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Analysis of earthy and musty odors in water samples by solid-phase microextraction coupled with gas chromatography/ion trap mass spectrometry

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Abstract

A method for the determination of the earthy and musty odors geosmin, 2-methylisoborneol (2-MIB), 2-isobutyl-3-methoxy pyrazine (IBMP), 2-isopropyl-3-methoxy pyrazine (IPMP) and 2,4,6-trichloroanisole (2,4,6-TCA) in water by headspace solid-phase microextraction (HSSPME) combined with gas chromatography–ion trap mass spectrometry (GC–ITMS) is described. Several parameters of the extraction and desorption procedure were studied and optimized (such as types of fibers, extraction temperature, extraction time, desorption temperature, desorption time, ionic strength and elutropic strength and pH of samples). The method shows good linearity over the concentration range 1–500 ng l^{-1} and gives detection limits of sub-part per trillion levels for all compounds. Good precision (5.9–9.8%) is obtained using IBMP as internal standard. Finally, the method was successfully applied to analyze earthy and musty odors in tap water and lake water.

Keywords: Solid-phase microextraction; Odor; Earthy-musty; Gas chromatography; Ion trap mass spectrometry

1. Introduction

Earthy and musty odors in drinking water are often caused by chemical by-products (e.g., geosmin, 2-methylisoborneol (2-MIB), 2-isobutyl-3-methoxy pyrazine (IBMP), 2-isopropyl-3-methoxy pyrazine (IPMP) and 2,4,6-trichloroanisole (2,4,6-TCA)) from the growth of blue–green algae, commonly found in lakes and reservoirs. Some people can smell the odor of these compounds in drinking water at concentrations of 10 ppt or less. Thus, many water utility companies and beverage manufacturers must detect geosmin, 2-MIB, IPMP and IBMP at concentrations of 1–3 ppt. The identification and quantification of trace amounts of taste- and odor-causing compounds is essential since these compounds dramatically impact the aesthetic quality and consumer acceptability of drinking water.

Current methods for detection and quantification at these nanogram per liter levels require large sample volumes (100–1000 ml) and intensive sample preconcentration procedures such as liquid–liquid extraction/Kuderna Danish concentration [1], or relatively complex equipment, e.g., closed-loop stripping analysis [2], simultaneous distillation extraction [3] or purge and trap [4]. These procedures can be time-consuming, resulting in low sample throughput, and may require expensive high-resolution mass spectrometers [5] to provide detection and specificity at low nanogram per liter concentrations.

Solid-phase microextraction (SPME), a relatively new technique developed by Pawliszyn and co-workers [6–9] eliminated most of the drawbacks in the preparation of an aqueous sample. SPME integrates sampling, extraction, concentration and sample introduction in a simple process, and most importantly, it uses no solvent during extraction. The extensive applications of SPME were almost based exclusively on separation and analysis by gas chromatography

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(GC) [10,11] or HPLC [12]. SPME has also been used to measure the concentrations of a number of important odor-causing VOCs in surface waters and algal cultures at ug l^{-1} levels [13–18].

The headspace SPME (HSSPME) technology using polydimethylsiloxane/divinylbenzene (PDMS/DVB) [16,17] or polydimethylsiloxane (PDMS) [4] fibers for trace VOC work has been reported. Lloyd et al. [4] applied headspace SPME using the PDMS fiber, 6 ml samples, and 5 min extraction time to quantify geosmin and 2-MIB in standards at concentrations as low as 0.1 ug l^{-1}, approximately 10 times odor threshold concentrations [17] (geosmin and MIB, range from 4 to 10 ng l^{-1} and 9 to 42 ng l^{-1}, respectively). At these concentrations, these authors found that SPME compared favorably with purge and trap analyses [4]. In order to determine the lower limits of detection by HSSPME, using 500 ml samples and 20 min extractions they attained detection limits of 10 ng l^{-1} for 2-MIB and geosmin in standard solutions, but did not quantify at these analyte concentrations in surface or drinking water samples. The use of PDMS/DVB fiber of HSSPME technology for trace VOC work has been studied by McCallum et al. [15]. These authors used headspace extraction with the PDMS/DVB fiber to measure nanogram per liter levels of geosmin and 2-MIB in spiked reagent and drinking water from a local reservoir. They obtained good precision (2–12% relative standard deviation (R.S.D.)), but used a specialized protocol with deuterated internal standards (d5-geosmin and d3-2-MIB) requiring gas chromatography–chemical ionization/electron impact ionisation–ion trap mass spectrometry (GC–CI/EI–ITMS), instrumentation not widely available in most labs.

