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Determination of trace amounts of off-flavor compounds in drinking water by stir bar sorptive extraction and thermal desorption GC-MS

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A method for the determination of trace amounts of off-flavor compounds including 2-methylisoborneol, geosmin and 2,4,6-trichloroanisole in drinking water was developed using the stir bar sorptive extraction technique followed by thermal desorption-GC-MS analysis. The extraction conditions such as extraction mode, salt addition, extraction temperature, sample volume and extraction time were examined. Water samples (20, 40 and 60 ml) were extracted for 60–240 min at room temperature (25 °C) using stir bars with a length of 10 mm and coated with a 500 μm layer of polydimethylsiloxane. The extract was analyzed by thermal desorption-GC-MS in the selected ion monitoring mode. The method showed good linearity over the concentration range from 0.1 or 0.2 or 0.5 to 100 ng l^{-1} for all the target analytes, and the correlation coefficients were greater than 0.9987. The detection limits ranged from 0.022 to 0.16 ng l^{-1}. The recoveries (89–109%) and precision (RSD: 0.80–3.7%) of the method were examined by analyzing raw water and tap water samples fortified at the 1 ng l^{-1} level. The method was successfully applied to low-level samples (raw water and tap water).

Introduction

Taste and odor compounds in drinking water are a major problem. 2-Methylisoborneol (MIB) and geosmin have received special attention as musty/muddy off-flavor compounds in drinking water. MIB and geosmin are produced by benthic algae, fungi, bacteria and actinomycetes commonly found in water.[1,2] 2,4,6-Trichloroanisole (TCA) is also a major odorous compound that is produced by the biomethylation of 2,4,6-trichlorophenol (TCP).[3] TCP is formed during the disinfection of drinking water with chlorine.[4] These compounds have an extremely low odor threshold. The odor threshold concentrations were reported to be as low as 0.6 ng l^{-1} for MIB, 1 ng l^{-1} for geosmin and 0.03 ng l^{-1} for TCA.[5,6] Although the human olfactory sensor can detect such extremely low levels, sensory analysis is not always reliable because there are large differences in the response, not only between individuals, but also of an individual from day to day.[7,8] For example, it was reported that there was about a 50–1000-fold difference in the results of odor threshold concentrations for MIB and geosmin obtained by 20 trained panelists.[9] The concentrations ranged from 0.1 to 115 ng l^{-1} for MIB and from 12.9 to 685 ng l^{-1} for geosmin.

Consequently, in order to supply high quality drinking water, these off-flavor compounds have to be monitored and controlled not only by sensory analysis, but also by reliable and highly sensitive instrumental analysis. Usually, it is essential to have enrichment or extraction steps before GC or GC-MS analysis. There are a variety of enrichment or extraction techniques for the determination of trace amounts of MIB and geosmin, such as closed-loop stripping analysis (CLSA),[10–12] purge-and-trap (P&T)[13,14] (P&T is used for TCA determination[3,4]), liquid–liquid extraction (LLE)[15] and solid-phase extraction (SPE).[16,17] More recently, optimized static headspace (SHS)[18] and solid-phase microextraction (SPME),[19–22] which are simple, solvent-free techniques requiring only a small sample volume, have been successfully applied to MIB and geosmin determination with detection limits below 10 ng l^{-1}. However, the sensitivity is still considered to be limited when compared with large volume sample (1 l) and solvent techniques such as CLSA and the large volume injection (LVI) method, which have sub-ng l^{-1} sensitivity.[12] Because SPME with polydimethylsiloxane (PDMS) is by nature an equilibrium technique based on the partitioning of the solute between the stationary phase and the aqueous sample, enrichment factors are dependent on the distribution coefficients of the analyte between the different phases. As a consequence, the limited enrichment on the SPME fiber is mainly due to the amount of PDMS phase (typically 0.5 μl or less). Increasing the amount of PDMS relative to the aqueous matrix would dramatically increase the enrichment of the analyte. Recently, a new sorptive extraction technique using stir bars coated with 50–300 μl of PDMS was developed.[23] The technique is known as stir bar sorptive extraction (SBSE).

The aim of this paper was to apply SBSE to determine sub-ng l^{-1} levels of off-flavor compounds including MIB, geosmin and TCA in drinking water. The method was applied to low-level samples, in which the target analytes were not detected by the optimized SHS method.[12] Because another goal was to evaluate simultaneous pre-treatment using different stir bars, all the extractions for the validation of the method and the determination were performed in parallel (normally 6 replicates × 3). After extraction, the stir bars were thermally desorbed in the thermal desorption system (autosampler) followed by GC-MS analysis.

