# Solid Phase Micro Extraction: an Alternative Technique for the Determination of Volatile Organic Compounds in Groundwater

By

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UNIVERSITY of the
WESTERN CAPE

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## DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

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**ABSTRACT**

Standard methods for sample preparation use toxic organic solvents and can be replaced by utilizing a new sample preparation and concentration technique. One such technique, compatible with capillary gas chromatography was developed in this study that shows promise of increased speed, cost-efficiency and ease of automation:

The solid phase micro extraction (SPME) process has two steps: partitioning of analytes between the coating of a SPME fiber and the sample matrix, followed by desorption of concentrated extracts directly into an analytical instrument. In the first step, the coated fiber is exposed to the sample or its headspace which causes



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the target analytes to partition from the sample matrix into the coating. The fiber bearing concentrated analytes is then transferred to an instrument for desorption, whereupon separation and quantitation of extracts can take place. SPME can be used as a sample preparation technique for liquid, gas and solid samples.

Results show that SPME, when fully optimized can successfully be used for the determination of volatile organic compounds in groundwater at a fraction of the equipment cost. The technique can also be used as a screening tool before the validated purge and trap methods are employed.

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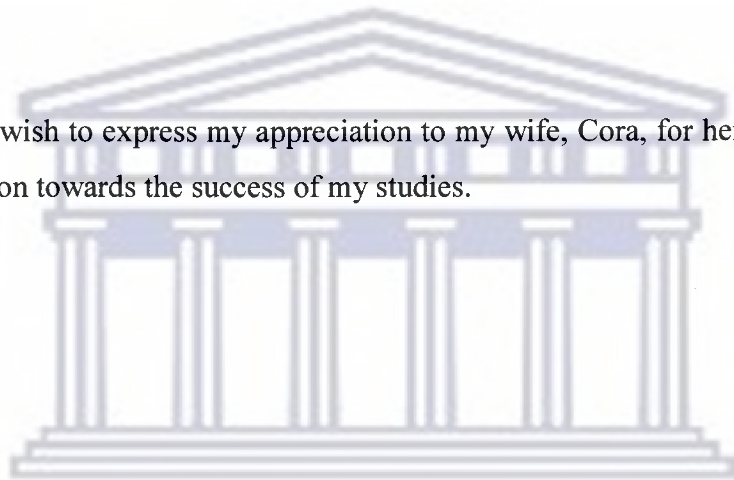

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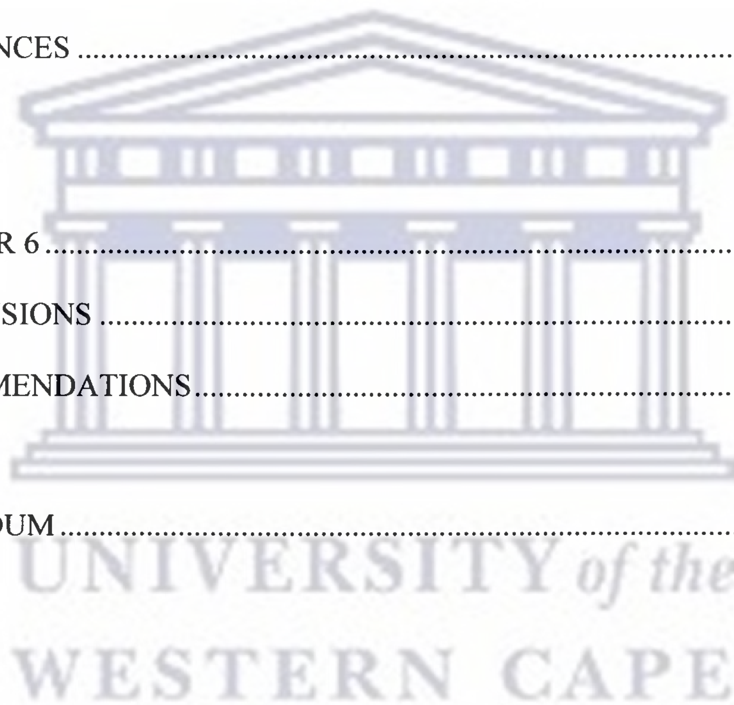
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# CHAPTER I

## 1.1 INTRODUCTION

### 1.1.1 Background to Study

Today producing without polluting is more than just a civilized concept; it is a mandate for the preservation of society. Cleaner production means conserving energy and natural resources, reducing the use of toxic substances and investing in the development of products and production processes towards minimized residues.

The rate of population increase in the urban centers of South Africa continues to increase. One of the consequences of this increasing rate of urbanization is the increase in the quantity of solid and liquid wastes. Many of these undesirable organic and inorganic substances if not well managed, can pollute groundwater.

The threat posed by organic contaminants to groundwater is recognized in many developed countries (Sililo,1999). During the last ten years environmental controls practiced by organic chemical industries have changed from "end of pipe technologies" for the treatment of liquid effluents and gaseous emissions as well as effectively confining industrial hazardous waste, to a clearer vision of source control and the minimization of residue.

The past sanctions era saw a certain degree of isolation of the South African industry from internationally acceptable environmental norms and practices. Soil and groundwater contamination standards are generally derived from established first world standards where they are usually set for worst-case situations (40 – 70 years continuous exposure) (Morris, 1996).



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South Africa with its diverse rainfall regions (the average rainfall of the country is less than 500mm, well below the world average of 860mm), has limited natural water resources to support its growing population (Van der Merwe, 1995; Laburn, 1995) and thus needs to preserve its additional groundwater reserves of nine billion $m^{3}$. (Holtzhausen, 2002).

### 1.1.2 The Need

A major limitation in the study of volatile organic contaminants in groundwater is the lack of reliable analytical facilities offering organic analysis in South Africa. Most of the universities' chemistry departments will offer Gas Chromatography (GC) or Gas Chromatography / Mass Spectrometry (GC/MS) analysis, but such institutions are seldom subjected to quality control audits. Consulting Engineers have been unable to find reliable analytical laboratories for analysis of organic compounds and therefore make use of the services of the Geochem Group Ltd. Commercial laboratories in the United Kingdom.

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### 1.1.3 The Problem

The majority of organic chemical analysis is conducted by Gas Chromatography coupled with mass spectrometry (GC/MS). This is primarily because, although it is relatively expensive, it is the most cost-effective analysis if the amount of information obtained per analytical rand spent is considered. If advances are to be made in the study of organic pollution of groundwater, cost-effective ways of sample preparation and analysis need to be investigated. One such method that shows promise is a technique called Solid Phase Microextraction (SPME) introduced by Janusz Pawliszyn (Pawliszyn, 1989).



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## 1.2 APPROACH

For the analysis of organic micro-pollutants in water by chromatographic techniques a pre-concentrated sample is needed. Present methods have various drawbacks, including cost and excessive preparation time. The objective of the proposed research was firstly to study the latest concentration technique designed for capillary gas chromatography that shows promise of increased speed, cost-effectiveness and ease of automation.

Initially the sample analysis time could be reduced in decreasing the time required to concentrate the sample using traditional concentration methods, by replacing this step with Solid-Phase Microextraction (SPME). It permits extraction without any solvent and reduces preparation time by as much as 70%. This technique won the prestigious R&D 100 Award in 1994 for innovative technology.

Secondly, investigations were undertaken to find the optimal conditions under which SPME would operate for the compounds of interest. The various factors that can influence the sensitivity namely; sample matrix, equilibrium times and the type of polymeric fiber were studied, since some of the requirements of a sorbent (fiber) are;

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- They should efficiently trap small concentrations of contaminants.
- Their capacity should be sufficiently high.
- They should selectively absorb contaminants in the presence of bulk matrix compounds, (example, water).
- Convenient quantitative methods of sample recovery should be available.

SPME fibers show promise of increased speed, ease of automation and cost-effectiveness since they can be reused. Use of SPME in the analysis of environmental samples was focused upon as to date most of the SPME work has centered on extraction of standard spikes from relatively clean water (Buchholz, 1994; Arthur, 1992).



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## 1.3 SCOPE AND LIMITATIONS OF THE STUDY

The objectives of this study were to develop and validate a method, which could serve as an alternative to conventional solvent-free sampling techniques, used for the determination of volatile organic compounds in groundwater. Application of the method to compounds that are of priority to the Department of Water Affairs and Forestry (DWAF). A limitation of this study was that the analytical instrumentation (GC/MS) used in this study was shared by organic chemists using the instrument for identification purposes and thus the detector was contaminated on occasions.

## 1.4 ARRANGEMENT AND PRESENTATION

This dissertation firstly (chapter 2) looks at the different techniques presently used by EPA and other organizations for sample preparations, and SPME as a solvent-free sampling / sample preparation / introduction technique of samples into a gas chromatograph. The second part (chapter 3) looks at the optimization of SPME; while chapter 4 discusses the SPME method development around the 10 target compounds and their environmental hazards. Lastly a case study was done on a landfill site (waste site) Vissershok, approximately 20 km northeast of Cape Town as an application of the developed technology.

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# CHAPTER 2

## LITERATURE REVIEW

### 2.1 WHAT IS GROUNDWATER?

Groundwater, simply stated, is the water which is located underground, below the earth's surface. Water in soils and other geologic formations is stored in a complex network of pores and voids between the solid matrix, which consists of clays, sand, gravel and other similar materials. Closer to the ground surface, in a region called the unsaturated zone, both water and air occupy the pores and voids. At greater depths, in a region known as the saturated zone, water completely fills all the pore spaces. It is the water in this zone that we refer to as groundwater.

The upper limit of the saturated zone is commonly referred to as the water table, and may occur at depths varying from a few meters to several hundred meters below ground surface. When the area of the saturated zone is large, and the ability of these zones to transmit water (i.e., their permeability) is sufficiently great to yield water to springs, rivers, and wells, they are referred to as aquifers (Hornsby, 1986).

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### 2.2 GROUNDWATER THREATS

Large scale production of synthetic halogenated organic compounds, which are often resistant to both biotic and abiotic degradation, has occurred in the last few decades (Hutzinger and Verkamp 1981). These same processes, perhaps operating at different rates, determine the transport and attenuation of organic contaminants in the saturated zone as well. The fundamental difference between the two zones is that the saturated zone pore spaces are completely filled with water (and at times certain dense non-aqueous phase liquids (DNAPL), while the pore spaces in the



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unsaturated zone are occupied by water (or DNAPL) and air, these fluid phases each contain dissolved contaminants that can interact with the mineral and organic constituents of the solid phase. (Rao, 990). Many halogenated organic compounds are not very soluble and tend to be highly lipophilic, therefore having the potential to bioaccumulate in some food chains. These chemical properties, along with their toxicity and resistance to degradation, present the potential for adverse health effects and ecosystem perturbations upon exposure (Rochkind et al. 1986).

## 2.3 HEALTH EFFECTS OF ORGANIC POLLUTANTS

Toxicity of an organic pollutant is defined as its inherent ability to cause an adverse health effect, such as the ability to induce cancer, birth defects and other illnesses in animals and humans (Rao et al., 1987). The severity of health effects from exposure to organic pollutants is dependent upon the dose (i.e., the amount and time of exposure). The short-term toxicity of a chemical, manifested over a period of hours or days, is referred to as an acute toxicity. On the other hand, the long-term toxicity, observed after several years of exposure to a chemical, is known as the chronic toxicity.

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Acute toxicity is easier to diagnose and treat because the health effects are exhibited over a short period of time and, after exposure to low doses, these effects are usually reversible; that is, when the exposure to the chemical ceases, so do the effects.

Chronic toxicity is more difficult to diagnose and to treat because in some cases its effects are latent, taking several years before the adverse health effects become evident and by then it may be too late to reverse or terminate the adverse effects. Because of the uncertainty of affliction and the protracted effects, it is the chronic toxicity of organic pollutants in drinking water that is the major concern of scientists and the public. On the basis of their chronic toxic effects, organic



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chemicals may be grouped into the following three major classes: carcinogens, mutagens and teratogens.

### 2.3.1 Carcinogens

Any chemical that causes cancer in either a direct or an indirect form is called a carcinogen. Although carcinogenesis is the most studied of all chronic effects, it is not entirely clear as to how carcinogens cause cancer. It is known, however, that these chemicals stimulate the formation of malignant tumors of various forms in many parts of the body.

Among the chemicals suspected to produce carcinogenic effects in humans are: vinyl chloride, a component of some resins used in construction; benzene, a product of petroleum refining and used as a solvent.

### 2.3.2 Mutagens

A chemical capable of producing an inheritable change in the genetic material is called a mutagen. Most of the chemicals suspected to be mutagenic have only been tested using microorganisms and animals. Chemicals that have been found to be mutagenic include: vinyl chloride; benzo(a)pyrene; bromoform; chlorodibromomethane; and the fungicides folpet and captan.

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### 2.3.3 Teratogens

Any chemical that acts during pregnancy to produce a physical or functional defect in the developing offspring is known as a teratogen. Scientific knowledge on teratogens is very limited. Some of the chemicals that have been shown to have teratogenic effects in animals are: nicotine, found in cigarettes; and the pesticides 2,4D, 2,3,5-T, and folpet.



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## 2.4 PRIORITY ORGANIC POLLUTANTS

Priority pollutants are compounds that may pose a threat to human health and the environment because they are toxic. The U.S. Environmental Protection Agency has prioritized 45 volatile compounds (USEPA, 1986, 1990). In South Africa the Department of Water Affairs and Forestry (DWAF) has singled out ten of these compounds namely: carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,2-dichloropropane, toluene, chlorobenzene, 1,4-dichlorobenzene and 1,3-dichlorobenzene (tender W7909). In communications with DWAF no definite answer was provided to explain why these compounds were singled out as priority compounds. Even in communications with the Institute for Water Quality Studies in Bloemfontein, no clear-cut answer was forthcoming. No South African references could be found where these compounds were studied apart from the trihalomethanes by the National Institute for Water Research (van Rensburg, 1981).

It was for this reason that these compounds were reviewed in relation with guidelines set out by the World Health Organization (WHO) for their health effects. Below is a table (2.1) formulated by the International Agency for Research on Cancer (IRAC) to categorize chemical substances with respect to their potential carcinogenic risk.

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**Table 2.1:** Categorization of chemicals according to there carcinogenic risk

| GROUP | CLASSIFICATION |
|---|---|
| Group 1 | The agent is carcinogenic to humans |
| Group 2A * | The agent is probably carcinogenic to humans |
| Group 2B * | The agent is possibly carcinogenic to humans |
| Group 3 | The agent is not classifiable as to its carcinogenicity to humans |
| Group 4 | The agent is probably not carcinogenic to humans |

Taken from: Guidelines for drinking-water quality (1993)



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* Group 2A. This category is used when there is limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals.
* Group 2B. This category is used for agents, mixtures, and exposure circumstances for which there is limited evidence of carcinogenicity in humans and less than sufficient evidence of carcinogenicity in experimental animals.

### 2.4.1 Carbon tetrachloride

This material has mostly been used in the manufacture of chlorofluorocarbon propellants and refrigerants, though this has been declining steadily due to their effect on the ozone layer. It is also used as a solvent for oils, fats, lacquers, varnishes, rubber waxes, and resins and as a starting material in the manufacture of organic compounds. Acute (short-term) oral exposure to carbon tetrachloride has been observed primarily to damage the liver and kidneys of humans. Chronic (long-term) oral exposure to carbon tetrachloride produces liver and kidney damage; cancer. Carbon tetrachloride has been classified in group 2B by the International Agency for Research on Cancer (IARC). The guideline value has been set at 2ng/l by the WHO

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### 2.4.2 1,1,1-Trichloroethane

It is largely used as a solvent in the metal plating industry and for removing grease from machined metal products, in textile processing and dyeing. Short-term and long-term exposure causes damage to the liver, nervous system and circulatory system. The IARC has placed 1,1,1 – trichloroethane in group 3. The guideline value has been set at 2mg/l by the WHO.



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### 2.4.3 Trichloroethylene

Trichloroethylene is mainly in dry cleaning and in metal degreasing operations. It induces lung and liver tumors in humans. Trichloroethylene in anaerobic groundwater may degrade to more toxic compounds, including vinyl chloride. The IARC has classified it in group 3. The WHO guideline is set at 70µg/l.

### 2.4.4 Tetrachloroethylene

The chemical is used in rubber coatings, solvent soaps, printing inks, adhesives and glues. At high concentration, tetrachloroethylene causes central nervous system depression. Tetrachloroethylene (TCE) may be a carcinogen in humans and may damage the developing fetus. TCE can also damage the liver and kidneys enough to cause death. IARC has classified TCE in group 2B and the WHO guideline is set at 40µg/l.

### 2.4.5 1,2-Dichloroethane

This solvent has been replaced as a degreaser by less toxic compounds. It once served as a solvent for processing pharmaceutical products; for fats, oils, waxes, gums, resins and particularly for rubber. Therapeutically, 1,2-dichloroethane was once used as a general anesthetic instead of chloroform. 1,2-dichloroethane is reasonably anticipated to be a human carcinogen based on evidence of carcinogenicity in experimental animals. The WHO guideline is 200µg/l and the IARC has classified 1,2-dichloroethane in Group 2B.

### 2.4.6 1,2-Dichloropropane

It is used as a chemical intermediate in the production of chlorinated organic chemicals, as an industrial solvent, in ion exchange manufacture, for paper coating



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and for petroleum catalyst regeneration. The use as a soil fumigant has been discontinued, and pesticide formulations containing 1,2-dichloropropane are no longer available in the United States. No studies are available regarding carcinogenic effects in humans from oral exposure to 1,2-dichloropropane, although gland tumors and liver tumors were reported in studies on rates and mice. The IARC classified 1,2-dichloropropane in Group 3 and the WHO guideline is set at 20μg/l.

### 2.4.7 Toluene

The largest chemical use for toluene is to make benzene, urethane, dyes, inks, perfumes, plastics and medicines. Over exposure to toluene mainly affects the central nervous system (the brain), causing headache, nausea, dizziness and clumsiness. Although no sign of cancer in animal experiments were shown, toluene is often contaminated with small amounts of benzene, which is known to cause leukemia and other cancers. The guideline value for toluene set by WHO is 0.7μg/l.

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### 2.4.8 Chlorobenzene

Chlorobenzene is used as a solvent for adhesives, drugs, rubber, paints and dry cleaning. Short-term health effects when exposed to chlorobenzene are anesthetic effects and impaired liver and kidney function. Long-term effects are liver, kidney and central nervous system damage. Limited evidence of carcinogenicity has been found in male rats, and the evidence thus suggests that chlorobenzene is of low acute toxicity. It has a WHO guideline of 0.3mg/l.

### 2.4.9 1,4-Dichlorobenzene

The compound is widely used as a moth killer, in the production of polyphenylene sulfide and the manufacture of certain resins in the pharmaceutical industry. 1,4-



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dichlorobenzene is not considered to be genotoxic, and the relevance for humans of the tumors observed in animals is doubtful (WHO. 1993). The IARC has placed 1,4-dichlorobenzene in group 2B and the WHO has set a guideline value of 0.3mg/l.

### 2.4.10 1,2-Dichlorobenzene

1,2-dichlorobenzene is of low acute toxicity by the oral route of exposure. The balance of evidence suggests that it is not genotoxic and there is no evidence for its carcinogenicity in rodents (WHO. 1993). The guideline value in drinking water has been set at 1mg/l.

## CURRENT EXTRACTION TECHNIQUES FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

### 2.5 COLLECTION OF ORGANIC POLLUTANTS

In general, most organic pollutants of interest in aqueous environmental samples, i.e., volatile organic compounds (VOC's), have to be extracted and enriched before their instrumental determination. This isolation from a sample matrix is often achieved by sampling and extraction steps separate from the instrumental analysis.

The renewed awareness of the pollution and hazards caused by organic solvents used for extraction processes (e.g., methylene chloride) has resulted in international initiatives towards the development of solvent-free sample preparation. Although several solvent-free methods have been known for some time, the enforcement of more stringent regulations on scientists and industry has prompted the shift in emphasis. A literature study was done on the different types of solvent-free techniques on the market, used for sample preparation.



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## 2.6 SOLVENT-FREE SAMPLE PREPARATION

Solvent–free sample preparation can be categorized according to the separation medium employed in the process, namely:

- Gas-phase extraction
- Membrane extraction
- Sorbent extraction

### 2.6.1 Gas-phase Extraction

These methods include:

- Static headspace sampling
- Purge and trap / Dynamic headspace sampling
- Supercritical fluid extraction (SFE)

Static headspace analysis has been used for decades to analyze volatile organic compounds (VOC's) in food, beverage, clinical and other samples (Charalambous, 1978). The sample is equilibrated with its headspace, and a small volume of the headspace is then directly injected into a gas chromatograph for analysis. This is however a low sensitivity technique as no concentrating of the analyte occurs. Another disadvantage of the technique is that "exhaustive extraction" cannot be achieved. Small amounts of analyte are therefore extracted at a time, reducing the sensitivity of the method considerably. It also requires careful calibration, where equilibration times between gas and liquid phase should be taken into consideration (Poole, C.F., 1991) ( Zhang et al 1994).

Dynamic headspace analysis makes use of a multiple partition concept. It allows for quantitative extraction of analytes (eg VOC's). The analytes are trapped on Tenax-GC contained in an 11-cm tube. Tenax-GC is a porous polymer based on 2,6-diphenyl- *p* -phenylene oxide. Trapped samples can easily be stored or shipped



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to another site for analysis. Efficient desorption from the Tenax occurs with helium flow at 300$^{o}$C. The desorbed volatiles are collected in a precolumn cooled by dry ice. The precolumn is then connected to the GC column, the dry ice is removed, and the analysis is started at room temperature. The precolumn contains the same liquid-liquid phase as the regular GC column. The technique is well developed for drinking water analysis in the United States. Apart from that, the method can achieve accurate and precise results as well as low detection limits. However this technique does suffer from drawbacks / limitations. The equipment is expensive and has been known to be prone to leaks and sample carry over (Westendorf), as well water management problems (Noij, 1987), thus rendering the technique incompatible with on-line operation (Poole, 1991). Thus the technology was discontinued by the Hewlett Packard Company in 1999 (Wrede, 2001).

