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Determination of 2-Methylisoborneol, Geosmin and 2,4,6-Trichloroanisole in Drinking Water by Dynamic Headspace Coupled to Selectable ^{1}D/^{2}D GC-MS with Simultaneous Olfactory Detection

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Abstract
A method for the determination of trace amounts of off-flavor compounds such as 2-methyl isoborneol (MIB), geosmin and 2,4,6-trichloroanisole (TCA) in drinking water is described based on dynamic headspace coupled to selectable one-dimensional or two-dimensional gas chromatography - mass spectrometry with simultaneous olfactory detection (DHS-^{1}D/^{2}D GC-O/MS). Automated DHS using a Tenax TA packed tube as trap was performed on a 10 mL-sample containing 30 % NaCl at 80ºC, and followed by thermal desorption of the trap. Combining heart-cutting with fast temperature programming (100ºC/min) of the second column resulted in improvements in both separation and analyte limits of determination due to decreased background signal of the monitored mass ion and the increased analyte peak height. Compared to DHS-^{1}D GC-O/MS analysis, signal-to-noise ratios (S/N) were improved by a factor of 12 for MIB, 9 for geosmin, and 3 for TCA. The method showed good linearity

over the concentration range from 1 to 100 ng/L with correlation coefficients (r^2) greater than 0.9942. The limits of detection (LODs) for these compounds ranged from 0.15 to 0.22 ng/L. Simultaneous olfactory- and MS detection was succesfully performed for the lowest level sample spiked at 1 ng/L.

Introduction

The naturally occurring compounds 2-methylisoborneol (MIB) and geosmin, have received a great deal of attention over the past decades since they lend a musty/earthy off-flavor to water. Similarly, halogenated anisoles, or haloanisoles, such as 2,4,6-trichloanisole (TCA), are highly odorous compounds produced by biomethylation of the equivalent halogenated phenols. Haloanisoles have extremely low odor thresholds ranging from sub-ng/L to 10 ng/L [1]. Conventional analytical methods therefore include both extraction and enrichment steps, e.g. closed-loop stripping analysis (CLSA) [2], purge and trap (P&T) [3], continuous liquid-liquid extraction (CLLE) [4], solid phase microextraction (SPME) [5, 6] and stir bar sorptive extraction (SBSE) [1, 7, 8] combined with gas chromatography - mass spectrometry (GC-MS) determination. These extraction and enrichment techniques in combination with GC-MS can provide highly sensitive analysis, but insufficient GC resolution often prevents reliable determination of MIB and geosmin even in clean samples such as drinking water because the target ions, e.g. m/z 95 for MIB and m/z 112 for geosmin are not unique to these compounds. Two-dimensional (^{2}D) GC-MS provides an effective way of improving analyte separation and reliability or the analysis. In 2010, we proposed a new heart-cutting ^{2}D GC-MS system referred to as "Selectable ^{1}D/^{2}D GC-MS" for simple and fast operation of both ^{1}D GC-MS and ^{2}D GC-MS with simultaneous olfactory detection and element-specific detection [9]. The selectable ^{1}D/^{2}D GC-MS system employs low thermal mass (LTM) GC, which can provide rapid heating and cooling for fast GC analysis as well as independent temperature control for multi-dimensional GC [10]. Therefore, faster temperature programming during the second dimension separation can often shorten the analysis time while improving analyte limits of determination due to the improved resolution resulting in decreased background signal of the monitored mass ion, narrower analyte peaks and increased peak heights. All this is gained in addition to the increased resolution achieved through heart-cutting.

Recently, a new dynamic headspace (DHS) system was introduced, which consists of a dual needle DHS module, replaceable adsorbent traps, an x-y-z robotic sampler, a small integrated thermal desorption unit (TDU), and a programmable temperature vaporizer (PTV) inlet. This design provides a fully automated and highly inert system with a very short and fully heated sample-path [11].

In this study, we describe a method for the determination of off-flavor compounds such as MIB, geosmin and TCA in drinking water at ng/L level by using DHS coupled to selectable ^{1}D/^{2}D GC-MS with simultaneous olfactory detection (DHS-^{1}D/^{2}D GC-O/MS).

