

DETERMINATION OF TERPENOID COMPOSITIONS IN CLEANING PRODUCTS BY SOLID PHASE MICROEXTRACTION (SPME) METHOD

Y. Huang¹ and S. C. Lee²

¹ Department of Civil and Structural Engineering, Research Center for Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China
Email: 08901343r@polyu.edu.hk

² Department of Civil and Structural Engineering, Research Center for Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China
Email: ceslee@polyu.edu.hk

ABSTRACT

Terpenoids, especially monoterpenes and monoterpene alcohols, are commonly used as solvents or odorants in household cleaning products. These unsaturated compounds of natural origin are very reactive and can pose health risk on occupants due to the formation of secondary pollutants via indoor chemistry. In this study, a solid phase microextraction (SPME) coupled with gas chromatography/mass spectrometry (SPME-GC/MS) method was applied for the determination of terpenoid compositions in four kinds of floor cleaners (FL). The analysis results demonstrated that chemical composition and concentration of individual terpenoid species varied broadly with cleaning products.

KEY WORDS

Terpenoids, cleaning products, chemical emissions, solid phase microextraction (SPME).

INTRODUCTION

Indoor volatile organic compounds (VOCs) have attracted more and more attentions recently. Many VOCs concentrations are higher in indoor than those in outdoor due to the presence of particular indoor emission sources (Weisel *et al.*, 2008). Many researches demonstrated that daily consumptions of household cleaning products would elevate concentrations of indoor air pollutants (Singer *et al.*, 2006). Recently, terpenes and terpene alcohols emitted from the household products have been attracted more attentions because these VOCs are prone to oxidation and are probably associated with health risks for occupants and workers, even though such products offer substantial benefits (e.g., promotion of hygiene and aesthetics) to human life (Kwon *et al.*, 2007; Nazaroff and Weschler, 2004). A few studies indicated that household products such as floor cleaners and detergents are significant emission sources for indoor air pollutants. Terpenoids can react rapidly with ozone, resulting in formation of reactive radicals, formaldehyde, and secondary organic aerosols (SOA) in indoor environment (Coleman *et al.*, 2008; Fan *et al.*, 2003). The formation of ultrafine particles ($D_p < 100$ nm) has been evidenced from ozonolysis of indoor emissions from building materials (Aoki and Tanabe, 2007), terpene-rich household products (Coleman *et al.*, 2008), cleaning products and air fresheners (Destailats *et al.*, 2006), and wood-based materials (Toftum *et al.*, 2008). The products generated from oxidations of fragrance terpenes contributed greatly to fragrance allergy and upper airway irritation (Matura *et al.*, 2005; WOLKOFF *et al.*, 2000). In addition, such secondary pollutants possibly contain multiple oxygen groups that can cause adverse health effects (Forester and Wells, 2009; Jarvis *et al.*, 2005). Therefore, to understand the roles of terpenoids associated with the consumption of cleaning products in indoor chemistry, it is important to characterize and quantify the terpenoid compositions in daily-consumed cleaning products indoors. The objective of this study is to determine terpenoid compositions in cleaning products by a solid phase microextraction (SPME) coupled with gas chromatography/mass spectrometry (SPME-GC/MS) method.

EXPERIMENTAL

Four kinds of floor cleaners (FL) were examined in this study. The samples were selected based on the extent of product consumption in Hong Kong and the scent of the products shown on the label of their containers.

Three milliliter of each aqueous household samples was extracted respectively with 2 ml of cyclohexane. Recovery test shows that a close to 100% of efficiency was found in the liquid-liquid extraction for terpenoids. The supernatant (cyclohexane) layer was transferred into a clean capped vial. Ten microliters of the extract was injected into a clean Tedlar bag (SKC Inc., Eighty Four, PA) with a micro-syringe (Hamilton, Reno, NV) through a septum. A manual SPME sampling holder consists of a 75 μm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). Once the sampling completed, the fiber was stored and then inserted into the GC injection port at 280°C for 4 min. The highest purity of terpenoids standards of α -pinene, camphene, β -pinene, myrcene, 3-carene, p-cymene, d-limonene, eucalyptol, γ -terpinene, terpinolene, linalool and α -terpineol were used as calibration standards.

