



Extracting Emissions from Air Fresheners Using Solid Phase Microextraction Devices

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ABSTRACT

Families all over the world commonly use air fresheners indoors. In this investigation, needle trap samplers (NTS), which are environmentally friendly analytical devices, are used to sample the gaseous products from three types of lavender fresheners—liquid, granular and oil. NTS are prepared using 60–80 mesh divinylbenzene (DVB) particles in 22 gauge stainless steel needles and utilized to extract indoor organic compounds. This investigation compares the extraction efficiency of NTS with that of commercially available 100- μm polydimethylsiloxane solid phase microextraction (PDMS-SPME) fiber samplers, when used to sample gaseous emission products from fresheners. The experimental results revealed that 60–80 mesh DVB-NTS outperformed SPME fibers during a 1-hr sampling period, and the main compounds that are extracted by NTS were ethanol, benzene, toluene, ethylbenzene, xylenes, dichloromethane, butenes and pentane. The potential use of small badge-sized or pen-sized NTS for indoor atmospheric and occupational hygiene applications is thoroughly evaluated.

Keywords: Needle trap sampler; Volatile organic compounds (VOCs); Sampler; Freshener; Solid phase microextraction; Indoor air.

INTRODUCTION

Air fresheners are typically utilized to scent the air in washrooms, houserooms and cars. The major constituents of air fresheners are fragrances and volatile organic solvents that can be responsible for both indoor and outdoor air pollution (Bridge, 2002). Fragrances are complex mixtures of volatile organic compounds (VOCs), formulated to have a specific smell. The VOCs break down, mix with other pollutants, and form new compounds that are more irritating or allergenic than the original substances (Forester and Wells, 2009). Many studies have focused on human dermal and respiratory allergies to fragrance compounds in cosmetics (Cheung, 2003; Wang *et al.*, 2011; Uter *et al.*, 2013; Politano, 2013; Kim *et al.*, 2013). Exposure to chemicals by inhalation seems to be the most effective means of inducing respiratory sensitization (Falko *et al.*, 2011). Forester and Wells (2009) noted that the oxygenated organic reaction products were formed from gas-phase reactions of hydroxyl radical ($\text{OH}\cdot$) and ozone (O_3) with the common terpene compounds in cleaning products, such as limonene, α -terpineol, and geraniol, and that various dicarbonyl reaction products such

as glyoxal and methylglyoxal, are formed; the latter have strong reductions, which can irrigate the eyes, skin and upper respiratory tract.

Despite the widespread use of fragrances and extensive indoor exposure to them, little information is available concerning the gaseous emissions of fragrance products (Bridge, 2002). Most importantly, 95% of the chemicals in fragrances are synthetic compounds that are derived from petroleum (Fukayama *et al.*, 1999). In research on the hazard of fragrance compounds, animals have been exposed to particular compounds to evaluate the safety of those compounds when inhaled. For example, Ferlow (2008) evaluated benzyl acetate, coumarin, hydroxycitronellal, musk ketone, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-g-2-benzopyran (HHCB) and phenyl ethyl alcohol (PEA), which are fragrance raw materials (FRMs), by exposing rats or hamsters to them. However, the actual emission characteristics of fragrance products have been seldom elucidated. This work concerns three common lavender air fresheners—liquid, granular and oil (Fig. 1) and evaluates their emission compounds and concentrations. Air samples were obtained using solid-phase microextraction (SPME) devices, SPME fibers and self-fabricated needle trap samplers (NTS), and then analyzed using gas chromatograph (GC) and mass spectroscopy (MS).

