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

By

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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.

Signature: _____ Date: _____

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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

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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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).

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.

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).

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;

- 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).

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).

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

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.

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

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.

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.

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.

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)

* 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

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.

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

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.

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-

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.

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

to another site for analysis. Efficient desorption from the Tenax occurs with helium flow at 300°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).