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Experimental

Materials

Standard solutions of MIB and geosmin at 100 μg ml^{-1} in methanol were purchased from Wako (Osaka, Japan) as the stock standard solutions. TCA, which was also purchased from Wako, was initially prepared at 100 μg ml^{-1} in methanol as the stock standard solution. The 100 μg ml^{-1} stock standard solutions of MIB, geosmin and TCA were then diluted and mixed with methanol to prepare the mixed working standard solutions. The stock standard solutions were kept at −20 °C. Sodium chloride (NaCl) of analytical grade (Wako) was previously heated at 400 °C for 6 h. Samples were from the Kobe City Waterworks Bureau, which obtains drinking water from the Sengari reservoir (Hyogo, Japan). Raw water was sampled in 1 l glass bottles from the reservoir and filtered before use. Tap water was sampled in 1 l glass bottles.

Apparatus

The stir bars coated with a 0.5 mm layer (24 μl) of PDMS (Twister™: the magnetic stirring rod is incorporated in a glass jacket and coated with PDMS) were obtained from Gerstel (Mullheim an der Ruhr, Germany). The stir bars could be used over 30 times with appropriate re-conditioning (see Experimental section). For the extractions, 12, 22, 43 and 62 ml headspace vials with Teflon-coated silicone septa from Agilent Technologies (Palo Alto, CA, USA) and GL Sciences (Tokyo, Japan) were used. The thermal desorption (TD)-GC-MS analysis was performed using a Gerstel TDS 2 thermodesorption system equipped with a Gerstel TDS-A autosampler and a Gerstel CIS 4 programmable temperature vaporization (PTV) inlet (Gerstel) and an Agilent 6890 gas chromatograph with a 5973 mass-selective detector (Agilent Technologies). The static headspace (SHS)-GC-MS analysis was performed using an Agilent 7694 headspace sampler and an Agilent 6890 gas chromatograph with a 5973 mass-slective detector (Agilent Technologies).

Sample preparation and TD-GC-MS

Prior to use, the stir bars were conditioned for 4 h at 300 °C in a flow of helium. For liquid sampling SBSE, headspace vials (12, 22, 43, 62 ml) and Teflon-coated silicone septa were used. A drinking water sample was placed in a headspace vial. A stir bar was added and then the vial was crimped with a Teflon-coated silicone septum. SBSE of the water samples was performed at 25, 40 and 60 °C from 5 to 480 min while stirring at 1000 rpm. For headspace sampling [headspace sorptive extraction (HSSE[24])], headspace vials (22, 43, 62 ml), Teflon-coated silicone septa and a home-made holder were used. A small hole was drilled in a septum, enclosing and fixing the home-made holder with a stir bar (PDMS). After inserting the sample and Teflon stir bar (for sample agitation), the vial was crimped with the septum including the stir bar (PDMS). HSSE of the water samples was performed for 60 min at 25, 40 and 60 °C while agitating the samples by stirring at 1000 rpm. NaCl (15% m/v) was added to evaluate the effect of salt addition in SBSE and HSSE before the vial was crimped. When adding NaCl, an ultrasonic bath was used for dissolution of the NaCl before the extraction because shaking by hand or with a shaker will cause the stir bar to break down or drop into the liquid phase in HSSE. Fig. 1 shows a diagram of the SBSE and HSSE set-ups. After extraction, the stir bars were easily removed with forceps (due to the magnetic attraction effect), rinsed with distilled water, dried with a lint-free tissue and placed in a glass thermal desorption tube. The thermal desorption tube was then placed in the thermal desorption unit, where the stir bar was thermally desorbed by programming the TDS 2 from 20 °C (held for 1 min) to 180 °C (held for 4 min) at 60 °C min^{-1}. The desorbed compounds were cryofocused in the CIS 4 at −150 °C. After desorption, the CIS 4 was programmed from −150 to 250 °C (held for 5 min) at 12 °C s^{-1} to inject the trapped compounds on to the analytical column. Injection was performed in the splitless mode and the split valve was closed for 3 min. The separations were carried out on a HP-5ms fused silica column (30 m × 0.25 mm id, 0.25 μm film thickness, Agilent Technologies). The oven temperature was programmed from 40 °C (held for 3 min) to 280 °C (held for 5 min) at 10 °C min^{-1}. Helium was used at the carrier gas at a flow rate of 1 ml min^{-1}. The mass spectrometer was operated in the selected ion monitoring (SIM) mode with electron ionization (ionization voltage: 70 eV). For SIM, six ions were monitored (*m/z* 95, 108 for MIB, *m/z* 195, 197 for TCA, *m/z* 112, 182 for geosmin: the underlined number is the *m/z* of the ion used for determination). A blank run of the stir bar was always performed after an analysis, but memory effects were never shown.

