Determination of geosmin and 2-methylisoborneol in water using solid-phase microextraction and gas chromatography-chemical ionisation/electron impact ionisation-ion-trap mass spectrometry

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A method for the determination of geosmin and 2-methylisoborneol (MIB) in water by solid-phase microextraction (SPME) is presented. Various SPME fibre chemistries have been compared for their efficiency in extracting MIB from water. Extraction conditions including the extraction time and temperature have been optimised. A 30 ml water sample is extracted for 20 min at 60 °C using a divinylbenzene fibre, and the extract analysed by gas chromatography with ion-trap mass spectrometry detection. d_5-Geosmin and d_3-MIB are added as internal standards to compensate for any variability in the SPME process which is not carried out to equilibrium. Chemical ionisation, using acetonitrile as the reagent gas, was found to give superior sensitivity to electron impact ionisation (EI) for the detection of MIB. EI was used as the ionisation mode for detection of geosmin. The method shows good linearity over the concentration range 5–40 ng l^{-1} and gives detection limits of 1 ng l^{-1} for both geosmin and MIB. Recovery (93–110%) and precision (3–12%) over this concentration range, for both raw and treated drinking waters, are comparable to currently employed methods such as closed-loop stripping analysis (CLSA). The method offers the advantage of being simple to use, with much shorter analysis times in comparison to CLSA.

Introduction

Aesthetic quality is one of the crucial parameters for drinking-water suppliers to consider when assessing water quality. The major reason for this is that consumers judge water by what they first perceive. Tastes and odours (T/O) account for the largest single class of consumer complaints to water utilities.[1] Two common odour-causing compounds in drinking water are geosmin and 2-methylisoborneol (MIB), known to be produced by certain *actinomycetes* bacteria and cyanobacteria.[2] These two compounds impart an earthy–musty odour in water at very low odour thresholds; as low as 4 ng l^{-1} for geosmin and 15 ng l^{-1} for MIB.[3] It is therefore important to have techniques available which allow for the analysis of these compounds at very low ng l^{-1} concentrations in both finished and raw drinking waters.

There are many different techniques available for the analysis of geosmin and MIB. Most involve pre-concentration and extraction of the sample before analysis by gas chromatography-mass spectrometry (GC-MS). Closed-loop stripping analysis (CLSA) is by far the most frequently applied technique for the extraction and concentration of both geosmin and MIB.[4] Open-stripping analysis (OSA), a variation of CLSA, has also been used for the analysis of T/O compounds in water. Cotsaris *et al.*[5] and Bruchet *et al.*[6] used the OSA technique and obtained improved recoveries of geosmin and MIB relative to those obtained using CLSA.

While these stripping techniques give very low detection limits, they are very time consuming and labour intensive. Because of this drawback, several other techniques for the concentration and extraction of geosmin and MIB in water have been developed recently. Bao *et al.*[7] reported a modified liquid–liquid microextraction technique combined with analysis of the extract by GC-ion trap MS. Palmentier *et al.*[8] recently reported a method for the analysis of geosmin and MIB in water which gave greatly improved sample throughput with similar sensitivity to CLSA.

During our recent studies on the removal of geosmin and MIB from drinking waters using activated carbons,[9] we required a method for the analysis of these compounds which would be relatively inexpensive to perform and ideally give high sample throughput. Solid-phase microextraction (SPME), a technique which has gained a lot of interest for the detection of trace compounds in environmental samples,[10] appeared to offer these advantages. In the only report at the time on the use of SPME for the analysis of geosmin and MIB in water, Brand[11] indicated significant promise for SPME analysis of these compounds. Using a polydimethylsiloxane fibre, he obtained detection limits for geosmin and MIB of 100–200 ng l^{-1}.

These early results suggested that the SPME method could be refined to give a simple technique, capable of detecting geosmin and MIB at low ng l^{-1} levels, while at the same time offering higher sample throughput than CLSA. The aim of this study was to develop such a method. We report here the development of an SPME method combined with GC-chemical ionisation/electron impact ionisation-ion-trap mass spectrometry (GC-CI/EI-ITMS) for the analysis of geosmin and MIB in water.

