
Electromagnetically vibrated Solid-Phase Microextraction for the analysis of organic compounds

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Abstract: A newly developed electromagnetically vibrated Solid-Phase Microextraction (SPME) device for extracting 1,4-dichlorobenzene and toluene from aqueous matrices was evaluated in terms of sorption equilibrium time, precision, and detection level relative to three other more conventional extraction techniques involving SPME, viz., static, magnetic stirring, and fibre insertion/retraction. Electromagnetic vibration at 420 cycles/s was found to be the most efficient extraction technique and also did not detrimentally impact the sustainability of the extracting performance of the SPME fibre. Therefore, electromagnetically vibrated SPME may be a more powerful tool for rapid sampling and solvent-free sample preparation relative to other more conventional extraction techniques used with SPME.

Keywords: detection level; electromagnetic vibration; extraction techniques; organic compounds; precision; SPME; solid-phase microextraction; sorption equilibrium time.

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1 Introduction

Solid-Phase Microextraction (SPME) was developed to address the need for rapid sampling and solvent-free sample preparation in extracting organic compounds from various sample matrices, including air, water, soil, biological and pharmaceutical samples (Belardi and Pawliszyn, 1989; Louch et al., 1992; Motlagh and Pawliszyn, 1993; Popp et al., 1994; Zhang et al., 1994; Eisert and Pawliszyn, 1997a, 1997b; Pawliszyn, 1997, 2001; Lord and Pawliszyn, 2000; Chen et al., 2003; Conder et al., 2003; van der Wal et al., 2004; Larroque et al., 2006; Dietz et al., 2006; Ouyang and Pawliszyn, 2006; Beceiro- González et al., 2007). SPME combines sampling, isolation and enrichment into a single step (Zhang et al., 1994; Eisert and Pawliszyn, 1997b; Ouyang and Pawliszyn, 2006), and consists of two processes:

- 1 sorption of organic compounds between the SPME fibre and the sample matrix
- 2 desorption of enriched organic compounds from the SPME fibre in analytical instruments (Zhang et al., 1994; Lord and Pawliszyn, 2000; Dietz et al., 2006).

In the sorption process, the SPME fibre is exposed to the sample matrix until sorption equilibrium of an organic compound between the SPME fibre and the sample matrix is achieved (Louch et al., 1992; Eisert and Pawliszyn, 1997a, 1997b; Pawliszyn, 1997, 2001; Conder et al., 2003; van der Wal et al., 2004; Ouyang and Pawliszyn, 2006). However, the time required to reach equilibrium in extracting organic compounds from the sample matrix to the SPME fibre can be long (i.e., from 0.5 h to 30 d), and is dependent on several factors including the physicochemical properties of the organic compounds, the physicochemical properties and thickness of the SPME fibre, and the temperature and chemistry of the sample matrix (Louch et al., 1992; Motlagh and Pawliszyn, 1993; Eisert and Pawliszyn, 1997a, 1997b; Lord and Pawliszyn, 2000; Ouyang and Pawliszyn, 2006).

Since the time required to reach equilibrium typically is longer (i.e., >0.5 h) under a static sorption condition, several different extraction techniques have been evaluated in an attempt to achieve equilibrium more rapidly, including magnetic stirring, fibre insertion/retraction, mechanical vibration, and sonication (Louch et al., 1992; Motlagh and Pawliszyn, 1993; Eisert and Pawliszyn, 1997a, 1997b; Koehler and Geppert, 1997; Lord and Pawliszyn, 2000; Ouyang and Pawliszyn, 2006). Although these extraction techniques facilitate mass transport of organic compounds between the SPME fibre and the sample matrix, their application has been problematic owing to the need to ensure that the rotational speed is constant, the flow around the coated fibre is reproducible, the transfer of vibratory motion to the fibre is consistent, and the sample is not heated during the extraction processes. In addition, these extraction techniques (i.e., magnetic stirring, fibre insertion/retraction, mechanical vibration, and sonication) have been applied to direct extraction from fluids in porous media and on-site field analysis when coupled with a portable isothermal Gas Chromatograph (GC) with practical limitations. Therefore, an alternative technique is needed to reduce the time to achieve sorption equilibrium without the inherent disadvantages from the conventional extraction techniques.