Experimental

Reagents and materials. Standard solutions of MIB, Geosmin, and TCA at 100 µg/mL in methanol were purchased from Sigma Aldrich Japan (Tokyo, Japan) and used as stock standard solutions. These were then diluted and mixed with methanol to prepare the mixed working standard solutions. The stock standard solutions were kept at -20ºC. Methanol of pesticide residue grade and sodium chloride (NaCl) of analytical grade were purchased from Kanto Kagaku (Tokyo, Japan). NaCl was heated to 350ºC for 6 h prior to use.

Instrumentation. DHS was performed using a GERSTEL DHS module (GERSTEL, Mülheim an der Ruhr, Germany) subsequently followed by thermal desorption (TD)–GC–MS analysis using a TDU thermal desorption unit equipped with an MPS autosampler and a CIS 4 programmable

Figure 1. DHS-^{1}D/^{2}D GC-O/MS system.

temperature vaporization (PTV) inlet (GERSTEL), dual LTM-GC system (Agilent Technologies, CA, USA) installed on an Agilent 7890 gas chromatograph (host GC) and a 5975C mass-selective detector. The LTM-GC system consists of dual wide format column modules (5 in.; 1 in. = 2.54 cm), LTM-heated transfer lines, cooling fan, temperature controller, power supply, and a specially constructed GC door. The GC was equipped with a switching device which consists of a capillary flow technology (CFT) Deans switch and a CFT 2-way splitter with make-up gas line and restrictor (Agilent Technologies) [9]. An Olfactory Detection Port (ODP 2) (GERSTEL) was used for olfactory detection. Figure 2 shows a schematic of the DHS-^{1}D/^{2}D GC-O/MS system.

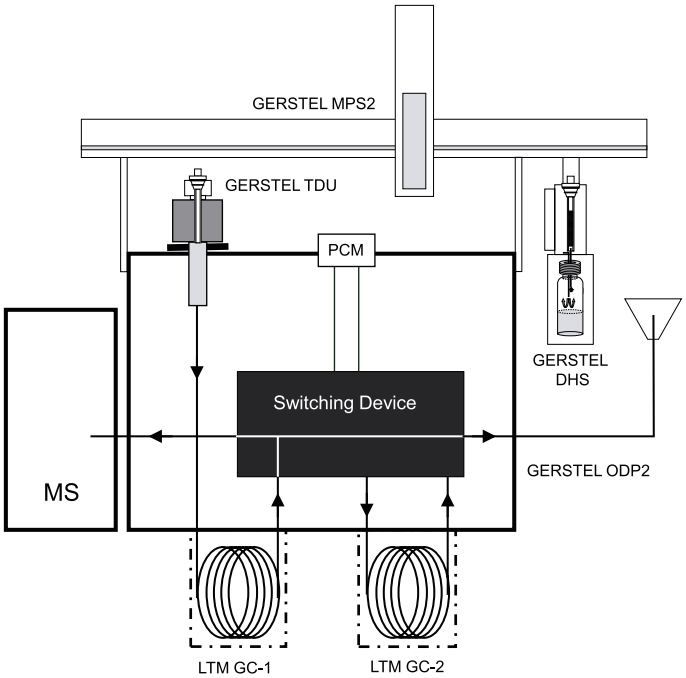

Figure 2. Flow diagram of a DHS-^{1}D/^{2}D GC-O/MS system.

Dynamic headspace and thermal desorption. A ten milliliter sample of water was poured into a 20 mL headspace vial. Three grams of NaCl was added to the sample and dissolved after the vial had been sealed with a screw cap. No further sample preparation was necessary.

Samples were initially incubated at 80ºC for 20 min in the agitator of the MPS at 500 rpm agitation speed. Then, samples were transferred to the DHS module at 80ºC and left for 5 min without agitation. Analytes in the headspace were purged with 60 mL of nitrogen gas at a flow rate of 10 mL/min and trapped at 20ºC on a TDU tube packed with Tenax TA. Following the dynamic headspace extraction step, the trap temperature was increased to 40 ºC and a dry purge with 600 mL of nitrogen gas was performed at a flow rate of 50 mL/min. The TDU tube was transported to, and subsequently desorbed in the TDU. The TDU was programmed from 30ºC (held for 0.5 min) to 240ºC (held for 3 min) at 720ºC/min with 50 mL/min desorption flow. Desorbed compounds were focused at 10ºC on a Tenax TA packed liner in the PTV inlet. After desorption, the PTV inlet was programmed from 10ºC to 240ºC (held for GC run time) at 720ºC /min to inject trapped compounds onto the analytical column. The injection was performed in the splitless mode with a 2 min splitless time.

