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Title: *A Solid Phase Microextraction/Gas Chromatography Method for Estimating the Concentrations of Chlorpyrifos, Endosulphan-Alpha, Endosulphan-Beta and Endosulphan Sulphate in Water*

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A SOLID PHASE MICROEXTRACTION /GAS CHROMATOGRAPHY METHOD FOR ESTIMATING THE CONCENTRATIONS OF CHLORPYRIFOS, ENDOSULPHAN-ALPHA, ENDOSULPHAN-BETA AND ENDOSULPHAN SULPHATE IN WATER

H.A. ADAM

This thesis is dedicated to my loving mother, father and Jasmine who often wonder what I am busy with late at night. Thank you to all of you, as well as close friends and family, for the constant motivation and support throughout my life. Please excuse the delay. It's been long overdue, but well worth the wait.

"If you can fill the unforgiving minute with sixty seconds' worth of distance run, yours is the earth and everything that's in it…"

Rudyard Kipling, 'IF'

Statement

A Solid Phase Microextraction/Gas Chromatography Method For Estimating The Concentrations Of Chlorpyrifos, Endosulphan-Alpha, Endosulphan-Beta And Endosulphan Sulphate In Water

I, Hassan Ali Adam, hereby declare that the work on which this thesis is based is my original work (except where acknowledgements indicate otherwise), and that neither the whole work nor any part of it has been, is being, or is to be submitted for another degree in this or any other Technikon or University.

9 February 2004

Hassan Ali Adam

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Abstract

The monitoring of pesticide contamination in surface and groundwater is an essential aspect of an assessment of the potential environmental and health impacts of widespread pesticide use. Previous research in three Western Cape farming areas found consistent (37% to 69% of samples) pesticide contamination of rural water sources. However, despite the need, monitoring of pesticides in water is not done due to lack of analytical capacity and the cost of analysis in South Africa. The Solid Phase Microextraction (SPME) sampling method has been developed over the last decade as a replacement for solvent-based analyte extraction procedures. The method utilizes a short, thin, solid rod of fused silica coated with an absorbent polymer. The fibre is exposed to the pesticide contaminated water sample under vigorous agitation. The pesticide is absorbed into the polymer coating; the mass absorbed depends on the partition coefficient of the pesticide between the sample phase and the polymeric coating, the exposure time and factors such as agitation rate, the diffusivity of the analyte in water and the polymeric coating, and the volume and thickness of the coating. After absorption, the fibre is directly inserted into the Gas Chromatograph (GC) injection port for analysis.

For extraction from a stirred solution a fibre will have a boundary region where the solution moves slowly near the fibre surface and faster further away until the analyte is practically perfectly mixed in the bulk solution by convection. The boundary region may be modelled as a layer of stationary solution surrounded by perfectly mixed solution. Mass transfer occurs from the sample across the fluid film adjacent to the fibre. The detailed theoretical analysis presented in this thesis demonstrated the analogous relationship between the heat transfer Biot Number and the Mass Transfer Biot Number, in determining the Mass Transfer Biot Number, as well as the importance of the Mass Transfer Biot Number in the mass transfer process.

SPME was evaluated as an analytical method for determining pesticides in water resources, and compared with another analytical technique, i.e. Solid Phase Extraction (SPE). The method was established for chlorpyrifos, endosulphan I (alpha) and II (beta) and endosulphan sulfate. The sensitivity and precision of the method were evaluated using samples taken in areas known to be contaminated with these

pesticides, and spiked laboratory blanks, using a 100 μm Supelco PDMS (Polydimethylsiloxane) fibre. SPME was evaluated by determining the effect of agitation (<625 RPM and absorption time (5-25 minutes) on reproducibility. Optimal experimental conditions included maximum agitation (625 RPM, 20 mm stirrer, 10 ml vial) and absorption time of 25 minutes. The SPME Method Detection Limits determined for the four analytes were found to be 0.01μg/l to 0.02μg/l, substantially lower than for SPE (0.05μg/l to 0.13μg/l). The SPME method reproducibility (95% confidence interval for replicate differences, n = 20) ranged from 3.1% to 4.1% at 1μg/l level, and mass absorbed into the fibre ranged from 40pg to 80pg (at 1μg/l level). The SPME method gave better precision and reproducibility, and was found to be quicker, simpler and less labour intensive compared to the solvent-based Solid Phase Extraction method.

Pesticide contaminant concentrations in surface streams may exhibit marked temporal variation, with time scales ranging from hours to months to that of an agricultural season. Temporal variations in concentration may relate to factors such as spraying and irrigation patterns, rainfall, soil characteristics, local meteorology and occasional spills of the pesticides during mixing. A great deal of data exists demonstrating the daily and seasonal variation, but little data is available on the hourly or diurnal variation of contaminant levels. Comparatively infrequent (typically weekly) grab samples may significantly over- or underestimate average concentrations. A sampling method that yields a Time Weighted Average (TWA) concentration over a comparatively extended period (24 hours or longer) using a single sample would give a more accurate picture of prevailing contaminant levels. One of the objectives of this project was the development of a method to obtain an integrated (TWA) sample, using SPME. The theoretical analysis presented in this report showed that the SPME system could be adapted to obtain a TWA sample of pesticides in water, at concentrations of the order of 1μg/l. The system could be operated with mass loadings of 20-30% of the equilibrium values, with a corresponding increase in method sensitivity (detection limit) providing that the linearity of the mass loading rate through the sampling period was preserved by operating the system at sufficiently low Mass Transfer Biot number for the sample period under consideration.

The preliminary experimental results confirmed that in principle and in a practical environmental setting, the SPME device could be adapted to obtain a TWA sample of the pesticides of interest, over a sampling period of several hours. The field test showed that a TWA sample could be obtained with minimal effort over a comparatively short sampling period of 3 hours. However, the TWA sample result significantly underestimated the average concentrations over a 24-hour sampling period, compared with the average of 24 hourly samples taken over the same period. SPME holds promise as an analytical method for full-scale monitoring of pesticides in water in South Africa.

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List of Nomenclature

Symbol	*Description*	*Units*
C_s	Concentration of the aqueous solution	µg/l
C_f	Concentration of analyte in SPME fibre	µg/l
K_{fs}	Distribution Constant between fibre and sample (dimensionless)	-
m_f	Mass of analyte on fibre	µg
V_f	Volume of SPME fibre	µl
C_0	Initial concentration of analytes in aqueous solution	µg/l
C_H^1	Equilibrium concentration of analytes in the headspace	µg/l
C_S^i	Equilibrium concentration of analytes in the aqueous solution	µg/l
C_f^i	Equilibrium concentration of analytes in the fibre coating	µg/l
V_H	Volume of headspace	L
V_S	Volume of aqueous solution	L
V_f	Volume of fibre coating	L
K_{fs1}	Values at absolute temperatures T_1	-
K_{fs2}	Values at absolute temperatures T_2	-
ΔH	Molar enthalpy change on analyte absorption into the fibre	kJ/kmol
R	Gas constant (in SPME calculations)	J/kmol.K
δ	Boundary Layer thickness	µm
R_d	Reynolds number	-
b	Fibre coating outer radius	µm
Sc	*Schmidt number of the liquid*	-
$u(r)$	Tangential velocity	s^{-1}
R	Radius (half-length) of the stir bar	m
N	Revolutions per second	rpm
D_{aw}	Analyte diffusion co-efficient in the sample	m^2/s

	fluid	
(b-a)	Fibre coating	m
a	Fibre coating inner radius	m
t_e	Equilibration time	s
D_{aw}	Analyte diffusion co-efficient in the sample fluid	m^2/s
C_{TWA}	Time weighted average concentration	µg/l
t_T	Total Time	s
l_f	Fibre Length	M
j	Mass Flux	$kg/m^2.s$
A	Cross-sectional area	m^2
Δx	Diffusion path	m
m_T	Total Mass	µg
R	Volumetric sampling rate (in TWA calculations)	m^3/s
D_s	Diffusivity of analyte in sample medium	m^2/s
D_f	Diffusivity of analyte in fibre coating	m^2/s
u_∞	Velocity of sample medium far from surface of fibre steel shaft face	m/s
$C_{s\infty}$	Sample analyte concentration far from influence of absorbing fibre	µg/l
x_l	Length of fibre	m
j_s	Mass flux in sample	kg/s
C_{si}	Sample concentration at the interface	µg/l
k_c	Mass transfer coefficient	-
j_f	Mass flux in fibre	kg/s
Bi	Biot number	-
h	Heat transfer coefficient	$kW/m^2.K$
L_c	Characteristic length	m
k	Conductivity	W/m.K
t*	Dimensionless time	-
F_0	Fourier Number	-

C^*	Dimensionless concentration	-
R_{ave}	Average volumetric sampling rate	m^3/s
D_{AB}	Diffusivity of substance B through A (water)	cm^2/s
ϕ_B	Association parameter	-
M_B	Molecular mass of solvent B	g/gmol
T	Absolute temperature	K
μ_B	Viscosity of B	cP
V_A	Molal volume of solute A at the normal boiling point	$cm^3/gmol$
δ_f	Film thickness	m
δ_c	Concentration boundary layer	m
x	Distance from the leading edge of the fibre	m
u_∞	Velocity at infinity	m/s
μ	Fluid viscosity	cP
ρ	Fluid density	kg/m^3
r_0	Fibre radius	m
Q	Energy tranfer	kJ/kg.K

List of Abbreviations

SPME	Solid Phase Microextraction
SPE	Solid Phase Extraction
GC	Gas Chromatography
TEL	Tetraethyllead
PAHs	Polycyclic aromatic hydrocarbons
TPH	Total petroleum hydrocarbons
PDMS	Polydimethylsiloxane
MDL	Method Detection Limit
TWA	Time Weighted Average
ECD	Electron Capture Detector
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

Chapter 1: Overview

1.1 Introduction and Background

A 3-year investigation into the presence of pesticides in rural water sources in Western Cape was undertaken with the financial support of the Water Research Commission (WRC) from 1997 to 1999. The study arose out of a concern for the lack of data in South Africa on the presence of pesticides in rural water sources [1]. South Africa is the highest pesticide user in Sub Saharan Africa and available evidence suggest the potential for environmental contamination is high [1,2,3].

The fact that low level exposures to pesticides over prolonged periods are increasingly being suspected of being associated with adverse chronic health impacts, such as cancer, reproductive impacts, immune deficiencies and neurological diseases, attention to the ascertainment of low levels of contamination is important. Queiroz, Silva and Carvalho (2001) [4] reported that due to the widespread use of Organophosphorus pesticides (OPs) in agriculture for crop protection, they have been found in groundwater, surface water and drinking water. In South Africa, data on pesticides in rural water sources are sparse. Previous studies conducted, especially in the Western Cape (South Africa), have found a number of pesticides present in rural water sources [5,6]. Previous local research results have been constrained by relatively high detection limits used in previous analyses [7].

The findings from the previous WRC project [7], conducted during the period from 1997 to 1999, demonstrated a significant spread of detections of pesticides throughout all three regions studied, namely the Hex River Valley, the Grabouw/Vyeboom area, and the Piketberg region, for both Chlorpyrifos and Endosulphan. Concentrations were generally low (between 0.05µg/l and 1µg/l), but there were exceptions with levels in excess of 10µg/l. Chlorpyrifos was detected most frequently in Piketberg, 62 (66%) out of 94 times sampled compared to Hex River, 96 (52%) out of 184 times and Grabouw 51 (49%) out of 104 times. Endosulphan was found most frequently in Grabouw, 72 (69%) out of 104 times compared to Hex River 85 (46%) out of 184 times and Piketberg, 37 (39%) out of 94 times. Of importance is the observation that the problem is not confined to the Hex River but is ever-present in all

three study-areas chosen for investigation. Out of 362 samples, there were 30% detects above the EU limit of 0.1μg/l for Chlorpyrifos and 37% for Endosulphan (London *et al*, 2001) [7]. In general, most organic pollutants of interest in aqueous environmental samples have to be extracted and enriched before their instrumental determination. This isolation of the analyte from a sample is often achieved by sampling and extraction steps separate from the instrumental analysis [8]. Determination of pesticides by chromatographic techniques, such as Gas Chromatograph (GC) analysis, requires an extensive and time consuming step of sample preparation that usually includes the extraction step and a cleaning-up procedure in order to obtain a final extract fully compatible with the chromatographic determination [9].

To extract 1μg/l of an analyte from a 1 litre sample requires about 25ml of solvent, or the ratio of solvent to analyte is about $25*10^6$: 1. The cost of the high purity solvents is significant. The discharge of these solvents into the environment is of concern [10].

In the last few years, several papers have outlined the need for a major simplification of sample preparation procedure. One approach was the miniaturization in scale (microextraction), resulting in a reduction of time and solvent consumption [11]. The introduction of microextraction methods has reduced the problem of chemical emissions into the environment and has been more cost-effective as well. In the microextraction method the solvent and chemical amounts for the extraction were reduced to 1/10 to 1/100 of the amounts used in macro methods [10].

The Solid Phase Extraction (SPE) method is described as being simpler and less time-consuming than classical extraction techniques, which it replaced, as many samples can be enriched in parallel [12,13,14]. Later, it was found that, an optimised selectivity could be achieved by using analyte-specific sorbents for different compounds. By coating the sorbent on a fine rod of fused silica (a fused-silica capillary column, where the polymeric film is on the outside), the limitations of SPE were overcome. This extraction technique, termed Solid Phase Microextraction was introduced in the late 1980's [15]. In 1990, Pawliszyn reported the first SPME device that was commercialised in 1993 by Supelco, together with the coated fibres used for the extraction [9].

Hence, Solid Phase Microextraction (SPME) was developed to address the need to facilitate rapid sample preparation in the laboratory. SPME is based on an immobilized liquid phase (Polydimethylsiloxane - PDMS) as a stationary phase and is used for the direct extraction of organic compounds from water by simply dipping the fibre into the aqueous sample [8]. SPME utilizes a short, thin, solid rod of fused silica that is coated with an absorbent polymer or adsorbent material, to absorb an analyte from a sample. The coated SPME fibre is attached to a metal rod, and a metal sheath that covers the fibre when not in use protects both. Note that it is the polymeric coating that absorbs the analyte rather than the silica fibre, although the literature frequently refers to absorption (or adsorption) into the *fibre* rather than the *fibre coating*. This convention will be followed in this report.

SPME has the advantage over SPE that the solvents are completely eliminated; blanks are greatly reduced, easy handling and high linearity for many analytes [16]. The extraction times may be greatly reduced as well, due to the fact that SPME is fast and simple [8]. SPME, also potentially has, better precision, lower detection limits and is more cost effective than SPE. The SPME method is relatively insensitive to matrix effects if standard parameters, such as pH, are controlled. Therefore, relatively high contents of other organics do not interfere with the extraction. Another advantage of SPME is that the fibres can be used repeatedly, whereas with SPE the activated carbon cartridge is discarded after use [8]. As mentioned before, it is a simple sample preparation method for gas and liquid chromatography (GC and LC) and has been mainly used for the analysis of aqueous samples of environmental pollution [17].

Although the introduction of SPME was first referenced in 1989, it was in 1994 when the first applications on pesticide determination appeared. These first applications were published by Eisert *et al.* [8]. Beltran *et al* [9] estimated that of about 400 references on the SPME technique, approximately 60 of them dealt with pesticide residue analysis. Among the different chemical classes of pesticides, organochlorine and organophosphorous have received major attention over the past few years [9]. Most papers have dealt with the application of SPME to the determination of pesticide residue in water samples, not only because of the environmental relevance, but due to the fact that the technique fits perfectly to extraction of aqueous matrices [9]. The majority of applications for SPME are in aqueous medium and very few in solid medium.

In SPME, the fibre is inserted into the sample, usually contained in a capped glass vial, absorption of the analyte occurs into the fibre coating. The transport of analytes from the matrix into the fibre coating begins as soon as the fibre has been placed in contact with the sample. At 'infinite time' the system reaches a dynamic equilibrium between the analyte in solution and that in the fibre. The distribution ratio between liquid (sample) and polymeric phases is a measure of the position of the equilibrium in the absorption process. The distribution constant may be a function of the concentration of the solute, chemical composition of the solute and the polymeric coating, pH, the temperature and the constituents of the sample [18]. The fibre is then removed from the sample and directly inserted into the sampling port of the Gas Chromatograph (GC), where it is thermally desorbed (i.e. a separation or extraction process that removes mixed organic contaminants using a thermal source) to determine the mass of the analyte.

Quantitation in water analysis by SPME is carried out, as performed in this thesis, by a calibration using external standards prepared with ultrapure water adding a minimum volume of pesticide standard solution and extracting them in the same way as a sample. There is vast number of applications of SPME for the analysis of different pesticides types in water samples [19]. Results from the first inter-laboratory study on pesticide analysis by SPME conducted in 1996, indicated that SPME is an accurate and fast method of sample preparation and analysis [20]. A subsequent study [21] confirmed these statements and added that the results proved that SPME is a reliable technique for quantitative analysis of the pesticide group studied in water [9].

Several papers can be found dealing with pesticide determination in more complex samples such as food samples (e.g. fruit and juices) [22], soil samples [23] and biological fluids (e.g. urine, serum and blood) [24]. When samples other than water are analysed, it is suggested, in most papers, that some sample pre-treatment be performed in order to simplify a sample matrix [9]. SPME has been used in many applications. It has been used in the extraction of polycyclic aromatic hydrocarbons (PAHs) in water [25]; used in the analysis of human breath [26]; applied to the analysis of caffeine in beverages [27]; and used to determine tetraethyllead (TEL) and inorganic lead in water [28].

Phenols have been monitored in industrial and municipal wastewaters and extracted from these waters using SPME. SPME has also been used for pharmaceutical applications [29]. The analysis of non-ionic surfactants (soluble compounds that reduces the surface tension of liquids, or reduce interfacial tension between two liquids or a liquid and a solid), comprising commercial detergents, has also been done using SPME. The surfactants have been linked to effects on the human endocrine system and have been detected in sewage treatment plant effluents.

SPME has been used in the field of fuel related hydrocarbons, particularly total petroleum hydrocarbons (TPH) analysis. This is because the polydimethylsiloxane (PDMS) fibre is an excellent extraction medium for virtually all non-polar hydrocarbons in both water and air. Researchers have also applied other analytical configurations to the determination of familiar compounds i.e. volatile organics have been detected using infrared spectroscopy (which is the use of the absorption, emission, or scattering of electromagnetic radiation by atoms or molecules to qualitatively or quantitatively study the atoms or molecules, or to study physical processes) [29].

For this research, the utility of the SPME fibres was evaluated as an alternative, cost-effective method for monitoring of water systems for the pollution by pesticides [7]. The SPME method was evaluated by establishing the optimum conditions for the sample extraction, assessing the reproducibility and determining the Method Detection Limit (MDL). Extensive laboratory assessment of the SPME fibres was conducted for the recovery and analysis of Chlorpyrifos and Endosulphan, the main pesticides under investigation. Field samples were analysed to confirm that the method could be applied to the real environmental samples.

Pesticide contaminant concentrations in surface streams may exhibit marked temporal variation, with time scales ranging from hours to months to that of an agricultural season. Temporal variations in concentration may relate to factors such as spraying and irrigation patterns, rainfall, soil characteristics, local meteorology and occasional spills of the pesticides during mixing. A great deal of data exists demonstrating the daily and seasonal variation [30], but little data is available on the hourly or diurnal variation of contaminant levels. Comparatively infrequent (typically weekly) grab samples may significantly over or underestimate average concentrations. An accurate assessment of the water quality in a

particular region currently requires a relatively frequent (and costly) sampling regime. The costs of attempting to assess water quality at a number of sites through frequent grab sampling are prohibitive.

In practice, grab sampling at intervals varying from twice per week through to weekly or at greater time intervals is practiced, and average values are inferred from these relatively infrequent samples. For example, the large scale (46 pesticides, 58 sampling sites over 3 years, 2 200 samples) USGS (United States Geological Survey) assessment of the status and trends in the quality of the United States' surface and ground water resources estimated the Time-Weighted Mean concentrations by associating each sample with the time interval halfway to the date of the preceding sample and halfway to the date of the succeeding sample. A sampling method that yields a time weighted average (TWA) concentration over a comparatively extended period (24 hours or longer) using a single sample would give a more accurate picture of prevailing contaminant levels. If the cost of the TWA sampling system is low by comparison with frequent grab sampling or the use of an Autosampler (automated grab sampling over 24 hours), the method would not only yield better data but would have cost advantages as well.

Lowering the cost of sampling and analysis, and more representative (with respect to time-variation) data would enable the implementation of a better water quality assessment, monitoring and management system. One of the specific objectives of this research project was thus to evaluate the utility of solid phase microextraction fibres and a programmable sampler as tools to achieve integrated sampling of water resources being tested for pesticide contamination.

It should be noted that an estimate of contaminant load – the mass flow of contaminants during a specified period - in these streams requires a simultaneous estimate of stream flow rates as well as measurements of contaminant concentrations.

The predominant application of SPME sampling uses the characteristic that, when an SPME fibre is exposed to a sample with analyte concentration C_s, for sufficient time for equilibrium to be reached, the analyte partitions between the sample and the fibre coating in accordance with:

$$C_f = K_{fs} * C_s, \quad \text{..... (1)}$$

Where K_{fs} is the distribution constant.

The concentration of the analyte in the fibre, C_f, is defined by:

$$C_f = m_f / V_f \quad \text{..... (2)}$$

The mass of the analyte on the fibre, m_f, is determined by Gas Chromatography (GC), and hence the fibre concentration and the sample concentration C_s may be calculated using the known fibre volume V_f and Equations 1 and 2. However, the mass-loading rate of analyte into the fibre decreases with time, and approaches zero asymptotically as equilibrium is approached. Thus true equilibrium is only reached at 'infinite time'.

If the K_{fs} value is accurately known and equilibrium is approached to within, say, 5% the sample concentration may be then calculated as follows:

$$C_s = (1/K_{fs}).C_f = (1/K_{fs}).(m_f/V_f). \quad \text{..... (3)}$$

In practice, the GC response for the unknown sample (Detector Counts) is compared to a calibration curve prepared by exposing the fibre to analytical standards of known concentration, under identical exposure conditions (stirrer speed) and for the same time period as for the unknown sample. In contrast, the use of an SPME fibre for the determination of the TWA concentration over a given period is based on sampling under non-equilibrium conditions. Under conditions sufficiently far from equilibrium, the mass-loading rate of analyte into the fibre coating is approximately linear with time and concentration. This unsteady state behaviour of the system, within suitable constraints, may therefore be used to obtain a TWA sample of analyte concentrations. In addition to the mass-loading rate over the sampling period, the retention of the analyte absorbed during sampling and sensitivity to low concentrations are important additional criteria for a quantitative estimate of time weighted average concentrations.

One of the objectives of this project was the development of a method to obtain an integrated (time weighted average) sample, using SPME. The sampling time period was not specified.

The data collected during the course of the project indicated that a sampling system yielding a 24-hour time weighted average sample would eliminate uncertainty as to the representivity, with respect to the 24-hour period, of a daily grab sample. Longer term, but more difficult, objectives would be to obtain a sample representative of the TWA concentration over a 7-day period, and the simultaneous estimate of the peak concentration that may have occurred during the same period.

1.2 Objectives of Project

- To establish and develop the Solid Phase Microextraction (SPME)/ Gas Chromatograph (GC) method, including estimates of reproducibility and method detection limit, for the analysis of Chlorpyrifos and Endosulphan-alpha, Endosulphan-beta and Endosulphan Sulfate at low μg/l levels in water, and to compare these results with other methods for pesticide analyses.

- To use the Solid Phase Microextraction (SPME)/ Gas Chromatograph method for the analysis of Chlorpyrifos and Endosulfan-alpha, Endosulfan-beta and Endosulfan Sulfate in field water samples.

- To develop a dynamic sampling system to enable the estimation of a time weighted average (TWA) concentration over a 24-hour period using a single SPME field sample, and to compare the results with programmable autosampler data.

1.3 Thesis Chapter Content

The outline of this thesis is as follows: Chapter 2 deals with the Solid Phase Microextraction/Gas Chromatography (SPME/GC) method, the theory and kinetics thereof; Chapter 3 deals with the method of estimating Time Weighted Average (TWA) using the SPME technique and explaining the theory and kinetics involved therein; Chapter 4 outlines the materials and methods implemented during the laboratory experiments and testing period of the SPME/GC method as well as the TWA method; Chapter 5 displays the results obtained and Chapter 6 discusses these results and outlines conclusion drawn from there. Chapter 7 discusses some recommendations for use of SPME. The Appendices follows which displays

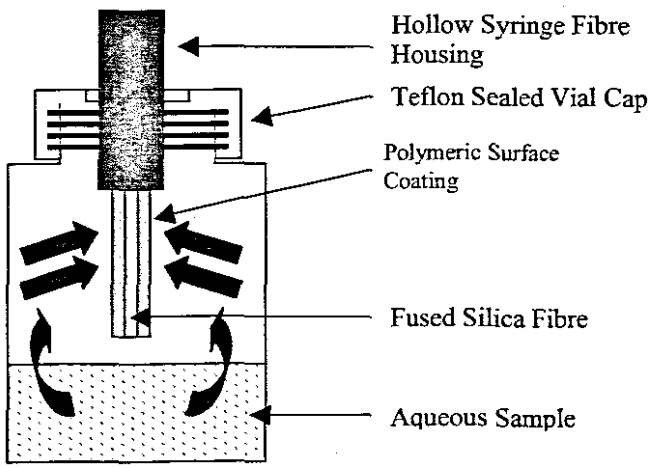
the figures referred to, where applicable, throughout the document. Finally, the list of references used is displayed at end of the thesis.

