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Trace Analysis of Taste-Odor Compounds in Water by "Salt-Free" Purge-and-Trap Sampling with GC-MS Detection

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Abstract

A novel, fully validated, purge-and-trap sampling method, with gas chromatography-mass spectrometric detection for simultaneous quantitation of geosmin (GSM) and 2-methylisoborneol (2-MIB) was developed. The procedure involved purging a 25 mL sample volume, containing 1% (v/v) methanol, at 60°C for 20 min. Quantitation was done by separation on an HP 5-MS capillary column (30 m x 0.25 mm x 0.25 μm), followed by mass spectrometric detection in the selected ion monitoring (SIM) mode and a multiplier voltage of 400 mV above the auto tune setting. The method was reproducible (RSD <15%) and linear ($r^2 \geq 0.995$) over the calibration range (5-100 ng/L). The relative recoveries of analytes from potable and raw water were between 80 and 120%; limits of quantitation (LOQ) achieved were 4 ng/L and 7 ng/L, for GSM and 2-MIB, respectively.

Keywords: Purge-and-trap; Salt-free extraction; Geosmin; 2-methylisoborneol; Gas chromatography-mass spectrometry; Methanol

Introduction

Geosmin (GSM) and 2-methylisoborneol (2-MIB) (Table 1), semi-volatile compounds produced by a wide range of aquatic and blue-green algae species, contribute to the earthy-musty taste and odor problems of water supplies [1].

The odor thresholds reported for these compounds in water range from 1-10 and 5-42 ng/L (Table 1), for GSM and 2-MIB respectively [2-4]. Sensitive analytical methods for their determination in water are therefore required to detect and quantitate values at this low ng/L level.

These compounds are saturated tertiary alcohols. Due to their hydrophilic nature, gas chromatographic analysis has been the preferred method of choice [5,6]. The latter, in combination with mass spectrometric detection, offers excellent sensitivity and selectivity [2]. Other detectors, like flame ionization [7], atomic emission [8], electron-capture [9] and olfactometry [10], have also been reported.

Regarding the extraction of 2-MIB and GSM from water samples, various extraction methods in the analysis include closed loop stripping analysis [11], solvent (liquid-liquid) extraction [12,13], or micro extraction [5], solid phase micro extraction with headspace [14], stir bar sorptive extraction [15] and solid phase extraction [16]. Some of these are time-consuming, labor-intensive, are complex for sample preparation or analysis or have poor sensitivity.

Purge-and-trap is a fairly rapid sample concentration-extraction technique. To date, there are comparatively fewer reports on the purge-trap extraction of 2-MIB and GSM [7,17-19]. Salting out of organic compounds by addition of sodium chloride has been used to maximize extraction of organic compounds from water matrices, leading to increased sensitivity. However, use of the latter can lead to salt build-up, blockage and corrosion of the sample pathway valves, lines, needles and sparge vessel. To date, there are no reports on purge-and-trap analytical methods that are based on 'salt-free' extraction. Furthermore, the absence of adequate method detail regarding the purge-trap parameters for published analytical procedures, and comprehensive method validation data, is noted.

Umgeni Water is the largest bulk potable water supplier in KwaZulu-Natal, South Africa, with a testing facility accredited in terms of ISO/IEC 17025. Taste and odor problems tend to be a frequent occurrence in the warm summer months in the Umgeni Catchment areas, in the province of KwaZulu-Natal, making routine monitoring of GSM and 2-MIB absolutely essential due to aesthetic implications for consumers. Our current liquid-liquid extraction method, with gas chromatography-mass spectrometry, was shown to give erratic results, as noted with the recoveries obtained on the quality control samples. The unavailability of a rapid, accurate and precise, fully validated test method prompted this research. It was anticipated that the purge-and-trap technology would be a much faster sample extraction technique for analysis of these odorants in water. A novel, fully validated, salt-free extraction procedure, is reported that has been found to be sensitive, accurate, and precise, with a scope applicable to raw and potable water samples.

Experimental

Chemicals and consumables

(±)-Geosmin (2 mg/mL) and 2-MIB (10 mg/mL) in methanol, of greater than 98% purity, were obtained from Sigma (St. Louis, USA) [21].