Selectable ^{1}D/^{2}D GC-MS with simultaneous olfactory detection. ^{1}D and ^{2}D GC-MS analysis with simultaneous olfactory detection was performed on the selectable ^{1}D/^{2}D GC-MS system previously described [9]. Separations were performed on a 30 m x 0.25 mm i.d., 0.25 µm film thickness DB-Wax column (Agilent) as the ^{1}D column and a 10 m x 0.18 mm i.d., 0.40 µm film thickness DB-5 column (Agilent) as the ^{2}D column. The column temperature for the DB-Wax was programmed from 40ºC (held for 2 min) to 240ºC (held) at 10ºC/min. The column temperature for the DB-5 was either 40ºC (held for GC run time) or programmed from 40ºC to 280ºC (held) at 100ºC/min. The host GC oven was kept at a constant temperature of 250°C. A split ratio of 1:2 was set between the MS and the ODP 2 sniffing port. The MS was operated in selected ion monitoring (SIM) mode using electron ionization (electron accelerating voltage: 70 V). For SIM, seven ions were monitored (m/z 18 for water; m/z **95** and 108 for MIB; m/z **112** and 125 for geosmin; and m/z **195** and 197 for TCA: the bold number is the m/z of the ion used for determination). The data acquisition speed was 10 Hz for each ion except for m/z 18 (3 Hz). The sniffing port temperature was set to 250°C. Pressure was 385 kPa, 314.8 kPa and 26 kPa for the inlet, a pneumatic control module (PCM) and an AUX of PCM, respectively.

Results and discussion

Water management and DHS conditions. Kolb indicated that both static and dynamic headspace GC has to deal with the "water problem", e.g. peak splitting and variability of retention time [12]. The purge gas remains permanently saturated with water vapor in DHS. Thus, a high amount of water is accumulated in the adsorbent trap. Since MIB, geosmin and TCA are not highly volatile, a dry purge step can be applied

before the final thermal desorption step. In order to optimize the dry purge conditions, we used a "pre-calculation approach" using an LVI calculator software (GERSTEL). Before the calculation we defined the basic conditions: the total purge gas volume should not exceed 1000 mL and the maximum amount of water going through the adsorbent trap should be 20 mg, with the DHS sampling temperature set to 80°C. Calculating based on these parameters 20 mg of water are contained in a saturated gas volume of 67 mL at 80°C. A Tenax TA adsorbent trap, kept at 40°C, can eliminate 20 mg water with a minimum total purge volume of 379 mL. We decided to select a sampling volume of 60 mL above the 10 mL sample kept at 80°C (containing the analytes at 15 ng each) and added an additional 340 mL dry purge for this study providing a total purge volume of 400 mL. Residual water on the Tenax TA tube and analyte breakthrough were monitored by TD-GC-MS. The chosen total purge volume of 400 mL worked fairly well for the removal of water from the Tenax TA tube without breakthrough of analytes. However, the SIM chromatogram for water (m/z 18) still included a large and very wide peak indicating the presence of an amount of water large enough to negatively impact the quality of the chromatography. Therefore, an additional dry purge volume of 200 mL was applied, bringing the total volume to 600 mL. The result was a complete removal of water from the Tenax TA tube without causing analyte breakthrough. Consequently, the dry purge volume was set to 600 mL in the DHS methods used for further study.

For method development, the pre-calculation approach can provide a good starting point with nearly optimal dry purge conditions. Based on the results obtained using the calculated dry purge parameters, the analyst can then relatively easily devise optimal conditions. In the present study, only an additional 200 mL dry purge volume was required as the 2nd and final step.