Supercritical fluid extraction (SFE) allows many difficult-to-prepare samples to be prepared for analysis – *without* organic solvents. Because supercritical fluid extraction, possess both gas-like mass transfer and liquid-like solvating characteristics, SFE is a very efficient solvent-free sample preparation technique, (Hawthorne S., 1990). It combines the high solvating characteristics of liquids with low viscosity and high penetrating ability of gases (Langenfield, 1993). The solvating power can be adjusted by changing the pressure or temperature, or by adding modifiers to the supercritical fluid. Samples are usually solids, but liquid samples can also be extracted by SFE if they are first deposited on an inert support (e.g., diatomaceous earth), or if a SFE fluid is purged through water as in a purge and trap procedure. Analytes are normally collected in a solvent in a capped collection vial. Liquid $CO_2$ is forced into the supercritical state by regulating its temperate and pressure. Supercritical $CO_2$ has solvent power and extracts lipophilic and volatile compounds. However, SFE requires high cost instrumentation and large amounts of high purity gas (Poole, 1991) (Zhang, 1994). Hewlett Packard Company has discontinued this type of instrument in 1998 (Wrede, 2001).



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### 2.6.2 Membrane Extraction

Membrane extraction with a sorbent interface (MESI) was first introduced in 1992. (Yang, 1994; Luo,1995). The extraction is based on the partitioning of organic compounds across a non-polar membrane. A small section of membrane material is mounted in a holder that allows one side of the membrane to be exposed to the sample matrix. The other side of the membrane is continuously swept with a carrier gas (nitrogen). As volatile compounds come in contact with the membrane surface, migration through the membrane begins. Compounds are then picked up by the carrier gas on the other side of the membrane and passed along to an adsorbent trap. After the sampling or extraction period is completed, the trap is very rapidly heated to desorb all of the compounds that have been collected on the adsorbent material. Desorbed analytes are picked up in the flow of the carrier gas and are transferred to the inlet of the GC analytical column for separation. This application compares favourably with conventional headspace analysis and has a significantly higher surface area-to-volume ratio, which allows greater mass transfer rates. The technique is still being developed and suffers from limited capability to analyze polar compounds and slow response of the membrane to changes in concentration (Zhang, 1994).

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### 2.6.3 Sorbent Extraction

The principle of using sorbent material to extract organic compounds from an aqueous media was developed several years ago. The technique is based on concentration of the analytes by the sorbent. By employing different sorbents, a variety of analytes can be extracted from gaseous or aqueous media. One of the most commonly known sorbent extraction techniques is Solid Phase Extraction (SPE). Analytes are extracted from aqueous media through a plastic cartridge containing dispersed sorbent on a particulate support. SPE has a number of attractive features, namely:



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- Its quite simple
- Is inexpensive ($C_{18}$ cartridges, R1000 00 per box of 30)
- Can be used in the field
- Can be automated
- Uses relatively little solvent.

Despite its advantages, SPE still exhibits some limitations, e.g. it still uses small amounts of hazardous solvent for the extraction of the analyte from the sorbent. It is limited to semi-volatile compounds. Low recovery due to interaction between sample matrix and analytes. Moreover, SPE cartridges are often blocked by solid and oily components, resulting in low breakthrough volume and low capacity (Gòrecki, 1996; (Zhang, 1994).

To overcome the limitation of SPE, the geometry of the sorbent has been improved, by coating the sorbent into a fine rod of fused silica, thus changing the geometry to a cylindrical shape. This cylindrical geometry was aptly named Solid Phase Microextraction (SPME), which allows for rapid mass transfer during extraction and desorption without encountering the problem of plugged cartridges (Gòrecki, 1996; Zhang, 1994).

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## 2.7 SOLID PHASE MICRO-EXTRACTION (SPME)

### 2.7.1 Background

SPME, a technique developed by Janusz Pawliszyn et. al. (Pawliszyn, 1989) is basically a miniaturization of the process of solid phase extraction of analytes from aqueous medium (Gorecki, 1996). The SPME device (figure 2.7) as developed by Supelco; Ontario, Canada (Shirey, 1994), consists of a phase coated polymeric fiber fastened into the end of a fine stainless steel tube contained within a syringe-like device. The fiber is withdrawn into a protective sheath in the standby position.



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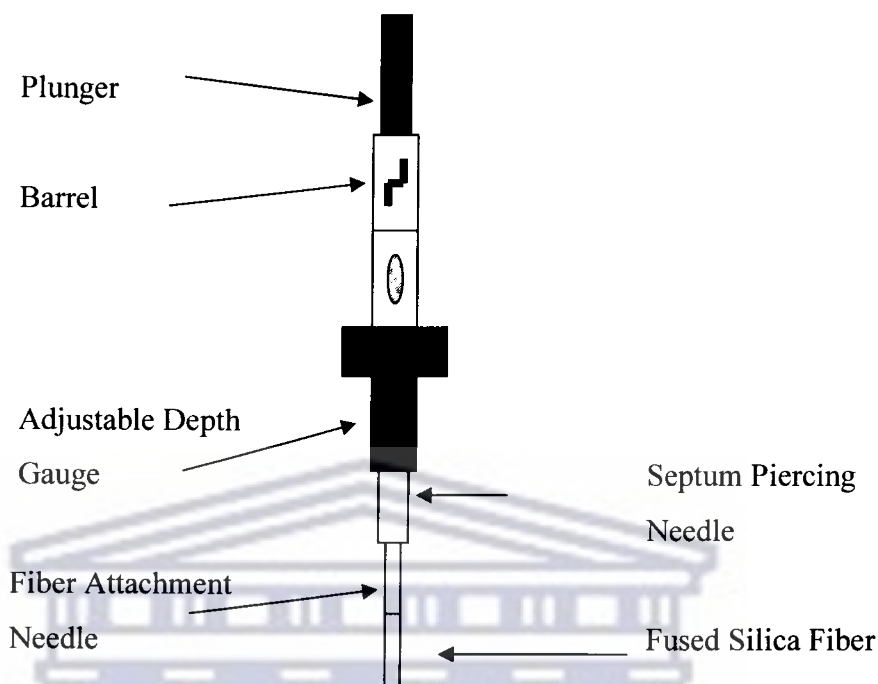
**Figure 2.7:** SPME device




Samples that contain VOC's, (aqueous or soil samples) are placed in a capped vial with a septum. The sheath is pushed through the septum and by lowering the plunger the fiber is exposed and immersed into the solution in the vial. The organic compounds (analytes) in the sample are subsequently absorbed onto the fiber. After a pre-determined time (until equilibrium is established) the fiber is withdrawn into the protective sheath and pulled from the sampling vial. With minimum delay, the sheath is inserted into the injection port of a Gas Chromatograph (GC) and the plunger pushed down, to expose the fiber to conditions where the analytes are thermally desorbed (200 to 250°C) and separated on the GC column.

Desoprtion usually takes 1-5 minutes. The fiber is withdrawn into the protective sheath and the sheath removed from the GC injector. A number of sorbent polymers used in the manufacturing of fused silica GC columns, are available on SPME fibers. SPME is relatively new and is not yet approved by government regulatory agencies. The fibers and the fiber holders are commercially available from Supelco Inc. They are versatile, may be adapted to any GC, and are capable of automation. Applications include volatiles and semi-volatiles in food

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(Nilsson,1996) (Peppard, 1994) ( Page, 1993) ( Keszler, 1998), polymers (Penton, 1998), and environmental samples (Arthur 1992) (Nilsson, 1998) (Llompart, 1998). Table 2.2 summarizes the phases that are available at the present time. These phases are continuously improved, as new materials become available.

**Table 2.2: Commercially Available SPME fibers**

| Phase | Features |
|---|---|
| 100μm PDMS* | Non-polar phase with high sample capacity, suitable for a wide variety of applications. |
| 30μm PDMS* | Useful for semi-volatile compounds such as pesticides. The thinner phase allows faster desorption, thus sample carry-over is minimized. |
| 7 μm PDMS* | For semi-volatiles. Bonded fiber which allows a higher desorption temperature than the above PDMS fibers (maximum operating temperature 320°C vs 260°C for the 100μm fiber. Shorter absorption and desorption times. |
| 65um PDMS*/ Divinylbenzene | Useful for polar volatiles. |
| 85μm Polyacrylate | Greater affinity for polar compounds (recommended for phenols). This phase is more of a solid than the PDMS phase; therefore diffusion rates are slow and equilibration times are relatively long. |
| 65μm Carbowax / divinylbenzene | Polar phase with a much stronger affinity for alcohols than the PDMS fibers. |
| 65umPDMS*/ Carboxen | Trace-level volatiles. |
| 50um Carbowax/ Templated Resin | Surfactants only |

*PDMS: Polydimethylsiloxane



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### 2.7.2 Principles of SPME

Henry's Law can be applied for volatile analytes in a liquid polymer such as polydimethylsiloxane (Zhang, 1993).
According to the Henry's law (Atkins, 1982)

$$p_f = K_f C_1^{\infty}$$
$$p_s = K_s C_2^{\infty}$$

Where $p_f$ and $p_s$ are the vapour pressures of analyte which are in equilibrium with the analyte in the coating and the aqueous solution, respectively; $K_f$ and $K_s$ are Henry's constant for the analyte in the polymer coating and the aqueous solution, respectively; $C_1^{\infty}$ and $C_2^{\infty}$ are the concentration of analyte in the coating and aqueous solution, respectively.

The main principle behind SPME is the partitioning of analytes between an aqueous sample matrix and the polymeric film on the fiber. The amount of analyte absorbed by the polymeric phase is related to the overall equilibrium of analytes in the two phase system. Since the total amount of an analyte should be the same during extraction, we have

$$C_0 V_s = C_1^{\infty} V_f + C_2^{\infty} V_s \quad (1)$$

Where,

$C_0$ = Is the initial concentration of analyte in the aqueous solution.

$C_1^{\infty}$ and $C_2^{\infty}$ = Are the equilibrium concentrations of the analyte in the coating and the solution, respectively



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$V_f$ and $V_s$ = Are the volumes of the coating and the aqueous phase, respectively.

The amount of analyte absorbed by the coating (i.e. the capacity of the coating), $n = C_1^{\infty} V_f$, can be expressed as

$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + V_s} \qquad (2)$$

Where,

$n$ = the number of moles of the analyte absorbed by the stationary phase.

$K_{fs}$ = the partition coefficient of analyte between the stationary and aqueous phase.

$V_f$ and $V_s$ = the volumes of the fiber coating and the sample respectively.

$C_0$ = the initial concentration of the analyte in aqueous phase.

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Since the coatings (sorbents) used in SPME have strong affinities for organic compounds, $K_{fs}$ values for analytes are large, which means that SPME has a very high concentrating effect. This in turn leads to good sensitivity.

In many cases the $K_{fs}$ values are however not large enough to ensure exhaustive extraction of the analytes from the sample matrix.

Since the sample volume, $V_s$, is much larger than that of the polymeric fiber coating, we can assume that $V_s >> K_{fs}V_f$ Equation (2) therefore simplifies to:

$$n = K_{fs} V_f C_0 \qquad (3)$$

Equation 3 clearly indicates, that since in SPME an exhaustive extraction does not occur, but an equilibrium is developed between the aqueous and "stationary"



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organic phase, the number of moles of analyte absorbed by the fiber is linearly related to the concentration of analyte aqueous phase

The mainstay of SPME success can be ascribed to the fact that the technique combines extraction, concentration and sample introduction of organic compounds in a single step.

## 2.8 FACTORS FOR MAXIMIZING SPME

The sensitivity and effectiveness of SPME are influenced by several measures that will be discussed below (Zhang, 1993; Zhang, 1994; Zhang, 1995; Page, 1993 and Eisert, 1996).

### 2.8.1 Mixing the sample during absorption

Since SPME is an equilibrium process, the rate of extraction of analytes is directly influenced by the diffusion rate of the analyte. In a static case, transport of analyte is limited by the diffusion in both the aqueous phase and the aqueous layer at the fiber surface, thus reducing the flux into the fiber. With extensive stirring equilibrium is determined by diffusion of the analyte through the water layer that remains on the surface of the fiber (Eisert, 1996).

### 2.8.2 Extraction Matrix

Changing the composition of the liquid phase or heating the sample, organic analytes can be driven out of an aqueous phase. Heating will alter the partitioning of the analyte between the headspace and the fiber, favoring the headspace. Salts are used to drive polar compounds into the headspace and thus Kfs is therefore dependent on the ionic strength of the sample (Penton, 1997).



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### 2.8.3 Maximizing the ratio of liquid to headspace volumes in the vials

This will enhance the sensitivity of non-polar samples (low partition coefficients). The magnitude of this effect varies with the partition coefficient. For polar compounds with larger partition coefficients sensitivity will not be increased as partitioning tends to favor the aqueous phase. Equilibrium time though will not be influenced from equation (l) and (2).

### 2.8.4 Polymeric Fiber

Changing the partition coefficient between the fiber and the other phases results in the analyte being driven into the fiber. With the continuously development of new fiber phases this can be achieved by changing to a fiber phase with better affinity for the analytes.

### 2.8.5 Matrix effects

The efficiency of SPME was not influenced when being extracted from samples with elevated suspended solids of 100mg/L (Rodgers, 1998). There are no significant effects when extracting from samples that contain an excess concentration of organics. The fiber selected for a specific analysis should be selective towards the specific compound to be analised (Eisert, 1996).

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# CHAPTER 3

## OPTIMIZATION OF SPME for VOC analysis

### 3.1 Introduction

A trace is a constituent that is found in a minor concentration in another material called the "matrix". In groundwater pollution sampling, water is the matrix from which the trace quantities of pollutants are collected. During sample extraction the trace quantities of pollutants are removed from the bulk of the matrix, water, onto an adsorbent (polymeric fiber). Since the sensitivity of SPME is influenced by various factors (2.8), the analytical method has to be optimized for the compounds of interest.

### 3.2 Analytical Instrumentation

The Gas Chromatography Ion Trap Mass Spectrometer (GC- ITMS) used in this study was a Finnigan GCQ system (Finnigan MAT, San Jose, CA, USA). The GC was a Finnigan Mat GCQ (figure 3.1). The chromatograph was fitted with a 30m x 0.25mm Rtx 5MS column coated with a 0.25um film of stationary phase (Restek Corp. Bellefonte,PA, USA). The ion trap MS was tuned to perfluorotri-butylamine (PFTBA) in accordance with the Ontario Municipal of Industrial Strategy for Abatement (MISA). When tuned to PFTBA the ion trap spectrometer (ITS) also met the tuning criteria as required by the United States Environmental Protection Agency (USEPA) method 524.2 (Eichelberger, 1989).

During GC-MS analysis in the electron impact mode, the ion trap temperature was set at 200$^{o}$C, and the scan rate at 1 scan per second. The mass scan range was set between 40 and 350 m/z. The injector in the splitless mode and transfer line temperatures were 250$^{o}$C and 275$^{o}$C during the GC/MS analysis. The initial



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**Figure 3.2**
GCQ Finnagan Mat, GC/MS instrument used as the analytical tool in this study.

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column temperature was set at 35°C and then programmed at 4°C/min to 100°C, ramped 5°C/min to 170°C and finally increased at 10°C/ min to 240°C. Helium was used as the carrier gas at a linear velocity of 40cm/sec. Data was collected via a GCQ software, volume II, Data system.

For the SPME analysis a SPME holder (cat. No 5-7330), SPME fiber Assembly kits (cat. No.5-7300), SPME fiber Assortment kit (cat. No.5-7306), Inlet liners75mm ID (cat. No.2-6375,01). Thermogreen LB-2 Septa (cat. No.2-3168), SPME Sampling Stand (cat. No.5-7410) and a Corning PC-200 ceramic Stirrer/Hot plate was purchased from Supelco, Bellefonte, PA, USA). Hamilton micro syringes (1μl, 10μl, 25μl, 50μl,100μl, 250μl and 500μl) were purchased from Hewlett Packard South Africa.



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## 3.3 Experimental:

### 3.3.1 Samples

A pure volatile organic compound standard mixture (2ml, 200ppm 54 compound VOC mix in methanol) as listed in table 3.1, that contained the 10 target compounds was purchased from Supelco (cat. No. 4-7933), to establish the retention times of all these compounds). Two types of injections were employed namely a direct injection (Hamilton syringe) and a SPME injection, to optimize the run time for all the 54 compounds in the mix to elute. Neat solutions of the 10 target compounds were also purchased from Supelco, ranging from 5ml – 15ml bottles.

**Table 3.1** VOC standard mixture (conc. 200ppm in methanol)

| | | |
|---|---|---|
| Chlorobenzene # | 1,4-dichlorobenzene # | Toluene # |
| 1,2-dichloroethane # | Trichloroethylene # | 1,2-dichloropropane # |
| Tetrachloroethylene # | 1,1,1-trichloroethane # | Carbon tetrachloride # |
| Chloroform | p-xylene | 1,2-dichlorobenzene# |
| Benzene | o-xylene | Methylbenzene |
| p-isopropyltoluene | n-butylbenzene | 1,2,4-trichlorobenzene |
| Naphthalene | 1,2,3-trichlorobenzene | 1,1-dichloropropene |
| Isopropylbenzene | n-propylbenzene | 2-chloro-toluene |
| Trans-1,3-dichloropropene | Cis-1,3-dichloropropene | 1,1,2-trichloroethane |
| 1,3-dichloropropane | 1,2-dibromethane | 1,1,1,2-tetrachloroethane |
| 1,1,2,2-tetrachloroethane | 1,2,3-trichloropropane | 1,2-dibromo-3-chloropropane |
| Hexachlorobutadiene | Bromoform | 4-chloro-toluene |
| Dibromomethane | Sec-butylbenzene | Tert-butylbenzene |



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**Table 3.1** continue

| Bromochloromethane | 1,3-dichlorobenzene | 2,2-dichloropropane |
|---|---|---|
| 1,1-dichloroethane | 1,1-dichloroethylene | Methylene chloride |
| Trans-1,2-dichloroethylene | Cis-1,2-dichloroethylene | Dibromochloromethane |
| Bromodichloromethane | Ethylbenzene | m-xylene |
| Styrene | Bromobenzene | 1,3,5-trimethylbenzene |

# denotes target compounds.

Three of the target compounds (1,2-dichloroetane, toluene and 1,4-dichlorobenzene) were used in the preliminary experiments to investigate some of the factors (2.4.2-2.4.5) that can influence the sensitivity of SPME. Only those factors relevant to the target compounds were identified and optimized. First a fiber blank was run, followed by SPME of the target compounds of concentration 1ppm.

### 3.3.2 Stirring versus Static conditions

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For this investigation solutions that contain 1,2-dichloroethne and 1,4-dichlorobenzene in milli-Q water where used. Amber 4ml glass vials, closed with a polypropylene cap and a PTFE/Silicone septa were used to sample the 2 target compounds. In two of the vials a small magnetic stirrer was placed for stirring. All four vials contained 2ml sample volume. The dial on the stirrer was set at 0.5 for two of the vials that gave a stirring rate of approximately 40 revolutions per minute (RPM).

**<u>The SPME operating steps that were followed are as follows:</u>**

- The needle with the retracted fiber was passed through the vial septum.



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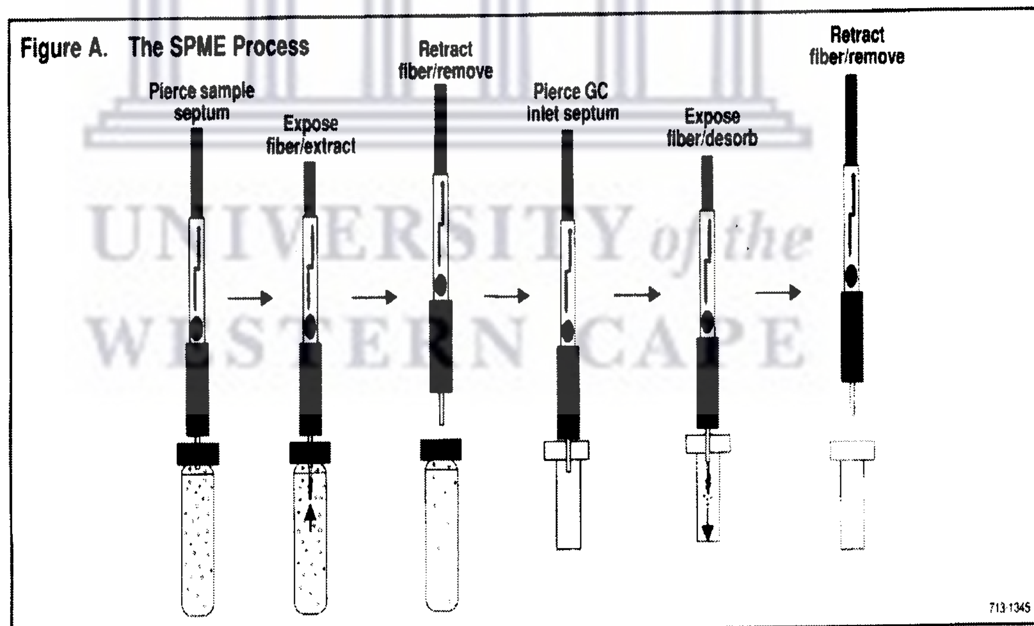
- The plunger was depressed to expose the fiber to the sample. The fiber was immersed in the liquid and the analytes absorbed to the phase on the fiber for 1,2,5, 10 and 20 minutes. For the dynamic senario (stirring) the vial was placed on a magnetic stirrer at 40 RPM.
- The fiber was retracted into the needle and removed from the sample vial.
- The needle was inserted into the GC injector port; transfer time less than 30 seconds.
- The plunger was depressed, exposing the fiber in the heated zone of the injector to desorb the analytes for 3min onto the column.
- The sample was analysed by GC/MS.
- The fiber was retracted and removed from the GC for resampling.

**Figure A** gives a schematic view of the extraction process.




### 3.3.3 Changing the Ionic Strength

For this investigation all 3 of the target compounds; 1,2-dichloroethane, toluene and 1,4- dichlorobenzene were used. Two different types of solutions that contain



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1ppm of the target compounds were made. One vial was filled with a 0.5% sodium chloride solution and the other with Milli Q water, which contained the target compounds. The same static SPME operating steps were used as in par. 3.3.2, except that the extraction time was only done for one time interval viz., 10 minutes.