A new odor method incorporating the dual-coated SPME fiber DVB/CAR/PDMS was proposed as method 6040D of the AWWA [13]. In a manufacturer's report, Supelcos [14], described an HSSPME method for the analysis of 2-MIB and geosmin with excellent linearity from 1 to 10 ug l^{-1} for standards in water. They employed a newly developed dual-coated fiber of polydimethylsiloxane/Carboxen/divinylbenzene. No estimates of precision, or application to drinking water or field samples were presented.

In this paper, we describe an HSSPME method. The effect of method variables on earthy and musty odors compounds (geosmin, 2-MIB, IBMP, IPMP and 2,4,6-TCA) recovery, measurement precision (%R.S.D.), detection limit and results of the quantitative sample analysis are presented.

2. Experimental

2.1. Reagents and materials

Reagent water used for procedural blanks and preparation of the solutions used for extraction efficiency experiments was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Sodium chloride, which was added to the samples before extraction, was conditioned by heating at 450 °C for 4 h before use. Tap water and lake water were collected from National Tsing Hua University and filtered through a 0.2 μm filter before use. They served as the environmental samples. The standards of geosmin, 2-MIB, IBMP, IPMP and 2,4,6-TCA were purchased from Supelco (Bellefonte, PA, USA). All standards were 100 μg ml^{-1} in methanol. Mixed stock standard solutions of 10 μg ml^{-1} were prepared by diluting each standard in methanol. Hydrochloric acid and HPLC-grade methanol were obtained from Tedia (Cincinnati, USA). All other chemicals and reagents are of analytical grade.

2.2. Apparatus

The SPME fiber assemblies and manual holder were obtained from Supelco (Bellefonte, PA, USA). Six commercially available SPME fibers were investigated for their extraction property in this study. These include 100 μm (coating thickness) polydimethylsiloxane, 65 μm polydimethylsiloxane/divinylbenzene, 85 μm polyacrylate (PA), 75 μm carboxen/polydimethylsiloxane , 65 μm Carbowax/divinylbenzene (CAR/DVB) and 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane coatings (Supelco, Bellefonte, PA, USA). The fibers were conditioned in the GC injector port according to the manufacturer's instructions. A magnetic stirrer, which was controlled by a magnetic stirrer (PMC DataPlate 720 Series, Dubuque, Iowa, USA), was used for stirring the water samples during the SPME procedure. Analyses were carried out in a Varian (Walnut Creek, CA, USA) CP-3800 GC system coupled to a Varian Saturn 2000 ion trap mass spectrometer. A 30 m × 0.25 mm i.d. (0.25 μm film thickness) DB-5 ms coating fused-silica capillary column (J & W Scientific, Folsom, CA, USA) was used. The oven temperature program was held at 60 °C for 3 min, raised to 150 °C at 5 °C min^{-1} then raised to 250 °C at 15 °C min^{-1}, and kept at 250 °C for 3 min. The carrier gas was helium of purity 99.9995% and kept at 1 ml min^{-1} constant flow. A 1079 universal capillary injector fitted with a 0.75 mm i.d. glass liner was held at 250 °C in splitless mode (3 min). The split vent was opened after 3 min. The transfer-line temperature was 280 °C and ion-trap temperature was 200 °C. The ion-trap mass spectrometer (GC/MS^1) was operated in the EI positive mode (70 eV) and perfluorotributylamine (FC-43) was used to achieve the best sensitivity working with the automatic gain control (AGC). Table 1 shows the parameters of the MS scan function (SIM mode) for the determination of analytes. IBMP (spiked concentration in samples is 10 ng l^{-1}) was used as an internal standard to calibrate the data by calculation of relative response factor (RRF). The quantitations were done as in Ref. [13].

