FULL PAPER
THE ANALYST
www.rsc.org/analyst

The determination of six taste and odour compounds in water using Ambersorb 572 and high resolution mass spectrometry

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Received 1st September 2000, Accepted 6th April 2001
First published as an Advance Article on the web 17th May 2001

A method for the analysis of six taste and odour causing compounds in aqueous samples using the granular adsorbent, Ambersorb 572, and gas chromatography-high resolution mass spectrometry (GC-HRMS) has been developed. This method for the determination of geosmin, 2-methylisoborneol (2-MIB), 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), 2,3,6-trichloroanisole (236-TCA) and 2,4,6-trichloroanisole (246-TCA) is highly productive [up to 40 samples per day + 23 quality control (QC) samples] and provides rapid (24–48 h) turnaround times. The analytes are extracted from water by the addition of Ambersorb 572 to the sample bottle and rolling for 1 h. The adsorbent is isolated by filtration and allowed to air dry for 1 h. The Ambersorb 572 is transferred to an autosampler vial and the analytes are desorbed into dichloromethane. The extract is analysed by GC-HRMS at 7000 resolving power (RP). Quantification is performed by isotope dilution and internal standard techniques utilizing d_3-geosmin, d_3-2-MIB, d_5-246-TCA and 2-*sec*-butyl-3-methoxypyrazine (s-BMP). Method precisions of 3.5–5.8% and accuracies of ±5.7–8.9% were obtained. Reporting detection limits (RDLs) of 1.0 ng L^{-1} were obtained for 2-MIB, geosmin, IPMP and IBMP, while RDLs of 2.0 ng L^{-1} were obtained for 236-TCA and 246-TCA.

Introduction

Taste and odour problems occur seasonally in drinking and surface waters. Naturally occurring taste and odour problems are the result of the growth and decay of algae, actinomycetes or other biological activity. Taste and odour problems can also result from chemical reactions occurring during the water treatment process, or effluent discharges into rivers, lakes and streams. Six compounds have been identified as being responsible for imparting earthy, musty taste and odour qualities to water, food and soil. The two compounds most often identified as responsible for causing the earthy, musty taste and odour qualities in water are geosmin [CAS No. 19700-21-1] and 2-methylisoborneol (2-MIB) [CAS No. 2371-42-8]. Both are semi-volatile metabolites of actinomycetes,[1–4] cyanobacteria[5,6] and certain blue–green algae.[7–9] Four other compounds identified as causing taste and odour problems in water are: 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), 2,3,6-trichloroanisole (236-TCA) and 2,4,6-trichloroanisole (246-TCA). IPMP [CAS No. 25773-40-4] has a musty potato-like odour and has been identified as a metabolite from one type of actinomycete.[3,4] IBMP [CAS No. 24683-00-9] has been identified as a major component responsible for the aroma in green bell peppers.[10] 236-TCA [CAS No. 50375-10-5] and 246-TCA [CAS No. 000087-40-1] have been detected in treated water supplies.[11] Trichlorophenols formed during chlorination in the water treatment process undergo microbial activity during residence in the distribution system and are biomethylated to the trichloroanisoles.[12] 246-TCA has also been identified in river water downstream from a bleached Kraft Pulp Mill effluent.[13]

Threshold odour concentrations (TOCs) for these six taste and odour compounds can vary widely, and are a function of the residual chlorine concentration and water temperature.[14] The TOCs of geosmin and 2-MIB have been widely reported[15] to be 10 ng L^{-1} for geosmin and 30 ng L^{-1} for 2-MIB, and most recently reported[16] at lower values of 3.8 ng L^{-1} and 15 ng L^{-1}, respectively. The TOCs of IPMP and IBMP are considerably lower than those of geosmin and 2-MIB at 0.2 ng L^{-1} and 1.0 ng L^{-1}, respectively.[16] The TOCs of 236-TCA and 246-TCA vary widely and have been reported to be in the ranges 20–30 ng L^{-1} for 236-TCA and 2–5 ng L^{-1} for 246-TCA,[13] although a TOC value of 0.9 ng L^{-1} for 246-TCA has been given.[16] In order to monitor drinking and surface waters for these taste and odour compounds, extraction methods and instrumental techniques with detection limits in the low ng L^{-1} range are required.

