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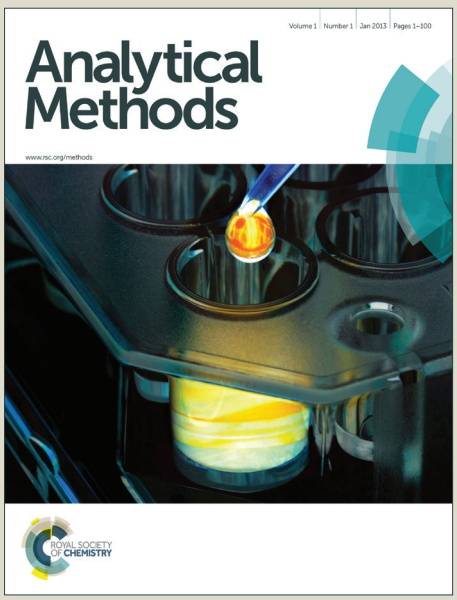

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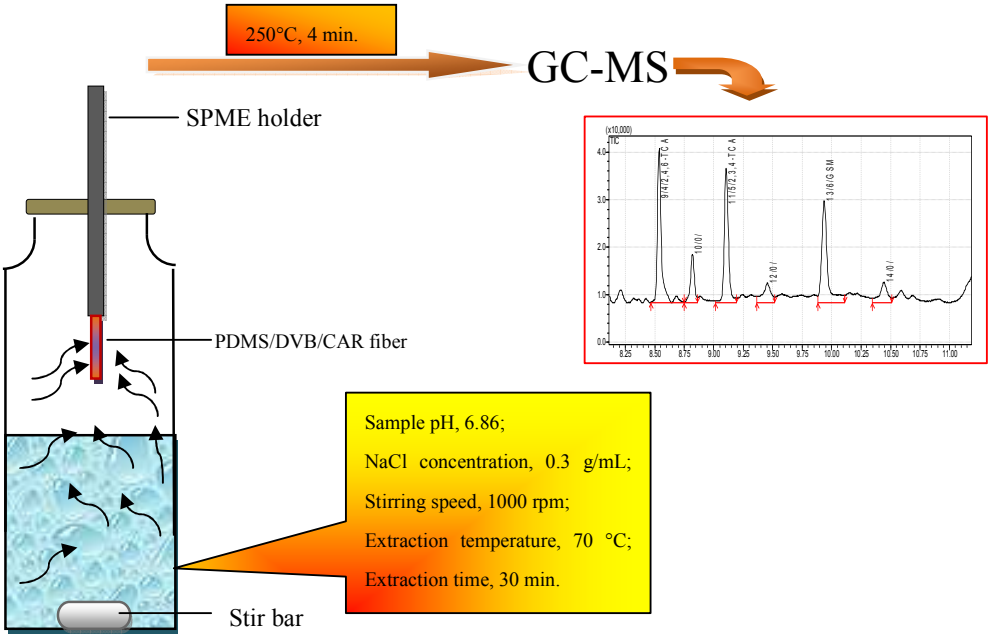
Graphical Abstract



Simultaneous determination of six earthy-musty odorous compounds in water by headspace solid-phase microextration coupled with gas chromatography-mass spectrometry

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Abstract

A simple, rapid, sensitive and high-efficiency method for simultaneous determination of six earthy-musty odorous compounds, 2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, 2-methylisoborneol, 2,4,6-trichloroanisole, 2,3,6-trichloroanisole, and geosmin, in water samples was developed by headspace solid-phase microextraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS). Experimental variables such as type of SPME fiber, desorption temperature, desorption time, sample pH, salt concentration, extraction temperature, stirring speed, and extraction time were optimized. The results show that polydimethylsiloxane/ divinylbenzene/carboxen fiber showed good extraction performance in terms of sensitivity and reproducibility. HS-SPME was carried out by using 20 mL water sample, addition of 6 g NaCl, stirring at 1000 rpm and temperature at 70 ℃ for 30 min to pre-concentrate the target analytes. After that, the fiber was desorbed at 250 ℃ for 4 min and determined by GC-MS. Under optimal conditions, the earthy-musty odorous compounds exhibited good linearity (R>0.986) over the concentration range of 2.5-250 ng/L. The repeatability and reproducibility of the method were lower than 6.5% and 9.2%, respectively. The limit of detection and limit of quantification values were lower than 1.0 ng/L and 2.5 ng/L, respectively. The analyte recoveries for different water samples such as tap, pond, river and waste water spiked at different concentrations were 92.8-114.1%.

Key words: headspace solid-phase microextration; odorous compounds; water; gas chromatography-mass spectrometry

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1. Introduction

The earthy and musty odor produced by blue algae, fungi, and actinomycetes in water environment has been widely reported [1, 2]. Geosmin (GSM) and 2-methylisoborneol (MIB) have been known to be the most common earthy-musty odorous compounds contributing to the undesirable earthy and musty smell of water [3]. Beside these compounds, 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), 2,3,6-trichloroanisole (2,3,6-TCA), and 2,4,6-trichloroanisole (2,4,6-TCA), have been also reported to contribute to the odor of water in recent year. IPMP and IBMP are the metabolites of actinomycetes and soil bacteria [4]. The compounds of 2,3,6-TCA and 2,4,6-TCA are most probably formed by bio-methylation of trichlorophenol [5]. Typically more than one earthy-musty odorous compound may simultaneously produce when algal bloom occurs. From this perspective, it is essential to devise a rapid, selective and efficient method that enables the simultaneous quantification of the principal compounds identified as responsible for the main odor.

The threshold odor concentrations of the earthy-musty odorous compounds are near or below nanogram/Liter [6]. In order to determine the origin of these compounds, it is necessary to quantify the molecules responsible on this side of their thresholds of perception in water by a highly sensitive method.