Experimental

Materials

Four different fibre chemistries were investigated for their extraction properties in this study. These included: 100 μm (coating thickness) polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA), 65 μm polydimethylsiloxane–divinylbenzene (DVB) and 75 μm polydimethylsiloxane–Carboxen (Carboxen) coatings (Supelco, Bellefonte, PA, USA). Reagent water used for procedural blanks and for 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. Reservoir water was collected from the Myponga reservoir (South Australia) and filtered through a 0.2 μm filter before use. (±)-Geosmin was obtained from Wako Chemicals (Tokyo, Japan) and (±)-d_5-geosmin was obtained from Ultrafine Chemicals (Manchester, UK).

R-(-)-2-Methylisoborneol (MIB) was prepared from R-(+)-camphor by a modification of the method of Wood and Snoeyink.[12] The modification consisted of the use of methylmagnesium iodide prepared from iodomethane in place of methyllithium used by Wood and Snoeyink. d_3-MIB was prepared in a similar way using d_3-iodomethane (Aldrich, Milwaukee, WI, USA).

Preparation of standards

To calibrate the GC-FID for optimisation of SPME extraction conditions, standard solutions of MIB ranging from 1–5 mg l^{-1} (1–5 ng μl^{-1}) were prepared in dichloromethane. A 1 μl portion of each standard solution was injected into the GC (splitless mode). From this, a calibration curve of response *vs.* the amount of MIB injected was constructed and used to calculate the percentage of MIB extracted by SPME.

For analysis of geosmin and MIB in natural waters by SPME and GC-CI/EI-ITMS the following standards were prepared. An internal standard (IS) solution in reagent water was prepared to give a solution at a concentration of 5 μg l^{-1} for both d_5-geosmin and d_3-MIB. This IS solution was prepared fresh every few weeks. Aqueous solutions of geosmin and MIB were prepared by dilution of 10 mg l^{-1} stock solutions (prepared in methanol) with the appropriate water. Calibration standards were prepared in reagent water at concentrations of 5, 10, 20, 30 and 40 ng l^{-1}.

SPME extractions

All SPME extractions carried out to optimise the extraction process were performed using the procedure described except where noted in the discussion. A 1 ml portion of a 5 μg l^{-1} aqueous solution of MIB (prepared by dilution of a 50 mg l^{-1} aqueous stock solution) was added to a 4 ml vial containing a magnetic stirrer bar (10 × 3 mm) and 0.35 g NaCl. The vial was sealed with a silicone–Teflon septum cap. The sealed vial was placed in a water-bath and stirred at 900 rpm. The various temperatures used in the extraction procedure were set using a Neslab RTE-211 Bath/Circulator (Activon, Sydney, Australia) to control the water-bath temperature. The syringe needle of the SPME device was then used to pierce the septum and the fibre extended to expose the fibre in the headspace for adsorption of the analyte. After a fixed time, the fibre was retracted back into the syringe and withdrawn from the vial.

SPME extraction of natural water samples was carried out as follows. 30 g of the water sample were weighed into a 40 ml vial containing 10.5 g of NaCl and a magnetic stirrer (20 × 8 mm); 50 μl of the internal standard mixture were added to the sample (to give 250 pg each of d_5-geosmin and of d_3-MIB) and the vial was quickly sealed with a silicone–Teflon cap. SPME extraction using a DVB fibre was performed as described earlier, with the sample heated to 60 °C using an extraction time of 20 min.

GC-FID analysis

For optimisation experiments, SPME extracts were analysed using a Hewlett Packard 5890 Series II GC with flame ionisation detection (FID). The injector port was fitted with a 0.8 mm id glass liner. A BPX5 25 m × 0.22 mm × 0.25 μm film column (SGE, Melbourne, Australia) was used. The oven temperature programme was as follows: hold at 45 °C for 1 min^{-1}; raise to 125 °C (10 °C min^{-1}); raise to 250 °C (50 °C min; hold for 2.5 min. The injector temperature was 250 °C (300 °C for the Carboxen fibres) with the split vent open after 1 min. The FID was heated to 280 °C. Hydrogen carrier gas was used at 50 cm s^{-1} at 45 °C.