Sample preparation and SHS-GC-MS

The water samples (raw water and tap water) were initially analyzed by the optimized SHS-GC-MS method.[12,25] A 15 ml drinking water sample was placed in a 20 ml headspace vial. A 4.5 g amount of NaCl was added and then the vial was crimped with a Teflon-coated silicone septum. The static headspace analysis of the water samples was performed at 80 °C, with shaking, for an equilibration time of 30 min using an Agilent 7694 headspace sampler with a 3 ml sample loop. After equilibration, injection was performed in the pulsed split mode.

Results and discussion

Selection of extraction mode

Because it was found that sampling from the liquid phase by SPME has a poor extractive behavior in comparison with sampling from the headspace,[19–22] the extraction modes were firstly examined with parameters such as sample volume, extraction temperature and salt addition. Fortified natural mineral water (100 ng l^{-1} for all the compounds) was used, and each analysis was carried out in six replicates. The extractions were performed for 60 min at 25, 40 and 60 °C. NaCl (15% m/v) was added to study the effect of salt addition (not more than 20% m/v NaCl could be dissolved in water within 30 min by the ultrasonic bath). The effect of sample volume on SBSE was investigated as follows: 10 ml of water sample were placed in a 12 ml vial, 20 ml in a 22 ml vial, 40 ml in a 43 ml vial and 60

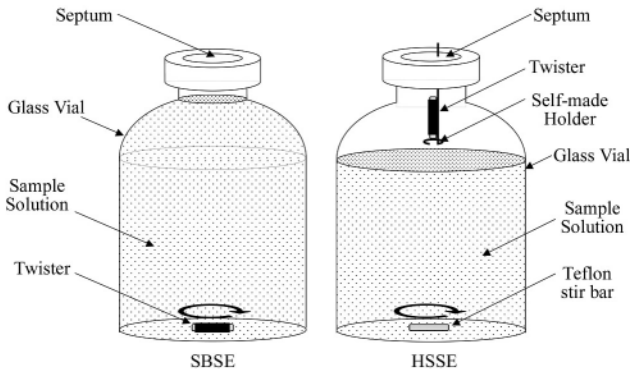

Fig. 1 Diagram of SBSE and HSSE set-ups.

ml in a 62 ml vial. The effect of sample volume on HSSE was evaluated by using a constant percentage headspace (about 27%),[21] but with different vials: 22, 43 and 62 ml. In this case, the sample volume was 16, 31 and 45 ml, respectively. Fig. 2 shows the typical results (SBSE at 25 °C without salt addition, HSSE at 60 °C with or without salt addition). With 15% salt addition and variation of the extraction temperature, the responses obtained by SBSE did not change appreciably, whereas the responses obtained by HSSE were 1.4–3.3 times higher than those obtained with no salt addition and ambient temperature extraction (25 °C). For all the compounds and conditions except MIB in SBSE, the responses significantly increased when the sample volume increased from 10 to 60 ml in SBSE and from 16 to 45 ml in HSSE. For MIB in SBSE, the highest response was obtained with a sample volume of 40 ml. For geosmin and TCA, the highest responses were obtained by SBSE using a 45 ml sample. HSSE at 60 °C using 60 ml of sample with 15% salt addition showed the highest response for MIB and the second highest responses for geosmin and TCA. However, the relative standard deviations (RSD) obtained under these conditions showed significantly higher values (8.8–19%) than those obtained by SBSE (less than 3%). In addition, HSSE requires additional procedures in sample preparation such as fixing the stir bar using the home-made holder, salt addition and dissolution by means of an ultrasonic bath, in contrast to SBSE. Because of the low RSD values, the highest sensitivity for geosmin and TCA and the simplicity of sample preparation, SBSE was selected as the extraction mode for further experiments.