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HPLC grade methanol was obtained from Merck Darmstadt. Ultrahigh purity helium gas (99.999%) for GC-MS was obtained from Air Products, Durban, South Africa. Water was obtained from a Milli-Q (MQ) (MILLIPORE) water purification system (Millipore, USA). The conductivity was on average 0.054 μS/cm (range: 0.048-0.060 μS/cm). Filter membranes (MILLIPORE, 0.45 um, 47 mm, Cat. No.: HAWG047S6) was obtained from Microsep, agents for Waters, South Africa. The Tenax 12" trap (U-shape, (#1) Tenax, Part # 12-0083-403), and the Proprietary # 9 trap, was obtained from LabHouse (South African agents for Teledyne Instruments, USA). The Supelco split liner (Part number: 2-0510, 05) was obtained from Capital Lab Supplies CC, South African agents for Supelco.

A suitable internal standard, cis-decahydro-1-naphthol [19], or naphthalene-d8 and biphenyl-d10 [21] was considered but was not available timeously at the time of the investigation; it was omitted. All experiments, method development and validation were conducted using the external calibration procedure.

However, the validated recovery of this method was on average acceptable at 95%. Future work must include its additional application to monitor recovery of the target analytes.

Standard solutions

A composite standard of 1 mg/L of GSM and 2-MIB in methanol was prepared from the commercial methanol solutions of Geosmin stock 2 mg/mL and the 2-MIB stock 10 mg/mL. This solution is stable for 6 months on storage at -20°C.

A working composite standard of 1 ug/L in MQ water was prepared from the above composite standard. This solution is stable for 5 days at ± 4°C.

Aqueous calibration standards, of concentration: 5, 10, 15, 20, 30, 50 and 100 ng/L, were prepared daily in MQ water, containing 1% (v/v) methanol, from the working standard. A MQ blank (0 ng/L) was used to check for any contamination.

Analytical quality control (AQC) samples were prepared at a suitable concentration (30 ng/L), falling within the calibration range, in Milli-Q water.

Samples

The reported procedures were used as a guide [22-24]. Grab, potable water samples, collected into 1 or 2 L glass bottles, were used directly. Raw water samples were filtered through a 0.45 μm (47 mm diameter) standard HPLC filter membrane prior to purging. Samples were analyzed immediately on receipt, or were stored, without any preservative, at ± 4°C overnight if necessary.

Purge-and-trap method

A commercial TELEDYNE TEKMAR purge-and-trap sample concentrator (Stratum model) coupled to a TELEDYNE TEKMAR AQUATEK 70 Vial Auto sampler (TEKMAR, USA) was used, which automatically dispensed 5-25 mL aliquots of water sample into a 25 mL fritted purging device (sparger).

A "wash" cycle for the purge-and-trap extractor and auto sampler, between GC-MS runs used hot water (90°C) for cleaning, and the trap was baked at 230°C for 8 min. These processes were adequate to reduce carryover of the technique to a negligible level. Detailed conditions are presented in Table 2.

GC-MS conditions

GC-MS Analyses were performed on an Agilent gas chromatograph 7890A equipped with an electronically controlled split/splitless injection port, a Supelco split liner and interfaced to a 5975C Inert mass-selective detector. The conventional GC separation employed a HP5-MS column, of dimensions 30 m x 0.25 mm x 0.25 μm. Helium was the carrier gas. Each compound was quantified based on peak area using one target ion and the presence of 3 qualifier ions. Acquisition was also performed in scan mode from 40 to 300 amu for identification purposes using the 1000 ng/L Working Standard. Detailed conditions are presented in Table 2. Table 3 reports the elution time of these compounds and their mass spectral characterization at four different ions.

Results and Discussion

Development and optimization of analytical aspects of method

Table 1 contains the most commonly accepted threshold values of these two compounds. According to low odor threshold concentrations reported, sensitivity is one of the most important performance parameters of a method for analysis of water odorants, beside selectivity.

Both compounds are saturated, tertiary alcohols; they are hydrophilic and not readily purged. Various reports indicate the use of sodium chloride as a "salting technique" to facilitate maximum extraction of these organic compounds from water matrix [18,19,22]. However, the latter was not tested due to advice from the Tekmar agent. The potential for sodium chloride leaks into the transfer line, leading to plugging of tubing and valves, as well as subsequently faster deterioration of the trap has cost implications for remediation of these resultant problems.

A combination of standards made in organic solvent (acetone, methanol, dichloromethane), injected by the GC liquid autosampler, and in water, extracted by the purge-and-trap, was both used to optimize all parameters.

