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Gas purge microsyringe extraction for quantitative direct gas chromatographic–mass spectrometric analysis of volatile and semivolatile chemicals

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ABSTRACT

Sample pretreatment before chromatographic analysis is the most time consuming and error prone part of analytical procedures, yet it is a key factor in the final success of the analysis. A quantitative and fast liquid phase microextraction technique termed as gas purge microsyringe extraction (GP-MSE) has been developed for simultaneous direct gas chromatography–mass spectrometry (GC–MS) analysis of volatile and semivolatile chemicals without cleanup process. Use of a gas flowing system, temperature control and a conventional microsyringe greatly increased the surface area of the liquid phase micro solvent, and led to quantitative recoveries of both volatile and semivolatile chemicals within short extraction time of only 2 min. Recoveries of polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and alkylphenols (APs) determined were 85–107%, and reproducibility was between 2.8% and 8.5%. In particular, the technique shows high sensitivity for semivolatile chemicals which is difficult to achieve in other sample pretreatment techniques such as headspace-liquid phase microextraction. The variables affecting extraction efficiency such as gas flow rate, extraction time, extracting solvent type, temperature of sample and extracting solvent were investigated. Finally, the technique was evaluated to determine PAHs, APs and OCPs from plant and soil samples. The experimental results demonstrated that the technique is economic, sensitive to both volatile and semivolatile chemicals, is fast, simple to operate, and allows quantitative extraction. On-site monitoring of volatile and semivolatile chemicals is now possible using this technique due to the simplification and speed of sample treatment.

1. Introduction

In recent years, highly efficient analytical instrumentation has been developed for the determination of target analytes. However, most analytical instruments cannot directly handle the matrix, so sample preparation is necessary and is the most challenging and time-consuming step. Recent research activities have been oriented towards the development of the miniaturization, integration and automation of sample preparation methods. For more than a decade, liquid phase microextraction (LPME) or headspace liquid phase microextraction (HS-LPME) has been used as an alternative to conventional extraction methods [1–3]. In this technique, the analytes are enriched from the sample matrix (or its headspace) into a microliter solvent drop hanging on the tip of a microsyringe, and after extraction, the extraction solvent is retracted into the syringe and then injected directly into instrument [4–6].

Compared to conventional extraction methods, LPME and HS-LPME are inexpensive, convenient, simple, sensitive, and integrate sampling, extraction, cleanup, concentration and other steps [7]. The approaches have been applied to a wide variety of volatile and semivolatile organic compounds from environmental [8–11], biological [12,13] and food [14–16] samples. However, several drawbacks limit the applications of LPME; these include lower enrichment factors [17,18], the fact that the extraction system is closed, so that the highest enrichment factors can be obtained when extraction equilibrium is established [17–19], a microdrop suspended on the needle of microsyringe is easily dislodged [18,20], the surface area of the organic solvent is limited [21,22], the extraction time is long (extraction time $\geq$ 20 min) [23–25], and most importantly, LPME and HS-LPME are not sensitive to semivolatile chemicals [18].

To improve the enrichment factors of HS-LPME, gas flow headspace liquid phase microextraction (GF-HS-LPME) was introduced in 2009 by Yang and co-workers [26]. It is fast, efficient and economic, and demonstrated higher enrichment factors relative to HS-LPME for volatile chemicals, since the absolute amount of target

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compounds in the gas phase is increased by extending extraction time in the gas flow condition (open system) [26]. However, this approach has not yet completely overcome problems of low enrichment for poorly volatile chemicals, and there remain some disadvantages in using it routinely, such as operational difficulties arising from the easy dislodgement of the microdrop, or incomplete extraction processes which lead to difficulties in quantitative determination.

To overcome these disadvantages, we have developed a novel gas purge microextraction technique using a common microsyringe that we term as "gas purge microsyringe extraction" (GP-MSE). A 100 μL microsyringe is used as a "holder" and "protector" of the organic solvent. Target compounds are brought to the inner wall of the microsyringe needle and barrel by inert gas flow, and are quantitatively trapped by the extraction solvent. Various operational conditions affecting extraction efficiency, such as gas flow rate, extraction time, nature of the extracting solvent, and temperatures of the extracting solvent and of the sample, have been systematically investigated. Analytical performance and applications to real sample analysis have also been investigated.

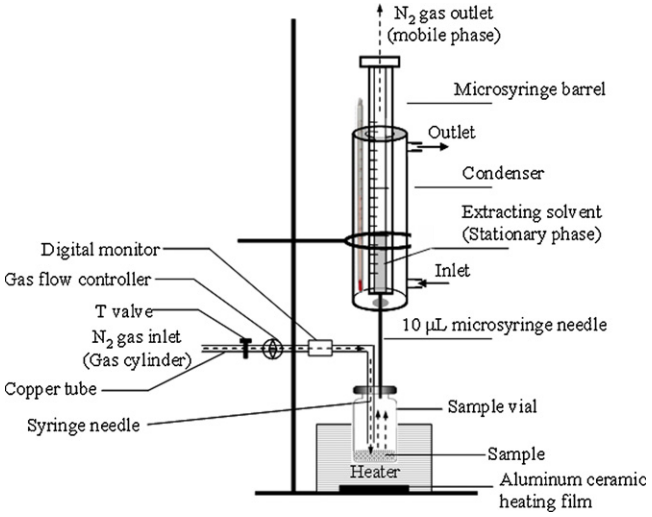

Fig. 1. Schematic illustration of the GP-MSE apparatus. The dotted line means gas flow pathway.