### 3.3.4 Effect of extraction temperature

1,2-dichloroethane and 1,3-dichlorobenzene solutions of 1ppm were used. One of the vials was extracted at room temperature (20°C as the room had an air conditioner). A number of vials that contained only water were used to establish the setting on the heating block that could be used for the second vial to be extracted at 50°C. When this was established the second vial was SPME'd for 5 minutes with the solution temperature at 50°C ± 5.

### 3.3.5 Different Polymeric Fiber

Solutions of trichloroethylene and 1,2-dichloroethane were SPME'd for 5 minutes using a 7 and 100μm PDMS fiber. Since SPME is an equilibrium extraction method that samples only a fraction of the available compounds in the sample, it was decided to do sequential extractions from a single vial (Zhang, 1993). All the extractions were done followed by SPME steps in 3.3.2.

## 3.4 Results and Discussion

The chromatograms 1 and 2 show that if the polymeric fiber is not properly conditioned before use, traces of the epoxy used to glue the fiber to the fiber attachment needle (figure 2.7) still remains on the fiber. For this reason it was decided that for each new fiber used, three conditioning runs would be done.



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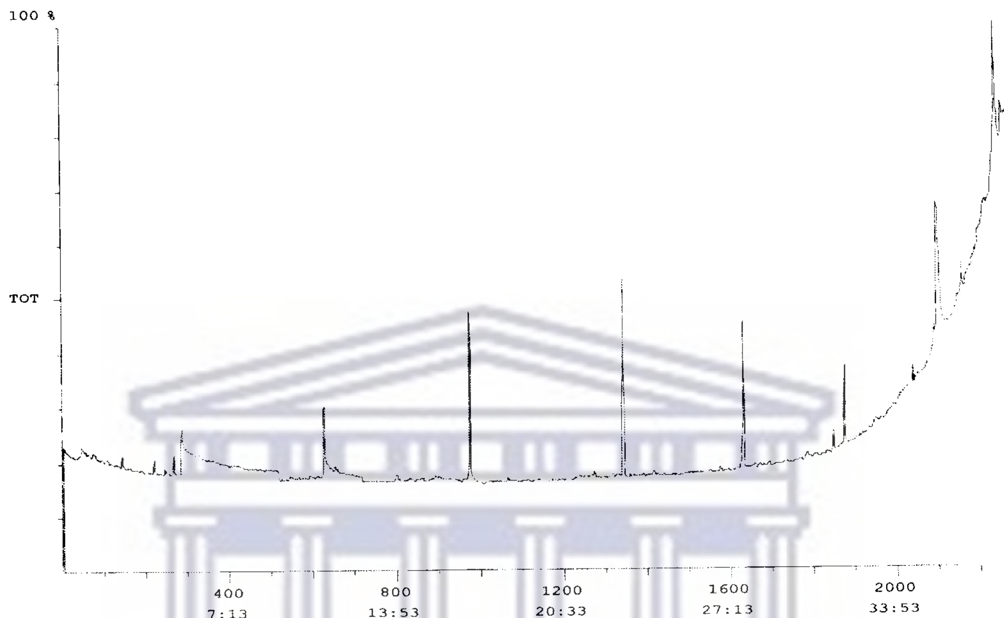
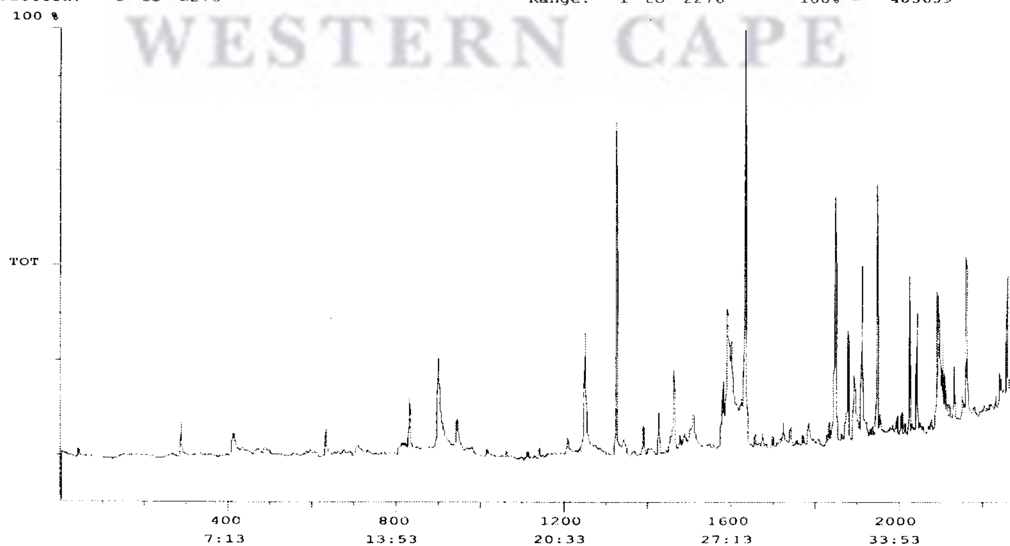
## CHROMATOGRAPH 1




The chromatograph of a newly conditioned fiber after 1hour

## CHROMATOGRAPH 2




The chromatograph of a new fiber conditioned for 2hours



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Although there were still peaks after this (chrom 3), these did not interfere as they elute long after the compounds of interest (chrom 5a) have eluted. To prevent their peak intensities from interfering the run was stopped after 18 minutes as these peaks eluted after 20 minutes even on a well conditioned fiber. Chromatograph 1 shows that very little of the epoxy has been removed from the fiber. The peaks from the glue used to attach the fiber to the steel rod are still evident in chromatograph 2. Although the peak intensities have shifted to the right, some of the smaller peaks at between 6 and 15 minutes may still interfere when low concentrations are to be detected. The peaks appearing at a retention time of approximately 27.5 minutes (chrom 2) is proof of this.

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## CHROMATOGRAPH 3

**The chromatograph of a well conditioned fiber**



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The "hot spot"(warmest part) in the injector port was established by trial and error to see at what length the adjustable needle gauge on the SPME holder could be set. This controls the depth of the fiber in the injection port. A setting of 4 on the gauge was used as this could also be used as the setting when extracting from the 4 ml vials. Although this condition was not optimal, this setting was retained since a setting of 3.5 caused the fiber in the injection port to break off on occasion.

The chromatographs 4 and 5b obtained for the two different injection techniques shows the advantages of SPME, over that of the classical injection method. The initial SPME of the 54 compound mixture, showed a much cleaner chromatograph in comparison to the direct syringe injection. The solvent peak is very evident on the direct injection (chrom. 4), while the SPME chromatograph shows a very clean extract (chrom. 5a and 5b). We could not overcome the interference from the solvent, even by switching the filament on at a later stage (that is the time when the MS start recording). Of the 54 compounds that were SPME'd, 47 were positively identified, by the instrument in the peak search mode. Positive identification of the compounds were made by making use of the MS library with the instrument. The library used in this instance was the Wiley library of spectra, which contains the spectrum of over 100,000 compounds.

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For the direct injection technique, compound identification was very difficult since many of the peaks co-eluted and overlapped. Although we could identify most of the compounds by means of the instrument library, this will be very difficult if only GC were to be used. Even by knowing the retention times, positive identification would still be difficult as the degree of overlapping will make identification a tedious task. To obtain a better chromatograph, a different temperature program as for that for the SPME'd chromatograph had to run. This was not investigated. Further optimization of the temperature program for the SPME protocol was not done as the 10 target compounds eluted within 15 minuteand the peaks of interest were well resolved. The identified peaks are listed in table 3.2 (page 37).



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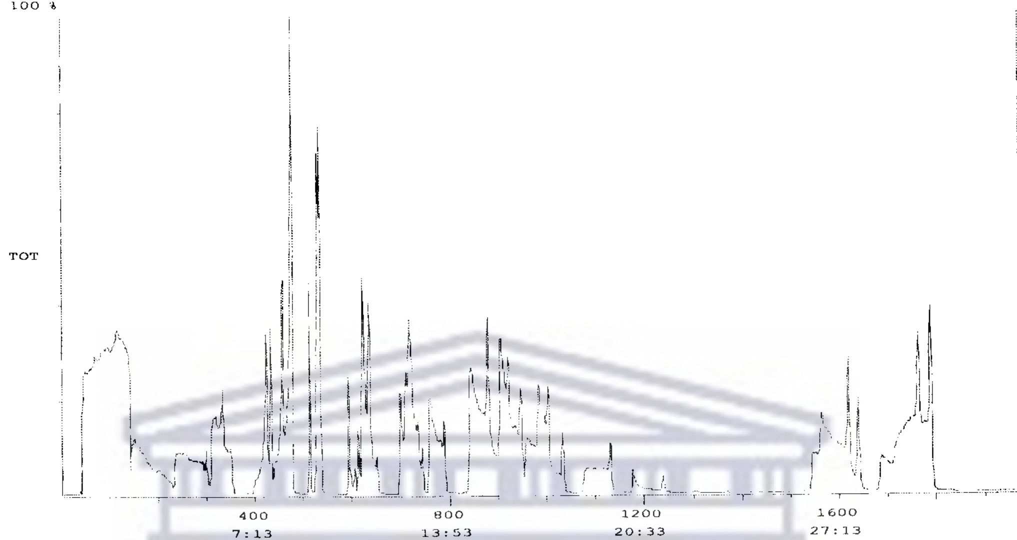
## CHROMATOGRAPH 4




**Chromatograph of a 54 compound mixture by 0.2µl direct injection: (solvent peak very much evident at the start of the chromatograph). The peaks are not clearly separated.**

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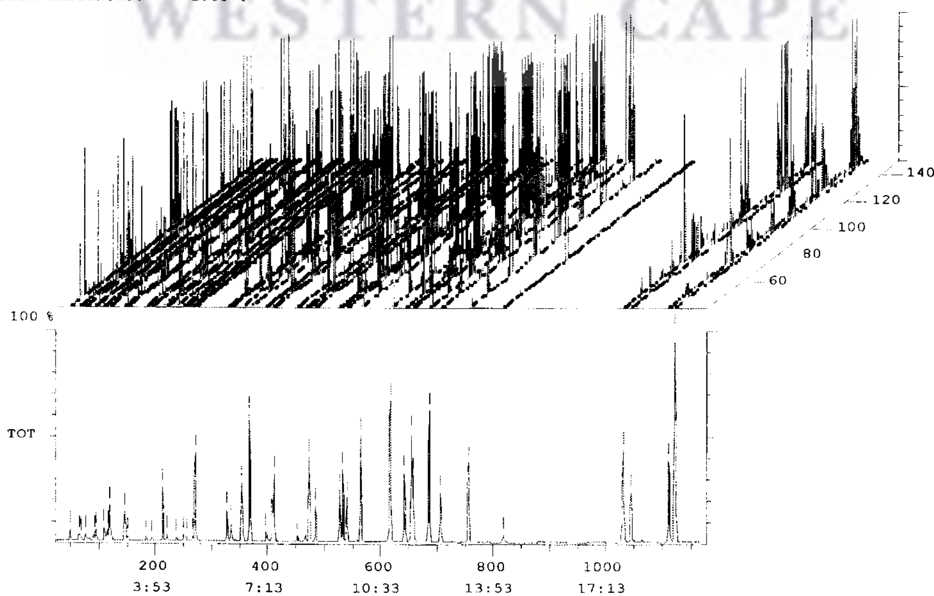
## CHROMATOGRAPH 5a



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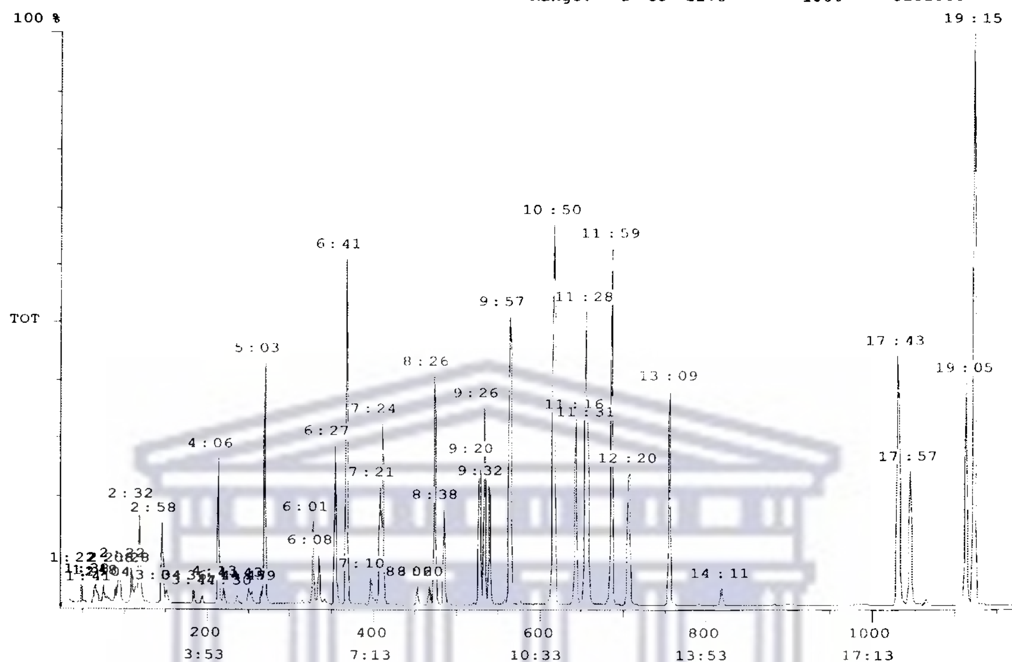
## CHROMATOGRAPH 5b




**Chromatograph of a 54 compound mixture SPME'd**

**Table 3.2:** Depicting the retention times of the compounds that could be identified from chromatograph 5b, obtained by the SPME method of injection.

| RETENTION TIMES (min.) | COMPOUNDS (as identified by Mass Spec.) |
|---|---|
| 1.38 | *Trans* 1,2 dichloroethene |
| 1.41 | Methylene chloride |
| 1.48 | *Cis*-1,2-dichloroethene |
| 1.53 | 1,1-dichloroethene |
| 2.07 | 2,2-dichloropropane |
| 2.21 | 1,1,1-trichloroethane |
| 2.28 | *Trans*-1,3-dichloropropane |
| 2.32 | Carbon Tetrachloride |
| 2.58 | Trichloroethylene |

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**Table 3.2** continue

| | |
|---|---|
| 3.04 | 1,1,2,2-tetrachloroethane |
| 3.36 | Cis-1,3-dichloropropane |
| 3.47 | 1,2-dichloropropane |
| 4.05 | Toluene |
| 4.14 | 1,1,2-trichloroethane |
| 4.30 | 1,3-Dichloropropane |
| 4.43 | dibromochloromethane |
| 5.03 | 1,1,1,2-tetrachloroethane |
| 6.01 | *Trans*-1,2-dichloroethylene |
| 6.08 | Tetrachloroethylene |
| 6.27 | Ethylbenzene |
| 6.41 | *p*-Xylene |
| 7.10 | Bromoform |
| 7.21 | Styrene |
| 7.24 | Chlorobenzene |
| 8.27 | *o*-xylene |
| 8.37 | Bromobenzene |
| 9.21 | 2-Chlorotoluene |
| 9.26 | Propylbenzene |
| 9.32 | 4-Chlorotoluene |
| 9.57 | Isopropylbenzene |
| 10.50 | Tert-butylbenzene |
| 11.15 | 1,4-Dichlorobenzene |
| 11.28 | Secbutylbenzene |
| 11.59 | p-isopropyltoluene |
| 12.20 | 1,2-Dichlorobenzene |
| 13.08 | n-butylbenzene |
| 17.44 | 1,2,3-trichlorobenzene |
| 17.59 | Naphthalene |
| 19.05 | 1,2,4-trichlorobenzene |
| 19.16 | hexachlorobutadiene |

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### 3.4.1 Stirring versus static conditions

| Time (min) | 1,2-dichloroethane (Static) | 1,2-dichloroethane Dynamic | 1,4-Dichlorobenzene (static) | 1,4-Dichlorobenzene (dynamic) |
|---|---|---|---|---|
| 1 | 551486 | 578560 | 948965 | 974993 |
| 2 | 751034 | 755140 | 986703 | 998503 |
| 5 | 754103 | 754667 | 1051024 | 1079956 |
| 10 | 753868 | 754023 | 1075521 | 1084515 |
| 20 | 752856 | 753106 | 1068414 | 1081531 |

**Table 3.3:** Peak areas of 1,2-dichloroethane and 1.4-dichlorobenzene obtained for static and dynamic extraction conditions

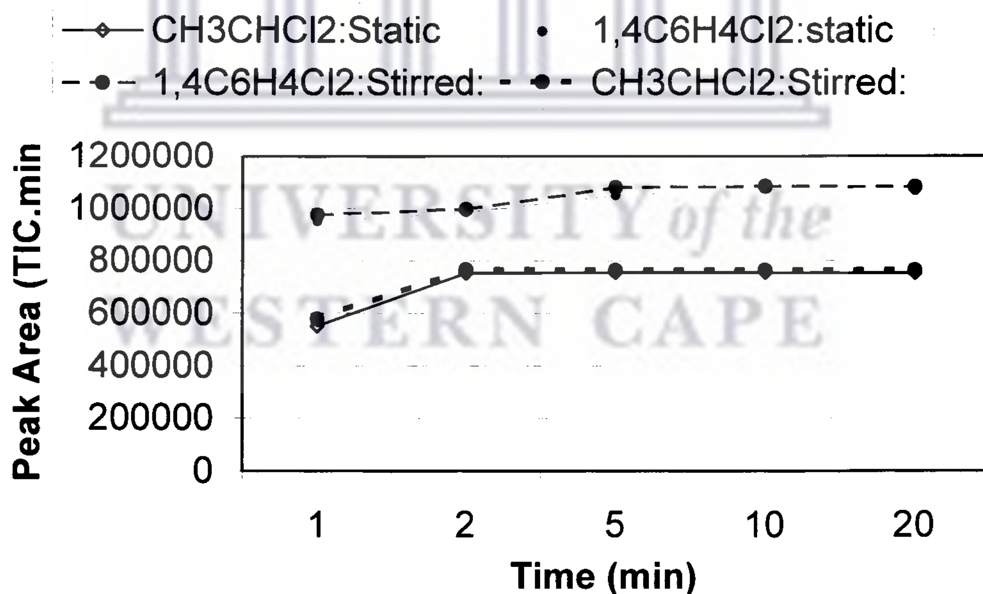


**Figure 3.2**; Time dependence for equilibrium of 1,2-dichloroethane and 1,4-dichloro benzene between the aqueous and the polydimethylsiloxane phase. Two exposure time profiles are shown: one with intensive stirring of the aqueous sample and the other without mixing.



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From figure 3.2 it is noticed that there is an effective increase in the response of one of the compounds. From the graph it can be observed that for 1,2-dichloroethane, a volatile compound with a high diffusion rate, equilibrium and maximum response was achieved in less than 2 min, regardless of whether the sample was mixed or not. With 1,4-dichlorobenzene, a less volatile compound than 1,2-dichloroethane the response was enhanced by approximately 5% after 5 min of mixing. The response though reaches a maximum after 10 min. as can be observed from the graph. It was thus decided from the data obtained from the graph (figure3.2), that all future SPME extractions would be done using the static conditions, since the water-fiber distribution coefficient ($K_{fw}$) for the compounds of interest is between 60 and 930 (Nilsson, 1995) and with that of 1,4-dichlorobenzene being the largest.

### 3.4.2 Changing the Ionic Strength

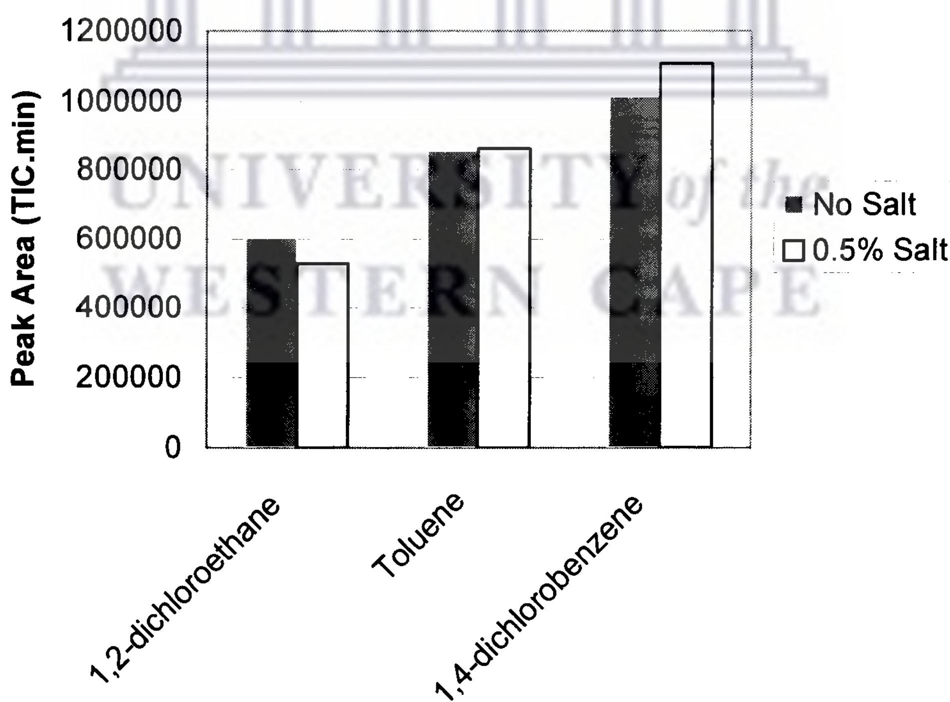


**Figure 3.3** Showing the effect of adding salt to volatiles in water. The more denser compounds will tend to be driven from solution into the headspace.



