Analysis of volatile organic compounds in water by sorptive extraction and gas chromatography – mass spectrometry

by

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Submitted in partial fulfillment of the requirements for the degree

Master of Science
Applied Science

In the Faculty of Natural, Agricultural and Information Science
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Summary

The Volatile Organic Compounds (VOCs) are a common occurrence in drinking water and potable water. A number of these substances have been labelled by the US Environmental Protection Agency (EPA) as being dangerous and harmful to human health.

Tastes and odours occur in drinking water and are most often considered as unacceptable by the end user and their presence in the water is of concern to the public.

In this thesis the multi-channel silicone rubber trap (MCT) was used to isolate these substances from water for analysis by capillary gas chromatography – mass spectrometry.

The water contaminants were purged from the sample and trapped on the MCT. The organic compounds absorbed on the MCT were thermally desorbed onto a cryogenic trap and then refocused onto the analytical column for analysis.

The mass spectrometer was used as the detector and it was operated in the *single ion monitoring* mode to obtain greater sensitivity and better resolution of the analysed substances

The results obtained from the study indicate that the MCT can be successfully used for the simultaneous analysis of VOCs and substances that cause tastes & odours, in water. The method is easy to implement, inexpensive and produces reliable results. This is ideal for a routine water laboratory analysing a large number of samples.

Samevatting

Drinkwater bevat 'n aantal vlugtige organiese stowwe waarvan somiges hulle oorsprong het in die chloor-disinfeksieproses. Van die stowwe is deur die Amerikaanse Agentskap vir Omgewingsbewaaring (EPA) gelys as gevaarlik en skadelik vir menslike gesondheid.

Ander stowwe wat 'n onaangename smaak en geur aan water gee is ook 'n bekommernis vir die verbruiker. Alhoewel die stowwe nie toksies is nie is hulle nie aanvaarbaar in die drinkwater nie.

Die multikanaalsilikoonrubber konsentreerder (MCT) is gebruik om die stowwe van water te ekstraeer en dan met gaschromatografie – massespektrometrie te analiseer. Die MCT is in ons labratorium vervaardig met 6mm glasbuis wat 16 silikoon rubber buisies bevat, 70mm in lengte en 0.3mm binne-deursne x 0.64mm buite-deursne. Die organiese stowwe word in die MCT opgevang deur gas deur die water monster te borrel. Daarna word dieselfde gas weereens deur die water gepomp in 'n geslote lus.

Die stowwe wat in die konsentreerder opgevang word,word dan termies gedesorbeer na 'n koueval toe, wat dan weer vehit word om die komponente op die analitise kolom te plaas.

Die massaspekrometer was in die enkel-ion bedryfswyse gebruik om verbeterde sensitiwiteit en resolusie te verkry.

Die metode vir die analise van die stowwe wat verantwoordelik is vir smaak en geur is eers geoptimiseer gevolg deur dieselfde prosedure vir die vlugtige organiese verbingings. Daarna is getoon dat die twee organiese groepe terselfdetyd geanaliseer kan word met die nuut-onwikkelde MCT metode.

Die metode is maklik om te implementer, goedkoop en uiters nuttig in 'n labratorium wat baie watermonsters analiseer.

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Abbreviations

MCT	Multi-channel Silicone Rubber Trap
VOC	Volatile Organic Carbon
THM	Trihalomethane
EPA	United States Environmental Protection Agency
MCL	Maximum contaminant level
GC	Gas chromatography / gas chromatographic
GC-MS	Gas chromatography – mass spectrometry
ppb	parts per billion
LLE	liquid – liquid extraction
SHS	Static headspace sampling
DHS	dynamic headspace sampling
P&T	Purge and trap
CLSA	Closed-loop stripping analysis
SPE	Solid phase extraction
OTT	Open tubular trapping
PTFE	polytetrafluoroethylene
SPME	Solid Phase Microextraction.
PAH	Polynuclear Aromatic Hydrocarbons
PDMS	Polydimethylsiloxane
2-MIB	2-methyl-isoborneol
SIM	single ion monitoring mode
NIST	National Institute of Standards and Technology

Chapter 1

Introduction

1.1 Background.

Clearly the primary objective of authorities providing drinking water to the public is to ensure that it is safe and aesthetically acceptable. A legacy which continues to plague many countries throughout the world is that drinking water can spread disease. With this knowledge the consumer will require that the safety of drinking water must be the overriding consideration in deciding between aesthetic and safety concerns. Generally however, aesthetic and safety problems operate in parallel as factors impairing the quality of drinking water. Improvement in the aesthetic quality often corresponds to an overall improvement of quality, which will be consistent with reducing health risks. A notable exception may be the taste associated with the disinfection of water by chlorination[1].

In South Africa, which has a shortage of drinking water resources, contamination of naturally occurring water such as rain, surface and ground waters by organic compounds has led to increased concern.

These organic contaminants can be broadly divided into two main categories.

- Substances of high to moderate volatility which include many of the chlorinated organic solvents and substances producing off-flavours in drinking water.
- Substances of moderate to low volatility which encompass many of the pesticides, aromatic compounds containing two or more benzene rings, polychlorinated biphenyls (PCBs) and polar water soluble organic compounds.

Because of the very large range of volatilities and polarities of the substances in the combined groups, no single method currently exists whereby all the substances can be analysed concurrently.

In the report that follows, emphasis will be placed mainly on those compounds that fall within this first group of volatile and semi-volatile substances.

During the late 1970's selected contaminants in water and drinking water began to receive increased attention[2]. As the list of contaminants considered detrimental to health continues to grow, more and more emphasis is placed on the monitoring and detection of these substances. A number of compounds, known as the Volatile Organic Compounds (VOCs), have been identified as contaminants in drinking water. The Environmental Protection Agency (EPA)[1] of the United States of America has published a list of 54 of these compounds, which are considered harmful to human health. A number

[1].Environmental Protection Agency, 401 M street, SE, Washington, DC 20460-0003 USA

of these substances have been classified as known or suspected human and mammalian carcinogens.

Included in this list are eight to ten compounds, known as the Trihalomethanes (THMs), which are most often formed during chlorine disinfection. Many of the other compounds listed find their way into drinking water from industrial run-off. With industrial expansion comes the greater likelihood of contamination of our water resources by these substances.

The EPA , in their *National Primary Drinking Water Regulations*[3], has set maximum contaminant levels (MCLs) for these VOCs which are in the low part-per-million range (ppm) i.e. 10^{-6} gl^{-1}. In December 1998, new, lower MCLs were set for the total THMs[4] allowable in drinking water. This necessitates the development of new methodology for the detection of these substances at these "new" low concentration levels.

The European Commission revised their Drinking Water Directive in 1997. Standards of 10 μgl^{-1} were set, for the total concentration of five chlorinated hydrocarbon compounds, amongst which are trichloroethene and tetrachloroethene. The suggested maximum allowable concentrations for these two substances have been set at 2$\mu gl^{-1}$and 3μgl^{-1}, respectively, by the Scientific Committee for Toxicity and Ecotoxicity of Chemical Compounds[5]. On the basis of the current proposals, maximum standards for THMs have been set at 100μg l^{-1} for the sum of four compounds, at the tap[6].

It is generally felt that the guidelines for drinking water, set by the World Health Organization in 1993, are far too lenient and do not take into consideration a number of aspects, especially the volatility of the particular substances in question[5].

The other substances of interest that fall into the volatile and semi-volatile group of contaminants are not included in the VOC listing of the EPA . These are the substances which impart off-flavours to drinking water. The *European Drinking Water Directive* stipulates a maximum taste and odour threshold equal to 3 for drinking water (dilution ratio with a reference water, beyond which no odour is perceived).

Because the aesthetic quality of drinking water is the only measure of quality available to most consumers, the detection of off-flavours is most often associated with unsafe water[7].

An earthy, musty, potato-bin like taste and odour occurs commonly in water and is usually detected in the early summer. This is most often produced by two compounds, geosmin (trans-1,10-dimethyl-trans-9-decalol) and 2-methyl-isoborneol (1,2,7,7-tetramethyl-exo-bicyclo[2.2.1]heptan-2-ol). These substances originate as degradation products of actinomycetes and cyanobacteria (blue-green algae)[8]. Since the original research done in developing a standard method for the determination of these two

compounds[9], numerous other substances have been identified with tastes and odours ranging from earthy/musty to fragrant, grassy and fishy.[10]

Taste and odour incidents from geosmin and 2-methyl-isoborneol (MIB) generally occur at the onset of warm weather when algal blooms occur. The human nose is extremely sensitive and odour threshold concentrations of $10ngl^{-1}$ (ppt) for geosmin, have been reported[9]. At these low concentration levels, most water facilities would have difficulty in removing these compounds from their finished product. The application of activated carbon filtration is usually required to remove these substances, but this is an expensive exercise.

A taste and odour incident, that occurred in a South African impoundment, was treated by dosing with $10mgl^{-1}$ of powdered activated charcoal to make the drinking water acceptable. The cost of this treatment, over a two month period, was in the region of R1 000 000[11]. Tastes and odours in drinking water are therefore a very real problem and constant monitoring for these substances is required to take quick action.

1.2 Approach.

The work that follows will introduce new technology in the field of analytical monitoring of drinking water and drinking water resources. The work will specifically be aimed at the isolation and concentration of the VOCs and taste

and odour producing substances, from an aqueous matrix. The main requirements are,

(i). that the technique should be easy to implement and readily available,

(ii). that the analytical results can be obtained in the shortest period possible, without sacrificing accuracy and precision and

(iii). that the technique should be inexpensive, thereby reducing the cost of monitoring which in turn would reduce the cost of producing a good quality drinking water.

1.3. Arrangement and Layout.

The dissertation will consist of the following:

Chapter 1. Introduction

Chapter 2. Discussion and presentation of the current state of analytical techniques for the isolation and separation of the substances in question. Theoretical discussion on each introduced technique.

Chapter 3. Experimental detail, analytical methodology and instrumentation.

Chapter 4. Presentation and discussion of results from the analysis of the taste & odour substances

Chapter 5. Presentation and discussion of results from the analysis of the VOCs

Chapter 6. Presentation of "real" samples. Discussion of results, conclusions and recommendations

Addendum I. Chromatograms

Addendum II. Publication in Journal of Chromatography A.

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Chapter 2

Isolation and Pre-Concentration Techniques for Organic Compounds in Water

2.1 Extraction of Water Samples

The type of samples that environmental analysts typically handle are either too dilute, too complex, or incompatible with the normal working of chromatographic instruments, used for their analysis[1]. Sample preparation is therefore an unavoidable step. Direct introduction of small volumes of water into the GC has been done, with some success. To meet the stringent standards set by the EPA and the European Commission, a total analyte content of at least an equivalent of between 0.1ml and 1.0ml of a water sample, must be introduced directly into the GC system for analysis. This has a number of experimental disadvantages, the main being that the evaporation of this amount of water results in a very large volume of vapour[2]. To avoid these problems various indirect methods have been developed. In these methods the compounds of interest are isolated from the water sample prior to analysis.

Trace analysis of organic compounds in water normally requires selective extraction procedures and then a concentration step prior to analysis. A complete scheme for trace analysis of organic compounds would generally

consist of the taking of the sample, selective extraction, clean-up procedures, preconcentration and analysis by high resolution capillary gas chromatography (GC), and/or gas chromatography with mass spectrometric detection (GC-MS). Determination of organic compounds, at the low part-per-billion (ppb) range, i.e. $10^{-6}gl^{-1}$ can be performed by combining sensitive and selective detection with sample preconcentration[3].

The basis of the isolation technique is to transfer the compounds of interest from the aqueous sample to a medium, which is more favourable for GC sample introduction. This is commonly known as phase switching. A concentration step is generally an integral part of the isolation procedure.

The techniques used for the isolation of volatile and semi-volatile organics contained in an aqueous phase can be divided into the following basic groups:

liquid-liquid extraction
gas-liquid extraction
solid-liquid extraction
permeation and other techniques.

2.2 Liquid – Liquid Extraction.

Liquid – liquid extraction (LLE) is essentially an equilibrium distribution technique, where the solutes of interest partition between the aqueous phase and an organic phase.

The extraction efficiency for LLE, θ, can be written as [2]:

$$\theta = 1 - \frac{1}{1 + K\left(\frac{V_{org}}{V_{aq}}\right)} \qquad (2\text{-}1)$$

where K is the distribution constant, and V_{org} and V_{aq} are the volumes of organic phase and the aqueous phase, respectively. Equation.2-1 shows that the higher the phase ratio ($= \frac{V_{org}}{V_{aq}}$) and the higher the distribution constant the higher will be the extraction yield. Therefore the selection of solvent plays an important role on the recovery of the solutes from the sample. In selecting a solvent, the partition coefficient, which is a measure of the affinity of the solute for the solvent, must be considered, as must the phase ratio and the number of extraction steps.[3, 4, 5]

Direct extraction with an immiscible organic solvent, although one of the oldest methods, can be very efficient. Extraction by shaking, with a solvent that is lighter or denser than water is the simplest and most rapid method. Multiple extractions, combining the extracts, will increase the recovery, but this requires large volumes of expensive ultra-pure solvents. Preconcentration by solvent evaporation is required which may cause serious losses of the compounds of interest [6]. Hence, methods that do not require a solvent concentration step are preferable for the recovery of volatile and semi-volatile, trace organic compounds from water.

Micro-extraction is one such method. The reduction of the water sample volume to 10ml and the organic solvent volume to 200µl has been successfully used for the analysis of THMs, with electron capture detection [7]. With the micro-extraction technique, the problem of impurities in the solvent is reduced, since sample concentration is generally not required. Although extraction efficiencies are only in the range of 40% - 60%, consistent and reliable results are obtained [8].

Continuous liquid-liquid extractors are available as an alternative extraction method. These can be operated simultaneously, unattended, for long periods of time (e.g. overnight)[9]. The countercurrent distribution apparatus can provide 1000 or more equilibration steps and allows the recovery of analytes that have extremely small distribution coefficient (K) values. Using equation (2-1) the relationship for the total recovery (R_{tot}) by countercurrent liquid-liquid extraction is:

$$R_{tot} = 1 - (1 - \theta)^n \qquad (2\text{-}2)$$

where R_{tot} is the total accumulative recovery for n extractions.

Although liquid-liquid extraction is still used extensively, it suffers from a number of disadvantages.

- A great amount of time is spent on the technique, particularly when multiple extractions are required.

- The sample volume required is relatively large (0.5l – 5l).
- Large volumes of ultra pure solvents, which are often toxic, are used.
- Concentration of the solvent is usually required, prior to analysis.
- The formation of emulsions during extraction is often troublesome.

2.3 Gas – Liquid Extraction

Gas phase extraction of volatile and semi-volatile organic compounds from an aqueous medium has been reported as being several times more efficient than any other extraction method [6]. Two distinct methods of gas extraction exist, headspace analysis and stripping or purging analysis.

Headspace analysis samples the vapour above the sample, either statically or in a dynamic mode. In static headspace sampling (SHS), an aliquot of the vapour phase (headspace), in thermodynamic equilibrium with the liquid phase, in a sealed container, is transferred for analysis. On the other hand, dynamic headspace sampling (DHS) is the purging of the vapour phase with an inert gas, driving the purged substances out of the vial, onto an in-line purge - trap concentrator.

With stripping analysis, the compounds are purged from the water sample by bubbling a gas through the water and collecting the substances on an in-line trap.

This technique can be divided into two types of analyses:

- Open-ended trapping or more commonly known as purge and trap (P&T)
- Closed loop stripping analysis (CLSA).

These two techniques will be discussed below under the headings of Purge & Trap and Closed Loop Stripping.

2.3.1 Static and Dynamic Headspace

Static headspace is a technique suitable for determining volatile compounds in solids and dirty liquid matrices such as blood, food and wastewater. In utilizing SHS, the sample is normally placed in a sealed vial, heated carefully in a regulated bath or oven and the compounds in the sample allowed to come to equilibrium in the gas phase. An aliquot of the gas phase is removed and injected into the GC for analysis. The relative concentrations of the analyte in the two phases are determined by the partition coefficient (K). This is defined as the ratio of the concentration of the analyte in the liquid phase to that in the gas phase [10]. The ratio of the volumes of the liquid and the gaseous phase in the headspace vial can affect the sensitivity of a headspace determination [11].

$$K = \frac{C_L}{C_G} \qquad (2\text{-}3)$$

$$C_0 V_0 = C_L V_0 + C_G \cdot (V_{HS} - V_0) \qquad (2\text{-}4)$$

combining Eq.(2-3) & Eq.(2-4)

$$C_G = {C_0 V_0}/{(V_0 \cdot (K-1) + V_{HS})} \qquad (2\text{-}5)$$

K is the partition coefficient. C_L and C_G are the concentrations of the analyte in the liquid and gas phases after equilibrium. C_0 is the original concentration of the analyte in the liquid sample, V_0 is the volume of the liquid phase and V_{HS} is the volume of the headspace.

To increase sensitivity, dynamic headspace sampling (DHS) is employed. In this case the phase equilibrium is continually displaced by purging the headspace out of the sample vial with an inert gas. The analytes are collected on a suitable adsorbent trap or are cold trapped directly on the GC column for analysis. Solutes can be detected at parts-per-billion(ppb) concentration levels and the method can be easily automated. Salting out with sodium sulphate or sodium chloride has been used to increase the sensitivity by increasing the ionic strength of the liquid phase [12]. Acids and bases can be forced into the headspace by adjusting the pH of the sample.[13]

2.4 Purge and Trap

This technique is probably the most widely used method for analysing volatile organics in water samples, particularly in water laboratories in the United States of America, where the method was first published in 1974 [14]. This

technique entails bubbling an inert gas through the water sample and trapping the purged solutes on an adsorbent trap or on a cryogenic trap. This is in essence an open-ended trapping technique where the purge gas is vented to the atmosphere after passing through the adsorbent trap. The trapped substances are then thermally desorbed on to the GC column for analysis. The solutes therefore pass from liquid phase to gas phase to solid phase to gas phase.

The recovery (R) of the purged compounds, from the sample, over a period of time can be expressed as [15]:

$$R = 1 - \exp\left(\frac{-Ft}{KV_L + V_G}\right) \qquad (2\text{-}6)$$

where R is the recovery of the solute. F is the flow rate of the purge gas, t the purging time, V_L, the sample volume and V_G the volume of the gas passed through the sample in time t. K is the gas/liquid partition coefficient of the solute. Equation (2-6) assumes that thermodynamic equilibrium exists between liquid and vapour in each bubble formed, that no breakthrough occurs on the adsorbent trap, that the sample matrix is non-volatile and that the partition coefficient is independent of concentration.

There are several potential problems that exist with this method of sample concentration [6], a) Cross contamination of the purging vessel occurs where low- and high-concentration samples are analysed in succession. b) Sample

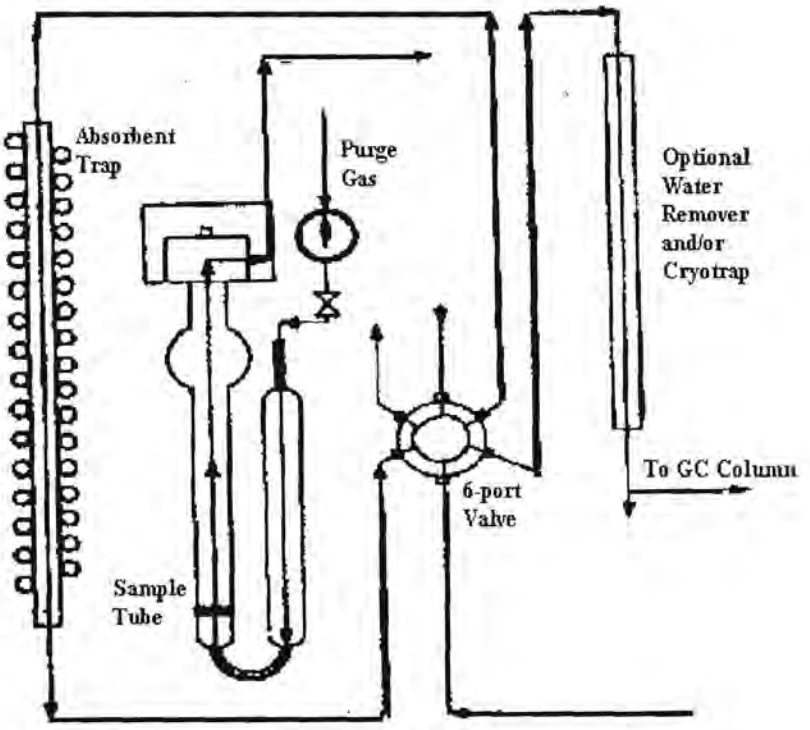

Figure 2.1 Purge and Trap Apparatus.

foaming can be a problem if samples are obtained from sources other than drinking water. c) Whereas contaminants in the continuously introduced GC carrier gas are often not a problem, the same does not hold for the purge gas. The latter needs to be extremely pure as contaminants from a large volume are concentrated in the trap.

Numerous commercial instruments are available on the market, some offering automated sample handling facilities. The desorption oven is an integral part of the instrument, capable of fast heating rates for the thermal desorption of the trapped substances. Most instruments have the option of a cryogenic trap to focus the substances prior to analysis by GC.

Purging directly onto the analytical column, also know as whole column cryotrapping, has been reported as an alternative to the use of the adsorbent and cryogenic trap on the instrument. Good resolution was obtained using a capillary column [16,17]. The method eliminates the need for a P&T unit. It is inherently, highly reliable as it is very simple; the level of background contamination is low because of the reduction in the number of steps and the need to retain very volatile compounds on a P&T trap is eliminated. [6]

The range of compounds isolated from water by the P&T technique has been extended beyond the highly volatile substances detected by the original method to many of the semi-volatile materials [6, 18]. The wide range of applications, good precision and elimination of an organic solvent step ensure that the technique will be continually developed.