As a result of the aforementioned considerations, the development and evaluation of an electromagnetically vibrated SPME device for extracting organic compounds from aqueous matrices are presented in this study. The evaluation was based on comparison in terms of sorption equilibrium time, precision, and detection level with three other more conventional extraction techniques involving SPME, viz., static, magnetic stirring, and fibre insertion/retraction. The effects of vibration frequency on the sorption equilibrium time and the sustainability of the extracting performance of the SPME fibre also were investigated. Finally, a perspective for future applications and further development of the electromagnetically vibrated SPME device is presented in terms of monitoring the transport of organic compounds from fluids through porous media and incorporation of an automated sampler, respectively. To the best of the authors' knowledge, electromagnetically vibrated SPME has never been studied.

2 Materials and methods

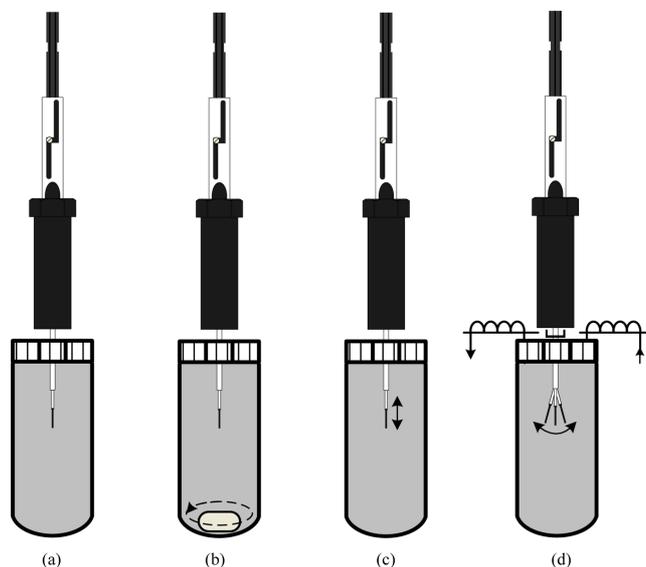
2.1 Solutions of organic compounds

On the basis of the negligible peak tailings or thermal stability in a GC (HP 5890 II, Hewlett-Packard Co., Palo Alto, California, USA) equipped with a Mass Selective Detector (MSD), two non-polar neutral organic compounds were used in this study, viz., 1,4-DCB and TOL. The organic compounds were purchased from Sigma-Aldrich Chemical Co. (St. Louis, Missouri, USA) and Fisher Scientific Co. (Pittsburgh, Pennsylvania, USA), respectively, and were of the highest available purity ($\geq 99.9\%$). Solutions of each organic compound were prepared by adding the exact amount of neat compound to nanopure water (Barnstead/Thermolyne, Dubuque, Iowa, USA) in a 0.5-L flat-bottom glass flask with a short neck (Pyrex Brand, Fisher Scientific Co., Pittsburgh, Pennsylvania, USA), and by mixing the contents using a magnetic stir bar [22.2 mm (L) \times 9.5 mm (O.D.)] at 600 rpm for 24 h before use. A bacterial inhibitor in the form of 200 mg/L of sodium azide, NaN_3 (Fisher Scientific Co, Pittsburgh, Pennsylvania, USA), was added to all solutions. Finally, diluted solutions of the organic compounds at ten different initial concentrations (i.e., 0.01, 0.1, 0.5, 1, 5, 10, 30, 50, 80, and 100 $\mu\text{mol/L}$) were transferred into 41-mL glass centrifuge vials (Kimble Glass Inc., Vineland, New Jersey, USA) and sealed immediately with the polytetrafluoroethylene-faced silicone septa and screw caps (National Scientific Co., Rockwood, Tennessee, USA) without headspace. In this study, large sample volumes (41 mL) were used, since there was concern that lesser volumes of analyte with greater partitioning into the SPME fibre would have been exhausted. For all tests, the volumes of both samples and standards for calibrations were the same during the analysis to avoid errors.

