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Analysis of odorous compounds in water by isolation by closed-loop stripping with a multichannel silicone rubber trap followed by gas chromatography–mass spectrometry☆

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Abstract

An alternative technique for the isolation and concentration of odorous compounds found in potable water is described. The method currently employed by water authorities is closed-loop stripping with the collection of these substances on a small activated carbon filter. The compounds of interest are then extracted from the carbon using a suitable solvent. The authors offer a multichannel silicone rubber trap as an alternative to the carbon filter. The absorbed compounds are thermally desorbed from the trap, directly on to the gas chromatographic column for analysis by GC–MS, thereby eliminating the solvent extraction step required by the carbon filter. The multichannel silicone rubber trap, producing equivalent results, offers a number of advantages over the carbon filter.

Keywords: Sample handling; Water analysis; Methylisoborneol; Geosmin

1. Introduction

Tastes and odors occurring in surface waters have received increased attention from the analyst over the past 35 years. The public's demand for aesthetically clean drinking water puts constant pressure on the water authorities to either prevent the formation of the compounds causing the organoleptic effects or to remove them during the water purification processes. The effective removal of these substances requires the large scale application of activated carbon, which is an expensive exercise [1].

Water generally acquires obnoxious tastes and odors indirectly from human influence, resulting in the rapid enhancement of the growth of aquatic organisms under eutrophic conditions or the contamination by wastewater disposal and/or agricultural run-off. A range of volatile and semi-volatile organic compounds may impart tastes and odors to a water making it unpalatable. Some of these substances can be detected by the human nose when present in trace amounts, at the low ng/l level. Microbial metabolites such as geosmin (*trans*-1,10-dimethyl-*trans*-decalol) and 2-methylisoborneol (MIB) belong to this category of compounds.

Geosmin was identified as early as 1965, first in actinomycetes and later in cyanobacteria or blue-green algae, as the main component imparting the 'earthy' odor to soil and water [2]. Five commonly found compounds imparting the earthy/musty odors

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Table 1
Characteristics of substances producing earthy odours [3]

Compound	Threshold odour concentration (ng/l)	Odour characteristics
Geosmin	10	Earthy/musty
2-Methylisoborneol	29	Earthy/musty camphorous
2-Isopropyl-3-methoxypyrazine	2	Earthy/musty potato-bin
2-Isobutyl-3-methoxypyrazine	2	Earthy/musty bell pepper
2,3,6-Trichloroanisole	7	Musty

to water are listed, with their threshold odor concentrations in Table 1 [3].

Grob [4,5] developed a closed-loop stripping analysis technique for the isolation of volatile organic compounds in an aqueous medium. In 1983, Krasner et al. [3] published a standard method, based on the closed-loop stripping analysis technique and mass spectrometry, for the analysis of taste and odor substances in water and drinking water, which is used routinely by most water laboratories. The technique combines a high concentration factor with a small sample size and a relatively fast processing time. The activated carbon in the trap is an excellent adsorbent but is dependent on the activity of the adsorption surface [6]. The compounds are extracted from the carbon with a solvent. Carbon disulfide or dichloromethane are most commonly used.

Alternative methods for the pre-concentration of the headspace have been proposed using open tubular traps, coated with a thick film of a GC stationary phase [7,8]. Pre-concentration with these traps occurs by sorption of the organic compounds, which diffuse into the stationary phase. This clearly has a number of advantages over the standard adsorption techniques.

Recently, Baltussen et al. [9] developed a trap packed with polydimethysiloxane particles, which was used for pre-concentration of organics directly from the aqueous phase. This demonstrates the stability of these phases and that their efficiency is not impaired in the presence of water.

Ortner and Rohwer [10] developed a multichannel silicon rubber trap, which has several channels in parallel to concentrate volatile organics from air. The trap consists of a quartz tube filled with silicone rubber tubes positioned next to each other. This trap is short in comparison to the other open tubular traps and may be used in standard commercial desorbers or programmed-temperature vaporizer (PTV) injectors, facilitating automated analyses.

The multichannel trap was tested in our laboratory, replacing the carbon filter in the closed-loop stripping analysis apparatus, to isolate geosmin and MIB from water, for analysis by gas chromatography with mass spectrometric detection.

