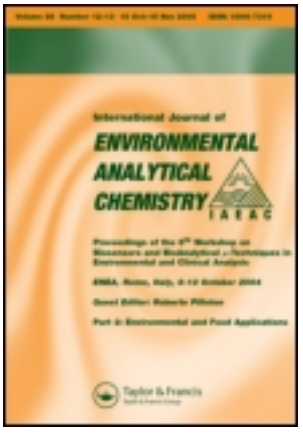

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Automated analysis of geosmin, 2-methyl-isoborneol, 2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine and 2,4,6-trichloroanisole in water by SPME-GC-ITDMS/MS

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This paper describes a method of determining the following compounds in water characterised by complex matrices (raw waters and drinking waters): geosmin, 2-methylisoborneol (2-MIB), 2-isobutyl-3-methoxypyrazine (IBM), 2-isopropyl-3-methoxypyrazine (IPM) and 2,4,6-trichloroanisole (TCA). The method is carried out using headspace solid-phase microextraction (HS-SPME) combined with gas chromatography (GC) and ion trap mass spectrometry (ITMS). Several parameters of extraction and desorption were optimised through the use of a Combi PAL autosampler to automate various tasks (temperature extraction, extraction time, stir speed). Quantities of NaCl and the liquid volume/total volume ratio were also optimised. Double fragmentation (tandem MS/MS) was optimised on the target compounds. The method resulted in good linearity obtained for concentrations of 1 to 100 ng L^{-1} and provided detection limits of approximately below 1 ng L^{-1}. Good precision (1–8%) was obtained. This method was successfully applied to the analysis of earthy and musty odours in municipal raw source waters with high concentrations of natural organic matter and in the corresponding treated waters. This is the first time MS/MS has been used to analyse odorous compounds in waters destined for human consumption. In addition, the method as developed is simple to use and lends itself to easy interpretation of chromatograms.

Keywords: off-flavour compounds; solid-phase microextraction; gas chromatography; ion trap mass spectrometry

1. Introduction

The odorant compounds most often detected in surface or drinking water are geosmin and 2-methylisoborneol (2-MIB) [1–3]. Other compounds are 2,4,6-trichloroanisole (TCA), 2-isobutyl-3-methoxypyrazine (IBM) and 2-isopropyl-3-methoxypyrazine (IPM) [4]. All of these compounds give water an earthy or musty flavour. Their olfactory threshold concentrations are very low (in the order of 10 ng L^{-1} or less) [3], resulting in a significant number of complaints from drinking water consumers [1,5,6].

Potential causes underlying the occurrence of geosmin and 2-MIB in water include the presence of cyanobacteria, actinomycetes and fungi [7]. In addition, TCA, IPM and IBM

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have also been reported to contribute to odours in water [8]. TCA is probably formed through bio-methylation of trichlorophenol [9] and IPM and IBM are metabolites of actinomycetes and soil bacteria [10]. Given this problem, the identification and quantification of these compounds is essential because their impact on customer perception is critical. In fact, many citizens abandon tap water, replacing it with bottled water, despite the fact that investments by municipalities in drinking water production have never been greater [11].

There are currently a large number of extraction processes for odorant molecules such as liquid-liquid extraction (LLE) [12], steam distillation extraction (SDE) [13], purge and trap (PT) [14], closed-loop stripping analysis (CLSA) [15] and stir bar sorptive extraction (SBSE) [16]. The most widely used method by far for the analysis of geosmin and of 2-MIB is the CLSA method. However, most of these methods require lengthy and careful sample preparation. Sometimes they require large volumes of samples (100–1000 mL) or the use of solvents. Quantities extracted during the concentration phase are sometimes low and eventually require a high-resolution mass spectrometer. For the vast majority of these methods, automation at various stages is not available at the present time. Consequently, the frequency of samples that can be analysed is limited.