Chapter 2: Solid Phase Microextraction/Gas Chromatography Theory

2.1 Solid Phase Microextraction (SPME) Theory

When the polymer-coated fibre is inserted into the sample (aqueous), the analytes partition between two phases, namely the fibre-coating phase and the aqueous phase. Transfer of the analyte from the sample to the SPME fibre is an equilibrium process, thus analytes are not completely extracted from the matrix. The liquid polymeric coatings provide a non-exhaustive liquid-liquid or gas liquid extraction. When a sample is placed in a closed vial, equilibrium forms between (1.) fibre coating to aqueous phase (i.e. water sample), (2.) headspace (the space between the surface of the liquid and the vial cap) to aqueous phase, and (3.) fibre coating to headspace. The analyte recovery is related to the overall equilibrium of the three phases that are present in the sampling vial.

Figure 2-1: Diagram of an SPME fibre performing headspace sampling [31]



The distribution of analyte among the 3 phases, after equilibrium, is given by Equation 4:

$$C_0V_S = C_H^iV_H + C_S^iV_S + C_f^iV_f \qquad \text{.....(4) [29]}$$

C_0 is the initial concentration of the analytes in the aqueous solution; C_H^i , C_S^i and C_f^i are the equilibrium concentrations of the analytes in the headspace, aqueous solution and fibre coating, respectively. V_H, V_S and V_f are volumes of headspace, aqueous solution and fibre coating, respectively. It should be noted that if no headspace exists in the closed vial, then the

headspace term ($C_H^i V_H$) is eliminated and the equilibrium is solely formed between the fibre and aqueous solution.

Partitioning between the fibre coating and the aqueous phase is described by a distribution constant (K_{fs}):

$$K_{fs} = C_f / C_s \qquad \text{.....(5) [31]}$$

Where, C_f is the concentration of analyte in the fibre coating and C_s is the concentration of the analyte in the aqueous phase. K_{fs} is the parameter that describes the properties of the fibre coating and its selectivity toward a specific analyte in comparison to other matrix components.

The PDMS coatings used for SPME have strong affinities for organic compounds, therefore K_{fs} values for targeted analytes are usually large and the SPME has a very high concentrating affect and leads to good sensitivity. For example, for a PDMS coated fibre the distribution constants are as follows [31]: Endosulphan-alpha: K_{fs} = 25000, Endosulphan-beta: K_{fs} = 10000, Endosulphan Sulfate: K_{fs} = 400

When the aqueous sample volume (V_s) is much larger than the stationary phase volume (V_f), the following equation is used:

$$m_f = K_{fs} V_f C_s^0 \qquad \text{.....(6) [29]}$$

Where, m_f is the amount extracted by the fibre coating. In general, for comparatively large sample volumes (usually > 5ml, but larger volumes may be necessary for high K_{fs} values), the amount of analyte absorbed by the fibre coating at equilibrium is directly proportional to the initial aqueous concentration; C_s^0, and equation 6 may be used. (The exact sample volume does not have to be known, ideal for field sampling and simplification of laboratory operations).

When sampling from a finite volume, the sample can significantly deplete – the fibre may extract sufficient analyte to reduce the concentration of the remaining sample. The equation to be used to estimate the mass extracted m_f is as follows:

$$m_f = K_{fs} V_f V_s C_s^0 / [(K_{fs} V_f) + V_s] \quad \text{.....(7) [29]}$$

2.2 Determination of the Distribution Constant (K_{fs}) Values

The distribution constant (partition coefficient) is defined by the relationship $C_s = K_{fs}.C_f$, at equilibrium. The time required to approach equilibrium values depends on a set of parameters, including K_{fs}, level of agitation, and boundary layer thickness. The time required to achieve 95% of equilibrium may be of the order of one hour or of the order of several days depending greatly on the K_{fs} value and the boundary layer thickness, which both have an influence on the extraction time and the approach to equilibrium. For the sampling system consisting of the fibre of thickness 100μm fully exposed in the sampling vial, under vigorous stirring, the time required to approach equilibrium may be determined theoretically but during this research the time was determined empirically, and was found to be approximately 2 hours for the analytes under consideration. Thus, the K_{fs} values were estimated by exposing the fully extended fibre in a vial containing 1 μg/l mixed standard solution, under vigorous stirring, for a period of 3 hours.

Previous experimental work [31] demonstrated that the arbitrarily chosen standard concentration of 1μg/l used in these experiments was well above the Method Detection Limit (MDL), and that good reproducibility of analytical results – the measurement of analyte mass (or concentration) on the fibre - could be achieved. The mass of analyte absorbed (the absolute extracted amount) was estimated by comparing the GC response to a calibration curve based on direct injection of a series of standards, that is, by external calibration. Although this is the generally accepted method for measuring the absolute extracted amount, the method has been criticized due to the differences between thermal absorption and liquid injection/vaporisation [32]. The known fibre volume was then used to calculate the concentration in the fibre, and hence the K_{fs} values.

The variation of K_{fs} values with temperature is given by [31]:

$$\frac{K_{fs1}}{K_{fs2}} = \exp\left[\frac{-\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \qquad \text{.....(8)}$$

In this equation, K_{fs1} and K_{fs2} refer to the values at absolute temperatures T_1 and T_2; ΔH is the molar enthalpy change on analyte absorption into the fibre and R is the gas constant. As ΔH is essentially constant over the temperature ranges applicable to SPME work, the percentage change in K_{fs} values with temperature may be estimated using this equation.

K_{fs} is affected by extraction conditions such as salting, pH, as well as temperature. Therefore, when sampling outdoors, the temperature effect must be considered when temperature variations occur. The effect of temperature must be considered when heating is used to increase sample extraction rate as well as to enhance the release of analytes. By using equation 8, a scenario demonstrating the effect of temperature may be illustrated. When a K_{fs} value for an analyte is greater than 1, the ΔH is greater than zero. Equation 8 shows that an increase in temperature should decrease the K_{fs} value [31].

2.3 Kinetics of the Extraction Process

The (analyte) mass transfer process involves the following: (1) Diffusion (in general, by convective and/or molecular processes) through the liquid sample, and (2) molecular diffusion into the fibre coating. One or both processes may be rate limiting, depending on the sampling conditions, the physical and thermodynamic properties of the materials in the system and the dimensions of the system.

The time required for the concentration of the analyte in the fibre coating to approach equilibrium is determined by the rate of mass transfer from the sample to the fibre, and diffusion within the fibre coating. In an agitated system, mixing in the bulk of the liquid is rapid. Mass transfer by molecular diffusion through the boundary layer adjacent to the fibre is a function of the boundary layer thickness. Rapid stirring reduces the boundary layer thickness and hence reduces the absorption time. Mass transfer from the surface of the

coating to the interior is rapid due to the short transfer path (100 μm) and the (usually) high K_{fs} values.

In liquids, diffusion coefficients (diffusivities) are several orders of magnitude lower than in gases. Thus rapid extraction of the analytes in aqueous media requires some form of agitation in order to reduce the boundary layer thickness. Agitation (mixing) of the sample accelerates the rate of mass transfer from the sample to the fibre - effectively reducing extraction times by decreasing the time required to approach equilibrium. No mixing occurs in the stagnant boundary layer adjacent to the fibre, but mixing occurs in the rest of the sample. Mass transfer occurs slowly through the boundary layer. The reproducibility of results is improved if the rate of mixing (usually controlled by the rotational speed of the magnetic stirrer) and the position of the fibre in the vial are the same from sample to sample. After a specified elapsed absorption time, the fibre is retracted back into the sheath and removed from the sampling vial. The sheath is inserted into the injection port of the GC and the plunger is lowered to expose the fibre to a high temperature, where the analytes are thermally desorbed.

Without agitation, extraction time may be of the order of hours [31], and the mass extracted may vary considerably from one analysis to the next (for the same analyte concentration) due to lack of control over the flow conditions in the vicinity of the fibre. The system being used for the experimental laboratory testing may be modelled as an unsteady state problem.

By optimizing the position of the fibre in a stirred sample, the extraction time may be shortened. The thickness of the boundary layer can be estimated from the empirical formulae of fluid mechanics. If the fibre is placed off-centre in the vial so that the fluid flows past the fibre at an angle to the fibre axis, the boundary layer thickness can be estimated using Equation 9:

$$\delta = 9.52\, b/(R_d^{0.62} Sc^{0.38}) \qquad \text{.....(9) [27]}$$

Where, R_d is the Reynolds number ($R_d = 2ub/v$, where u and v are the linear speed of the fluid and kinematic viscosity), b is the coated fibre radius and Sc is the Schmidt number of the liquid (equaling v/D, where D is the diffusion coefficient of the analyte in the liquid.)

The tangential velocity in water agitated by stir bar in a cylindrical container is predicted by using Equation 10 or Equation 11:

$$u(r) = 1.05\pi Nr[2 - (r/0.74R)^2], \text{ for } 0 < r \leq 0.74R \quad \text{.....(10) [31]}$$

$$u(r) = 0.575\pi NR^2 1/r \quad \text{.....(11) [31]}$$

Where, R is the radius (half-length) of the stir bar and N the revolutions per second.

Figure 2-2 illustrates the graphical form of equations 10 and 11 and figure 2-3 graphically illustrates the process by which the analytes move from the aqueous matrix into the SPME fibre.

Figure 2-2: Curve of Tangential Velocity versus r/R

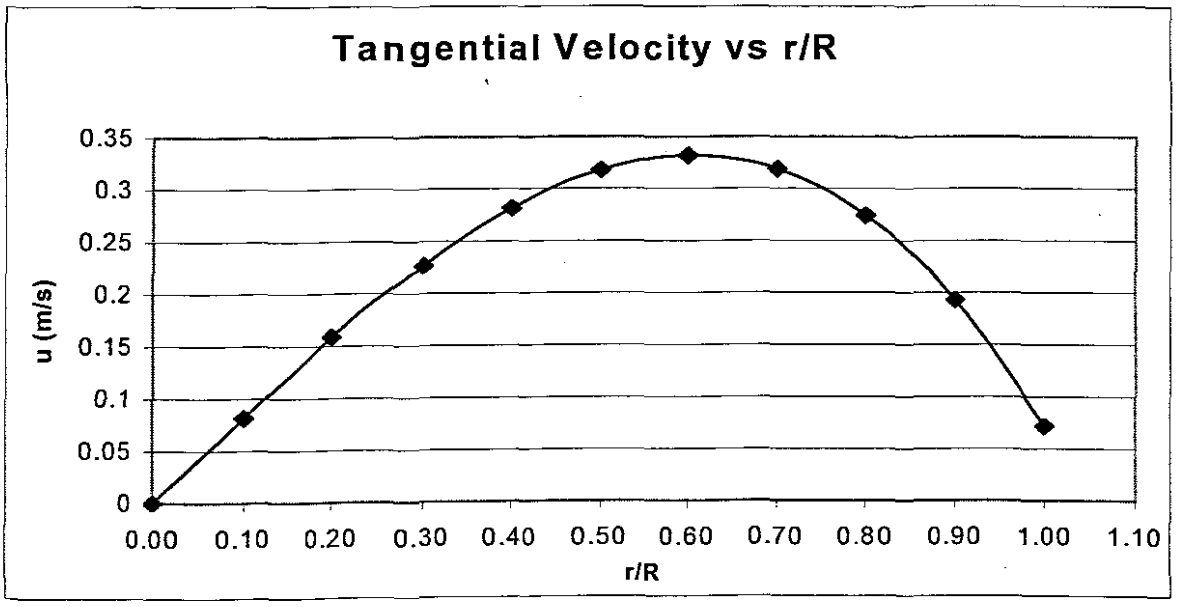


Figure 2-3: Schematic Model of Mass Transfer to the Fibre Coating

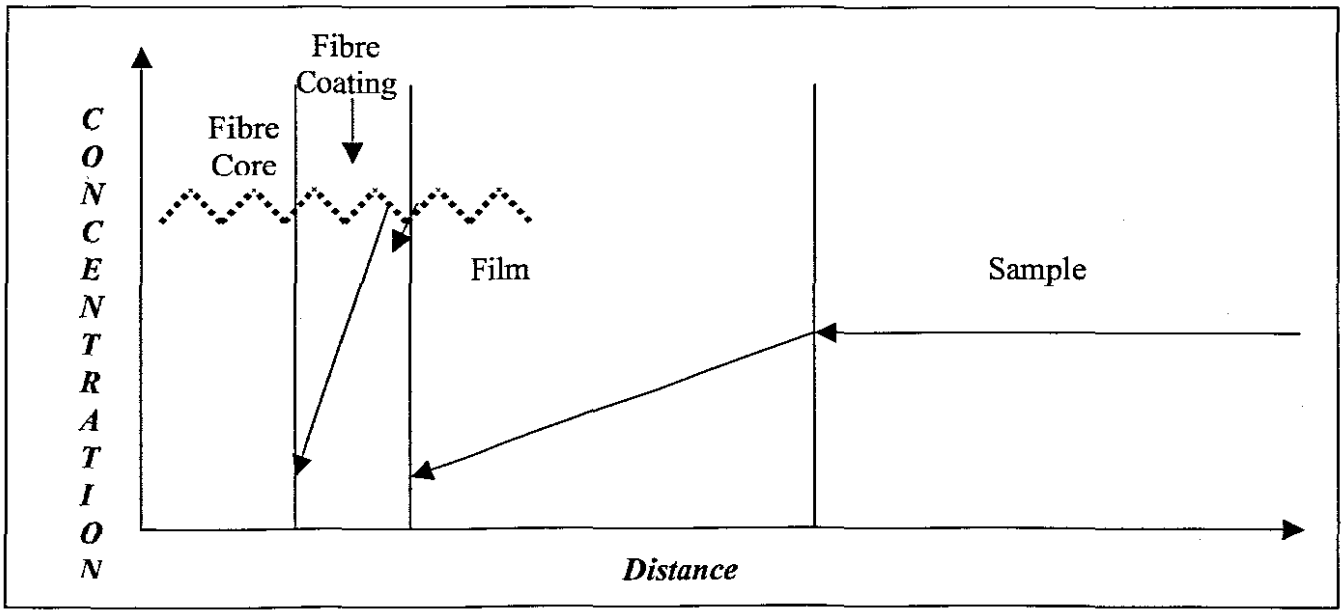
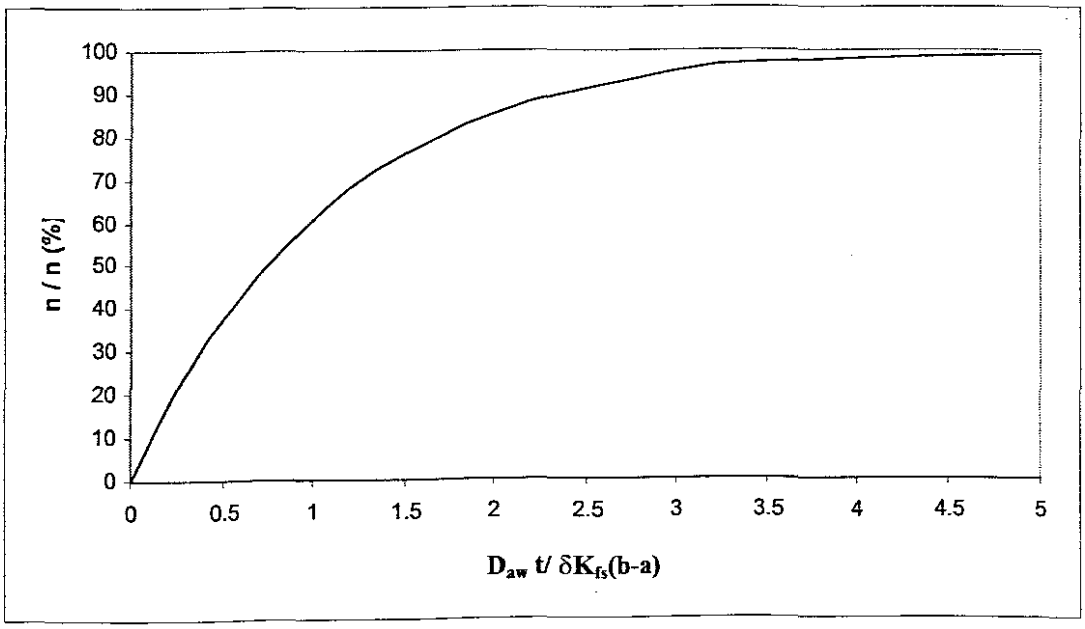


Figure 2-4 is a schematic diagram showing the approach to equilibrium.

Figure 2-4: Rate of Approach to Equilibrium versus Dimensionless Time [29]



In Figure 2-4, the y-axis is the percentage of total analyte mass absorbed by the fibre at equilibrium. As the time increases, the mass absorbed increases. Time is represented as a dimensionless unit, on the x-axis, of the analyte diffusion co-efficient in the sample fluid (D_{aw}), divided by the boundary layer thickness (δ), the distribution constant between the fibre

and sample (K_{fs}), the fibre coating (b-a) where 'a' is the fibre coating inner radius and 'b' is the fibre coating outer radius, and the time to reach equilibrium.

Figure 2-4 indicates that equilibrium is approached asymptotically, implying that the system requires 'infinite' time to reach equilibrium. A change in mass extracted cannot be determined if it is smaller than the experimental error (usually 5 %). The equilibration time is dependent on the K_{fs}, the analyte diffusion co-efficient in the coating. Also, the extraction time will be longer when using thicker fibre coatings because analytes must travel longer and further to completely penetrate the coating. A thicker coating may be chosen to improve sensitivity, but an increase in extraction time may occur. Lastly, a thicker boundary layer will increase extraction time.

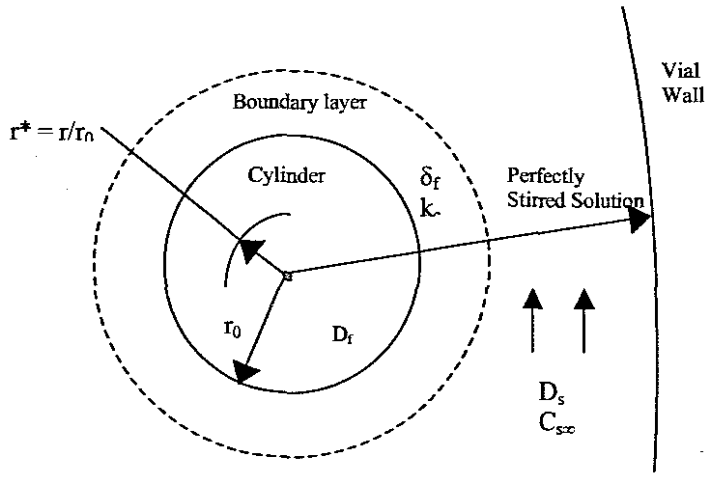
An approximation to the equilibration time, the time required to reach 95% of the equilibrium concentration, for an agitated solution with a boundary layer can be determined using the following equation:

$$t_e = t_{95\%} = 3\delta K_{fs}(b-a) / D_{aw} \qquad \text{.....(12) [29]}$$

Where, δ is the boundary layer thickness, K_{fs} is the analyte's distribution constant between the fibre and sample, *(b-a)* is the fibre coating thickness and D_{aw} is the analyte diffusion co-efficient in the sample fluid. This equation may be used to estimate the equilibration time when the extraction time is controlled by the diffusion of the analyte through the boundary layer.

2.4 Theoretical Analysis of Analytes Diffusing into the SPME Fibre Coating

Figure 2-5: Theoretical SPME Extraction Process: Unsteady Diffusion into an Infinite Cylinder with radius r_0



Nomenclature: D_s and D_f are the diffusivities of the analyte in the aqueous sample medium and the fibre coating respectively. $C_{s\infty}$ is the sample analyte concentration, C_f is the analyte concentration in the fibre and r_0 is the fibre radius.

For extraction from a stirred solution a fibre will have a boundary region where the solution moves slowly near the fibre surface and faster further away until the analyte is practically perfectly mixed in the bulk solution by convection. The boundary region can be modelled as a layer of stationary solution surrounded by perfectly mixed solution. Mass transfer occurs from the sample across the fluid film of thickness δ_f adjacent to the fibre. The concentration boundary layer thickness is δ_c.

Fick's Second Law is derived from the sample unsteady state mass balance, which is:

$$\frac{\partial C_s}{\partial t} = \frac{D_s}{r} \cdot \frac{\partial}{\partial r}\left(r \frac{\partial C_s}{\partial r} \right) \qquad \text{.....(13) [41]}$$

A mass balance around the fibre coating yields:

$$\frac{\partial C_f}{\partial t} = \frac{D_f}{r}.\frac{\partial}{\partial r}\left(r\frac{\partial C_f}{\partial r}\right) \qquad \text{.....(14) [41]}$$

Where, C_f is the concentration at any time $t \geq 0$ and r_0 in the fibre and D_f is the diffusivity of the analyte in the fibre.

Let C_s be the concentration in the sample, $C_{s\infty}$ the concentration at any distance within the sample, C_{s0} the initial concentration of sample in the fibre vicinity ($C_{s0} = 0$), and C_f is fibre concentration. After obtaining equations 13 and 14 (detailed derivation in APPENDIX G), the variables may then be defined in dimensionless form as follows:

Dimensionless Concentrations: $$C_s^* = \frac{C_{s\infty} - C_s}{C_{s\infty} - C_{s0}} \qquad \text{.....(15)}$$

And, $$C_f^* = \frac{K_{fs}.C_{s\infty} - C_f}{K_{fs}.C_{s\infty} - C_{f0}} \qquad \text{.....(16)}$$

Where, $$K_{fs} = C_f / C_s \qquad \text{.....(5)}$$

Dimensionless radius (distance): $$r^* = \frac{r}{r_0} \qquad \text{.....(17)}$$

Dimensionless time: $$t^* = \left(\frac{D_f.t}{r_0^2}\right) \qquad \text{.....(18)}$$

Now, equations 13 and 14 may be expressed in dimensionless form as follows:

$$\frac{\partial C^*}{\partial t^*} = \frac{1}{r^*}.\left[\frac{\partial}{\partial r}.\left(r^*.\frac{\partial C^*}{\partial r^*}\right)\right] \qquad \text{.....(19)}$$

Equations 13 and 14, as well as the dimensionless equation 19, are subject to an initial condition and two boundary conditions, which are as follows:

Initial condition: at $t = 0$, $C_s = C_{s0}$ and $C_f = C_{f0}$

Using the definitions Equations 15, 16 and 18, the dimensionless initial conditions are:

$$t^* = 0,\ C_s^* = 1 \text{ and } C_f^* = 1 \qquad \text{.....(20)}$$

For the fibre, the first boundary condition (BC1) is:

$$\left.\frac{\partial C_f}{\partial r}\right|_{r=0} = 0 \qquad \text{.....(21)}$$

and in dimensionless form:

$$\left.\frac{\partial C_f^*}{\partial r^*}\right|_{r^*=0} = 0 \qquad \text{.....(22)}$$

At the interface, the mass leaving the sample is equal to the mass being absorbed by the fibre. As this is true, the second boundary condition may be based on a mass balance across the fibre-sample interface. The mass flux equation describing the mass transfer from the fluid bulk ($C_{s\infty}$) to the interface (C_{si}) is as follows:

$$j_s = k_c (C_{s\infty} - C_{si}) \qquad \text{.....(23)}$$

Where j_s is the mass flux in the sample, C_{si} is the sample concentration at interface and k_c is the mass transfer coefficient. Equation 23 is based on the idea that mass transfer occurs across a fluid film of thickness δ_f. Note: the mass flux (j) is the rate of mass flow per unit area. $C_{s\infty}$, the concentration at any distance within the sample, is assumed to remain constant or change slowly in relation to the overall response time of the system.

The mass flux j_f in the fibre may be described by Fick's First Law, which states that:

$$\mathbf{j_f = -D_f \frac{dC_f}{dr}} \qquad \text{.....(24)}$$

The mass flux across the interface ($r = r_0$), as well as the mass transfer rates must be equal except with a difference in sign (i.e. $j_s = -j_f$). The second boundary condition (BC2) is then as follows:

$$k_c\left(C_{s\infty} - C_{si}\right) = D_f \left.\frac{dC_f}{dr}\right|_{r=r_0} \qquad \text{.....(25)}$$

Note: at the interface, $r = r_0$ and $C_f = C_{fi} = K_{fs}.C_{si}$. The second boundary condition then becomes:

$$\frac{dC_s^*}{dr^*} = -\frac{k_c.r_0}{K_{fs}.D_f} C_s^*\left(1, t^*\right)$$

$$= -Bi.C_s^*\left(1, t^*\right) \qquad \text{.....(26)}$$

The Mass Transfer Biot number may be defined as the ratio of mass transfer resistance in the fibre to that in the film, where R_{fibre} and R_{film} are analogous to $R_{conduction}$ and $R_{convection}$ (in the heat transfer case), respectively:

$$Bi_{MT} = \frac{R_{fibre}}{R_{film}}$$

Where,

$$R_{fibre} = \frac{r_0}{D_f.K_{fs}}$$

and,

$$R_{film} = \frac{\delta_f}{D_s}$$

The Mass Transfer Biot number may, therefore, be defined as:

$$\mathbf{Bi_{MT}} = \left(\frac{\mathbf{D_s}}{\mathbf{D_f}}\right).\left(\frac{r_0 - r_i}{\delta_f}\right).\left(\frac{1}{K_{fs}}\right) \qquad \text{.....(27)}$$

Where, $(r_0 - r_i)$ refers to the fibre coating radius (fibre coating outer radius – fibre coating inner radius).

The Mass Transfer Biot number is similar to the Biot number for heat transfer, which states that $Bi = \frac{hL_c}{k}$, where h is the heat transfer coefficient, L_c is the characteristic length and k is the conductivity. If the Mass Transfer Biot number is greater than or less than 1, lumped

parameter approximations may be used. For $Bi_{MT} < 0.1$, the resistance to mass transfer in the fibre is negligible compared to that in the aqueous sample. For $Bi_{MT} > 1$, the resistance to mass transfer is negligible in the aqueous sample compared with resistance in the fibre.