2. Closed-loop stripping analysis

The volatile organic compounds are trapped in the multichannel trap by pumping the purge gas, in a closed circuit, through the aqueous phase and the trap. The trap retains the volatile and semi-volatile organic compounds allowing the purge gas through, to return to repurge the sample via the pump.

If the volume of gas pumped through the trap is such that the least sorbed compound does not break through then the proportions of the compounds sorbed by the trap will be equal to their corresponding mean proportions in the gaseous phase. This can be regarded as conservation trapping. If the volume of gas pumped through the trap is large enough to bring the whole system to equilibrium then equilibrium trapping occurs. In the latter case, the proportion of the component entrapped is given by Eq. (1) [11]:

$$R_t = C^*_{iG}(V_{Gt} + K_{SG}V_S) \quad (1)$$

where C^*_{iG} is the final (equilibrium) concentration of the solute (i) in the gaseous phase, V_{Gt} is the void volume of the trap, K_{SG} is the actual sorbent-gas distribution constant of the solute and V_S is the volume of the sorbent in the trap.

3. Experimental

3.1. Instrumentation

The multichannel traps were made from 6 mm O.D.×3 mm I.D.×160 mm quartz tubing in which 16 silicone rubber tubes, 90 mm in length, were inserted [10]. The traps were conditioned overnight at 280°C under hydrogen, at a flow rate of 25 ml/min.

The closed-loop stripping analysis apparatus was constructed in-house and used a standard metal bellows circulating pump with a pumping speed of 1500 ml/min. The water samples (250 ml) were purged at 40°C and the transfer line, ahead of the trap, was maintained at 60°C.

The analytical instrumentation consisted of a CP-4010 PTI/TCT injector from Chrompack (Middelburg, The Netherlands) mounted on an HP5988 quadrupole Mass spectrometer fitted with an HP5890 gas chromatograph (Hewlett-Packard). The CP-4010 consisted of a desorption oven connected to a fused-silica capillary cryotrap. The thermally desorbed components are refocused on the cold trap, which is flash heated to inject the trapped substances on to the analytical column. The cryotrap was cooled to −80°C and the trapped components were desorbed at 180°C at a flow rate of 60 ml/min. The injection temperature of the cryotrap was 200°C held for 1 min. With this procedure, quantitative transfer of the trapped substances to the column is achieved.

The analytical column was a PS-089 low-bleed, glass capillary column (25 m×0.32 mm I.D., 0.25 μm film thickness), manufactured in the laboratory. The column was initially held at 40°C for 2 min and then programmed to 200°C at 4°C/min and then to 280°C at 20°C/min.

The mass spectrometer was operated in the selected ion monitoring (SIM) mode (Table 2); the source temperature was 220°C and the interface temperature was 280°C.

3.2. Standards

A solution of deuterated geosmin and MIB (Manchester, UK) standards in methanol and a solution of the non-deuterated geosmin and MIB standards were used in all the evaluation experiments. These sets of standards were used to determine to what extent the deuterated and non-deuterated standards would be separated in the GC analysis. Little has been published on the use of deuterated MIB and geosmin as standards and it was therefore decided to use these standards for future internal calibration to increase the accuracy of the determinations, particularly at low concentrations.

Table 2
m/z Values used for SIM analysis

Compound	SIM m/z values
MIB	95, 135[a], 168
[$^2H_3$]MIB	95, 138[a], 171
Geosmin	112[a], 182
[$^2H_3$]Geosmin	115[a], 185

[a] Ions used for quantitation.

4. Results and discussion

All of the multichannel traps were conditioned, as above, and 20 ng of each deuterated standard was injected on to a trap with a microsyringe and analysed to determine the background peaks and the position of these two standards in the chromatogram. The analysis was done at full-scan mode, scanning from 10–400 u (Fig. 1). Six silicone peaks of note, resulting directly from the trap, were observed in this trace [10], but these did not interfere at all with the deuterated MIB and geosmin standards.