Solid-phase microextraction (SPME) is a method developed by Pawliszyn and colleagues [17]. SPME is used in the extraction of a large number of odorant compounds present in water, in addition to those mentioned in this study. This method is applied with success in other fields such as water chemistry, notably in the agro-processing industry and in oenology [18]. It eliminates most of the disadvantages associated with the preparation of water samples. SPME integrates sampling, extraction, concentration and introduction into a simple process without resorting to the use of a solvent. It also requires small sample volume (15 mL in this present work), contrary to other methods mentioned previously. It can be conducted manually or by automation. The SPME method presented in this paper uses the Combi PAL autosampler type. The use of an autosampler eliminates constraints induced by various phases of the SPME by combining heating, sample stirring, penetration depth in the sample fibre and the injection in the GC column in an automated manner. Furthermore, the fact of adopting this type of autosampler serves to optimise repeatability, reduce random factors resulting from multiple human handlings and increase the number of the analysed samples. Also, the Combi PAL ensures a greater stability in extraction conditions and is very useful when a high number of samples must be analysed. Once SPME is completed, it is most often coupled with gas or liquid chromatography analysis.

According to the literature, detection and quantification of the molecules targeted in this study are generally made using a quadripole mass spectrometer (QUAD) in selected ion monitoring (SIM) mode [19]. Methods carried out on an ion-trap mass spectrometer are less common, as is the case in SIM mode or in complete spectrum (SCAN) [20]. This latter mode allows identification, but detection limits are inferior to those of other previously mentioned modes. There are some methods targeting molecules in tandem MS/MS mode carried out on an ion-trap mass spectrometer, yet their operational conditions are rarely revealed. Furthermore, the SIM mode is not always available for most ionic trap mass spectrometers and the SCAN mode does not allow threshold limits of detection as low as those obtained in the tandem MS/MS and SIM modes.

In this study, we describe a method of analysing odorant compounds in drinking water based on headspace solid-phase microextraction, (HS-SPME) automated on a Combi PAL autosampler coupled with GC-ITMS analysis with electronic impact (EI). This method

was selected mainly because MS/MS allows for enhanced selectivity and sensitivity and ensures a high reproducibility in complex matrices.

Different parameters of SPME extraction are optimised: extraction temperature, extraction time, headspace volume/sample volume ratio and stir speed. Optimisation of the SPME parameters of extraction, detection and recovery and the precision and limits of detection of the method to analyse geosmin, 2-MIB, IBM, IPM and TCA are presented. The tandem MS/MS mode is tested on the target molecules.

2. Experimental

2.1 *Reagent and materials*

Water serving to prepare the solutions used in the study was obtained by means of the Milli-Q purification system (Millipore, Bedford, MA, USA). Sodium chloride added to the samples prior to extraction was conditioned by heating at 450°C for 4 hours prior to its use. The tap water tested originated from the Quebec City (Canada) distribution system and the raw water from the St. Lawrence River, also in the Quebec City area. These waters were used as samples. Geosmin, 2-MIB, IBM, IPM and TCA standards were purchased from Supelco (Bellefonte, PA, USA). All of the standards were prepared in methanol at $100\,\mu g\,mL^{-1}$. All of the chemical products used in this project were of analytical grade.

2.2 *Apparatus*

The Combi PAL SPME autosampler model was obtained from CTC Analytics (Zwingen, Switzerland). The Stable Flex 50/30 µm DVB\CAR/PDMS SPME type fibres were obtained from Supelco (Bellefonte, PA, USA). The fibres were conditioned according to manufacturer instructions at 250°C for 1 hour in the port provided for this purpose on the Combi PAL autosampler. The choice of these fibres was made based on available literature [15–17]. The analyses were performed on a Varian 3900 gas chromatography attached to a Varian mass spectrometer (Walnut Creek, CA, USA) Saturn 2100T in tandem MS/MS mode. Table 1 presents the parameters of the mass spectrometer in tandem MS/MS mode for each of the analytes. A 30-m long and 0.25 mm internal diameter DB-5 capillary column (silicon film thickness of 0.25 µm) from J&W Scientific (Folsom, CA, USA) was used. The oven temperature was maintained at 60°C for 2 min and raised to 200°C at $5°C\,min^{-1}$, for a total runtime of 30 min. The carrier gas was 99.9995% helium, delivered at a constant flow of $1\,mL\,min^{-1}$. A 1079 universal capillary

Table 1. Parameters for mass spectrometer (MS/MS mode) for the determination of analytes.

