

Calibration of solid-phase microextraction for measuring indoor gas phase SVOC concentration

Mengyan Gong^{1,*}, Dustin Poppendieck¹

¹Indoor Air Quality and Ventilation Group, Engineering Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA

*Corresponding email: mengyan.gong@nist.gov

SUMMARY

The most common method to calibrate solid-phase microextraction (SPME) for measuring gas phase semi-volatile organic compound (SVOC) concentrations, i.e., splitless liquid injection, may be associated with large measurement uncertainty. This study aims to evaluate the direct syringe-fiber loading method for calibrating SPME by examining repeatability, influence of solvent evaporation, and linearity of standard curves for several typical indoor SVOCs. The direct loading method has been successfully validated for DEHP. Evaluation for TDCPP, B[a]P and PCB-52, and application to DEHP concentration in air of a sealed chamber with PVC flooring will be conducted.

KEYWORDS

SPME, SVOC emissions, DEHP, PVC flooring, Indoor air quality

1 INTRODUCTION

Measurement of gas phase SVOC concentrations is required for indoor exposure assessment. Compared with other SVOC sampling techniques, e.g., sorbent tube and polyurethane foam, SPME has advantages of small sampling volume, ease of sample preparation and sampling, and simple injection (Ouyang and Pawliszyn, 2008). In addition, SPME is the only suitable method for sampling in sealed environments, e.g., the sealed stainless steel chamber used in Cao et al. (2016). Therefore, SPME has been increasingly used to sample gas phase SVOCs in both sealed and ventilated environments. However, to use SPME to measure SVOC concentration in air, quantification of the absolute amount of analyte on the SPME fiber is required. To calibrate the amount of analyte on the fiber, a separate liquid splitless injection to a gas chromatography–mass spectrometer (GC-MS) is often used, which assumes that SPME injection has the same transfer efficiency as liquid splitless injection. However, the transfer efficiencies can be significantly different for the two injection techniques (Ouyang et al., 2005). Thus, calibrating with liquid splitless injection may cause large uncertainties in measured SVOC concentrations. The purpose of this study is to improve and evaluate the current direct syringe-fiber loading method by determining the reproducibility, influence of solvent evaporation, and linearity for several typical indoor SVOCs, and demonstrating the method's applicability by measuring bis(2-ethylhexyl) phthalate (DEHP) concentration in air of a sealed chamber with PVC flooring.

2 METHODS

For calibration, as shown in Figure 1, 1 μL of standard liquid at different concentrations and 1 μL of a corresponding internal standard were spiked onto the SPME fiber. After the solvent evaporated, the SPME fiber was injected into the GC-MS. We used several typical SVOCs, e.g. DEHP, Tris(1,3-dichloro-2-propyl)phosphate (TDCPP),

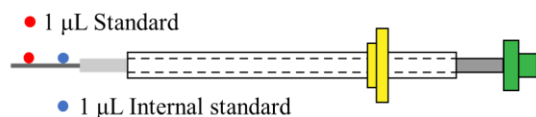


Figure 1. Illustration of direct loading of calibration liquid onto SPME fiber.

Benzo[a]pyrene (B[a]P), and 2,2',5,5'-Tetrachlorobiphenyl (PCB-52) (and their corresponding internal standards DEHP-d₄, TDCPP-d₁₅, BaP-d₁₂ and ¹³C PCB-52) to evaluate this method.

First, the repeatability of standard loading was examined by running the same standard multiple times. Second, to examine the standard loss during solvent evaporation, 1 μL of standard liquid was spiked onto the fiber and evaporated for different times, while 1 μL internal standard was spiked onto the fiber but evaporated for a fixed time for each sample. Third, the linearity of the standard curve was evaluated. After evaluation of the calibration method, SPME will be used to sample in a specially designed sealed chamber containing PVC flooring for different times at 25 °C, as show in Figure 2. The DEHP concentration in the air of the sealed chamber was then calculated based on the method described in Cao et al. (2016).



Figure 2. SPME sampling from a sealed chamber.

3 RESULTS AND DISCUSSION

The results show that the response ratio of DEHP and DEHP-d₄ for multiple injections are consistent with relative standard deviations less than 10 %. Figure 3 shows that the evaporation time of DEHP doesn't significantly influence the response. Hence, if the evaporation time of DEHP is within the examined time range (less than 32 min), the evaporation loss will be insignificant. The linearity of the standard curve for direct loading is high with R² larger than 0.99, as shown in Figure 4. Based on these results, it appears that the direct loading method can be used to calibrate the amount of DEHP sorbed to SPME. However, since different chemicals have varying evaporation rates, the method may not work for chemicals with higher volatility, and application for other chemicals needs to be further examined.

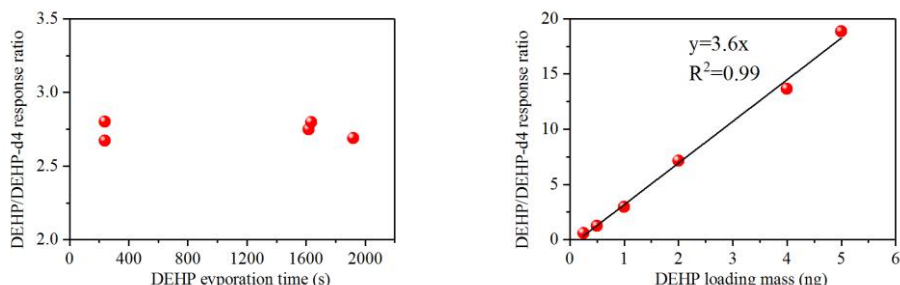


Figure 3. Influence of DEHP evaporation loss. Figure 4. SPME calibration curve for DEHP.

4 CONCLUSIONS

The method of calibrating SPME by direct syringe-fiber loading has been validated for DEHP. Evaluation for other selected SVOCs and application of the method for measurement of DEHP concentration in air of sealed chamber with PVC flooring will be conducted. If successful, the direct loading method could be used as a calibration method for using SPME to measure gas phase SVOC concentrations. However, the applicability of this method for chemicals not evaluated in this study needs to be examined using the procedure in this study.

5. REFERENCES

- Cao J, Zhang X, Little JC, Zhang Y. 2016. *Indoor Air*. 27(2), 417-426.
Ouyang G, Chen Y, Setkova L, Pawliszyn J. 2005. *Journal of Chromatography A*, 1097(2): 9-16.
Ouyang G, Pawliszyn J. 2008. *Analytica Chimica Acta*, 627(2): 184-197.