GC-CI/EI-ITMS analysis

Analysis of SPME extracts of natural water samples were performed with a Varian Star 3400CX GC coupled to a Varian Saturn 2000 ion-trap mass spectrometer. A DB-5ms 30 m × 0.25 mm × 0.25 μm film column (J&W Scientific, Folsom, CA, USA) was used. The oven temperature programme was as follows: hold at 50 °C for 4 min; raise to 150 °C (10 °C min^{-1}); raise to 250 °C (25 °C min^{-1}); hold for 3 min. The carrier gas used was helium (100 kPa). A 1078 universal capillary injector fitted with a 0.8 mm id glass liner was held at 250 °C. The split vent was opened after 4 min. The transfer line temperature was 250 °C and the ion-trap temperature was 180 °C. The MS was tuned to FC-43 (perfluorotributylamine). The MS was scanned from 65–199 u every 0.5 s after the first 6 min. The SECI scan mode was used for the first 7 min of acquisition (with CH_3CN as reagent gas) and then EI for the next 8 min. The electron multiplier and automatic gain control were set automatically.

Results and discussion

Optimisation of extraction conditions

When optimising extraction conditions in any SPME method there are a number of variables which must be considered. The major factors to be considered include: extraction mode (*i.e.*, direct *vs.* headspace sampling); salt concentration; sample volume; fibre coating and extraction time and temperature. Each of these parameters were examined systematically to find the optimum conditions for extraction. Only MIB was examined because it is known to have similar adsorption properties to geosmin, and in general, geosmin is more strongly adsorbed by hydrophobic surfaces than MIB.[13,14] In optimising the extraction of the more weakly adsorbed MIB, it was thought that geosmin would be at least as efficiently extracted. Using a solution of MIB in reagent water (5 μg l^{-1}) and a 100 μm PDMS fibre, each of the above parameters (excluding the last two listed) were examined for their influence on extraction efficiency. All extractions were performed for 10 min, at ambient temperature for immersion sampling and at 40 °C for headspace sampling. The extraction efficiency was measured by calculating the mass extracted from the solution after analysis by GC-FID, which had been previously calibrated by injection of known masses of MIB.

All samples were stirred so as to produce the agitation necessary for efficient transfer of the analyte from the aqueous phase to the fibre.[15] Headspace sampling (35% extraction) proved to be more efficient than immersion sampling (12% extraction), and was further improved by saturating the sample with NaCl (50% extraction).

The efficiency of headspace extraction was also examined as a function of the sample volume at a fixed headspace : sample volume ratio (3 : 1). Not surprisingly, there was a decrease in the percentage extracted with increasing sample volume.[16] The decrease in extraction efficiency on increasing the sample volume is, however, offset by the increased mass of material available for extraction in the larger samples. Using a smaller headspace : sample volume ratio (1 : 3), more efficient extractions could be obtained at higher sample volumes, thus maximising the mass of material on the fibre. Optimum sensitivity was obtained using 30 ml of sample in a 40 ml vial.

Having established the best extraction conditions, the influence of fibre coating, and the effects of extraction time on each different coating, were examined using the conditions derived earlier (*i.e.*, 1 ml sample of 5 μg l^{-1} MIB in 4 ml vial, saturated NaCl, stirring, headspace sampling). These results, presented as adsorption time profiles, are shown in Fig. 1 and 2. The results indicate that while the PDMS fibre showed superior kinetics, this fibre gave the poorest extraction efficiency (Fig. 1). The polyacrylate fibre gave extraction efficiency intermediate to the PDMS fibre and the Carboxen or DVB fibre, but