Compound	Retention time (min)	Segment (min)	Quantitative ion MSMS (m/z)	Parent ion (m/z)	Excitation storage level (m/z)	Excitation amplitude (V)	Scan (m/z)
IPM	12.9	12.5–13.5	109	137	60.2	56	50–150
IBM	15.5	15–15.8	95	124	54.5	53	50–150
2-MIB	16.1	15.8–16.5	67	95	41.6	0.30	50–150
TCA	19.9	19.5–20.5	169	196	86.3	0.63	50–200
Geosmin	22.3	22–23	97	112	49.1	37	50–150

injector fitted with a 0.75 mm internal diameter low-volume glass liner was held at 260°C for 3 minutes in splitless mode. Then the split was opened at 10 : 1. The transfer line was set at 250°C and the ion trap at 200°C. The ion-trap mass spectrometer was used in EI positive mode (70 eV) and the perfluorotributylamine (FC-43) was used to obtain the best work sensitivity with the automatic gain control (AGC).

2.3 *SPME procedure*

For the purpose of optimising extraction conditions, experiments were conducted to observe the impact of the extraction temperature, exposure time, sample volume, stir speed during extraction and the quantity of added NaCl. Parameters such as mode of extraction and choice of fibre were selected based on available literature [4,19].

For each optimisation test of the extraction parameters, four replicates containing 100 ng L^{-1} of geosmin, 2-MIB, IBM, IPM and TCA were analysed. The analyses were conducted in SCAN mode. When optimum parameters of extraction were found, optimisation of detection was made in tandem MS/MS mode.

The first experiments in the optimisation of extraction were conducted with 20 mL vials containing 10 mL of standard solutions, to which was added 3 g of NaCl. The extraction time was 20 min and the stir speed was 250 rpm. Optimisation dealt with the extraction temperature. The following temperatures were tested: 40, 50 and 60°C. Then four periods of exposure of the fibre were tested: 20, 40, 60 and 80 min. Following this, the headspace/sample volume ratio was tested for a constant vial volume of 20 mL. Then 1/2 and 1/4 ratios were explored. The quantity of NaCl and the stir speed were also optimised: 3 g and 5 g of NaCl were tested in 20 mL vials containing 10 or 15 mL of standard sample. Two stir speeds were tested: 250 rpm min^{-1} and 500 rpm min^{-1}.

2.4 *Tandem MS/MS procedure*

The steps in the tandem MS/MS process involve ionising analytes using CI or EI, isolating parent ions (like SIM or SIS) and dissociating parent ions. Dissociating parent ions consists of a collision with an inert atom (He). Collision energy must be determined experimentally using the automating method development (AMD). Ions produced are analysed using the same procedure as with collection of a full-scan mass spectrum. In this work, we used EI mode to ionise analytes. All final parameters are presented in the results and in Table 1.