2.2 Solid-Phase Microextraction

Solid-Phase Microextraction (SPME) was performed manually using a 100 μm polydimethylsiloxane (PDMS) fibre (Supelco, Bellefonte, Pennsylvania, USA) at $22 \pm 1^\circ\text{C}$ for all experiments. Since the extraction time increases with thickness of the coating (Louch et al., 1992; Zhang et al., 1994; Eisert and Pawliszyn, 1997b), a relatively thick, 100- μm PDMS fibre was selected to increase the likelihood that the sorption equilibrium time would be long under conventional extraction conditions, such that a significant reduction in the sorption equilibrium time might result under the modified extraction conditions. Also, the PDMS fibre includes a non-polar liquid coating with greater partitioning of non-polar organic compounds compared with other fibre coatings. Prior to use, the PDMS fibre was conditioned at 250°C under high-purity helium flow for 0.5 h. With the PDMS fibre retracted, the needle was passed through the septum of a sample vial. Then, the PDMS fibre was directly exposed to the aqueous matrix under various extraction techniques, as illustrated in Figure 1. Finally, the PDMS fibre was retracted into the needle, and the needle was removed from the sample vial. For all experiments, the depth of the PDMS fibre within a sample vial was consistent, and SPME was performed as a minimum in triplicate for statistical analysis.

Figure 1 Illustration of the four different extraction techniques evaluated in this study: (a) static condition; (b) magnetic stirring at 600 rpm; (c) fibre insertion and retraction at 10 insertion-retraction cycles/min; (d) electromagnetic vibration at constant and controlled frequencies (i.e., 10, 200, 420, and 800 cycles/s)



The method detection limit, or MDL, defined as the lowest concentration level of organic compounds that can be measured with 99% confidence that the concentration of the organic compound is greater than zero, was determined from the analysis of the organic compounds for each extraction technique using the EPA procedure described by Berthouex and Brown (1994).

2.2.1 Magnetic stirring

After the stable and optimum stirring rate in the aqueous matrix for a 41-mL glass centrifuge vial was determined prior to extraction experiments, the speed of the magnetic stirrer (Fisher Scientific Co. Pittsburgh, Pennsylvania, USA) using an octagonal magnetic stir bar [12.7 mm (L) \times 7.9 mm (O.D.)] was set at 600 rpm (note that 600 rpm did not represent the maximum stirring rate). Also, the PDMS fibre was exposed for periods up to 30 min.

2.2.2 Fibre insertion and retraction

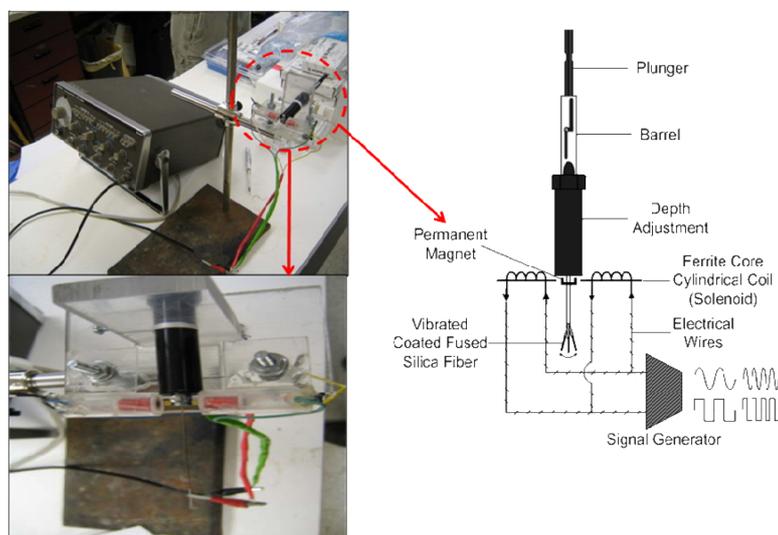
To minimise the thickness of the boundary (i.e., stagnant-water) layer at the surface of the PDMS fibre, the PDMS fibre was inserted into and retracted from the aqueous matrix repeatedly. In this method, the PDMS fibre was inserted/retracted manually at a rate of 10 cycles/min for periods up to 60 min.

2.2.3 Electromagnetic vibration

Electromagnetic vibration was performed using the newly developed electromagnetically vibrated SPME device. The newly developed SPME device consists of a permanent

magnet, solenoids, and a signal generator, as illustrated in Figure 2. Two single-layer magnetically coupled solenoids with a common axis around the SPME needle and an installed permanent magnet gave rise to mutual inductance effects in a frequency oscillator circuit around the SPME needle. Thus, electromagnetic vibration was generated via magnetic forces between two single-layer magnetically coupled solenoids. The SPME fibre was vibrated at constant and controlled frequencies for periods up to 30 min by adjusting the sine waves at constant and controlled frequencies of 10, 250, 420, and 800 cycles/s via the signal generator (Hewlett-Packard Co. Palo Alto, California, USA), regardless of the direction (horizontal or vertical).