Gas chromatography-mass spectrometry (GC-MS) is usually used for quantification of the earthy-musty odorous compounds [6-18]. However, a pre-concentration step is required in order to measure the earthy-musty odorous compounds at low nanogram/Liter level. Unlike the unique separation method, a wide variety of enrichment and extraction techniques including purge and trap (PT) [6-8], closed-loop stripping analysis [9], solid-phase extraction (SPE) [10, 11], stir bar sorptive extraction (SBSE) [12, 13], headspace solid-phase micro extraction (HS-SPME) [14, 15], liquid-liquid extraction (LLE) [16], and liquid-phase micro extraction (LPME) [17, 18] have been used to pre-concentrate earthy-musty odorous compounds. PT coupled with GC-MS shows satisfactory sensitivity for the measurement of earthy-musty odorous compounds in waters. However, the PT instruments are expensive and have more complicated flow paths. A carry-over effect often arises after the analysis of

complex and/or highly dissolved solids samples. Closed loop stripping and LLE are tedious, time consuming, and consume large amount of solvents. SPE and SBSE have high recoveries and high capacity, but they are relatively time-consuming for extraction. LPME using a microdrop of solvent from microsyringe is fast and inexpensive, but attention must be paid to the stability of droplet during extraction. HS-SPME using a fused-silica fiber coated on the outside with a stationary phase provides potentially attractive features for the extraction of earthy-musty odorous compounds because it has important advantages over conventional extraction techniques due to its ease of use, being rather rapid, potable and solvent-free.

HS-SPME was developed by Arthur and Pawliszyn in 1990 [19]. This technique eliminates most of the drawbacks in the preparation of an aqueous sample and allows the quantification of a large number of molecules with sufficiently low limits of detection and good linearity over a considerable dynamic range. Nakamura et al. reported that carboxen (CAR)/PDMS, PDMS/divinylbenzene (DVB) and PDMS fibers showed similar extraction performances for MIB and GSM [20]. Saito et al. developed a new HS-SPME method for MIB and GSM in environmental water by using a PDMS/DVB fiber for effective sample enrichment [14]. In order to determine different earthy-musty odorous compounds, Sung et al. employed a PDMS/DVB/CAR fiber for simultaneous extraction of GSM, MIB, IPMP, and 2,4,6-TCA in water. But the method requires gas chromatography-ion trap mass spectrometry for the subsequent quantification, which is not widely available in most labs [21]. In a recent report, a PDMS/DVB metal alloy fiber was used to pre-concentrate GSM, 2,4,6-TCA, and MIB in different water matrices. But the cost of the metal alloy fiber is high [22]. Although HS-SPME has been widely used to determine GSM and MIB, its application for simultaneous determination of other syngenetic earthy-musty odorous compounds such as IPMP and 2,3,6-TCA by GC-MS is relatively few. Therefore, it is desirable to develop a simple and efficient method for simultaneous determination of these compounds to increase the detection efficiency.

The aim of the present study was to develop a new HS-SPME method for simultaneous determination of GSM, 2-MIB, IPMP, IBMP, 2,3,6-TCA, and 2,4,6-TCA in water samples. Experimental variables such as type of SPME fiber, desorption temperature, desorption time, sample pH, salt concentration, extraction temperature, stirring speed, and extraction time were

controlled and optimized. The recovery, repeatability, reproducibility, linearity, limits of detection (LOD), limits of quantification (LOQ), and quantitative data for real water samples are discussed.

2. Materials and methods

2.1. Reagents and materials

Methanol, sodium chloride (NaCl), hydrochloric acid (HCl), citric acid and sodium hydroxide (NaOH) were analytical grade from Guangzhou Chemical Reagent Factory (Guangzhou, China). Standards of GSM and MIB were certified reference material from Supelco (Bellefonte, PA, USA) as solutions of 100 mg/L in methanol. Standards of IBMP (99%), IPMP (98%), 2,3,6-TCA （98%）and 2,4,6-TCA (98%) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Disodium hydrogenphosphate (Na_2HPO_4) and potassium dihydrogenphosphate (KH_2PO_4) were analytical grade from Shanghai Reagents (Shanghai, China). Sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) was analytical grade from Nanjing Senking Chemical Co., Ltd. (Nanjing, China). All other chemicals and solvents were analytical-reagent grade and used without further purification. The SPME fiber assemblies and manual holder were obtained from Supelco (Bellefonte, PA, USA).

2.2 Preparation of standard solutions and buffer solutions

Stock standard solutions of 10.0 mg/L were prepared in methanol. Fresh mixed standard solutions of 10.0 μg/L were prepared in methanol weekly before the extraction. Typically, standards of 5.0, 10, 25, 50, and 100 ng/L were used. Working solutions were prepared by dilution of standard stock solution in de-ionized water. All aqueous working solutions were freshly prepared before each extraction in order to eliminate volatilization losses. The citrate solution was prepared by adding 20 mL of 1.0 mol/L NaOH solution to dissolve 2.101 g of citric acid, and diluting to 100 mL with de-ionized water. To obtain buffer solutions with pH values between 2.0 and 4.0, suitable volumes of 0.10 mol/L HCl were added to citrate solution. The buffer solutions with pH 6.86 were obtained by dissolving 0.353 g of Na_2HPO_4 and 0.339 g of KH_2PO_4, and diluting to 100 mL with de-ionized water. The buffer solutions with pH 9.18 were obtained by dissolving 0.380 g of $Na_2B_4O_7 \cdot 10H_2O$, and diluting to 100 mL

with de-ionized water. The buffer solutions with pH 10.0 were obtained by adding suitable volumes of 1.0 mol/L NaOH to the sodium tetraborate solution. All solutions were stored in the dark at 4 ℃.

