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Simultaneous picogram determination of "earthy-musty" odorous compounds in water using solid-phase microextraction and gas chromatography–mass spectrometry coupled with initial cool programmable temperature vaporizer inlet

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Abstract

"Earthy-musty" off-flavor problem in water samples are due to organic compounds present at the sub-part-per-trillion level. Most of the developments in the analysis of tastes and odorous compounds focus on the extraction pre-concentration technique, with detection at picogram per liter level of the earthy-musty off-flavor compounds difficult to be achieved. In this study, a simple, efficient and sensitive method for the analysis of odorous compounds has been developed by the application of solid-phase microextraction (SPME) and gas chromatography–mass spectrometry (GC–MS) with initial cool programmable temperature vaporizer (PTV) inlet for the first time. Compared with initial hot PTV inlet, the initial cool inlet could greatly improve the system sensitivity, especially for the compounds with good volatility, e.g. 2-methylisoborneol (MIB). StableFlex divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber was found to possess the best extraction efficiency towards these odorous compounds in water. Various SPME and PTV conditions have been studied and optimized in detail. The optimized method has been validated with good linearity, precision and accuracy. The method detection limits (MDL) of the targeted odorous compounds were found to be 0.32 ng/L for 2,4,6-trichloroanisole (2,4,6-TCA), 0.14 ng/L for 2,3,6-trichloroanisole (2,3,6-TCA), 0.16 ng/L for 2,3,4-trichloroanisole (2,3,4-TCA), 0.38 ng/L for 2,4,6-tribromoanisole (2,4,6-TBA), 0.16 ng/L for gesomin and 0.15 ng/L for MIB. To the best of our knowledge, this represents the best sensitivity achieved for analysis of gesomin and MIB in water via the simple and efficient SPME method. The current method has been successfully applied in the analyses of different water samples.

Keywords: Water; Odorous; Solid-phase microextraction; Programmable temperature vaporizer; GC–MS

1. Introduction

Surface water supplies are more likely to be affected by substances causing undesirable tastes and odors [1]. It was commonly accepted that earthy-musty smell is associated with the presence of geosmin, MIB and haloanisoles [2–4]. Among the eight odor groups described in the water flavor wheel, the earth-musty odors are specially troublesome because they are particularly unpleasant and often encountered in water [5]. These semi-volatile compounds have a muddy, musty odor described by the human nose when present at concentrations more than 0.004–0.02 μg/L for geosmin and MIB [6–9], as well as 30 pg/L for haloanisoles in water [10,11]. These olfactory detection limits are well below the conventional analytical methods.

Traditional analytical methods for monitoring these tastes and odors concentrations include closed-loop stripping [12], liquid–liquid extraction [13,14], steam distillation [15] and purge and trap [16,17]. Some of these methods have poor sensitivity, some of them are more complex for sample preparation or analysis. Most of the developments in the analysis of tastes and odor compounds focus on the extraction pre-concentration technique, such as membrane based extraction [18], microliquid–liquid extraction [14,19] and stir bar sorptive extraction [20,21]. However, detection at picogram per liter level of the earthy-musty off-flavor compounds has not been achieved, although numerous extraction techniques have been

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applied. Since GC–MS can be highly selective and sensitive, it is often the method of choice for organic residue analysis and/or confirmation [22,23]. However, for analysis of tastes and odor compounds at picogram per liter level, sensitivity of GC–MS is usually a challenge.

SPME is a solvent free extraction technique that enables the extraction and concentration steps to be carried out simultaneously [24–26], which has received much more attention in recent years due to its high efficiency for the extraction of organic compounds with different polarity, volatility and solubility from water samples [27–33]. A manufacturer's report [34] described a headspace SPME (HS-SPME) method for the analysis of MIB and geosmin with excellent linearity from 1 to 10 ng/L for standards in water.

So far, all the reported SPME processes were performed on the hot GC injection inlet, since most of the gas chromatograph systems are equipped with standard split/splitless type inlets. With the development of programmable temperature vaporizers (PTVs) technique [35,36], it has been commonly used for large volume injection (LVI), but with rare application in SPME. One Gerstel application note firstly demonstrated the advantage of combination of hot PTV inlet and SMPE technique [37]. The significant improvement versus split/splitless type inlet was considered to be contributed from the use of septumless head (SLH) instead of a septum for sealing the inlet. However, the main advantage of the application of PTV inlet is that the sample is not introduced into a hot oxidative environment, but into a cool system followed by an increasing temperature ramp to minimize the thermal decomposition of the labile analytes. Unfortunately, until now, there is no report on the combination of SPME and PTV process starting from a cool inlet.