2. Experimental

2.1. Materials and chemicals

Eighteen polycyclic aromatic hydrocarbons (PAHs), five organochlorine pesticide (OCP) standards, tetrachloro-m-xylene (TCMX) and [$^2H_{10}$] phenanthrene were purchased from Supelco (Bellefonte, PA, USA). Two alkylphenol (AP) standards were purchased from Chem Service (Hatfield, PA, USA). The purity of standards was higher than 99%. The gas mass flow controller and digital monitor were purchased from Beijing Metron Instruments Co., Ltd. (China). Organic solvents (hexane, dichloromethane, methanol, acetone and ethyl acetate) were HPLC grade obtained from Caledon (Georgetown, Ont., Canada). Stock standard solutions of PAHs (20 mg L^{-1}), APs (340 mg L^{-1}) and OCPs (0.4 mg L^{-1}) were prepared in methanol, acetone and hexane, respectively. The PAHs and APs were diluted to 80 μg L^{-1} and 1.36 mg L^{-1}, with dichloromethane, respectively. OCPs were diluted to 1.60 μg L^{-1} with hexane. Standard working solutions of different concentrations were prepared by diluting the stock solutions with dichloromethane. The internal standard ($^2H_{10}$-phenanthrene) was spiked into hexane (200 μg L^{-1}), when it was used as an extracting solvent for PAHs and APs. The internal standard (TCMX) was spiked into hexane (20 μg L^{-1}), when it was used as extracting solvent for OCPs. The standard solutions and extracting solvent were stored in the dark at 0–4 °C till used.

2.2. Sample preparation

The real plant and soil samples were taken from the Changbai Mountain and were extracted with dichloromethane for 12 h with Soxhlet extraction. The extract was used for evaluation of cleanup ability of the GP-MSE. The standard solutions were spiked into the blank samples (plant and soil) at levels of 80 ng g^{-1}, 1.36 μg g^{-1} and 1.60 ng g^{-1}, respectively, for PAHs, APs and OCPs. The sub-samples of 0.01 and 5.0 g were used for GP-MSE and Soxhlet extraction, respectively.

2.3. GP-MSE apparatus and mechanism

Based on previous studies on the gas flow headspace liquid phase microextraction (GF-HS-LPME) in our laboratory [26], an apparatus for GP-MSE was fabricated (Fig. 1). It consists mainly of a microsyringe, sample vial, gas flow system, heater and condenser. A 100 μL volume microsyringe barrel (Hamilton, 710RN) was used to hold the liquid phase organic solvent, and 10 μL narrow microsyringe needle (Hamilton, RN, needle size: 26s) was fitted to the bottom of the microsyringe barrel to avoid run off of the organic solvent from the microsyringe barrel. Conventional screw capped GC vials with PTFE-lined septa was used as a sample vial. The gas flow system consisted of a copper tube, T valve, gas mass flow controller, digital monitor, and conventional syringe needle. One end of the copper tube was connected to syringe needle, which was inserted into sample vial through the septum of the screw cap, and the tip of the needle was positioned just below the vial cap. The other end of the copper tube was connected to a nitrogen gas cylinder. An alumina ceramic heating film was used to heat the sample vial. The ceramic heater generates heat when an electric current is applied, and can raise its temperature to 280 °C within tens of seconds. For cooling the microsyringe barrel and organic solvent phase, a modified air-cooled condenser cut off to 6 cm length was used, and ice–salt–water was used as cooling carrier. A mercury thermometer was inserted into the condenser to measure the cooling temperature.

The extraction was conducted as follows: (1) the standard sample or real sample was put into the sample vial, then it was tightly closed with the septum-lined screw cap; (2) the sample vial was positioned in the heater; (3) the gas flow line, heater, condenser and microsyringe were installed (using a microsyringe cleaning apparatus developed in our lab [27], the microsyringe was thoroughly washed with methanol, dichloromethane, and then with hexane, and rinsed again at least five times with extracting solvent); (4) the syringe needle was carefully inserted into the sample vial through the cap septum till the tip of the needle just protruded 1 mm from the cap; (5) to start the extraction, a suitable extracting solvent was added into extraction syringe barrel by another microsyringe, at the same time, applying heating power and opening the inert gas valve; (6) the gas flow carried target chemicals through the inner syringe needle and barrel, and the evaporated chemicals were trapped by the solvent. Compared to other HS-LPME techniques, the stability of the micro extracting solvent in the GP-MSE is significantly increased using microsyringe barrel and cooling; (7) after a defined period of time, the syringe was removed from the apparatus, and its plunger was re-inserted (solvent position was controlled by inert gas flow before removal of the syringe), and the extracting solvent was directly injected into the GC-MS or GC-ECD for analysis. To optimize recovery during the extraction, the gas