2.3. HS-SPME

Four commercially available SPME fibers were investigated for their extraction performance. These included 85 μm (coating thickness) polyacrylate (PA), 100 μm PDMS, 65 μm PDMS/DVB, and 50/30 μm PDMS/DVB/CAR coating fibers. The fibers were conditioned in the GC injection port at 260 ℃ in accordance with the supplier's instructions before first use. An 85-2B magnetic stirrer (Jinan Medical Instrument Factory, Jiangsu, China) was used for stirring the water samples during the HS-SPME procedure. Before the SPME, the pH of the samples solution was adjusted to pH 6.86 by adding suitable volumes of Na_2HPO_4-KH_2PO_4 buffer solution. After placing 6.0 g of NaCl and a stir bar in a 45 ml vial, aliquots of 20 ml of standard solutions (25 ng/L in water) or real samples were added. The vial was sealed with a silicone-teflon septum cap and placed in a water bath. The rotation rate of stir bar was controlled at 1000 ± 50 rpm. The temperature of the water bath was 70 ± 2 ℃, unless otherwise specified. The outer needle of fiber was used to penetrate the septum and the fiber extended into the headspace for extraction. After 30 min exposure, the fiber was immediately inserted into the GC injection port for desorption.

2.4 Instrumental conditions

A GC-2010 gas chromatography coupled with mass spectrometry detector (Shimadzu, Kyoto, Japan) was used in electron ionization mode. A DB-5MS UI capillary column (Agilent, CA, USA) with 30 m × 0.25 mm I.D. and 0.25 μm film thickness was used to separate the samples. Helium (>99.999% pure) was used as carrier gas at a constant column flow of 1.00 mL/min. The GC oven temperature program was set at an initial temperature of 50 ℃ for 2 min, raised to 150 ℃ (hold for 5 min) at 25 ℃/min, then increased to 250 ℃ (hold for 3 min) at 40 ℃/min. The injector was set in splitless mode and injector temperature was 250 ℃. Electron ionization was performed at 70 eV, the source and GC interface temperature were set at 230 ℃ and 250 ℃, respectively. Data acquisition was performed in scan mode from 40 to 300 a.m.u. for identification purposes and in time-scheduled selected ion monitoring (SIM)

mode using the retention windows as indicated in Table 1.

2.5. Sample collection

Tap water was sampled from the main area of the water supply network of Guangzhou, Guangdong. River water was collected from Panyu sections of Pear River (Guangzhou, Guangdong). Pond water was sampled from Dongshan Lake (Guangzhou, Guangdong). Waste water was collected from the waste water discharge ports of Shaji river (Guangzhou, Guangdong). All the samples were collected from the surface of water and stored in 500 mL amber-class bottles with PTFE septa, respectively. During the sampling, the bottles were filled to be headspace free and immediately transported to the laboratory. All the samples were kept at 4 ℃ between sampling analysis.

3. Results and discussion

3.1 Method development

SPME is an equilibrium process that involves the partitioning of analytes between the sample and the extraction phase. Extraction conditions must be systematically optimized to increase the partitioning of analytes in the coated fiber. In order to obtain a reproducible, fast and sensitive method based on HS-SPME, influences of several parameters including type of SPME fiber, desorption temperature, desorption time, sample pH, salt concentration, extraction temperature, stirring speed, and extraction time have to be considered. Therefore, a series of aqueous solutions (20 mL) spiked at 25 ng/L with each of the earthy-musty odorous compounds was extracted, in triplicate, to evaluate the effect of the experimental parameters on the extraction efficiency. To identify the optimal conditions, peak area responses for the analytes were used for evaluation.

3.1.1 Type of SPME fiber

The type of SPME fiber is one of the most important aspects of optimization. Both the parity and thickness of the fiber coating will influence the fiber extraction efficiency. A thick fiber coating will extract more analytes than will a thin coating. The small pores in carboxen particles make this carbon molecular sieve particularly effective for extracting small molecules. Divinylbenzene polymer increases the available surface area and thus improves

the extraction of small polar molecules. PDMS/DVB is considered to be effective for low molecular weight amines and alcohols. CAR/PDMS is suitable for volatile organic compounds [20]. As the target anaytes were different in their physical-chemical property, four commercially available SPME fibers which was different in fiber coating and thickness was investigated as candidate extraction fiber. These included 85μm PA, 100μm PDMS, 65μm PDMS/DVB, and 50/30μm PDMS/DVB/CAR coating fibers. As shown in Fig. 1, the PDMS/DVB/CAR fiber provided the highest peak area responses for all the target compounds. However, PDMS and PDMS/DVB that were adsorbent type fibers had limited peak area responses. PA fiber which was a polar fiber exhibited the lowest peak area responses. Given that PDMS/DVB/CAR fiber showed the highest peak area responses for all the target analytes, this fiber was selected for further experiments.

3.1.2 Desorption temperature

In order to obtain the optimal desorption temperature for a fast desorption of the extracted analytes, the effect of the desorption temperature on the peak area responses for the analytes was investigated by changing the GC injection port temperature from 220 to 260 ℃ for 3 min. As illustrated in Fig. 2a, the peak area responses for all analytes increased rapidly when the temperature increased from 220 to 240 ℃ and increased slightly after the temperature beyond 240 ℃. This result indicated the extracted analytes could not be completely desorbed at this temperature range when the desorption time was 3 min. Thus, higher desorption temperature and longer desorption time should employ to release the extracted analytes. However, the maximum endurable temperature of the PDMS/DVB/CAR fiber is 270 ℃. Thus, 250 ℃ was chosen as the optimal desorption temperature to avoid possible damage of the fiber.

3.1.3 Desorption time

Different desorption times (0.50, 1.0, 2.0, 3.0, 4.0, and 5.0 min) were tested on the injection port at 250 ℃. Fig. 2b shows the desorption time profile of the extracted analytes. The peak area responses of the analytes increased significantly with an increase in desorption time from 0.50 to 4.0 min. The peak area responses maintained constant when the desorption time increased further. The peak area responses of IPMP, IBMP, MIB, 2,3,6-TCA, 2,4,6-TCA, and GSM at 4.0min were 2.1, 2.9, 1.9, 2.7, 3.5, and 2.5 times higher, respectively, than those at

0.5 min. Consequently, 4.0 min was selected to be the optimum desorption time for subsequent studies. Using the selected desorption conditions, a vial with de-ionized water was analyzed after the sample injection, and no carry-over effect was observed.