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Graph (figure 3.3) indicates that adding sodium chloride to volatiles in water can have a negative effect on compounds with very low distribution coefficients as indicated by 1,2-dichloroethane. The addition of salt drives the organic compound into the headspace which in turn can lead to lower sensitivity of this compound. Toluene show no significant increase in peak area, while that of 1,4-dichlorobenzene shows an increase of 10%. This may be attributed to the fact that 1,4-dichlorobenzene that is heavier compound (more dens) than 1,2-dichloroethane, has a larger distribution coefficient (930) and the addition of salt will tend to drive the compound out of solution and into the fiber. There is thus an increase in the rate of diffusion of 1,4-dichlorobenzene. The fact that the addition of salt has a negative effect on 1,2-dichloroethane, leads to the assumption that salt additions will also have a negative effect on some of the other more volatile compounds as well, lead to the decision that the addition of salt will not be employed. This ties in with results obtained in previous studies (Eisert, 1996)

### 3.4.3 Effect of Extraction Temperature

As with the case of (fig.3.4) it was noticed that an increase in temperature leads to a decrease in the measurement of very volatile compounds see fig.3.4. The higher temperature on the other hand enhances the peak area of 1,4-dichlorobenzene by more than 25%. It is evident from fig.3.2 that very short equilibration times are necessary when the sample will be heated. The extraction temperature does have a very direct influence on diffusion and partitioning of the compounds. It was noticed from the literature (Nilsson, 1995), that the distribution coefficient ($K_{fw}$) of 1,2-dichloroethane decreases with a temperature increase thus lowering the amount absorbed onto the fiber. If the concentration of this compound in an environmental sample is very low it will be less likely to be detected if the sample is heated. Heating the sample will reduce the equilibration times but, due to the fact that the adsorption process is exothermic, the sensitivity will decrease, i.e. the fiber coating/water distribution coefficients will decrease. Room temperature extraction will thus give more consistent results. As with many compounds, the



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characteristics of the compound will also be changed by heating and multiple extraction from a single vial will thus not be possible when there is a sample shortage.

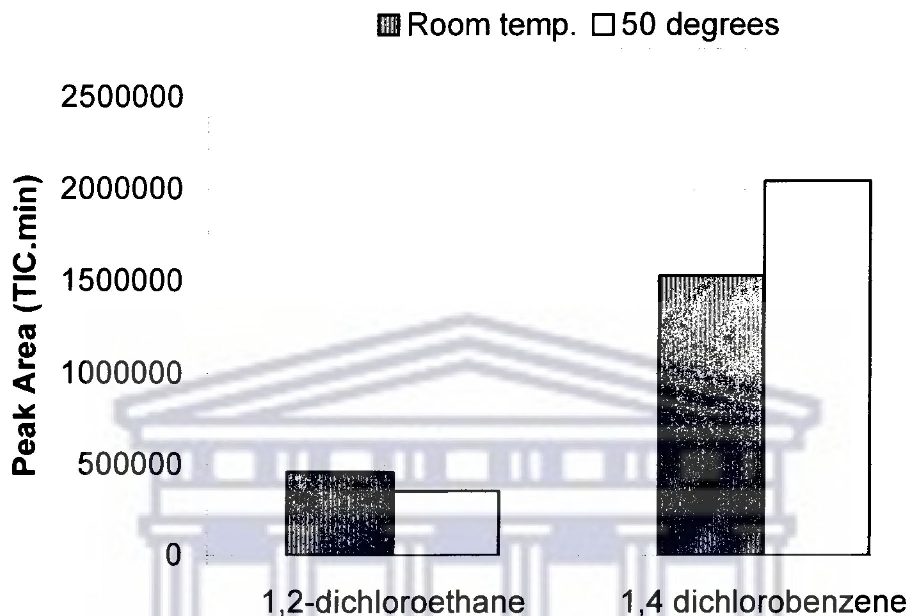


**Figure.3.4**: Peak areas for 1,2-dichloroethane and 1,4dichlorobenzene at room temperature and at 50°C

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### 3.4.4 Different Polymeric fibers

From equation 1 (par 2.7.2, p 20), the amount of analyte extracted by the fiber coating is directly proportional to the volume of the coating. The sensitivity of the extraction method can thus be improved by increasing the coating volume (by increasing the thickness of the coating, the length of the fiber, or both). As the 100µm PDMS polymeric fibers were giving larger TIC peak areas than the 7µm, it was decided to only use the former as the fiber of choice in this study.



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**Table 3.4:** Peak ratios for direct extractions, using different fiber coating diameter (thickness)

| Compound | 7µm/100µm PDMS fiber |
|---|---|
| 1,2-dichloroethane | 0.82 |
| Trichloroethylene | 0.73 |

.

**REFERENCES**


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Nilsson T., Pelusio F., Montanarella L., Larsen B., Facchetti S. and Madsen J.O. (1995) An Evaluation of Solid-Phase Microextraction for Analysis of Volatile Organic Compounds in Drinking Water. *J. High Resol. Chromatogr.* **18** p.617-624.

Zhang Z. and Pawliszyn J. (1993) Headspace Solid-Phase Microextraction *Anal. Chem.* **65** p. 1843-1852.


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# CHAPTER 4

## Method Validation of SPME

### 4.1 Introduction

In chapter 3 the optimal conditions for SPME were established. Next it was necessary to look at the quantitative efficiency of SPME before any real environmental sample could be collected and analysed. The method thus had to be validated in order to determine if standard samples could quantitatively be absorbed and desorbed from the fibers, a prerequisite for accurate quantitation of organic pollution samples in chromatographic methods (Paul, W.L., 1991, Hewlett Packard product note, 1993). The validity is ensured when the methods measure what and only what they purport to measure.

### 4.2 What is Method Validation

Validation is the process of evaluation of products or analytical methods to ensure compliance with product or method requirements. Validation is thus defined as documental evidence that a system performs as expected. The most frequently validation criteria are:

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- Selectivity (specificity)
- Precision
- Accuracy
- Linearity
- Range
- Limit of Detection
- Limit of quantification
- Ruggedness
- Stability



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### 4.2.1 Selectivity (specificity)

The terms selectivity and specificity are often used interchangeably. The term specific however refers to a method, which produces a response for only a single analyte. (Massart, D.L. et al 1988). The term selective refers to a method that provides responses for a number of chemical entities that may or may not be distinguished. The selectivity of an analytical method can thus be defined as its ability to measure accurately an analyte in the presence of interferences that may be expected to be present in the sample matrix. (VS Pharmacopeial convention, 1990).

### 4.2.2 Precision

Precision of a method is measured by injecting a series of standards. The measured standard deviation can be subdivided into two categories, viz., repeatability and reproducibility. Repeatability is obtained if the analysis is carried out in one laboratory by one operator, using one piece of equipment over a relatively short time span. Reproducibility is defined as long-term variability of the measurement process that may be determined for a method run within a single laboratory but on different days. Precision in retention times and peak area is a major criterion of a separation system (The United States Pharmacopeial convention, 1990).

### 4.2.3 Accuracy

The accuracy of an analytical method is the degree of agreement of test results generated by the method to the true value (Karnes, 1991). This can be established using external, internal or standard addition protocols.



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### 4.2.4 Linearity

The linearity of an analytical method is its ability to elicit test results that are directly, or by means of well-defined mathematical transformations, proportional to the concentration of analytes in samples within a given range (Shaw,1991).

### 4.2.5 Range

The range of an analytical method is the interval between the upper and lower levels (including these levels) that have been demonstrated to be determined with precision, accuracy and linearity using the method as written (Wilson, 1990).

### 4.2.6 Limit of detection and quantitation.

The limit of detection is the point at which a measured value is larger than the uncertainty associated with it (Conacher, 1990). In other words the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is larger than zero and is determined from analysis of a sample in a given matrix containing the analyte. The limit of quantification is the injected amount that results in a reproducible measurement of peak areas (equivalent to amounts).

### 4.2.7 Stability

The fact that certain components have been quantitatively introduced is no guarantee that they will be present or remain in that proportion in a mixture. Many solutes readily decompose prior to chromatographic investigations. Under these circumstances, method development should investigate the stability of the analytes (Szepesi, 1989).



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### 4.2.8 Ruggedness

Ruggedness text, examines the effect operational and environmental conditions have on the analysis results. It is the degree of variance in test results obtained by the analysis of the same samples under a variety of difference test conditions (Good Laboratory Practice, 1993). Ruggedness is affected by a number of factors namely;

- Different room temperature and humidity in separate labs.
- Analysts with different experience.
- Instruments from various vendors.
- Reagents from different suppliers.
- Columns from different batches.

## 4.3 Analytical Instrumentation

All GC-MS analyses of standard samples were performed on the Finnigan GCQ system (figure 3.2) using the same parameter settings as described in paragraph 3.2, page 18. System suitability tests were performed periodically to determine the adequacy or effectiveness of the instrument.

Based on tune gas report results, action was taken either to clean the MS lenses or recalibrate the instrument with the tuning gas. The calibration gas perfluorotributylamine (molecular mass 671) with m/e fragmentations 69, 100, 131, 264, 414, 464, 502, and 602 were used in this instance. Instrument tuning as prescribe in the maintenance manual were performed when the fragmentation ion intensity for the m/e 131 peak were less than 99.5% and the shoulder peaks to the right of all the peak shown in figure 4.1 were of any significant height.



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**Figure 4.1:** A typical tune report

GCQ Tune Report    Source: EI    Tue Sep 11 18:47:48 2001
Instrument: 200536    Operator: GCQ

m/z 69    m/z 131    m/z 264    m/z 414    m/z 502

| Theory | Actual | Intensity | % Base Pk |
|---|---|---|---|
| 69.0 | 69.0 | 325260 | 25.7 |
| 131.0 | 131.1 | 1264428 | 100.0 |
| 264.0 | 263.9 | 769311 | 60.8 |
| 414.0 | 414.0 | 191049 | 15.1 |
| 502.0 | 501.9 | 102817 | 8.1 |
| 614.0 | 614.0 | 6556 | 0.5 |

**Calibration Parameters**

| | |
|---|---|
| Multiplier Volts | = 1250 |
| Multiplier Gain | = Unknown |
| Mass Slope | = 63.56 |
| Mass Intercept | = 193.34 |
| Resej Slope | = 0.0186 |
| Resej Intercept | = 1.41 |
| Waveform Cal | = 0.07, 70.64, 21.59, -24.00 |

**Automatic Tune**

| | |
|---|---|
| Multiplier Gain: | Not Run |
| Lens Tune: | Passed |
| Resej Amp: | Passed |
| Mass Calibration: | Passed |
| Waveform Cal: | Passed |

**Tune file: autotune2**

| | |
|---|---|
| Lens 1 | = -26.90 |
| Lens 3 | = -24.33 |
| Gate Lens On | = -104.40 |
| Gate Lens Off | = 100.00 |
| Elec Lens On | = 15.00 |
| Elec Lens Off | = 65.00 |
| EE On | = -70.00 |
| EE Off | = -20.00 |
| Trap Offset | = -10.00 |
| Emission Curr | = 250.00 |

| | |
|---|---|
| High Mass Adjust | = 50 % |
| AGC Target | = 50 |
| Injection Wf | = Off |

No Environmental Tuning Factors

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The impurities deposited on the lenses were in many instances the reason for the instrument requiring maintenance. A target value of -30 for lenses 1 and 3 indicated that the MS required cleaning. After cleaning, this value normally came down to –20 and went up to –30 as analyses were performed with the instrument.



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## 4.4 Experimental

### 4.4.1 Preparation of standard samples

A 1000 ppm (v/v) stock solution of all 10 target compounds listed in table 3.1 was made up in methanol. The stock solutions were used to make any further standard solutions by diluting the exact amount of stock solution with de-ionized water from a Milli Q system.

### 4.4.2 Conditioning of Polymeric fiber

Before the polymeric fibers could be used in analyses they had to be conditioned to ensure minimal decomposition by products being observed in the chromatograph. The polymeric fiber was conditioned at 250°C for approximately 3 hours. The blank fiber was then injected (blank run), using the same temperature program to be used for the analysis of the standard samples.

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### 4.4.3 Determination of distribution constants

The determination of the distribution coefficients (K values) was attempted for the target compounds, in order to compare them in the literature. This was established by performing two different types of injections. A compound mixture (1ppm) of all ten compounds in methanol was made up. Of this solution 0.2µl in a Hamilton syringe was used, and the peak area obtained was recorded. For SPME 2ml of the compound mixture was placed in a 4ml vial and the sample was SPME'd for 15minutes and injected into the GC, the peak areas for each of the compounds were calculated and recorded. Knowing the amount of sample injected (i.e. 0.2µl for the direct injection), one could calculate the concentration of the injected amount of compound that produced the peak area. The amount of analyte absorbed onto the fiber at equilibrium could be calculated by making use of cross



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multiplication. The following formula (equation 3, p 21) was then used to calculate the distribution coefficient of all the target compounds, since there is a linear relationship between the number of moles and the concentration of analyte at equilibrium

Number of moles absorbed $\propto$ concentration of analyte

$$n = K_{fs} V_f C_0 \tag{3}$$

$K_{fs}$ = distribution coefficient

$V_f$ = Volume of the coating

$C_0$ = Initial concentration

So if known, the concentration of the analyte, the volume of the coating around the fiber ($6.91*10^{-7}$ litres, as reported by the fiber manufacturer for the 100μm fiber) and the mass absorbed onto the fiber, one can calculate K the distribution coefficient.

Table 4.1 shows the results obtained for all the target compounds.

**Table 4.1**: Comparation of distribution coefficients determined experimentally

| Compound | Distribution Coefficients | | |
|---|---|---|---|
| | **Found @ 20°C** | **Nilsson et al.** | **Eisert et al.** |
| 1,2-dichloroethane | 65 | - | 93 |
| 1,2-dichloropropane | 110 | - | 191 |
| Trichloroethylene | 312 | - | - |
| Tetrachloroethylene | 998 | 912 | - |
| Toluene | 619 | 930 | 759 |
| Carbon tetrachloride | 704 | 631 | - |
| 1,1,1-trichloroethane | 168 | 316 | 151 |
| Chlorobenzene | 405 | 417 | - |
| 1,2-dichlorobenzene | 915 | 812 | - |
| 1,4-dichlorobenzene | 930 | 933 | - |



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The values obtained for the distribution constants in table 4.1 compared well with those obtained by Nilsson et al. (Nilsson et al. 1995) and Eisert and Levsen (Eisert et al. 1996). Apart from 111-trichloroethane which is the 3rd most volatile compound ( 47% difference for Nilsson and 11% for Eisert) the distribution constants of all the other values are within ten percent of those reported. The values obtained for 1,2-dichloroethane, 1,2-dichloropropane and toluene had differences of more than ten percent. Although the values for 1,2-dichloropropane and 1,2-dichloroethane are lower than those published in the literature, this may be explained in terms of the volatility of these two compounds (see table 4.1.1). Values obtained for toluene was difficult to reconcile (table 4.1.). A possible reason for this may be the different extraction temperatures employed for the determination of these parameters. According to the literature references the measurements were done at 40, 60 and 80°C.

**Table 4.2:** Differences in distribution constants for three of the target compounds.

| **Compound** | **Found @ 20°C** | **Literature** | **% Difference** |
|---|---|---|---|
| 1,2-dichloroethane | 65 | 93 | 30 |
| 1,2-dichloropropane | 110 | 191 | 42 |
| Toluene | 619 | 930 | 67 |

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### 4.4.4 Establishing sample equilibrium times

Four working solutions of each of the 10 target compounds was prepared by adding 2µl of a 100ppm (v/v) solution from each of the ten compounds into a 4ml amber glass vial that contained 1998µl of de-ionized water to give a final concentration of 0.1ppm (v/v). The 100ppm (v/v) was prepared from the 1000 ppm (v/v) stock solution. Each of the vials of the 10 compounds were SPME'd for 5, 10, 20 and 40 minutes to establish if there would be any increase in the amount of organic material extracted by the fiber with time. This was done by exposing the fiber for the four different time intervals followed by GC analyses of the



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different compounds. Since SPME is an equilibrium extraction method (equation 3) which samples only a fraction of the available compound concentration in the sample, as opposed to exhaustive methods (i.e. liquid-liquid extraction, Purge and trap, SPE), sequential extractions from a single vial were also performed on two of the target compounds. This was done in order to establish whether it would be possible when samples were available in limited amounts.

#### 4.4.4.1: Results and Discussion

The peak areas (TIC.min) for the ten target compounds are summarized in Table 4.3 (a), (b) and (c).

**Table 4.2(a):** Equilibrium time investigation

| Time (min) | Peak area Toluene | Peak area Chlorobenzene | Peak area Trichloroethylene | Peak area Tetrachloroethylene |
|---|---|---|---|---|
| 5 | 3020058 | 6005605 | 1950800 | 1328000 |
| 10 | 4705350 | 9388452 | 3100400 | 1500106 |
| 20 | 4693000 | 9350041 | 3000125 | 1497500 |
| 40 | 4590010 | 9288995 | 2950600 | 1450085 |

**Table 4.2(b):** Equilibrium time investigation

| Time (min) | Peak area Carbon Tetrachloride | Peak area 1,2-dichloropropane | Peak area 1,2-dichloroethane |
|---|---|---|---|
| 5 | 256001 | 2215470 | 126000 |
| 10 | 326100 | 3269200 | 142004 |
| 20 | 323000 | 3198009 | 138505 |
| 40 | 298500 | 2980060 | 135450 |



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**Table 4.2(c):** Equilibrium time investigation

| **Time (min)** | **Peak area 1,2-dichlorobenzene** | **Peak area 1,4-dichlorobenzene** | **Peak area 1,1,1-trichloroethane** |
|---|---|---|---|
| 5 | 2145608 | 1378625 | 285905 |
| 10 | 3286500 | 1595004 | 357249 |
| 20 | 3200452 | 1597008 | 360004 |
| 40 | 2900238 | 1564420 | 3525550 |

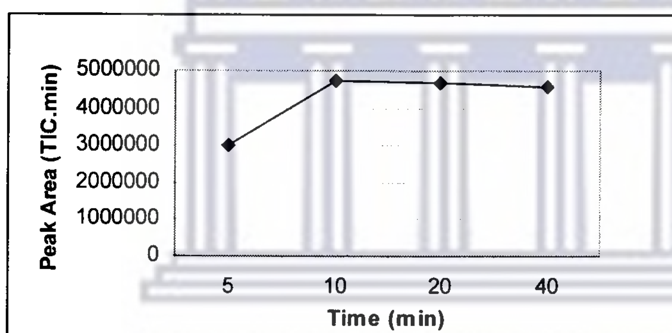


**Figure 4.1:** Time profile of the mass of toluene absorbed by the fiber coating

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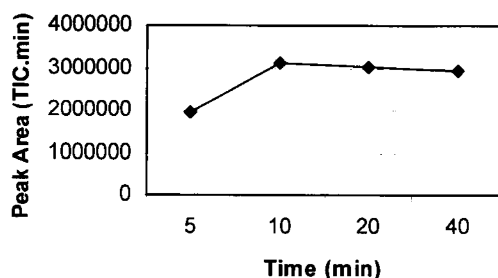


**Figure 4.2:** Time profile of the mass of trichloroethylene absorbed by the fiber coating



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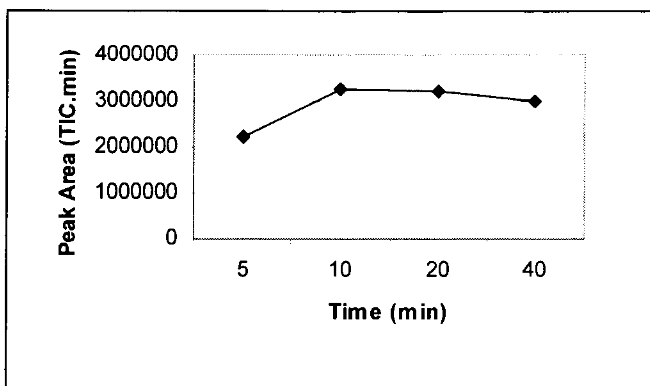


**Figure 4.3:** Time profile of the mass of 1,2-dichloropropane absorbed by the fiber coating

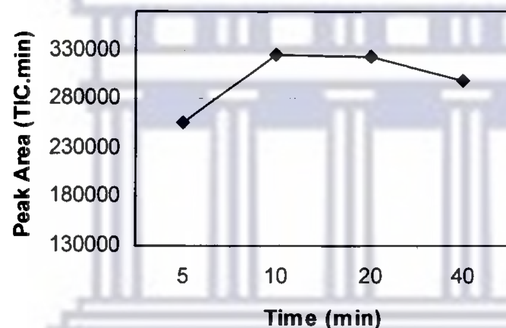


**Figure 4.4:** Time profile of the mass of carbon tetrachloride absorbed by the fiber coating

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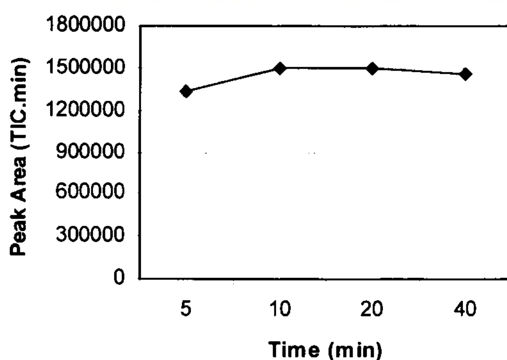


**Figure 4.5:** Time profile of the mass of tetrachloroethylene absorbed by the fiber coating



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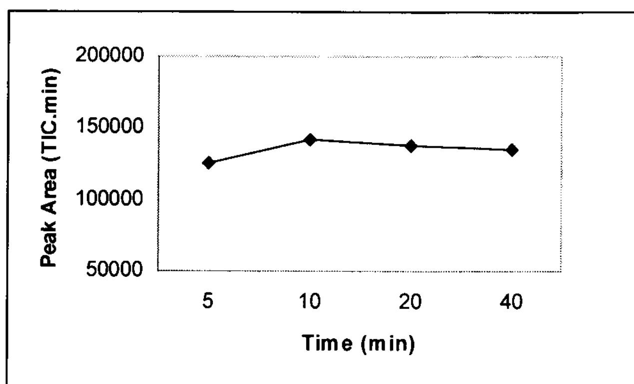