2.5 Closed Loop Stripping Analysis

The method of CLSA for the measurement of purgeable, intermediate-molecular-weight organic compounds in drinking water at the ngl^{-1} was first described in 1973. Several papers from the same group, dealing with the development of the method, have been published [19,20]. It is an interesting variant of the P&T method, in which volatile compounds in the liquid phase are trapped on a sorbent trap by pumping the purge gas in a closed circuit via the trap and the liquid phase. In the original method the sorbent was a carbon trap, which adsorbed the organics and allowed the purge gas to pass through

the filter to repurge the sample, via the pump. The trapped organic compounds are then extracted from the trap with a small amount of a suitable solvent (8-10µl). Carbon disulphide is a solvent that is commonly used. An aliquot of the extract is then analysed by GC or GC-MS.

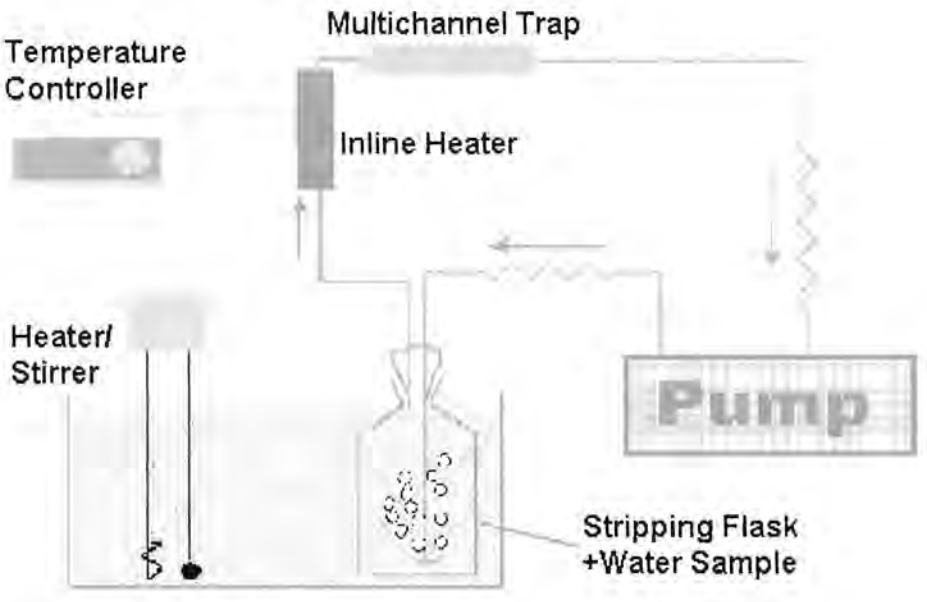

Figure 2.2 Closed Loop Stripping Apparatus

Considering the situation in the trap, the CLSA method can be applied in two ways. In the early stage of the process, frontal chromatography of the components being accumulated takes place in the trap. If the volume of gas pumped is such that it does not cause the zone of the least retained compound to leave the trap, the proportions of the components deposited on the trap will be equal to their corresponding mean proportions in the gaseous phase. This case is considered as conservation trapping. If the volume of gas pumped through is large enough to bring the whole system to a state of

equilibrium, then equilibrium trapping occurs. In the latter case, the proportion of the components entrapped [R_t] is given by [6]:

$$R_t = C^*_{iG}(V_{Gt} + K_{SG}V_S) \qquad (2\text{-}7)$$

where C^*_{iG} is the final (equilibrium) concentration of the solute (i) in the gaseous phase; V_{Gt} the void volume of the trap; K_{SG} the sorbent-gas distribution constant for the solute and V_S the volume of the sorbent in the trap. CLSA has a high reproducibility as all steps can be accurately standardised. It is less influenced by the sample conditions such as high organic or inorganic particulate material. There is no alternative procedure with such a wide range of sensitivity and the recovery of polar substances is equal to or better than that obtain by extraction with solvent or solid sorbents [20]. New developments in the technique have made use of adsorbents other than carbon. Tenax GC has been used as sorbent for the analysis of apple juice and the adsorbed substances thermally desorbed [21].

As a result of the high sensitivity of this technique, a standard method for the analysis of tastes and odours was developed [22]. This method is used extensively in water laboratories for regular monitoring of taste and odour incidents. The human nose is an extremely sensitive detector and sensory evaluation by trained human noses has set threshold odour concentrations in the low ngl^{-1} range (Table .2.1) [22]. The CLSA technique is well suited to

these analyses, being able to detect these substances, at the required low concentration levels.

Table 2.1. Characteristics of Odour-Causing Compounds

Compound	Threshold Odour Concentration (ng ℓ^{-1})	Odour Characteristics
Geosmin	10	Earthy, musty
2-methylisoborneol	29	Earthy, musty, campherous
2-isopropyl-3-methoxy pyrazine	2	earthy, musty potato-bin
2-isobutyl-3-methoxy pyrazine	2	earthy, musty, bell-pepper
2,3,6-trichloroanisole	7	musty

The widely used procedure for extracting the trapped substances from the carbon trap consists of collecting, in a sample tube, several small portions of solvent which have been repeatedly passed through the filter bed, by temperature gradient [20]. This gradient is obtained by warming the capillary receptacle with the fingers and then cooling it. This technique has a number of weak points. The procedure is rather laborious and requires a skilled operator. Losses of solvent by evaporation occur easily, particularly when a very volatile solvent, such as carbon disulphide is used. More over, with trace analysis it would be desirable to analyse the first portion of the extract, which provides

the highest available concentration. However, this portion is distributed over large glass surfaces and dilution is unavoidable with further rinsing [20].

Contamination of the carbon filter, resulting in an unacceptably high background, is of concern. In some cases solvent extraction does not clean the carbon bed and it has been necessary to treat the filter with hydrogen peroxide, achieving clean-up by oxidation [23].

2.6 Solid – Liquid Extraction

The direct trace enrichment of organic compounds by adsorption on solid materials has become a very popular technique. Some desirable attributes of solid sorbents are a high specific surface area, inertness and the ability to adsorb a wide variety of organic compounds from large volumes of water. Sorbent extraction is based on the distribution of the dissolved compounds between the solid sorbent and the water. Provided the sorbent is correctly chosen, the partition coefficient is shifted even more towards the sorbent than in LLE. The principle is thus analogous to that of LLE, the differences being in the extraction materials used and therefore in the resulting enrichment factor.

Commonly used solid sorbents are activated charcoal, macro-reticular porous polymers, polyurethane foams, bonded-phase material and ion-exchange resins [15]. Compounds retained on the solid phase are removed by eluting with a solvent which has a greater affinity for the analytes than the sorbent. The different mechanisms of retention or elution are due to intermolecular

forces between the analyte, the active sites on the surface of the adsorbent and the liquid phase. These mechanisms are identical to those involved in column liquid chromatography. Where the sorbent is thermally stable, thermal desorption of the analytes sometimes replaces solvent elution, ensuring the highest degree of sample enrichment [24].

Modern techniques necessitate that the sample (water) be passed through a column, pre-packed with the sorbent of choice. Highly selective extractions can be achieved by choosing sorbents that will attract only the analyte of interest. The major advantages of sorbent extraction over LLE are [25] :

Samples can easily be collected in the field and then brought to the laboratory for analysis.

- Small volumes of solvent are required for extraction.
- Sample preparation time and requirements are reduced.
- Selective adsorption and elution yield lower background interferences
- Sorption techniques are easily automated and can be used on-line.

Sorption techniques can be divided into two main groups, solid-phase extraction (SPE) and open tubular trapping (OTT).

2.6.1 Solid Phase Extraction

The design of a solid phase extraction (SPE) cartridge consists of a short column, often an open syringe barrel, containing a sorbent packed between polypropylene frits. Packing capacities range from 20mg to 10g with reservoir volumes of as much as 30ml. A variety of sorbent materials are available for SPE analysis but the most popular are the polymers and chemically bonded silica phases, which are used in liquid chromatography. These phases are classified as polar, non-polar and ion-exchange, according to the chemical characteristics of the functional group chemically bonded to the silica or co-polymer(Table 2.2)[26]. For better adsorption and specificity, the SPE sorbent can be chemically modified with a reactive compound or loaded with a solution containing a reactive group to form a derivative of the analyte.

The general procedure in SPE analysis is: (1) conditioning of the cartridge and eluting any interfering substances, (2) extraction of the sample, (3) drying of the cartridge, and (4) elution of the retained compounds.

Key factors to be considered in SPE are the extraction volume of the sample, the flow rate, the amount of solid sorbent in the cartridge and, finally, the use of organic modifiers.

The SPE method is strongly dependent on the volume of sample analysed, as the retention and consequently, recovery of compounds depends largely on the volume of sample flowing through the cartridge. The retention of compounds in a SPE cartridge can be described by a chromatographic process. As the sample flows through the SPE cartridge, the substances

Table 2.2. Commonly used SPE phases

NONPOLAR		
C18	Octadecylsilane	-Si-$(CH_2)_{17}$-CH_3
C8	Octylsilane	-Si-$(CH_2)_7$-CH_3
C2	Ethylsilane	-Si-CH_2-CH_3
PH	Phenylsilane	-Si-(C_6H_6)
CH	Cyclohexylsilane	-Si-$(C_6H_6$
POLAR		
Si	Silica	-SI-OH
CN	Cyanopropylsilane	-Si-CH_2-CH_2-CH_2-CN
2OH	Diolsilaane	-Si-CH_2-CH_2-CH_2OCH_2(CHOH)-CH_2OH)
NH_2	Aminopropylsilane	-Si-CH_2-CH_2-CH_2-NH_2
PSA	N-propylethylenediaminesilane	-Si-CH_2-CH_2-CH_2-$NHCH_2CH_2NH_2$
ION EXCHANGE		
SCX	Benzenesulfonylpropylsilane	-Si-CH_2-CH_2-$CH_2(C_6H_4$-SO_3^-
PRS	Sulfonylpropylsilane	-Si-CH_2-CH_2-CH_2-SO_3^-
CBA	Carboxymethylsilane	-Si-CH_2COO^-
DEA	Diethylaminopropylsilane	-Si-CH_2-CH_2-$CH_2^+NH(CH_2CH_3)_2$
SAX	Triethylaminopropylsilane	-Si-CH_2-CH_2-$CH_2^+N(CH_3)_3$

move along the sorbent with the elution characteristics of a chromatographic column. This process is equivalent to frontal chromatographic analysis and it is thus important to know the volume of sample that can be passed through a sorbent bed before the analyte of interest commences to elute from the column i.e. the breakthrough volume. The breakthrough volume limits the maximum sample volume that can be used for a particular substance, which in turn restricts the maximum pre-concentration factor that can be obtained.

Trace analysis of environmental samples is often affected by this restriction. When the volume of sample available is small, the breakthrough volume is not usually a consideration. It is important though, when the volume of the sample is large, as in environmental samples, where the breakthrough volume may easily be exceeded. The homogeneity of the sorbent bed, the quality of the sorbent and the sample flow rate, which contribute to the number of theoretical plates, will influence the breakthrough volume. But since the primary function of an SPE device is retention and not separation of the analytes, only the minimum efficiency is required for a cartridge to function adequately.

The design of the SPE cartridge has several disadvantages, which can be summarized as follows [27].

1. The small cross-sectional area of the extraction cartridges results in slow sample processing rates and a low tolerance to blockage by particles and adsorbed matrix components.
2. Channeling reduces the capacity of the cartridge to retain analytes.
3. Inconsistency in the quality of the sorbents occurs between batches and between manufacturers.
4. Irreversible adsorption of some analytes does occur.
5. Contaminants originating from the packing material or cartridge body can interfere with the analysis.

Points (I) and (2) above, result directly from the design of the cartridge and can be improved, while point (3) is a manufacturing problem and points (4) & (5) result from the analytical conditions

.

2.6.2 Solid Phase Extraction Disk

One of the most important developments of solid phase extraction materials was the introduction of the membrane filter disk. Known as "Empore Disks", these were developed by 3M (St. Paul, MN, USA) at the end of the 1980's, and were first reported by Hagen et al [28]. They were developed especially to overcome the problem of the small cross-sectional area and slow processing rates of the conventional SPE extraction cartridge.

The solid phase extraction disks are constructed of membranes, consisting of a fibrillated polytetrafluoroethylene (PTFE) matrix in which sorbents such as bonded silicas, polymers or ion exchangers are enmeshed. The membranes are available in diameters of 4mm to 96 mm, are 0.5 mm thick and the adsorbent accounts for up to 90% of the mass of the membrane. The main feature of these disks is their internal structure which permits a high flow-rate of a water sample without channelling occurring, thereby avoiding the loss of the analyte.[29]

The extraction process with the disks can be performed in three different ways [30]: (1) a standard filtration apparatus - where the sample is passed through the disk with the aid of a vacuum source - is the method generally used.

Analytes are retained on the sorbent and are then removed with a small volume of a suitable organic solvent; (2) the membrane is suspended in the liquid sample for a controlled period of time, then allowed to dry briefly in air and finally the analytes are directly detected by means of a solid state spectroscopic technique; (3) this option is similar to the second but the analytes are desorbed by suspending the disk in a solvent and then detected by analysing the extract.

Extraction disks are most often used when the sample volume is very large and the concentration of the analytes is low, e.g., in the trace analysis of organic pollutants in water.

The advantages of disk extraction technology over cartridge extraction technology can be summarised as follows. (1) Less time is required for sample processing because of the larger cross-sectional area of the disk, which decreases the pressure drop and lowers the linear velocity allowing higher volume flow rates through the disk. (2) Reduced plugging by solid particles occurs because of the larger cross-sectional area of the disk. (3) Channelling does not occur because of the use of smaller diameter sorbents and a greater mechanical stability of the sorbent bed. (4) Cleaner extracts are obtained, with fewer interferences, due to the optimisation of the bed mass to reduce non-specific matrix adsorption.

When analysing large volumes of environmental water samples with suspended matter, increased surface area and reduced plugging of the

extraction discs are important considerations. Stabilizing the disc bed by entrapping the sorbent particles addresses the problem of channelling which is the dominant cause of poor sampling reproducibility when using conventional cartridges.

The kinetic properties of the particle loaded membranes differ from those of the cartridge sampling devices [30]. The heterogeneous structure of the membranes probably contributes unfavourably to their kinetic properties. Over the typical flow-rate range of 10-100mlmin^{-1} for a 47mm diameter disk with a 38mm active sampling area, the particle loaded membrane will provide about four to nine theoretical plates with the largest values in the region of the optimum flow-rate (about 13 mlmin^{-1}) [30].

Some of the disadvantages of particle loaded membranes are that (1) they require 4-6 times higher volumes of eluents; (2) they are about 4 times more expensive than their cartridge counterparts and (3) the discs are not available in as many different sorbent phases as found in cartridges.

2.6.3 Solid Phase Microextraction

The difficulty of handling small volumes of solvents in solid phase extraction techniques comprises a major limitation to this approach. To overcome the limitations of conventional SPE techniques, Pawliszyn et al. at the University of Waterloo [31,32], dispersed a minute quantity of the extracting phase on a fine rod made of fused silica. The permanently attached sorbent allows reuse of the same extraction phase. The resulting technique is called Solid Phase

Microextraction (SPME). This technique allows extraction and concentration of the analytes in a single step. The fibre most often used in the SPME device is a fused silica rod mounted in the syringe needle and coated with various materials, such as polydimethylsiloxane, polyamide, liquid crystal polyacrylate, Carbowax or graphite (Figure2.3).

The coated fibre is introduced directly into an aqueous sample, where the analytes diffuse or dissolve into the fibre until equilibrium is established. The

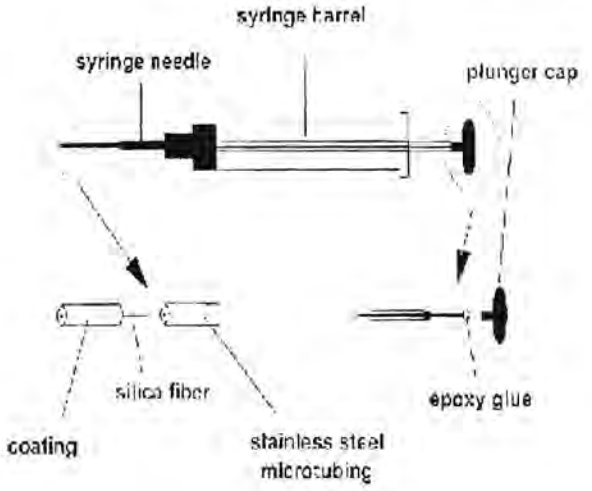

Figure 2.3 A custom made SPME

amount of analyte extracted is therefore dependent on its distribution coefficient. Typically the SPME extraction is considered to be complete when the analyte concentration has reached distribution equilibrium between the sample matrix and the fibre coating. The extracted amount is constant within the limits of experimental error and is independent of further increase of extraction time.

The equilibrium conditions can be described as[33]:

$$n = \frac{K_{fs} V_f V_s C_0}{K_{fs} V_f + V_s} \qquad (2.8)$$

where n is the amount extracted by the coating, K_{fs} is the coating/sample matrix distribution constant. V_s is the sample volume, V_f is the fibre coating and C_0 is the initial concentration of the analyte in the sample.

In most cases the K_{fs} values are not large enough to exhaustively extract all of the analytes in the matrix. Instead SPME, like static headspace analysis, is an equilibrium sampling method and can be used to accurately determine the concentration of target analytes in a sample matrix only through proper calibration. Factors such as the volume of the coating and the coating characteristics can influence the amount of analyte extracted by SPME as will *in situ* derivatization of target analytes, modification of the matrix, heating the sample and cooling the coating. The primary factors that affect the linear range and limit of detection of the technique are the fibre's stationary phase and the GC detector. As the stationary phase volume increases, more analyte is absorbed and the linear range increases. Consequently, compounds with low distribution constants will require thicker films than compounds with high distribution constants. The type of stationary phase used will determine the distribution constant for a specific analyte and therefore the quantity absorbed. The detection limits are therefore better for compounds with high distribution constants [32].

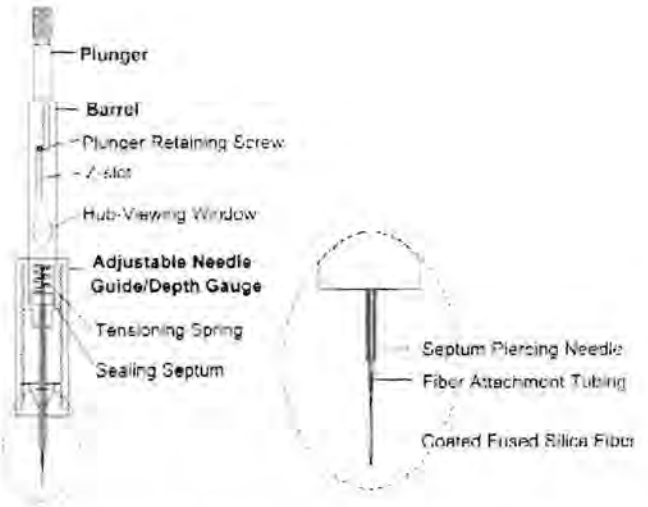

Figure 2.4 The first commercial SPME from Supelco

The partition coefficient (K_{fs}) of an analyte is also partially dependent on the sample matrix and therefore changing the nature of the matrix will influence the coating/matrix partition. Increasing the ionic strength of a water sample by the addition of sodium chloride will reduce the solubility of an analyte, shifting the partitioning into the polymer coating. Neutral forms of analytes are more efficiently extracted by non-ionic polymeric coatings, and therefore the pH of the aqueous sample must be adjusted to prevent ionisation of the analytes [34,35].

The speed of extraction is controlled by the mass transport of the analytes from the sample matrix to the coating. It has been reported that, at room temperature, equilibration can take up to 60 minutes [36] for compounds of high molecular mass. The time taken to reach equilibrium can be reduced by agitation, stirring or sonication [33,37]. Increasing the temperature of the sample also reduces the time taken to reach equilibrium, due to faster

diffusion of the molecules through the water, but the total amount absorbed by the fibre is lowered, as the distribution coefficients decrease with temperature[36].

If the sample volume V_s is very large ($V_s >> K_{fs}V_f$) then equation 2-8 can be reduced to

$$n \cong K_{fs} V_f C_0 \qquad (2\text{-}9)$$

and thus the amount of analyte extracted by the fibre coating is independent of the sample volume. This feature, combined with the simple geometry of SPME, will reduce analysis times by combining sample extraction, sample concentration and injection into a single uninterrupted process.

SPME preserves all the advantages of SPE such as being simple to manage, low in cost, easy to automate and allows on-site sampling, yet at the same time, eliminates the disadvantages of SPE such as plugging and the use of solvents. No special thermal desorption equipment and modification of the gas chromatograph is required. SPME with thermal desorption completely eliminates the use of organic solvents and integrates both the extraction and injection processes into a single step. The geometry of SPME enables placement of the sorbent into a sample, or the headspace above the sample, to extract the analytes. Sampling from the headspace with SPME will permit the extraction of analytes from very complex matrices such as sludges and water with a solids content.

Open Tubular Trapping

Open tubular traps (OTT) consist of uncoated [38] or coated [,39 ,40] capillary columns and are alternative devices used for extracting analytes from a water sample. The water sample is generally passed through the trap and the organic compounds present in the sample are absorbed on the capillary wall or coating. The use of crosslinked silicone stationary phases used for gas chromatographic columns is an attractive alternative to the use of classical solid adsorbents. The analytes in this case are not adsorbed onto the surface of the stationary phase but are partitioned into the stationary phase and the process is similar to liquid-liquid extraction.

Although the sorbent material used in OTT is very similar to the active part of a solid phase microextraction (SPME) device, extraction is fundamentally different from SPME in that it is normally not an equilibrium method. Instead extraction occurs by the movement of the analyte molecules through the trap by a normal chromatographic process which results in multi-equilibrium extractions, like countercurrent LLE, or disks, or SPE traps and therefore also facilitates complete extraction below a given breakthrough volume. The micropollutants are then either thermally desorbed with cryogenic refocusing or extracted with a small volume of suitable solvent.