3.1.4 Sample pH

The sample pH could affect the chemical form of the analytes and hence affect the equilibrium between the sample and the extraction phase. The effect of sample pH on the peak area responses for the analytes was investigated over the pH range of 2.0-10.0 under the optimal desorption condition. As revealed in Fig. 3a, the peak area responses for 2,4,6-TCA and 2,3,6-TCA remained relatively constant over the pH range of 2.0-10.0. While the peak area responses for IPMP, IBMP, GSM and MIB increased when the pH value increased from 2.0 to 6.86. Thereafter, the peak area responses for IPMP, IBMP, GSM and MIB remained relatively constant on further increase in sample pH. For example, the peak area responses for IPMP at pH 2.0 were 21.6% lower than that at pH 6.86. Similar results were also found for IBMP, GSM and MIB. The pH-dependent behavior of the analytes was attributed to dehydration of analytes under acidic conditions and this could be mitigated by adjusting the sample to a neutral pH. Therefore, the pH of the water sample should be adjusted to approximately 7 if the sample had previously been acidified for heavy metal analysis [23]. In subsequent experiments, the pH of the water sample was adjusted to pH 6.86 by Na_2HPO_4-KH_2PO_4 buffer solution.

3.1.5 Salt concentration

Generally, the addition of salt increases the ionic strength of the aqueous solution and would affect the solubility of organic compound. Increasing the ionic strength can affect the affinity of the analytes for the extraction phase since less water molecules are available for the solubilization of the analytes, which facilitates their transference towards the headspace [24]. The influence of salt concentration on the peak area responses of the analytes at pH 6.86 was investigated by adding NaCl to give concentrations of 0, 0.1, 0.2, 0.3, and 0.4 g/mL. The temperature of the water bath was controlled at 50℃ as the initial extraction temperature in order to increase the mass transfer rate of the analytes. As shown in Fig. 3b, the peak area responses of the analytes increased significantly with an increase in salt concentration from 0 to 0.2 g/mL, reaching a plateau in salt concentration from 0.3 to 0.4 g/mL. From the

optimization studies, 0.3 g/mL was considered to be the most appropriate concentration to achieve maximum peak area responses for the analytes.

3.1.6 Extraction temperature

Extraction temperature has some potential effects on the kinetics and thermodynamics in the extraction process by increasing the mass transfer rates and the partition coefficients of an analyte, accordingly shortening the equilibrium time. At the same time, a higher extraction temperature also leads to a higher vapor pressure of the analyte and consequently increases the analyte concentration in the headspace [25]. The effect of extraction temperature on the peak area responses of the analytes was investigated from 40 to 80 ℃. As illustrated in Fig. 4a, the peak area responses of all target analytes increased with extraction temperature from 40 to 70 ℃. However, the peak area responses of all target analytes decreased when the extraction temperature increased further. The reduction in peak area responses may arise from the decreasing absorption of the analytes onto the fiber at higher temperature [21]. Therefore, the extraction temperature selected for further studies was 70 ℃.

3.1.7 Stirring speed

Agitation of a sample is assumed to reduce the time required to establish the partition equilibrium between the aqueous and the gaseous phases as the transfer coefficients of the analytes in the aqueous phase are enhanced. Besides, stirring the sample induces convection in the headspace, which would also facilitate the mass transference towards the extraction phase. The effect of stirring speed on the extraction efficiency was evaluated by changing the stirring speed from 400 to 1200 rpm. The results, shown in Fig. 4b, revealed that all target analytes showed a similar trend, i.e., the extraction efficiency increased with stirring speed up to 1000 rpm, and remained constant beyond 1000 rpm. The peak area responses of the analytes at 1000 rpm were two to three times higher than those at 400 rpm. Comparing the results obtained at 1000 and 1200 rpm, the peak area responses for all the analytes were comparable. However, the RSDs (7.2-10%) of the peak areas at 1200 rpm were higher than those (5.5-7.8%) at 1000 rpm. Thus, 1000 rpm was chosen as the optimal stirring speed for the extraction.

3.1.8 Extraction time

The effect of extraction time on the peak area responses for the analytes was investigated by

extracting the analytes for 10, 20, 30, 40, 50, and 60 min, respectively. The results in Fig. 5 indicated that all analytes responded similarly to the effect of extraction time on signal response, i.e., the peak area responses for the analytes increased dramatically with the increase in extraction time from 10 to 30 min. Then, the peak area responses increased slightly when the extraction time increased from 30 min to 60 min. These results indicated that the equilibrium was still not reached within 60 min. According to the non-equilibrium theory of HS-SPME, HS-SPME quantitative analysis can be utilized in a non-equilibrium situation if the extraction conditions are kept constant [26]. To ensure a rapid and efficient extraction, 30 min was chosen as the optimal extraction time.

The optimal experimental conditions used in the present work can be summarized as follows: fiber, PDMS/DVB/CAR; sample pH, 6.86; NaCl concentration, 0.3 g/mL; stirring speed, 1000 rpm; extraction temperature, 70 ℃; extraction time, 30 min; desorption temperature, 250 ℃; and desorption time, 4 min.

