New concepts in sorption based sample preparation for chromatography

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1 Introduction and Scope

1.1 General Introduction

Since its discovery nearly a century ago by the Russian botanist Tswett, chromatography has developed into the most important tool in analytical chemistry today. Initial developments in column and paper chromatography, employing a liquid as the mobile phase, have resulted in high performance liquid chromatography (HPLC) which is now a routine analytical tool. Though in principle any compound can be analyzed by HPLC, these systems are characterized by a low resolving power, thereby limiting the number of compounds that can be resolved in a single run. In 1941 gas chromatography was first proposed by Martin and Synge employing an inert gas as the mobile phase. Due to the introduction of open tubular capillary GC columns by Golay and its further development, GC is now the most powerful chromatographic technique combining unsurpassed separation power with extremely low detectability. It has to be noted, however, that only volatile or volatilizable compounds are emenable to GC analysis.

In the last 20 years chromatographic instrumentation has matured into routine equipment ready for use in many different fields including environmental, clinical, forensic, petroleum and polymer analysis. Especially the hyphenation of chromatography with mass spectrometry has resulted in powerful systems for the identification and quantification of unknowns in complex mixtures (GC-MS, LC-MS).

Despite the many features of state-of-the-art chromatographic instrumentation, direct introduction of the sample into the analytical instrument is often impossible. This can be due to the presence of particles (LC) or non-volatile sample constituents (GC) but most often the concentration of the sample analytes is simply too low. Especially in the analysis of environmental samples, enrichment is of vital importance because samples are too dilute and often too complex for direct injection. The samples need to undergo a chain of specific treatments to make them compatible with the analytical techniques (sample preparation). During these processing steps, specific performance is aimed at, however, often additional undesired effects can occur, especially if particular interfering compounds are present. Therefore, the dictum "The best sample preparation is no sample preparation" is very correct, however, sample preparation usually is hard to avoid.

An important factor in sample preparation is the required amount of organic solvent for extraction and enrichment. State of the art procedures are designed to minimize the consumption of organic solvents, which can be achieved through miniaturization. In some cases, the use of solvents can even be completely avoided. Using 100 mL dichloromethane to extract semi-volatile analytes from a water sample may serve as a typical example of how not to proceed.

1.2 Sample Preparation by Adsorption

Many sample preparation techniques rely on the trapping of the analytes of interest from the sample (gas, liquid or solid) on an adsorbent material. Adsorbents are porous materials with a high internal surface area (typically 5-1000 m^2/g) and the analytes are temporarily stored on the adsorbent surface. Adsorbent trapping separates the analytes from matrix constituents (*e.g.* water, oxygen) that can compromise the performance of the overall analytical procedure. Following analyte trapping and matrix removal, the trapped analytes can be released with a small amount of organic solvent (typically mL's). An aliquot (typically µL's) of this desorption liquid is subsequently injected into the analytical instrument. Though this approach works quite successfully, it is likely to result in poor sensitivity as only a fraction of the sample is used.

An alternative to liquid desorption is desorption by means of heating the adsorbent (thermal desorption). A thermal desorption unit, can rather conveniently be coupled to a gas chromatograph. Thermal desorption is performed under the flow of an inert gas which is usually the carrier gas of a gas chromatographic instrument. If cryogenic focusing is employed, quantitative transfer of the analytes trapped on the adsorbent material to the chromatographic column is possible. This will result in a considerable sensitivity increase compared to liquid desorption. Therefore thermal desorption is an attractive alternative for many classical procedures involving liquid desorption. It has to be noted, however, that analytes subjected to thermal desorption must be thermally stable to result in successful analysis, otherwise decomposition will occur. Since volatile and thermally stable analytes are emenable to GC analysis, thermal desorption is in practice only used in combination with gas chromatography.

Adsorbents for thermal desorption can be subdivided into three categories. The first category is that of inorganic carbon based materials such as carbon blacks, carbon molecular sieves and activated carbon. These materials generally exhibit a very high affinity for organic compounds and are most often applied for gaseous samples. Carbon molecular sieves can be used to retain C_2-C_3 hydrocarbons or even methane whereas the activated carbons and carbon blacks are more suited for less volatile analytes. Due to their inorganic nature, these materials can be heated to high temperatures (400-450°C) without significant degradation.

The second category is that of inorganic materials based on silica and alumina. Silica type materials can be used as such for the trapping of analytes from both gaseous and liquid samples and are generally suited for larger molecules than the inorganic carbon based adsorbents. These materials are thermally stable up to 400-600°C. Additionally, these materials can be covered with organic surface groups, resulting in materials such as octadecylsilica (ODS). These materials are very successful for the enrichment of liquid samples. Organic coated silicas, however, exhibit poor thermal stability at elevated temperatures (> 100°C) as the organic groups tend to be expelled from the surface.

The third category is that of the polymeric adsorbents. This is the largest and most diverse group and comprises many commonly applied materials such as Tenax and Chromosorb. Most of these materials have a synthetic nature and consist of polymeric building blocks like styrene. One of the most important drawbacks of these types of materials is that (especially upon heating) depolymerization occurs, emitting monomeric units and reaction products thereof. Unfortunately these include many of the target analytes such as styrene and benzene. At moderate temperatures where adsorbent degradation is still not very pronounced, small quantities of emitted compounds can easily lead to the attribution of false positives. Especially Tenax, which is the most commonly applied organic adsorbent, is notorious for its background of benzaldehyde, acetophenone, benzophenone and other aldehydes and ketones. In practice the maximum temperatures range from 150°C for some Chromosorbs through 350°C for Tenax. However, traces of water or oxygen strongly promote degradation reactions and can lead to a significantly deteriorated background.

Table 1 lists some of the generally used adsorbents and their composition. The last column (temperature limit) is an indication of the temperature up to which the material is reasonably stable which means that it does not degrade to such an extent that the chromatographic analysis is compromised.

In all cases, the adsorbent surface contains active groups (adsorptive sites) that can initiate an interaction with the analytes and bond them onto the surface. Depending on the nature of adsorbent and analyte, the interaction can range from VanderWaals type bonding which is very weak to very strong ionic interactions. The strength of the interaction also determines the required desorption step. Generally, liquid desorption can destroy strong adsorbent-analyte interactions whereas thermal desorption is only able to destroy the relatively weak VanderWaals type interactions.

At present, many standardized methods exist for the enrichment of analytes from gaseous and liquid samples on adsorbent cartridges followed by liquid desorption and injection into the chromatographic system. Unfortunately, relatively few standardized analytical methods exist that take advantage of the high sensitivity of thermal desorption. The reason for this lies in the fact that though a wide variety of adsorbents is available, none is universally suited for thermal desorption. Many

adsorbents exhibit a too strong interaction with the trapped analytes (most inorganic adsorbents), requiring very high desorption temperatures that lead to degradation reactions. This limits the use of inorganic adsorbents to highly volatile apolar analytes only. On the other hand, organic adsorbents often provide poor blanks due to thermal decomposition of the adsorbent itself. The organic nature of the adsorbent will result in blanks containing some of the (organic) compounds of interest. Moreover, most adsorbents exhibit, even at lower temperatures, a significant catalytic activity preventing their use for the enrichment of chemically labile compounds. This is of course another highly undesirable effect that prevents the application of organic adsorbents in many instances.

Table 1 Commonly applied adsorbents for the enrichment of aqueous and gaseous samples.

Adsorbent	Adsorbent type*	Composition	Temperature Limit (°C)
Carbon Molecular Sieve	1	Carbon	>400
Activated Charcoal	1	Carbon	>400
Graphitized Carbon Blacks	1	Carbon	>400
Silica	2	SiO_2	>400
Octadecyl silica	2	SiO_2 with C_{18} surface groups	<100
Florisil	2	Magnesium silicate	
Tenax	3	Poly-2,6-diphenylphenyleneoxide	350
Chromosorb 102	3	Styrene-Divinylbenzene	180
Chromosorb 104	3	Acrylonitrile-Divinylbenzene	180
Porapak Q	3	Ethylvinylbenzene-Divinylbenzene	180

*Adsorbent types: 1, inorganic carbon based; 2, inorganic silica and alumina based; 3, organic polymers

1.3 Sample Preparation by Sorption

The problems outlined in **Section 1.2** associated with thermal desorption of adsorbents have prompted several research groups to focus on another class of materials namely that of sorption type materials. Contrary to adsorbents, sorption (dissolution or partitioning) materials are a group of polymeric materials that are above their glass transition point (T_g) at all temperatures employed. In this temperature range sorbents are in a gum-like or liquid-like state and show similar behavior as organic solvents. Sorbents are in principle homogeneous, non-porous materials in which the analytes actually dissolve. The analytes therefore do not undergo a real (temporary) bond with the material but are retained on a dissolution basis. It has to be noted that all sorption materials only work in the sorption regime above their glass transition point. This

means that upon cooling any sorbent loses the sorption mechanism below its glass transition point and is then turned into an adsorbent with a low specific surface area.

In practice there are only a few materials that are able to operate in the sorption mode at sampling temperatures around 0-25°C. These materials include siloxane polymers and several acrylates. The most commonly used sorbent is a 100% methyl substituted polysiloxane, namely polydimethylsiloxane (PDMS). This material is also one of the most popular stationary phases in capillary gas chromatography (CGC) and its properties have been extensively studied in the literature. Apart from the advantages associated with sorption, additional advantages of PDMS include its very high inertness and high thermal stability. Probably the strongest advantage of PDMS is that its degradation products can easily be recognized with a mass spectrometer as they all contain silicon and are consequently never associated with the analytes of interest. Therefore, there is no chance to misidentify a breakdown product as an actually sampled analyte as is the case with adsorbents such as Tenax. Although in principle polysiloxanes with more polar substitutions such as phenyl or cyanopropyl groups or the polar polyacrylates can be used, the thermal stability of these materials is never of the same quality as that of PDMS resulting in similar blank problems as those encountered with adsorbents. Therefore in this thesis attention will be almost exclusively focussed on PDMS.

1.4 Scope of this Thesis

This thesis will focus on the description and development of novel sample preparation strategies based on (polydimethylsiloxane) sorption. Due to the favorable characteristics of sorbents for thermal desorption, primary focus is on the use of these materials in thermal desorption-gas chromatographic systems. Additionally, typical properties of PDMS such as a very high linearity, the absence of displacement effects and catalytic activity and its very high inertness are described in detail and compared against other, existing, technologies. An import factor is also the comparison of the newly proposed techniques with existing technologies and to highlight those areas where most room for improvement is available. Several new concepts for sorptive sample enrichment are proposed and described in detail.

The first concept is that of Gum Phase Extraction (GPE) which is based on a packed bed of sorbent particles for sample enrichment. GPE is similar to solid phase extraction for liquid samples or adsorbent based air sampling techniques, but with the distinct advantages of sorbents as described in **Section 1.3**. The dynamic nature of GPE requires the sample to be either pumped (liquids) or sucked (gases) through the bed. GPE is often operated in a conventional way, with the intention to trap all analytes from a sample, an approach called breakthrough sampling. Breakthrough sampling has important advantages such as straightforward, simple and matrix-independent calibration. Breakthrough sampling is very successful but often fails for weakly retained

solutes. For a large number of compounds, superior performance was observed by employing GPE compared to classical adsorbent based enrichment techniques.

The second new concept is that of equilibrium gum phase extraction (EGPE). This technique is very similar to GPE, but instead of employing breakthrough sampling, the PDMS sorbent is in EGPE completely saturated to equilibrium so that the maximum amount of all analytes is sorbed. EGPE therefore achieved a higher sensitivity for all compounds than GPE, however at the expense of a somewhat more complicated calibration. EGPE has proven to be very successful for the enrichment of volatile compounds, such as ethyleneoxide and epichlorohydrin from gaseous samples.

The third concept presented in this thesis is that of Stir Bar Sorptive Extraction (SBSE). This technique is based on a sorbent coated stir bar for stirring and extraction of liquid samples. The static nature of SBSE permits only the application of equilibrium extraction. SBSE has proven to be a technique that can offer high and reproducible extraction recoveries for a wide variety of matrices.

Chapter 2 presents an overview of the current state-of-the-art in sample preparation methods. This includes commonly employed techniques like solid phase extraction (SPE), micro liquid-liquid extraction (μLLE) and adsorptive air sampling. In addition to this, in **Chapter 3** an overview of sorption based techniques is presented and several limitations of the existing techniques will be addressed leading to the criteria for the introduction of the new concepts proposed above. The first new concept of this thesis, GPE, is described in **Chapter 4** with applications for gaseous samples whereas in **Chapter 5** application in aqueous samples are described. In addition to these applications, **Chapter 5** also describes an automated system for GPE coupled to thermal desorption-GC-MS for aqueous samples. The second concept, EGPE, is described in **Chapter 6**, also with some typical applications. The third concept, SBSE, is presented from a theoretical viewpoint in **Chapter 7** with some introductory applications. A comparison between SPME and SBSE will also be given in this chapter. Additionally, selected typical applications of SBSE are listed in **Chapter 8**.

The novel sorptive sample preparation concepts described in this thesis show good performance for a large number of practical, real-life analytical problems that cannot easily be solved by other approaches. However, this thesis is the first research on these new techniques and therefore a large amount of additional developmental work is needed in order for these concepts to become equally well documented as, for example SPE. Import aspects such as inter-laboratory validation, long term stability and routine performance could not be investigated within the framework of this thesis but should be part of future research.

2 State-of-the-art in Sample Preparation

In this chapter the present state of the art in sample preparation is presented taking into account modern methodologies except those using sorption materials. These sorptive techniques are described in **Chapter 3**. First some basic concepts are introduced and subsequently the available techniques for the enrichment of gaseous, aqueous and solid samples are described. It has to be noted, however, that focus is only on the newer and more innovative techniques. At present, analytical techniques for the extraction and preconcentration of compounds from solid and liquid samples are quite well developed. Only relatively small room for improvement exists. For gaseous samples, this situation is completely different. Here only a few universally reliable methods are available and these are often either of low sensitivity or can only handle a very limited range of compounds. This is an important reason that this chapter, and in fact this entire thesis, is more oriented towards analytical method development for gaseous samples than it is for liquid or solid samples. The generally good compatibility of gaseous samples with gas chromatography also puts most focus on this separation technique. In the remaining chapters of this thesis solid samples are never used and therefore analytical techniques for solid samples are only very briefly described here.

2.1 Basic Concepts

All sample preparation methods basically ensure the transfer of the analytes of interest from their original surroundings (sample matrix) into a form more suitable for introduction into the analytical instrument. This can be achieved by many different techniques which all have their strengths for specific analyte/matrix combinations. Most often, the sample is placed in direct contact with the extraction phase (extractant) to accomplish transfer of the analytes into the extractant. Subsequently, the extractant can be further processed or in some cases it can be directly introduced into the analytical device. Several basic concepts in sample preparation are described in **Sections 2.1.1** and **2.1.2** leading to a classification of sample preparation procedures in **Section 2.1.3.**

2.1.1 Static Sampling

Static sampling techniques bring the entire amount of extractant in contact with the entire amount of sample at the start of the method; the same amount of extractant is continuously kept in contact with the same portion of sample. This means that in static techniques neither the sample nor the extractant is renewed. Static techniques rely on the diffusion of sample analytes into the extractant with the ultimate goal of reaching equilibrium between both phases. Usually, selection of the extractant phase is based on the so-called 'like-like' principle. A substance will always have the highest affinity for a phase with similar properties as itself. This means that if an apolar compound is to be extracted from a polar matrix, an apolar extractant should be used. It has to be noted that mixing procedures such as stirring, shaking or sonnication are often applied to speed up diffusion of analytes from the sample into the extractant. This, however, only has an influence on the required time for equilibration but does not affect the equilibrium itself or other properties of the static process.

The most important factor governing static extraction is the distribution constant (K) which is defined as:

Equation 1

$$K = \frac{C_E}{C_S} = \frac{m_E}{m_S} \times \frac{V_S}{V_E} = \frac{m_E}{m_S} \times \beta$$

where: C_S is the concentration of analyte in the sample, in g/L; C_E is the concentration of analyte in the extractant, in g/L; m_S is the mass of analyte remaining in the sample, in g; m_E is the mass of analyte in the extractant phase, in g; V_E is the volume of the extractant, in L and V_S is the volume of sample, in L. ß is the phase ratio of the static extraction system and defined as V_S/V_E. For future equations, the total mass of analyte in the system is defined as m_{tot} (m_E+m_S). Rewriting **Equation 1** leads to a more useful expression, that of the extraction efficiency (? = m_E/m_{tot}):

Equation 2

$$\eta = \frac{1}{\frac{\beta}{K} + 1}$$

The extraction efficiency is usually expressed as a percent value and as such generally known as recovery. From **Equation 2** it is important to note that the only two parameters affecting the recovery of an analyte are ß and K. For very high partitioning constants, the numerator becomes one, leading to an extraction recovery of 100%. Very high phase ratios (small volume of extractant relative to the sample volume) leads to a large numerator and consequently to a low recovery. In practice, K is often a more or less fixed constant depending mainly on properties of the analyte and on the characteristics of the sample and extractant phases. ß is chosen by the phase volumes applied, usually in such a way as to ensure a high recovery with a minimal

amount of extractant. It has to be noted, however, that under static conditions, extraction is never complete and that a certain portion of the analytes always remains in the sample.

Static sampling often is an easy, reliable and straightforward technique. However, since it relies on the equilibrium distribution of compounds rather than on complete extraction, care should be taken that the distribution constant (K) is equal in all experiments, including calibration and actual samples. Though this seems to be a simple requirement on first sight, in practice this is often not the case. In chemical equilibria, temperature has a dominant effect on equilibrium and distribution constants. Therefore, careful control of the temperature, often within 0.5ºC is necessary. In the laboratory this requirement can easily be met, but in field sampling applications, this can be problematic. As was already pointed out in the previous chapter, a distinction between adsorption and sorption extraction phases has to be made. Sorption phases (including all organic solvents, water, ideal gases and polymeric materials at a temperature above their glass transition point) retain solutes purely with a dissolution mechanism. The analytes partition into the bulk of these phases where they can freely diffuse through the entire amount of sorbent. Therefore they experience the bulk properties of the sorbent and as long as the total amount of sorbed compounds is less than 1%, these bulk properties do not chance significantly with concentration. This kind of "high" concentration levels are, however, only seldom found in practice and therefore static sorptive extraction is a very reliable approach.

Static extraction performed with an adsorbing phase is, unfortunately, a much more complicated situation. Here, the analytes are retained on an active surface which contains a fixed number of adsorptive sites. The equilibrium that is reached is that between analytes present in the sample and those adsorbed on the adsorbent surface. This means that if the sample concentration becomes rather high, all adsorptive sites become occupied and an increase in sample concentration will not lead to an increase in the amount of adsorbed compound which is of course a highly undesirable effect. However, analyte concentration levels are usually low enough to circumvent this effect so that in the case a single compound is adsorbed from an otherwise clean sample this is not a real problem. When multiple analytes are adsorbed simultaneously this becomes problematic. Not only do the different analytes compete for the same adsorptive sites but matrix compounds, present at relatively high concentration levels and that are of no interest for a particular analysis (*e.g.* salts, humic acids, proteins) can block adsorptive sites leading to unpredictable and irreproducible results. Therefore the application of adsorbents in static sampling is limited to clean and diluted samples. In special cases, particularly if the sample is a solid, the sample itself may also exhibit adsorbing properties, preventing the reliable use of static sampling techniques.

2.1.2 Dynamic Sampling

The opposite of static sampling is dynamic sampling where the entire amount of extractant is not immediately brought into contact with the entire amount of the sample. Whereas in static sampling mixing, stirring and other dynamic processes are only a means for faster equilibration, dynamic sampling procedures essentially require these basic dynamic processes to ensure complete extraction. Many of the dynamic techniques resemble chromatography in that they are also based on the use of a stationary phase (often the extractant) and a moving, mobile phase (often the sample).

In the case of gaseous or liquid samples, the sample is most often pumped through the extractant that can, for example, typically be a packed bed. The analytes will be retained in the bed and consequently the concentration of analyte in the sample will decrease through the bed. Initially the concentration of analyte in the outgoing sample phase will be zero. Usually sampling is stopped when the first analyte of interest starts to elute from the trap. This is called "breakthrough sampling" which will be discussed in this section. However, it is also possible to continue sampling beyond the breakthrough point until all analytes are in equilibrium with the extractant. This is a relatively new technique, called "equilibrium sampling" which will be presented in **Chapter 6**.

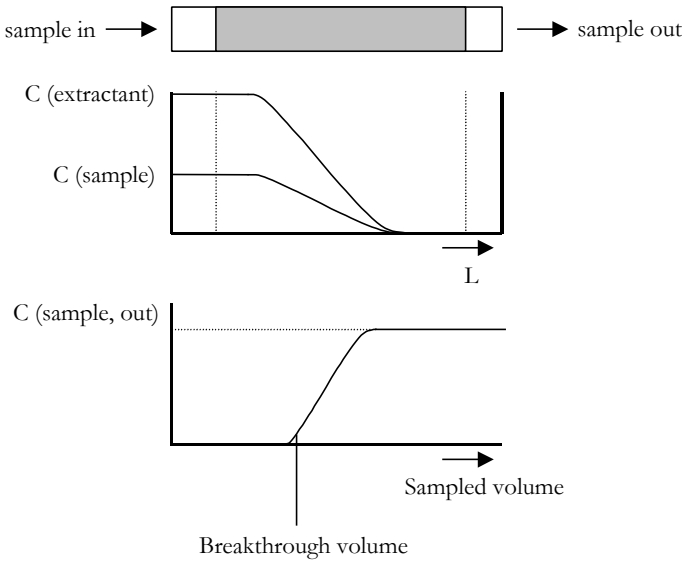

Figure 1 Principle of dynamic breakthrough sampling. On top, the sample is pumped through the extraction trap and the concentration profiles in the sample and in the extractant are shown below. The lowest figure shows the analyte concentration in the outgoing (extracted) sample as a function of the sampled volume.

Dynamic breakthrough sampling is probably the most often used technique for the enrichment of liquid and gaseous samples. The principles of breakthrough sampling are outlined in **Figure 1**. Here a situation where the sample (liquid, gas) is pumped through the extractant is shown. The extractant is presented as a packed bed but this can in principle also be another device through which the sample can be delivered under controlled circumstances, such as an open tubular capillary. During sampling analytes are passed from the sample to the extractant phase.

The most important parameter in breakthrough sampling is the breakthrough volume which determines the maximum volume of sample that can be passed through the trapping device before analytes are no longer fully retained. It is important that there is not a single definition of breakthrough volume, rather the breakthrough volume depends on the analyte loss accepted. The accepted analyte loss is usually 5 or 10%. A general equation for the calculation of the breakthrough volume is:

Equation 3 $$V_B = V_0 \times (1+k) \times f(N,b)$$

where: V_B is the breakthrough volume, in L; V_0 is the void volume of the trap, in L; k is the retention factor and f(N,b) is a function accounting for the theoretical plates in the trap and the accepted breakthrough loss (b). The retention factor is the same as that defined in chromatography and corresponds to K/ß, with ß defined here as V_0/V_E. For strongly retained compounds (k >> 1), **Equation 3** reduces to:

Equation 4 $$V_B = V_E \times K \times f(N,b)$$

This equation depends only on the volume of extractant used, the distribution constant of analyte for the extractant and a function depending on the number of theoretical plates in the trap and the accepted breakthrough loss. Since both V_E and K are usually readily determined from simple experiments, only an expression for f(N,b) has to be found. In the literature there has been some controversy regarding the definition of the breakthrough factor. Therefore in **Section 2.1.2.1** the definitions of the breakthrough factor will be presented and in the subsequent **Sections 2.1.2.2** through **2.1.2.4** three different approaches for the estimation of f(N,b) will be presented.

2.1.2.1 Definition of the Breakthrough Factor (b)

In the literature two definitions for the breakthrough loss or breakthrough factor (b) are used side by side. The first and most commonly applied breakthrough factor is based on the momentary loss of analyte which will be referred to as the differential breakthrough factor (b_D). The second breakthrough definition is based on the total loss of analyte and will be referred to as the integral breakthrough factor (b_I). Mathematically, the differential breakthrough factor is defined as:

Equation 5

$$b_D = \frac{C_{O,V}}{C_I}$$

where: $C_{O,V}$ is the concentration of analyte in the outgoing sample at a certain volume V and C_I is the concentration of analyte in the original sample. This is graphically presented in **Figure 2** where the 10% breakthrough factor is presented on the curve.

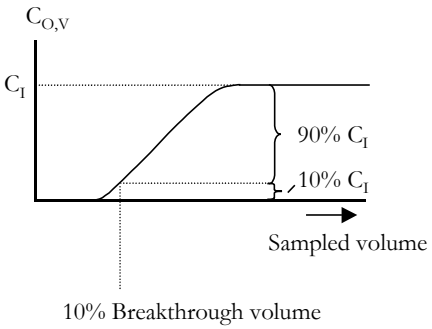

Figure 2 Illustration of the definition of the differential breakthrough factor (b_D). Shown here is the 10% breakthrough volume under differential conditions.

Though the differential definition is very simple in practice as will be shown in **Section 2.1.2.2**, for real life sampling it often does not represent a very useful situation. This is because the b_D value only represents the momentary loss at the point sampling is stopped, the breakthrough volume. Since the momentary analyte loss increases with increasing sampled volume, as can be observed from **Figure 2**, this means that though at the predicted breakthrough volume the momentary analyte loss will be b_D, the overall amount of analyte lost will be less than b_D. Therefore if a sample loss of 10% is accepted (a b_D of 0.1), at the calculated breakthrough volume the actual overall analyte loss will always be less than 10%. Not only does this lead to a reduced sensitivity as a larger sample volume could have been taken, it is also impossible to correct for sample losses since the exact analyte loss it not known.

The arguments presented above have led to the adoption of the integral breakthrough factor b_I which is defined as:

Equation 6

$$b_I = \frac{\int_0^{V_B} C_{O,V}\, dV}{\int_0^{V_B} C_I\, dV} = \frac{\int_0^{V_B} C_{O,V}\, dV}{C_I\, V_B}$$

As can be observed from **Figure 3** the integral definition of the breakthrough volume is based on the amount of analyte lost from the trap relative to the total amount of analyte sampled. At the breakthrough volume under integral breakthrough conditions, the amount of analyte lost is exactly equal to b_I. Therefore the predicted breakthrough volume under integral conditions represents the true maximum volume that can be sampled before the predetermined portion of analyte (b_I) is lost.

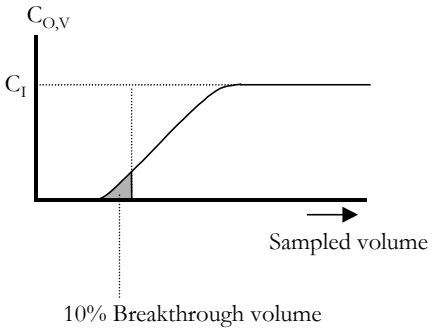

Figure 3 Illustration of the definition of integral breakthrough. Shown here is the 10% breakthrough volume under integral conditions.

In practice care should be taken when comparing different approaches for the calculation of f(N,b) since b can be either a differential or integral based parameter. Moreover, if breakthrough factors are determined experimentally by analysis of the extraction trap, integral rather than differential breakthrough factors are determined.

2.1.2.2 Differential Gaussian Breakthrough

This model for analyte breakthrough was initially developed by Werkhoven-Goewie[1] and assumes that analytes elute from the extraction column as Gaussian shaped bands.

The expression then found for f(N,b) from **Equation 4** is:

Equation 7

$$f(N,b) = 1 - \frac{a_G(b_D)}{\sqrt{N}}$$

b_D	$a_G(b_D)$
0.1 %	3.090
1 %	2.326
2.5 %	1.960
5 %	1.645
10 %	1.280

where: N represents the number of theoretical plates in the trap and a_G is a constant dependent on the accepted breakthrough level. Values for a_G are listed in the table of **Equation 7**. **Figure 4** shows a graph of f(N,b) for different values of b_D. It is clear that at any b_D a non-negative breakthrough volume is only obtained at a certain, critical plate number ($N_{crit} = a_G^2$). In practice, this implies that at very low plate numbers immediate breakthrough is expected. However, a sample loss of 10% before sampling is even started is very unrealistic and is in fact an artifact of the Gaussian theory which is only valid at a relatively high plate number. Therefore care should be taken with the use of values predicted by **Equation 7**, which should preferably only be used if an f(N,b) in excess of 0.5 (50 %) is predicted.

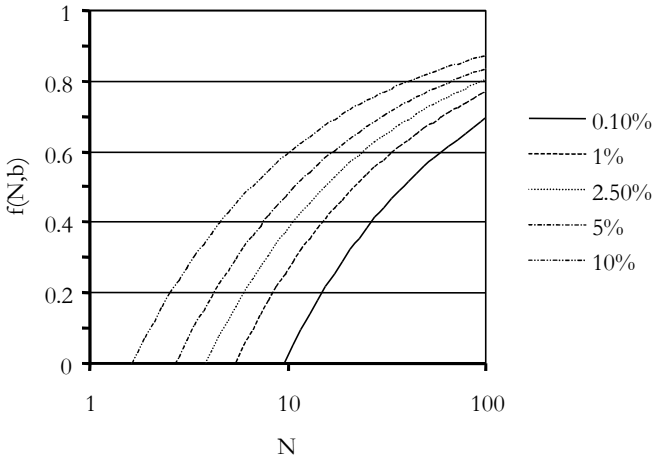

Figure 4 Predicted f(N,b) from the differential Gaussian breakthrough model (**Equation 7**). Five curves are drawn for different breakthrough fractions (b_D).

With the theory presented above it is possible to calculate breakthrough volumes, only an expression for the calculation of plate numbers is required. For capillary (open tubular) traps this can be the Golay equation which gives an exact

theoretical description of the plate number whereas for packed columns semi-empirical equations such as those proposed by van Deemter and Knox can be used.

2.1.2.3 Integrated Gaussian Breakthrough

Analogous to the theory presented in the previous section, the integral definition of the breakthrough factor (b_I) can also be used in conjunction with the Gaussian peak elution theory to obtain an expression for f(N,b). However, no literature is available covering this topic. Additionally, the obtained expressions will be much more complicated than **Equation 7** while still resulting in unrealistic breakthrough volumes at low plate numbers. Therefore integrated Gaussian breakthrough is not described in detail here.

2.1.2.4 Integrated Lövkvist Breakthrough

The problems associated with Gaussian breakthrough at low plate numbers have led researchers to develop alternative, more realistic, expressions for f(N,b). Lövkvist and Jönsson[2] compared several dedicated equations for breakthrough curves at low plate numbers and suggested the following expression for f(N,b) which they found to be valid for strongly retained compounds:

Equation 8

$$f(N,b) = \left(a_{L,0} + \frac{a_{L,1}}{N} + \frac{a_{L,2}}{N^2} \right)^{-\frac{1}{2}}$$

where $a_{L,0}$, $a_{L,1}$ and $a_{L,2}$ are constants depending on the breakthrough factor (b_I). Values for the parameters $a_{L,0}$ through $a_{L,2}$ are listed in **Table 1**.

Table 1 Parameters of **Equation 8** as a function of the breakthrough level (b_I).

b_I	$a_{L,0} = (1-b_I)^2$	$a_{L,1}$	$a_{L,2}$
0.5 %	0.990025	17.92	26.74
1 %	0.9801	13.59	17.6
2 %	0.9604	9.686	10.69
5 %	0.9025	5.360	4.603
10 %	0.81	2.787	1.941

Breakthrough curves predicted by **Equation 8** are shown in **Figure 5**. It is clear that non-negative breakthrough volumes are predicted at any plate number. For high plate numbers, f(N,b) can become larger than one indicating a breakthrough volume in excess of the retention volume. This is not an artifact of **Equation 8** but is

a result of the definition of the integral breakthrough factor. For a trap with an infinite plate number (N = 8) no analyte is lost before the retention volume is reached. Therefore at V_R, the breakthrough factor is still zero. At sample volumes in excess of the retention volume the amount of analyte sampled at the trap front is equal to the amount lost at the trap end, hence the breakthrough factor increases from this point on.

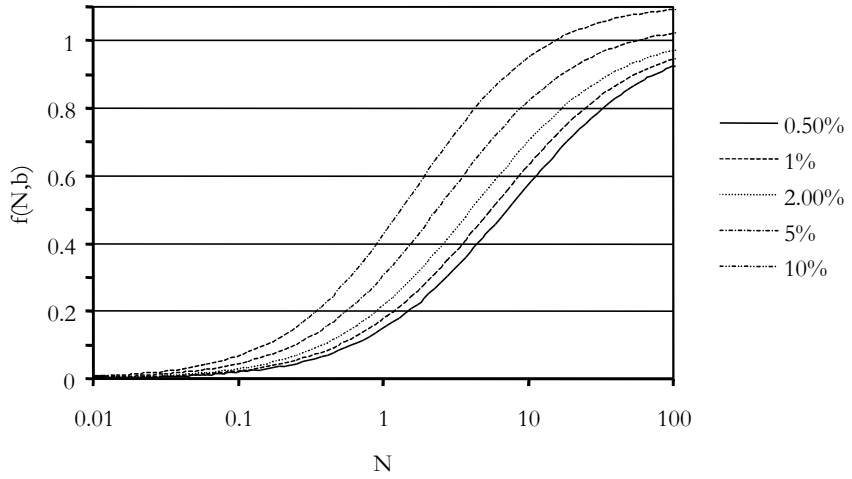

Figure 5 Predicted f(N,b) from the integrated Lövkvist breakthrough model (**Equation 8**). Five curves are drawn for breakthrough factions (b_f) of 0.5 to 10 %.

The authors of **Equation 8** recommend the use of their breakthrough expression with a modified Knox equation[3,4] for the prediction of the plate numbers:

Equation 9

$$h_r = 3\upsilon^{1/3} + \frac{1.5}{\upsilon} + 0.05\upsilon$$

where: h_r is the reduced plate height and ? is the reduced velocity in the trapping column. These reduced parameters are defined as:

Equation 10

$$h_r = \frac{H}{d_p} = \frac{L}{N \times d_p} \qquad \upsilon = \frac{u \times d_p}{D_m}$$

where: H is the plate height, in m; d_p is the diameter of packing particles, in m; L is the length of the trapping column, in m; u is the superficial linear velocity in the trap, in m/s and D_m is the diffusion constant in the mobile phase, in m^2/s. **Equations 9** and **10** are only valid in situation where a pressure drop over the packed bed can be neglected.