Salted closed-loop stripping (CLS) extraction followed by gas chromatography-mass spectrometry (GC-MS) is the most widely used method for the analysis of these six taste and odour compounds in water. Internal standard quantification using chloroalkanes gave detection limits of 0.8 ng L^{-1} for five taste and odour compounds.[17] Geosmin and 2-MIB have also been analysed using salted CLS with isotope dilution mass spectrometry.[18] Solid phase micro-extraction (SPME) GC-MS methods for the analysis of taste and odour compounds have recently been reported and are showing promise.[19–21]

Taste and odour compounds can also be isolated from water using adsorbents. Several adsorbents have been studied for the removal of taste and odour compounds from water, including powdered and granular activated carbon,[22] Filtrasorb 300[23] and Zeolite-Y.[24] Seven commercially available adsorbents were compared with solvent extraction methods by Blok *et al.*[25] for the extraction of taste and odour compounds in water. However, all adsorbents were found to have high artifact background levels, even after extensive clean-up. Geosmin and 2-MIB were successfully analysed using the adsorbent Ambersorb 572 and isotope dilution gas chromatography-high resolution mass spectrometry (GC-HRMS).[26] This method was highly productive with detection limits below the TOCs. Studies were initiated to incorporate four additional compounds (IPMP, IBMP, 236-TCA, 246-TCA) into the existing geosmin/2-MIB

DOI: 10.1039/b008013f

Ambersorb 572 isotope dilution GC-HRMS method, while increasing the number of quality control (QC) samples and maintaining high productivity and rapid turnaround times with detection limits at or below the TOC values. This has resulted in a comprehensive method for identifying sources of taste and odour events.

Experimental

Materials

High purity water used for method blanks and method recovery/laboratory control samples were obtained from a carbon-filtered/deionized/reverse osmosis/UV-treatment system (Biolab Equipment Canada Ltd., Oakville, Ontario, Canada). Ambersorb XEN-572 (Rohm and Haas Canada Inc., Scarborough, Ontario, Canada) was conditioned at 320 ± 5 °C for 3 h before use. Geosmin (98%) and 2-MIB (98%) were obtained from Dalton Chemical Laboratories Inc. (Downsview, Ontario, Canada). d_3-Geosmin (98%) and d_3-2-MIB (97%) were obtained from CSIRO-DWR (Griffith, Australia). IPMP (97%), IBMP (99%), 2-*sec*-butyl-3-methoxypyrazine (s-BMP) (99%), 236-TCA (98%) and 246-TCA (99%) were obtained from Sigma-Aldrich Canada Ltd. (Oakville, Ontario, Canada). d_5-246-TCA was obtained from CDN Isotopes Inc. (Pointe-Claire, Quebec, Canada). Dichloromethane and methanol were distilled-in-glass grade (Caledon Laboratories, Georgetown, Ontario, Canada).

Sample preparation

Field samples were collected in 1 L amber glass bottles with Teflon-lined caps, and shipped in coolers packed with ice to the laboratory. Upon receipt, each bottle was spiked with 20 µL of the internal standard solution containing d_3-geosmin (0.77 ng µL^{-1}), d_3-2-MIB (0.82 ng µL^{-1}), d_5-246-TCA (1.1 ng µL^{-1}) and s-BMP (0.32 ng µL^{-1}), mixed and then stored in a refrigerator at 4 ± 3 °C until the start of sample preparation (within 3 days). For each set of samples extracted, three method blanks (MB), consisting of 500 mL of high purity water, and a series of 10 method recovery (MR)/laboratory control samples (LCS), consisting of 500 mL of high purity water spiked with the six taste and odour compounds at 1.0, 2.5, 5.0, 10, 20, 40, 60, 80, 96 and 160 ng L^{-1} and 10 µL of internal standard, were processed. A 500 mL aliquot of the field sample was transferred to a clean 1 L amber glass bottle and approximately 200 mg (measured in a 400 µL flat-bottomed autosampler vial insert) of Ambersorb 572 was added to each sample and QC bottle (MB + MR + LCS). The bottles were rolled for 1 h at 50 rpm on a roller apparatus (Hotpack Corporation, Philadelphia, PA, USA) with a variable speed controller (Leeson Speedmaster Motor Control, Grafton, WI, USA). The Ambersorb 572 was isolated from the water by filtering the bottle contents through a 55 mm Whatman No. 4 filter paper (VWR Canlab, Mississauga, Ontario, Canada) on a filtration apparatus (Peter Petersen Glassblowing, Harriston, Ontario, Canada). The sample bottle and filtration apparatus walls were rinsed with high purity water to ensure complete transfer of the Ambersorb 572. The filtration apparatus was left under vacuum for 1 min to remove as much water as practical from the Ambersorb 572. The filter paper with the Ambersorb 572 was transferred using forceps to a disposable 57 mm aluminium weighing dish (VWR Canlab, Mississauga, Ontario, Canada) and allowed to air dry for a minimum of 1 h. The air-dried Ambersorb 572 was transferred to a 2 mL autosampler vial and approximately 400 µL of dichloromethane was added. The vial was tapped to expel any air bubbles from the Ambersorb 572 and was then capped with a Teflon-lined crimp cap. The extracts could be analysed immediately by GC-HRMS or stored at 4 ± 3 °C in the dark until the instrument was available.