3.2Validation of the method

The analytical figures of merit of the proposed method under the optimal conditions were evaluated and presented in Table 1. The linear ranges of the method were from 2.5 to 100 ng/L, and all the correlation coefficients were better than 0.986. The repeatability of the method was evaluated through extracting de-ionized water spiked at 5 ng/L (5 replicates), and the relative standard deviations (RSDs) were 4.4-6.5%. The reproducibility of the method was checked by extracting the same water samples over 5 successive days and the RSDs were 5.3-9.2%. Overall, the method showed good repeatability and reproducibility. The LOD and LOQ values for the method were calculated as three or ten times the signal-to-noise ratio (S/N), respectively. The LOD and LOQ values were found to be lower than 1.0 ng/L and 2.5 ng/L, respectively. Since most of studies have focused on the well-known earthy-musty algal metabolites GSM and MIB, whereas there are only a few studies on other cyanobacterial metabolites such as 2,3,6-TCA and 2,4,6-TCA. The obtained results for MIB and GSM with this method were compared with those methods reported in the literature and given in Table 2. The values obtained in the present study are similar to those reported by Saito et al. [14], and greatly improved when compared with those obtained by ultrasound-assisted dispersive

liquid-liquid microextraction (USADLLME) techniques [18]. Compared with LLE and USADLLME, the HS-SPME technique need little experiment effort to perform an analysis. In addition, it does not need toxic solvent, which is environmental friendly.

3.3 Real water analysis

The proposed SPME technique coupled with GC-MS analysis was used to measure the earthy-musty odorous compounds in four kinds of water samples. These water samples included tap, pond, river and waste water. All water samples were extracted without any pre-treatment. There were no earthy-musty odorous compounds that detected in the tap water samples. However, MIB was detected in the pond and, river, and waste water samples and the corresponding concentrations were 9.3 ± 0.5, 3.7 ± 0.3 and 15.4 ± 0.8 ng/L, respectively. The compound of 2,4,6-TCA was found in the waste water samples and the corresponding concentration was 2.8 ± 0.2 ng/L. To confirm the validity of this method, know amounts of target analytes were spiked at concentrations of 10, 25, and 50 ng/L, respectively. The analyte recoveries for the spiked samples are listed in Table 3. The overall recoveries of the target analytes in different water samples were 92.8-114.1%, and the RSDs were 3.8-8.5%. Fig. 6 showed the typical chromatograms for tap, pond, river and waste water samples and samples spiked at 25 ng/L. The chromatographic profiles for the different water samples were free of interferences, indicating that the HS-SPME GC-MS system was suitable for the analysis of the different types of water samples. These results also indicated that the method was reliable and the sample matrix had negligible effect on the extraction efficiency.

4. Conclusions

A simple, rapid, sensitive and high-efficiency method for simultaneous determination of six earthy-musty odorous compounds in water samples was developed. The HS-SPME technique was shown to be effective in extraction of target analtyes in real samples, resulting in good chromatographic behavior. Several water samples such as pond, river, and waste water samples have been polluted by MIB or (and) 2,4,6-TCA. The MIB might arise from the algal bloom in different water environments. The 2,4,6-TCA in waste water samples might arise from the pollution of chlorophenols. The chlorophenols can originate from various

contaminants such as those found in some pesticides and wood preservatives. The present result revealed that much attention should be paid to the pollutions of the water environments. The method provides a useful tool for screening the earthy-musty odorous compounds in water samples.

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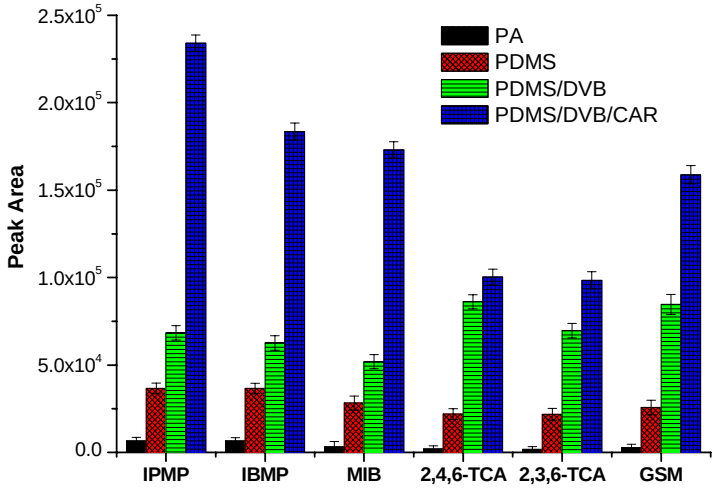
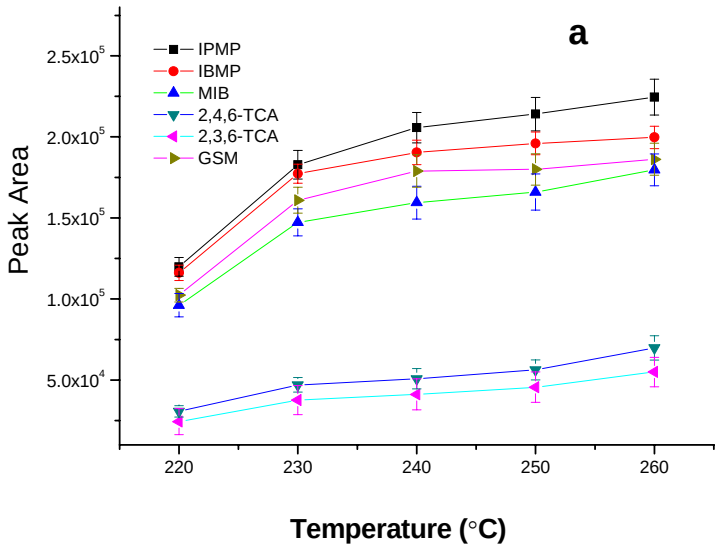


Fig. 1 Analyte responses for different SPME fibers. Extraction conditions: extraction temperature, 50 ℃; extraction time, 30 min; stirring speed, 500 rpm. Desorption condition: temperature, 250 ℃; desorption time, 4 min. Spiked concentration of each analyte, 25 ng/L.



