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Short Communication

Sampling free and particle-bound chemicals using solid-phase microextraction and needle trap device simultaneously

The possibility of sampling the free and particle-bound concentrations of organic compounds was studied using two different sampling techniques at the same time: needle trap device (NTD) and solid-phase microextraction (SPME). In this study, a mosquito coil was used to produce gaseous (free) and particle-bound compounds. Allethrin, the active ingredient in mosquito coils, was chosen as the target analyte. Under the same sampling conditions, the amount of allethrin extracted from the mosquito-coil smoke was higher for the NTD compared to the SPME fiber, while the extracted amounts were almost the same for both devices when sampling gaseous samples of allethrin. These results can be explained by the fact that the SPME fiber can only extract free molecules (based on diffusion), whereas the NTD, an exhaustive sampling device, collects both free and particle-bound allethrin. Breakthrough for NTD and carryover for both NTD and SPME were negligible under the given sampling and desorption conditions.

Keywords: Aerosol / Allethrin / Mosquito coil / Needle trap device / Solid-phase microextraction

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1 Introduction

During the last two decades, trace gases and aerosols have become more and more important in almost all areas of air quality-related concerns, including public and occupational health, indoor air quality, photochemical smog, stratospheric ozone depletion, global climate change, and genesis of atmospheric acidity [1]. Although atmospheric fine particulate matter is dominantly inorganic, significant quantities of organic, including large and complex macromolecules, are often present in ambient aerosols in readily detectable concentrations [1]. In order to analyze aerosol samples they are usually collected using a collecting method and are then analyzed by different methods. Collecting methods include diffusion-based collection, gravitational settling, impaction, electrostatic and thermal precipitation, filtration (the most commonly used). Wet analysis, thermal decomposition-based methods, spectroscopic methods, aerosol MS, emission spectrometry (aerosol metal concentration), and measurement of aerosol carbon are common analyzing systems [1]. These methods are mostly used for analyzing the particles or total concentration of chemicals in an aerosol sample. But in the presence of particles in the air sample, a fraction of chemicals can become bound to the surface of the aerosol particles. Determining free and particle-bound concentrations of these compounds is important from the environmental pollution point of view.

The objective of this study is to use a simple and fast method for the determination of both free and particle-bound chemicals. Mosquito coils were selected as a source of particles and chemicals. These coils, which are widely used as mosquito repellents in Asia, Africa, and South America, are derived from joss or incense sticks. They contain various insecticides, organic fillers, dyes, binders, and other additives with high smoldering capabilities. When a mosquito coil burns, the insecticide evaporates with the smoke and is distributed throughout the room, thus repelling mosquitoes. Mosquito coils normally contain pyrethroids, derived either from natural pyrethrum flowers or from one of the various synthetic analogs, *e.g.*, allethrin. When exposed to these pyrethroids, mosquitoes are immobilized, paralyzed, and finally rendered unconscious [2].

Combusting mosquito coils also generate large amounts of submicrometer particles and gaseous pollu-

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Abbreviations: GW, glass wool; **NTD,** needle trap devices; **SPME,** solid-phase microextraction tants. These particles, which may be coated with a wide range of organic compounds, can reach the lower respiratory tract of humans. The size of particles in mosquito-coil smoke is known to be around 30 μm [3]. Some of these organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), are carcinogens or suspected carcinogens. These are generated through incomplete combustion of the biomass making up the base materials of the mosquito coil [4]. Determining free and particle-bound concentrations of these compounds is important from the environmental pollution point of view.

Two sampling methods including solid-phase microextraction (SPME) and needle trap device (NTD) were used in combination in this study. SPME has been utilized for indoor and outdoor air sampling [5–12]. The analytes present in air samples partition into the SPME coating while being exposed to the fiber. Equilibrium can be achieved by static or dynamic methods, and calibration can be performed using a standard gas generating system or standard gas mixtures [13–17]. In the use of an NTD, the extraction phase (*i.e.*, a sorbent) is packed into a needle with a small hole in its side. Analytes are trapped on the sorbent as the gaseous sample passes through the needle. After sampling, the NTD is inserted into the hot injector of a gas chromatograph. The carrier gas flows into the needle through the hole in the side of the needle, passes through the sorbent, and carries the thermally desorbed analytes into the column. The NTD has been used for sampling BTEX from permanent marker fumes and from various points inside houses [18], and as a time-weighted average diffusive sampling device for air sampling [19]. This device has also been used for extraction of BTEX [20], formic and acetic acid [21] from headspace of aqueous solutions.