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METHOD

SPME, which is extensively used to sample gaseous

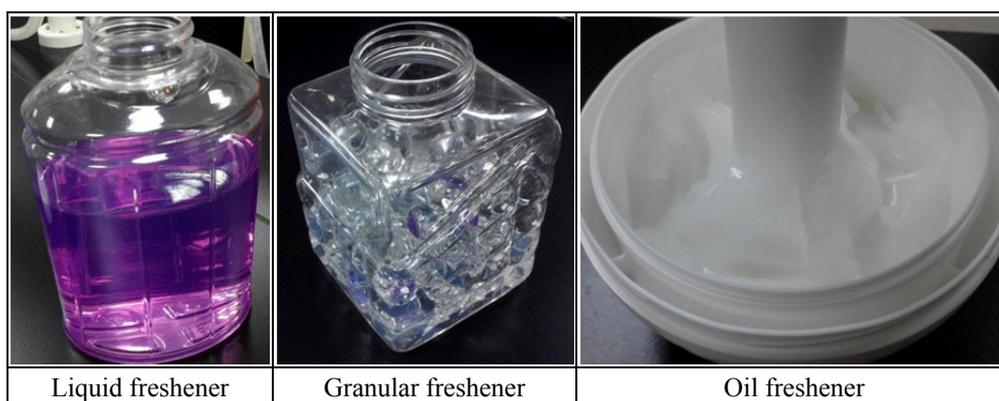


Fig. 1. Fresheners tested in this work.

organic compounds, is environmentally friendly because it is solvent-free and SPME devices can be reused (Lord and Pawliszyn, 2000). The sampling and analyzing pollutants using NTS required only small amounts of analytical reagents (as it involves thermal desorption with GC-FID and no solvent). Therefore, NTS is a fully satisfactory green analytical method that can be applied indoors.

NTS were made by utilizing 22 G stainless steel needles (ID 0.41 mm and OD 0.71 mm), which were purchased locally, and divinylbenzene (DVB) particles were used as adsorbents packed inside NTS. 100 μm -PDMS SPME fibers were also used and their sampling efficiencies were compared with those of NTS. Sampling devices of PDMS SPME fibers and DVB-NTS have been evaluated the excellent extraction of BTEX (Cheng *et al.* 2014a, b).

Fig. 2 presents that the NTS is composed of mainly a

stainless steel needle that is packed with DVB particles (60–80 mesh). The procedures developed by Cheng *et al.* (2011, 2013, 2014a, b) were used to examine all NTS in terms of the desired sampling flow rates (mL min^{-1}) when drawn by an aspirating pump through the packing phase to examine the uniformity of the packing phase in an NTS. When the relative standard deviations (RSD) in triplicate sampling flow rate tests did not exceed 5%, the filled materials in the NTS were considered to be uniformly immobilized. Benzene, toluene, ethylbenzene and p-xylene (BTEX) were mixed in a glass bulb, and then extracted using NTS to evaluate the mass of adsorbed VOCs. BTEX were analyzed using a GC with a flame ionization detector (FID). Supplement I presents the experimental data from qualification tests. Five NTS passed the qualification tests and were applied for the chamber sampling.

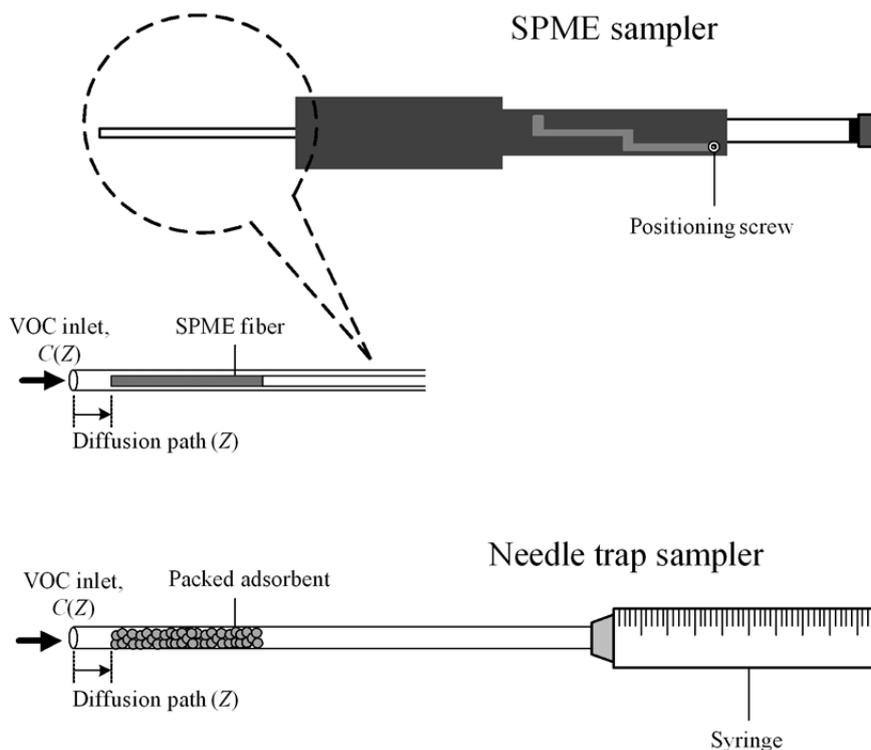


Fig. 2. Schematic SPME fiber and needle trap samplers.