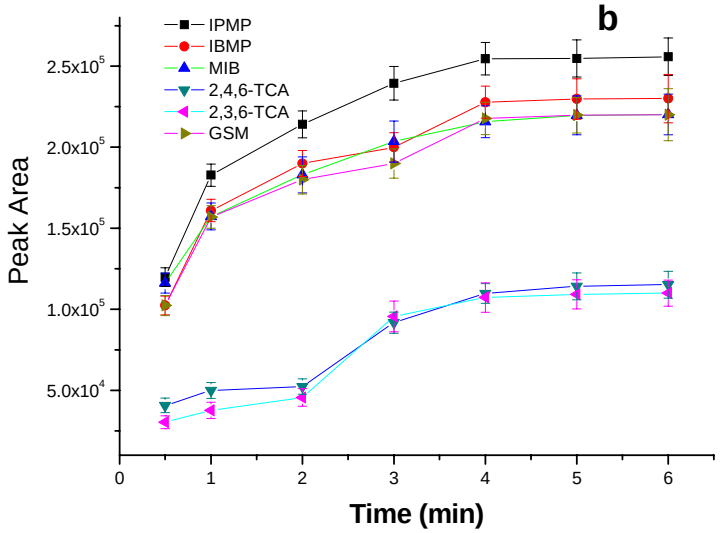
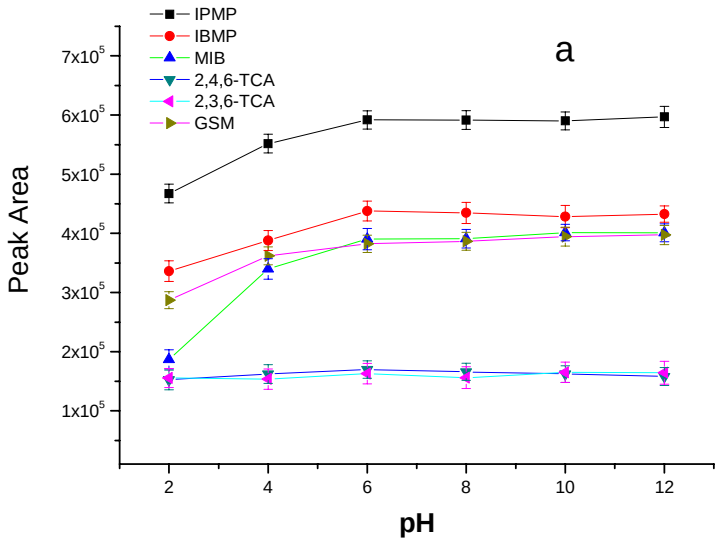


Fig. 2 Effect of desorption condition on analyte responses. (a) desorption temperature; (b) desorption time. Other parameters, as in Fig. 1.



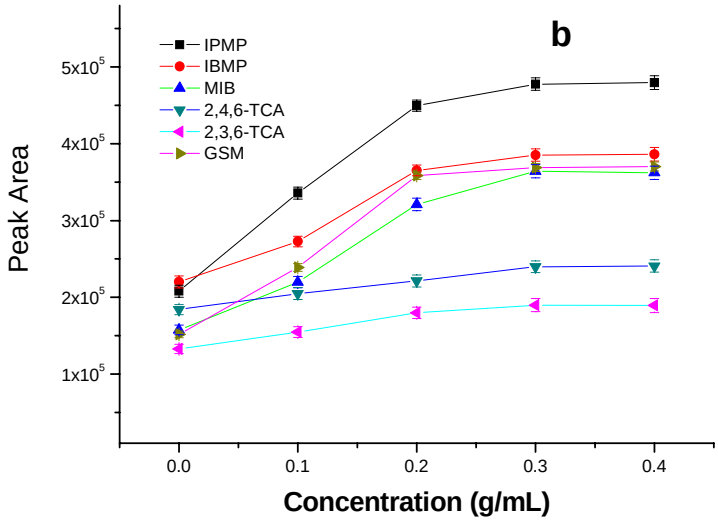
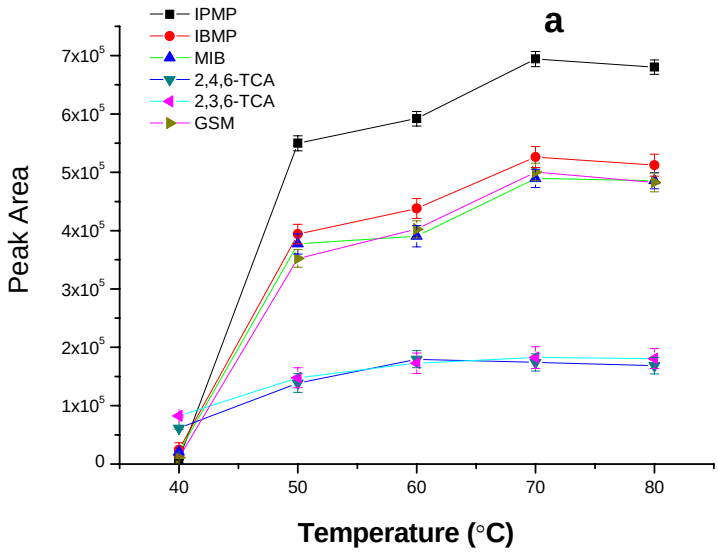


Fig. 3 Effect of solution property on analyte responses. (a) pH. Other parameters, as in Fig. 1. (b) NaCl concentration. Extraction conditions: sample pH 6.86. Other parameters, as in Fig. 1.