In this study, we developed a simultaneous sampling method, which combines SPME with NTD in order to differentiate between gaseous-phase and particulate-phase concentrations of insecticides in mosquito-coil smoke. Identification of organic compounds released by burning mosquito coils was also performed.

2 Experimental

2.1 Chemicals and supplies

Two brands of mosquito coil were used: coil A from Summer Lights Outdoors (Toronto, ON, Canada) and coil B from Coghlan's (Winnipeg, MB, Canada) containing 0.25 and 0.35% allethrin, respectively. Allethrin and all other standards were purchased from Sigma–Aldrich (St. Louis, MO, USA).

The needles were purchased from Dyna Medical Corporation (London, ON, Canada). Divinylbenzene (HayeSep Q, 80–100 mesh size particles), which was used as a sorbent in the needle trap, was purchased from Restek (Bellefonte, PA, USA). The PDMS/DVB SPME fibers (65 μm) were purchased from Supelco (Mississauga, ON, Canada). The bidirectional syringe pump was purchased from Kloehn (Las Vegas, NV, USA). All gases were supplied by Praxair (Kitchener, ON, Canada) and were of ultra-high purity.

2.2 Needle trap device (NTD)

The NTD consisted of a 3.5 in. long, 22-G stainless steel needle with DVB packing. A small hole was drilled on the side of the needle 30 mm from the opening end for passing carrier gas into the injector during the desorption step [22]. It is crucial to immobilize sorbent particles inside the positioned needle without bleeding and with minimized flow restriction. Therefore, a stainless-steel spring plug was first fixed in position; then DVB particles were packed by aspirating a few grains at a time until the desired length was packed. Packing was then completed by applying a very small amount of epoxy glue at the end of the sorbent layer, in order to hold the sorbent particles firmly. To avoid complete blockage of the NTD by the epoxy-resin plug, air was also drawn continuously through the NTD while the epoxy resin was curing. Ten millimeter packing was positioned at a less than 1 mm distance from the opening of the NTD [18–21].

2.3 Sampling by SPME fiber and NTD

Mosquito coils were burnt in a chamber, which is shown schematically in Fig. 1. Purified air was led into the chamber at a flow rate of 0.5 L/min while mosquito coil was burning. For sampling, the SPME and NTD needles were inserted into the chamber through the septa, which sealed the sampling ports installed on the side of the chamber. A DVB/PDMS fiber was exposed in the chamber for 20 min and then injected into the GC/MS. For sampling by NTD from the chamber, a bidirectional syringe pump was used. This syringe pump offers a high resolution and syringe driving force, allowing users to work with a large syringe range. It also permits the versatility to choose many different valve options for virtually any application that requires precision fluid metering [23].

2.4 Microwave-assisted standard gas generator

A microwave-assisted standard gas generation system [24] was used to produce gaseous samples of allethrin. A commercial domestic microwave oven 1100 W, model DMW1153BL from Danby (Guelph, ON, Canada) and 1 L gas-sampling bulbs from Supelco were used for standard gas preparation. The bulbs were purged with nitrogen before use. For each sample, a new piece of fresh glass wool (GW) (∼10 mg) was set inside the sampling port of the bulb and moistened with pure water (15 μL). The port was then sealed with a Teflon-faced silicon rubber sep-

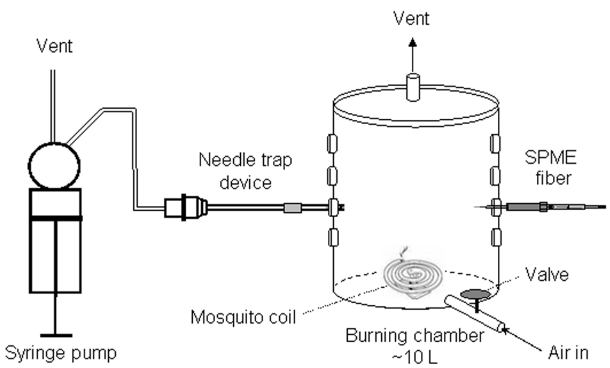

Figure 1. Schematic diagram of the system used for sampling burning mosquito coils with SPME and NTD.

tum, through which a 1 μL aliquot of the standard solution of allethrin in methanol (5%) was injected onto the GW. Finally, the bulb was placed in the microwave oven and radiated at full power for 1.5 min. A commercial SPME fiber and NTD were used for sampling the gaseous allethrin from the bulbs.