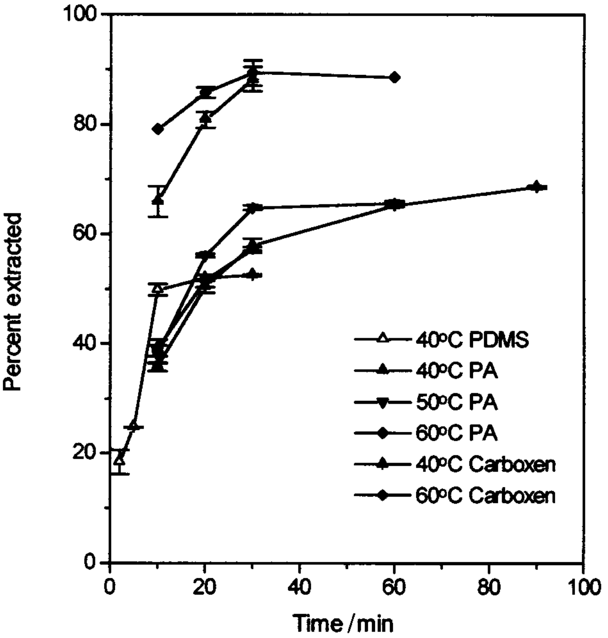

Fig. 1 Adsorption time profiles for SPME of MIB using various fibre coatings. Extraction conditions include: 1 ml of 5 μg l^{-1} solution in a 4 ml vial, saturated NaCl, stirring, headspace sampling.

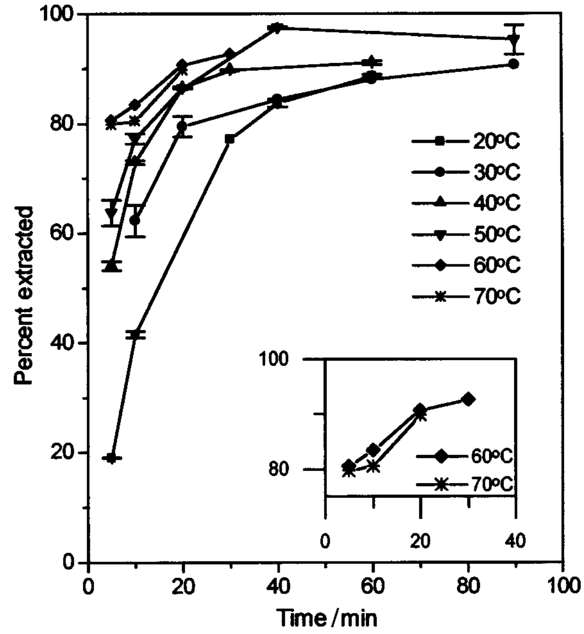

Fig. 2 Adsorption time profiles for SPME of MIB using a DVB fibre. Extraction conditions as in Fig. 1.