2.1.3 Classification of Extraction Approaches

After the introduction of several basic concepts in the previous sections, an overview of the most commonly applied techniques for sample enrichment is presented here. Extraction of the sample can be performed with either a gas, liquid or solid and as the sample itself can also be either a gas, liquid or solid this yields nine theoretical combinations. However, the miscibility of gases will prevent the extraction of one gas with another. Similarly, two solid phases (as powders) will also intermix and additionally the diffusion between two solids will be too slow for practical applications. Therefore, the sample preparation procedures will be divided in seven groups based on the aggregation state of both extractant and sample as is shown in **Table 2**.

Table 2 Classification of some commonly applied sample preparation methods according to the aggregation state of the sample and the extractant. The most important techniques in each group are shown. Techniques shown in *italic* (SPME and OTT) are based on sorption and will be discussed in **Chapter 3**. For the sake of simplicity, supercritical fluids are considered to be liquids.

	Sample		
Extractant	Gas	Liquid	Solid
Gas	--	Static Headspace Purge and Trap	Static Headspace Dynamic Headspace
Liquid	Impringer Denuder *OTT*[2]	Liquid/Liquid Extraction *SPME*[1] *OTT*[2]	Sonication Soxhlet Extraction SFE[3]
Solid	ATD[4] ALD[5]	Solid Phase Extraction	--

1 Solid Phase Microextraction
2 Open Tubular Trapping
3 Supercritical Fluid Extraction
4 Adsorption with Thermal desorption
5 Adsorption with Liquid desorption

2.2 Enrichment of Air and Gaseous Samples

Organic air pollutants can exist either in the continuous gas phase or in solid or liquid particles suspended in the gaseous phase. Volatile compounds (with a boiling point below *ca.* 100°C) exist primarily in the gaseous phase whereas relatively non-volatile compounds (boiling point above 400°C) exhibit a more pronounced presence in the particle-bound state. Semi-volatile compounds (boiling point between 100 and 400°C) exist in an equilibrium between the gaseous and particle-bound state.

Non-volatile compounds can be very easily enriched from the gaseous sample by means of sampling through a filter with narrow pores (typically 0.45 μm). This simple but often applied approach will not be discussed here. For the volatile and semi-volatile compounds the techniques from **Sections 2.2.1** through **2.2.3** can be applied.

2.2.1 Impringer and Denuder Techniques

Airborne organic contaminants can be removed from a gaseous sample by bringing the sample in contact with an appropriate solvent. This can be done in either an impringer or in a so-called denuder.

An impringer is designed to distribute the total gas flow in a manner that yields a stream of finely divided bubbles rising in the solvent. Impringers have a vertical design such that the gas bubbles slowly rise through the solvent layer and the solvent can effectively solubilize the analytes. Chemical reagents can also be added to the solvent to convert the analytes into derivatives more suitable for the final chromatographic analysis. Analogously, derivatives with lower vapor pressure can be prepared to prevent evaporative losses during sampling. Denuders differ only from impringers in their set-up. Contrary to impringer, denuders are based on an open tube coated on the inside with the absorbing liquid. The sample will be sucked through the denuder by means of a vacuum pump. Advantages of denuders over impringers include the higher sampling flow rates (up to several liters/min) and since less absorbing liquid is necessary a more concentrated extract can be obtained.

Denuder and impringer techniques apply common (organic) solvents or even water for retention of the analytes. This not only has the advantage that an immense number of phases is available but also that there is a lot of room to "play" with the chemistry in the liquid phase. Therefore it is possible to select conditions favorable for trapping a certain type of compounds while (largely) excluding those of minor interest. For example, if a certain analysis is aimed at the determination of basic compounds in air but non-polars and acids are of no interest, water with a low pH can be used as the trapping liquid. The basic compounds will be converted into their ionic form and lose their volatility, stay trapped and be enriched over time. Acids can also dissolve in water but will not be converted and will thus also be vaporized from the sample. Apolar compounds on the other hand will only show very low affinity for the highly polar water phase and will remain in the gas phase.

A typical application of diffusion denuders was described by Frank *et al.*[5] for the enrichment of halogen containing acids from ambient air. A denuder which was 3 m long with an inner diameter of 8 mm and coated with a solution of sodium carbonate in a glycerol/water mixture was used. The acids were trapped in this basic liquid and remain there in an ionic form. After sampling of 10 m^3 air, the denuder trap

was rinsed with water to remove the glycerol layer. Subsequently, the obtained solution was acidified with sulfuric acid upon which the acids were converted back into their non-ionic form. This acidified aqueous solution was extracted with diethylether to transfer the analytes to an organic environment more suitable for final derivatization with 1-pentafluorobenzyl-diazoethane. The resulting extract was analyzed with gas chromatography coupled to negative ion chemical ionization mass spectrometry operated in the selected ion monitoring mode (NICI-MS-SIM). This was the most sensitive technique for the analytes under investigation here. Though the above described procedure allowed detection limits below the 0.1 pg/m^3 level it is characterized by several marked disadvantages. The many (manual) handling steps prevent automation and the 3 m long denuders are not very practical for use in large sampling programs. Since several steps require the use of relatively large amounts of solvents of which eventually only an aliquot (less than 0.1 % of the equivalent of the total sample volume) will be injected, a reduced sensitivity is obtained. This can be circumvented by applying the large sample volume of 10 m^3 but this leads to a sampling time of 2.5 days which can be impractical. In practice, the severe drawbacks of denuder and impringer samplers only justify the use of these techniques for difficult compounds such as the free halogenated acids analyzed here.

2.2.2 Dynamic Adsorptive Extraction-Liquid Desorption

Dynamic sampling onto small, packed adsorbent cartridges is probably the most applied technique for the enrichment of both volatiles and semi-volatiles from gaseous samples. Though the analytes can be desorbed thermally (**Section 2.2.3**) most commonly the analytes are released from the adsorbent by a small amount of organic solvent.

A typical adsorption/liquid desorption (ALD) trap contains 0.5-20 g of adsorbing material but even larger cartridges have been applied. Through these cartridges, air is sampled at flow rates up to several liters per minute to a total volume of ten to several hundred liters. Most often inorganic carbon-based adsorbents are employed that allow trapping of volatile compounds (as volatile as C_2 and C_3 alkanes) from relatively large sample volumes but the weaker organic adsorbents such as Tenax and Chromosorb (C_6 alkanes and higher) can also be used. Trapping of organic compounds from gaseous samples is primarily based on volatility with the addition that polar analytes are much more strongly retained than apolar analytes.

Desorption of the analytes from the adsorbents is usually performed with organic solvents. Here the common like-like principle from chromatography applies again; for the desorption of apolar compounds an apolar solvent should be used whereas (semi)-polar solutes are desorbed with a more polar solvent. With the proper selection of desorption solvent(s) selectivity can be introduced in the desorption step. For example, a first desorption with pentane can be done to collect the apolar

compounds, subsequently a desorption with acetone for the medium-polars and finally a desorption with methanol for the collection of the polars. The most common desorption solvent, however, is carbondisulfide (CS_2) since interest is often focused on apolar compounds. In gas chromatography with flame ionization detection (GC-FID), CS_2 has the advantage that it is one of the few solvents that show no response.

Though ALD techniques are very simple and require virtually no instrumentation besides a GC and the adsorbent traps, their application, especially in trace analysis, is hindered by several drawbacks. First, from the desorption solvent (1-5 mL) only an aliquot (1-5 μL) can be injected into a standard GC. Therefore a reduction in sensitivity by a factor 1000 is obtained compared to ATD, unless special techniques such as large volume injection are employed. Second, the presence of a large solvent peak precludes the analysis of highly volatile compounds and a boiling point difference between the analytes and solvent of 50-75°C should be kept. In recent years, much attention has been paid to somewhat overcome this problem by means of large volume injection (LVI). This technique allows the introduction of up to several hundred μL's in a modified gas chromatographic instrument. The main drawback of LVI is that certain elements (liners and/or retention gaps) have to be replaced frequently. Additionally, LVI cannot easily be applied for compounds eluting close to the solvent, *i.e.* volatiles.

Haraguchi *et al.*[6] employed an XAD-2 type resin for the trapping of pesticides from urban air samples. A high capacity trap containing 20 g of XAD resin was employed together with a quartz fiber filter to prevent particulate matter from reaching the resin. Air samples were collected at a flow rate of 500 L/min for 24 hours so that a total volume of 720 m^3 was collected. After sampling, the XAD resin was extracted with two times 100 mL of dichloromethane which was concentrated to 1 mL on a Kuderna-Danish evaporator and further under a nitrogen stream. This extract was fractionated over a silica gel column and eluted with in turn 20 mL hexane, 25 mL hexane-benzene (1:1 v/v) and finally 15 mL benzene-methanol (1:1 v/v). These three factions were again concentrated to 1 mL and for the final quantitation 1 μL of each extract was injected in a GC-MS system operated in the selected ion monitoring mode (SIM). Three chromatograms are thus obtained per sample. In real life samples pesticides were encountered at the 0.05-5 ng/m^3 level with detection limits in the 0.05-0.2 ng/m^3 range. Despite the many handling steps relative standard deviations were below 20% for most compounds. This example clearly illustrates the benefits of ALD regarding the opportunity for the introduction of selectivity in the desorption or in subsequent fractionation procedures. However, the concentration disadvantage is also pronounced. Since only 1 μL from the 1 mL extract is injected, only the equivalent of 720 L of air (0.1% of the sample) is introduced in the GC column and the majority of the sample is discarded. In principle, the sampling could be shortened to less than 2 minutes if the entire amount of trapped analytes could be transferred to the analytical instrument.

Kawata *et al.*[7] presented a similar method for the determination of pesticides in air employing activated carbon trapping and desorption with acetone and toluene/ethanol (4:1 v/v). Air was sampled at a flow rate of 0.1-0.2 L/min for seven days on a trap containing 5 g of activated carbon. Detection limits were in the 0.1-1 ng/m^3 range depending on the pesticide. In rural samples pesticides were detected up to a level of 430 ng/m^3 for fenobucarb. Again only 0.1% of the sample was injected onto the column.

Another ALD approach concerns the application of diffusive (passive) samplers. Contrary to active sampling, a pump is not employed. The sampler is placed for a period of typically four to six weeks at the sampling site. Analytes will diffuse into the sampler and will be trapped on the (strong) adsorbent. The adsorbent capacity should be very high to prevent saturation effects. Begerow *et al.*[8] presented a method for the monitoring of volatile hydrocarbons, ketones and esters using charcoal diffusive samplers. The samplers were desorbed with 1.5 mL CS_2 of which 2 μL was injected in a dual column GC-ECD-FID system. A time consuming concentration step was thus not necessary. Unfortunately it was found that the blank adsorbent also generates traces of benzene, *n*-hexane, toluene at the 0.1-1 μg/m^3 level. This precludes trace determination of these compounds below their respective blank levels and requires establishing of blank levels for each lot of adsorbent samplers used.

In a comparative study[9] the reaction of adsorbed fluoranthene with gas phase N_2O_5 (present in ambient air) was investigated for both Tenax and polyurethane foam (PUF). These authors found conversion on Tenax to five nitrofluoroanthene isomers while PUF showed no catalytic reactions. This clearly illustrates the risk of artifact formation with adsorbents.

An extension of ALD is reactive trapping of analytes that are very volatile or instable. By using an adsorbent impregnated with a reagent, upon sampling a reaction between target and reagent is taking place transforming the analyte into a form more suitable for subsequent analysis. Examples include the reactive trapping of ethyleneoxide (EO), a highly volatile and reactive epoxide, on a carbon molecular sieve (ASTM D5578) or charcoal (NIOSH 1614 and OSHA 50) cartridge impregnated with hydrobromic acid (HBr). Upon trapping, EO is converted into 2-bromoethanol which is much less volatile than EO itself and will remain on the adsorbent. The derivative is eluted with acetone and conveniently analyzed using GC-ECD.

Another commonly applied reactive trapping procedure is the trapping of aldehydes and ketones on a silica adsorbent impregnated with 2,4-dinitrophenyl-hydrazine/H_3PO_4. The aldehydes/ketones are converted into their hydrazone derivatives and can be determined with HPLC/UV-VIS.

2.2.3 Dynamic Adsorptive Extraction-Thermal Desorption

Though ALD techniques described in **Section 2.2.2** generally perform well, the lack of sensitivity of these techniques and the problems associated with the analysis of highly volatiles have prompted many groups to develop procedures for thermal desorption of packed adsorbent beds. In practice, the adsorbent beds require desorption under a carrier gas flow rate of 50-200 mL/min which prevents direct thermal desorption onto a capillary GC column. A typical set-up for thermal desorption is schematically shown in **Figure 6**. The adsorbent trap is desorbed onto an intermediate cold trap from which the analytes are subsequently desorbed onto the analytical GC column. As can be observed from **Figure 6**, the thermal desorption system contains a valve which, when properly switched, allows the transfer of the entire amount of trapped analytes onto the GC column. Alternatively either one or both analyte transfers can be performed in the split mode to result in a single split or even double split transfer for high concentration flexibility.

Commonly applied materials in ATD are carbon-based materials such as activated carbon and carbon molecular sieves and porous organic polymers such as Tenax and Chromosorb. These are all relatively strong adsorbents giving excellent performance for apolar (semi)-volatiles (benzene, toluene, xylene [BTX], polyaromatic hydrocarbons [PAHs] and polychlorinated biphenyls [PCBs]). Unfortunately their application to the analysis of polar solutes is rather limited. Lack of retention during sampling is generally not the problem as the analytes are strongly retained on the active adsorbent surface. This strong retention, however, often precludes rapid and complete desorption resulting in low recoveries and a severe risk of carryover. Moreover, the long residence times of the analytes on the hot and active adsorbent surface during desorption often results in reactions initiated by the adsorbent surface itself or with other adsorbed species. These reactions can result in permanent adsorption and/or in artifact formation which are clearly undesirable effects[10].

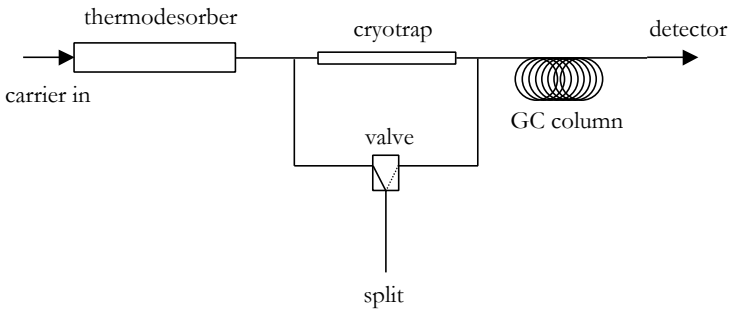

Figure 6 Schematic set-up of a thermal desorption instrument. From left to right the flow path of the carrier gas is shown. In the thermodesorber, the analytes are thermally released and are transported to the cryotrap. The split valve controls the split/splitless state of the system.

In a number of comparative studies, the performance of Tenax was compared to carbon based adsorbents. Rothweiler *et al.*[11] investigated the enrichment of apolar and polar volatile organic compounds (VOCs) on both Tenax and Carbotrap. They found that good performance was only observed for a limited number of compounds. On Tenax these included the apolar pentadecane, toluene and benzene and some polar analytes such as aniline, phenol, hexanal and dimethylformamide. However, for a wide range of polar analytes such as diethylamine, acetic acid, 1,2-ethanediol and mercaptoethanol dramatically poor performance was observed with total disappearal of several compounds. On Carbotrap the situation was even worse with quantitative recoveries of styrene and toluene only and recoveries below 50% for 15 out of the 24 test solutes. These effects were also observed by other authors[12,13]. The conclusion of Rothweiler *et al.*[11] was: "Tenax TA and Carbotrap do not seem to be suitable adsorbents for the enrichment of many polar compounds". Nowadays, reasonably good results can be obtained with Tenax for many apolar to slightly polar solutes but the application of carbon type materials should be carried out with more care. Holzer *et al.*[14] concluded: "Carbon type adsorbents unfortunately have a very narrow range of application and are far too reactive".

Tenax seems generally to be the best all-round adsorbent and is often the first choice unless highly volatile analytes are to be trapped[15]. Then the use of strong carbon based materials is the only alternative, however, this will also limit the application range on the semi-volatile end. Multi-stage adsorbent traps containing two or more adsorbent layers of different strength can extend the working range in terms of volatility[16]. Here the sample first comes into contact with the weakest adsorbent which will only retain the least volatile analytes. More volatile solutes will be retained in progressively stronger adsorbents. In this way the volatility range can be greatly enhanced, however, this does not improve the results for polar solutes.

The most commonly applied ATD adsorbent, Tenax, has been excessively studied. Many authors have reported on the retention characteristics of Tenax for many different compounds including hydrocarbons, aromatics, halogenated hydrocarbons and aromatics, phenols and alcohols[17,18,19,20]. **Figure 7** shows the specific retention volumes (V_r in L/g) for several compound classes on Tenax. From this figure it is clear that most compounds follow the same general trend which is indicated by the line. This trend can be used to estimate the retention volume for an unknown compound. However, some points are markedly below the line and these correspond to the two most polar compound classes, that of the alcohols and phenols. These analytes exhibit a relatively weak interaction with Tenax and are best enriched on alternative phases.

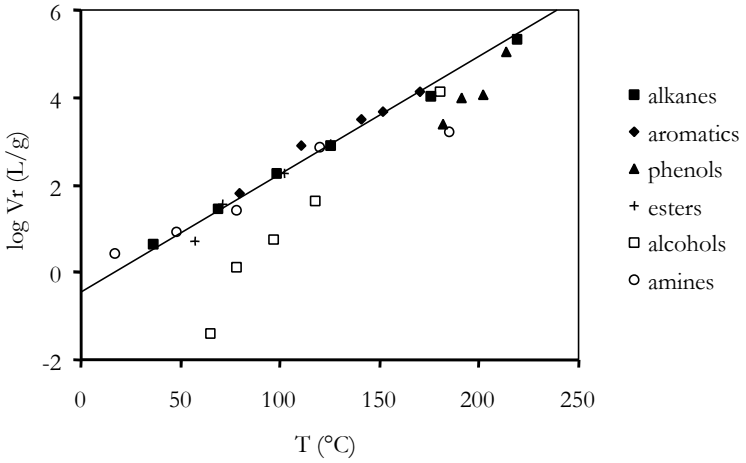

Figure 7 Specific retention volumes of several compound classes on Tenax TA as a function of their boiling point. Literature data was extracted from the publication of J. Pankow[21].

As was already stated above, a major problem with adsorbents is the formation of artifacts. Many of the organic adsorbents, including Tenax, possess a polymeric structure based on polymeric building blocks such as styrene, divinylbenzene and other monomers. Since all polymers are in equilibrium with their monomer, as is shown in **Equation 11**, at any temperature, any polymeric phase contains a certain amount of monomer (and dimer, trimer *etc.*).

Equation 11

$$M_n \leftrightarrow M + M_{n-1}$$

At ambient temperatures the monomeric content is usually very low but upon heating this equilibrium moves in the direction of free monomer due to the entropy effect. This is the reason that the blanks of most polymeric materials show distinct peaks corresponding to their monomeric building blocks. Not only at elevated temperature but also upon contact with reactive species during adsorption, such as ozone (O_3) and nitrogen oxides (NO_x) normally present in ambient outdoor air, artifact formation can be greatly enhanced. These species can partially oxidize the adsorbent structure and catalyze the reaction of **Equation 11**. Artifact forming reactions are discussed for Tenax, the most commonly used and best studied adsorbent.

For Tenax, degradation reactions have been extensively studied in the literature including reaction with ozone[22,23,24], nitrogen dioxide[25], nitrogenoxide[25,26], sulfur dioxide[26], sulfuric acid[26] and chlorine[22]. Clausen and Wolkoff[27] identified a number of potential Tenax artifacts and these include phenol, benzaldehyde, acetophenone, decanal, dibutylphthalate, 2,6-diphenyl-p-quinone (DPQ) and 2,6-diphenylhydro-quinone (DPHQ). The latter two compounds are direct derivatives of the Tenax monomer structure, whereas dibutylphthalate might be an additive. Their structures are listed in **Figure 8**. Though degradation of Tenax to its monomer is undesired, in practice it often does not present a real problem as these are generally not among the analytes of interest. The presence of the other small organic compounds is much more problematic as these are compounds of general interest and some are even included in environmental priority lists.

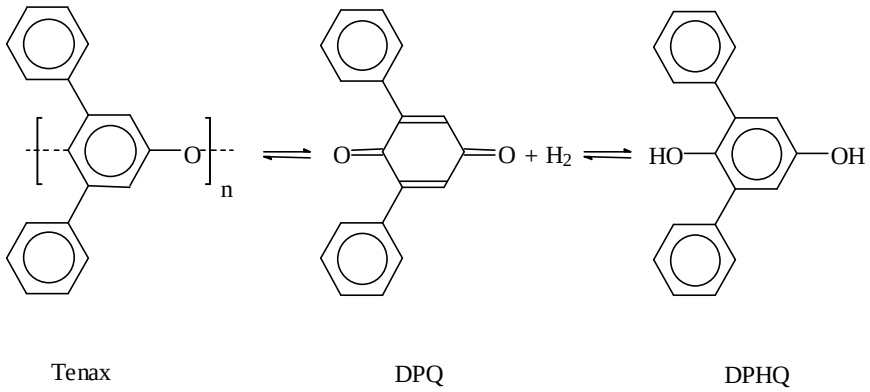

Figure 8 Degradation reaction of Tenax.

Another artifact forming reaction is that of adsorbed analytes with reactive species in the gas phase. This has been studied for the reaction of adsorbed terpenes with ozone[28,29,30]. Although one group found there was no reaction between adsorbed terpenes and ozone[31], it is nowadays generally agreed that degradative losses are hard to avoid. In several studies comparing equal spiking levels in both ozone rich and ozone free air, typical changes in recovery from 10% for compounds relatively insensitive to ozone up to total loss of ozone-sensitive (reactive) compounds[29,30] have been recorded. This has prompted several groups to apply ozone scrubbers in front of the actual Tenax trapping device[32]. This can prevent analyte decomposition by ozone but can also cause adsorption of low volatility and/or polar compounds resulting in a shift of the enrichment problem from the adsorbent to the filter. Selective filtering of the sample can only give good results in those cases where only a specific type of compounds are of interest and can definitely not be universally applied.

Another commonly encountered problem in ATD procedures is that of humidity present in the sample. If excessive amounts of water are present in the sample, a relatively large amount may be enriched on the adsorbent leading to problems during desorption and in the GC column. The application of Tenax can be advantageous in this respect, as it exhibits a very low affinity for water. Many volatiles are in practice trapped at sub-ambient temperatures[33, 34, 35, 36]. This causes even more problems as water can easily be "frozen out" of the sample at temperatures below the sample's dew point. This will lead to a blockage of the sampling device and prevents accurate enrichment. A device to remove water from the gaseous sample can be employed such as a cold trap, a packed bed of drying agent[37] (*e.g.* calcium chloride) or a Nafion dryer membrane[38]. However, with all these approaches the risk of losses of analytes of interest is obvious and careful evaluation of the sampling method has to be carried out.

The primary practical disadvantage of the thermal desorption approach described above is the necessity of a cold trap. Usually, the cold trap is cooled with liquid nitrogen for cooling down to -150ºC during the desorption step which can typically take between 10 and 20 minutes. This results in the consumption of between 1 and 5 liters of liquid nitrogen depending on the system, actual trapping temperature and carrier gas flow rate. Not only can this become an important cost aspect of the entire procedure, frequent refilling of the nitrogen dewar is inconvenient and time consuming. As an alternative, if only temperatures down to -60ºC are required cooling by liquid carbon dioxide may be employed. Though this a much cheaper alternative, frequent replacement of the CO_2 cylinder will still be required. If a close look at the thermodesorption instrument is given, it is clear that the only reason the cryotrap is needed is the flow incompatibility between the (packed) concentration trap and the capillary column. In this context, it seems logical to develop capillary concentration traps with similar diameters as GC columns to resolve this problem. Several specific capillary traps were developed by Grob and Habich[39]

2.3 Enrichment of Water and Liquid Samples

In the analysis of aqueous samples and liquid samples in general, a distinction between the analysis of volatiles on one side and that of semi- and non-volatiles is often made. The range of volatiles typically extends up to analytes with a boiling point similar to that of *n*-decane. These analytes are classically analyzed by Purge and Trap (**Section 2.3.1**) which permits sub-µg/L detection limits in a variety of aqueous samples and can thus easily cope with regulatory limits. Semi-volatiles analytes include compounds with a boiling point starting at that of *n*-decane and extending upwards. This group contains many environmentally relevant compounds including pesticides, polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Liquid-liquid extraction (**Section 2.3.3**) is a technique particularly suited for the analysis of semi-volatiles but its widespread use has often been questioned due to the large consumption of organic

solvents. As a result of this, liquid-liquid extraction is increasingly replaced by other techniques, of which the most important one is solid phase extraction (**Section 2.3.4**).

2.3.1 Dynamic Gas Phase Extraction (Purge and Trap)

Dynamic gas phase extraction of aqueous samples is known as purge and trap (P&T). Purge and trap is generally used for the enrichment of apolar volatile organics prior to GC analysis. An inert gas is bubbled through the water sample, causing the purgeable organics to move from the aqueous to the gaseous phase. The opposite effect as that of an impringer (**Section 2.2.1**) is obtained. After liberation from the water phase, the analytes are trapped on an adsorbent such as Tenax or charcoal. The trap containing the adsorbent is built into a desorption chamber equipped with a heating device which, when activated, permits the thermal desorption of the trapped compounds. This technique has the distinct merit of providing a clean sample, free from its often very dirty matrix. A purge and trap device mounted on a GC equipped with an electron capture detector (ECD) and a photoionization detector (PID) in series or a mass spectrometer (MS) is routinely employed to monitor a wide range of organics in aqueous samples[40]. Alternatively a GC with an electrolytic conductivity detector (ELCD) and PID can be used[41]. For unknown compounds, the mass spectrometer is the detector of choice and has proven itself for a wide variety of samples including environmental[38,42,] juices[43], coffee, tea or tobacco extracts[44] and many other applications. Detection limits in the sub-µg/L range are readily obtained for a wide range of apolar volatiles. Due to the fact that P&T analyses are relatively straightforward and well known to a broader scientific community, no examples are given here.

Though P&T performs well for a wide variety of volatile apolar compounds, its performance for more polar compounds is rather limited. Here the like-like principle applies again as these compounds are very well dissolved in the polar water phase. Consequently quantitative purging from the aqueous phase is impossible. Compounds with poor performance in P&T include small acids such as acetic acid, small aliphatic amines such as dimethylamine, free alcohols such as methanol and ethanol and small analytes with multiple functional groups such as ethylenediamine. For these compounds, currently no high-performance trace-level analysis techniques exist.

A variation on the P&T principle is closed loop stripping analysis[45]. In a P&T instrument the gaseous stripping phase is re-circulated in a closed system with the advantage that larger sample volumes can be used, resulting in better detection limits. In practice P&T techniques are simple and reliable and should be the technique of choice if the analytes of interest can indeed be purged from the water sample, however P&T can in practice only be applied to the analysis of non-polar volatiles.

2.3.2 Static Gas Phase Extraction (Headspace)

Headspace analysis is the static equivalent of Purge and Trap. Contrary to P&T, where the extraction gas phase is supplied to the sample, in headspace analysis the gas phase above the sample (the headspace) is directly injected into the gas chromatograph. Due to the static (equilibrium) nature of the extraction process proper temperature control is of great importance, as exhaustive extraction generally does not occur. Heating of the sample is often applied in order to transfer as much analyte as possible from the sample to the gas phase. The most simple way to transfer (a portion of) the gas phase to the GC is by means of a syringe piercing the septum followed by withdrawal of the desired amount of gas and subsequent injection into the GC. However, as a significant pressure increase can occur during heating this may lead to erroneous data. Balanced pressure sampling systems are therefore often used. These apply a pressurization step (with the carrier gas pressure) between equilibration and injection to ensure consistent sampling pressure[46]. Alternatively, many headspace systems use a gas supply for controlled pressurization of the sample. After the equilibration time, it is then possible to let the gas phase expand through a sample loop and inject a pre-defined amount of gas phase into the GC.

2.3.3 Liquid Phase Extraction (Liquid-Liquid Extraction)

At present the most widely used method for sample preparation in water analysis is liquid-liquid extraction (LLE). LLE can easily be carried out manually by shaking the sample with an extraction solvent in a separatory funnel or automatically with a continuous liquid-liquid extractor. Continuous LLE is recommended by the EPA for the extraction of semi-volatiles (base/neutral/acid-extractables). Depending on the extraction conditions used, extracts can contain intermediate to low polarity, semi-volatile compounds (universal extraction for neutral semi-volatiles) or acidic/basic compounds (selective extraction) by adjusting the pH. Classical LLE procedures use large volumes (up to several hundred milliliters) of organic solvents which are often much more toxic than the trace contaminants to be determined. The volume of extract is usually too large for direct injection and, in order to obtain sufficient sensitivity, an additional evaporation step (Kuderna-Danish) is necessary. Not only will the highly volatile analytes be lost, care has to be taken to avoid contamination of the sample. Moreover, solvent impurities will be concentrated often masking target compounds.

At present, several authors have reported on micro liquid-liquid extraction (μLLE) in the vial of a standard injection autosampler. This is a promising new approach that seems suitable for a number of applications. By using highly sensitive and selective detectors, eventually in combination with large volume injection, sub-μg/L detection limits can be obtained. A typical μLLE procedure will be outlined below for trihalomethanes as an example[47].

The trihalomethanes chloroform, dichlorobromomethane, chlorodibromomethane and bromoform are commonly present in tap water at concentrations less than 25 μg/L (ppb) and originate from organic material during the chlorination of drinking water. According to World Health Organization (WHO) regulations[48] the sum of these compounds should not exceed 100 μg/L. There is, therefore, a need to monitor the presence of these compounds in drinking water using reliable methods. The use of fast analysis and automation saves laboratory time and expense.

Trihalomethanes can be analyzed in drinking water samples using various techniques including static headspace, purge and trap, liquid-liquid extraction and direct aqueous injection[49,50]. Static headspace and P&T are highly sensitive techniques but both require dedicated instrumentation. Although direct aqueous injection gives reliable results, the use of retention gaps that have to be replaced on regular time intervals is required. Micro liquid-liquid extraction with *n*-pentane can be an alternative.

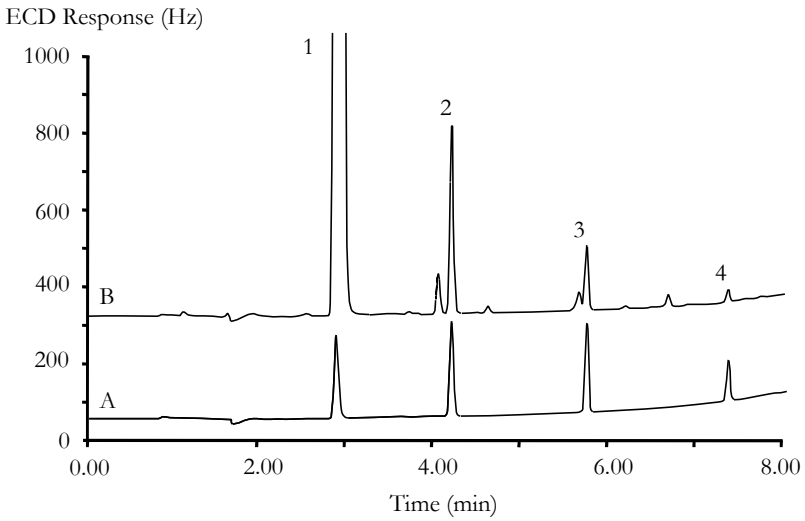

Figure 9 GC-ECD chromatogram of the micro liquid-liquid extraction of an aqueous sample with *n*-pentane. Lower trace (A) is the analysis of blank sample spiked to a level of 5 μg/L (ppb) with the target analytes. Upper trace (B) is the analysis of a water sample contaminated with chloroform. Peak assignment and concentrations in the water sample: 1, 5* mg/L (ppm) chloroform; 2, 11 ppb dichlorobromomethane; 3, 3.8 ppb dibromochloromethane; 4, 1.1 ppb bromoform. *Extrapolated out of the liner range (1-100 ppb).

One milliliter tap water aliquots were pipetted into 2 mL vials and to this 0.5 mL *n*-pentane was added. The compounds were extracted for 1 min on a vortex mixer. Subsequently, 1 μL from the *n*-pentane layer was injected into a GC-ECD system equipped with an on-column injector. Linear calibration curves were made

over the 1-100 μg/L range, which is the concentration range that is usually monitored in tap water samples. Chromatograms obtained from both the analysis of a spiked blank water sample (5 μg/L) and that of a tap water sample contaminated with chloroform are shown in **Figure 9**. Chloroform was found to be present at a level far exceeding the linear calibration range. Extrapolating resulted in a concentration estimate of 5 mg/L which is severely over the maximum permissible concentration level.

2.3.4 Solid Phase Extraction

In solid phase extraction (SPE), the water sample is pumped through a packed adsorbent bed. This innovative extraction procedure is gaining wide acceptance, being much faster and more versatile than most classical techniques. The principle of retention is analogous to high-performance liquid chromatography (HPLC). SPE is suitable for low, medium and high polarity pollutants depending on the solid adsorbent phase used. Most often, the extraction cartridges are packed with a hydrophobic material such as C_{18} or C_8 silica or a styrene-divinylbenzene copolymer. With SPE, large sample volumes can be handled using a relatively small amount of solid phase. This in turn requires only a small volume of solvent for solid phase stripping resulting in a significant sensitivity increase over classical techniques such as LLE. Moreover, consequently the need for an additional evaporative concentration step is reduced with a considerable increase in speed of analysis and a reduction in the risk on contamination. Unfortunately selectivity during analyte trapping is generally low due to the hydrophobic interaction mechanism. Selectivity can be drastically improved by selective washing steps or by the use of more selective adsorbents, *e.g.* incorporating immobilized antibodies[51, 52, 53].