Aliquots of 4 ng of each of the deuterated and non-deuterated standards were then placed directly onto the trap and analysed in the single ion mode to determine the separation obtained between the deuterated and non-deuterated compounds. The reconstructed total ion trace (the sum of the single ions) indicates poor separation is obtained on the 25 m PS-089 column but the integration of the single ion peaks (Figs. 2 and 3) can be accomplished without any difficulty. The peaks in the reconstructed single ion traces (Figs. 2 and 3) of the m/z values used for the identification of the compounds in a SIM analysis are clearly discernible. $m/z=95$ Is the major peak in both the deuterated and non-deuterated MIB but as a result of the overlap of these two compounds, insufficient separation is obtained for its use in

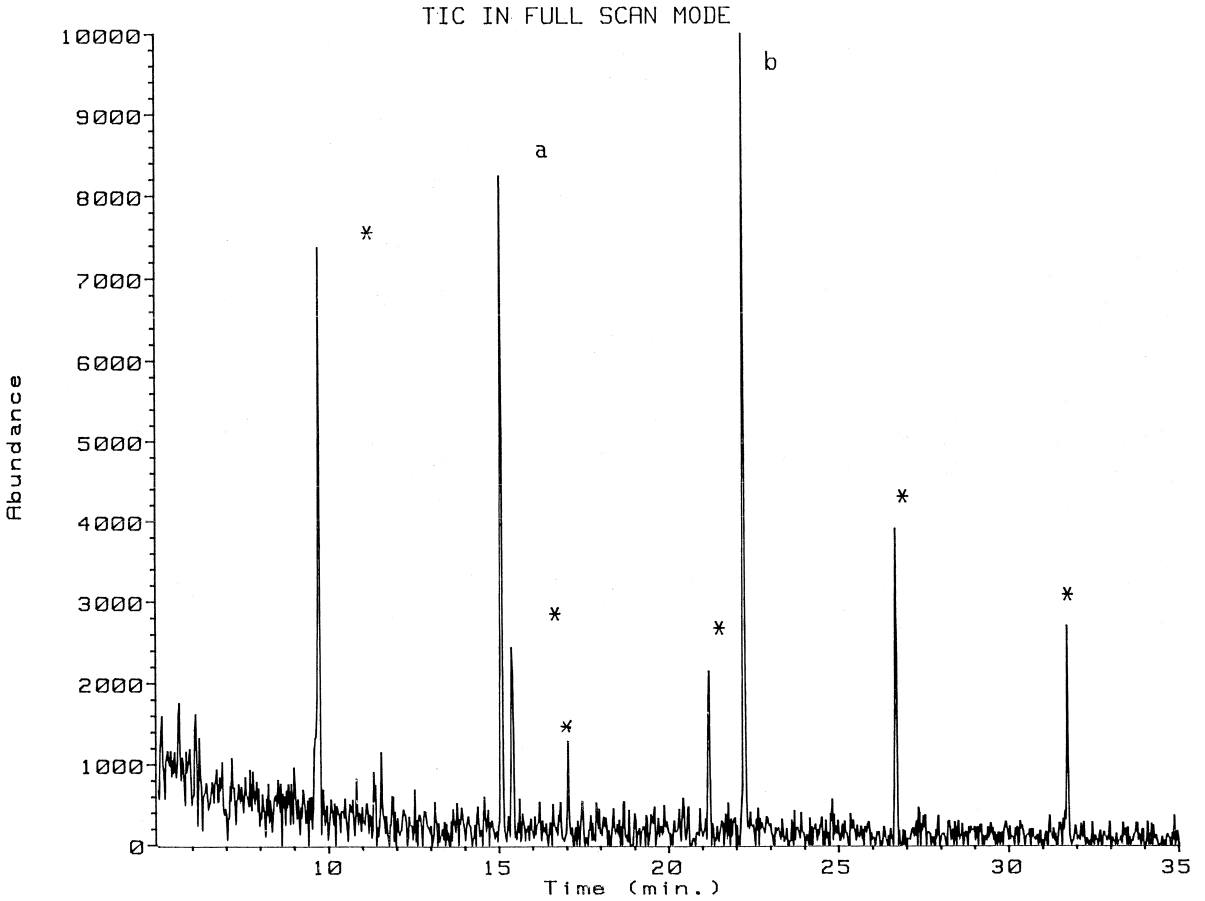

Fig. 1. Deuterated MIB and deuterated geosmin added to the multichannel silicone rubber trap and analysed in full scan mode to observe the trap background. (a) Deuterated MIB; (b) deuterated geosmin; * silicone peak background.

quantitative calculations based on internal calibration methods. This is a disadvantage, since peaks $m/z=138$ and $m/z=135$, with much lower abundances (ca. 20% of the $m/z=95$ peak) have to be used, which consequently affects the lower limit of detection of the compound. This, of course, does not apply to quantitative calculations using external calibration procedures. Clearly, the use of a longer or different column would also be an option in obtaining baseline separation for the isotopic compounds, allowing the implementation of an internal calibration procedure with the strongest ions.