To determine the linearity of the SPME fibre response over a set time period, the Mass Transfer Biot number is essential. Exact solutions are therefore required to define conditions needed for linearity with respect to time (for all Mass Transfer Biot Numbers). A solution is given in the form of a dimensionless concentration profile, which is in the form:

$$C^* = \sum_{n=1}^{\infty} C_n . \exp\left(-\zeta_n^2 Fo\right) J_0\left(\zeta_n r^*\right) \quad \text{.....(28) [41]}$$

Where,

$$C_n = \frac{2.}{\zeta_n} \frac{J_1(\zeta_n)}{J_0^2(\zeta_n) + J_1^2(\zeta_n)} \quad \text{.....(29) [41]}$$

And, ζ_n is given by the equation:

$$Bi = \zeta_n \frac{J_1(\zeta_n)}{J_0(\zeta_n)} \quad \text{.....(30) [41]}$$

C_n and ζ_n are both functions of the Mass Transfer Biot Number.

In the heat transfer case, an energy balance for the total energy transfer in the infinite cylinder over a time interval $\Delta t = t$ is as follows:

$$\frac{Q}{Q_0} = 1 - \frac{2\theta_0^*}{\zeta_1} J_1(\zeta_1)$$

Where, θ_0^* is the centreline temperature: $\theta_0^* = C_1 . \exp\left(-\zeta_1^2 F_0\right)$

In the mass transfer case, the similar situation applies, but θ_0^* is substituted for C_0^* and $\frac{Q}{Q_0}$ is substituted with $\frac{m}{m_0}$. The mass balance for the total mass transfer into the fibre is as follows:

$$\frac{m}{m_0} = 1 - \frac{2C_0^*}{\zeta_1} J_1(\zeta_1) \qquad \text{.....(31)}$$

The values of the coefficients C_1 and ζ_1 are listed in Incropera [41]. The quantities J_1 and J_0 are Bessel functions of the first kind and their values are tabulated in Incropera [41]. Bessel functions are found for systems with cylindrical symmetry. These functions are found when solving wave equations.

Equation 31 may be plotted in order to determine the linearity range of mass absorbed into the fibre with respect to time for a range of Mass Transfer Biot numbers. From the plot in Figure 2-6 (dimensionless mass onto fibre versus time in minutes), as well as Figure 2-7 (all dimensionless axes), it is observed that the rate of mass absorption is strongly influenced by the Mass Transfer Biot number, which in turn is a strong function of the K_{fs} value. The graphs in both figures illustrate that in the case of the $Bi_{MT} > 10$, the diffusion in the fibre is the controlling parameter for rate of extraction. If the Bi_{MT} is between 0.5 and 0.1, both the diffusion in the fibre and diffusion in the aqueous solution are controlling parameters. However, if $Bi_{MT} < 0.1$, the diffusion in the aqueous solution is the controlling parameter. The trend of the curves, in both Figures 2-6 and 2-7, is similar to that of Figure 2-4.

Figure 2-6: Mass transfer to fibre vs time
Parameter: Biot Number {Bi = $[D_s/D_f]*[r_o/\delta_f]*[1/K_{fs}]$}

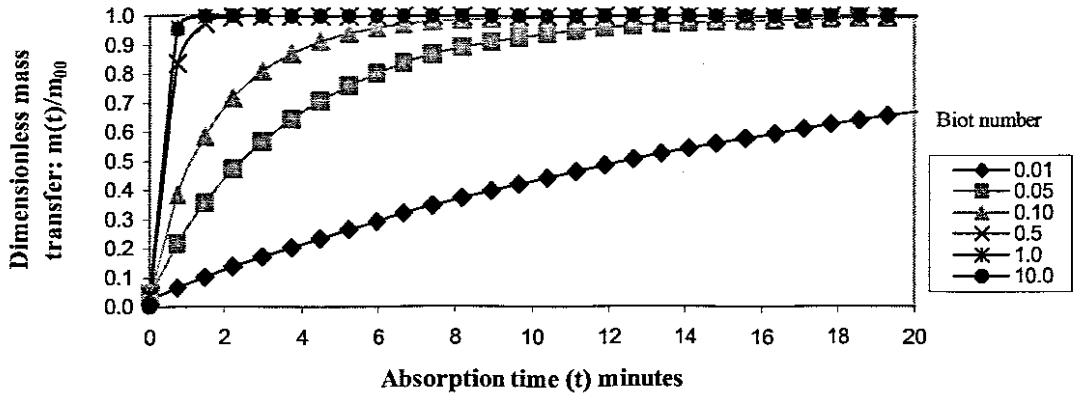


Figure 2-7: Mass transfer to fibre vs dimensionless time
Parameter: Biot Number {Bi = $[D_s/D_f]*[r_o/\delta_f]*[1/K_{fs}]$}

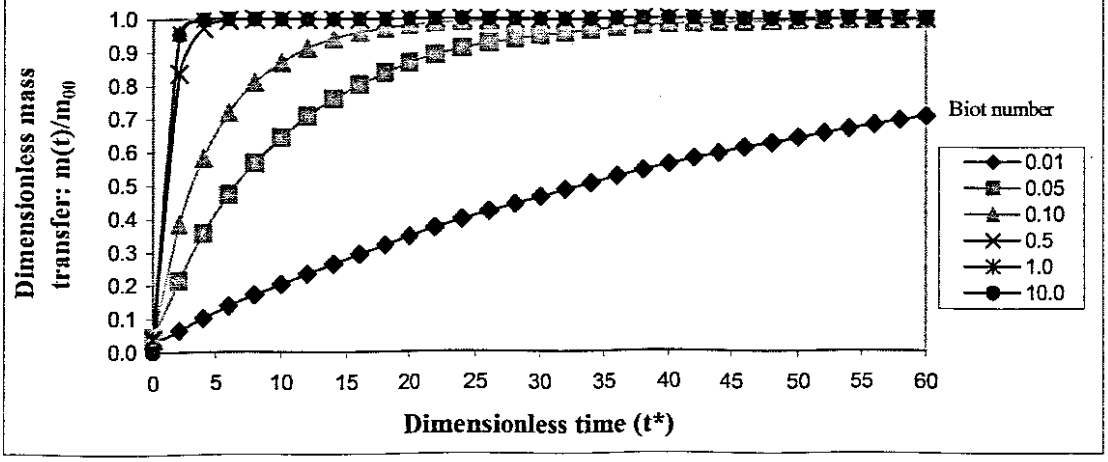
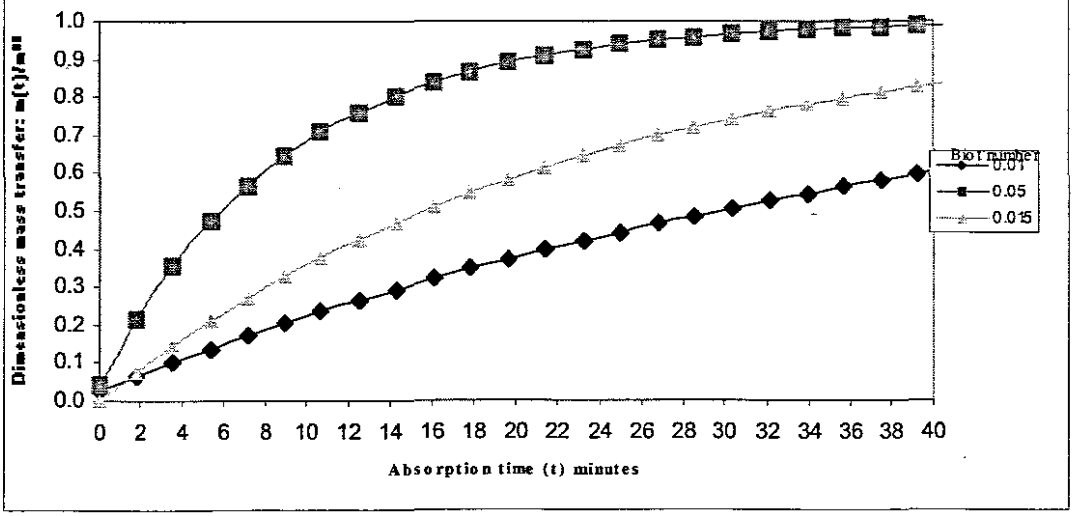


Figure 2-8: Mass transfer to fibre vs time

Parameter: Biot Number $\{Bi = [D_s/D_f]*[r_o/d_f]*[1/K_{fs}]\}$



2.5 Gas Chromatography (GC) Theory

2.5.1 Gas Chromatography (GC)

Gas chromatography is a sensitive and selective method for the qualitative and quantitative determination of substances that are stable in the vapour phase. Gas chromatography is based on phenomenon that occurs when a mixture of volatile materials is transported by a carrier gas eluent through a column containing an absorbing material coated on a solid material. Each volatile component is partitioned between the stationary phase and carrier gas. The length of time required for a volatile analyte to pass through the column depends upon the degree to which it is retained by the stationary phase. The time at which an analyte emerges, and its quantity may be measured via suitable detectors.

The gas chromatograph consists of different components. The carrier gas is a gas constituting the mobile phase. It must be very pure and is generally argon, helium, nitrogen or hydrogen. This gas must be chemically unreactive toward the sample and chromatograph components. A sample is injected as a single compact plug into the carrier gas stream immediately ahead of the column entrance. If the sample is liquid, it is important to heat the injection chamber to vapourize the liquid quickly, otherwise tailing occurs, which in turn causes spreading of the peak. If the sample is heated too much, thermal decomposition may occur and produce inaccurate results.

The column, through which the carrier gas and analyte species flow and in which separations occur, is the key component of the gas chromatograph. Superior results are usually obtained with a capillary column consisting of a very long, small-diameter quartz tube with the stationary liquid phase coated on the inside of the column. A column is usually chosen for its ability to separate compounds in a group of compounds from each other.

A component that primarily determines the sensitivity of gas chromatographic analysis, and the selectivity as well is the detector. The detector shows when an analyte peak is emerging from a column and responds to the quantity of the analyte in the peak.

2.5.2 Electron Capture Detector (ECD)

The principle of the ECD is that some organic compounds take up electrons in an ionized gas (particularly those compounds containing Chlorine, and Fluorine) [33], changing a current flowing through the gas. With the ECD, the carrier gas is passed over material containing a radioactive element that emits electrons (β-emitter). β-Emitters used for this purpose may be Nickel-63 [34] or tritium adsorbed on platinum or titanium foil. Electrons from the β-emitter ionize the carrier gas causing more electrons to be released. The carrier gas is then electrically conducting. When a solute, that is capable of picking up electrons, is present in the carrier gas, the number of free electrons is decreased and the current is therefore decreased.

ECD has an insensitivity toward hydrocarbons, which means that ECD-detectable compounds may be measured in high-hydrocarbon backgrounds. ECD does not respond to alcohols or amines either. The detector is non-destructive and sample peaks may therefore be collected after detection [35].

Chapter 3: Time Weighted Average

3.1 Prior Work Using SPME to Determine the Time Weighted Average Concentration of Air Contaminants, Based on the Steady State Assumption

Thus far, attempts to use SPME to obtain a TWA sample have focused on the analysis of volatile or semi-volatile compounds (e.g. hydrocarbon mixtures) in air [36,37,38], based on the following theoretical approach.

Consider a stream with time varying pollutant concentration, C(t). The Time Weighted Average Concentration, C_{TWA}, over a total time period t_T, for a medium with time varying concentration C(t), may be defined as:

$$C_{TWA} = \frac{1}{t_T}\int_0^{t_T} C(t)dt \qquad \text{.....(32)}$$

Continuous measurements of concentration are generally not available, and the TWA concentration is calculated by taking a number of grab samples (say n samples), with measured concentrations C_i, at time intervals t_i. The time intervals are not necessarily equal, and each sample is assumed to be representative of the interval between samples. The TWA Concentration is then approximated by:

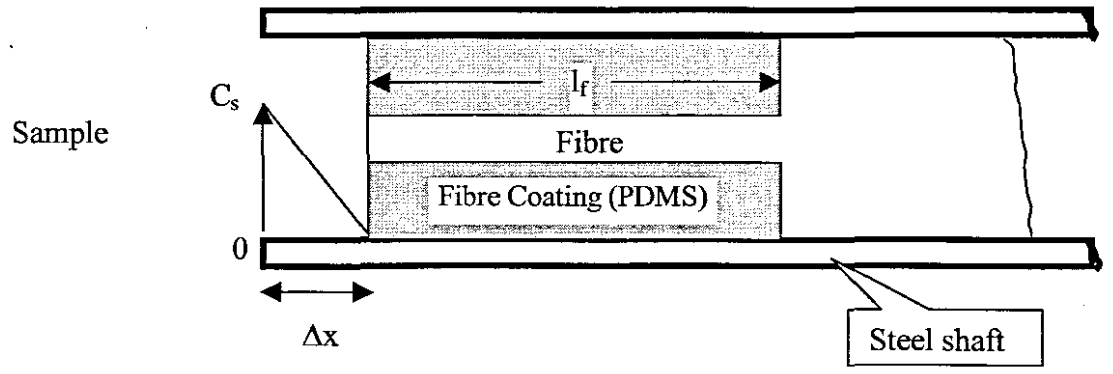
$$C_{TWA} = \frac{\sum_{i=1}^{n} C_i t_i}{\sum_i t_i} \qquad \text{.....(33)}$$

The total time over the sampling period is $t_T = \Sigma t_i$.

Martos and Pawliszyn [36] (and other researchers [37]) demonstrated that the SPME fibre could be used as a passive (diffusive) sampler to obtain the time weighted average concentrations of volatile and semi-volatile compounds in air. In these applications, the device was operated in pseudo-steady state mode and the steady state assumption was made to estimate the TWA concentration.

This approach used the arrangement shown in Figure 3-1:

Figure 3-1: SPME Arrangement for Time Weighted Average Sampling, using a Retracted Fibre



The concentration at the face of the steel shaft was assumed to equal the free stream concentration $C_{s\infty}$ (the 'free stream concentration' is the concentration far from the influence of the fibre, at an 'infinite distance from the fibre) and the concentration was assumed to be approximately zero at the fibre-sample interface. The fibre, length l_f, was retracted a distance Δx into the steel shaft. Under these pseudo steady state conditions, Fick's First Law was assumed to be valid. The conditions are pseudo steady state in the sense that the concentration at the interface is clearly increasing with time, but the time dependent change is much slower than that which occurs immediately after the fibre is exposed to the sample.

Hence, for analyte diffusivity in the sample D_s, constant (mass) concentration gradient dC/dx and (mass) flux **j**, Fick's First Law is:

$$j = -D_s \frac{dC}{dx} \qquad \text{.....(34)}$$

The flux j has units of mass/(time*area).

For constant cross-sectional area A,

$$j = \frac{1}{A}\frac{dm}{dt} = -Ds\frac{dC}{dx} \qquad \text{.....(35)}$$

The rate of mass transfer to the fibre is implicitly controlled by diffusion in the sample phase. The finite diffusion path Δx may be fixed by withdrawing the fibre into the steel sheath and assuming that, for relatively short sampling times the concentration at the fibre–sample interface is approximately zero, hence the sampling rate or mass loading rate dm/dt, with units of mass/time, may be approximated by:

$$\frac{dm}{dt} = \frac{A.Ds}{\Delta x}(C_s - C_i) = R(C_s - C_i), \qquad \text{.....(36)}$$

Where, R = A.Ds/Δx is the volumetric sampling rate, with units of volume/time.

If the interfacial concentration C_i = 0, the mass loading rate (mass sampling rate) is proportional to the sample concentration C_s, and is given by

$$\frac{dm}{dt} = \frac{A.Ds}{\Delta x}(C_s) = R.C_s. \qquad \text{.....(37)}$$

In practice, the factor R, the volumetric sampling rate is determined empirically by measuring the mass loading rate for a known concentration C_s.

The total mass m_T absorbed onto the fibre to time t_T is thus given by:

$$m_T = R.\int_{t=0}^{t_T} C_{s\infty}(t)dt \qquad \text{..... (38)}$$

The sampling rate is measured empirically by exposing the fibre to a standard solution or solutions, for increasing time periods. The total mass loaded onto the fibre, m_T, is determined by GC analysis. The GC calibration curve is prepared using direct injection of standards.

Hence the mass m_T may be determined directly and the TWA, for a given exposure time t = t_T, may be calculated using equations 32 and 38:

$$C_{TWA} = m_T/(R.t_T)$$

Martos and Pawliszyn [36] recommended that the application of this analysis be restricted to a fibre loading of less than 5% of the equilibrium loading value. While this is consistent with the assumption that the concentration at the interface is approximately zero, it is clearly a

significant restriction since it reduces the sensitivity of the method – the overall sensitivity of the method is directly related to the total mass loaded onto the fibre.

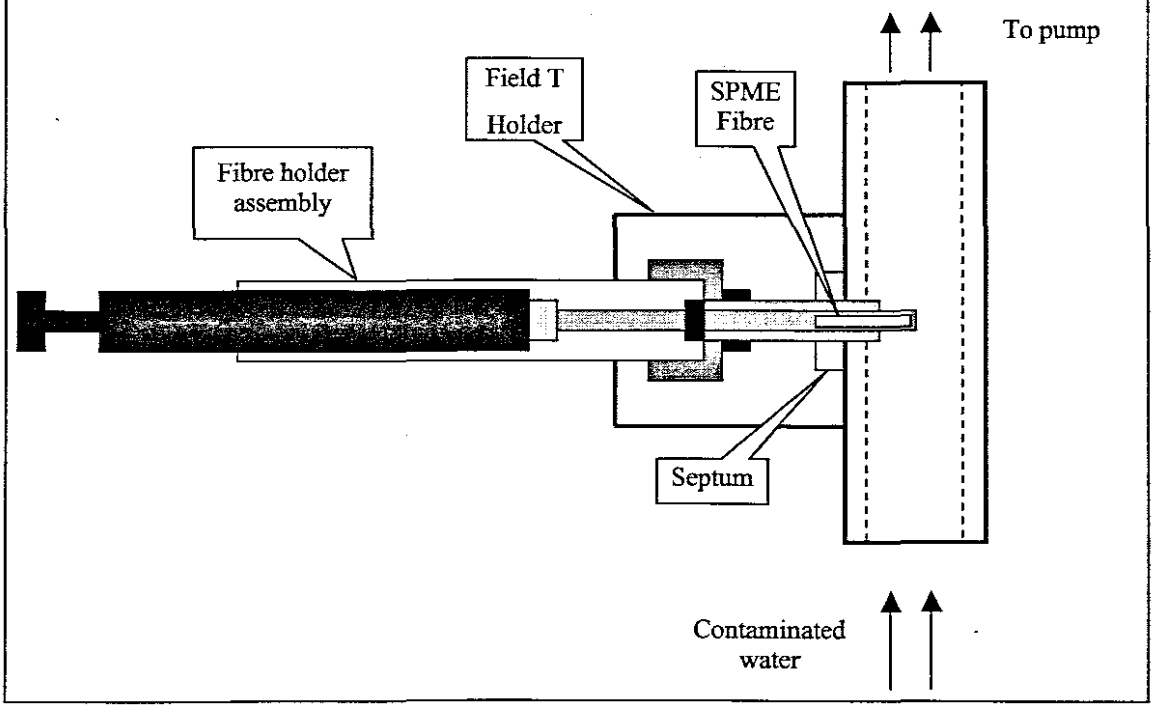
3.2 The Theoretical Basis for the Application of SPME to Obtain a TWA Concentration of Pesticides (analytes) in Water

The application of SPME to the TWA sampling of pesticides in water has to contend with factors significantly different compared with the sampling of air pollutant concentrations. Diffusivities in water are two to four orders of magnitude lower than diffusivities in air [39]; analyte concentrations may be two to three orders of magnitude lower, of the order of 0.1 to 10 ppb compared with several hundred ppb, as well. A theoretical framework that restricts the sampling method to 5% of the equilibrium fibre concentration would not produce the required sensitivity at low contaminant concentrations. A more detailed theoretical framework is required to determine feasible experimental or operating conditions, and the limitations of the method, for the application of SPME to TWA sampling.

The proposed experimental sampling device is similar to that used for air sampling, except that the fibre may be positioned flush with the entrance of the steel shaft, or retracted by distance Δx from the entrance of the steel shaft (see Figure 3-1).

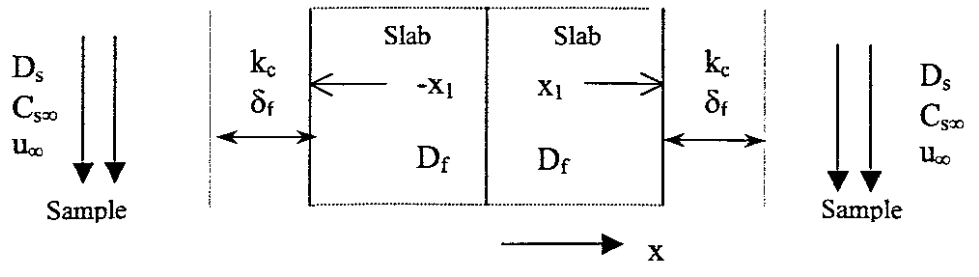
The fibre holder is located in a custom-made field sample 'T' holder that is designed to protect the fibre and to enable a well defined velocity field to be created past the sampling device, as shown in Figure 3-2.

Figure 3-2: Schematic diagram of the field sampling device



In TWA air sampling, the fibre holder with retracted fibre is simply exposed to the air being sampled. For TWA sampling in water, a defined flow field past the retracted fibre is required. (The need for a defined flow field past the steel sheath housing the fibre created by the flow induced by a pump (Figure 3-2) is clarified in the analysis below.) The theoretical analysis of the system is based on the model depicted in Figure 3-3.

Figure 3-3: Theoretical model for the sampling system: Unsteady diffusion into an infinite slab of thickness $2x_1$



Nomenclature: D_s and D_f are the diffusivities of the analyte in the sample medium (water) and the fibre coating respectively, u_∞ is the velocity of the sample medium far from the surface of the face of the steel shaft, $C_{s\infty}$ is the sample analyte concentration far from the

influence of the absorbing fibre, C_f is the analyte concentration in the fibre and x_1 the length of the fibre.

The theoretical model assumes that symmetrical diffusion from both sides of the infinite plate occurs. By symmetry, no mass transfer across the centreline occurs. This models mass transfer into a fibre of length x_1, with no transfer beyond the end of the fibre. Mass transfer occurs from the sample across the film of fluid of thickness δ_f adjacent to the fibre face. The concentration boundary layer thickness, the distance to a point at which the concentration reaches 99% of the free stream sample concentration $C_{s\infty}$, is designated δ_c, and the film thickness is δ_f. The concentration gradient at $x = \delta_c$ is by definition negligible and thus no mass transfer occurs in the x direction across the concentration boundary layer. Molecular mass transfer in the direction of flow is assumed to be negligible by comparison with convective mass transfer (that is, mass transfer due to the bulk fluid motion) in the flow direction. In all the situations under consideration, the flow is well within the laminar flow regime. (Convective mass transfer may occur in laminar flow – it should not be assumed to be mass transfer due to turbulence in the flow.)

Fick's Second Law may be derived from an unsteady state mass balance in the sample:

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} \qquad \text{.....(39) [41]}$$

Similarly, a mass balance over a shell perpendicular to the x direction in the slab, the analogue for the fibre coating, yields:

$$\frac{\partial C_f}{\partial t} = D_f \frac{\partial^2 C_f}{\partial x^2}. \qquad \text{.....(40) [41]}$$

In Equation 40, C_f is the concentration at any time $t >= 0$ and point x in the fibre, and D_f is the diffusivity of the analyte in the fibre. The subscripts s and f refer to the sample phase (typically air or water) and the fibre coating phase respectively; the subscript 'i' refers to the interface and '∞' refers to infinity with respect to distance from the fibre face.

Let C_s be the concentration in the sample, $C_{s\infty}$ the free stream concentration, C_{s0} the initial concentration of the fibre and the sample in the vicinity of the fibre ($C_{s0} = 0$), C_f the fibre

concentration, C_{fCL} the fibre concentration at the model centreline corresponding to the end of the fibre and C_{fi} the concentration at the interface on the fibre side.

At the interface: $C_{fi} = K_{fs}*C_{si}$. As before, K_{fs} is the distribution constant.

The following dimensionless variables may then be defined [40]:

Dimensionless concentrations: $Cs^* = \frac{Cs_\infty - Cs}{Cs_\infty - Cs_0}$ and $C_f^* = \frac{K_{fs}.Cs_\infty - C_f}{K_{fs}.Cs_\infty - C_{f0}}$. .....(41)

Dimensionless distance: $x^* = x/x_1$ .....(42)

and dimensionless time: $t^* = (D_f t/x_1^2)$ or $t^* = (D_s t/\delta_f^2)$ .....(43)

Equations 39 and 40, expressed in terms of these dimensionless variables, become:

$$\frac{\partial C^*}{\partial t^*} = \frac{\partial^2 C^*}{\partial x^{*2}} \qquad .....(44)$$

Note that the dimensionless distance and time may equivalently be expressed in terms of any characteristic length other than x_1. The differential Equations 39 and 40, and the dimensionless equivalent Equation 44, are subject to the following conditions.

The initial condition is:

At t=0, $C_s = C_{s0}$, $C_f = C_{f0}$. That is, at $t^* = 0$; $C_s^* = 1$ and $C_f^* = 1$ . .....(45)

For the fibre, the first boundary condition, BC1, is:

$$\frac{\partial C_f}{\partial x} = 0\Big|_{x=0}, \text{ (i.e. by symmetry)} \qquad .....(46)$$

That is, the concentration gradient at the centreline is zero and no mass transfer occurs across the centreline.

Therefore this boundary condition, expressed in terms of dimensionless variables, becomes:

$$\frac{\partial C_f^*}{\partial x^*} = 0\Big|_{x^*=0}. \qquad \ldots\ldots\ldots (47)$$

The second boundary condition, BC2, is based on a mass balance across the fibre-sample interface. At the interface, the mass leaving the sample is equal to the mass being absorbed by the fibre. Thus BC2 is derived from the following relationships.