In this study, the first case of combination of SPME process and GC–MS with cool PTV inlet will be applied. Variable SPME and PTV-GC–MS conditions will be investigated in detail. Via initial cool PTV inlet, a reliable and efficient method for the analysis of tastes and odor compounds at sub-part-per-trillion level in water using SPME-GC–MS technique will be developed, validated and applied in the real water sample analysis.

2. Experimental

2.1. Chemicals and reagents

The standard compounds of MIB, geosmin, 2,3,4-TCA and 2,4,6-TBA were purchased from Dr. Ehrenstorfer Gmbh (Augsburg, Germany). 2,4,6-TCA and 2,3,6-TCA were purchased from Aldrich (Saint Quentin Fallavier, France). Their chemical structures, volatility, together with their odor threshold concentrations as well as specific ions are listed in Table 1. Methanol and acetone were HPLC grade and obtained from Merck (Darmstadt, Germany). Sodium chloride (Reagent grade) was obtained form Merck and dried at Nabertherm furnace oven (Bremen, Germany) at 450 °C for 5 h. Deionized water was obtained by passing tap water through an USF-ELGA option 15 system and an USF Maxima system (Vivendi Water, UK) with the resistance greater than 18.2 MΩ cm^{-1} and on-line TOC less than 2 μg/L.

2.2. Materials

SPME fiber assembly holder and six commercial available fibers (polydiemthylsiloxane (PDMS) 100 μm, non-bonded; polydiemthylsiloxane/divinylbenzene (PDMS/DVB) 65 μm, partially crosslinked; polydimethylsiloxane/divinylbenzene (PDMS/DVB) Stableflex 65 μm, highly crosslinked; polyacrylate (PA) 85 μm, partially crosslinked; Carbowax/divinylbenzene (CW/DVB) 65 μm, partially crosslinked; stableflex divinylbenzene/Carboxen/polydimethylsioxane (DVB/CAR/PDMS) 50/30 μm, highly crosslinked) were obtained from Supelco (Bellefonte, PA,USA). Headspace vials (22 mL) with PTFE-coated silicone septa were purchased from Agilent Technologies (Singapore).

2.3. Instrumentation and chromatographic conditions

Analyses were carried out with an Agilent 6890 series GC system coupled with a 5973 series mass spectral detector. An Agilent programmable temperature vaporizer inlet (G2619A) was applied as the GC injector. The GC column used was HP-5MS 30 m × 0.25 mm, 0.25 μm. The carrier gas was helium with flow rate at 1.2 mL/min. The GC oven temperature programme was as follows: hold at 40 °C for 6.13 min; raise to 200 °C (20 °C/min); raise to 280 °C (10 °C/min); raise to 300 °C (20 °C/min); hold for 3 min. The PTV injector was set at splitless mode with inlet temperature programme as follows: hold at 40 °C for 2 min; raise to 265 °C with ramp rate of 500 °C/min; hold at 265 °C for 5 min to re-condition of the fiber. The purge flow was 50 mL/min starting from 6.5 min. PTV inlet constant column pressure was set as 14 psi. The GC–MS transfer line temperature was maintained at 280 °C. The electron impact (EI) ionization mode was used with an electron energy of 70 eV and tune to perfluorotributylamine (PFTBA). The mass spectra was obtained at a mass-to-charge ratio scan range from 50 to 700 amu to determine appropriate masses for selected ion monitoring (SIM). The EI ion source of the mass spectrometer was 230 °C. The solvent delay time was set to 3 min. Selected ion monitoring mode was used in quantitation. The dwell time was set to 100 ms for each ion.

2.4. Mass spectra of MIB, geosmin and haloanisoles

To achieve the best sensitivity, in this study, PTV-GC–MS was run at selective ion mode (SIM), with quantitation ions of these odorous compounds shown in Table 1. Excellent separation was obtained by combination of SPME extraction and cool splitless PTV-GC–MS, indicated in Fig. 1.