3. Results and discussion

3.1 *Optimisation of extraction conditions*

3.1.1 *Extraction mode (DI or HS)*

Two modes of extraction are available when using SPME, direct immersion (DI-SPME) and headspace (HS-SPME). The different resides in either direct contact or no contact with the aqueous medium. The choice of HS-SPME or DI-SPME mode depends on the molecules to be analysed. A study conducted by McCallum *et al.* [17] dealing with geosmin and 2-MIB showed the greater efficiency of the headspace mode compared to the DI mode. HS sampling (35% of extraction) proved to be more efficient than DI

sampling (12% extraction). The addition of NaCl even increased extraction to 50% in HS-SPME. It should be noted that the fibre used is of the PDMS-DVB type for an extraction time of 20 min at 60°C. More recently, the same type of study was conducted by Zhang *et al.* [19] on geosmin, 2-MIB and TCA but with a DVB/CAR/PDMS fibre for 30 min at 60°C. Zhang *et al.* [19] showed that the HS-SPME mode is 30% more efficient than the DI-SPME mode for 2-MIB and TCA, and that this efficiency can be up to 10 times greater with regard to geosmin.

3.1.2 *Choice of fibre*

The choice of fibre for the extraction is important because the affinity of analytes with the fibre varies on the basis of their composition. McCallum *et al.* [20] tested several fibres for the extraction of 2-MIB and geosmin with exposure times of 30 min. Polydimethylsiloxane/divinylbenzene fibre (PDMS/DVB) and the fibre in polydimethylsiloxane/carboxene (PDMS/CAR) have extraction efficiencies quite superior to those of polydimethylsiloxane (PDMS) alone, or polyacrilate (PA). The percentages extracted by PDMS and PA are approximately 50% and 90% for PDMS/DVB and PDMS/CAR. On the other hand, with shorter exposure times (<10 min), the PDMS has extraction kinetics much faster than the other fibres. More recent studies undertaken by Sung *et al.* [4] and Zhang *et al.* [19] compared the extraction efficiency of geosmin, 2-MIB, IBM, IPM and TCA with new fibres. Thus, the divinylbenzene/carboxene/polydimethylsiloxane (DVB/CAR/PDMS) fibre was compared with those mentioned in the previous study. It appears in the studies of Sung *et al.* [4] and those of Zhang *et al.* [19] that the DVB/CAR/PDMS fibre is far from the most efficient when the extraction time is 30 min or greater, at an extraction temperature of 50°C.

3.1.3 *Effect of the extraction temperature*

Extraction temperature plays an important role on the extraction of analytes because it influences the quantity of analytes transferred onto the SPME fibre by means of two equilibriums: the partition coefficient of the analytes between the gaseous phase and the aqueous phase and the equilibrium existing between the fibre and the gas phase [21]. Therefore, it is important to heat sufficiently in order to increase the proportion of analytes in the gas phase; but at the same time, one must not overheat the analytes adsorbed into the fibre, otherwise they are desorbed.

The literature provides different optimal values of extraction temperatures for the analytes chosen. Some like Sung *et al.* [4] promote a temperature of 50°C for an exposure time of 30 min with a DVB/CAR/PDMS fibre, whereas a publication by Supelco [22] recommends a temperature of 65°C for the same exposure time as for the same fibre. Finally, Penton [18] recommends a temperature of 40°C to best extract TCA in wine. Figure 1 shows that among these three extraction temperatures, the optimum temperature seems to be 60°C, which corresponds to the average temperature recommended in scientific literature.

3.1.4 *Effect of the fibre run through time*

Analyte extraction efficiency increases with the exposure time of the fibre until equilibrium is reached. We studied extraction times between 20 and 80 minutes.