2.5 GC/MS analysis

GC was performed on a Varian 3800 gas chromatograph (Mississauga, ON, Canada) coupled with a Saturn 4000 IT-MS system. Separation was performed using a 30 m × 0.25 mm, 0.25 μm RTX-5 column from Restek (Bellefonte, PA, USA). The column was initially set at 40°C and kept at this temperature for 3 min, then ramped at 10°C/min to 250°C, for a total run time of 24 min.

3 Results and discussion

3.1 Identification of compounds

Figure 2 shows GC/MS chromatograms of mosquito-coil smoke injected from the SPME fiber and NTD. The retention times of all analytes were almost identical for both SPME fiber and NTD. The organic compounds released by burning both mosquito coils (A and B) were identified based on the MS library, linear temperature program retention index (LTPRI), and/or standard injection. Table 1 shows the identified compounds and their retention times, as well as the calculated and reference LTPRI for both coils. The results show that burning mosquito coils produce a large number of harmful organic compounds, especially benzene (a human carcinogen, according to the Environmental Protection Agency (EPA)) in addition to their active ingredient, allethrin.

3.2 Free and particle-bound allethrin

The GC/MS chromatograms of mosquito-coil smoke injected from the SPME fiber and NTD (Fig. 2) show that the SPME fiber exhibited higher extraction efficiency for semivolatile organic compounds located in the middle of the chromatogram. This can be explained by the higher partition coefficients of semivolatile compounds (*e.g.*, phenol) between the gas phase and the SPME fiber, compared with the very low partition coefficients of more volatile compounds (*e.g.*, benzene and toluene). Less volatile compounds (*e.g.*, allethrin) tend to deposit on other surfaces, such as the chamber walls and, more importantly, on particles present in the smoke. The chromatogram from the DVB-NTD shows higher extraction recoveries of more volatile compounds, resulting from the larger volume of the extraction phase. However, the DVB-NTD chromatogram also shows higher extraction efficiency for allethrin. Since allethrin has a high boiling point (~280°C at 1 atm), it is expected to be present in the smoke mostly as particle-bound species [3].

We assume that SPME can collect free chemicals rather than particles, whereas NTD is able to collect both free and particle-bound chemicals. Therefore, the absolute amount of allethrin extracted with NTD is higher than

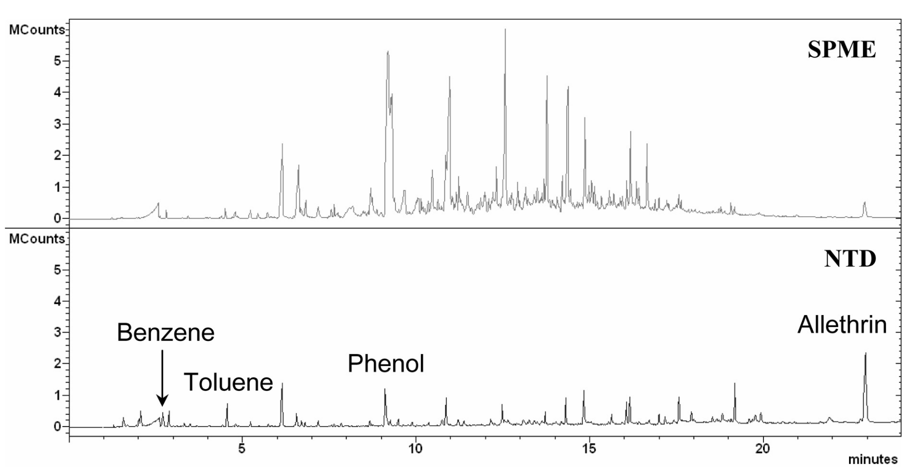

Figure 2. GC/MS chromatograms of mosquito-coil smoke sampled with the SPME fiber and NTD. Extraction time for SPME: 10 min, sampling volume for NTD: 18 mL.