2.5. HS-SPME procedure

2.5.1. Extraction procedure for SPME

Ten milliliters of water sample was placed into a 22 mL headspace vial containing a magnetic stirrer (12 mm × 3 mm). After addition of 4.0 g of NaCl, the vial was sealed with a silicon-PTFE septum cap. The sealed vial was placed in a water-bath and stirred at 700 rpm, with the water-bath temperature being con-

Table 1
Analyzed odorous compounds

Name/abbreviation	Taste	Odor threshold (ng/L)	GC–MS monitored ion at SIM mode	Boiling point (°C)
2-Methylisoborneol (MIB)	Earthy	5–10	95[a]; 108, 110	165
Geosmin	Camphor	1–10	112[a]; 125	270
2,4,6-Trichloroanisole	Musty	0.1–2	195[a]; 210	241
2,3,6-Trichloroanisole	Musty	0.1–2	210[a]; 167	227
2,3,4-Trichloroanisole	Musty	0.2–2	210[a]; 195	*Not available*
2,4,6-Tribromoanisole	Musty	0.15–10	344[a]; 331	298

[a] Quantitated ion.

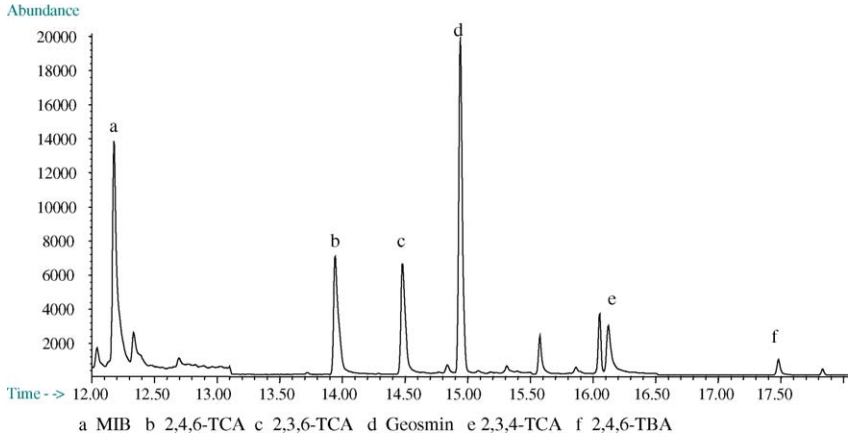

Fig. 1. Chromatograms of 50 ng/L earthy-musty compounds.

trolled at 60 °C by magnetic digital ceramic hotplates/stirrers SM26 (Stuart Scientific, Staffordshire, UK). After the syringe needle of the SPME device being pierced through the septum, the fiber was plunged out to be exposed in the headspace for adsorption of the analyte. Thirty minutes later, the fiber was retracted back into the syringe and withdrawn from the vial, followed by immediate fit into the PTV-GC–MS inlet for desorption.

2.5.2. Desorption procedure for SPME

After the SPME fiber and holder were removed from the sample vial, it was immediately fit into cool PTV inlet. After plunging the fiber out from the syringe holder to desorb the extracted analytes, both the PTV programme and GC programme started. Eight minutes later, the SPME fiber was retracted back into holder, removed away from PTV inlet and used directly for next SPME extraction.

3. Results and discussion

3.1. Optimization of HS-SPME process

3.1.1. Selection of extraction mode

For SPME application, there are two types of extraction modes commonly used, for analytes with different properties. When extracting semivolatile compounds from aqueous matrix, the fiber is usually immersed directly into the sample, which is known as directly immersion sampling (DI-SPME). If the fiber is exposed in the vapor phase above the liquid or solid sample, it is headspace sampling (HS-SPME). Headspace sampling is generally used for more volatile compounds. It has the advantage of faster extraction time and improving selectivity.

Experiments were conducted under the same condition at 60 °C for 30 min, except the extraction mode being different. Extraction fiber used was DVB/CAR/PDMS. The results indicated that extraction efficiency of HS-SPME is much higher than DI-SPME. The response intensities of all six-target compounds via DI-SPME were at least 30% less than that via HS-SPME. Interestingly, for geosmin, the response intensity obtained via HS-SPME is about 10 times higher than that from DI-SPME (Fig. 2). Therefore, HS-SPME was applied for all of the following experiments.

3.1.2. Selection of fiber coating materials

Six types of commercial available SPME fibers were evaluated for odorous application. The fibers used are: PDMS, PDMS/DVB Stableflex, PDMS/DVB, PA, CW/DVB, DVB/CAR/PDMS. SPME extraction process was conducted at 60 °C for 30 min with constantly stirring at speed of 700 rpm.