RESULTS AND DISCUSSION

Table 1 lists the calibration slopes, intercepts, and coefficients of determination, and limit of detections (LOD) for the 12 terpenoids. The coefficients of determination are >0.98 , except myrcene (0.971), linalool (0.973), p-cymene (0.975) and α -terpineol (0.978). The LODs in mixing ratio were 0.31-0.50 ppbv for the 12 terpenoids. The values demonstrate that the SPME method is reliable for quantification of terpenoids at standard conditions.

Large variations in the concentration were showed. For FC, the highest total quantified terpenoids concentration was seen in FC#1 with a mean of 4145 $\mu\text{g/g}$, which is at >15 times higher than that in the other three samples, ranging from 139 to 265 $\mu\text{g/g}$. d-Limonene, eucalyptol, linalool and α -terpineol are the major quantified terpenoids in FC. Among these compounds, eucalyptol is a sole compound that can be detected in all FC samples. Its mass concentrations ranged from 20.0 ± 0.7 to 210 ± 50.1 $\mu\text{g/g}$. Only in FC#1, other monoterpenes such as β -pinene (11.0 ± 4.5 $\mu\text{g/g}$), myrcene (215 ± 12.1 $\mu\text{g/g}$), and p-cymene (142.8 ± 13.1 $\mu\text{g/g}$) were quantified, while they were undetectable in the rest of samples. Linalool and d-limonene were the two most abundant terpenoids in FC#1, which contributed 55.9% and 30.2%, respectively, to the total quantified terpenoids concentration. However, the contribution of linalool was significantly small in the FC#2 (35.8%) and FC#3 (21.3%) and even no linalool was found in the FC#4. For d-limonene, it only contributed 8.9% in the FC#2 and none was found in FC#3 and FC#4. It should be noted that α -terpineol was the most abundant terpenoids in FC#2-FC#4, contributing 43.0-83.7% to the total quantified concentration, but cannot be detected in FC#1. The concentrations and compositions of monoterpenes and monoterpenoids do not indicate any relationship with the fragrance presented in the FC samples. According to the information provided by the manufacturers, no fragrance was added in FC#1 and FC#4 but no similarity was seen on their composition profiles. For FC#2 and FC#3, both were added with lemon and pinene scent respectively. Again, the mass concentrations and contributions of terpenoids varied greatly. The results demonstrate that the fragrance should not be a major contributor to the terpenoids emission from the FL.

Table 1 Physical Properties, Linear Regression Parameters for Calibration Curves, Limits of Detection (LODs), and Method Precisions

Terpenoids	Formula	MW	Quantification Ion	Boiling Point (°C)	Slope	Intercept	R ²	LOD (ppbv)	RSD
α-Pinene	C ₁₀ H ₁₆	136.23	77,93,121	155-156	233.8	3135.4	0.980	0.44	1.9%
Camphene	C ₁₀ H ₁₆	136.23	79,93,121	159-160	176.2	2573.8	0.983	0.48	3.3%
β-Pinene	C ₁₀ H ₁₆	136.23	69,79,93	155-156	298.9	2192.0	0.986	0.39	4.4%
Myrcene	C ₁₀ H ₁₆	136.23	69,93	167	194.7	-166.8	0.971	0.33	5.2%
3-Carene	C ₁₀ H ₁₆	136.23	77,93,121	168-169	367.2	281.6	0.986	0.45	2.3%
p-ymene	C ₁₀ H ₁₄	134.22	91,119,134	176-178	1485.3	6733.3	0.975	0.50	6.7%
d-Limonene	C ₁₀ H ₁₆	136.23	68,93	170-180	161.5	755.9	0.985	0.50	4.6%
Eucalyptol	C ₁₀ H ₁₈ O	154.25	81,108,111	176-177	189.9	1341.7	0.985	0.33	6.0%
γ-Terpinene	C ₁₀ H ₁₆	136.23	93,119,136	182	172.0	-70.1	0.987	0.31	1.1%
Terpinolene	C ₁₀ H ₁₆	136.23	93,121,136	184-185	103.7	-208.4	0.992	0.42	2.9%
Linalool	C ₁₀ H ₁₈ O	154.25	55,71,93	194-197	106.8	1061.4	0.973	0.37	3.8%
α-Terpineol	C ₁₀ H ₁₈ O	154.25	59,93,136	217-218	194.3	1097.9	0.978	0.35	1.3%

Table 2 Terpenoids composition of cleaning products and air fresheners (in the unit of µg terpenoids / g household products)