The most significant differences between OTT devices and packed SPE traps are their permeability (low pressure drop) and the absence of band

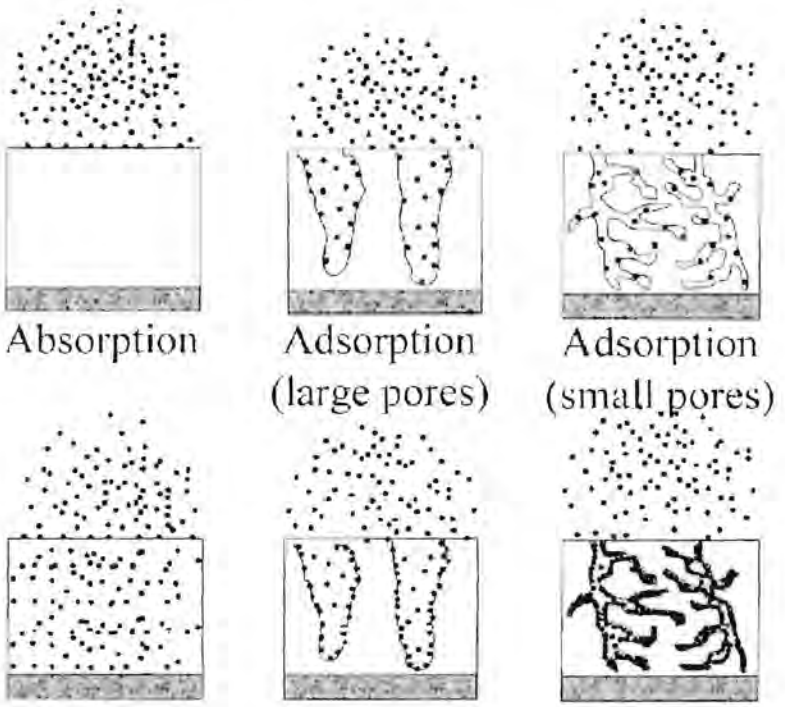

Figure 2.5. Absorption & adsorption processes

broadening effects which result from channelling occurring in the packing (the A-term in the Van Deemter equation,). As with SPE, the maximum volume of a sample that can be passed through a sorption column is determined by the breakthrough volume of the solute (V_b). The breakthrough volume of a component in a sorption column is often represented by the following equation [41]

$$V_b = V_0(1+k)(1-\frac{3}{\sqrt{N}}) \qquad (2\text{-}10)$$

where V_o is the void volume of the trapping column, k the capacity factor of the solute in the trap and N the plate number of the trapping column (with N>9).

The process of trapping analytes in an open tubular trap is analogous to frontal elution in open-tubular Liquid Chromatography using extremely wide-bore columns. Values for N (Equation 2-10) can be obtained from the Golay equation which describes band broadening in an open-tubular trap:

$$H = \frac{2D_m}{u} + \frac{1+6k+11k^2}{96(k+1)^2}\frac{d_e^2}{D_m}u + \frac{2}{3}\frac{k}{(k+1)^2}\frac{d_f^2}{D_s}u \qquad (2\text{-}11)$$

where D_m is the diffusion coefficient of the solute in the mobile phase, u the linear velocity, d_f the stationary phase thickness and D_s the diffusion coefficient of the solute in the stationary phase.

From the two equations above it is seen that the absorption process of pollutants from water in OTTs is influenced by the following chromatographic constants; the internal diameter (ID) and the phase thickness (d_f) of the capillary trap; the sampling conditions (flow velocity and total volume eluted) and the physical-chemical properties of the analytes. Equation 2-10 indicates that an increase in the capacity factor (k) will cause a marked increase in breakthrough volume. The capacity factor (k) of a trap is defined as the ratio of the concentration distribution constant (K) to the phase ratio (β) i.e. $k=K/\beta$, but from the last two terms of Equation 2-11, it can be seen that increasing the internal diameter and the stationary phase thickness in a column leads to reduced chromatographic efficiency. It is therefore necessary to find the right

balance between the different needs arising from retention and chromatographic efficiency

It was noted from studies done by Zlatkis et al. [38] that the efficiency of trapping is greatly dependent on the flow rate of the aqueous solution through trapping capillaries. The lower the flow rate, the better the removal of trace organics, primarily because of a longer residence time of the solution inside the capillary trap, since the possibility of organics coming into contact with the trapping surface is enhanced [38]. A decrease in flow rate will decrease the plate height (Equation 2-11), which in turn will increase the number of theoretical plates of the trap and the increase of theoretical plates will increase the breakthrough volume of the trap (Equation 2-10).

The breakthrough volume is also affected by temperature since the diffusion coefficient of the analytes in the mobile phase and the capacity factor are affected. Mol et al. [41] determined that the capacity factors of PAHs decreased by a factor of 2.2-3.4 with increased temperature. Generally it was found that trapping of the analytes at room temperature is preferable to using elevated temperatures.

Water retained in the trap poses a problem and needs to be removed from the trap after sampling prior to thermal desorption. Incomplete elimination of water will often interfere with the GC analysis. An advantage of OTTs over SPE devices is that complete removal of water, remaining in the trap after sampling, can be accomplished by simply purging the capillary with a low flow

of nitrogen gas. [41]. The removal of water from the packed SPE adsorption traps requires longer purging which can lead to the loss of the more volatile compounds. Any remaining water in the trap leads to reduced extraction efficiency as a portion of the pores of the packing material become blocked by the residual water.

The use of open tubular extraction traps has two principle disadvantages compared to the SPE packed traps [2]: (1) the retention power is generally not as great and (2) much lower sampling flow rates are used because of the single large diameter open channel and slow diffusion of the analytes in water.

2.6.4.1 Open Tubular Trap Configurations

Zlatkis et al. [38] concentrated organics from water samples by passing aqueous samples through uncoated plastic and metal capillary tubing. It was found that plastic materials and uncoated silicone in particular are capable of extracting trace quantities of organics in solution extremely efficiently. This prompted the use of coated capillary columns, of varying lengths, internal diameters and film thicknesses, to be used as OTTs. The analytical GC column has been used , off-line, to concentrate substances from water. The trapped analytes are analysed either directly [40] or after refocusing at the column inlet [42].

Blomberg et al. [39] use a capillary column, 2 metres in length, with a very thick stationary phase of 95 µm, as an OTT. This was attached to the

analytical column and a two oven configuration was necessary for the thermal desorption of sampled analytes from the OTT onto the GC column.

Burger devised a method to increase the phase thickness by inserting a silicone rubber tube into a 0.53 mm id. fused silica capillary by an innovative stretch and freeze method [43]. These commercial polymer tubes produced film thicknesses of 145 µm and a corresponding increase in retention [44].The traps were up to a meter in length which required a dual oven GC configuration for desorption and analysis.

Figure 2.6 Schematic of the multichannel silicone rubber trap

The low sampling flow rates required to prevent immediate breakthrough of the analytes in OTT, stems from the slow radial transfer in the tube The geometric deformation of OTTs (eg. coiling, stitching, weaving) [45] was found to increase the radial mass transfer rate due to centrifugal forces which are active and generate a so-called secondary flow in a radial direction. Mol et al. [45] showed that the plate heights for the same volume flow rate decreased with the deformed OTTs compared to the straight single channel OTT.

In our laboratory we have developed an OTT which is as long as the conventional desorption tube used in most commercial thermal desorbers –viz ca. 10cm long. This shorter more manageable trap, consists of a filled silica glass tube containing a number silicone rubber tubes, positioned parallel to each other[46]. (Figure 2.6).

Roughly the same internal volume and phase ratio is obtained when compared to the equivalent single channel trap with the same total length of silicone tube. The linear flow velocity through this multi-channel silicone rubber trap (MCT) is a lot lower than through a single channel trap at the same volume flow rate, which should result in a reduced theoretical plate height and thus provide similar number of theoretical plates as that of a long single channel trap. The multichannel trap was developed to fit most commercial thermal desorption devices .

The partitioning characteristics of the silicone rubber, which is identical to that of a non-polar GC stationary phase, has prompted other authors to use this medium for sample collection and concentration. Baltussen et al. [47] made a packed bed trap from crushed silicone rubber tubes which proves to be an attractive alternative for certain LLE and SPE applications.

Very recently, a procedure combining the sensitivity of packed PDMS beds with the application range (in terms of volatility) of SPME was introduced [48]. Stir bar sorptive extraction (SBSE) applies stir bars varying in length from 1 to

4 cm coated with a relatively thick layer of PDMS (0.3-1 mm) resulting in PDMS volumes varying from 55 ml to 220 µl. After a certain stirring time, the stir bar is removed from the aqueous sample and thermally desorbed on-line with a gas chromatograph. Due to the much larger volume of the PDMS-phase extraction efficiency is far better than for SPME.

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Chapter 3

Methodology and Instrumentation

3.1 Introduction

The multi-channel silicone rubber trap (MCT), which has been developed and tested in our laboratory [1], is used to develop a method to simultaneously analyse water samples for substances that cause tastes and odours and the volatile organic carbon compounds (VOC).

Currently, the standard method used for the analysis of tastes and odours is the Grob closed-loop stripping technique [2] using a small carbon trap. The standard method used most often for the analysis of the VOCs is a purge and trap method from the EPA, known as Method 524 which uses GC-MS for the analysis.

The major concern of most of the sorption techniques that are employed today is, the volume of sample that can be passed through the concentrating device before break-through of the analytes occurs. This is of particularly importance for the open-ended concentrating techniques used, such as purge & trap and solid phase extraction.

Details of the break-through volumes and elution curves for the MCT have been studied [3] and are available from a PhD thesis by Ortner [4]. This study concerned the direct extraction of organic compounds from water by passing the water sample

through the MCT, which necessitated the determination of break-through volumes of the substances being studied.

To bypass the necessity of having to consider break-through volumes it was decided to make use of the closed-loop stripping technique. This technique is similar to the purge & trap technique where the water sample is purged by bubbling a gas through the sample and the analytes then collected on a sorption trap. However, with closed-loop stripping the purge gas is re-circulated after passing through the sorption tube in a closed loop, to re-purge the sample. Under these conditions, equilibrium extraction occurs, since the sample is purged until the whole system reaches a state of equilibrium. This state of equilibrium will generally occur far beyond the break-through volume for most compounds.

The MCT was selected as the sorbent because the compounds are absorbed directly into the silicone rubber used, with all compounds partitioning independently into the sorbent. The silicone rubber can consequently be considered a liquid phase. The compounds of interest diffuse into the material as opposed to the surface adsorption that occurs with the commonly employed adsorbents such as activated carbon, carbon molecular sieves and the porous polymers such as Tenax and Chromosorb. The silicone rubber has been shown to be inert and permanent adsorption and reactions on the silicone rubber are negligible[5].

3.2 Equilibrium trapping theory.

One of the advantages of silicone rubber (polydimethylsiloxane) is that it has been used for many years as a gas chromatographic column stationary phase. Retention data of many compounds are available in the literature in the form of Kovats retention indices[6]. Baltussen and co-workers published a simple approach to calculate equilibrium constants (K) from retention index data [7]. In equilibrium trapping the gaseous phase is in complete equilibrium with the sorbent. With an infinitely large sample and open-ended trapping the concentration of the compound C in the gas phase can be calculated by:

$$C = \frac{m_{sorbed}}{V_r} = \frac{m_{sorbed}}{V_o(1 + K/\beta)} \approx \frac{m_{sorbed}}{V_{SR}K} \quad \text{for} \quad K>>1 \qquad (3.1)$$

where m_{sorbed} is the amount of compound. V_r is the retention volume of the trap, V_0 is the dead volume of the trap, V_{SR} is the volume of the silicone rubber in the trap and β is the phase ratio. The volume of the silicone rubber in the trap can be determined by weighing the amount of silicone rubber in the trap and multiplying by $0.825 g.cm^{-3}$, for the determination of β.[7] The distribution coefficient of the compound is K and m_{sorbed} is determined from a calibration curve [5].

In a three phase closed system, such as CLSA, the concentration of the extracted analyte in the silicone rubber is related to the overall equilibrium of the analyte in the

three phases. The total amount of the analyte in the system remains the same as the initial amount, therefore:

$$C_0 V_s = C_f^{\infty} V_f + C_h^{\infty} V_h + C_s^{\infty} V_s \qquad (3.2)$$

where C_0 is the initial concentration of the analyte in the matrix; C_f^{∞}, C_h^{∞} and C_s^{∞} are the equilibrium concentrations of the analyte in the silicone phase, the headspace and the matrix respectively; V_f, V_h and V_s are the volumes of the silicone rubber, the headspace and the matrix, respectively. Defining the silicone rubber/gas distribution constant as $K_{fh} = C_f^{\infty} / C_h^{\infty}$ and the gas/sample matrix distribution constant as $K_{hs} = C_h^{\infty} / C_s^{\infty}$, the mass of the analyte absorbed into the silicone rubber $n = C_f^{\infty} V_f$ can be expressed as [8]

$$n = \frac{K_{fh} K_{hs} V_f C_0 V_s}{K_{fh} K_{hs} V_f + K_{hs} V_h + V_s} \qquad (3.3)$$

The proper expression for the above distribution constants should involve appropriate activities, but the concentrations are a good approximation when considering trace levels of the analytes in a sample and assuming a pure matrix [8].

The multichannel silicone rubber traps were made in the laboratory from 6mm od x3mm id x 160mm quartz tubing containing 16 silicone rubber tubes, 90mm in length, placed linearly next to each other[1].

The traps were conditioned overnight at 280°C with hydrogen flowing through the trap at 25ml/min

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3.3 Optimisation of the methods.

The closed-loop stripping extraction technique was independently optimised for the taste and odour analyses and the volatile organic compound analysis. Limits of detection were determined and calibration curves were drawn to determine the linear range of the analyses

3.3.1 Taste and Odour Analysis.

Only Geosmin and 2-methylisoborneol, the two most commonly occurring substances that produce off-flavours in potable water, were chosen for this analysis. Both produce a musty, potato-bin type of taste and odour in drinking water and generally occur in the warmer months as by-products of blue-green algae.

The internal standards used in general for the closed-loop stripping analysis of these two substances are the linear 1-chloroalkanes. However the use of these compounds has a number of disadvantages, two of which are that they "strip" (purge from the aqueous sample) faster than 2-MIB and Geosmin and are sensitive to changes in the closed-loop stripping analysis parameters[9]. When isotopically

labelled compounds are used as internal standards, the accuracy of the determination is not sensitive to variations in the stripping time or the water temperature[10].

It was therefore decided to use these labelled standards for internal calibration, thereby increasing the accuracy of the determinations, particularly at low concentration levels. The identical chemical and physical behaviour of 2-MIB and Geosmin to their labelled analogues make the deuterated compounds ideal internal standards [9].

The closed-loop stripping analysis apparatus was constructed in-house and used a standard, metal bellows, circulating pump with a pumping speed of 1500ml/min (Figure.2.1). The water samples (250ml) were purged at 40^{0}C and the transfer line, ahead of the trap, was maintained at 60^{0}C to prevent the water vapour condensing in the trap.

The analytical instrumentation consisted of a CP-4010 PTI/TCT injector from ChromPack[1] (Figure 3.1) 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

[1] ChromPack, P O Box 8033, 4330 EA Middelburg. The Netherlands.

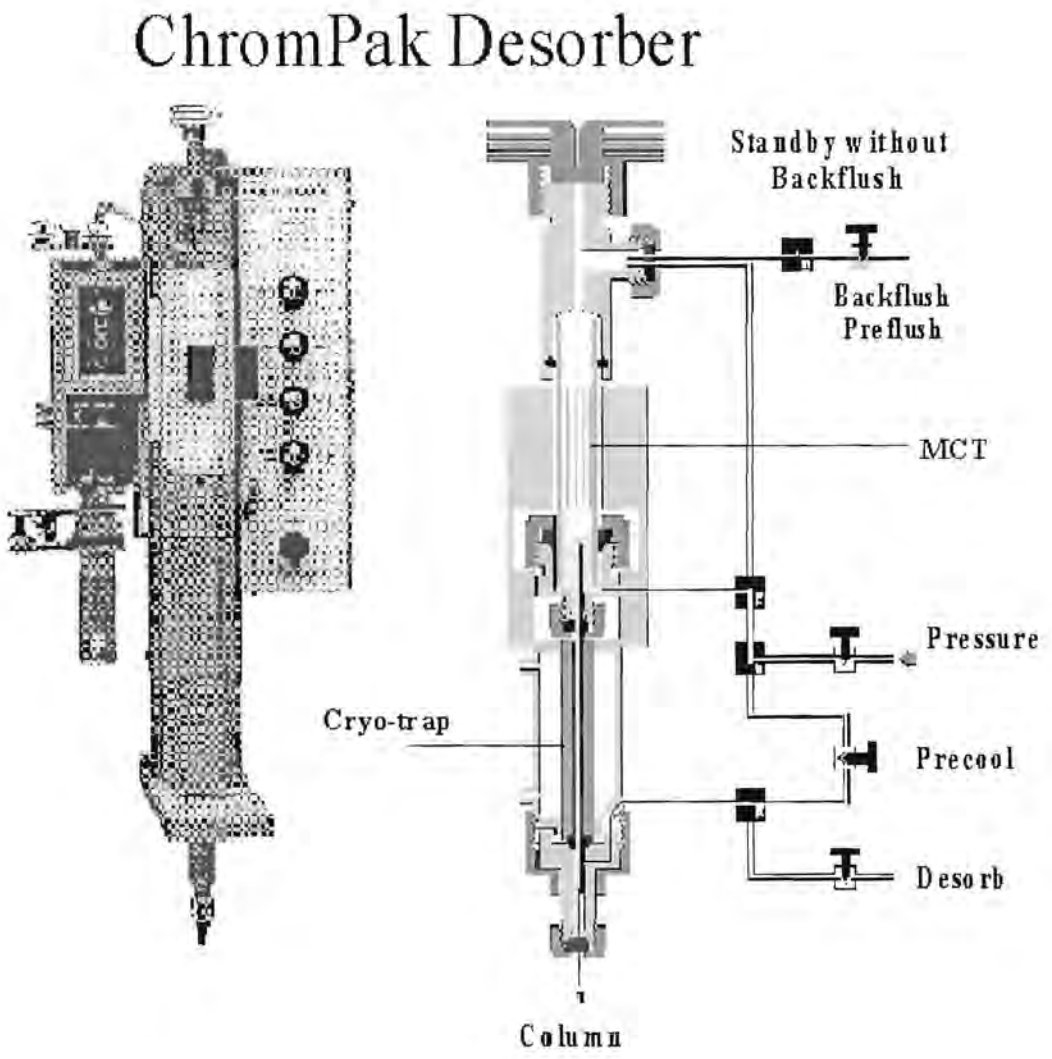

Figure 3.1. Chrompak CP-4010 PTI/TCT injector with detailed schematic drawing

to inject the trapped substances on to the analytical column. The cryotrap was cooled to 80^{0}C and the trapped components were desorbed at 180^{0}C at a flow rate of 60ml/min. The injection temperature of the cryotrap was 200^{0}C, held for 1 minute. 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 (25m x 0.32mm id, 0.25µm film thickness) with fused silica legs, manufactured in house. The column was initially held at 40^{0}C for 2 min. and then programmed to 200^{0}C at 4^{0}C/min and then to 280^{0}C at 20^{0}C/min.

[^{2}H $_3$]Geosmin (d3-Geosmin)and [^{2}H $_3$]2-MIB (d3-2-MIB)[1] standards were obtained for isotope dilution. A standard solution containing the deuterated and the non-deuterated Geosmin and 2-MIB standards in methanol was prepared and used in all the evaluation experiments.

Twenty nanogram of each standard was injected on to the chromatographic column to determine if the gas chromatographic conditions were correct for the analysis and to what extent the deuterated and non-deuterated compounds would be separated on the GC column.

The mass spectrometer was operated in the SIM mode with a source temperature 220^{0}C and an interface temperature 280^{0}C. The operation of the mass spectrometer in the single ion mode was necessary to achieve the sensitivity required to detect the very low odour threshold levels of Geosmin and 2-MIB and to accurately quantify these compounds

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[1] Ultra Fine Chemicals, Synergy House, Manchester Park, Manchester. M1555Y England.

3.3.2Volatile Organic Carbon Analysis

The method most often used to analyse water samples for the volatile organic carbon compounds is the purge and trap method using a trap packed with Tenax to

Table 3.1 Table of volatile organic compound standards used, the ions monitored and the retention time.

Volatile Organic Compounds							
Compound Name	Selected Ion		R.T.	Compound Name	Selected Ion		R.T.
	Primary	Secondary			Primary	Secondary	
1,1-Dichloroethene	96	61, 63	1.76	Styrene	104	78	17.35
trans- 1,2-Dichloroethene	96	61, 98	2.18	0-Xylene	106	91	17.51
1,1-Dichloroethane	62	98	2.30	1,1,2,2-Tetrachloroethane	83	131,85	18.80
cis-1,2-Dichloroethene	96	61, 98	2.76	1,2,3-Trichloropropane	75	77	19.28
Chloroform	83	85	2.88	Isopropylbenzene (Cumene)	105	120	19.85
Methylene chloride	84	86, 49	2.90	Bromobenzene	156	77, 158	20.03
2,2-Dichloropropane	63	112	2.91	2-Chlorotoluene	91	126	21.58
1,1,1-Trichloroethane	97	99, 61	3.58	n-Propylbenzene	91	120	21.93
1,1-Dichloropropene	75	110, 77	3.83	4-Chlorotoluene	91	126	22.03
Benzene	78		3.98	1,3,5-Trimethylbenzene	105	120	23.00
Carbon tetrachloride	117	119	4.01	p-Isopropyltoluene	119	134, 91	24.66
Trichloroethylene	95	97, 130, 132	5.30	1,2,4-Trimethylbenzene	105	120	24.73
Bromodichloromethane	83	85, 127	5.55	1,3-Dichlorobenzene	146	111, 148	25.33
cis-1,3-dichloropropene	75	77, 39	7.25	1,4-Dichlorobenzene	146	111, 148	25.80
trans-1,3-Dichloropropene	75	77, 39	8.86	sec-Butylbenzene	105	134	25.91
Toluene	91	91	8.98	tert-Butylbenzene	119	91, 134	26.91
1,1,2-Trichlroethane	83	97,85	9.18	1,2-Dichlorobenzene	146	111, 148	27.26
1,3-Dichloropropane	76	78	10.0	n-Butyl benzene	91	92, 134	29.03
Dibromochloromethane	129	127	10.5	1,2-Dibromo-3-chloropropane	75	155, 157	30.40
1,2-Dibromoethane	107	109, 188	11.2	1,2,4-Trichlorobenzene	180	182, 145	36.63
tetrachloroethylene	164	129, 131, 166	11.7	Naphthalene	128		37.00
Chlorobenzene	112	77, 114	14.1	1,2,3-Trichlorobenzene	180	182, 145	38.78
1,1,1,2-Tetrachloroethane	131	133, 119	14.3	Hexachlorobutadiene	225	223, 227	39.28
Ethylbenzene	91	106	15.3	Bromochloromethane	128	49, 130	
m-Xylene	106	91	15.9	1,2-Dichloroethane	62	98	
p-Xylene	106	91	15.9	1,2-Dichloropropane	63	112	
Bromoform	173	175, 254	16.6				

collect the volatile compounds. This method has been developed to the extent, that most water laboratories can easily implement it for routine analysis.
However it suffers from the break-through of the volatile compounds, the same problem found in most open ended trapping techniques where the outlet of the trap is vented to the atmosphere. This is of particular importance in the analysis of the VOCs since these have a large range of boiling points, from the very volatile to those compounds of medium volatility.