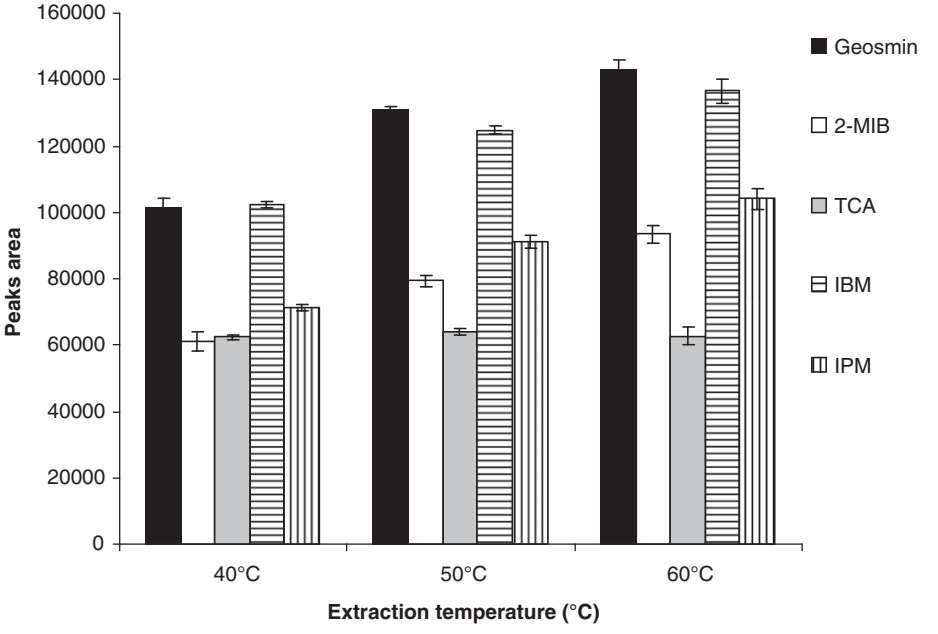

Figure 1. Relative extraction efficiencies of *musty and earthy* compounds for three different extraction temperatures. Concentration, 100 ng L^{-1}; extraction time, 20 min; desorption temperature, 250°C; desorption time, 2 min; stirring rate, 250 rpm.

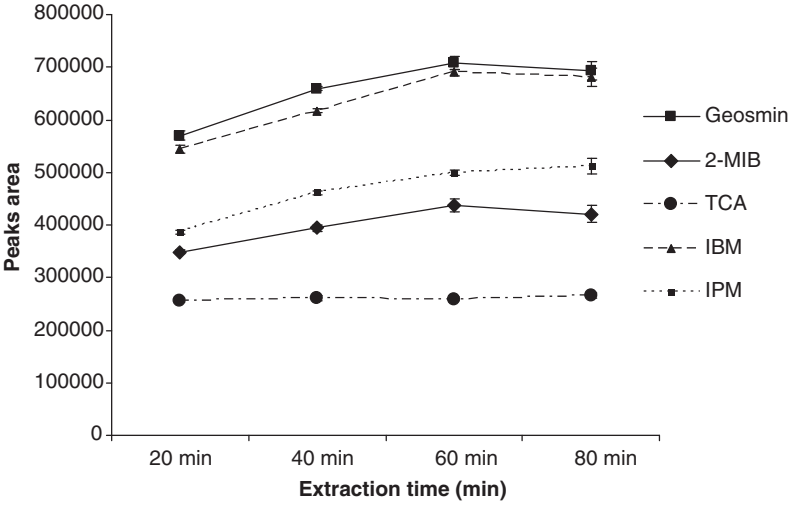

Figure 2. Relative extraction efficiencies of *musty and earthy* compounds for different extraction times. Concentration, 100 ng L^{-1}; extraction temperature, 60°C; desorption temperature, 250°C; desorption time, 2 min; stirring rate, 250 rpm.

As illustrated in Figure 2, at a run through time of 60 min, we nearly approached equilibrium for most of the analytes. However, the objective of the method is to achieve optimum performances in the shortest possible time. The run through time selected was 60 min.

3.1.5 *Effect of the headspace volume/sample volume ratio and NaCl mass*

The headspace volume/sample volume ratio plays an important role in the partition coefficient of the analytes between the gaseous and liquid phases. An increase in sample volume decreases the percentage of analytes extracted. McCallum *et al.* [20] propose a ratio of 1/3 as being the optimum for sensitivity (which corresponds to a 30 mL sample for a 40 mL vial with 10.5 g of NaCl). Lloyd *et al.* [23] indicate that the optimum headspace volume/total volume should be 25% or less. Sung *et al.* [4] propose a vial volume of 60 mL containing 45 mL of sample with 30% of NaCl used to saturate the liquid phase and send the analytes in the gaseous phase.