Extraction time and extraction efficiency

The distribution coefficients of the analytes between water and PDMS ($k_{PDMS/w}$) were correlated with the octanol–water distribution coefficients ($k_{o/w}$).[26–28] Compounds with a high $k_{o/w}$ are more lipophilic; by contrast, compounds with a low $k_{o/w}$ are hydrophilic. The mass of analyte extracted into PDMS at full equilibration (expected recovery) is calculated by the following equations:[23]

$$k_{o/w} \approx k_{PDMS/w} = C_{PDMS}/C_w = (m_{PDMS}/m_w)(V_w/V_{PDMS})$$

where C_{PDMS} is the analyte concentration in PDMS, C_w the analyte concentration in water, m_{PDMS} the mass of analyte in PDMS, m_w the mass of analyte in water, V_{PDMS} the volume of PDMS and V_w the volume of water. $V_w/V_{PDMS} = \beta$, the phase ratio of the water–PDMS system:

$$k_{o/w}/\beta = m_{PDMS}/m_w = m_{PDMS}/(m_0 - m_{PDMS})$$

$$\text{Recovery} = m_{PDMS}/m_0 = k_{o/w}/\beta/(1 + k_{o/w}/\beta)$$

where m_0 is the total amount of analyte originally present in the water sample.

The extraction time profiles (equilibration curves) and the extraction efficiencies of the off-flavor compounds for 20, 40 and 60 ml water samples using a stir bar coated with 24 μl of PDMS were determined. Fortified natural mineral water (100 ng l^{-1} for all the compounds) was used. Eight extraction times between 5 and 480 min were examined. Replicate analyses ($n = 6$) were performed at each extraction time. The recoveries of the target compounds by SBSE were calculated by comparing the peak areas with those of a direct analysis of a standard solution used for the calibration graphs, which was spiked on a stir bar placed in a thermal desorption tube. The extraction efficiencies were calculated by comparing the expected recoveries at full equilibration with the measured recoveries. Fig. 3 shows the extraction time profiles and the effect of variation of sample volume. Table 1 shows the $P_{o/w}$ (log $k_{o/w}$) and the extraction efficiencies. From the extraction efficiencies, TCA, with the highest $P_{o/w}$, reached extraction equilibrium (full equilibration) the earliest, whereas MIB, with the lowest $P_{o/w}$, reached equilibrium the slowest or did not reach equilibrium at all, even after 480 min. For all the compounds, the extraction equilibrium gradually lengthened when the sample volume increased from 20 to 60 ml. The time needed to reach the extraction equilibrium depends not only on $P_{o/w}$ but also on the sample volume (phase ratio). The extraction efficiency decreased on increasing the sample volume; however, the responses increased with the increased mass of analyte in the larger samples, except for MIB, in 5–60 min. For MIB, the responses obtained with a sample volume of 60 ml were lower than those obtained with 40 ml of sample in 5–60 min.

In order to obtain the maximum sensitivity with this method, a 480 min extraction using a sample volume of 60 ml is