A series of water standards were prepared containing 2 ng/l, 4 ng/l, 8 ng/l and 16 ng/l of the deuterated standards and these were extracted by the closed-loop stripping analysis and the multichannel trap and analysed in the SIM mode. The resulting integrated areas of the single ion peaks were used to draw calibration curves for $m/z=95$, $m/z=138$ and $m/z=115$ (Fig. 4). These curves appear to be linear at the higher concentrations but fall off rapidly below 4 ng/l for both deuterated-MIB and deuterated-geosmin. This type of loss is often observed were active surfaces occur in the analytical instrumentation, as was the case in the closed-loop stripping analysis apparatus, built in this laboratory. This curve therefore suggests a lower limit of detection for the method of 4 ng/l, which is well below the reported odor threshold of 10 ng/l (Table 1).

(Duplicate analyses were done on the equivalent of 4 ng/l of each of the deuterated standards placed directly onto the trap. Percentage recoveries were

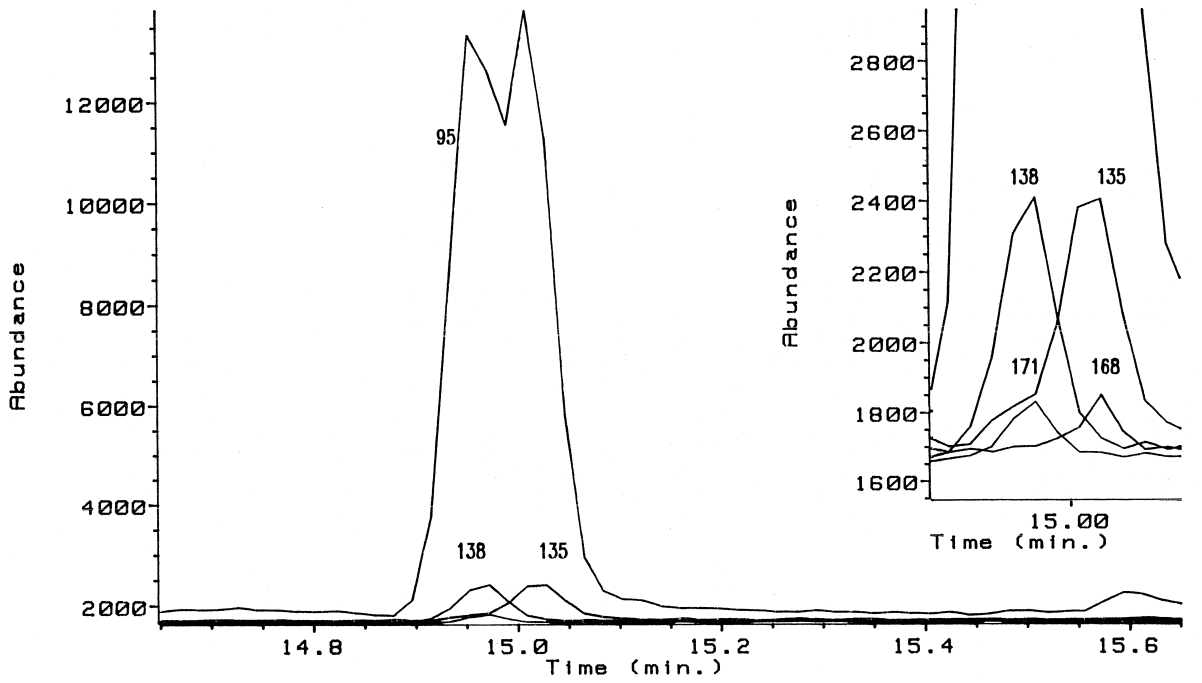

Fig. 2. Separation of deuterated MIB and non-deuterated MIB using the *m*/*z* values listed in Table 2 (*m*/*z* 95, 138, 135, 171, 168).

