

Optimization of a Passive Sampling Method for Determination of Airborne Naphthalene for Residential Indoor Air Monitoring.

Amanda J. Wheeler^{1*}, Phil Fellin², Henrik Li², Mark D. Gibson³, Judy Read Guernsey³, Keith Van Ryswsk¹, Leonora Marro⁴, Huda Masoud⁴, Roger Sutcliffe¹ and Marie-Eve Héroux¹

¹Water, Air and Climate Change Bureau, Health Canada, Ottawa, Ontario, Canada, ²AirZOne One Ltd., 222 Matheson Boulevard East, Mississauga, Ontario, Canada, ³Department of Community Health and Epidemiology, Dalhousie University, Halifax, Nova Scotia, Canada, ⁴Environmental Health Sciences Research Bureau, Health Canada, Ottawa, Ontario, Canada

* *Corresponding email: Amanda.Wheeler@hc-sc.gc.ca*

SUMMARY

Several exposure studies of indoor air contaminants have used passive sampling devices (PSDs) to determine VOC levels. An existing passive method to determine airborne naphthalene at low levels offers reproducible but low recoveries, considered unacceptable for producing quantitative results. Given the need to determine airborne naphthalene quantitatively with high sensitivity and high quality, optimization of the passive sampling method was undertaken. Seven solvent combinations were evaluated to determine the extraction efficiency, toluene being the most promising. Detailed assessments of toluene extracts allowed optimization of chromatographic performance and characterization of the new method. Passive sampling was then conducted as part of an indoor air exposure study in up to 6 locations within residences including the living room, garage, basement, bathroom, main bedroom and kitchen for both 7-day and 24-hr integrated samples. Results indicate summer naphthalene concentrations were highest in the garage, followed by the basement and then living room.

IMPLICATIONS

Up to 99.0% of human exposure to naphthalene is from indoor air (Government of Canada, 2008). IARC has classified naphthalene as a possible human carcinogen, and reliable residential indoor exposure data are lacking. This research provides a suitable analytical approach and passive sampling design to assess indoor air quality.

KEYWORDS

Indoor air quality, method development, analytical procedure, naphthalene, monitoring.

INTRODUCTION

Passive sampling methods offer significant advantages compared to active sampling methods, in particular they are unobtrusive and easy to deploy when measuring personal exposures and indoor concentrations of airborne volatile organic compounds (VOCs). Health Canada has long supported development of PSD-based methods for indoor air quality and personal breathing-zone exposure assessments. Initially, PSDs were evaluated in test atmospheres and in ambient monitoring situations against reference methods to verify performance. Subsequently, PSDs were used in large scale surveys to determine levels of 26 target VOCs, including naphthalene, in Canadian residences (Fellin and Otson, 1994; Héroux et al., 2008). For the target VOCs, except naphthalene, recovery efficiencies were greater than 80% and sensitivities were approximately $0.2 \mu\text{g}/\text{m}^3$. For naphthalene, the recovery efficiency was

approximately 30%, so efforts were made to improve the quality of the data. The extraction efficiencies could not easily be optimized because use of common solvents caused chromatographic interference in determination of the other target VOCs, hence only naphthalene can be measured with this new extraction method. Although other methods are available for determination of naphthalene, they are generally expensive or have other disadvantages such as high and unpredictable blank levels.

METHODS

As originally configured, the passive method used 3M OVM 3500 PSDs and gas chromatography-mass spectrometry (GC-MS) in selected ion monitoring (SIM) mode. For the initial study, the solvents selected were carbon disulphide (CS₂), dichloromethane (DCM), DCM with 30% acetone, DCM with 30% methanol, toluene, acetonitrile and chloroform (CHCl₃). Duplicate 3M PSDs were spiked at 1 and 10 µg/sample levels to test precision of analysis. Additionally to test recovery from the collection medium, fourteen PSDs were also spiked with 10 µg naphthalene (10 µL solution) and left for 2 hours to dry. Two mL of each solvent were then used to extract naphthalene from the samplers. Naphthalene solution was also spiked into vials containing 2 mL of solvent for comparison to establish recovery as well as precision. Toluene was found to be the best solvent for extracting naphthalene, with a recovery of 72%. Recoveries with the other solvents were poor and ranged from 10% to 20%. The original method for determination of 26 VOCs was modified to allow improvement of the peak-to-width ratio for naphthalene and overall sensitivity. This also reduced the analysis time. Subsequently, toluene was used in a detailed study to determine the method detection limit (MDL) and the extraction recovery efficiency over a range of concentrations characteristic of indoor levels. Finally, the active (charcoal sorbent tube) and passive methods were compared by collecting collocated samples in indoor environments. Although only a small number of collocated samples were collected, which unfortunately had very low naphthalene levels and thus did not allow statistical treatment, the concurrence between the two methods was good.