Instrumental analysis

A Hewlett-Packard 5890 series II gas chromatograph (Hewlett-Packard Canada, Mississauga, Ontario, Canada), coupled to a VG ZAB-2F (Micromass, Manchester, UK) double-focusing, reverse geometry magnetic sector mass spectrometer, was used to analyse the extracts. A CTC A200S autosampler (Leap Technologies, Chapel Hill, NC, USA) was used to inject a 2 µL aliquot into a split/splitless injector. A DB-1701 (30 m × 0.25 mm id with 0.25 µm film thickness) column (J&W Scientific, Folsom, CA, USA) was used for analyte separation. The split/splitless injector was operated in the splitless mode at 200 °C. The GC transfer line temperature was set to 230 °C. The GC oven temperature was programmed as follows: 38 °C, held for 1 min, then ramped at 10 °C min^{-1} to 155 °C, then ramped again at 30 °C min^{-1} to 250 °C and held for 3 min. Data were acquired using a DEC VAXstation 3100 (M76) with DEC VMS v 5.4 and VG OPUS 2000 (v 2.1) software.

The mass spectrometer was operated in the positive ion electron ionization (EI) mode and tuned to 7000 resolving power (RP) (10% valley definition) using *m*/*z* 130.9920 of perfluorotributylamine (PFTBA) (SCM PCR Incorporated, Product No. 18201-4). Selected ion recording (SIR) was carried out in four separate experiment functions (see Table 1 for the ions monitored and dwell times).

Data analysis

The MR samples were used to generate calibration curves covering the range of taste and odour concentrations from 1.0 to 160 ng L^{-1}. The calibration curves were plots of unlabelled/deuterated compound peak area ratios or analyte/internal standard peak area ratios in the MR sample extracts *versus* the concentrations (ng L^{-1}) of unlabelled compounds in the MR samples. The amount of deuterated compound or internal standard added to the MR samples was fixed [d_3-geosmin (16.3 ng L^{-1}), d_3-2-MIB (15.4 ng L^{-1}), d_5-246-TCA (22.6 ng L^{-1}) and s-BMP (6.4 ng L^{-1})], while the amount of unlabelled analyte was varied (1.0–160 ng L^{-1}). Quantification for QC (MB + LCS) and samples was performed by interpolating a linear response between two adjacent MR samples (calibration points) encompassing the particular sample. The average concentration of 2-MIB in the method blanks over a 6 month period was calculated to be 0.16 ng L^{-1}. This includes 2-MIB from all possible sources, *i.e.* the high purity water and isotopic impurity of the deuterated internal standard (d_3-2-MIB) added.