Table 1. Identified compounds in the smoke of mosquito coils

Compound	Mosquito coil (A)		Mosquito coil (B)		Reference LTPRI[a)]
	RT (min)	Calculated LTPRI	RT (min)	Calculated LTPRI	
Benzene	2.68	664	2.62	660	664
Toluene	4.53	775	4.50	773	774
3-Furaldehyde	6.11	852	6.08	851	832
2-Furanmethanol	6.64	878	6.58	875	865
1-(2-Furanyl)-ethanone	7.65	928	7.63	927	910
5-Methyl-2-furancarboxaldehyde	8.7	983	8.68	982	978
Phenol	9.19	1010	9.09	1004	998
2-Methylphenol	10.45	1082	10.44	1082	1055
4-Methylphenol	10.85	1106	10.83	1105	1084
2-Methylbenzofuran	11.23	1130	11.23	1130	1149
2-Methoxy-4-methyl- phenol	12.3	1198	12.31	1199	1201
4,7-Dimethylbenzofuran	12.92	1241	12.92	1241	1214
2,3-Dimethoxytoluene	13.16	1257	13.16	1257	1237
4-Ethyl-2-methoxy -phenol	13.77	1300	13.77	1300	1297
2-Methyl-naphthalene	14.21	1332	14.22	1332	1306
1-Methyl-naphthalene	14.45	1349	14.45	1349	1316
2-Methoxy-4-propyl-phenol	14.92	1383	14.98	1388	1369
1,4-Dimethyl-naphthalene	15.96	1464	15.95	1462	1447
Hexadecene	16.36	1495	16.36	1495	1590
Cadinene	16.92	1522	16.89	1521	1523
Allethrin (cis)	22.82	1848	22.81	1848	–
Allethrin (trans)	22.92	1854	22.9	1853	–

a) From NIST Chemistry WebBook (http://webbook.nist.gov/chemistry).

that extracted with SPME fibers. This fact can be explained based on the theory of SPME and NTD. Mass transfer processes involved in sampling by SPME are commonly described by the boundary layer model [25]. Analyte flux in the bulk of the sample is assumed to be controlled by convection, whereas analyte flux within the boundary layer is controlled by diffusion. In many cases, the diffusion of analytes through the boundary layer controls the extraction rate. There is a concentration gradient in the boundary layer, which causes a continuous diffusion of analyte to the surface. Diffusion coefficient for pesticides in the air is about 0.05 cm^2/s (5×10^{-6} m^2/s), which is about 2 million times greater than the diffusion coefficient of a 10 μm particle. It means that the number of pesticide molecules deposited on the fiber is much greater than the number of 10 μm particles. NTD acts like a filter and aerosol particles can be collected on the sorbent in the needle by passing the aerosol sample through the device. A common misconception is that aerosol filters work like microscopic sieves in which only particles smaller than the holes can get through. This view may be true for the liquid filtration of solid particles, but it does not explain how aerosol filtration works [26]. Particles are removed by a filter when they collide and attach to the surface of the sorbent. Deposition mechanisms of an aerosol particle on a sorbent are: interception, inertial impaction, diffusion, and gravitational settling. Interception and impaction are negligible

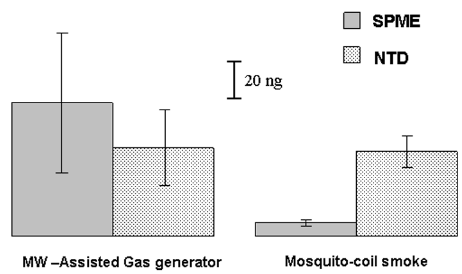

Figure 3. Amount of allethrin extracted from mosquito-coil smoke and from MW-assisted gas generator.

for small particles, but increase by increasing particle size. Diffusion is the only important mechanism for particles below 0.2 μm, and its importance decreases for particles above that size. For all particle sizes, gravity settling is small compared with the other mechanisms. The range of particle size collected in NTD depends on parameters such as sorbent particle size and sampling flow rate. Regular NTDs used in this study are appropriate for the studied particles size (>10 μm). By choosing appropriate sorbent particle size and sampling flow rate we can collect particles with different range of sizes.