The pseudo steady state mass flux equation describing mass transfer from the bulk of the fluid (at concentration $C_{s\infty}$) to the interface (at concentration C_{si}) is:

$$j_s = k_c\,[C_{s\infty} - C_{si}]\,; \qquad \ldots\ldots\ldots (48)$$

Where, $\mathbf{j}_s$ is the mass flux in the sample, C_{si} the sample concentration at the interface and k_c is the mass transfer coefficient. Equation 48 is based on the concept that mass transfer is occurring across a film of fluid, of thickness δ_f (See Figure 3.3) The concentration boundary layer occurs, by definition, at the distance from the interface at which the concentration reaches 99% of the free stream concentration $C_{s\infty}$. The boundary layer thickness is not constant across the interface. A detailed analysis of the boundary layer shows that the film thickness, $\delta_f = (2/3)\delta c$ [39]. In laminar flow, $k_c = D_s/\delta_f$. Note that the flux **j** is the rate of mass flow per unit area.

The sample free stream concentration $C_{s\infty}$ is assumed to remain constant or to change slowly in relation to the overall response time of the system. For the situations under consideration, the interfacial concentration changes slowly compared with the initial transient response. This is the pseudo steady state assumption. The equation thus expresses the mass flux from the sample fluid across the interface under the specified conditions.

The mass flux $\mathbf{j}_f$ in the fibre may be described by Fick's First Law:

$$j_f = -D_f \frac{dC_f}{dx} \qquad \text{..... (49)}$$

At the interface ($x=x_1$), the mass flux (mass transfer rate per unit area) across the interface and therefore the mass transfer rates (the area refers to the same interfacial area) must be equal but opposite in sign; i.e., $j_s = -j_f$.

Thus the second boundary condition, at the sample-fibre interface, is:

$$k_c[C_{s\infty} - C_{si}] = +D_f \frac{dC_f}{dx}\Big|_{x=x1} \qquad \text{..... (50)}$$

At the interface, $x=x_1$ and $C_f = C_{fi} = K_{fs}.C_{si}$. The second boundary condition (BC2) then becomes:

$$\frac{dCs^*}{dx^*} = -\frac{k_c.x_1}{K_{fs}.D_f} Cs^*(1,t^*) = -Bi^* Cs^*(1,t^*) \qquad \text{..... (51)}$$

In laminar flow, $k_c = \frac{D_s}{\delta_f}$**. Therefore, in Equation 51 the Mass Transfer Biot Number (Bi_{MT}) is defined by:**

$$\mathbf{Bi_{MT}} = \frac{k_c.x_1}{K_{fs}.D_f} = \left(\frac{D_s}{D_f}\right)\left(\frac{x_1}{\delta_f}\right)\left(\frac{1}{K_{fs}}\right). \qquad \text{..... (52)}$$

The Mass Transfer Biot Number may be interpreted as the ratio of the mass transfer resistance in the fibre, $R_{fibre} = \frac{x_1}{D_f.K_{fs}}$, to that in the film, $R_{film} = \frac{\delta_f}{D_s}$. That is, $\mathbf{Bi_{MT}} = \frac{\mathbf{R_{fibre}}}{\mathbf{R_{film}}}$.

Note that, in the initial transient period (of the order of seconds) the system behaves as if it is far from its boundaries and the Mass Transfer Biot number during this period is given by:

$$Bi = \left(\frac{D_s}{D_f}\right)\left(\frac{1}{K_{fs}}\right) \qquad \text{.....(53)}$$

The Biot Number for mass transfer is analogous to the Biot number for heat transfer, namely $Bi = hL_c/k$, where h is the heat transfer coefficient, L_c a characteristic length and k the

conductivity. Equation 44, with the initial condition (Equation 45) and the boundary conditions (Equations 46 and 50) are identical to the corresponding heat transfer equations. The dimensionless time t* corresponds to the Fourier Number F_0. Thus the solutions to this set of equations (Equations 44, subject to 45, 47 and 51) are identical to the corresponding solutions to the heat transfer equations [41].

If the Mass Transfer Biot number <<1 or >> 1, lumped parameter approximations may be used. In the mass transfer situation under consideration, Bi_{MT} <<1 (say <0.1) infers that the resistance to mass transfer in the fibre is negligible compared to that in the sample fluid. For Bi_{MT} >>1 (say Bi_{MT} >10), the inference is that the resistance to mass transfer in the sample fluid is negligible compared with resistance in the fibre. In each of these special cases, simplified expressions for the concentration profiles and the mass transfer rate in the system may be obtained, as given, for example, by Pawliszyn for the case of mass transfer to a cylindrical fibre placed perpendicular to the flow field [31].

The Mass Transfer Biot Number is important in the estimation of the linearity of the response of SPME fibre over a given time period. Thus, to define the necessary conditions for linearity with respect to time, the generally applicable (for all Mass Transfer Biot Numbers) exact solutions to the problem are required.

One solution to Equation 44 and the associated initial condition and boundary conditions is in the form of an infinite series involving sine and cosine functions. The dimensionless concentration profiles given by this series are [40]:

$$C^* = \sum_{n=1}^{\infty} C_n \exp[(-\xi_n^2 . t^*)(\cos \xi_n . x^*)] \qquad \text{.....(54)}$$

Where,

$$C_n = \frac{4.\sin\xi_n}{2.\xi_n + \sin(2.\xi_n)} \qquad \text{.....(55)}$$

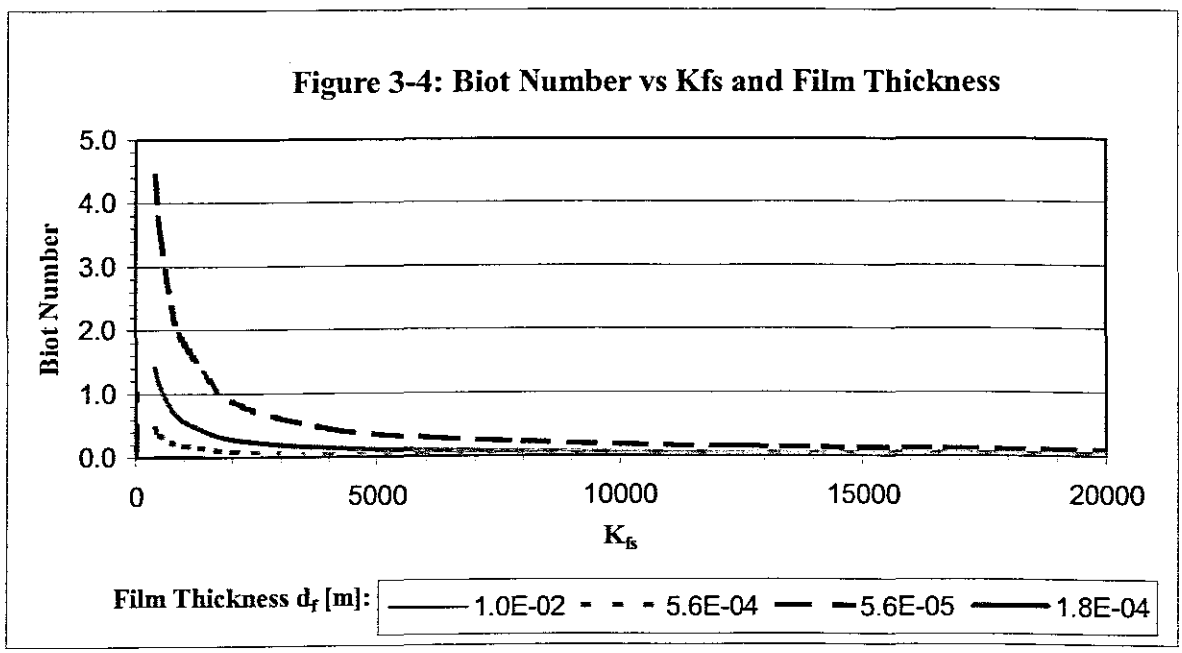
And, ξ_n is given by: $\xi_n . \tan(\xi_n) = Bi$ .....(56)

Note that the concentration at the interface, C^*_i, occurs at $x_1^*=1$. Thus Cos(0) = 1 in Equation 54, at the interface.

The second boundary condition implies that the free stream concentration of the sample, $C_{s\infty}$, remains constant throughout the sampling period. A theoretical analysis that allows $C_{s\infty}$ to vary with time, a situation representative of real-time environmental sampling, is possible but would introduce considerable additional complexity into the theoretical solution. Instead of a rigorous theoretical analysis including a time-varying $C_{s\infty}$, the underlying assumption was made that the sampling system behaves as if it is exposed to a series of discrete exposures $C_{s\infty,i}$ for time intervals t_i, and that the mass transferred to the fibre during each of these exposures is additive. The validity and limitations of this assumption must be tested experimentally. The assumption is in any case not valid if the concentration $C_{s\infty,i}$ drops below the interfacial concentration C_{si}.

For given values of D_s, D_f and x_1, the Mass Transfer Biot number may be plotted against the distribution constant K_{fs} and film thickness δ_f as in Figure 3-4.

Figure 3-4: Biot Number vs Kfs and Film Thickness



The range of film thickness values used in Figure 3.4 corresponds to different sample flow velocities past the fibre.

The ratio of mass transferred at time t or t* (m) to the equilibrium mass transferred (m_∞) is given by:

$$\frac{m(t^*)}{m_\infty} = 1 - \sum_{n=1}^{\infty} [C_n.\exp(\xi_n^2.t^*)].\frac{\sin\xi_n}{\xi_n} \qquad \text{..... (57)}$$

Where, the constants C_n and ξ_n are functions of the Mass Transfer Biot number.

This analysis is not necessarily restricted by the approximation that $C_i \sim 0$, or $C_i < 5\%$ of $C_{s\infty}$. Thus, Equation 36, rather than the approximation given by Equation 37, must be used to estimate the total mass transferred to the fibre over the sampling period.

The sampling rate is given by:

$$\frac{dm}{dt} = \frac{A.D_s}{\Delta x}(C_s - C_i) = R.(Cs - Ci) \qquad \text{.....(36)}$$

The total mass loaded into the fibre is then given by:

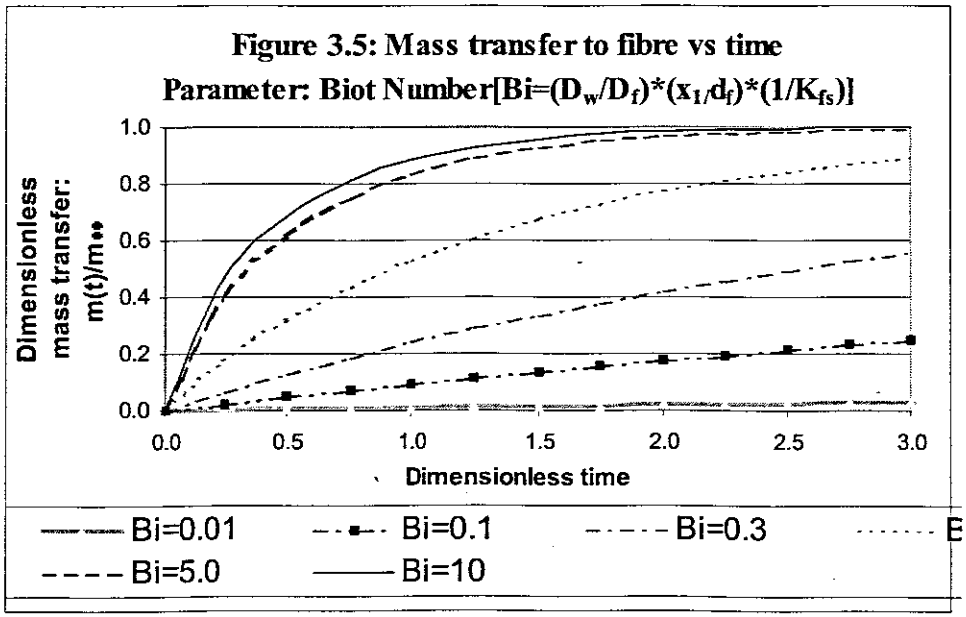
$$m_T = R.\int_{t=0}^{tT} [C_{s\infty}(t) - C_i(t)]dt \qquad \text{..... (58)}$$

Since the concentration difference (the mass transfer driving force) is assumed to be approximately linear with respect to time for the conditions under consideration, an average volumetric sampling rate R_{ave} over the sampling period may be approximated by the relationships:

$$m_T = R_{ave}.\int_{t=0}^{tT} C_{s\infty}(t)dt\,; \qquad \text{..... (59)}$$

The average volumetric sampling rate is the arithmetic average over the time period, $R_{ave} = 0.5(R_0+R_{tT})$. As before, m_T may be measured using gas chromatography, R_{ave} may be determined empirically and the time weighted average concentration may be calculated using Equations 32 and 59.

Equation 58 may be plotted (Figure 3.5) in order to ascertain the range of linearity of the mass absorbed into the fibre with respect to time, for a range of Mass Transfer Biot numbers. Figure 3-5 was plotted using a four-term (n=1 to 4) approximation of the infinite series, Equation 35. The rate of mass transferred to the fibre is clearly strongly influenced by the Mass Transfer Biot number. (The analysis may be extended to determine the conditions required to obtain a TWA over any period)



Chapter 4: Materials and Methods

4.1 Reagents and Equipment for SPME/GC Method

A 20 ml aqueous sample of the analyte was placed in a borosilicate glass vial sealed with a cap and septum. The SPME fibre holder protective sheath was used to pierce the septum and the plunger was lowered to expose the fibre directly to the sample. Constant temperature, extraction time, agitation and fibre position were maintained to ensure reproducibility. The fibre was then withdrawn into the protective sheath and the holder removed from the sampling vial. The fibre holder was inserted directly into the GC injection port to thermally desorb the analytes from the fibre coating. The concentration of analytes was determined by comparing the detector counts to standard calibration curves. Calibration was done using standards prepared from ultrapure water and a minimum volume of pesticide standard solution; extracted in the same way as a sample.

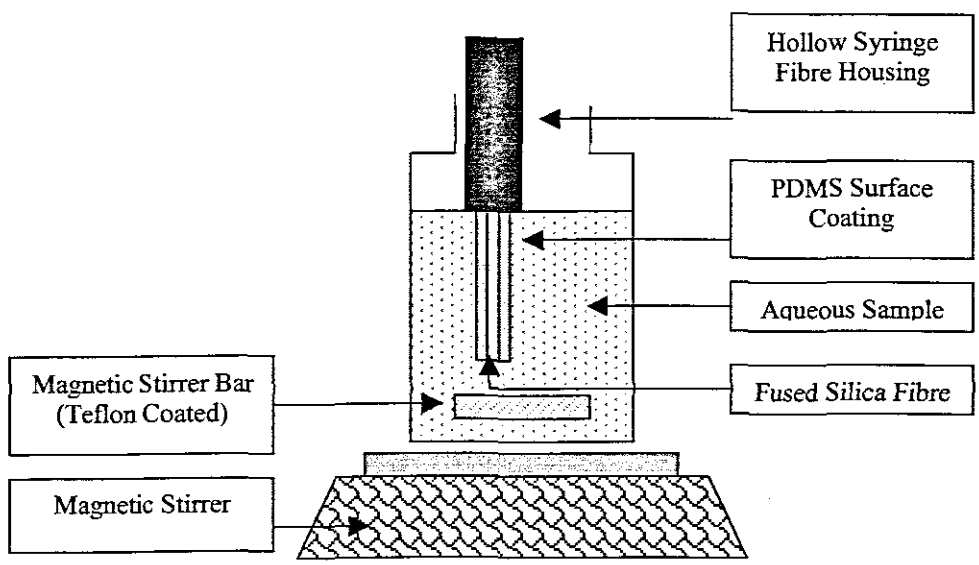
The 100μm fibre (PDMS) was the coating size specification that was chosen for the experimental work. Various coating thicknesses and fibres are available (7, 30, 65, 75, 85μm), but the 100μm fibre was selected for maximum sensitivity. The SPME fibres were supplied by Supelco[1] (distributed by Anatech in South Africa[2]). Stock standards of Chlorpyrifos and Endosulphan (alpha, beta, sulfate) (crystals, Chem Service Inc.[3]) were prepared using methanol (analytical grade, Merck[4]) as the solvent. A Heidolph MR3001K Magnetic Stirrer was used, together with Teflon coated stirrer bar (Length = 20mm; Diameter = 5mm), to agitate the aqueous sample. The analysis was performed using a Varian model 3300 Gas Chromatograph (GC), equipped with an electron capture detector (ECD). The Packed Column detector has a temperature range of 120°C to 420°C. The GC conditions used were: Injector temperature of 250°C, Column temperature of 170°C (initial) and 290°C (final) and a Detector temperature of 300°C. The Delta chromatography data system (Version 5.0) was used for data processing (Supplied by Digital Solutions Pty (Ltd))[5]. Nitrogen 4.5 (99.995%) was used as a carrier gas supplied by Fedgas. The GC temperature program was as

[1] Supelco, Supelco Park, Bellefonte, PA, 16823-0048 USA
[2] Anatech Instruments (Pty.) Ltd, P.O.Box 98485, Gauteng, South Africa
[3] Chem Service Inc., 660 Tower Lane, P.O.Box 599, West Chester, PA, 19381-0599 USA (www.chemservice.com)
[4] Merck Laboratory Supplies (Pty.) Ltd, 259 Davidson Road, Wadeville, Germiston (www.merck.co.za)
[5] Digital Solutions (Pty.) Ltd., P.O.Box 178, Margate, QLD, Australia, 4019

follows: initial GC column temperature was 170°C, increased to a final temperature of 290°C with an increment of 7°C/min. At 290°C the hold time was 5 minutes. The GC cycle time was set at 25 minutes; 22 minutes for the elution of the analytes and 3 minutes for the GC to stabilize and return to the original temperature settings after the temperature program had elapsed. Prior to the first extraction, the fibres were conditioned at 250°C for 1 hour as was recommended by the manufacturer.

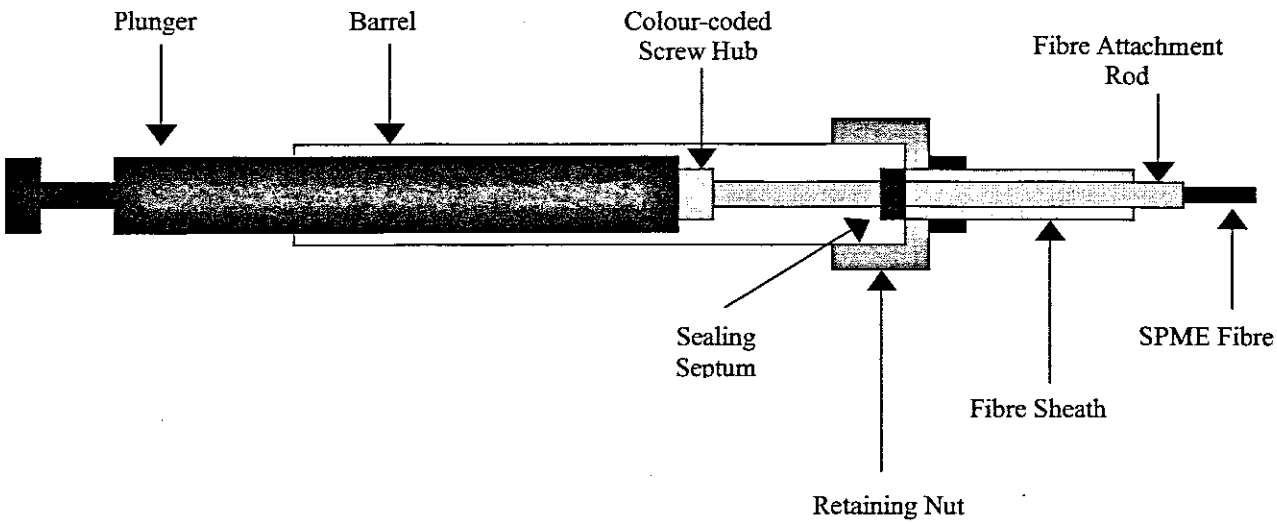
SPME extractions were performed in duplicate and triplicate. Aqueous sampling, rather than headspace sampling, was used. The SPME desorption was achieved at the GC injection temperature of 250°C and desorption time of 5 minutes. These parameters were similar to those in literature, gave sharp peaks and in practice showed no evidence of carryover in the replicate analyses.

Figure 4-1: Diagram of an SPME fibre exposed to an aqueous contaminant sample



The fibre is placed off-centre, as illustrated in the diagram, at the position of maximum tangential velocity, and requires minimum extraction time i.e. extraction of the analyte from the sample [31].

Figure 4-2: Schematic Diagram of an SPME fibre with Holder (Supelco Supplied)



The SPME procedure involves the partitioning of analytes between the sample and the fibre coating and desorption of the concentrated analytes from the fibre coating in the GC port. For the extraction procedure, an aqueous sample containing organic analytes is placed in a vial and sealed with a cap and septum. The SPME protective sheath pierces the septum and the plunger is lowered to expose the fibre directly to the aqueous sample. Analytes are then extracted from the sample matrix into the fibre coating. The time for the analyte concentration in the fibre to approach equilibrium is determined by the mass transfer rate from sample to fibre.

The thickest available Polydimethylsiloxane (PDMS) SPME fibre was used for all of the experimental work reported on. One reason for the choice of the thickest fibre coating is because the thicker the coating, the more analyte will be extracted and the lower the detection limit. The 100μm fibre retains a greater mass of the volatile analytes, therefore, it was selected as the fibre of choice to be used for the analysis. The PDMS coating was chosen because it has a high affinity for the pesticides of interest in this study, and was recommended in the commercial and scientific literature.

4.2 Materials and Methods for TWA

In order to estimate the Mass Transfer Biot Number (using Equation 51) applicable to the experimental arrangement values of the diffusivities D_s and D_f, the fibre length x_1, the film thickness δ_f and the distribution constants K_{fs} are required. Only the value of x_1 (10mm) is known. The values of D_s, D_f and δ_f were calculated and the K_{fs} values were measured, using the procedures outlined in Chapter 2.

4.2.1 Calculation of Diffusivities

The correlation of Wilke and Chang [42] was used to calculate the diffusivities of chlorpyrifos and endosulphan in water. The basic correlation is:

$$D_{AB} = \frac{7.4 * 10^{-8} (\Phi_B . M_B)^{0.5} . T}{\mu_B . V_A^{0.6}}, \qquad \ldots\ldots (60)$$

Where D_{AB} is the diffusivity of substance B through A (water), ϕ_B the association parameter, M_B the molecular mass of solvent B, T the absolute temperature (K), μ_B the viscosity of B (cP) and V_A the molal volume of solute A at the normal boiling point (cm^3/g). In this equation, the diffusivity is given in units of cm^2/s.

Reliable correlations for the estimation of diffusivities in the fibre polymer coating do not appear to be available. Pawliszyn [31] indicates that the diffusivity of an analyte in PDMS is about 5 to 6 times lower than that in water. A ratio of 6:1 was used, i.e., $D_f = (1/6)*D_s$.

4.2.2 Assessment of Analyte Retention on the Fibre

In the field sampling setting, the sampling system is exposed to a fluctuating sample concentration over a period up to 24 hours. The theoretical basis of the method assumes that the analyte absorbed by the fibre does not desorb during periods of low analyte concentration during the sampling period. That is, the estimate of the time weighted average concentration given by equation 32 and equation 58 assume 100% retention of the analyte during the sampling period.

A preliminary assessment of analyte retention was done using the fibre exposed to 3mm. The fibre was exposed to a spiked analyte solution (1µg/l) for a period of 15 minutes, under

vigorous stirring, and then exposed to analyte-free water for periods of 30 minutes to 180 minutes.

4.2.3 Linearity of Mass Absorbed with Respect to Exposure Time and Concentration

The theoretical curves indicate that the system has to be operated at Mass Transfer Biot Number values less than 0.3 (approximately) for linearity with respect to exposure time to be achieved over a 24-hour period.

The effective diffusion path length, the film thickness δ_f, of the pesticide in water, may be estimated using the following relationship derived from an analysis of laminar boundary layer flow over a flat plate [39]:

$$\frac{\delta c}{x} = 4.64\left(\frac{\mu}{x.u_\infty.\rho}\right)^{1/2}\left(\frac{D\rho}{\mu}\right)^{1/3} \quad \ldots\ldots\ldots (61)$$

Where δ_c is the concentration boundary layer, x is the distance from the leading edge of the fibre (stationary plate), u_∞ the velocity at infinity, μ the fluid viscosity, D the diffusivity and ρ the fluid density. Note that Equation 61 is of the form:

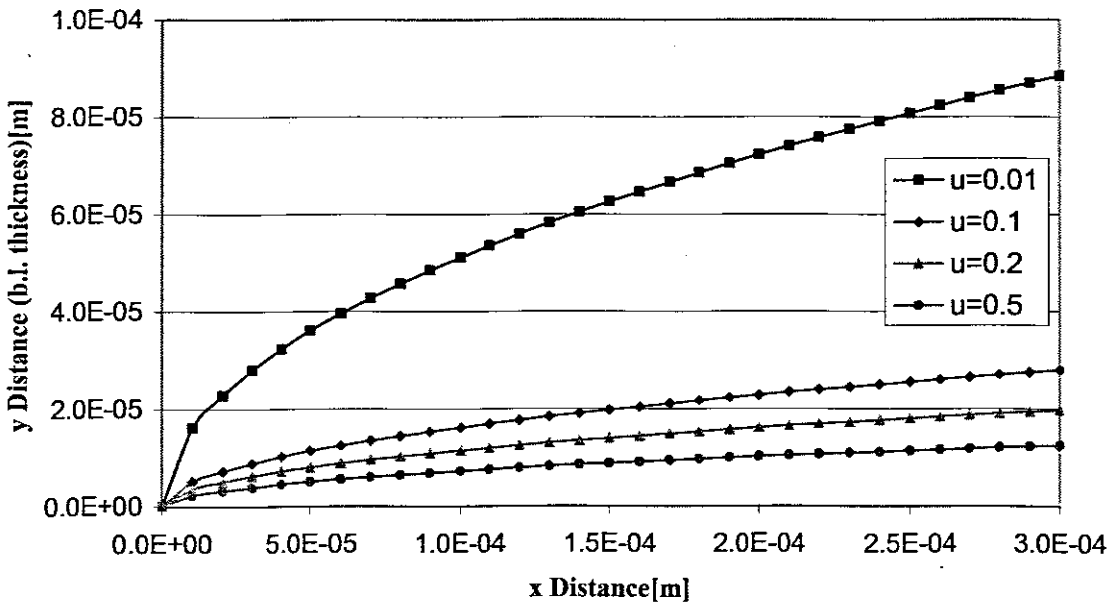
$$\frac{\delta c}{x} = 4.64\left(\frac{1}{Re}\right)^{1/2}\left(\frac{1}{Sc}\right)^{1/3}$$

Where Re is the Reynold's Number $(\frac{x.u_\infty.\rho}{\mu})$ and Sc is the Schmidt Number $(\frac{\mu}{D.\rho})$.