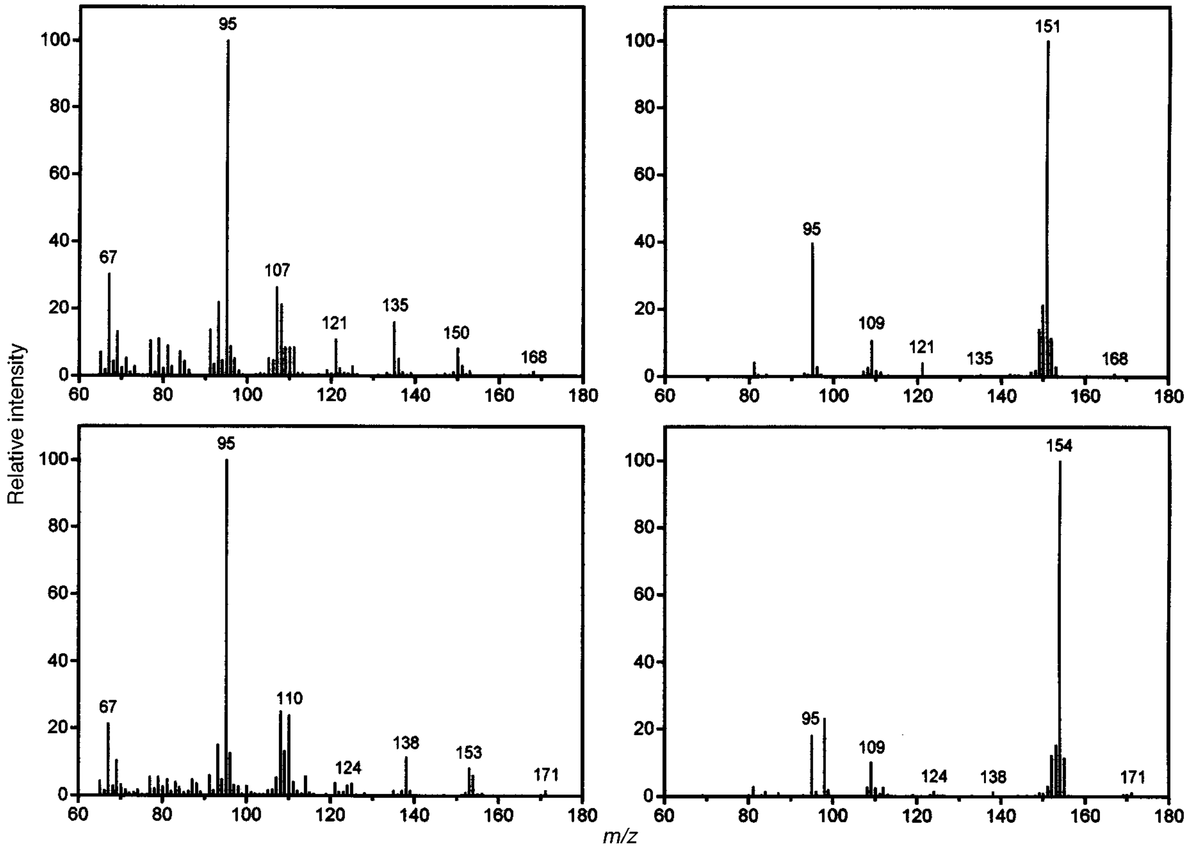

Fig. 3 EI-mass spectrum of MIB (top left) and d_3-MIB (bottom left). CI-mass spectrum of MIB (top right) and d_3-MIB (bottom right). CI reagent gas was acetonitrile.

had the poorest adsorption kinetics (Fig. 1). Both the Carboxen and the DVB fibres exhibited ≈90% extraction efficiency at equilibrium. However, since equilibrium times for these fibres were 30–40 min or more, and we desired shorter analysis times to maximise sample throughput, the DVB fibre was thought to be preferable. At shorter extraction times (< 30 min), the DVB fibre gave slightly higher extraction of MIB than the Carboxen fibre.

The effect of variation on extraction temperature is also shown in Fig. 1 and 2 for the different fibres examined. For each fibre type an optimum temperature was found, which under non-equilibrium conditions (< 30 min) gave a better percentage extraction than if higher or lower temperatures were chosen. This optimum temperature varied for each fibre type. The variation in temperature at which this occurs for the different fibres is a consequence of the variation in solute–fibre surface adsorption enthalpy and the sensitivity of both the water–headspace[17,18] and headspace–fibre[19] partition coefficients to temperature.

From the above experiments a set of optimum extraction conditions were identified. Included in the choice of optimum conditions was the extraction time. While more MIB was extracted using the DVB fibre at 50 °C than at 60 °C, this was only achieved for extraction times of 40 min or more. As shorter extraction times were desirable, it was felt that the slightly lower amount extracted after 20 min exposure at 60 °C was more than compensated for by the reduced extraction time. The optimised extraction conditions used in subsequent work are summarised as: mixing: vigorous magnetic stirring; extraction mode: headspace sampling (solution saturated with NaCl); sample volume: 30 ml sample in 40 ml vial; fibre coating: DVB; extraction time and temperature: 20 min at 60 °C.

Optimisation of GC-MS analysis

In order that analysis times could be kept to a minimum, it was decided to use a 20 min extraction time with a DVB fibre. As can be seen from Fig. 2, after 20 min extraction, the system has not reached equilibrium and so any variation in extraction time can be expected to result in some variation in the amount of geosmin and MIB extracted. To overcome this possible source of variance, deuterated internal standards[20] were incorporated into the analytical procedure.

When pre-concentration and extraction was carried out by SPME, the molecular ion signal for MIB was very weak, even at a concentration of 5 μg l^{-1}. The reason for this becomes obvious upon inspection of the mass spectra of MIB and d$_3$-MIB produced using electron impact ionisation (EI; Fig. 3). The molecular ion in each case is only a very small percentage of the total ion current. While the base peak ion at *m/z* 95 gives maximum sensitivity, this ion cannot be used because it is common to both MIB and the labelled internal standard, which are not chromatographically resolved. Further inspection of the EI spectra in Fig. 3 shows that there are more intense ion pairs (unlabelled and labelled) other than the molecular ions which might be used for quantification. Palmentier *et al.*[8] used the ions at *m/z* 150 and 153 for quantification in their analytical method. However, they pointed out that high resolution mass spectrometry was required in this case, because the signal at *m/z* 153 originates from both d$_3$-MIB and MIB and the *m/z* 153 ions from each compound are indistinguishable at low resolution.