According to the assembly of sampling chamber (Cheng et al., 2011, 2013, 2014a, b; Uhde and Schulz, 2015), 10 g of air freshener was placed in a circular glass chamber (with inner dimensions of a diameter of 30 cm, a height of 22 cm and a total volume of about 17.5 L) at 27°C. Air was then pumped into the chamber at a flow rate of 0.5 L min⁻¹ as the freshener emitted the gaseous compounds. Gas samples were collected in triplicate using 1-L Teflon bags and then analyzed with GC/MS to quantify the gaseous emission products of the fresheners. The NTS and SPME were inserted into the chamber through the septa, which sealed the sampling ports on the chamber wall. The commercial PDMS SPME fibers and NTS were simultaneously exposed in the chamber for sampling, before being analyzed by GC/FID.

RESULTS AND DISCUSSION

Table 1 presents the main gaseous emission products identified by GC/MS analysis. The liquid freshener emitted the most organic compounds (especially, cis-2-butene and dichloromethane) among all of the tested fresheners. Cis-

2-butene is extremely flammable, but it presents a very weak biohazard to humans. Notably, the International Agency for Research on Cancer (IARC) and American Conference of Governmental Industrial Hygienists (ACGIH) have specified dichloromethane as a possible or suspected human carcinogen (Kent, 1998). Fortunately, the 8-hr time weight average (TWA) permissible exposure limit (PEL) for dichloromethane, established by Occupational Safety and Health Administration (OSHA) is 50 ppm, which is much higher than the measured concentration of 25.9 ppb (0.0259 ppm). Liquid and granular fresheners emitted more ethanol than the oil freshener. However, the oil freshener emitted acetone, which was not emitted by the liquid or granular fresheners. Ethyl acetate emissions were similar among three types of fresheners. The liquid freshener emitted the most aromatic compounds and vegetable scents (1,8-cineole, α -terpinolene and L-camphor), whereas the oil freshener emitted the least. Briefly, the liquid freshener emitted more gaseous pollutants indoors than the other two fresheners.

Fig. 3 displays a chromatogram of the emissions from the liquid freshener that was obtained by NTS sampling

Table 1. Main gaseous by-products of fresheners extracted.

Chemicals	Concentration (ppb) ^a		
	Liquid freshener	Granular freshener	Oil freshener
Alkane compounds			
1-Butene			1.80
Butane			3.40
Trans-2-Butene		1.00	
Cis-2-Butene	5.75	0.30	
Isopentane			1.30
Pentane	2.55	1.25	1.6
Hexane			2.30
Aromatic compounds			
Benzene	0.30	0.30	
Toluene	2.00	1.34	0.30
Ethylbenzene	0.40	1.50	0.70
<i>m/p</i> -Xylene	0.85	1.25	1.40
<i>o</i> -Xylene	1.65	1.30	0.10
Styrene	0.35	0.45	
<i>n</i> -Propylbenzene	0.75		
1,3,5-Trimethylbenzene	1.65	0.50	
1,2,4-Trimethylbenzene	1.55	0.85	
1,2,3-Trimethylbenzene	1.60	0.40	
<i>o</i> -Ethyltoluene	0.70	0.25	
Chlorinated compounds			
Dichloromethane	25.9	1.5	2.1
Oxygenated compounds and others			
Ethanol	8.31	8.62	0.03
Ethyl acetate	12.87	14.5	11.7
Methyl ethyl ketone (MEK)		4.45	
Acetone			8.5
1,8-Cineole	0.79	0.093	0.055
α -Terpinolene	0.21	0.072	0.026
L-Camphor	0.22	0.052	0.015