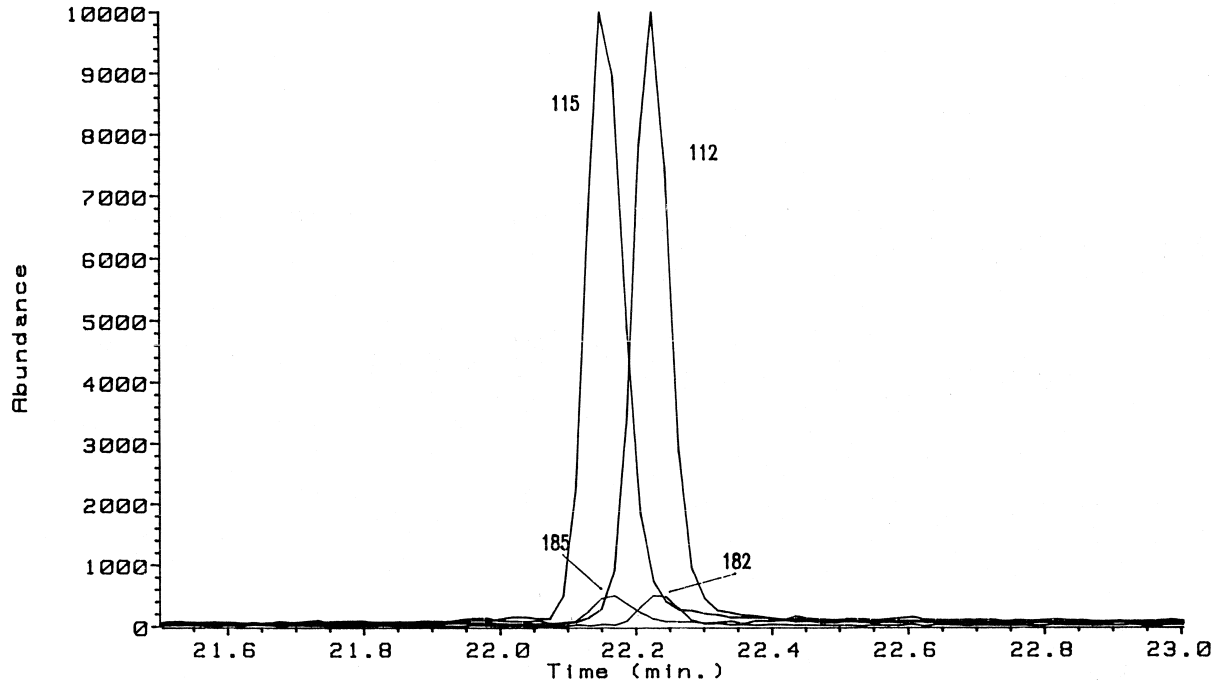

Fig. 3. Separation of deuterated-geosmin and non-deuterated geosmin using the *m*/*z* values listed in Table 2 (*m*/*z* 115, 112, 185, 182).

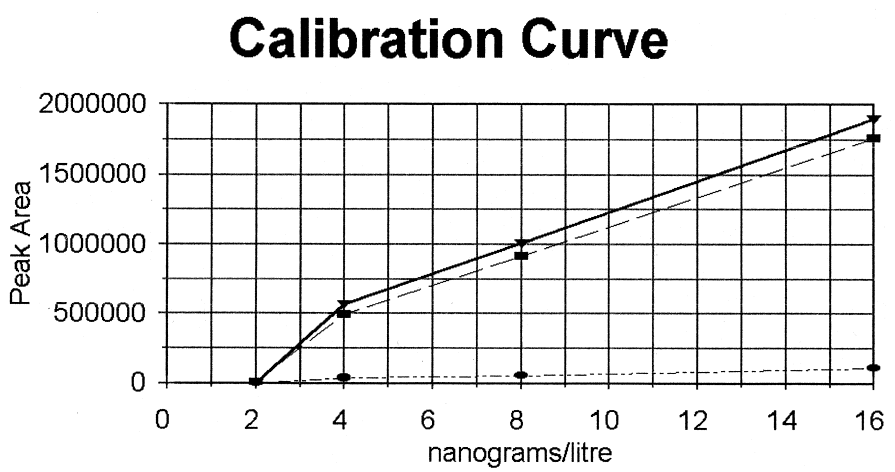

Fig. 4. (a) Deuterated MIB m/z 95; (b) deuterated geosmin m/z 115; (c) deuterated MIB m/z 138.

calculated using the average peak areas from these duplicate determinations and the peak areas from the determination of the 4 ng/l standard were used to calculate the calibration curve.)