Table 1 Ions monitored (there is an interchannel delay time of 20 ms between scans)

Function	Analyte	*m*/*z*	Dwell time/ms
1	PFTBA	118.9920	5
	IBMP	124.0637	100
	PFTBA (Lockmass)	130.9920	30
	IPMP	137.0715	100
	s-BMP	138.0793	75
2	PFTBA (Lockmass)	130.9920	30
	2-MIB	150.1409	200
	d_3-2-MIB	153.1597	100
3	236-/246-TCA	209.9406	200
	d_5-246-TCA	216.9690	100
	PFTBA (Lockmass)	218.9856	30
4	Geosmin	112.0888	150
	d_3-Geosmin	115.1076	50
	PFTBA (Lockmass)	118.9920	3

The average concentration of geosmin in the method blanks was calculated to be 0.29 ng L^{-1}, while the concentrations of 236-TCA and 246-TCA were calculated to be 0.21 ng L^{-1} and 0.20 ng L^{-1}, respectively. These concentrations are less than the maximum isotopic impurity of 2% which would result in concentrations of 0.4 ng L^{-1} in the method blanks. Therefore, the results were not corrected for the isotopic purity of the internal standards.

Results and discussion

Taste and odour episodes resulting from the presence of geosmin and/or 2-MIB in southern Ontario drinking water supplies can result in a large number of samples (up to 30 or more) being submitted in a short period of time, as the effectiveness of treatments and the levels of suspect compounds are monitored. Therefore, a method with low detection limits, high sample capacity and fast turnaround times is essential in order to monitor the effectiveness of treatments, or to determine when expensive water treatments can be discontinued. However, other compounds may also be responsible for causing or contributing to taste and odour problems in water. The Ministry of the Environment (MOE) (for the province of Ontario) uses an Ambersorb 572 isotope dilution GC-HRMS method[26] for the determination of geosmin and 2-MIB in aqueous samples. The Ambersorb 572 preparation method has no clean-up steps. Any organic compound that is adsorbed onto the Ambersorb 572 and desorbed into dichloromethane will be in the final extracts. To keep the sample preparation procedure simple, the number of sample preparation steps was kept to a minimum. HRMS was necessary to achieve the low ng L^{-1} detection limits and to minimize the possibility of interferences (see discussion on butyl stearate). There are interferences as a result of using the deuterated internal standards (see discussion on internal standards). HRMS was used to circumvent these interference problems. Quantification of geosmin and 2-MIB was performed using deuterium-labelled internal standards. This method increased productivity by a factor of 20 (up to 40 samples per day) and reduced turnaround times (24–48 h) over the previously employed CLS method, that utilized a single CLS system.

The deuterated analogues, d_3-geosmin, d_3-2-MIB and d_5-246-TCA, were used as internal standards for geosmin, 2-MIB and 236-TCA/246-TCA. There are no deuterated analogues of IPMP or IBMP commercially available. The possibility of ordering custom-synthesized deuterated analogues of IPMP and IBMP was investigated, but was found to be prohibitively expensive at a cost of approximately \$10 000 (US) for each standard synthesized. Therefore, an alternative internal standard was sought. The compounds 2-*sec*-butyl-3-methoxypyrazine (s-BMP) and 2-ethyl-3-methoxypyrazine (EMP) were assessed for suitability as internal standards for IPMP and IBMP. Extraction studies showed that either s-BMP or EMP could be used as an internal standard for IPMP and IBMP, because neither compound was believed to be found in real samples. Both compounds were found to have chromatographic retention times that were suitable for analysis. Ambersorb 572 recovery experiments using high purity water and spiked matrix samples showed that the recoveries were similar to the other compounds being analysed with no interferences. s-BMP was eventually chosen as the internal standard because it eluted between IPMP and IBMP.

