FACTORS INFLUENCING THE USE OF SOLID PHASE MICROEXTRACTION TECHNIQUES FOR ENVIRONMENTAL ANALYSIS OF INDUSTRIAL WASTE WATER

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LIST OF ABBREVIATIONS

SPME:	Solid phase microextraction
SPE:	Solid phase extraction
GC:	Gas chromatograph
HPLC:	High performance liquid chromatograph
NAC:	Non-acidic compounds
GC-MS:	Gas chromatograph – Mass spectrometer
VOCs:	Volatile Organic Compounds
BTEX:	Benzene, Toluene, Ethylbenzenes, Xylenes
PAHs:	Polycyclic Aromatic Hydrocarbons
PDMS:	Polydimethylsiloxane
PA:	Polyacrylate
DVB:	Divinylbenzene
CAR:	Carboxen
CW:	Carbowax
ppm:	Parts per million
ppb:	Parts per billion
ppt:	Parts per trillion
STD DEV:	Standard deviation
RSD:	Relative standard deviation

LOD:	Limit of detection
LOQ:	Limit of quantification
MEK:	Methyl-Ethyl Ketone
rpm:	Revolutions per minute

ABSTRACT

The goal of an analytical laboratory is to have a high sample throughput, quick turnaround time and reduced operating costs.

In most of the cases, a sample preparation step is necessary to prepare the sample for the specific analysis. Generally, a sample preparation step is incorporated in the analysis to eliminate interferences from the sample and to result in a "cleaner" sample that produces a signal with an enhanced signal response.

In chromatographic analysis, the sample preparation step is in most cases the rate determining step. This is because most of the sample preparation steps are outdated, time- and labor-intensive, contain multiple steps that can lead to the loss of analytes and involve the use of toxic organic solvents. It should also be noted that the possibility of errors increases significantly if the number of steps are increased. The errors can be due to human, systematic or contamination inconsistencies.

A sample preparation technique should be reproducible and cost effective. SPME meets these requirements. It is quick, sensitive and versatile; and no solvents or complicated apparatus are required. SPME consists of only two steps, namely the concentration and extraction of analytes out of the sample matrix, followed by desorption using a GC or HPLC.

The successful analytical extraction of small polar organic compounds from water samples is very difficult and the commonly used liquid-liquid extraction techniques are often not suitable for some polar analytes. The required recovery of target compounds out of the aqueous phase can not be achieved because of low partition coefficients. Continuous direct injections of water samples into a GC lead to the removal of the stationary phase of the gas chromatographic column and ultimate deterioration of the column, which increases maintenance costs (Chapter 1). Direct injections are sometimes not

sensitive enough for the very low level of organic pollutants in waste water streams, an aspect that will be demonstrated in the presentation of data in later chapters.

SPME is a potential alternative technique for the sampling of these pollutants in environmental waste water, particularly because of the diverse range of possible organic contaminants (Chapter 2).

An investigation was launched to compare two methods for the analysis of organic analytes in industrial waste water. The current method in use is a direct injection NAC method. Data from this technique has been unsatisfactory and this has led to the development of a SPME method, specific to the needs of an industrial client (Chapter 3). Comparisons between these two methods show that SPME gives a more effective picture of the pollution status.

The effectiveness of SPME depends on the efficiency of extraction. The various factors that have an influence on the extraction were investigated, in particular fiber choice, extraction duration, temperature and sample pH. It was found that fiber selection is dependent on the molecular weight, polarity, functionality and concentration level of the analyte of interest. According to the results, extraction time before equilibrium is achieved, affects the extraction process significantly. The amount of analyte extracted after equilibrium has been reached will remain similar, but for pre-equilibrium extraction, it is crucial to keep the extraction time constant. Associated with equilibrium effects is the variation of temperature and its influence on the extraction concentrations of the analytes. The higher the sampling temperature, the greater the extraction efficiency of the analytes will become, until a maximum is reached. The pH of the sample influenced the amount of acidic and basic analytes sorbed; basic compounds partitioning towards the fiber when the matrix had a high pH and similarly, acidic compounds partitioning towards the fiber when the pH was low. Polar analytes were driven out of the solution when the ionic strength of the sample was increased (Chapter 4).

Before SPME can be quantitatively used in analysis, all these factors should be optimized for maximum sensitivity, precision and ruggedness.

Quantification with SPME can be done using either an internal standard, or external standards with calibration graphs. For simple matrices, an internal standard can be used, provided the compound chosen is similar in characteristic to the target analytes. In this study it was found that the internal standard approach was not an appropriate method for quantification, simply because the range of organic compounds in the waste water was so diverse that no internal standard could be chosen to represent the group in response.

It was concluded that SPME was a suitable method for qualitative analysis, because more analytes could be detected. For quantitative analysis, it is important to optimize and control the extraction process. This makes the procedure sensitive to subtle changes that can affect data and therefore may not be rugged enough for routine analysis.

OPSOMMING

Die doel van 'n analitiese laboratorium is om so veel as moontlik monsters in die kortste moontlike tyd, teen die laagste koste te analiseer.

In die meeste gevalle is 'n monstervoorbereidingstap nodig om die monster vir 'n spesifieke analise voor te berei. Die rede waarom so 'n stap nodig is, is om steurings te probeer elimineer. Die resultaat is 'n "skoner" monster wat 'n sterk sein van die hoogste analiet konsentrasie lewer.

Dis verbasend om kennis te neem van die feit dat die monstervoorbereidingstap van die meeste chromatografiese analises, die analise tyd bepaal. Dit word toegeskryf aan die feit dat dit meestal verouderde, tyd- en arbeidsintensiewe, veelvoudige stappe bevat wat tot die verlies van analiete lei. Van die stappe sluit die gebruik van toksiese organiese oplosmiddels, wat 'n gesondheidsrisiko inhou, in. Dit moet ook in gedagte gehou word dat met elke addisionele stap, die moontlikheid van foute verhoog. Dit kan wissel van menslike-, sistematiese- of kontaminasie foute.

Die voorbereidingstap moet reproduseerbaar en koste effektief wees. SPME tegnieke voldoen aan hierdie vereistes. SPME is 'n metode waarin die analiete ge-ekstraëer, gekonsentreer en in die GC in een stap gevoer word. Van die voordele van SPME is dat dit vinnig, sensitief, veelsydig is en geen oplosmiddels of gekompliseerde apparate benodig nie. SPME bestaan uit twee stappe, naamlik die ekstraksie van die analiete uit die monster matriks en die desorpsie daarvan in 'n GC of HPLC.

Die ekstraksie van klein polêre analiete (bv. organiese komponente) vanuit 'n water matriks is gekompliseerd en algemene ekstraksie tegnieke is nie geskik vir bepalings van polêre analiete nie. In vloeistof-vloeistof ekstraksie en soliede fase ekstraksie is die oplosmiddel wat gebruik word in baie gevalle dieselfde verbinding as wat geanaliseer moet word. Die direkte inspuiting van 'n watermonster in 'n GC lei tot die verwydering van die stationêre fase van

die kolom. Dit beteken dat die kolom beskadig word en dat die kolom meer dikwels vervang moet word, wat die onderhoudskostes verhoog (Hoofstuk 1). Die lae vlakke van organiese besoedelstowwe in afvalstrome verhoog ook die kompleksiteit van sulke analises. SPME is 'n potensiële alternatiewe tegniek vir die analisering van sulke besoedelstowwe in die afvalwater (Hoofstuk 2).

'n Ondersoek was geloods om twee verskillende metodes vir die analise vir organiese analiete in industriële afval water te vergelyk. Die een metode is die sogenaamde die NAC metode en die ander metode is die SPME metode (Hoofstuk 3).

Verskeie faktore wat 'n invloed op die SPME ekstraksie kan hê, is ook ondersoek. Dit is gevind dat die keuse van die SPME vesel is gebaseer op die molekulêre gewig, polariteit, funksionele groepe teenwoordig en die konsentrasievlakke van die analiet. Volgens die resultate is die ekstraksie tyd, voor ewewig ingestel is, krities. Die konsentrasie van die analiet sal konstant raak na ewewig bereik is, maar voordat ewewig bereik is, moet die ekstraksietyd konstant gehou word. Dit blyk uit die resultate dat die variasie van temperatuur 'n invloed gehad het op die ewewig en die konsentrasies beïnvloed. Die konsentrasies het toegeneem met 'n toename in die temperatuur. Daar is gevind dat daar 'n toename in die analiet konsentrasie was, as die monster volume vergroot is. Die effek van die pH het 'n toename in konsentrasie vir suur en basis analiete tot gevolg gehad. Hoe meer basies die monstermatriks was, hoe groter die toename in konsentrasie vir basis analiete. Dieselfde het gegeld vir die ekstraksie van suur analiete in 'n suur matriks. Die ioonsterkte het die ekstraksie van polêre analiete beïnvloed. Hoe meer ionies die oplossing was, hoe hoër was die waargeneemde polêre analiet konsentrasie in die oplossing. Dit blyk uit hierdie ondersoek dat al bogenoemde faktore in ag geneem moet word voordat daar met ekstraksie begin word.

Verskillende metodes vir kwantifisering is ook ondersoek. Die eksterne standaard metode vir kwantifisering is met die interne standaard metode vir kwantifisering vergelyk (Hoofstuk 4). Volgens die resultate was die interne

standaard metode nie geskik vir die kwantifisering vir die SPME metode nie. Hierdie bewering is gebaseer op die feit dat die SPME vesel 'n affiniteit vir dioksaan het. Die gevolg is dat 'n skynbaar hoër konsentrasie as werklik waargeneem word.

Die gevolgtrekking is gemaak dat SPME 'n geskikte metode vir kwalitatiewe analiese is, omdat meer analiete geïdentifiseer kon word. SPME was nie 'n geskikte metode vir kwantitatiewe analises nie.

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CHAPTER 1

MOTIVATION AND OBJECTIVES

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The motivation and objectives of this study is outlined.

1.1. MOTIVATION

The water quality that is required for industries depends upon its intended use. Process water is required for washing, rinsing, direct contact cooling, solution makeup, chemical reactions, process condensation and gas scrubbing operations. Water impurities can therefore result in serious operating problems, such as deposit formation, corrosion of metals, foaming in steam generating systems and microbiological fouling.

The spent process waters normally contain the largest amount of contamination in plant effluents. This is usually caused by leakages of process liquors into the water system. Storage and transport of raw material may require attention as a potential source of contamination and as such must be considered in the overall analytical procedure. Good environmental governance requires a regular monitoring of industrial effluent.

Currently, dissolved organic compounds in waste water streams are analyzed by injecting the aqueous medium directly into a gas chromatograph (GC). This results in the quick deterioration of the GC column due to the removal of the stationary phase. The frequent

replacement of capillary columns leads to high maintenance costs for routine laboratories.

In order to increase sample throughput and decrease the maintenance costs, new technology needs to be investigated. SPME, which involves the extraction of the analytes from the water, can be a potential alternative method to direct injection of water samples into the GC and may eliminate the problems associated with an aqueous sample. It is a simple, cost-effective, time-saving extraction technique; highly sensitive and versatile because it can be used with any GC fitted with a detector of choice, or with split/splitless or on-column injection. No solvent or complicated apparatus is required, which also lowers the analysis costs. Also, any problems with solvent use and disposal of solvent waste are eliminated.

1.2. OBJECTIVES

The objectives of this study are to:

(i) investigate the sampling factors that can have an influence on SPME analysis;

(ii) compare the external standard method of quantification of VOCs in waste water streams with the internal standard method currently in use;

(iii) compare the Non-Acidic Compounds method (NAC) with SPME. The NAC method is currently applied and involves the use of an internal standard and direct injection in a GC.

CHAPTER 2

LITERATURE REVIEW

In this Chapter...

A brief introduction to SPME is given. How the analytes are extracted from the sample matrix and the desorption of the extracted analytes by means of a GC or high performance liquid chromatograph (HPLC) is discussed. The factors that influence the extraction process and the methods of quantification are reviewed. The advantages and disadvantages of SPME are also given.

2.1. INTRODUCTION

The industry demands rapid, sensitive, low cost analysis for the monitoring of effluents and contaminated sites. Aqueous samples vary from drinking water, groundwater or wastewater to wet sludge. The organic compounds in these samples are divided into either volatile or semivolatile/nonvolatile groups. Normally the volatile analytes are arbitrary defined as having boiling points below 200°C [1].

The standard sample preparation step for the isolation and concentration of organic compounds from an aqueous medium is usually liquid-liquid extraction involving the use of appropriate solvents. These extractions can be inappropriate for some samples due to excessive emulsion formation that prevents post-extraction separation of the organic and aqueous phases [1]. The extraction of small polar analytes (e.g. organic compounds) from water samples is very difficult and many commonly used extraction techniques are not suitable for polar analytes or are very

time-consuming. It is usually the sample preparation step that is the major source of error in an analysis [2].

Solid phase extraction (SPE) is an alternative method of extracting organic compounds from aqueous samples. It can be classified as a liquid-solid extraction process, in which the analyte of interest is adsorbed onto a particular adsorbent. The aqueous sample is passed through a coated membrane or particulate bed mounted in a filtration apparatus. Specific functional groups in the coated support have an affinity for the target analyte. These functional groups retain the analyte effectively on the solid phase. Once the filtration is completed, the analyte is quantitatively eluted from the solid with an appropriate solvent. Solid phase coatings can be designed for a specific application, for example the coating of C_{18} is used for the removal of non-polar analytes from the aqueous phase [1].

For volatile organic analytes in the water and wastewater samples, the most widely used method is the dynamic headspace analysis, also known as Purge and Trap. The volatiles are purged from a liquid sample by bubbling an inert gas through the sample. It is then swept onto a solid sorbent trap where it is retained and concentrated. The organic analytes are then thermally desorbed from the trap using additional inert gas and directed to the injector of a GC for separation and quantification. Static, or equilibrium, headspace is a variation on Purge and Trap in which an aliquot of the headspace of a heated, enclosed sample is taken at equilibrium [1].

SPME, introduced in 1990, is a sample preparation method that can integrate sampling, extraction, concentration and sample introduction into a single step, resulting in a high sample throughput [2]. Its main advantages over the SPE and "Purge and Trap" methods are the exclusion of solvents and simplicity of execution.

This technique consists of a fused-silica fiber that is connected to a stainless steel tube which is used to increase the mechanical strength of the fiber. This stainless steel tube is contained in a specially designed syringe (see Figure 2.1).

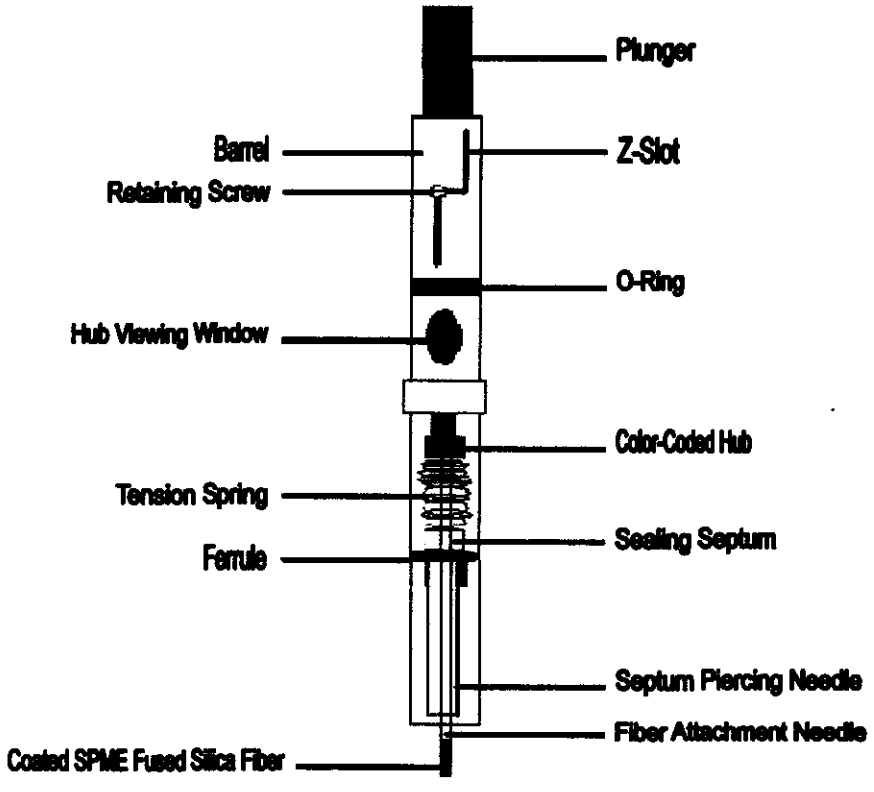

Figure 2.1: A cross sectional diagram of the fiber assembly and the fiber holder [3].

2.2. EXTRACTION OF ANALYTES

SPME utilizes a fused-silica fiber, which is coated with a polymeric stationary phase, for the extraction of analytes from the sample matrix. The fiber is mounted in a syringe-like device for protection. The stationary phase can be a viscous liquid or a porous solid [4].

Traditional sample preparation methods strive to completely remove the analytes of interest from the sample matrix. With SPME the amount of analyte that is removed by the fiber is proportional to the concentration of the compound in the sample. This is accomplished when the analyte distribution between the fiber and the sample reach equilibrium; or before equilibrium, if the sampling parameters are carefully controlled. SPME permits much shorter sampling times due to its ability to be used quantitatively before equilibrium is reached [5].

There are different extraction modes and the appropriate extraction mode should be selected based on the sample matrix, analyte volatility and its affinity to the matrix. Three different exposure techniques exist: headspace sampling, direct sampling from the aqueous phase and direct exposure using membrane protected extraction [1,10]. Headspace sampling is considered for volatile analytes (VOCs) such as benzene, toluene, ethylbenzenes and xylenes (BTEX). This sampling method is preferred due to faster equilibration times and high selectivity when extremely contaminated samples are analyzed. Direct sampling is used for clean, aqueous samples, such as groundwater. Semi- and non-volatile compounds will be extracted by using this mode [1]. Figure 2.2 illustrates the difference between headspace and direct sampling.

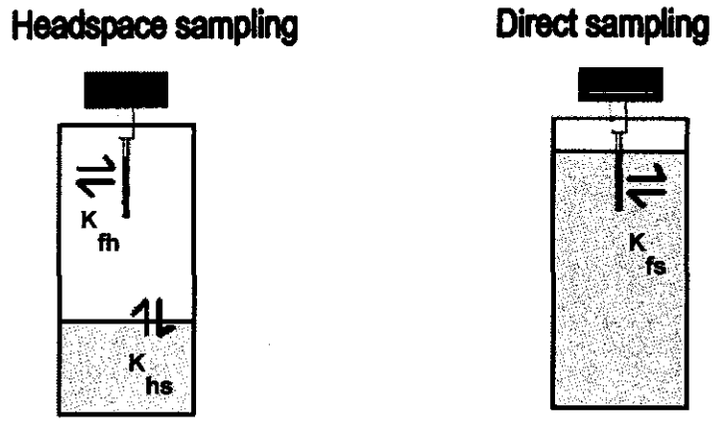

Figure 2.2: The different equilibriums that occur with headspace sampling and with direct sampling methods.

For dirty samples, the sample can be extracted with the fiber being protected by a membrane [10].

Independent of the extraction mode selected, the fiber coating removes the compounds from the sample matrix by absorption in the case of a liquid coating or adsorption in the case of a solid coating. Absorption is defined as the assimilation of molecules, or other substances, into the physical structure of a liquid or solid without a chemical reaction. Adsorption is defined as the physical adhesion of molecules to the surfaces of solids without a chemical reaction [5,9].

During SPME, the fiber is lowered into the vial by pressing the plunger down. The fiber is exposed to the sample matrix for a predetermined time. During this time, analytes are extracted from the sample matrix (see Figure 2.3). Once extraction is completed, the fiber is withdrawn from the vial and introduced into a GC or a HPLC injector. The extracted analytes are then desorbed from the fiber coating and quantitatively analyzed by using GC or HPLC [2].

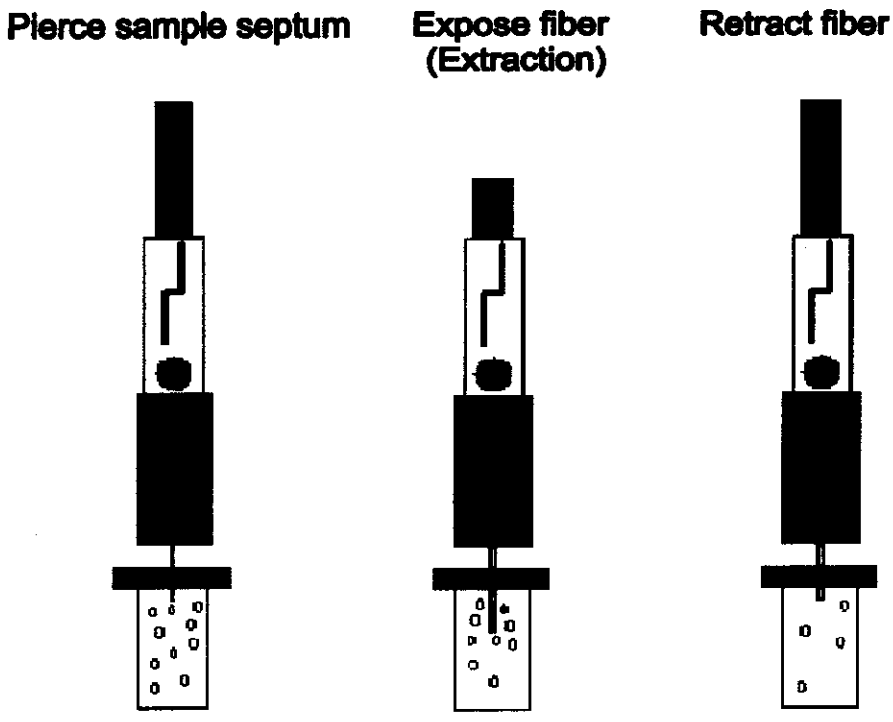

Figure 2.3: The process of extracting the analytes out of the sample matrix and exposure of the fiber to the sample [3].

2.3. DESORPTION OF EXTRACTED ANALYTES

Desorption of the analytes from the fiber depends on various factors, namely the boiling point of the analyte, the thickness of the fiber coating and the temperature at which the fiber is introduced [11]. Two desorption techniques are used for SPME to transfer the extracted analytes from the fiber to a chromatographic column. The first technique involves the coupling to a GC and the second technique involves a HPLC [1].