The results in Fig. 3 indicate that the extraction efficiency of these SPME fibers towards the odorous compounds follow the order as: DVB/CAR/PDMS > PDMS > DVB/PDMS stableflex > DVB/PDMS > CW/DVB > PA. The extraction efficiency on MIB and geosmin can be greatly different by using different SPME fibers, while the difference are smaller on trichloroanisoles and no big difference on tribromoanisole. It is interesting to see that the lower response intensities were generated by CW/DVB and PA fiber, which are fairly polar SPME fiber, meaning that the polar SPME fiber are not suitable for such application. Non-polar PDMS fiber has demon-

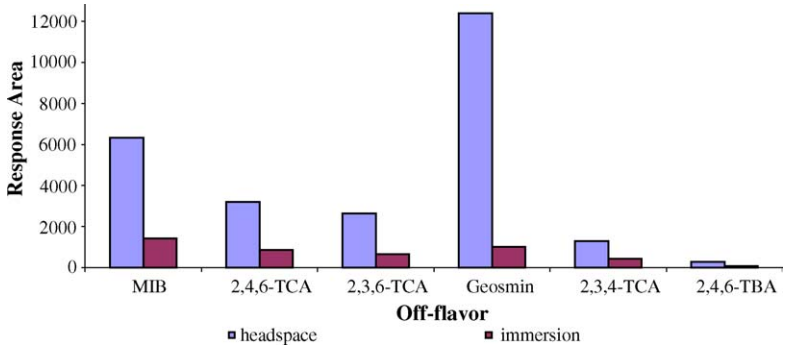

Fig. 2. Influence of extraction mode on the extraction efficiency of off-flavor.

strated the second best extraction efficiency, only lower than fiber of DVB/CAR/PDMS. The DVB/CAR/PDMS showed the best extraction efficiency, especially towards MIB and gesmin, could be resulted from the combination of the following points: (a) high affinity of DVB for small alcohol; (b) non-polar PDMS stationary phase; (c) increased SPME fiber surface area via porous carboxen particles, which is much more efficient to small molecular analytes. Based on the above experiments, fiber DVB/CAR/PDMS was chosen for our following SPME analysis.

3.2. GC conditions

3.2.1. Injection mode and initial inlet temperature

Both splitless and pulsed splitless modes for PTV inlet were evaluated for trace level odorous compounds analyses. Peak tailing was found in the pulsed splitless mode, response area was also smaller than that obtained in splitless mode. Therefore, in the following work, the PTV inlet was always set at splitless mode.

One of the major differences between PTV inlet and normal split/splitless inlet is that PTV is designed to have the capability of holding the sample in the cool inlet liner until the entire sample (usually large volume) being injected. Then, the PTV is heated rapidly via a temperature ramp to sweep the injected samples to the column. Herein, the initial cool inlet could help to reduce the evaporation of analytes during injection period, thus avoid loss of target components. Initial cool inlet could also help to minimize the thermal decomposition of the labile analytes. In principle, these advantages of PTV inlet could also help SPME process by keeping the absorbed analytes in the fiber at cool temperature during injection period to improve its sensitivity. However, so far, there is no report on the combination of SPME process with such an initial cool inlet.

In our experiments, multi baffle deactivated borosilicated glass liner (part No. 5183-2037, 1.5 mm I.D., 150 μL) was employed. This liner has a small internal diameter and small volume than normal liner, which allows sharp peaks to be generated after column separation to improve separation and enhance sensitivity.

Experiments were performed on the same SPME extraction process and GC–MS conditions, except the PTV initial inlet temperature being different. Cool PTV inlet means the initial PTV inlet temperature was set at 40 °C, followed with a temperature programme as: hold at 40 °C for 2 min followed by raising to 265 °C with ramp rate of 500 °C/min; hold at 265 °C for 5 min to re-condition of the fiber. The hot inlet means the inlet temperature was hold at 265 °C constantly. The results in Fig. 4 indicated that the response intensities will increase from 20 to 300% via cool inlet than that via hot inlet. For MIB and geosmin, their response areas increase 300 and 80%, respectively. The response intensities for haloanisoles increased 20–60%. Obviously, towards the parameters of MIB with relative better volatility, much more improvement on the response intensity could be achieved by cool PTV inlet than that towards haloanisoles. This could be easily clarified as that the cool PTV inlet helped to retain the absorbed analytes on the SPME fiber before they are swept into GC column, thus avoid the loss of analytes during desorption process. This experiment clearly indicated, for the first time, that the application of initial cool PTV inlet can greatly improve the sensitivity of SPME analysis, especially towards the analyte with high volatility, such as MIB.