Optimization of the GCMS conditions: Retention times were established by both injections of suitable liquid methanol standards that were analyzed by standard GC-MS and by comparison with library spectra from the Chemstation software. A relatively higher concentration of an aqueous standard (1000 ng/L) was analyzed by purge-and-trap.
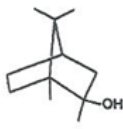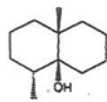
Compound	Structure	Odor threshold (ng/L)
2-MIB		9-42 [2-4] 5-10 [2-4]
GSM		4-10 [2-4] 1-10 [2-4]

Table 1: Structure and threshold concentration of taste-odor compounds in water.

Injection technique: A pulsed split injection technique was chosen to maximize efficient transfer of the analytes to the GC column. It was noted that a low split ratio of 2:1 was found to give maximum peak area response for the target analytes. The use of 240°C compared to the reported 200°C [18] was found to be optimum.

Mass spectrometer acquisition: The selected ion monitoring mode (SIM) was chosen. In SIM mode only a few selected ion fragments are monitored and overall detector sensitivity is maximized. An injection of a 1000 ng/L composite standard was made with the MS in scan mode to determine analyte retention times and the best ions for SIM mode. Validation studies initially included comparison of four ions per analyte Table 3. It was found that ion 95, for 2-MIB, and ion 112, for GSM gave optimum linearity, accuracy and precision.

Effect of dwell time: Dwell times were varied in 50 msec increments to optimize area precision (Table 3).

The method validation parameters (specificity, selectivity, linear range, accuracy, precision, limit of detection and quantitation) were then determined. All results are based on the response for ion 95 and 112 for 2-MIB and GSM respectively. Qualitative identification was based on retention time analysis. Mass spectral verification was done by comparison of relative abundance values of the quantification and qualification ions to the same values obtained from the standard samples.

Optimization of the purge-and-trap parameters: Standard USEPA purge-and-trap conditions for volatiles methodology [23] was initially used as a guide.

Sample size: Most USEPA methods are designed for 5 mL samples. A 25 mL sample aliquot was used and a fritted sparge vessel was chosen for more efficient purging.

Effect of trap: A Proprietary # 9 trap was initially used [25]. Overall

Variable	Value	Variable	Value
Purge-trap:			
Valve oven temperature	140°C	Dry purge flow	100 mL/min
Transfer line temperature	140°C	GC start	Start of desorb
Sample mount temperature	90°C	Desorb preheat temperature	175°C
Purge ready temperature	45°C	Desorb drain	On
Sample preheat time	1 min	Desorb time	4 min
Sample temperature	60°C	Desorb temperature	180°C
Purge time	20 min	Desorb flow	400 mL/min
Purge temperature	0°C	Bake rinse	On
Purge flow	35 mL/min	Number of bake rinses	3
Condenser ready temperature	40°C	Bake drain time	0.80 min
Condenser purge temperature	20°C	Bake drain flow	300 mL/min
Rinse loop time	3 min	Bake time	8.00 min
Purge loop time	1.40 min	Bake temperature	230°C
Dry purge time	3.00 min	Bake flow	200 mL/min
Dry purge temperature	20°C	Condenser bake temperature	200°C
GC-MS:			
GC		MS	
Oven:		Mode	EI/SIM
Helium gas flow	1 mL/min	Electron energy	70 ev
Initial temperature/time	40°C/3 min	Emission current	34.6 µA
Ramp rate 1	5°C/min	EM volts	Atune + 400
Final temperature 1/final time 1	160°C/2 min	Transfer line temperature	280°C
Ramp rate 2	20°C/min	Source temperature	230°C
Final temperature 2/final time 2	280°C/2 min	Quadrupole temperature	150°C
Injector:		Solvent delay	13 min
Injector mode	Pulsed (23 psi), Split (4 min)		
Split ratio	2:1		
Injector temperature	240°C		

Table 2: Purge-and-trap, and GC-MS parameters.

Compound	t_R (min)	Retention window (min)	Quantitation ion (*m/z*) (dwell time)[a]	Qualifier ions (*m/z*) (dwell time)[a]
2-MIB	17.474	13.00- 20.00 [b]	*95* (400)	*107* (300) *108* (100) *135* (400)
GSM	23.567	20.00-25.00	*112* (100)	*97* (450) *111* (350) *125* (300)

[a] In msec
[b] Solvent delay of 13 min.

