

An improved method for calibrating solid-phase microextraction by direct loading

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KEYWORDS

SPME, semivolatile organic compounds, tris(2-chloro-1-methylethyl) phosphate, spray polyurethane foam

1 INTRODUCTION

Solid-phase microextraction (SPME) has been widely used as a sampling technique for a variety of organic compounds due to its advantages of small sampling volume, ease of sampling, and simple injection (Ouyang and Pawliszyn 2008). Recently, Cao et al. (2016) developed an improved method for measuring the emission parameters for semivolatile organic compounds (SVOC), which shortened experimental times. In the method by Cao et al. (2016), the SVOC equilibrium concentration in a sealed chamber was measured using SPME sampling. Hence, calibration of SPME is required, which requires that the absolute amount of SVOC adsorption onto the SPME fiber be measured. To do this, Cao et al. (2016) calibrated SPME using liquid splitless injection and assumed that the SPME injection and liquid splitless injection have the same transfer efficiency. However, it is known that the transfer efficiency for both SPME injection and splitless injection are influenced by factors such as the type of liner, temperature of injector, and cross-sectional area of the space between column and liner, so that transfer efficiencies could be significantly different for the two injection techniques (Ouyang, Chen et al. 2005). Hence, calibrating SPME using liquid splitless injection may cause large uncertainties. Among the loading techniques that have been used for SPME, direct syringe-fiber loading has been shown to have transfer efficiencies greater than 95 % for chemicals with low volatility (Zhao, Ouyang et al. 2007). The present study aims to first investigate the applicability of the syringe-fiber loading approach for calibrating SPME, and then apply it to experiments measuring the Tris(2-chloro-1-methylethyl) Phosphate (TCPP) partition coefficient between spray polyurethane foam (SPF) and air based on the method by Cao et al. (2016).

2 METHODOLOGIES

The structure of SPME is shown in Figure 1. Instead of spiking the liquid calibration solution onto the fiber as in the previous loading method (Zhao, Ouyang et al. 2007), we spiked the liquid onto the stainless steel rod just above the fiber to avoid damaging the easily breakable SPME fiber (100 μm in diameter). In addition, to eliminate the influence of changing the gas chromatograph-mass spectrometer (GC-MS) response, the internal standard was also spiked onto the stainless-steel rod. Here, we took TCPP as an example to evaluate this method. First, a series of experiments were run to examine the influence of evaporation loss during spiking by exposing the SPME stainless steel in a fume hood for different times. As shown in Figure 2, 1 μL TCPP liquid and 1 μL internal standard (triamyl phosphate, TAP) were spiked onto the end of the SPME stainless steel rod successively. Second, SPME was used to sample in a specially designed sealed chamber containing SPF for different times at 25 $^{\circ}\text{C}$, as show in Figure 3. Then, 1 μL of TAP was spiked onto the stainless-steel rod after pushing the fiber out. Experiments were run to examine the TCPP loss from SPME fiber when it is exposed to the surrounding fume hood air during the process of spiking TAP. Third, standard curves were run to calculate the SPME adsorption amount for different sampling times. Finally, the partition coefficient between TCPP in SPF and air was calculated based on the method described in Cao et al.(2016).

3 RESULTS AND DISCUSSION

Figure 4a shows the response ratio of two TCPP isomers (TCPP1 and TCPP2) and TAP (internal standard) when the TCPP standard was evaporated from the stainless-steel rod for different times. The standard deviations of the ratio for standards with both high and low TCPP concentration is less than 10 %, except for TCPP2 at lower concentration, which is 15 %. Hence, the TCPP loss from the stainless-steel rod during spiking was minimal. Figure 4b shows the response ratio of TCPP and TAP when SPME samples were first taken for 5 min and then the fiber was exposed to surrounding air for different times. The standard deviation for TCPP1 and TCPP2 is 6 % and 11 %, respectively, which indicates that the TCPP loss from the SPME fiber during spiking was also minimal. The linear correlation coefficients of the standard curve with TCPP concentrations from 0.1 ng/ μ L to 2.5 ng/ μ L were larger than 0.98. The calculated SPME adsorption amount for different sampling times is shown in Figure 5. Based on Figure 5 and the initial TCPP concentration in SPF we measured in other experiments (8.3×10^{11} μ g/ m^3 and 2.1×10^{11} μ g/ m^3 for TCPP1 and TCPP 2), the calculated partition coefficient between SPF and air at 25 °C is 1.0×10^7 and 1.2×10^7 for TCPP1 and TCPP2, respectively.