Determination of off-flavor compounds in drinking water. Figure 3 illustrates a sum of SIM chromatograms obtained by DHS-^{1}D GC-O/MS of spiked natural water at 10 ng/L. MIB, geosmin and TCA were clearly detected both by olfactory detection and MS. The retention times (RT) were 16.34 min for MIB, 19.30 min for TCA, and 19.55 min for geosmin. However, the blank chromatogram of a non-spiked natural water

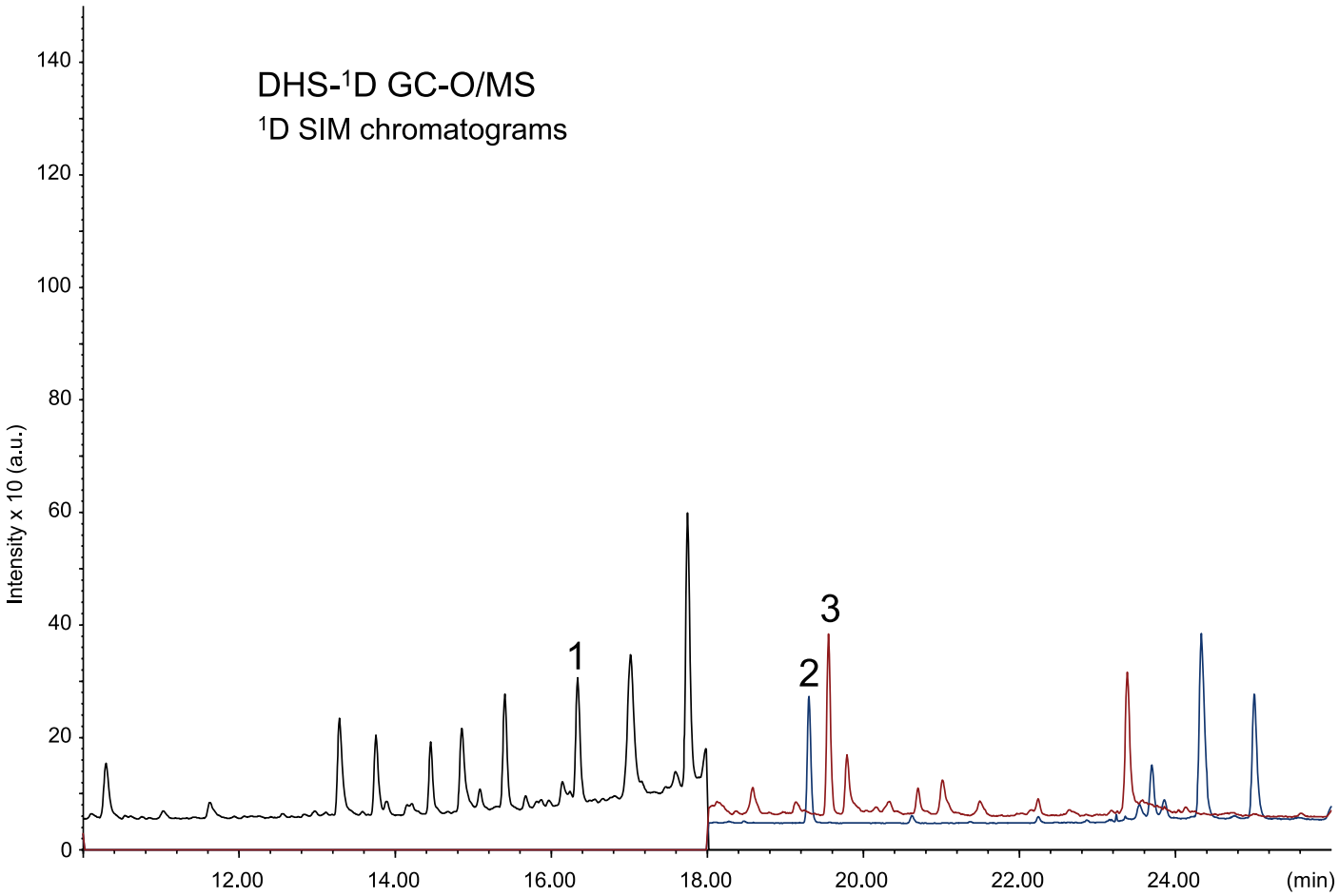

Figure 3. Sum of SIM chromatograms obtained by DHS-^{1}D GC-O/MS of spiked water at 10 ng/L each. 1. MIB (m/z 95), 2. TCA (m/z 195), 3. Geosmin (m/z 112).