2.3.1. Desorption, using a GC

For a GC analysis, the extracted analytes are thermally desorbed through the insertion of the needle into a hot GC injection port. The fiber is exposed immediately and should be placed at the hottest part of the injector. As temperature increases, the coating to gas distribution constant decreases and the ability of the fiber coating to retain analytes diminishes (see Figure 2.4). The constant flow of the carrier gas within the GC injector helps with the discharge of analytes from the fiber coating and transfers these analytes to a cool column for refocusing [1].

To ensure a fast transfer of the analytes, the highest possible desorption temperature that is amenable for the target analytes and the fiber coating should be used [1].

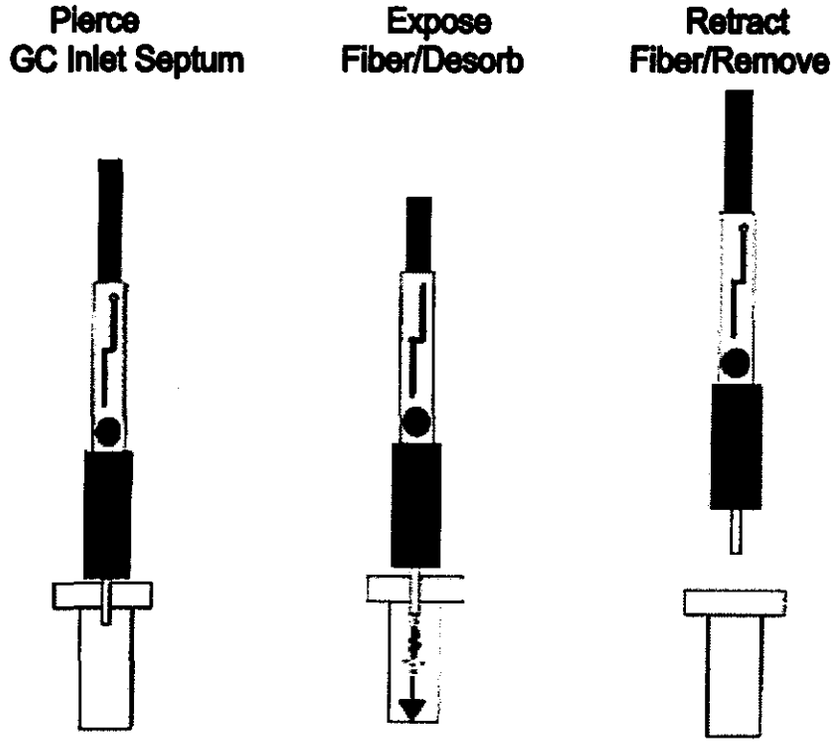

Figure 2.4: The desorption process in a GC, showing the exposure of the fiber in the injection port [3].

2.3.2. Desorption, using a HPLC

For HPLC analysis, the extracted analytes are desorbed into an organic solvent. HPLC analysis is preferred for nonvolatile and thermally labile analytes. The fiber is inserted into a desorption chamber which replaces the injection loop on the injector valve. When the valve is in the load position, the SPME fiber is introduced into the desorption chamber and the mobile phase is then used to release the analytes from the fiber [1].

The linear flow rate can be maximized by choosing small inner diameter tubing, which is imperative due to a low volumetric flow rate in HPLC. The major disadvantage of this injection procedure is carryover, which is mostly related to poor desorption conditions. Moreover, the elution power of the initial eluent composition is mostly not sufficient for a quantitative desorption of the extracted analytes, e.g. high molecular weight compounds [1].

Heating of the interface might increase the driving force of desorption, but it is limited to the thermal stability of the target analytes. An alternative approach is to fill the desorption chamber with a pure organic solvent to increase the desorption power, but this can lead to peak broadening [1].

2.4. FACTORS INFLUENCING THE SPME PROCESS

SPME is an equilibrium technique and therefore not all the analytes are completely extracted from the matrix. Generally a sample is placed in a closed vial and an equilibrium forms between three phases, namely the sample matrix' headspace above the sample and the polymeric coating of the fiber (see Figure 2.2). The recovery of the analyte is related to the overall equilibrium of the three phases present in the sampling vial. The total amount of analyte does not change during the extraction process.

The distribution of the analyte among the three phases after equilibrium is represented as follows [1]:

$$C_o V_s = C_h^{\omega} V_h + C_s^{\omega} V_s + C_f^{\omega} V_f \qquad (2.1)$$

where:

C_o: the initial concentration of the analyte in the aqueous solution

C_h^{ω}, C_s^{ω}, C_f^{ω}: the equilibrium concentration of the analyte in the headspace, aqueous solution and the fiber coating, respectively

V_h, V_s, V_f: the volumes of the headspace, aqueous solution and the fiber coating, respectively

Using Henry's partitioning law and substituting for equilibrium concentrations, the amount of analyte extracted by the fiber, n, can be represented as follows:

$$n_f = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s + K_{hs} V_h} \qquad (2.2)$$

If no headspace exists in the closed vial, and direct sampling is applied, the equation simplifies to:

$$n_f = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s} \qquad (2.3)$$

where:

n_f: the amount extracted by the fiber coating

K_{fs} : the distribution constant

V_s : the volume of the aqueous phase

V_f : the volume of the stationary phase

C_o : the initial concentration of analytes in the aqueous phase

The distribution constants (K) between the three different phases are [1]:

$$K_{fh} = \frac{C_f}{C_h} \qquad (2.4)$$

$$K_{hs} = \frac{C_h}{C_s} \qquad (2.5)$$

$$K_{fs} = \frac{C_f}{C_s} \qquad (2.6)$$

In both instances, the amount of analyte extracted is proportional to the initial concentration of the analyte in the sample matrix.

2.4.1. Direct or headspace sampling

Direct sampling is more suitable for analytes that are semi-volatile, where headspace sampling is more sensitive for analytes that are volatile. It is also believed that direct sampling is best used for low concentration aqueous based sample matrices. The decision on which of these two methods should be used, will depend on the analytes that need to be extracted [11,14].

In headspace sampling, equilibrium is more rapidly obtained than in direct sampling. This is because there is no liquid to hinder diffusion of

the analytes onto the fiber coating. The headspace sampling works on the principle that the sample is equilibrated with its headspace and the aqueous phase and analytes are extracted from the headspace. The fiber does not have any direct contact with the aqueous phase. The extracted analytes are then directly transferred to a GC or HPLC for separation [2].

The headspace sampling method is limited to volatile analysis, but its applications can be broaden when used in combination with thermal desorption for the analysis of solid samples such as soils and polymers. This procedure has found application in the investigations of petroleum contamination of soils as well as the determination of the residue monomers and anti-oxidants in polymers.

2.4.2. Fiber selection

Because there is a continuous development of new fiber coatings, it has become a difficult task to select an appropriate fiber for a specific application. During the selection process, it is important to determine whether to use an adsorbent type fiber or an absorbent type fiber [19].

With the absorbent fiber coating, the fiber extracts by means of partitioning of analytes into a liquid-like phase. This allows analytes to migrate in and out of the fiber coating. The ability of the coating to retain and release the analyte depends on the thickness of the coating and the size of the analyte. The polarity of the fiber coating can be used to discriminate between analytes. There is virtually no competition between specific types of analytes and the sample capacity can be improved by increasing the thickness of the fiber coating [19]. PDMS, a nonpolar coating and PA, a polar coating, are two examples of absorbent fibers that are commercially available.

An adsorbent fiber coating functions by means of a physically interaction with the analytes. This type of fiber coating is generally a solid that contains pores, creating high surface areas. Extraction is accomplished by trapping the analytes in the internal pores. Pore size distribution will control the fiber applications in terms of molecular size of the adsorbates, as well as their polarity. Analytes compete for pores, because of limited number of sites. This results in reduced capacity and probable displacement of analytes with low distribution constants by those with higher distribution constants [19]. Fibers that are adsorbent in function, contain molecular sieves such as carboxen; carbowax and divinylbenzene (See Figure 2.5).

A nonpolar analyte is most effectively extracted with a nonpolar fiber coating, while a polar analyte is most effectively extracted with a polar coating. A derivatizing agent can be placed into the fiber coating to change an absorbent fiber coating to make it more like an adsorbent fiber coating. The derivatizing agent chemically reacts with the analytes and binds them to the fiber coating. Adsorbent type fiber coatings can also be altered in this way [19, 12].

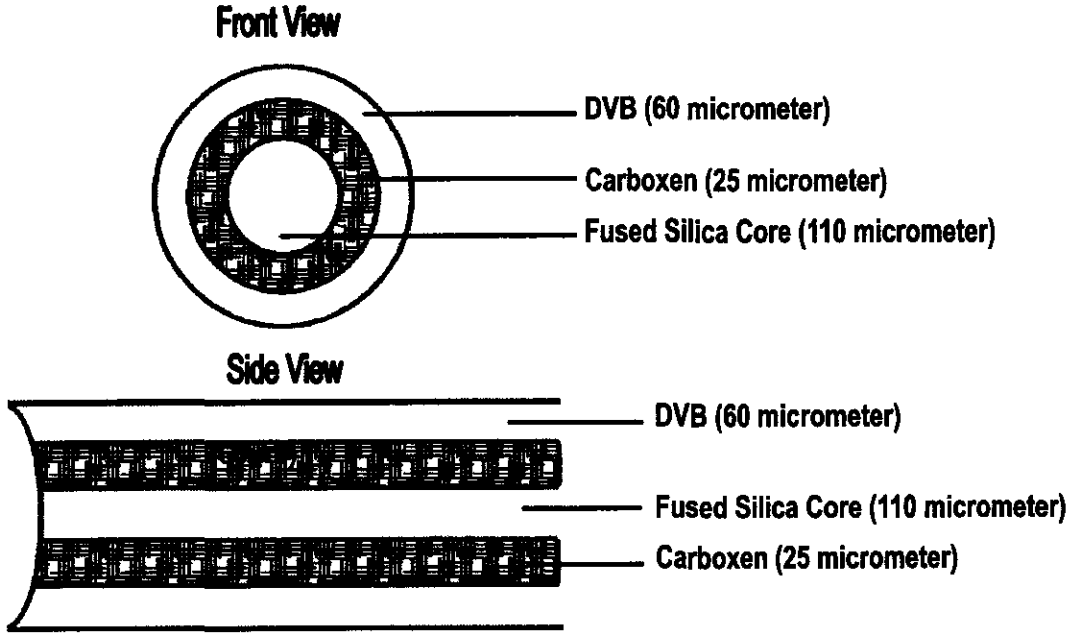

Figure 2.5: An illustration of a dual coated SPME fiber, in this case a CAR-DVB fiber [3].

The ability of the fiber coating to crosslink and bond determines its stability. There are three classifications used to describe the stability of the coating, namely nonbonded, crosslinked and bonded [1]. (See Table 2.1)

Nonbonded phases are stable, but do not contain any crosslinking agents. These phases tend to swell in organic solvents, because these phases are not solvent resistant. Nonbonded fiber coatings have less thermal stability than the bonded fiber coating. Partial crosslinked fiber coatings contain crosslinking agents. These agents can be vinyl groups. The stationary phase crosslinks itself and thus produce a more stable coating. However, the coating does not tend to bond to the fused silica. Advantages of a partially crosslinked fiber coating is that it is more solvent resistant than the nonbonded fiber coating and that it has better thermal stability. Most of these fibers can be exposed to a variety of solvents, but care must be taken to prevent

the fiber coating from being stripped off the fused silica core due to the swelling that might occur. Bonded fiber coatings also contain crosslinking agents. The difference between the partially crosslinked fiber coating and the bonded fiber coating is that with the bonded fiber coating, the coating is crosslinked not only to itself, but also to the fused silica core. These coatings are very resistant to a variety of solvents and have good thermal stability [1].

Fiber name	Thickness of coating	Type of fiber	Polarity	Coating stability	Application
Polydimethyl-siloxane (PDMS)	7μm	Absorbent	Nonpolar	Bonded	VOCs, polycyclic aromatic hydrocarbons (PAHs) and BTEX
	30μm			Nonbonded	VOCs, PAHs and BTEX
	100μm			Nonbonded	VOCs, PAHs and BTEX
Polyacrylate (PA)	85μm	Absorbent	Polar	Crosslinked	Polar organic analytes
Polydimethyl-siloxane/di-vinylbenzene (PDMS/DVB)	65μm, 60μm	Adsorbent	Bipolar	Crosslinked	VOCs and aromatics
Carbowax/di-vinylbenzene (CW/DVB)	65μm	Adsorbent	Polar	Crosslinked	Polar organic analytes
Carboxen/poly-dimethyl-siloxane (CAR/PDMS)	75μm	Adsorbent	Bipolar	Crosslinked	VOCs

Table 2.1: Types of SPME fiber coatings and their characteristics [1, 19].

When selecting the appropriate fiber for the extraction of the analytes of interest, the physical characteristics of the analyte and the detection levels must be considered. Factors that should be kept in mind are the molecular weight of the analyte, boiling point, vapor pressure, polarity, functional group and the concentration range. These factors should be matched with the variables in the fiber coatings, such as the film thickness, polarity and porosity [1].

The selectivity can be altered by changing the polymer coating and coating thickness. It has been suggested that a thick fiber coating would be more suited for volatile compounds and a thin fiber coating for semi volatile compounds [12]. This is because a fiber with a thicker coating is used to retain volatile compounds and to transfer them to the gas chromatograph without loss, but a thin coating is used to ensure fast diffusion and release of higher boiling compounds during thermal desorption. If a thick coating should be used for high boiling compounds, the desorption rate will be prolonged and compounds could be carried over to the next extraction [12].

The detection limit for SPME differs from compound to compound and in turn is dependent on the distribution constants between the fiber, matrix and analyte. Using a nonpolar polymeric coating, a nonpolar compound in an aqueous matrix with a high distribution constant will have a lower detection limit than a more polar compound in the same matrix with a lower distribution constant. Under these conditions, compounds with the lowest detection limits include branched aromatic compounds and chlorinated alkenes. In the case of extremely volatile compounds, the compounds can desorp from the fiber before the fiber is inserted in the injection port. It is therefore advisable when analyzing volatile compounds that the time between extraction and desorption should be minimized [22].

2.4.2.1. Polydimethylsiloxane (PDMS) and Polyacrylate (PA) fiber coatings

According to Alonso *et al.* [16] the first fiber coatings to be used in SPME were the PDMS and PA fibers. PDMS is a rugged liquid coating that can withstand very high temperatures. This nonpolar coating has a high affinity for nonpolar analytes such as benzene, xylenes, volatile organic compounds and pesticides. This fiber extracts analytes with a molecular weight range of 60-275 g/mol. On the other hand, the PA fiber coating is a solid polymer with a low density at room temperature, is polar in nature and extracts more polar analytes, such as phenolic compound, from aqueous solutions. This fiber extracts analytes with a molecular weight range of 80-300 g/mol. Coatings with more porous and adsorbent materials, like divinylbenzene (DVB) and carboxen (CAR), were blended in the PDMS (see Figure 2.6). This makes PDMS more polar and extends its range of target analytes to compounds such as alcohols and ethers.

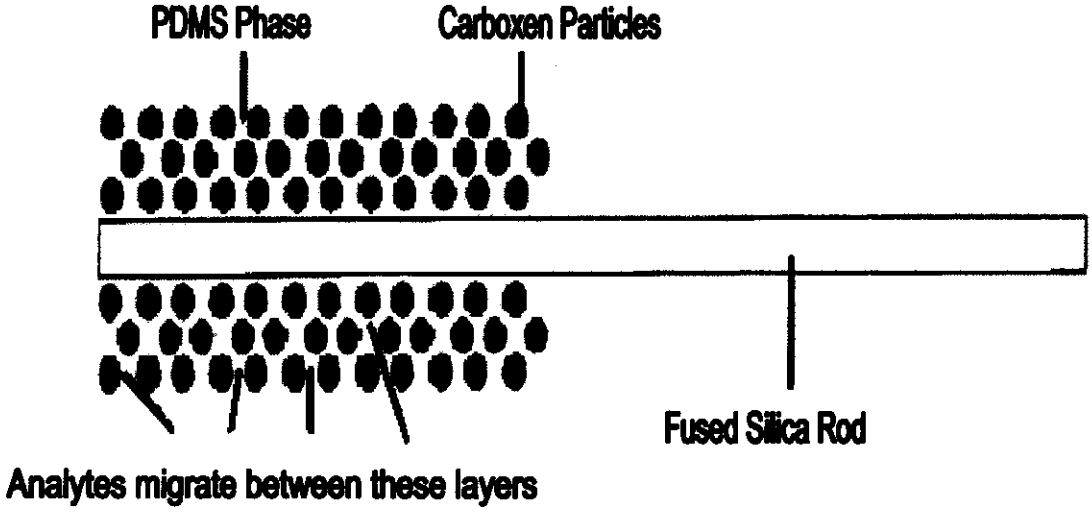

Figure 2.6: The physical characteristics of the CAR-PDMS combination fiber [3].

2.4.2.2. Carboxen (CAR) fiber coating

When CAR is blended with PDMS, it results in a bipolar phase which can extract smaller analytes. CAR is a range of porous, synthetic carbons that has distinctive pore designs. It has an even distribution of micro (<1.5 nm), meso (1.5-100 nm) and macro (>100 nm) pores. These pore sizes are critical in determining which analytes will be stronger retained. For the optimum extraction, the pore diameter should be at least twice the size of the molecule that is being extracted [1, 23].

Usually, poor desorption is caused by hysteresis. Hysteresis is known as the condensation of an analyte in the pore. The adsorption and the desorption branches of an isotherm are not coincident over the whole pressure range. It occurs with midsize volatiles that are trapped in the mesopores and must reverse direction to be desorbed. Slit-like pores have a much higher chance of hysteresis than the open tapered pores of CAR. High temperatures help to minimize the effects of hysteresis by releasing relatively large molecules that are trapped in the macropores [1, 23, 39].

Tuduri *et al.* [20] state that CAR is an adsorbent that contains approximately 1/3 macropores, 1/3 mesopores and 1/3 micropores. This can lead to slow mass transfer of analytes.

CAR is used for the extraction of C_2-C_{12} hydrocarbon range. Molecules larger than C_{12} are strongly retained on the coating and are not easily desorbed. Thus, CAR should not be used for analytes larger than C_{12} or for analytes with boiling points greater than 200°C [1].

2.4.2.3. Carbowax (CW) fiber coating

The CW fiber coating tends to swell in water and is easily sheared off the fused silica core. This problem was overcome when a highly crosslinked CW was synthesized. The increase in crosslinking reduces the risk in swelling and solubility in water, but also slightly reduces the polarity. Another problem of the CW fiber coating is that it is sensitive to oxygen at temperatures above 220°C. Thus, oxygen in the carrier gas or leaking through the septum can oxidize the fiber coating. This result in the darkening of the fiber coating, the coating becomes powdery and it can be easily removed from the fused silica core [1].

2.4.2.4. Divinylbenzene (DVB) fiber coating

The DVB fiber coating contains pores that have the ability to adsorb analytes and physically retain them. This results in stronger retention of the analytes that fit into the pores. Thus, fiber coatings that contain porous materials are generally better for trace level analysis (parts per trillion or parts per billion) [1].

The surface area of the DVB coating is approximately 750 m^2/g. The porosity distribution is primarily mesoporous, with some macro and some micro pores. It is therefore ideal for trapping C_6-C_{15} analytes, but can also trap larger molecules [1].

DVB is a solid particle and therefore it must be suspended in a liquid phase to be able to be coated onto the fiber. This blending of DVB with a liquid phase increases the diversity of the fiber and its ability to extract a wide molecular weight range of analytes. When it is blended with PDMS, the character of the coating allows for the lower molecular

masses to be included into quantitative extraction; while being blended with CW, the molecular mass range is extended further [1].

2.4.3. Extraction time

If the extraction time is varied, the concentrations of the analytes will also vary on the fiber, until equilibrium is reached (see Figure 2.7). Once equilibrium is reached, the concentration of the analyte on the fiber will become constant. Controlling the extraction time is critical when working in the pre-equilibrium state. Consistent timing is more important than reaching full equilibrium as this allows for shorter extraction times. The time is determined by the length of time required to obtain precise extraction for the analyte with the highest distribution constant. Note that when working with trace amounts, it is important to operate at maximum sensitivity and in this instance the duration of the extraction may by critical [12, 21, 25]. A stopwatch should be used to time each extraction precisely to ensure good reproducibility [5].

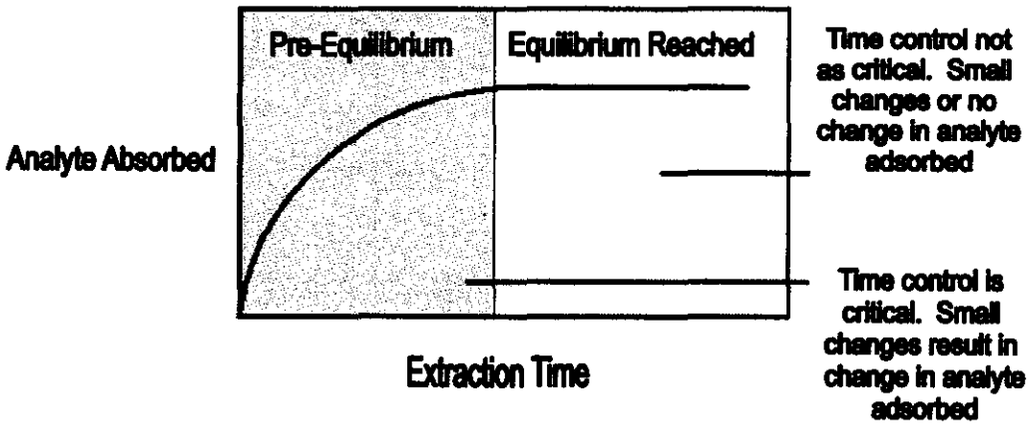

Figure 2.7: A diagram to illustrate the time dependence before equilibrium is reached [24].

In practice, a change in the mass extracted cannot be determined if it is smaller than the experimental error, which is typically 5%. Therefore, the equilibration time is assumed to be achieved when 95% of the equilibrium amount of the analyte is extracted from the sample matrix [1].

According to Alpendurada [21] compounds with low diffusion coefficients have long equilibrium times and the shortest acceptable time is chosen according to the analyte's detection limit.

According to Alonso *et al.* [16] the extraction time depends on the type and the properties of the analyte, the sample and the fiber coating. In their study, they observed that the extraction time for direct sampling is longer than the time needed by headspace sampling.