In order to show that the particle-bound allethrin is collected by the NTD, a microwave-assisted gas generator was used to produce particle-free (gaseous) allethrin. Both SPME and NTD were used for sampling under the same conditions as with the mosquito-coil study. The

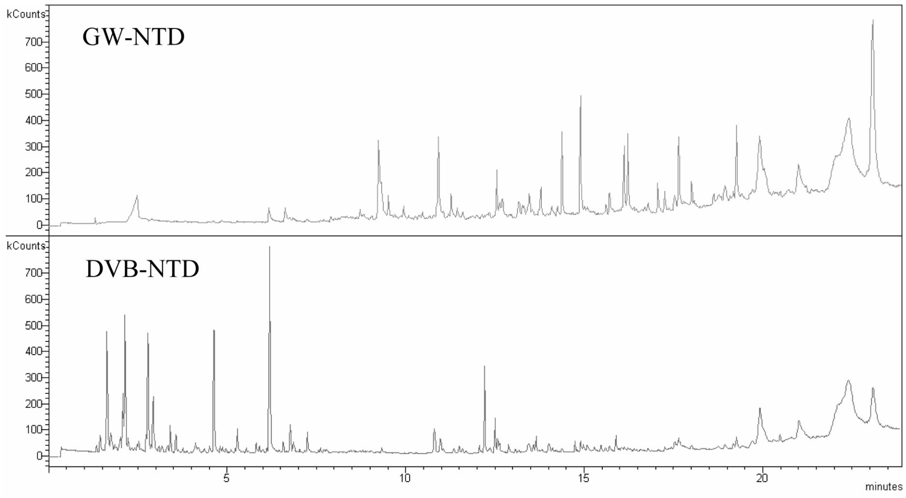

Figure 4. GC/MS chromatogram of glass wool needle trap (front NTD) and DVB needle trap (back NTD).

quantities of allethrin extracted from the gas generator using the SPME fiber and NTD are shown in Fig. 3. SPME extracted more (or at least equal) amounts from this system compared with NTD. Comparing these results with those obtained from mosquito-coil smoke – where more allethrin was extracted by NTD than SPME fiber – it can be concluded that allethrin is present as both particle-bound and free molecules in mosquito-coil smoke. In addition, while NTD can extract particle-bound molecules, SPME can extract only free alletrin molecules.

In order to prove that NTD can collect both gaseous and particle-bound compounds at the same time, two NTDs, connected in a series with a polytetrafluoroethylene (PTFE) connector, were used for sampling mosquito-coil smoke. The front needle was packed with GW and the back needle was packed with DVB. Mosquito-coil smoke passed first through the GW-NTD and then through the DVB-NTD; therefore, the particles and particle-bound organic compounds were trapped on the GW inside the GW-NTD, and the more volatile and gaseous organic compounds, which passed through the GW-NTD, were collected on the DVB-NTD.

GC/MS chromatographs obtained by both needles are shown in Fig. 4. As expected, the chromatogram obtained from the GW-NTD shows higher peak intensities for less volatile compounds, while the chromatogram obtained from the DVB-NTD shows higher peak intensities for more volatile compounds. However, peaks are more sparsely distributed through the whole volatility range in the chromatogram obtained by the single DVB-NTD, shown in the lower trace of Fig. 2. This shows that a NTD packed with sorbent-particles can extract both gaseous and particle-bound organic compounds simultaneously. It should be noted that using a filter to discriminate gaseous and particle-bound compounds is not recommended, as some unexpected reactions may occur on the GW. In addition, gaseous compounds may be collected on the trapped particles on the filter, thus causing qualitative and quantitative errors. The use of SPME fiber (for measuring free concentration) and the NTD (for measuring total concentration) promises to minimize such adverse effects of filters.

4 Concluding remarks

This study showed that SPME and NTD have the potential to be used simultaneously to differentiate between free (gaseous) and particle-bound compounds in air samples, such as mosquito-coil smoke. An SPME fiber can only extract free molecules, whereas an NTD can collect both free and particle-bound molecules. This method is simpler, faster, and less expensive than alternative methods such as filtration and aerosol MS. It should be mentioned that this study was focused on comparing the free and particle-bound amount of allethrin extracted by SPME and NTD. Determination of absolute amount of free and particle-bound species requires further investigation including calibration by a standard gas generator system with permeation tubes for allethrin.