Early break-through occurs for the volatile substances, which then leaves the less volatile substances incompletely extracted from the water sample.

The use of the closed-loop stripping analysis technique will ensure that all compounds are in equilibrium with the vapour-gas phase and the sorbent. A constant partitioning will occur and if the mass of the sorbent is large enough, equilibrium will shift toward the sorbent phase. The VOCs can therefore be accurately quantified and the only parameters that will affect the equilibrium, besides the sample matrix, are the stripping temperature and the sorbent mass. It has been found that equilibrium is attained sooner at elevated temperatures but the individual equilibrium constants also change at higher temperatures. The MCT is therefore well suited to trap the VOCs for analysis by GC-MS.

To optimise the conditions for extraction and analysis a mixture of 53 compounds was selected. This mixture is a commercially available set of calibration standards

used for the analysis of surface and drinking waters (Table 3.1). The set of standards was chosen so that the CLSA method with the MCT sorption trap could be calibrated and evaluated against "real samples" done in an existing water laboratory.

The large number of compounds being analysed restricted the application of isotope dilution techniques for quantitative analysis. Two internal standards were selected for quantitative work, neither of which have the likelihood of being found in a surface or drinking water sample. The more volatile standard chosen was fluorobenzene and the less volatile, d5-chlorobenzene, a deuterium labelled chlorobenzene.

Fluorobenzene has a base peak/molecular ion at m/z=97 and d5-chlorobenzene a base peak/molecular ion at m/z=117.The closed-loop stripping analysis apparatus used was the same as that described above (3.3.1). The closed-loop stripping was done at ambient temperature (25^0C) and the MCT was heated to 3^0C – 5^0C higher than the trap to prevent water condensing in the trap.

The analytical instrumentation used was a Varian 3300 gas chromatograph fitted with the Chrompak thermal desorber (see 3.3.1) and connected to a Finnegan Mat ITD 800 ion trap detector mass spectrometer. The analytical column in the GC was a DB5 fused silica capillary column (30m x 0.25mmID, 0.25µm film thickness)

The GC oven temperature was held at 35^0C for 8 minutes and then programmed to 150^0C at 3^0C.min^{-1} and then to 280^0C at 20^0C min^{-1}. The interface temperature of the

mass spectrometer was held at 250^{0}C and the source temperature at 210^{0}C. The mass spectrometer was used in the full scan mode, scanning from 35 to 400 daltons. Analysis of the resulting data was done on reconstructed single ion chromatograms, using the ions for the various compounds as listed in Table 3.1.

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Chapter 4

Analysis of Taste & Odour Compounds

4.1 Analytical Conditions

Initially, the equivalent of a 20ng aliquot of each deuterated and non-deuterated standard was placed onto the front end of the MCT with a micro-syringe. The standards were then thermally desorbed from the trap onto the gas chromatographic column using the desorption conditions as in **3.3.1** above. Retention times of the standards and peak shapes were found to be satisfactory using these conditions.

The analysis was done in full scan mode, to be assured of the identity of the

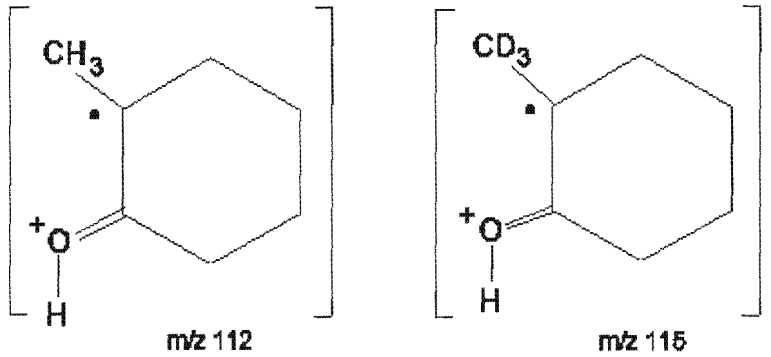

Figure 4.1 Base peak fragments for Geosmin and d3-Geosmin showing the retention of the labelled methy group.

resulting peaks, scanning from 10-400 daltons. The base peaks for Geosmin and d3-Geosmin differ by three Daltons, being m/z=112 and m/z=115 m/z respectively. This indicates that the major fragment of the d3-Geosmin retains the deuterated labelling. Figure 4.1 is a schematic diagram of the deuterated and non-deuterated

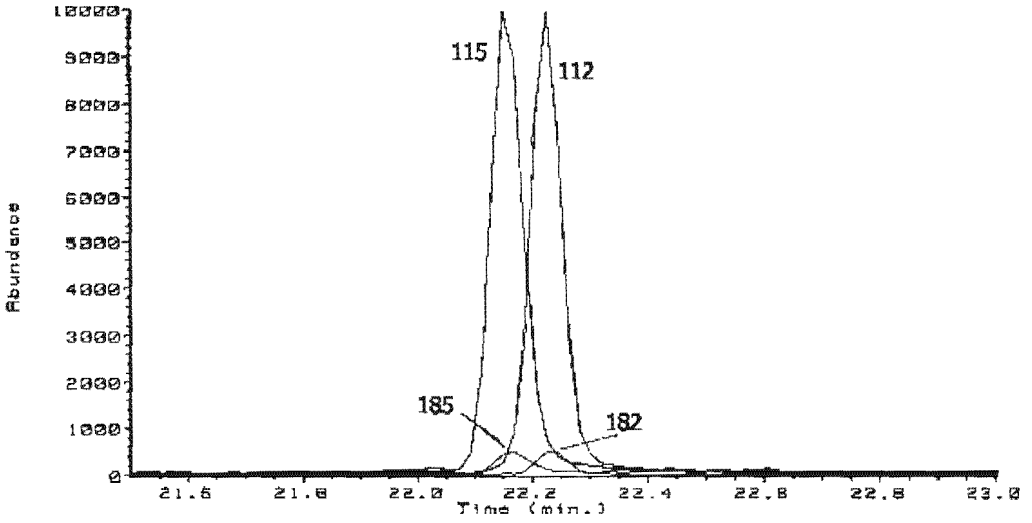

Figure 4.2 Single ion trace of Geosmin and d3-Geosmin using the base peak and molecular ions

base peak fragments, which clearly shows the retention of the deuterium labelled methyl group. These ions are therefore ideal for single ion monitoring methods, as separation will be achieved by the mass spectrometer detector.

This can be clearly observed in Figure 4.2. which is a reconstructed single ion trace of the Geosmin and d3-Geosmin standards using the base peak ions, m/z=112 and m/z=115 as well as the molecular ions, m/z=182 and m/z=185 respectively [1]. Complete separation is achieved which is essential for quantitative analysis and is not reliant on the separation by the gas chromatographic column. The molecular ions

may also be used for the single ion trace as proof of identification of the geosmin in a real sample.

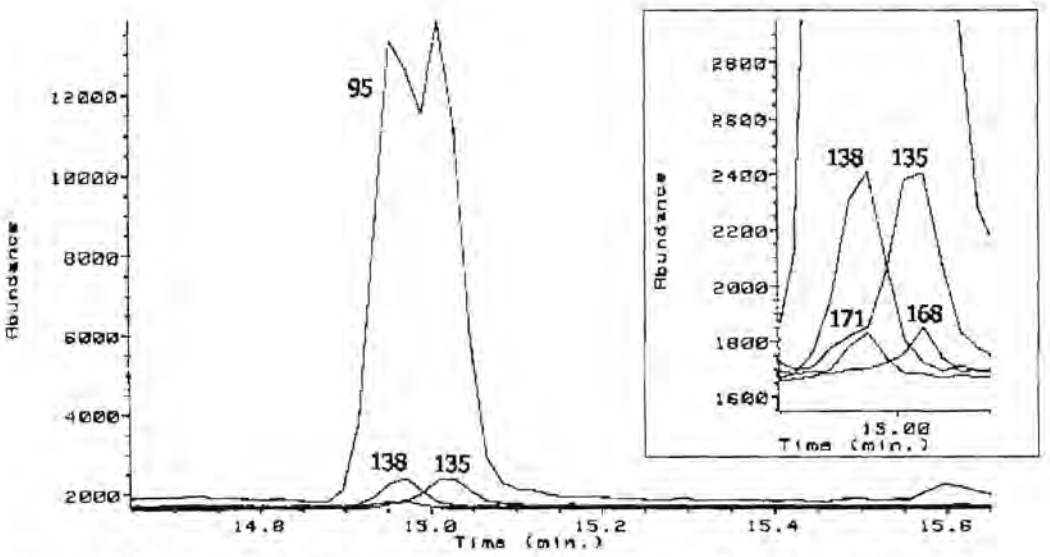

Figure 4.3. Single ion trace of 2-MIB and d3-2-MIB using the m/z values as listed in Table 3.1

Both the deuterated and non-deuterated 2-MIB have a base peak at m/z 95. This can be observed in Figure 4.3 which is a reconstructed single ion trace of m/z=95. Insufficient separation is achieved chromatographically so that this m/z is not suitable for the analysis.

To make use of the m/z=95 peak for quantification it will be necessary to improve the chromatographic separation, either by changing the analysis parameters or by making use of a column of a different polarity. Some authors [2] have made use of high-resolution mass spectrometry to overcome this problem by using accurate masses.

Making use of an external standard method is of course another option.

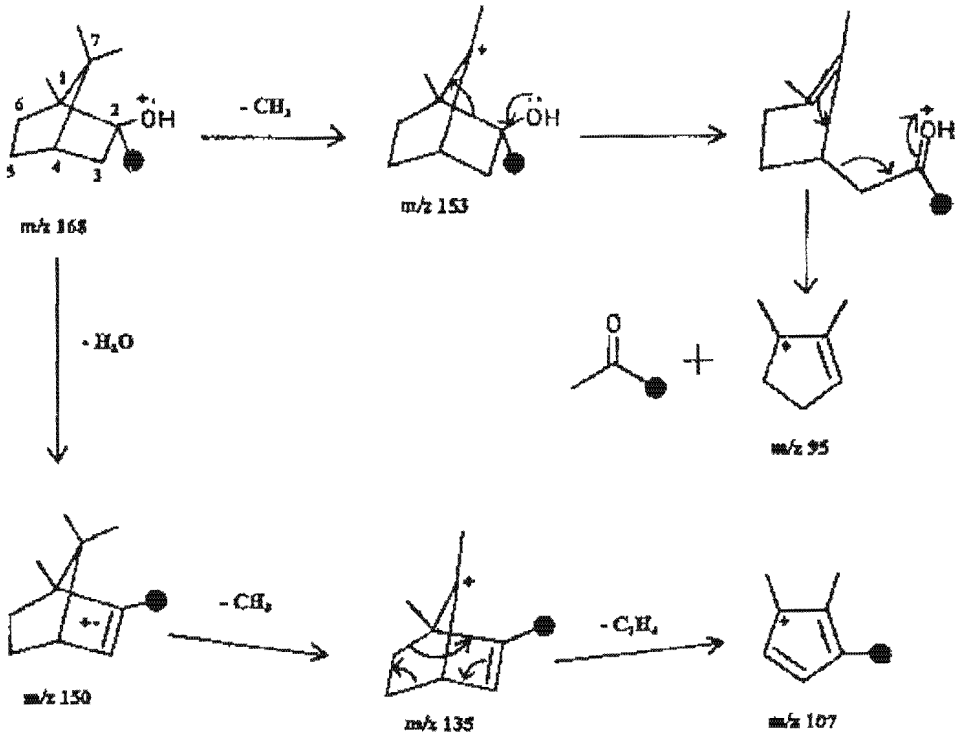

Figure 4.4. Suggested framentation for 2-MIB. The solid circle represents the d3 labelled methyl group.

Figure 4.4 is a proposed fragmentation pathway for the labelled 2-MIB, [2] which clearly shows the loss of the labelled methyl group to give a stable ion at m/z=95. Other fragments such as the m/z=135 and m/z=138 retain the isotopic labelling and can be used for quantitative analysis [1], but these ions occur at much lower abundance (ca 20% of the m/z=95 peak abundance) than that of the base peak at m/z=95.(Figure 4.3). It is therefore quite probable that the lower limit of detection of this compound might not be reached if these low intensity ions are used for the analysis.

According to Kort et al.[3] there is no simple way of incorporating the deuterium label into the 2-MIB base peak.

From the analyses described above a selection of ions were chosen to use in the single ion mode MS analysis. This list is tabled in Table 4.1.

Table 4. 1 m/z Values used for SIM analysis

Compound	SIM m/e values
2-Methylisoborneol	95, 135*, 168
D3-2-Methylisoborneole	95,138*, 171
Geosmin	112*, 182
D3-Geosmin	115*, 185
* ions used for quantitation	

The deuterated standards were now added to a distilled water sample, at a concentration level equivalent to 20ng/litre water. A 250ml aliquot was then extracted with the closed-loop stripping apparatus and the organic compounds present were trapped on the multi-channel silicone rubber trap. The sample was purged at ambient temperature for 45 minutes to ensure that equilibrium conditions were reached. The trap was then placed into the thermal desorber ensuring that the end where the stripping gas from the CLSA entered the trap, was the end where the trapped compounds would exit the trap on desorption Figure 4.5 is a reconstructed total ion chromatogram of the analysis.

A number of siloxane peaks were observed in the chromatogram which are easily recognised by their distinctive mass spectra. These originate from the MCT and are breakdown products of the silicone rubber. These peaks always occur at the same retention time and the same intensity under the same conditions and generally do

not interfere with the analysis. No extra peaks occur in the background after continued use of the trap. Background peaks can therefore, never be interpreted as

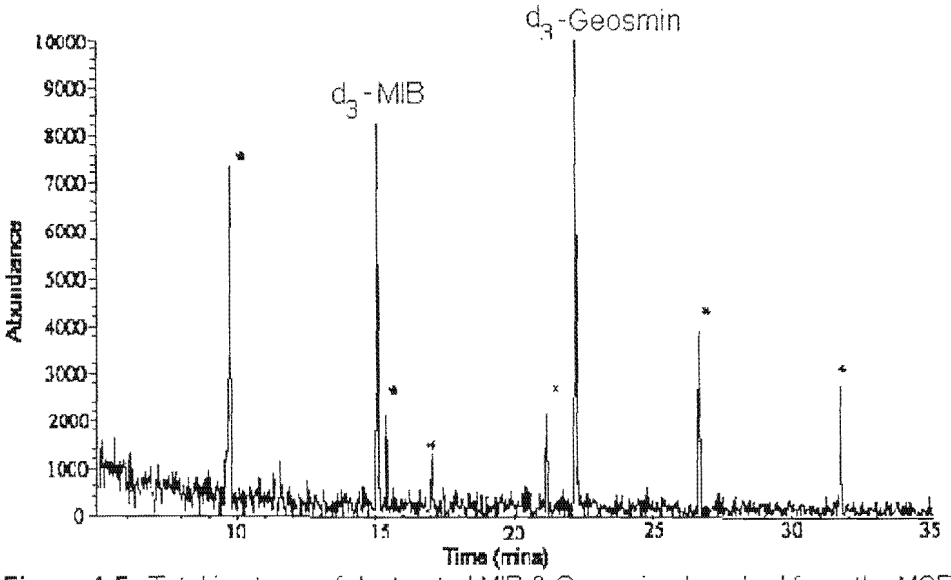

Figure 4.5. Total ion trace of deuterated MIB & Geosmin, desorbed from the MSRT and analysed at full-scan. Siloxane background peaks are marked with a *.

resulting from the sample (Figure 4.5). These peaks will be filtered out when the single ion monitoring mode is used and therefore will not have any affect on the analysis.

To determine the linearity of the analytical method, a calibration curve was drawn from data obtained from a series of pure water samples spiked with $2ngl^{-1}$, $4ngl^{-1}$, $8ngl^{-1}$ and $16ngl^{-1}$ of each of the labelled geosmin and MIB standards. (Figure 4.6).

Samples of 250 ml of the water were purged using the CLSA technique and the multi-channel silicone rubber trap to absorb the purged compounds. The mass spectrometer was run in the single ion monitoring mode using the ions listed above. The curve was drawn for m/z values of 95 & 138 for the deuterated MIB and 115 for the deuterated geosmin. The linearity of the curve is surprisingly good for

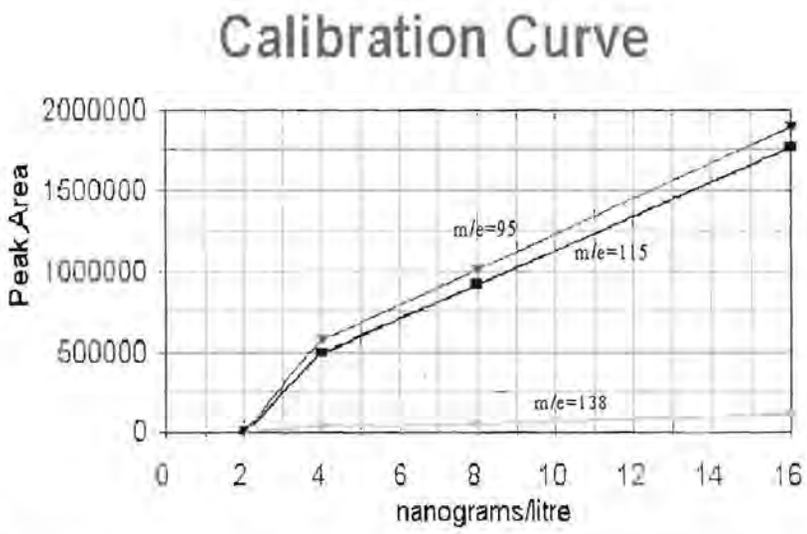

Figure 4.6 Deuterated Geosmin and 2-MIB calibration curves.

concentrations of 4ngl^{-1} and above but drops off sharply from 4ngl^{-1} to 2ngl^{-1}. This is a typical sign of activity in the analytical system, which is not surprising since the CLSA, equipment, including the pump, is constructed from (untreated) steel.

Taking 4ngl^{-1} as the lower detection limit, it is still well below the reported odour threshold levels of 10ngl^{-1} and 29ngl^{-1}, for these two compounds (Table 2.1) and therefore of little consequence. It is probable that with a deactivated system this curve will maintain linearity below 4ngl^{-1}.

Finally a drinking water sample was spiked with 8ngl^{-1} of the deuterated standards and extracted using the closed-loop stripping analysis technique and the MCT. The analysis was done in the SIM mode using the ions selected in Table 4.1. No geosmin or 2-MIB was detected in the selected ion (sum of the selected single ions) chromatogram at levels above 4ngl^{-1}(Figure 4 7).

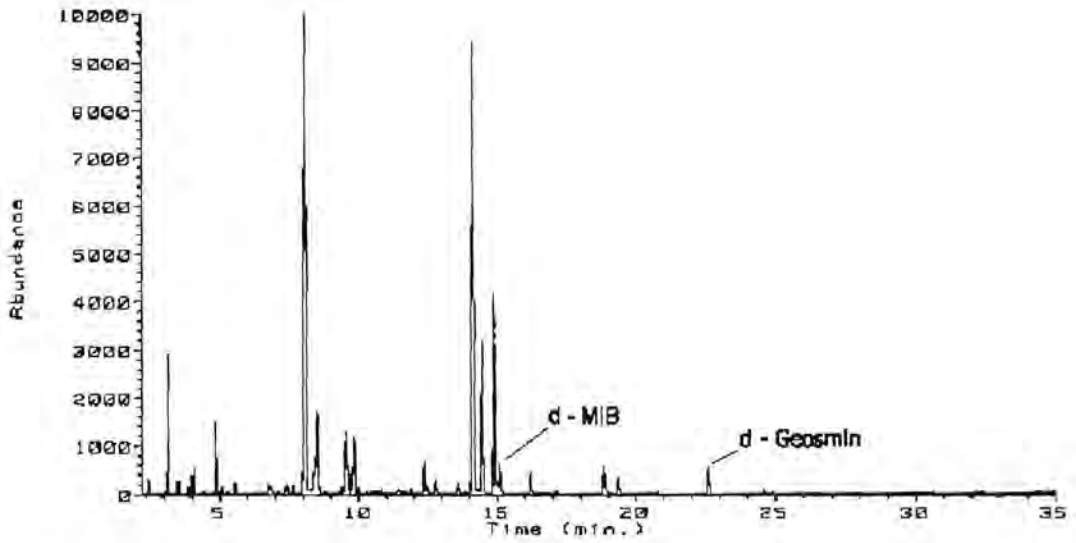

Figure 4.7. SIM analysis of drinking water sample.

Numerous peaks were observed with the same ions as those selected for the analysis, in particular the ions m/z=112 and m/z=138. These peaks did not interfere or overlap with the standard peaks. These substances originated from the water sample itself and not from the trap.