For most applications, SPE is presently carried out using cartridges containing 100 mg to 1 g of an apolar phase as a low efficiency packed bed in a disposable (plastic) cartridge. These cartridges perform very well for apolar to medium polar solutes, provided the sampling rate is low to prevent breakthrough (typically 10-20 mL/min, which results in a sampling time of one hour for a one liter sample), and that drying of the cartridge prior to desorption is complete (which typically takes 30 minutes). As an alternative to the standard SPE cartridges, extraction disks (46 mm diameter) were introduced several years ago (3M, St. Paul, MN, USA) allowing higher sampling flow rates (one liter in 10 minutes) and reduced drying times. These disks are made by impregnating small adsorbent particles (12 μm compared to 40 μm in conventional SPE cartridges) embedded in an inert polytetrafluoroethylene (PTFE, Teflon) network. Due to the larger size of these disks, the trapping capacity is improved compared to conventional SPE cartridges but this also leads to a somewhat larger desorption volume. The net result will still be a more concentrated extract compared to conventional SPE traps but the exact outcome will have to be determined for a specific analytical problem. Recently, miniaturized disk extraction cartridges (10 mm diameter) also became available. They have the same benefits as the larger disks but have the

distinct advantage of only requiring 0.5 mL for desorption[54]. Unfortunately, the reduced diameter also implies that the sample capacity of the small disks is reduced.

In environmental analysis, the desired detection limits are 1 μg/L in river and ground water and 0.1 μg/L in drinking water. With classical SPE, these detection limits can be reached by extraction of a one liter sample, eluting with 10 mL solvent, concentrating to 1 mL (concentration factor 1000), and injection of 1-2 μL extract into a GC using a splitless or on-column injector. Though this approach works rather well, it would be desired to speed up the entire procedure and to eliminate the concentration step, by using the miniaturized disks. However, by using these as such it is impossible to reach the desired concentration factor. Recent developments in sample introduction for GC, namely large volume injection via a programmable temperature vaporizing (PTV) injector, have helped to overcome this problem. By operating the PTV in the so-called solvent venting mode, sample volumes significantly in excess of 1-2 μL can be injected[55]. Using the 10 mm disks to extract 20 mL water samples, desorption with 500 μL solvent and subsequent injection of 40 μL extract ensures transfer of the same amount of analytes to the GC as the classical SPE approach. This is illustrated in **Table 3**.

Table 3 Comparison of classical SPE and SPE using miniaturized disk cartridges.

	Classical SPE	Miniaturized SPE disks
Sample concentration	0.1 ng/mL	0.1 ng/mL
Sample volume	1000 mL	20 mL
Extraction	1g cartridge or 46 mm disk	10 mm disk cartridge
Desorption	10 mL	0.5 mL
Concentration to	1 mL	-
Final concentration	100 ng/mL	4 ng/mL
Injection volume	2 μL	50 μL
Injected amount	200 pg	200 pg

Though off-line SPE is commonly applied for limited sample series with the liquid phase separation techniques LC[56] and CE[57] and GC, the on-line coupling of SPE with chromatography is ideal for the automated analysis of a large number of samples. Miniaturized extraction disks as described above or miniaturized classical SPE cartridges open up possibilities to realize this. Numerous papers concerning the on-line combination of SPE with GC and GC-MS have appeared from the group of Brinkman, who worked quite extensively on this particular hyphenation[58,59,60]. Many different systems for SPE-GC were developed, most of which are based on a large volume on-column interface on the gas chromatograph. The performance of such a system for SPE-GC-(MS) was discussed by Louter *et al.*[61] in a recent review. This system for

on-line SPE-GC, based on an on-column type interface on the gas chromatograph, contains typically 4 multiport switching valves for proper (automated) operation of the SPE process and for transfer of the final SPE eluate to the GC. Louter *et al.*[60] showed that on-line SPE-GC-MS typically results in detection limits in the low-ng/L range from sample volumes as low as 1-10 mL. Obviously, only small sample volumes are required since all analytes are transferred fully to the gas chromatographic instrument (on-line). In another study, an ion trap tandem mass spectrometric detector (MS/MS) was used, which is probably the most selective detector available today. This high selectivity results in the almost complete elimination of any background interferences and consequently, next to its high selectivity, a very high sensitivity is also attained. Verma *et al.*[62] showed with an on-line SPE-GC-MS-MS system employing 10 mL samples that detection limits as low as 0.01 ng/L are feasible for certain compounds, like trifluralin. Other compounds exhibited detection limits in the 0.01-1 ng/L range.

One of the most critical steps in a SPE procedure often is complete drying of the SPE adsorbent prior to liquid desorption. This process is rather critical as insufficient drying will result in a "wet" SPE extract that will be transferred to the GC column. This can be problematic for long series of samples as large amounts of water are known to have a detrimental effect on the GC stationary phase coating. Hankemeier *et al.*[63] proposed the incorporation of a cartridge packed with drying material in the SPE procedure. The SPE extract is passed through this drying bed to remove (adsorb) water prior to injection onto the GC column. Though this approach is likely to extend column lifetime, it also offers a new source for analyte loss. Polar compounds are, according to the like-like principle, easily adsorbed on the drying material, similar as for water itself. This was found to be particularly the case if an apolar solvent such as pentane or hexane was used, If the SPE cartridge was eluted with ethylacetate good performance was observed for all compounds under investigation[63].

In addition to on-line SPE-GC, several papers have also appeared on so called at-line SPE-GC[64]. The at-line technique does not transfer the entire amount of analyte present in the original sample to the GC column at once, but the SPE extract is first collected in a glass vial by means of a robotized system. Subsequently, an aliquot of this extract is automatically injected into the gas chromatograph. This has the disadvantage that a reduced sensitivity is obtained compared to a fully on-line system but it also has a very important advantage, *i.e.* more than one analysis can be performed on one single sample.

Coupling of solid-phase extraction with GC is a very attractive option for the monitoring of a wide range of pollutants in water samples due to its very high separating power and easy interfacing with a wide number of highly sensitive and selective detectors. Though off-line SPE-GC is well established and many methods for *e.g.* pesticides[65] and chlorinated phenols[66] exist, an on-line set-up is desirable for the automated processing of large sample numbers. Using normal off-line SPE procedures a final extract of typically 1-5 mL is obtained. This volume is however far too large

for introduction into a standard GC instrument that only accepts a volume of typically 1 μL. The application of large-volume injection techniques is therefore required. Several authors described on-line SPE-GC set-ups based on either the PTV interface[67], on-column interface[68,69,70] and the loop type interface[71,72]. As these techniques also exhibit a maximum practical volume of 100-200 μL miniaturization of the SPE procedure is essential.

So far, the discussion on SPE has been limited to its combination with gas chromatography due to the extensive use of gas chromatography in this thesis. Though SPE-GC is a very powerful technique with many interesting applications, the coupling of SPE to liquid chromatography should not be overlooked. The hyphenation of SPE with LC was in fact realized some 10 years earlier than that with GC. Coupling SPE, a liquid phase enrichment method (with intermediate adsorbent trapping) to the liquid phase separation technique LC seems very logical. Proper selection of SPE adsorbent, SPE desorption solvent and LC conditions allows direct elution of the SPE extract into the analytical LC system. Particularly the easy on-line interfacing of SPE with LC is an important advantage over SPE-GC where a critical solvent evaporation step (*e.g.* on-column, PTV) is always required.

On-line SPE-LC approaches for the analysis of pesticides and phenols were described by the group of Brinkman[73,74] and by Masque *et al.*[75, 76]. The latter authors used UV detection with which detection limits at the μg/L level in tap and river water samples were obtained. Using an automated on-line SPE-LC method with UV detection and employing sample volumes of 200 mL, detection limits of 10-50 ng/L depending on the analytes were obtained[77]. In a comparative study of ten adsorbents[78] the authors determined that when using a C_{18} bonded silica analytical column, a styrene-divinylbenzene copolymer (PRLP-S) was ideal for on-line sample enrichment.

Though many of the SPE-LC-UV systems show good performance for a wide number of applications they are all hindered by one major drawback. It is very difficult to make positive identifications based on a UV spectrum alone as a typical UV spectrum contains only a limited amount of relatively unspecific information. With the availability of sensitive interfaces for on-line coupling of LC to mass spectrometry (atmospheric-pressure chemical ionization [APCI] and electrospray ionization [ESI]) the use of LC-MS for confirmatory analysis becomes more and more interesting. Several groups described on-line SPE-LC-MS for the detection of pesticides in aqueous samples at the low ng/L level[79,80,81].

In addition to the above mentioned on-line hyphenations of solid phase extraction at least two additional, less common, approaches are relevant within the context of this thesis. The first is the combination of SPE with supercritical fluid extraction (SFE). Though off-line SPE-SFE followed by GC analysis was described by Tang and Ho[82], approaches involving the on-line coupling of SPE with supercritical fluid chromatography (SFC) seem more promising[83]. Using a miniaturized SPE

approach and diode-array detection, identification of several common pesticides by comparison of acquired DAD spectra with that of a library was possible at the 0.1-1 μg/L level in river water samples.

The second approach is the application of solid phase extraction but with thermal desorption instead of liquid desorption with an organic solvent. In order to prevent degradation of both the adsorbent and the trapped analytes at the elevated temperatures used (up to 300°C) desorption is performed under a stream of inert gas. Most commonly helium is applied which allows easy interfacing with GC and GC-MS. Several systems for on-line SPE-TD-GC were described in the literature[84,85,86] and are all build up around a programmable temperature vaporizing (PTV) injector. A short adsorbent bed is placed in the glass liner of the PTV and introduction of the water sample is done with a syringe in a similar fashion as a standard splitless injection. After introduction of the aqueous sample it is essential to dry the adsorbent packing and vent the excess water through the split exit to prevent the introduction of large amounts of water into the GC column. This not only interferes with the chromatography of the analytical column but will also destroy the stationary phase. In addition to venting, it was found advantageous to backflush the analytical column during this process to ensure that absolutely no water is entering the column[84, 85]. In a comparative study of 8 adsorbents, Vreuls *et al.*[87] selected Tenax adsorbents to be the most suitable for SPE-TD resulting in the widest volatile range that could be handled. Stronger retaining materials such as carbon based adsorbents were found to result in a small application range due to the loss of volatiles during drying on one side and incomplete desorption of semi-volatiles on the other. Reported detection limits are in the order of 0.01 μg/L[86] (0.5 mL sample, ECD) to 0.5 μg/L[86] (0.5 mL sample, FID). However, the major drawback of the system is that the deposition of salts and other non-volatile sample constituents may lead to the destruction of labile compounds. A frequent change of insert is therefore required for real-life samples[86].

In addition to direct SPE procedures, the use of dialysis-SPE is also briefly described here. Dialysis membranes are a very effective means of separating large molecules and particulate matter from smaller analytes and in this way to obtain a rather clean sample. Dialysis can, for example, be directly applied to biological matrices such as those present in fermentations[88] or urine, plasma and blood samples. A sample (donor liquid) flows at one side of the dialysis membrane and a clean liquid (acceptor fluid) at the other. Compounds that can diffuse through the membrane (*i.e.* have a lower molecular mass than the membrane's cutoff value) will pass from the donor into the acceptor fluid. The one disadvantage of dialysis is that concentration is difficult to achieve and often the sample is diluted instead of concentrated. Therefore, dialysis is in practice almost always combined with solid-phase extraction resulting in dialysis-SPE[89]. The SPE process is operated as described above followed by (on-line) chromatographic analysis. The particular interesting feature of dialysis-SPE is that the dialysis membrane will prevent fouling of the SPE cartridge, whereas the SPE cartridge starts with a more

or less ideal sample, free of most contamination. Reproducible and robust operation is often observed.

2.4 Enrichment of Soil, Sludge, Sediment and Solid Samples

In this section, several techniques are described for the extraction and enrichment of compounds from solid samples. However, since this thesis focuses on the analysis of particularly gaseous and also liquid samples only, the techniques for solid samples described in this section are presented in much less detail compared to **Sections 2.2** and **2.3**.

2.4.1 Static and Dynamic Gas Phase Extraction

These techniques were discussed in **Sections 2.3.1** and **2.3.2** for liquid samples. For solid samples both can be applied with features analogous to those described before.

2.4.2 Dynamic Gas Phase Extraction (Thermal Desorption)

Thermal desorption (TD) on-line coupled to CGC-MS is a powerful technique for the analysis of air volatiles collected on adsorbent tubes (**Section 2.2.3**), for the enrichment of residual monomers in polymers, for the analysis of residual solvents in pharmaceutical products, *etc.* The same principle can be applied for the determination of volatiles in solid matrices. The solid material is placed into a TD tube and brought directly into the TD unit. The temperature is programmed to typically 350ºC and the released volatiles are transported with the carrier gas to a cold trap. After desorption, the trap is rapidly heated and the trapped solutes are introduced into the capillary GC column as a sharp injection band. The method has been criticized because of the small sample size loaded into the TD cartridge which is typically in the order of 500 mg. Standard deviations can therefore be quite high but this simple procedure can still rapidly yield a fingerprint of the pollution. A possibility to circumvent the sample size problem was presented by Yokouchi *et al.*[90] by using an intermediate desorption step of solid sample onto a Tenax trap and subsequently a second thermal desorption of the Tenax trap onto the analytical column. Using this approach large sample volumes could be handled.

A method for the determination of PAHs and PCBs in soil was described by Wormann and Hoffman[91]. The sample was crushed in a jaw crusher and subsequently 500 mg was put in a thermal desorption tube (4 mm ID). This was the only sample preparation needed. The soil is desorbed at 350ºC for 20 minutes while

trapping the thermally released analytes in a cold trap kept at -150ºC with the aid of liquid nitrogen. After thermal desorption is complete, the tube is cooled down and removed. Subsequently the cryotrap is heated and analysis is performed. The authors found that reliable results could be obtained even for the highest boiling PAHs and PCBs.

2.4.3 Liquid Extraction (Soxhlet)

Soxhlet extraction is a very commonly applied classical technique for solid samples that requires no further introduction. Despite its good performance for a wide range of compounds, it suffers from several severe disadvantages including long extraction times (up to 24 hours), the use of large volumes of organic solvents requiring additional concentration steps and the loss of volatile analytes. This has prompted researchers to developed alternatives of which the most important are briefly highlighted in **Sections 2.4.4** through **2.4.7**.

2.4.4 Supercritical Fluid Extraction (SFE)

In supercritical fluid extraction the extraction phase, usually carbon dioxide, is above its critical temperature and pressure and hence is in its supercritical state. **Figure 10** shows a schematic layout of a state-of-the-art SFE instrument. The primary advantage of supercritical fluid extraction is that under optimized conditions a very selective extraction can be made. This is of particular interest in environmental analysis where trace concentrations of target compounds are often to be determined in a complicated matrix[83]. Proper use of the selectivity aspect allows to prepare extracts that are directly amenable to chromatographic analysis.

The system, as shown in **Figure 10**, contains several points where selectivity can be introduced. In first instance, the extraction selectivity can be controlled by the nature of the supercritical medium (selectivity 1). The choice of supercritical fluid, almost always CO_2 to which an organic solvent (called modifier) is often added, obviously has a strong effect on the resulting extraction performance. The reasons for adding a polar or apolar modifier to the CO_2 are threefold: (i) to increase the solubility of the target compounds; (ii) to destroy analyte-matrix interactions; and (iii) to enhance diffusion by swelling of the matrix. The second opportunity for selectivity concerns the density of the supercritical medium and the temperature (selectivity 2). After leaching of the sample, the extract is collected on a solid trap filled with an apolar or polar adsorbent, which can be selected according to the application (selectivity 4). The trap is then rinsed with a solvent, the polarity of which can be chosen to desorb the solutes of interest in a selective way (selectivity 3). Last but not least, an adsorbent can be added in the extraction thimble (selectivity 5). This facilitates the retention of unwanted polar solutes (fixation) and the enhancement of recoveries of apolar solutes (exaltation).

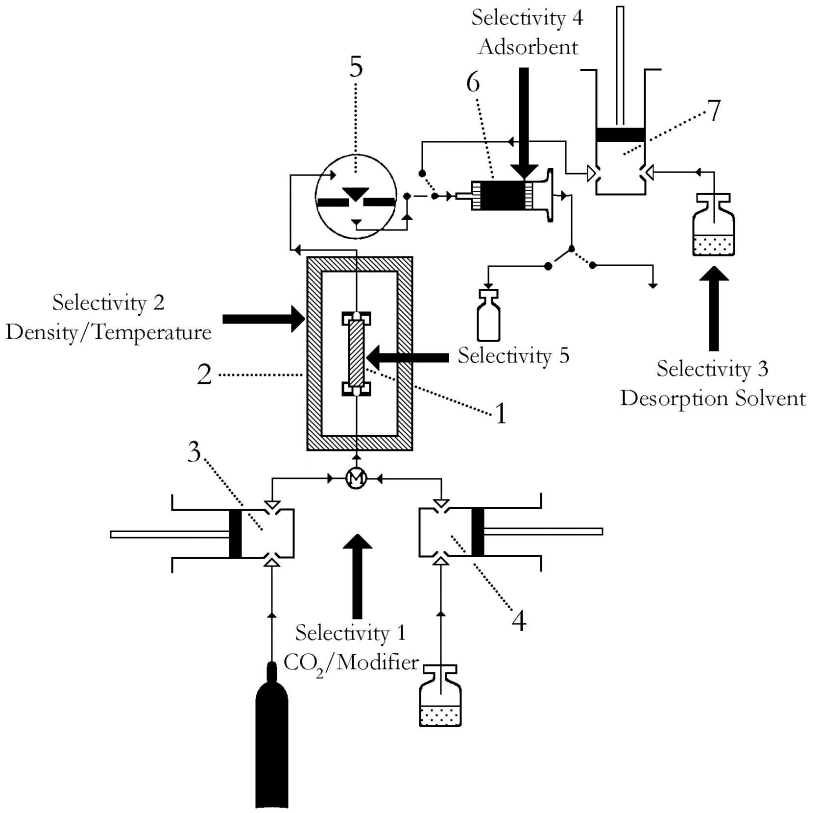

Figure 10 State of the art supercritical fluid extraction (SFE) instrument. 1, extraction cartridge; 2, oven; 3, CO_2 pumping module; 4, independent modifier pumps; 5, variable restrictor; 6, solid phase trap; 7, pump to deliver rinse solvents.

2.4.5 Accelerated Solvent Extraction (ASE)

ASE is a promising technique for the extraction of a large number of pollutants from solid matrices. It is similar to Soxhlet extraction but extraction now takes place at an elevated temperature and pressure. Under these conditions extraction processes are much faster and thus the speed of extraction is greatly increased compared to conventional methods. In environmental analysis, ASE is applicable to virtually all extractable organics from the priority pollutant lists[92] and generally provides good and consistent recoveries with short extraction times (15-30 min). Disadvantages of the procedure can be: the lack of sensitivity, which means that further clean-up steps are needed; and that the sample is diluted and often requires further concentration. For the extraction of PCBs from fish tissue, the selectivity problem can be overcome by adding

alumina to the extraction cell[93]. An extract that could be directly analyzed by GC-ECD was obtained. Large volume injection can eventually avoid the concentration step.

2.4.6 Microwave Assisted Solvent Extraction (MASE)

Microwave assisted solvent extraction (MASE) was invented and patented by J.R.J. Paré and J. Lapante[94]. It is based on the use of microwave radiation to enhance the extraction properties of solvents[95,96,97]. This objective is similar to ASE, which uses elevated temperatures above the normal atmospheric boiling point of the solvent for enhanced extraction performance. Two set-ups of MASE exist.

The first is the open cell, where extraction takes place at atmospheric pressure. Microwave radiation is focused on the vessel containing the extraction solvent. A reflux condensor ensures that escaping solvent vapors flow back into the extraction vessel. Budinski *et al.*[98] described the application of such a focused open-cell microwave system for the extraction of PAHs from soils and sediments. It was found that the extraction time and power of irradiation are not important parameters and that the classical solvent for Soxhlet extraction (dichloromethane) can also be used in MASE. Additionally, the humidity of the sample was identified as the most important variable. Optimal extraction was obtained when the sample contains 30% water. Quantitative recoveries were obtained for all PAHs under investigation in a 10 min extraction period.

The second MASE approach is that using a closed vessel. This approach uses, in addition to the microwave energy, also an increase in extraction temperature above the normal solvent boiling point similarly to ASE, also associated with a pressure increase. Tomaniová *et al.* evaluated this closed cell technique for the extraction of PAHs from plant materials. They found excellent performance, in terms of recovery, for pollen and spruce needles whereas poor performance of conventional ultrasonic extraction was observed. Optimal extraction was found to take place at 140ºC which is the maximum temperature the instrument allowed.

2.4.7 Liquid Extraction (Micro Sonication)

A method, which often provides good results for solid samples, is ultrasonic treatment with an organic solvent. Surprisingly, the same quantitative data were obtained for the extraction of PCBs from a certified sediment sample, SM 1939 (BCR, Brussels, Belgium) compared to an optimized SFE procedure[99]. A 0.5 g sample was extracted with 10 mL *n*-hexane in an ultrasonic bath for 30 minutes and, after filtration and concentration to 0.5 mL, was injected into a GC-ECD instrument. If large volume injection is applied, the concentration step can be omitted.

2.5 Conclusions

At this point, following the presentation of the most popular classical tools for sample preparation, some remarks towards the applicability of these techniques to certain analyte/matrix combinations will be presented. Particularly those areas that could use some improvement are addressed. As already mentioned in **Section 2.4**, solid samples will not be discussed in this thesis and therefore also not in this section.

For liquid samples, a variety of very good techniques is available. Today, the most important techniques are purge and trap (P&T, section **2.3.1**) for volatile compounds (up to decane) and solid phase extraction (SPE, section **2.3.4**) for semivolatiles (starting at octane). This means that these techniques should be combined if a total analytical profile of the sample is desired. The existence of an overlap region form octane to decane is in this respect helpful as it enables a comparison between SPE and P&T data in this region and might correct for some experimental errors. A somewhat larger area of overlap, though, would be desirable. Concerning the polarity of analytes, both techniques work well for a wide range of compounds, particularly for apolar to slightly polar compounds, but often fail for more polar compounds. P&T for example is very successful for volatile apolar compounds such as dichloromethane which can be stripped for the liquid phase with great ease. Polar compounds such as acetic acid, acetone or ethanol can only be purged from the liquid phase with very low recoveries and the determination of these compounds at trace levels in aqueous samples is even at present problematic. For SPE the same is true, but a much larger polarity range can be handled. On the instrumental side, some improvement in the analysis of liquid samples would be favorable as the instrumentation for automated (on-line) SPE-GC and P&T-GC is rather complicated. Simplification here would be an advantage. Also the introduction of a new technique with a wider ranger of application, in terms of both volatility and polarity, than P&T would be of great use.

For gaseous samples the situation is not so favorable as for liquid (aqueous) samples. The most successful and most widely employed techniques are those based on adsorptive trapping (**Sections 2.2.2** and **2.2.3**). The volatility range that can be handled on a single adsorbent material is rather small but by means of combining several adsorbents with different strengths into a single tube typical application ranges from C_2 to C_{15} or from C_5 to C_{22} can be obtained. One of the complicating factors in air analysis, however, is the low detection limit that is usually required, typically in the sub µg/L range. By employing liquid desorption techniques, as was discussed in the text, extremely large sample volumes are required, often leading to unacceptably long sampling times. Reduction of the sample volume by thermal desorption then seems a very attractive alternative. Unfortunately, the nature of adsorbents, which are often also used in other scientific areas for their catalytical activity, often prevents the accurate analysis of polar and/or reactive compounds. These can often be very easily trapped but react on the adsorbent to form either different compounds (artifact formation) or become permanently adsorbed. Both effects are clearly undesired. Adsorbent activity

always plays a more important role in thermal desorption than in liquid desorption, due to the high temperatures used. In this way, the simple translation of classical low sensitivity adsorption-liquid desorption techniques to the modern adsorption-thermal desorption is impossible. The sensitive and rapid enrichment of (medium-) polar compounds in gaseous samples is still a very difficult task. It is the aim of this thesis to offer introduce new, alternative materials to adsorbents to make facilitate the analysis of this particular class of compounds.

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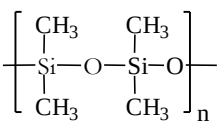
3 Sorptive Sample Preparation Methods

As was discussed in the previous chapter, a large part of the sample enrichment procedures currently available rely on the adsorption of the analytes of interest onto a suitable adsorbent. Unfortunately, their applicability for the enrichment of polar and/or high molecular weight compounds, especially coupled to thermal desorption, is limited. Polar solutes can easily be adsorbed but can also be readily converted into different compounds on the surface catalyzed by active surface groups[1]. High molecular weight compounds cannot be desorbed due to extremely strong interactions with the adsorbent and low volatility. As a solution, at least to a part of these problems, sample preparation techniques based on (polydimethylsiloxane) sorption will be described in this chapter. First, the basic principles of sorption will be outlined including the mechanism and potential advantages. Subsequently, two techniques for sorptive sample preparation namely, open tubular trapping (OTT) and solid phase microextraction (SPME) will be presented. Two new sorptive sample enrichment techniques, developed in the context of this thesis namely gum phase extraction (GPE) and stir bar sorptive extraction (SBSE) are described in detail.

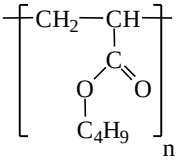
3.1 Principles of Sorption

Though the principles of sorption were briefly addressed in **Chapter 1**, a more detailed description of the advantages and limitations of sorptive materials is presented. Sorption materials are a group of polymeric materials that are above their glass transition temperature (T_g) at all temperatures used during the process of sampling - storage - desorption. This might seem a trivial requirement at first, the consequences of this are enormous. At temperatures above their T_g, polymeric materials no longer behave as pure solid materials but enter a gum-like, or even liquid-like, state with properties similar to those of organic solvents like diffusion and distribution constants. The most commonly used sorbent is the apolar polydimethylsiloxane (PDMS), a 100% methyl substituted siloxane polymer. Its structure is shown in **Figure 1**. The reason why this material is so popular is that it is very inert, reducing the risk of losses of instable and/or polar analytes by irreversible adsorption or by catalytic (surface) reactions. Retention data can be found in the literature for numerous compounds. Additionally, PDMS synthesis is relatively simple and leads to very reproducible

properties. Moreover, its degradation products are very well known and can easily be identified with the use of a mass spectrometer. These advantages and the lack of availability of other materials as stable, reproducible and inert as PDMS account for its widespread use in sorptive sample preparation techniques. Alternative materials, such as the polar poly(butyl)acrylates, are used for more polar analytes that have a low affinity for PDMS and consequently do not partition very well into this material. Mechanical stability of sorbents is usually provided by means of crosslinking which ensures that the extraction phase will retain its shape, even at elevated temperatures.



polydimethylsiloxane



polybutylacrylate

Figure 1 Structure of commonly applied sorbents for sample enrichment. Glass transition temperatures[2]: polydimethylsiloxane (-125°C) and polybutylacrylate (-54°C).

It is important to realize that using sorbents, preconcentration of analytes occurs by *sorption* of the analytes *into* the polymeric liquid phase instead of *adsorption onto* a solid adsorbent surface. Different sorptive enrichment procedures exist that are based on different approaches and geometries in which the sorbent is used for sample extraction. Two important techniques, that have been well-described in the literature, can be discerned. The first, open tubular trapping, is the oldest technique and employs a (thick film) capillary GC column for sampling. This technique will be discussed in **Section 3.2.** The second technique, solid phase microextraction (SPME) is based on a PDMS coating on the needle of a syringe-like device. This innovative approach is increasingly being used and discussed in **Section 3.3**.

3.2 Open Tubular Trapping

Though open tubular traps coated with adsorbent particles have been used in the past[3,4], focus has been on sorbent coated capillaries due to their favorable characteristics similar to those of capillary GC columns. In some cases short capillary traps, that can be desorbed in the injector of a gas chromatograph such as the PTV or split/splitless injector, were used[5]. More commonly coated lengths of fused silica columns with an inner diameter of 0.3-0.5 mm are employed. A typical film thickness of 10-15 μm is used[6] but in some cases high capacity open tubular traps with extremely thick films of 100 μm[7] or even 165 μm[8] are preferred. Films up to 15 μm can still be prepared in short columns by procedures commonly employed for the preparation of thick film capillary

columns[9]. However, the use of a low molecular weight methyl siloxane polymer was suggested by Bicchi *et al.* as it allows the preparation of 15 μm films in capillary traps up to five meter in length[10]. Immobilization of the stationary phase is carried out by the addition of dicumyl peroxide to the coating solution. Film stability is further enhanced by treatment with azo-*t*-butane. Both agents effect crosslinking upon heating. It was found that in order to get a perfectly immobilized and stable film, conditioning during one week at 250ºC was required. In case of thicker films, classical coating techniques will not be suitable, as the deposited film will quickly rearrange into droplets due to drainage and Rayleigh instability[11]. An approach that allows the preparation of very thick film traps and circumvents the problems associated with dynamic coating was described by Roeraade *et al.*[12,13]. Fixation was carried out by heat-accelerated crosslinking of a suitable pre-polymer where the column is pulled through an oven at the same speed as the evaporation of the coating liquid. In this way, stable films up to 100 μm could be obtained. For the production of traps with even thicker films, an innovative process was described by Burger *et al.*[8] Instead of using coating solutions or pre-polymers, these authors started with (crosslinked) polydimethylsiloxane tubing (0.65 mm outer diameter, O.D. and 0.3 mm inner diameter, I.D.) which was stretched and subsequently submerged into liquid nitrogen. At this temperature the tubing loses its flexibility and will remain fixed in the stretched position. While still being submerged in liquid nitrogen, the tubing is pushed in a fused silica capillary with an I.D. of 530 μm and is subsequently removed from the liquid nitrogen. Equilibration at room temperature causes the tubing to shrink in length and expand in diameter to become fixed inside the capillary. This allows for the production of very thick films. The advantage of this approach is that a very stable capillary is obtained with a low background profile and favorable sorption characteristics. The maximum length of an open tubular trap prepared in this way was found to be one meter as longer traps will require excessively large liquid nitrogen containers. In almost all cases, open tubular traps are used in the breakthrough mode, where complete trapping of all analytes is ensured. Sampling is stopped prior to saturation of the stationary phase with the least retained compounds to be analyzed.

3.2.1 Gaseous Samples

Open tubular traps have been applied to the analysis of gaseous samples by many groups[5,6,7,8,14]. Most commonly, traps with a length of up to 1-3 meter are used for the retention of gaseous analytes. Sampling is usually done by means of a vacuum pump which is applied at the outlet of the open tubular trap. The reverse, pushing the sample through a trap by means of a pump is not a very good approach since this can easily lead to contamination of the sample by compounds released by the pump or changes in the composition of the actual sample by (ad)sorption of analytes inside the pump. The limitation of sampling by sucking implies that the restriction by the open tubular trap should not be too large, otherwise a very low flow rate will result leading to excessively long sampling times. On the other hand, a long open tubular trap is desired to have a

high capacity (expressed as K^*V_E, see **Chapter 2 Equation 4**), especially for highly volatiles. In practice, an optimal compromise between sample capacity and sampling speed has to be found.

Open tubular traps were successfully employed for a range of gaseous samples including wine headspace[15], plant volatiles[6,10,16], pheromones[17] and environmental air samples[13,18]. For a wide variety of compounds such as alkanes, aromatics, esters and alcohols good performance was observed at trace concentration levels illustrating the favorable properties of sorbents. Particularly for gaseous samples, the use of very thick film traps seems essential as sufficient trapping capacity from samples up to *ca.* one liter is provided by these traps, even for more volatile analytes. The disadvantage of the use of films up to 200 μm is that desorption is slow and cryofocusing of the thermally released analytes prior to injection onto the analytical capillary column becomes essential. Cryotrapping can be performed either in a separate device or on-column[19] with liquid carbon dioxide or nitrogen resulting in full utilization of the analytical column's efficiency.

The use of open tubular traps for the enrichment of samples for high-speed narrow-bore capillary gas chromatography was described by Pham-Tuan *et al.*[20] Using equilibrium sampling (also described in **Chapter 6**), the open tubular trap was fully saturated with the sample prior to thermal desorption. Subsequently, only a small part (time sliced injection) was injected into the analytical column. This allows the use of open tubular enrichment without the need for cryotrapping or other focusing techniques. This is essential for field applications of (micro) GC's, where cryofocusing is very impractical.

Using open tubular traps coated with 80 μm PDMS films, Blomberg and Roeraade[21] demonstrated the viability of OTT for the fraction collection of compounds eluting from a capillary GC column. Over extended time periods and from multiple GC runs compounds were trapped quantitatively on the OTT. Recovery of the collected volatiles was accomplished by either thermal desorption or by extraction of the OTT with pentane. Complete recoveries could be obtained by either method.

3.2.2 Liquid Samples

Open tubular trapping can be an attractive technique to classical techniques for the enrichment of aqueous samples. The main advantage of OTT over alternative techniques is that complete water removal from the trap can be obtained by purging with a short plug of gas through the capillary. Long drying times, such as in solid phase extraction on cartridges or disks, are not required. The main disadvantage of OTT is the low retention power for the trapping of compounds from aqueous samples. This is particularly the case for more polar compounds that do not partition strongly into the stationary phase. Additionally, due to the low diffusion coefficient of compounds in the

liquid phase, the flow rate during sampling is rather critical and only very low flow rates can be tolerated[22]. An HPLC pump can effectively be used to deliver the sample contamination free to the capillary trap so that pressure limitations do not play a role as was the case for gaseous samples.

Though open tubular traps with films below 15 μm can be successfully applied, low breakthrough volumes often result due to the low amount of stationary phase present. The use of thick film traps[23], with films up to 165 μm, seems more promising as they allow the retention of analytes from larger sample volumes. Thinner film traps could be used for sample volumes up to 2.5 mL if swelling of the stationary phase with chloroform was applied. This was demonstrated for analytes ranging from the apolar toluene to the more polar dimethylphenol and chloroaniline by Mol *et al.*[24]. Kaiser and Rieder[25] described an OTT technique using the same capillary for both analyte enrichment and for the actual chromatographic separation. This was achieved by backflushing the capillary between these two steps and cryotrapping the analytes at the head of the column.

3.3 Solid Phase Microextraction

Solid Phase Microextraction (SPME) is a powerful and innovative extraction procedure introduced by Arthur and Pawliszyn in 1990[26]. SPME employs a fused silica fiber with an outer diameter of typically 150 μm which is coated with an (ad)sorbent layer of 5 up to 100 μm. This fiber can simply be inserted into a gaseous or aqueous sample for analyte extraction and into the heated zone of a gas chromatographic injector for desorption[27]. The small size of the SPME fiber and its cylindrical shape allow to fit the fiber in the needle of a syringe-like device. The SPME fiber is attached to the syringe plunger and this set-up can be used to either expose the fiber for extraction or desorption or to retract the fiber for storage and piercing of injector or sample vial septa. The latter is necessary as the coated fused silica fiber has a very low mechanical strength and cannot as such be directly inserted through septa.