Table 1
Parameters of the MS scan function (SIM mode) for the determination of analytes

Compound	Retention time (min)	Segment (min)	Quantitative ions (*m*/*z*)	Secondary ions (*m*/*z*)	Scan (*m*/*z*)
IPMP	11.0	10.0–11.2	137	152.124	120–155
IBMP	13.24	11.2–14.0	124	151.94	90–155
2-MIB	14.25	14.0–17.5	95	107.93	85–115
2,4,6-TCA	17.87	17.5–18.5	197	195.212	190–220
Geosmin	20.25	18.5–21.4	112	126.97	90–130

2.3. SPME procedure

In the beginning, the extraction conditions shown in the Standard Methods 6040D [13] were followed. After placing 13.5 g NaCl and a stir bar in a 60 ml vial, aliquots of 45 ml of standard solutions (50 ng l^{-1} in water) or real samples were added. When using internal standard method, 10 μl IBMP (45 μg l^{-1}) was added to sample. 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 550 ± 10 rpm. The temperature of the water bath was 65 ± 2 °C, 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.

3. Results and discussion

3.1. Fiber evaluation

Fiber coatings dominate the recoveries of analytes. In this study, six commercial fibers (PDMS, PDMS/DVB, PA, CAR/PDMS, CW/DVB and DVB/CAR/PDMS) were chosen for evaluation. Fig. 1 shows the relative extraction efficiencies of earthy and musty odors (expressed by peak areas of each compound). As shown in Fig. 1, the most suitable fiber for the extraction of the compounds studied was the DVB/CAR/PDMS-coated fiber, which extracted all of the analytes with the best efficiency. Thus, the DVB/CAR/PDMS fiber was chosen for further optimization.

3.2. Effect of Extraction temperature

Extraction temperature plays an important role on the extraction of analytes because it influences the mass transfer rates and the partition coefficients of analytes. We studied the SPME analyses run at selected extraction temperatures (20–80 °C), the extraction efficiency of all analytes increased with extraction temperature from 20 to 50 °C. However, when temperature raised from 50 to 80 °C, a decrease is observed. This is most likely due to the heating of the fiber, as reported by Zhang and Pawliszyn [19], resulting in decreased absorption of the analyte onto the fiber. When temperature control is possible, 50 °C is the optimal choice.

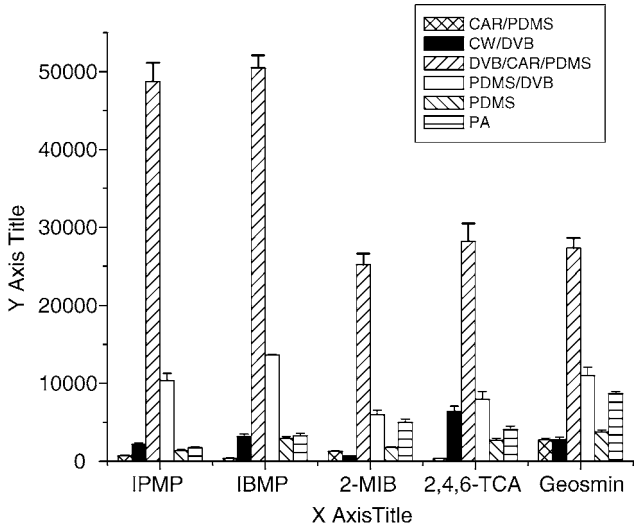

Fig. 1. Relative extraction efficiencies of earthy and musty odors compounds with six commercial fibers (PDMS, PDMS/DVB, PA, CAR/PDMS, CW/DVB and DVB/CAR/PDMS). Concentration, 50 ng l^{-1}; extraction temperature, 50 °C; extraction time, 30 min; desorption temperature, 250 °C; desorption time, 2 min; stirring rate, 500 rpm.

3.3. Extraction-time profile

The extraction efficiencies of analytes increase with extraction time until it reaches equilibrium. We studied the extraction-time profile between 10 and 120 min. However, since equilibrium times for these fibers were 90 min or more, and we desired shorter analysis times to maximize sample throughput, an extraction time for 30 min was selected for further experiments. This provides sufficient extraction efficiency and allows the headspace SPME procedure to be performed approximately in the same time as that required for GC analysis (30.67 min).