Figure 2 Pictorial and schematic views of the electromagnetically vibrated SPME device developed in this study (see online version for colours)



2.3 Gas Chromatography

Concentrations of 1,4-DCB and TOL were measured using a GC/MSD. To achieve better resolution and a more consistent retention time, the SPME inlet guide, a Merlin microseal and a 0.75 mm (I.D.) liner (Supelco, Bellefonte, Pennsylvania, USA) were used for all experiments. Thermal desorption of both compounds from the PDMS fibre into the GC injector was performed for 6 min, and no carry-over was observed after thermal desorption. Organic compounds were separated on a 30 m (L) \times 0.25 mm (I.D.), 1 μ m HP-5MS column (Agilent Technologies, Inc., Santa Clara, California, USA). High-purity helium flowed through the column at 1 mL/min, and the temperatures for the inlet and the detector were 250°C and 280°C, respectively. The oven temperature was maintained at an initial value of 40°C for 5 min, raised at 8°C/min to 180°C, increased at 40°C/min to 260°C, and finally held at 260°C for 2 min.

External calibrations using ten different initial concentrations were performed to quantify the organic compounds and to investigate the linearity in the response under the identical sampling procedure and GC conditions. The GC was calibrated before use with a midpoint concentration standard. Any deviation from peak area greater than 10%

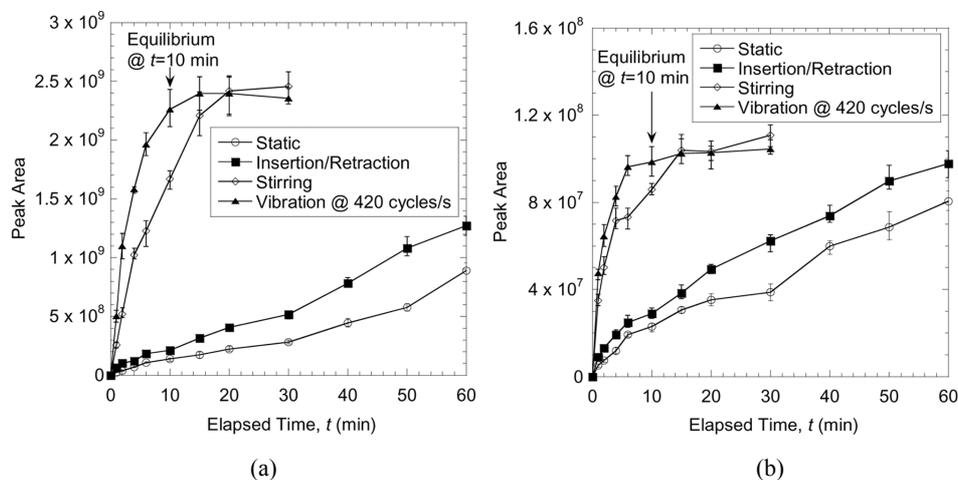
required re-injection of the entire standard. Resolution, separation, and retention times of the peaks were monitored carefully to ensure that the GC was functioning properly.

3 Results and discussion

3.1 Sorption equilibrium time among extraction techniques

The sorption-time profiles for 1,4-DCB and TOL at an initial concentration of 100 $\mu\text{mol/L}$ using a static condition, insertion/retraction, magnetic stirring, and electromagnetic vibration at 420 cycles/s are compared in Figure 3. Consistent with Eisert and Pawliszyn (1997a, 1997b), the equilibrium time in this study was defined as the time after which the peak area became constant, and corresponded to at least 95% of the peak area extracted from the sample matrix at equilibrium. As shown in Figure 3, equilibrium based on electromagnetic vibration at 420 cycles/s for both 1,4-DCB and TOL was achieved after approximately 10 min, whereas equilibrium based on stirring at 600 rpm for 1,4-DCB and TOL was achieved after about 20 min and 15 min, respectively. However, equilibrium for both compounds based on either insertion/retraction or a static condition was not achieved before 60 min. Therefore, electromagnetic vibration at 420 cycles/s was found to be the most efficient extraction technique in terms of reducing the sorption equilibrium time for both compounds evaluated in this study.