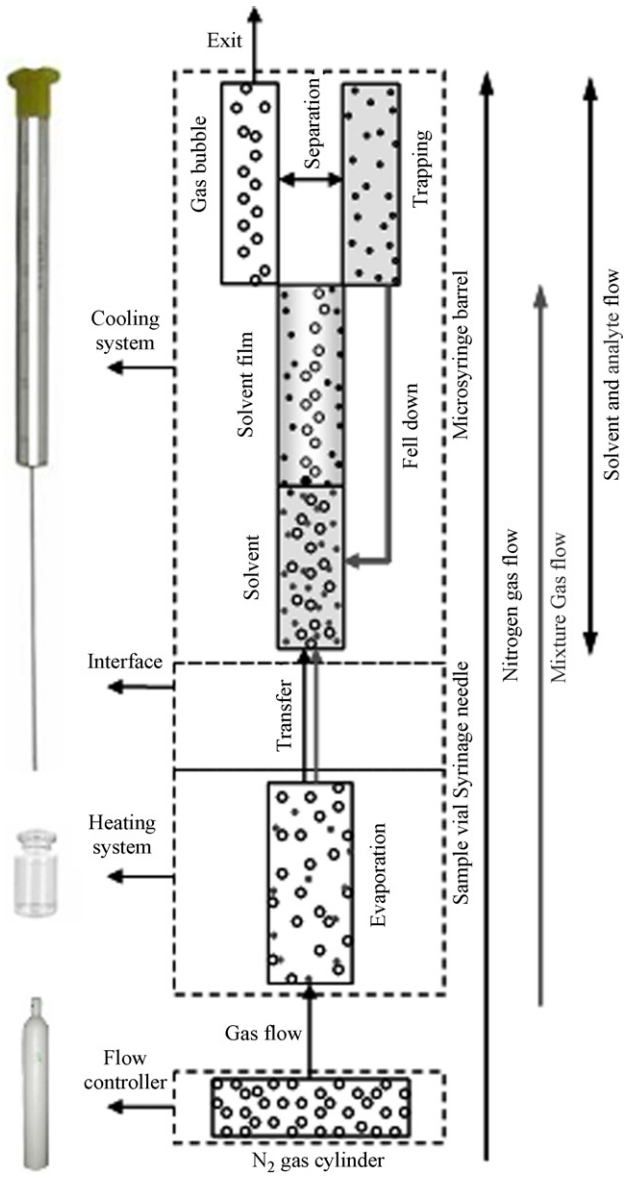

Fig. 2. Schematic illustration of the extracting mechanism of GP-MSE. ● is target compound; ○ is inert gas bubble; gray color means organic solvent.

flow rate, extraction time, extracting solvent type, heater and condenser temperature were systemically investigated in this study.

The mechanism of the GP-MSE is similar to the partitioning of analytes in gas–liquid chromatography (shown in Fig. 2). The target compounds (volatile and semivolatile chemicals) in the sample vial are quickly evaporated into the gas phase from the sample matrix at high temperature (similar to the processes in a GC injector); they are carried into the organic solvent phase (analogous to partitioning in a GC stationary phase) by inert gas flow. When the extraction solvent is displaced by the inert gas flow, a small gas bubble is generated in the microsyringe barrel and a very thin organic solvent film (OSF) is automatically generated on the inner side of the microsyringe barrel. The target compounds in the vapor phase are partitioned between the OSF and the gas phase. When the extraction solvent film collapses due to gravity, the target compound-enriched OSF accumulates in the bulk organic solvent. The surface area of the interface and stability of the micro organic solvent should be significantly increased in this process, which should lead to increase extraction efficiency and reproducibility, respectively. The GP-MSE therefore overcomes the difficulties of dislodgment of microdrops, and the syringe can be directly injected to the GC without multiple cleanup and desorption steps. The most important feature is that GP-MSE is a quantitative extraction process. Consequently, very simple quantitative analysis is possible by the GP-MSE technique.

2.4. Instrument analysis

Analysis of PAHs and APs was carried out on a Shimadzu GC 2010 equipped with DB5 fused-silica capillary column (30 m × 0.25 mm; thickness 0.25 μm) and detected on a Shimadzu QPMS 2010 quadrupole mass spectrometer system. For PAHs, the column temperature was maintained at 80 °C for 2 min and then programmed to increase by 20 °C min^{-1} to 100 °C, by 10 °C min^{-1} to 280 °C, and then held for 21 min, column flow was 1.20 mL min^{-1}. For APs, the column temperature was maintained at 80 °C for 2 min and then programmed to increase by 20 °C min^{-1} to 100 °C, by 10 °C min^{-1} to 200 °C, by 20 °C min^{-1} to 280 °C, and then held for 20 min, column flow was 0.6 mL min^{-1}. Other operating conditions were as follows: injection temperature was 280 °C in splitless mode; helium (99.999% pure) was used as a carrier gas. GC–MS interface temperature was 280 °C. The electron ionization – selected ion mode (EI-SIM) was used for quantification of analytes. Solvent cut time was 5.0 min. The ion source temperature and energy of ionizing electron were set at 200 °C and 70 eV, respectively.

The OCPs were analyzed using a Shimadzu GC 2010 equipped with a DB5 fused-silica capillary column (30 m × 0.25 mm; thickness 0.25 μm) and detected on a ^{63}Ni electron capture detector. Helium gas was used as the carrier gas, mixture gas of CH_4 and Ar (V_{CH4}:V_{Ar} = 5:95) was used as the make-up gas, the column flow was 1.0 mL min^{-1}. The temperature program was set at 100 °C for 1 min, 100–140 °C at 5 °C min^{-1}, 140 °C for 1 min, 140–250 °C at 1.5 °C min^{-1}, 250 °C for 1 min, 250–300 °C at 10 °C min^{-1}, 300 °C for 2 min. Other operating conditions were as follows: the injection temperature was maintained at 275 °C in splitless mode, the detector temperature was maintained at 300 °C.

To evaluate cleanup ability of the GP-MSE technique, interfering chemicals in the Soxhlet extract and GP-MSE extract were analyzed using a Shimadzu HPLC 6A system equipped with a Shimadzu SPD-6AV UV detector, a GRACE VYDAC C_{18} 250 mm × 4.6 mm I.D. column was used. The mobile phase was CH_3OH–H_2O (9:1). The constant flow was kept at 1 mL min^{-1}. The injection volume was 20 μL for the samples and the detection was performed at the wavelength of 254 nm.

3. Results and discussion

The gas flow HS-LPME technique was proposed in preliminary study in our lab in 2009 [26] to increase the enrichment factor. Although it was successfully increased to about three-fold for volatile chemicals using this technique, further enrichment factor is difficult and it is insensitive to semi-volatile chemicals because of limitations of the organic solvent surface area and difficult in the evaporation of semi-volatile chemicals. Furthermore, in the gas flow system, it is very difficult to control the microdrop hanging on the microsyringe needle. To overcome these disadvantages of the gas flow HS-LPME technique, the GP-MSE technique was developed during a series of preliminary experiments. It was found that the organic solvent surface area and stability were dramatically increased in the GP-MSE system, and it was also shown to be very highly sensitive to both volatile and semivolatile chemicals within a short extraction time.