3.4. Effect of desorption temperature

The desorption temperature (230–270 °C) profile is studied. Peak areas of 2-MIB and geosmin increased with desorption temperature from 230 to 240 °C and maintained constant from 240 to 270 °C. IPMP reached maximum response at 250 °C. Peak areas of IBMP and 2, 4, 6-TCA were raised with desorption temperature. However, the maximum endurable temperature of the CAR/PDMS/DVB fiber is 270 °C. Hence, we chose 265 °C as optimal desorption temperature to avoid damage of fiber.

Table 2
The slopes[a], coefficient of determination (R^{2a}); relative standard deviation (R.S.D.)[b]; and method detection limits (MDLs)[c] for the analysis of earthy and musty odors compounds in tap water and lake water with headspace SPME-GC-ITDMS

Compound	Slope[a] (counts (ng l)$^{-1}$	(R^2)[a]	R.S.D.[d] (%)	R.S.D.[e] (%)	MDL[f] ng l^{-1}	MDL[g] ng l^{-1}	MDL[h] ng l^{-1}
IPMP	0.1044	0.998	5.0	10.2	0.34	0.38	0.32
2-MIB	0.0674	0.999	5.3	8.0	0.59	0.65	0.66
2,4,6-TCA	0.0871	0.9983	9.8	20.8	0.40	0.41	0.47
Geosmin	0.0805	0.9999	7.2	9.4	0.48	0.44	0.49

[a] Calibration curves with compounds concentration: 1, 5, 10, 50, 100, 250, and 500 ng l^{-1}.
[b] R.S.D. is obtained by seven replicate runs of sample.
[c] MDLs are calculated as three times the standard deviation of seven replicated runs of sample.
[d] Using IBMP as the internal standard. Compound concentration: 10 ng l^{-1}.
[e] Without internal standard. Compound concentration: 10 ng l^{-1}.
[f] Standard solution. Compound concentration: 1 ng l^{-1}.
[g] Spiked tap water sample. Compound concentration: 1 ng l^{-1}.
[h] Spiked lake water sample. Compound concentration: 1 ng l^{-1}.

3.5. Effect of desorption time

The desorption time (1–5 min) profile is studied. Peak areas of 2-MIB remained constant as a result of its fast desorption from fiber. As to others, desorption time of 3 min was enough for complete desorption. Consequently, 3 min was the optimal time.

3.6. Effect of stirring rate

Sample agitation enhances extraction efficiency and decreases extraction time. The studied stirring rate (0–750 rpm) shows that the extraction efficiencies increased with stirring rate. Stirring at 650 rpm produces a factor of 2.4–3.5 improvement in the responses of analytes compared to no stir-

Table 3
Performance comparisons with Ref. [13–18]

References	Odor compounds	Fiber/SPME optimized condition	Performance
This study	Geosmin, 2-MIB,IPMP, 2,4,6-TCA and IBMP (IS[a])	DVB/CAR/PDMS, 60 ml vial containing 45 ml water sample with 30% NaCl, with optimized stirring rate, extraction time and temperature: 30 min at 50 °C.	Linearity, 1–500 ng l^{-1}; MDL, 0.34–0.59 ng l^{-1}; R.S.D., 5.0–9.8%
[13]	Geosmin, 2-MIB, IPMP and IBMP (IS[a])	DVB/CAR/PDMS, 60 ml vial containing 45 ml water sample with 30% NaCl, no stirring, extraction time and temperature: 30 min at 65 °C	Linearity, 10–100 ng l^{-1}; MDL, 1 ng l^{-1}
[14]	Geosmin, 2-MIB, IBMP, IPMP and 2,4,6-TCA (IS[a])	DVB/CAR/PDMS, 40 ml vial containing 25 ml water sample with 25% NaCl, with rapid stirring, extraction time and temperature: 30 min at 65 °C.	Linearity, 1–10 ng l^{-1}; MDL, 1 ng l^{-1}
[15]	Geosmin and 2-MIB	PDMS, 11.5 ml vial containing 6 ml water sample with 40% NaCl, with rapid stirring, extraction time and temperature: 5 min at 22 °C.	Linearity, 0.1–30 ng l^{-1}; MDL, 10 ng l^{-1}
[16]	Geosmin, 2-MIB, d_5-geosmin(IS[a]) and d_3-MIB(IS[a])	PDMS/DVB, 40 ml vial containing 30 ml water sample with 25% NaCl, with vigorous stirring, extraction time and temperature: 20 min at 60 °C.	Linearity, 5–40 ng l^{-1}; RSD, 3–12%; MDL, 0.8–0.9 ng l^{-1}
[17]	Geosmin, 2-MIB, and other odors. Total 34 organic compounds	PDMS/DVB, 62 ml vial containing 40 ml water sample with 30%NaCl, with stirring, extraction time and temperature: 40 min at room temperature.	Linearity, 2–300 ng l^{-1}; RSD, 5.3–6.8%; MDL, 0.5–0.7 ng l^{-1}
[18]	Geosmin, 2-MIB and Biphenyl-d_{10} (IS[a])	PDMS/DVB, 30 ml vial containing 25 ml water sample with 24%NaCl, with possible maximum stirring, extraction time and temperature: 60 min at 65 °C.	Linearity, 1–100 ng l^{-1}; RSD, 5–12%