Suitable ions to monitor the four new analytes and internal standards were chosen. The base peaks of IPMP (*m*/*z* 137.0715 $[M - CH_3]$), IBMP (*m*/*z* 124.0637 $[M - C_3H_6]$) and s-BMP (*m*/*z* 138.0793 $[M - C_2H_4]$) and the molecular ion of 236-TCA/246-TCA (*m*/*z* 209.9406) were chosen for optimum sensitivity. Initially, the molecular ion of d_5-246-TCA (*m*/*z* 214.9720) was chosen to be monitored as the internal standard for quantification. It was discovered that there was an interference with the molecular ion of d_5-246-TCA (*m*/*z* 214.9720) coming from an isotope peak of the PFTBA fragment ion, C_4NF_8 (*m*/*z* 213.9903). There are two possible interferences coming from PFTBA. These are listed in Table 2. The first potential interference could come from the ^{15}N ($^{12}C_4{}^{15}NF_8$, *m*/*z* 214.9873) isotope peak of the C_4NF_8 PFTBA fragment ion, but is not considered likely due to the very low natural abundance of ^{15}N (0.37%). The more plausible interference with the molecular ion of d_5-246-TCA (*m*/*z* 214.9720) is from the ^{13}C ($^{13}C_1{}^{12}C_3{}^{14}NF_8$, *m*/*z* 214.9937) isotope peak from the same PFTBA fragment ion (C_4NF_8, *m*/*z* 213.9903). The RP required to separate these interferences from d_5-246-TCA were calculated to be 9874 for the ^{13}C and 13938 for the ^{15}N isotope peak of PFTBA. There was another interference problem with the d_5-246-TCA molecular ion (*m*/*z* 214.9720) coming from the $[M + 4]$ ^{13}C isotope peak of 246-TCA (*m*/*z* 214.9380). The RP required to separate these two masses is 6294. With the mass spectrometer operated at 7000 RP, these two masses could easily be resolved. However, this interference problem could cause quantification problems when monitoring these ions using low resolution mass spectrometry (LRMS) instruments, as they would have the same nominal mass. Therefore, the $[M + 2]$ molecular ion isotope peak (*m*/*z* 216.9690) of d_5-246-TCA was chosen. Table 2 shows all the ions from 246-TCA, d_5-246-TCA and PFTBA associated with this interference problem.

In the original two analyte Ambersorb method, the $[M - H_2O]^{+}$& ions of 2-MIB (*m*/*z* 150.1409) and d_3-2-MIB (*m*/*z* 153.1597) were monitored.[26] The $[M - CH_3]^{+}$ fragment ion of 2-MIB (*m*/*z* 153.1297) will interfere with the $[M - H_2O]^{+}$& fragment ion of d_3-2-MIB (*m*/*z* 153.1597) used for quantification. The RP required to differentiate these two masses is 4811. Operating the mass spectrometer at 7000 RP minimizes the effects of this interference. However, these two ions cannot be differentiated using LRMS instrumentation and therefore the less intense molecular ions or chemical ionization (CI) may have to be used. The base peak (*m*/*z* 95) of 2-MIB could not be monitored for isotope dilution quantification because the label is lost in d_3-2-MIB.

The original GC temperature program from the geosmin/2-MIB method[26] afforded the baseline separation of all components, except for 236-TCA and geosmin. Because they were not baseline separated, these two analytes would have had to be placed in the same voltage switching function. Monitoring the *m*/*z* 112.0888 of geosmin and the molecular ion for 236-TCA (*m*/*z* 209.9406) requires a change in the accelerating voltage (ΔV) of 60%. ΔV should be kept to $< 30\%$ to minimize losses in sensitivity that are proportional to ΔV. The GC temperature program was modified to enable the baseline separation of all the analytes including 236-TCA and geosmin. This allowed four separate SIR voltage scanning acquisition functions (with their appropriate magnet settings) to be set up

Table 2 Ions and interferences of 246-TCA, d_5-246-TCA and PFTBA

Analyte	Formula	Ion	*m*/*z*
246-TCA[a]	$C_7H_5Cl_3O$	$[M]$	209.9406
246-TCA	$C_7H_5{}^{35}Cl_1{}^{37}Cl_2O$	$[M + 4]$	213.9347
246-TCA[b]	$^{13}C_1{}^{12}C_6H_5{}^{35}Cl_1{}^{37}Cl_2O$	$[M + 5]$	214.9380
d_5-246-TCA	$C_7D_5Cl_3O$	$[M]$	214.9720
d_5-246-TCA[a]	$C_7D_5{}^{35}Cl_2{}^{37}Cl_1O$	$[M + 2]$	216.9690
PFTBA fragment	C_4NF_8	$[M - C_8F_{19}]$	213.9903
PFTBA fragment[b]	$C_4{}^{15}NF_8$	$[M - C_8F_{19}]$	214.9873
PFTBA fragment[b]	$^{13}C_1{}^{12}C_3NF_8$	$[M - C_8F_{19}]$	214.9937
PFTBA (Lockmass)[a]	C_4F_9	$[M - C_8NF_{18}]$	218.9856

[a] Ions monitored. [b] Interferences with the molecular ion of d_5-246-TCA.

for optimizing the sensitivity for all six analytes. The trade-off was that the GC run time was increased by 72% in order to produce this separation.