Based on the results of preliminary studies, a series of optimization experiments were carried out. Except where otherwise stated,

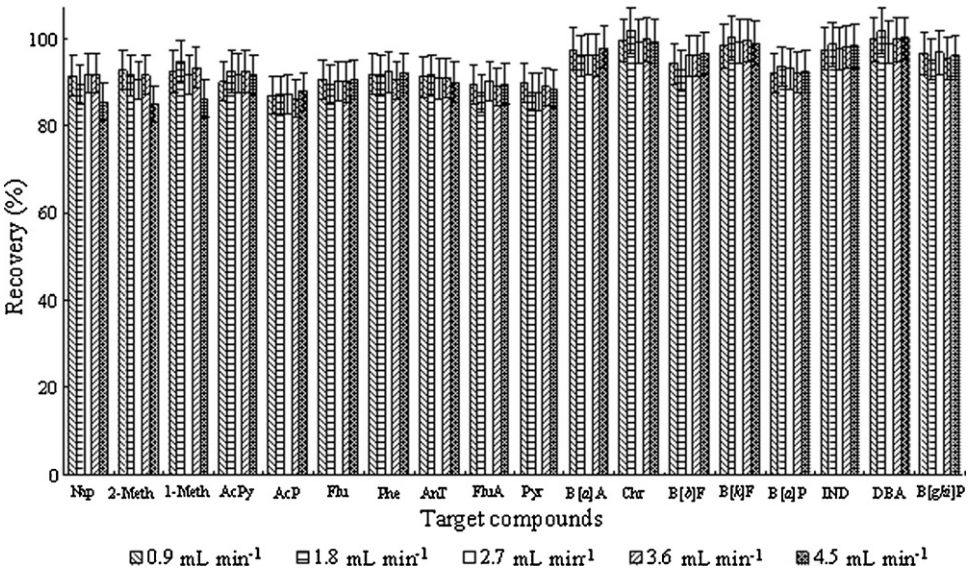

Fig. 3. Effect of gas flow rate on the extraction efficiency. Extracting solvent: hexane; solvent volume: 10 μL; extraction time: 2 min; heater temperatures: 280 °C; cooling temperature: 0 °C, amount of PAHs: 0.8 ng.

10 μL hexane was used as an extraction solvent (stationary phase); gas flow rate was to 1.80 mL min^{-1}; extraction time was set to 2 min; heater temperatures and microsyringe temperatures were set to 280 and 0 °C, respectively; the absolute amount of PAHs used was 0.8 ng; the final volume of extracting solvent was controlled at 1–3 μL.

3.1. Effect of gas flow rate on the extraction efficiency

In the GP-MSE technique, analytes are evaporated from sample matrix, and then the inert gas flow carried them to the extraction part. So, gas flow is one of the basic necessary parameters for increasing extraction efficiency. To understand the effect of gas flow rate on the extraction efficiency, gas flow rates were controlled at 0.9, 1.8, 2.7, 3.6 and 4.5 mL min^{-1} (0.9 and 4.5 mL min^{-1} were the minimum and maximum rates of the gas mass flow controller), and then the results were compared. Fig. 3 shows that recoveries of target compounds were basically unchanged with varying gas flow rates. The experimental data demonstrate that most chemicals were exhaustively moved to the extraction part after gasification under the gas flow condition. It must be pointed out that the gas flow is an important parameter in the GP-MSE, while the flow rate does not greatly affect the recovery of the target chemicals. To simplify gas flow rate and organic solvent volume control, a gas flow rate of 1.8 mL min^{-1} was used in the following experiments.

3.2. Effect of extraction time on the extraction efficiency

Extraction time is an important factor in HS-LPME and GF-HS-LPME, since enrichment factors increase with time up to an equilibrium state [17–22]. In most previous studies, extraction time was controlled at 20 min. However, shorter extraction time was required in the GP-MSE technique. As shown in Fig. 4, the extraction was finished within 2 min, and the recoveries of the target compounds were higher than 85%, they were not varied with increasing extraction time after 2 min. This indicates that after trapping by the

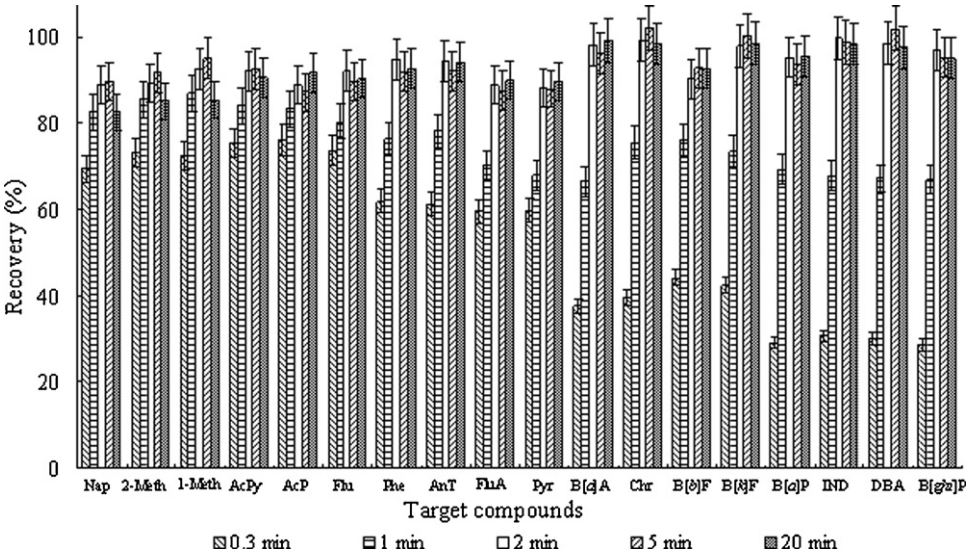

Fig. 4. Effect of extraction time on the extraction efficiency. Extracting solvent: hexane; solvent volume: 10 μL; gas flow rate: 1.8 mL min^{-1}; heater temperatures: 280 °C; cooling temperature: 0 °C, amount of PAHs: 0.8 ng.