**Figure 4.6:** Time profile of the mass of 1,2-dichloroethane absorbed by the fiber coating

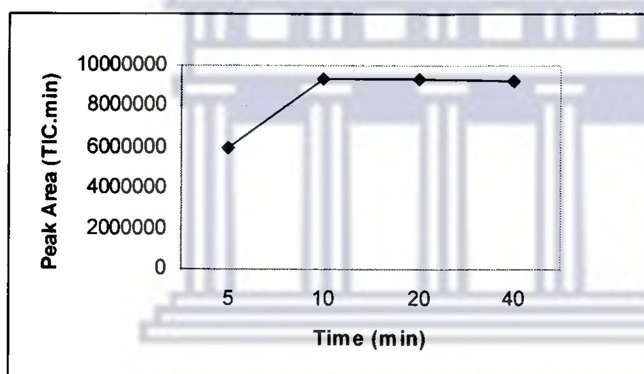


**Figure 4.7:** Time profile of the mass of chlorobenzene absorbed by the fiber coating

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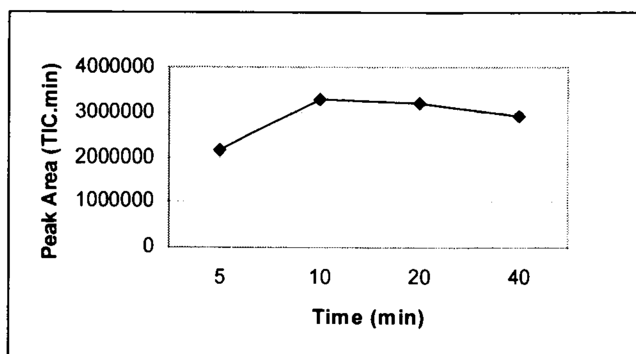


**Figure 4.8:** Time profile of the mass of 1,2-dichlorobenzene absorbed by the fiber coating



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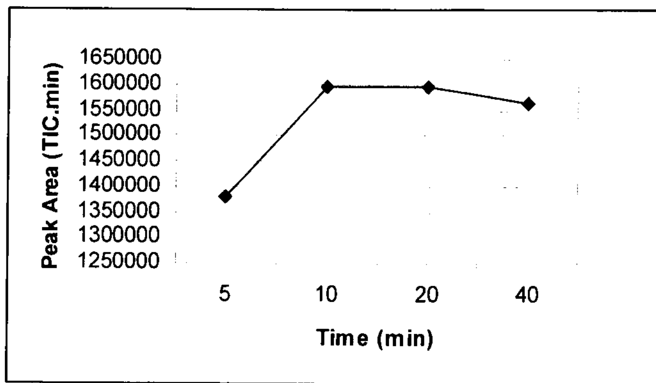


**Figure 4.9:** Time profile of the mass of 1,4-dichlorobenzene absorbed by the fiber coating

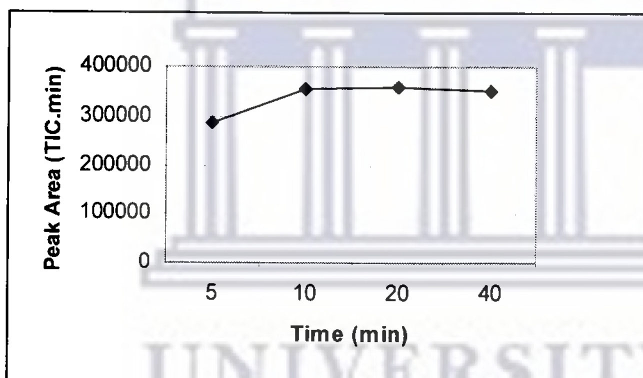


**Figure 4.10:** Time profile of the mass of 1,1,1-trichloroethane absorbed by the fiber coating

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From the time profile graphs it is clear that initially there was a steep increase in the mass of organic material absorbed. After 10 minutes the graphs started to level off. Equilibrium was also reached quicker for compounds with lower K-values. From the graph for 1,2-dichlorobenzene and 1,4-dichlorobenzene there was an increase of 40 percent in the amount of organic material absorbed onto the fiber between time intervals 5 and 10 minutes. The diffusion of the analyte through the water layer around the fiber coating was thus much slower than that of the low K-value compounds. As the fiber was exposed for a longer period of time desorption



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of the organic material started to take place (although from p23 no significant effect when extracting from samples with an excess concentration of organics, the fiber have a greater affinity for the compounds under discussion, table 2.2). This is very much in evidence in the graphs of the compounds with very high K-values. The sharp rate of desorption shown by some of the compounds gave an indication that there are no more available sites on the fiber for adsorption to take place. From the literature it was shown (Wei, 1997) that when salt was used to enhance extraction of the organic compound, in fact a decrease in extraction efficiency became more evident beyond the equilibrium time of the specific compounds. When salt was added, the lower extraction efficiency was attributed to the degradation of the specific compound in saturated saline solutions. The extraction conditions employed in this study was therefore standardized to 15 minutes of exposure time.

### 4.4.5 Equilibration times of Compound Mixture

To see if there would be any interaction between the 10 target compounds for available sites on the fiber, 20 µl of a 100 ppm (v/v) of each of the 10 compounds was added to 1800 µl of de-ionized water to provide a final concentration of 1 ppm (v/v) of the 10 compound mixture. This was repeated to provide 4 vials of the identical concentration. The 4 vials were also SPME'd 5, 10, 20 and 40 minutes respectively and analysed. The results are listed in table 4.4 (a), (b) and (c)

**Table 4.4(a):** Compound mixture equilibrium time investigation

| **Time (min)** | **Peak area Toluene** | **Peak area Chlorobenzene** | **Peak area Trichloroethylene** | **Peak area Tetrachloroethylene** |
|---|---|---|---|---|
| 5 | 2790500 | 6315040 | 2530050 | 1407301 |
| 10 | 4290805 | 10040090 | 3598305 | 1523640 |
| 20 | 4340058 | 10160095 | 3468451 | 1519480 |
| 40 | 4120095 | 9475045 | 3175841 | 1481709 |



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Table 4.4(b): Compound mixture equilibrium time investigation

| Time (min) | Peak area Carbon Tetrachloride | Peak area 1,2-dichloropropane | Peak area 1,2-dichloroethane |
|---|---|---|---|
| 5 | 703540 | 349634 | 139000 |
| 10 | 74915 | 394704 | 146004 |
| 20 | 760099 | 395000 | 146100 |
| 40 | 751998 | 386580 | 145505 |

Table 4.4(c): Compound mixture equilibrium time investigation

| Time (min) | Peak area 1,2-dichlorobenzene | Peak area 1,4-dichlorobenzene | Peak area 1,1,1-trichloroethane |
|---|---|---|---|
| 5 | 5890005 | 3974138 | 507505 |
| 10 | 8960500 | 5814005 | 583051 |
| 20 | 8961005 | 5839045 | 583900 |
| 40 | 8384400 | 5684055 | 564054 |

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The trend followed by the single compounds and that of the compound mixture are very similar. None of the compounds was thus negatively influenced by the greater affinity of the fiber some of the compounds. The fiber has a greater affinity towards those compounds that produced higher peak areas. This was established by SPME 0.1ppm single compound solutions and looking at the peak areas obtained for each of the compounds under discussion. The peak areas were lower for the most volatile compounds.



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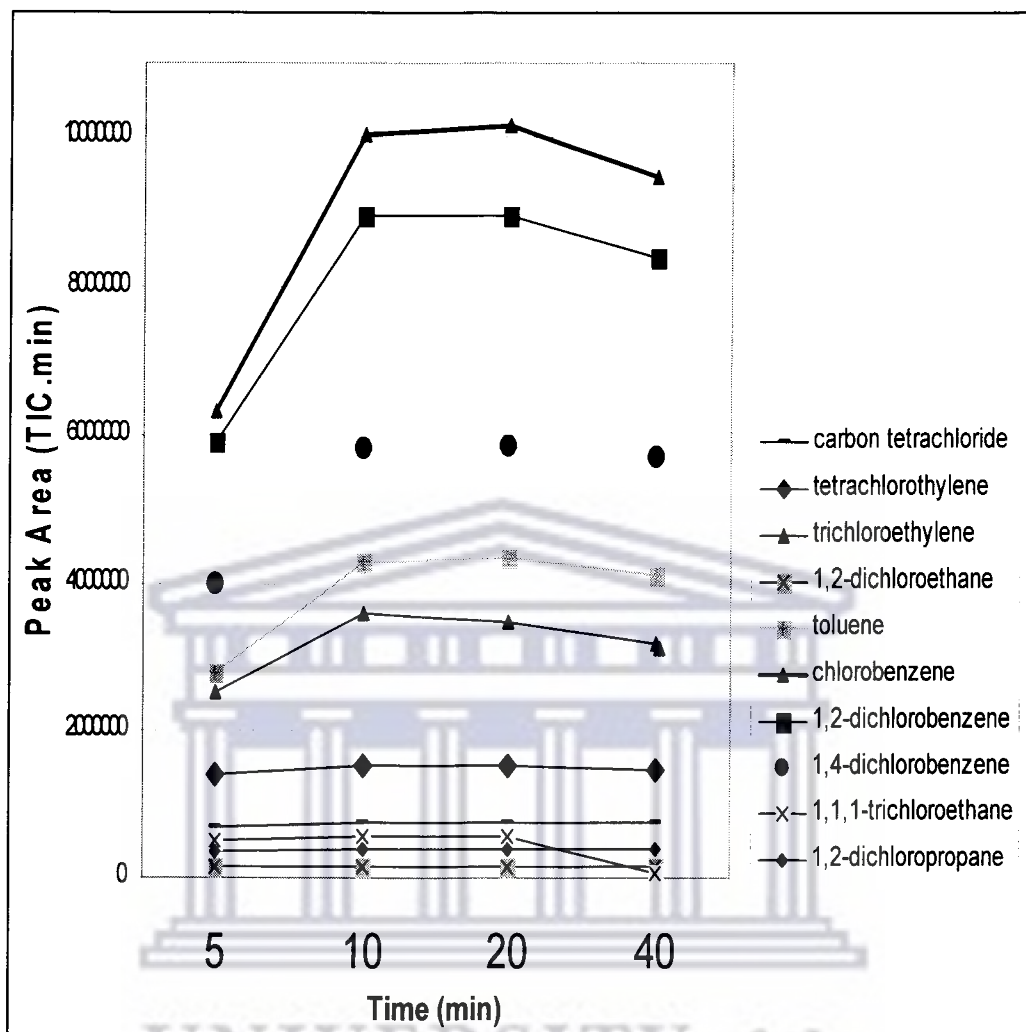


**Figure 4.11**: Time profiles of the mass absorbed of each of the ten target compounds.

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### 4.4.6 Reproducibility and Precision of SPME

To check the reproducibility of SPME, 6 compound mixtures of 1.25ppm were injected. The peak areas for each run (n=6) were recorded and the mean, standard deviation and relative standard deviation calculated. Table 4.5 depicts the peak areas for each of the six injections while table 4.6 give a summary of the mean standard deviation and relative standard deviations



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**Table 4.5:** Peak areas (TIC.min) of VOC's to check the precision of SPME

| **1,1,1-trichloro ethane** | **Carbon Tetra-chloride** | **Trichloro ethylene** | **Toluene** | **Tetrachloro ethylene** | **Chloro benzene** |
|---|---|---|---|---|---|
| 369756 | 568068 | 915523 | 1028145 | 2177083 | 1359792 |
| 438447 | 739745 | 1084247 | 1201788 | 2839462 | 1713051 |
| 448613 | 688362 | 997357 | 1323431 | 3008360 | 1839018 |
| 420418 | 667319 | 999831 | 1190341 | 2740801 | 1663874 |
| 395849 | 605650 | 937041 | 1083404 | 2259314 | 1389578 |
| 410034 | 660901 | 979848 | 1170841 | 2618410 | 1590041 |

**Table 4.6:** Summary of statistical results

| **Compound** | **mean** | **SD** | **% RSD** |
|---|---|---|---|
| 1,1,1-trichloroethane | 413852.8 | 28773.2 | 6.95 |
| Carbon Tetrachloride | 655007.5 | 60784.7 | 9.28 |
| Trichloroethylene | 985641.2 | 58947.1 | 5.98 |
| Toluene | 1166325 | 102476 | 8.79 |
| Tetrachloroethylene | 2607238 | 328291.1 | 12.59 |
| Chlorobenzene | 1592559 | 187475 | 11.77 |

**Remarks:**

The variation of between 6.95 and 12.59% compares well with the prescribed limit set by the EPA of 20% for the determination of VOC making use of validated analytical methods (USEPA, 1992). The retention time differences of all six compounds as depicted in fig.14 3 were all within ±0.03 relative retention time (RRT) units for each of the six different injections and therefore meets the required



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±0.06( RRT) as set out by the USEPA. One can thus conclude that SPME meets the requirements as set out by the USEPA, for precision measurements.

**Figure 4.12:**

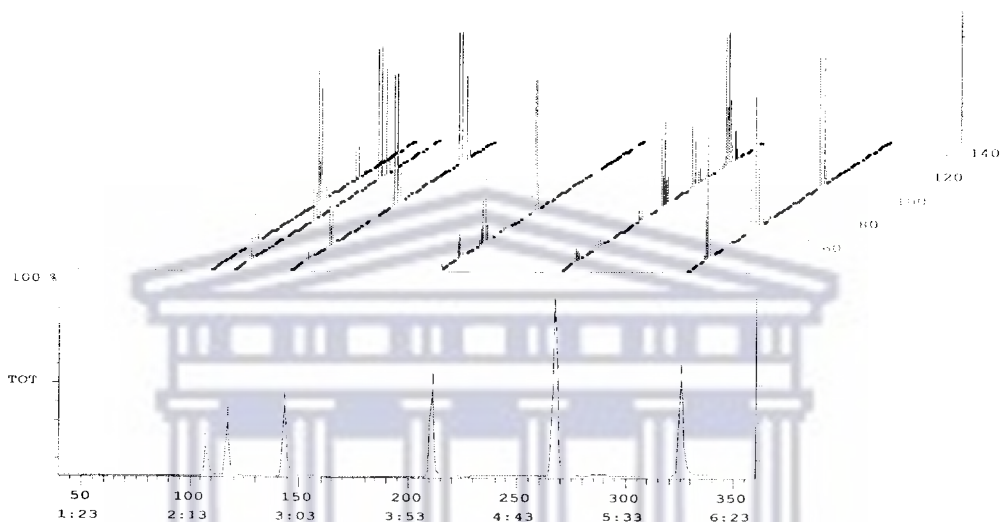
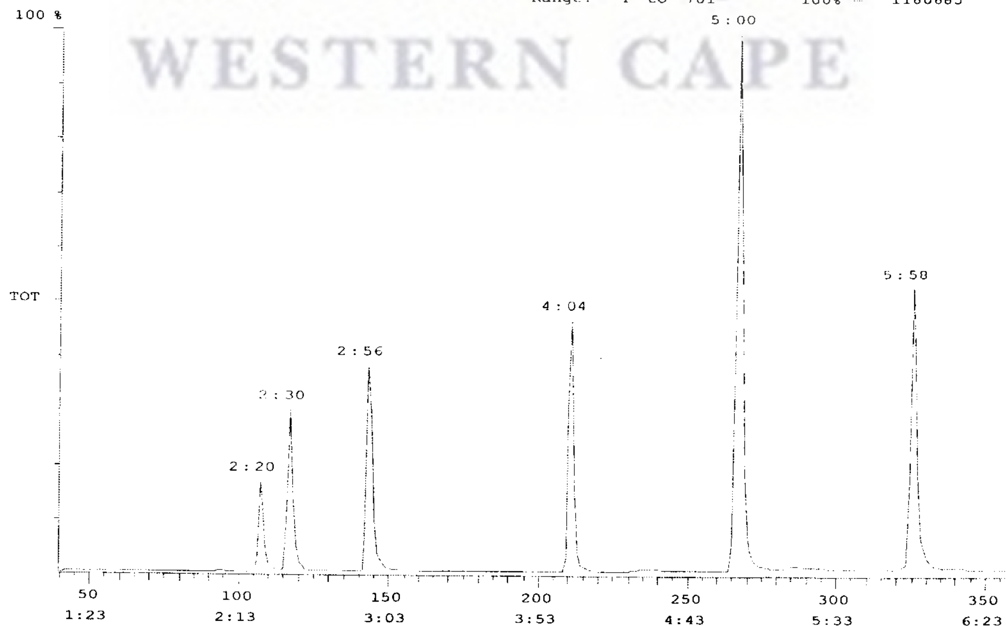



**Figure 4.13:** Chromatograph to check the reproducibility and precision of SPME

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### 4.4.7 Linearity and detection of SPME

#### 4.4.7.1 Objective

Calibration data to measure the linearity of SPME over an entire range of concentrations were investigated. Linearity enables one to use a simple equation like $\frac{\text{peak area (sample)}}{\text{peak area (std)}} \times \text{conc of standard}$ ; for the calculation of the relevant organic compound concentrations without having to calibrate the SPME device, prior to each sample analysis.

#### 4.4.7.2 Procedure

**General experimental conditions**

The same instrument conditions applied to paragraph 3.2 (p.27) was used. Sample volumes were 4ml of each calibration standard (table 4.7) in an amber glass vial, with distilled water as the dilution matrix. The adsorption time and temperature were 15 minutes and 20°C respectively.

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**Table 4.7:** Spiked volatile organic compound series

| Volatile Organic Compound | Concentration (ppb) | | | |
|---|---|---|---|---|
| Toluene | 250 | 500 | 1000 | 2500 |
| Trichloroethylene | 250 | 500 | 1000 | 2500 |
| 1,2-dichloropropane | 250 | 500 | 1000 | 2500 |
| Carbon Tetrachloride | 250 | 500 | 1000 | 2500 |
| Tetrachloroethylene | 250 | 500 | 1000 | 2500 |
| 1,2-dichloroethane | 250 | 500 | 1000 | 2500 |
| Chlorobenzene | 250 | 500 | 1000 | 2500 |
| 1,2-dichlorobenzene | 250 | 500 | 1000 | 2500 |
| 1,4-dichlorobenzene | 250 | 500 | 1000 | 2500 |
| 1,1,1-trichloroethane | 250 | 500 | 1000 | 2500 |



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**Results and discussion**

The results obtained for each of the different calibration standard are listed in table 4.7(a), (b) and (c).

**Table 4.8(a):** Calibration data

| Conc. (ppb) | Peak area Toluene | Peak area Chlorobenzene | Peak area Trichloroethylene | Peak area Tetrachloroethylene |
|---|---|---|---|---|
| 250 | 963550 | 325254 | 765542 | 1360000 |
| 500 | 1856855 | 410000 | 1448331 | 1488000 |
| 1000 | 3605800 | 655580 | 3537989 | 2718000 |
| 2500 | 7693254 | 1235561 | 9925518 | 6940020 |

**Table 4.8(b):** Calibration data

| Conc. (ppb) | Peak area Carbon Tetrachloride | Peak area 1,2-dichloropropane | Peak area 1,2-dichloroethane |
|---|---|---|---|
| 250 | 601157 | 92671 | 47556 |
| 500 | 1180958 | 141727 | 58090 |
| 1000 | 1995529 | 260481 | 129866 |
| 2500 | 3405799 | 630910 | 415523 |

**Table 4.8 (c):** Calibration data

| Conc. (ppb) | Peak area 1,2-dichlorobenzene | Peak area 1,4-dichlorobenzene | Peak area 1,1,1-trichloroethane |
|---|---|---|---|
| 250 | 2018530 | 795530 | 160130 |
| 500 | 4258925 | 1599508 | 299420 |
| 1000 | 7855100 | 3355423 | 591892 |
| 2500 | 16085005 | 7954360 | 1235373 |



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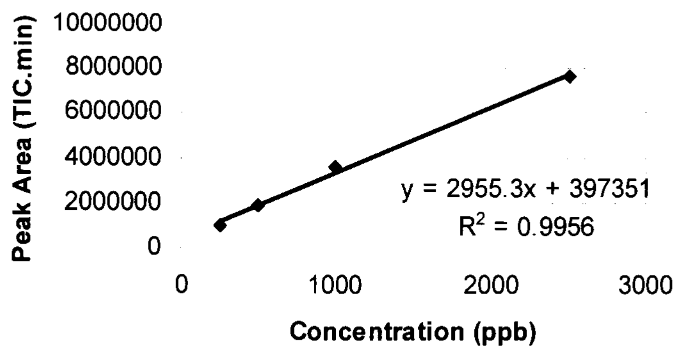


**Figure 4.14(a)** Calibration curve of toluene

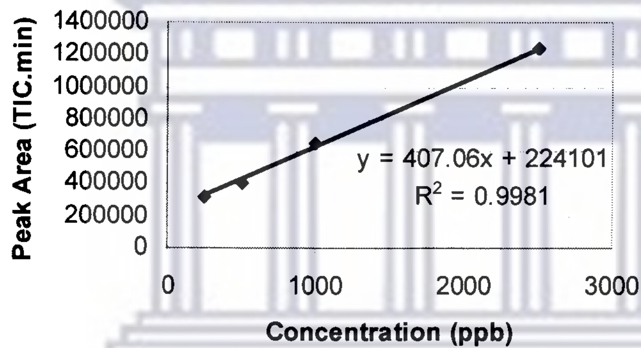


**Figure 4.14(b)** Calibration curve of chlorobenzene

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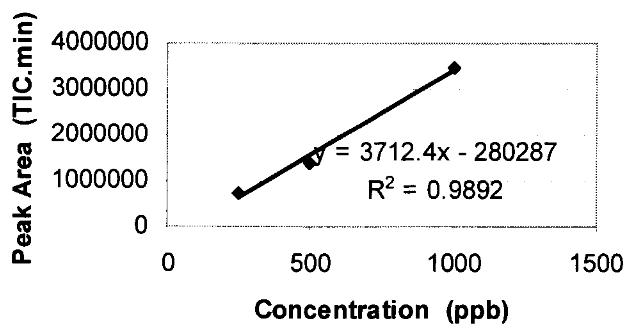


**Figure 4.14(c)** Calibration curve of trichloroethylene



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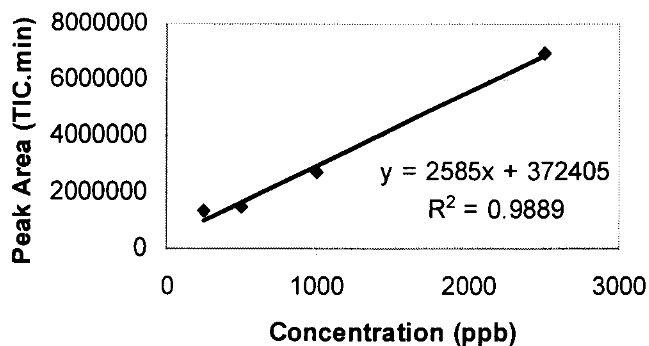