Extraction times vary between 15-40 minutes, but can be as short as 30 seconds. Extraction times can be shortened when [14]:

- Analyzing small compounds with a molecular weight of less than 150 g/mol.
- Using a thinner, absorbent type of fiber coating.
- Using the headspace technique instead of the direct sampling.
- Working with high concentration analytes.

2.4.4. Temperature

The effect of temperature on SPME manifests itself in equilibrium effects and coupled to that, mass transport. Constant temperature is required for consistent distribution of analytes within the respective phases of the process. Mass transport of analytes from the matrix into the fiber coating is faster at higher temperatures. Very often, when

direct sampling is carried out, the temperature effects are most noticeable with high boilers, in that a temperature increase may improve the sensitivity [1].

Where volatility may be a problem, as in headspace sampling, an increase in the sample temperature increases the analyte concentration in the headspace, thereby resulting in faster extractions [1].

Thus, a predetermined optimum temperature for the process is important for precise quantification. It is common practice to stabilize the sample at the predetermined optimal temperature before the final fiber coating is exposed to the sample matrix, using a calibrated thermometer alongside the sample to ensure constant extraction temperatures under thermo-stated conditions [5]. Ideally, sampling at ambient temperatures should not be undertaken because of the variation in room temperature that can cause non-reproducible results.

Heating methods, like microwave heating, can generate convective currents in the sample matrix that improves transfer of analytes from the sample matrix to the extracting fiber coating. Microwave heating releases analytes from the sample matrix quicker, which results in greater sensitivity for most of the analytes [1, 2].

Increasing the temperature will increase the sensitivity for the higher boiling point analytes but decrease the sensitivity for the lower boiling point analytes [1].

2.4.5. Volume

The sensitivity of SPME is proportional to the amount of moles of analyte extracted from the sample matrix. If the sample volume

increases, so does the amount of analyte extracted. This continues until the volume of the sample becomes significantly larger than the product of the distribution constant and the volume of the fiber coating. After this point, the sensitivity of the technique does not improve with further increase in the volume. However the sample volume cannot be considered without taking fiber capacity into account [21].

The K_{fs} values for the targeted analytes are normally quite large, because the coatings used in SPME have strong affinities for organic analytes. This means that SPME has a very high concentrating affect and leads to good sensitivity, provided that the volume ratio (V_f/V_s) should be very small [2].

The optimum volume required for maximum sensitivity in SPME analysis is determined predominantly by the K values for the VOCs in the matrix. $K_{fs}V_f$ represents the coating capacity and when $K_{fs}V_f << V_s$, there will be no increase in sensitivity. The limiting sample volume can be calculated assuming an error of measurement, e.g. 5%, from:

$$V_s = \frac{100 K_{fs} V_f}{E(5)} \qquad (2.7)$$

V_f can therefore be estimated at 20 $K_{fs}V_f$. K values up to 200 and 100µm fiber (0.65µl) gives a limiting sample volume of 2.0ml. Since most VOCs have K values = 1000+, for the same fiber there is a substantial variation in the amount extracted when the sample volume changes from 2 to 10ml.

For volatile compounds at very low concentrations such as 50ppb and less, changes in sample volume do not affect response, because the equilibrium can be assumed constant at very low concentrations. At higher concentrations the sample volume becomes more significant. With a large volume of more than 5ml, containing a high concentration

of analytes, the amount of analytes removed from the sample is not sufficient to change the concentration. It is best to keep sample volumes between 1ml and 5ml, because analyte concentrations are not usually known [12].

Because, the total amount of analytes in the three phases is constant at equilibrium, lowering the headspace volume will increase the amount of the analytes in the other two phases. Thus, an increase in sensitivity of SPME-based methods will be observed [1].

2.4.6. pH

The pH of the sample matrix can have an influence on the extraction processes of acidic and basic analytes. A change in pH affects the recovery of slightly acid or basic analytes, because they need to be kept in the undissociated form. A sample with a pH of 12, has a higher recovery of more basic and neutral analytes, whereas a sample with a pH of 2, the acidic and neutral analytes have higher recoveries [21, 27].

The selective extraction of acidic analytes on the SPME fiber is understood from the relationship between adsorption and polarity. Dissociated and undissociated forms of the acidic analyte coexist in the aqueous solution, and the distribution of these acid species is determined by the pK_a of the acid and the pH of the solution. The polarity of these two forms differs significantly. The dissociated form is too hydrophilic to be extracted on a hydrophobic surface of the fiber. Thus, only the undissociated species are extracted on the SPME fiber [1, 28].

Research at J.T. Baker indicated that acetone reacts with certain aromatic primary amines under acidic conditions. This leads to the appearance of low recoveries for basic compounds [27].

2.4.7. Agitation

Agitation influences the equilibration time. There are different agitation methods, such as magnetic stirring, which requires a stirring bar in the vial; the vortex technique, the vial is moved rapidly in a circular motion; fiber movement; flow through; and sonication. The magnetic stirring technique is most commonly used due to its availability in analytical laboratories [21].

Agitation of the sample enhances extraction of analytes and reduces the extraction time. Constant stirring is necessary to ensure good precision. Inconsistent stirring causes poor extraction reproducibility and is worse than no stirring [12].

2.4.7.1. Agitation in headspace sampling

Extraction by means of headspace sampling is very fast and magnetic stirring does not affect the diffusion of analytes from the headspace to the fiber. When the concentration in the headspace is dramatically reduced by the SPME fiber exposure, the mass transport between the aqueous sample matrix and the headspace slows down the extraction process. Without agitation, physical breakdown of the sample matrix is not achieved and analytes trapped in the interior will not be released to the headspace. Agitation is used to ensure equilibrium conditions between the headspace and the aqueous phase during the extraction

process, thus reducing the depletion of the headspace concentration [1].

The release of volatile analytes into the headspace is relatively easy because the analytes tend to vaporize once they are dissociated from their matrix. For semi-volatile analytes, the low volatility and relatively large molecular size may slow the mass transfer from the matrix to the headspace. This increases the extraction time. By agitating the sample, a fresh aqueous surface is generated which helps the less volatile analytes to escape to the headspace [1].

2.4.7.2. Agitation in direct sampling

Agitation provides a continuously refreshed sample to the fiber, which results in more collisions of the analytes with the SPME fiber and therefore a decrease in the extraction time.

Stagnant samples need a much longer equilibration time due to low diffusion coefficients for analytes in water. The mass transport of the analytes is limited by migration through the sample matrix surrounding the fiber surface. The analytes closest to the fiber penetrate the fiber coating faster than the distant analytes which have to migrate through the water towards it. This result in a static aqueous layer depleted of analytes, around the fiber. The rate of mass transport is high initially, but as the water layer around the fiber is depleted of analytes, diffusion through the water limits the rate of mass transport. This depleted water layer affects the extraction rate of analytes with high distribution constants, because more analytes have to pass through the static water layer to reach the fiber coating [1, 13].

For direct sampling, a thin layer of water forms around the surface of the fiber coating, known as the Prandtl boundary layer. This layer is

unavoidable, even with rigorous stirring. This layer is thinner for samples that are agitated than for samples that are not agitated. The agitation conditions and the viscosity of the sample determine the thickness of this boundary layer. If this layer is thick, the diffusion of the analytes through this layer determines the equilibration time. The more analytes that travel through the boundary layer, the longer the extraction process is. The time required to reach equilibrium by agitation is ten times less than under no agitation. The equilibration time for an agitated sample with a boundary layer can be determined by Equation 2.8 [1, 26, 29].

$$t_e = t_{95\%} = \frac{3\delta K_{fs}\Phi}{D_s} \qquad (2.8)$$

where:

δ: boundary layer thickness

K_{fs}: distribution constant of the analyte between the fiber and sample

Φ: fiber coating thickness

D_s: diffusion coefficient of the analyte in the sample matrix

2.4.8. Addition of salt

The addition of an electrolyte in the sample matrix decreases the solubility of hydrophobic analytes in the aqueous phase. The extraction efficiency of analyte-to-stationary phase can be increased by adding salt to the sample matrix. This addition can increase the response by 10- to 500-fold by shifting the equilibrium toward the fiber [30, 31].

Salt addition, usually sodium chloride or sodium sulphate, increases the ionic strength of the sample matrix. When water acts as a solvent and salt is added, the salt form ions. The ions in the solution polarize the water molecules near them. The stability of the ion is dependent on the extent to which this can take place. It is in effect stabilizing itself by spreading its charge. These ions stabilize themselves in solution by collecting around them a solvation "envelope" of water molecules. The result is that analytes are "pushed" out of the solution and onto the fiber. The salt makes the organic analytes less soluble and increasing the distribution constant of these compounds. The amount of analytes extracted increases with an increase salt concentration in the sample matrix until saturation. The addition of salt has a stronger effect on the extraction of polar analytes [16, 21, 32].

The addition of salt is mainly used to drive polar analytes out of the solution, because it has a relatively insignificantly effect on the non-polar analytes [1].

2.5. QUANTIFICATION METHODS USED IN SPME

2.5.1. Method of external standardization

This method compares the detector responses of the sample to the responses of the target analytes. Standard mixtures, over the range of the expected concentrations in the sample matrix, are prepared. SPME is applied to each standard solution and then to the sample matrix. A calibration curve is constructed from the detector responses of the calibration standards. The sample detector response is then plotted onto the calibration curve and the comparison of the sample detector response to the calibration curve determines the concentration of the analyte in the sample matrix [24].

This method is suitable for simple sample matrixes, such as gaseous or liquid samples, that do not have interferences or organic solvents. It is also used for homogeneous samples [24].

This method is not recommended for samples with complex matrixes, such as proteins and fats. These samples have the tendency of adsorbing the target analytes or it may vary in the type and total number of analytes that are present [24].

2.5.2. Method of internal standardization

This method requires the addition of a known amount of a known compound into the calibration standards and into the sample matrix. The internal standard should be similar in analytical behaviour to the target analytes but should not be found in the sample. The target analytes are determined according to the concentration of the internal standard [24].

This method is best suitable for complex gaseous or liquid matrices, or less complex solid samples that can be dissolved in a liquid to perform headspace sampling [24].

It is not recommended for samples where the easier external standardization method can be used. More complex liquid or solid matrices, such as protein and fats, should also be avoided. These samples adsorb the target analytes [24].

2.5.3. Method of standard addition

This technique uses the addition of a known concentration of the actual analyte of interest to multiple aliquots of the sample. The sample matrix is then analyzed. The detector response of the sample matrix is plotted against the amount spiked for each analysis. A straight line is extrapolated and the x-intercept of the graph represents the concentration of the unknown analyte (see Figure 2.8) [24].

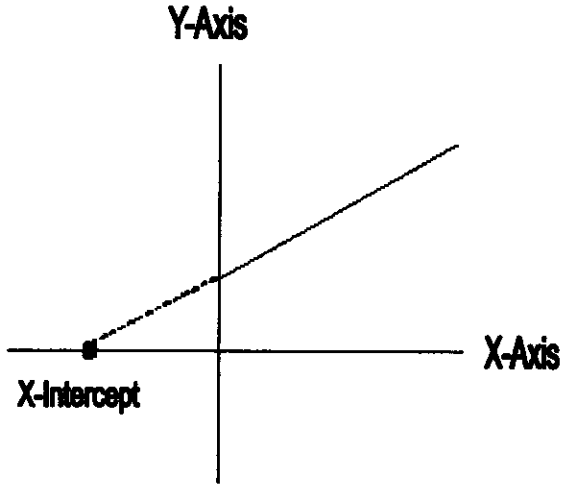

Figure 2.8: Extrapolation of curve to obtain the x-intercept

This method is suitable for a sample matrix where a blank matrix is not available or for a sample matrix that varies in the type and total number of analytes that are present [24].

This technique is not recommended for a sample matrix where the easier external or internal standardization methods can be used [24].

2.6. ADVANTAGES AND DISADVANTAGES OF SPME

2.6.1. Advantages of SPME

SPME offers various advantages [21, 30, 33, 34]:

(i) sample loss is minimized because the analytes are trapped on the fiber;
(ii) convenient because the fiber holder is small and easy to operate and no complicated procedures are involved;
(iii) rapid because the extraction time can be manipulated according to the analytes and the desorption time is also fast;
(iv) analytical cost is low due to the fact that no solvents are used;
(v) eliminating the use of organic solvents reduces the health risk involved that may be toxic to humans;
(vi) selective because it can be used for a wide variety of analytes by modifying the fiber coatings;
(vii) allow automation because it can be used with an autosampler on a GC;
(viii) smaller samples are utilized and therefore exposure to contaminants in the sample is reduced.

2.6.2. Disadvantages of SPME

SPME has also limitations [21, 30, 33, 34]:

(i) the performance of the fiber differs from batch to batch and the quality of the fiber depends on the manufacturer's standards;
(ii) fibers are fragile and can easily break;

(iii) new fibers and fibers that have not been used for some time should be conditioned prior to extraction otherwise contaminants are carried over;

(iv) even with careful conditioning some bleeding of the fiber coating can occur, reducing the lifetime of the fiber;

(v) in some cases, even at high temperatures, the carry-over of the fiber can be a problem. Therefore blank GC runs should be performed between sampling;

(vi) suspended matter in the sample matrix can damage the fiber during agitation and can lead to poor extraction of analytes;

(vii) high molecular mass compounds can change the properties of the fiber coating, leaving it unusable;

(viii) the formation of gas bubbles on the fiber surface affects the mass transfer rates.

2.7. CONCLUSION

It follows from the literature survey that a large number of factors can influence the analysis of VOCs by SPME.

The potential use of SPME for the analyses of VOC compounds in complex waste water streams of a petrochemical industry will be tested in this study. A complete investigation of the factors that influence the possible routine use of SPME in such matrixes will be performed.

CHAPTER 3

METHODOLOGIES

In this Chapter...

An overview on the sampling procedure, analysis procedures and the calculations that will be followed in this study, is given.

3.1. INTRODUCTION

Because SPME deals with the analysis of trace levels of pollutants, caution was taken in preventing contamination by thoroughly washing the glassware before standards were prepared. High purity chemicals (Fluka Chemica) and Millipore milli-Q deionized water (12Ω.cm) were used for the preparation of standards.

SPME fibers were conditioned for a predetermined time and temperature as were recommended by the manufacturer. The PDMS fiber was conditioned at a temperature of 250°C for 1 hour, CAR-PDMS conditioned at 280°C for 50 minutes and the CW-DVB fiber at 250°C for 50 minutes.

The sample that was used as a test sample was a routine sample from a waste water stream of a plant at a petrochemical industry. The plant requests, on a daily basis, the analysis of organic analytes such as BTEX in its waste water stream. These analytes are by-products of petrochemical refining, coal burning operations and leaks from underground storage tanks. The sample matrix was mainly water with low levels of organic analytes.

In Table 3.1 a summary is given for the different sampling parameters that were used for the study of the factors that have an influence on the extraction process.

EXTRACTION TIME
1, 5, 10, 20, 30 and 40 minutes
EXTRACTION TEMPERATURE
22°C ± 0.5°C, 40°C ± 0.5°C and 50°C ± 0.5°C
TYPE OF FIBER
Polydimethylsiloxane
Carbowax-Divinylbenzene
Carboxen-Polydimethylsiloxane
SAMPLE VOLUME
1.5ml, 5ml and 10ml
ADDITION OF SALT
0g, 0.3g ± 0.1g and 0.8g ± 0.1g Na_2SO_4 in 1.5ml samples
SAMPLE pH
pH 1, pH 7 and pH 10

Table 3.1: Summary of the different sampling parameters that were used for the study of the factors that have an influence on the extraction process.

3.2. SAMPLING PROCEDURE

3.2.1. Sampling procedure for monitoring factors that influence SPME

3.2.1.1. Internal standard approach

An aliquot of 1.5ml, 5ml or 10ml were taken from the sample. It was pipetted into a 1.5ml, 5ml or 10ml vial, respectively. Dioxane was used as internal standard. For the 1.5ml sample a volume of 5µl dioxane was added, 16.7µl dioxane was added to the 5ml sample and 33.3µl dioxane was added to the 10ml sample. These volumes for the dioxane were added to represent 0.32% of the sample. Sodium sulphate was added to drive the equilibrium towards the fiber. The sodium sulphate mass that was added to a volume of 1.5ml was 0g, (0.30 ± 0.01) g or (0.80 ± 0.01) g.

The vial was then placed in a waterbath of (22.0 ± 0.5) °C, (40.0 ± 0.5) °C or (50.0 ± 0.5) °C for a period of 20 minutes to reach the desired temperature. Agitation of (20 ± 5) rpm (revolutions per minute) was used because fast agitation could stir particles vigorously and the particles could damage the fiber coating. Analytes were directly extracted with the 75µm Carboxen-PDMS, 65µm Carbowax-DVB or 100µm PDMS fiber. The extraction times varied from 1 minute to 40 minutes. The pH of the sample matrix was also altered between pH 1, pH 7 or pH 10. The sample was then manually injected in a 6890N Agilent GC with a PONA column (50m x 0.2mm x 0.5µm) and a flame ionization detector (FID) (See Figure 3.1).

The column flow rate of the hydrogen carrier gas was 1 ml/min and the detector temperature was set at 300°C. Split injection with a split ratio of 10:1 was used. The GC oven was kept at 120°C for 10 minutes after the injection, where after the temperature was increased at a rate of 5°C/minute up to 290°C and this temperature was held for 10 minutes.

A narrow liner (0.75mm inner diameter) was used to achieve a high linear flow around the fiber during the desorption process, which in effect reduced the desorption time. The fiber was kept in the injector for 15 minutes to avoid carry-over effects caused by impurities.

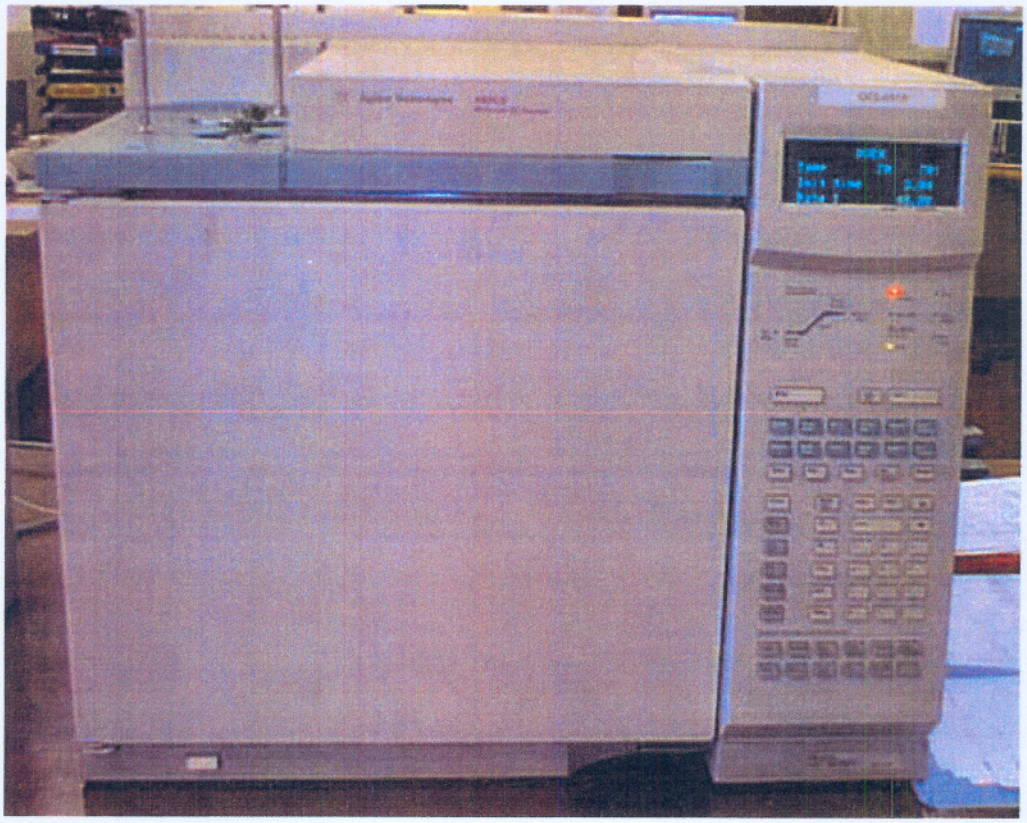

Figure 3.1: The Agilent 6890 GC that was used for desorption and analysis of analytes from the SPME fiber.

By using the experimental setup described above, chromatograms in which the different compounds are well separated and rather easily identifiable has been obtained (see Figure 3.2).