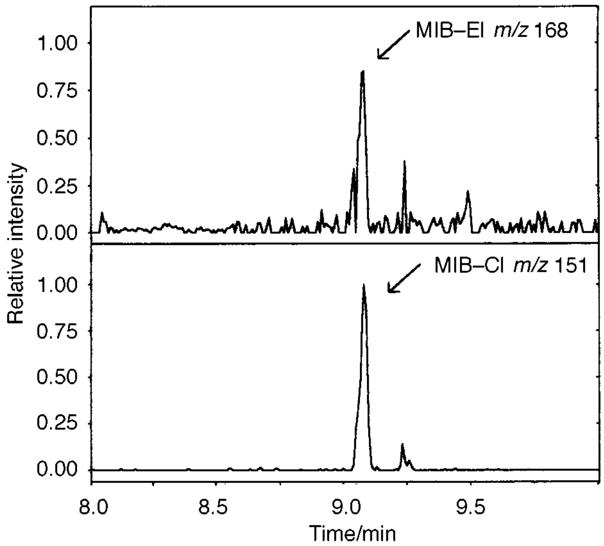

Fig. 4 Extracted ion chromatograms from SPME analysis of MIB using EI and CI ITMS detection. Portions of 1 ml of 5 μg l^{-1} solutions in 4 ml vials were extracted using a DVB fibre at 60 °C for 20 min.

Since the EI spectra of MIB and d$_3$-MIB exhibited considerable fragmentation giving primarily low molecular weight ions with loss of the label, chemical ionisation (CI) was investigated. CI is known to be a "soft" ionisation technique generally resulting in less fragmentation. In particular, CI spectra of highly branched alcohols (ROH) with greater than five carbons are known to produce very intense R$^+$ ions on loss of water from the MH$^+$ ion, especially when reagent ions with high proton affinities (weak proton donors) are used.[21] The CI spectra of MIB and d$_3$-MIB produced using acetonitrile as a mild proton donor reagent gas[22] are shown in Fig. 3. In contrast to the EI spectrum, the CI spectrum of d$_3$-MIB exhibits a base peak which is derived from an ion containing the deuterium label as desired. Using CI to generate the ions, quantification of MIB using the extracted ions *m/z* 151 and 154 could be achieved with considerably enhanced sensitivity relative to that achieved using EI and the molecular ions at *m/z* 168 and 171. The magnitude of this sensitivity enhancement can be seen in Fig. 4, which shows extracted ion chromatograms of SPME extracts from a solution of MIB produced using both EI and CI.

For the analysis of geosmin, d$_5$-geosmin was used as an internal standard. In this case, the EI spectrum of the labelled compound produced a base peak at *m/z* 114 which contained two deuterium atoms, in agreement with the fragmentation proposed by Korth *et al.*[20] The spectra produced using CI did not exhibit ions containing the deuterium label with greater intensity than the EI base peak. Therefore, quantification of

Table 1 Method data for SPME analysis of geosmin and MIB

	Geosmin	MIB
Internal standard (IS)	d$_5$-Geosmin	d$_3$-MIB
Quantification ions (Analyte/IS)	112/114	151/154
Ionisation mode	EI	CI
Calibration range/ng l^{-1}	5–40	5–40
r^{2a}	0.995	0.992
Detection limit^b/ng l^{-1}	0.8	0.9

[a] Correlation coefficient from the linear regression line for response ratio (analyte/IS) *vs.* amount ratio (analyte/IS). [b] Detection limits[23,24] were calculated as 3 × standard deviation of replicate measurements of a sample spiked at 5 ng l^{-1}.