In our study 20 mL vials were used because this is required for the Combi Pal autosampler. Various tests were conducted, with 10 mL and 15 mL samplings placed in the 20 mL vials. Tests were carried out with the addition of 3 or 5 g of NaCl under various stir rates (250 and 500 rpm). It appears quite clear that a volume of 15 mL with 5 g of NaCl mixed at 500 rpm achieves superior extraction conditions than other conditions. This is in agreement with Sung *et al.* and McCallum *et al.* [4,20].

3.1.6 *Effect of the desorbing temperature and desorbing time*

The desorbing temperature and desorbing time were selected from the literature, in particular the study of Sung *et al.* [4] recommending a temperature of 265°C. However, other authors suggest 250°C [19,24]. A temperature of 260°C was selected for desorption at the injector level. The desorbing time was the one recommended by Sung *et al.* [4], i.e. 3 minutes.

3.2 *Tandem MS/MS optimisation*

Tandem MS/MS optimisation was conducted using AMD to find the best parameters. In AMD, different parameters must be optimised: scan time, multiplier voltage, emission current, excitation storage level and excitation amplitude.

The aim of AMD is to find the parameters that fragment parent ions into products. In the final spectra, parent ions should be present at approximately 5% and product ions should have an intensity of 100%. At the onset, the scan time was established at 0.1 s/scan, the multiplier voltage at 200 V and the emission current at 50 μA [24].

The excitation storage level was calculated using the MS 'q' calculator for the ion parent m/z. The best excitation amplitude was found by looking at the spectra. As mentioned above, parent ions should be present at approximately 5% and daughter ions should have an intensity of 100%. When all the excitation amplitudes were determined, the optimisation was completed and we conducted the analysis in MS/MS mode retaining the AMD parameters except for the scan time, which was set at 0.55 s/scan.

All of the parameters are presented in Table 1. The chromatograms of Figure 3 show that the chromatographic resolution and the shape of the peaks are perfectly acceptable. The comparison of MS scan and MS/MS (Figure 3) shows definite proof of the benefits of the latter, in particular with regard to its capacity to improve the resolution and the interpretation of the chromatographic picks.

3.3 *Detection limits of the method, precision, linearity and comparison with the literature*

Optimum conditions of extraction and of desorption are as follows: a Stable Flex PDMS/CAR/DVB fibre; extraction temperature of 60°C; extraction time of 30 min, a stir speed