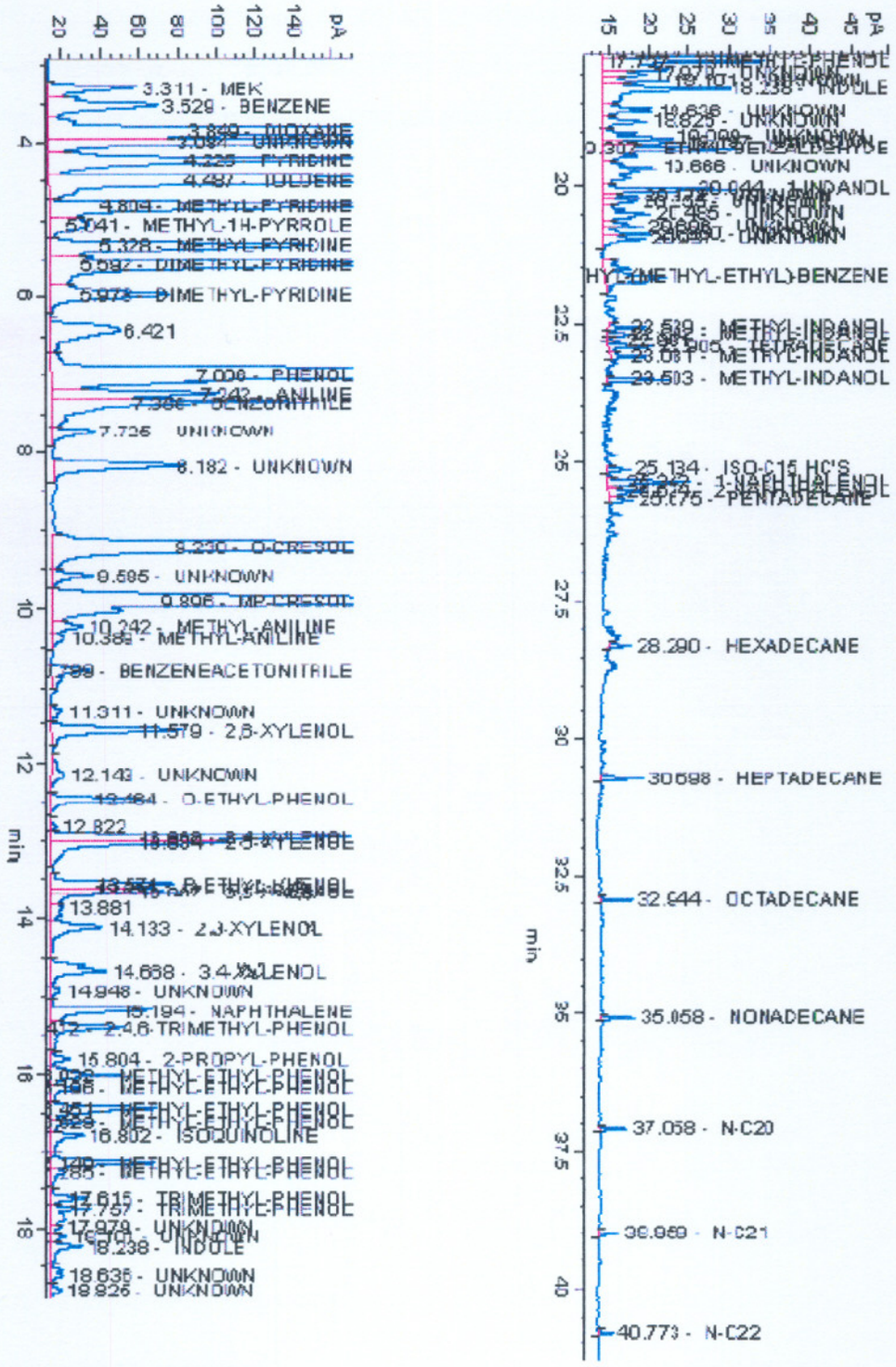

Figure 3.2: A SPME chromatogram of an industrial sample using the internal standard method.

As can be seen from the chromatogram above, the sample is highly complex and a large number of species are present.

3.2.1.2. External standard approach

A standard calibration solution with the components and concentrations, as given in Table 3.2, were prepared:

Components	**Mass %**
Toluene (Fluka Chemica)	0.0089
Phenol (Fluka Chemica)	0.3012
O-Cresol (Fluca Chemica)	0.0398
M/P-Cresol (Fluca Chemica)	0.0173

Table 3.2: Components and concentrations of the external standard solution.

The standard solution was injected first into the GC to calibrate the response of each compound by the FID detector. The sample, prepared under various conditions, was then injected at the same conditions.

The sample was prepared under the same conditions as mentioned in Paragraph 3.2.1.1. The difference between these two methods is that for the internal standard a known amount of analyte is added to the sample. This analyte is used as reference to calculate the unknown concentrations of the analytes present in the sample.

3.2.2. Sampling procedure for the comparison between SPME and NAC

3.2.2.1. Internal standard approach

An aliquot of 1.5ml was taken from the sample. It was pipetted into a 1.5ml vial and 5µl of dioxane was added to the sample. The dioxane was used as internal standard and represented 0.32% of the sample. For the SPME method the analytes were extracted with the Carboxen-PDMS fiber at 22°C, for 20 minutes at pH7 with (0.30 ± 0.01) g of sodium sulphate. The sample was then manually injected on the gas chromatograph.

The GC conditions were the same as mentioned in Paragraph 3.2.1.1 but with a difference in split ratios. Split injection with a split ratio of 150:1 was used for the NAC method and a split ratio of 10:1 was used for the SPME method. A bigger split ration was used for the NAC method to avoid the overloading of the GC column with water.

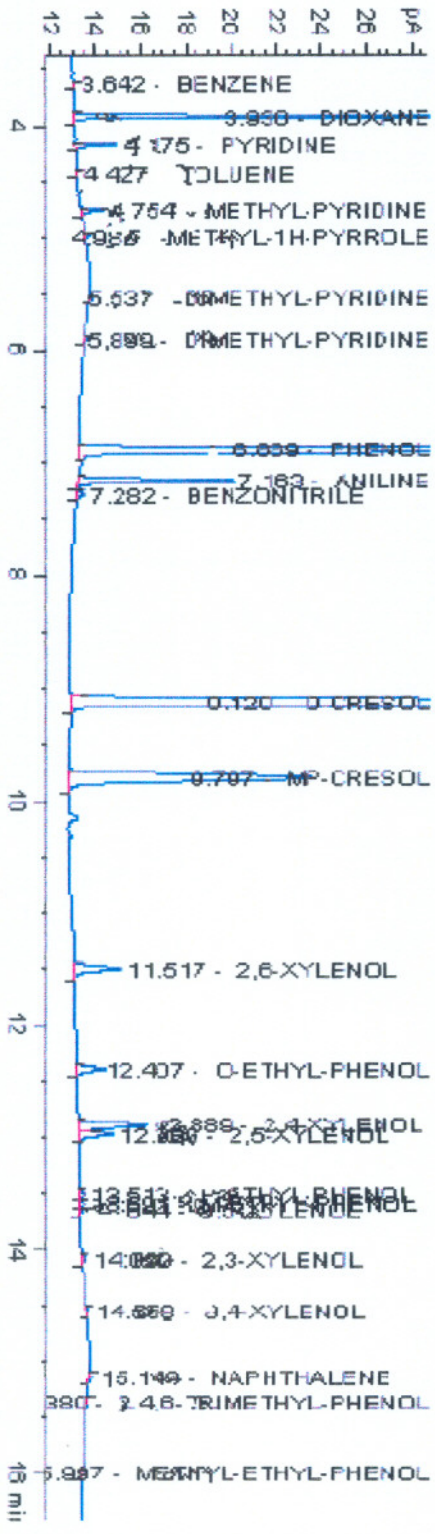

Figure 3.3: A NAC chromatogram of an industrial sample using the internal standard method.

When comparing the Figure 3.2 with Figure 3.3, it can be seen that a lesser number of peaks are found by following the NAC method than by following the SPME method.

3.2.2.2. External standard approach

A standard was prepared and analyzed (see Table 3.2). For the SPME method, the analytes were extracted with the Carboxen-PDMS fiber at (22.0 ± 0.5) °C, for 20 minutes at pH7 with (0.30 ± 0.01) g of sodium sulphate added to the 1.5ml vial.

The sample was then injected in the GC under the same conditions that were used as for the standard (see Paragraph 3.2.1.1).

3.3. ANALYSIS PROCEDURE

All the extractions were carried out with a manual SPME holder and were injected manually. A gradient programmable gas chromatograph (6890N Agilent Technologies) was used for the NAC method, as well as for the SPME method. It was equipped with a PONA column (50m x 0.2mm x 0.5µm) and a flame ionization detector (FID).

The sample was also injected on a 6890 Agilent MS, with a PONA column. The Wiley library was used to identify the peaks on the chromatogram.

3.4. CALCULATIONS

The concentration of the analyte identified on the chromatogram was calculated using Equation 3.1.

$$C_x = \frac{Area_x}{Area_{std}} xC_{std} \qquad (3.1)$$

where:

C_x :	concentration of component in sample
C_{std} :	concentration of internal/external standard
$Area_{std}$:	area of the internal/external standard
$Area_x$:	area of the component in sample

The percentage increase was calculated using Equation 3.2.

$$\%Increase = \frac{(Mass\%_{20\,min} - Mass\%_{1\,min})}{Mass\%_{1\,min}} x100 \qquad (3.2)$$

The percentage yield was calculated using Equation 3.3

$$\%Yield = \frac{Actual}{Theoretical} x100 \qquad (3.3)$$

3.5. CONCLUSION

During this study, the best methods for the sample preparation and analysis of an industrial waste water stream for VOCs, was investigated. The methods involved the NAC and SPME method with the internal and external standard approach of quantification.

CHAPTER 4

EVALUATION OF EXPERIMENTAL RESULTS

In this Chapter...

The experimental data that was obtained is presented. Factors that influence the extraction process when using SPME were investigated. The data was quantified using an internal standard as well as an external standard approach and the data was compared with the NAC method. All the experimental results obtained are represented in table form and given in Appendix A.

4.1. INTERNAL STANDARD APPROACH

4.1.1. Evaluation of the results for the different fibers used

The use of the PDMS, CW-DVB and CAR/PDMS fibers were decided upon because the PDMS fiber is recommended for the extraction of VOCs and BTEX compounds and the CAR-PDMS fiber is known as a suitable fiber for extracting VOCs. The CW-DVB fiber is marketed as a good extractor for polar organic analytes. The decision to use these three fibers was also made because they have different polarities. The PDMS is a nonpolar fiber, the CW-DVB being a polar fiber and the CAR-PDMS being a bipolar fiber.

The PDMS fiber is not generally suited as a stationary phase for extracting phenols, due to the fact that it is a nonpolar fiber and phenol is a polar analyte. It is used for detecting most of phenols only in the

mg/l concentration range and has little affinity for the nitro-containing phenols.

The PDMS fiber and the CAR-PDMS fiber are supposed to extract more or less the same analytes, because both fibers contain the nonpolar PDMS stationary phase. The difference between the two fibers is that the CAR-PDMS contains the polar CAR stationary phase, which makes this fiber a bipolar fiber. This fiber is supposed to extract more polar analytes than the PDMS fiber. The results are given in Table A.1 (p. 79 - 80) and graphically displayed in Figure 4.1. The GC conditions that were used are described in Paragraph 3.2.1.1.

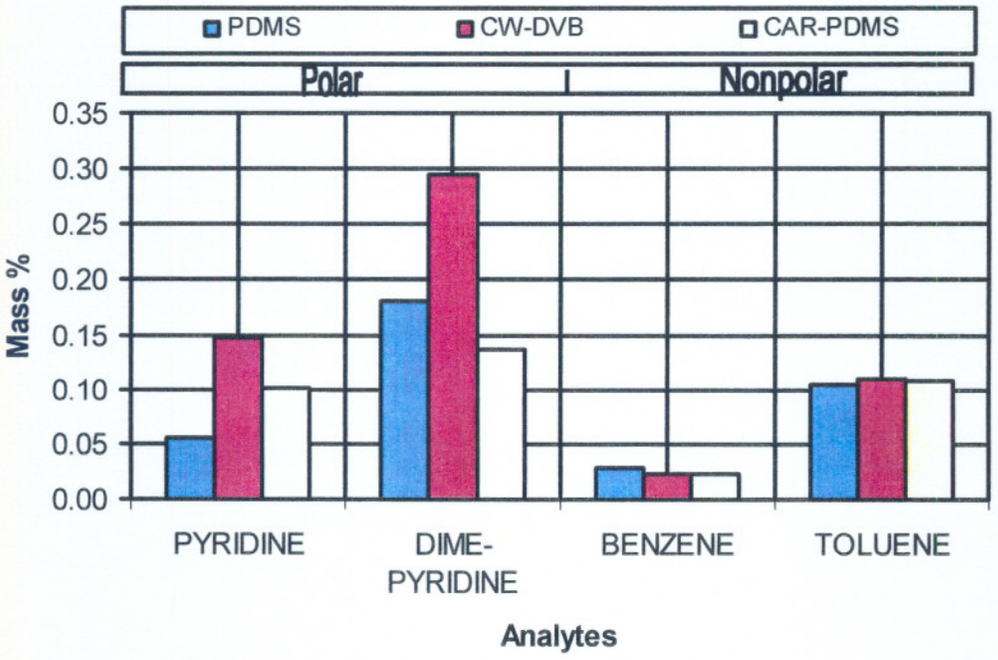

Figure 4.1: A comparison between the three fibers for polar and nonpolar analytes, based on the results of the internal standard approach.

It follows from Figure 4.1 that a very good correlation between the PDMS, CW-DVB and CAR-PDMS fibers is found for nonpolar analytes. A clear difference in response is however observed for the polar analytes. For each of these analytes a higher response is observed for the CW-DVB fiber. This observation can be explained by the fact that CW-DVB is more suited for polar analytes because it has a more polar character than the other fibers.

	FIBER		
COMPOUND	**PDMS**	**CW-DVB**	**CAR-PDMS**
Pyridine	1.000 :	2.637 :	1.827
Dimethyl-pyridine	1.332 :	2.158 :	1.000
Benzene	1.172 :	1.002 :	1.000
Toluene	1.000 :	1.045 :	1.028

Table 4.1: Ratios between different fibers for a particular analyte using the internal standard approach

According to the ratios in Table 4.1, pyridine was the analyte that was most affected by the variation in fibers and toluene the least affected.

The dielectric constant represents the polarity of the analyte. A high constant represents a highly polar analyte and it is these analytes that show the biggest difference between the three selected fibers (see Table 4.2).

COMPOUND	DIELECTRIC CONSTANT AT 20°C
Phenol	12.400
Pyridine	12.300
Toluene	2.379
Benzene	2.284
O-cresol	6.760
M/P-cresol	12.750
Dimethyl-pyridine	8.465
2.3-Xylenol	4.810
Naphthalene	2.540
2.6-Xylenol	4.900

Table 4.2: Components and their dielectric constants

The PDMS, CW-DVB and CAR-PDMS fibers were also compared by using the external standard approach. Results are given in Table A.9 (p. 95) and graphically presented in Figure 4.2.

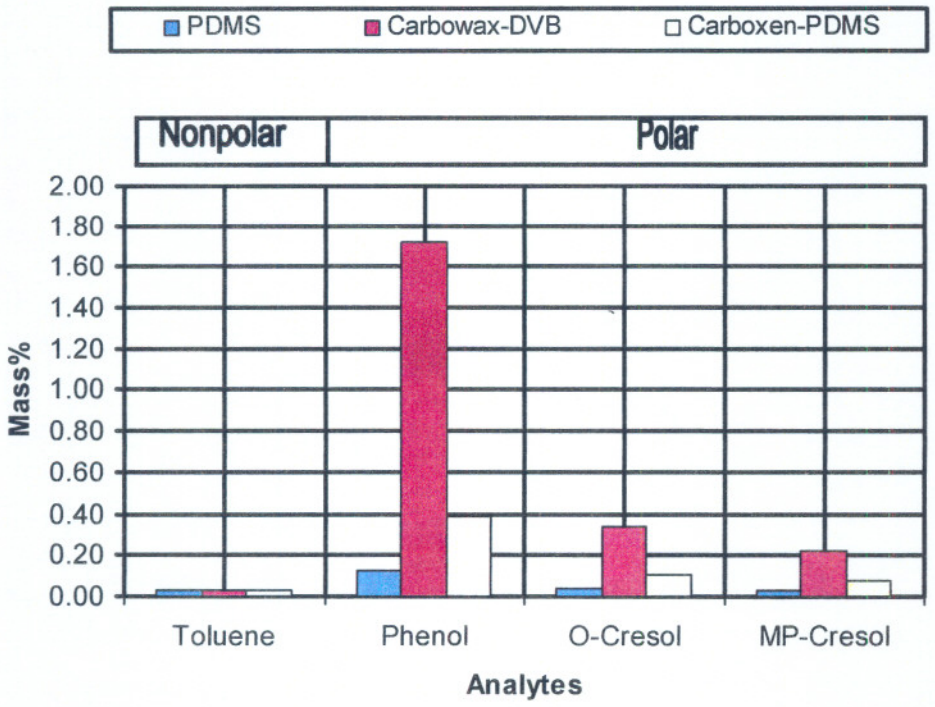

Figure 4.2: A comparison between the three fibers for polar and nonpolar analytes, based on the results of the external standard approach.

As seen in Figure 4.2, the same general observation for the internal standard approach was found with the external standard approach.

For polar analytes, specifically referring to phenol, o-cresol, m/p-cresol, the xylenols and the ethyl-phenols, it should be noted that the responses are more or less ten times greater for the CW-DVB fiber than with the PDMS and CAR-PDMS fibers (see Table A.1). This is due to the fact that the CW-DVB fiber is a polar fiber and thus extracts polar analytes much better than the nonpolar fibers.

	FIBER		
COMPOUND	**PDMS**	**CW-DVB**	**CAR-PDMS**
Toluene	1.033 :	1.000 :	1.108
Phenol	1.000 :	13.410 :	3.034
O-cresol	1.012 :	8.783 :	2.620
M/P-cresol	1.000 :	7.529 :	2.724

Table 4.3: Ratios between different fibers for a particular analyte using the external standard approach

It follows from Table 4.3 that phenol shows the biggest concentration differences between the different fibers and toluene the least.

As seen in Table A.1, great care has to be taken in selecting the correct SPME fiber for a particular application. It can be concluded that the polarity of the analyte of interest must be taken into account when selecting the appropriate SPME fiber.

4.1.2. Influence of the extraction time on the extraction process

If the extraction time was prolonged, the concentrations of the analytes increased until a plateau was reached. The plateau represents the equilibrium conditions between the fiber and the matrix (see figures 4.3 - 4.8). Results are given in Table A.2, Table A.3 and Table A.4 (p. 81 – 86) . The GC conditions are described in Paragraph 3.2.1.1.

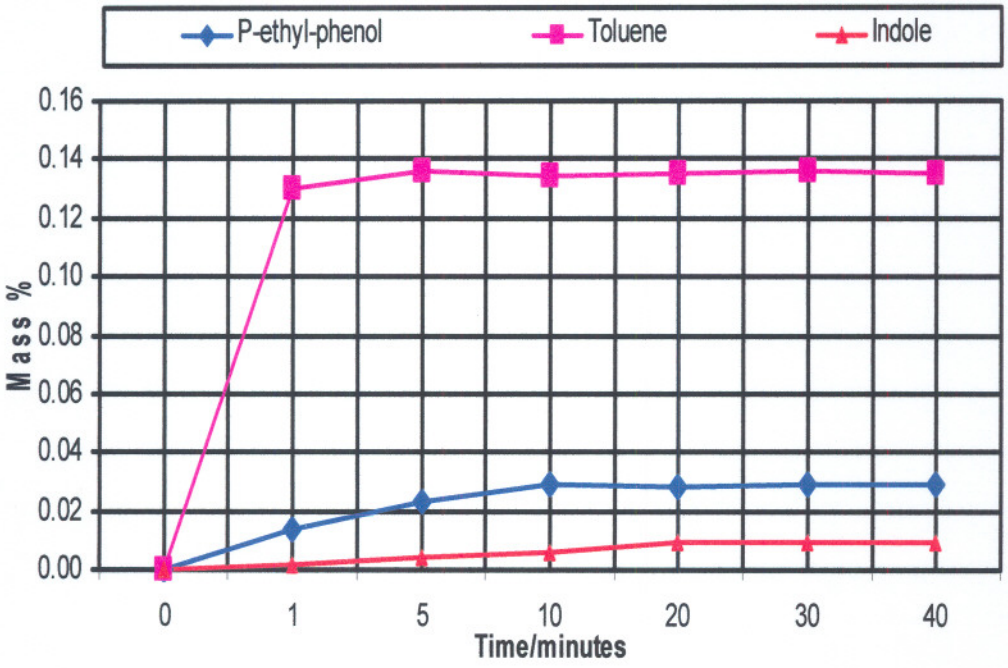

Figure 4.3: Influence of the extraction time for the PDMS fiber and following the internal standard approach.

It follows from Figure 4.3 that toluene reached equilibrium before *p*-ethyl phenol and indole. This could be due to the fact that toluene is a much smaller molecule than *p*-ethyl phenol and indole with a lower molecular weight.

The percentage increase in concentration of the different compounds in Figure 4.3 for the PDMS fiber was calculated by using Equation 3.2. The results are given in Table 4.4.

COMPOUND	Mass % for 1 minute	Mass % for 20 minutes	% Increase
P-ethyl-phenol	0.014	0.028	103
Toluene	0.13	0.135	4
Indole	0.002	0.009	379

Table 4.4: Percentage increase in 20 minutes for the PDMS fiber using the internal standard approach

It follows from Table 4.4 that indole had the highest percentage increase and toluene had the lowest percentage increase.

The influence of the extraction time was also investigated for the CAR-PDMS fiber (see Figure 4.4) by following the internal standard approach. Results are given in Table A.4 (p. 85 – 86).

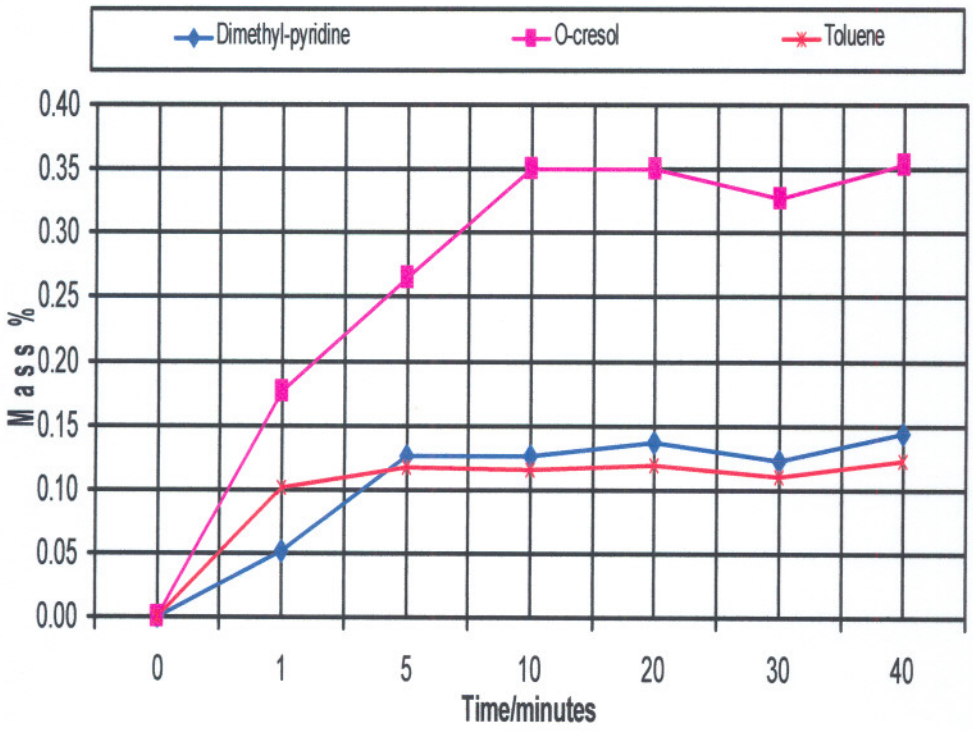

Figure 4.4: Influence of the extraction time for the CAR-PDMS fiber and following the internal standard approach.