**Figure 4.14(d)** Calibration curve of tetrachloroethylene

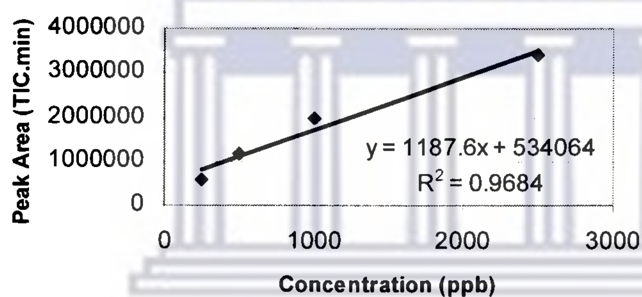


**Figure 4.14(e)** Calibration curve of carbon tetrachloride

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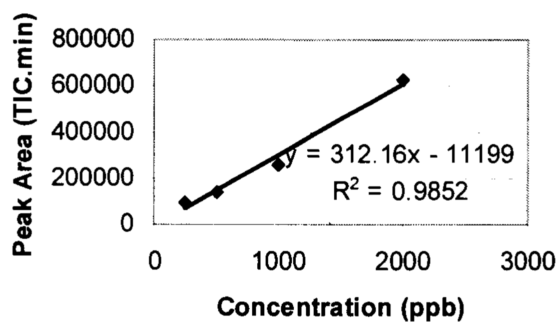


**Figure 4.14(f)** Calibration curve of 1,2-dichloropropane



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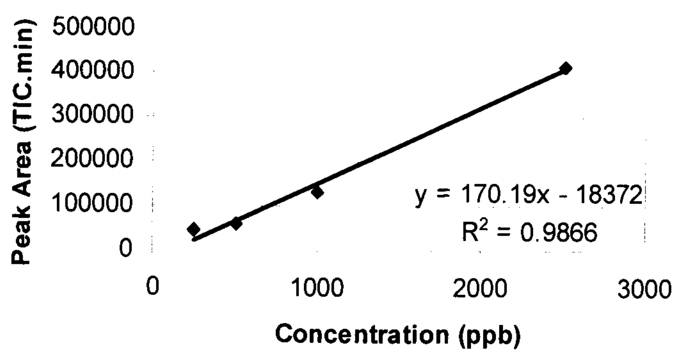


**Figure 4.14(g)** Calibration curve of 1,2-dichloroethane

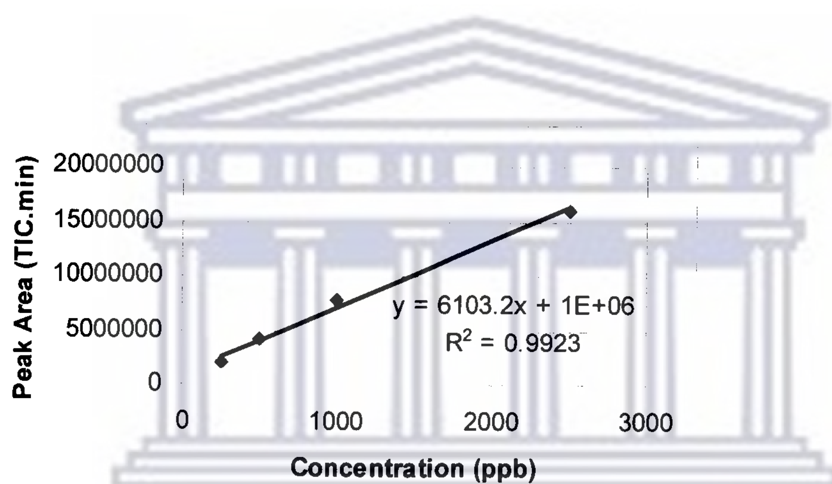


**Figure 4.14(h)** Calibration curve of 1,2-dichlorobenzene

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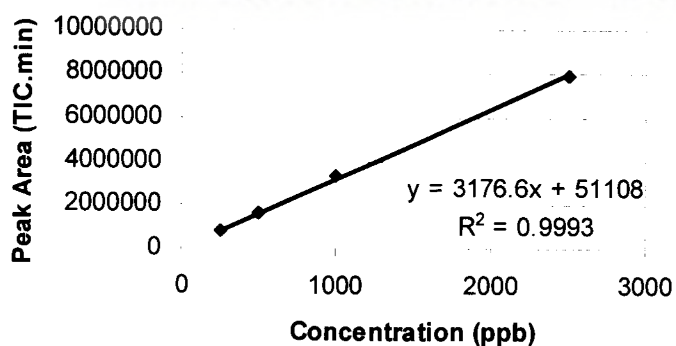


**Figure 4.14(i)** Calibration curve of 1,4-dichlorobenzene



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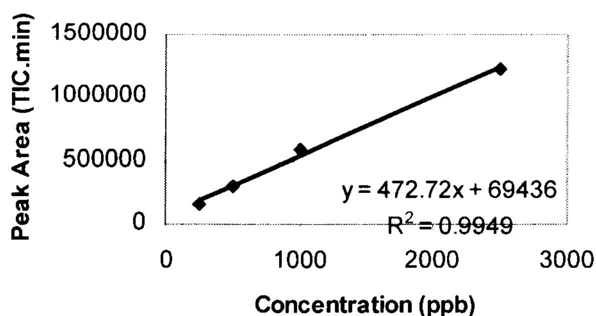


**Figure 4.14(j)** Calibration curve of 1,1,1-trichloroethane

**Remarks:**

The external calibration curves for each of the ten target compounds shows a fair degree of linearity. The experimentally determined linear range of SPME for the analytes with large distribution constants gives linear correlation coefficients ($R^2$) of 0.9993 (1,4-dichlorobenzene) while for those with lower distribution constants, $R^2$ figures as low as 0.9684 (carbon tetrachloride) are observed as indicated on the graphs. Recoveries figures, as low as 50% were observed for those compounds with lower distribution coefficients when using the external calibration curves. The values obtained are depicted in table 4.6

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Table 4.6: Recoveries making use of external calibration standards

| Compound | Expected conc. (ppb) | Found conc.(ppb) | % Recovery |
|---|---|---|---|
| 1,1,1-trichloroethane | 250 | 156.8 | 62.7 |
| Carbon Tetrachloride | 250 | 129.5 | 51.8 |
| Trichloroethylene | 250 | 198.5 | 79.4 |
| Toluene | 250 | 207 | 82.8 |
| Tetrachloroethylene | 250 | 237 | 94.8 |
| Chlorobenzene | 250 | 258 | 103.2 |

Since SPME is an equilibrium technique, competitive adsorption to glassware can reduce the amount of analyte absorbed by the fiber. Further investigation also revealed spiked peaks coming from the fiber used for the analysis. This was confirmed using the GC/MS library to identify these compounds (fig. 4.15). Because the fibers are made from polydimethylsiloxane (PDMS), these were the type of compounds that was identified by the MS. Degradation of PDMS has been extensively studied by (Patai et al, 1991) (Blum et al, 1991) ( Welsch et al, 1991). Thermal degradation of PDMS under inert conditions gives rise to pure dimethylcyclosiloxanes where neither C-H nor Si-C bonds are broken. The main products of degradation under these conditions are low molecular weight cyclosiloxanes with hexamethylcyclotrisiloxane predominating. Trace amounts of hexamethyldisiloxane and octametyltrisiloxane were also detected as noticed from fig. 4.15. The changes in fiber conditions had thus a direct influence on recovery values. The equation as mentioned in 4.4.7.1 can thus not be used in all instances. The addition of an internal standard can account for analyte losses to glassware, volatilization or experimental conditions. Due to the cost of deuterated internal standards and the none availability of a compound that could be used as an internal standard, standard addition were looked at to improve the accuracy of SPME for those compounds with lower distribution coefficients and to counter the change in fiber condition.



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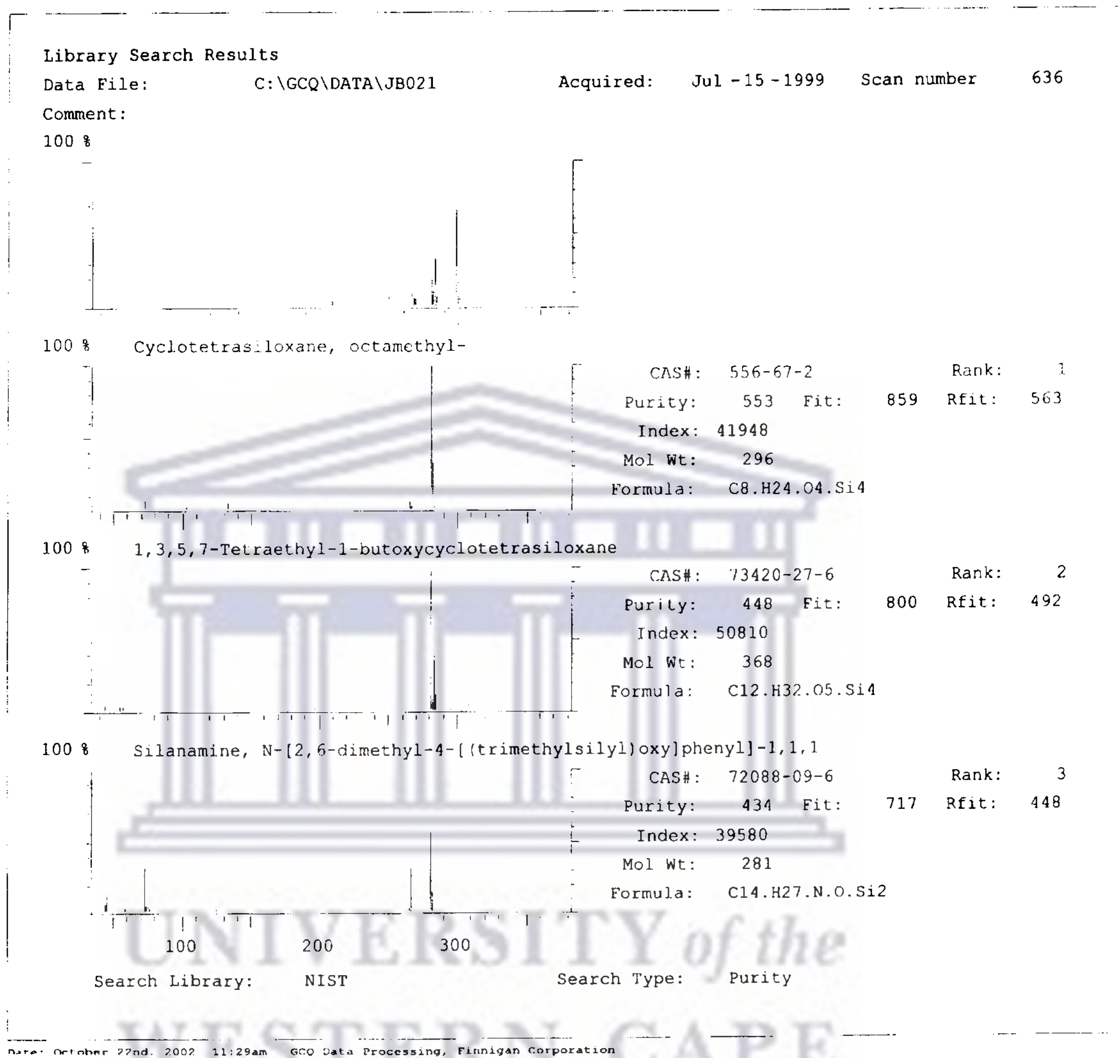
**Figure 4.15**: Degradation of polymeric fiber




## 4.5 Standard Addition

The standard addition method is employed when it is impossible to suppress interferences from matrix elements. It involves the addition of a small amount of analyte solution of known concentration to an unknown sample and both vials analysed using the same instrument parameters and procedures.



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### 4.5.1 Procedure

Four vials, each containing 100ppb of the six compounds mix used for the precision studying 4.4.6 were again made up with deionised water as the dilution matrix. To three of the vials a further 50, 100 and 200ppb of the six compounds mix were added to increase the effective concentrations to 150, 200 and 300ppb respectively. All four vials were SPME'd making use of the same experimental conditions as that employed in par. 3.2 p. 27. Figure 4.16, 4.17 and 4.18 depicts the chromatographs for three of these solutions. The recoveries were calculated with the use of linear regression and are summarized in table 4.7.

**Figure 4.16**: 100ppb Compound mix for standard addition

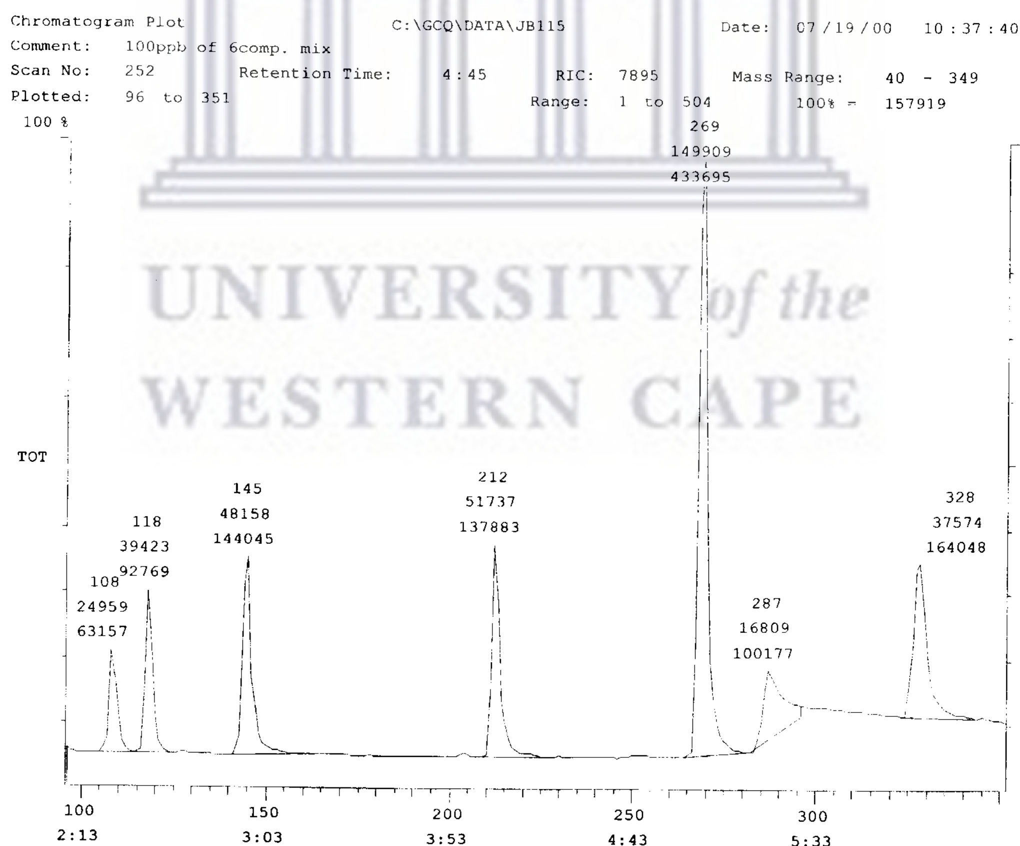


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**Figure 4.17:** Compound mix spiked with a further 50ppb for standard addition

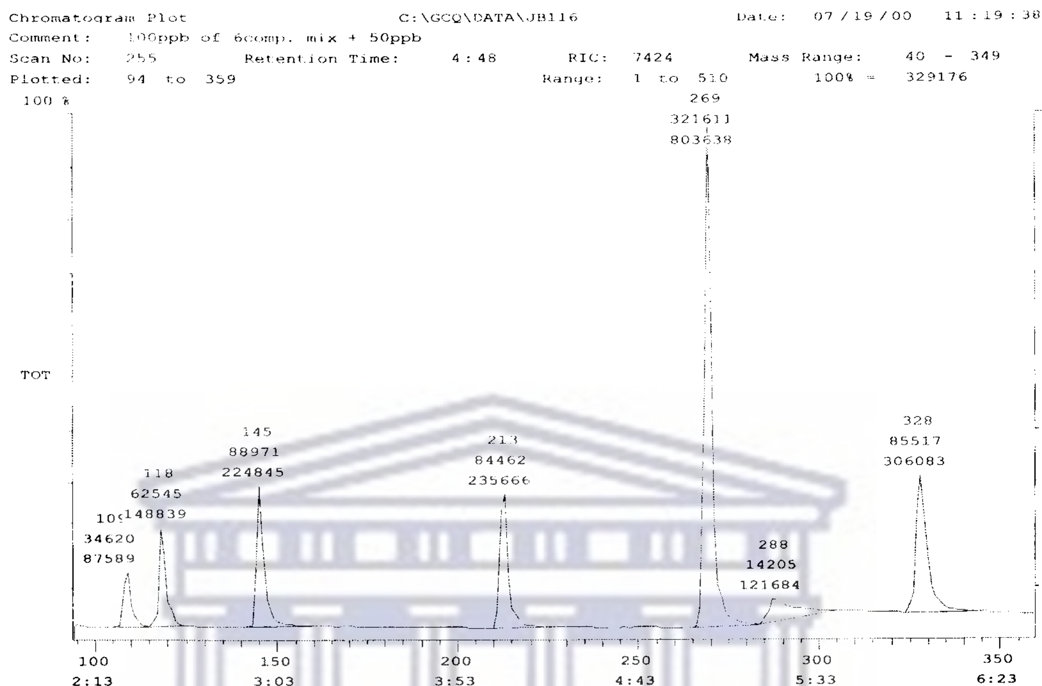


**Figure 4.18:** Compound mix spiked with a further 100ppb for standard addition

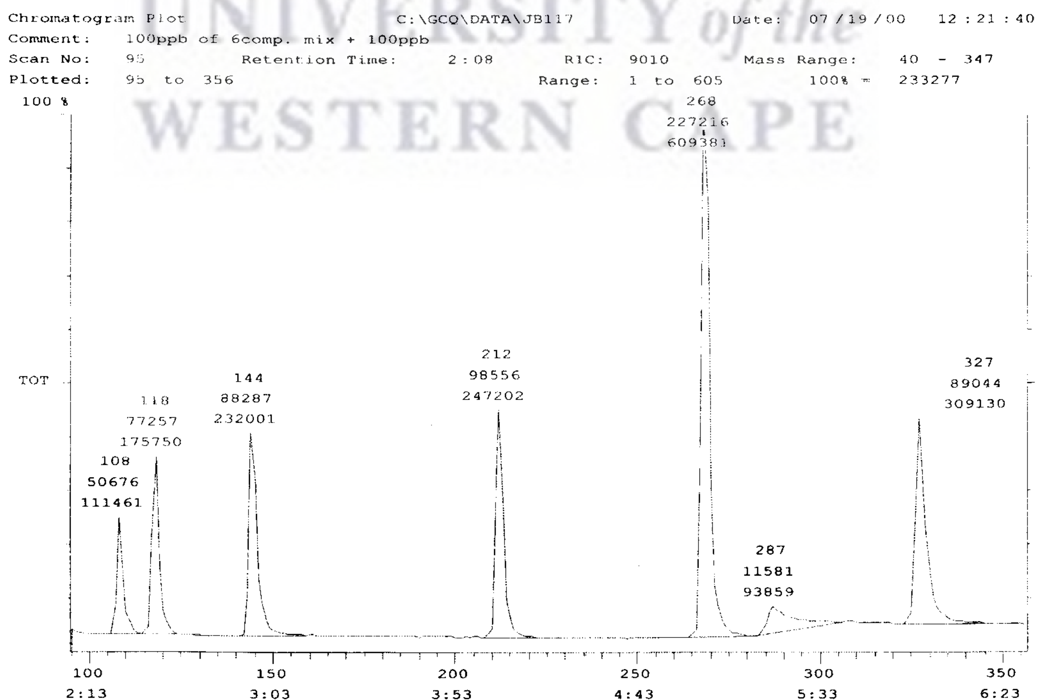


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**Table 4.7:** Recoveries using standard addition

| Compound | Expected conc. (ppb) | Found conc.(ppb) | % Recovery |
|---|---|---|---|
| 1,1,1-trichloroethane | 100 | 89.2 | 89.2 |
| Carbon Tetrachloride | 100 | 84.3 | 84.3 |
| Trichloroethylene | 100 | 98.5 | 98.5 |
| Toluene | 100 | 112.0 | 112.0 |
| Tetrachloroethylene | 100 | 99.5 | 99.5 |
| Chlorobenzene | 100 | 108.7 | 108.7. |

**Remarks:**

Although the recoveries for the low boiling point compounds are slightly lower than for the high boiling point compounds as expected when one keep in mind the optimization studies results in chapter 3, standard addition should be employed as the analytical method of choice for SPME analysis since all sample interferences can be overcome. The recovery figures also compares well with that obtained by the USEPA when using validated methods, like the purge and trap.

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## 4.6 Method Detection Limit Studies

The lowest possible standard to be detected by the method was investigated. EPA requirements is that the signal to noise ratio should be at least 3 times the standard deviation of a compound for qualitative analysis and at least 10 times the standard deviation for quantitative analysis.

**Pocedure**

A 100ppb compound mixture containing six of the target compounds were SPME'd . The peaks were integrated with the aid of instrument software.