The schematics of the SPME device and the SPME extraction process are shown in **Figure 2**. The process is build up on six basic steps and these are followed from left to right. First, the SPME device is used to pierce the septum of the sample vial. Second, the clean and conditioned SPME fiber is exposed to the sample under stirring. This static extraction condition is maintained until equilibrium between gaseous or liquid sample and the fiber is reached. Third, the fiber is again retracted in the SPME needle and the SPME assembly is removed from the sample vial. For desorption, the SPME needle is inserted through the septum of a GC injector, typically a split/splitless or PTV injector. In the hot injector chamber, the SPME fiber is again exposed and the analytes are thermally desorbed. Finally, upon completion of the thermal desorption step, the SPME fiber is retracted and the SPME device is removed from the analytical instrument.

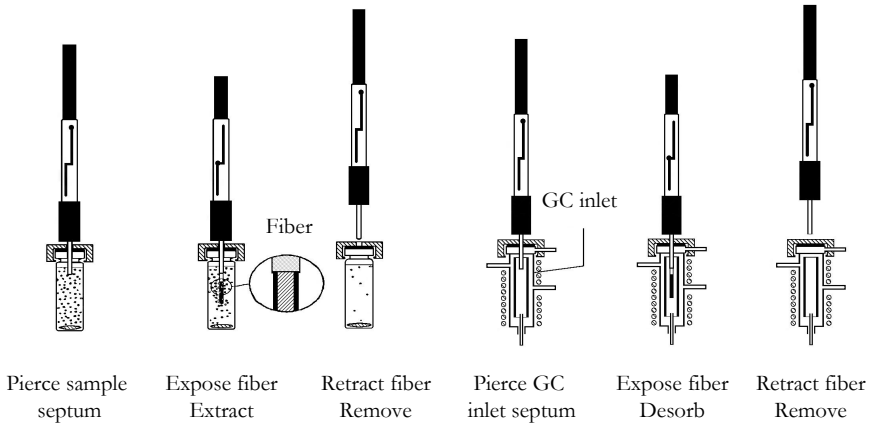


Figure 2 Schematic description of the SPME extraction process.

An interesting feature of SPME extraction is that partitioning constants between sample and fiber can be estimated from literature data, at least for the PDMS sorbent. This was shown by the group of Pawliszyn for both gaseous[28] and aqueous[29] samples. Linear temperature programmed retention indices[30] were used for the estimation of equilibrium constants between the PDMS fiber and a gaseous sample. This is based on the assumption that the behavior of solutes in a gas chromatographic column is similar to that of the same solutes in the gas phase/SPME coating equilibrium. By comparison of retention indices determined on a capillary GC column and with the SPME extraction device, the validity of this concept was confirmed. For the determination of water-PDMS distribution constants, a combination of the gas/PDMS equilibrium constant and Henry's law (water/gas equilibrium) was made to yield a value for the water/PDMS distribution coefficient[31]. This approach can be applied for many volatile solutes, for which a Henry constant is readily available. For semi-volatiles, the water/PDMS distribution constant may be approximated by the octanol water coefficient (this thesis, **Chapter 5**). It is important that these approaches are valid not only for headspace SPME but also for direct SPME (where the fiber is actually dipped into the water solution). Identical extraction coefficients are obtained in both cases.

Numerous applications for the determination of pesticides and other priority pollutants in aqueous samples have been described in the literature and some are listed in **Table 1**. Detection limits have been reported over a very wide concentration range, from as low as 0.01 ng/L (ppt) up to high concentration detection limits of 9 mg/L (ppm). This is partly due to the difference in analytical systems used, such as the low sensitivity FID and the high sensitivity ECD, ion trap detector (ITD) and other

forms of mass spectrometry. More important, the polarity of the target compounds also differs widely form very apolar (PAHs, PCBs) to polar (some pesticides) which also has a strong influence on the extent to which analytes partition from the polar water matrix into the SPME fiber. Fortunately, most compounds can be monitored below the desired 1 μg/L (ppb) level for surface water. The limit for drinking water analysis (0.1 μg/L), on the other side, cannot be reached for a large group of analytes, not even if the high sensitivity GC-ECD or GC-MS is applied. This lack in sensitivity is the most important disadvantage of SPME and is partly caused by the fact that sorbents feature significantly lower analyte capacity than typical adsorbents. Add to this the extremely low amount of sorbent coated onto the SPME fiber, up to 0.5 μL, and overcoming this sensitivity problem seems hard to achieve. As a result, sorption SPME is today, almost 10 years after its introduction, still not as widely accepted as deserved despite its clear instrumental advantages, simplicity and low cost.

In order to improve the capacity of SPME fibers, several "new" SPME coatings have been introduced[32,43]. These include materials such as copolymers of PDMS with divinylbenzene (PDMS/DVB) and Carbowax (PDMS/WAX) and physical mixtures of PDMS with adsorbents such as Carboxen. Though these materials do indeed exhibit a significantly increased capacity for many solutes, an important drawback is that the true sorption mechanism is lost as these materials are no longer pure polymeric sorbents. For example, Carbowax is below its glass transition temperature (*ca.* 70°C) and Carboxen itself is an inorganic adsorbent. Application of these materials in static sampling is likely to result in irreproducible results as adsorption of matrix compounds (salts, humic acids, proteins *etc.*) will compete with the target analytes for available adsorbent sites. This complicates reliable quantitation of SPME procedures.

In a comparative study on the extraction of benzodiazepines from biological fluids[33] several SPME fibers were compared, namely PDMS, PDMS/DVB, Acrylate and WAX/DVB. It was found that the performance of the PDMS fiber for the extraction of the polar benzodiazepines was very poor as these analytes do not partition strongly into the apolar PDMS bulk. The other fibers, which are more polar in nature, were able to extract a significantly higher amount of analyte. The highest recoveries were observed on the WAX/DVB fiber, closely followed by the Acrylate fiber which yielded recovies at least half that of the WAX/DVB fiber for all compounds. The authors preferred the WAX/DVB fiber for its higher recoveries and obtained detection limits in the order of 0.02-0.1 mg/L (ppm) from 1-2 mL samples using an ion trap mass spectrometer. Though the addition of salt was found to have a positive influence on the recoveries (salting out effect), the influence of (high concentrations of) other matrix compounds (*e.g.* proteins) was not investigated though this is also likely to cause a pronounced effect. If the acrylate sorbent phase would have been used, these effects would have played a much less important role and therefore, the acrylate fiber might more likely be preferred for its favorable sorption characteristics.

Table 1 Overview of the performance of typical SPME extraction procedures for pesticides and other priority pollutants from aqueous samples.

Compounds	SPME fiber	Sample Volume	Technique	Detection Limit
VOC, VHOC[34]	PDMS, 100 μm	50 mL	GC-ITD	0.001-1 μg/L
PAHs, PCBs[35]	PDMS, 15 μm	40 mL	GC-ITD	low ng/L
N-herbicides[36]	Acrylate, 95 μm	4 mL	GC-FID GC-NPD GC-ITD	0.2-20 μg/L 0.01-6 μg/L 0.01-15 ng/L
N,P-Pesticides[37]	PDMS, 100 μm	4 mL	GC-NPD GC-ITD	0.02-37 μg/L 0.01-8 μg/L
Cl-pesticides[38]	PDMS, 100 μm	35 mL	GC-FID GC-ECD GC-MS	2-9000 μg/L 0.05-9 μg/L 0.02-800 μg/L
P-insecticides[39]	Acrylate, 85 μm	4 mL	GC-FID GC-NPD GC-ITD	0.2-5 μg/L 0.01-0.5 μg/L 0.002-0.1 μg/L
P-pesticides[40]	PDMS, 100 μm Acrylate, 85 μm	3 mL	GC-NPD	0.002-0.1 μg/L 0.001-0.1 μg/L
Triazine herbicides[40]	Acrylate, 85 μm	3 mL	GC-NPD	0.01-0.09 μg/L
2,6-dinitroaniline herbicides[40]	Acrylate, 85 μm	3 mL	GC-NPD	0.008-0.06 μg/L
P-pesticides[41]	PDMS, 100 μm Acrylate, 85 μm	3 mL	GC-NPD	0.02-0.5 μg/L 0.006-0.1 μg/L
Cl-pesticides[42]	PDMS, 100 μm	110 mL	GC-ECD	0.3-11 ng/L
Anilines[43]	PDMS/DVB, **	5 mL	GC-FID	0.18-3.17 μg/L
Phenolic compounds*,[44]	Acrylate, 95 μm	40 mL	GC-FID GC-MS	0.6-30 μg/L 0.01-1.6 μg/L

Abbreviations: VOC, volatile organics; VHOC, volatile halogenated organics compounds; PAHs, polyaromatic hydrocarbons, PCBs, polychlorinated biphenyls, ITD, ion trap detector; FID, flame ionization detector; NPD, nitrogen phosphorous detector; ECD, electron capture detector. *Phenols were derivatized with acetic anhydride prior to analysis. **No film thickness was mentioned.

Alternatively to SPME sampling directly into the aqueous phase, SPME may also be employed for the extraction of compounds present in the sample's headspace, headspace-SPME. This was described from a theoretical viewpoint by Zhang an Pawliszyn[45] and Ai[46]. In headspace-SPME, volatilized analytes are extracted and concentrated in the SPME coating and this can have several advantages over direct SPME extraction in the liquid phase. For analytes that partition strongly into the SPME fiber equilibration times can be substantially reduced due to higher diffusion coefficients in the gaseous phase compared to the liquid phase[45]. Using headspace-SPME samples containing high molecular weight or particulate material can be analyzed with greater accuracy. Additionally, fiber lifetime is extended as these unwanted

compounds do not come into contact with the fiber. This was demonstrated for the analysis of serum samples by Namera *et al.*[47] and for urine samples by Fustinoni *et al.*[48]. In both cases rapid equilibration was observed in conjunction with a high reproducibility and detection limits in the low μg/L to ng/L level depending on analyte polarity and detector used.

Llompart *et al.*[49] compared headspace-SPME to conventional headspace analysis (at 95°C) and liquid-liquid extraction for a range of (semi-)volatile compounds. It was found that headspace-SPME gave similar quantitative results as both conventional techniques, however, for most compounds a large increase in sensitivity was obtained.

In a study into wine bouquet components using headspace-SPME, de la Calle-Garcia *et al.*[50] used an acrylate fiber for the extraction of terpenoids and related compounds. Generally good performance was observed but it was noted that the extraction recovery depended strongly on the number of extractions performed on the same fiber. During the first 35 headspace-SPME extractions peak areas decreased by as much as a factor 4, which complicated quantitation. This problem is still not well explained but could be overcome by the use of internal standards.

Headspace-SPME is not only a successful approach for the analysis of gaseous and liquid samples but can also be applied for the analysis for solid samples or even air samples directly. Fromberg *et al.*[51] applied headspace-SPME for the determination of a range of chlorinated and nitrated aromatics in soil. It was found that analyte recoveries depend on many parameters including the soil humidity and the type of soil. It was found that matrix effects, especially those determined by the organic carbon content, are so large that quantitation of unknown samples is impossible. Additionally, equilibration times were very large for high MW analytes that partition strongly into the SPME fiber but only diffuse slowly from the sample through the gas phase to the fiber. Equilibration times up to 10 hours were found for certain analyte/matrix combinations. Only low MW, apolar analytes could be quantitated in certain unknown soils. Other applications of headspace-SPME include the analysis of monoterpenes from conifer needles[52], organic acids in tobacco[53], volatiles in apple fruit[54], terpenoids in herb based formulations (including drops)[55] and the analysis of methylmercury in fish tissue[56]. In general, long equilibration times are found for solid samples, except for volatiles with difficult quantitation for many analytes. SPME can therefore be considered as a tool for "fast" sample screening but the generation of accurate quantitative data is often difficult. An approach to circumvent the long equilibration times in the headspace SPME extraction of solids was proposed by Moens *et al.*[57]. These authors developed a method for the simultaneous determination of organomercury, -lead and -tin compounds in sediment samples. The approach is based on liberation of the target analytes from the solid matrix by ultrasonic liquid extraction followed by liquid phase derivatization. Finally the analytes were sorbed into a PDMS coated SPME fiber and analysis was performed on a CGC-ICPMS instrument.

Detection limits at the ng/L level were reported while the total analysis time, including the gas chromatographic determination, was in the order of 75 min.

SPME with PDMS fibers can also be employed for direct air sampling[27] using equilibrium constants derived directly from GC retention data. In an application of SPME for the analysis of volatiles in human breath[58] several compounds including acetaldehyde, acetone, ethanol and isoprene were monitored. Most compounds reached equilibrium within 30 s on the various SPME fibers and sampling times could be as short as 10 s under optimized conditions which enables rapid sampling and monitoring.

So far the discussion around SPME has been limited to gas chromatography. However, coupling of solid phase microextraction to liquid chromatography[59] or even LC-MS[60] has been shown to be an alternative to GC, particularly for polar compounds that cannot be analyzed by GC such as polar pesticides[61] or inorganic and/or charged substances such as metal ions[62]. The latter were converted into crown ether complexes prior to extraction. Especially the applicability of SPME to the analysis of polar pesticides seems rather difficult as these analytes will exhibit low partitioning constants into the SPME fiber coatings. Low recoveries are observed resulting in detection limits above the 1 μg/L level for most compounds on a conventional 4.6 mm I.D. column and above the 0.5 μg/L level on a miniaturized column with an I.D. of 1.5 mm[61]. These authors propose the development of stronger (adsorbent-type) coatings but this will result in loss of the sorption behavior and advantages and is not to be recommended.

SPME relies on an equilibrium between the sample and the sorbent coated fiber. To increase the speed at which this equilibrium is reached, the sample is almost always stirred during extraction. Though this is a rather straightforward approach, it is not ideally suited for automated sampling due to the large amount of stir bars needed, the manual recovering thereof and possible carryover problems. Alternative mixing techniques such as vibration of the SPME fiber was investigated in the work of Eisert *et al.*[63]. It has to be noted however, that at present more than 99% of all SPME experiments are performed manually with stir bar agitation.

3.4 Summary Sorptive Techniques – Advantages and Limitations

In **Sections 3.2** and **3.3**, open tubular trapping and solid phase microextraction have been described as the two most successful sorptive enrichment techniques available today. Despite the clear advantages of sorption materials, OTT and SPME suffer from several pronounced disadvantages, originating primarily from the geometry in which the sorbents are applied in these techniques. In both cases, this strongly restricts the application of sorption materials. In order to evaluate this more closer, a distinction between gaseous and aqueous samples has to be made in this respect.

Aqueous samples have the advantage that they are easily contained in a glass bottle, vial or other storage medium if care is taken to avoid analyte adsorption on inner walls. This enables the use of both static (SPME) and dynamic (OTT) sampling. SPME has already proven to be rather successful for aqueous samples but suffers from a lack of sensitivity caused by the limited amount of sorbent (0.5 μL) on the fiber and the weak nature of the sorption process. Open tubular trapping can employ columns with a large amount of stationary phase but due to the slow analyte diffusion in the liquid phase, only very low sampling flow rates are allowed resulting in long sampling times. Moreover, complicated equipment such as pumps, valves and a second GC oven for thermal desorption is needed for operation of the open tubular traps. This strongly prevents their widespread use.

Gaseous samples are, contrary to aqueous, not easily contained since they are much less stable and large sample volumes (sometimes up to several 100 liters) are often needed to achieve adequate sensitivity. Therefore, in many cases static sampling (*e.g.* SPME) is not a very good option. Additionally, accurate control of the flow and mass transfer process around the fiber in the gaseous phase seems rather difficult to achieve. Open tubular trapping seems much more promising but as the sample cannot be pumped through the column, a tradeoff between capacity (long trap) and sampling speed (short column) has to be made. To retain sufficient trapping capacity, typical sampling flow rates in open tubular trapping are below 15 mL/min. Open tubular trapping is therefore also limited by the capacity of the sorption phase, resulting in severe practical limitations, primarily in terms of sampling speed.

3.5 Conclusion

Though sorption materials exhibit clear advantages in terms of inertness, stability and versatility, the presently available techniques OTT and SPME cannot fully exploit these advantages due to severe sensitivity restrictions and practical limitations. New approaches for sorptive sample enrichment should be able to overcome these problems by applying at least 50-100 μL of sorbent material without the introduction of any flow and/or sampling restrictions. Two new techniques, developed within the context of this thesis, that circumvent existing problems associated with OTT and SPME are presented. **Chapters 4**, **5** and **6** describe the first, gum phase extraction (GPE), a dynamic sorptive sampling technique using a packed bed consisting of up to 400 μL of pure PDMS particles. **Chapter 7** describes the second technique, stir bar sorptive extraction which is a static extraction technique, similar to SPME, but employing up to 200 μL of (PDMS) sorbent. Since it is a static technique, it is most suited for aqueous samples. It is important to note, at this point, that both techniques employ roughly the same amount of PDMS sorbent. The capacity of the sorbent in both techniques, primarily determined by the volume of sorbent used and the distribution constant ($K*V_E$) is equal. Hence the sensitivity of both techniques are approximately the same.

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4 Gum Phase Extraction for Gaseous Samples

In this chapter, gum phase extraction will be described as a new and powerful sample enrichment technique for gaseous samples. Liquid samples will be discussed in **Chapter 5**. Based on a packed bed of pure and homogeneous sorbent particles, gum phase extraction, particularly in combination with thermal desorption, provides a rapid, sensitive and reliable alternative to classical sample enrichment techniques based on packed adsorbent beds.

4.1 Characteristics and Performance of Gum Phase Extraction (GPE)*

4.1.1 Summary

In this part the determination of volatile and semi-volatile organic components in air and gaseous (headspace) samples with the primary focus on polar analytes is described. Samples were analyzed by preconcentration on different (ad)sorbents followed by thermal desorption and analysis by capillary gas chromatography. The performance of a cartridge filled with 100% polydimethylsiloxane (PDMS) particles was compared to the performance of adsorbents like Tenax TA and Carbotrap 300. Though the PDMS phase is apolar it showed adequate retention for both polar and apolar components. The blank runs of the PDMS trap were significantly better than those of most adsorbents and did not deteriorate as was the case with all adsorbents investigated. With respect to trapping efficiencies, the PDMS phase performed better for most of

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Sorption Tubes Packed with Polydimethylsiloxane: A New and Promising Technique for the Preconcentration of Volatiles and Semivolatiles from Air and Gaseous Samples, E. Baltussen, F. David, P. Sandra, H.-G. Janssen and C. Cramers, Journal of High Resolution Chromatography 21 (1998) 333

the analytes under investigation compared to the adsorbents. For a range of analytes including triethylamine, butanone, diacetyl, nicotine and acetic acid the PDMS phase performed exceptionally well whereas all adsorbents showed unsatisfactory performance. The packed PDMS traps were employed for the determination of organic acids, polyaromatic hydrocarbons (PAH's) and nitro-PAH's in air and for the analysis of the headspace of cacao and hop.

4.1.2 Introduction

Most of the analytical procedures presently used for the preconcentration of volatile organic compounds (VOCs) in air and gaseous samples are based on adsorption of the analytes of interest on a suitable adsorbent material[1,2,3] followed by either liquid or thermal desorption. In the thermal desorption method, the desorbed analytes are re-focused in a cold trap prior to transfer onto the analytical column. Common adsorbents include carbon-based materials such as activated carbon and carbon molecular sieve[4,5] and porous organic polymers such as Tenax and Chromosorb[6]. These are all relatively strong adsorbents giving excellent performance for apolar volatiles. Unfortunately, their application to the analysis of polar solutes is rather limited, as will be shown in this chapter.

Lack of retention during sampling is generally not the problem, (polar) analytes are strongly retained on most adsorbents. This strong retention, however, often precludes rapid and complete desorption resulting in low recoveries and a severe risk of carryover. Moreover, the long residence times of the analytes on the hot and active adsorbent surface during desorption might result in reactions of the analytes, of the analytes with the surface itself or of the analytes with other adsorbed species. These reactions can result in permanent adsorption and/or in artifact formation which are clearly undesired effects. Another complicating factor when working with adsorbents is that the organics which have to be determined can occasionally be formed due to degradation reactions from the adsorbent itself. This is for example the case with Tenax where acetophenone and benzaldehyde are easily formed and with Chromosorb leading to styrene and a-methylstyrene.

From the above it is clear that an alternative to the classic adsorbents is necessary for adequate handling of samples containing polar solutes. Several years ago, an alternative method for the preconcentration of organic components from air was developed by Burger and Munro[7], Bicchi *et al.* [8,9,10] and Roeraade and Blomberg[11]. These authors used an open tubular trapping column (OTT) coated with a thick film of a GC stationary phase for sample enrichment. In this method, preconcentration occurs by *sorption* of the analytes *into* the bulk of the liquid phase instead of *adsorption onto* an active surface. The most commonly used GC stationary phase for this purpose is 100% polydimethylsiloxane (PDMS). Preconcentration by sorption has some clear advantages over adsorption onto an active surface. In the sorption mode, polar solutes desorb fast

at low temperatures due to a weak interaction of the analytes with the PDMS material. Moreover, PDMS is much more inert than a standard adsorbent minimizing the losses of instable and/or polar analytes. Another advantage of the PDMS phase is that its degradation products can be easily identified with the use of a mass spectrometric detector as they generate characteristic silicone mass fragments. Peaks originating from the sorbent can therefore not be mistaken as being from a sampled analyte. For practical purposes, the advantages of PDMS are that, since the analytes are retained in the bulk of this material, retention of the solutes on this phase is more reproducible than in the case of adsorbents. For example, a high water content of the gas sample does not affect retention of the analytes. Also, poor batch to batch reproducibility as is sometimes encountered when working with adsorbents is absent in the case of PDMS.

Despite several clear advantages of open tubular traps over classic adsorbents, they never gained widespread acceptance. This is due to several limitations of open tubular traps. Open tubular traps have only a limited sample capacity because only a small amount of stationary phase is present per unit of trap length. For adequate retention, long traps are necessary (up to several meters). Since the air sample has to be sucked through the trap by applying a vacuum to the outlet, open tubular traps allow only low sampling flow rates (typically in the order of 10 ml/min). Because an air volume of 0.5 - 5 liters is generally required for adequate detection limits, this implies that long sampling times are necessary. An other disadvantage of OTT's is that an additional GC oven is required for thermal desorption of the OTT with efficient refocusing of the enriched analytes.

In an attempt to overcome the problems associated with OTT's, Ortner and Rohwer[12] designed a multi-channel OTT. This short trap contains several channels in parallel and should tolerate significantly higher flow rates since the pressure drop over the trap is very small. This device extends the useful flow rate regime up to only 15 ml/min. Due to the unfavorable geometry of the trap, at higher flow rates, the number of plates generated by the trap becomes too low to ensure quantitative trapping. On the instrumental side, the multi-channel OTT has the advantage that it can be desorbed in a standard GC injector.

In this section, the applicability of a packed bed containing 100% polydimethylsiloxane (PDMS) particles for use as a sorption device in the enrichment of gaseous samples is investigated. The analytes from a gaseous sample are first trapped on the PDMS preconcentration trap. Subsequently the trap is heated and the analytes are thermally desorbed onto the GC column. A theory model is derived that allows the prediction of breakthrough volumes from gas chromatographic retention data and trap properties. The applicability of the system is demonstrated by the analysis of various environmental and industrial samples. The packed PDMS traps have the same advantages as open tubular traps with respect to inertness and thermal desorption characteristics but they allow sampling flow rates as high as 2.5 l/min. The performance of packed PDMS traps has been compared to that of common adsorbents like

Tenax TA, Carbotrap 300, Chromosorb 101 and Lichrolut EN. The performance of PDMS is illustrated with several examples.

4.1.3 Theory

Sampling in (ad)sorption/thermal desorption systems for air enrichment is usually performed in the breakthrough sampling mode. In this sampling mode, air is sampled through the preconcentration device until the most volatile compound is no longer quantitatively retained by the sorbent and starts to elute (or break through) from the trap. This implies that the breakthrough volume of the trap, *i.e.* the volume of air that can be passed through the trap before breakthrough starts to occur is determined by the most volatile compound. Less volatile compounds are still far from breakthrough. The potentially higher sensitivity for these solutes cannot be achieved due to breakthrough of the least volatile analyte. The sorption characteristics of PDMS packed sorption tubes are addressed.

The required minimum breakthrough volume can be estimated from the desired concentration detection limits and the detector sensitivity. As an example, for the determination of pesticides in air, a minimum detectable concentration of at least 1 ppt (1 ng/m^3) is desired[13]. If the flame ionization detector (FID) detector is used, roughly 0.5 ng of solute is required for accurate peak recognition and integration. This implies that 500 liters of air needs to be sampled onto the trap, *i.e.* the breakthrough volume should be more than 500 L. From the flow rate applied, the total sampling time required can be calculated. If air is sampled at a 'normal' flow rate of 100 mL/min, sampling 500 L of air would take 5000 min, which is, of course, unacceptably long. The possibility of using high sampling flows (up to 5 L/min) was investigated.

In order to fully apprehend the possibilities of packed PDMS sampling tubes it is necessary to investigate the retention volume and especially the breakthrough volume of compounds on these traps. According to the theory described by Lövkvist and Jönsson[14] the breakthrough volume of an enrichment trap (V_b, allowing 5% breakthrough) is given by:

Equation 1

$$V_b = V_o \times (1+k) \times \left(0.9025 + \frac{5.360}{N} + \frac{4.603}{N^2} \right)^{\frac{1}{2}}$$

where: V_0 is the trap dead volume, k the capacity factor and N the plate number of the trap. V_0 is a trap specific parameter, the capacity factor is a thermodynamic parameter depending on the solute, trapping material, phase ratio of the trap and on the temperature. The plate number is a kinetic parameter that depends on the flow rate in the trap and on solute and trapping material properties.

The breakthrough level is defined as the amount of analyte that has eluted from the trap relative to the amount of analyte that has been sampled. If the sampling flow rate is kept constant, the breakthrough level is given by:

Equation 2

$$b = \frac{\text{total amount of analyte eluted from trap}}{\text{total amount of analyte sampled}} = \frac{\int_0^t C_o(t)dt}{\int_0^t C_i(t)dt}$$

where $C_o(t)$ is the concentration in the gas leaving the trap outlet and $C_i(t)$ is the concentration in the gas entering the trap. The capacity factor can be calculated by:

Equation 3

$$k = \frac{K}{\beta}$$

In this equation ß is the phase ratio of the trap which can be determined experimentally or can be calculated as will be demonstrated later. For alkanes the values for the equilibrium distribution coefficient (K) can be obtained from the equation published by Millen and Hawkes[15]:

Equation 4

$$K = \exp\left(\frac{950 + 905 \times C}{1.987 \times T} - 0.59 \times C - 1.8\right)$$

Here T represents the absolute temperature and C is the carbon number of the alkane. The last parameter in **Equation 1**, N, can be calculated from the well-known Knox equation[16,17]:

Equation 5

$$h_r = 3v^{1/3} + \frac{1.5}{v} + 0.05v$$

with:

Equation 6

$$h_r = \frac{H}{d_p} = \frac{L}{N \times d_p}$$

Equation 7

$$v = \frac{u \times d_p}{D_m}$$

where: H is the plate height, d_p is the particle diameter, u is the linear velocity during sampling, L is the length of the packed bed and D_m is the diffusion coefficient in the gas phase. A method for the estimation of D_m values has been published by Fuller *et al.*[18].

From **Equation 5** it can be seen that at high sampling velocities (*i.e.* high sampling flow rates) the reduced plate height will be very high and hence the plate number will be very low. Using **Equation 1**, the breakthrough volume of a trap can be calculated as a function of the plate number. **Figure 1** shows the calculated breakthrough volume as a function of N for a trap with a dead volume of 1 mL and a solute with a capacity factor of $1*10^6$. From **Figure 1** it is clear that even at very low plate numbers reasonable breakthrough volumes can still be obtained.

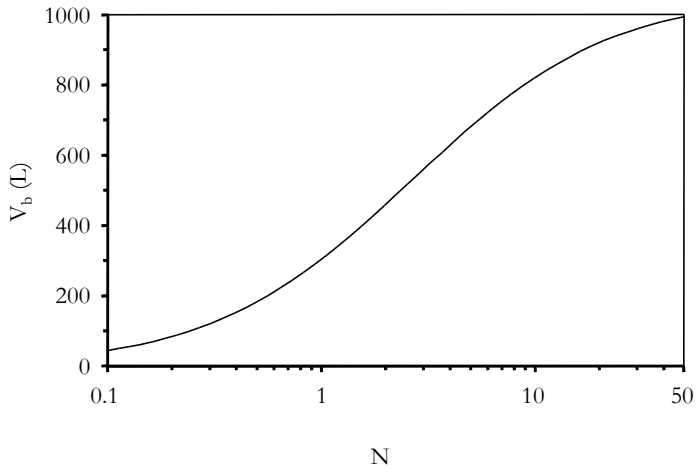

Figure 1 Breakthrough volume as a function of the number of theoretical plates according to the theory of Lövkvist and Jönsson[14]. V_0 = 1mL, $k=1*10^6$.

To illustrate the possibilities of packed PDMS sampling tubes the presented theory is used to calculate the breakthrough volume for *n*-pentadecane. For this solute, **Equation** 4 yields an equilibrium constant of $1.62*10^6$ at 20°C. If a preconcentration tube is used with a dead volume of 1 mL and a phase ratio of 1 this leads to a retention volume of 1621 liters. Typical values for d_p and the inner diameter of the sampling tube are 0.5 and 4 mm, respectively. A typical bed length is 5 cm. If a sampling flow rate of 1500 mL/min is used this results in a reduced velocity of 420 and a plate number of 2.3 (D_m for pentadecane in air is estimated to be $5.8*10^{-6}$ m^2/s). Even at this very low plate number, **Equation 1** yields a breakthrough volume of 800 L. This means that a detection limit of 1 ppt can be obtained for pentadecane using FID detection.

The approach presented above only allows the calculation of breakthrough volumes for alkanes. In order to be able to estimate the breakthrough volume for other (non-alkane) solutes a universal equation for the calculation of equilibrium constants

has to be derived. This can be done using the well known Kováts retention indices (RI) which are available for numerous compounds[19] and are easy to determine experimentally. The Kováts retention index is defined as:

Equation 8

$$RI = 100 \times \frac{\log(t'_A) - \log(t'_Z)}{\log(t'_{Z+1}) - \log(t'_Z)} + 100 \times Z = 100 \times \frac{\log(K_A) - \log(K_Z)}{\log(K_{Z+1}) - \log(K_Z)} + 100 \times Z$$

where: Z is the number of carbons in the *n*-alkane eluting just before the compound of interest (A). t_i' is the net retention time and K_i is the equilibrium constant of the component i. Using this definition the equilibrium constant for a given component can be calculated by:

Equation 9

$$\log(K_A) = \log(K_Z) + \left(\frac{RI}{100} - Z\right) \times \left(\log(K_{Z+1}) - \log(K_Z)\right)$$

The procedure to calculate V_b for a non *n*-alkanes is to first look up the retention index of this solute at the trapping temperature in published data sets, then calculate K_{Z+1} and K_Z with **Equation 4** and calculate K_A with **Equation 9**. At the sampling flow rate chosen, u and N are calculated with **Equation 5** through **7**. Finally, **Equation 1** yields V_b. If the retention index value at the trapping temperature is not available, the retention index at the nearest available temperature can be used. For the 100% polydimethylsiloxane trap used this will not result in a large deviation as the temperature dependence of the retention index on such phases is generally small.

4.1.4 Experimental

4.1.4.1 Test Solutes

To characterize the (ad)sorbent cartridges, 7 test solutions containing components of different polarity and volatility were prepared. The compositions of these test solutions are listed in **Table 1**. Test mixture 1 was purchased from Supelco (Bellefonte, PA, USA) and diluted 10 times in methanol (Labscan, Dublin, Ireland). It contains apolar to slightly polar aromatic components. Test mix 2 was also obtained from Supelco and contains the 6 most volatile analytes marked as priority pollutants. This mixture was also diluted 10 times in methanol. Test mixtures 3-6 were prepared in-house from the respective pure components in methanol and contain polar components of environmental interest and of interest to *e.g.* the flavor industry. Test mixture 7 was also prepared in-house but the test solutes were dissolved in ethylacetate (Labscan) instead of methanol to prevent esterification.

Table 1 Analytes under investigation were present in the listed 7 test mixtures. Mixtures 1-6 were in methanol, mixture 7 in ethylacetate. For each compounds out of the total ion chromatogram (TIC) the Quant. ion was extracted and integrated for quantitation. The ratio between the Qual. ion and Quant. ion was used for confirmation of the peak identity.

Test mix	Component	Conc. (µg/ml)	Quant. Ion	Qual. Ion
1	Benzene	200	77	78
	Toluene	200	92	91
	Ethylbenzene	200	91	106
	m-Xylene	200	91	106
	Styrene	200	104	78
	Bromobenzene	200	156	158
	1,3,5-trimethylbenzene	200	105	120
	1,2,4-trimethylbenzene	200	105	120
	p-Isopropylbenzene	200	119	134
	Butylbenzene	200	91	134
	1,2,3-Trichlorobenzene	200	180	182
	Naphthalene	200	128	102
	1,2,4-Trichlorobenzene	200	180	182
2	Dichlorodifluoromethane	200	85	87
	Chloromethane	200	50	52
	Vinylchloride	200	62	64
	Bromomethane	200	94	96
	Dichloromethane	200	64	66
	Trichlorofluoromethane	200	101	103
3	Triethylamine	145	86	101
	Pyridine	196	79	78
4	Dimethylsulfide	169	62	61
	Carbondisulfide	253	76	78
	Isopropanol	157	46	59
	Methyl,t-butyl ether	148	73	57
	2-Butanone	161	72	43
	Diacetyl	196	86	43
	Methylmethacrylate	187	100	99
	Methylisothiocyanate	301	73	72
5	N-Nitrosodimethylamine	500	74	42
6	*n*-Decane	100	71	85
	1-Octanol	100	84	83
	n-Undecane	100	71	85
	2,6-Dimethylphenol	100	122	107
	2,6-Dimethylaniline	100	121	106

	n-Dodecane	100	71	85
	Decylamine	100	100	157
	n-Tridecane	100	71	85
	Nicotine	100	133	162
	n-Tetradecane	100	71	85
7	Acetic Acid	100	45	60 / 43
	Propionic Acid	100	74	73 / 57
	n-Butanoic Acid	100	73	55 / 88
	n-Pentanoic Acid	100	73	55 / 87

4.1.4.2 Sorbent and Adsorbent Cartridges

Four adsorbents for air preconcentration were compared with a polydimethylsiloxane filled air sampling cartridge. All cartridges were 177.8 mm long, had an inner diameter (I.D.) of 4 mm and an outer diameter (O.D.) of 6 mm. The (ad)sorbents were:

Carbotrap 300 - A standard adsorbent cartridge filled with 300 mg Carbotrap C (20/40 mesh), 200 mg Carbotrap B (20/40 mesh) and 125 mg Carbosieve S-III (60/80 mesh). This adsorbent cartridge was obtained from Supelco. The length of the adsorbent bed was 7 cm. The bed was kept in place by a glass frit on the sample inlet side and a plug of glass wool at the outlet side.