The conclusion that can be drawn from Figure 4.4 is that dimethyl-pyridine reached equilibrium at more or less 5 minutes, whereas the o-cresol reached equilibrium at more or less 10 minutes. A possible explanation can be that dimethyl-pyridine is a nitrogen-containing compound and because the CAR-PDMS is an adsorbent fiber, it interacts quicker with this analyte than with o-cresol.

It is interesting to note that more or less the same mass% is obtained in the same time scale for both the PDMS and CAR-PDMS fibers (see Figure 4.3 and Figure 4.4). An interesting result that requires an explanation is that for most of the analytes, a decrease in response was recorded after about 30 minutes (see Table A.4). This is due to the fact that the fiber coating depleted and a new fiber was used for the 40 minute extraction.

The percentage increase was calculated by using Equation 3.2. It follows in Table 4.5.

COMPOUND	Mass % for 1 minute	Mass % for 20 minutes	% Increase
Dimethyl-pyridine	0.052	0.137	162
O-cresol	0.176	0.351	99
Toluene	0.102	0.119	17

Table 4.5: Percentage increase in 20 minutes for the CAR-PDMS fiber using the internal standard approach

It follows from Table 4.5 that dimethyl-pyridine had the highest percentage increase, whereas toluene had the lowest percentage increase.

The variation in extraction time was also compared for the CW-DVB fiber. The results are displayed in Table A.3 (p. 83 – 84) and graphically illustrated in Figure 4.5.

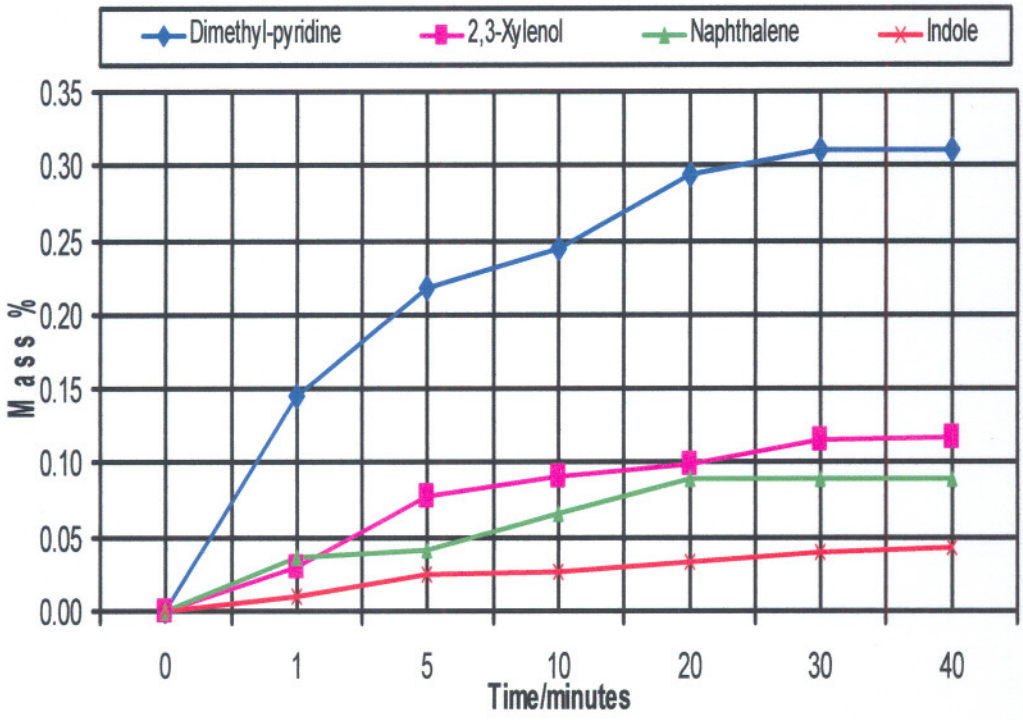

Figure 4.5: Influence of the extraction time for the CW-DVB fiber and following the internal standard approach.

It follows from Figure 4.5 that naphthalene reached equilibrium before the other analytes. This is probably because naphthalene is nonpolar and the other analytes are polar.

COMPOUND	Mass % for 1 minute	Mass % for 20 minutes	% Increase
Dimethyl-pyridine	0.146	0.295	102
2,3-xylenol	0.030	0.100	235
Naphthalene	0.037	0.089	140
Indole	0.010	0.033	236

Table 4.6: Percentage increase in 20 minutes for the CW-DVB fiber using the internal standard approach

It can be seen from Table 4.6 that indole had the highest percentage increase and dimethyl-pyridine had the lowest increase.

The internal standard was also affected by the variation in extraction time. The area responses are presented in Table 4.7 and graphically displayed in Figure 4.6.

	Time/minutes						
Fiber	**0**	**1**	**5**	**10**	**20**	**30**	**40**
CAR/PDMS	0	913	1439	1465	1880	1983	1981
CW/DVB	0	459	725	736	779	746	764
PDMS	0	608	913	976	1005	1240	1187

Table 4.7: Area responses for dioxane using the internal standard approach

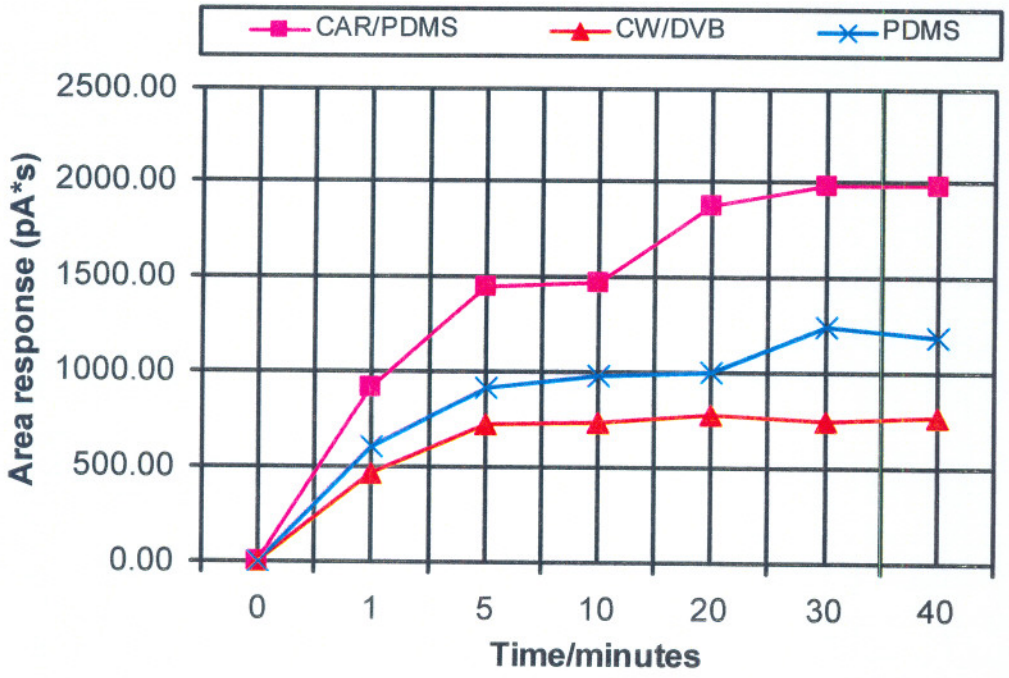

Figure 4.6: Influence of the extraction time on the area response of dioxane

From Figure 4.6 it can be observed that the area response of the internal standard increased with an increase in extraction time.

In Figure 4.7 the extraction time was varied for the PDMS fiber and the external standard approach was used. The concentrations were calculated using a standard as reference. The results are given in Table A.12 (p. 98).

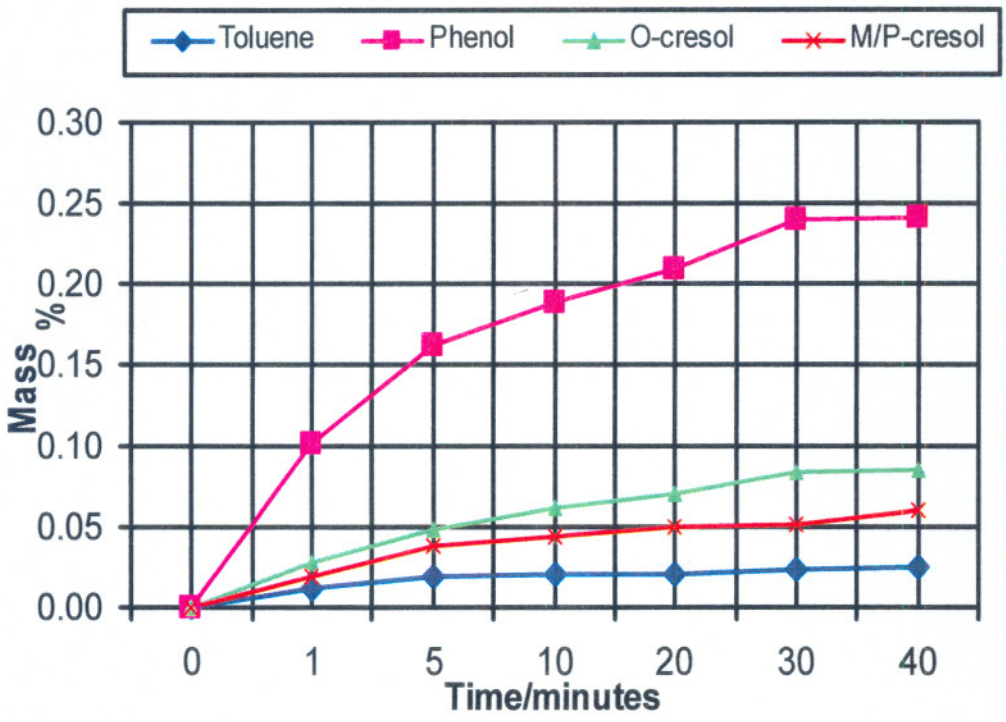

Figure 4.7: Influence of the extraction time for the PDMS fiber and following the external standard approach.

As can be seen in Figure 4.7, the concentrations for phenol, o-cresol and m/p-cresol reached equilibrium at more or less 30 minutes. Toluene reached equilibrium at 5 minutes. It should be noted that toluene is a nonpolar analyte, whereas the other analytes are polar.

The percentage increase was calculate for the PDMS fiber using Equation 3.2 and presented in Table 4.8.

COMPOUND	Mass % for 1 minute	Mass % for 20 minutes	% Increase
Toluene	0.012	0.021	73
Phenol	0.102	0.210	107
O-cresol	0.028	0.070	147
M/P-cresol	0.019	0.050	161

Table 4.8: Percentage increase for the PDMS fiber using the external standard approach

The observation from Table 4.8 is that m/p-cresol had the highest percentage increase. Toluene had the lowest percentage increase.

The extraction time was also varied for the CAR-PDMS and the external standard approach was followed (see Figure 4.8). The results are given in Table A.10 (p. 96).

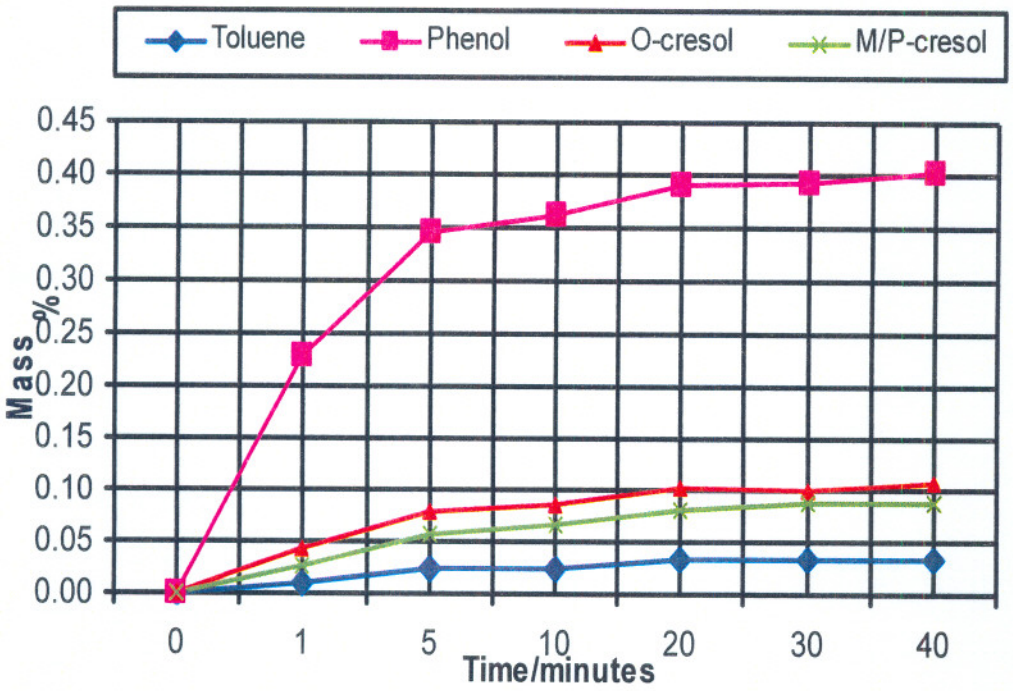

Figure 4.8: Influence of the extraction time for the CAR-PDMS fiber and following the external standard approach.

It follows from Figure 4.8 that the same observation is made for the CAR-PDMS as with the PDMS fiber.

The percentage increase was calculated for the CAR-PDMS fiber and presented in Table 4.9.

COMPOUND	Mass % for 1 minute	Mass % for 20 minutes	% Increase
Toluene	0.010	0.033	232
Phenol	0.229	0.390	70
O-cresol	0.043	0.102	137
M/P-cresol	0.027	0.082	201

Table 4.9: Percentage increase for the CAR-PDMS fiber using the external standard approach

The variation of the extraction time was also investigated for the CW-DVB fiber. The external standard approach was used and the results are given in Table A.11 (p. 97) and graphically presented in Figure 4.9.

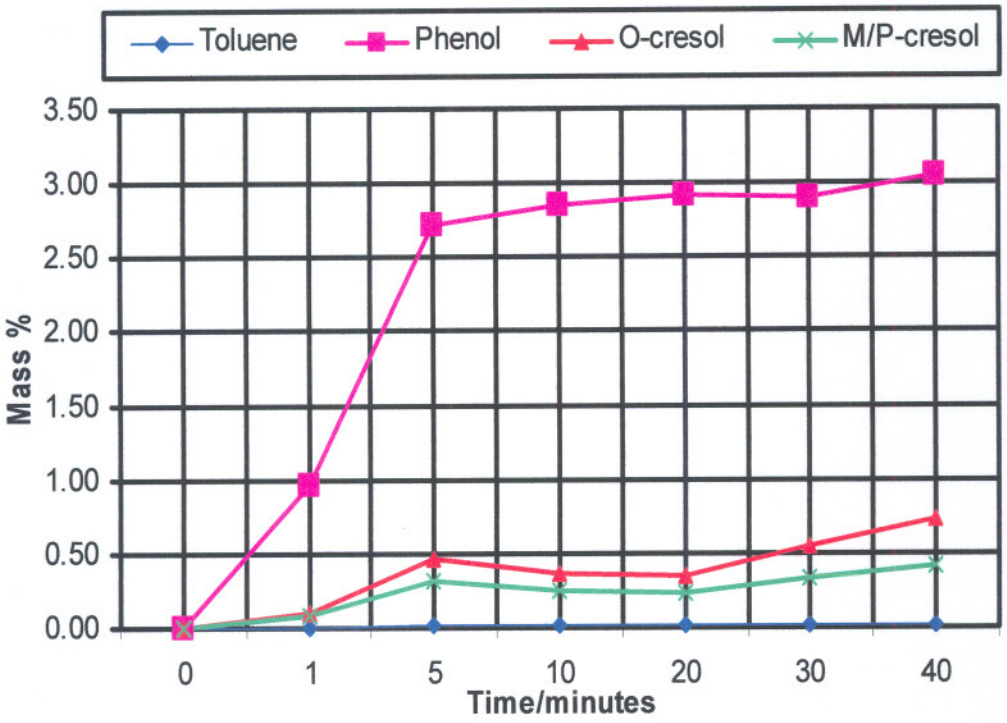

Figure 4.9: Influence of the extraction time for the CW-DVB fiber and following the external standard approach.

It follows from Figure 4.9 that the corresponding results are found for the CW-DVB as with the PDMS and CAR-PDMS fibers.

COMPOUND	Mass % for 1 minute	Mass % for 20 minutes	% Increase
Toluene	0.008	0.011	41
Phenol	0.962	2.914	203
O-cresol	0.104	0.343	230
M/P-cresol	0.077	0.226	195

Table 4.10: Percentage increase for the CW-DVB fiber using the external standard approach

The results in Table 4.10 show that o-cresol had the highest percentage increase, whereas toluene had the lowest increase.
It can be concluded from the abovementioned results that extraction time plays a crucial role in the extraction process. The time should be consistent to produce repeatable results.

4.1.3. Influence of the extraction temperature on the extraction process

The CAR-PDMS fiber was chosen for this experiment because it is a bipolar fiber and represents the midway for the nonpolar and the polar fibers. An extraction time of 20 minutes were selected because it follows that most of the analytes reached equilibrium by this time (see figures 4.4 to 4.9).

Most of the analytes showed an increase in the concentration at elevated temperatures. The heat that was added is a form of energy that increases the molecular diffusion speed of the molecules. At a particular instant, different molecules have different speeds and therefore, different kinetic energies. The different speeds can be explained by the fact that larger molecules move slower than smaller molecules at the same temperature. The average kinetic energy of all the molecules is assumed to be directly proportional to the

temperature. The temperature actually gives a quantitative measure of the average motion of molecules [36].

The effect of raising the temperature is that the kinetic energy of the molecules is increased and that the molecules move more energetically. Thus, the molecules can collide more frequently, and more vigorously, with the fiber. Therefore, the mass transport of analytes from the matrix onto the fiber coating is faster at higher temperatures (see figures 4.10 and 4.11).

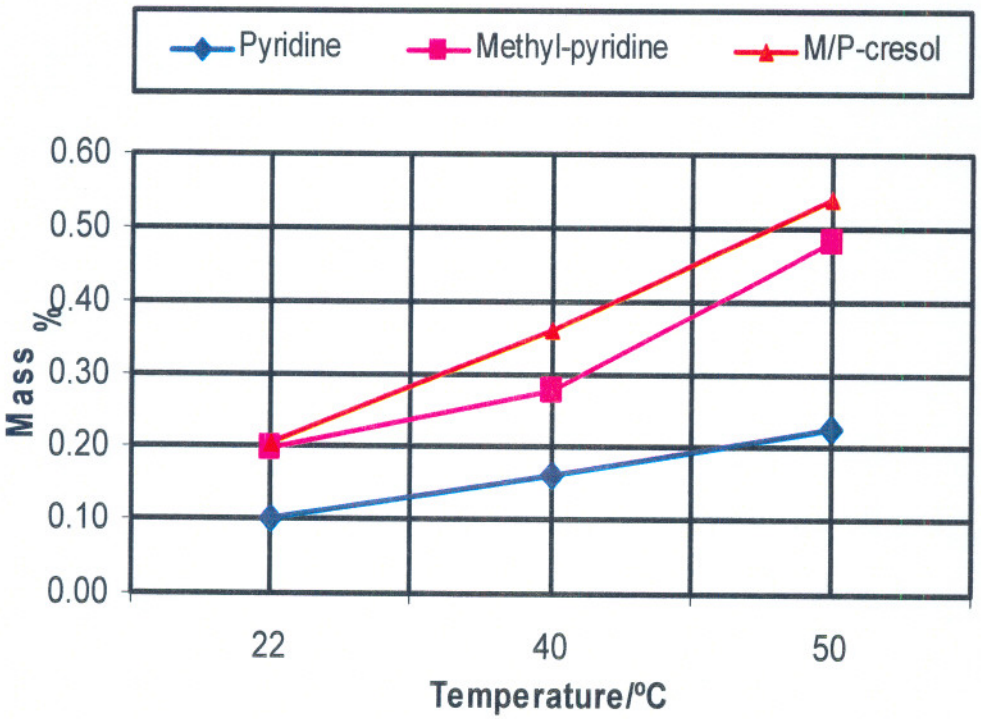

Figure 4.10: The temperature dependence of the analyte concentration by using the results from the internal standard approach.

It follows from Figure 4.10 that there is definitely a significant increase in analyte concentration when the temperature is increased.

The temperature variation was also investigated for the external standard approach. The data is presented in Table A.13 (p. 99) and displayed graphically in Figure 4.11.

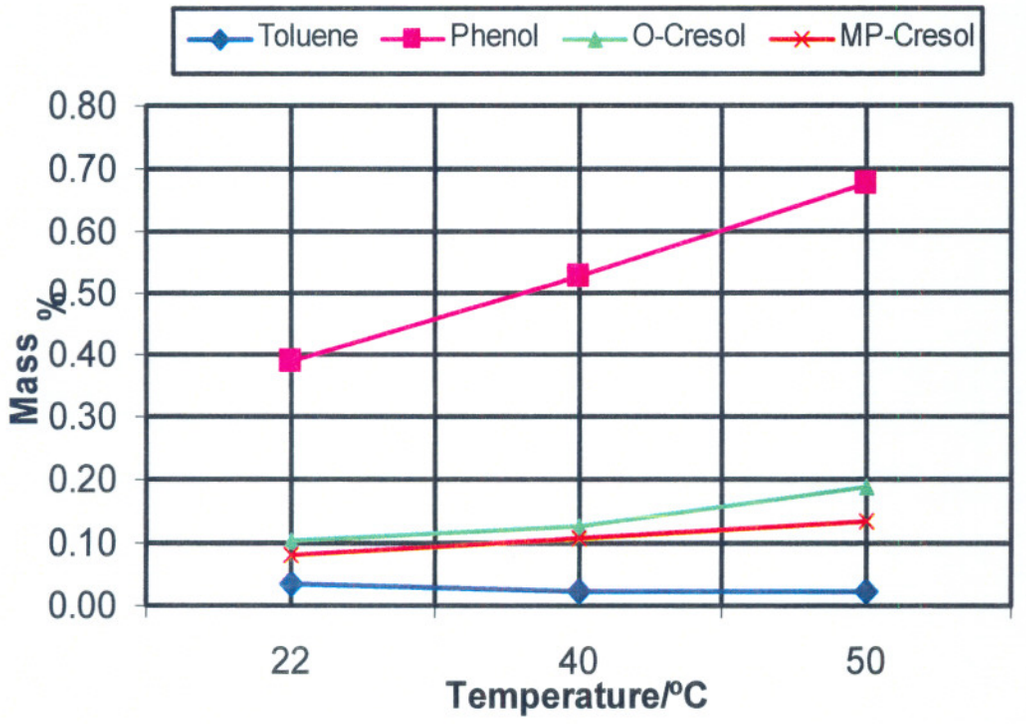

Figure 4.11: The temperature dependence of the analyte concentration by using the results from the external standard approach.