With the new GC temperature program, there was an interference problem with the analysis of geosmin when the base peak ion [M − C_5H_{10}] of geosmin (*m*/*z* 112.0888) was monitored. The interference was present in sufficient concentration (low µg L^{-1}) that it was identified by full scans at 7000 RP. Butyl stearate [CAS No. 123-95-5], a common analytical extraction artifact from plastics, has a low abundance C_8H_{16} ion (*m*/*z* 112.1252) that interferes with the *m*/*z* 112.0888 ion ($C_7H_{12}O$) of geosmin. The RP required to differentiate these two ions is only 3078, assuming similar concentrations. However, butyl stearate was present in a large excess (low µg L^{-1}) and therefore interfered with the geosmin *m*/*z* 112.0888 ion present in low ng L^{-1} concentration, even at 7000 RP. The two compounds were not resolved chromatographically on certain columns: when the 30 m DB-1701 column was shortened to maintain chromatographic performance, or when '1701'-type columns from different manufacturers were used. Fig. 1 shows the mass chromatograms of an MR sample containing geosmin (*m*/*z* 112.0888) and d$_3$-geosmin (*m*/*z* 115.1076) run on two different '1701'-type columns under the same conditions. On column A, geosmin and its internal standard elute at approximately 14:50 min with the broad intense peak of the butyl stearate interference in the *m*/*z* 112.0888 mass chromatogram. On column B, geosmin elutes at 14:19 min and its internal standard elutes approximately 1 s earlier at 14:18 min with no interference from the butyl stearate, even though they elute earlier than on column A under the same conditions. To maintain the separation of these two compounds on some '1701' columns, the temperature program must be changed and/or the head pressure on the GC (under constant pressure operation) must be adjusted as the column is shortened, or a new column must be used.

To determine if problems with the selected ions would arise, spiked high purity water and spiked matrix samples (raw, surface and treated water) were extracted and analysed. No interferences were observed. These extraction studies showed that the recoveries for the four new compounds and internal standards were sufficient to establish that none of the sample preparation extraction parameters from the original method, including the sample volume, the amount of Ambersorb 572 used or the rolling and drying time, needed to be changed. Absolute recoveries were not monitored. The use of isotope dilution for four of the six compounds monitored compensated for any losses of the native compounds during the sample preparation procedure. A ten point calibration curve system, using the MR samples to generate calibration curves, covering the range 1.0–160 ng L^{-1} that was expected in real samples, was used. The calibration curves are non-linear in the low ng L^{-1} concentration range. Quantification was performed by interpolating a linear response between two adjacent MR samples (calibration points) using the appropriate pair of target analyte and internal standard peak areas. The calibration curve for 2-MIB is shown in Fig. 2 and the calibration curve data are given in Table 3. The calibration curve is non-linear in the 1–10 ng L^{-1} range. Therefore, the concentrations in the method blanks, samples and MR samples that are in the non-linear part of the curve would not be adequately represented by a linear regression plot.

The method performance data are listed in Table 4. The within-run precision for the ten point calibration curve Ambersorb 572 method was determined from 5 series of 10 samples spiked at 5.0 and 10 ng L^{-1}, that were extracted and analyzed on

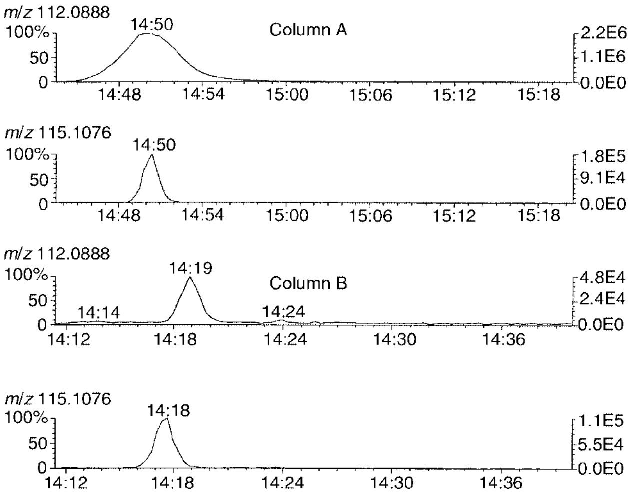

Fig. 1 Mass chromatograms of ions *m*/*z* 112.0888 (geosmin) and *m*/*z* 115.1076 (d$_3$-geosmin) showing butyl stearate interference.