The (effective) film thickness δ_f is then given by: $\delta_f = (2/3)\delta_c$ ..... (62)

The concentration boundary layer thickness and hence the film thickness δ_f are thus functions of the parameters of Equation 61. The concentration boundary layer thickness varies with distance x from the leading edge of the fibre, and the free stream velocity u_∞ (the velocity far from the influence of the fibre). Figure 4-3 illustrates this functional relationship.

Figure 4-3: Concentration Boundary Layer Thickness versus x distance (m) and velocity u (m/s)



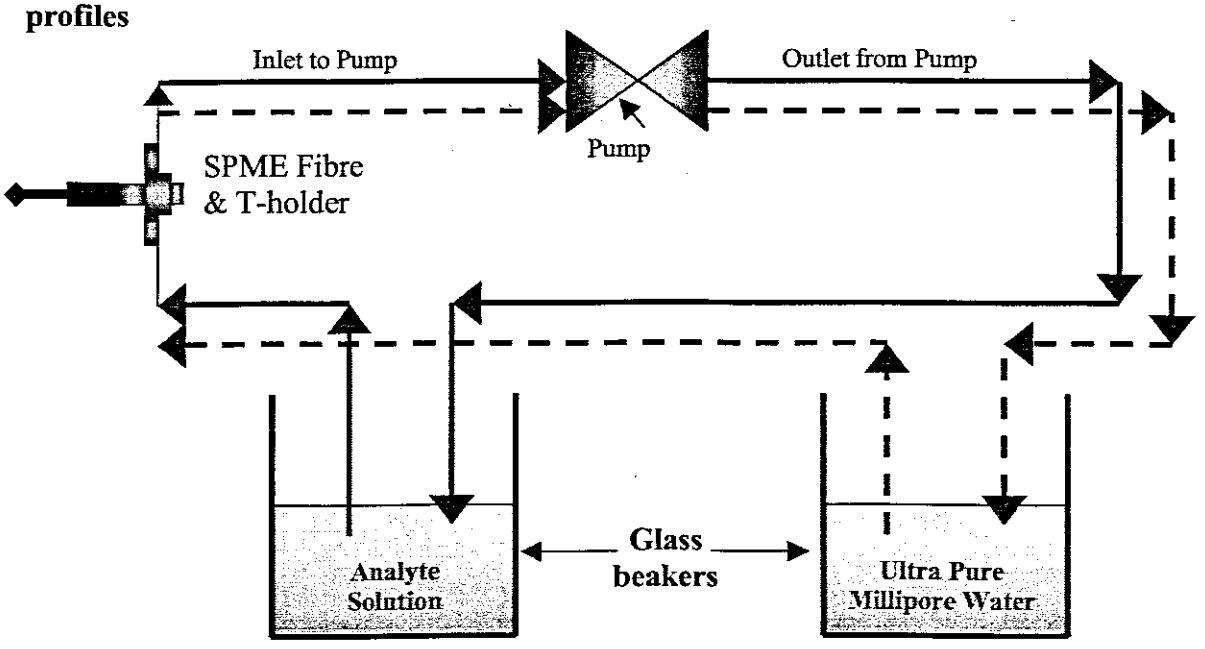
The theoretical analysis indicates that the required Mass Transfer Biot Number could be achieved with the fibre mounted flush with the steel sheath for analyte-fibre systems with K_{fs} values above 10 000. However, for systems with lower K_{fs} values, the fibre should be retracted by about 0.5mm. The exact and reproducible positioning of the fibre in the 0.5mm retracted location required an adaptation of the fibre holder. On the other hand, positioning of the fibre flush with the steel shaft could be accomplished easily, with the aid of a low powered microscope. Thus the first linearity experiment was conducted with the fibre mounted flush with the steel shaft, for exposure (absorption) periods of up to 6 hours. The fibre was exposed to 1ug/l standard solutions for periods of 1, 2, 4 and 6 hours, to ascertain if the mass absorbed increased linearly with time over this period. A second set of experiments was planned with the fibre retracted by 0.5mm, with exposure periods of up to 24 hours but could not be carried out due to lack of time to modify the fibre holder.

The linearity of the GC detector response to concentration over the range of concentrations of interest was demonstrated with a set of direct injection runs.

4.2.4 Exposure to different concentration profiles

The procedure used to test the assumption that exposure to different concentration profiles with the same theoretical TWA would yield the same (within experimental error) mass absorbed into the fibre was tested using a procedure based on that reported by Martos and Pawliszyn [36]. The fibre was positioned flush with the steel shaft, in a custom-made fibre holder and exposed to two different concentration profiles – the first consisting of an alternating series of 30 minute exposures to 1.0µg/l chlorpyrifos spiked into Millipore water, the second consisting of exposure to the 1.0µg/l solution continuously for 90 minutes, then to the pure water only for the remainder of the period. In each case the mass absorbed into the fibre was ascertained by comparison against a direct injection calibration curve; the masses obtained for the two profiles were compared to each other.

Figure 4-4: System for assessing effect of exposure to different concentration profiles



Exposure to the solution or the pure water was achieved by changing the suction line (Figure 4-4) from the one beaker to the other at the required time. The pumping rate was constant throughout the period. The constant flow rate and the location of the fibre in the T-holder ensured a constant velocity (0.1m/s) of the sample stream in relation to the face of the fibre.

In the first exposure pattern, the fibre system was exposed to the 1µg/l analyte solution and the pure water alternately for periods of 30 minutes at a time, for a total exposure-to-analyte

time of 90 minutes over a three-hour period. In the second exposure pattern, the fibre system was exposed to the analyte solution for a continuous period of 90 minutes, then to the pure water for 90 minutes. The theoretical time weighted average concentrations for the two exposure patterns were thus identical at 0.5µg/l. The mass absorbed into the fibre in each case was ascertained using GC.

The exposure profiles used are shown schematically in Figures 4-5a and 4-5b.

Figure 4-5a: First Exposure Pattern

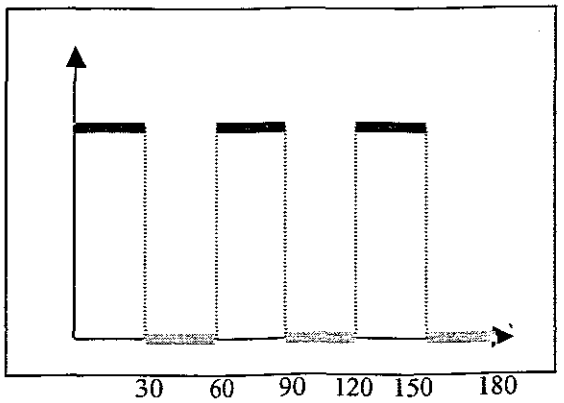
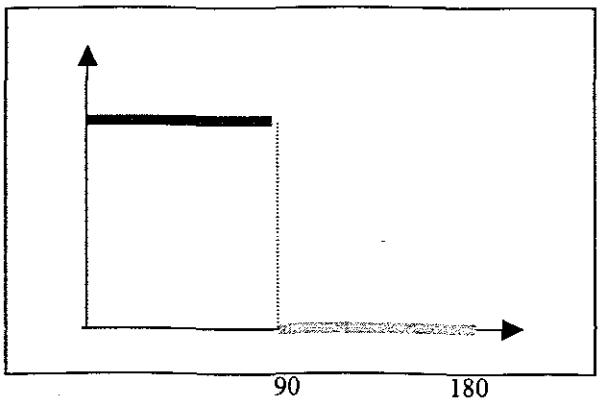


Figure 4-5b: Second Exposure Pattern



4.2.5 Comparison Between 24 x 1-hour Grab Samples and the 24-hour TWA Sample

Field-testing of the Time Weighted Average sampling system was done at sites Bdr. At each site the Autosampler (Model: Buhler Montec XIAN 1000) was located close to the stream being sampled, and the Teflon suction line was positioned in the stream to allow the vacuum pump to sample the stream. The arrangement is shown in Figures 4-6a and 4-6b.

Figure 4-6a: Autosampler with suction line to drain (Bdr) sampling point

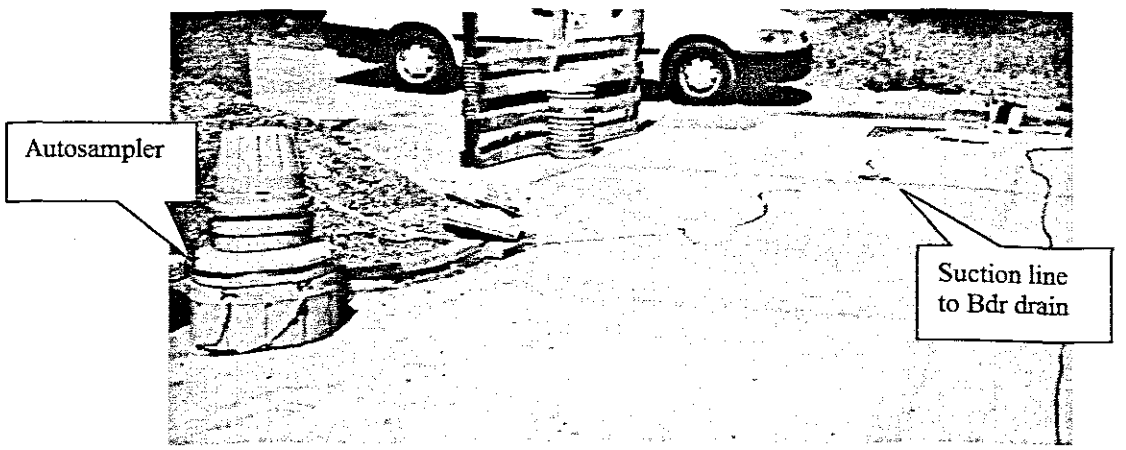
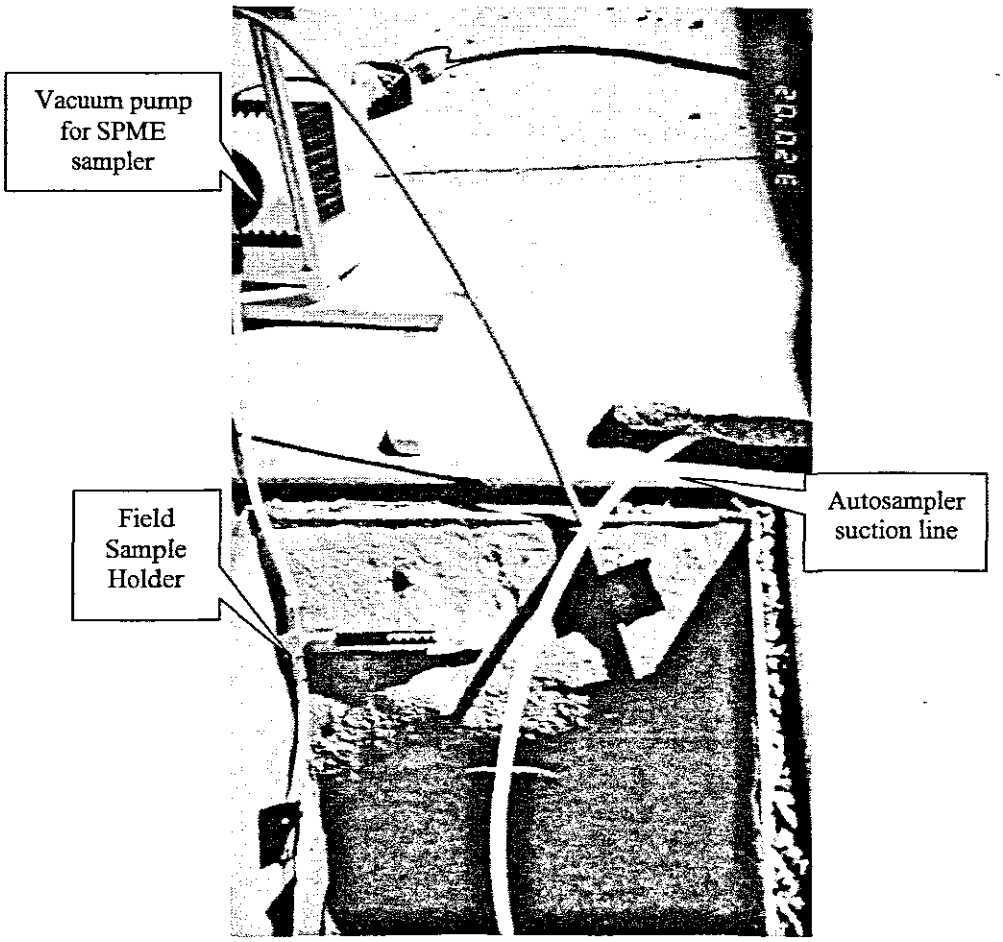


Figure 4-6b: Field Sampler Holder, BDR sampling point



The Autosampler was programmed to collect 24 x 1 litre samples, taken at hourly intervals, over a 24-hour period. The SPME fibre was positioned in the Field Fibre Holder as required for TWA sampling, mounted flush with the steel shaft. The TWA sampling system was exposed to the same stream by using a pumping circuit as shown in Figure 4-6b, with the pump suction located close to the suction line of the Autosampler. This arrangement thus allowed the two devices to sample essentially the same stream, over the same time period.

The 24 hourly samples were returned to the laboratory, refrigerated as normal, and were analysed using the standard SPME method. The fibre holder was simultaneously returned to the laboratory for analysis. The mass of analyte absorbed into the fibre was established by comparison with a direct injection (external) calibration curve. The single TWA fibre analysis was done within 5 days of sample collection; the 24 hourly samples were all analysed within 30 days of sampling.

Chapter 5: Results

A. SPME Results

5.1 Evaluating the Effect of Agitation

A series of laboratory runs was conducted to test the effect of agitation of the sample. The effect of agitation was tested on all four analytes, individually, as well as the effect on the reproducibility of results without stirring (agitation). There were two parts to the experiment. The effect of a complete absence of agitation on reproducibility was assessed by exposing the SPME fibre to the spiked analyte solution (5µg/l) in the borosilicate glass vial, for absorption times ranging from 5 minutes to 25 minutes. A set of experimental runs was then conducted with the SPME fibre exposed to a newly prepared spiked analyte solution (5µg/l), stirred at 625 RPM, for absorption times of 5 to 25 minutes. In all cases, the fibre was exposed to its full length of 10mm; stirring (for the second set of runs) was achieved using a magnetic stirrer and a Teflon-coated magnetic stirrer bar located inside the glass vial containing the spiked analyte solution.

Figure 5-1 illustrates the relationships between GC readings (detection counts) and absorption time for a 5µg/l chlorpyrifos standard stirred (625 RPM) and unstirred. Without stirring, the data are scattered, particularly at low absorption times. With stirring, good reproducibility between replicate runs was achieved, demonstrating the importance of agitation when using SPME.

Figure 5-1: Detector Counts (proportional to mass absorbed for stirred and unstirred Chlorpyrifos sample) versus Absorption time

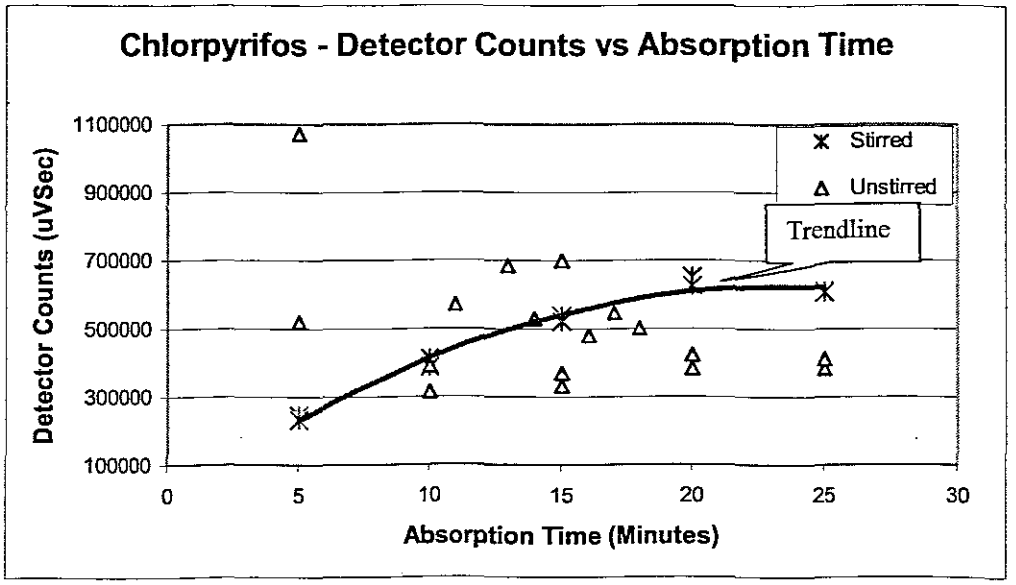
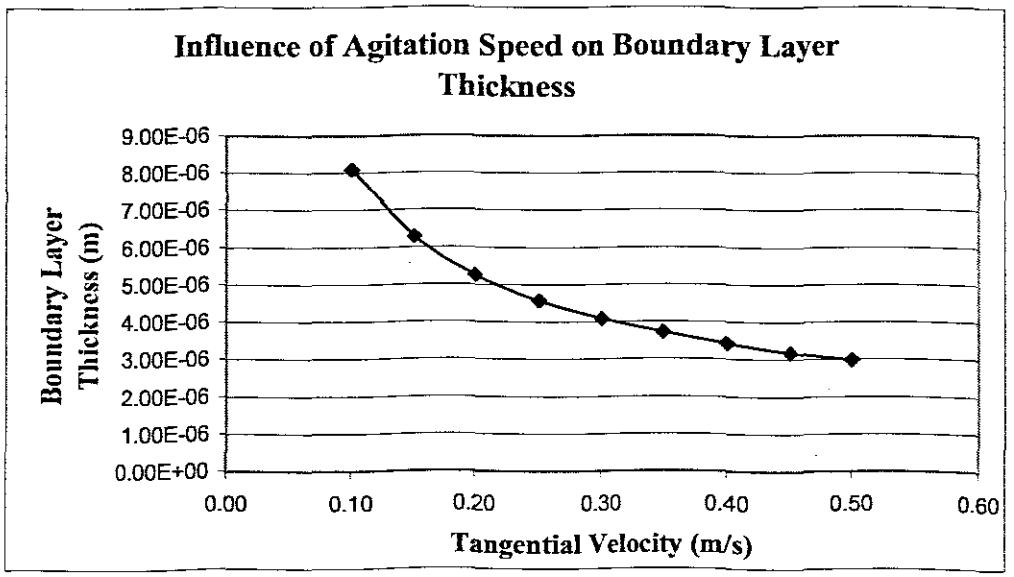


Figure 5-2 illustrates that by increasing the stirrer speed (agitation speed) of an aqueous sample, the thickness of the stagnant layer (which is found between the sample and the fibre coating) known as the boundary layer can be reduced which in turn will increase analyte extraction time. (Equation 9 was used to generate the graph in Figure 5-2).

Figure 5-2: The Influence of Agitation Speed on the Boundary Layer Thickness



5.2 Determination of Optimum Absorption Time

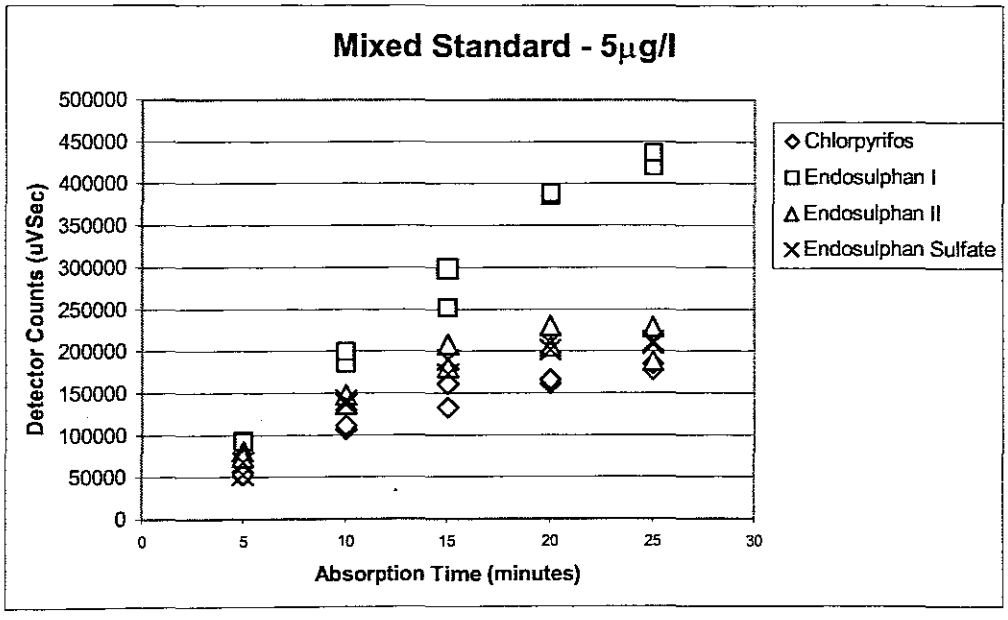
Experimental runs were performed on a stirred (625 RPM) 5 µg/l spiked mixed analyte solution (10 ml) containing all four analytes, namely chlopyrifos, endosulphan-alpha, endosulphan-beta and endosulphan sulfate, at different absorption times (5, 10, 15, 20, 25 minutes) in order to establish the optimum absorption time to be used for SPME. The temperature was maintained at 20°C. The SPME fibre was fully exposed (10mm) to the spiked analyte solution. These runs were replicated in order to determine reproducibility.

Table 5-1 and Figure 5-3 show that for 5 µg/L standard stirred (625 RPM) samples of any of the four pesticides analysed, reproducibility, as a percentage (%) relative difference, is good (a range of ± 2.3% to ± 12.0%) for absorption times of 5 to 25 minutes, but generally improved with increasing absorption time. However the longer absorption time is preferable as an increase in absorption time increases the mass absorbed (as reflected in the detector counts) and hence the sensitivity of the method.

Table 5-1: Range of Absorption Times for Four Analytes in a Mixed Standard – 5µg/l (ppb)

	Chlorpyrifos		Endosulphan-alpha		Endosulphan-beta		Endosulphan Sulfate	
Absorption Time	Detector Counts	Differences	Detector Counts	Differences	Detector Counts	Differences	Detector Counts	Differences
(Minutes)	(µVSec)	(%)	(µVSec)	(%)	(µVSec)	(%)	(µVSec)	(%)
5	52871	0.7	93417	1.2	81295	9.4	53573	23.3
5	53250		92258		74017		67693	
10	106597	4.6	185283	7.3	136663	7.9	136954	3.3
10	111632		199417		147887		141519	
15	160836	18.9	298104	16.6	208106	13.9	190070	9.3
15	133091		252293		181132		173144	
20	161511	3.0	385601	0.7	230428	11.3	201886	3.5
20	166415		388437		205737		209095	
25	177905	3.9	420641	3.8	188768	19.3	211686	1.3
25	185009		436853		229008		208903	

Figure 5-3: Reproducibility versus Absorption times for four analytes in a mixed standard (5µg/l)



5.3 Reproducibility of the SPME Method

The initial experiments (described in *5.1* and *5.2*) established the standard experimental conditions for SPME. In order to assess the overall reproducibility of SPME under the standardized conditions, replicate runs were done on spiked 10 ml, 5 µg/l standard samples as well as field samples. Field samples were collected in February 2001 from a sub-surface drain, farm dam and river site in the Hex River, Western Cape. These sites were found to be consistently contaminated in a previous study [7] conducted in this region. Reproducibility was assessed from the mean and standard deviation of differences between readings for each replicate set, by using a two-tailed Student t-test. The t_{calc} and the 95% Confidence Interval (n = 20) was determined for each analyte.

Table 5-3 shows, firstly, that all four analytes could be detected in different environmental samples. The range of concentrations is similar to that found in the previous project in the Hex River Valley, using SPE. Secondly, good reproducibility was obtained for all sites and for all the pesticides analysed, ranging from 0.3% to 10.5% in relative differences between replicates. This range was narrower (better) than that obtained (1.6%-42.9%) for SPE (Table 5-2). (Refer to APPENDIX E for the Calibration Curves used for quantification of unknown water samples).