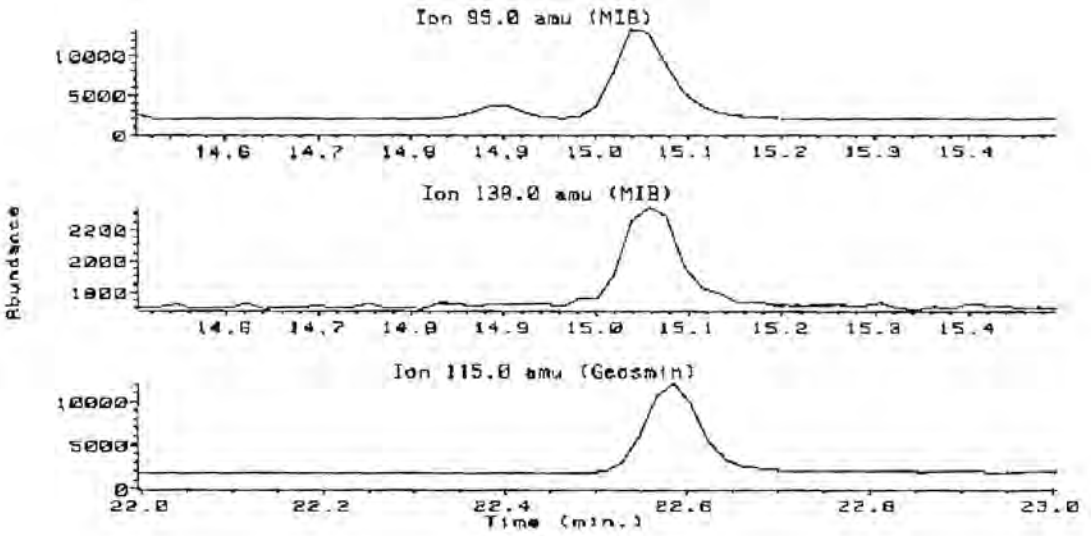

Figure 4.8 Single ion traces for deuterated Geosmin and 2-MIB standards in a drinking water sample.

At this concentration level, good sensitivity and peak shapes are obtained for the m/z values chosen. The single ion peak at m/z=138 was found to have a signal-to-noise ratio of about 20:1 (Figure 4.8)

4.2 Conclusion

The multi-channel trap is an excellent alternative to the carbon filter used for the determination of tastes and odours in drinking water. The retention of these substances by the silicone rubber is based on dissolution as opposed to the adsorption onto the activated carbon in the standard filter. This is a major advantage since the sorption properties of the multi-channel trap remain constant in contrast to the reliance on the activity of the carbon filter, which deteriorates with usage. The multi-channel traps can be used repeatedly for extended periods without change in their sorption properties.

Although these traps produce background peaks, these are distinctive, remain constant without deterioration and are easily identified by mass spectrometry

The elimination of the micro-extraction step required to extract the adsorbed substances from the carbon filter with organic solvent is a major advantage of using the MCT.

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Chapter 5

Analysis of Volatile Organic Compounds

5.1 Analyses

To calibrate the analytical method, 1µℓ of the mixed VOC standard mixture in methanol (Table 3.2), was placed on the front of the MCT with a micro-syringe. This equated to 20ng of each individual compound in the mixture. The trap was then placed into the desorber for analysis. The desorption temperature was set at 180^0C for 5 minutes with the cryogenic trap at -80^0C. The injection temperature of the cryogenic trap was set to 200^0C and the injection was completed after a preset time of 1 minute.

The reconstructed chromatograms (Figure 5.1) demonstrate that the selected analytical conditions are adequate for the separation of the mixture of compounds in the standard solution. As was expected, a number of siloxane derived peaks were observed but these did not interfere with the determination of the compounds of interest (Figure 5.1). The siloxane degradation products can be observed from the single ion trace m/z=73. The substituted benzene compounds are clearly visible in the single ion trace m/z=91. This demonstrates that the selected 53 standard compounds can be analysed using the desorption conditions as above.

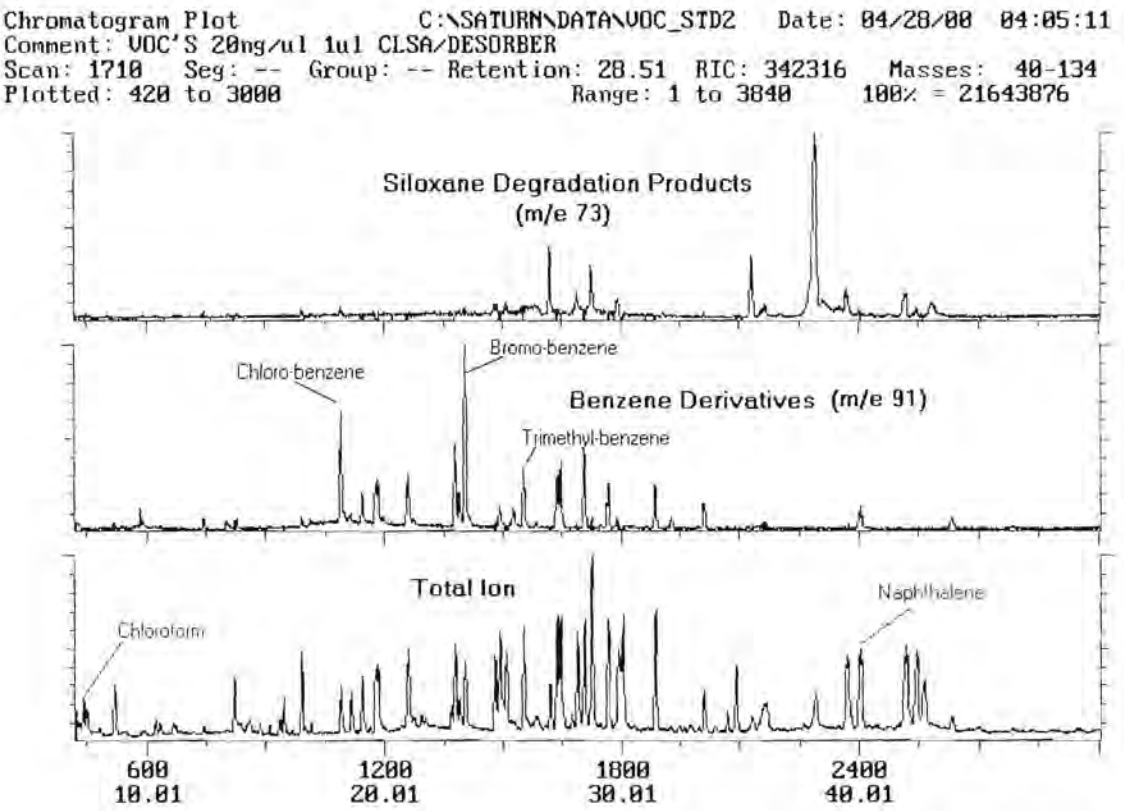

Figure 5.1. Reconstructed chromatograms of the VOC standard mixture at 20ng per compound

After the MCT had been conditioned, as described in Chapter 3 above, a blank determination of the trap was done. One gram of anhydrous sodium sulphate was added to a 200ml pure (milli-Q) water sample in a clean glass flask to assist the purging process by increasing the ionic strength of the sample.

The flask and a clean, conditioned, multi-channel trap were then connected to the CLSA apparatus and the purging was started.

The sample was purged for 45 minutes at a purge gas flow rate of 1.5lmin^{-1}.

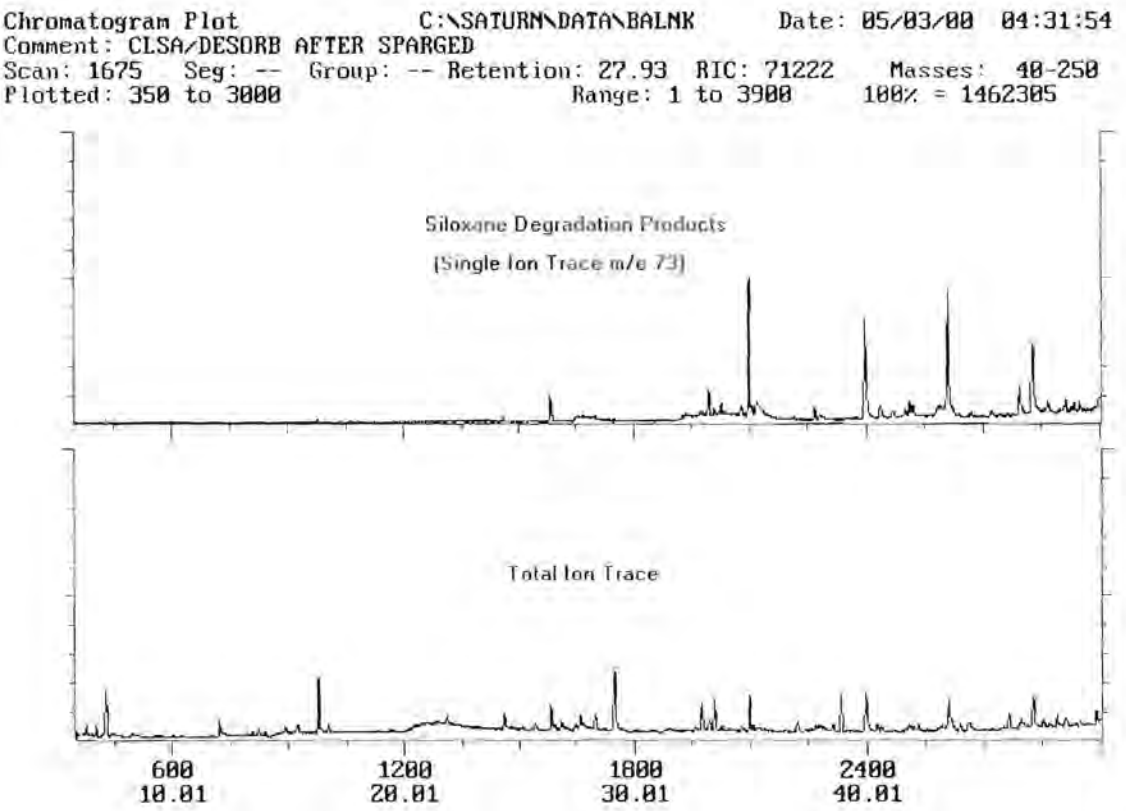

Figure 5.2 Analysis of Water Blank

It is important that the sample temperature is kept 2-3°C lower than the trap temperature to prevent water condensing in the trap. Figure 5.2 is a reconstructed total ion trace and a reconstructed single ion trace of silicone peaks (m/z=73) of this blank determination. Background peaks of the pure water can be seen to be present in the total ion trace, which do not result from the trap. These peaks may of course, originate from the added sodium sulphate. Generally it would be necessary to bake the anhydrous sodium sulphate in an oven at 400°C overnight to remove all organic contamination.

To determine to what degree the analytical technique would produce repeatable results, a water sample containing a known amount of the standard compounds was analysed in quadruplicate. The water sample was spiked with the equivalent

Table 5.1 Relative Standard Deviation of selected VOC standards at 200ngl^{-1}.

Compound Name	R.S.D. 0.2ug/l	S/N Ratio 0.2ug/l	S/N=3 LOD in ng/l	Area (x1000) Recov_1	Recov_2	Recov_3	Mean	Stand.Dev
Chloroform	19.7%	140	85.714	338	388.3	259.6	328.6	64.9
trichloroethylene	12.2%	16148	0.743	83.7	74.5	95	84.4	10.3
dibromomethane	21.4%	4410	2.721	23.3	15.8	23.8	21.0	4.5
tetrachloroethylene	5.8%	46081	0.260	227.6	250.7	226.4	234.9	13.7
tetrachloroethane	10.2%	51192	0.234	244.2	222.2	198.9	221.8	22.7
ethyl benzene	16.2%	974	12.320	1254	1295.8	949.6	1166.5	189.0
bromobenzene	17.6%	80751	0.149	470.5	450.5	334	418.3	73.7
butylbenzene	11.9%	631968	0.019	3527.7	3164.7	2779.1	3157.2	374.4
trichlorobenzene	7.2%	208549	0.058	1302.9	1135.4	1181.8	1206.7	86.5
naphthalene	12.4%	528396	0.023	3532.8	2756.3	3114.7	3134.6	388.6

of 200ngl^{-1} (200X10^{-9}g/litre). A 250ml aliquot was then subjected to the closed-loop stripping technique and analysed under the conditions as described above.

Table 5.1 is a listing of a selected number of compounds in the standard mixture (Appendix I), indicating the area of the peaks obtained from the reconstructed chromatograms of their characteristic ions, which are listed in Table 3.1 above.

The relative standard deviation was calculated from the standard deviation and the mean value of the four determinations. Signal-to-noise ratios were determined at the 0.2ugl^{-1} concentration range. Limits of Detection (LOD) were then calculated in ngl^{-1}, assuming that the LOD occurs at a signal to noise ratio of 3 and that the signal for the compounds is linear over this range (Table 5.1).

With the same solution of standards (200ngl^{-1}) used in the Standard Deviation measurements, an experiment was conducted to determine what percentage recovery can be expected using the MCT analysis technique. The equivalent of 250ml of spiked water sample (i.e. 50ng per compound) was placed directly onto a

clean, previously conditioned MCT and immediately analysed by desorbing the compounds and focusing them on the cryo-trap, and then thermally injecting them onto the column for analysis.

The water sample containing the standards was then analysed in triplicate. The peak areas, obtained from reconstructed single ion traces, and the calculated recoveries , are given in Table 5.2

Table 5.2 Percentage recovery of selected compounds at 200ngl^{-1} concentration.of a selected number of standards

Ret.Time (mins)	Compound Name	Peak Area (x1000)		% Recovery
		Mean (n=3)	Direct Analysis	
15.7	Tetrachloroehtylene	234.9	287.2	82%
18.5	tetrachloroethane	221.8	228.7	97%
19.0	ethyl benzene	1166.5	2099.8	56%
23.2	bromo-benzene	418.3	739.2	57%
28.0	butyl benzene	3157.2	3175	99%
37.5	trichlorobenzene	1206.7	1252.5	96%
38.0	naphthalene	3134.6	4018.9	78%

Because of the interference of the methanol solvent peak in the mass chromatogram, which occurred in the analysis of the standards placed directly on to the trap, recovery data is only available for later eluting substances.

One of the major objectives of this study was to determine whether the combination of the multi-channel silicone rubber trap and closed-loop stripping technique, could

be applied to simultaneously analyse a water sample for two different groups of substances that are commonly found in drinking and fresh water supplies.

With this in mind a water sample was prepared containing the VOC standards at a concentration level of 10ngl^{-1} per compound and geosmin at a concentration of 20ngl^{-1}. One litre of this sample was purged with the CLSA, collecting the compounds on the MCT and analysing them under the conditions described above.

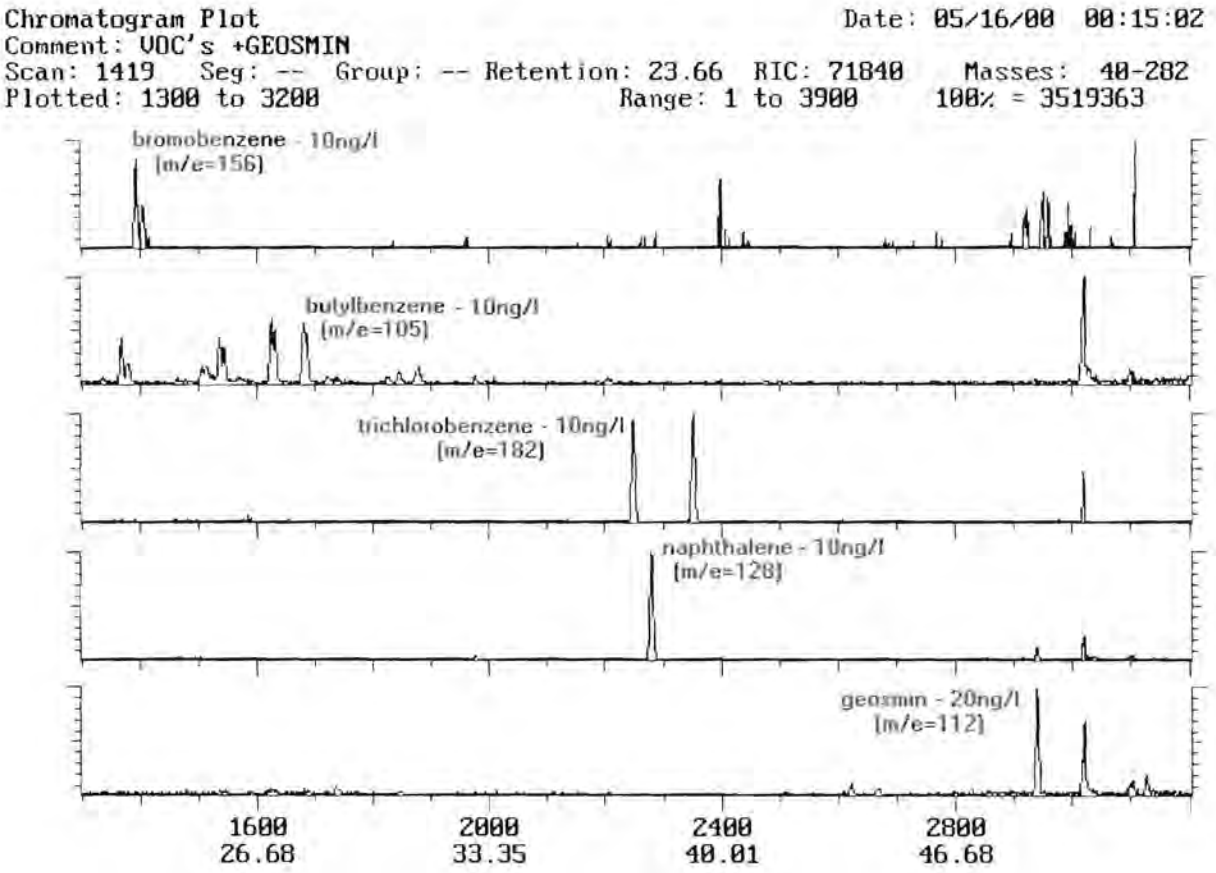

Figure 5.3 Analysis of water sample containing both the volatile organic compounds and taste and odour substances (geosmin).

5.2 Conclusion

Figure 5.3 depicts a series of reconstructed single-ion traces of some of the common VOCs and geosmin, a substance that causes tastes and odours in water. This demonstrates that this analysis is, in fact possible and at low concentration levels as well. The concentration level of the VOCs is well below that required by US-EPA and the European Water Commission and the concentration of the geosmin is at the taste & odour threshold level of the human nose. A single method can replace, for example, the two standard methods; one from the EPA for the VOCs and the other for taste & odour from Standard Methods.

Chapter 6

Discussion of Results and Conclusion

6.1 Analysis Results of "Real" Water Samples

6.1.1 Volatile Organic Compounds

Three water samples were obtained from a water laboratory that routinely analyses water for the presence of VOCs. The laboratory makes use of the P&T method recommended by the EPA (Method 524) for isolating the analytes and GC-MS, in single-ion monitoring mode, for the analysis. These samples were analysed using the same conditions as described above. The volume of the samples were 50ml to which was added 1.2ugl^{-1} of d5-chlorobenzene and 200ngl^{-1} of d3-geosmin as internal standards. After consulting the analysis sheets of the samples supplied by the water laboratory, it was decided to use higher concentrations of the internal standards than those used in the development of the method because the values for the VOCs reported are in the ugl^{-1} range. This water laboratory does not conduct the analyses for taste and odour compounds. Table 6.1 lists the compounds detected in the samples by both the MCT analytical technique and the water laboratory. The concentrations of these compounds are listed to compare the results obtained by the MCT technique with the results from the water laboratory.

Although the same compounds were detected in both analyses the correlation of the results are very poor. The only correlation is that the same order of magnitude

Table 6.1 Analytical results of water samples obtained from a water laboratory

Compound Name	Concentration in ugl^{-1}					
	MCT Method			Water Laboratory		
	BH-A02	SW-N4	BN-X1	BH-A02	SW-N4	BN-X1
chloroform	0.56	9.06	2.83	<1	<100	8
1,1,1-trichloroethane	0.1	ND	ND	ND	<100	ND
trichloroethylene	0.23	8.83	3.95	2	<100	490
1,3-dichloropropene	ND	0.09	ND	ND	<100	ND
toluene	0.76	1.23	20.15	<1	<100	<1
chlorodibromomethane	0.72	9.10	1.59	ND	<100	ND
tetrachloroethylene	6.2	1.62	24.43	2	<100	81
chlorobenzene	ND	0.58	ND	ND	<100	<1
ethyl benzene	0.02	0.02	0.38	ND	<100	ND
m & p-dimethyl benzene	0.03	ND	0.45	ND	<100	<1
o-dimethyl benzene	0.02	0.03	0.59	ND	<100	<1
methylethyl benzene	0.008	ND	0.06	ND	<100	ND
1,4-dichlorobenzene	0.1	0.12	0.99	ND	<100	2
sec-butyl benzene	ND	ND	0.1	ND	<100	ND
1,2,3-trichlorobenzene	0.003	0.006	0.06	ND	<100	ND
naphthalene	0.009	0.01	0.1	ND	<100	ND

can be found between the results. One explanation for this poor correlation is that there was a large period of time between the initial analysis conducted by the water laboratory and the analysis with the MCT. To get any meaningful results from such an exercise, a carefully controlled inter-laboratory calibration study will need to be conducted with fresh samples.

From the results listed it is quite clear that low concentration levels of the VOCs can be detected using the MCT concentration technique with CLSA. These levels are well within the required MCL set by the EPA. With the large volume of silicone rubber packed in the MCT, the capacity of the trap permits a large concentration range to be sampled.