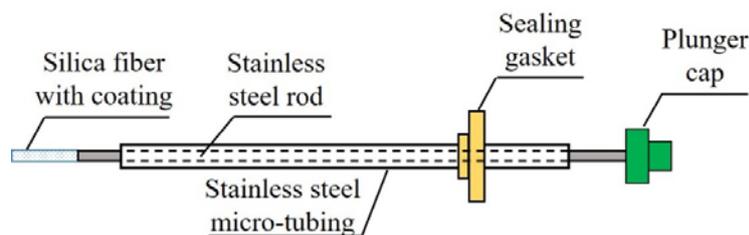


Figure 1. Structure of SPME (Pawliszyn, Pawliszyn et al. 1997)



Figure 2. Illustration of direct loading of calibration liquid onto SPME stainless steel rod

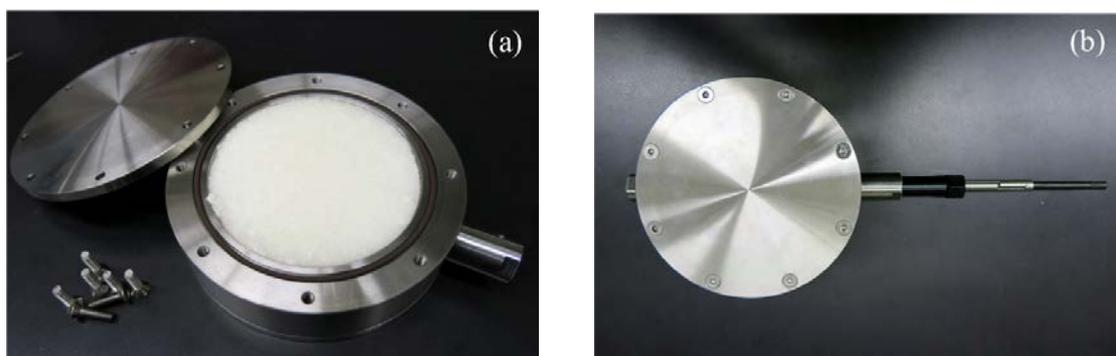


Figure 3. SPME sampling from a sealed chamber (a) chamber; (b) sampling

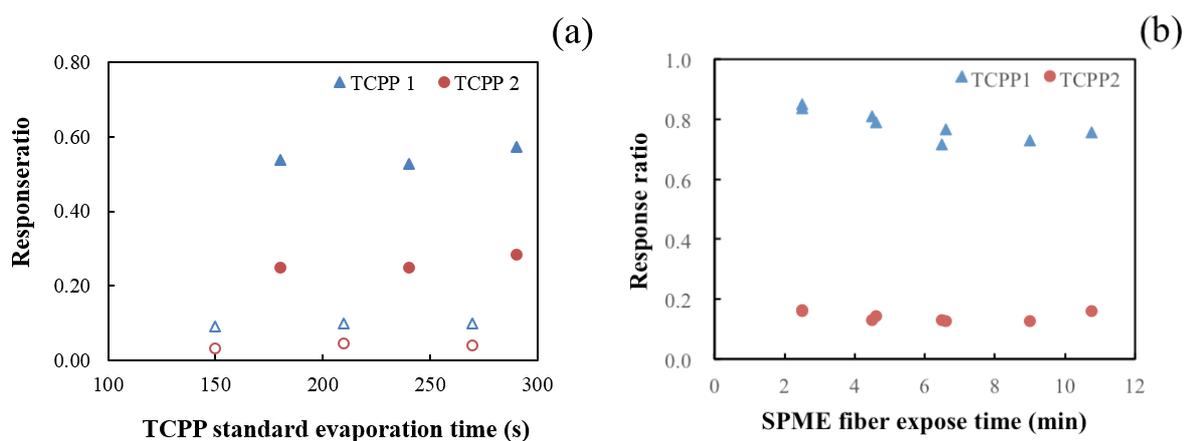


Figure 4. Evaluation of TCPP loss during spiking (a) TCPP standard, lower ratios for 0.1 ng/μL standard, higher ratios for 1 ng/μL standard; (b) SPME fiber

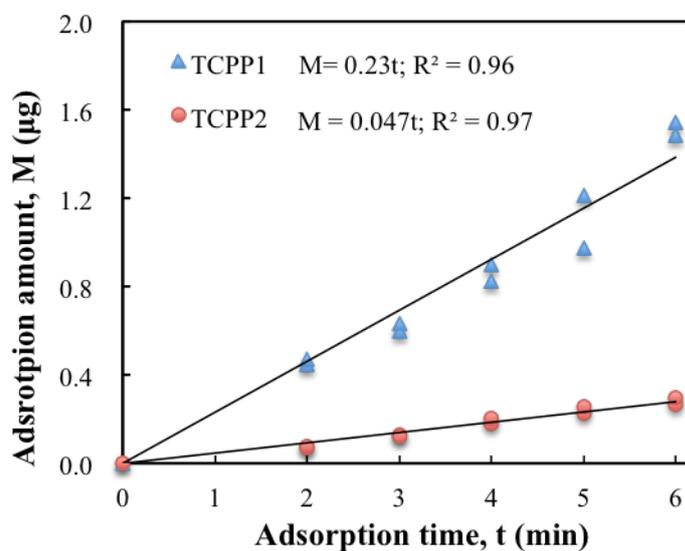


Figure 5. SPME adsorption amount of TCPP

4 CONCLUSIONS

The improved method for calibrating SPME by direct syringe-stainless steel rod loading for TCPP has been preliminarily validated. In addition, the method has been successfully used for measurement of the TCPP partition coefficient between SPF and air. However, more tests for

TCPP standards at higher concentrations and the applicability of this method for chemicals with different physical properties are needed to completely evaluate this method.

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