[a] IS means internal standard.

ring. Comparing the results obtained at 650 and 750 rpm, the extraction efficiencies were comparable. However, poor precision (R.S.D.: 14.6–25.4%) was obtained at 750 rpm. Thus, we chose 650 rpm as stirring rate.

3.7. Effect of ionic strength

The effect of ionic strength determined by preparing standards with NaCl concentrations ranging from 0 to 30% (w/v). The analytes studied, with the exception to 2,4,6-trichloroanisole, showed a significant increase in extraction efficiency with the addition of salt. Salt addition of 30%, compared to no salt added, offers an improvement in the extraction efficiency of about 2.6–3.2 times. The suitability of the headspace SPME technique for the extraction of compounds in water depends on the transfer of analyte from the aqueous phase to the gaseous phase. Salt addition could significantly decrease their solubility in water, resulting in a higher concentration of these compounds in the headspace. Finally, 30% of NaCl was added to all samples in further experiments.

3.8. Effect of elutropic strength

The organic solvent in the solutions enhances the solubility of analytes, thus reduces the extraction efficiency. The effect of elutropic strength of the sample on extraction was studied by preparing a series of samples that contained methanol at concentrations from 0 to 10% (v/v). The results were as expected, that the extraction efficiency decreased as elutropic strength increased.

3.9. Effect of pH

The pH (3.0–9.0) effect was studied. The recoveries of IBMP and IPMP were reduced somewhat at pH 3.0 because of their protonation. No significant variation in the recoveries of the analytes was observed in the pH range 5.0–9.0. The original pH of the sample solutions 5.0 was used for further study.

3.10. Method detection limits, precision, linearity and comparison with published results

The optimized extraction and desorption conditions used in subsequent work are summarized as: fiber, DVB/CAR/PDMS; extraction temperature, 50 °C; stirring rate, 650 rpm, faster stirring rate results in poor precision; extraction time, 30 min; desorption temperature, 265 °C; desorption time, 3 min; ionic strength, 30% NaCl; sample pH, 5.0. The coefficient of determination (R^2), precision (R.S.D.s) and method detection limits (MDL) are shown in Table 2. Precision, based on USEPA SW-846, was calculated as three times the standard deviation of seven replicate runs of standard solution (1 ng l^{-1}). The R.S.D.s range from 8.0 to 20.8% (without using internal standard) and from 5.0 to 9.8% (using IBMP as the internal standard).

Table 4
The concentration and recovery of earthy and musty odors compounds in tap water and lake water

Compound	Tap water		Lake water	
	Concentration (ng l^{-1})	Recovery[a] (%)	Concentration (ng l^{-1})	Recovery[a] (%)
IPMP	N.D.[b]	103.2 ± 4.9	N.D.[b]	90.5 ± 4.5
2-MIB	0.75	85.7 ± 5.0	0.81	101.4 ± 5.2
2,4,6-TCA	N.D.[b]	92.2 ± 9.6	N.D.[b]	87.1 ± 10.0
Geosmin	0.54	113.4 ± 7.2	1.27	106.0 ± 7.8

[a] Spiked compound concentration: 10 ng l^{-1}.
[b] N.D. = not detected.

The linearity of this method, for analyzing the earthy and musty odors was investigated over the range 1–500 ng l^{-1}. The correlation coefficients were better than 0.998.