The authors declared no conflict of interest.

5 References

[1] Pawliszyn, J. (Ed.), *Sampling and Sample Preparation for Field and Laboratory*, Elsevier, Amsterdam 2002.
[2] Liu, W. K., Wong, M. H., Mui, Y. L., *Toxicol. Lett.* 1987, *39*, 223–230.
[3] Chang, J., Lin, J., *Chemosphere* 1998, *36*, 617–624.
[4] Liu, W., Zhang, J., Hashim, J. H., Jalaludin, J., Hashim, Z., Goldstein, B. D., *Environ. Health Perspect.* 2003, *111*, 1454–1460.
[5] Pacolay, B. D., Ham, J. E., Wells, J. R., *J. Chromatogr. A* 2006, *1131*, 275–280.
[6] Hippelein, M., *Chemosphere* 2006, *65*, 271–277.
[7] Koziel, J. A., Cai, L., Wright, D. W., Hoff, S. J., *J. Chromatogr. Sci.* 2006, *44*, 451–457.

[8] Barro, R., Garcia-Jares, C., Llompart, M., Cela, R., *J. Chromatogr. Sci.* 2006, *44*, 430 – 437.
[9] Larroque, V., Desauziers, V., Mocho, P., *J. Chromatogr. A* 2006, *1124*, 106 – 111.
[10] Vilela-Parreira, F., de Souza-Bergo, P. L., de Carvalho-Rabelo, C., de Lourdes-Cardeal, Z., *J. Sep. Sci.* 2006, *29*, 346 – 350.
[11] Larroque, V., Desauziers, V., Mocho, P., *J. Environ. Monit.* 2006, *8*, 106 – 111.
[12] Wei, M. C., Chang, W. T., Jen, J. F., *Anal. Bioanal. Chem.* 2007, *387*, 999 – 1005.
[13] Koziel, J., Noah, J., Pawliszyn, J., *Environ. Sci. Technol.* 2001, *35*, 1481 – 1486.
[14] Gorlo, D., Zygmunt, B., Dudek, M., Jaszek, A., Pilarczyk, M., Namiesnik, J., *Fresenius J. Anal. Chem.* 1999, *363*, 696 – 699.
[15] Jia, M., Koziel, J., Pawliszyn, J., *Field Anal. Chem. Technol.* 2000, *4*, 73 – 84.
[16] Koziel, J., Jia, M., Khaled, A., Noah, J., Pawliszyn, J., *Anal. Chim. Acta* 1999, *400*, 153.
[17] Ferrari, F., Sanusi, A., Millet, M., Montury, M., *Anal. Bioanal. Chem.* 2004, *379*, 476 – 483.
[18] Eom, I.-Y., Tugulea, A. M., Pawliszyn, J., *J. Chromatogr. A* 2008, *1196 – 1197*, 3 – 9.
[19] Gong, Y., Eom, I.-Y., Lou, D.-W., Hein, D., Pawliszyn, J., *Anal. Chem.* 2008, *80*, 7275 – 7282.
[20] Eom, I.-Y., Niri, V. H., Pawliszyn, J., *J. Chromatogr. A* 2008, *1196 – 1197*, 10 – 14.
[21] Lou, D.-W., Lee, X., Pawliszyn, J., *J. Chromatogr. A* 2008, *1201*, 228 – 234.
[22] Wang, A., Fang, F., Pawliszyn, J., *J. Chromatogr. A* 2005, *1072*, 127 – 135.
[23] Amornthammarong, N., Jakmunee, J., Li, J., Dasgupta, P. K., *Anal. Chem.* 2006, *78*, 1890 – 1896.
[24] Xiong, G., Pawliszyn, J., *Anal. Chem.* 2002, *74*, 2446 – 2449.
[25] Pawliszyn, J., *Solid-Phase Microextraction: Theory and Practice*, Wiley-VCH, Chichester 1997.
[26] Hinds, W. C., *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, John Wiley & Sons, Inc., New York 1999.