As can be seen in Figure 4.11, phenol, o-cresol and m/p-cresol displayed an increase in response when the temperature was increased.

It was also found that an increase in temperature favored the higher boiling point analytes. This conclusion is clearly illustrated in Figure 4.12.

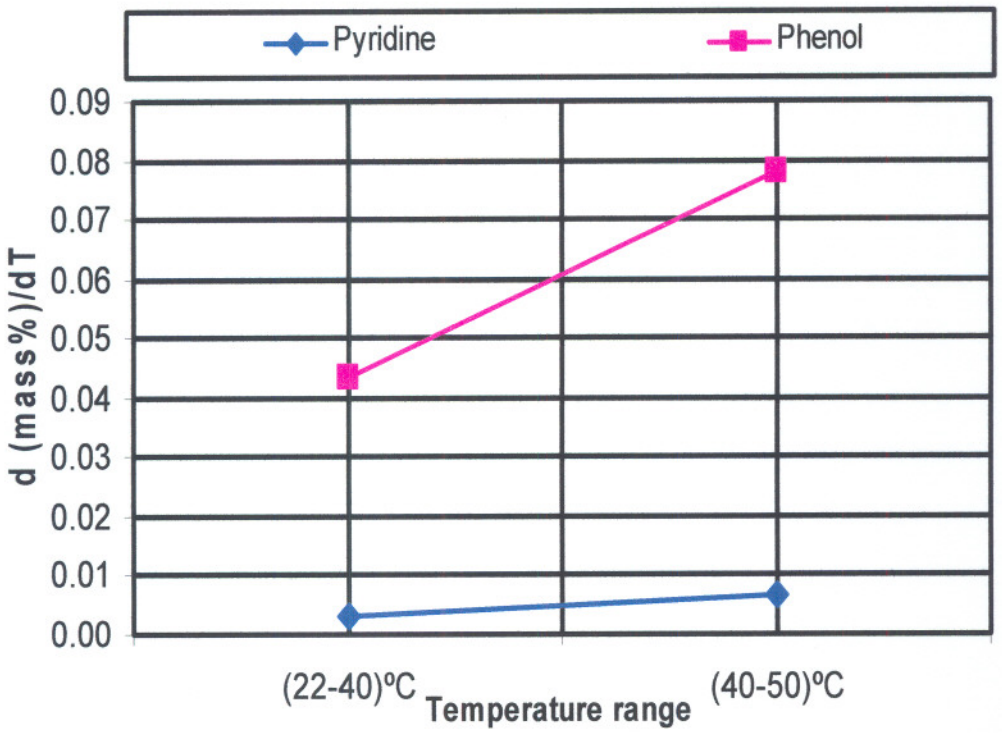

Figure 4.12: The temperature dependence of the extraction process by following the internal standard approach.

The temperature dependence of the extraction process was estimated by comparing the slopes of the results obtained by the internal standard method. It follows from Figure 4.12 are that an increase in temperature did not affect the sensitivity for the lower boiling point analytes as much as the case for higher boiling point analytes. Pyridine has a boiling point of 115°C whereas phenol has a boiling point of 182°C. Increase in temperature had a major effect on the concentration for phenol, but for pyridine the effect was less significant. It can also be observed from the figure that phenol has stronger temperature dependence than pyridine and the quantification thereof will therefore be more temperature sensitive.

It can be concluded that the temperature of the sample has a major effect on the extraction efficiency of analytes. The temperature should be kept constant and should be monitored with a thermometer to

assure consistent extraction. It not only influences the measured concentration of a specific compound but also the relative ratio between different compounds.

4.1.4. Influence of the sample volume

In order to investigate the influence of the sample volume, the CAR-PDMS fiber and the same conditions mentioned in Paragraph 4.2.3 was selected for the reasons mentioned in Paragraph 4.2.3. An extraction temperature of 22°C was decided upon because it was the same as room temperature and no heating or cooling of the water bath was necessary. The ionic strength of the added salt was kept constant.

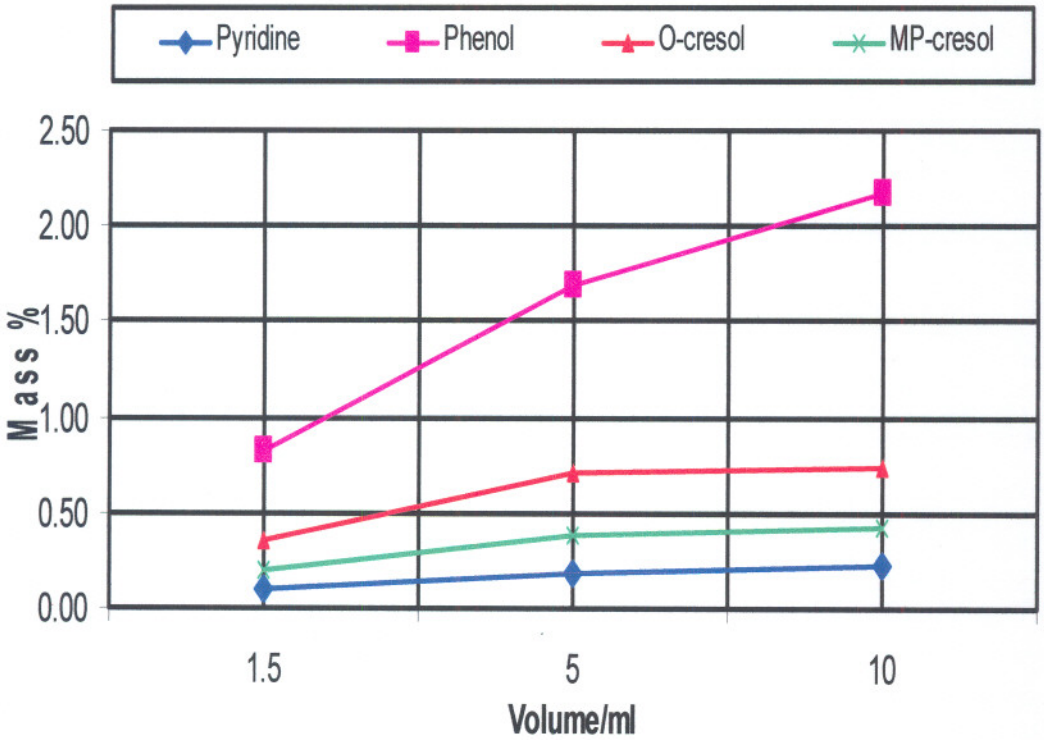

Figure 4.13: The influence of the extraction volume on the observed concentration of analytes.

As can be observed from Figure 4.13, almost all of the analytes showed an increase in response when the sample volume was increased. For analytes with a high concentration, like phenol, the sample volume had a stronger influence.

The percentage increase for the variation of volume was calculated and is given in Table 4.11.

COMPOUND	Mass % for 1.5ml	Mass % for 10ml	% Increase
Pyridine	0.102	0.229	125
Phenol	0.825	2.167	163
O-cresol	0.351	0.738	110
M/P-cresol	0.206	0.430	109

Table 4.11: Percentage increase for the variation of volume using the internal standard approach

It can be concluded from this results that the extraction volume should be kept constant to ensure reproducible results.

4.1.5. Evaluation of the effect of pH of the sample matrix on the extraction process

The decision on the type of fiber, temperature and extraction time was made based on the manufacturer recommendations and practical laboratory considerations. A volume of 1.5ml was decided upon due to the fact that it is a small volume and less sample would be wasted. A pH of 2, 7 and 10 was decided upon to represent an acidic, a neutral and a basic sample matrix. The matrix was made acidic by the

addition of hydrochloric acid and made basic by adding sodium hydroxide to the sample matrix. The results are given in Table A.7 (p. 91 – 92) and are graphically presented in Figure 4.14.

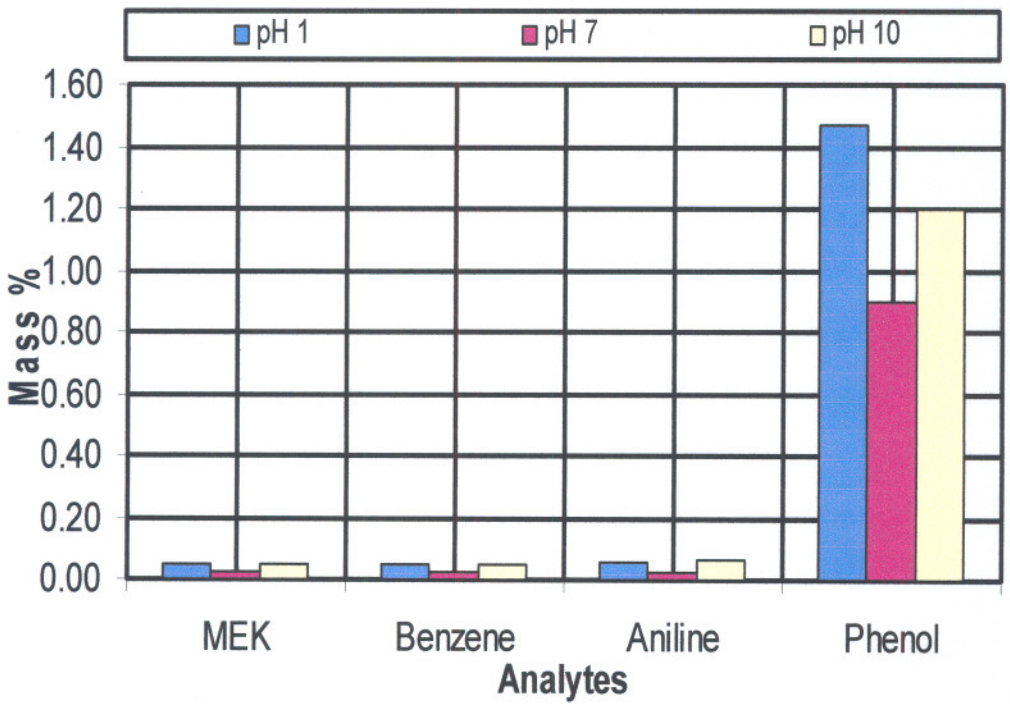

Figure 4.14: The effect of pH on the extraction process, using the internal standard approach.

It follows from Figure 4.14 that a more or less constant difference in the mass% is found for all the analytes at different pH values. This constant difference points to the internal standard (dioxane) used in this study. Dioxane is a neutral analyte and will be extracted more effectively in a basic or acidic matrix. This will have an effect on the concentrations of the other analytes, because the concentrations of these analytes are calculated using the response of the internal standard (see Equation 3.1). Therefore, these results increased with a pH of 1 and also for a pH of 10.

The variation of the pH was also investigated by following the external standard method. The results are graphically presented in Figure 4.15 and given in Table A.15 (p. 101).

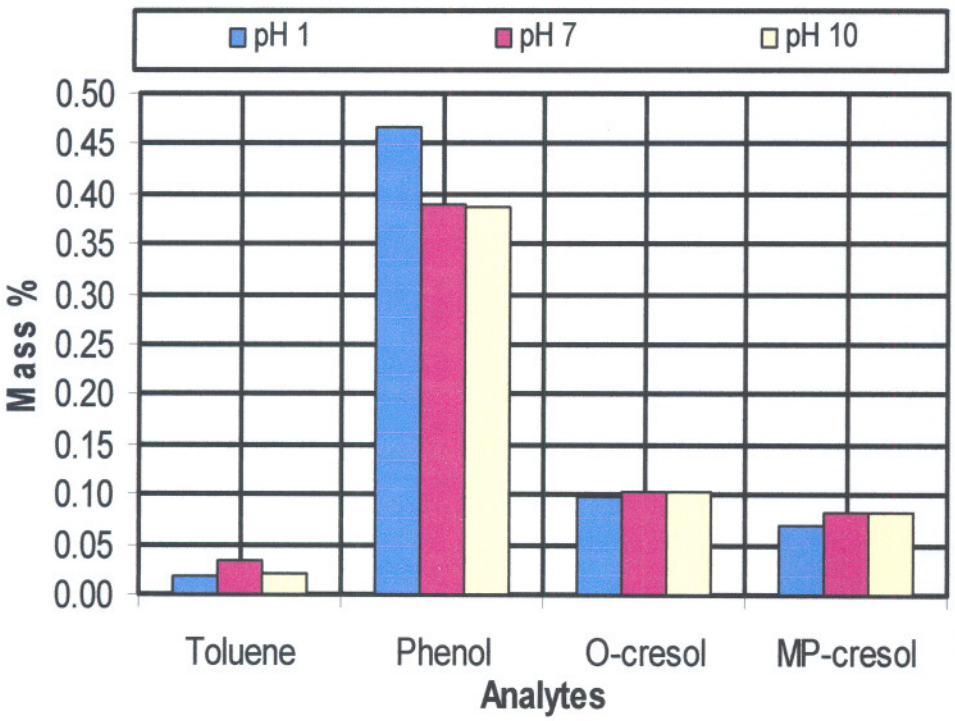

Figure 4.15: The effect of pH on the extraction process, using the external standard approach.

In the case where the external standard methodology is followed, the concentration of each analyte is determined by using its concentration in the prepared standard as reference. With these results it is clear that with a neutral pH analyte the pH do not have a major effect on the extraction process. Phenol is a monoprotic acid with a K_a value of 1.3 x 10^{-10}. Thus, phenol is extracted more effectively in a matrix of pH 1, as can be seen from Figure 4.15.

It is evident from Figure 4.14 and Figure 4.15 that a change in the pH of the sample matrix can have an influence on the extraction of acidic and basic analytes. A change in pH affects the extraction efficiency of

slightly acid or basic analytes. A sample with a pH of 10 has a higher extraction efficiency of more basic and neutral analytes, whereas a sample with a pH of 2, the acidic and neutral analytes has higher extraction efficiencies. This may be explained by the fact that the matrix adjusted itself in such a way as to counteract the effect of the pH change.

4.1.6. Influence of the ionic strength of the sample matrix

The variables were chosen on the criteria mentioned in Paragraph 4.2.3 and Paragraph 4.2.4. The ionic strength was varied between an unsaturated, saturated (0.3g Na_2SO_4 added to 1.5ml) and oversaturated (0.8g Na_2SO_4 added to 1.5ml) sample matrix. Results are given in Table A.8 (p. 93 – 94) and Table A.16 (p. 102) and graphically presented in Figure 4.16 and Figure 4.17.

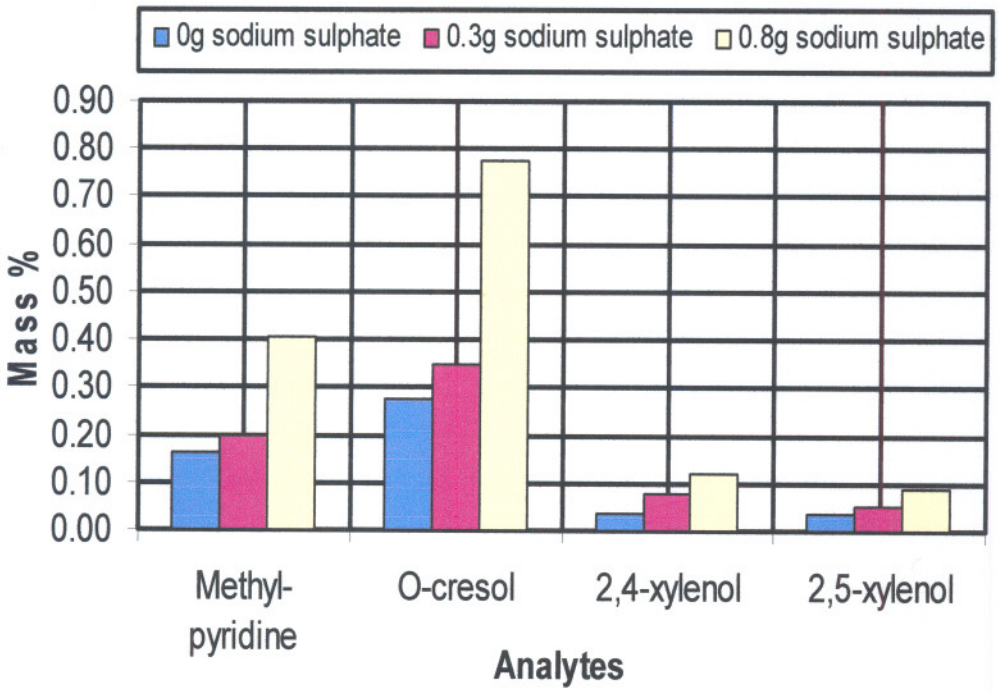

Figure 4.16: The effect of the ionic strength on the extraction process by following the internal standard approach.

It is evident from Figure 4.16 that all the analytes showed an increase in mass% with an increase in the ionic strength of the sample. This is in agreement with literature reports [37].

The increase in ionic strength makes the organic compounds less soluble by polarizing the water molecules. This interaction between the salt ions and the water molecules is called hydrolysis. This results in an equilibrium shift of the analytes towards the fiber.

A possible reason can be that the dielectric constant of the analytes decrease when the ionic strength increase. The analytes thus become less "polar" and therefore less soluble in the sample matrix when more salt was added.

The percentage increase for the variation in ionic strength was calculated. The results are given in Table 4.12.

COMPOUND	Mass% for 0g	Mass% for 0.8g	% Increase
Methyl-pyridine	0.162	0.405	149
O-cresol	0.276	0.776	181
2,4-Xylenol	0.036	0.122	239
2,5-Xylenol	0.037	0.087	136

Table 4.12: Percentage increase for the variation of ionic strength using the internal standard approach

The ionic strength was also investigated using the external standard approach.

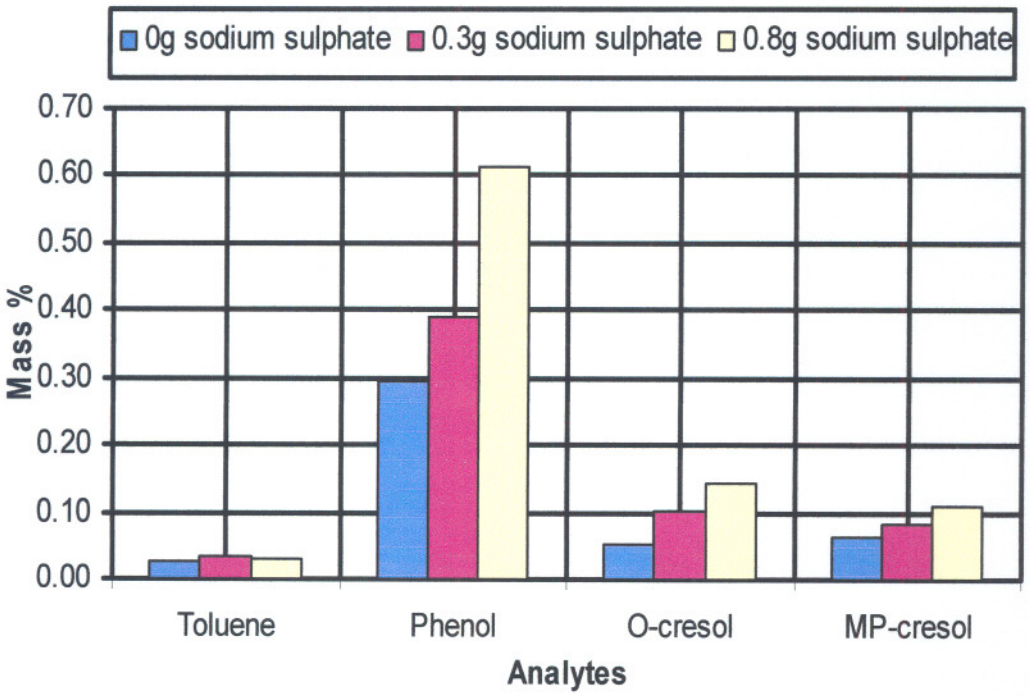

Figure 4.17: The effect of the ionic strength on the extraction process by following the external standard approach.

According to these results (see Figure 4.16 and Figure 4.17), the polar analytes were more affected by the increase in the amount of salt added to the sample matrix. The interaction between the salt ions and the water molecules (hydrolysis) made these polar analytes less soluble in the water. This results in an increase in extraction efficiency.

It can be concluded from Figure 4.16 and Figure 4.17 that the ionic strength of the sample matrix has a strong influence on the extraction efficiency of the polar analytes. The influence is less significant for nonpolar analytes.

4.2. EXTERNAL STANDARD APPROACH

All the variables that were investigated for the internal standard approach, was also investigated for the external standard approach.

For the internal standard approach the dioxane is extracted to a high extent. This results that the reported concentrations of analytes in the sample matrix are much higher than in reality. The external standard is a better method for extracting BTEX and VOCs because standards are prepared and the responses from the GC is calibrated according to these values.

Between the internal standard approach and the external standard approach, the emphasis fell on the internal standard approach. This is due to the fact the NAC method uses the internal standard approach for quantitation.

4.3. COMPARISON BETWEEN SPME AND NAC

4.3.1. Internal standard approach

The responses of the analytes were much higher for the SPME method than for the NAC method (see Table A.17 on p. 103). This was due to the fact that with the NAC method, the water was also injected and the peak responses appeared much smaller. The SPME method eliminated the water by making use of a concentrating effect. This result that peaks appeared much bigger and more analytes were detected than with the NAC method. Since the overall concentration of analytes in the sample is the same, care has to be taken calculating these values when using SPME extraction techniques.

4.3.2. External standard approach

Due to the difference between the internal and external methods (see Paragraph 2.5), the responses recorded using the SPME method, were lower than the responses of the NAC method using the external standard approach (see Table A.18 on p.104). This difference can be explained by the fact that different methods of calculations were used. All the analytes in the sample matrix were extracted although only some of the analyte concentrations were calculated using the external standard as reference. Therefore, some analytes could not have been calculated although they occupied pores on the fiber. The signals recorded for analytes when standards were introduced were higher, because more of the fiber pores were available for the analytes of interest and no interfering analytes were present.