6.1.2 Taste and Odour Compounds

2-MIB was detected in two of the samples obtained from the water laboratory but no geosmin was detected in any of the samples. Concentrations of 2-MIB detected were as follows:

Sample BH-A02	$73ngl^{-1}$
Sample BN-X1	$132ngl^{-1}$

Considering that only 50ml of sample was used, for the analysis, the actual amounts collected on the MCT were between 3 and 6ng. These peaks have signal to noise ratios of between 10:1 and 18:1, respectively which is approximately 3 – 6 times the detection limit. Theoretically, the method detection limit of 1ng would yield a concentration of $20ngl^{-1}$ using a 50ml sample volume, which is the limit of detection of the human nose. This means that the larger volumes (ca 1 litre), that were traditionally used in the CLSA method for the taste and odour compounds are no longer required.

6.1.3 Other Compounds

A number of other compounds were tentatively identified from their mass spectra by searching the National Institute of Standards and Technology (NIST) mass spectral library (Table 6.2). These substances do not include the methyl silicones and they were not quantified. The reconstructed total ion chromatograms of the water samples analysed by the MCT and CLSA can be found in Addendum I.

Table 6.2 Substances tentatively identified in the water samples

Compound Name	Sample Name		
	BN-X1	SW-N4	BH-A02
cyclohexane	X		X
methyl butanol	X		
benzothiophene	X		
dodecanol	X		X
pentamethylbenzene	X		
methyl naphthalene	X		
biphenyl	X		
heptadecane	X	X	
n-butanol		X	X
undecane		X	X
ethyl hexanol		X	X
methyl decane		X	
dibutyl phthalate		X	X
eicosane		X	

6.2 Conclusion

The object of this research was to develop a method to simultaneously analyse two different groups of volatile organic compounds. This has been achieved as indicated by the results reported above.

VOCs are known to break through early in silicone rubber traps in an open ended purge system such as P&T. CLSA offers efficient concentration by equilibrium partitioning between the sample and the silicone rubber. With samples that are muddy or "dirty", CLSA offers the same advantages as headspace SPME and P&T. However it benefits from the large amount of extracting phase and constant degradation peaks that are easily recognised by the mass spectrometer. VOCs

(MDL_{EPA} =500ngl^{-1}) can be detected at 10ngl^{-1} simultaneously with taste and odour compounds at 20ngl^{-1} concentration range with the closed loop silicone rubber system. As opposed to the standard CLSA [1] our solventless CLSA method is cheaper and simpler and does not produce artefacts like S_8 from CS_2 and activated charcoal surfaces.

CLSA with silicone rubber traps and thermal desorption is a versatile, solventless technique offering extreme sensitivity. A single GC-MS analysis will give the same information as would be obtained from two separate standard water analysis techniques. The simplicity of the method lends itself to the use in a laboratory that conducts routine analyses on water samples. One disadvantage is the requirement of a thermal desorption apparatus which will require quite a large initial capital outlay. This will easily be recouped by a laboratory that has a large sample throughput.

References

1 Krasner, S.W., Hwang, C.J. and McGuire, M.J.. 1983 A standard method for the quantification of earthy-musty oderants in water, sediments and algal cultures. *Wat.Sci.Technol,* **15** , 127-138