Table 5-2: Comparison between SPME and SPE Replicate Pairs (Samples obtained and analysed for the four analytes)

	Chlorpyrifos		Endosulphan-alpha		Endosulphan-beta		Endosulphan Sulfate	
Sample	Differences (%)		Differences (%)		Differences (%)		Differences (%)	
Name	SPE	SPME	SPE	SPME	SPE	SPME	SPE	SPME
Bdr*	26.2	1.9	31.8	4.7	27.1	5.3	41.0	3.2
Dd**	17.1	1.6	24.1	0.3	25.3	10.5	42.9	0.5
Gr***	14.8	2.1	12.6	4.3	22.8	3.6	22.5	7.6

*a) Concentration; *Sub-surface drain-Site B; **Farm Dam-Site D; ***River-Site G*

Table 5-3: Field Sample Results (Samples obtained and analysed for the four analytes)

		Chlorpyrifos		Endosulphan-alpha		Endosulphan-beta		Endosulphan Sulfate	
Sample	Run	Conc.[a]	Differences	Conc.[a]	Differences	Conc.[a]	Differences	Conc.[a]	Differences
Name		Cs° (µg/l)	(%)	Cs° (µg/l)	(%)	Cs° (µg/l)	(%)	Cs° (µg/l)	(%)
Bdr*	A	5.6	1.9	4.9	4.7	1.5	5.3	5.9	3.2
Bdr	B	6.0		6.0		1.9		6.7	
Dd**	A	1.5	1.6	1.3	0.3	1.0	10.5	1.9	0.5
Dd	B	1.6		1.3		0.6		2.0	
Gr***	A	0.2	2.1	0.2	4.3	0.1	3.6	0.2	7.6
Gr	B	0.3		0.2		0.1		0.3	

Table 5-4 summarizes the results obtained from experiments evaluating the reproducibility of 20 samples, including 17 mixed-standard laboratory spiked samples and 3 field samples (concentration range 0.1µg/l to 6.7µg/l for all four analytes). The mean (signed) differences, the mean absolute differences and the standard deviation of the mean absolute differences between replicates were -0.05pg to 1.05pg, 0.715pg to 1.63pg, and 0.97pg to 2.99pg, respectively. The relative standard deviation (absolute difference*100/mean value) varied between 3.1% and 4.1% at the 1µg/l and mass absorbed onto the fibre ranged from 40pg to 80pg (at 1µg/l level). The mean differences of < 1pg demonstrates the absence of carryover; mean absolute differences of < 1.6pg demonstrate good reproducibility for all the analytes measured.

Table 5-4: Reproducibility as Standard Deviations of % Relative Differences of Replicate Values *of samples containing all four analytes*

	Chlorpyrifos	Endosulphan-Alpha	Endosulphan-Beta	Endosulphan Sulfate
Mean Difference (pg)	1.05	0.74	-0.05	0.76
Mean AD** (pg)	1.63	1.52	0.72	1.11
SD* of Mean AD** (pg)	2.16	2.99	0.97	2.04

*SD: Standard Deviation; **AD: Absolute Difference

5.4 Determination of the Method Detection Limit

There are several approaches to defining and determining the Method Detection Limit [43]. The US EPA method [44] of using low concentration spikes (of the each of the four analytes to be studied) into a blank matrix and then calculating the MDL from the standard deviation of 7-10 repeat runs was used:

$$\text{Thus: MDL} = \frac{3 * (\text{Standard deviation}) * (\text{Concentration in Solution [Cs]})}{\text{Mean Peak Area}}$$

The MDL is applicable for concentrations ≤ 10 times the MDL [18]. Experimental runs were therefore conducted at successively lower concentrations of the analyte in a range of analyte concentrations detected in previous studies (i.e. 1.00µg/l, 0.04µg/l and 0.02µg/l) in order to determine the MDL of SPME. The MDL was calculated from 7 repeat runs at each concentration, for each analyte.

As per definition, the MDL's were estimated as the average of the 3*Standard Deviation figures for the 0.02µg/l and 0.04µg/l concentration levels. Table 3 shows that SPME has low MDL's (< 0.02 µg/l) for all four analytes tested. These MDL's are much lower than those of SPE, which were experimentally determined by London et al for the same compounds [7]: chlorpyrifos = 0.05µg/l; endosulphan-alpha = 0.11µg/l; endosulphan-beta = 0.13µg/l; and endosulphan Sulfate = 0.13µg/l.

Table 5-5: MDL values for three mixed standards at three concentration levels

	Chlorpyrifos		Endosulphan-alpha		Endosulphan-beta		Endosulphan Sulfate	
Conc. (µg/l)	Std. Dev.[a]	3*Std. Dev. µg/l	Std Dev.	3*Std. Dev. µg/l	Std Dev.	3*Std. Dev. µg/l	Std Dev.	3*Std. Dev. µg/l
0.02	1780	0.002	44251	0.024	10299	0.008	3680	0.003
0.04	5482	0.009	8726	0.008	19315	0.019	13139	0.015
0.1	25573	0.021	37406	0.013	34274	0.016	20966	0.014
	MDL	*0.010*	MDL	*0.016*	MDL	*0.014*	MDL	*0.009*

[a] Standard deviation (of Detector Counts)

5.5 Equilibrium Runs

The reproducibility of analyses depends primarily on reproducing extraction conditions - stirrer speed, temperature of the sample during extraction, position of the fibre rather than extracting for long enough to approach the equilibrium partitioning of the analyte between the fibre and the sample. Nonetheless, an experiment was conducted to estimate the time required to approach equilibrium.

The tests were done at 20°C. The SPME fibre fully exposed (10mm) to a mixed standard, containing all four analytes, of concentration 1µg/l (ppb) for a range of absorption times - 20 minutes to 140 minutes. The mixed standard in glass vial was stirred at maximum (N = 625 RPM), using the magnetic stirrer and Teflon coated stirrer bar set-up. The results for Endosulphan Sulfate Standard at the 1µg/l level are shown in Figure 5-4.

Maximum counts (directly proportional to mass absorbed) were reached at about 80 minutes. Thereafter, an apparent decrease in concentration (mass absorbed) occurred. All the analytes yielded similar results (refer to APPENDIX F).

Figure 5-4: Graph of Detector Counts versus Absorption Time for 1μg/l Endosulphan Sulfate

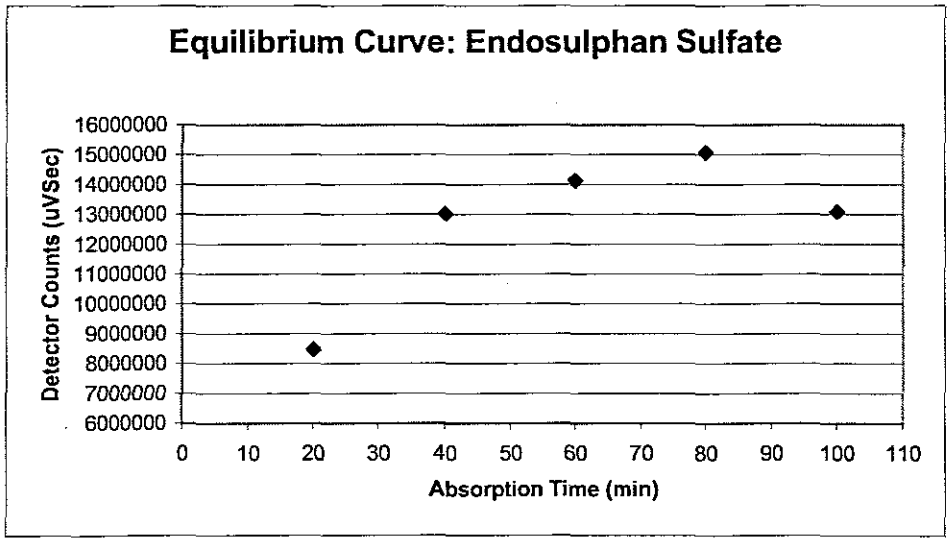
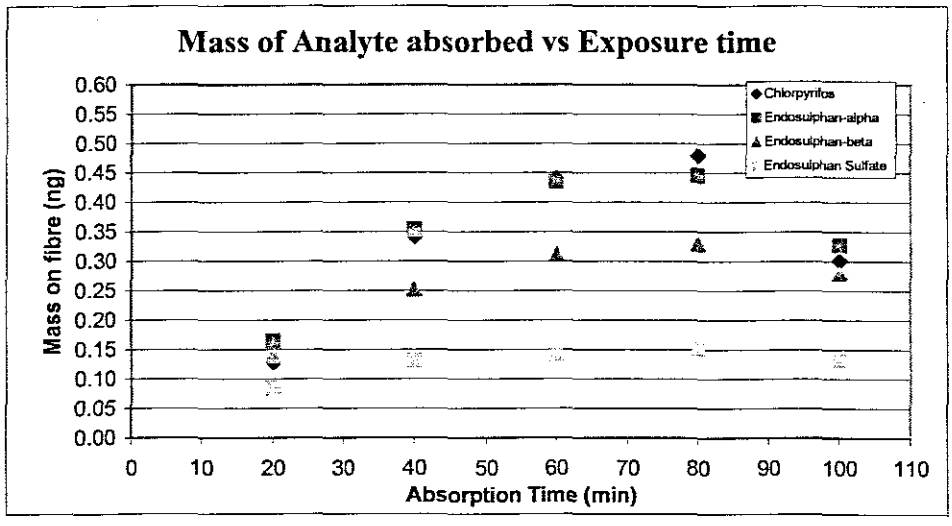


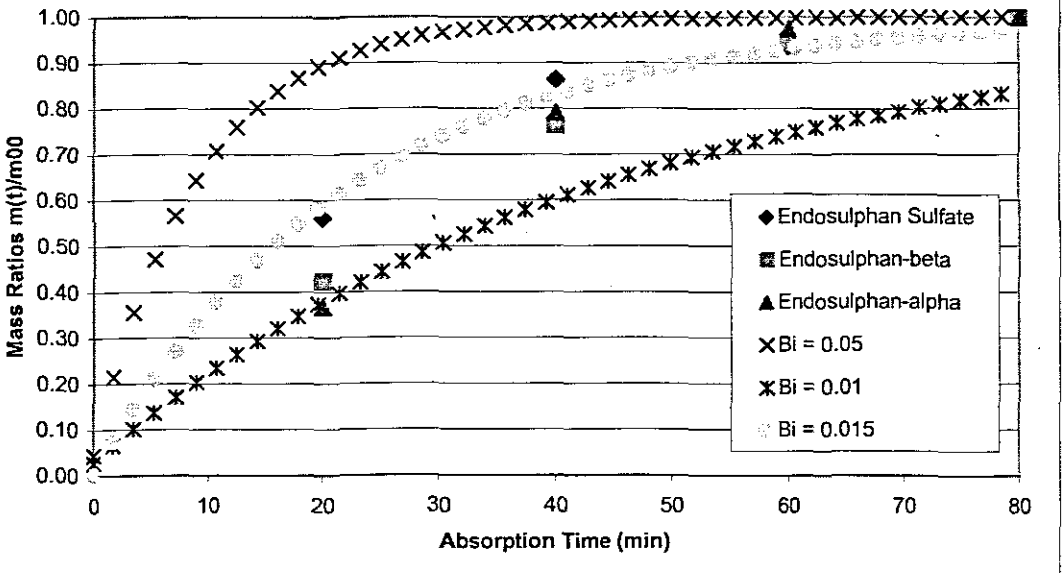
Figure 5-5: Graph of Mass of Analyte Absorbed onto fibre versus Exposure Time



The mass absorbed by the fibre coating, at equilibrium, is *proportional* to K_{fs}, which is defined by Equation 5. Fig 5-5 shows that equilibrium, under the experimental conditions, is approached at about 80 minutes. At 80 minutes, the data indicate that the ratios of mass extracted, relative to that of endosulphan sulfate (0.15ng) were 0.33ng/0.15ng = 2.2:1 for endosulphan-beta, 0.45ng/0.15ng = 2.9:1 for endosulphan-alpha and 0.48ng/0.15ng = 3.2:1 for chlorpyrifos. The literature K_{fs} values for endosulphan-alpha, -beta, and -sulfate are 25000, 10000, and 400, respectively [29]. No K_{fs} value is available for chlorpyrifos. Based on

these values, the expected ratios of mass extracted (at equilibrium) are 10000/400 = 25:1 for endosulphan-alpha, and 25000/400 = 62.5:1 endosulphan-beta. These ratios are considerably higher than calculated based on the data given in Fig 5-5, but show the expected trend in value. The lack of close numerical agreement for these ratios is not unexpected, given the reported lack of agreement of experimentally measured K_{fs} values between researchers [46]. Langenfeld *et al* [46] compared experimentally determined values for K_{fs} to published K_{fs} values and reported significant differences, up to a factor of 5 between them, for the same compound, e.g. toluene: K_{fs} published / K_{fs} experimental = 758 / 147 ≈ 5.

Figure 5-6: Mass Transfer to Fibre Profiles



The times to reach 95% of the equilibrium mass, m_0, given by the rigorous theoretical analysis, Equation 31 and Fig 2-8 are 27 minutes, 70 minutes and 132 minutes for endosulphan sulfate, endosulphan-beta and endosulphan-beta, respectively. These theoretical values may be compared with the values predicted by the simplified analysis given by Equation 12: 28 minutes, 80 minutes and 132 minutes for endosulphan sulfate, endosulphan-beta and endosulphan-alpha, respectively. The differences are less than 10%. If Fig 5-5 is used to estimate the time to 95% of equilibrium, the times are approximately 70 minutes for all three analytes. The factors that may be responsible for the differences between the theoretically determined times and the experimentally approximated times are the uncertainty in the diffusivities and average boundary layer thickness, δ_f. The diffusivities for the

endosulphan analytes are not available in literature and need to be calculated. Equation 31 was used to calculate the total mass transfer to the fibre for each individual Mass Transfer Biot Number in Figure 5-6.

B. Time Weighted Average Results

5.6 Estimate of Diffusivities

The diffusivities of chlorpyrifos and endosulphan in water were estimated using Equation 60. The required parameters for chlorpyrifos and endosulphan, and the resulting diffusivities, are given in Table 5-6.

Table 5-6: Calculation of diffusivities in water, at 20 °C (293K)

Parameter	Units	Water	Chlorpyrifos	Endosulphan
Molecular Mass, M_B (water)		18.0		
Temperature	K	293		
Viscosity, μ_B (water)	cP	0.993		
Association Parameter, ϕ_B (water)		2.26		
Molal Volume, V_A	cm^3/g		310-320	320
Calculated Diffusivity (Equation 60)	**cm^2/s**		**$0.44*10^{-5}$**	**$0.44*10^{-5}$**
Calculated Diffusivity	**m^2/s**		**$0.44*10^{-9}$**	**$0.44*10^{-9}$**

In order to see whether the calculated estimates of the diffusivities are valid, they may be compared with the experimental values, in m^2/s units, for ethanol ($0.84*10^{-9}$), benzyl alchohol ($0.82*10^{-9}$), acetic acid ($1.21*10^{-9}$) and sucrose ($0.52*10^{-9}$) [39]. The calculated values fall within the expected range of values for diffusivities in water at infinite dilution. The diffusivity varies in direct proportion to the absolute temperature. For small changes in temperature, the variation in diffusivity is negligible. For a 5°C variation in temperature, the change is less than 2%.

5.7 Determination of the Distribution Constant Values (K_{fs})

The experimentally estimated K_{fs} values and the literature values are presented in Table 5-7.

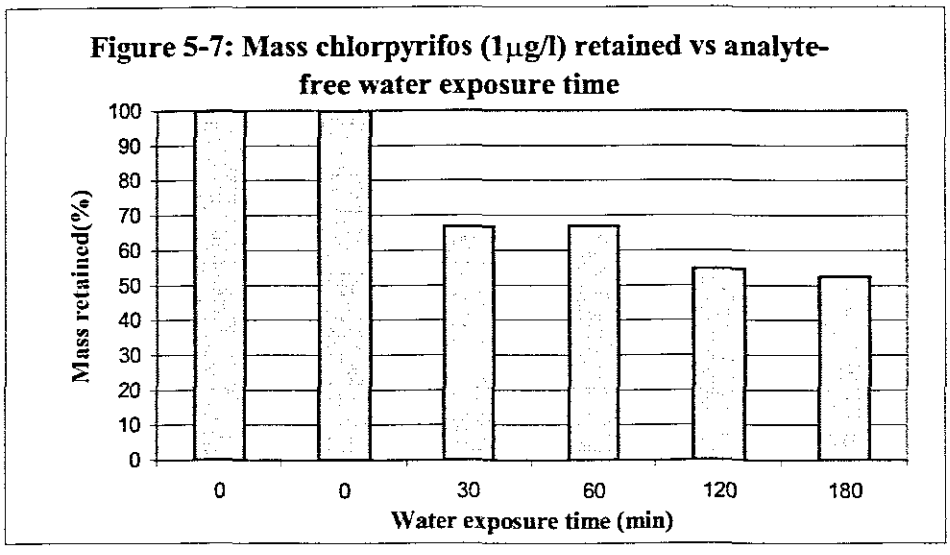
Table 5-7: The literature and measured (at 20 °C) K_{fs} values

Analyte	Chlorpyrifos	Endosulphan-alpha	Endosulphan-beta	Endosulphan Sulphate
K_{fs} (literature values) [29]	(No value)	25000	10000	400
K_{fs} (experimental)	**520-580**	**2300-2900**	**1200-2300**	**420-620**

The exposure time of 60 minutes, used in these experiments, was greater than the equilibrium extraction times of 45 minutes quoted by MacGillivray [29]. However, MacGillivray does not quote the temperatures at which the values were measured thus a direct comparison is not possible. The difference between the measured Endosulphan values and the literature values appear to be greater than that due to possible temperature differences and non-equilibrium conditions. Large differences in published K_{fs} values have previously been reported [46].

5.8 Assessment of Analyte Retention on Fibre

The results, for the fibre protruding by 3mm from the end of the steel shaft, exposed to a spiked standard (1µg/l) for 15 minutes and then to analyte-free water, are shown in Figure 5-7.



5.9 Linearity of Mass Absorbed with Respect to Exposure Time and Concentration

The linearity of mass absorbed with respect to exposure time is a function of the Mass Transfer Biot number:

$$Bi_{MT} = \frac{k_c.x_1}{K_{fs}.D_f} = \left(\frac{D_s}{D_f}\right)\left(\frac{x_1}{\delta_f}\right)\left(\frac{1}{K_{fs}}\right) \quad \ldots\ldots (52)$$

The calculation of the experimental Mass Transfer Biot numbers (using Equation 52) requires an estimate of δ_f, the effective film thickness. If the fibre is positioned flush with the steel sheath, Equations 60 and 61 may be used to estimate the film thickness. For velocities in the range of 0.01m/s (which corresponds to a slow moving stream) to 0.5m/s, the film thickness ranges from 0.18mm to 0.025mm. If the fibre is retracted to a distance 0.5mm from the rim of the sheath, the film thickness is effectively 0.5mm plus δ_f.

The system parameters are shown in Table 5-8. The Mass Transfer Biot number values for a range of parameter values are given in Table 5-9.

Table 5-8: Values of the System Parameters

Parameter	Units	Value
Fibre diameter	[m]	$0.300*10^{-3}$
Sheath cross-sectional area	[m^2]	$7.07*10^{-8}$
Fibre cross-sectional area	[m^2]	$6.12*10^{-8}$
Diffusivity in water: D_s (average)	[m^2/s]	$4.2*10^{-9}$
Diffusivity in polymer: D_f (=1/6Ds)	[m^2/s]	$0.7*10^{-9}$
Fibre length, x1	[m]	0.010
Water density (20 °C)	[kg/m^3]	998
Water viscosity	[$N.s/m^2$]	0.001

Table 5-9: Mass Transfer Biot Number versus K_{fs} and Calculated Film Thickness

Velocity u_∞ [m/s] →	0.01	0.05	0.1	0.5	Fibre Retracted by 5.0E-4m, u_∞= 0.1	Initial Bi_{MT} case
Film thickness, δ_f [m] →	1.8E-04	8.0E-05	5.6E-05	2.5E-05	5.6E-04	1.0E-02
K_{fs}	**Biot**	**Biot**	**Biot**	**Biot**	**Biot**	**Biot**
400	1.402	3.134	4.433	9.912	0.449	0.025
1000	0.561	1.254	1.773	3.965	0.180	0.010
6000	0.093	0.209	0.296	0.661	0.030	0.002
10000	0.056	0.125	0.177	0.396	0.018	0.001
15000	0.037	0.084	0.118	0.264	0.012	0.001
20000	0.028	0.063	0.089	0.198	0.009	0.001
25000	0.022	0.050	0.071	0.159	0.007	0.000

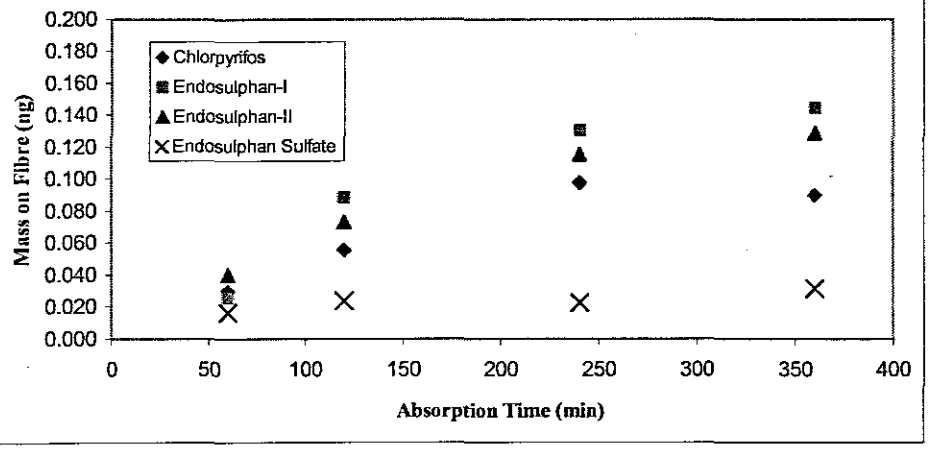
The Mass Transfer Biot Number may fall in the range of 0.1 to 10, depending on the values of the various parameters in the equation, indicating that the lumped parameter models (Bi_{MT} <0.1 or Bi_{MT} >10) are not necessarily good approximations. The Mass Transfer Biot numbers for the experimentally determined K_{fs} values, and the experimental velocity of 0.1m/s are given in Table 5-10.

Table 5-10: Experimental K_{fs} and Mass Transfer Biot Numbers

Analyte	K_{fs} Values		Calculated Mass Transfer Biot numbers	
	Literature	Measured	Based on Literature K_{fs}	Based on Measured K_{fs}
Chlorpyrifos	-	520-580		3.1 – 3.4
Endosulphan-alpha	25 000	2300 - 2900	0.07	0.6 – 0.8
Endosulphan-beta	10 000	1200 - 2300	0.18	0.8 – 1.6
Endosulphan Sulfate	400	420 - 620	4.2	4.4 – 6.9

The mass of analyte absorbed with exposure time is shown in Figure 5-8.

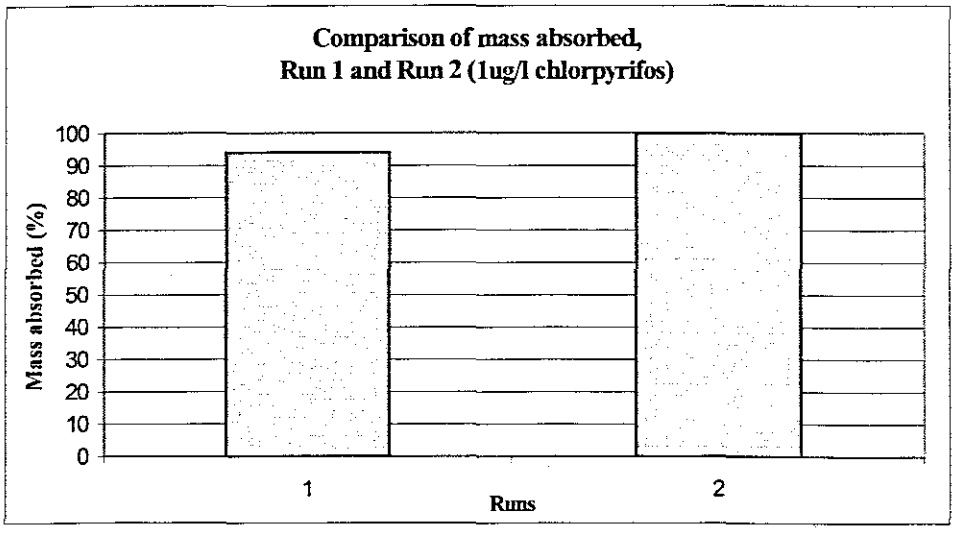
Figure 5-8: Mass of analyte absorbed vs exposure time



5.10 Exposure to Different Concentration Profiles

The results of the mass absorbed using two concentration profiles (both 1μg/l) are given in Figure 5-9. The results for the two concentration profiles are within 6% of each other.

Figure 5-9: Comparison of Mass Absorbed, Run1 and Run2 (1μg/l Chlorpyrifos)



5.11 Comparison Between 24 x 1-Hour Grab Samples and the 24 Hour TWA Sample

Figure 5-10 displays the results of the 24 autosampler grab samples, taken hourly at the sampling point Bdr, over the period 28/29 March 2002.

Figure 5-10: Concentrations of Hourly Bdr Samples

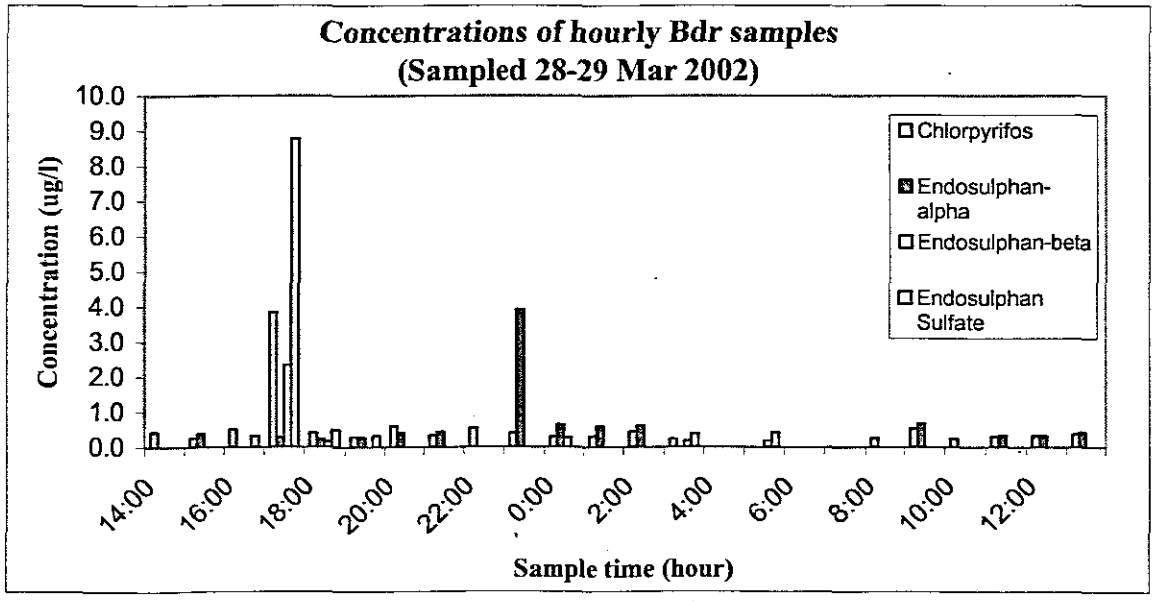


Table 5-11 contains the results of the 24-hourly field samples, as well as the means and standard deviations of the 24-hourly values.