Finally, a drinking water sample was spiked with 8ng/l of the deuterated standards and extracted using the multichannel trap. The analysis was done in the SIM mode and Fig. 5 is a diagram of the reconstructed total ion chromatogram obtained. This sample did not have any geosmin or MIB present at concentration levels exceeding 4ng/l. Numerous peaks with the same ions ($m/z=112$ and $m/z=128$) selected for the analysis, were observed in this trace, yet none of these peaks overlapped the standard

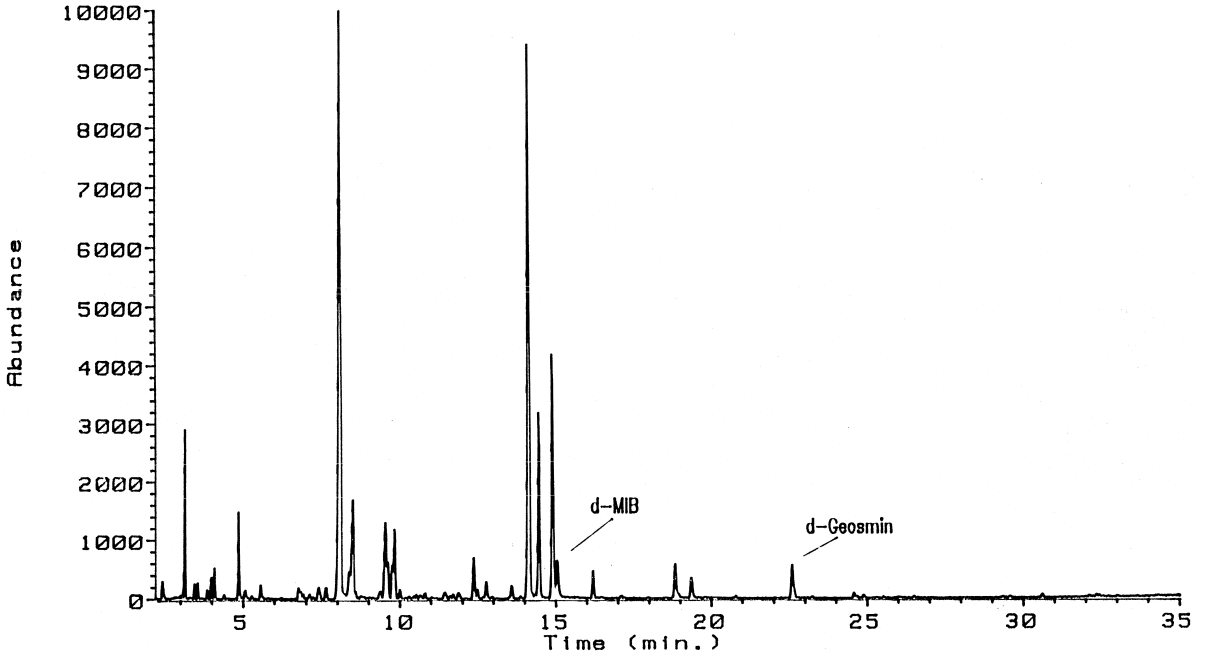

Fig. 5. Reconstructed total ion chromatogram (TIC) (sum of the SIM ions) for the SIM analysis of a drinking water spiked with 8 ng/l of deuterated MIB (d-MIB) and geosmin (d-geosmin) standards, extracted with the MCSRT.