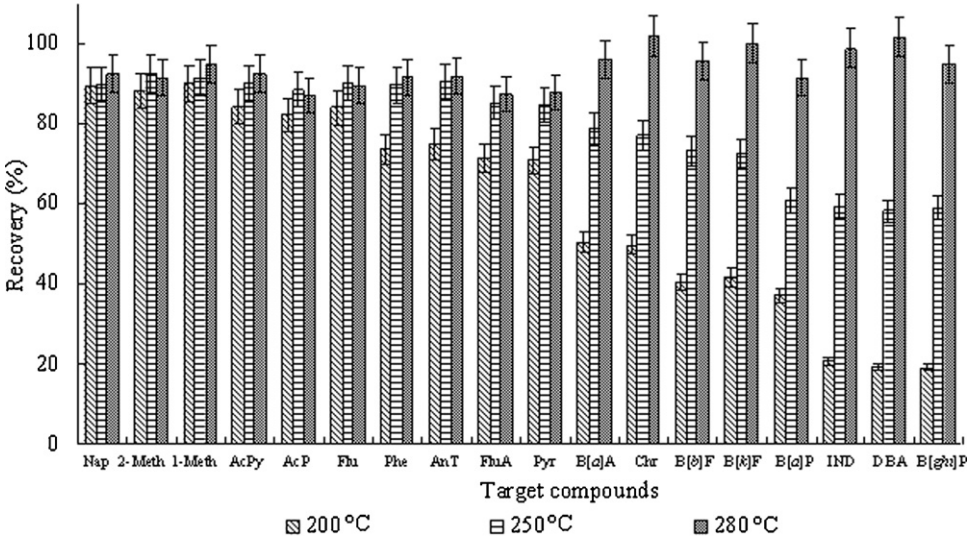

Fig. 5. Effect of sample temperatures on extraction efficiency. Extracting solvent: hexane; solvent volume: 10 μL; gas flow rate: 1.8 mL min^{-1}; extraction time: 2 min; cooling temperature: 0 °C, amount of PAHs: 0.8 ng.

organic solvent, chemicals were not evaporated from the GP-MSE system. To confirm this, standard solutions (the absolute amount of analytes was 0.8 ng) were put in the microsyringe barrel, and then conducted simulate exposure experiment for 20 min. A few losses of volatile chemicals such as naphthalene and methylnaphthalene occurred, but most of the remaining chemicals did not change (see Fig. S1 in the supplementary information). Therefore, the extraction time can be chosen to match the properties of target chemicals or experimental objectives, such as the volatility of target compounds and the distribution coefficient of target compounds between gas phase and sample matrix. An extraction time of 2 min was used in the following experiments, taking account of both the simplicity of operation and reproducibility.

3.3. Effect of extracting solvent on the extraction efficiency

The "like-dissolve-like" rule is an old and well-established principle in extraction techniques which can be applied in GP-MSE. Five organic solvents (dichloromethane, methanol, hexane, acetone and ethyl acetate) were selected and the results were compared. The model PAHs selected has high solubility in those organic solvents, so similar recoveries were obtained for all cases. Based on the toxicity and suitability on the GC–MS analysis of the solvent selected, the hexane was used as an extracting solvent in the following experiments.

3.4. Effect of temperatures of sample and extracting solvent on the extraction efficiency

Although high temperatures favour high enrichment factors in the HS-LPME and GF-HS-LPME techniques [26,28–30], they lead to loss of liquid phase organic solvent by evaporation, because the liquid phase organic solvent is exposed through the headspace of the sample vial. To resolve this problem, the gas flow microsyringe system was designed as the liquid phase organic solvent and sample vial separated by the syringe needle. The extraction solvent is perfectly maintained as in the liquid phase at the high temperature of sample vial, because condenser cooling and thermal were isolated by the syringe needle. Analogous to chromatographic injection temperature conditions, the evaporation temperatures of the sample were set to 200, 250 and 280 °C and the results were compared. The results are shown in Fig. 5. Clearly, high temperatures favour high recoveries of the target chemicals. For high boiling point chemicals such as benzo[ghi]perylene, recoveries at high sample temperature (280 °C) were much higher than those at low sample temperature (200 °C) with 5 folds increasing factor.

Since gas phase extracts were extracted by organic phase in an exothermic process, lower temperatures of extraction solvent favour high enrichment factors of the analytes. Furthermore, cooling the extraction solvent favours the protection of solvent evaporation. Since at a high temperature, gas flow was continuously supplied from the sample vial, the organic solvent was quickly evaporated and exited from the microsyringe barrel if without cooling. Fortunately, the extraction process is fast (2 min), the gas flow rate is very slow (1.8 mL min^{-1}) and the microsyringe glassware has high thermal capacity (C_p = 0.84 J g^{-1} K^{-1}) [31,32], so a simple ice-water cooling system is enough to keep the extracting organic solvent as a liquid phase under the given operation conditions. Based on the above considerations and preliminary experience, 0 °C was chosen as solvent temperature in this study. In these conditions, just only 10 μL of organic solvent (hexane) was used for quantitative extraction of target chemicals for dried samples, and about 1–3 μL of organic solvent remained in the microsyringe, the volume was suitable for direct analysis of GC–MS.