sample showed that MIB would co-elute with sample matrix. In order to separate MIB from the sample matrix, a heart-cut from 16.05-16.30 min was performed to transfer the co-eluting compounds to the second dimension column. ^{2}D GC–O/MS analysis was performed just after the ^{1}D GC–O/MS run without any instrument set-up change. Figure 4 shows SIM chromatograms (m/z 95, 107, and 135) obtained by DHS-^{1}D GC-O/MS (a) and DHS-^{2}D GC-O/MS (b) of spiked natural water at 10 ng/L. Following the heart-cut, MIB was clearly separated from other compounds in the ^{2}D separation. Also, it was interesting to observe that the peaks obtained on the ^{2}D SIM chromatograms using a short, narrow bore column (e.g. 10 m x 0.18 mm i.d., 0.40 µm film thickness) are very sharp even when using a moderate temperature programming rate of 20ºC/min. In order to separate MIB from the sample matrix and reach lower limits of determination for all target compounds, two heart-cuts from 16.05-16.30 min and 19.00-20.00 min were performed to transfer all target compounds to the ^{2}D column.

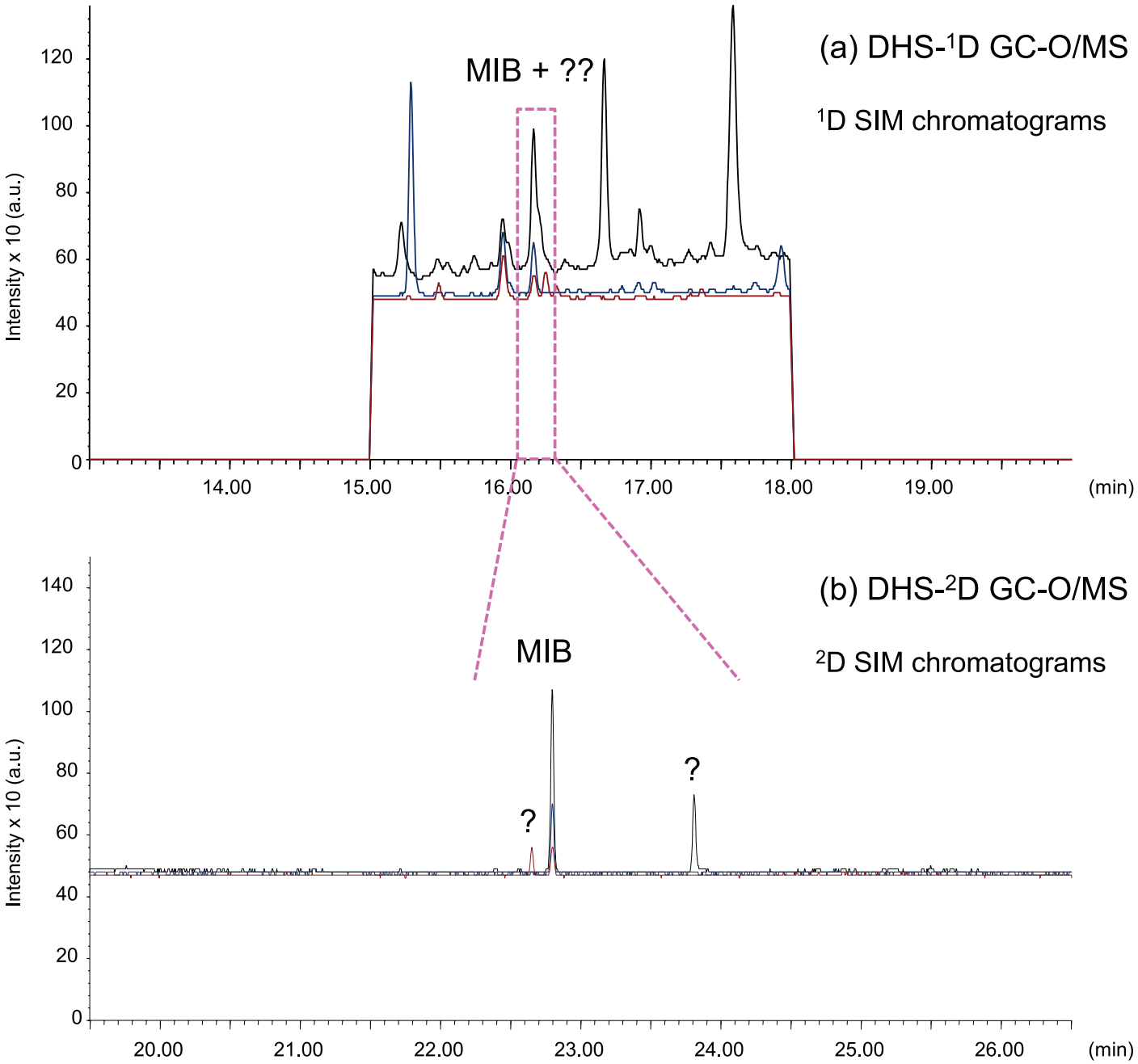

Figure 4. SIM chromatograms (m/z 95, 107, and 135) obtained by DHS-^{1}D GC-O/MS (a) and DHS-^{1}D/^{2}D GC-O/MS (b) of spiked water at 10 ng/L each.