Tenax TA - A standard adsorbent cartridge containing Tenax TA was obtained from Gerstel (Müllheim a/d Ruhr, Germany). The adsorbent bed was 6.1 cm long and was kept in place by two metal frits.

Chromosorb 101 - This adsorbent was obtained from Alltech (Deerfield, IL, USA). An empty glass tube (Gerstel) was filled with Chromosorb 101 to result in a bed length of 6.2 cm. The bed was kept in place by two plugs of silylated glass wool.

Lichrolut EN - Standard SPE cartridges containing Lichrolut EN (Merck, Darmstadt, Germany) were emptied and the SPE material was transferred into an empty glass tube. The bed was 5.5 cm long and kept in place by two plugs of silylated glass wool. Although Lichrolut EN is an adsorbent intended for liquid desorption, in this study it was used for thermal desorption.

PDMS - Polydimethylsiloxane (PDMS) particles were prepared in-house from a 95.5% dimethyl, 0.5% vinyl polysiloxane polymer (Petrarch Systems, Bristol, PA, USA). This polymer was crosslinked with benzoylperoxide at 140°C and a large chunk of raw, crosslinked, PDMS is obtained. PDMS particles are obtained by grinding the raw PDMS under liquid nitrogen. The obtained particles were sieved in the range

240-400 μm and 325 mg was transferred into an empty glass tube. This corresponds to a V_0 of 0.334 mL. The phase ratio (ß) of the trap was determined to be 0.85. The PDMS particles were kept in place by two small pieces of Silastic silicone tubing (Dow Corning, Midland, MI, USA) which were pushed onto the PDMS bed. The resultant PDMS plugs appeared to work well under real-life sampling conditions. It is important to realize that in this sampling cartridge no active adsorbent surface is present since the PDMS particles are truly homogeneous, *i.e.* the material is not coated an adsorbent support. Even the active sites originating from glass wool or metal plugs were eliminated by the PDMS "frits". The resulting PDMS bed was 6 cm long (including the "frits" which also participate in retaining analytes).

All cartridges were thermally desorbed at 250°C except the PDMS cartridge which was desorbed at 200°C. Each cartridge was conditioned 25°C in excess of the desorption temperature for 2 hours at a helium flow of 150 mL/min.

4.1.4.3 Instrumental Set-Up

The instrumental set-up used in all experiments consists of a Gerstel TDS-2 thermo-desorption system mounted on an HP6890 gas chromatograph (Hewlett Packard, Little Falls, DE, USA). The TDS-2 system consists of two programmable temperature vaporization (PTV) injectors in series. The first PTV injector is the TDS-2 unit in which the packed (ad)sorbent cartridges are thermally desorbed. The second PTV injector is a CIS-4 (Gerstel), used as a cryotrap/reinjection device. For all experiments an HP 5972 mass selective detector was used. All chromatograms were recorded in the full scan mode in the mass range from 40 to 300 amu. A schematic drawing of the system is shown in **Figure 2**. The TDS-2 system contains 2 valves which control the split/splitless state of the system. The four different flow modes are listed in **Table 2**. In order to efficiently cryotrap even the most volatile analytes, it was found necessary to pack the liner of the CIS-4 with approximately 10 mg of Tenax TA. This packed CIS liner was used for all solutes.

Table 2 Flow modes of the TDS-2 thermal desorption system.

Flow mode	Valve 1	Valve 2
Split desorption	------	———
Splitless desorption	———	———
Split injection	———	———
Splitless injection	———	------

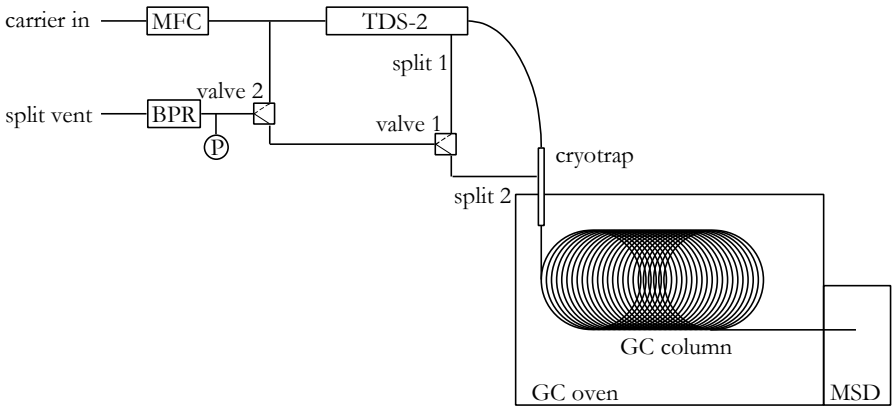

Figure 2 Gerstel TDS-2 thermodesorption system with CIS-4 cryotrap. MFC: Mass flow controller, BPR: Back pressure regulator, P: Pressure Gauge, valve 1 and valve 2: split/splitless valves.

The temperature program of the TDS-2 started at 40°C. The temperature was then ramped at 50°C/min to an upper temperature of 250°C where the cartridge was kept for 5 minutes. This program was used for all cartridges except for the PDMS-packed tube for which a temperature of 200°C was found to be sufficient. During thermal desorption, the CIS-4 was kept at -100°C with liquid nitrogen. After the thermal desorption program is complete, the TDS-2 is cooled down to ambient temperature and the (ad)sorbent tube is removed and replaced by an empty one. Subsequently, the temperature of the CIS-4 is increased to 250°C at 10°C/s to ensure narrow injection bands. Transfer of the analytes from the TDS-2 to the CIS-4 and from the cryotrap onto the column was performed in the splitless mode by proper switching of valves 1 and 2 (**Table 2**). The GC initial temperature was 40°C which was maintained for 3 minutes. The temperature was then ramped to 250°C at 10°C/min.

The analytical column used for test mixtures 1-6 was a home-made poly(5%)diphenyl(95%)dimethylsiloxane fused silica open tubular (FSOT) column had the following dimensions: 60 m long, 0.25 mm I.D. and 1.2 μm film thickness. For the free organic acids in test mixture 7, a home made free fatty acid phase (FFAP) FSOT column was used. The dimensions of this column were: length 60 m, I.D. 0.25 mm, film thickness 0.25 μm. For the analysis of the headspace samples and for the analysis of PAHs and nitro-PAHs an HP-5MS column was used which was 30 m long, 0.25 mm I.D. with a film thickness of 0.25 μm.

Model experiments were performed to study the breakthrough volumes of the test solutes on the (ad)sorbents. In order to load the test solutions onto the (ad)sorbent cartridges in a reproducible manner, the cartridge was placed inside the

oven of an HP 5890 GC (Hewlett Packard). The inlet of the cartridge was connected to the injector (split/splitless) and the outlet was connected to the detector (FID) via 530 μm I.D. fused silica tubing. Both the injector and detector were kept at 200°C while the GC oven was at 30°C. The flow through the cartridge was kept at 55 ± 2 mL/min. 1 μL of a test solution was injected into the split/splitless injector which was constantly kept in the splitless mode to ensure transfer of the entire sample onto the (ad)sorbent tube. The solvent exiting the cartridge can be monitored on the FID detector. For practical purposes, a concentration detection limit of roughly 1 ng/m^3 is desired. With a detection limit of approximately 0.5 pg (MSD, SIM), 500 ml of sample is required to attain the desired sensitivity. To simulate this, after injection of the standard, the tube remains in the GC oven for 10 minutes and thus 550 ± 20 mL of gas is passed through the sampling tube. Next the tubes were inserted into the thermodesorption system for thermal desorption and GC/MS analysis.

4.1.4.4 Quantification

For quantification purposes, 1 μL of the standard solution was injected into a plug of deactivated glass wool placed in an empty glass tube. This tube was then directly desorbed thermally and analyzed as described earlier. Recoveries of the test analytes on the different (ad)sorbents were calculated relative to these standard runs. Since several (ad)sorbents produced a considerable background all chromatograms were integrated using only 1 ion per component (Quantitative ion). A second ion was used for confirmation of the presence of the analyte (Qualitative ion). A relative deviation of 20% in the ratio between the two ions was considered acceptable.

4.1.5 Results And Discussion

4.1.5.1 Standards

After thorough conditioning of the Tenax TA packed CIS liner, the five adsorbent cartridges and the GC columns, the first experiments concerned the blank chromatograms of the adsorbents. Since Lichrolut EN showed a very poor blank, it was attempted to clean this material with supercritical fluid extraction (SFE). **Figure 3** shows blank chromatograms of Carbotrap 300, Tenax TA and PDMS.

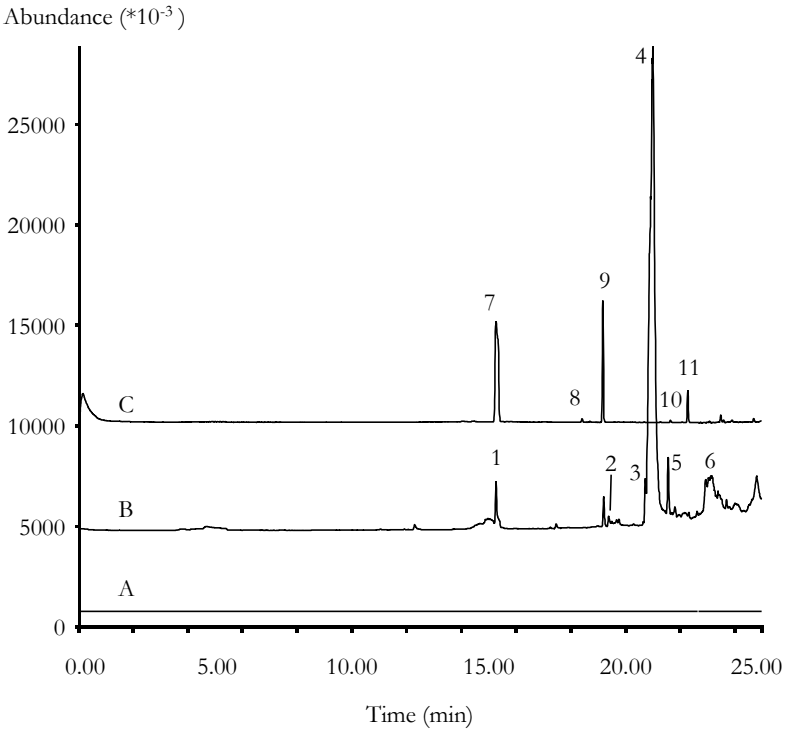

Figure 3 Blank chromatogram of Carbotrap 300 (A), Tenax TA (B) and polydimethylsiloxane (C). Numbers indicate peaks identified and listed in **Table 3.**

Figure 4 shows blank runs of Chromosorb 101, Lichrolut EN and Lichrolut EN after SFE (30 minutes, density = 0.5 g/ml, 50°C, 2 ml/min). **Table 3** lists some compounds identified in the blank chromatograms. For quantification purposes it is required that an analyte that has to be determined is not detected in the blank. Also, no peaks should be present co-eluting with the analyte unless they can be discerned by the detector (*i.e.* generate different ions on the mass spectrometric detector).

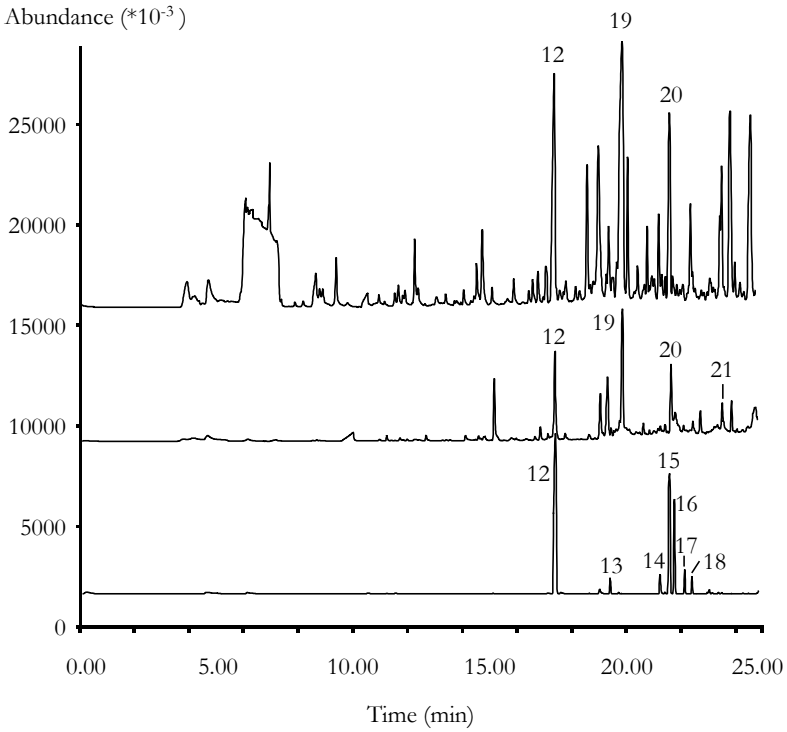

Figure 4 Blank chromatogram of Chromosorb 101 (A), Lichrolut EN (B) and Lichrolut EN after SFE (30 minutes at 2 ml/min CO_2 with a density of 0.5 g/ml) (C). Numbers indicate peaks identified which are listed in **Table 3**.

Table 3 Peaks identified in the blank chromatograms.

no	Compound	no	Compound
1	Propionic acid	12	Styrene
2	2(5H)Furanone, 3-methyl	13	Styrene, 2-methyl
3	2-Pyrrolidone, 1-methyl	14	Acetophenone
4	Hexadecanol	15	Benzene, 2-ethenyl, 1,4-dimethyl
5	2,5-pyrrolidinedione, 1-methyl	16	Benzene, 1-ethenyl, 4-ethyl
6	Dibutylphthalate	17	Benzene, diethenyl
7	Siloxane fragment (M^*=207)	18	Benzene, diethenyl
8	Siloxane fragment (M^*=267)	19	Benzene, 1-ethenyl, 3-methyl
9	Siloxane fragment (M^*=281)	20	Benzaldehyde, 3-methyl
10	Siloxane fragment (M^*=267)	21	Benzaldehyde, ethyl
11	Siloxane fragment (M^*=267)		

[*] Highest observed mass peak (scanning to 300 amu)

From **Figure 3** and **4** it is clear that Carbotrap 300 exhibits by far the best blank; no peaks are present. All other adsorbents give rise to more or less pronounced peaks in the blank runs. Several of these peaks were identified and are listed in **Table 3**. Both Chromosorb 101 and Lichrolut EN gave rise to a large background of aromatic compounds and are therefore not suited for the analysis of this class of analytes. Especially the blank chromatogram of Lichrolut EN was cluttered with peaks. SFE seemed to worsen this and therefore the experiments with Lichrolut EN were discontinued. In the blank run of the PDMS material some peaks were present but they could be readily identified as siloxane breakdown products and do therefore not interfere in normal air analysis.

Recovery and carry-over data found for the various materials are listed in **Table 4**. Recoveries were measured as described in **Section 4.1.4.4**. Carryover was measured by performing a blank of the (ad)sorbent after each analysis. If a compound was detected in the blank, its peak area was measured and expressed as a relative value to the peak found in the original analytical run. These can be found in **Table 4** for all compounds and are listed in parentheses. For practical purposes, recoveries between 70 and 130% are considered acceptable and carryover is required to be less than 1% at the level of 100 ng/solute which is used here (detection limit is ± 0.1 ng in full scan mode). As can be seen from **Table 4**, the performance of the three (ad)sorbents for the aromatics sample (1) is comparable.

Table 4 Recoveries (%) of the test solutions on the (ad)sorbents. Values in parentheses indicate carryover (%). Benzene to 1,2,4-trichlorobenzene were not studied for Chromosorb 101 due to a very poor blank.

Component	Carbotrap	Tenax TA	Chromosorb	PDMS
Benzene	44.2 (0.4)	133.0 (0.8)		0.9 (nd)
Toluene	54.5 (1.8)	129.4 (3.8)		54.6 (nd)
Ethylbenzene	73.1 (0.3)	103.8 (0.2)		106.1 (nd)
m-Xylene	73.1 (0.3)	103.9 (0.3)		106.1 (nd)
Styrene	77.8 (0.2)	101.3 (0.2)		99.1 (nd)
Bromobenzene	97.1 (0.2)	118.8 (0.2)		112.4 (0.2)
1,3,5-trimethylbenzene	93.9 (0.7)	91.2 (0.3)		93.7 (nd)
1,2,4-trimethylbenzene	93.8 (0.2)	92.8 (0.2)		93.9 (0.2)
p-Isopropylbenzene	96.7 (0.3)	91.7 (0.2)		92.3 (0.1)
Butylbenzene	96.6 (0.6)	91.9 (0.3)		93.8 (0.2)
1,2,3-Trichlorobenzene	120.0 (0.9)	97.5 (0.7)		105.2 (0.7)
Naphthalene	106.1 (1.8)	97.5 (1.5)		99.2 (0.7)
1,2,4-Trichlorobenzene	117.9 (0.8)	100.2 (0.6)		103.1 (0.6)
Dichlorodifluoromethane	60.6 (nd)	nd (nd)	nd (nd)	nd (nd)
Chloromethane	235.8 (45.7)	nd (nd)	nd (nd)	nd (nd)
Vinylchloride	282 (nd)	nd (nd)	nd (nd)	nd (nd)

Dichloromethane	253.6 (nd)	nd (nd)	nd (nd)	nd (nd)
Trichlorofluoromethane	231.7 (nd)	nd (nd)	nd (nd)	nd (nd)
Triethylamine	23.7 (0.3)	77.8 (4.0)	16.1 (1.4)	71.3 (0.4)
Pyridine	42.9 (3.6)	90.5 (3.2)	46.4 (1.9)	77.5 (nd)
Dimethylsulfide	26.9 (nd)	nd (nd)	nd (nd)	2.9 (nd)
Carbondisulfide	25.4 (3.6)	nd (nd)	nd (nd)	nd (nd)
Isopropanol	nd (nd)	nd (nd)	nd (nd)	nd (nd)
Methyl,t-butyl ether	69.5 (nd)	40.9 (nd)	nd (nd)	104.2 (nd)
2-Butanone	nd (nd)	80.3 (5.5)	57.2 (2.1)	77.6 (0.3)
Diacetyl	nd (nd)	58.1 (5.5)	46.3 (2.0)	73.5 (nd)
Methylmethacrylate	60.2 (0.4)	89.0 (nd)	59.5 (0.1)	102.2 (nd)
Methylisothiocyanate	57.4 (0.4)	74.9 (1.0)	55.8 (0.1)	27.4 (nd)
N-Nitrosodimethylamine	76.5 (0.6)	99.1 (nd)	97.9 (nd)	102.2 (nd)
n-Decane	111.5 (nd)	103.6 (nd)	96.2 (nd)	110.4 (nd)
1-Octanol	97.9 (0.3)	89.7 (1.0)	86.3 (0.6)	90.0 (0.3)
n-Undecane	118.9 (nd)	105.3 (nd)	82.1 (nd)	110.8 (nd)
2,6-Dimethylphenol	110.1 (0.2)	99.2 (nd)	92.2 (0.5)	104.2 (nd)
2,6-Dimethylaniline	119.8 (2.1)	106.0 (nd)	95.8 (0.7)	105.8 (nd)
n-Dodecane	111.5 (nd)	97.0 (nd)	89.6 (nd)	106.9 (nd)
Decylamine	42.1 (5.7)	116.2 (0.3)	4.3 (2.8)	100.7 (0.1)
n-Tridecane	99.4 (nd)	86.4 (0.5)	84.7 (1.2)	97.7 (0.3)
Nicotine	nd (nd)	63.5 (3.2)	58.9 (6.5)	98.1 (0.3)
n-Tetradecane	0.5 (0.3)	80.7 (0.8)	79.9 (0.6)	91.5 (0.5)
Acetic Acid	396.4 (33.6)	133.1 (0.6)	70.2 (nd)	108.5 (nd)
Propionic Acid	144.8 (12.6)	122.0 (nd)	132.6 (nd)	91.7 (nd)
n-Butanoic Acid	114.7 (nd)	99.5 (nd)	110.7 (nd)	95.1 (nd)
n-Pentanoic Acid	98.8 (nd)	93.3 (nd)	108.8 (nd)	102.9 (nd)

nd: not detected

On both the PDMS material and on Carbotrap 300, benzene and toluene are (partially) lost. The PDMS phase does not exhibit an adequate retaining power to retain these volatile solutes. The loss of benzene and toluene on Carbotrap 300 is not understood since this adsorbent should have a high affinity for these solutes. Incomplete desorption of benzene and toluene from Carbotrap is also unlikely since less volatile solutes (*i.e.* xylene) were recovered quantitatively. For the heavier analytes an increased carry-over is observed which is smallest in the case of PDMS. On Tenax, the recovery for benzene is too high and the carry-over for toluene is also too high. The last observation is unexplained since toluene should readily desorb at the conditions chosen. It is however possible that these solutes appear as Tenax breakdown products.

For the group of the very volatiles, as known, Carbotrap performs best. The other (ad)sorbents cannot be applied. Bromomethane is missing in the list because it was neither detected in the standard, nor in any of the sample chromatograms. Very high recoveries were observed for the other compounds except for dichlorodifluoromethane which was partially lost in the sampling process. These high recoveries were, most likely, caused by the fact that analyte losses occur during the injection of the standard solution used for calibration. PDMS performed best or equally well as the adsorbents for polar analytes except for methylisothiocyanate for which a surprisingly low recovery was observed. From all analyses it is clear that one of the great advantages of PDMS is that it shows virtually no background, only a few distinct peaks are present. This is illustrated in **Figure 5** where the fifth analysis of the analysis series of standard 1 on each (ad)sorbent (except Chromosorb 101) is shown.

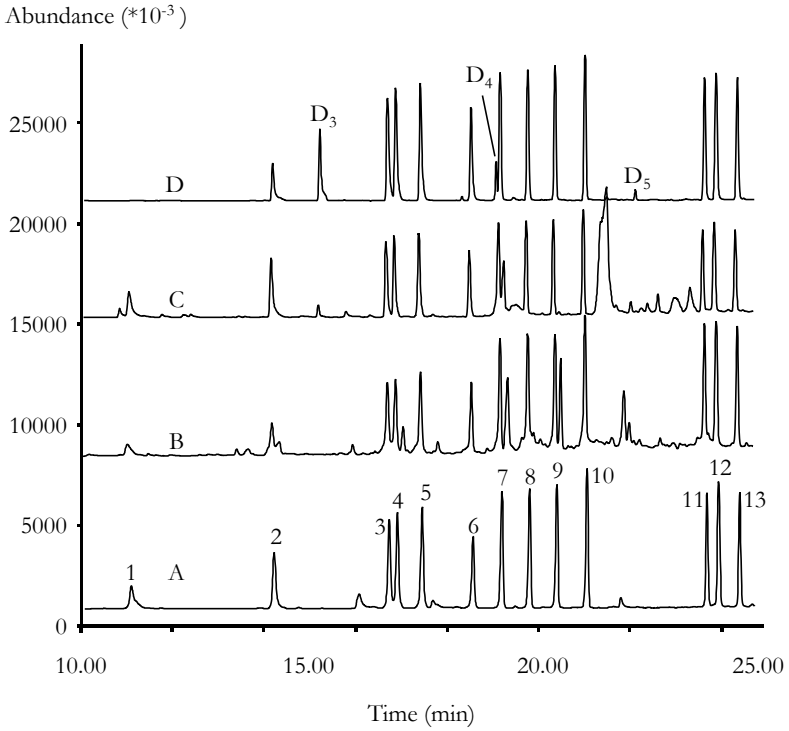

Figure 5 Chromatogram of test mixture 1. A : chromatogram of a 1 µl standard injection. Other 3 chromatograms are obtained by sampling the aromatic components from the gas phase. Chromatogram shown is the fifth analysis with the respective (ad)sorbent. B : Carbotrap 300, C : Tenax TA, D : Polydimethylsiloxane. Numbers indicate solutes in test mixture 1, order as in **Table 1**. D_3, D_4 and D_5 indicate the cyclic siloxane degradation products.

From comparison with the standard, it is clear that the chromatogram obtained from PDMS is closest to that of the standard, only a few (known) degradation products are present. All other chromatograms are cluttered with interfering background peaks. The adsorbents can generate very good blanks but when used more than one time a highly increased background appears which can only be prevented by thorough re-conditioning. The excellent stability appears to be one of the strongest advantages of PDMS. There are several distinct peaks present in the blank, however, these are always of the same intensity and retention time, *i.e.* no extra background peaks appear after repeated use. When using the PDMS material, peaks present in the background can easily be identified with the use of a mass spectrometric detector. Background peaks can therefore never be misinterpreted as actually sampled components as is the case with adsorbents. This is a great advantage for accurate sample identification and quantification. The characteristic degradation products can even be used as retention-time markers. In the following sections several applications performed on PDMS traps for real-world samples will be shown.

4.1.5.2 Determination of Organic Acids in Air

Inspired by the results of the test chromatograms, the PDMS material was employed to determine organic acids in laboratory air. Acetic acid, propionic acid, *n*-butyric acid and *n*-pentanoic acid were analyzed underivatized. Ambient air was sampled for 10 minutes at a flow rate of 50 mL/min. The MSD was, contrary to the earlier experiments, used in the selected ion monitoring mode (SIM). Two ions were used per component as listed in **Table 1**. The chromatogram is shown in **Figure 6**. The four acids were found to be present at levels between 1.08 and 2.21 $\mu g/m^3$. The detection limit for these solutes was estimated to be 1-5 ng/m^3.

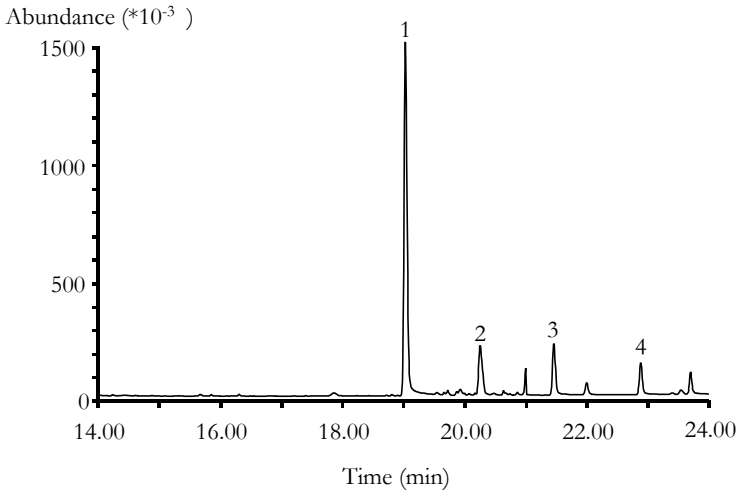

Figure 6 Chromatogram of the analysis of organic acids in air. Column: FFAP, 60 m x 0.25 mm I.D. x 0.25 μm. Peaks: 1, Acetic acid 2.21 μg/m^3; 2, Propionic acid 1.08 μg/m^3; 3, *n*-Butanoic acid 1.31 μg/m^3; 4, *n*-Pentanoic acid 1.15 μg/m^3.

4.1.5.3 Determination of PAHs and Nitro-PAHs in Air

The 27 solutes under investigation here are listed in **Table 5**. The analytical column was exchanged for the 0.25 μm HP-5MS column. All experiments were performed in the SIM mode using two ions per component which are listed in **Table 5**. Initially the recoveries of the solutes were determined versus a 1 μL cold splitless injection. Similar to the earlier experiments, spiked PDMS tubes were prepared by injecting 1 μL into a splitless GC injector. The flow rate through the PDMS cartridge was increased to 1031 mL/min. 10.3 L of He was passed through the cartridge. Under these conditions, the 5% breakthrough volume for naphthalene was calculated to be 11.3 liters[20] and all PAHs are thus retained quantitatively. Recoveries of the PAHs and nitro-PAHs calculated are listed in **Table 5**. Laboratory air was sampled for 10 minutes at a flow rate of 1062 mL/min. The chromatograms obtained for both the standard and the air analysis are shown in **Figure 7A and 7B**. The 16 PAHs were all detected and the concentrations found in laboratory air are listed in **Table 6**. With the present set-up PAHs can be quantitatively determined using sample volumes of only 10 liters.

Table 5 PAH's and nitro-PAH's determined in laboratory air

No	Component	Concentration in standard (mg/L)	Quant. Ion	Qual. Ion	Recovery (%)
1	Naphthalene	40	128	102	113.1
2	Acenaphthylene	80	152	153	104.8
3	Acenaphthene	40	153	152	84.0
4	Fluorene	4	166	165	120.2
5	Phenanthrene	4	178	176	104.3
6	Anthracene	4	178	176	101.5
7	Fluoranthene	8	202	200	90.5
8	Pyrene	4	202	200	88.6
9	Benz(a)anthracene	4	228	226	86.6
10	Chrysene	4	228	226	90.3
11	Benz(b)fluoranthene	8	252	126	99.7
12	Benz(k)fluoranthene	4	252	126	98.3
13	Benz(a)pyrene	4	252	126	97.8
14	Indeno(123cd)pyrene	4	276	138	102.4
15	Dibenz(ah)anthracene	8	278	138	104.7
16	Benzo(ghi)perylene	8	276	138	103.4
17	1-Nitronaphthalene	20	173	127	82.4
18	2-Nitronaphthalene	20	173	127	83.1
19	2-Nitrobiphenyl	20	199	152	92.1
20	3-Nitrobiphenyl	20	199	152	92.8
21	1,5-Dinitronaphthalene	20	218	126	93.0
22	1,3-Dinitronaphthalene	20	218	126	92.4
23	2,2-Dinitrobiphenyl	20	198	168	102.9
24	9-Nitroanthracene	20	223	176	96.8
25	1,8-Dinitronaphthalene	20	172	114	102.0
26	1-Nitropyrene	20	247	201	102.9
27	2,5-Dinitrofluorene	20	256	239	86.8

Nitro-PAHs were also determined in laboratory air by sampling for five hours at 588 mL/min. This relatively large sample volume is required because nitro-aromatics occur at concentrations typically around or below 0.1 ng/m^3. **Figure 8A** shows a chromatogram of the nitro-PAHs standard. **Figure 8B** shows the chromatogram obtained for the analysis of laboratory air. Only the part containing 1-nitropyrene is shown, all other solutes could not be determined because too many interfering peaks were present without sample clean-up. 1-nitropyrene (peak 26) was positively identified and found present at a concentration of 0.1 ng/m^3.

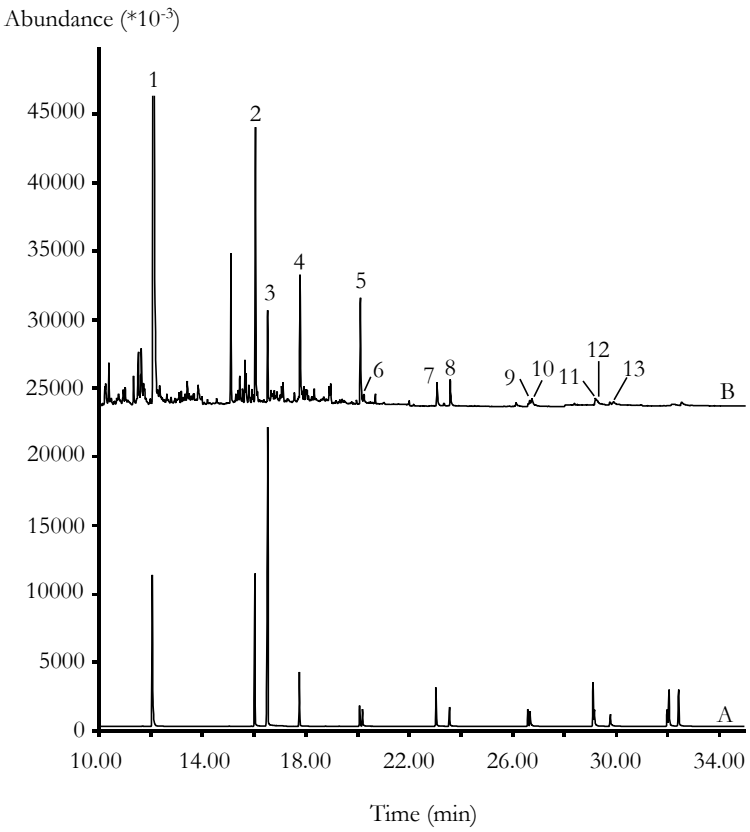

Figure 7 Chromatogram of the PAH standard (A) and of the air sample (B), for peak identification see **Table 5**. Quantitative data are listed in **Table 6**.

Table 6 PAHs determined in ambient air.

No	Component	Concentration (ng/m^3)	No	Component	Concentration (ng/m^3)
1	Naphthalene	2035	9	Benz(a)anthracene	7.68
2	Acenaphthylene	107	10	Chrysene	7.56
3	Acenaphthene	45.3	11	Benz(b)fluoranthene	7.73
4	Fluorene	22.2	12	Benz(k)fluoranthene	7.50
5	Phenanthrene	47.6	13	Benzo(a)pyrene	1.99
6	Anthracene	51.7	14	Indeno(123cd)pyrene	2.73
7	Fluoranthene	11.2	15	Dibenz(ah)anthracene	1.12
8	Pyrene	10.9	16	Benzo(ghi)perylene	4.19

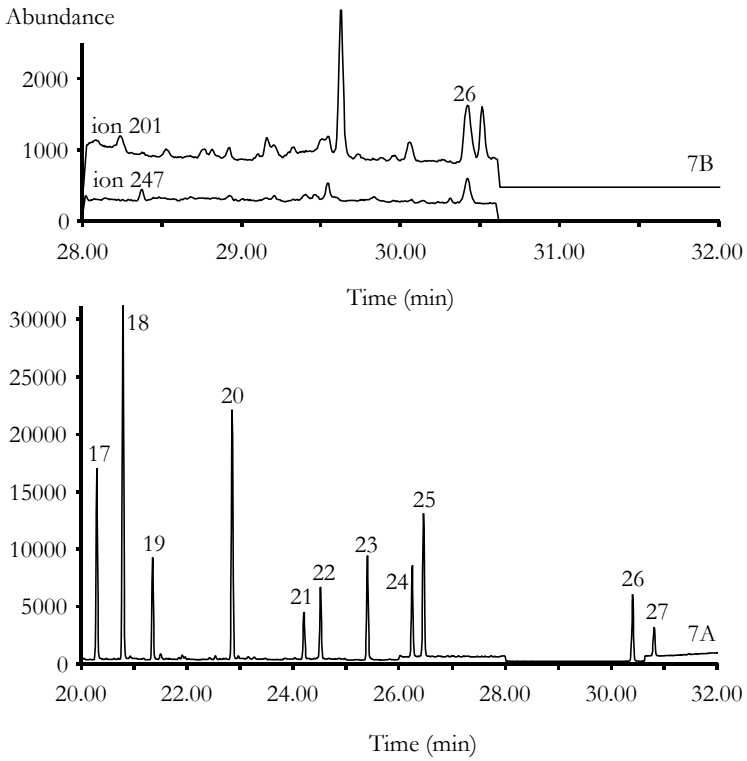

Figure 8 Chromatogram of the nitro-PAH standard (A) and of the air sample (B). For conditions and concentrations see text. Peak numbers as in **Table 5**.