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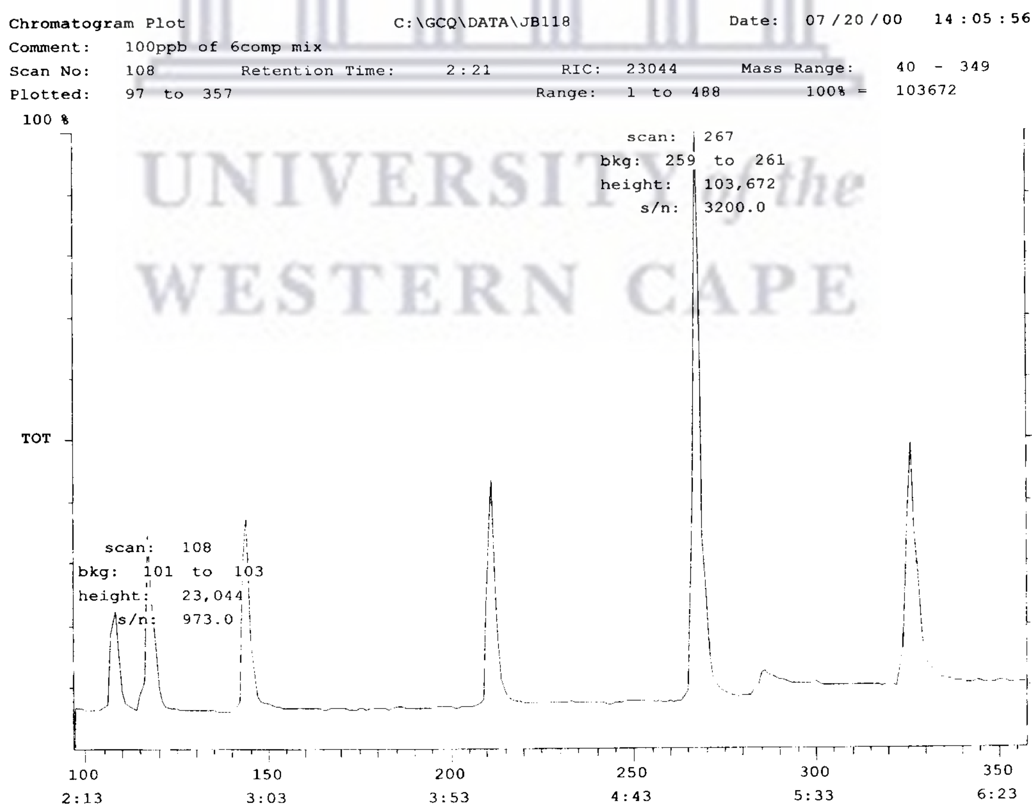
**Remarks:**

The signal to noise ratio for the compound with the lowest intensity is 973 units and that of the most intense peak is 3200 units. Inspection of the base line showed no spikes between the standard peaks. The chromatogram in figure 4.19 indicates that when the experimental conditions are optimal (clean MS source, no vial contamination) that SPME method detection can be in parts per trillion (ppt.) levels for low boiling point compounds (compounds with smaller K values) and in the sub ppt. levels for the ones with large K values.

The assumption can thus be made that taking into consideration the conditions under which this research are taking place (instrument sharing) that sub ppb levels can be measured.

**Figure 4.19:** Signal to noise ratio of six compound mix



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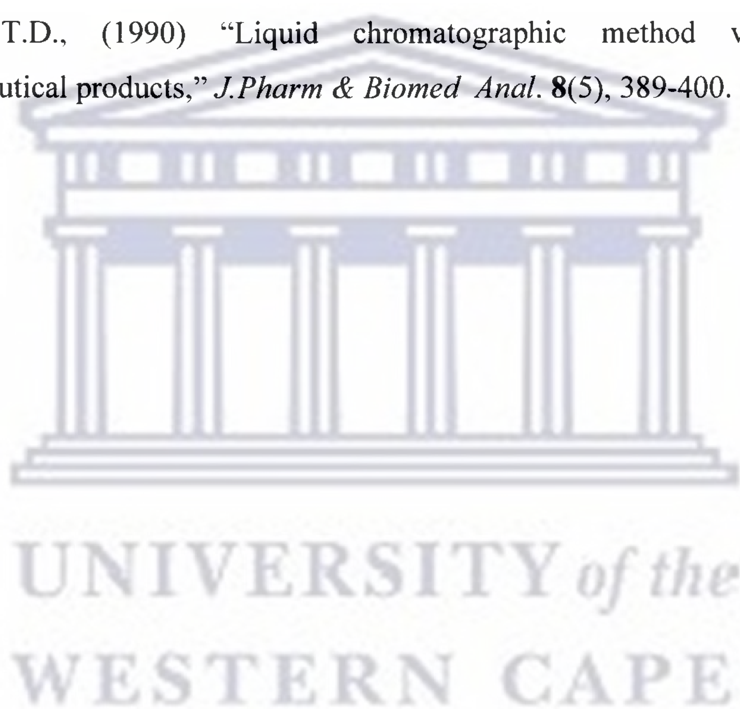




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# CHAPTER 5

## Case study of Volatile Organic Compounds in the Vissershok Landfill site in Durbanville in the Western Cape

### 5.1 Introduction

The initial objective of the project was to investigate the use of SPME as an alternative technique for the analysis of volatile organic compounds in groundwater. As to date the method has just focused on the extraction of standards spiked in relatively clean water. The method was further extended to include complex water samples that contained hundreds of organic and inorganic compounds. For this study samples were collected from the Vissershok landfill site, just outside of Durbanville in the Western Cape.

### 5.2 Background to Vissershok landfill

Vissershok Waste Management Facility is situated between the N7 National Road and the Atlantis railway line approximately 20km northeast of Cape Town. (See figure 5.1). The closure of Aloes hazardous waste facility in Port Elizabeth and the redirecting of all the hazardous waste to Vissershok, has placed an additional burden on the site management. The site has been in use for more than two decades and is classified as a H:H facility which can accept most hazardous waste types. Although the groundwater yields of the aquifer is of low yield (0.01 to 0.13 L/s) (Weaver, 1995), and the aquifer is classified as being of low yield and of no significance, monitoring boreholes were drilled around the site to assess the extent of pollution from the landfill site. These boreholes are depicted in figure 5.2, with borehole V1-09 being the up-gradient reference borehole.



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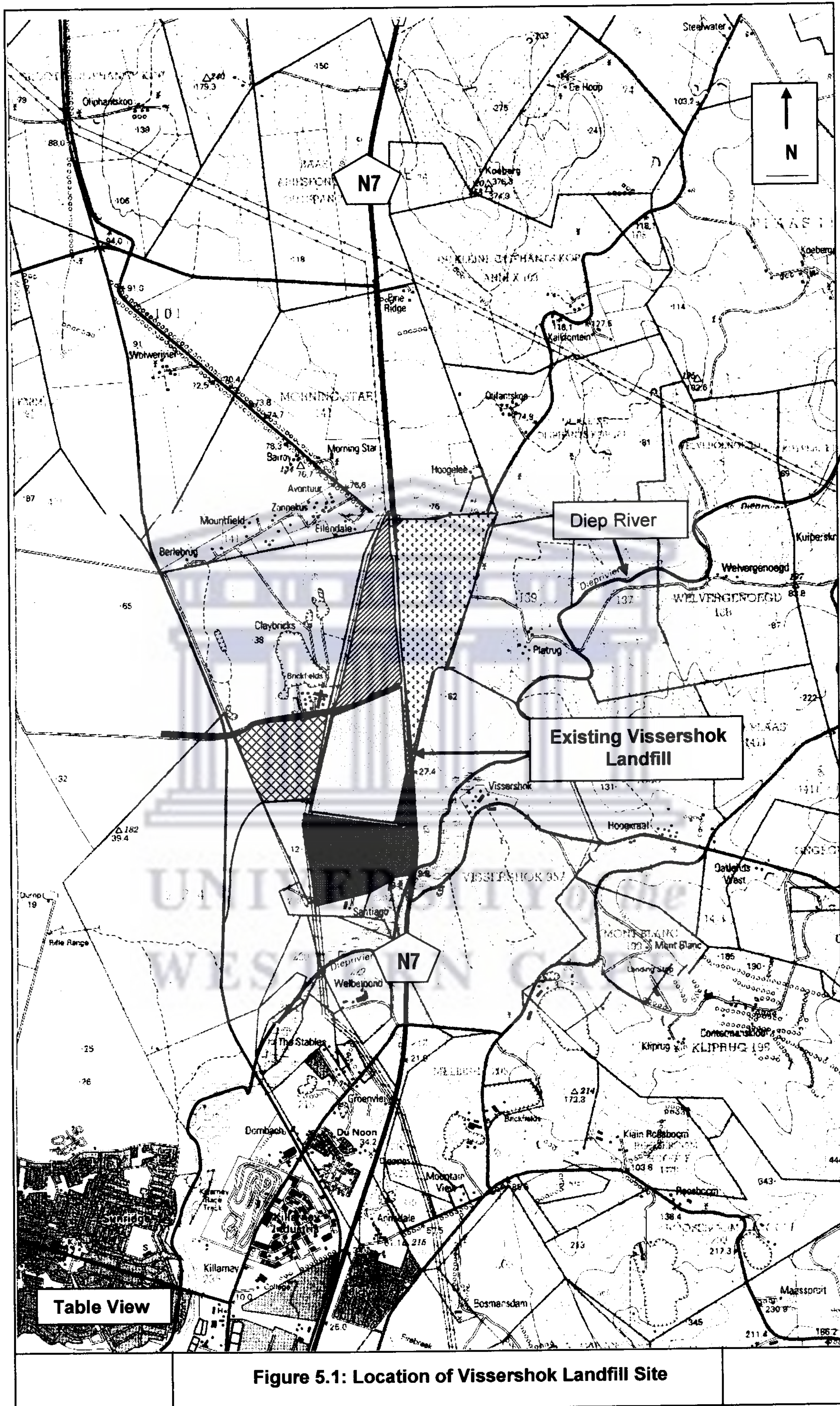


Figure 5.1: Location of Vissershok Landfill Site



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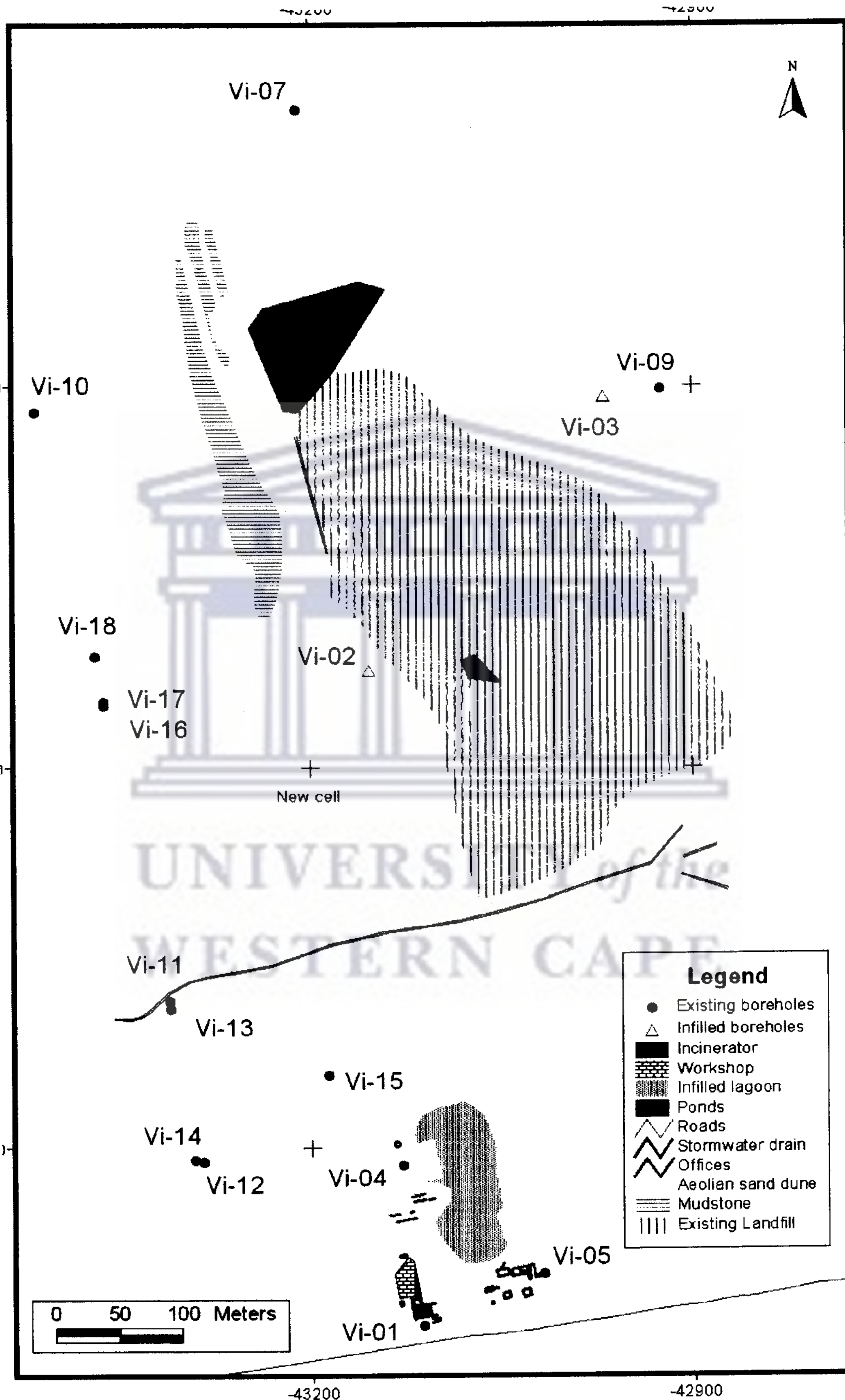


**Figure 5.2:** Location of sampling boreholes



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## 5.3 Sample Analysis

In order to gain some idea of the nature of the pollution in the groundwater, samples were taken from one leachate sump and eight boreholes, and analysed for chloride and conductivity as an indication of mineral pollution. Total Organic Carbon (TOC) was determined to provide an indication of organic pollution and ammonia analysis provided an indication of decomposed proteinaceous matter. Anions such as chloride do not enter into redox reactions, do not form complexes with other ions, do not significantly absorb onto mineral surfaces, and do not undergo biological transformations that remove them from solution. As a result they can be used as tracers of groundwater contamination. Total organic carbon is useful for mass balance considerations. However, TOC measurements give no indication of the specific compounds present. To acquire such data, class or compound specific analyses is required.

### 5.3.1 Collection and Analyses of Groundwater Samples

#### 5.3.1.1 Sampling for Inorganic ions and TOC

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Samples were collected in a 250ml plastic PVC bottle from all the eight boreholes and the leachate cell. The boreholes sampled were Vi-01, Vi-04, Vi-05, Vi-07, Vi-09, Vi-10, V1-14, Vi-16 and leachate collected from one of the open ponds. These samples were kept at 4°C until analysed for, conductivity by means of a platinum electrode and for chloride, ammonia and total organic carbon by means of automated colormetric methods (see addendum). Table 5.1 lists the average results for the parameters analysed in the analytical laboratory of the CSIR, Stellenbosch, over four sampling runs between 2000 and 2001.



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**Table 5.1:** Summary of the results for the parameters tested in Stellenbosch Laboratory

| Sample point | Conductivity (mS/m@25⁰C) | Chloride (mg/L) | Total Organic Carbon (mg/L) | Ammonia (mg/L) |
|---|---|---|---|---|
| Vi-01 | 605 | 1668 | 4.9 | 0.3 |
| Vi-04 | 437 | 1249 | 12.0 | 6.4 |
| Vi-05 | 1465 | 4611 | <1 | <0.1 |
| Vi-07 | 218 | 630 | 1.2 | <0.1 |
| Vi-09 | 211 | 560 | 1.6 | <0.1 |
| Vi-10 | 1048 | 2487 | 3.4 | 0.6 |
| Vi-14 | 312 | 791 | 8.2 | 0.8 |
| Vi-16 | 852 | 2610 | 1.9 | 0.3 |
| Leachate sump | 3160 | 5976 | 1221 | 1535 |

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#### 5.3.1.2 Results and discussion

The salinities as indicated by the measured conductivity vary considerably in the study area. From the hydrochemical data in table 5.1 it is very difficult to conclude if any of the boreholes are being contaminated by leachate seepage. Apart from borehole Vi-04 and Vi-14, whose total organic carbon values are much higher than the background figure of less than 2ppm, all the other boreholes shows the same trend as that of the reference borehole Vi-09. These two holes also indicate slightly elevated ammonia levels. The slight pollution of these two boreholes can be considered to be related to the evaporation lagoons which are located to the right of the boreholes (fig. 5.2). The extent of contamination is also decreasing as water is moving further away from the evaporation lagoons (the groundwater flow is from northeast to southwest). As the groundwater has a sodium chloride character



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(Tredoux, 1996), chloride is the main anion and its trends confirm the identified conductivity trends.

## 5.4 Sampling for VOC's

Samples were collected in 4ml amber glass vials. Ten vials were filled from each of the previously mentioned borehole. Vials were capped with a PVC top with Teflon septa. These samples were kept on ice until analysed the day following sampling. The sample for the leachate was scooped from the leachate cell as it was emerging from the waste to ensure that the leachate was as fresh as possible, since the compounds of interest were very volatile. The same experimental conditions applied.

### 5.4.1 Results and discussion

No VOC's were detected in any of these samples that were analysed. Apart from the leachate chromatograph the other samples chromatograms had no significant peaks. The leachate compounds could not be positively identified. The reason for not detecting any VOC's in the groundwater, can be attributed to the fact that the initial concentration of these compounds may be well below the detection limit. Another factor to consider is that of the "salting-out "effect. From the hydrochemical data one can observe that these waters have elevated conductivity levels and the fact that the water shows a sodium chloride character (Tredoux, 1996), will tend to drive any VOC's present, to the water surface in the borehole as discussed in chapter 3. A third factor that could have influenced the detection was instrument contamination (figures 5.3 and 5.4). Problems were encountered with a ghost peak that was eluting right in the beginning of the chromatographic run. Cleaning of the instrument did not solve this problem, nor did the purchase of a new column. The intensity of this peak was such that the concentration of any ppb detection was not possible. The source of contamination could not be traced to any



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of the solutions, vials, septa or syringes used as even air injected with a Hamilton syringe yielded the same peak. The peak was identified as sulphamide by means of the MS library and the assumption was made that it may have come from one of the organometallic compounds analyzed, as the instrument was shared with other users. Whether SPME can be used to do environmental thus still remained unanswered. It was thus decided to simulate the groundwater contamination to see if the matrix would influence the extraction capabilities of SPME in complicated real environmental samples.

**Figure 5.3**: Proof of instrument contamination

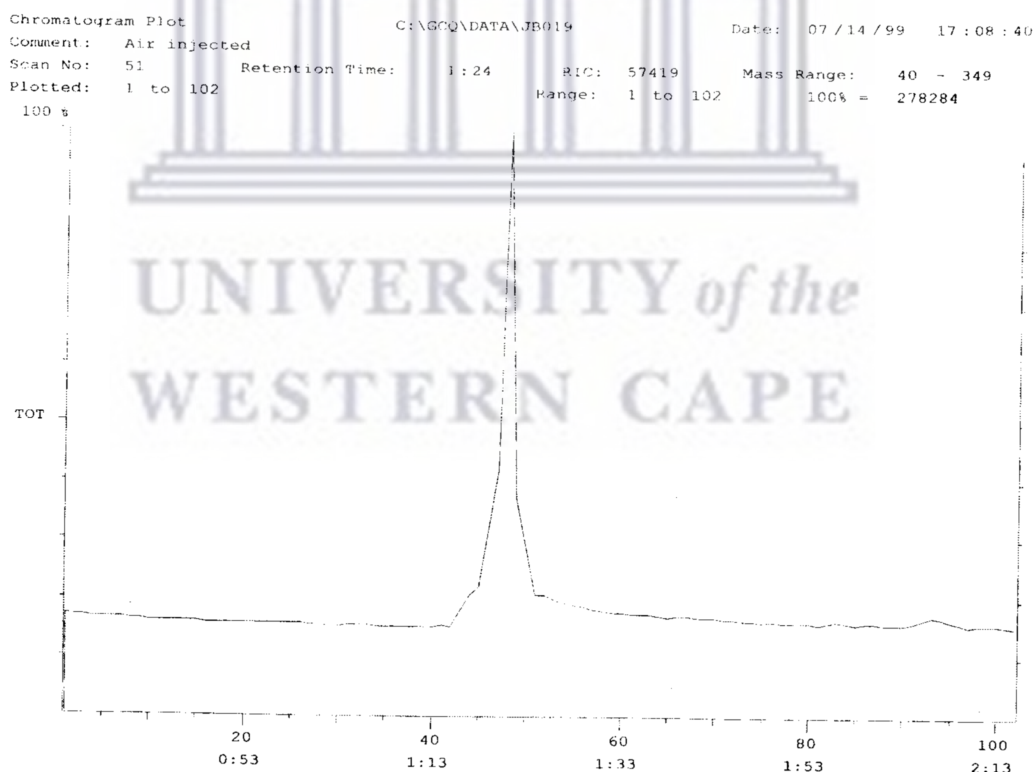


**Figure 5.3:** indicates the contamination of the GC/MS and the eluting peak at a retention time of 1.24 minutes. The intensity is such that later eluting compounds are overshadowed and cannot be detected in trace amounts.

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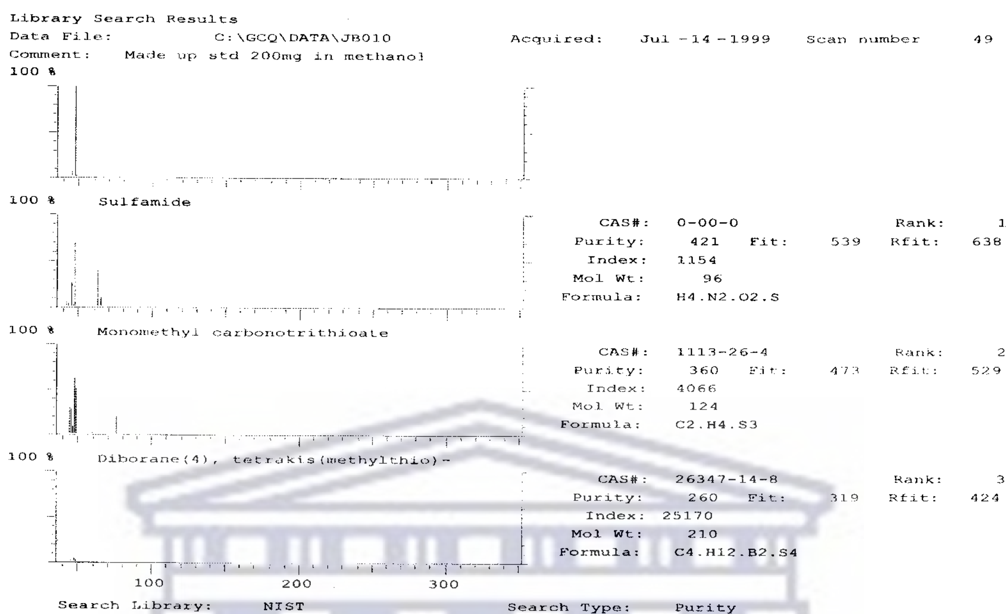
**Figure 5.4:** Contamination identification




## 5.5 Groundwater Simulations

For this study the ground water was spiked with a known concentration of each the ten target compounds and the samples SPME'd . The same experimental conditions as established were employed

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### 5.5.1 Procedure

A 2ppm (v/v) of the ten target compound mixture in borehole Vi-09 and Vi-10 were made as they had the lowest and the highest electrical conductivities. These solutions were analysed by means of standard addition protocol as per par. 4.5.