Table 3: Details of the GC-MS program for the assay.

precision and accuracy, by recovery study, was 28% and 36-152% respectively, for the ions m/z 95 or 107, and 112, for 2-MIB and GSM. Significant improvement in these two parameters was noted on the use of the #1 Tenax trap.

Effect of purge cycle temperature: The recommended [18] temperature of 80°C was initially used to heat samples during the purge cycle.

Effect of purge cycle time: A purge time of 20 minutes was found to be optimum as compared to the reported time of 11 minutes [18].

Effect of purge cycle flow of helium gas: The flow rate of 40 mL/min was initially tested but it was later found that 35 mL/min was optimum.

Effect of trap desorb time: A time of 4 min was found to be optimum.

Effect of addition of methanol: It was found that addition of methanol, not exceeding 1% by volume, to the water sample had the most significant effect and led to increased sensitivity (peak area counts), without significantly affecting chromatographic peak shape. The latter addition necessitated the lowering of the purge temperature from 80 to 60°C to prevent evaporation of methanol.

This effect is simply illustrated in Table 4. Three calibration standards in MQ water were prepared, without methanol and with 1% (v/v) methanol added. A simple 3-point calibration curve was plotted and regression statistics determined. The gradient m (sensitivity) is greater in the case of methanol addition. For a given calibration standard concentration, a relatively increased area response was noted for both analytes, resulting in the steeper slope (m) of the corresponding graphs. Use of the determetion of signal: noise ratios were not as effective in showing differences.

Initial work also involved the use of the following percentage of methanol, using the Number # 9 proprietary Trap: 1, 2, 3, 4 and 5% (v/v). Using a 100 ng/L composite standard in MQ water, it was noted that, for methanol percentages > 1% (v/v), especially for 4% and 5% (v/v), the peak shape and symmetry of the extracted ion of m/z 112 for GSM began to exhibit tailing and asymmetry. There was also reduced sensitivity as noted by reduced peak height for m/z 112 for GSM.

Other alcohols were also briefly investigated, on the Number 9 Proprietary Trap : iso-propanol, and Butanol. For the use of 4% (v/v) Butanol, there was significant shift in retention times of both compounds, eluting much later; it was also difficult to confirm their exact elution times, on the SIM mode.

A similar, 3-point calibration was not done for these methanol percentages above 1% (v/v), or for the other alcohols, that were briefly investigated.

Method validation criteria

Analysis of blanks: Evaluation of MQ water (calibration standard 0 ng/L), over more than a year, and also checked between standards and real samples run, indicated average values of well below the LOQ for 2-MIB and GSM respectively.

Specificity/selectivity: An extracted sample of potable water, and the same matrix (sample) spiked with target compounds at concentration of 30 ng/L showed that there were no interfering peaks from the sample matrix (Figure 1). The unspiked sample showed 2-MIB and GSM at 17.469 and 23.583 min and the spiked sample showed 2-MIB and GSM at 17.469 and 23.563 min, respectively.

The retention times, determined over 10 days, averaged 17.474 ± 0.024 min (RSD = 0.57%) and 23.567 ± 0.009 min (RSD = 0.04%) for 2-MIB and GSM respectively (Figure 1).

Effect of matrices: Raw water (dam and river) matrix, containing 1% methanol, was spiked with both target analytes at concentrations of 0, 5, 10, 20, 30, 50 and 100 ng/L. A plot of spiked analyte concentration versus analyte response, afforded the following equations: $r^2 = 0.999$ (SD = 0.002, RSD = 0.16%), $r^2 = 0.998$ (SD = 0.002, RSD = 0.18%) (averaged over 3 days), $y = 969x + 698$, $y = 760x + 2680$, for 2-MIB and GSM, respectively.

Typical values of 2-MIB and GSM, for MQ water and potable water, were well below the LOQ.

Linear range: Calibration standard solutions, at concentrations of 5, 10, 20, 30, 50 and 100 ng/L, were prepared in MQ water: methanol (99:1, v/v). The data were fitted to a line by the equation $y = ax$, forced through zero, where y is the peak area and a the slope. Regression analysis showed good linearity. The correlation coefficients, determined over 23 days, averaged 0.999 (SD = 0.002, RSD% = 0.11) and 0.999 (SD = 0.002, RSD = 0.12%) for 2-MIB and GSM, respectively.