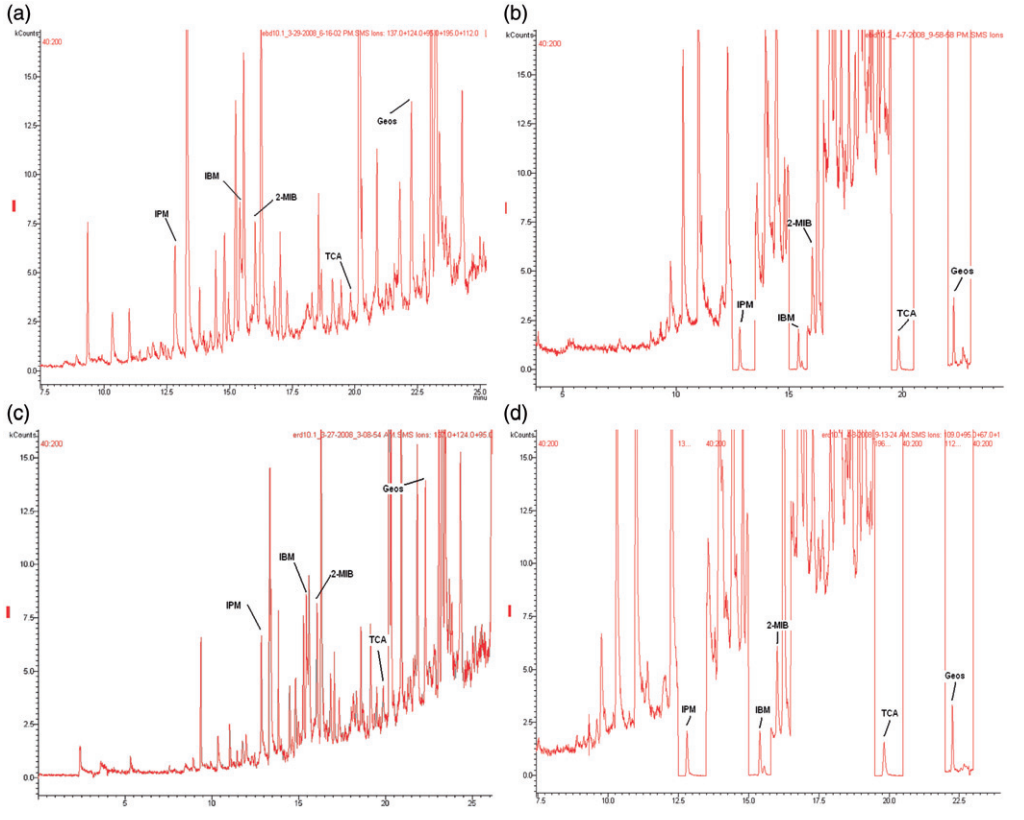

Figure 3. Comparison between MS scan and MS/MS chromatograms in tap water and raw water. (a) Raw water spike 10 ng L^{-1} (MS scan); (b) Raw water spike 10 ng L^{-1} (MS/MS); (c) Drinking water spike 10 ng L^{-1} (MS scan); and (d) Drinking water spike 10 ng L^{-1} (MS/MS).

rate of 500 rpm; desorbing temperature of 260°C; desorbing time of 3 min; vial volume of 20 mL; liquid volume of 15 mL; NaCl mass of 5 g. The coefficient of determination (R^2), precision (RSD), and limits of detection of the method as well as the recovery in drinking water and in natural water are indicated in Tables 2 and 3.

The precision calculation is based on the USEPA SW-846 method. It was calculated as being three times the standard deviation of seven replicas of a standard solution (5 ng L^{-1}). Relative standard deviations are included between 1% and 8%. The linearity of this method for the analysis of musty and earthy odours was evaluated over a range of 1 to 100 ng L^{-1}. Correlation coefficients exceeded 0.997 (Table 2). The detection limits of the method were calculated (based on the weakest analysed concentration, 5 ng L^{-1}) as three times the standard deviation of seven replicas made from deionised water (Table 2).

As a comparison, the method conducted by McCallum *et al.* [20] in HS-SPME with detection on GC-ITMS and ionisation by electronic impact for the geosmin and chemical ionisation (CI) with acetonitrile for the 2-MIB achieved detection limits in the order of 1 ng L^{-1} for the two compounds. The use of CI in the McCallum *et al.* [20] method is due to the necessity of introducing an internal standard to compensate for the extraction time of 20 min at 60°C, which is lower than the time needed to reach equilibrium. The type of

Table 2. Coefficient of determination (R^{2a}); relative standard deviation (R.S.D.)[b]; and method detection limits (MDLs)[c] for the analysis of earthy and musty odours compounds in deionised water with headspace SPME-GC-ITDMSMS.

Compound	$(R^2)^a$	RSD[b] (%)	MDL[c] (ng L^{-1})
IPM	0.998	5.3	0.7
IBM	0.999	4.5	0.6
2-MIB	0.997	7.5	1.4
TCA	0.998	15	2.4
Geosmin	0.999	3.2	0.4

Notes: [a]Calibration curves with compounds concentration: 1, 5, 10, 20, 50, 75, 100 ng L^{-1}.
[b]RSD is obtained by seven replicats runs of sample.
[c]MDLs are calculated as three times the standard deviation of seven replicated runs of sample (without internal standard).