3.5. Evaluation of the method performance

In this study, a PAH standard mixture of eighteen compounds was used to evaluate reproducibility, detection limit (DL which is spiked amount to the plant sample), linearity of matrix spiked and recovery of the GP-MSE technique. The reproducibility and the detection limit were represented by the relative standard deviation (RSD) and three times of the signal-to-noise ratio, respectively. The RSD values ranged from 3.0% to 8.5% and the DL ranged from 10.0 pg for naphthalene to 18.0 pg for benzo[ghi]perylene. To investigate linearity of matrix spiked, five different levels of PAH standard mixture (20, 40, 100, 500 pg and 2.0 ng) were injected to the sample matrix. All of the target compounds responded linearly (R^2 = 0.9861–0.9987). The recoveries of PAHs in a 0.8 ng sample of standard mixture ranged from 87.5% to 101.9%. The results are summarized in Table 1.

Based on similarity of the extraction mechanism, the performances of the GP-MSE technique were compared to those of the HS-LPME (headspace-liquid phase microextraction) technique. First, all of the chemicals spiked (eighteen PAHs) were quantitatively trapped in GP-MSE technique while the same chem-

Table 1
Characteristics of the GP-MSE technique.

Compound	DL (pg)	Linearity (R^2)	RSD (%) (n = 6)	Recovery (%)
Nap	10.0	0.9926	7.3	87.5
2-Meth	10.0	0.9972	6.4	89.6
1-Meth	10.0	0.9963	3.0	95.0
AcPy	15.0	0.9937	7.5	92.5
AcP	13.0	0.9963	7.6	95.1
Flu	12.0	0.9927	8.3	89.6
Phe	10.0	0.9963	5.0	91.7
AnT	10.0	0.9932	6.9	91.9
FluA	10.0	0.9987	7.8	98.4
Pyr	10.0	0.9935	8.1	87.9
B[a]A	15.0	0.9963	7.5	96.1
Chr	15.0	0.9904	4.4	101.9
B[b]F	14.0	0.9917	6.6	100.7
B[k]F	14.0	0.9893	7.7	100.3
B[a]P	15.0	0.9892	8.5	91.6
IND	18.0	0.9899	5.7	98.8
DBA	18.0	0.9885	5.5	101.8
B[ghi]P	18.0	0.9861	4.7	95.1

DL = detection limits (three times of the signal-to-noise ratio). *Abbreviations*: Nap = naphthalene; 2-Meth = 2-methylnaphthalene; 1-Meth = 1-methylnaphthalene; AcPy = acenaphthylene; AcP = acenaphthene; Flu = fluorene; Phe = phenanthrene; AnT = anthracene; FluA = fluoranthene; Pyr = pyrene; B[a]A = beazo[a]anthracee; Chr = chrysene; B[b]F = beazo[b]fluoranthene; B[k]F = beazo[k]fluoranthene; B[a]P = beazo[a]pyrene; IND = indeno[1,2,3-cd]pyrene; DBA = dibenz[a,h]anthracene; B[ghi]P = benzo[ghi]perylene.

icals were only partially trapped in the HS-LPME technique (see Fig. S2 in the supplementary information). Furthermore, extraction efficiencies were significantly decreased with increasing boiling point of the target chemicals in the HS-LPME technique, due to low vapor pressure of the chemicals. Second, only 2 min of extraction time was required for the GP-MSE technique while over 20 min of extraction time was needed for HS-LPME. Third, the control of liquid phase micro organic solvent was much simpler even at high sample temperature such as 280 °C in the case of GP-MSE, while it was a very difficult procedure requiring care in the HS-LPME technique even at room temperatures.

In consideration of SPME method which has the advantages of being simple, low-cost and solvent free in sample pretreatment, the GP-MSE technique was simply compared with the HS-SPME (headspace-solid phase microextraction) technique. It was reported that the HS-SPME takes more than 30 min to extract most PAHs, and still cannot determine the high-ring PAHs (over four ring PAHs) due to limitation of evaporation temperature [10,33]. At high temperature such as 280 °C, the analytes absorbed by solid fiber would be desorpted to gas phase because the SPME is adsorption/desorption procedure. It is easily found that the detection limit of the HS-SPME (LPME) ranged from 5.9 ng for naphthalene to 246 ng for pyrene [29,34]. It is two or three orders higher than those determined in GP-MSE for any PAHs analyzed.

3.6. Application

The method was applied for the analysis of some real plant and soil samples collected from the Changbai Mountain, and the results were compared with those of Soxhlet extraction methods including silica-alumina column chromatographic cleanup steps. Target compounds included eighteen PAHs, two alkylphenols (APs) and five organochlorine pesticides (OCPs). GP-MSE conditions were as follows: gas flow rate was 1.8 mL min^{-1}, extraction time was 2 min, 10 μL hexane was used as an extracting solvent, and temperatures of sample and extracting solvent are 280 °C and 0 °C, respectively. For spiked samples, recoveries of "spiked" target analytes including PAHs, OCPs and APs determined ranged from 88% to 105% in plant samples with 7.8% of average RSD,

Table 2
Quantitative results of GP-MSE for various chemicals.