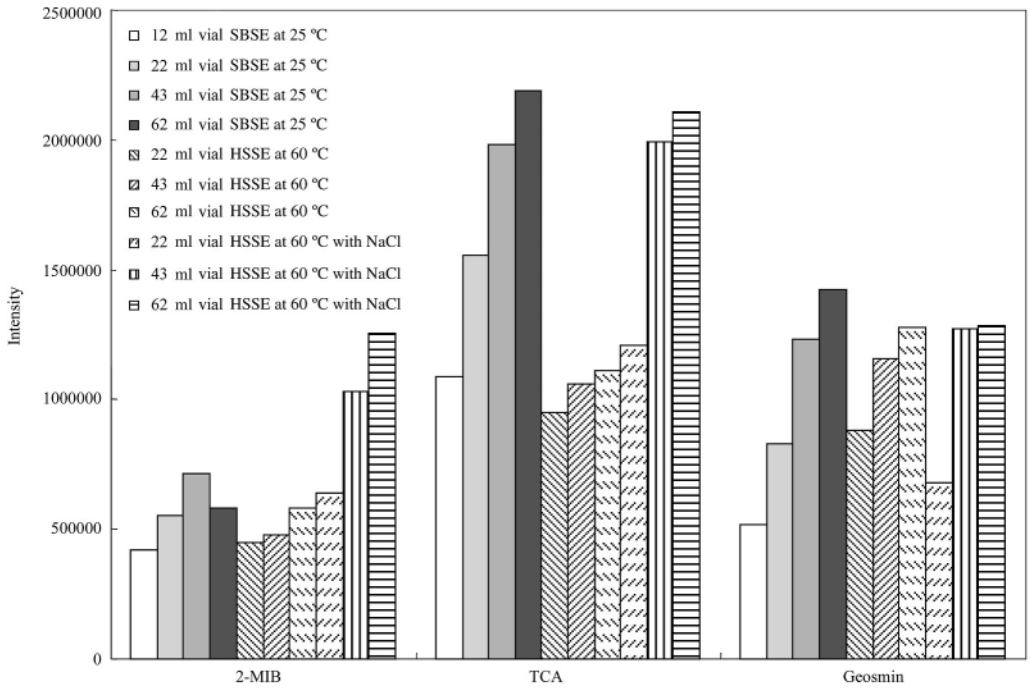

Fig. 2 Comparison of the responses of off-flavor compounds in water by SBSE at 25 °C without salt addition and HSSE at 60 °C with or without salt addition. The extraction time was 60 min.

required. Although several samples can be extracted in parallel by using SBSE, the time and sample throughput should be considered in the selection of the optimum extraction time. In practice, full equilibration is not essential for an accurate determination. A timed stirring period can also be used for calibration, as is the case in SPME. However, if the equilibration curve rises rapidly, a short extraction time will not only result in a loss of sensitivity but also of precision.[29] The extraction time was selected so as to give more than 80% extraction efficiency for TCA, which has the equilibration curve with the largest slope and the lowest odor threshold concentration. Consequently, 60, 120 and 240 min extraction times were selected for sample volumes of 20, 40 and 60 ml, respectively, for further experiments.

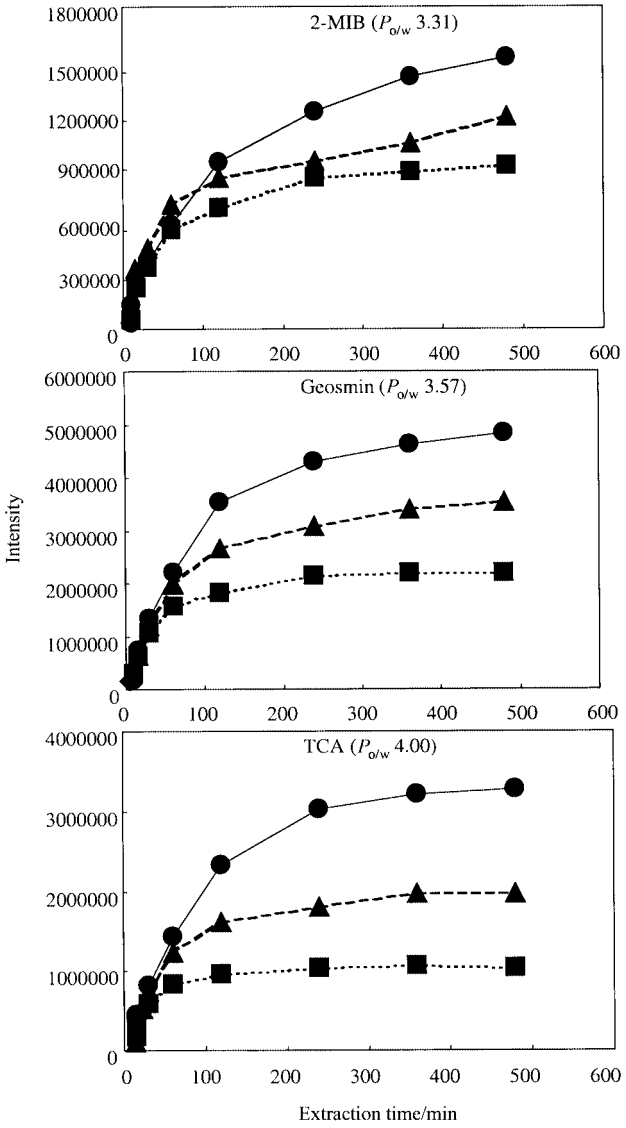

Fig. 3 Extraction time profiles and the effect of variation of sample volume for the off-flavor compounds studied in water by SBSE-TD-GC-MS. ■, 20 ml sample; ▲, 40 ml sample; ● 60 ml sample.