The analysis protocol involved extracting the samples with 2 mL of toluene for one hour on a mechanical shaker. The toluene extraction solvent was spiked with deuterated 1,2-dichlorobenzene-d₄ (1.34 ng/µL). The extraction solvent was then transferred to a 1.5 mL autosampler vial and analyzed via GC-MS (HP5890 II GC & HP5792 MS). The GC was equipped with a capillary column (J&W 123-1364 DB-624, 60 m x 0.32 mm x 1.8 µm). The carrier gas (helium) head pressure was 6.0 PSI and injector and detector temperatures were kept constant at 220°C and 260°C, respectively. The temperature program yielded a 12.9 min retention time (initial temperature, 80°C for 1 min, 80°C to 260°C at 15°C/min, hold for 1.5 min). The MS was configured to quantify the following 3 characteristic ions of naphthalene: 128, 102 and 64 amu. The ion ratios and peak integration were verified manually for each sample. The air concentrations were calculated using the mass adsorbed on each sampler, the specific uptake rate for naphthalene, exposure times to the nearest one minute and laboratory blank PSDs analyzed at the same time as the samples.

Based on a brief survey of indoor airborne naphthalene concentrations, recovery verification was targeted at levels between 0.1 and 10 µg/m³. The nominal sampling rates are 25 mL/min for the PSDs. Indoor air levels are likely to be biased on the low side i.e., less than 1 µg/m³, so the test levels were chosen to correspond to about 0.3, 0.8, 1.2, 4.0 and 10 µg/m³ corresponding to nominal spiking levels of 11, 29, 44, 150, and 360 ng for PSDs. Each was determined in triplicate to assess method precision. At the same time the standard was spiked

into a solvent aliquot equal to the extraction amount for each sorbent to allow comparison at each level. The recoveries ranged from 79% to 87% over the five levels (average 84%). The precision of determination was 3% Relative Standard Deviation (RSD) for triplicate measurements over the range of concentrations.

The MDL, including handling and extraction was determined by the CFR 40 method (the standard deviation of determination of 8 low level standards or blank media multiplied by 3.28 is defined as the detection limit at 95% confidence interval). Low level spikes were made at 0.008 ng/ μ L. The data show a MDL of 0.05 μ g/m³.

Having developed an improved analytical method, the PSD monitoring of naphthalene was pilot tested as part of a residential indoor air exposure study conducted by Health Canada in collaboration with Dalhousie University in the greater Halifax Regional Municipality (HRM), Nova Scotia, Canada. A range of air parameters typically found within residences were measured indoors and outdoors for seven consecutive 24-hour periods in 50 homes in both the winter (January to April 2009) and the summer (June to September 2009) sampling phases, with 42 homes participating in both seasons. Ten homes were recruited from each of the following construction year categories: 1945 and before, 1946-1960, 1961-1980, 1981-2000, and 2001-2008. The most recent age category was oversampled to include sufficient numbers of newer homes in the study. An effort was made to include 10 homes using gas stoves.

Naphthalene concentrations were first measured using PSDs indoors in the winter season, starting in March 2009. In order to capture the main sources of naphthalene and the variation in indoor concentrations, PSDs were installed in up to six different locations and for three different sampling times in a subset of participants' homes. The measurements were taken in the basement, bathroom, garage, kitchen, living room and main bedroom. These samplers were deployed for a 24-hr period during the week (Tuesdays) and weekend (Saturdays); and for a 7-day integrated period. Based on the results from the winter sampling phase, it was decided that summer sampling would be conducted in each house for one 7-day period only, with PSDs installed in the living room and if present, in the basement and attached garage. Blank and duplicate samples (10% each) were deployed randomly in the field for 24-hr's or 7-days, depending on the season.