Figure 5 illustrates the sum of the SIM chromatograms obtained by DHS-^{1}D/^{2}D GC-O/MS of spiked natural water at 10 ng/L. Directly following the second heart-cut, the compounds remaining on the ^{1}D column were back flushed and the fast GC temperature program with a column heating rate of 100ºC/min for the ^{2}D separation was started. Using the described system, the ^{1}D SIM chromatograms and the ^{2}D SIM chromatograms were combined into a single GC/MS run. The ^{1}D separation was performed over 20.00 minutes while also monitoring water with the added possibility of checking the background signal during heart-cutting. The ^{2}D separation was performed from 20.50 min (after pressure equilibration). MIB was clearly separated from the sample matrix, even under fast GC conditions with a column temperature programming rate of 100ºC/min. MIB, geosmin and TCA were all detected using both olfactory detection and MS. Only two minor segments of the ^{1}D chromatogram were heart-cut to the ^{2}D column and the ^{2}D background signals for the monitored ions were therefore all significantly decreased. The resulting analyte peaks were very narrow thanks to fast GC conditions with temperature programming rate of 100ºC/min. In combination, these two improvements lead to significantly improved signal to noise ratios, especially for MIB and geosmin. Compared to ^{1}D GC-O/MS analysis, the signal-to-noise ratio (S/N) was 12 times higher for MIB, 9 times higher for geosmin, and 3 times higher for TCA.

