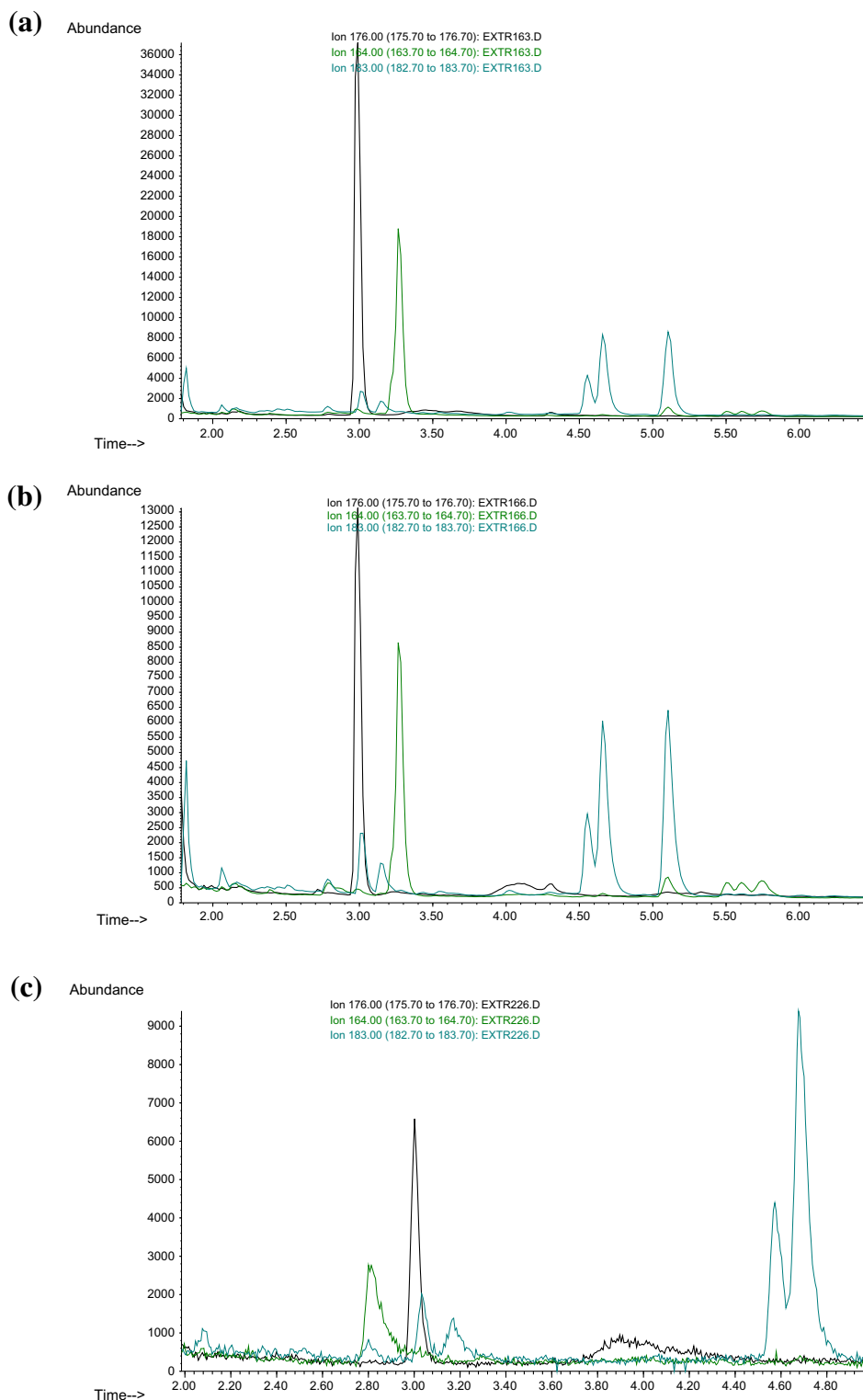


Figure 3 Chromatograms obtained for floor deposition residue extracts: 20 min after treatment without cleaning (a) and with ordinary cleaning (b) and seven days after treatment without cleaning (c).

washed three times with household detergent then rinsed with distilled water and dried in indoor conditions.

2.4.3. Recovery studies

The recovery rate of the analytes on the woollen surfaces was investigated separately. Fortification of the woollen surfaces was made by pipetting 50 μ L volume of standard solution onto the center of the surface. The overall recoveries on the sampling surfaces were determined by spiking the woollen piece. Spiking level was 50 μ g.

2.4.4. Extraction

The woollen piece was transferred to Soxhlet apparatus and extracted for three cycles with 150 mL acetone. The extract was reduced to 0.5 mL on a Rotavapor system. The final volume was adjusted to 5 mL with acetone.

3. Results and discussion

3.1. Validation of the GC–MS method

All compounds are baseline-separated. Analytes showed more isomers in the chromatogram were integrated by peak summing. Reproducibility was checked by injecting a mixed standard solution (10 μ g/mL) ten times. Standard derivations were found to be inferior to 0.1% for retention times and inferior to 12% for the concentration values.

3.2. Recovery studies

In the beginning, quantitative analyses were carried out using calibration curves obtained from mixed standard solutions. Recovery rates of spiked woollen pieces ranged from 102% to 87%.

When using standard mix solution, the following mean recoveries were obtained for piperonyl butoxide ($97.01 \pm 0.44\%$), tetramethrin ($90.63 \pm 0.73\%$) and permethrin ($96.33 \pm 5.66\%$).

3.3. Estimation and prediction of deposition rates

According to the calculated standard derivation listed in Table 1, the rate of particle precipitation from aerosol flow does not vary with application. For the fixed flow rate and the given insecticide aerosol particle concentrations the quantity of active ingredient seems greater compared to the OMS perspective (Chavasse and Yap, 1999). Fig. 1 presents chromatogram obtained from the SIM analysis of two second aerosol insecticide pulverization solution. Retention times are the following: piperonyl butoxide (3.00 min), tetramethrin (3.25 min) and permethrin (two peaks, 4.58 min and 4.69 min).

3.4. Deposition rates on indoor surfaces

The rates of deposition insecticide on table and floor surfaces are respectively listed in Table 2. The amount of collecting from floor surface is two times as low as that from table surface. To within experimental accuracy the amount of insecticide found on table surface is independent of the method of obtaining (velocity of aerosol flow, precipitation of particle). Additionally, these results demonstrate the non ability of the

adopted cleaning procedure to remove the contaminant from the studied surfaces. These results reveal also, the persistence of the three molecules issued from only two second pulverisation. Figs. 2 and 3 present each one three chromatograms obtained from the SIM analysis of deposition residue extracts on table and floor, respectively.

4. Conclusion

We have described a GC–MS assay for the simultaneous quantification and confirmation of piperonyl butoxide, tetramethrin and permethrin in indoor surfaces with a simplified sampling and extraction procedure. The selected aerosol insecticide could be controlled by GC–MS; the method was simple and rapid. Application of this technique showed that it is able to control the real aerosol content.

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