Figure 3 Sorption-time profiles for 1,4-dichlorobenzene and toluene with the initial concentration of 100 $\mu\text{mol/L}$ using four extraction techniques (the error bars indicate the maximum and minimum values): (a) 1,4-dichlorobenzene and (b) toluene

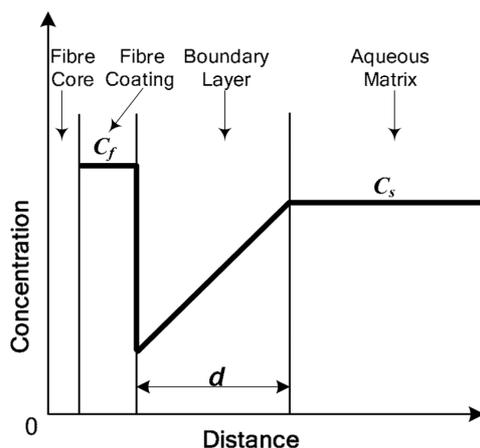


3.2 Mass transport of organic compounds

Regardless of the extraction level or technique, a fluid in contact with an SPME fibre surface is always stagnant (Young, 1989). As the distance from the SPME fibre surface increases, the fluid movement progressively increases until the fluid movement corresponds to that for the bulk fluid in a sample matrix. Organic compounds must first

diffuse through this stagnant water layer before the organic compounds can be sorbed into the fibre coating. Assuming that no convection occurs in the boundary (i.e., stagnant-water) layer surrounding the SPME fibre, and perfect extraction occurs in the aqueous matrix, the boundary layer model for mass transfer kinetics illustrated in Figure 4 was proposed by Pawliszyn (1997, 2001) to explain the mass transport of organic compounds between the SPME fibre and aqueous matrix.

Figure 4 Boundary layer model for mass transfer kinetics between an SPME fibre and an aqueous matrix as proposed by Pawliszyn (1997, 2001)



In this model, mass transport of an organic compound in a bulk aqueous matrix is assumed to be controlled by convection, whereas that in the boundary layer is assumed to be controlled by diffusion. Also, the mass transfer limitation is assumed to be controlled by the diffusion of an organic compound through this boundary layer, not by the diffusion of an organic compound within the fibre coating. The thickness of the boundary layer was expected to be different for the different extraction techniques evaluated in this study, since the thickness of the boundary layer in general depends on the extraction level, viscosity, and temperature of the fluid and the diffusion coefficient of the organic compound (Louch et al., 1992; Eisert and Pawliszyn, 1997a, 1997b; Pawliszyn, 1997, 2001; Conder et al., 2003; Ouyang and Pawliszyn, 2006). For example, since equilibrium was achieved faster in the order of electromagnetic vibration < stirring < insertion/retraction \approx static condition, the thickness of the boundary layer would be expected to have increased in the same order. Thus, the most likely reason that electromagnetic vibration was more effective in reducing the sorption equilibrium time was a greater reduction in the thickness of the boundary layer, thereby facilitating mass transport of organic compounds from the aqueous matrix to the PDMS fibre and decreasing the time required to achieve sorption equilibrium.

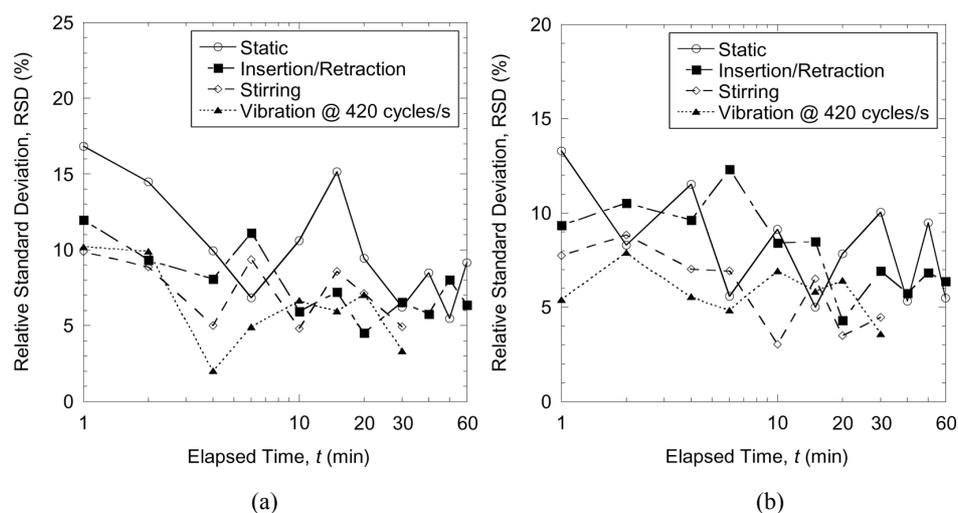
Except for electromagnetic vibration, the equilibrium of TOL was achieved faster than the equilibrium of 1,4-DCB (see Figure 3). Since the diffusion coefficient for TOL in aqueous matrix is greater than that of 1,4-DCB, or $9.5 \times 10^{-6} \text{ cm}^2/\text{s}$ vs.