Compounds	% Recovery (% RSD, n = 3)	Concentration (ng g^{-1})					
		Plant sample		Soil sample			
	Standard sample	Spiked plant sample	Spiked soil sample	GP-MSE	Soxhlet extraction	GP-MSE	Soxhlet extraction
PAHs							
Nap	92.5 (4.3)	89.2 (7.3)	90.5 (8.9)	14.39	14.41	12.35	12.28
2-Meth	91.6 (3.4)	89.6 (8.0)	90.0 (9.3)	7.25	7.23	6.02	5.96
1-Meth	95.0 (3.3)	90.3 (8.2)	92.0 (8.5)	7.43	7.41	6.69	6.73
AcPy	92.5 (4.5)	88.3 (6.5)	89.8 (7.5)	2.12	2.08	3.02	2.98
AcP	87.1 (4.6)	89.9 (7.8)	85.5 (7.5)	1.97	1.95	2.43	2.50
Flu	89.6 (3.3)	102.4 (7.3)	89.0 (7.4)	5.06	5.11	6.11	6.03
Phe	91.7 (3.0)	90.3 (8.0)	90.6 (8.6)	16.85	16.79	18.89	18.79
AnT	91.9 (6.9)	104.5 (6.8)	91.1 (7.9)	2.78	2.81	2.13	2.28
FluA	87.4 (7.8)	90.5 (7.7)	93.6 (8.1)	8.97	9.01	10.17	10.31
Pyr	87.9 (8.1)	99.0 (8.0)	94.8 (8.3)	9.52	9.47	12.61	12.47
B[a]A	96.1 (7.5)	93.9 (8.4)	106.0 (8.3)	2.98	3.01	4.92	5.03
Chr	101.9 (8.5)	91.0 (8.5)	97.6 (8.2)	6.75	6.69	9.41	9.53
B[b]F	95.7 (5.6)	90.5 (8.3)	103.6 (8.4)	5.87	5.81	5.81	5.92
B[k]F	100.3 (6.7)	89.9 (8.2)	94.1 (8.4)	2.25	2.19	2.46	2.51
B[a]P	91.6 (5.5)	89.4 (7.8)	95.6 (6.8)	3.05	3.10	2.57	2.54
IND	98.8 (7.7)	88.9 (7.8)	98.4 (8.5)	4.97	4.96	2.62	2.68
DBA	101.8 (6.5)	91.4 (8.0)	97.1 (8.4)	1.45	1.39	0.87	0.85
B[ghi]P	95.1 (7.7)	90.4 (7.6)	98.6 (8.3)	3.57	3.58	2.91	3.01
APs							
4-*t*-OP	89.0 (4.9)	91.0 (7.8)	94.6 (8.2)	3.25	3.14	2.37	2.29
4-*t*-NP	90.2 (5.0)	94.3 (7.2)	96.1 (6.9)	11.67	11.53	19.01	19.11
OCPs							
α-HCH	92.6 (6.8)	90.0 (7.0)	97.3 (6.8)	0.78	0.75	2.68	2.73
γ-HCH	92.2 (5.3)	90.0 (6.3)	95.8 (5.9)	0.64	0.67	4.52	4.47
p,p′-DDE	94.0 (4.9)	88.9 (5.2)	93.8 (4.7)	1.42	1.35	0.47	0.45
p,p′-DDD	92.4 (5.0)	89.6 (4.9)	92.1 (7.0)	0.59	0.63	5.81	5.95
p,p′-DDT	92.1 (5.9)	90.2 (6.0)	96.0 (6.7)	0.72	0.76	0.29	0.31

Abbreviations: 4-*t*-OP = 4-*t*-octylphenol; 4-*t*-NP = 4-*t*-nonylphenol; α-HCH = alpha-hexachlorocyclohexane; γ-HCH = gamma-hexachlorocyclohexane; *p,p′*-DDE = *p,p′*-dichlorodiphenyldichloroethylene; *p,p′*-DDD = *p,p′*-dichlorodiphenyldichloroethane; *p,p′*-DDT = *p,p′*-dichloro-diphenyl-trichlorothane.

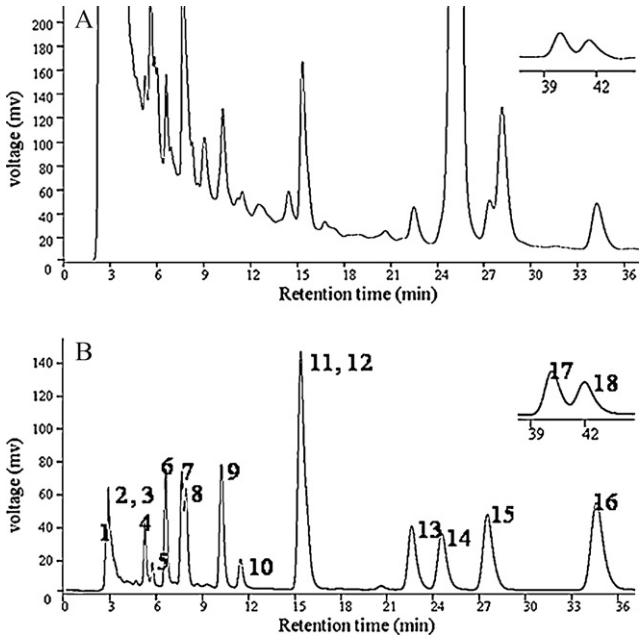

Fig. 6. Comparison of real sample HPLC chromatograms. "a" is obtained from Soxhlet extract without cleanup and "b" is obtained from GP-MSE extract. The GP-MSE was carried out under the following conditions. Extracting solvent: hexane; solvent volume: 10 μL; gas flow rare: 1.8 mL min^{-1}; extraction time: 2 min; heater temperatures: 280 °C; cooling temperature: 0 °C, amount of PAHs: 0.8 ng. Peak number: 1, naphthalene; 2, 2-methylnaphthalene; 3, 1-methylnaphthalene; 4, acenaphthylene; 5, acenaphthene; 6, fluorene; 7, phenanthrene; 8, anthracene; 9, fluoranthene; 10, pyrene; 11, beazo[a]anthracene; 12, chrysene; 13, beazo[b]fluoranthene; 14, Beazo[k]fluoranthene; 15, beazo[a]pyrene; 16, indeno[1,2,3-cd]pyrene; 17, dibenz[a,h]anthracene; 18, benzo[ghi]perylene.

and 85% to 107% in the soil samples with 8.3% of average RSD (shown in Table 2). For real samples, the results of GP-MSE were similar to the results obtained from Soxhlet extraction (shown in Table 2). It is clear that volatile and semivolatile chemicals can be simultaneously extracted from environmental samples using the GP-MSE technique with improved reliability and convenience.