Limit of detection (LOD) and limit of quantitation (LOQ): Standards in MQ water were serially diluted. The LOQ was found to be 7 ng/L and 4 ng/L, with CV = 8.42% (accuracy = 82 %), and 9.56% (accuracy = 94%), for 2-MIB and GSM, respectively. Our laboratory water quality tests methods (assays) generally utilize this technique for LOD and LOQ determination.

For comparison purposes, use of the S/N method for chromatographic methods, gave an LOD of 1 ng/L for both 2-MIB and GSM, at 3:1. The LOQ was 2 ng/L for both 2-MIB and GSM, respectively, at a S: N ratio of 10:1.

Standard Concentration (ng/L)	0% MeOH 2-MIB (peak area)#	1% MeOH 2-MIB (peak area) #	0% MeOH GSM (peak area) #	1% MeOH GSM (peak area) #
5	4593	5764	3019	5047
30	24720	30441	11257	20711
100	88803	101491	41476	77076
Regression statistics				
r^2	1.000	1.000	0.997	0.998
a (gradient)	883	1009	411	768
c (y-intercept)	0	483	106	-299

#Mean of 2 runs

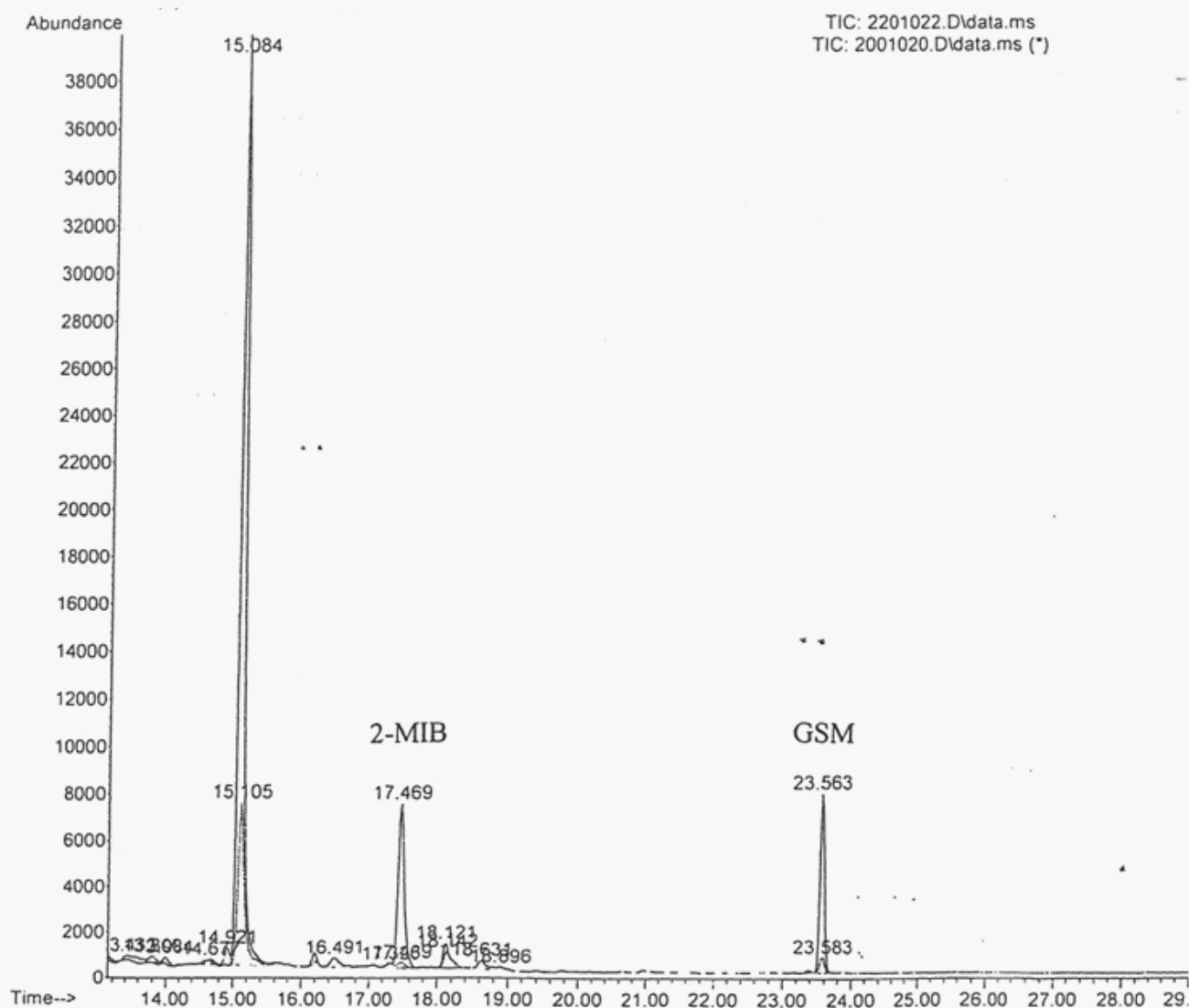**Table 4:** Effect of methanol addition on sensitivity.