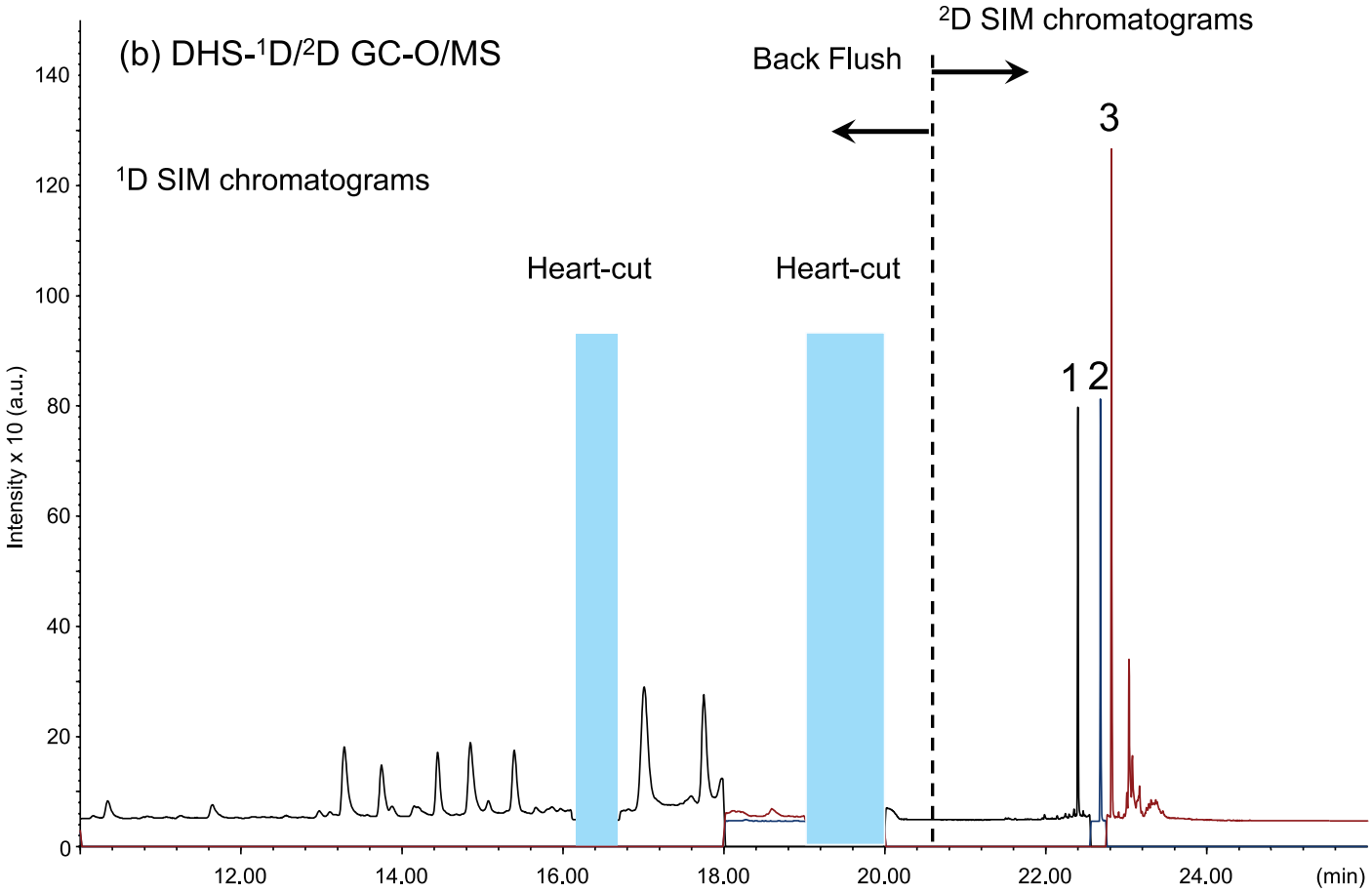

Figure 5. Sum of SIM chromatograms obtained by DHS-^{1}D/^{2}D GC-O/MS of spiked water at 10 ng/L each. 1. MIB (m/z 95), 2. TCA (m/z 195), 3. Geosmin (m/z 112).

The linearity of the DHS-^{1}D/^{2}D GC-O/MS method was determined over a concentration range from 1 to 100 ng/L by running standards at 7 concentration levels. For all analytes, good linearity was achieved with correlation coefficients (r^2) above 0.9942. The limits of detection (LODs) were estimated using low concentration spikes and calculating the standard deviation of the determination. The LODs were defined as 3 times the standard deviation (n = 6) obtained for an analyte concentration not higher than 10 times the LOD [13]. The LODs were calculated with repeated analyses (n = 6) of spiked natural water at 1 ng/L (lowest concentration measured for the calibration curves). Very low LODs in the range of 0.15–0.22 ng/L were obtained.

For all analytes, simultaneous olfactory and MS detection was successfully performed for the lowest level sample spiked at 1 ng/L. Figure 6 shows SIM chromatograms obtained by DHS-^{1}D/^{2}D GC-O/MS of spiked natural water at 1 ng/L (a) and non-spiked natural water (b). The linearity, the repeatability at 1 ng/L and the LODs of the method are listed in Table 1.