During experiments on the real complex samples, it was found that GP-MSE technique gives extremely clean extract which is suitable for direct GC–MS analysis. To evaluate the cleanup ability of the GP-MSE, the PAH spiked plant extracts obtained from GP-MSE were compared to those obtained from Soxhlet extraction using HPLC analysis. The plant extracts could include many kinds of interfering chemicals such as pigments, carbohydrates and phospholipids. There are large numbers of unknown peaks in the liquid chromatograms of original Soxhlet extracts (Fig. 6a), while the unknown peaks were usually absent in that of the GP-MSE extracts (Fig. 6b), probably due to their limited evaporation at the given temperature. The extracts obtained from GP-MSE and Soxhlet (including silica-alumina column chromatographic cleanup steps) were compared using GC–MS (shown in Supplementary information Fig. S3). Although clean chromatograms were obtained from two kinds of extracts, less unknown peaks appeared in the GP-MSE extracts. Furthermore, the spiked PAHs were quantitatively determined using GP-MSE with over 90% extraction efficiency. This indicates that further cleanup steps such as silica cleanup could be omitted in the GP-MSE technique, while the clean up steps is necessary for the Soxhlet extract. This allows simplification of the analytical procedure.

4. Conclusion

GP-MSE is a powerful sample pretreatment technique with excellent analytical performance. The technique eliminates cleanup procedures which are necessary in other sample treatment techniques such as LLE, Soxhlet extraction, sonic extraction, and even in direct-LPME, because the gas phase chemicals which could be analyzed with GC–MS without any instrumental problems are only trapped by extracting solvent in the GP-MSE system. The results show that GP-MSE integrates sample extraction, cleanup and concentration. Future modifications of this method may include further automation of the device, and additional applications, such as in the fields of metabolomics, phytochemistry, food chemistry, biochemistry, and environment chemistry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.01.018.

References

[1] J. Cacho, V. Ferreira, P. Fernandez, Anal. Chim. Acta 264 (1992) 311.
[2] Y. Wang, Y.C. Kwok, Y. He, H.K. Lee, Anal. Chem. 70 (1998) 4610.
[3] Y. He, J.K. Lee, Anal. Chem. 69 (1997) 4634.
[4] L. Hou, H.K. Lee, J. Chromatogr. A 976 (2002) 377.
[5] Y. Yamini, M. Hojjati, M. Haji-Hosseini, M. Shamsipur, Talanta 62 (2004) 265.
[6] G. Ouyang, W. Zhao, J. Pawliszyn, J. Chromatogr. A 1138 (2007) 47.
[7] C. Nerín, J. Salafranca, M. Aznar, R. Batlle, Anal. Bioanal. Chem. 393 (2009) 809.
[8] L. Zhao, H.K. Lee, J. Chromatogr. A 919 (2001) 381.
[9] C. Basheer, J.P. Obbard, H.K. Lee, J. Chromatogr. A 1068 (2005) 221.
[10] M.C. Wei, J.F. Jen, Talanta 72 (2007) 1269.
[11] K. Demeestere, J. Dewulf, B.D. Witte, H.V. Langenhove, J. Chromatogr. A 1153 (2007) 130.
[12] J. Romero, P. López, C. Rubio, R. Batlle, C. Nerín, J. Chromatogr. A 1166 (2007) 24.
[13] S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. B 817 (2005) 3.
[14] P. Das, M. Gupta, A. Jain, K.K. Verma, J. Chromatogr. A 1023 (2004) 33.
[15] A. Rodríguez, S. Pedersen-Bjergaard, K.E. Rasmussen, C. Nerín, J. Chromatogr. A 1198–1199 (2008) 38.
[16] R. Batlle, C. Nerín, J. Chromatogr. A 1045 (2004) 29.
[17] E. Psillakis, N. Kalogerakis, Trends Anal. Chem. 22 (2003) 565.
[18] A.S. Yazdi, A. Amiri, Trends Anal. Chem. 29 (2010) 1.
[19] G. Ouyang, W. Zhao, J. Pawliszyn, Anal. Chem. 77 (2005) 8122.
[20] L. Xu, H.K. Lee, J. Chromatogr. A 1216 (2009) 5483.
[21] M.C. Alcudia-León, R. Lucena, S. Cárdenas, M. Valcárcel, Anal. Chem. 81 (2009) 8957.
[22] T.S. Ho, T. Vasskog, T. Anderssen, E. Jensen, K.E. Rasmussen, S. Pedersen-Bjergaard, Anal. Chim. Acta 592 (2007) 1.
[23] H. Xu, Z. Ding, L. Lv, D. Song, Y.Q. Feng, Anal. Chim. Acta 636 (2009) 28.
[24] A. Saleh, Y. Yamini, M. Faraji, M. Rezaee, M. Ghambarian, J. Chromatogr. A 1216 (2009) 6673.
[25] S. Berijani, Y. Assadi, M. Anbia, M.R.M. Hosseoni, E. Aghaee, J. Chromatogr. A 1123 (2006) 1.
[26] C. Yang, J. Qiu, C. Ren, X. Piao, X. Li, X. Wu, D. Li, J. Chromatogr. A 1216 (2009) 7694.
[27] D. Li, C. Yang, C. Ren, China Patent ZL 200820071370.4, May 20, 2008.
[28] X. Yan, C. Yang, C. Ren, D. Li, J. Chromatogr. A 1205 (2008) 182.
[29] S. Shariati-Feizabadi, Y. Yamini, N. Bahramifar, Anal. Chim. Acta 489 (2003) 21.
[30] L.M. Zhao, H.K. Lee, J. Chromatogr. A 931 (2001) 95.
[31] http://www.engineeringtoolbox.com/specific-heat-solids-d_154.html.
[32] http://en.wikipedia.org/wiki/Specific_heat_capacity#Heat_capacity.
[33] R.A. Doong, S.M. Chang, Y.C. Sun, J. Chromatogr. A 879 (2000) 177.
[34] X. Jiang, C. Basheer, J. Zhang, H.K. Lee, J. Chromatogr. A 1087 (2005) 289.