Table 3. Concentration and recovery of earthy and musty odours compounds in tap water and river water.

		Tap water		River water	
Compound	Concentration added (ng L^{-1})	Concentration measured (ng L^{-1})	Recovery (%)	Concentration measured (ng L^{-1})	Recovery (%)
IPM	0	ND[a]	–	ND[a]	–
IBM	0	ND[a]	–	ND[a]	–
2-MIB	0	ND[a]	–	ND[a]	–
TCA	0	ND[a]	–	ND[a]	–
Geosmin	0	ND[a]	–	2.1	–
IPM	10	8.4	85	9.5	95
IBM	10	9.0	90	9.3	93.5
2-MIB	10	8.1	80	7.9	80
TCA	10	8.9	90	9.9	99.5
Geosmin	10	9.8	99	11.8	97
IPM	50	43.9	88	43.9	88
IBM	50	46.3	93	47.4	95
2-MIB	50	38.9	78	39	78
TCA	50	49.5	99	52.7	105
Geosmin	50	48.9	98	52.3	100

Notes: [a]ND: not detected.

fibre used was polydimethylsiloxane/divinylbenzene (PDMS/DVB). Detection on an ion-trap detector was performed in SCAN mode. The recovery of the analytes on natural water and tap water was between 93% and 110% with a precision of 2% to 12%. It should be noted that SPME extraction was carried out manually.

More recently, a method developed by Sung *et al.* [4] in SPME-GC-MS in SIM mode on an ion-trap mass spectrometer was used to analyse geosmin, 2-MIB, TCA, IBM and IPM with detection limits between 0.34 and 0.59 ng L^{-1}. The fibre used was DVB/CAR/PDMS, extraction occurred at 50°C for 30 min in a 60 mL vial containing 45 mL

and 30% of NaCl. The precision of the analysis was between 8% and 20% without an internal standard and between 5% and 10% with an internal standard (internal standard: IBM).

Detection limits and the precision obtained in the tandem MS/MS mode with a Combi PAL autosampler for the SPME extraction were similar in the case of geosmin, 2-MIB, TCA, IBM and IPM, to the results obtained in SIM mode by Sung *et al*. [4].

3.4 *Recovery and applicability to drinking water and natural water*

Application of the method to drinking water from a distribution network and to natural waters (raw water) is feasible, since recoveries ranged between 80% and 105% (Table 3). This suggests that the proposed method, which is based on a simple calibration curve, may be used routinely to analyse musty and earthy odours in samples of drinking water and river water. Recoveries were calculated based on the average of four replicas at 10 and 50 ng L^{-1} in drinking water and in water from the St. Lawrence River. As shown in Table 3, IPM, IBM, 2-MIB and TCA were not detected in the drinking water and natural water. On the other hand, geosmin was detected in the river water.

As shown in Figure 3, the identification of the analytes in the real water (drinking and natural) was based on the retention time of various analytes, as well as by the mass spectrum.

4. Conclusions

The method presented in this paper is simple. Given the automation of tasks by means of the autosampler, a large number of samples may be analysed in series. Moreover, the Combi Pal allows standardisation of the tasks and enhances reproductibility.

Many parameters of extraction were studied and optimised (temperature and time of extraction, volume headspace ratio: sample, NaCl mass, shaking). Other, non-optimised parameters (injector temperature, desorption time, choice of fibre) were chosen based on a rigorous analysis of the literature. The tandem MS/MS mode was also studied and optimised. This method allows proper linearity over a range from 1 to 100 ng L^{-1} and provides detection limits at approximately below 1 ng L^{-1} for IBM, IPM, TCA, 2-MIB and geosmin. Good precision was obtained (1–8%).

In summary, this method allows great sensitivity for the analysis of musty and earthy smelling odorant compounds found in drinking water and natural waters characterised by a complex matrix.

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