^a The method detection limits: 1butene 0.35 ppb, butane 0.80 ppb, trans-2-butene 0.55 ppb, cis-2-butene 0.45 ppb, benzene 1.60 ppb, toluene 1.35 ppb, dichloromethane 0.75 ppb, ethyl acetate 0.82 ppb, MEK 1.54 ppb, acetone 3.41 ppb, and the other compounds 0.25 ppb.

and GC-FID analysis. The chromatograph peaks of analyzed compounds were separated and integrated. Fig. 4 plots the integral area analyzed by GC-FID of the main aromatic compounds that were emitted by the liquid freshener when the SPME fiber and NTS was used with a TWA sampling time of 60 min. The comparison reveals that the adsorption of VOCs by the NTS that was packed with 60–80 mesh DVB exceeded or was close to that by the 100- μ m PDMS SPME fibers. NTS extracted more ethylbenzene and trimethylbenzenes than did the 100- μ m PDMS SPME fibers, but almost the same masses of other compounds. These experimental results indicated that NTS and SPME fibers can extract organic compounds of close quality; however, the material cost of man-made NTS is much cheaper (US\$ 12.3 per piece) than the price of SPME devices (US\$ 138.5 per coating SPME fiber). For spreading the application of NTS, the multiple functional samplers, which can write, detect temperature and relative humidity, and extract gaseous

compounds via a NTS, have been developed and designed as “pen-like” ones, shown in Fig. 5. Three 1.5-volt mercury cells in series supplied the electric power.

CONCLUSIONS

Method 1501 of the National Institute for Occupational Safety and Health (2003) requires workers to clip a charcoal sorbent tube (around 7 cm) connected to an active personal sampling pump via a flexible tube when assessing exposure to organic compounds. Workers commonly complain about the inconvenience of carrying the apparatus to perform this assessment. Packed NTS is recommended to be an alternative as a passive personal sampling of gaseous compounds in work places. This study evaluated that the potential use of small pen-sized sampler for occupational hygiene. The pen-like NTS device has been successfully applied as a personal sampler at work places where solvent gas emitted.

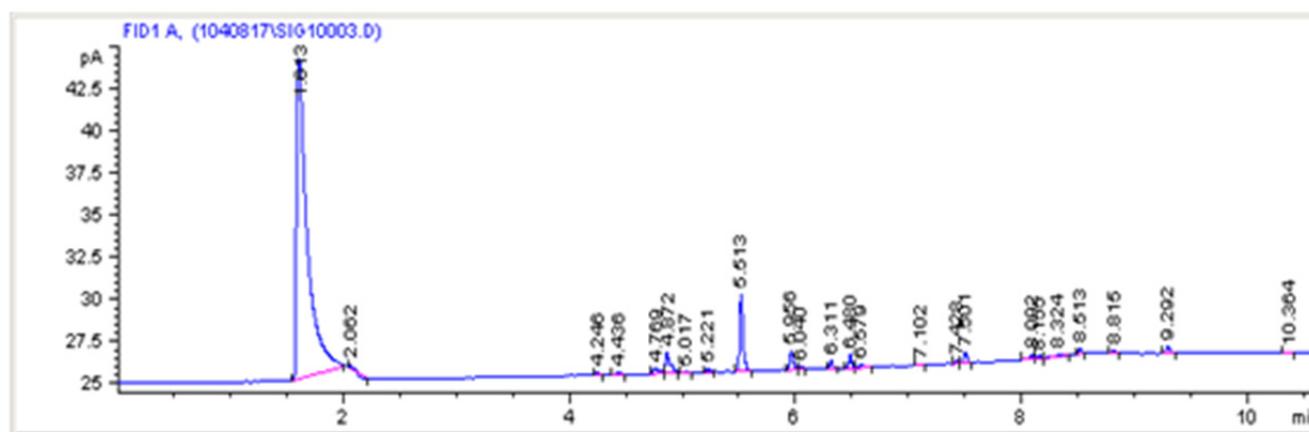


Fig. 3. Chromatograph diagram of freshener emissions by needle trap sampling and GC-FID analysis. Retention times in compound sequence: ethanol 1.6 min; benzene 4.2 min; toluene 4.4 min; ethylbenzene 4.7 min; p-xylene 4.8 min; styrene 5.2 min; dichloromethane 5.5 min; butenes 5.9–6.0 min; pentane 6.3 min; trimethylbenzenes 6.4–6.5 min; compounds of vegetable scents ≥ 7.1 min.