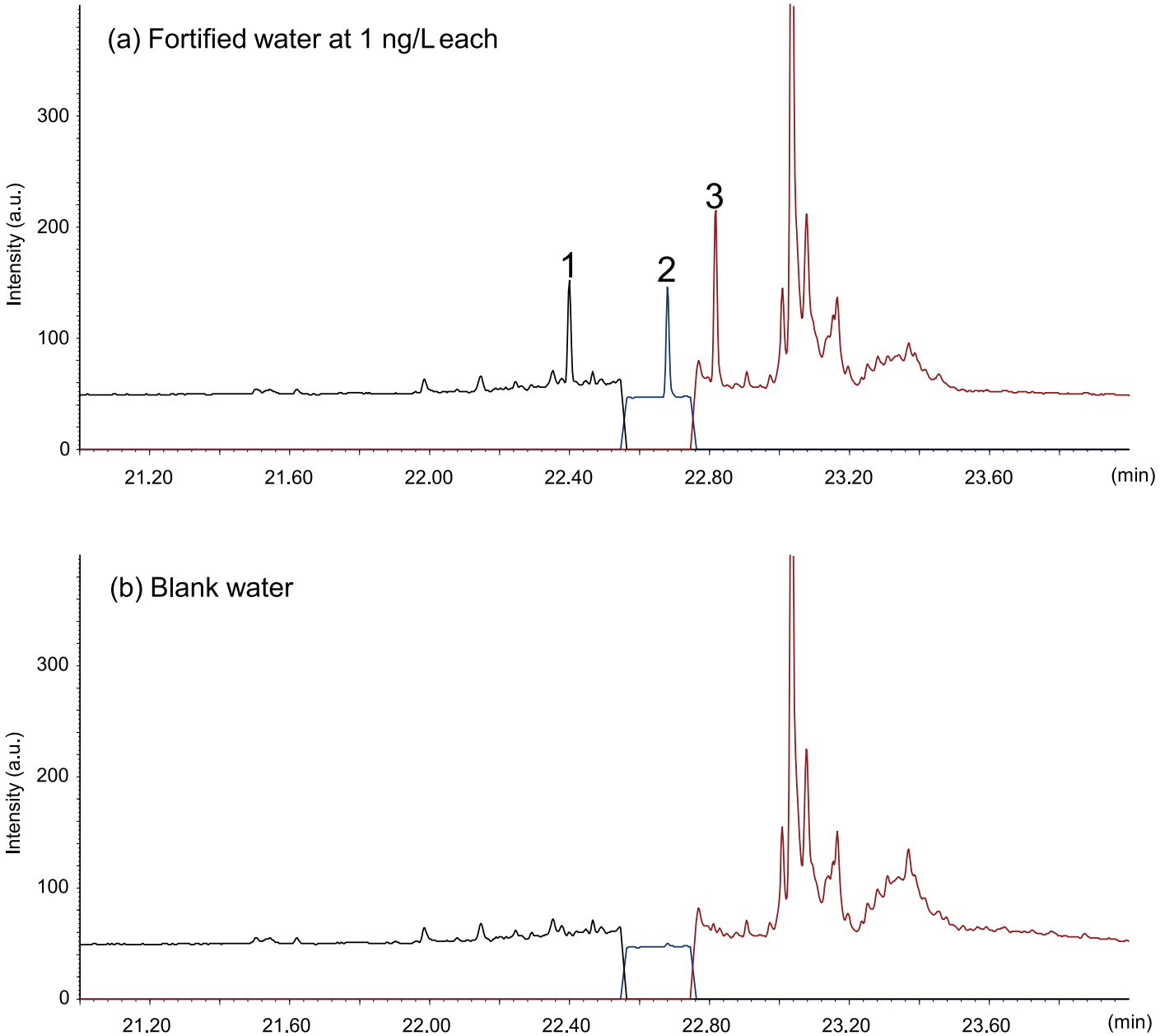

Figure 6. Comparison of SIM chromatograms obtained by DHS-1D/2D GC-O/MS. (a) Spiked water at 1 ng/L each, (b) Blank water. 1. MIB (m/z 95), 2. TCA (m/z 195), 3. Geosmin (m/z 112)

Table 1. Linearity, repeatability and LOD obtained by DHS-^{1}D/^{2}D GC-O/MS.

Compound	m/z [a]	r^2 [b]	RSD (%) n = 6 [c]	LOD (ng/L) [d]
MIB	95	0.9968	8.0	0.22
TCA	195	0.9942	5.8	0.15
Geosmin	112	0.9976	7.5	0.19

[a] Selected ions for quantification
[b] Linearity of calibration curve between 1 and 100 ng/L (7 concentration levels)
[c] Repeatability is examined with six replicate analyses of fortified natural water spiked at 1 ng/L
[d] The LOD is defined as 3 times the standard deviation (for six replicates) at 1 ng/L

Conclusion

The determination of off-flavor compounds such as MIB, geosmin and TCA in drinking water using the DHS technique followed by selectable $^{1}D/^{2}D$ GC-O/MS was described. The proposed DHS method can provide many practical advantages: It is fully automated; no solvent is required for the extraction; only a small sample volume (10 mL) is needed; and it provides both high sensitivity and high selectivity.

The LODs at sub-ng/L level are comparable to those of other solvent free and miniaturized methods like SPME and SBSE. The DHS approach, however, covers a broader analyte polarity range. In addition, the ^{2}D GC separation can eliminate false positives and results in more reliable quantification. Moreover, simultaneous olfactory and MS detection is possible providing additional confirmation of the identity of the detected compound.

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