$7.9 \times 10^{-6} \text{ cm}^2/\text{s}$ at 20°C (Montgomery, 1996), molecules of TOL should diffuse faster than those of 1, 4-DCB through the boundary layer, all other conditions being the same. Additionally, since the distribution of TOL between the PDMS fibre and the aqueous matrix was lower than that of 1, 4-DCB, fewer molecules of TOL relative to 1, 4-DCB would be expected to diffuse through this boundary layer prior to equilibrium. Thus, the time required to achieve sorption equilibrium for TOL was expected to be shorter than that for 1, 4-DCB. In accordance with the aforementioned considerations, the time required for sorption equilibrium of organic compounds between the PDMS fibre and the aqueous matrix was found to be a complex function of the extraction level and techniques, and the diffusion and distribution of the organic compounds.

3.3 Precision and detection limits among extraction techniques

The Relative Standard Deviation (RSD)-time profiles for 1, 4-DCB and TOL for an initial concentration of $100 \mu\text{mol/L}$ using a static condition, insertion/retraction, magnetic stirring and electromagnetic vibration at 420 cycles/s are compared in Figure 5. The RSD values for both compounds were obtained from triplicate tests. As shown in Figure 5, the RSD values for both compounds based on both the static and the insertion/retraction techniques were generally greater than those for the techniques based on magnetic stirring and electromagnetic vibration at 420 cycles/s, indicating that precision can be improved by using both magnetic stirring and electromagnetic vibration. However, in all cases, the RSD values gradually decreased as the time for the SPME fibre exposed to aqueous matrix increased. These results suggest that a greater precision was obtained for the equilibrium extraction than that for the non-equilibrium extraction. After equilibrium, the RSD values based on electromagnetic vibration at 420 cycles/s for both compounds were lower than 7.1%, whereas those based on magnetic stirring were lower than 8.6%.

Figure 5 Relative standard deviation-time profiles for 1, 4-dichlorobenzene and toluene for an initial concentration of $100 \mu\text{mol/L}$ using four extraction techniques (relative standard deviation was obtained from triplicate tests with manual PDMS-GC-MSD method): (a) 1, 4-dichlorobenzene and (b) toluene



The MDL values and the coefficients of determination (r^2) for external calibrations are summarised in Table 1. For both organic compounds, the MDL values based on electromagnetic vibration at 420 cycles/s were lower than those for other extraction techniques, whereas the r^2 values based on electromagnetic vibration at 420 cycles/s were higher than those for the other extraction techniques. These results indicate that both precision and linearity can be enhanced by using the electromagnetic vibration technique relative to the other extraction techniques evaluated in this study.

Table 1 Method Detection Limit (MDL) and coefficient of determination (r^2) for linear regression for the extraction techniques evaluated in this study

<i>Organic compound</i>	<i>Extraction technique</i>	<i>MDL</i> ($\mu\text{mol/L}$)	<i>r</i> ²
1, 4-Dichlorobenzene	Static sorption	1.04	0.935
	Magnetic stirring @ 600 rpm	0.31	0.974
	Fibre insertion/retraction @ 10 insertion/retraction cycles/min	0.90	0.929
	Electromagnetic vibration @ 420 cycles/s	0.12	0.985
Toluene	Static sorption	2.08	0.916
	Magnetic stirring @ 600 rpm	0.45	0.990
	Fibre insertion/retraction @ 10 insertion/retraction cycles/min	1.28	0.954
	Electromagnetic vibration @ 420 cycles/s	0.23	0.998