Figure 1: Overlay total ion chromatogram of potable water after extraction: unspiked and spiked, at 30ng/L: 2-MIB (RT 17.469 min.), GSM (RT 23.583 min, 23.563 min).

The serial dilution technique, although results in higher LOD and LOQ, would tend to be more accurate, as selection of the "noise" region in a chromatogram, using the S/N method, is biased due to choice by the analyst.

Stability: Stability was assessed by monitoring the change in area responses of the target analytes of all the primary, secondary stock standards, calibration standards, and AQC samples with time. A variance exceeding ± 20% for response and recovery was used as a guide. All stock standards are stable for 6 months on storage at -20˚C. The working stock is stable for 12 months on storage at -20˚C. The working composite standard is stable for 5 days at ± 4˚C. For general batch processing, a maximum time of ± 24 hr can be allowed for entire completion of a run of all calibration standards and samples. It was noted that area counts for geosmin, especially at low concentration,

tend to decrease on standing of the sample at room temperature.

Future work should consider the additional use of a suitable internal standard [19,21] to ascertain the stability of these analytes, standards and real samples.

Carry-over evaluation: An air blank was run after assay of a 100 ng/L standard solution in MQ water. Signal responses for presence of 2-MIB and GSM were virtually non-detectable or well below the limit of detection.

Accuracy: The accuracy was determined by assessing recovery of added analytes to MQ and raw water, and analyzing internal AQC material.

For MQ water, overall accuracy was 83.80 ± 6 (RSD = 6.71%) and

Compound	Concentration added (ng/L)	Concentration found Mean ± SD (ng/L)#	RSD (%)	Accuracy/ Recovery Mean ± SD (%)	RSD (%)	Bias (%)
MQ water						
2-MIB	5	3.88 ± 0.60	15.46	77.62 ± 11.92	15.36	-22.38
	10	9.10 ± 0.15	1.65	90.96 ± 1.48	1.63	-9.04
	30	28.15 ± 1.91	6.79	93.83 ± 6.36	6.78	-15.17
	100	81.77 ± 7.44	9.10	81.77 ± 7.44	9.10	-18.23
Mean				83.80		
GSM	5	3.89 ± 0.53	13.63	77.74 ± 10.66	13.77	-22.26
	10	8.00 ± 0.71	8.88	79.95 ± 7.06	8.83	-20.05
	30	30.02 ± 1.57	5.23	100.07 ± 5.22	5.22	+0.07
	100	85.63 ± 7.80	9.11	85.63 ± 7.80	9.11	-18.23
Mean				85.85		
Raw water						
2-MIB	5	8.20 ± 0.78	9.51	164.00 ± 15.59	9.51	+64.00
	10	7.31 ± 0.82	11.22	73.08 ± 8.17	11.18	- 26.92
	30	32.36 ± 0.83	2.57	107.87 ± 2.78	2.58	+ 7.87
	100	124.59 ± 2.86	2.30	124.59 ± 2.86	2.30	+24.59
Mean			6.40	117.39	6.39	+17.39
GSM	5	6.43 ± 0.27	4.20	83.37 ± 5.40	6.48	-16.63
	10	8.75 ± 0.55	6.29	87.49 ± 5.53	6.32	-12.51
	30	29.52 ± 0.98	3.32	93.57 ± 3.27	3.95	- 6.43
	100	103.47 ± 3.86	3.53	103.47 ± 3.86	3.73	+3.47
Mean			4.34	91.98	5.12	-8.03

#After blank correction

Table 5: Accuracy, bias and precision of analytes (n = 10).