Table 5-11: Hourly Pesticide Concentrations at Bdr (28 March 2002)

Sample	Sampling Time	Chlorpyrifos Concentration (µg/l)	Endosulphan-alpha Concentration (µg/l)	Endosulphan-beta Concentration (µg/l)	Endosulphan Sulfate Concentration (µg/l)
BDR 1	14:00	0.44	0.00	0.00	0.00
BDR 2	15:00	0.26	0.37	0.00	0.00
BDR 3	16:00	0.50	0.00	0.00	0.31
BDR 4	17:00	3.84	0.27	2.33	8.78
BDR 5	18:00	0.41	0.23	0.16	0.49
BDR 6	19:00	0.29	0.27	0.00	0.33
BDR 7	20:00	0.61	0.42	0.00	0.00
BDR 8	21:00	0.33	0.43	0.00	0.00
BDR 9	22:00	0.54	0.00	0.00	0.00
BDR 10	23:00	0.40	3.95	0.00	0.00
BDR 11	00:00	0.30	0.64	0.28	0.00
BDR 12	01:00	0.31	0.59	0.00	0.00
BDR 13	02:00	0.44	0.60	0.00	0.00
BDR 14	03:00	0.23	0.00	0.18	0.39
BDR 15	04:00	0.00	0.00	0.00	0.00
BDR 16	05:00	0.00	0.00	0.19	0.41
BDR 17	06:00	0.00	0.00	0.00	0.00
BDR 18	07:00	0.00	0.00	0.00	0.00
BDR 19	08:00	0.27	0.00	0.00	0.00
BDR 20	09:00	0.53	0.67	0.00	0.00
BDR 21	10:00	0.25	0.00	0.00	0.00
BDR 22	11:00	0.30	0.34	0.00	0.00
BDR 23	12:00	0.32	0.32	0.00	0.00
BDR 24	13:00	0.37	0.42	0.00	0.00
	Mean:	0.45	0.40	0.13	0.45
	Standard Deviation:	0.74	0.79	0.48	1.78

The TWA sample was obtained over the same sampling period, with the sampling pump set to give a flow velocity of 0.1m/s past the SPME fibre positioned flush with the steel shaft. Under these conditions the Mass Transfer Biot numbers, based on literature values for K_{fs}, were in the range of 0.2 to less than 0.01 for 3 of the analytes, but greater than 4 for endosulphan sulfate. The Mass Transfer Biot numbers based on the experimentally determined K_{fs} values range from 0.8 to 4.4. If the latter K_{fs} and Mass Transfer Biot numbers values are correct, the mass absorbed into the fibre would approach equilibrium rapidly and the TWA would be underestimated.

The mass of analyte absorbed into the fibre was determined by comparison with a direct injection calibration curve using external standards. Table 5-12 summarises the mass absorbed of the different analytes.

Table 5-12: Mass of Analyte Absorbed During 24 hour TWA sampling

Analyte	Chlorpyrifos	Endosulphan-alpha	Endosulphan-beta	Endosulphan Sulfate
Mass absorbed (m_T)[pg]	0.28	0.19	0.00	0.00
Corrected mass (m_T)[pg]	0.52	0.36	0.00	0.00

The mass loading rate is given by:

$$\frac{dm}{dt} = \frac{A.D_s}{\Delta x}(C_s - C_i) = R.(Cs - Ci) \qquad \text{.....(36)}$$

The total mass loaded into the fibre is then:

$$m_T = R.\int_{t=0}^{tT}[C_{s\infty}(t) - C_i(t)]dt \qquad \text{..... (58)}$$

The factor R may be calculated with A= $7.1*10^{-8}$ m^2, D_s = $0.44*10^{-9}$ m^2/s and $\Delta x = \delta_f$ = $5.6*10^{-5}$ m; hence the initial volumetric sampling rate, R = $0.56*10^{-12}$ m^3/s. In the absence of experimental mass sampling rates to define the rate of decrease in sampling rate with time over the sampling period, the initial sampling rate R was used to estimate C_{TWA}:

$$C_{TWA} = m_T/(R.t_T);\ t_T = 24 \text{ hours};\ t_T = 8.64*10^4 \text{ s}$$

Table 5-13 compares these estimates against the 24 hour mean values of Table 5-12.

Table 5-13: Comparison of TWA sample concentrations versus average of 24 hour grab samples

Analyte	Chlorpyrifos	Endosulphan-alpha	Endosulphan-beta	Endosulphan Sulfate
C_{TWA} [µg/l]	0.01	0.01	0.00	0.00
Average of 24 x hourly samples [µg/l]	0.45	0.45	0.40	0.13

From the results it is clear that the TWA sample under-predicts the average values as measured using the 24-hourly grab samples over the sampling period. The TWA method failed to detect the Endosulphan-beta and Endosulphan Sulfate analytes. Analyte loss from fibre due to periods of low concentration may be the cause of the under-prediction of the actual concentrations. Derivitisation may be a solution to this problem. The second contributing factor to the under-prediction of the TWA concentration is that the flush mounted fibre configuration used does not display linearity (with respect to mass absorbed versus time) beyond about 4 hours for 3 of the 4 analytes, as shown in Figure 5-7.

Chapter 6: Discussion

This study found SPME to be a highly effective method for extracting and analysing the two pesticides, endosulphan and chlorpyrifos, in water. Previous studies [38] have shown that it can be employed on many of the other pesticides families (i.e. organophosphorus compounds, triazines, thiocarbamates, urea derivatives, and dinitroanilines). Reproducibility was found to be better than for SPE. This is consistent with a previous study that has shown SPME to be a reliable method [45]. An important finding was that the MDL of SPME was an order of magnitude lower than that found for SPE; the greater sensitivity is a prerequisite for the detection of pesticides at low environmental concentrations.

Only a handful of laboratories in South Africa have MDL's, for pesticides, lower than 0.1µg/l. SPME was successfully employed on environmental samples. Although a limitation in the study was that only three environmental samples were analysed, the range of concentrations was representative as it was similar to that found in a previous study in which SPE was used. This study indicates that SPME holds great promise as an analytical method that can be used for systematic monitoring of pesticides in water, in South Africa.

It is not necessary for samples to reach equilibrium, which was more than 60 minutes for the four analytes evaluated and would have increased the analytical time for SPME. A previous study [4] reported that sensitivity of SPME is not affected if equilibrium is not achieved and another study [17] reported that if equilibration times are excessively long, shorter extraction times could be used. Based on the findings from the previous reported studies, an exposure time of 25 minutes was chosen to be adequate to allow sufficient mass of analyte to be absorbed into it, in order to obtain significant peaks on the Gas Chromatograph (GC).

At temperatures higher than 20°C, thermal swelling or expansion may occur. This is expected to cause the fibre coating radius to change according to equation: $r = r_0 (1 + \alpha T)$ [31], where r_0 is the radius at 0°C and α is the linear thermal expansion co-efficient. Pawliszyn [31] stated that for PDMS, α is noted to be $2.7 \times 10^{-4}\ °C^{-1}$ (negligible for SPME extraction conditions). With an increase in temperature, extraction of analytes is faster, but loss of sensitivity occurs due to a decrease in the distribution constant. Therefore, although the rate of analyte mass

extraction at 30°C was 20% higher than at 20°C, it was more practical to use the controlled laboratory temperature of 20°C.

In Chapter 2 the Mass Transfer Biot number, Bi_{MT}, was defined as $Bi_{MT} = \left(\frac{\mathbf{D_s}}{\mathbf{D_f}}\right).\left(\frac{r_0}{\delta_f}\right).\left(\frac{1}{K_{fs}}\right)$. The Mass Transfer Biot number is *inversely proportional* to the K_{fs} and to δ_f, the momentum film thickness. The Mass Transfer Biot number increases with an increase in agitation rate, which decreases the δ_f. A higher Mass Transfer Biot number results in an increase in the rate of analyte absorption into the fibre coating, but has no effect on the amount of analyte being absorbed into the fibre coating. The theoretical analysis in figure 5-2 clearly illustrates the inverse proportionality of the relationship between the boundary layer thickness and the agitation rate. Experimental results qualitatively confirmed the theoretical analysis and demonstrated that the maximum agitation rate of 625 RPM achieved the highest rate of analyte mass extraction for each analyte, with good reproducibility between replicate pairs, as opposed to results at low or no agitation. Beyond the agitation rate of 625 RPM, vortexing occurred, which would ultimately lead to the lack of good reproducibility between replicate pairs.

Fig 2-6 and Fig 2-8 show that the smaller the Mass Transfer Biot Number, the longer the time taken for the analyte extraction, on to the fibre, to reach equilibrium. Using Equation 31 and Fig 2-8, the theoretical times to reach 95% of the equilibrium mass may be determined and compared with the values predicted by the simplified analysis, using Equation 12. The differences are less than 10%. The experimental results in Fig 5-6 show similar profiles to the theoretical analysis in Fig 2-8. The practical implication of this is that there is, qualitatively, agreement between this set of experimental results and the theoretical analysis, using the Mass Transfer Biot number as a parameter. A quantitative comparison would entail direct measurement of diffusivities and K_{fs} values as well as more detailed experimental work. In a given experimental system, factors that remain constant or nearly constant are the analyte diffusivities and the fibre coating radius.

In the environment, pesticide contaminant concentrations in surface streams display variations over time, from hours to days to weeks. Irregular grab samples, usually once weekly, may provide a poor estimate of the average concentration of the stream sampled. If

grab samples are taken less frequently, then a greater uncertainty will arise. Therefore, a sampling method that yields a Time Weighted Average (TWA) concentration over a comparatively extended period (24 hours) using a single sample should, theoretically, give a more accurate picture of current contaminant levels.

The theoretical analysis showed that the SPME system could be adapted to obtain a Time Weighted Average sample of pesticides in water, at concentrations of the order of 1μg/l. The system could be operated with mass loadings of 20-30% of the equilibrium values, with a corresponding increase in method sensitivity (detection limit) providing that the linearity of the mass loading rate through the sampling period was preserved by operating the system at a low Mass Transfer Biot number for the sample period under consideration. The theoretical analysis also demonstrated the impossibility of satisfying both linearity and sensitivity criteria with a single fibre located in a particular configuration if the analytes of interest have a wide range of K_{fs} values (in this case the ratio of the highest to lowest K_{fs} values, based on literature data, is approximately 50:1). A multi-fibre system would be required for these cases.

The laboratory based experiment showed that a similar (agreement within 6%) TWA sample was obtained for two markedly different exposure patterns with the same theoretical TWA concentration. However, this test does not confirm that the absolute value of the measured concentration is accurate, and it is thus not a definitive test of the validity of the result.

For the integrated-sampling method (TWA) to be successful, analyte retention on the fibre is essential in order to predict the occurrence of a maximum peak concentration of the analyte in a stream over a set time period (e.g. 24 hours). It is essential that the analytes do not desorb from the fibre coating when exposed to very low or zero concentrations within a stream. Results, using PDMS, show that the fibre fails to retain, for the time period required (in Fig 5-6 for 3-hour period when conducting analyte retention test with 1μg/l chlorpyrifos sample), 100% of the analyte absorbed, with losses over 50% over a 3-hour period. The retention for each analyte is different as each analyte has different K_{fs} values, which in turn means that the mass extracted onto a fibre for each analyte is different. All four analyte, however, do display losses from the fibre coating over extended exposure periods to analyte-free water. Based on limited experimental data, this loss factor was assumed to be constant, and the calculated

TWA result was adjusted accordingly. This calculation was based on limited experimental data; hence its validity has yet to be confirmed experimentally. The loss of analyte hinders the sensitivity, and quite possibly the reproducibility, of the method.

Chemically fixing the absorbed analyte onto the fibre or using a different type of fibre coating may overcome this loss of analyte from the fibre. Fibres containing porous materials are better for the analysis of ppb levels of analytes with low distribution constants. Due to the fact that pores have the ability to adsorb and physically retain analytes, the result is better retention of analytes that fit into the pores [29]. Divinylbenzene (DVB) is a solid porous particle with a high degree of porosity and, due to its solid nature, is suspended in a liquid phase to coat it onto a fibre. DVB may be blended with PDMS with the combination reported to produce better retention of smaller analytes than PDMS alone [29].

Chapter 7: Conclusions and Recommendations

This study confirmed that the SPME method is a reliable, simpler and faster extraction method than SPE, as well as a viable and preferred alternative to SPE in the analysis of the four analytes, i.e. chlorpyrifos, endosulphan-alpha, -beta, -sulfate, in aqueous media (water), particularly when analysing at very low concentrations. The MDL of SPME was also found to be an order of magnitude lower than SPE (SPME MDL: 0.01µg/l to 0.02µg/l compared to SPE MDL: 0.05µg/l to 0.13µg/l). The SPME method was successfully used on 3 typical environmental samples. Reproducibility, between replicates, which is defined as the agreement (or lack thereof) between values for sample runs obtained in like determinations at different times during the experimental testing program, ranged from 3.1% to 4.1% at the 1µg/l level; the mass absorbed onto the fibre ranged from 40pg to 80pg (at the 1µg/l level). In the SPME method the fibre directly extracts the analyte from an agitated sample. It is then directly inserted into the injection port of the Gas Chromatograph (GC) for quantification. The advantage of this simplicity is that the time consuming sample preparation step performed in the SPE method, which may lead to a loss of volatile analytes, is omitted. Other advantages of the sample-free SPME method are higher sensitivity and smaller sample volume. SPME is therefore recommended for consideration as an analytical method if the full-scale monitoring of pesticides in water is to be implemented in South Africa.

The theoretical analysis in Fig 5-2 clearly illustrates the inverse proportionality of the relationship between the boundary layer thickness and the agitation rate. Experimental results qualitatively confirmed the theoretical analysis and demonstrated that the maximum agitation rate of 625 RPM achieved the highest rate of analyte mass extraction for each analyte, with good reproducibility between replicate pairs. The theoretical times to reach 95% of the equilibrium mass were determined (using equation 31) and compared with the values predicted by the simplified analysis (equation 12). The differences were less than 10%. The experimental results in Fig 5-6 showed similar profiles to the theoretical analysis in Fig 2-8. The practical implication of this is that there is agreement, qualitatively, between the set of experimental results and the theoretical analysis. The experimentally determined times to 95% of equilibrium were approximately 70 minutes for all three endosulphan analytes. Factors that may be responsible for the differences between the theoretically determined

times and the experimentally approximated times are the uncertainty in the diffusivities and the average boundary layer thickness, δ_f.

The primary purpose of obtaining the 24 x hourly samples, using the autosampler, was to provide the basis of comparison for the SPME Fibre TWA sample. However, analysis of these 24 samples yielded an important observation. While only one set of hourly samples was taken, the 24 x hourly grab samples revealed that the diurnal variation in analyte concentration is considerable, confirming that a single grab sample of a contaminated stream or river is very likely to overestimate or underestimate the average value over a given day. A single grab sample would then provide a poor estimate of the time-averaged concentration of the stream sampled. The uncertainty is even greater if grab samples are taken less frequently than daily, as is usually the case. Thus, regardless of the precision of the analytical method applied to the (single) grab sample, an assessment of the level of contamination of the stream is subject to the far greater uncertainty because the grab sample provides a poor representation of the time averaged concentration than uncertainty due to lack of analytical precision.

Insufficient experimental results have been obtained, to date, to provide estimates of the accuracy and sensitivity of the TWA sampling method. The preliminary work reported on shows that a limitation of the method was the loss of analyte from the PDMS fibre coating. This problem, however, could be overcome by using a different fibre coating or by chemically fixing the absorbed analyte onto the fibre coating. Further work is required to develop the TWA sample method. The drawbacks of the method, i.e. the loss of analyte during periods of low sample concentration and the different response characteristics of fibre-coating/analyte systems (K_{fs} values), may limit the application of the method. The possibility of using the SPME fibre system to obtain peak concentrations over a given period may be more promising.

APPENDICES

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APPENDIX A: Table of Commercially Available SPME Fibres

Table A-1: Summary of Different SPME fibres commercially available[a] for GC and GC/MS [29]

Phase	Coating Volume	Application
1. Polydimethylsiloxane Three film thicknesses are available: ❖ 7μm ❖ 30μm ❖ 100μm	 0.026μl 0.132μl 0.612μl	Non-polar phase (for many semipolar compounds: aromatics, esters, many pesticides) 100μm used for relatively volatile compounds; the thinner phases are for non-polar and semipolar compounds of low viscosity.
2. 85-μm Polyacrylate	0.521μl	Polar compounds such as phenols, esters.
3. 65-μm Carbowax/ Divinylbenzene	0.357μl	More polar than polyacrylate, for alcohols.
4. 75-μm PDMS/ Divinylbenzene	0.436μl	Moderately polar, for amines.
5. 65-μm Carboxen/ PDMS	0.357μl	Highly volatile compounds including vinyl chlorides, sulphur gases.

a) Supplied by Supelco (supplier's dimensions)

APPENDIX B: Apparatus and Analytical Methods to be Used

- Solid phase microextraction fibres - manual sampling and autosampling (Supelco supplies; Anatech is the distribution agent)
- Solid phase microextraction fibre holder for manual sampling (Supelco supplies; Anatech is the distribution agent)
- Varian 8200 CX Autosampler
- Magnetic stirrer (Heidolph Model: MR 3001K) - (Labotec supplies); and Teflon coated magnetic stirrer bar (Peninsula Technikon)
- Millipore Water - Milli-RO4 Water Purification System (Millipore supplies), and Milli-Q Reagent Grade Water System (Millipore supplies)
- Pesticide analyses will be done using the Varian 3300 Gas Chromatograph

APPENDIX C: Preparation of Analytical Standards of the Four Pesticides

C.1 Suppliers' Pesticides' Standards Data:

C.1.1 Chlorpyrifos:

- Catalogue Number: PS-674
- Lot Number: 219-91B
- Purity: 99.2%
- Expiration Date: 02/03
- Invoice Number: CS204701
- PO Number: 2000030977

C.1.2 Endosulphan (alpha isomer):

- Catalogue Number: PS-81-1
- Lot Number: 232-85A
- Purity: 99.5%
- Expiration Date: 10/02
- Invoice Number: CS204701
- PO Number: 2000030977

C.1.3 Endosulphan (beta isomer):

- Catalogue Number: PS-81-2
- Lot Number: 225-108B
- Purity: 99.5%
- Expiration Date: 08/05
- Invoice Number: CS204701
- PO Number: 2000030977

C.1.4 Endosulphan Sulfate:

- Catalogue Number: PS-81-3
- Lot Number: 225-43A
- Purity: 99.5%

- Expiration Date: 06/02
- Invoice Number: CS204701
- PO Number: 2000030977

C.2 Preparation of the Stock Standards of each pesticide:

- Weigh out, separately, approximately 0.0100g of Chlorpyrifos (pure compound), 0.0100g of Endosulphan-alpha, 0.0100g of Endosulphan-beta and 0.0100g of Endosulphan Sulfate, using a weigh bath
- Throw mass weighed of Chlorpyrifos, Endosulphan-alpha, Endosulphan-beta and Endosulphan Sulfate, into separate 100ml volumetric flasks
- The contents in each flask are to be dissolved in methanol
- Dilute to the 100ml mark in each of the volumetric flasks

Note: The concentrations of the stock standards:

Chlorpyrifos = 0.0099g => 99mg/ml (i.e. 99000µg/l); 99ppm

Endosulphan-alpha = 0.0105g => 105mg/ml (i.e. 105000µg/l); 105ppm

Endosulphan-beta = 0.0101g => 101mg/ml (i.e. 101000µg/l); 101ppm

Endosulphan Sulfate = 0.0102g => 102mg/ml (i.e. 102000µg/l); 102ppm

C.3 Preparation of the 1ppm Mixed Stock Standard for each pesticide:

***Note:** *the 1ml pipette should be constantly rinsed with distilled water before and after pipetting of different compounds or solutions; this should be done in all the preparations that follow**

- Use the 100ppm stock standards of each analyte, as prepared above, for the 1ppm mixed stock standard
- Use a 1ml pipette to pipette out 1ml of the Chlorpyrifos 100ppm stock standard in the 100ml volumetric flask
- Pour the contents, from the 1ml pipette, into a clean 100ml volumetric flask
- Repeat the pipetting of 1ml of the other three analytes (i.e. Endosulphan-alpha, Endosulphan-beta and Endosulphan Sulfate) and add each of them to the same 100ml volumetric flask
- Dissolve the contents in the 100ml volumetric flask, all four analytes at 100pm concentration, in methanol
- Dilute to the 100ml mark in the volumetric flask

Note: 1ml of each analyte at a concentration of 100ppm in a 100ml volumetric flask renders a concentration of 1ppm

APPENDIX D: Fibre Care Guidelines (Supplier's Suggestion)

1. A new fibre needs to be conditioned by desorbing for approximately 60 minutes in an injector that is about 10°C hotter than the temperature to be used during analysis. The GC column should be temperature programmed and this procedure should be repeated until there are no major peaks present.
2. The fibre and injector septum should be changed after 100 runs. If, however, after 100 runs the fibre and injector septum are still in a condition, then further runs with the same fibre may be embarked upon.
3. Standards and samples are prepared and diluted in storage containers and then transferred to manual sampling glass vials for analysis.
   - Samples should be stored in the refrigerator and the glass vials may be chilled before adding the sample.
   - The samples should be transferred to the vials with a pipette of sufficient capacity to deliver the entire sample in one step. (For 10.0ml volume, a 10ml Grade-A pipette should be used).
4. For the liquid sampling, 10.0ml should be used for a 10.0ml glass vial. (Note: The glass vial should not be filled right to the top)
5. From literature it is suggested that a fair absorption time is 20-25 minutes with 3 minutes desorption. Preferably, conditions should be optimised for each analysis. It is not necessary to achieve equilibrium if the total analysis time will be prolonged, because for many samples, relative standard deviations under 5% may be obtained before reaching equilibrium.

The life of the SPME fibre varies with experimental conditions but there is no visible or evident deterioration in chromatography up to 100 runs when desorbing into an injector heated to 220°C. A possible sign of an aging fibre is deterioration of precision, which may also be due to an aging GC septum. Therefore, it is preferable to change the septum when changing the fibre.

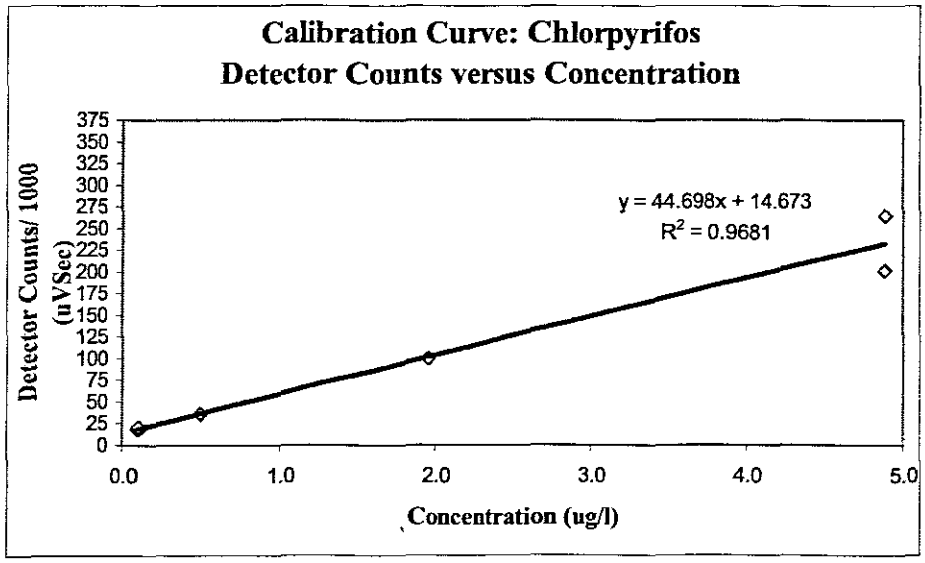
The glass sampling vials should not be filled to the top due to the possibility of carryover if the liquid sample enters the fibre sheath and is not fully desorbed. Good precision may be

obtained without achieving equilibrium. A reasonable point for sampling is 20-25 minutes, but absorption times may be longer if the GC cycle time permits. At least 3 minutes is recommended to desorb all traces of the analyte to minimize carryover. The injector temperature is normally at least 200°C but should not be higher than the temperature limit of the analytical column or the SPME fibre. (Note: if carryover is present, a longer desorption time and possibly a higher injector temperature should be used as well.)

A new fibre needs to be desorbed for 15 to 20 minutes. When a new fibre is desorbed for 3 minutes, followed by a GC run, after 6 runs the blank is clean. For a fibre that has been used, the first run each day should be a blank. Peaks known as Ghost peaks may occasionally appear from the vial septa. If this occurs, a different septum brand should be used or the septa should be baked before use.