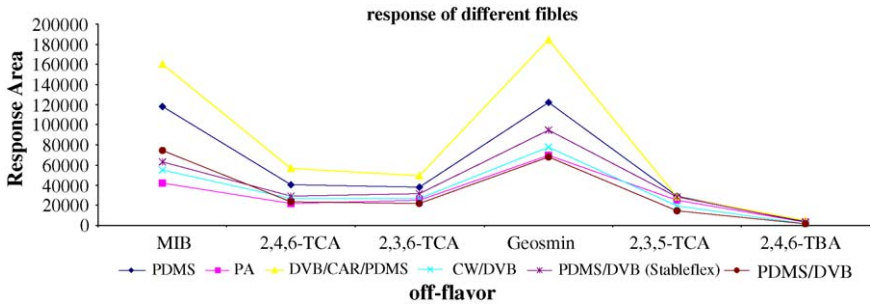

Fig. 3. Influence of different fibers coating on extraction efficiency.

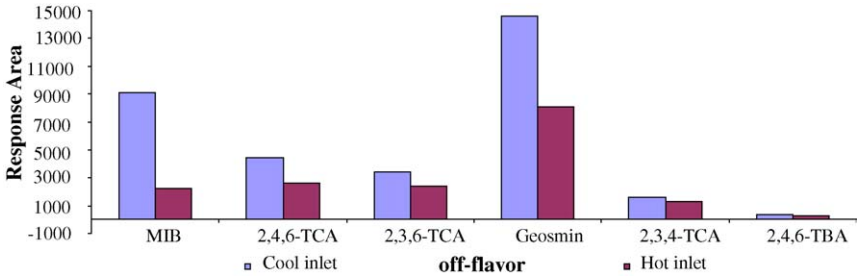

Fig. 4. Influence of initial inlet temperature on the response of off-flavor.

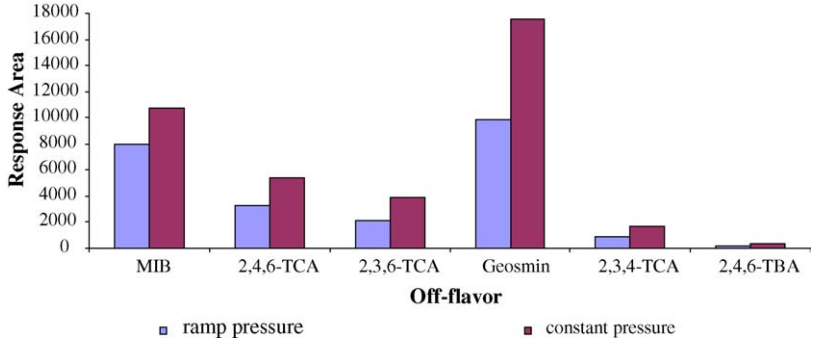

Fig. 5. Influence of initial column pressure on the response of off-flavor. Ramp pressure: initial column is 0.58 psi, 30 psi/min, final column pressure is 14.0 psi. Constant pressure: column is 14.0 psi.

3.2.2. *Inlet temperature programme and column pressure*

After the SPME fiber being fit into PTV inlet, the PTV inlet will be heated to 265 °C with a certain temperature ramp rate. In our experiment, five different temperature ramp rates (100, 200, 300, 400 and 500 °C/min) were investigated to study its effect to analytical results. It was found that with the increase of the ramp rate, the response intensities for all odorous compounds increase as well. This could be understood as that low inlet temperature ramp may cause the desoption process lasted long time, which will make the chromatographic peak broadening and reduce the analysis sensitivity. Therefore, 500 °C/min is the optimum temperature ramp in our current study.

Column pressure not only affects the retention time of analytes but also affects the response of analytes. According to an earlier report, during PTV injection, the column head pressure should be set to 0 psi followed by a pressure ramp program during solvent elimination process [38]. It would help to prevent analytes going into the column, which possibly would cause sample diffusion and peak broadening and tailing. However, our study indicates that operation under column constant pressure is better than ramp pressure as showed in Fig. 5. Increase of initial pressure will increase the response intensity of analyte. It could be understood as that increase of the initial column pressure will facilitate desorbing the analytes adsorbed on SPME fiber, thus increase the possibility of analyte going into the column, and avoid analyte being vented out of system. However, if the column pressure is higher than 14 psi, the analyte response intensity starts to drop. It is because too high gas pressure in PTV inlet would sweep the analyte to the vent, thus cause loss of the analytes. Therefore, the best column pressure in our study was set at 14 psi.