Table 2 Recovery and precision for tap water measurements

	Geosmin	MIB	Geosmin	MIB	Geosmin	MIB
Spike concentration/ ng l^{-1}	0	0	10	10	50	50
Measured concentration^a/ng l^{-1}	ND^b	ND^b	10.0	9.5	46.5	52.0
Recovery (%)	—	—	100.3	94.5	93.0	103.9
RSD (%)	—	—	2.0	9.0	10.5	4.7

[a] Average of four repeat analyses. [b] ND = not detected = < 1 ng l^{-1}.

Table 3 Recovery and precision for reservoir water measurements

	Geosmin	MIB	Geosmin	MIB	Geosmin	MIB	Geosmin	MIB
Spike concentration/ng l^{-1}	0	0	5	5	10	10	20	20
Measured concentration[a]/ng l^{-1}	ND[b]	22.3	4.7	4.9	9.3	11.0	19.5	20.4
Recovery (%)	—	—	94.1	97.4	93.0	109.5	97.5	101.9
RSD (%)	—	14.9	6.2	5.0	9.1	1.4	11.4	6.7

[a] Average of three repeat analyses. [b] ND = not detected = < 1 ng l^{-1}

geosmin was achieved using EI and the ion pair at *m/z* 112 and 114.

It was also noted that while a desorption time of 1 min at 250 °C was satisfactory for analysis of MIB, when these conditions were used for desorption of geosmin, significant carryover was observed in the analysis of subsequent samples. By extending the desorption time to 4 min the problem of geosmin memory effects was eliminated, without the need to increase the desorption temperature and thereby shorten the life of the fibre.

SPME GC-CI/EI-ITMS analysis of natural water samples

Using the optimised SPME extraction conditions and the GC-CI/EI-ITMS conditions described in the above sections, calibration curves were constructed by analysis of reagent water samples fortified with geosmin and MIB in the concentration range in which these compounds can be expected in the environment. The details of the method are summarised in Table 1. The method detection limits of around 1 ng l^{-1} for both geosmin and MIB mean that the method can be used to detect these compounds at concentrations below their odour threshold.

The accuracy and precision of the method were examined by measuring recoveries of the compounds from both finished (tap) water and raw (reservoir) water. The reservoir water contained a background level of 22 ng l^{-1} MIB which was subtracted from the results obtained for the fortified samples to calculate recoveries. The results of these experiments are shown in Tables 2 and 3. The results show good recoveries (93–110%), indicating acceptable accuracy with concentrations at or below odour thresholds.

The reservoir water used in these recovery experiments was chosen to represent a natural water sample with a relatively high organic loading (dissolved organic carbon = 10.1 mg l^{-1}). We have noted when performing SPME analyses of geosmin, MIB and other analytes from water containing considerable amounts of other organics, that the amount extracted can be highly matrix dependent. The decrease in the amount extracted probably results from two effects. Firstly, when using a porous DVB fibre, the partitioning of the analyte into the fibre occurs by adsorption within the porous structure.[25] This means that in a system which is highly heterogeneous, such as a natural water sample, there may be significant competitive adsorption resulting in a decrease in the amount of analyte extracted. For headspace sampling this effect is, however, likely to be less important. The second effect is the likely change in the solubility of the analyte resulting from the presence of significant quantities of other organics. The presence of natural organic material (NOM) is known to significantly enhance the water solubility of non-polar organics through association with the non-polar moieties present in the NOM.[26] This will result in a decrease in the coefficient for the water–headspace partition and a subsequent decrease in the amount adsorbed by the fibre. The good recoveries of geosmin and MIB using this method even in the reservoir water with relatively high NOM content, indicate the applicability of the method for a broad range of water types.

The precision of the method was also very good, showing low relative standard deviations (ranging from 2–12%). Typically, SPME methods give 1–12% precision with concentrations generally in the high ng l^{-1} to low µg l^{-1} range.[27] These results are also comparable to those reported for the standard CLSA method, which has been shown to give mean recoveries of 105% and precision of 15% in the 4–20 ng l^{-1} concentration range.[28]

Clearly the method described above has many advantages over the current methods, such as CLSA, used for analysing geosmin and MIB in water. Detection limits are low, comparable to those obtained with CLSA, but SPME is much simpler, less labour and time intensive, and importantly is relatively inexpensive to set up and run. In addition, the method has the potential for automation, which would further increase sample throughput and decrease analysis costs.

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