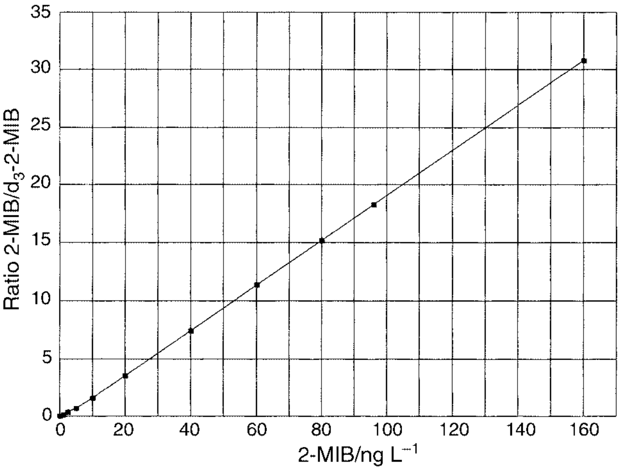

Fig. 2 Calibration curve for 2-MIB.

Table 3 Calibration curve data for 2-MIB in Fig. 2

Spike/ng L^{-1}	Ratio 2-MIB/d$_3$-2-MIB	Slope	*y* intercept
0.0	0.0	0.0	0.0
1.0	0.136	0.1356	0.0
2.5	0.338	0.1348	0.0009
5.0	0.663	0.1300	0.0126
10	1.587	0.1849	−0.2616
20	3.510	0.1923	−0.3355
40	7.458	0.1974	−0.4371
60	11.335	0.1939	−0.2973
80	15.164	0.1915	−0.1533
96	18.256	0.1932	−0.2948
160	30.800	0.1960	−0.5594

Table 4 Method performance data

Compound	Within-run precision (%)	Between-run precision (RSD[a]) (%)	Accuracy (%)	MDL[b]/ ng L^{-1}
Geosmin	1.9–3.4	3.5	±6.4	0.81
2-MIB	3.7–5.0	4.9	±8.3	0.60
IPMP	2.1–4.5	4.5	±8.9	0.50
IBMP	1.5–3.6	4.2	±6.6	0.37
236-TCA	4.4–5.8	5.8	±5.9	1.5
246-TCA	2.6–4.9	4.5	±5.7	1.0
Geosmin[c]	4.2–9.5	7.7	±11	2.0
2-MIB[c]	3.7–6.4	5.5	±6	1.5

[a] RSD, relative standard deviation.[b] MDL, method detection limit.Performance data from previous Ambersorb 572 method.

5 different days. The between-run precision was determined using the 50 values for the within-run precision. The accuracy data were calculated using the percentage difference between the between-run average and theoretical values plus the between-run precision relative standard deviation. The method detection limits (MDLs) were calculated using the Municipal/Industrial Strategy for Abatement (MISA) Estimation of Analytical MDL[27] and the within-run precision data. The detection limits were determined to be less than 1.0 ng L^{-1} for geosmin, 2-MIB, IPMP and IBMP, while detection limits for 236-TCA and 246-TCA were less than 2.0 ng L^{-1}. The performance data using the original geosmin/2-MIB method are also listed in Table 4 for comparison. The reporting detection limits (RDLs) were set to 1.0 ng L^{-1} for geosmin, 2-MIB, IPMP and IBMP, while RDLs for 236-TCA and 246-TCA were set to 2.0 ng L^{-1} Improved method precision reduced the MDLs for geosmin and 2-MIB.

Field samples used for method development and method comparison were collected in 1 L amber glass bottles with Teflon-lined caps. Because of known decomposition problems with geosmin and 2-MIB in the matrix,[28,29] sample bottles were shipped to the laboratory in ice-packed coolers. Upon arrival at the laboratory, each bottle was spiked with 20 μL of the internal standard solution containing d$_3$-geosmin (0.77 ng μL^{-1}), d$_3$-2-MIB (0.82 ng μL^{-1}), d$_5$-246-TCA (1.1 ng μL^{-1}) and s-BMP (0.32 ng μL^{-1}), mixed and then stored in a refrigerator at 4 ± 3 °C until the start of sample preparation (within 3 days). Compensation for any decomposition of the analytes from this point on could be made. Also, storing the samples at 4 ± 3 °C helps to reduce the rate of decomposition. No stability data for the four new target compounds were found in the literature.