85.85 ± 10 (RSD = 11.71%) for 2-MIB and GSM respectively. For raw water, corresponding values were 117.39 ± 37.76% (RSD = 6.39%) and 91.98 ± 8.73 (RSD = 9.49%) for 2-MIB and GSM respectively (Table 5).

A freshly prepared AQC, at 30 ng/L in MQ water, assayed over 24 days, gave mean recovery of 91% ± 10 (RSD = 10.48%) and 97 % ± 9 (RSD = 8.81%) for 2-MIB and GSM respectively. The corresponding bias was -9.09% and -3.22% for 2-MIB and GSM.

Precision: Instrument precision (repeatability) was determined by assay of 10 replicates of standards at 5,10,30 and 100 ng/L. For MQ water, using peak areas, RSD% was 15.41%, 1.62, 6.77, 5.98 (mean = 7.45%) for 2-MIB, and 13.69, 8.65, 5.21, 3.42 (mean = 7.74%) for GSM, at the latter 4 concentrations, respectively.

Method precision was determined for both repeatability and reproducibility by analysis of standards at 5, 10, 30 and 100 ng/L in MQ water and raw water. Repeatability was studied by replicate analysis for n = 10 aliquots. Reproducibility was determined by assaying two to four aliquots of freshly prepared standard, 30 ng/L, on n = 24 different days.

Repeatability for MQ water was on average 8.25% and 9.21%, at 5, 10, 30, 100 ng/L, for 2-MIB and GSM respectively. The corresponding average for raw water was 6.40% and 4.34% for 2-MIB and GSM respectively (Table 5).

Raw water (dam and river) and a potable water sample were also analyzed, for n = 10 replicates, with following results: dam: 2-MIB < 7 ng/L (RSD = 0%), GSM = 3.93 ng/L (RSD% = 9.57%); river: 2-MIB < 7 ng/L (RSD = 0%), GSM = 6.07 ng/L (RSD% = 10.71%); potable: 2-MIB = 0.84 ng/L (RSD = 10.71%), GSM = 2.84 ng/L (RSD% = 14.08%).

Reproducibility for the AQC was 14.06% and 13.70% for 2-MIB (mean concentration = 28 ng/L, SD = 4) and GSM (mean concentration = 28 ng/L, SD = 4), respectively.

Application: A raw water sample and a potable sample were analyzed over 3 days**.** For the raw water sample, the assay values were: < 7 ng/L for 2-MIB, and 6 ng/L (RSD = 3.45%) for GSM.

For the potable water sample, the assay values were below the limit of quantification: < 7 ng/L for 2-MIB, and < 4 ng/L for GSM.

Comparison of current method with other purge-trap methods

A summary of common purge-trap method validation parameters, for assay of these two target analytes, is summarized in Table 6.

Lloyd et al. [7] used 150 mL of sample, with internal standard, purged for 1 hr at 80°C with nitrogen gas at 500 mL/min. Trapped analytes from the carbopack/carbosieve trap were then desorbed by use of 10 mL of hexane. Further steps involved removal of organic solvent by drying under nitrogen gas to 100 µL and final injection of 1 uL. Their reported limit of detection for both compounds was 10 ng/L. Beside inadequate sensitivity, other disadvantages are: large sample volume, long purge time, long extraction time for solvent evaporation from 10 mL to 100 µL. They reported very little method validation criteria data (Table 6). Their linear range was 0.1-30 µg/L (100-30 000 ng/L) with correlation coefficient of 0.9947 for both target compounds.

An improved procedure was reported in a technical bulletin by OI Analytical [18] where the analytical range was 1-100 ng/L, with good area precision. However, significant validation data is again not reported (Table 6).

A more recent publication [19] showed good overall improvement in the assay. However, the reproducibility of the analysis is not reported.