The MDLs were calculated (based on the lowest level analyzed, 1 ng l^{-1}) as three times the standard deviation of seven replicate runs, and those based on deionized water, tap water and lake water were compared. The MDL of spike 1 ng l^{-1} standards in deionized water, tap water and lake water were in the range of 0.34–0.59 ng l^{-1}, 0.38–0.65 ng l^{-1} and 0.32–0.66 ng l^{-1}, respectively. No significant difference in MDL was found among sample solutions prepared with deionized water, tap water and lake water.

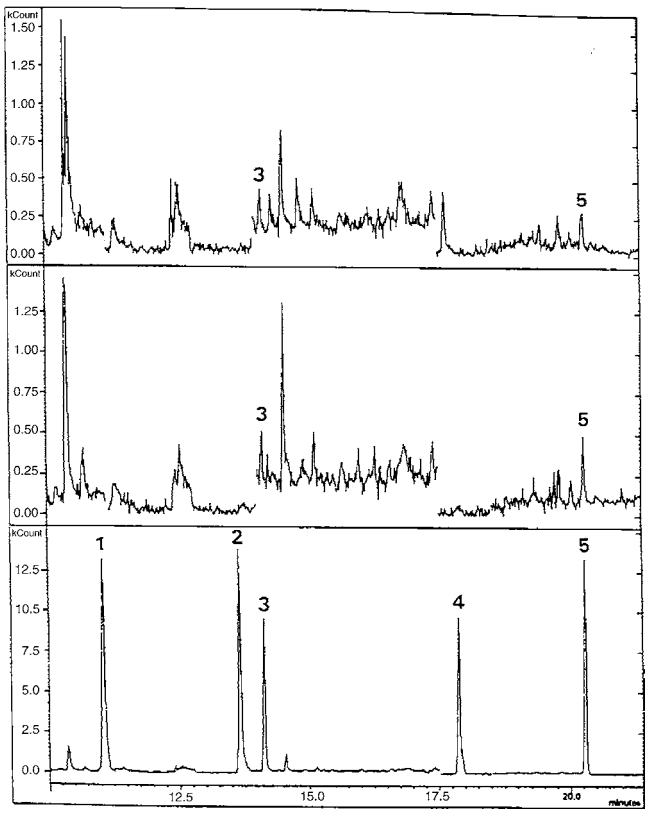

Fig. 2. GC–MS chromatograms of: tap water; lake water and 50 ng l^{-1} 1 standard solution 1 = IPMP; 2 = IBMP; 3 = 2-MIB; 4 = 2,4,6-TCA; 5 = geosmin.