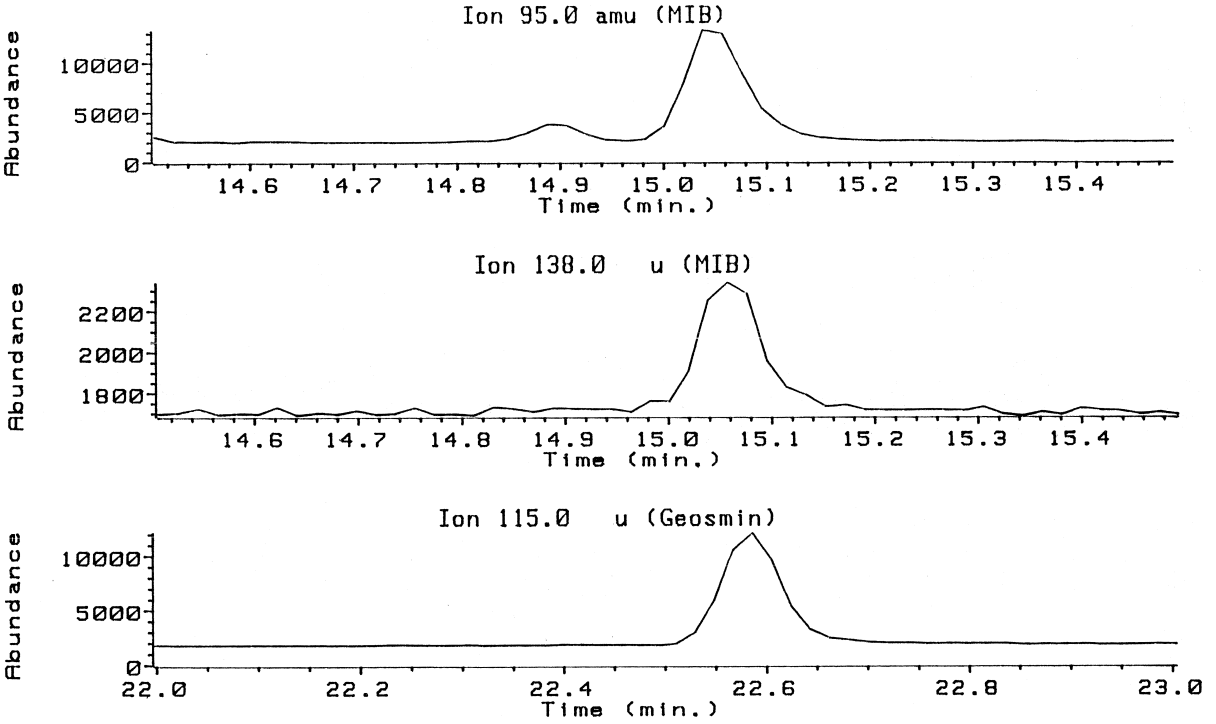

Fig. 6. Reconstructed single ion traces from the spiked water sample (Fig. 6) for deuterated MIB (m/z 95, 138) and deuterated geosmin (m/z 115).

peaks. These substances originated from the water sample and not from the trap. At this concentration level, good sensitivity and peak shapes are obtained for the m/z values that were used for quantitative calculations (Fig. 6). The single ion peak $m/z=138$ was found to have a signal-to-noise ratio of about 20:1.

5. Conclusions

The multichannel silicone rubber trap is an excellent alternative to the carbon filter used for the determination of tastes and odors in drinking water. The retention of these substances by the silicone is based on dissolution into the polymer as opposed to the adsorption onto the activated carbon in the standard filter. This is a major advantage since the sorption properties of the multichannel trap remain constant [9] in contrast to the reliance on the activity of the carbon filter, which deteriorates with usage. The multichannel traps can therefore be used repeatedly over long periods without change in sorption properties.

Although these traps produce background peaks, these are distinctive and remain constant without deterioration [8] and are easily identified by mass spectrometry. Any type of background is generally undesirable, but the stability of these low-level peaks suggests that they can be put to use as retention markers.

Other advantages of the multichannel trap are its simple design, permitting laboratories to manufacture their traps to their own specifications, which reduces the cost of analyses quite considerably. The elimination of the micro-extraction of the carbon filter with organic solvent, which requires a certain amount of skill and experience makes the multichannel trap much easier to use.

A major disadvantage of using the multichannel trap is that is requires a desorber or PTV injector for thermally desorbing the sample onto the gas chromatographic column.

Although the presence of water does not alter the

sorption properties of the trap, water that condensed onto the trap during purging, if not completely removed, tended to freeze in the cryo-trap, reducing the flow rate through the cold-trap. This condensate was effectively removed by centrifuging the trap at 2500 rpm for 10 min. Purging at higher sample temperatures in the closed-loop stripping apparatus, in an attempt to shorten the purge time, resulted in more water condensing in the trap and consequently greater difficulty in removing the water. Longer centrifuge periods were required to remove this water. Some of the commercial desorbers on the market, as in the case of that used in our laboratory, have a 'back-flush' facility, which effectively removes the remaining traces of water from the trap.

The multichannel trap has clearly been shown to be a suitable alternative to the carbon filter for the analysis of tastes and odors in water, doing away with the necessity of micro-extraction with organic solvent. It is ideally suited for the water laboratory where these analyses are conducted routinely.

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