4.1.5.4 Headspace Sampling

The applicability of packed PDMS traps for headspace analysis was tested by the analysis of cacao powder and hops. Both headspace samples were pushed through the PDMS trap with a stream of nitrogen at a flow rate of 51 mL/min for 10 minutes. Transfer from the TDS-2 to the CIS-4 occurred in the splitless mode whereas transfer from the CIS-4 to the column was performed in the split mode. This was necessary to ensure a sharp band width for the most volatile analytes. **Figure 9** shows the chromatogram of the cacao sample and **Figure 10** shows the analysis of the hops sample.

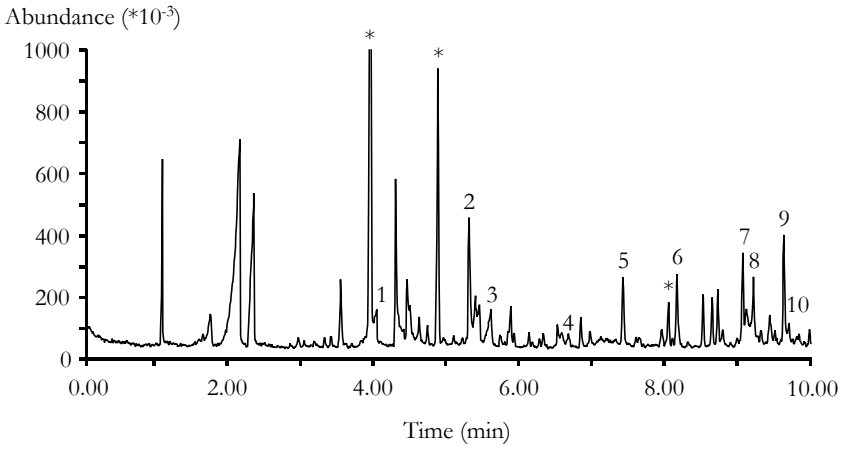

Figure 9 Chromatogram of cacao headspace, 10 min x 51 ml/min. Other conditions see text. Peak assignment: 1, 1,3-butanediol; 2, 4-methylpentanone; 3, *n*-butanoic acid; 4, dimethylpyrazine; 5, benzaldehyde; 6, trimethylpyrazine; 7, tetramethylpyrazine; 8, methylbenzoate; 9, unidentified; 10, mequinol; *, siloxane degradation product.

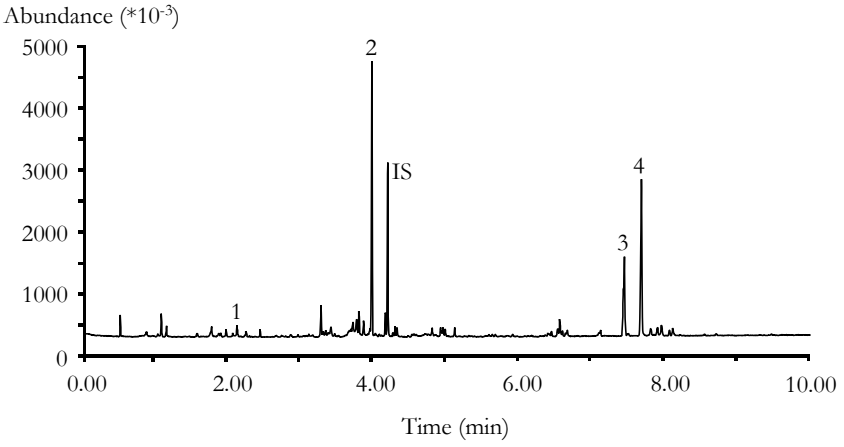

Figure 10 Chromatogram of hop headspace, 10 min x 51 ml/min. Peak assignment: 1, pentanal, 2, myrcene; 3, humulene; 4, a-caryophyllene; IS, internal standard.

4.1.6 Conclusion

Polydimethylsiloxane (PDMS) is an excellent alternative to classical adsorbents in the analysis of volatile and/or polar components in air. Retention on the PDMS phase is based on dissolution into this non-porous polymeric material rather than on adsorption onto an active adsorbent surface. The PDMS traps used proved to be more inert than the adsorbents Tenax TA, Chromosorb 101 and Carbotrap 300. Although the blank chromatograms of the PDMS phase contain some distinct peaks, they can easily be identified with the use of a mass spectrometric detection system. Also, the PDMS cartridge generates a more stable and constant background which does not deteriorate after several analyses. Contrary to PDMS, the adsorbent cartridges showed significantly increased backgrounds even after only a single analysis, requiring a severe conditioning step after each analysis. This is, of course, highly impractical.

For both polar and apolar analytes, the PDMS sorbent has proven to perform better or equal compared to the adsorbents included in the study. PDMS showed superior performance for analytes such as triethylamine, butanone, diacetyl, nicotine, acetic acid *etc.* for which all adsorbents under investigation showed unsatisfactory performance. With a sample volume of 500 mL and using MS detection in the SIM mode, detection limits were 1-5 ng/m^3 or better for all solutes investigated.

Several air and headspace samples were analyzed. Four organic acids (acetic, propionic, *n*-butyric, *n*-pentanoic) were determined in ambient air at a level of 1-2 $\mu g/m^3$. Additionally, the 16 priority PAHs and some nitro-PAHs were determined in laboratory air. All PAHs could be quantitated in air at levels between 2.0 $\mu g/m^3$ and 1.1 ng/m^3. Of the nitro-PAHs only 1-nitropyrene was detected, the analysis of all other nitro-PAHs was hampered by the presence of excessive levels of background. Finally, headspace samples were analyzed of cacao and hops. Several pyrazines, hydrocarbons and other solutes were identified. Packed PDMS traps clearly have shown to be a viable alternative for the active adsorbents used almost exclusively in air monitoring.

4.2 Reactivity and Inertness for Sulfur Compounds*

4.2.1 Summary

The performance of the sorbent polydimethylsiloxane (PDMS) was compared to that of the adsorbents Carbotrap and Tenax for the enrichment of volatile reactive sulfur compounds. These included: 1- and 2-propanethiol, tetrahydro-thiophene, 2-thio-ethanol and 2-ethylthio-ethanol. Several artifact forming reactions were identified on both Tenax and Carbotrap including: H_2S elimination and dimerization of thiols. Additionally, permanent adsorption was also observed for heavier solutes. These effects are absent when PDMS is applied. This superior performance is explained by the absence of catalytic or adsorptive activity on PDMS.

4.2.2 Introduction

The performance of packed polydimethylsiloxane (PDMS) traps as an alternative to adsorbents for air sampling was evaluated and compared to that of the adsorbents Chromosorb, Lichrolut EN and Carbotrap 300 and Tenax in **Section 4.1**. For many polar (and/or reactive) compounds much better performance in terms of recoveries was obtained on PDMS because of its inertness. Moreover, PDMS degradation results in a series of cyclic siloxane oligomers which can easily be detected and identified with the use of a mass spectrometer and do not interfere with the solutes of interest. Additionally, permanent adsorption and reactivity of PDMS are suspected to be minimal. In this section, adsorbent reactivity and its influence on analyte conversion/stability was studied with the use of several sulfur solutes as model compounds.

4.2.3 Experimental

4.2.3.1 Thermal Desorption Cartridges

Three materials namely PDMS, Carbotrap 300 and Tenax are compared. Prepacked Tenax and PDMS traps were obtained from Gerstel (Müllheim a/d Ruhr, Germany) and prepacked Carbotrap 300 cartridges were obtained from Supelco (Bellefonte, PA, USA). The Carbotrap 300 cartridge is a multi stage adsorbent trap containing Carbotrap C, Carbotrap B and Carbosieve SIII. PDMS traps were conditioned for 1 h at 300°C and then for 4 h at 250°C. After this procedure, no peaks appear in the blank

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chromatogram with the exception of the cyclic siloxanes. Tenax traps, obtained in sealed glass containers, were conditioned at 275°C for 2 h before use to guarantee proper blanks. Carbotrap 300 tubes were conditioned at 325°C for 2 h. Conditioning was performed under a flow rate of 15 mL/min for all materials. Thermal desorption temperatures were 225°C for PDMS, 250°C for Tenax and 300°C for Carbotrap 300 during 5 min if not otherwise stated.

4.2.3.2 Experimental Set-Up

A Gerstel TDS-2 Thermodesorption system mounted on a HP6980-HP5972 GC/MSD system (Hewlett Packard, Little Falls, DE, USA) was used. A CIS-4 programmable vaporizing injector (PTV, Gerstel) is used to cryofocus the analytes, prior to their transfer onto the analytical column. The system was used in a modified form suitable only for split desorption and is schematically shown in **Figure 11**. The modification consists of eliminating the transfer capillary from the thermodesorption unit to the PTV cryotrap. The analytical column is pushed through the PTV liner and connected directly to the thermodesorption unit. This implies that the analytes are cryotrapped on the analytical column instead of on the glass liner of the PTV. This minimizes component degradation in the analytical system and allows to focus entirely on the thermal desorption process. Observed component loss can thus be totally attributed to processes occurring in the thermodesorption unit.

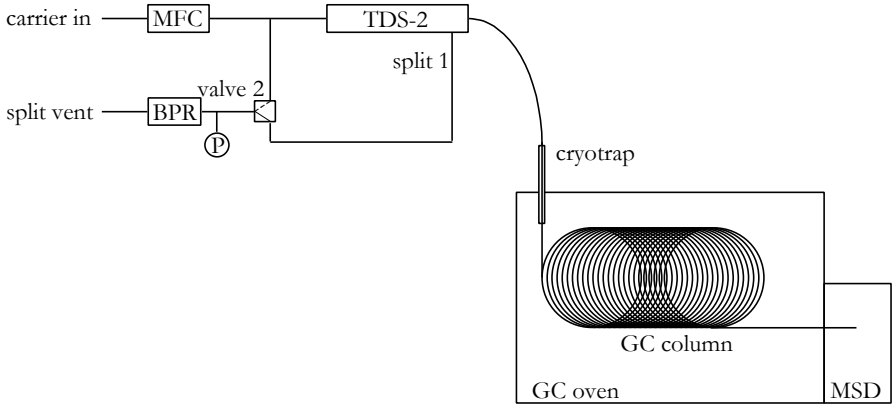
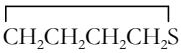


Figure 11 Analytical system used for split desorption. Compared to **Figure 2**, split 2 and valve 1 are eliminated and the analytical column is connected directly to the TDS-2 unit. The cryotrap is used in an on-column fashion.

Analyses were performed on a laboratory-made 50 m L x 250 μm I.D. fused silica column coated with a 1 μm film of OV-1 or on a 30 m L x 250 μm I.D. x 0.25 μm HP-5MS column (Hewlett Packard). Column head pressure was maintained at 50 kPa and the split flow at 15.0 mL/min. For both columns, the temperature program started at 35°C which was kept for 4 min and then programmed to 275°C at 15°C/min. The MSD was operated in the scan mode, scanning from 40-300 amu at 2.8 scans/s.

Table 7 Composition of the test mixtures. M_w, molecular weight; T_b, boiling point.

Mix	Nr	Component	Structure	Concentration (μg/L)	M_w	T_b[21]
1	1	2-Propanethiol	$CH_3CHSHCH_3$	450	76	52.6
1	2	2-Methyl-2-propanethiol	$(CH_3)_2CSHCH_3$	2250	90	88.5
1	3	1-Propanethiol	$CH_3CH_2CH_2SH$	300	76	67.8
2	4	Tetrahydrothiophene		1000	88	121
2	5	1-Pentanethiol	$CH_3CH_2CH_2CH_2CH_2SH$	1000	104	126.6
2	6	1-Hexanethiol	$CH_3CH_2CH_2CH_2CH_2CH_2SH$	1000	118	151
3	7	2-Thio-ethanol	$HSCH_2CH_2OH$	1000	78	158
3	8	Methyl-3-thio-propanoate	$HSCH_2CH_2COOCH_3$	1000	120	
3	9	2-Ethylthio-ethanol	$CH_3CH_2SCH_2CH_2OH$	1000	106	184

4.2.3.3 Standards

For this investigation, three standard solutions in *n*-pentane were prepared. The first solution contains three "volatile" thiols (1-3), standard 2 contains three 'heavy' thiols (4-6) and finally standard 3 contains three analytes with both a thiol and an alcohol or ester group (7-9). The compositions of the test mixtures are given in **Table 7**.

Gaseous standards were prepared by the method described in **Section 4.1.4.3**. Briefly, a TDS cartridge is connected to a split/splitless injector operated in the splitless mode and the flow is adjusted to 15 mL/min. The injector temperature was maintained at 200°C. After injection of 1 μL of the standard into the GC injector the flow is maintained for 10 min to simulate a sampled volume of 150 mL (Tenax, Carbotrap 300, PDMS) or 50 mL (PDMS). Calculation of recoveries is done versus a 1 μL injection into a TDS tube filled with deactivated glass wool and desorbed immediately after spiking.

4.2.4 Results and Discussion

Initial recovery studies were performed on a 30 m L x 320 μm I.D. x 4 μm d_f CP-Sil5CB column (Chrompack, Middelburg, the Netherlands) which is a thick-film column specially deactivated for the analysis of volatile sulfur compounds. Incomplete recoveries were observed which could not be attributed to permanent adsorption or artifact formation. Possible artifact solutes can have a relatively high molecular weight which prevents their elution from the thick-film column. Further experiments were therefore carried out on the 1 μm column.

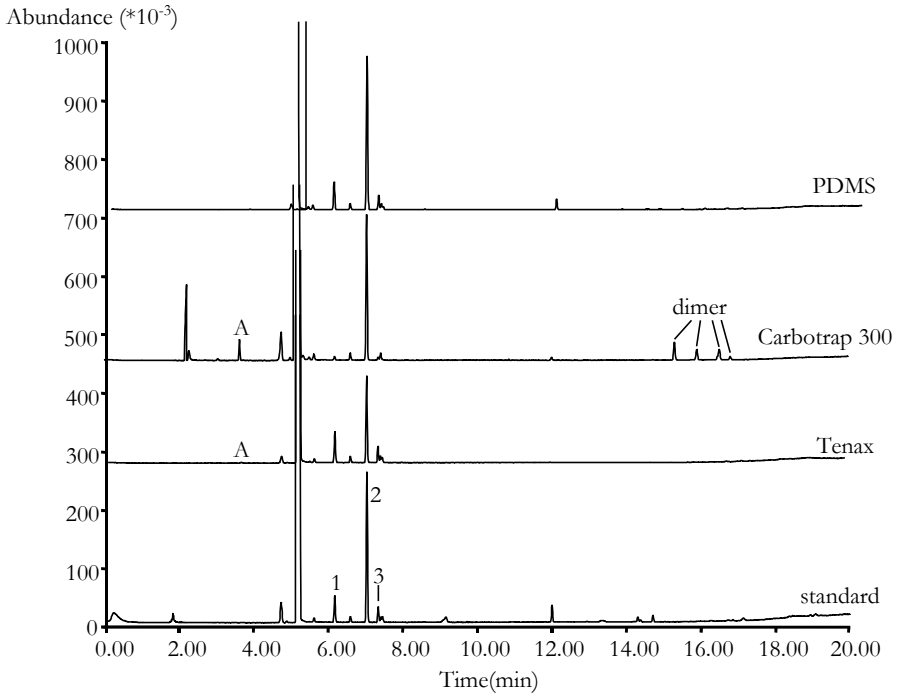


Figure 12 Chromatograms of mixture 1 injected directly (standard) or enriched from an artificial gaseous sample on Tenax, Carbotrap 300 or PDMS. Sample volume was 150 mL (Carbotrap 300 and Tenax) or 50 mL (PDMS). Peak 1: 2-propanethiol, 2: 2-methyl-2-propanethiol, 3: 1-propanethiol, A: 2-methyl-1-propene. The chromatogram of Carbotrap 300 also reveals the presence of dimers.

Figure 12 shows the chromatograms obtained for the analysis of test mixture 1 on the three tubes and the chromatogram obtained by direct injection of the standard solution. **Table 8** lists the recoveries on the three sampling tubes. Recoveries are determined relative to the direct injection of the same amounts. For the most volatile solutes in a 150 mL sample, PDMS gives low recoveries. This is due to the fact

that the breakthrough volumes for these solutes is lower than 150 mL. If only 50 mL is sampled, good recoveries are obtained, which is in agreement with theoretical predictions. The limitation of the sampling volume on PDMS (and the consequential lower sensitivity) can be overcome by equilibrium sorption, as described in **Chapter 6**. Theoretical and literature data predict that the breakthrough volumes of these solutes are larger than 150 mL for both Tenax and Carbotrap 300. For Tenax, good results are indeed obtained for 2-propanethiol and 1-propanethiol, but 2-methyl-2-propanethiol is partly lost. On Carbotrap 300, both 2-propanethiol and 1-propanethiol show low recovery. It is remarkable that the performance of the adsorbents Tenax and Carbotrap 300 is very poor for the analytes used here, even at the relatively high concentration levels used and in the absence of humidity.

On both adsorbents an early eluting compound (A) is formed. This compound was identified as 2-methyl-2-butene which originates from compound 2 by elimination of H_2S. This artifact tends to occur more on Carbotrap 300 than on Tenax although the loss of compound 2 is more prevalent on Tenax (**Table 8**). Probably, the formed 2-methyl-2-butene is too volatile to be trapped on Tenax and is lost immediately when formed.

Table 8 Recoveries (in %) for the test solutes from a 150 mL sample on three enrichment materials. Desorption temperatures: 225°C (PDMS), 250°C (Tenax), 300°C (Carbotrap 300). PDMS[1] recoveries from a 50 mL sample. Tenax[2] desorption at 300°C.

Nr	Component	PDMS	Tenax	Carbotrap 300	PDMS[1]	Tenax[2]
1	2-Propanethiol	2	112	28	101	
2	2-Methyl-2-propanethiol	14	53	92	101	
3	1- Propanethiol	25	99	0	103	
4	Tetrahydrothiophene	110	96	100		
5	1-Pentanethiol	100	99	71		
6	1-Hexanethiol	100	99	60		
7	2-Thio-ethanol	100	98	96		96
8	Methyl-3-thio-propanoate	102	59	69		64
9	2-Ethylthio-ethanol	98	57	96		51

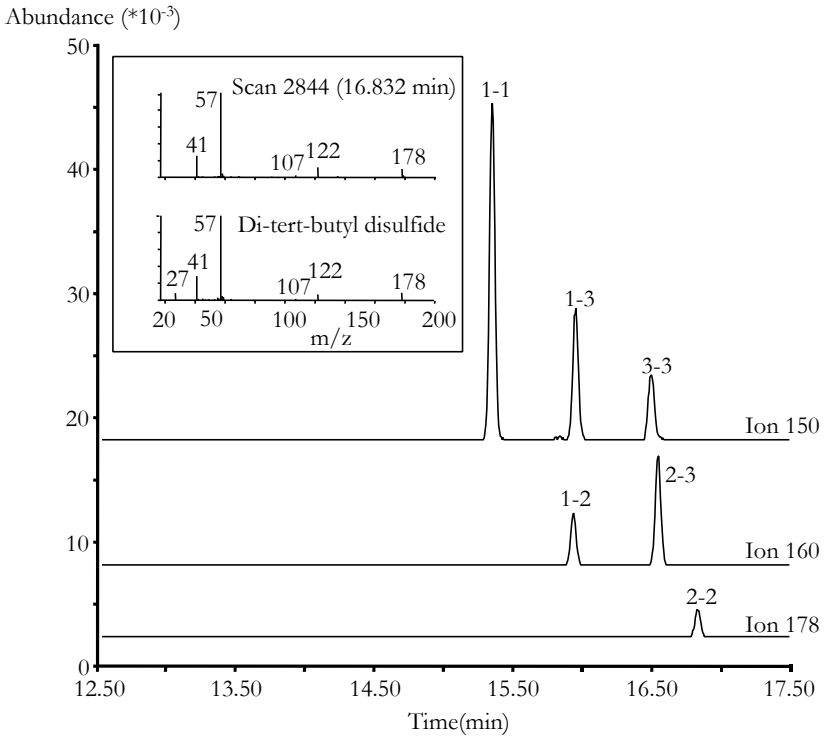


Figure 13 Extracted ion chromatograms of mixture 1 on Carbotrap 300. Ions correspond to the dimers formed between compounds 1, 2 and 3. Insert shows the spectrum recorded for dimer 2-2 and the library spectrum.

In the case of Carbotrap 300, several peaks are detected between 15 and 17 min. These have been identified as the dimers of the thiols (disulfides) in mixture 1 and are formed by H_2 elimination of two thiols. Between the three thiols from mixture 1, six different dimers can be formed and they are all present. This is illustrated in **Figure 13** showing the extracted ion traces corresponding to the molecular masses of the dimers, m/z 150 for dimers 1-1, 1-3 and 3-3, m/z 164 for dimers 1-2 and 2-3 and m/z 178 for dimer 2-2. The insert of **Figure 13** shows the mass spectrum of the 2-2 dimer eluting at 16.83 min together with the library spectrum. If ion extraction is performed on the Tenax chromatogram of mixture 1, the dimers are also observed but at a level 100 times lower than on Carbotrap 300. H_2S and H_2 elimination reactions were not observed on the PDMS sorbent illustrating its superior inertness.

For mixture 2, similar results as for mixture 1 were obtained. Tetrahydrothiophene appeared to be a relatively inert component and was recovered quantitatively from all three materials. 1-Pentanethiol and 1-hexanethiol were quantitatively recovered from both Tenax and PDMS. On Carbotrap 300, significantly lower recoveries were

observed. Similar to the observations for mixture 1, this was suspected to be due to dimerization with the formation of disulfides. These dimers could not be eluted from the 1 μm OV-1 column, but their formation was confirmed by using a thin film (0.25 μm) HP-5MS column. Dimers originating from 1-pentanethiol and 1-hexanethiol (5-5, 5-6 and 6-6) could easily be detected for Carbotrap 300 and in lesser extent for Tenax.

For test mixture 3, 2-thio-ethanol was recovered quantitatively from all enrichment materials. The two analytes with the highest molecular weight were only fully recovered from PDMS whereas on Tenax and Carbotrap 300 losses occurred. Since in the case of 2-ethylthio-ethanol dimerization cannot occur and for 3-thiomethylpropionate the dimer was not detected, it is assumed that these solutes cannot be completely desorbed from the adsorbent due to their high polarity and relatively high molecular weight compared to the other analytes (permanent adsorption). For these compounds no artifacts were observed, indeed an indication of incomplete desorption or permanent adsorption. It was attempted to improve the recoveries from Tenax by increasing the desorption temperature but this did not significantly improve the recoveries (**Table 8**).

4.2.5 Conclusion

The "enrichment performance" of PDMS versus that of the two most popular adsorbents, Tenax and Carbotrap 300, for nine reactive sulfur compounds was investigated. Several artifacts were identified and include dimerization, H_2S elimination and permanent adsorption. These reactions occurred on both Tenax and Carbotrap 300 but not on the PDMS phase. The inertness of polydimethylsiloxane and the absence of catalytic activity and adsorptive sites make this material very interesting for the enrichment of reactive (sulfur) compounds. For the most volatile solutes, the breakthrough volumes on PDMS are, however, much lower in comparison to Tenax or Carbotrap 300. Equilibrium sorption can help to overcome this problem.

4.3 GPE versus SPME - Analysis of Plant Volatiles*

4.3.1 Summary

In this section a comparison of dynamic sampling on PDMS and Tenax and of static solid phase micro extraction using PDMS and PA fibers for the enrichment of volatiles emitted by *Jasminum officinale* is made. Additionally, the headspace of a rose was analyzed using SPME with the PDMS and PA fibers to illustrate the effect of fiber polarity on the extraction efficiency of various solutes.

4.3.2 Experimental

4.3.2.1 Plant Material

A flowering *Jasminum officinale* plant (height *ca.* 18 cm, width 14 cm) was purchased from a local flower shop. The jasmine plant had a pronounced and characteristic smell. Additionally, new experimental roses with a pleasant but relatively weak smell were kindly donated by Dr. Heursel of the Institute of Horticulture, Melle, Belgium.

4.3.2.2 Sampling Unit

A schematic diagram of the sampling assembly used for *in vitro* experiments is shown in **Figure 14**. The plant was placed on a glass plate of 30 cm x 30 cm (1) and a Pyrex glass bell (15 cm I.D., 20 cm height, volume *ca.* 3.5 l) is positioned over the plant. Both units can be tightly joined by a screw system (5). For the analysis of a single rose, the headspace volume was reduced with a closed glass cylinder (14 cm I.D., 17 cm height, volume *ca.* 2.7 L) which was introduced into the glass bell. The rose was placed on top of this cylinder during sampling. The glass bell has a gas inlet (4) and outlet (3) made of Sovirel no. 10 connections and equipped with Teflon lined septa (Alltech, Deerfield, IL, USA). The entire system is air-tight to avoid outside air contamination. Pure air can be introduced for dynamic sampling via inlet 4 equipped with a pressure regulator. Both static and dynamic sampling takes place at outlet 3.

* *Published as:*
Monitoring Volatiles Emitted by Living Plants. Part 1 - Dynamic and Static Sorptive and Adsorptive Sampling , E. Baltussen, J. Vercammen, P. Sandra, T. Sandra, F. David, in preparation

4.3.2.3 Capillary GC-MS

The capillary GC-MS system consisted of an HP 6890 GC connected to an HP 5972 MSD operated in the electron impact mode (Hewlett-Packard, Little Falls, DE, USA). Full scan spectra were taken from m/z 40 to 300 at a scan rate of 3 scans/s. Identification was done via a Wiley database. The column used during all experiments was a 30 m L x 250 μm I.D. x 0.25 μm d_f HP-5MS capillary column (Hewlett Packard). The oven was programmed from 40°C to 325°C at a rate of 15°C/min. Helium was the carrier gas at a flow rate of 1 mL/min. The instrument was equipped with a CIS-4 programmable temperature vaporizing injector (PTV, Gerstel, Müllheim a/d Ruhr, Germany) for static sampling and with a thermal desorption (TD/PTV, Gerstel) unit for dynamic sampling.

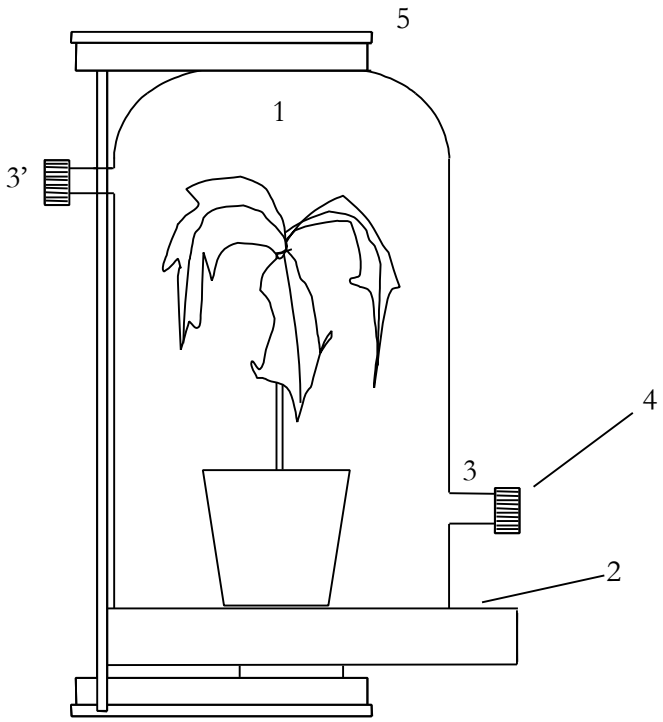


Figure 14 Schematic representation of the sampling unit (1), with a and b being 15 cm and 20 cm respectively. The set-up is placed on a glass plate (2). The unit is equipped with two openings: an outlet opening (3) were dynamic, as well as static, sampling takes place and an inlet opening (4) where purified air enters the system.

4.3.2.4 Static Sampling

Solid phase microextraction (SPME) on polydimethylsiloxane (PDMS) and polyacrylate (PA) fibers was used for static sampling. Both fibers were purchased from Supelco (Bellefonte, PA, USA) and had a coating length of 1 cm. The film thickness of the PDMS fiber was 100 μm and of the PA fiber 85 μm. The fibers were placed in a manual SPME holder (Supelco, Bellefonte, PA, USA). Prior to use, the fibers were conditioned into a hot GC injection port at 250°C during 1 hour for the PDMS fiber and at 280°C for 2 hours for the PA fiber, as recommended by Supelco. Static sampling was carried out, after the plant or flower had equilibrated for 1 hour, by inserting the SPME needle through the septum (**Figure 14**/3) and exposing the fiber to the headspace for 30 min. The fiber was then retracted and the SPME device was transferred manually to the CIS-4 PTV injector. Thermal desorption was done by programming the injector from 50°C to 250°C at a rate of 12°C/sec. The desorption time was 5 min with the splitless valve closed for 1.5 min.

4.3.2.5 Dynamic Sampling

After the plant material was equilibrated in the sampling assembly for 1 hour, dynamic sampling was performed by connecting a packed enrichment tube to the outlet of the sampling unit and applying a flow of air at 100 mL/min for 10 min. Concentration tubes packed with PDMS or Tenax were purchased from Gerstel. Conditioning of the PDMS cartridge was performed by heating at 250ºC for 24 hours under a flow of 100 mL/min helium. Preconditioned Tenax cartridges, flame sealed in a glass container, were used without further treatment. Desorption of the trapped components was carried out using a Gerstel TDS-2 thermal desorption unit mounted on top of the CIS-4 PTV injector. For all experiments desorption was in the splitless mode using helium at a flow rate of 150 mL/min. The TDS-2 was programmed from 20ºC to 225ºC at 60ºC/min with a final time of 5 min. To quantitatively trap the analytes released from the TDS and to guarantee small initial injection bands, the PTV was cooled to -150ºC with liquid nitrogen. When desorption was completed, the PTV was heated from -150ºC to 325ºC at 12ºC/sec with the split valve closed for 1.50 min. Full details of the system including a schematic lay-out and operation of the different valves, have been described[20].

4.3.3 Results and Discussion

4.3.3.1 Evaluation of PDMS and PA Blank Levels

Trace and ultratrace enrichment by sorptive or adsorptive extraction, requires that background signals from the used materials are minimal. In this respect, also the *in vitro* sampling unit should be critically evaluated. SPME background profiles for PDMS and

PA fibers, recorded after the conditioning procedure described in the experimental section and placing them in the sampling unit for 30 min, are given in **Figure 15**.

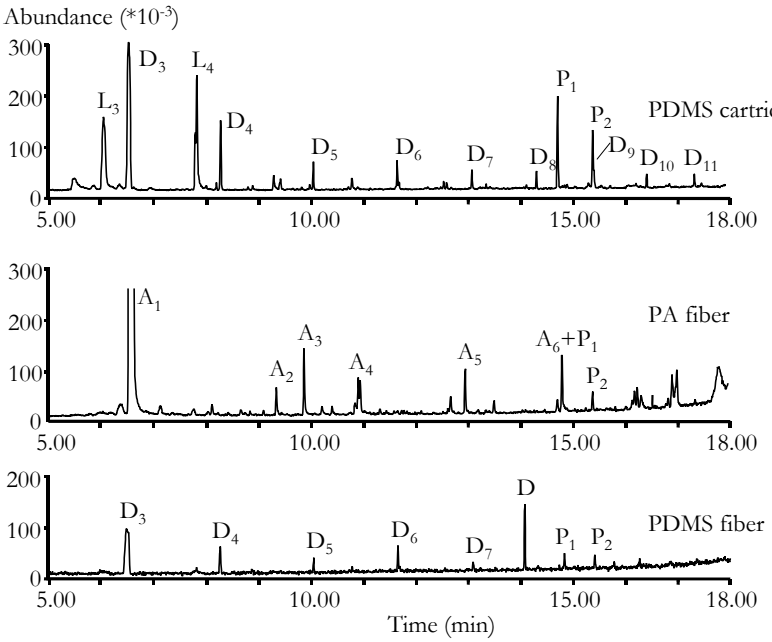


Figure 15 Lower trace is the result of a blank run of the PDMS coated fiber, 100 µm. The middle trace of the PA coated fiber, 85 µm and the upper trace of the packed PDMS concentration tube. An abundance of 100 000 corresponds to an amount of analyte of roughly 1 ng. Peak labeled D_x are cyclic siloxane degradation products. Peaks labeled A_x were identified as acrylate degradation products and their structures are given in the text.

With the exception of peaks P_1 and P_2, all signals detected in the blank run of the PDMS fiber originate from the decomposition of the polymer itself. D_x refers to cyclic PDMS oligomers of dimethylsiloxane with x being the number of silicon atoms in the ring structure. P_1 and P_2 have been identified as di-isobutylphthalate and di-n-butylphthalate, respectively, and are system peaks most probably present as plasticizers in the septa used in the sampling assembly. It has to be noted that acceptable blank values for the latter compounds could only be obtained after thorough washing of the interior of the glass bell with p.a. dichloromethane. The bell is then placed in an oven for 30 min at 60°C. Subsequently, the bell is flushed with purified air for 2 hours at a flow rate of 1 L/min. Initially, for flushing and dynamic sampling, laboratory air was used instead of pure air from a gas container. High molecular weight fatty acids like palmitic, stearic and oleic acid together with different phthalates were showing up at quantities of several nanograms for static sampling and at concentrations levels of 100 ng/L for dynamic sampling.