3.3. *Optimized SPME-PTV-GC–MS process*

DVB/CAR/PDMS fiber was used for SPME process. All analyses were conducted at HS-SPME mode, with water-bath temperature set at 60 °C. The SPME fiber adsorption time was 30 min. PTV injector was set at splitless mode with initial temperature at 40 °C followed with an increasing temperature programme with ramp rate of 500 °C/min to final temperature of 265 °C. The PTV constant column pressure was set at 14 psi. All detection was conducted by MSD at SIM mode with selected ions specified in Table 1.

Table 2
Protocols for method validation

	MIB	2,4,6-TCA	2,3,6-TCA	Gesomin	2,3,4-TCA	2,4,6-TBA
Linear range (μg/L)	0.5–50	0.5–50	0.5–50	0.5–50	0.5–50	0.5–50
Linear regression (r^2)	0.993	0.997	0.998	0.994	0.999	0.996
Within-batch RSD (%)	3.91	4.1	2.3	1	2.6	1
Between-batch RSD (%)	3.3	6.9	4.7	5.5	8.1	6.3
MDL (ng/L)	0.15	0.32	0.14	0.16	0.16	0.38

3.4. Method validation and real sample application

This developed method was validated according to USP/ICH guideline [39].

3.4.1. Calibration and linearity

Linearity is the ability of the method of elicited test results that are directly proportional to analytes concentration within a given range. The calibration curve linear range for the six off-flavor compounds was determined over five to seven concentration levels. The linear range is 0.5–50 ng/L. Linear regression r^2 were from 0.993 to 0.999 (Table 2.). These results show the developed method possesses good linearity.

3.4.2. Precision

Precision (repeatability) is the measure of the degree of the repeatability of an analytical method under normal operation and is normally expressed as the relative standard deviation (RSD) for a statistically significant number of samples. It is the degree of agreement among individual test results when the procedure is carried out repeatedly.

Precision was measured by comparing standard deviation of the response from the injection in triplicate of different standard spiked DI water solution. The repeatability of six off-flavor compounds was determined by analysis of standard mixture spiked DI water at the concentration of 10 ng/L. The RSD of each off-flavor standard is listed in Table 2. The within-batch RSD is within the range of 1.0–4.1% while the between batch RSD is 3.3–8.1%, showing extremely satisfactory results.

3.4.3. Accuracy and real water sample analysis

Accuracy is a measure of the closeness of a result to the true value and should be established across the specified range of the analytical procedure. Accuracy is usually expressed as the recovery of the analyte.

$$\text{Recovery}\,(\%) = \frac{C_{\text{spiked sample}} - C_{\text{sample}}}{C_{\text{spiking standard}}} \times 100$$

Samples were prepared by spike 10 and 20 ng/L off-flavor standards in different real water matrics and extracted with SPME fiber for 30 min. The recovery of each off-flavor standard is listed in Table 3. The recovery of haloanisole was about 60% while the recovery of geosmin and MIB were above 80%.

3.4.4. Method detection limit (MDL)

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measure and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

MDL = $t_{(n-1,1-\alpha=0.99)}$ (S), $t_{(n-1,1-\alpha=0.99)}$ is the students t-value appropriate for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom. S is the standard deviation of the replicate analyses. When the number of replicates = 7, $t_{(n-1,1-\alpha=0.99)} = 3.14$ [40].

Method detection limits of these six off-flavor compounds were determined by spiking 1 ng/L off-flavor mix standard in