	β-Pinene		Myrcene		p-Cymene		d-Limonene		Eucalyptol		Linalool		α-Terpineol	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
FL #1	11.0	4.5	215.0	12.1	142.8	13.1	1250.0	236.5	210.0	50.1	2317.2	571.6		
FL #2							23.6	3.1	32.5	3.3	94.7	8.4	113.8	9.8
FL #3									20.0	0.7	29.7	2.1	89.6	1.1
FL #4									40.7	9.6			208.6	28.1

CONCLUSIONS

A solid phase microextraction (SPME) coupled with gas chromatography/mass spectrometry (SPME-GC/MS) was developed for the determination of terpenoids released from cleaning products and air fresheners. The SPME-GC/MS analysis results suggested that the chemical composition and concentrations of individual terpenoid varied broadly with household products. The concentration of total terpenoids for sample FC1 was the highest up to 4060.8 µg/g, followed by FC2 of 793.9 µg/g, FC4 of 249.3 µg/g and FC3 of 139.2 µg/g.

ACKNOWLEDGMENTS

This project is financially supported by the Postgraduate Studentship (RPH5) and Research Grant (1-ZV3X) of the Hong Kong Polytechnic University (HKPU). This study is also in part supported by Research Grants Council of Hong Kong (PolyU 5175/09E).The authors would like to thank Mr. W.F. Tam at HKPU for technical support.

REFERENCES

- Aoki, T., and S. Tanabe (2007)." Generation of sub-micron particles and secondary pollutants from building materials by ozone reaction", *Atmospheric Environment*, 41(15), 3139-3150.
- Coleman, B. K., M. M. Lunden, H. Destailats, and W. W. Nazaroff (2008)." Secondary organic aerosol from ozone-initiated reactions with terpene-rich household products", *Atmospheric Environment*, 42(35), 8234-8245.
- Destailats, H., M. M. Lunden, B. C. Singer, B. K. Coleman, A. T. Hodgson, C. J. Weschler, and W. W. Nazaroff (2006)." Indoor secondary pollutants from household product emissions in the presence of ozone: A bench-scale chamber study", *Environmental Science & Technology*, 40(14), 4421-4428.

- Fan, Z., P. Liyoy, C. Weschler, N. Fiedler, H. Kipen, and J. Zhang (2003)." Ozone-Initiated Reactions with Mixtures of Volatile Organic Compounds under Simulated Indoor Conditions", *Environmental Science & Technology*, 37(9), 1811-1821.
- Forester, C. D., and J. R. Wells (2009)." Yields of Carbonyl Products from Gas-Phase Reactions of Fragrance Compounds with OH Radical and Ozone", *Environmental Science & Technology*, 43(10), 3561-3568.
- Jarvis, J., M. J. Seed, R. Elton, L. Sawyer, and R. Agius (2005)." Relationship between chemical structure and the occupational asthma hazard of low molecular weight organic compounds", *Occupational and Environmental Medicine*, 62(4), 243-250.
- Kwon, K. D., W. K. Jo, H. J. Lim, and W. S. Jeong (2007)." Characterization of emissions composition for selected household products available in Korea", *Journal of Hazardous Materials*, 148(1-2), 192-198.
- Matura, M., M. Skold, A. Borje, K. E. Andersen, M. Bruze, P. Frosch, A. Goossens, J. D. Johansen, C. Svedman, I. R. White, and A.-t. Karlberg (2005)." Selected oxidized fragrance terpenes are common contact allergens", *Contact Dermatitis*, 52(6), 320-328.
- Nazaroff, W. W., and C. J. Weschler (2004)." Cleaning products and air fresheners: exposure to primary and secondary air pollutants", *Atmospheric Environment*, 38(18), 2841-2865.
- Singer, B. C., H. Destailats, A. T. Hodgson, and W. W. Nazaroff (2006)." Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids", *Indoor Air*, 16(3), 179-191.
- Toftum, J., S. Feund, T. Salthammer, and C. J. Weschler (2008)." Secondary organic aerosols from ozone-initiated reactions with emissions from wood-based materials and a "green" paint", *Atmospheric Environment*, 42(33), 7632-7640.
- Weisel, C. P., S. Alimokhtari, and P. F. Sanders (2008)." Indoor Air VOC Concentrations in Suburban and Rural New Jersey", *Environmental Science & Technology*, 42(22), 8231-8238.
- WOLKOFF, P., P. A. CLAUSEN, C. K. WILKINS, and G. D. NIELSEN (2000)." Formation of Strong Airway Irritants in Terpene/Ozone Mixtures", *Indoor Air*, 10(2), 82-91.