The quantity of D_3 in **Figure 15** (PDMS fiber) corresponds to *ca.* 1 ng (abundance of 10^5). Background peaks of PDMS and the sampling unit are, however, very characteristic and will not disturb the elucidation, identification and quantification of plant volatiles. In the blank profile of PA, for which the exact structure is unknown, a number of peaks is detected with 2-ethoxy-(2-ethoxy-(2-ethoxy-)) ethanol (A_1) as main compound and in a quantity of 5 to 10 nanogram. Other compounds are trimethylsilylpropionate (A_2), 1-(2-methylphenyl) ethanone (A_3), 1,3-dihydro-5-methyl-2N-imidazole (A_4), benzophenone (A_5) and N,N,N',N'-tetrabutyl methanediamine (A_6). Compounds A_3 and A_5 are known flavor compounds and can thus interfere in the determination of plant volatiles. The same phthalates as for PDMS are present in the PA trace (P_1 is overlapping with A_6) which emphasizes they are sampling assembly contaminants. The upper trace in **Figure 15** shows the blank of a PDMS concentration tube after dynamic sampling at 100 mL/min for 10 min in an empty sampling unit.

Table 9 Peak areas of the compounds detected in the headspace of *Jasminum officinale* relative to benzylacetate. Absolute amounts of benzyl acetate relative to dynamic sampling with PDMS are: 85% for Tenax, 2.4% SPME, PDMS and 6.2% SPME, PA.

		Dynamic Sampling		Static Sampling	
		PDMS	Tenax	PDMS	PA
1	3-hexenylacetate	1.82	2.32	nd*	nd*
2	2-hexenylacetate	1.25	2.11	nd*	nd*
3	benzylalcohol	0.64	0.63	nd*	0.75
4	4-methylphenol	12.71	12.05	14.53	26.72
5	linalool	11.87	11.13	6.68	7.87
6	benzylcyanide	1.18	0.90	2.38	0.92
7	benzylacetate	100.00	100.00	100.00	100.00
8	3-hexenylbutyrate	11.62	15.23	9.02	4.13
9	2- hexenylbutyrate	1.25	1.78	0.88	0.46
10	2-methoxy-4-methylphenol	2.23	1.54	2.30	5.42
11	methylsalicylate	0.23	0.21	0.08	0.31
12	3-hexenyl, 2-methylbutanoate	0.34	0.38	0.50	0.15
13	phenylethylacetate	2.57	2.24	4.38	3.95
14	eugenol	2.90	1.71	6.43	7.51
15	methylcinnamate	0.18	0.23	0.75	0.28
16	isoeugenol 1	0.24	0.13	1.17	0.31
17	trans-caryophyllene	0.16	0.16	0.29	0.10
18	isoeugenol 2	7.03	4.12	29.9	19.4
19	nerolidol	0.25	0.20	0.88	0.38
20	hexadecanoic acid, methylester	0.29	0.23	2.13	2.87

*nd = not detected

The same solutes as for the PDMS fiber are detected together with the linear oligomers containing 3 (L_1) and 4 (L_2) silicon atoms. The concentration is only *ca.* 3 times higher which is amazingly low considering the fact that a tube contains 300 mg PDMS whereas the PDMS fiber contains less than 1 mg. Di-iso-butylphthalate (P_1) and di-n-butylphthalate (P_2), the system peaks, are present in higher quantities because of the dynamic character of this sampling mode.

4.3.3.2 Static Sampling Using SPME with PDMS and PA Fibers

The total ion chromatograms of the headspace of *Jasminum officinale* using static SPME sampling are shown in **Figure 16**. The upper trace is the chromatogram obtained with the PDMS fiber (B) and the lower trace with the PA fiber (A). The identification of the peaks is listed in **Table 9**.

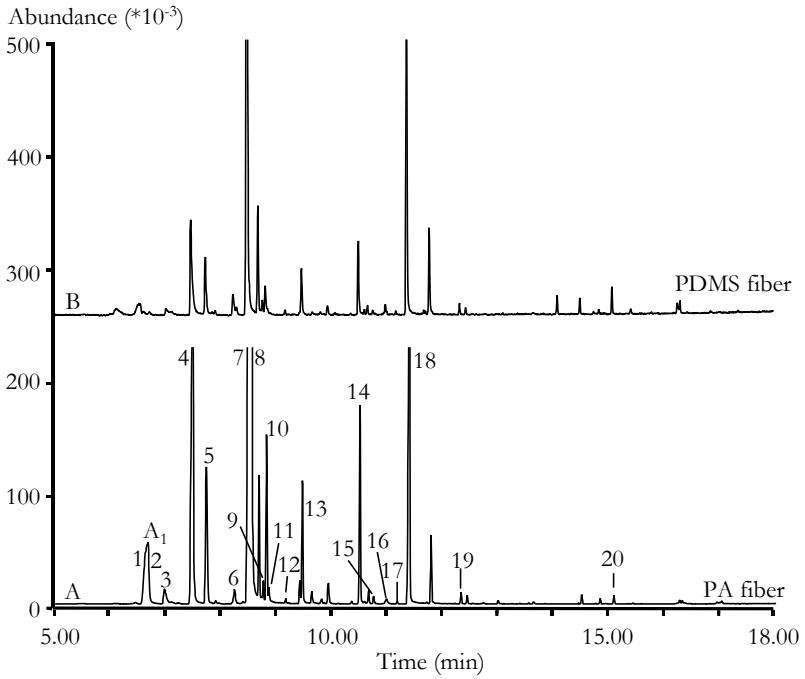


Figure 16 TICs of *Jasmonium officinale*. A: SPME with PA coated fiber. B: SPME with PDMS coated fiber. For conditions see experimental part. For peak identification see **Table 9**.

Comparison of both chromatograms shows that the volatiles emitted by *Jasminum officinale* which are medium polar to polar in nature, exhibit more affinity for the polar PA fiber than for the apolar PDMS fiber. The recoveries for benzylalcohol (peak 3), 4-methyl phenol (peak 4), linalool (peak 5), 2-methoxy-4-methyl phenol (peak 10) and eugenol (peak 14) are substantially lower in the PDMS trace compared to the PA trace. 3-hexenyl acetate (peak 1) and 2-hexenyl acetate (peak 2) could only be elucidated by ion extraction because they are co-eluting with A_1 in a broad peak which is the result of insufficient stationary phase focusing of the highly volatiles on the thin film column applied.

The apolar/polar discrimination effect which is entirely due to the different distribution coefficients in the apolar PDMS versus the polar PA fiber (like-like principle) is even better illustrated in the case of the roses. One rose was placed on top of the reducing cylinder and sampling on PA and PDMS was carried out (**Figure 17**). The identification of the peaks are listed in **Table 10**.

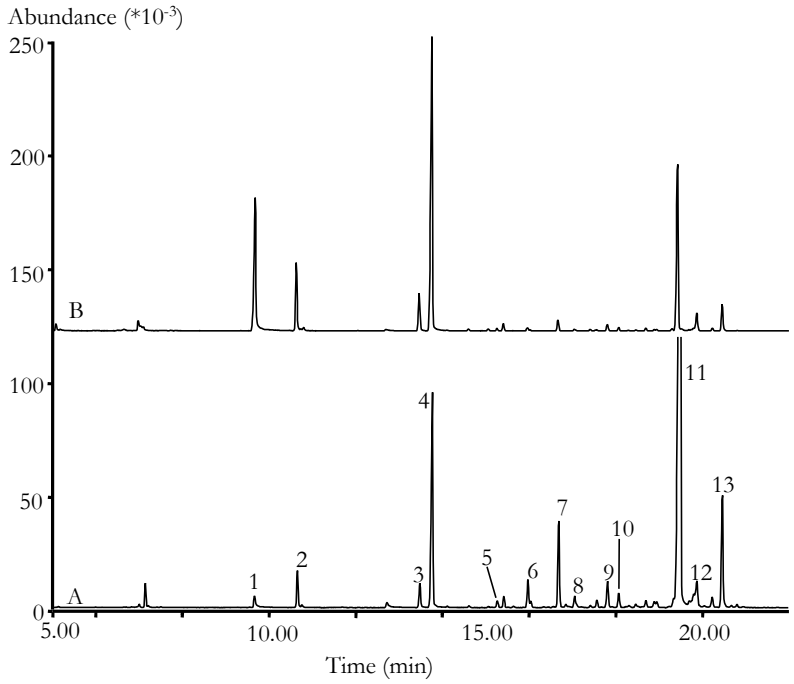


Figure 17 TICs of a single rose. Lower trace (A): SPME with PDMS coated fiber, upper trace (B): SPME with PA coated fiber. For conditions see experimental part. For peak identification see **Table 10**.

Table 10 Composition of the rose headspace as observed with SPME on a PA and a PDMS fiber. Listed are peak area values, relative to 2-phenylacetate, in %.

		PA	PDMS
Peak Number	Compound	Relative area	Relative area
1	phenylethylalcohol	419	56
2	1-ethenyl-4-methoxybenzene	155	126
3	2-phenylethylacetate	100	100
4	1-(ethylthio)-2-methylbenzene	869	872
5	3, 7-dimethyl 2, 6 octadienoic acid, methyl ester	--	--
6	a-cubelene	--	81
7	copaene	29	345
8	terpene 1	--	53
9	terpene 2	--	113
10	terpene 3	--	59
11	germacrene D	474	4331
12	terpene 4	61	215
13	terpene 5	71	465

The polar compound phenylethylalcohol (peak 1) exhibits on the PA fiber an increase in abundance by a factor of 10, the medium polar compounds like peaks 2, 3 and 4 an increase by *ca.* 1.5 while the apolar sesquiterpenes (peaks 6 to 13) show an intensity increase by a factor of at least 5 on the PDMS fiber compared to the PA fiber. This discrimination effect of SPME is tiresome in real sampling because one can never predict whether a signal molecule under biotic or abiotic stress[22], will be polar or apolar in nature. Dynamic sampling is much more promising in this respect.

4.3.3.3 Dynamic Sampling on Cartridges Packed with Tenax and PDMS

Figure 18 shows the total ion chromatograms of the headspace of *Jasminum officinale* with Tenax (A) and PDMS (B) as adsorbent and sorbent, respectively. The peak identification is listed in **Table 9**. The chromatograms were obtained after sampling for 10 min at a flow rate of 100 mL/min. Both chromatograms look very similar but additional peaks, assigned with T_x and arising from Tenax decomposition, are noted in **Figure 18A**. T_1 is benzaldehyde, T_2 acetophenone, T_3 and T_4 correspond to 2,6-diphenylquinone and 2,6-diphenyl-hydroquinone and represent degradation products of the monomeric Tenax structure. Additionally, the time window between 13 and 17 min contains several unidentified peaks which are typical for Tenax and are not present in the PDMS profile. The Tenax background thus hampers accurate

quantification of two important flavor compounds namely benzaldehyde and acetophenone which moreover possess biological activity as attractants for insects[33-36]. In fact, benzaldehyde was also identified in the PDMS trace applying ion extraction at m/z 105 but its concentration was ten times lower than in the case of Tenax sampling.

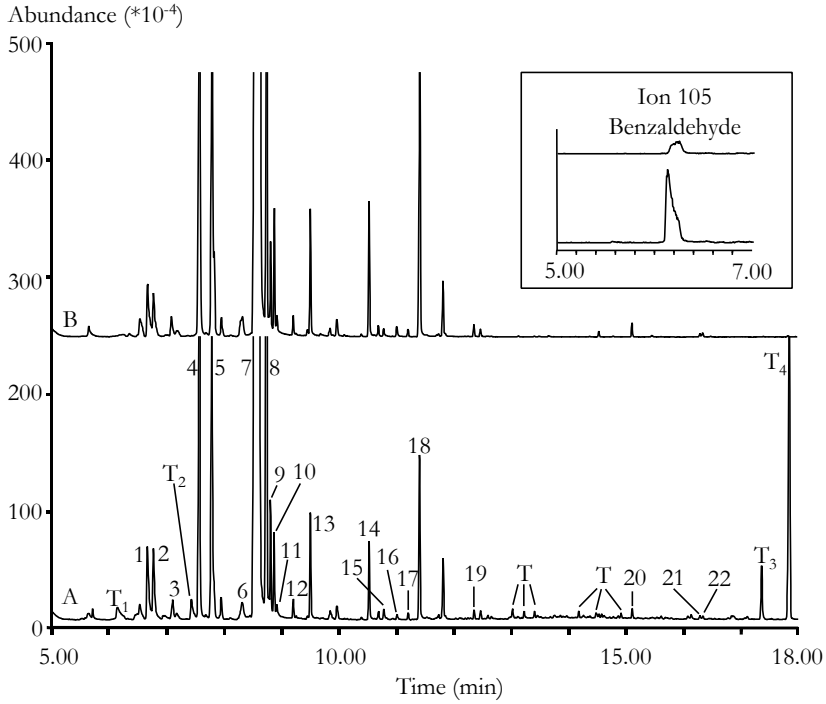


Figure 18 TICs of the headspace of *Jasminum officinale*. Lower Trace (A) with Tenax as enrichment material and upper trace (B) with PDMS as enrichment material. For conditions see text. For peak identification see **Table 9**. Peaks Labeled T_x are Tenax degradation products. T_1 is benzaldehyde, T_2 is acetophenone and T_3 and T_4 correspond to the Tenax monomeric structure, see text. Insert shows the extracted ion chromatogram of ion 105 from the TIC, which is specific for benzaldehyde.

Careful evaluation of the chromatograms in **Figure 18** also reveals a boiling point discrimination effect in the Tenax profile compared to the PDMS profile. Responses of the identified analytes on PDMS and on Tenax, relative to the areas of benzyl acetate, which was attributed 100, are given in **Table 9**. The higher molecular weight compounds show stronger retention on Tenax compared to PDMS and different desorption conditions (*i.e.* higher temperatures or longer desorption times) than the standard conditions (see experimental section) should be applied. This favors, however, the use of PDMS for which diffusion is fast and at low temperatures which decreases the risk of artifact formation.

Comparing **Figure 16** with **Figure 18**, in first instance indicates that the highly volatile solutes show less band broadening for dynamic sampling compared to static sampling. This is because of efficient cryofocusing at –150ºC in dynamic sampling compared to the much slower release of the trapped solutes from the SPME fiber. On the other hand, for the *Jasminum officinale* plant, the dynamic PDMS profile strongly resembles the static PA profile! Whatever the nature of the emitted volatiles, dynamic sorption on PDMS operated in the breakthrough mode, will always better reflect the headspace composition than SPME sampling. Also note that the dynamic sampling shown in **Figure 18** displays a 10 times higher sensitivity compared to the SPME chromatograms in **Figure 16**.

4.3.4 Conclusion

There was little difference in dynamic sampling between PDMS and Tenax when globally comparing the obtained results. Tenax, however, has some important disadvantages when compared to the PDMS material: degradation products of the material can be mistakenly interpreted as compounds emitted by the plant. This was observed for benzaldehyde and acetophenone. The yield of higher molecular weight compounds was also lower when compared to dynamic sampling with PDMS. This is due to the stronger retaining capacity of Tenax (adsorption) resulting in incomplete desorption. In addition to these observations, sampling with Tenax as trapping material can also give rise to catalytic degradation of polar and/or unstable analytes, which renders the results somewhat less reliable.

Dynamic sampling with PDMS and static sampling using SPME with PDMS and with PA fibers give, in general, similar results. Large differences in extracted amounts were obtained for compounds being emitted in trace amounts and/or having a low affinity for the used fiber material. In these cases dynamic enrichment with PDMS was more sensitive and straightforward because one single material can trap the apolar as well as the polar analytes. Dynamic sampling, with PDMS used as the packing material for preconcentration tubes, can, therefore, be a viable alternative to the static sampling technique with SPME. In this way dynamic sampling with PDMS can introduce new frontiers in the domain of plant volatile research.

4.4 Determination of Nicotine in Hospital Air*

4.4.1 Summary

A novel method for the enrichment of nicotine from gaseous samples is presented. It is based on the sampling of 6 liters of air onto a cartridge packed with 100 % polydimethylsiloxane (PDMS) particles. The analytes are dissolved (partitioned) into the PDMS phase which results in much better recoveries and reproducibilities compared to those obtained on common adsorbents. The PDMS tube is then placed in a thermal desorption (TD) unit connected to a CGC-NPD or CGC-MS system. The procedure was employed for routinely monitoring air in a hospital. Nicotine was typically found at levels ranging from 5 to 250 $\mu g/m^3$ (ppb) depending on the location and number of smokers present. Additionally, the efficiency of nicotine filters was determined by sampling simultaneously at the filter in- and outlet and was found to be 46 %.

4.4.2 Introduction

The use of sorptive preconcentration on cartridges packed with PDMS particles for the determination of nicotine in air samples is described. PDMS as a preconcentration phase is compared to the adsorbents Carbotrap, Tenax and Chromosorb 101 for the enrichment of nicotine from gaseous samples. In order to overcome the shortcomings of adsorbents, we recently introduced a new retaining material, namely 100% polydimethylsiloxane (PDMS), which is a well known stationary phase (OV-1, SE-30, HP-1 *etc.*) in gas chromatography. The analytes are retained by dissolution into the pure, homogeneous PDMS particles, *i.e.* no active adsorbent surface is present. This minimizes the risk of permanent adsorption and/or decomposition of the sampled analytes. As an application, we describe the monitoring of nicotine, the tracer of cigarette smoke, in the air of a hospital in Eindhoven. The concentration of nicotine was followed over several 12 hour periods. Additionally, the effectiveness of a nicotine filter was investigated by measuring simultaneously at the in- and outlet of the filter.

* *Published as:*
Monitoring of Nicotine in Air Using Sorptive Enrichment on Polydimethylsiloxane and TD-CGC-NPD, E. Baltussen, A. den Boer, P. Sandra, H.-G. Janssen and C. Cramers, Chromatographia 49 (1999) 520

4.4.3 Experimental

4.4.3.1 Sampling Cartridges and Air Sampling

Thermal desorption tubes (6 mm O.D., 4 mm I.D.) filled with PDMS particles were obtained from Gerstel (Müllheim a/d Ruhr, Germany). These cartridges contain *ca.* 400 mg of PDMS material which is kept in place by means of two plugs of deactivated glass wool. Before use, the PDMS cartridges are thermally conditioned at 325ºC for 1 hour and subsequently at 225ºC for 4 hours to ensure good blank profiles. Sampling tubes filled with Carbotrap 300 or Carbotrap 302 were obtained from Supelco (Bellefonte, PA, USA). Sampling tubes filled with Tenax TA were obtained from Gerstel (Müllheim a/d Ruhr, Germany). Thermal desorption tubes filled with Chromosorb 101 (Alltech, Deerfield, IL, USA) were home made using empty glass tubes obtained from Gerstel. All adsorbents were conditioned at 300ºC for 5 hours.

Spiked air samples were generated according to the procedure described previously, see **Section 4.1.4.3**. Hereto the sampling tube was connected to a clean air source in which 1 μL of a standard solution containing nicotine was injected. After injection of the liquid standard the flow was maintained for 10 minutes at 600 mL/min to simulate as closely as possible the sampling of an actual air sample. Field sampling was also performed at a flow rate of 600 mL/min for 10 minutes but now using a high volume air pump (Verder, Vleuten, the Netherlands).

4.4.3.2 Experimental Set-Up

An experimental set-up similar to the one described previously (**Section 4.1.4.3**) was used. It consists of a thermal desorption system (TDS-2, Gerstel) where the PDMS packed cartridges are thermally desorbed at 225ºC for 5 minutes. The thermally released analytes are cryogenically refocused in a CIS-4 PTV injector (Gerstel) which is equipped with an empty, deactivated glass liner (Gerstel). The system is mounted on an HP 6890 gas chromatograph (GC, Hewlett Packard, Little Falls, DE, USA) which was equipped with an HP-VOC column which was 30 m long, had an inner diameter of 200 μm and a film thickness of 1.1 μm. The detector used was an HP 5972 mass selective detector (MSD). This set-up was used for characterization of the blank profiles of the PDMS traps and to identify the solutes of interest in cigarette smoke.

For routine monitoring of nicotine in hospital air an alternative system was used. The TD unit was connected to a HP 5890A (Hewlett Packard) equipped with a nitrogen-phosphorous detector (NPD). The NPD was operated under a hydrogen flow rate of 3 mL/min and an air flow rate of 100 mL/min. The bead current was adjusted to obtain a background signal of *ca.* 20 mV.

This system was equipped with a 15 m x 150 μm CP-SIL5CB column with a film thickness of 2 μm (Chrompack, Middelburg, the Netherlands).

4.4.4 Results and Discussion

4.4.4.1 System Evaluation and Smoke Characterization

Initial experiments focussed on the characterization of cigarette smoke. Hereto, 10 mL smoke of a cigarette was drawn through a PDMS packed sampling tube. This small (but very concentrated) sample was sufficient to detect and identify the principal components. The chromatogram of this analysis is shown in **Figure 19**.

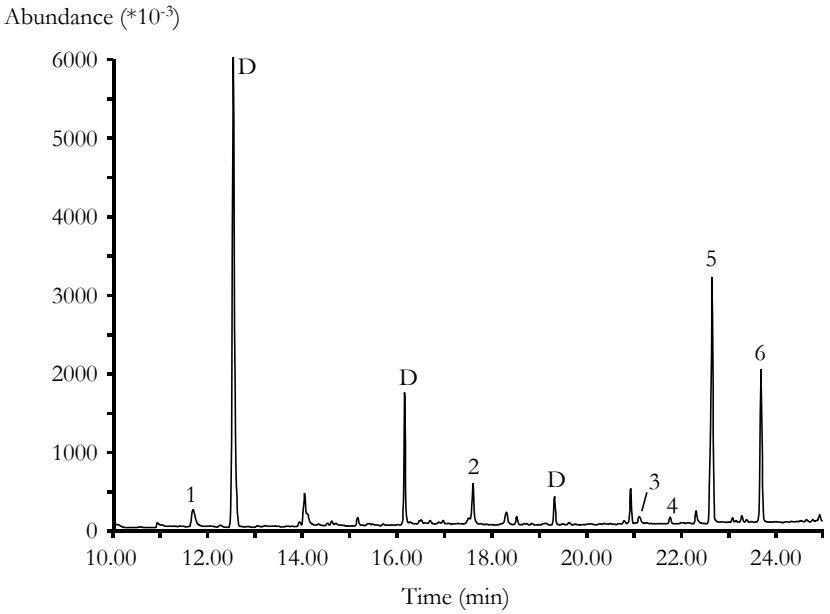


Figure 19 Chromatogram on the PDMS-TD-GC-MS set-up of the analysis of 10 mL cigarette smoke. Identified solutes: D=silicone degradation products; 1=toluene; 2=monoterpene; 3=glycerol diacetate; 4=substituted naphthalene; 5=triacetin; 6=nicotine.

As expected, nicotine is one of the major components and therefore was selected for further monitoring studies. Next to nicotine a number of other peaks are present, however, none of these are as specific for cigarette smoke as nicotine. Glycerol diacetate and triacetin are known to be cigarette tobacco and filter additives. The presence of toluene could be positively confirmed which is not possible on Tenax which gives blanks containing this analyte and thus prohibiting its analysis. Also

interesting in this chromatogram is the presence of the siloxane degradation peaks (labeled as D in **Figure 19**). These could, from their mass spectrum, be assigned as cyclic siloxane degradation products (D_3, D_4, D_5 *etc.*) hence there is no risk of misidentifying these sorbent degradation products as actually sampled analytes.

4.4.4.2 Performance of PDMS Versus Adsorbents

In order to evaluate PDMS for the enrichment of nicotine and to illustrate the advantages of sorption over adsorption, several experiments were performed with spiked air samples. At two concentrations, namely: 100 μg/m^3 and 2 μg/m^3, recoveries from 6 liter air samples were established for PDMS and all adsorbent cartridges used here. The results are listed in **Table 11**. Each recovery was determined as the average of 3 experiments on 3 different tubes.

Table 11 Recoveries (REC, %) of nicotine from 6 liter air samples at a level of 100 μg/m^3 and 2 μg/m^3. Relative standard deviations (RSD, %) were determined from 3 replicate analyses (n.d.: not detected).

	100 μg/m^3		2 μg/m^3	
	REC	RSD	REC	RSD
Carbotrap 300	n.d.	-	n.d.	-
Carbotrap 302	n.d.	-	n.d.	-
Tenax TA	73	13	52	34
Chromosorb 101	61	18	7	21
PDMS	98	6	105	8

It is clear from this table that poor performance is observed for all adsorbents. On the carbon based Carbotrap phases nicotine is completely lost. On Tenax and Chromosorb 101 the situation is better but a significant loss of analyte is still observed. The low recoveries on the adsorbents are not caused by losses of nicotine due to breakthrough from the trap. Instead, the interaction of polar analytes (such as nicotine) with the adsorbents is very strong. This precludes complete release of the sampled analytes thus causing poor recoveries. The analytes can either become permanently fixed to the adsorbent surface or be converted into other components (artifact formation). On the PDMS traps, the analytes are not retained on an active surface, rather they are dissolved into the PDMS layer. This provides a much more inert environment and allows quantitative trapping and release of the solutes in question. Lower concentrations than those shown in **Table 11** were not tested since they were not encountered at the problem locations (polluted areas). However, on the basis of the sorption mechanism good performance at lower concentration levels is suspected[23].

4.4.4.3 Routine Monitoring

It was asked to monitor background nicotine levels in the air of a hospital. Therefore, several locations including totally non-smoking rooms and special smoking rooms were selected. Several samples were taken in these rooms to determine the background levels. In **Figure 20**, chromatograms are presented using PDMS-TD-CGC-MS. **Figure 20A** is the result of the analysis of a spiked air sample. Nicotine was added at a concentration of 73 $\mu g/m^3$. **Figure 20B** and **Figure 20C** show chromatograms of a typically highly smoke polluted and low smoke contaminated samples, respectively. The analysis of nicotine should thus be possible at environmentally relevant concentrations using NPD detection. In real life samples the detection limit is around 0.1 $\mu g/m^3$ with the set-up used. This limit is primarily determined by the presence of chemical interferences (*e.g.* components co-eluting with nicotine and also having a non-zero NPD response). Lowering the detection limit is possible using more selective detection techniques such as GC-MS in the selected ion monitoring mode[24] or even GC-ECD using a nicotine derivative[25]. However, for routine monitoring the reliable and cheap NPD is appropriate.

The time dependence (day profile) of the concentration of nicotine was determined over a number of 12 hour periods. 13 PDMS sampling tubes were prepared and the absence of nicotine was confirmed by blank analyses. Air samples were taken in a room at intervals of 1 hour starting at 7 AM until 7 PM. During the sampling periods the rooms under investigation were used as normal. This resulted in significant day-to-day differences depending both on the number of persons present and their smoking behavior. In **Figure 21** a typical profile for a 12 hour monitoring period is presented for a smoking room. At the start of the day, the nicotine level is low since the room has not been used at night. During the day several peaks appear in the profile corresponding to the intensity of smoking in the room.

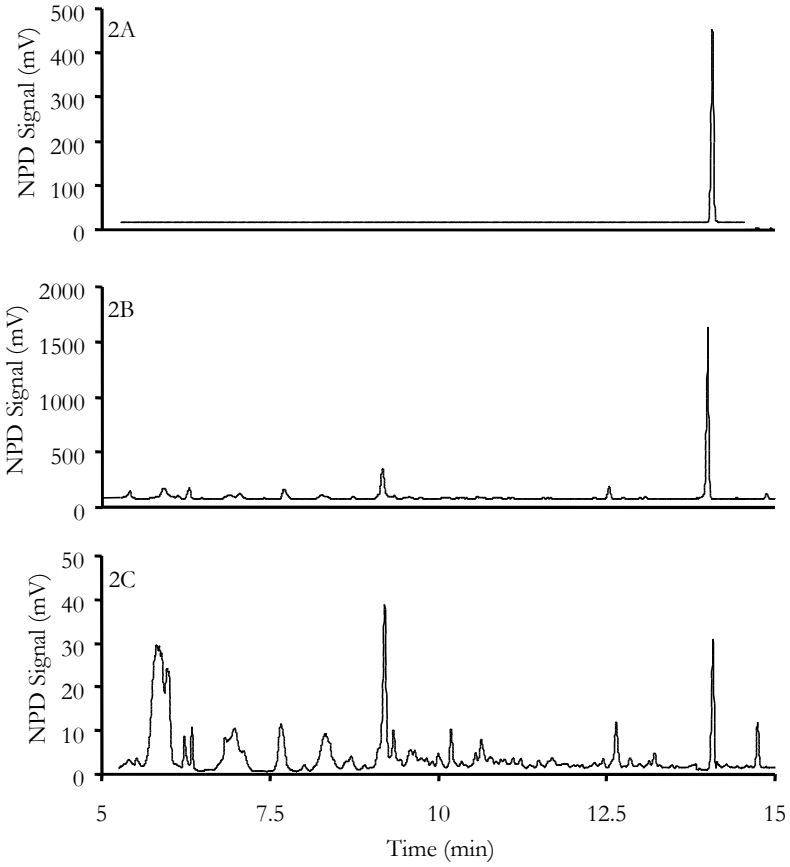


Figure 20 Chromatograms of the analysis of nicotine in air by PDMS-TD-CGC-MS. Chromatogram A is obtained from an air sample spiked at a level of 73 μg/m^3. Chromatogram B is an example of a highly smoke polluted room and C of a low by smoke polluted area. The concentrations of nicotine found are 250 and 4.86 μg/m^3 respectively.

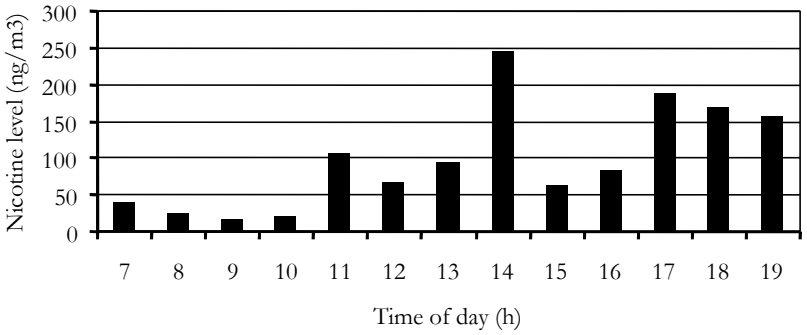


Figure 21 Profile of the nicotine concentration in a hospital smoking room during a working day.

4.4.4.4 Filter Efficiency

To reduce the nicotine level in the smoking room it was decided to install extra filters. These filters function independently from the air conditioning system and circulate the total room volume roughly 1.5 times per hour. The filters are based on a fine particulate filter, a carbon adsorbent and an electrostatic filter placed in series. A more detailed description of the filter system is given elsewhere[26]. The efficiency of these filters was determined by sampling simultaneously at the filter in- and outlet. From 5 replicate measurements (10 chromatographic runs), a filter efficiency of 46 % was measured. Slightly less than half of the nicotine was removed from the air. The relative standard deviation was 14 %. **Figure 22A** represents the air entering the filter unit while **Figure 22B** is a chromatogram of the air exiting the filter unit. The figures show that the nicotine peak clearly diminishes, but that the background (as observed on the NPD) increases. This effect was observed during all filter efficiency measurements. Most likely substances previously adsorbed on the filter are eluting out of the filter by the flow through it.

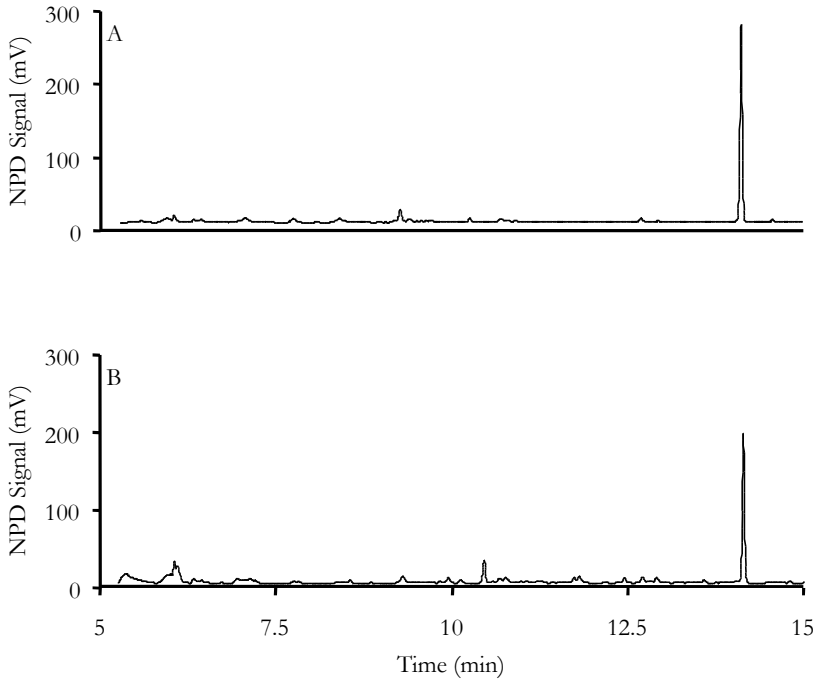


Figure 22 Chromatograms of the filter efficiency determination. Chromatogram A is taken directly before the filter and chromatogram B is taken directly after the filter.

4.4.5 Conclusion

A new method for the enrichment and determination of nicotine in gaseous samples was described. It was shown that the sorbent PDMS exhibits superior performance over adsorbents for the enrichment of samples in the 2-200 $\mu g/m^3$ (ppb) range. This can be extended into lower concentrations by applying GC-MS. The method could be applied to monitor nicotine levels in hospital rooms and to evaluate the effectiveness of filter systems.

4.5 Fast Analysis of PAHs in Air with Liquid Chromatography*

4.5.1 Introduction

Most preconcentration methods for the enrichment of semi-volatile components from air samples are based on the sampling of extremely large air volumes onto glass fiber filters or active adsorbent materials. Sampled volumes can be as high as 1000 m^3 or more and require very long sampling times even at flow rates up to several m^3/min. After preconcentration the trapped analytes are most commonly desorbed by an organic solvent (*e.g.* dichloromethane) of which a volume of up to 100 mL is not uncommon. After extraction this volume has to be concentrated and even then only a small portion of the sample is actually analyzed. These type of procedures are very complex, time-consuming and prone to artifacts by the many (manual) sample handling steps. A significant shortening of the sampling time (necessary air volume) is the subject of the work described here.