Table 3
Recoveries of six off-flavor compounds in difference matrix

	MIB		2,4,6-TCA		2,3,6-TCA		Geosmin		2,3,4-TCA		2,4,6-TBA	
	Measured concentration (ng/L)	Recovery	Measured concentration (ng/L)	Recovery	Measured concentration (ng/L)	Recovery	Measured concentration (ng/L)	Recovery	Measured concentration (ng/L)	Recovery	Measured concentration (ng/L)	Recovery
Treated water												
Treated water	0.68	–	0.63	–	0.60	–	0.45	–	0.84	–	0.21	–
Spike (10 ng/L)	9.47	0.88	7.27	0.66	6.89	0.63	9.64	0.92	7.44	0.66	8.79	0.86
Spike (20 ng/L)	16.94	0.81	12.75	0.61	12.41	0.59	17.09	0.83	12.85	0.60	16.52	0.82
Surface water												
Surface water	0.57	–	0.87	–	0.60	–	0.40	–	0.77	–	0.84	–
Spike (10 ng/L)	8.65	0.81	7.48	0.70	6.85	0.63	8.78	0.84	7.35	0.66	7.63	0.68
Spike (20 ng/L)	16.86	0.81	14.79	0.70	12.81	0.60	17.10	0.84	12.02	0.56	13.69	0.64
Wastewater												
Wastewater	13.46	–	17.19	–	1.61	–	12.68	–	3.00	–	3.96	–
Spike (10 ng/L)	21.63	0.82	24.67	0.75	9.11	0.75	22.43	0.99	9.41	0.64	11.64	0.77
Spike (20 ng/L)	30.45	0.85	29.53	0.62	16.07	0.72	32.32	0.98	15.48	0.62	18.14	0.71

DI water, extracted by CAR/DVB/PDMS fiber for 30 min at 60 °C. MDL of each compound was found to be 0.32 ng/L for 2,4,6-TCA, 0.14 ng/L for 2,3,6-TCA, 0.16 ng/L for 2,3,4-TCA, 0.38 ng/L for 2,4,6-TBA, 0.16 ng/L for gesomin and 0.15 ng/L for MIB, respectively. To the best of our knowledge, this represents the best sensitivity achieved for analysis of gesomin and MIB in water via the simple and efficient SPME method.

The MDL results clearly indicated that current developed method is a very efficient method for the analysis of odorous compounds in water. Especially for MIB and geosmin, their detection limits are far below their smell thresholds.

4. Conclusions

A simple, efficient and sensitive method for the analysis of odorous compounds in water has been developed by the application of SPME-PTV-GC–MS with initial cool inlet for the first time. CAR/DVB/PDMS fiber was found to possess the best extraction efficiency towards these odorous compounds. Compared with initial hot PTV inlet, the initial cool inlet could greatly improve the system sensitivity, especially for the compounds with good volatility, e.g. geosmin and MIB. Various SPME and PTV conditions have been studied and optimized in detail. The optimized method has been validated with good linearity, precision and accuracy. MDLs of each targeted odorous compounds were found to be 0.32 ng/L for 2,4,6-TCA, 0.14 ng/L for 2,3,6-TCA, 0.16 ng/L for 2,3,4-TCA and 0.38 ng/L for 2,4,6-TBA, 0.16 ng/L for gesomin and 0.15 ng/L for MIB. To the best of our knowledge, this represents the best sensitivity achieved for analysis of gesomin and MIB in water via the simple and efficient SPME method. Current method has been successfully been applied in the analyses of different real water samples.