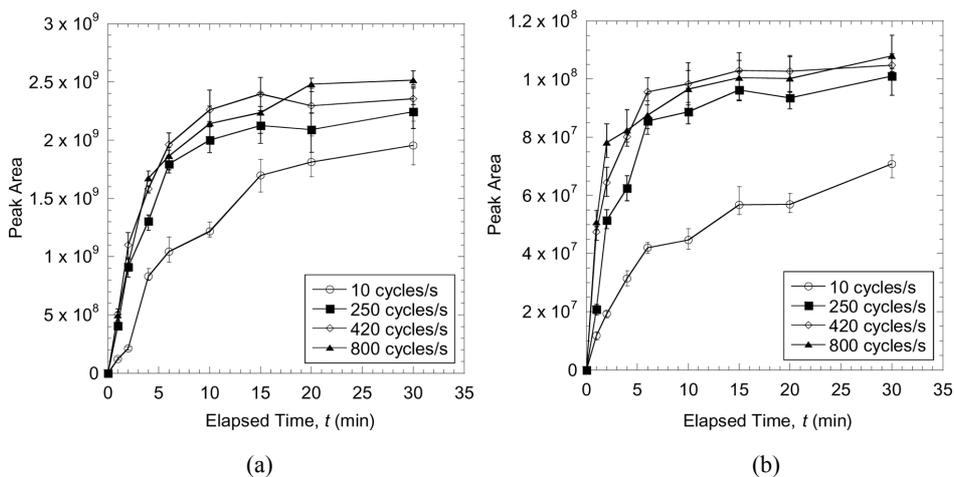
3.4 Effect of frequency

The effect of frequency on the sorption of organic compounds to the PDMS fibre is shown in Figure 6. As the frequency of electromagnetic vibration increased from 10 cycles/s to 250 cycles/s, the rate of sorption increased significantly for both organic compounds. However, as the frequency of electromagnetic vibration increased from 250 cycles/s to 800 cycles/s, the sorption-time profiles for both organic compounds were not significantly affected. Instead, the peak areas between 250 cycles/s and 800 cycles/s were within the experimental error at several elapsed times. These results indicate that frequencies greater than 250 cycles/s were not significantly effective in terms of reducing the thickness of the boundary layer and decreasing the time required to achieve sorption equilibrium.

As illustrated in Figure 4, the stagnant boundary layer surrounding the PDMS fibre still remains despite the vigorous vibration of the PDMS fibre (Young, 1989). Thus, for frequencies greater than 250 cycles/s, the final equilibrium sorption time is still a function of the diffusion of the organic compound through this boundary layer, but is independent of the vibration frequency. As a result, the time required to achieve

sorption equilibrium cannot be reduced further by increasing the frequency or the convection around the PDMS fibre owing to the existence of this boundary layer surrounding the PDMS fibre.

Figure 6 Effect of frequency (10, 250, 420, and 800 cycles/s) on the sorption of 1, 4-dichlorobenzene and toluene with the initial concentration of 100 $\mu\text{mol/L}$ to PDMS fibre (the error bars indicate the maximum and minimum values): (a) 1, 4-dichlorobenzene and (b) toluene