ADDENDUM I

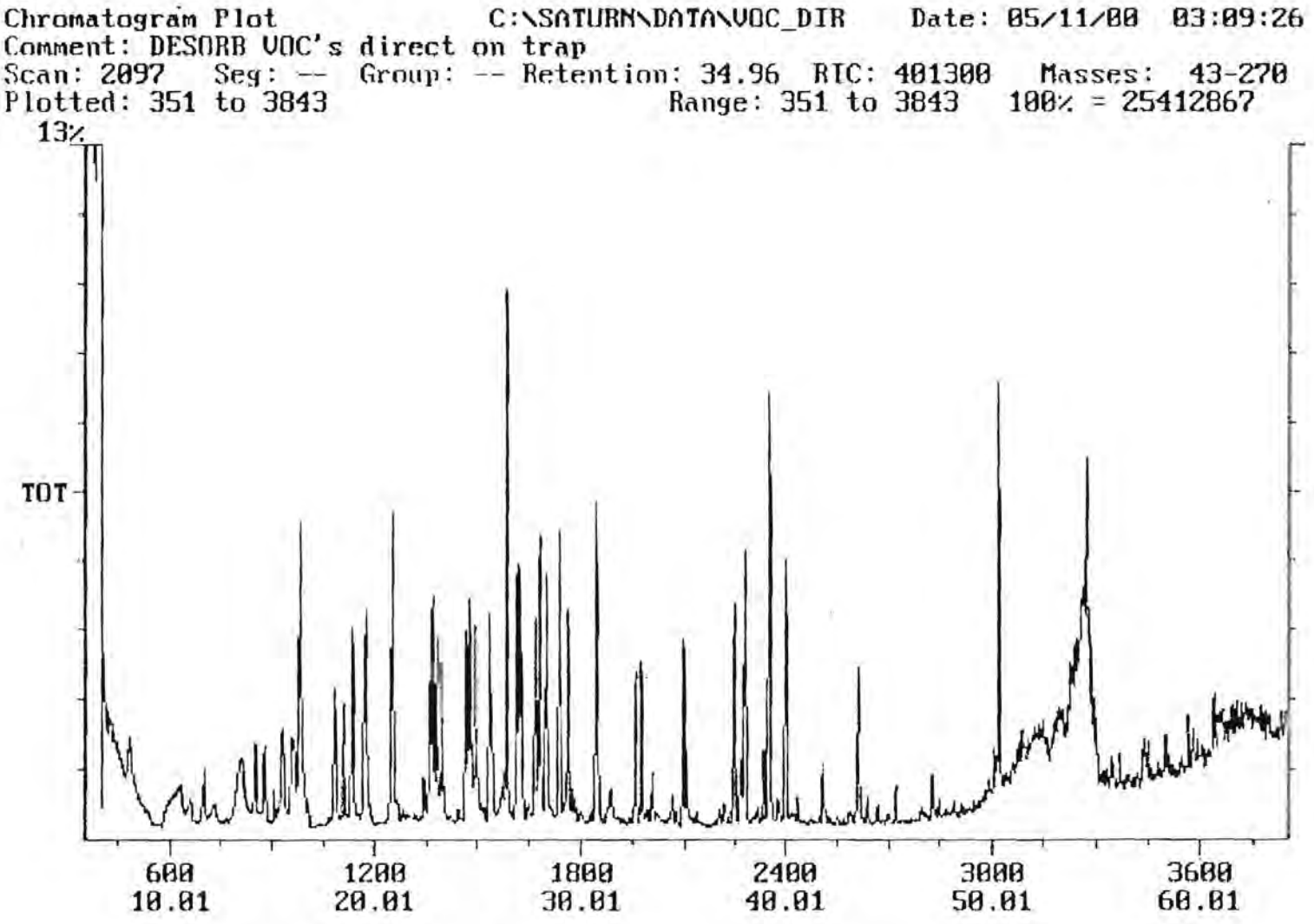

Figure I.1 Direct injetion of VOC standards

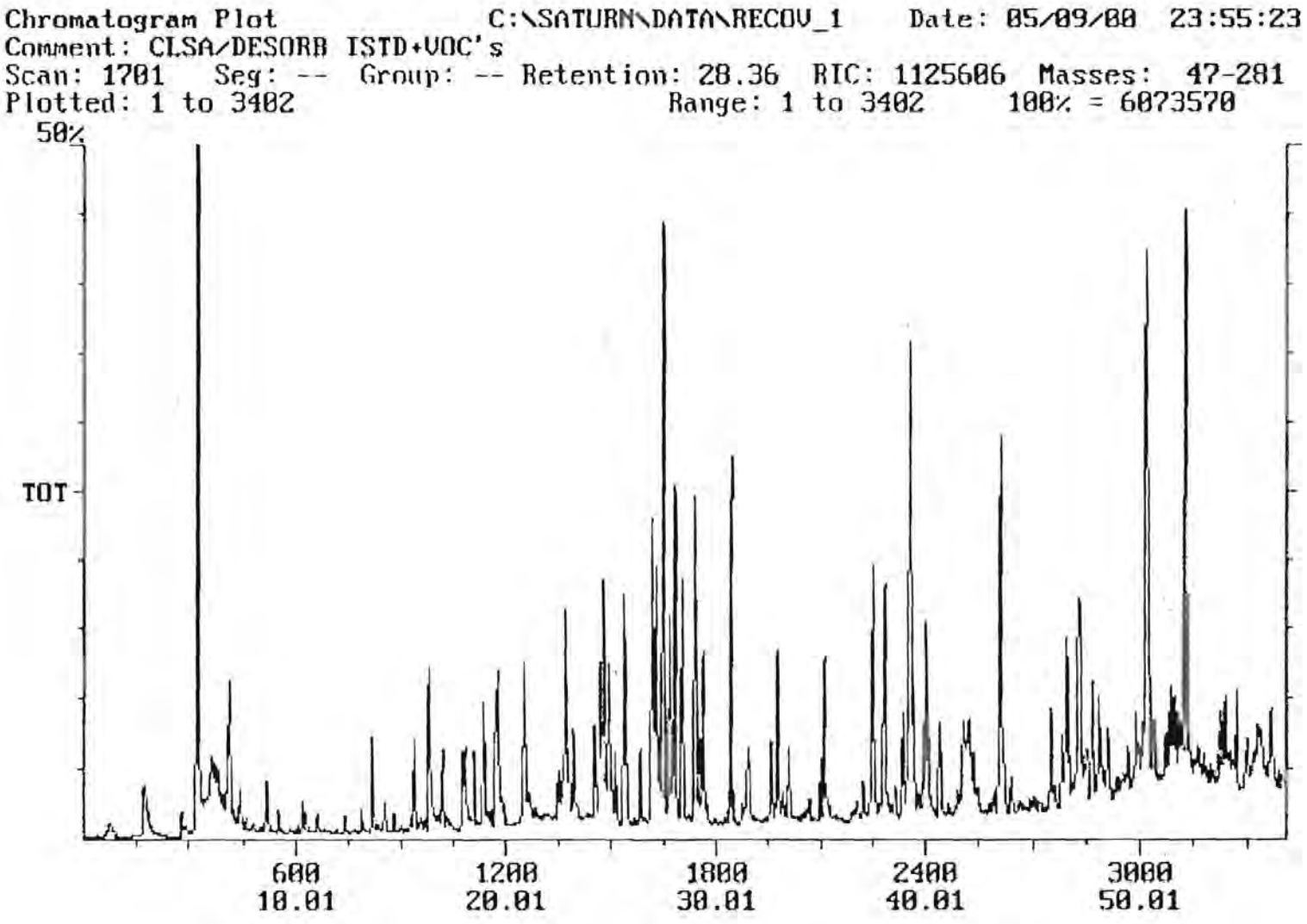

Figure I.2 Chromatogram of VOC recovery data

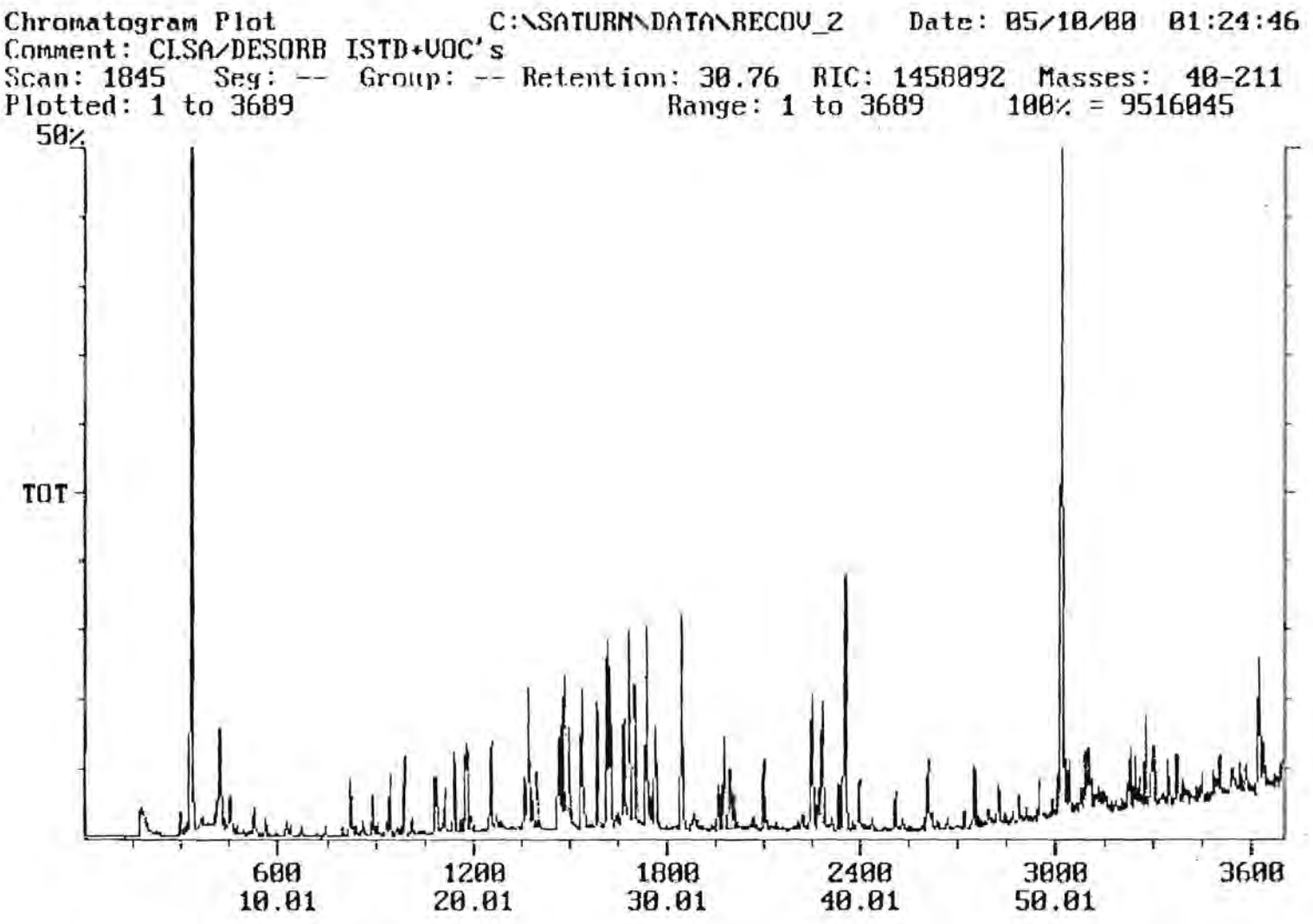

Figure I.3 Chromatogram of VOC recovery data

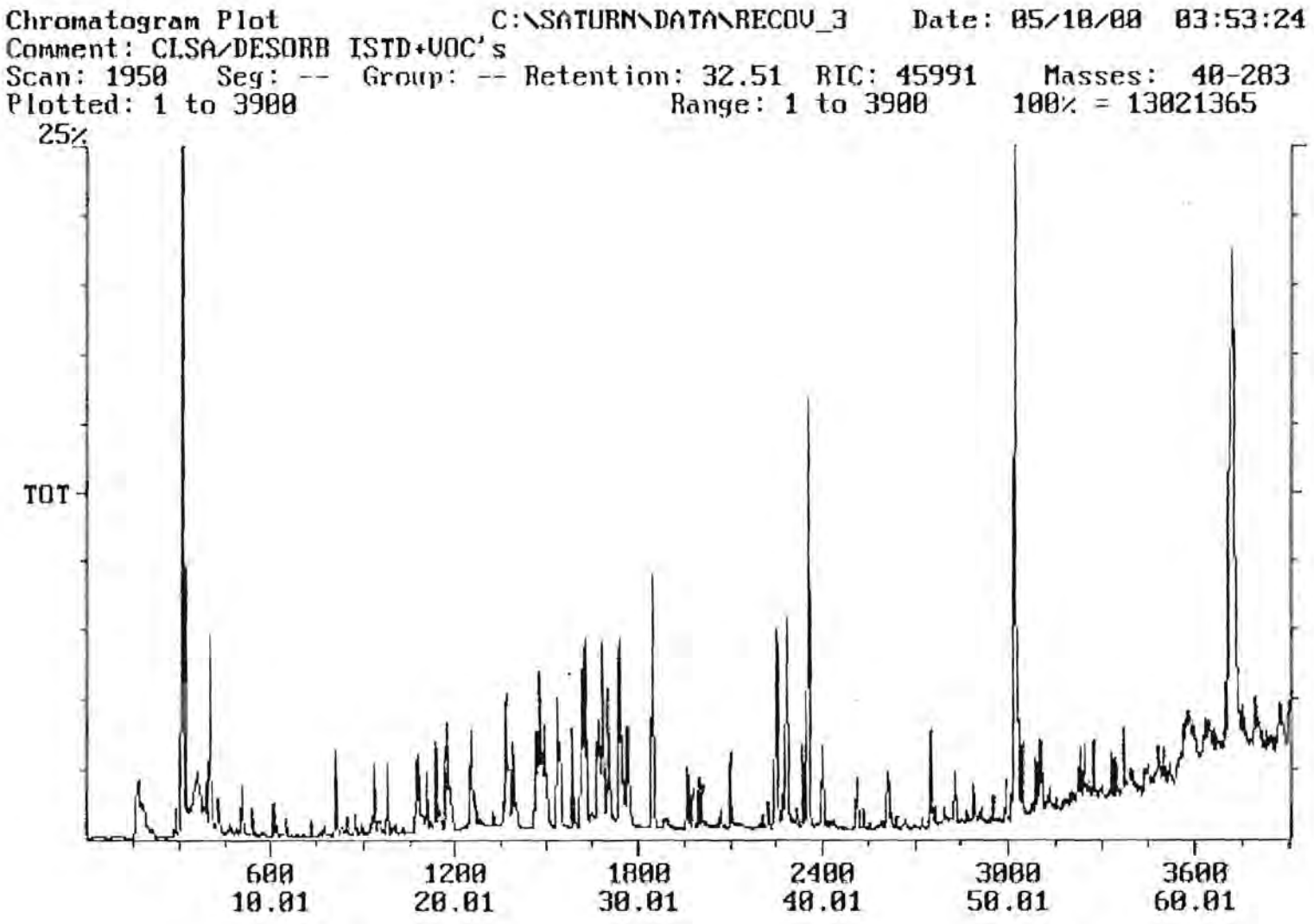

Figure I.4 Chromatogram of VOC recovery data

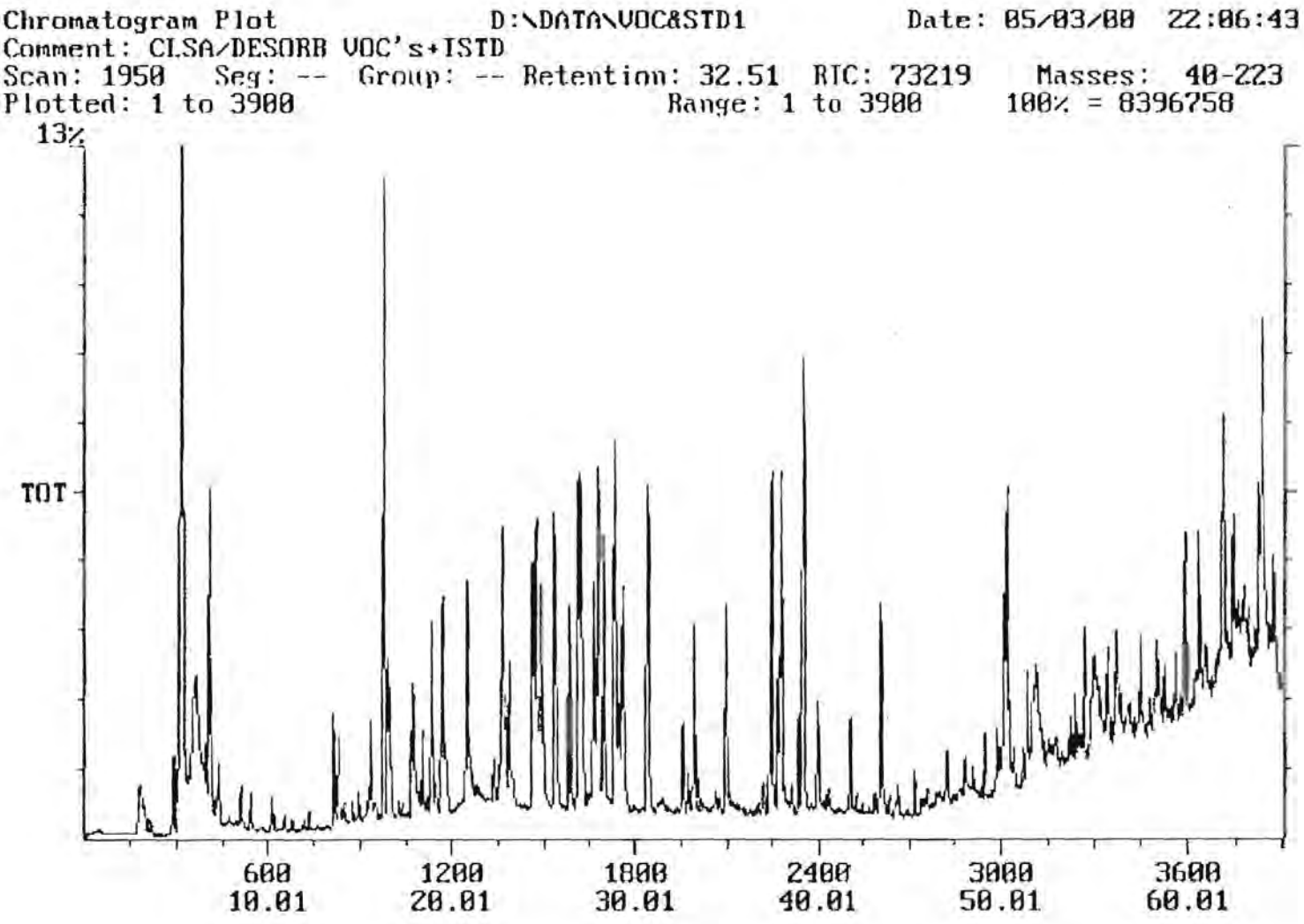

Figure I.5 Chromatogram of analysis for statistical data

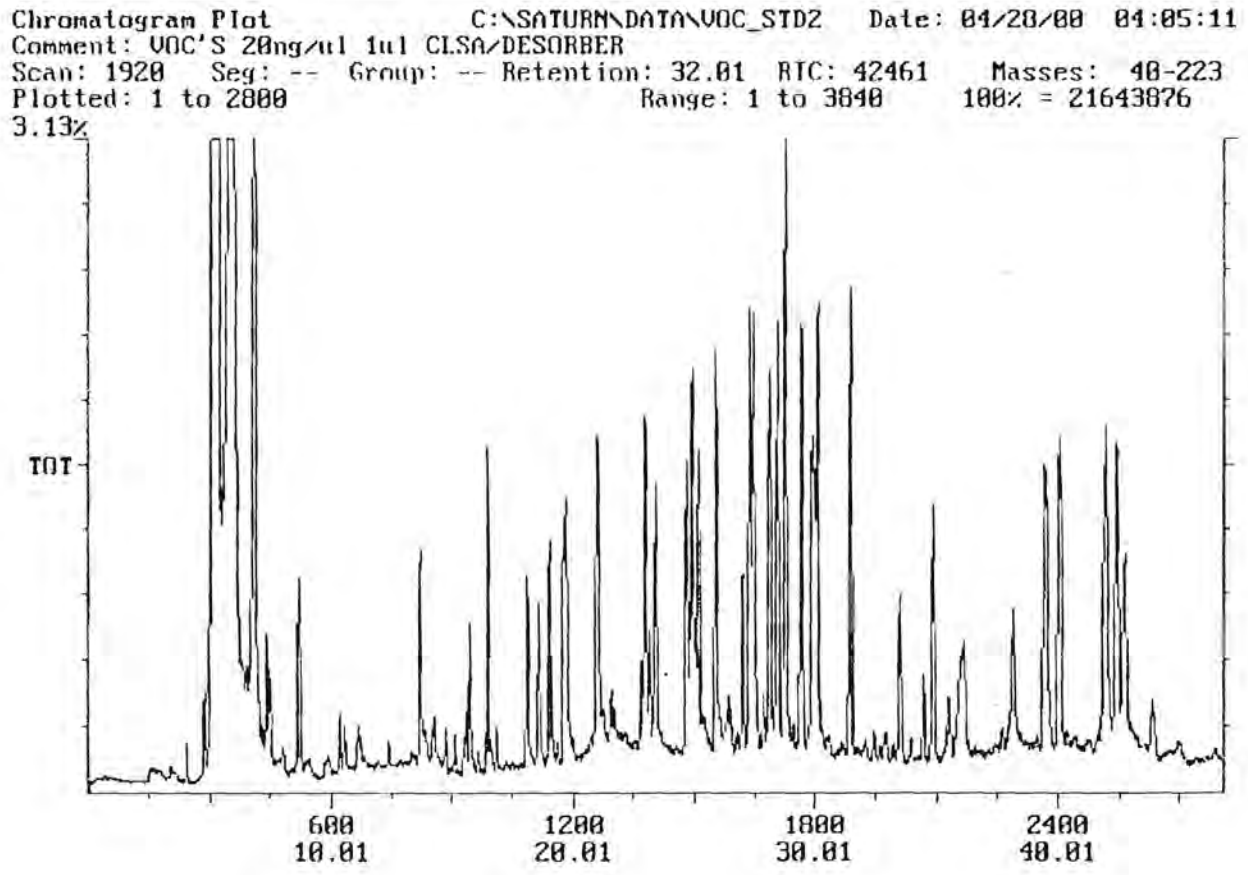

Figure I.6 Chromatogram of analysis for statistical data

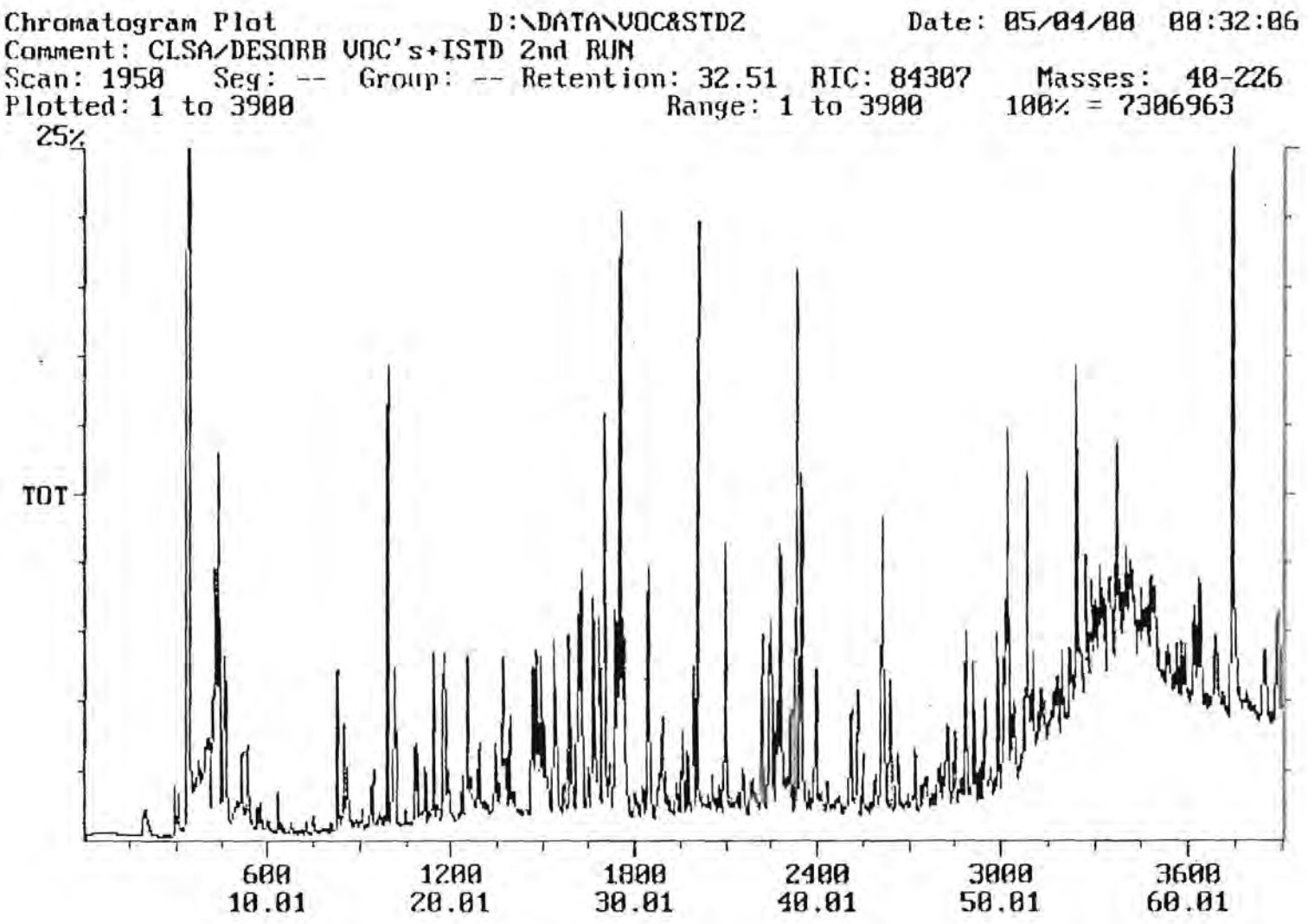

Figure I.7 Chromatogram of analysis for statistical data

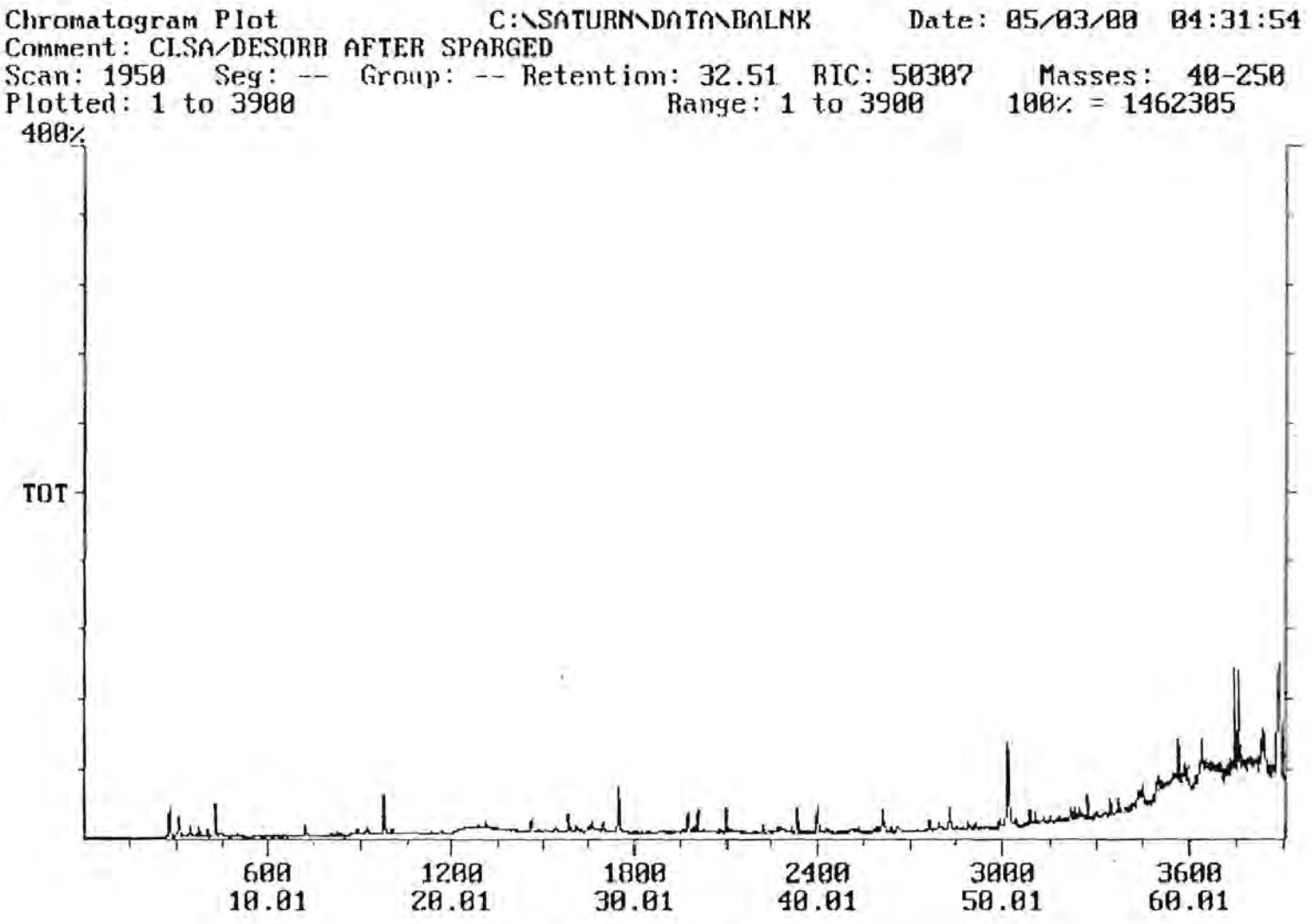

Figure I.8 Chromatogram of blank analysis.