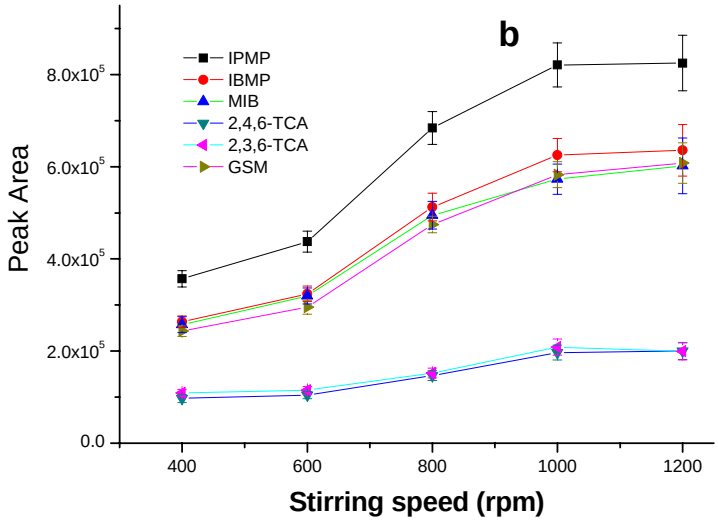


Fig. 4 Effect of extraction temperature and stirring speed on analyte responses. (a) Extraction temperature. Extraction conditions: sample pH, 6.86; NaCl concentration, 0.30 g/mL. Other parameters, as in Fig. 1. (b) Stirring speed. Extraction conditions: sample pH, 6.86; NaCl concentration, 0.30 g/mL. extraction temperature, 70 ℃; Other parameters, as in Fig. 1.

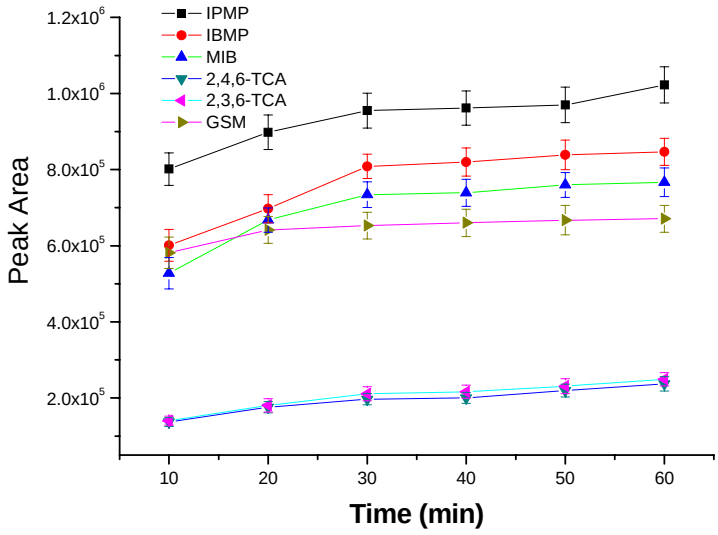


Fig. 5 Effect of extraction time on analyte responses. Extraction conditions: sample pH, 6.86; NaCl concentration, 0.30 g/mL. extraction temperature, 70 ℃; stirring speed, 1000 rpm. Other parameters, as in Fig. 1.

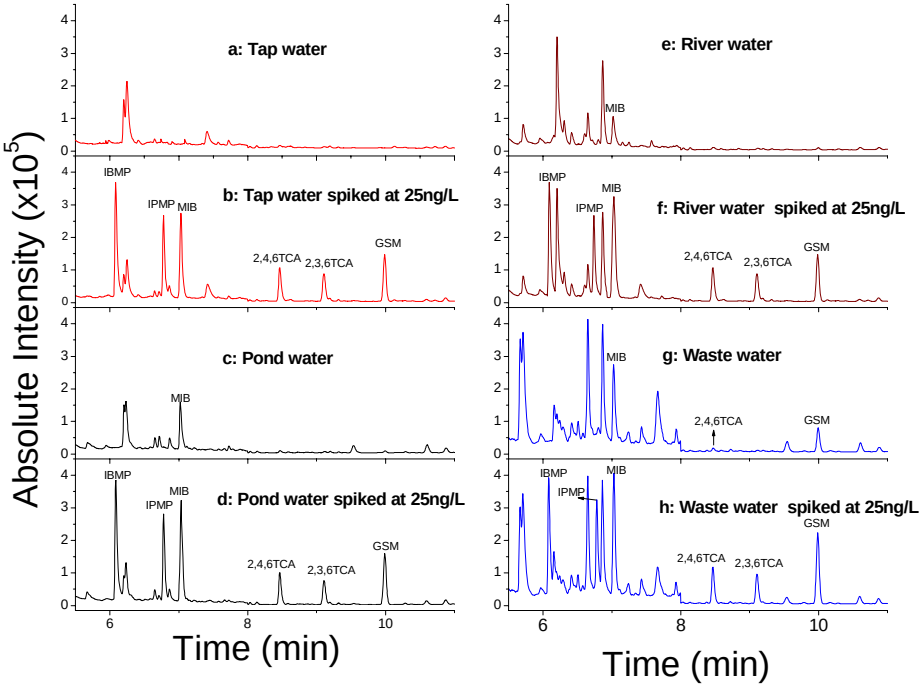


Fig. 6 Total ion chromatogram for GC-MS analysis of extract. (a) Tap water; (b) Tap water spiked at 25 ng/L; (c) pond water; (d) pond water spiked at 25 ng/L; (e) river water; (f) river water spiked at 25 ng/L; (g) waste water; (h) waste water spiked at 25 ng/L.