Table 1 Extraction efficiencies

			Extraction efficiency (%)[a]							
			Extraction time/min							
Compound	$P_{o/w}$	Sample volume/ml	5	15	30	60	120	240	360	480
MIB	3.31	20	6	24	36	58	70	87	92	94
		40	5	20	27	41	50	56	62	71
		60	1	5	15	24	38	50	58	62
Geosmin	3.57	20	13	28	47	70	81	95	98	98
		40	5	17	31	51	69	79	88	91
		60	3	14	25	41	66	80	86	90
TCA	4.00	20	16	36	58	82	95	101	103	101
		40	6	27	37	62	81	91	99	99
		60	4	14	23	41	67	86	92	94

[a] The extraction efficiencies were calculated by comparing the expected recoveries at full equilibration with the measured recoveries.

Method validation and determination of off-flavor compounds in drinking water

In order to validate the methods (20 ml sample with 60 min extraction, 40 ml sample with 120 min extraction and 60 ml sample with 240 min extraction), fortified blank water (natural mineral water) and raw water samples were prepared. The linearity was examined by analysing the fortified natural mineral water samples. The eight data points for the external calibration graphs were linear over the range from 0.1 or 0.2 or 0.5 to 100 ng l^{-1} with correlation coefficients better than 0.9987. There are several methods to determine the method detection limits (MDL). The most widely accepted definition is based on estimating the MDL using low concentration spikes and calculating the standard deviation of the determination. The MDL is then defined as three times the standard deviation (for six replicates) obtained for an analyte concentration no higher than ten times the MDL.[29] The MDL were calculated to be 0.071–0.16 ng l^{-1} for a 20 ml sample, 0.030–0.13 ng l^{-1} for a 40 ml sample and 0.022–0.041 ng l^{-1} for a 60 ml sample by repeated analysis ($n = 6$) of fortified blank water spiked at 0.1–0.5 ng l^{-1} (lowest concentrations of the calibration graphs). The recoveries and precision of the methods were assessed by replicate analysis ($n = 6$) of raw water and tap water samples fortified at the 1 ng l^{-1} level. The non-spiked and spiked samples were initially analyzed by SHS-GC-MS,[12,25] however, the target analytes were not detected. The MDL of the SHS method were calculated to be 1.2–4.0 ng l^{-1} by triplicate analysis of fortified natural mineral water spiked at 10 ng l^{-1}. The recoveries were calculated by subtracting the results for the non-spiked sample from those for the spiked sample. All the results were obtained by using calibration graphs obtained from fortified natural mineral water samples. The results showed good recoveries and precision for all the compounds under all the conditions. The recoveries and precision were 89–104% (RSD 0.85–3.7%) for raw water and 100–109% (RSD 0.8–3.5%) for tap water. Consequently, the method recoveries appeared not to be influenced by the type of water that was analyzed. Validation of the method is summarized in Table 2. Fig. 4 shows the SIM chromatograms obtained with the proposed method after a 120 min extraction of a natural mineral water sample (40 ml) fortified at the 1.0 ng l^{-1} level. The results for the non-spiked samples are shown in Table 3. The data in Table 3 show that the concentrations obtained under all the conditions were comparable. Consequently, all the conditions are applicable to the practical analysis of low-level samples.

Conclusion

The determination of trace amounts of off-flavor compounds such as MIB, geosmin and TCA in drinking water using the SBSE technique followed by TD-GC-MS was described. The proposed method has many practical advantages such as a small sample volume (20–60 ml) and the simplicity of the extraction; it is also solvent-free and of high sensitivity. The SBSE technique could be performed in parallel (normally 6 replicates × 3) at room temperature without salt addition, thereby saving time and effort. Compared with conventional solvent-free techniques such as the optimized SHS and SPME, the proposed

Table 2 Method validation for SBSE determination of MIB, geosmin and TCA[a]

Compound	Sample volume/ml	Correlation coefficient (r^2)	MDL/ng l^{-1}	Tap water		Raw water	
				Recovery (%)	RSD (%), $n=6$	Recovery (%)	RSD (%), $n=6$
MIB	20	0.9995 (0.5–100)[b]	0.16	105	2.4	95	1.3
	40	0.9987 (0.2–100)	0.13	102	1.9	104	1.4
	60	0.9992 (0.1–100)	0.041	100	3.1	94	0.85
Geosmin	20	0.9998 (0.5–100)	0.11	108	2.4	102	3.7
	40	0.9998 (0.2–100)	0.030	104	2.8	102	1.6
	60	0.9996 (0.1–100)	0.025	103	3.5	103	1.8
TCA	20	0.9999 (0.5–100)	0.071	109	3.3	89	2.9
	40	0.9991 (0.2–100)	0.046	101	0.80	93	2.3
	60	0.9999 (0.1–100)	0.022	104	2.0	89	1.2