Values below the MDL for naphthalene (0.05 μ g/m³) were replaced with half the MDL. Levels of naphthalene were compared in the same household during the winter and summer seasons only for the living room measurements using a paired t-test. Normality assumption was assessed using the Anderson-Darling test. If the normality assumption was not satisfied then the non-parametric Wilcoxon Signed Rank (WSR) test was used to compare the differences between the levels of naphthalene during the two seasons in the same homes. For other homes that were sampled in only one season, levels of naphthalene were compared using a two sample t-test. Assumptions of normality and equal variance were tested using the Anderson-Darling test and Bartlett's test, respectively. When the assumptions were not satisfied for either the original or log-transformed data, then the non-parametric Kruskal Wallance (KW) test was used. Levels of naphthalene were also compared between locations: basement, living room and garage, by season. In order to maximize the use of the data, separate paired t-tests were used to assess the difference between locations, and Bonferroni corrections were used to adjust for multiple comparisons within houses. Comparisons were only carried out on a minimum sample size of 10 observations per group.

RESULTS

The precision of sampling and analysis based on replicate deployment of collocated samples was 14.9% RSD (n = 60 duplicates). Concentrations in both seasons were not blank-corrected because more than 50% of the blanks were below the MDL. For samples below the MDL ($0.05\mu\text{g}/\text{m}^3$), half MDL was used for concentration calculations.

A total of 55 homes were sampled for naphthalene in Halifax. Of these, only 13 were sampled during both the winter and summer, 5 during only the winter and 37 during the summer. During the winter season different measurements were taken in a sample of homes, including: single 24-hr periods (on Tuesday and Saturday to identify any weekday and weekend variability), and a single 7-day integrated sample. Both the single day summary statistics as well as the weekly summary statistics for naphthalene are reported in Table 1.

Naphthalene levels in the living room in homes sampled during both the winter and summer were similar to one another (paired t-test=0.70, $p=0.497$, $n=13$). For the remaining single season homes, no statistical tests were completed. Valid average levels of naphthalene in the living room for the 36 available summer homes were $0.45\mu\text{g}/\text{m}^3$, with a standard deviation of $0.54\mu\text{g}/\text{m}^3$, and a median of $0.27\mu\text{g}/\text{m}^3$. Average levels of naphthalene in the living room for the 5 winter homes were $0.20\mu\text{g}/\text{m}^3$, with a standard deviation $0.04\mu\text{g}/\text{m}^3$, and a median of $0.19\mu\text{g}/\text{m}^3$.

Weekly levels of naphthalene were compared in the three locations of homes: basement, living room and garage, by season. There was no significant difference between locations during the winter ($p>0.05$) (see Table 1). For homes sampled during the summer, levels of naphthalene were significantly higher in the garage when compared to the living room (WSR=101, adjusted $p <0.0001$, $n=20$) and basement (WSR=70.5, adjusted $p =0.003$, $n=18$). As well, levels of naphthalene were statistically higher in the basement compared to the living room (WSR=309, adjusted $p <0.0001$, $n=45$).

DISCUSSION

A recent review of the residential indoor naphthalene literature reported median naphthalene concentrations, measured using different sampling methods, ranging from 0.17 to $4.59\mu\text{g}/\text{m}^3$ (Jia and Batterman, 2010). Our indoor living room results are on the lower end of what was reported by Jia and Batterman, 2010; the only exception being the higher concentrations measured in the garage during the summer sampling (median = $2.34\mu\text{g}/\text{m}^3$). Naphthalene is a product of incomplete combustion, and can off-gas and volatilize from vehicles and stored petroleum products (Jia and Batterman, 2010; Schauer et al, 2002; Marr et al, 1999). These sources could have contributed to the higher levels found in the attached garages in our study. Similar results in attached garages have been reported by Batterman et al (2006a; 2006b). It is hypothesized that the higher concentrations found in the basement, compared to the living room, could be explained by the migration of naphthalene from the attached garages to the basements.