The percentage yield was calculated for the NAC and SPME method using Equation 3.3. Data is presented in Table B.1 (p. 105) and the results are given in Table 4.13.

COMPOUND	% YIELD USING SPME	% YIELD USING NAC
Toluene	966.67	22.22
Phenol	498.34	93.36
O-cresol	817.50	100.00
M/P-cresol	652.94	47.06

Table 4.13: Percentage yield for the SPME and NAC method

It follows from Table 4.13 that SPME had a greater percentage yield than the NAC method. This is due to the concentrating effect of the SPME method.

4.4. STATISTICAL EVALUATION

A statistical method of comparing the reproducibility of results was applied. The F-test is a statistical method that permits the comparison of the precision of two sets of measurements. By applying this test to the results for SPME and NAC, it was found that there are no significant differences between the two sets of measurements. The result of the F-test is given in Table B.2 – B.5 (p. 106-109).

The results in Table B.1 show that for the NAC method the standard deviations are smaller than for the SPME. The standard error for SPME is also much larger than the standard error for NAC. This means that using the NAC method, the error of a single measurement is smaller compared with the SPME method.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In this Chapter...

The overall results are evaluated and a summary is given of the findings. Recommendations are made for further research.

5.1. CONCLUSION

The following overall conclusions can be drawn from the results presented in Chapter 4. The sensitivity of the SPME method was increased when a bipolar, thin fiber coating was used. For this study the observation was that the CAR-PDMS fiber was the most appropriate fiber for the extraction of VOCs and BTEX analytes in the waste water samples of a petrochemical plant.

The recorded mass% of analytes increased when the temperatures was increased. It is therefore crucial to keep the temperature constant for the extraction process. This can be done by monitoring the sample matrix by means of a thermometer.

Because some of the analytes reach equilibrium before the other analytes, it is important to keep the extraction time as consistent as possible if the extraction process is done in the pre-equilibrium stage. The extraction time can be monitored with a stopwatch to ensure repeatable results.

Sample volume has an effect on the extraction process. Because the analyte response increases with an increase in volume, the volume should be kept constant.

The observed conclusion is that a pH~7 for the sample matrix is most appropriate for this study. This is because no preference under these conditions is given for the acidic, neutral and basic analytes, whereas for acidic and basic matrixes preference is given for certain analytes.

The addition of salt to the sample matrix had a major influence on the extraction process. The increase in ionic strength decrease the analyte's solubility and this effect resulted in an increase in recorded mass%.

For the comparison of the two methods of quantification it was found that the internal standard approach is a better method for quantification when used for the NAC method. The external standard approach is a time-consuming method when used for the NAC method. This is due to the fact that a large number of standards should be prepared, because the concentrations of the analytes in the sample are unknown, even the analytes are sometimes unknown.

The internal standard approach should be used with caution when using the SPME method. The analyte, which serves as internal standard, can be extracted in some extent more and to some extent less than the true concentration and therefore can lead to incorrect calculation of the analytes in the sample matrix. The external standard method is compatible with the SPME method.

SPME is a fast and convenient sample preparation technique, but the NAC method proves to be a more appropriate method of quantification under these conditions. SPME was an appropriate technique for qualitative analysis, because more analytes were detected due to the elimination of water from the sample analyzed but are not good for the

quantification of analytes because of its sensitivity to a large number of extraction conditions.

If a sensitivity analysis is done, it is observed that the most important factor that influences the SPME technique is the selection of the appropriate fiber for a specific analyte. The other factors are also important and should be kept constant throughout a study.

5.2. RECOMMENDATION

Choosing an appropriate analyte as internal standard is very difficult, because of the high selectivity of SPME fibers. It is recommended that the internal standard approach should be used with caution, because higher selectivity of the internal standard leads to higher recorded mass% for the analytes. This is due to the fact that the concentrations of the analytes are directly related to the concentration of the internal standard.

SPME is a fast and convenient sample preparation technique, but for this study it should be used for qualitative analysis. The sensitivity of SPME to a large number of factors, as indicated in this study, makes it less suitable for the use in a routine laboratory. SPME is not recommended for quantitative analysis of multi-component samples in an industrial environment. It won't comply with a routine laboratory, which rely on critical quantitative analysis.

CHAPTER 6

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APPENDIX A

EXPERIMENTAL RESULTS

A.1. INTERNAL STANDARD APPROACH

Table A.1: Analysis results of the same sample using three different fibers by following the internal standard approach.

TEMP	22°C		
SALT	0.3015 grams		
pH	No adjustments		
VOLUME	1.5 ml		
TIME	20 min		
FIBER	PDMS	CW-DVB	CAR-PDMS
Component	**Mass %**	**Mass %**	**Mass %**
METHYL-ETHYL KETONE (MEK)	0.011	0.021	0.027
BENZENE	0.028	0.024	0.024
UNKNOWN	0.186	0.309	0.108
DIOXANE	0.320	0.320	0.320
PYRIDINE	0.056	0.147	0.102
TOLUENE	0.105	0.110	0.108
METHYL-PYRIDINE	0.133	0.291	0.196
METHYL-1H-PYRROLE	0.014	0.050	0.018
DIMETHYL-PYRIDINE	0.182	0.295	0.137
PHENOL	0.589	11.917	0.825
ANILINE	0.026	0.234	0.025
BENZONITRILE	0.046	0.133	0.037
O-CRESOL	0.308	3.954	0.351
MP-CRESOL	0.161	1.779	0.206
METHYL-ANILINE	0.019	0.043	0.013
BENZENEACETONITRILE	0.029	0.053	0.027
2,6-XYLENOL	0.035	0.198	0.035
O-ETHYL-PHENOL	0.026	0.176	0.027

2,4-XYLENOL	0.063	0.530	0.077
2,5-XYLENOL	0.036	0.208	0.049
P-ETHYL-PHENOL	0.028	0.245	0.033
M-ETHYL-PHENOL	0.013	0.159	0.022
3,5-XYLENOL	0.021	0.149	0.026
2,3-XYLENOL	0.019	0.100	0.020
3,4-XYLENOL	0.026	0.127	0.025
NAPHTHALENE	0.058	0.089	0.025
2,4,6-TRIMETHYL-PHENOL	0.019	0.056	0.026
2-PROPYL-PHENOL	0.006	0.018	0.006
METHYL-ETHYL-PHENOL	0.108	0.433	0.127
ISOQUINOLINE	0.009	0.023	0.011
TRIMETHYL-PHENOL	0.022	0.069	0.023
INDOLE	0.009	0.033	0.007
ETHYL-BENZALDEHYDE	0.010	0.034	0.010
1-INDANOL	0.006	0.031	0.005
METHYL-INDOLE	0.006	0.013	0.003
DIMETHYL-(METHYL-ETHYL)-BENZENE	0.015	0.028	0.009
METHYL-INDANOL	0.011	0.038	0.010
TETRADECANE	0.000	0.011	0.003
1-NAPHTHALENOL	0.003	0.034	0.002
2-NAPHTHALENOL	0.006	0.010	0.005
PENTADECANE	0.000	0.001	0.004
HEXADECANE	0.000	0.004	0.001
HEPTADECANE	0.000	0.001	0.001
OCTADECANE	0.000	0.004	0.001
NONADECANE	0.000	0.003	0.001
N-C20	0.000	0.002	0.001
N-C21	0.000	0.001	0.001
N-C22	0.000	0.001	0.000
N-C23	0.000	0.000	0.000
N-C24	0.000	0.000	0.000
N-C25	0.000	0.000	0.000
N-C26	0.000	0.000	0.000
N-C27	0.000	0.000	0.000

Table A.2: Extraction times for the PDMS fiber, using the internal standard method.

FIBER	PDMS					
TEMP	22°C					
SALT	0.3099 grams					
pH	No adjustments					
VOLUME	1.5 ml					
TIME	1 min	5 min	10 min	20 min	30 min	40 min
Component	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**
MEK	0.009	0.011	0.008	0.011	0.010	0.008
BENZENE	0.028	0.027	0.026	0.028	0.029	0.032
UNKNOWN	0.045	0.144	0.171	0.186	0.173	0.199
DIOXANE	0.320	0.320	0.320	0.320	0.320	0.320
PYRIDINE	0.075	0.063	0.064	0.056	0.068	0.086
TOLUENE	0.130	0.136	0.134	0.135	0.136	0.135
METHYL-PYRIDINE	0.132	0.154	0.165	0.133	0.176	0.226
METHYL-1H-PYRROLE	0.022	0.022	0.023	0.014	0.029	0.048
DIMETHYL-PYRIDINE	0.153	0.230	0.256	0.182	0.253	0.341
PHENOL	0.577	0.617	0.667	0.589	0.650	0.705
ANILINE	0.032	0.028	0.033	0.026	0.033	0.038
BENZONITRILE	0.045	0.052	0.063	0.046	0.052	0.059
O-CRESOL	0.274	0.313	0.372	0.308	0.359	0.424
MP-CRESOL	0.127	0.167	0.180	0.161	0.169	0.203
METHYL-ANILINE	0.006	0.011	0.017	0.019	0.015	0.020
BENZENEACETONITRILE	0.010	0.025	0.031	0.029	0.026	0.031
2,6-XYLENOL	0.022	0.037	0.042	0.035	0.042	0.050
O-ETHYL-PHENOL	0.014	0.028	0.032	0.026	0.032	0.037
2,4-XYLENOL	0.036	0.058	0.077	0.063	0.077	0.088
2,5-XYLENOL	0.019	0.035	0.035	0.036	0.036	0.044
P-ETHYL-PHENOL	0.014	0.023	0.029	0.028	0.029	0.029
M-ETHYL-PHENOL	0.009	0.010	0.014	0.013	0.018	0.015
3,5-XYLENOL	0.011	0.019	0.023	0.021	0.020	0.030
2,3-XYLENOL	0.008	0.016	0.019	0.019	0.019	0.021
3,4-XYLENOL	0.010	0.019	0.022	0.026	0.033	0.026
NAPHTHALENE	0.019	0.053	0.041	0.058	0.048	0.045

2,4,6-TRIMETHYL-PHENOL	0.006	0.017	0.018	0.019	0.029	0.020
2-PROPYL-PHENOL	0.001	0.004	0.005	0.006	0.032	0.006
METHYL-ETHYL-PHENOL	0.035	0.088	0.109	0.108	0.199	0.133
ISOQUINOLINE	0.004	0.007	0.008	0.009	0.020	0.009
TRIMETHYL-PHENOL	0.007	0.013	0.019	0.022	0.030	0.030
INDOLE	0.002	0.004	0.006	0.009	0.009	0.009
ETHYL-BENZALDEHYDE	0.002	0.007	0.006	0.010	0.009	0.011
1-INDANOL	0.002	0.005	0.004	0.006	0.005	0.006
METHYL-INDOLE	0.000	0.002	0.000	0.006	0.005	0.003
DIMETHYL-(METHYL-ETHYL)-BENZENE	0.002	0.007	0.010	0.015	0.006	0.008
METHYL-INDANOL	0.001	0.006	0.007	0.011	0.007	0.008
TETRADECANE	0.000	0.000	0.000	0.000	0.000	0.000
1-NAPHTHALENOL	0.001	0.002	0.003	0.003	0.003	0.002
2-NAPHTHALENOL	0.000	0.003	0.002	0.006	0.003	0.003
PENTADECANE	0.000	0.000	0.000	0.000	0.000	0.000
HEXADECANE	0.000	0.000	0.000	0.000	0.000	0.000
HEPTADECANE	0.000	0.000	0.000	0.000	0.000	0.000
OCTADECANE	0.000	0.000	0.000	0.000	0.000	0.000
NONADECANE	0.000	0.000	0.000	0.000	0.000	0.000
N-C20	0.000	0.000	0.000	0.000	0.000	0.000
N-C21	0.000	0.000	0.000	0.000	0.000	0.000
N-C22	0.000	0.000	0.000	0.000	0.000	0.000
N-C23	0.000	0.000	0.000	0.000	0.000	0.000
N-C24	0.000	0.000	0.000	0.000	0.000	0.000
N-C25	0.000	0.000	0.000	0.000	0.000	0.000
N-C26	0.000	0.000	0.000	0.000	0.000	0.000
N-C27	0.000	0.000	0.000	0.000	0.000	0.000

Table A.3: Extraction times for the Carbowax-DVB fiber, using the internal standard method.

FIBER	CW-DVB					
TEMP	22°C					
SALT	0.2998 grams					
pH	No adjustments					
VOLUME	1.5 ml					
TIME	1 min	5 min	10 min	20 min	30 min	40 min
Component	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**
MEK	0.030	0.024	0.018	0.021	0.024	0.021
BENZENE	0.027	0.027	0.021	0.024	0.027	0.028
UNKNOWN	0.138	0.192	0.269	0.309	0.288	0.269
DIOXANE	0.320	0.320	0.320	0.320	0.320	0.320
PYRIDINE	0.122	0.165	0.131	0.147	0.186	0.186
TOLUENE	0.116	0.109	0.131	0.138	0.133	0.122
METHYL-PYRIDINE	0.161	0.269	0.216	0.291	0.365	0.302
METHYL-1H-PYRROLE	0.031	0.045	0.043	0.050	0.058	0.054
DIMETHYL-PYRIDINE	0.146	0.217	0.245	0.295	0.311	0.311
PHENOL	8.212	16.020	11.405	11.917	12.927	12.482
ANILINE	0.165	0.279	0.227	0.234	0.289	0.272
BENZONITRILE	0.068	0.105	0.119	0.133	0.144	0.129
O-CRESOL	1.555	4.024	3.439	3.954	4.802	4.760
MP-CRESOL	0.783	1.875	1.595	1.779	1.971	1.906
METHYL-ANILINE	0.017	0.037	0.053	0.043	0.050	0.044
BENZENEACETONITRILE	0.019	0.033	0.055	0.053	0.064	0.053
2,6-XYLENOL	0.057	0.157	0.165	0.198	0.290	0.287
O-ETHYL-PHENOL	0.049	0.158	0.142	0.176	0.238	0.247
2,4-XYLENOL	0.157	0.452	0.432	0.530	0.715	0.737
2,5-XYLENOL	0.060	0.170	0.157	0.208	0.242	0.251
P-ETHYL-PHENOL	0.070	0.209	0.195	0.245	0.294	0.311
M-ETHYL-PHENOL	0.050	0.153	0.128	0.159	0.200	0.215
3,5-XYLENOL	0.051	0.125	0.122	0.149	0.164	0.153
2,3-XYLENOL	0.030	0.078	0.090	0.100	0.116	0.118
3,4-XYLENOL	0.037	0.103	0.098	0.127	0.151	0.153
NAPHTHALENE	0.037	0.042	0.066	0.089	0.089	0.089

2,4,6-TRIMETHYL-PHENOL	0.014	0.034	0.041	0.056	0.075	0.074
2-PROPYL-PHENOL	0.004	0.011	0.012	0.018	0.023	0.026
METHYL-ETHYL-PHENOL	0.112	0.310	0.322	0.433	0.548	0.586
ISOQUINOLINE	0.007	0.018	0.018	0.023	0.026	0.025
TRIMETHYL-PHENOL	0.018	0.050	0.052	0.069	0.088	0.092
INDOLE	0.010	0.025	0.026	0.033	0.040	0.042
ETHYL-BENZALDEHYDE	0.010	0.027	0.027	0.034	0.039	0.040
1-INDANOL	0.009	0.026	0.024	0.031	0.034	0.036
METHYL-INDOLE	0.002	0.007	0.007	0.013	0.012	0.013
DIMETHYL-(METHYL-ETHYL)-BENZENE	0.010	0.021	0.022	0.028	0.035	0.037
METHYL-INDANOL	0.010	0.027	0.025	0.038	0.042	0.043
TETRADECANE	0.003	0.007	0.007	0.011	0.011	0.012
1-NAPHTHALENOL	0.009	0.027	0.026	0.034	0.040	0.044
2-NAPHTHALENOL	0.002	0.006	0.007	0.010	0.013	0.014
PENTADECANE	0.000	0.001	0.000	0.001	0.002	0.001
HEXADECANE	0.002	0.002	0.001	0.004	0.003	0.002
HEPTADECANE	0.001	0.001	0.002	0.001	0.001	0.001
OCTADECANE	0.001	0.001	0.001	0.004	0.002	0.001
NONADECANE	0.001	0.002	0.002	0.003	0.004	0.005
N-C20	0.000	0.000	0.001	0.002	0.001	0.001
N-C21	0.000	0.000	0.001	0.001	0.001	0.001
N-C22	0.000	0.000	0.000	0.001	0.001	0.001
N-C23	0.000	0.000	0.000	0.000	0.000	0.000
N-C24	0.000	0.000	0.000	0.000	0.000	0.000
N-C25	0.000	0.000	0.000	0.000	0.000	0.000
N-C26	0.000	0.000	0.000	0.000	0.000	0.000
N-C27	0.000	0.000	0.000	0.000	0.000	0.000

Table A.4: Extraction times for the Carboxen-PDMS fiber, using the internal standard method.

FIBER	CAR-PDMS					
TEMP	22°C					
SALT	0.3107 grams					
pH	No adjustments					
VOLUME	1.5 ml					
TIME	1min	5min	10min	20min	30min	40min
Component	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**
MEK	0.038	0.030	0.030	0.027	0.023	0.027
BENZENE	0.027	0.022	0.025	0.024	0.022	0.024
UNKNOWN	0.018	0.038	0.054	0.108	0.087	0.107
DIOXANE	0.320	0.320	0.320	0.320	0.320	0.320
PYRIDINE	0.068	0.084	0.107	0.102	0.093	0.101
TOLUENE	0.102	0.117	0.115	0.119	0.111	0.123
METHYL-PYRIDINE	0.133	0.127	0.190	0.196	0.147	0.195
METHYL-1H-PYRROLE	0.015	0.016	0.011	0.018	0.016	0.017
DIMETHYL-PYRIDINE	0.052	0.126	0.126	0.137	0.122	0.143
PHENOL	0.587	0.699	0.885	0.825	0.746	0.798
ANILINE	0.077	0.036	0.040	0.025	0.020	0.022
BENZONITRILE	0.016	0.053	0.070	0.037	0.034	0.035
O-CRESOL	0.176	0.266	0.351	0.351	0.327	0.353
MP-CRESOL	0.099	0.141	0.200	0.206	0.190	0.192
METHYL-ANILINE	0.001	0.007	0.009	0.013	0.011	0.012
BENZENEACETONITRILE	0.001	0.008	0.016	0.027	0.024	0.033
2,6-XYLENOL	0.008	0.019	0.031	0.035	0.031	0.036
O-ETHYL-PHENOL	0.005	0.014	0.023	0.027	0.024	0.028
2,4-XYLENOL	0.012	0.035	0.066	0.077	0.070	0.082
2,5-XYLENOL	0.014	0.026	0.041	0.049	0.045	0.049
P-ETHYL-PHENOL	0.006	0.013	0.025	0.033	0.029	0.035
M-ETHYL-PHENOL	0.009	0.010	0.017	0.022	0.018	0.019
3,5-XYLENOL	0.006	0.015	0.025	0.026	0.026	0.030
2,3-XYLENOL	0.004	0.008	0.013	0.020	0.017	0.019
3,4-XYLENOL	0.003	0.009	0.017	0.025	0.021	0.025
NAPHTHALENE	0.003	0.009	0.014	0.025	0.019	0.024

2,4,6-TRIMETHYL-PHENOL	0.003	0.008	0.014	0.026	0.021	0.025
2-PROPYL-PHENOL	0.002	0.001	0.003	0.006	0.005	0.006
METHYL-ETHYL-PHENOL	0.009	0.038	0.075	0.127	0.101	0.129
ISOQUINOLINE	0.001	0.002	0.004	0.011	0.008	0.012
TRIMETHYL-PHENOL	0.001	0.006	0.014	0.023	0.020	0.023
INDOLE	0.000	0.002	0.004	0.007	0.006	0.007
ETHYL-BENZALDEHYDE	0.001	0.002	0.005	0.010	0.007	0.008
1-INDANOL	0.001	0.001	0.003	0.005	0.004	0.005
METHYL-INDOLE	0.000	0.000	0.000	0.003	0.001	0.003
DIMETHYL-(METHYL-ETHYL)-BENZENE	0.000	0.000	0.005	0.009	0.007	0.010
METHYL-INDANOL	0.000	0.002	0.004	0.010	0.007	0.011
TETRADECANE	0.000	0.001	0.001	0.003	0.002	0.003
1-NAPHTHALENOL	0.000	0.000	0.001	0.002	0.001	0.002
2-NAPHTHALENOL	0.001	0.001	0.002	0.005	0.004	0.007
PENTADECANE	0.000	0.000	0.001	0.004	0.003	0.005
HEXADECANE	0.000	0.000	0.000	0.001	0.000	0.001
HEPTADECANE	0.000	0.001	0.001	0.001	0.001	0.001
OCTADECANE	0.000	0.000	0.001	0.001	0.001	0.001
NONADECANE	0.000	0.000	0.001	0.001	0.001	0.001
N-C20	0.000	0.000	0.001	0.001	0.001	0.001
N-C21	0.000	0.000	0.000	0.001	0.000	0.001
N-C22	0.000	0.000	0.000	0.000	0.000	0.000
N-C23	0.000	0.000	0.000	0.000	0.000	0.000
N-C24	0.000	0.000	0.000	0.000	0.000	0.000
N-C25	0.000	0.000	0.000	0.000	0.000	0.000
N-C26	0.000	0.000	0.000	0.000	0.000	0.000
N-C27	0.000	0.000	0.000	0.000	0.000	0.000

Table A.5: The effect of sample temperature on the extraction process, using the internal standard method.