[a] The MDL (method detection limits) were calculated as three times the standard deviation ($3s$) of replicate analyses ($n=6$) of fortified natural mineral water (spiked at the lowest concentrations of the calibration graph). The recoveries and precision were also examined by replicate analysis ($n=6$) of raw water and tap water fortified at the 1 ng l^{-1} level. [b] Values in parentheses are the linear ranges of the calibration graphs (ng l^{-1}).

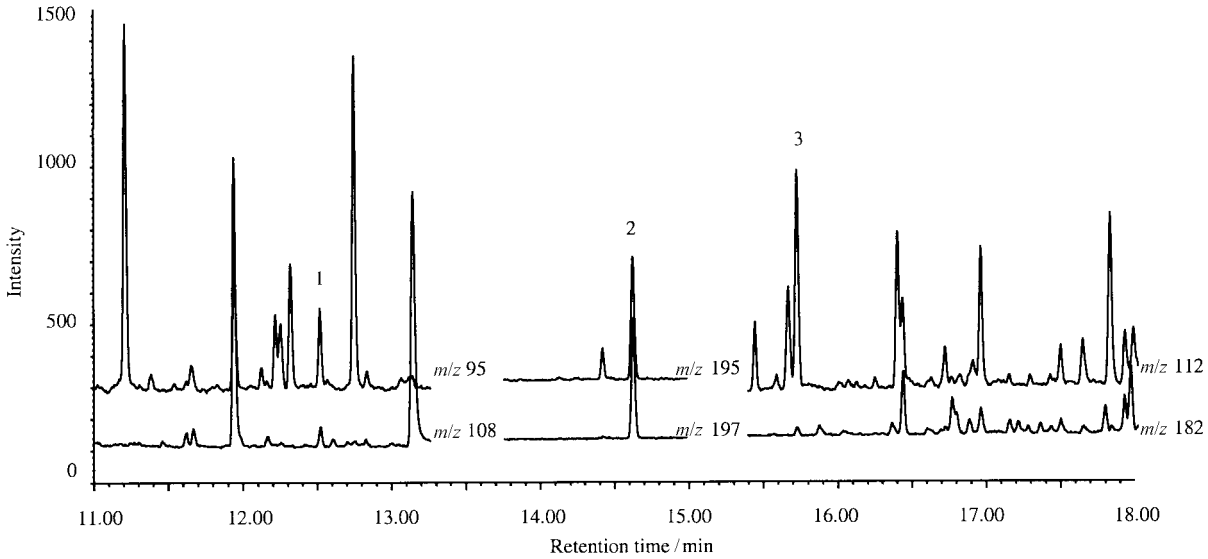

Fig. 4 SIM chromatograms obtained by SBSE-TD-GC-MS of fortified natural mineral water (40 ml) spiked at 1 ngl^{-1}. The extraction time was 120 min. 1, MIB; 2, TCA; 3, geosmin.

Table 3 Results of analysis of tap water and raw water (non-spiked) by SBSE-TD-GC-MS. The extraction times for the 20, 40 and 60 ml samples were 60, 120 and 240 min, respectively

Compound	Sample volume/ml	Tap water		Raw water	
		ng l^{-1}	RSD (%), $n=6$	ng l^{-1}	RSD(%), $n=6$
MIB	20	ND[a]	—	1.3	2.9
	40	ND[a]	—	1.3	7.4
	60	ND[a]	—	1.3	3.4
Geosmin	20	ND[a]	—	1.3	3.2
	40	ND[a]	—	1.3	2.9
	60	ND[a]	—	1.4	0.64
TCA	20	0.21	1.4	0.16	6.1
	40	0.21	0.71	0.18	4.2
	60	0.22	3.1	0.17	2.0

[a] ND = Not detected.

method showed about 10 times higher sensitivity. The maximum sensitivity (MDL; 0.022–0041 ng l^{-1}) was obtained with the largest sample volume (60 ml) and the longest extraction time (240 min); however, a smaller sample volume (20, 40 ml) and a shorter extraction time (60, 120 min) also led to sub-ng l^{-1} detection limits (ranging from 0.030 to 0.16 ng l^{-1}). The recoveries of the method showed good results (89–109%) with acceptable precision (RSD: 0.80–3.7%) for raw water and tap water fortified at the 1 ng l^{-1} level. Also, the method allowed the determination of ng l^{-1} or sub-ng l^{-1} levels of MIB, geosmin and TCA in raw water and tap water with a low RSD (ranging from 0.64–7.4%).