Use of "salting out" % NaCl (m/v)	LOD[a] 2-MIB	LOQ[a] 2-MIB	LOD[a] GSM	LOQ[a] GSM	R% 2-MIB	R% GSM	Repeat =ability RSD (%) 2-MIB	Reproduc =ability RSD (%) 2-MIB	Repeat =ability RSD (%) GSM	Reproduc =ability RSD (%) GSM	Ref.
-	0.1 ųg/kg	Above 0.5 ųg/kg	0.1ug/kg	Above 0.5 ųg/kg	38.9	59	No data	< 7%	No data	No data	[17]
-	No data	No data	No data	No data	No data	No data	1-48%	No data	1-34%	No data	[7]
10	1	No data	1	No data	No data	No data	6.6	No data	4.7	No data	[18]
25	1[d]	3.3[d]	2[d]	6.7[d]	85	94	6.4	No data	7.9	No data	[19]
-	1	7 (2)[d]	1	4 (2)[d]	83.80[b] 117.39[c]	85.85[b] 91.98[c]	8.22[b] 6.40[c]	14.06[b]	9.23[b] 4.34[c]	13.70[b]	This study

[a] Units: ng/L, unless indicated otherwise
[b] MQ water
[c] Raw water
[d] using the S:N ratio method
LOD = limit of detection; LOQ = limit of quantitation; 2-MIB = 2-methylisoborneol; GSM = geosmin; R = Recovery; Ref .= reference

Table 6: Comparison of reported purge-and-trap, and GC-MS method validation parameters.

Regarding sensitivity, our method gave a similar LOD of 1 ng/L for 2-MIB, but a better LOD of 1 ng/L for GSM, based on the S/N ratio method. Regarding the LOQ, we achieved results of 7 ng/L and 4 ng/L for 2-MIB and GSM using the serial dilution method. Corresponding results [19] were 3.3 and 6.7 ng/L, but using the S/N ratio method. A fairly long (75 m), fused silica capillary column was also used [19]. The use of wide bore columns and jet separators allows for necessary decrease in carrier gas flow rate prior to entering the mass spectrometer. However, problems include susceptibility to column contamination by high level samples, poor chromatographic behavior of early eluting compounds, long analysis times and frailty of the jet separator. Regarding the correlation coefficient, 0.9931 and 0.9943 was reported for 2-MIB and GSM [19]. We consistently obtained an r^2 of $\geq$ 0.995 for both analytes.

Although recovery for our current assay in raw water exceeds the commonly acceptable 80-120% range, at 5 ng/L in raw water, overall recovery was 95 % for both analytes in potable and raw water.

The common method used to optimize sensitivity is addition of salt to the water matrix, be it headspace or purge-trap sampling. Our analytical procedure is based on addition of 1% by volume of methanol; the 0.1 % (v/v) methanol (1 mL) present in the 1000 ng/L composite standard has negligible effect on the final methanol concentration in the calibration standards used. It appears that an increase in organic content, by methanol addition, reduces the number of polar water molecules available to bind to the polar target solutes, i.e. has a similar effect as increasing ionic strength of the medium by addition of inorganic salt, leading to increased sensitivity during the purge cycle with helium gas.

Conclusion

Commercial stock standards in methanol must be stored at -10˚C to -20˚C [20]. Contrary to conventional purge-trap theory, for typical volatile organic compounds, like benzene or toluene, where one can use typically 40:1 or higher split ratio, a low split ratio (2:1), approaching splitless injection, was found to be optimum for sensitivity. The latter finding can be related to the relatively polar nature of GSM and 2-MIB, which tend to bind more strongly to the polar water matrix. The

septum purge vent needs to be capped to prevent further losses. The Tenax trap also required replacement at approximately 6-monthly, or shorter, time intervals, depending on the number of samples analyzed. A good quality check is the AQC sample, or other suitable standard, which can be used for monitoring area counts and assay values.

Future work should look at the effect of having samples in the purge-trap auto sampler rack maintained at $\pm$ 4˚C, in view of the relative instability of GSM. We have recently acquired the newly launched OI Analytical Eclipse purge-trap sample concentrator, the Eclipse 4661 model, which provides for sample chilling down to $\pm$ 4°C, in the autosampler rack; method development and validation is currently in progress.

The study of the option of using methanol, instead of conventional salt, to other sampling techniques (e.g., headspace- solid phase micro extraction) involving assay of these compounds, is recommended.

It is apparent that assay of these taste-odorants in water, specifically by the purge-trap extraction technique is not simple. However, in the light of previously published analytical methods to date, our current method is a significant improvement.

A salt-free, sensitive, fully automated analytical method for determination of water odorants by purge-trap, with GC separation and mass selective detection has been developed and fully validated. The new method was shown to be accurate, precise, rapid and reliable. The method was applied to potable, dam and river samples.

Overall regular maintenance of critical equipment components of the entire analytical system, and use of clean glassware, is critical in achieving good sensitivity, accuracy and precision.

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