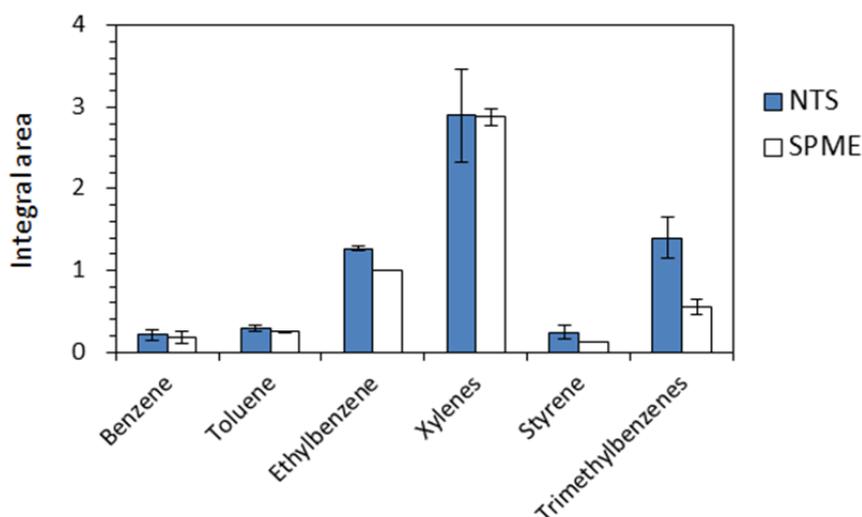
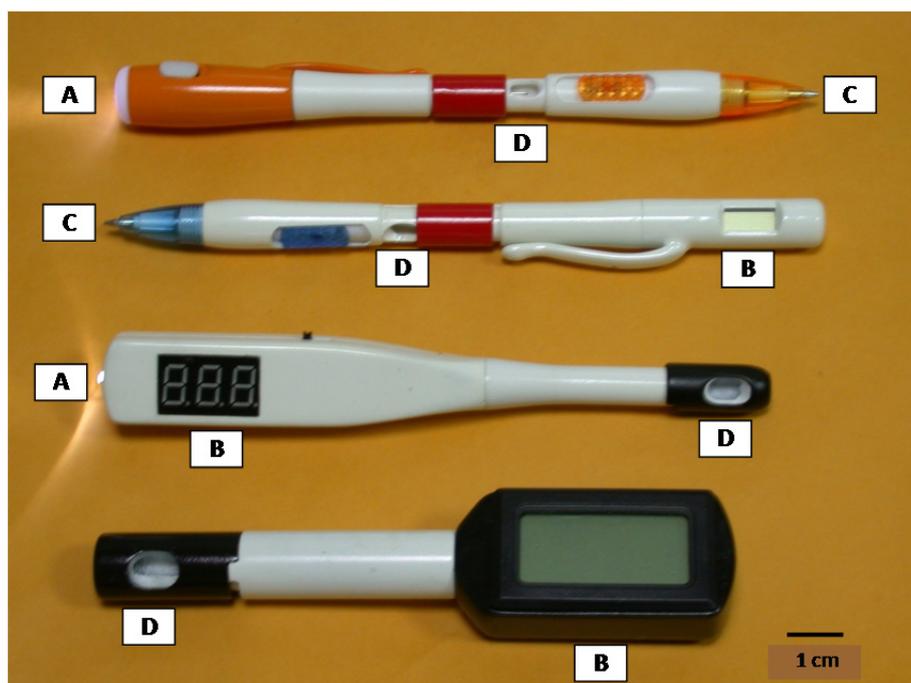


Fig. 4. Freshener emission sampling and analysis: aromatic compounds integral area extracted by 60–80 mesh DVB NTS and SPME fibers using GC-FID analysis.



Function notes:

- A. LED Lights
- B. Temperature/relative humidity display monitor
- C. Mechanical ball pen
- D. Sampling hole for NTS

Fig. 5. Multiple functional pen NTS sampler.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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