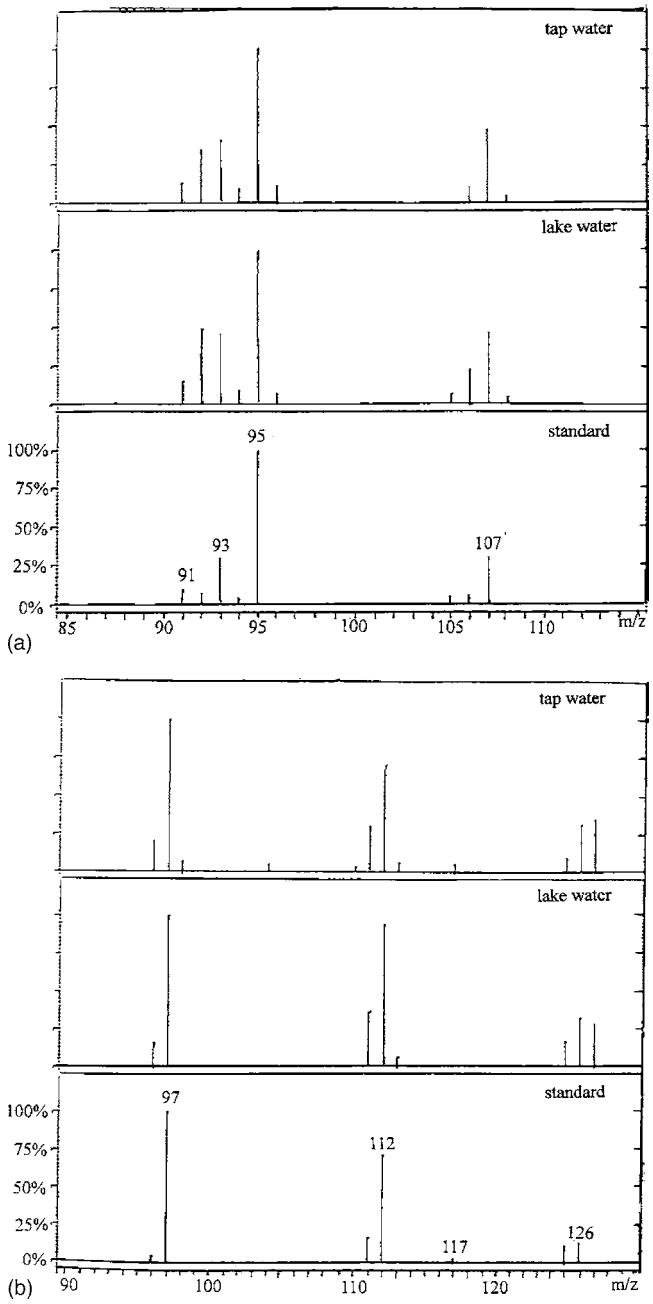

Fig. 3. Mass spectrum of (a) 2-MIB; and (b) geosmin in tap water, lake water and standard solution.

This method is developed from 6040D method [13], the major modifications are as follows: this method has four analytes (add 2,4,6-TCA), a controlled stirring rate 650 rpm (6040D, optional use of stirring) and extraction temperature, 50 °C (6040D, 65 °C). With this modification, the detection limits and the linearity of this study are lower and better than 6040D [13]. A manufacturer's report (Supelco) [14] also uses PDMS/CAR/DVB fiber for earthy and musty odors compounds analysis, but they did not do estimates of precision or application to drinking water or field samples. By comparison with methods, which used PDMS/DVB [16–18] and PDMS [15] fibers, as studied in previous fibers evaluation, the responses obtained with the DVB/CAR/PDMS fiber were 2.5–5 times higher than those obtained with the PDMS/DVB or PDMS fibers. The detection limits and the linearity of this study are also lower and better than those studies. A performance comparison of the proposed method with others is shown in Table 3.

3.11. Test on environmental samples

Tap water and lake water were used to confirm the applicability of this method for the analysis of these earthy and musty odors compounds in water samples. The results are shown in Table 4. The recoveries of these compounds were, almost not affected by the matrix of tap water and lake-water. Good recoveries (spiked concentration, 10 ng l^{-1}; 85.7–113.4% for tap water; 87.1–106.0% for lake water) were obtained. This indicated that the proposed method based on a simple calibration curve could be used to analyze these earthy and musty odors compounds in water samples.

As shown in Table 3, in the non-spiked tap and lake water samples, compounds including geosmin, 2-methylisoborneol, 2-isopropyl-3-methoxy pyrazine and 2,4,6-trichloroanisole were detected. The 2-MIB and geosmin were detected both in tap and lake water samples. The concentration of 2-MIB and geosmin in lake water was higher than in tap water. Figs. 2 and 3 show chromatograms and mass spectrum obtained after extraction of tap water, lake water and 50 ng l^{-1} standard solution by the proposed headspace SPME optimum procedure. The chromatograms shown in Fig. 2 indicate that the GC resolution and peak shapes are perfectly acceptable. The mass spectrum of 2-MIB and geosmin in tap and lake water matched very well with the corresponding spectrum of 2-MIB and geosmin standard, thus confirming the identity of these compounds by mass spectrometry.

4. Conclusion

This proposed HSSPME method is much simpler than the conventional closed-loop stripping analysis and purge and trap approaches and does not require the use of organic solvent.

Several parameters of extraction and desorption procedure were studied and optimized (such as types of fibers, extraction temperature, extraction time, desorption temperature, desorption time, ionic strength and elutropic strength, pH of samples). The method shows good linearity over the concentration range 1–500 ng l^{-1} and gives detection limits of sub-part-per trillion levels for all compounds. Good precision (5.9–9.8%) is obtained using IBMP as internal standard. The HS/SPME method achieves high-sensitivity for the analysis of earthy and musty odors compounds in tap and lake water. Finally, the method was successfully applied to analyze earthy and musty odors in tap water and lake water.

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