Table 1: Descriptive Statistics of Naphthalene Concentrations ($\mu\text{g}/\text{m}^3$)

Duration	Season	Location	N	Mean	Std. Dev.	Minimum	25 th	Median	75 th	90 th	Maximum	%BDL (n)*
Measurement on single Days												
Saturday	Winter	Basement	14	0.64	0.96	0.025	0.025	0.27	0.91	1.75	3.49	28.6 (4)
Saturday	Winter	Bathroom	16	0.86	1.84	0.025	0.07	0.24	0.44	3.72	6.89	25.0 (4)
Saturday	Winter	Garage	4	0.58	0.45	0.11	0.20	0.55	0.95	1.08	1.08	0.0 (0)
Saturday	Winter	Kitchen	16	0.79	1.66	0.025	0.025	0.08	0.52	4.60	5.36	50.0 (8)
Saturday	Winter	Living Room	16	0.89	1.94	0.025	0.025	0.21	0.42	4.62	6.82	31.3 (5)
Saturday	Winter	Main Bedroom	16	0.75	1.71	0.025	0.025	0.03	0.32	4.12	5.94	56.3 (9)
Weekly measurement												
Weekly	Summer	Basement	45	1.35	1.93	0.025	0.27	0.61	1.39	4.46	9.16	6.7 (3)
Weekly	Summer	Garage	20	5.52	6.78	0.19	1.09	2.34	8.10	16.09	24.16	0.0 (0)
Weekly	Summer	Living Room	49	0.67	1.46	0.025	0.17	0.23	0.39	1.49	7.95	10.2 (5)
Weekly	Winter	Basement	16	0.71	1.16	0.05	0.14	0.20	0.87	2.20	4.52	0.0 (0)
Weekly	Winter	Bathroom	18	0.92	2.01	0.09	0.18	0.26	0.38	4.13	8.10	0.0 (0)
Weekly	Winter	Garage	4	0.84	0.71	0.23	0.28	0.69	1.41	1.76	1.76	0.0 (0)
Weekly	Winter	Kitchen	18	0.88	1.83	0.06	0.18	0.23	0.37	5.05	6.60	0.0 (0)
Weekly	Winter	Living Room	18	0.92	1.94	0.09	0.18	0.24	0.37	5.29	7.03	0.0 (0)
Weekly	Winter	Main Bedroom	18	0.94	2.05	0.07	0.14	0.25	0.34	4.94	7.81	0.0 (0)

* = percent below the detection limit.

CONCLUSION

An optimized passive sampling method was developed to determine naphthalene in indoor air, with increased recovery averaging 84%. The sampler was successfully tested as part of an exposure study, with results being generally consistent with previous monitoring campaigns where naphthalene was sampled. During the summer, higher concentrations were found in garages and basements, compared to living room measurements. There was insufficient data available to test this relationship in the winter and this deserves further evaluation. Further research is needed to better identify sources that contribute to naphthalene levels in residential environments.

ACKNOWLEDGEMENTS

Funding provided under contracts #: 4500196514 and 4500195911 from Health Canada.

REFERENCES

Batterman, S., Jia, C., Hatzivasilis, G. and Godwin, C. (2006) Simultaneous measurement of ventilation using tracer gas techniques and VOC concentrations in homes, garages and vehicles. *J. Environ. Monit.*, 2006, 8, 249–256.

Batterman, S., Hatzivasilis, G. and Jia, C. (2006). Concentrations and emissions of gasoline and other vapors from residential vehicle garages. *Atmos Environ*, 40 (10), 1828-1844.

Fellin, P. & R. Otson (1994) Assessment of the influence of climatic factors on concentration levels of volatile organic compounds (VOCs) in Canadian homes. *Atmospheric Environment*, 28, 3581-3586.

Government of Canada, 2008. Proposed Risk Management Approach for Naphthalene. July 2008. http://www.ec.gc.ca/ese-ees/B68532E6-50EB-4368-92FC-7FA0B36AD64D/batch1_91-20-3_rm_en.pdf

Héroux, M. È., Gauvin D., Gilbert N. L., Guay M., Dupuis G., Legris M. & Lévesque B. (2008) Housing characteristics and indoor concentrations of selected volatile organic compounds (VOCs) in Quebec City, Canada. *Indoor and Built Environment*, 17, 128-137.

Jia C. and Batterman S. (2010). A Critical Review of Naphthalene Sources and Exposure Relevant to Indoor and Outdoor Air. *Int. J. Environ. Res. Public Health*. 7:2903-2939.

Schauer, J.J., Kleeman, M.J., Gass, G.R., Simoneit, B.R.T. (2002) Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles. *Environ. Sci. Technol.* 36, 1169-1180.

Marr, L.C., Kirchstetter, T.W., Harley, R.A., Miguel, A.H., Hering, S.V., Hammond, S.K. (1999) Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environ. Sci. Technol.* 33, 3091-3099.