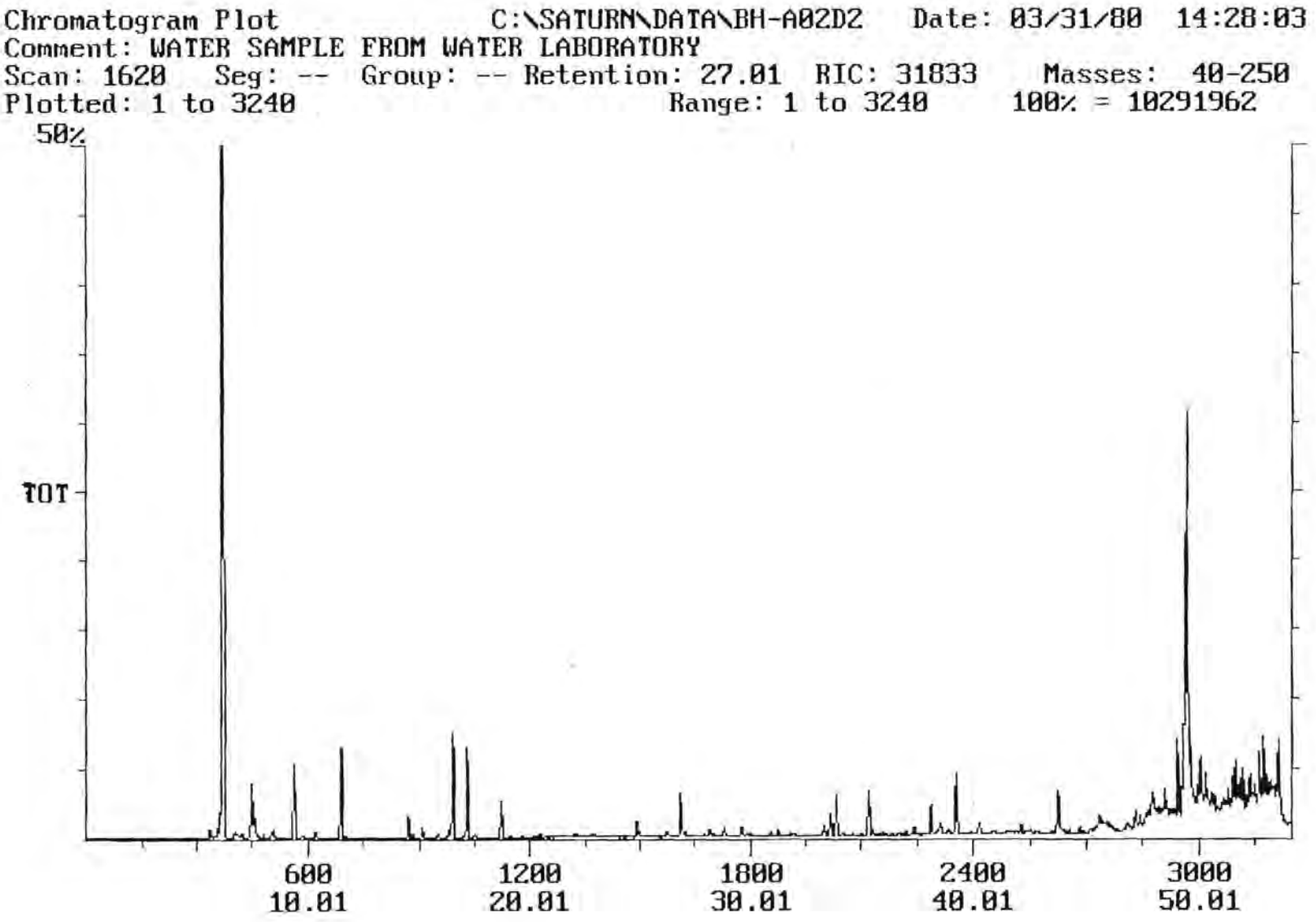

Figure I.9 Chromatogram of water sample BH-A0

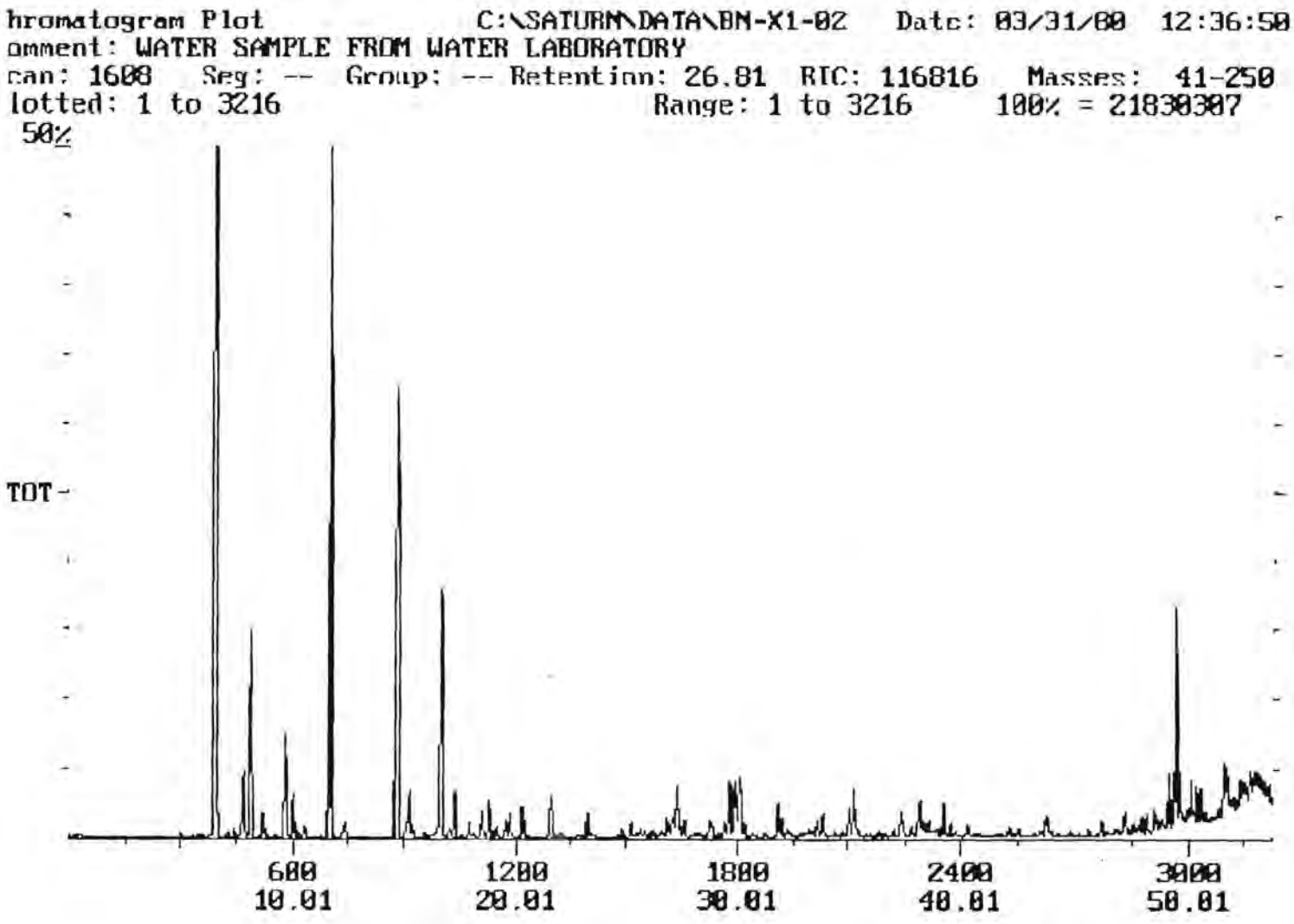

Figure I.10 Chromatogram of water sample BN-X1

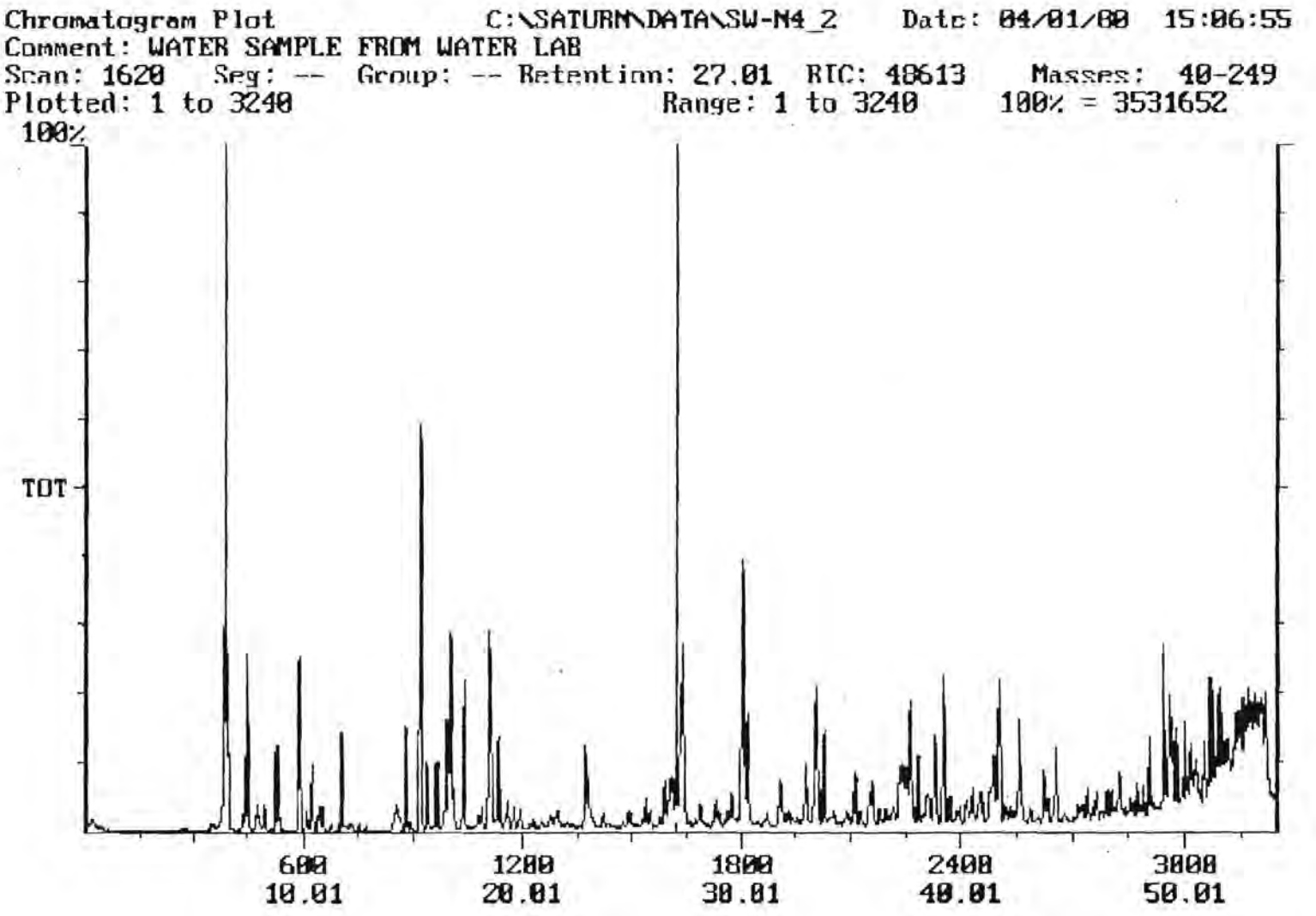

Figure I.11 Chromatogram of water sample SW-N4

Standard Deviation of VOCs at 200ng/l

Compound Name	R.S.D. 0.2ug/l	S/N Ratio 0.2ug/l	LOD.S/N=3 ng/l	Area (x1000)				
				Recov_1	Recov_2	Recov_3	Mean	Stand.Dev
Dichloromethane	26.3%	140	85.714	428	535	720	561.0	147.7
Chloroform	19.7%	193	62.176	338	388.3	259.6	328.6	64.9
trichloroethane	3.5%	117	102.564	63	67	67	65.7	2.3
tetrachloromethane	8.3%	1533	7.828	296	257	257	270.0	22.5
trichloroethylene	12.2%	16148	0.743	83.7	74.5	95	84.4	10.3
dibromomethane	21.4%	4410	2.721	23.3	15.8	23.8	21.0	4.5
bromodichloromethane	10.2%	354	33.898	115	97.9	119.2	110.7	11.3
dichloropropene	15.3%	481	24.948	120	93	125	112.7	17.2
methyl benzene	4.6%	4377	2.742	794	753	825	790.7	36.1
trichloroethane	34.3%	114	105.263	120	84	60	88.0	30.2
dibromochloromethane	40.7%	13813	0.869	66	69.4	130	88.5	36.0
tetrachloroethylene	5.8%	46081	0.260	227.6	250.7	226.4	234.9	13.7
chlorobenzene	9.5%	91807	0.131	529	540.6	452	507.2	48.2
tetrachloroethane	10.2%	51192	0.234	244.2	222.2	198.9	221.8	22.7
ethyl benzene	16.2%	974	12.320	1254	1295.8	949.6	1166.5	189.0
m-dimethyl benzene	19.3%	20	600.000	1339	1134	905	1126.0	217.1
p-dimethyl benzene	15.8%	1360	8.824	1145	1115	848	1036.0	163.5
isopropyl benzene	17.7%	136	88.235	1716	1855	1302	1624.3	287.7
bromobenzene	17.6%	80751	0.149	470.5	450.5	334	418.3	73.7
methy (methylethyl)benzene	11.4%	922	13.015	2760	2507	2192	2486.3	284.6
chloromethyl benzene	75.1%	143992	0.083	634	1309	232	725.0	544.2
propyl benzene	6.6%	12.6	952.381	2220	2402	2108	2243.3	148.4
trimethyl benzene	9.3%	376	31.915	1940	1830	1612	1794.0	166.9
dibromochloropropane	6.2%	51705	0.232	327	297	334	319.3	19.7
dichlorobenzene	15.2%	188169	0.064	1096	1022	809.6	975.9	148.7
butylbenzene	11.9%	1208	9.934	3527.7	3164.7	2779.1	3157.2	374.4
trichlorobenzene	7.2%	208549	0.058	1302.9	1135.4	1181.8	1206.7	86.5
naphthalene	12.4%	528396	0.023	3532.8	2756.3	3114.7	3134.6	388.6
hexachlorobutadiene	13.1%	166519	0.072	1191	948	964	1034.3	135.9

NB Some of the S/N ratios are deceptively small in some cases, since baseline separation was not achieved in all of the peaks.

ADDENDUM II

ELSEVIER

Journal of Chromatography A, 849 (1999) 521–528

JOURNAL OF CHROMATOGRAPHY A

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. © 1999 Published by Elsevier Science B.V. All rights reserved.

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.

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.

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.

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

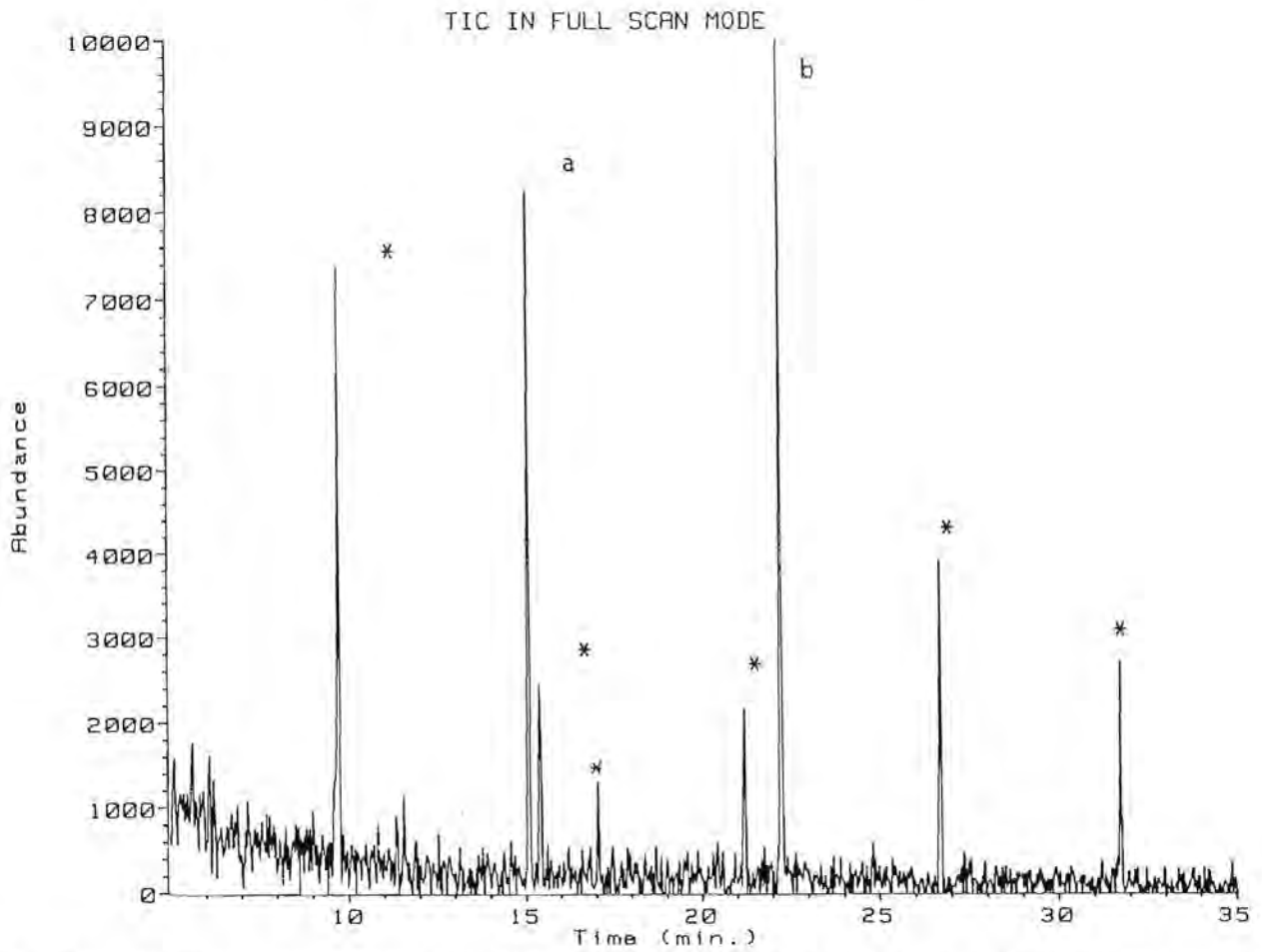

Fig. 1. Deuterated MIB and deuterated geosmin added to the multichannel silicone rubber trap and analysed in full scan mode to observe the trap background. (a) Deuterated MIB; (b) deuterated geosmin; * silicone peak background.

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

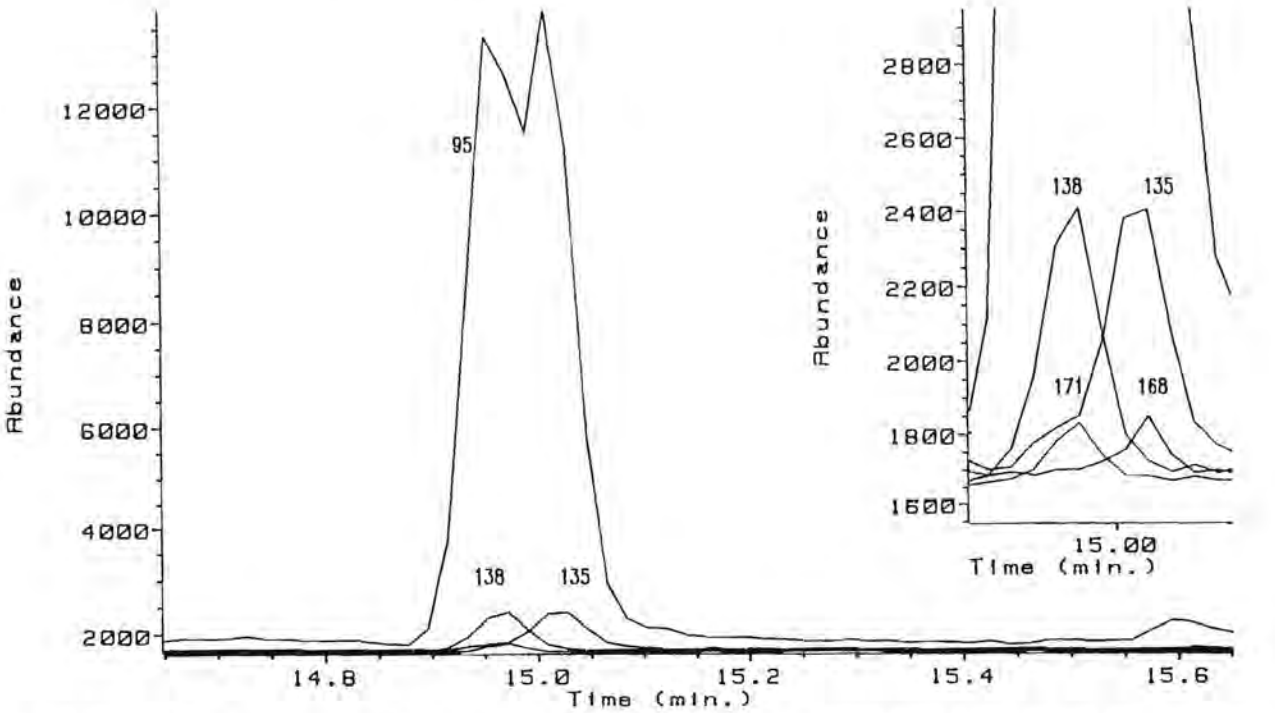

Fig. 2. Separation of deuterated MIB and non-deuterated MIB using the m/z values listed in Table 2 (m/z 95, 138, 135, 171, 168).

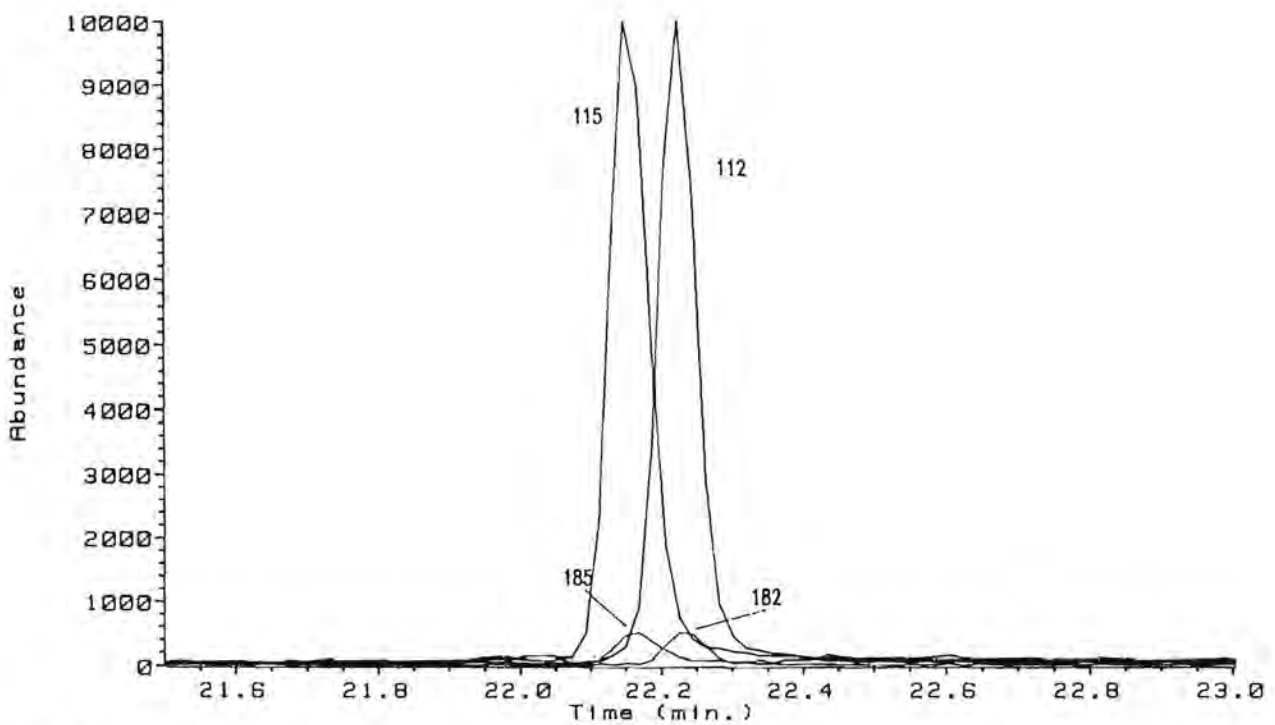

Fig. 3. Separation of deuterated-geosmin and non-deuterated geosmin using the m/z values listed in Table 2 (m/z 115, 112, 185, 182).

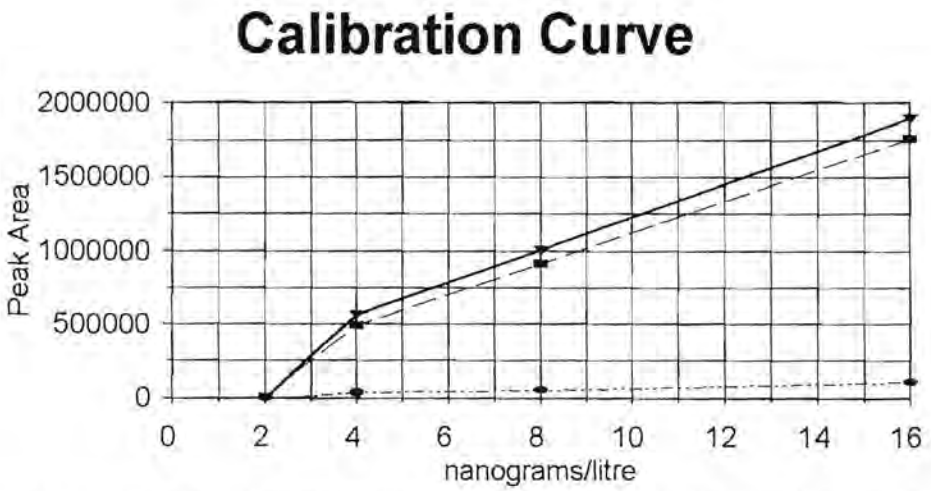

Fig. 4. (a) Deuterated MIB m/z 95; (b) deuterated geosmin m/z 115; (c) deuterated MIB m/z 138.

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

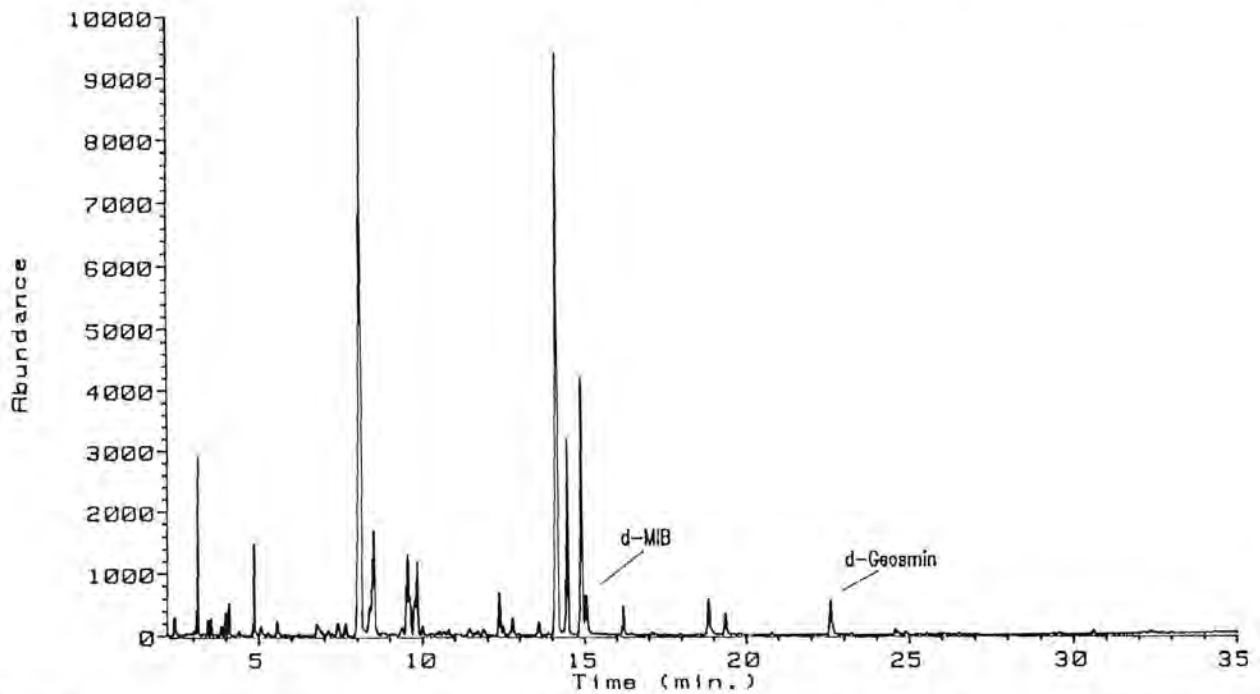

Fig. 5. Reconstructed total ion chromatogram (TIC) (sum of the SIM ions) for the SIM analysis of a drinking water spiked with 8 ng/l of deuterated MIB (d-MIB) and geosmin (d-geosmin) standards, extracted with the MCSRT.

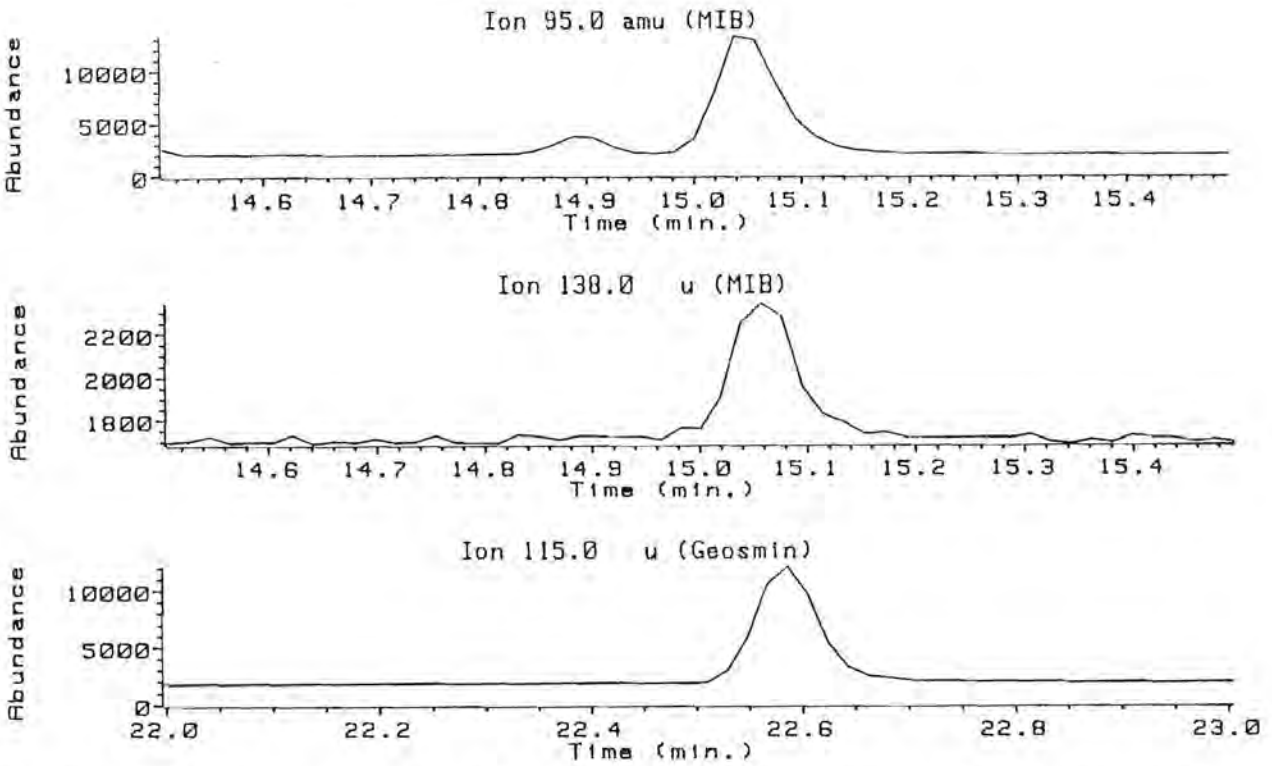

Fig. 6. Reconstructed single ion traces from the spiked water sample (Fig. 6) for deuterated MIB (m/z 95, 138) and deuterated geosmin (m/z 115).

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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