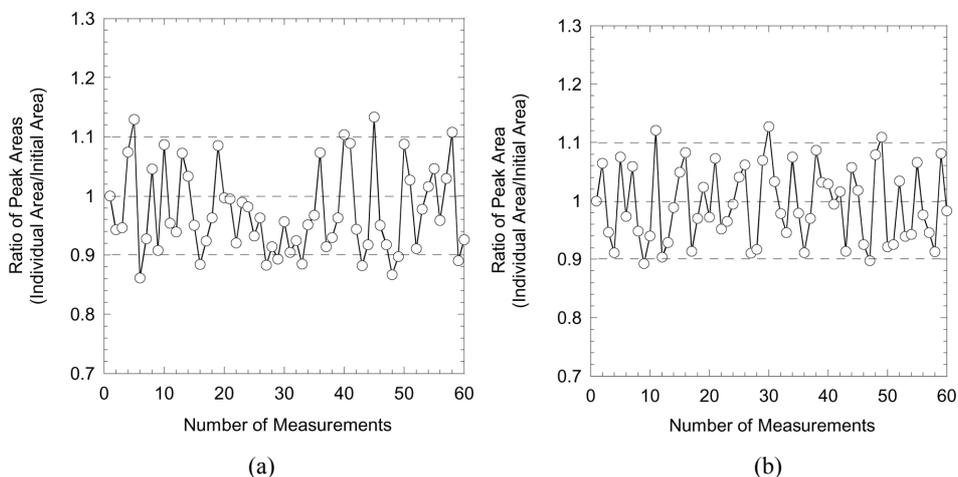


3.5 Effect of electromagnetic vibration on sustainability of extraction performance

Since convection or mechanical stresses resulting from electromagnetic vibration at high frequency (i.e., ≥ 250 cycles/s) might damage the PDMS fibre, the sustainability of extracting performance of the PDMS fibre exposed to each organic compound at an initial concentration of 100 $\mu\text{mol/L}$ using the electromagnetic vibration at 420 cycles/s was investigated. To ensure the comparability of the results, the ratios of peak area for individual measurement to peak area for initial measurement were used for evaluating the sustainability of the extracting performance for the PDMS fibre.

As shown in Figure 7, the extraction capacity of the PDMS fibre did not diminish significantly until the PDMS fibre had been used 60 times. According to the supplier (Supelco, Bellefonte, Pennsylvania, USA), the recommended usage of commercial PDMS fibres is around 50 times owing to the potential for damage caused primarily by the high temperature of the injection port of the GC. Thus, the effect of electromagnetic vibration at 420 cycles/s on the sustainability of the extracting performance for the PDMS fibre was insignificant. Overall, the PDMS fibre performed stably and consistently over a period of usage of up to 60 times despite the forces associated with electromagnetic vibration at 420 cycles/s.

Figure 7 Effect of electromagnetic vibration at 420 cycles/s on the lifetime and performance for PDMS fibre exposed to 1, 4-dichlorobenzene and toluene with the initial concentration of 100 $\mu\text{mol/L}$: (a) 1, 4-dichlorobenzene and (b) toluene



3.6 Future applications and development

The results from this study indicated that the newly-developed electromagnetically vibrated SPME device significantly increased the precision during the extraction of two organic compounds in aqueous matrix, and reduced the required sorption equilibrium time. As a result, the electromagnetically vibrated SPME device may be a powerful tool for rapid sampling and solvent-free sample preparation compared with more conventional extraction techniques. Further research should be conducted to evaluate the potential use of the electromagnetically vibrated SPME device for efficiently monitoring the transport of organic compounds through porous media, particularly with respect to potential detrimental effects caused by sampling.

Another promising application of the electromagnetically vibrated SPME device is the possibility of incorporating the device with a fully automated sampler for use with extraction and injection into analytical instruments. Although a recently commercialised SPME autosampler (Varian, Palo Alto, California, USA) mechanically vibrates the SPME fibre by agitating the vial holder during the extraction processes (Eisert and Pawliszyn, 1997a, 1997b), this indirect vibration frequency of the SPME fibre may be inefficient owing to an inconsistent and irreproducible transfer of vibratory motion to the SPME fibre. In contrast, the electromagnetically vibrated SPME device evaluated in this study directly vibrates the SPME fibre itself by the magnetic forces generated in a frequency oscillator circuit. Therefore, the SPME fibre is vibrated at consistent and controlled frequencies without significant dampening, and equilibrium is achieved more rapidly with greater precision and linearity. As a result, an automated sampler with an electromagnetically vibrated SPME may increase precision and reduce the time for the analysis of organic compounds.

4 Summary and conclusions

The feasibility of employing a newly-developed electromagnetically vibrated SPME device in extracting organic compounds from an aqueous matrix was evaluated relative to more conventional extraction techniques involving SPME, viz., static, magnetic stirring, and fibre insertion/retraction in terms of sorption equilibrium time, precision, and detection level. The results showed that equilibrium was achieved faster in the order of electromagnetic vibration < stirring < insertion/retraction \approx static condition, and that both precision and linearity can be enhanced by using electromagnetic vibration. In addition, no significant detrimental effect of electromagnetic vibration at 420 cycles/s was observed in terms of the sustainability in the performance of the PDMS fibre. As a result, the electromagnetically vibrated SPME device may be a powerful tool for rapid sampling and solvent-free sample preparation compared with more conventional extraction techniques. Nonetheless, further study is warranted to evaluate the potential for monitoring the transport of organic compounds through porous media, and for incorporating the device with an automated sampler for use with the extraction and injection into analytical instruments.

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