Table 1 Performance parameters for the method

Compound	Retention time (min)	Retention window (min)	Selected ion (m/z)	Range (ng/L)	r	Repeatability (n=5, RSD%)	Reproducibility (n=5, RSD%)	LOD (ng/L)	LOQ (ng/L)
IPMP	6.732	5.2-8.0	137[a],124, 152	1.3-100	0.9997	4.4	5.6	0.39	1.3
IBMP	7.148	5.2-8.0	124[a],151, 81	1.7-100	0.9997	4.0	5.3	0.51	1.7
MIB	7.388	5.2-8.0	95[a],108, 110	1.2-100	0.9997	4.5	6.2	0.35	1.2
2,4,6-TCA	8.536	8.0-12.0	195[a],197, 210	2.5-100	0.9867	6.5	9.1	0.76	2.5
2,3,6-TCA	9.106	8.0-12.0	210[a],195, 212	1.8-100	0.9967	6.6	9.2	0.53	1.8
GSM	9.942	8.0-12.0	112[a],111, 125	1.5-100	0.9996	6.2	8.9	0.44	1.5

a: The selected ion for quantitation

Table 2 Comparison of different pre-concentration methods for the determination of 2-MIB and GSM in water samples

Preconcentration method[a]	Sample volume(mL)	Extraction phase	Organic solvent volume(μL)	Extraction time (min)	LOD (ng/L)		RSD (%)		Reference
					MIB	GSM	MIB	GSM	
LLE	250	pentane	1000	30	0.1	0.1	6.9	6.3	[16]
USADLLME	12	Tetrachloroethylene	8	3	9	2	10.1	10.4	[18]
PT	20	Tenax Trap	/	20	1	2	6.4	7.9	[6]
SBSE	20	PDMS stir bar	/	20	0.33	0.15	9.2	3.7	[12]
SPME	2	PDMS/DVB fiber	/	30	0.9	0.6	<3.7	<8.0	[14]
SPME	20	PDMS/DVB/CAR fiber	/	30	0.35	0.44	4.5	6.2	This work

a: In all case GC-MS has been used for separation and quantification.

Table 3 Analysis of real water samples and the recovery data (n=3）

Sample type	Compound	DC[a] (X±SD,ng/L)	Spiked at 10 ng/L			Spiked at 25 ng/L			Spiked at 50 ng/L		
			DC (X±SD,ng/L)	Recovery (%)	RSD (%)	DC (X±SD,ng/L)	Recovery (%)	RSD (%)	DC (X±SD,ng/L)	Recovery (%)	RSD (%)
Tap water	IPMP	ND[b]	10.7 ± 0.5	106.7	4.7	26.8 ± 1.2	107.3	4.5	51.8 ± 2.8	103.7	5.4
	IBMP	ND	10.6 ± 0.5	106.1	4.7	26.1 ± 1.0	104.5	3.8	51.6 ± 2.4	103.2	4.7
	MIB	ND	10.3 ± 0.7	102.9	6.8	26.7 ± 1.6	106.8	6.0	50.4 ± 2.5	100.7	5.0
	2,4,6-TCA	ND	9.8 ± 0.6	98.0	6.1	26.9 ± 1.5	99.4	6.0	48.9 ± 3.0	97.8	6.1

	2,3,6-TCA	ND	9.7 ± 0.6	96.6	6.2	24.4 ± 1.3	97.4	5.3	48.4 ± 2.7	96.7	5.6
	GSM	ND	10.4 ± 0.5	103.9	4.8	25.5 ± 1.4	102.1	5.5	50.4 ± 2.5	100.9	5.0
	IPMP	ND	10.5 ± 0.6	104.7	5.7	26.8 ± 1.5	107.2	5.6	48.5 ± 2.5	96.9	5.2
	IBMP	ND	9.6 ± 0.5	96.3	5.2	26.7 ± 1.4	106.7	5.2	48.4 ± 2.1	96.7	4.3
Pond	MIB	9.3 ± 0.5	19.2 ±12	99.1	6.2	33.5 ± 2.0	96.6	6.0	59.8 ± 3.1	101.0	5.2
water	2,4,6-TCA	ND	9.5 ± 0.7	95.1	7.4	24.3 ± 1.4	97.3	5.8	48.7 ± 2.5	97.3	5.1
	2,3,6-TCA	ND	9.7 ± 0.7	97.0	7.2	24.8 ± 1.3	96.7	6.2	47.8 ± 2.3	95.5	4.8
	GSM	ND	11.4 ± 0.6	114.1	5.3	27.0 ± 1.5	108.0	5.6	49.5 ± 2.5	99.0	5.1
	IPMP	ND	10.7 ± 0.7	106.7	6.6	26.4 ± 1.5	105.8	5.7	48.0 ± 2.5	96.0	5.2
	IBMP	ND	10.6 ± 0.6	106.1	5.7	25.5 ± 1.4	102.2	5.5	49.4 ± 2.3	98.8	4.7
River	MIB	3.7 ± 0.3	13.3 ± 0.8	95.6	6.0	29.1 ± 1.8	101.5	6.2	51.8 ± 2.7	96.2	5.2
water	2,4,6-TCA	ND	9.6 ± 0.7	95.5	7.3	24.5 ± 1.4	98.0	5.7	48.8 ± 2.4	97.6	4.9
	2,3,6-TCA	ND	9.7 ± 0.8	96.6	8.3	24.2 ± 1.5	96.8	6.2	48.6 ± 2.5	97.1	5.1
	GSM	ND	11.4 ± 0.7	113.9	6.1	25.8 ± 1.4	103.2	5.4	49.2 ± 2.3	98.4	4.7
	IPMP	ND	10.5 ± 0.7	104.7	6.7	25.0 ± 1.5	99.9	6.0	48.5 ± 2.5	96.9	5.2
	IBMP	ND	9.6 ± 0.6	96.3	6.2	26.1 ± 1.6	104.2	6.1	48.4 ± 2.9	96.7	6.0
Waste	MIB	15.4 ± 0.8	25.2 ± 1.6	98.6	6.3	38.8 ± 2.2	93.7	5.7	62.8 ± 3.5	94.9	5.6
water	2,4,6-TCA	2.8 ± 0.2	12.1 ± 0.8	93.1	6.6	27.0 ± 1.8	96.7	6.7	52.7 ± 3.8	99.7	7.2
	2,3,6-TCA	ND	9.3 ± 0.7	92.8	7.5	24.5 ± 1.7	98.2	6.9	49.7 ± 3.7	99.3	7.4
	GSM	ND	22.4 ± 1.9	94.0	8.5	38.4 ± 2.9	101.7	7.5	59.8 ± 3.5	93.5	5.9

a: DC=Detected concentration

b: ND=Not detected.