FIBER	CAR-PDMS		
SALT	0.2886 grams		
pH	No adjustments		
VOLUME	1.5 ml		
TIME	20 min		
TEMP	22°C	40°C	50°C
Component	**Mass %**	**Mass %**	**Mass %**
MEK	0.027	0.044	0.039
BENZENE	0.024	0.036	0.042
UNKNOWN	0.108	0.139	0.176
DIOXANE	0.320	0.320	0.320
PYRIDINE	0.102	0.161	0.227
TOLUENE	0.108	0.115	0.115
METHYL-PYRIDINE	0.196	0.275	0.483
METHYL-1H-PYRROLE	0.018	0.027	0.041
DIMETHYL-PYRIDINE	0.137	0.172	0.245
PHENOL	0.825	1.607	2.388
ANILINE	0.025	0.072	0.105
BENZONITRILE	0.037	0.093	0.138
O-CRESOL	0.351	0.619	1.071
MP-CRESOL	0.206	0.360	0.538
METHYL-ANILINE	0.013	0.022	0.040
BENZENEACETONITRILE	0.027	0.032	0.031
2,6-XYLENOL	0.035	0.048	0.081
O-ETHYL-PHENOL	0.027	0.036	0.059
2,4-XYLENOL	0.077	0.109	0.187
2,5-XYLENOL	0.049	0.067	0.126
P-ETHYL-PHENOL	0.033	0.048	0.079
M-ETHYL-PHENOL	0.022	0.033	0.049
3,5-XYLENOL	0.026	0.037	0.087
2,3-XYLENOL	0.020	0.024	0.049
3,4-XYLENOL	0.025	0.030	0.050
NAPHTHALENE	0.025	0.038	0.020

2,4,6-TRIMETHYL-PHENOL	0.026	0.026	0.025
2-PROPYL-PHENOL	0.006	0.007	0.007
METHYL-ETHYL-PHENOL	0.127	0.141	0.177
ISOQUINOLINE	0.011	0.010	0.014
TRIMETHYL-PHENOL	0.023	0.024	0.032
INDOLE	0.007	0.008	0.017
ETHYL-BENZALDEHYDE	0.010	0.010	0.016
1-INDANOL	0.005	0.007	0.010
METHYL-INDOLE	0.003	0.006	0.004
DIMETHYL-(METHYL-ETHYL)-BENZENE	0.009	0.010	0.013
METHYL-INDANOL	0.010	0.013	0.018
TETRADECANE	0.003	0.003	0.004
1-NAPHTHALENOL	0.002	0.005	0.004
2-NAPHTHALENOL	0.005	0.003	0.003
PENTADECANE	0.004	0.002	0.002
HEXADECANE	0.001	0.001	0.001
HEPTADECANE	0.001	0.002	0.001
OCTADECANE	0.001	0.001	0.000
NONADECANE	0.001	0.001	0.000
N-C20	0.001	0.000	0.000
N-C21	0.001	0.000	0.000
N-C22	0.000	0.000	0.000
N-C23	0.000	0.000	0.000
N-C24	0.000	0.000	0.000
N-C25	0.000	0.000	0.000
N-C26	0.000	0.000	0.000
N-C27	0.000	0.000	0.000

Table A.6: The effect of sample volume on the extraction process, using the internal standard method.

FIBER	CAR-PDMS		
TEMP	22°C		
pH	No adjustments		
TIME	20 min		
VOLUME	1.5 ml	5 ml	10 ml
SALT	0.3005g	0.9979g	2.0037g
Component	**Mass %**	**Mass %**	**Mass %**
MEK	0.027	0.050	0.069
BENZENE	0.024	0.050	0.059
UNKNOWN	0.108	0.212	0.138
DIOXANE	0.320	0.320	0.320
PYRIDINE	0.102	0.185	0.229
TOLUENE	0.108	0.125	0.095
METHYL-PYRIDINE	0.196	0.360	0.392
METHYL-1H-PYRROLE	0.018	0.028	0.029
DIMETHYL-PYRIDINE	0.137	0.235	0.209
PHENOL	0.825	1.684	2.167
ANILINE	0.025	0.070	0.086
BENZONITRILE	0.037	0.132	0.126
O-CRESOL	0.351	0.708	0.738
MP-CRESOL	0.206	0.382	0.430
METHYL-ANILINE	0.013	0.035	0.025
BENZENEACETONITRILE	0.027	0.076	0.036
2,6-XYLENOL	0.035	0.070	0.059
O-ETHYL-PHENOL	0.027	0.051	0.049
2,4-XYLENOL	0.077	0.145	0.137
2,5-XYLENOL	0.049	0.098	0.115
P-ETHYL-PHENOL	0.033	0.066	0.057
M-ETHYL-PHENOL	0.022	0.034	0.035
3,5-XYLENOL	0.026	0.072	0.082
2,3-XYLENOL	0.020	0.035	0.037
3,4-XYLENOL	0.025	0.046	0.041
NAPHTHALENE	0.025	0.030	0.015

2,4,6-TRIMETHYL-PHENOL	0.026	0.031	0.023
2-PROPYL-PHENOL	0.006	0.008	0.006
METHYL-ETHYL-PHENOL	0.127	0.231	0.208
ISOQUINOLINE	0.011	0.020	0.018
TRIMETHYL-PHENOL	0.023	0.042	0.038
INDOLE	0.007	0.012	0.015
ETHYL-BENZALDEHYDE	0.010	0.014	0.015
1-INDANOL	0.005	0.009	0.008
METHYL-INDOLE	0.003	0.005	0.003
DIMETHYL-(METHYL-ETHYL)-BENZENE	0.009	0.016	0.014
METHYL-INDANOL	0.010	0.019	0.013
TETRADECANE	0.003	0.006	0.004
1-NAPHTHALENOL	0.002	0.007	0.004
2-NAPHTHALENOL	0.005	0.006	0.003
PENTADECANE	0.004	0.002	0.001
HEXADECANE	0.001	0.001	0.001
HEPTADECANE	0.001	0.001	0.001
OCTADECANE	0.001	0.000	0.000
NONADECANE	0.001	0.000	0.000
N-C20	0.001	0.000	0.000
N-C21	0.001	0.000	0.000
N-C22	0.000	0.000	0.000
N-C23	0.000	0.000	0.000
N-C24	0.000	0.000	0.000
N-C25	0.000	0.000	0.000
N-C26	0.000	0.000	0.000
N-C27	0.000	0.000	0.000

Table A.7: The effect of sample pH on the extraction process, using the internal standard method.

FIBER	CAR-PDMS		
TEMP	22°C		
TIME	20 min		
VOLUME	1.5 ml		
SALT	0.2964g		
pH	pH 1	pH 7	pH 10
Component	**Mass %**	**Mass %**	**Mass %**
MEK	0.046	0.027	0.048
BENZENE	0.052	0.024	0.049
UNKNOWN	0.258	0.108	0.276
DIOXANE	0.320	0.320	0.320
PYRIDINE	0.021	0.102	0.172
TOLUENE	0.115	0.108	0.114
METHYL-PYRIDINE	0.059	0.196	0.310
METHYL-1H-PYRROLE	0.037	0.018	0.026
DIMETHYL-PYRIDINE	0.379	0.137	0.273
PHENOL	1.472	0.825	1.199
ANILINE	0.055	0.025	0.068
BENZONITRILE	0.092	0.037	0.136
O-CRESOL	0.532	0.351	0.548
MP-CRESOL	0.255	0.206	0.295
METHYL-ANILINE	0.000	0.013	0.035
BENZENEACETONITRILE	0.214	0.027	0.071
2,6-XYLENOL	0.042	0.035	0.053
O-ETHYL-PHENOL	0.027	0.027	0.047
2,4-XYLENOL	0.116	0.077	0.130
2,5-XYLENOL	0.109	0.049	0.082
P-ETHYL-PHENOL	0.048	0.033	0.057
M-ETHYL-PHENOL	0.037	0.022	0.032
3,5-XYLENOL	0.061	0.026	0.040
2,3-XYLENOL	0.039	0.020	0.037
3,4-XYLENOL	0.040	0.025	0.037
NAPHTHALENE	0.032	0.025	0.040

2,4,6-TRIMETHYL-PHENOL	0.039	0.026	0.044
2-PROPYL-PHENOL	0.010	0.006	0.012
METHYL-ETHYL-PHENOL	0.160	0.127	0.229
ISOQUINOLINE	0.001	0.011	0.024
TRIMETHYL-PHENOL	0.019	0.023	0.047
INDOLE	0.006	0.007	0.014
ETHYL-BENZALDEHYDE	0.007	0.010	0.016
1-INDANOL	0.006	0.005	0.011
METHYL-INDOLE	0.002	0.003	0.003
DIMETHYL-(METHYL-ETHYL)-BENZENE	0.009	0.009	0.026
METHYL-INDANOL	0.008	0.010	0.028
TETRADECANE	0.002	0.003	0.007
1-NAPHTHALENOL	0.003	0.002	0.005
2-NAPHTHALENOL	0.002	0.005	0.004
PENTADECANE	0.001	0.004	0.001
HEXADECANE	0.000	0.001	0.001
HEPTADECANE	0.001	0.001	0.001
OCTADECANE	0.000	0.001	0.000
NONADECANE	0.000	0.001	0.000
N-C20	0.000	0.001	0.000
N-C21	0.000	0.001	0.000
N-C22	0.000	0.000	0.000
N-C23	0.000	0.000	0.000
N-C24	0.000	0.000	0.000
N-C25	0.000	0.000	0.000
N-C26	0.000	0.000	0.000
N-C27	0.000	0.000	0.000

Table A.8: The effect of salt concentrations on the extraction process, using the internal standard method.

FIBER	CAR-PDMS		
TEMP	22°C		
pH	No adjustments		
TIME	20 min		
VOLUME	1.5 ml		
SALT	0.0000g	0.3087g	0.8001g
Component	**Mass %**	**Mass %**	**Mass %**
MEK	0.032	0.027	0.054
BENZENE	0.030	0.024	0.056
UNKNOWN	0.169	0.108	0.093
DIOXANE	0.320	0.320	0.320
PYRIDINE	0.105	0.102	0.233
TOLUENE	0.151	0.108	0.092
METHYL-PYRIDINE	0.162	0.196	0.405
METHYL-1H-PYRROLE	0.000	0.018	0.034
DIMETHYL-PYRIDINE	0.196	0.137	0.198
PHENOL	0.918	0.825	1.928
ANILINE	0.041	0.025	0.081
BENZONITRILE	0.112	0.037	0.119
O-CRESOL	0.276	0.351	0.776
MP-CRESOL	0.232	0.206	0.401
METHYL-ANILINE	0.014	0.013	0.025
BENZENEACETONITRILE	0.031	0.027	0.019
2,6-XYLENOL	0.020	0.035	0.062
O-ETHYL-PHENOL	0.014	0.027	0.045
2,4-XYLENOL	0.036	0.077	0.122
2,5-XYLENOL	0.037	0.049	0.087
P-ETHYL-PHENOL	0.021	0.033	0.045
M-ETHYL-PHENOL	0.010	0.022	0.031
3,5-XYLENOL	0.017	0.026	0.060
2,3-XYLENOL	0.018	0.020	0.027
3,4-XYLENOL	0.018	0.025	0.032
NAPHTHALENE	0.062	0.025	0.011

2,4,6-TRIMETHYL-PHENOL	0.044	0.026	0.018
2-PROPYL-PHENOL	0.009	0.006	0.004
METHYL-ETHYL-PHENOL	0.093	0.127	0.103
ISOQUINOLINE	0.011	0.011	0.006
TRIMETHYL-PHENOL	0.025	0.023	0.016
INDOLE	0.007	0.007	0.008
ETHYL-BENZALDEHYDE	0.010	0.010	0.009
1-INDANOL	0.004	0.005	0.005
METHYL-INDOLE	0.006	0.003	0.001
DIMETHYL-(METHYL-ETHYL)-BENZENE	0.007	0.009	0.004
METHYL-INDANOL	0.010	0.010	0.004
TETRADECANE	0.004	0.003	0.001
1-NAPHTHALENOL	0.003	0.002	0.002
2-NAPHTHALENOL	0.002	0.005	0.001
PENTADECANE	0.001	0.004	0.001
HEXADECANE	0.000	0.001	0.000
HEPTADECANE	0.000	0.001	0.001
OCTADECANE	0.000	0.001	0.000
NONADECANE	0.000	0.001	0.000
N-C20	0.000	0.001	0.000
N-C21	0.000	0.001	0.000
N-C22	0.000	0.000	0.000
N-C23	0.000	0.000	0.000
N-C24	0.000	0.000	0.000
N-C25	0.000	0.000	0.000
N-C26	0.000	0.000	0.000
N-C27	0.000	0.000	0.000

A.2. EXTERNAL STANDARD APPROACH

Table A.9: The effect of different fibers, using the external standard method.

Temperature	22°C		
Time	20 min		
Volume	1.5 ml		
Salt	0.2913g		
pH	No adjustments		
Fiber	PDMS	Carbowax-DVB	Carboxen-PDMS
Component	**Mass %**	**Mass %**	**Mass %**
Toluene	0.031	0.030	0.033
Phenol	0.128	1.722	0.390
O-Cresol	0.039	0.343	0.102
MP-Cresol	0.030	0.226	0.082

Table A.10: Extraction times for the Carboxen-PDMS fiber, using the external standard method.

Fiber	Carboxen-PDMS					
Temperature	22°C					
Salt	0.3040g					
pH	No adjustments					
Volume	1,5 ml					
Time	1 min	5 min	10 min	20 min	30 min	40 min
Component	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**
Toluene	0.010	0.025	0.024	0.033	0.033	0.033
Phenol	0.229	0.346	0.362	0.390	0.392	0.404
O-Cresol	0.043	0.078	0.085	0.102	0.100	0.107
MP-Cresol	0.027	0.058	0.066	0.082	0.087	0.088

Table A.11: Extraction times for the Carbowax-DVB fiber, using the external standard method.

Fiber	Carbowax-DVB					
Temperature	22°C					
Salt	0.3102g					
pH	No adjustments					
Volume	1,5 ml					
Time	1 min	5 min	10 min	20 min	30 min	40 min
Component	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**
Toluene	0.008	0.013	0.013	0.011	0.014	0.014
Phenol	0.962	2.719	2.856	2.914	2.899	3.044
O-Cresol	0.104	0.466	0.360	0.343	0.555	0.725
MP-Cresol	0.077	0.316	0.246	0.226	0.332	0.420

Table A.12: Extraction times for the PDMS fiber, using the external standard method.

Fiber	PDMS					
Temperature	22°C					
Salt	0.3007g					
pH	No adjustments					
Volume	1,5 ml					
Time	1 min	5 min	10 min	20 min	30 min	40 min
Component	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**	**Mass %**
Toluene	0.012	0.019	0.020	0.021	0.023	0.024
Phenol	0.102	0.163	0.188	0.210	0.240	0.242
O-Cresol	0.028	0.049	0.062	0.070	0.084	0.086
MP-Cresol	0.019	0.038	0.043	0.050	0.052	0.060

Table A.13: The effect of sample temperature on the extraction process, using the external standard method.

Fiber	Carboxen-PDMS		
Time	20 min		
Salt	0.2979g		
pH	No adjustments		
Volume	1,5 ml		
Temperature	22°C	40°C	50°C
Component	**Mass %**	**Mass %**	**Mass %**
Toluene	0.033	0.022	0.022
Phenol	0.390	0.528	0.675
O-Cresol	0.102	0.125	0.190
MP-Cresol	0.082	0.106	0.135

Table A.14: The effect of sample volume on the extraction process, using the external standard method.

Fiber	Carboxen-PDMS		
Temperature	22°C		
pH	No adjustments		
Time	20 min		
Volume	1.5 ml	5 ml	10 ml
Salt	0.3101g	1.0187g	1.9943g
Component	**Mass %**	**Mass %**	**Mass %**
Toluene	0.033	0.023	0.011
Phenol	0.390	0.590	0.460
O-Cresol	0.102	0.146	0.092
MP-Cresol	0.082	0.114	0.078

Table A.15: The effect of sample pH on the extraction process, using the external standard method.

Fiber	Carboxen-PDMS		
Temperature	22°C		
Time	20 min		
Volume	1.5 ml		
Salt	0.3049g		
pH	pH 1	pH 7	pH 10
Component	**Mass %**	**Mass %**	**Mass %**
Toluene	0.019	0.033	0.019
Phenol	0.466	0.390	0.387
O-Cresol	0.099	0.102	0.104
MP-Cresol	0.069	0.082	0.081

Table A.16: The effect of salt concentrations on the extraction process, using the external standard method.

Fiber	Carboxen-PDMS		
Temperature	22°C		
pH	No adjustments		
Volume	1,5 ml		
Time	20 min		
Salt	0.0000g	0.2910g	0.8117g
Component	**Mass %**	**Mass %**	**Mass %**
Toluene	0.026	0.033	0.016
Phenol	0.297	0.390	0.614
O-Cresol	0.052	0.102	0.145
MP-Cresol	0.064	0.082	0.109

A.3. COMPARISON BETWEEN SPME AND NAC

A.3.1. Internal standard approach

Table A.17: Sample results for the NAC and SPME method, using the internal standard method.

METHOD	NAC	SPME
COMPONENT	MASS %	MASS %
BENZENE	0.002	0.024
DIOXANE	0.320	0.320
PYRIDINE	0.008	0.102
TOLUENE	0.002	0.108
DIMETHYL-PYRIDINE	0.006	0.137
PHENOL	0.280	0.825
ANILINE	0.006	0.025
O-CRESOL	0.038	0.351
MP-CRESOL	0.018	0.206
2,6-XYLENOL	0.001	0.035
O-ETHYL-PHENOL	0.001	0.027
2,4-XYLENOL	0.003	0.077
2,5-XYLENOL	0.001	0.049
P-ETHYL-PHENOL	0.001	0.033
M-ETHYL-PHENOL	0.001	0.022
3,5-XYLENOL	0.001	0.026

A.3.2. External standard approach

Table A.18: Sample results for the NAC and SPME method, using the external standard method.

Method	NAC	SPME
Component	**Mass %**	**Mass %**
Toluene	0.088	0.033
Phenol	4.556	0.390
O-Cresol	0.568	0.102
MP-Cresol	0.482	0.082

APPENDIX B

STATISTICAL EVALUATION

For the evaluation of all the statistical data, a 95% confidence level was used.

NAC							
Compound	**True value of standard**	**Injection1**	**Injection 2**	**Injection 3**	**MEAN**	**STD DEV**	**RSD**
TOLUENE	**0.009**	0.002	0.002	0.002	**0.002**	**0.000**	**0.00**
PHENOL	**0.301**	0.271	0.278	0.293	**0.281**	**0.011**	**3.91%**
O-CRESOL	**0.040**	0.041	0.039	0.039	**0.04**	**0.001**	**2.50%**
MP-CRESOL	**0.017**	0.007	0.009	0.008	**0.008**	**0.001**	**12.50%**
SPME							
Compound	**True value of standard**	**Injection1**	**Injection 2**	**Injection 3**	**MEAN**	**STD DEV**	**RSD**
TOLUENE	**0.009**	0.091	0.081	0.088	**0.087**	**0.005**	**5.75%**
PHENOL	**0.301**	1.622	1.415	1.463	**1.5**	**0.108**	**7.20%**
O-CRESOL	**0.040**	0.365	0.301	0.314	**0.327**	**0.034**	**10.40%**
MP-CRESOL	**0.017**	0.109	0.112	0.113	**0.111**	**0.002**	**1.80%**

Table B.1: Standard results for the NAC and SPME method; including the mean, standard deviation and relative standard deviation.

F-Test

(i) Toluene

(a) Is there a significant difference in the two sets of measurements?

(b) Assume that:

H_o : $\sigma^2_{NAC} = \sigma^2_{SPME}$: No significant difference in the two sets of measurements

H_1 : $\sigma^2_{NAC} \neq \sigma^2_{SPME}$: Significant difference in the two sets of measurements

Or

H_1 : $\sigma^2_{NAC} > \sigma^2_{SPME}$: NAC method more precise than SPME

(c)

F-Test Two-Sample for Variances		
Toluene		
	NAC	*SPME*
Mean	0.002	0.087
Variance	0.000	0.000
Observations	3.000	3.000
df	2.000	2.000
F	0.000	
P(F<=f) one-tail	0.000	
F Critical one-tail	0.053	

Table B.2: F-test for toluene

(d) Since $F_{calculated} < F_{critical}$, H_o can't be rejected.

Therefore, there is no significant difference in the two sets of measurements

(ii) Phenol

(a) Is there a significant difference in the two sets of measurements?

(b) Assume that:

H_o : $\sigma^2_{NAC} = \sigma^2_{SPME}$: No significant difference in the two sets of measurements

H_1 : $\sigma^2_{NAC} \neq \sigma^2_{SPME}$: Significant difference in the two sets of measurements

Or

H_1 : $\sigma^2_{NAC} > \sigma^2_{SPME}$: NAC method more precise than SPME

(c)

F-Test Two-Sample for Variances		
Phenol		
	NAC	*SPME*
Mean	0.281	1.500
Variance	0.000	0.012
Observations	3.000	3.000
df	2.000	2.000
F	0.011	
P(F<=f) one-tail	0.011	
F Critical one-tail	0.053	

Table B.3: F-test for phenol

(d) Since $F_{calculated} < F_{critical}$, H_o can't be rejected.

Therefore, there is no significant difference in the two sets of measurements

(iii) O-cresol

(a) Is there a significant difference in the two sets of measurements?

(b) Assume that:

H_o : $\sigma^2_{NAC} = \sigma^2_{SPME}$: No significant difference in the two sets of measurements

H_1 : $\sigma^2_{NAC} \neq \sigma^2_{SPME}$: Significant difference in the two sets of measurements

Or

H_1 : $\sigma^2_{NAC} > \sigma^2_{SPME}$: NAC method more precise than SPME

(c)

F-Test Two-Sample for Variances		
O-cresol		
	NAC	*SPME*
Mean	0.040	0.327
Variance	0.000	0.001
Observations	3.000	3.000
df	2.000	2.000
F	0.001	
P(F<=f) one-tail	0.001	
F Critical one-tail	0.053	

Table B.4: F-test for O-cresol

(d) Since $F_{calculated} < F_{critical}$, H_o can't be rejected.

Therefore, there is no significant difference in the two sets of measurements

*(iv) **MP-cresol***

(a) Is there a significant difference in the two sets of measurements?

(b) Assume that:

H_o : $\sigma^2_{NAC} = \sigma^2_{SPME}$: No significant difference in the two sets of measurements

H_1 : $\sigma^2_{NAC} \neq \sigma^2_{SPME}$: Significant difference in the two sets of measurements

Or

H_1 : $\sigma^2_{NAC} > \sigma^2_{SPME}$: NAC method more precise than SPME

(c)

F-Test Two-Sample for Variances		
MP-cresol		
	NAC	*SPME*
Mean	0.008	0.111
Variance	0.000	0.000
Observations	3.000	3.000
df	2.000	2.000
F	0.231	
P(F<=f) one-tail	0.187	
F Critical one-tail	0.053	

Table B.5: F-test for MP-cresol

(d) Since $F_{calculated} < F_{critical}$, H_o can be rejected.
Therefore, there is a significant difference in the two sets of measurements