### 5.5.2 Results and discussion

The chromatographs and retention times for the ten target compound mixture are shown in figures 5.5 and 5.6 and table 5.2.



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**Figure 5.5:** Chromatograph of ten target compounds

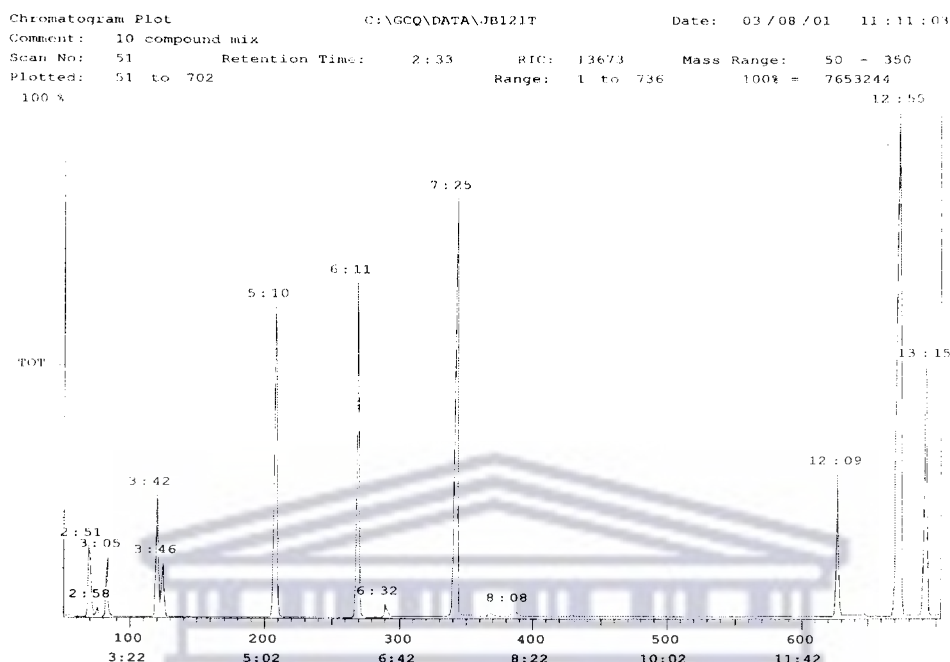


**Figure 5.6:** Peak detection

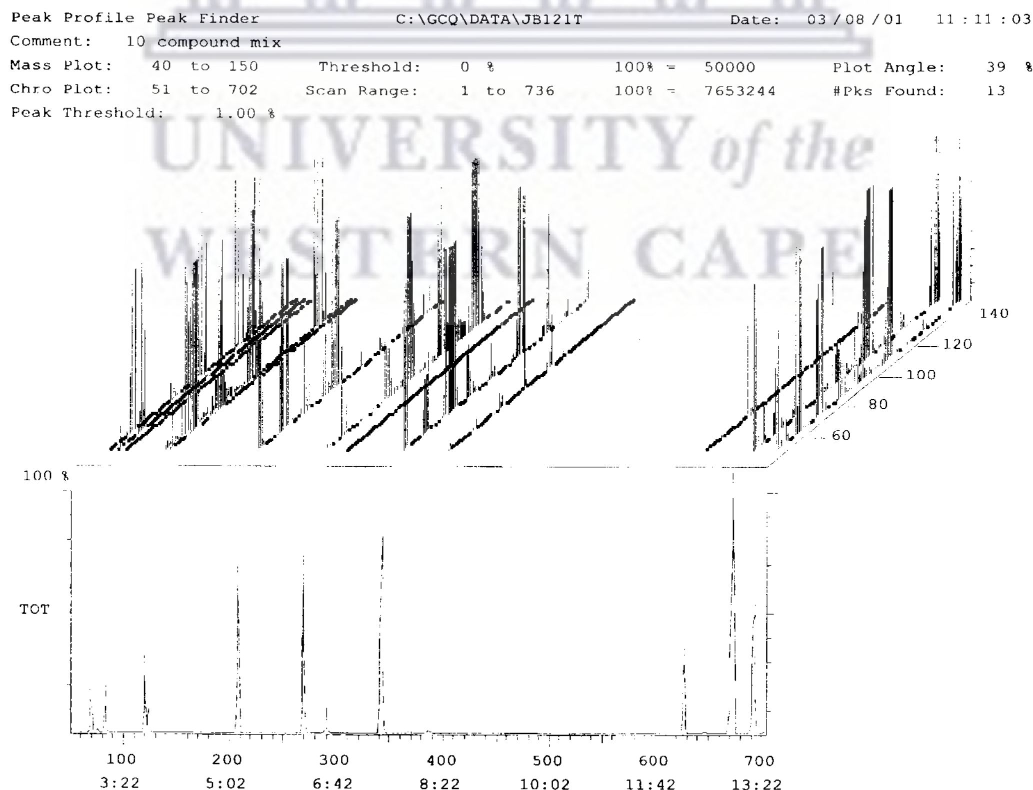




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**Table 5.2:** Ten target compound mixture retention times.

| Compound | Retention time (min) |
|---|---|
| 1,1,1-trichloroethane | 2.51 |
| Carbon Tetrachloride | 3.05 |
| Trichloroethylene | 3.42 |
| 1,2-dichloroethane | 3.46 |
| Toluene | 5.10 |
| 1,2-dichloropropane | 6.11 |
| Chlorobenzene | 7.25 |
| Tetrachloroethylene | 12.09 |
| 1,4-dichlorobenzene | 12.55 |
| 1,2-dichlorobenzene | 13.15 |

**Remarks:**

From the retention times of the ten compound mix one can notice that instrument conditions have changed. Although the new column, was exactly the same phase as the previous, there was an increase in retention time of up to 2 minutes for some of the compounds. From figure 5.7 the signal to noise ratio (99) for the compound 1.1.1-trichloroethane has decreased dramatically even though the concentration used in the study was 20 times higher than that used in the validation. No recoveries studies could be done as the intensity of the contamination peak (fig. 5.3) was not very consistent. The degree of intensity varied per run and thus all chromatographs were not affected in the same way. Even though the same results as in chap. 4 could not be obtained, one can draw the logical conclusion that it is possible to extract VOC's in complex sample matrixes as was proved by the extraction of the target compounds from groundwater.



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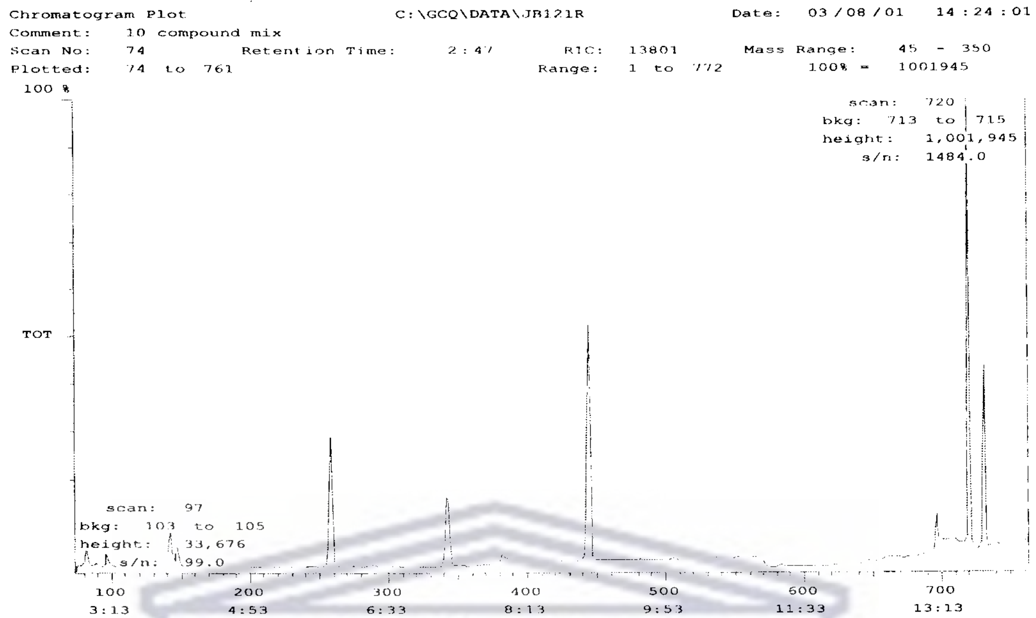


**Figure 5.7**: Signal to noise ratio of target compounds

## References


Tredoux, G (1996). Vissershok Waste Disposal Site: Geohydrochemical data evaluation. *Report No 4/96, Watertek, CSIR,* Stellenbosch

Weaver, J (1995). Vissershok Waste Disposal Site: Report on drilling and test-pumping of six boreholes, *Report No 31/95, Watertek, CSIR*, Stellenbosch




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# CHAPTER 6

## CONCLUSIONS

It has been demonstrated that SPME can be successfully used for determining VOC's in groundwater. The technique can be used successfully as a screening technique for determining the concentration levels of VOC's in groundwater samples prior to quantitative analysis by purge and trap. No extra samples are required for SPME analysis of VOC's in the groundwater samples as the SPME fiber can be inserted directly into the sample without effecting the concentration of the sample, ( the amount extracted by the fiber with each exposure are less than 2% of the total amount of compound present in the sample) . Contamination of the purge and trap are therefore eliminated as SPME will give an indication of the sample concentration.

This method, once optimized, can be utilized to successfully decrease the labour time, and the analysis time. The cost effectiveness of the method; 1999 cost for start up was R11 000-00 which far outweighs the cost implications of the validated methods for sample preparation as the cost of a new purge and trap unit are in the region of R200 000 -00 , which does not include the consumables needed to do the VOC trapping.

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We have noticed that method is not very rugged, and is thus affected by small uncontrolled changes in its operating conditions.

### Recommendations

A standard addition protocol should be employed for SPME. The condition of the fiber need to be inspected on a regular basis as it was seen to start decomposing after being exposed to high temperature over a period of time. The amount of extraction can be shortened from 100 as applied in this study to ±25 extractions. This is still cost effective as the cost of one fiber is roughly R400-00, and the charge for VOC determination by means of purge and trap is about R1100-00 per



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sample. The study could be extended to include the whole USEPA, VOC target compounds of 54 can be quantified by means of SPME .

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## ADDENDUM A

ELECTRICAL CONDUCTIVITY

Introduction and scope

This method is applicable to the determination of the electrical conductivity of water samples.

PRINCIPLE

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current.
The physical measurement made in a laboratory determination is usually of resistance. The resistance of a conductor is inversely proportional to its cross-sectional area and directly proportional to its length. The magnitude of the resistance measured in an aqueous solution therefore depends on the characteristics of the conductivity cell used, and is not meaningful without knowledge of these characteristics.

The term "conductivity" is preferred and is usually reported in micromhos per centimeter. The SI units use the Siemens (the reciprocal of the ohm and conductivity is reported as millisiemens per meter (mS/m). 1 mS/m = 10µmhos/cm. To report results in SI units, divide µmhos/cm by 10.

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REAGENTS

Dry KC1 at 105°C for two hours and cool in a dessicator. To prepare a solution of a particular conductivity, select the corresponding mass of KC1 from the table below. Weigh out the exact mass and transfer quantitatively to 1 liter volumetric flask. Dissolve the appropriate mass of KC1 in approximately 500 ml reagent grade water and dilute to 1000mL.

Potassium chloride solutions KC1

| Molar KCl | Mass KCl g/l | Conductivity mS/m @25°C |
|---|---|---|
| 0.05 | 0.3728 | 71.8 |
| 0.1 | 7.4560 | 1289.0 |



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De-ionised distilled water.

Pass distilled water through a mixed bed de-ioniser and discard the first liter. Conductivity should be less than 1 mS/m @25°C.

EQUIPMENT

Conductivity meter with platinum electrode cell
Thermometer

INTERFERENCES

Electrolytic conductivity (as opposed to metallic conductivity) increases with temperature at a rate of approximately 1,9%/°C. Significant errors can result from in accurate temperature measurement.

SAMPLING AND SAMPLE PREPARATION

No special sampling techniques are necessary. Use plastic or glass bottles with tightly fitting tops to prevent loss of sample due to evaporation. If conductivity is not determined immediately, sample can be stored for up to 28 days in a refrigerator.

ANALYTICAL PROCEDURE

Rinse cell with one or more portions of sample. Adjust temperature. Measure the sample conductivity.

CALCULATION OF RESULTS

Direct reading @25°C from conductivity meter

REFERENCES

Standard Methods for the examination of water and wastewater 18 Edition 1992
2510 B Laboratory Method

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**ADDENDUM B**

CHLORIDE

Introduction and scope

This method is applicable to the determination of chloride in surface, ground, drinking and wastewater over a range of 5 to 500 mg/L as C1. Higher concentrations may be determined by diluting the sample.

PRINCIPLE

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms a highly coloured ferric thiocyanate, of which the intensity is proportional to the chloride concentration.

An automated technique (Auto Analyser) is used.

REAGENTS

A 2000mg/L C1 standard is made.

Dissolve 6,5928g sodium chloride (NaC1) in water and make up to 2000mL with deionised water

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Prepare working standards in 200 mL volumetric flasks as follows.

| mL stock in 200mL flask | 2.5 | 5 | 10 | 15 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|---|---|---|
| Standard conc. as $Cl^-$ mg/L | 25 | 50 | 100 | 150 | 200 | 300 | 400 | 500 |
| | | | | | | | | |

Stock mercuric thiocyanate solution

Dissolve 4,17g mercuric thiocyanate in about 500mL methanol, dilute to 1000mL with methanol, mix, and filter.

Stock ferric nitrate solution

Dissolve 202g $Fe(NO_3)_3 .9H_2O$ in 500mL water, then carefully add 21 mL conc nitric acid. Dilute to 1000mL with water and store in an amber bottle.



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Colour reagent

Add 150mL stock $Hg(SCN)_2$ solution to 150mL stock $Fe(NO_3)_3$ solution, mix, and dilute to 1000mL, filter and store in an amber glass bottle.

EQUIPMENT

Autoanalyser system consisting of the following:
Recorder, Colorimeter, Mixing manifold with appropriate coils, Proportioning pump and an automatic sampler.

INTERFERENCES

No interferences of significance. However, filter turbid samples.

SAMPLING AND SAMPLEE PREPARATION

Collect representative samples in clean, chemically resistant glass or plastic bottles. No special preservative is necessary if the sample is to be stored.

ANALYTICAL PROCEDURE

Major anions (sulphate and chloride) in natural waters are usually in proportion to the total dissolved salts of that water. In other words, by determining the electrical conductivity of a sample, an appropriate dilution can be made so that the sample falls within the range of the working standards; the following table is used:
Set up manifold and complete system.
Switch on chart recorder and colourimeter and allow to warn up for ±30 minutes or until a stable baseline is obtained.

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CALCULATION OF RESULTS

Prepare standard curves by plotting peak heights of standards processed through the manifold against C1 concentrations in standards. Compute sample C1 concentration by comparing sample peak height with standard curve.

REFERENCES

Standard Methods for the examination of water and wastewater 18th Edition 1992
4500-$C1^-$ E Automated Ferriccyanide Method



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**ADDENDUM C**

AMMONIA – Nitrogen Automated

Introduction and scope

This method is applicable to the determination of ammomium in surface, ground, drinking and waste waters over a range of 0.1 to 5,0mg/L. High concentrations may be determined by diluting the sample, or adjusting the colorimeter's scale expansion setting or recorder's sensitivity.

PRINCIPLE

Alkaline salicylate and hypochlorite react with ammonia to form a green-blue colour, the absorption of which is proportional to the ammonia concentration. The colour is intensified by the addition of sodium nitro prusside.

INTERFERENCES

In alkaline solution calcium and magnesium will interfere by forming a precipitate. Sodium citrate buffer prevents this interference.

EQUIPMENT

AutoaAnalyser system consisting of the following:
Recorder, Colorimeter, Mixing manifold with appropriate coils, Proportioning pump and an automatic sampler.

STANDARDS

Ammonia-N stock standard 1000mg/L solution.

Dry at 105°C for two hours and a cool in dessicator; $NH_4CI$.
Dissolved 3,819g NH $_4$CI in water and dilute to 1000mL.

Dilute 20mL of stock solution to 1000mL – 20mg/L.

Prepare working standards in 200mL volumetric flasks as follows:

| mL, 20mg/L in 200mL flask | 5 | 10 | 15 | 25 | 50 |
|---|---|---|---|---|---|
| Standard conc. $NH_4$-N mg/L | 0.5 | 1.0 | 1.5 | 2.5 | 5.0 |



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REAGENTS

Sodium salicylate solution
Dissolve 90g of sodium salicylate in 800mL water and make up to 1000mL.

Sodium nitroprusside solution
Dissolve 0,5g of sodium nitroprusside in 800mL water and make up to 1000mL.

Sodium hypochlorite solution
Dilute 75mL of commercial bleach (Javell) to 250mL with water.

Buffer solution

| | |
|---|---|
| Sodium Citrate | 300g |
| EDTA | 10g |
| Sodium hydroxide | 5g |

Dissolve and make up to 1000mL with water.

ANALYTICAL PROCEDURE

Set up manifold and complete system. Switch on pump, colorimeter, chart recorder and allow to stabilize so as to obtain a stable baseline with all reagents, feeding water through the sample line.

CALCULATION

Prepared standard curves by plotting peak heights of standards processed through the manifold against $NH_4$ - N concentrations in standards. Compute sample $NH_4$ - N concentration by comparing sample peak height with standard curve.

REFERENCES

Standard methods for the examination of water and wastewater 18th Edition 1992. 4500 – $NH_3$ Automated phenate method.
South African National Scientific Programmes Report No. 44, July 1998



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**ADDENDUM D**

DISSOLVED ORGANIC CARBON (DOC)

Introduction and scope

This method is applicable to the determination of dissolved organic carbon over the range 0,1 to 20,0 mg/L as C. Higher concentrations may be determined by diluting the sample.

PRINCIPLE

This method utilizes an automated Persulphate-Ultraviolet oxidation method using colourimetric detection of $CO_2$ by persulphate in the presence of ultra violet light. The $CO_2$ produced diffuses through a gas permeable membrane and is measured by the decrease in absorbance of a phenolphthalein solution.

Inorganic carbon is removed by acidifying the sample to pH 2 or less to convert the inorganic species to $CO_2$, and then purging the sample with a purified gas ($N_2$) to strip off the $CO_2$.

REAGENTS

Stock Organic Carbon solution

Dissolve 2,1254g potassium biphthalate (dried at 105ºC for 24 hours) in 500mL and make up to 1000mL with water.

Dilute 40 mL of stock solution to 200mL - 200 mg/L as C

Prepare working standards in 200 mL volumetric flasks as follows.

| mL, 200mg/L in 200mL flask | 5 | 10 | 15 | 20 |
|---|---|---|---|---|
| Standard conc. mg/L as Carbon | 5.0 | 10.0 | 15.0 | 20 |

Dilute Sulphuric acid - ±1,0 Normal

Add 28mL conc suplhuric acid to 800mL water and dilute to 1000mL.

Potassium persulphate solution



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Dissolve 24g potassium persulphate in 800mL water and dilute to 2000mL.

Phenolphthalein 1%

Dissolve 1,0g of phenolphthalein in 80mL methanol and dilute to 100mL with methanol.

Sodium Carbonate 0,1M

Dissolve 10,6g sodium carbonate in 800 mL deionised water and make up to 1000mL.

Sodium bicarbonate 0,1M

Dissolve 8,4g sodium bicarbonate in 800 mL deionised water and make up to 1000mL.

Carbonate-Bicarbonate Buffer

Mix 150mL of the 01,M sodium carbonate solution with 300mL of the 0.1M sodium bicarbonate solution. Use this solution for the preparation of the colour reagent.

Phenolphthalein colour reagent

Pipette 1,0mL of the 1%Phenolphthalein solution into a 1000mL volumetric flask. Add 800mL deionised water and 15,0mL of the carbonate-bicarbonate buffer mixture and 0,5mL of Brij 35.

Dilute to 1000mOL with deionised water.

Hydroxylamine ammonium chloride

Dissolve 70g of hydroxylamine ammonium chloride in 800mL deionised water, add 28mL of conc. Sulphuric acid, mix well and make up to 1000mL with deionised water.

EQUIPMENT

Automated system consisting of the following:
Recorder, Colourimeter, Mixing manifold with appropriate coils, Proportioning pump and an automatic sampler.

INTERFRENCES

Persulphate oxidation of organic molecules is slowed in the presence of chloride by the preferential oxidation of chloride; at a concentration of 0,1% chloride, oxidation of organic matter may be inhibited completely. To remove this interference and hydroxylamine ammonium chloride.



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SAMPLING AND SAMPE PREPARATION

Because the detection limit is relatively high, (1 mg/L), polyethylene bottles can be used if it can be shown that the bottles have no influence on the results. Refrigerate samples that cannot be analysed immediately at 4°C. Acidify unstable samples.

ANALYTICAL PROCEDURE

Set up manifold and complete system.
Obtain a stable baseline with all reagents, feeding water through the sample line.

CALCULATION OF RESULTS

Prepare standard curves by plotting peak heights of standards processed through the manifold against DOC concentrations in standards. Compute sample DOC concentration by comparing sample peak height with standard curve.

REFERENCES

AutoAnalyster Applications. AAII Method no. G-107-94.
DOC in Water and Wastewater

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