APPENDIX E: Calibration Curves

Figure E-1: Calibration Curve of Chlorpyrifos – Detector Counts versus Concentration (1)*



**All Calibration Curves were generated using Microsoft Excel, and fitted with a linear trendline.*

Figure E-2: Calibration Curve of Endosulphan Sulfate - Detector Counts versus Concentration (1)

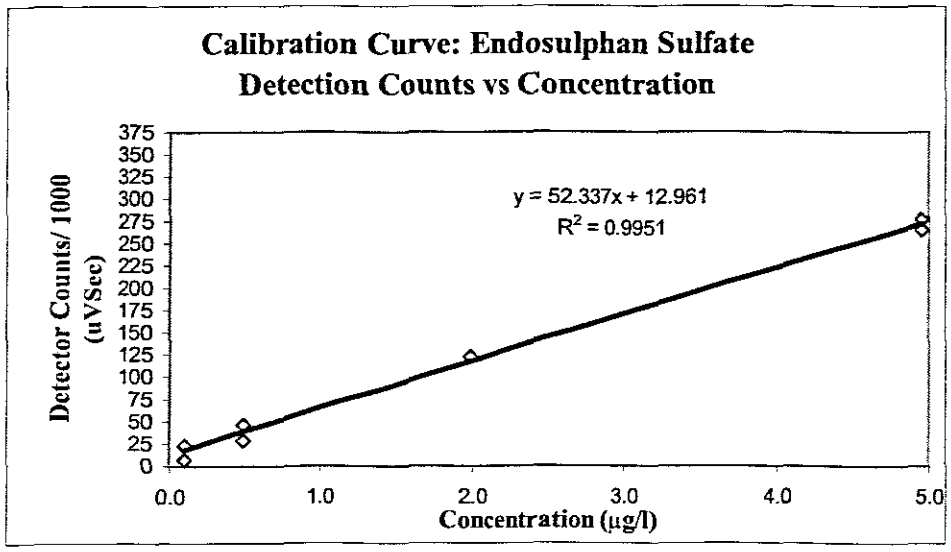


Figure E-3: Calibration Curve of Endosulphan-beta - Detector Counts versus Concentration (1)

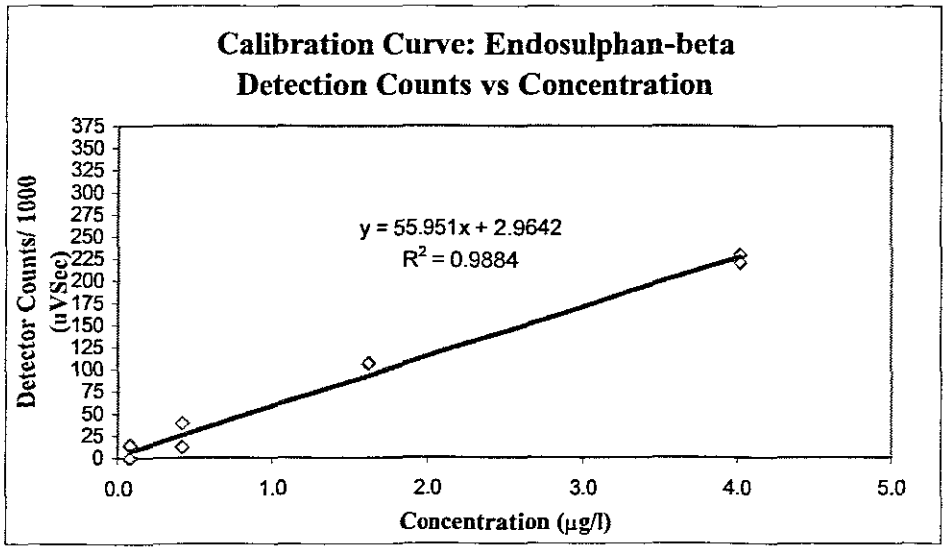


Figure E-4: Calibration Curve of Endosulphan-alpha - Detector Counts versus Concentration (1)

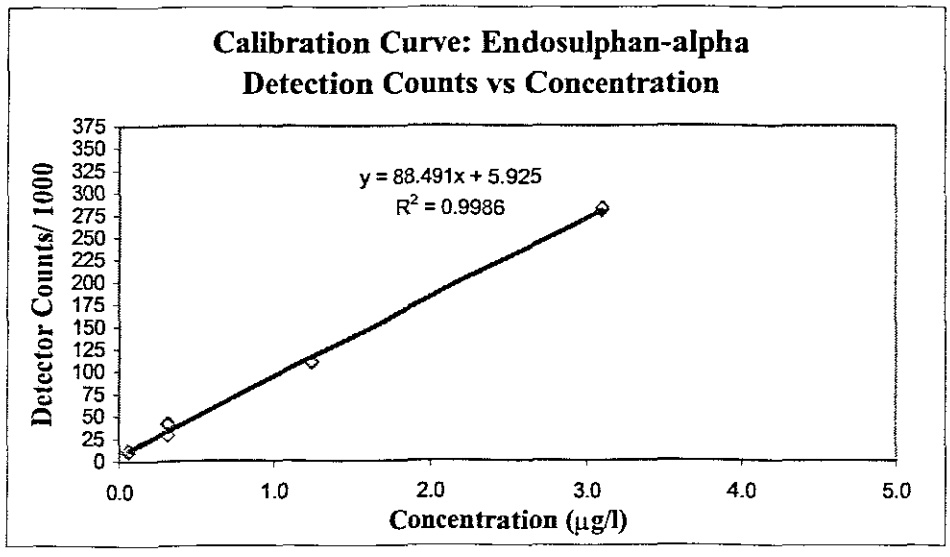


Figure E-5:Calibration Curve of Chlorpyrifos – Detector Counts versus Concentration (2)

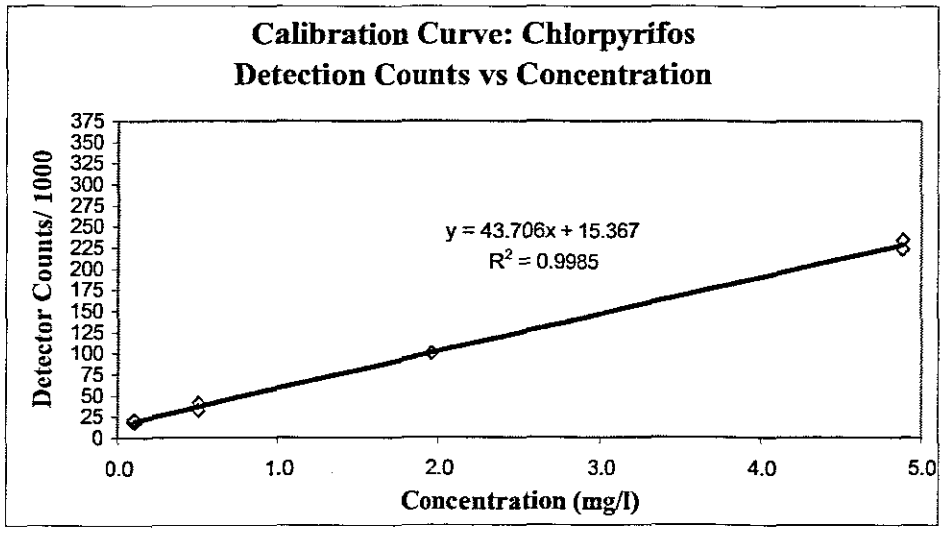


Figure E-6:Calibration Curve of Endosulphan Sulfate – Detector Counts versus Concentration (2)

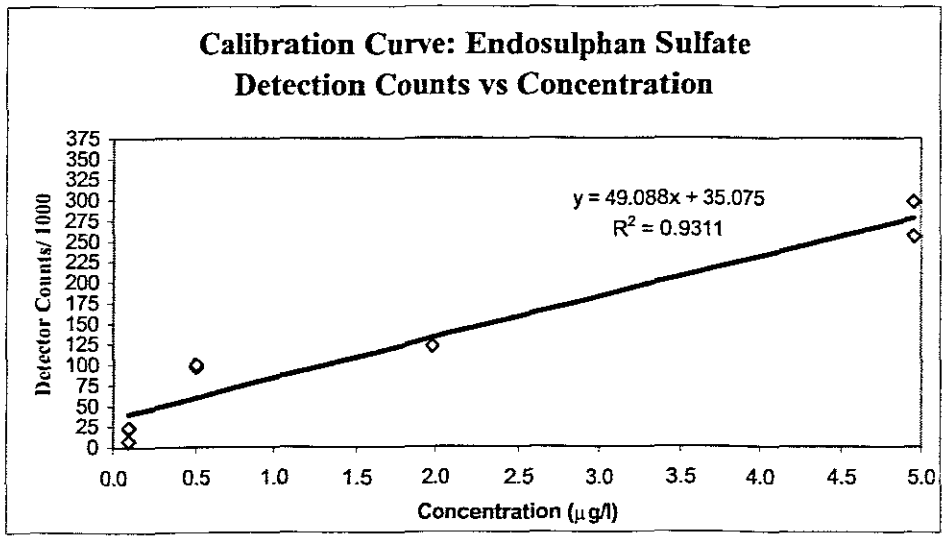


Figure E-7: Calibration Curve of Endosulphan-beta - Detector Counts versus Concentration (2)

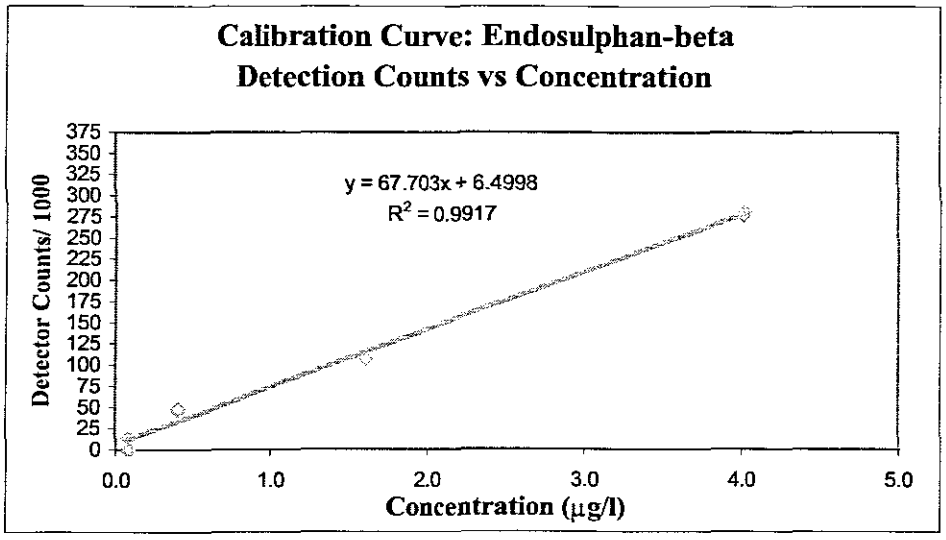
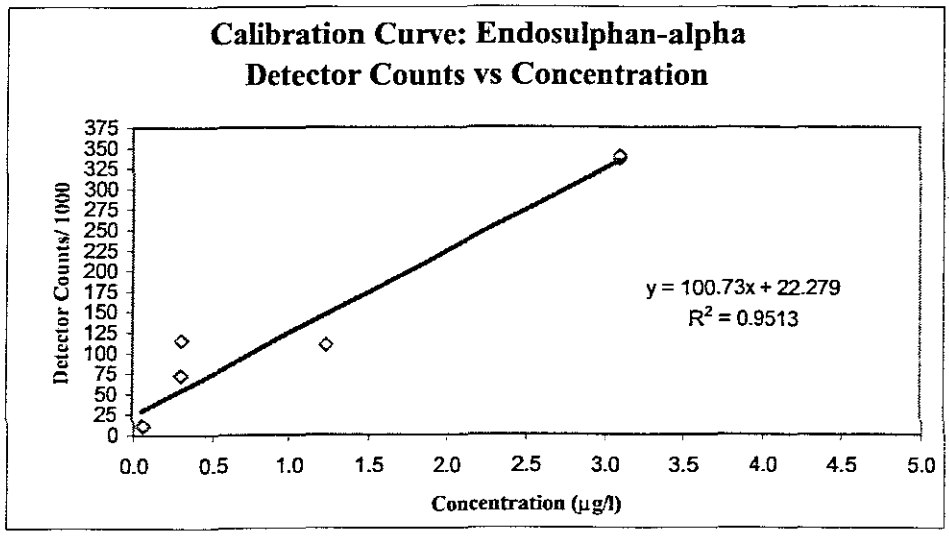


Figure E-8: Calibration Curve of Endosulphan-alpha - Detector Counts versus Concentration (2)



APPENDIX F: Equilibrium Runs for Four Analytes

Figure F-1: Graph of Detector Counts versus Absorption Time for 1μg/l Chlorpyrifos

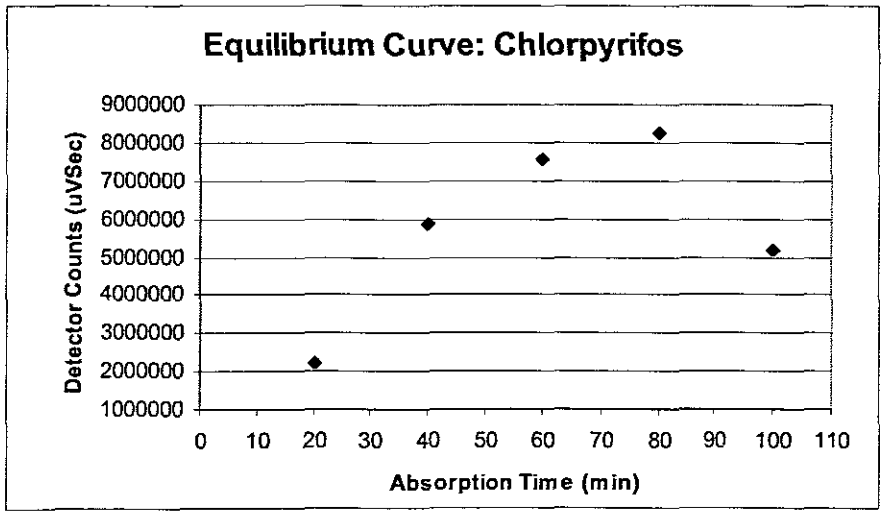


Figure F-2: Graph of Detector Counts versus Absorption Time for 1μg/l Endosulphan-alpha

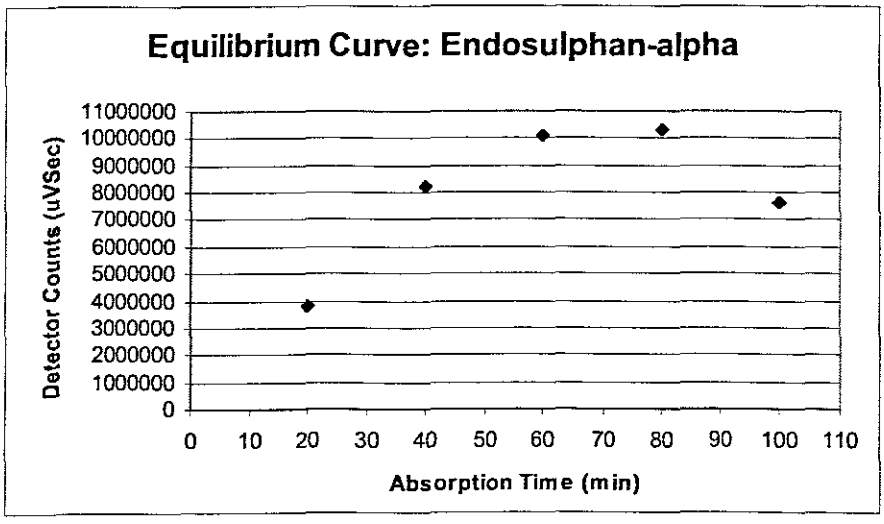
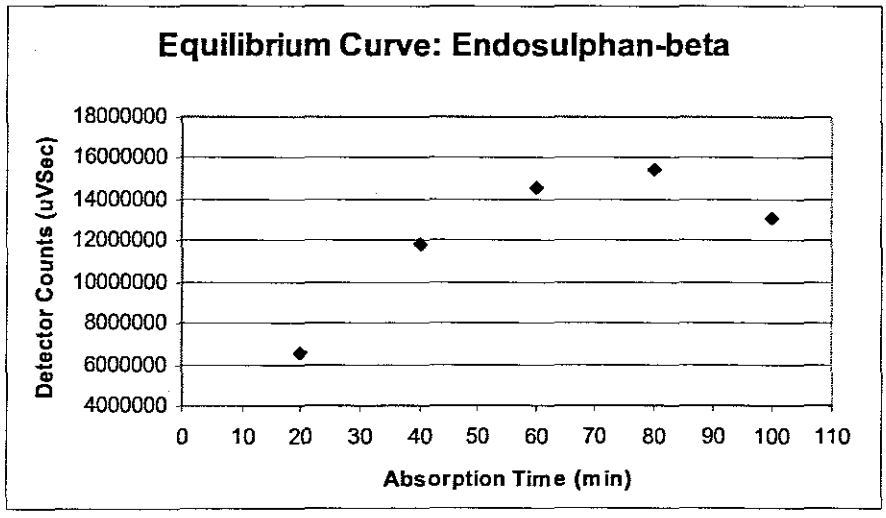
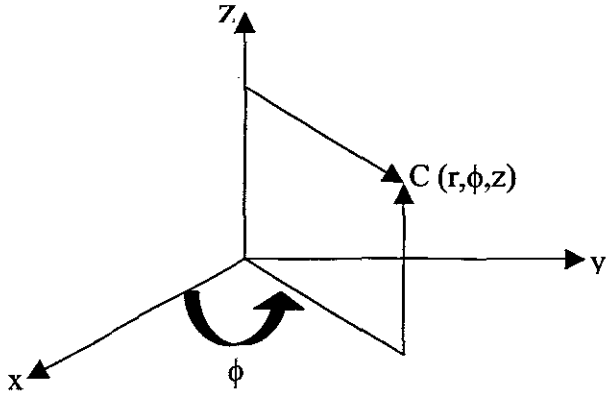


Figure F-3: Graph of Detector Counts versus Absorption Time for 1µg/l Endosulphan-beta



APPENDIX G: Theoretical Analysis: Mass Transfer Derivation for the Infinite Cylinder

Radial Co-ordinate system:



$$m_{r+dr} = m_r + \frac{\partial m_r}{\partial r} dr \qquad \text{.....G.1}$$

$$m_{\phi+d\phi} = m_\phi + \frac{1}{r}.\frac{\partial m_\phi}{\partial \phi} d\phi$$

$$m_{z+dz} = m_z + \frac{\partial m_z}{\partial z} dz$$

But,

$m_{\phi+d\phi}$ = 0 (due to the assumption of symmetry in cylinder)

m_{z+dz} = 0 (due to the assumption of infinite cylinder)

Where, 'm' is the mass flow rate.

On rate basis, the general form for the conservation of mass is:

$$\mathbf{j_{in} + j_{gen} - j_{out} = j_{st}} \qquad \text{.....G.2}$$

Where, mass in is:

$$\mathbf{j_{in} = m_r.(r\Delta\phi.\Delta z)} \qquad \text{.....G.3}$$

Mass out is:

$$\mathbf{j_{out} = j_{r+\Delta r}.(r+\Delta r).\Delta\phi.\Delta z} \qquad \text{.....G.4}$$

And, mass accumulated is:

$$\mathbf{j_{acc}} = \frac{\partial C}{\partial t}\Delta r(r\Delta\phi)\Delta z \qquad \text{.....G.5}$$

Therefore, Equation G.2 becomes:

$$\mathbf{j_{in} - j_{out} + j_{acc} = 0}$$

Where, 'j' is the mass flux.

$$m_r.(r\Delta\phi.\Delta z) - m_{r+\Delta r}.(r+\Delta r).\Delta\phi.\Delta z + \frac{dC}{dt}.r\Delta r.\Delta\phi.\Delta z \qquad \text{.....G.6}$$

From Fick's Law (mass flux equation) in general terms:

$$j_r = -D_{AB}\frac{\partial C}{\partial r} \quad \text{(Radial)} \qquad \text{.....G.7}$$

Then, Equation G.6 becomes:

$$\left(-D_{AB}\frac{dC}{dr}\bigg|_r\right).(r\Delta\phi.\Delta z) - \left(-D_{AB}\frac{dC}{dr}\bigg|_{r+\Delta r}\right).(r+\Delta r).\Delta\phi.\Delta z + (r.\Delta r.\Delta\phi.\Delta z)\frac{dC}{dt} = 0$$

.....G.8

Now,

$$f(r) = \frac{dC}{dr}$$

$$\lim_{\Delta r\to 0}\left(\frac{(r+\Delta r)f(r)_{r+\Delta r} - r\,f(r)_r}{\Delta r}\right) = \frac{\partial}{\partial r}(r\,\partial f(r))$$

Therefore, Equation G.8 becomes:

$$\frac{\partial}{\partial r}\left(D_{AB}.r\frac{\partial C}{\partial r}\right) = r\frac{\partial C}{\partial t}$$

$$\frac{D_{AB}}{r}.\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) = \frac{\partial C}{\partial t} \qquad \text{.....G.9 [41]}$$

In dimensionless form:

$$C^* = \frac{C}{C_i} = \frac{C - C_\infty}{C_i - C_\infty} \qquad \text{.....G.10}$$

$$r^* = \frac{r}{r_0} \qquad \text{.....G.11}$$

$$t^* = \frac{D_{AB}\, t}{r_0^2} \qquad \text{.....G.12}$$

Rewriting Equation G.10:

$$C = C^*(C_i - C_\infty) + C_\infty$$

Now,

$$\frac{\partial C}{\partial r} = \left(\frac{C_i - C_\infty}{r_0}\right).\left(\frac{\partial C^*}{\partial r^*}\right)$$

$$\partial r = r_0 . \partial r^*$$

$$\partial t = \frac{r_0^2}{D_{AB}} . \partial t^*$$

Equation G.1 => LHS:

$$\left(\frac{1}{r^* . r_0}\right).\left[\frac{\partial}{\partial r}.\left(r.\frac{\partial C}{\partial r}\right)\right] = \left(\frac{1}{r^* . r_0}\right).\left[\frac{1}{r}.\frac{\partial}{\partial r^*}.\left((r^* . r).\left(\frac{C_i - C_\infty}{r_0}\right).\left(\frac{\partial C^*}{\partial r^*}\right)\right)\right]$$

$$= \left(\frac{C_i - C_\infty}{r^* . r_0^2}\right).\left[\frac{\partial}{\partial r}.\left(r^* . \frac{\partial C^*}{\partial r^*}\right)\right]$$

Equation G.1 => RHS:

$$\frac{1}{D_{AB}}.\frac{\partial C}{\partial t} = \frac{1}{D_{AB}}.(C_i - C_\infty).\left(\frac{\partial C^*}{\partial t}\right)$$

$$= \frac{1}{D_{AB}}.(C_i - C_\infty).\left(\frac{D_{AB}}{r_0^2}.\frac{\partial C^*}{\partial t^*}\right)$$

Now: LHS = RHS:

$$\left(\frac{C_i - C_\infty}{r^*.r_0^2}\right).\left[\frac{\partial}{\partial r}.\left(r^*.\frac{\partial C^*}{\partial r^*}\right)\right] = (C_i - C_\infty).\left(\frac{1}{r_0^2}.\frac{\partial C^*}{\partial t^*}\right)$$

Therefore, the dimensionless form of Equation G.1 is:

$$\left(\frac{1}{r^*}\right).\left[\frac{\partial}{\partial r}.\left(r^*.\frac{\partial C^*}{\partial r^*}\right)\right] = \frac{\partial C^*}{\partial t^*} \qquad \text{where,} \quad t^* = F_0$$

Initial Condition:

$$C(r,0) = C_i; \quad C^* = \frac{C - C_\infty}{C_i - C_\infty}$$

Then, $\dfrac{C_i - C_\infty}{C_i - C_\infty} = 1$

BC1:

$$\left.\frac{\partial C}{\partial r}\right|_{r=0} = 0; \quad \frac{\partial C}{\partial r} = \left(\frac{C_i - C_\infty}{r_0}\right).\frac{\partial C^*}{\partial r^*} = 0$$

Therefore, $\left.\dfrac{\partial C^*}{\partial r^*}\right|_{r=0} = 0$

BC2:

$$-D_{AB}\left.\frac{\partial C}{\partial r}\right|_{r=r_0} = k_c[C(r_0,t) - C_\infty]$$

$$-\frac{D_{AB}}{r_0}.\left[(C_i - C_\infty).\frac{\partial C^*}{\partial r^*}\right]_{r^*=1} = k_c\left[(C_i - C_\infty).C^*(r^*,t)\right]_{r^*=1} - C_\infty + C_\infty\Big]$$

$$\text{Then, } \left[\frac{\partial C^*}{\partial r^*}\right]_{r^*=1} = -\frac{k_c r_0}{D_{AB}}\left[C^*(1,t^*)\right] = -Bi.C^*(1,t^*)$$

The Mass Transfer Biot number for the flat plate and the infinite cylinder are similar in relation to each other, with the only difference being the co-ordinate system:

Flat Plate Mass Transfer Biot Number: $Bi_{MT} = \frac{k_c x_1}{D_{AB}}$

And, the Infinite Cylinder Mass Transfer Biot Number: $Bi_{MT} = \frac{k_c r_0}{D_{AB}}$

Total Mass Absorbed onto Fibre:

Let, $m_\infty = V.\Delta C$

$= V(C_i - C_\infty)$

And, $m = -\int_v (C - C_i)dV$

Therefore, $\frac{m}{m_\infty} = -\frac{1}{V(C_i - C_\infty)}\int_v (C - C_i)dV$

Now, $C - C_i = \left[(C_i - C_\infty)\theta^* + T_\infty\right] - T_i$

$= \left[(C_i - C_\infty)\theta^*\right] - (C_i - C_\infty)$

$= (\theta^* - 1).(C_i - C_\infty)$

$= -(1 - \theta^*).(C_i - C_\infty)$

Therefore, $$\frac{m}{m_\infty} = \frac{1}{V(C_i - C_\infty)} \int_v (C_i - C_\infty).(1-\theta^*)dV \qquad \text{.....(sign change)}$$

$$\frac{m}{m_\infty} = \frac{1}{V} \int_v (1-\theta^*)dV$$

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