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References

1 P. E. Persson, *Water Sci. Technol.*, 1983, **15**, 1.
2 J. Mallevialle and I. H. Suffet, *Identification and Treatment of Tastes and Odors in Drinking Water*, American Water Works Association Research Foundation, Denver, CO, 1987.
3 A. Nystrom, A. Grimvall, C. Krantz-Rulcker, R. Savenhed and K. Akerstrand, *Water Sci. Technol.*, 1992, **25**, 241.
4 S. Karlsson, S. Kaugare, A. Grimvall, H. Boren and R. Savenhed, *Water Sci. Technol.*, 1995, **31**, 99.
5 K. Takahashi, K. Kido and R. Shirachi, *Yosui to Haisui*, 1992, **34**(2), 127.
6 N. M. Griffiths and G. R. Fenwick, *Chem. Senses Flavor*, 1977, **2**, 487.
7 J. E. Amoore, *J. Am. Water Works Assoc.*, 1986, **78**, 70.
8 P.-E. Persson, *Water Res.*, 1980, **14**, 1113.

9 Japan Water Works Association, *Manual of Analytical Methods for a Water Supply*, November 15, 1993.
10 K. Grob, *J. Chromatogr*., 1973, **84**, 225.
11 S. W. Krasner, C. J. Hwang and M. J. McGuire, *Water Sci. Technol*., 1983, **15**, 127.
12 L. Malleret, A. Bruchet and M.-C. Hennion, *Anal. Chem*., 2001, **73**, 1485.
13 M. W. Buettner and G. A. Schelk, *Proceedings of AWWA WQTC*, 1992, American Water Works Association, Denver, CO, 1992, pp. 1083–1100.
14 J. E. George, G. Payne, D. Conn, G. Ward and J. J. Thoma, *Proceedings of AWWA WQTC*, 1997, American Water Works Association, Denver, CO, 1998, pp. 88–98.
15 P. B. Johnsen and J.-C. W. Kuan, *J. Chromatogr*., 1987, **409**, 337.
16 V. C. Blok, G. P. Slater and E. M. Giblin, *Water Sci. Technol*., 1983, **15**, 149.
17 E. D. Conte, S. C. Conway, D. W. Miller and P. W. Perschbacher, *Water Res*., 1996, **30**, 2125.
18 J. Nakagawa, Y. Takahashi and M. Takeuchi, *Annu. Rep. Tokyo Metr. Res. Lab. P.H*., 1996, **47**, 253.
19 S. W. Lloyd, J. M. Lea and P. V. Zimba, *Water Res*., 1997, **32**, 2140.
20 R. McCallum, P. Pendleton, R. Schumann and M. Trinh, *Analyst*, 1998, **123**, 2155.
21 M. Bao, O. Griffini, D. Burrini, D. Santianni, K. Barbieri and M. Mascini, *Analyst*, 1999, **124**, 459.
22 S. B. Watson, B. Brownlee, T. Satchwill and E. E. Hargesheimer, *Water Res*., 1999, **34**, 2818.
23 E. Baltussen, P. Sandra, F. David and C. Cramers, *J. Microcolumn Sep*., 1999, **11**, 737.
24 B. Tienport, F. David, C. Bicchi and P. Sandra, *J. Microcolumn Sep*., 2000, **12**, 577.
25 N. Ochiai, N. Sakui, S. Daishima and D. B. Cardin, *Proceedings of 22nd ISCC*, Japan, 1999, I.O.P.M.S., Kortrijk, Belgium, 1999, CD-ROM paper PE203.
26 J. Dugay, C. Miege and M.-C. Hennion, *J. Chromatogr*., 1998, **795**, 27.
27 L. S. DeBruin, P. D. Josephy and J. B. Pawliszyn, *Anal. Chem*., 1998, **70**, 1986.
28 J. Beltran, F. J. Lopez, O. Cepria and F. Hernandez, *J. Chromatogr*., 1998, **808**, 257.
29 J. Pawliszyn, *Solid Phase Microextraction Theory and Practice*, Wiley-VCH, New York, 1997, pp. 123–125, 137.