References

[1] P. Levallois, J. Grondin, S. Guingras, Water Sci. Technol. 40 (1999) 135.
[2] J. Mallevialle, I.H. Suffet (Eds.), Identification and Treatment of Tastes and Odors in Drinking Water, American Water Works Association Research Foundation/Lyonnaise des Eaux, AWWA, Denver, CO, 1987.
[3] S.E. Jensen, C.L. Anders, L.J. Goatcher, S.E. Hrudey, Water Res. 28 (1994) 1393.
[4] A. Bruchet, Water Sci. Technol. 40 (1999) 15.
[5] I.H. Suffet, A. Corado, D. Chou, S. Butterworth, M.J. MacGuire, J. Am. Water Works Assoc. 88 (1996) 168.
[6] S.B. Watson, B. Brownlee, T. Satchwill, E.E. Hargesheimer, Water Res. 34 (2000) 2818.
[7] S.W. Krasner, C.J. Huang, M.J. McGuire, Water Sci. Technol. 15 (1983) 127.
[8] P.-E. Persson, Water Sci. Technol. 15 (1983) 1.
[9] W.F. Young, H. Horth, R. Crane, T. Ogden, M. Arnott, Water Res. 30 (1996) 331.
[10] L. Malleret, A. Bruchet, Water Sci. Technol. Water Supply 1 (2001) 1.
[11] L. Malleret, A. Bruchet, M.-C. Hennion, Anal. Chem. 73 (2001) 1485.
[12] M.J. McGuire, S.W. Krasner, C.J. Hwang, G. Izaguirre, J. Am. Water Works Assoc. 73 (1981) 530.
[13] P.B. Johnsen, J.-C.W. Kuan, J. Chromatogr. 409 (1987) 337.
[14] M.-L. Bao, K. Barbieri, D. Burrini, O. Griffini, F. Pantani, Water Res. 31 (1997) 1719.
[15] C. Anselme, J. Mallevialle, F. Fiessinger, I.H. Suffet, Correlation Between Sensory Analyses and Chromatographic Profiles: Comparison of Two Extraction Methods, presented at the AWWA WQTC, Houston, TX, 1985.
[16] P.B. Johnsen, S.W. Lloyd, Can. J. Fish Aquat. Sci. 49 (1992) 2406.
[17] US Environmental Protection Agency (EPA), Methods for the Determination of Organic Compounds in Drinking Water, EPA-600/4-88/039; Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1988, Method 524.2.
[18] A.K. Zander, P. Pingert, Water Res. 31 (1997) 301.
[19] B.G. Brownlee, L. Gaminie, W.D. Gummer, G.A. Macinnis, Water Sci. Technol. 20 (1998) 91.
[20] O. Nobuo, S. Kikuo, T. Masahiko, Y. Satoru, D. Shigeki, H. Arnd, H. Andreas, Analyst 126 (2001) 1652.
[21] D. Benanou, F. Acobas, M.R. De Roubin, Stir Bar Sorptive Extraction: A New Way to Extract Off-Flavor Compounds in the Aquatic Environment, Agilent publication number 5988-8900EN, 2003.
[22] A. Diaz, F. Ventura, T. Galceran, J. Chromatogr. A 1064 (2005) 97.
[23] F.J. Arrebola, S.C. Aguado, N. Sanchez-Morito, Anal. Lett. 37 (2004) 99.
[24] J. Pawliszyn, Solid Phase Microextraction—Theory and Practice, Wiley–VCH, New York, 1997.
[25] A.D. Harmon, in: R. Marsili (Ed.), Techniques for Analyzing Food Aroma, Marcel Dekker, New York, 1997, p. 81.
[26] H. Kataoka, H.L. Lord, J. Pawliszyn, J. Chromatogr. A 880 (2000) 35.
[27] R.C. Barth, P.S. Fair, J. Am. Water Works Assoc. 84 (1992) 94.
[28] P.G. Desideri, L. Lepri, L. Checchini, Microchim. Acta 107 (1992) 55.
[29] D. Bourgeois, J. Gaudet, P. Dveau, V.N. Mallet, Bull. Environ. Contain. Toxicol. 50 (1993) 433.
[30] V. Furtula, J.M. Davies, A. Mazumder, Water Qual. Res. J. Can. 39 (2004) 215.
[31] T.F. Lin, C.L. Liu, F.C. Yang, H.W. Hung, Water Res. 37 (2003) 21.
[32] S.B. Watson, B. Brownlee, T. Satchwill, E. McCauley, Water Sci. Technol. 40 (1999) 251.
[33] L.R. Zimmerman, A.C. Ziegler, E.M. Thurman, Method of Analysis and Quality-Assurance Practices by US Geological Survey Organic Geochemistry Research Group—Determination of Geosmin and Methylisoborneol in Water using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry US Geological Survey Open-File Report 02-337.
[34] Solid phase microextraction of odors in drinking water, for analysis by GC/MS, Application Note 147, Supelco, Bellefonte, PA, 1998.
[35] K. Grob, G. Karrer, M.-L. Riekkola, J. Chromatogr. 334 (1985) 129.
[36] W. Engewald, J. Teske, J. Efer, J. Chromatogr. A 856 (1999) 259.
[37] Benefits of Using Programmed Temperature Vaporized (PTVs) Instead of Hot Split/Splitless Inlets for Measurements of Volatiles by Liquid, Headspace, and Solid Phase MicroExtraction (SPME) Techniques, Gerstel Application Note AN/2001/07, 2001.
[38] P.L. Wylie, Trace Level Pesticide Analysis by GC/MS Using Large-Volume Injection, Agilent Application Note 5966-1214E.
[39] E.S. Michael, S.K. Ira, Analytical Method Development and Validation, Marcel Dekker, New York, 1997, p. 53.
[40] US-EPA SW-846, Test Methods for Evaluating Solid Wastes Physical/Chemical Methods, Revision 1, Chapter 1, 1992, pp. 26–27.