Table 5 shows the results of 10 of 150 samples (raw and treated waters) analysed using the old and new methods. Geosmin was found to be the source of the taste and odour problem. None of the four new taste and odour compounds were found in these samples. Results for geosmin and 2-MIB show good agreement between the two methods.

A six analyte taste and odour method was developed to provide a more thorough characterization of taste and odour events. The performance data for the new method were improved over the previous method and lower detection limits were achieved. In 1999, this method was successfully applied to over 150 samples (raw, surface and treated water) from around the province in less than 3 months. In the year 2000 (January to December), 854 samples and 494 QC samples (114 MB + 380 MR/LCS) were analysed as part of a province-wide taste and odour screening of raw and treated water from selected water treatment plants (WTPs) and a Lake Ontario water quality survey. The concentration of taste and odour compounds found in the WTPs from around the province ranged from not detected (ND) to 150 ng L^{-1} for geosmin and from ND to 92 ng L^{-1} for 2-MIB. For the 2000 water quality survey along the north to west shores of Lake Ontario, an investigation was undertaken to determine the biological origins of taste and odour problems affecting seven WTPs from Grimsby to Cobourg. These WTPs experienced high concentrations of geosmin in the summers of 1998 and 1999.[30] Raw and treated WTP water, along with surface and subsurface water from Lake Ontario, was sampled. The concentration of geosmin did not reach the high levels seen in 1998 (77 ng L^{-1}) or 1999 (130 ng L^{-1}), but reached a peak at 13 ng L^{-1} (see Table 6). However, the pattern of the increasing and peaking geosmin concentration in late summer was similar to that seen in the previous years, indicating that the cause of geosmin production was the same. None of the four additional taste and odour compounds was observed in any of the samples above their respective detection limits.

Table 5 Results of 10 samples analysed using the old and new methods (ND, not detected; method detection limit in parentheses)

Sample	Geosmin (new)/ ng L^{-1}	Geosmin (old)/ ng L^{-1}	2-MIB (new)/ ng L^{-1}	2-MIB (old)/ ng L^{-1}
1, treated	4.4	3.3	ND (1.0)	ND (2.0)
2, treated	3.5	3.6	ND (1.0)	ND (2.0)
3, raw	8.5	8.0	ND (1.0)	ND (2.0)
4, treated	8.9	8.7	ND (1.0)	ND (2.0)
5, treated	8.8	8.4	ND (1.0)	ND (2.0)
6, raw	9.5	7.7	ND (1.0)	ND (2.0)
7, treated	8.8	8.4	ND (1.0)	ND (2.0)
8, raw	19	15	ND (1.0)	ND (2.0)
9, treated	2.6	2.0	ND (1.0)	ND (2.0)
10, raw	2.7	2.9	ND (1.0)	ND (2.0)

Table 6 Geosmin and 2-MIB concentrations from 1998 to 2000 in raw water (ND, not detected; WTP, water treatment plant; WSS, water supply system)

	Geosmin			2-MIB		
Sample	1998	1999	2000	1998	1999	2000
Ajax WTP	37	102	9.8	10	8.0	ND
Cobourg WTP	ND	ND	13	ND	ND	1.5
Grimsby WTP	5.0	28	5.3	28	45	ND
Hamilton WSS	ND	130	8.3	ND	16	1.7
Lakeview WSS	23	127	11	3.0	105	ND
Oakville WTP	54	125	9.9	ND	8.0	ND
R.L. Clark WTP	77	120	9.7	ND	ND	1.7

The high productivity of the Ambersorb method has been maintained, allowing 23 QC samples and 40 samples to be analysed with a turnaround time of 24–48 h. These fast turnaround times, combined with high sample capacities and low detection limits, allow fast feedback for process changes during water treatment or changes in environmental concentrations. Future work includes sampling points in the distribution systems for 2001.

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