A new method for the preconcentration of volatile and semi-volatile components was recently introduced by Baltussen *et al.*[20,27]. It is based on the use of polydimethylsiloxane (PDMS) for the trapping of the analytes of interest from the gaseous sample. Contrary to adsorbent materials, retention on the PDMS phase is not based on an adsorption phenomenon, it is rather based on partitioning (= dissolution) of the analytes into the PDMS phase. Advantages of sorption were addressed in **Chapter 3** and this chapter, the most important ones being: prediction of breakthrough volumes from GC retention data, high degree of inertness and absence of displacement effects. Sorptive PDMS preconcentration has been evaluated for the analysis of both gaseous and aqueous samples by capillary GC/MS. In a recent publication[23] the analysis of the 16 EPA priority PAHs was described using PDMS preconcentration and thermal desorption coupled on-line to capillary GC/MS. Though good detection limits were obtained, the procedure itself is still rather lengthy. This was primarily due to the fact that the GC separation is rather time consuming, *i.e.* 50 minutes including cooldown.

The viability of sorptive PDMS preconcentration of air samples coupled on-line with fast LC analysis was evaluated. One of the most important factors determining sampling (and thus overall analysis time) is the required sample volume. This can be calculated from the detector sensitivity and the detection limits desired. With the use of a fluorescence detector, which is the most sensitive LC detector for PAHs, the detection limit is in the order of 40 pg for benzo[a]pyrene. The desired detection limit is

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in the order of 1 ng/m^3 since this is typically the expected concentration[23,28]. A simple calculation results in a required sample volume of 25 liters. This volume can be sampled at a flow rate of 5 L/min which means a total sampling time of only 5 minutes. Another important factor that has to be considered is breakthrough of the most volatile PAHs (*e.g.* naphthalene) due to insufficient retention on the PDMS trap. In a previous publication[20], a theoretical model for calculating breakthrough volumes on the PDMS trap was described. This model will be applied here to describe the losses of the more volatile analytes during sampling.

4.5.2 Theoretical Breakthrough

The model is based on the breakthrough equation of Lövkvist and Jönsson[14], using the Knox equation[16,17] for the calculation of plate numbers on the short PDMS column. Additionally, the retention data for alkanes on the PDMS phase are known from literature[15] and combining this with Kováts retention indices[19], breakthrough volumes can be calculated for any component.

The parameters for the PDMS trap used in this report were; inner diameter: 4.6 mm, length: 50 mm, average particle diameter: 375 μm and sampling flow rate: 5000 mL/min. 371 mg (0.449 mL) of PDMS material was fitted into the cartridge. Retention and breakthrough volumes for the volatile PAHs are listed in **Table 12**. It is clear from this table that, at the required sample volume of 25 liters, naphthalene is partially lost, since its breakthrough volume is only 12.6 liter under the conditions used here. For all other PAHs, quantitative retention is expected since the breakthrough volumes are significantly in excess of 25 liter (*i.e.* 115 liter or more).

Table 12 Retention data of PAHs on the PDMS trap. Trap parameters: diameter: 4.6 mm, length: 50 mm, particle diameter: 375 μm. PDMS trap contains 371 mg of PDMS material (= 0.449 mL). Temperature = 20°C.

Solute	Retention Index[19]	Retention volume (L)	Breakthrough volume (L)
Naphthalene	1187.75	30.0	12.6
Acenaphthylene	1428.30	288	115
Acenaphthene	1460.73	391	156
Fluorene	1574.92	349	886

4.5.3 Experimental

4.5.3.1 Packed PDMS Traps

The packed PDMS preconcentration trap used for the on-line LC experiments described here consisted of a short metal LC-type column with an inner diameter of 4.6 mm. The length of the PDMS trap was 50 mm. On both inlet and outlet this column was fitted with standard Valco adapters. The metal preconcentration column was filled with PDMS particles prepared according to the procedure outlined previously[20,27]. Before use, the PDMS particles were sieved in the range 250-500 μm. This relatively large particle diameter was chosen to allow high sampling flow rates during the air sampling step. From the thus obtained particles a slurry was prepared in methanol which was used to fill the PDMS column by applying a vacuum on the trap outlet. After the methanol was removed by the vacuum pump, the PDMS trap was closed by the inlet fitting.

In order to clean the PDMS trap it was connected to a LC pump. The cartridge was flushed with subsequently 25 mL methanol (MeOH) - 10 mL isopropanol (IPA) - 25 mL iso-octane - 10 mL IPA and finally 25 mL MeOH. The cartridge was then dried with nitrogen for 10 minutes (flow *ca.* 10 L/min). By comparing the filled trap weight with that of the empty trap it was determined that 371 mg PDMS was present in the trap.

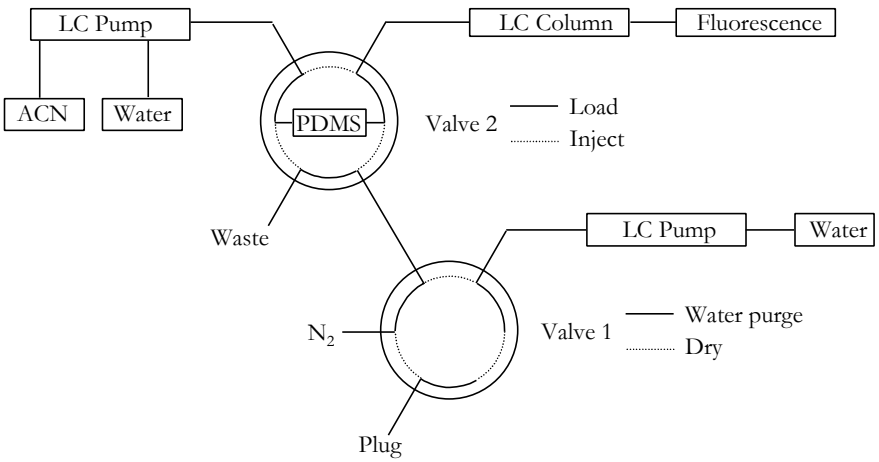

Figure 23 Schematic overview of the experimental set-up.

4.5.3.2 Experimental Set-Up

The experimental set-up used for all experiments is shown in **Figure 23**. It is built up around two Valco 6 port valves (Valco, Houston, TX, USA). Valve 1 is used as a selection valve to purge the cartridge with either nitrogen (grade 5.0) or HPLC grade water which was prepared using a Millipore system (Millipore, Bedford, MA, USA). Valve 2 is used to couple the PDMS precolumn on-line to the main LC column or to connect it to valve 1 for the pre/post-treatment procedures as will be described later.

The chromatographic system consisted of a gradient pump (LKB, Bromma, Sweden) which was supplied with gradient grade water and acetonitrile obtained from Biosolve (Valkenswaard, the Netherlands). The analytical column was a 150 mm x 4 mm I.D. Chromspher PAH (Chrompack, Middelburg, the Netherlands) and the detector was a model 1046A programmable fluorescence detector (Hewlett Packard, Waldbronn, Germany).

Table 13 Fluorescence program, Ex an Em are excitation and emission wavelengths respectively.

No.	Solute	Ex (nm)	Em (nm)
1	Naphthalene	230	330
2	Acenaphthylene	-	-
3	Acenaphthene	210	316
4	Fluorene	210	316
5	Phenanthrene	250	350
6	Anthracene	250	350
7	Fluoranthene	237	440
8	Pyrene	237	440
9	Benz[a]anthracene	277	376
10	Chrysene	277	376
11	Benz[b]fluoranthene	255	426
12	Benz[k]fluoranthene	255	426
13	Benz[a]pyrene	255	426
14	Dibenz[a,h]anthracene	230	400
15	Benz[g,h,i]perylene	230	400
16	Indeno[1,2,3-cd]pyrene	250	490

4.5.3.3 Air Sampling and On-Line LC Analysis

The analytical procedure starts with the sampling of air during 5 minutes at a flow rate of 5 L/min. A total air volume of 25 liters is thus taken. After sampling is complete the

PDMS trap is disconnected from the air pump and connected to valve 2 of the chromatographic system. At that time valve 1 is in the water purge position and valve 2 is in the load position. In order to purge the air still present in the PDMS trap, which would otherwise disturb the chromatographic analysis, the PDMS trap is flushed with water for 15 seconds at 5 mL/min.

Immediately thereafter valve 2 is switched to the inject position putting the PDMS trap in front of the analytical column. At the same time, the gradient and fluorescence programs are started. For maximum sensitivity, the excitation and emission wavelengths of the detector are programmed in time to provide optimum conditions for all compounds. The fluorescence program is listed in **Table 13**. Once the gradient program is finished and all analytes are eluted from the column, valve 2 is switched back to the load position and the gradient pump is programmed back to its initial conditions (50% AcCN). The acetonitrile still remaining in the PDMS trap is purged by switching valve 1 to the dry position and applying nitrogen at a pressure of 5 bar for 30 seconds. The PDMS cartridge is now ready for the second sampling. An overview of the total analytical procedure is listed in **Table 14**.

Table 14 Analytical procedure

Step	Time (min)	Valve 1	Valve 2	Remarks
Sample, 5 min at 5 L/min	-5.25	water purge	load	50% AcCN
Water purge	-0.25			
Start Analysis	0		inject	to 100% AcCN in 5 min
Gradient Ramp Finish	5			100% AcCN
Analysis End	7	Dry	load	100% AcCN
Purge Cartridge				Clean cartridge: N_2, 5 bar
Cartridge ready	7.5			PDMS ready for next run
Gradient ready	8	water purge		50%AcCN

4.5.4 Results and Discussion

In a first series of experiments, the recoveries of the PAHs were investigated. In order to simulate the loading of air samples the PDMS trap was connected with a short piece of 530 μm fused silica tubing to the split/splitless injector of an HP 5890 GC (Hewlett Packard, Little Falls, USA). The carrier gas flow regulator was bypassed to allow a flow of 5000 mL/min through the PDMS trap. The injector was kept in the splitless mode continuously. Spiked air samples were simulated by injecting 1 μL of a standard solution of PAHs in dichloromethane into the split/splitless injector and keeping the PDMS trap under the flow of 5000 mL/min for 5 minutes. Recoveries were calculated versus direct spiking of 1 μL of standard solution onto the PDMS cartridge. For the latter

experiment, the PDMS cartridge was opened and the needle tip is positioned in the middle of the PDMS bed. The results are listed in **Table 15**. It is clear from this table that good recoveries are observed for all PAHs except for naphthalene, for which losses were expected from the calculated breakthrough volumes. With the exception of naphthalene, relative standard deviations were within 15 % (n=5).

Concerning the analytical procedure, it can be stated that purging of air remaining in the PDMS cartridge prior to the chromatographic analysis is a critical and essential step. If this step is omitted, or not performed well, air remaining in the cartridge is pushed onto the analytical column. When the extraction cartridge was put in front of the column, the pressure on the HPLC pump immediately dropped to zero. As soon as the air had been compressed (and most likely been dissolved in the mobile phase), the pressure slowly came back to the normal value. The tubing exiting the fluorescence detector was made from a transparent material. Shortly after the column dead time, bubbles appeared in this tubing due to the air that was again released from the mobile phase. This resulted in a very unstable detector signal which continued for several minutes and prevented the detection of the first (1-8) PAHs. In summary, omitting the water purge step resulted in a disturbed detector signal, unstable pump pressure and changing retention times. All these problems could be efficiently circumvented by an appropriate water purge step.

Table 15 Recoveries of the 16 PAHs at the indicated concentration level.

No.	Solute	C (ng/m^3)	Recovery (%)	RSD (n=5, %)
1	Naphthalene	1000	45	27
3	Acenaphthene	1000	98	11
4	Fluorene	1000	106	13
5	Phenanthrene	1000	110	15
6	Anthracene	1000	105	10
7	Fluoranthene	1000	92	9
8	Pyrene	1000	96	13
9	Benz[a]anthracene	1000	110	14
10	Chrysene	1000	115	8
11	Benz[b]fluoranthene	100	101	8
12	Benz[k]fluoranthene	100	93	12
13	Benz[a]pyrene	100	106	15
14	Dibenz[a,h]anthracene	100	92	6
15	Benz[g,h,I]perylene	100	97	12
16	Indeno[1,2,3-cd]pyrene	100	91	15

The PDMS trap was applied for the analysis of PAHs in actual air samples. A chromatogram of 25 liters of ambient air taken in Eindhoven is shown in **Figure 24**. Most of the PAHs can be observed in the chromatogram (only acenaphthylene and indeno[1,2,3-cd]pyrene are missing). Several solutes were not quantitated because they were either not sampled quantitatively (naphthalene) or were present at too low concentrations (PAHs 7 through 10). The most important PAHs could be reliably quantitated. The concentrations determined are listed in the caption of **Figure 24**, and the most toxic PAH, benz[a]pyrene, was found at a concentration of 7.1 ng/m^3.

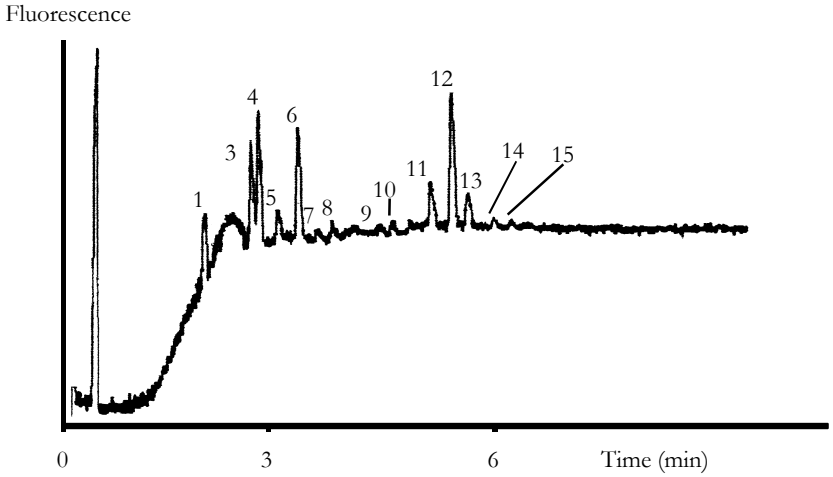

Figure 24 Chromatogram of 25 liters of an air sample, concentrated on the PDMS trap. For peak identification, see **Table 15**. Components quantitated: 3, 51 ng/m^3; 4, 110 ng/m^3; 5, 70 ng/m^3; 6, 20 ng/m^3; 11, 12 ng/m^3; 12, 6.8 ng/m^3; 13, 7.1 ng/m^3. Components were identified on the basis of retention times.

4.5.5 Conclusion

A new method for the analysis of PAHs in air is described. It is based on the preconcentration of 25 liters of an air sample onto a packed PDMS cartridge. The retained solutes are subsequently analyzed on-line by liquid chromatography with fluorescence detection.

The proposed method was evaluated for the analysis of the 16 EPA priority PAHs. Under real-life conditions the method worked well for the analytes under investigation. All solutes, with the exception of naphthalene, were recovered quantitatively. In an actual air sample, the most important PAHs were detected at levels between 7 and 110 ng/m^3.

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5 Gum Phase Extraction for Liquid Samples

Following the introduction of gum phase extraction in the previous chapter, including an overview of its applications in the analysis of gaseous samples, gum phase extraction for aqueous samples is described in this chapter.

5.1 A Retention Model for Gum Phase Extraction of Aqueous Samples: Application to the Automated Analysis of Pesticides and PAHs in Water Samples*

5.1.1 Summary

An automated method for the gum phase extraction (GPE) of aqueous samples is presented. It is based on sorption of the analytes of interest into a packed bed containing 100% polydimethylsiloxane (PDMS) particles followed by thermal desorption for complete transfer of the enriched solutes onto the GC column. Compared to other solvent-less sample preparation techniques for water samples, several improvements can be noted of which the most obvious are an enhanced sensitivity and improved blanks. Moreover, degradation products formed from the PDMS material can easily be identified with the use of a mass spectrometric detector. As these products contain silicone, they do not interfere with the target solutes (pesticides, PAHs). A theory model is derived which allows calculation of breakthrough volumes from octanol/water partitioning coefficients ($K_{O/W}$). Alternatively, the $K_{O/W}$ value required for complete retention can be calculated using only the sample volume and trap specific parameters. For a sample volume of 10 mL, theory predicts a required log $K_{O/W}$ of 1.77 for the trap used here which was found to be in good agreement with experimental results. For the most apolar solutes, with a log $K_{O/W}$ in excess of seven, poor recoveries were found. This is most likely due to adsorption of these apolar

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solutes in the system. With the current set-up, detection limits are in the order of 10 ng/L using mass spectrometric detection in the full scan mode.

5.1.2 Introduction

Trace analysis of organic micropollutants in water by gas chromatography-mass spectrometry (GC-MS) is basically hindered by two problems. The first problem is that the water sample is generally too dilute for direct injection, *i.e.* the water sample has to be concentrated. The second problem is that water is not compatible with most GC stationary phases and therefore its transfer onto the GC column should be prevented. To overcome these problems a number of different methods for phase switching, *i.e.* transferring the analytes from a large volume of water to a small volume of an organic solvent have been developed.

The most popular methods for phase switching are liquid/liquid extraction (LLE)[1,2,3] and solid phase extraction (SPE)[4,5]. Nowadays, LLE is more and more replaced by SPE because the latter technique requires less solvent, is faster, easier to automate and can easily be connected on-line to both GC as well as HPLC[6]. Although SPE has clear advantages over LLE it still suffers from some of disadvantages. The most important one being the fact that the retention behavior (breakthrough volume) can depend on both analyte and matrix concentration.

Recently, several solvent-less extraction techniques were proposed in literature. One of these methods uses SPE but now with thermal desorption (SPETD) instead of liquid desorption[2,7,8]. The major advantage of this approach is that organic solvents are completely banned. It was, however, found to be difficult to find adsorbents with both favorable adsorption and thermal desorption characteristics. For practical purposes, Tenax appeared to be the best compromise for SPETD.

A second approach is to trap the analytes in an open-tubular capillary coated with crosslinked polydimethylsiloxane (PDMS) as the retaining phase[9,10]. The water sample can be pumped through this column and analytes present in the water sample will partition into the PDMS phase. After a drying step the analytes can be thermally desorbed and are (cryogenically) refocused onto the head of the analytical column. Alternatively, both extraction and gas chromatography can be performed in the same column[11]. Advantages of using an open tubular trapping (OTT) column coated with PDMS are the good thermal stability, high degree of inertness and well documented retention properties. However, due to a number of reasons OTT has never gained widespread acceptance. First, as the amount of stationary phase per trap length is low, long traps are necessary. Second, long traps generally require a second GC oven for thermal desorption and allow only low sampling flow rates. Finally, OTTs

were only found to be suitable for very apolar compounds (*e.g.* PAHs) and polar solutes are virtually not retained by the relatively thin PDMS layer.

The third approach is called solid phase microextraction (SPME) which has recently been evaluated for the extraction of a wide variety of pesticides[12,13], PAHs, PCBs[14] and other solutes from water samples. SPME is based on the sorption (partitioning) of the analytes present in the water sample into a layer of stationary phase coated onto a syringe-like device. The most commonly used stationary phases for SPME are PDMS[12] and polyacrylate[15]. The main advantage of this method is its simplicity. For SPME, only standard GC instrumentation is required. The main disadvantage is that since this method is based on a partitioning equilibrium, extraction is in some cases incomplete which renders quantitation difficult. Each analyte should be individually calibrated and the extraction yield should be determined for each solute. Also, sensitivity is moderate in those cases where extraction is incomplete. SPME is especially suited as a rapid screening method, although for certain solutes, *e.g.* very apolar ones, long extraction times are necessary, even when stirring is applied.

Recently, a new approach for the analysis of semi-volatiles in aqueous samples, gum phase extraction (GPE) was proposed[16]. Here, an extraction cartridge containing 100% polydimethylsiloxane (PDMS) particles was used as the retaining phase. After applying the water sample, the PDMS-packed cartridge has to be dried. Subsequently, the PDMS trap can be directly thermally desorbed and the analytes released are transferred onto the GC column. The system was shown to be applicable for the analysis of selected PAHs and organo-chlorine pesticides (OCPs) in tap and river water samples. This approach combines several of the advantages of the solvent-less preconcentration methods described above. Compared to Tenax which is used in SPETD, the PDMS material has the advantage that degradation products from the sorbent can readily be identified with the use of a mass spectrometric detector as they generate characteristic silicone mass fragments. Therefore, false positives are unlikely to occur. A significant improvement compared to OTT is the fact that an increased amount of stationary phase is present in the trap. Therefore, the sample capacity is significantly increased. Moreover, the packed bed allows the use of higher sampling flow rates (1-10 mL/min) so that sampling times can be less than 10 minutes for sample volumes up to 100 mL. A disadvantage compared to OTT is that drying of the trap, which is extremely fast in the case of an OTT, is rather long for gum phase extraction. Relative to SPME, increased sensitivity and improved quantitation is attained since all analytes are transferred to the analytical system rather than only a fraction governed by the distribution coefficient.

An automated system for GPE of liquid samples is described which allows fully automated sample preparation for water samples. A theory model is presented which allows prediction of breakthrough volumes from octanol/water partitioning coefficients. This enables the user to predict the retention of solutes, and thus the suitability of the system for a certain application without any experiments. System

performance was measured using the complete list of priority PAHs and OCPs. Additionally, several triazine herbicides were also investigated. Retention characteristics of the PDMS trap for the analytes under investigation were compared with the retention behavior predicted by theory. Agreement and dissimilarities between theory and experiment are discussed in detail.

5.1.3 Theory

A theory model was developed which allows estimation of retention and breakthrough volumes of selected components on polydimethylsiloxane traps from octanol/water partitioning coefficients ($K_{O/W}$)[17]. This model was applied to the HPLC-UV and HPLC-MS analysis of several phenylurea herbicides from aqueous samples. The herbicides investigated in that work are relatively polar analytes, and can easily be lost due to insufficient retention on the PDMS trap. In this report a wide range of analytes is studied, ranging from very polar (deisopropylatrazine) to very apolar (indeno[123cd]pyrene).

As has been shown previously, the retention volume of an analyte can be calculated by[17]:

Equation 1

$$V_r = V_0 \times \left(1 + \frac{K_{PDMS/W}}{\beta}\right) \approx V_0 \times \left(1 + \frac{K_{O/W}}{\beta}\right)$$

where V_r is the retention volume, V_0 is the trap void volume, $K_{PDMS/W}$ is the PDMS/water distribution coefficient and ß is the phase ratio of the trap. For many compounds, $K_{PDMS/W}$ can be substituted by the octanol/water partitioning constant, $K_{O/W}$, which is tabulated for numerous compounds[18,19]. For a given trap, V_o and ß can be determined experimentally[20]. Once the retention volume is known, breakthrough volumes (accepting 5% sample loss) can be calculated according to the equations derived by Lövkvist and Jönsson[21]:

Equation 2

$$V_b = V_r \times \left(0.9025 + \frac{5.360}{N} + \frac{4.603}{N^2}\right)^{-\frac{1}{2}}$$

where V_b is the 5% breakthrough volume and N is the plate number of the trap. Plate numbers can be calculated from the Knox equation, as was previously shown[17,20]. Therefore, with the equations presented here, breakthrough volumes can be predicted using only literature data and trap specific parameters as input data. Using the equations described above, the required $K_{O/W}$ for quantitative trapping can be expressed as:

Equation 3

$$\left(K_{O/W}\right)_{req} = \beta \times \left(\frac{V_S}{V_0 \times \left(0.9025 + \frac{5.360}{N} + \frac{4.603}{N^2} \right)^{-\frac{1}{2}}} - 1 \right)$$

where V_S is the sample volume. From **Equation 2** and **Equation 3** it can be rapidly predicted whether the SE-TD method will give quantitative trapping for a given solute. In this way the need for trial and error method development is eliminated.

The equations shown above described analyte losses due to incomplete trapping from the water sample. In principle, analytes can also be lost during drying of the PDMS phase. Since no losses of the analytes under investigation due to volatility was observed, equations describing this process are not shown here.

Table 1 Composition of the test mixture (master standard) containing PAHs, organochlorine pesticides (OCPs) and triazine herbicides (TRIA) in methanol. Concentrations are those in the spiked water sample and recoveries are at this level.

No	Component	Class	Conc. (µg/L)	Quant. Ion	Qual. Ion	log ($K_{O/W}$)	Recovery (%)
1	Naphthalene	PAHs	4	128	101	3.01 [19]	76
2	Acenaphthylene	PAHs	8	153	152	4.07 [19]	128
3	Acenaphthene	PAHs	4	153	152	3.92 [19]	120
4	Fluorene	PAHs	0.4	166	167	4.18 [19]	108
5	Deisopropylatrazine	TRIA	2	158	145	1.15 [18]	0.0
6	Desethylatrazine	TRIA	2	172	174	1.51 [18]	1.5
7	α-BHC	OCPs	4	181	183	3.81 [18]	112
8	Simazine	TRIA	2	186	201	2.06 [18]	75
9	Atrazine	TRIA	2	200	215	2.40 [18]	76
10	β-BHC	OCPs	4	181	183	3.80 [18]	126
11	Propazine	TRIA	2	214	229	2.91 [18]	78
12	γ-BHC	OCPs	4	181	183	3.72 [18]	125
13	Terbutylazine	TRIA	2	173	214	3.06 [18]	127
14	Phenanthrene	PAHs	4	178	176	4.46 [19]	120
15	Anthracene	PAHs	4	178	176	4.45 [19]	116
16	δ-BHC	OCPs	2	181	183	4.14 [18]	120
17	Sebutylazine	TRIA	2	200	202		76
18	Metribuzin	TRIA	2	198	182	1.70 [18]	4.6
19	Heptachlor	OCPs	4	272	274	5.27 [18]	114

20	Prometryn	TRIA	2	184	226	3.34 [18]	80
21	Terbutryn	TRIA	2	226	185	3.72 [18]	79
22	Aldrin	OCPs	2	263	293	6.50 [18]	128
23	Cyanazine	TRIA	2	225	227	1.66 [18]	6.5
24	Fluoranthene	PAHs	0.8	202	200	5.53 [19]	108
25	Heptachlor-epoxide	OCPs	4	351	388	5.40 [18]	129
26	Pyrene	PAHs	0.4	202	200	5.32 [19]	111
27	Endosulfan I	OCPs	4	241	277		128
28	p,p'-DDE	OCPs	4	246	248	5.69 [18]	103
29	Dieldrin	OCPs	4	263	277	4.54 [18]	108
30	Endrin	OCPs	4	263	281	4.56 [18]	107
31	Endosulfan II	OCPs	4	159	195		112
32	p,p'-DDD	OCPs	4	235	237	4.28 [19]	101
33	Endrin-aldehyde	OCPs	4	345	347		78
34	Endosulfan-sulfate	OCPs	4	272	387		117
35	p,p'-DDT	OCPs	4	235	237	6.38 [18]	121
36	Endrin-ketone	OCPs	4	317	281		101
37	Benz[a]anthracene	PAHs	4	228	226	5.61 [19]	106
38	Chrysene	PAHs	4	228	226	5.61 [19]	105
39	Methoxychlor	OCPs	4	274	212	3.31 [18]	77
40	Benz[b]fluoranthene	PAHs	0.8	252	250	6.57 [19]	108
41	Benz[k]fluoranthene	PAHs	0.4	252	250	6.84 [19]	108
42	Benz[a]pyrene	PAHs	0.4	252	250	6.04 [19]	101
43	Indeno[123cd]pyrene	PAHs	0.4	276	274	7.66 [19]	25
44	Dibenz[ah]anthracene	PAHs	0.8	278	276	7.97 [19]	20
45	Benz[ghi]perylene	PAHs	0.8	276	274	7.23 [19]	23

5.1.4 Experimental

5.1.4.1 Test Solutes

Three groups of test analytes were selected. The full range of EPA priority polyaromatic hydrocarbons (PAHs) and organo chlorine pesticides (OCPs) was used. The analytes monitored are listed in **Table 1**. For both classes of analytes, certified standard solutions were obtained from Supelco (Bellefonte, PA, USA). These analytes were diluted with methanol. Additionally, a test mixture containing 11 triazine herbicides (TRIA) was prepared in methanol at a concentration of 1000 ppm. The three mixtures were combined into one mixture (master standard) which was used for all experiments. The exact composition of the mixture is listed in **Table 1**. Spiked tap water sample was prepared by adding 10 μL of the master standard to 95 mL of tap

water to which 4.99 mL of methanol was added. The resulting concentrations are also listed in **Table 1**.

5.1.4.2 PDMS Cartridges

PDMS particles were obtained from Gerstel (Müllheim a/d Ruhr, Germany). The particles were sieved into the range 240-400 μm (average d_p = 320 μm). In the present work, a novel trap design was used. The starting dimensions of the PDMS extraction cartridges are: 4 mm I.D., 6 mm O.D., 177.8 mm length. Since this cartridge can only be partially filled, a relatively large empty volume remains. This caused problems during the drying step. To facilitate drying of the packed PDMS bed, the extraction tube was narrowed on the end were no PDMS is present. The inner diameter in this section of the tube was reduced to 0.8 mm. The glass tube was filled with 339 mg of the PDMS phase. This results in a bed length of 71 mm. The phase ratio of the trap is 0.85 and V_0 is 0.41 ml. To keep the PDMS bed in place two plugs of knitted Silastic® tubing were pushed onto the bed. Thus, a packed PDMS extraction cartridge is obtained which contains no active sites since neither glasswool nor an active adsorbent or support material is present. In fact, the extraction cartridge consists only of the retaining silicone phase and the glass wall, hence degradation of the analytes is minimized.

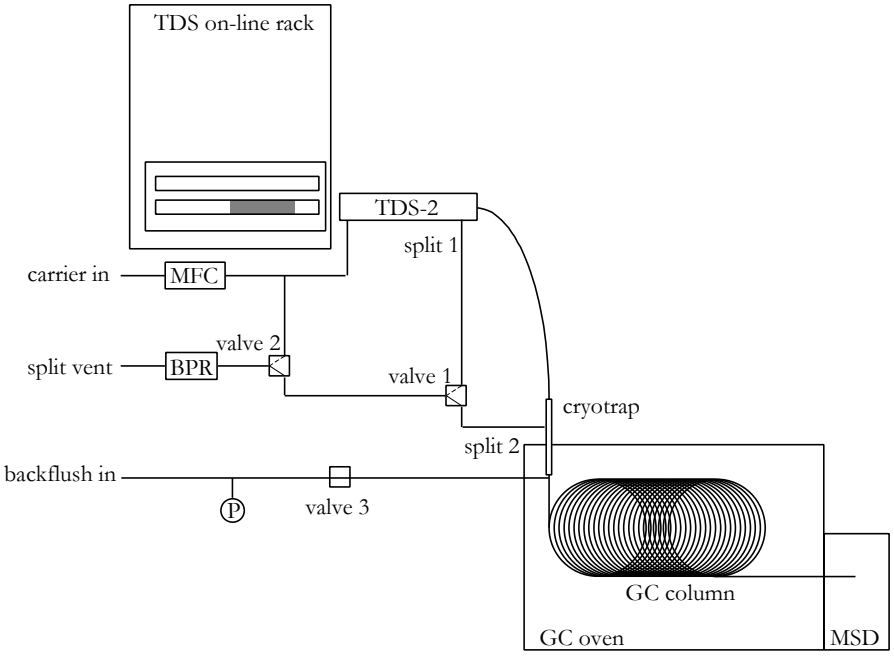

Figure 1 Schematic overview of the Gerstel TDS-2 Thermodesorption system and TDS on-line rack. MFC = Mass flow controller, BPR = Back pressure regulator.

5.1.4.3 Instrumental Set-Up

The instrumental set-up described previously[16], was modified to allow automated operation. It consists of a Gerstel TDS-2 thermodesorption system (Gerstel GmbH, Müllheim a/d Ruhr, Germany) mounted on an HP 6890 Gas Chromatograph (Hewlett Packard, Little Falls, DE, USA). A CIS-4 PTV injector (Gerstel) was used for cryogenic focusing of the thermally released analytes. For full automation of the total procedure, a TDS on-line rack (Gerstel) was used. This is a modification of the existing TDS-autosampler (Gerstel) that enables automated sorptive extraction/thermal desorption (SE/TD) of water samples. In **Figure 1** a schematic representation of the thermo-desorption system and the TDS on-line rack is shown. In **Figure 2** the system used for loading the samples onto the cartridge and for the drying step is shown. The combined set-up in **Figure 1** and **Figure 2** is controlled by the Gerstel controller. One of the most important modifications necessary for reliable operation is the backflush adapter installed directly at the bottom of the CIS-4 cryotrap. During the internal drying step, when water vapor is exiting the PDMS cartridge, this water vapor is prevented from entering the GC column by applying a gas pressure at the backflush line that exceeds the pressure of the carrier gas. In this way, both the cryotrap and the transfer line are backflushed. The combined carrier gas flow and backflush gas flow exit via split exit 1.

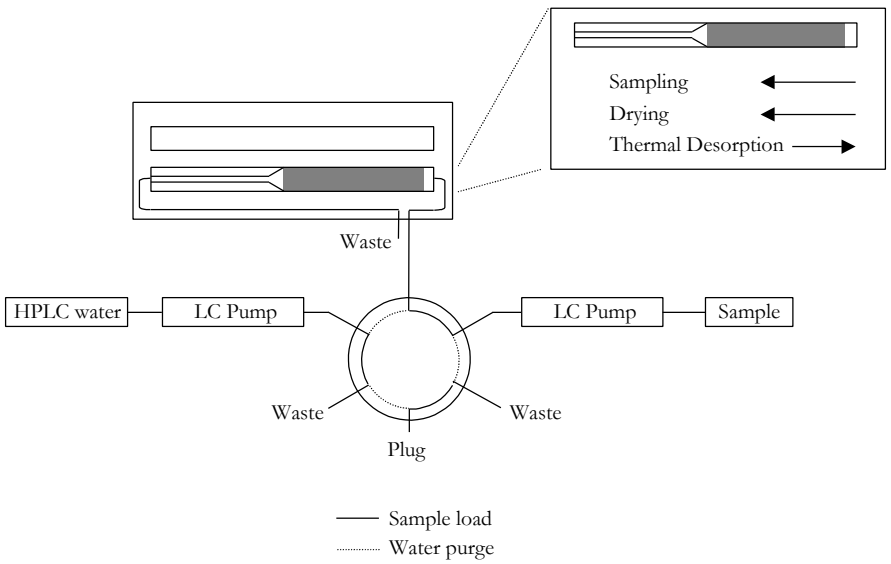

Figure 2 Schematic representation of the system used for loading the aqueous samples. Insert shows the design of the PDMS extraction cartridge. Diameter of the tube is 4 mm where PDMS is present and 0.8 mm at the narrow end. Arrows indicate flow directions during sampling, drying and thermal desorption.

For all experiments an HP-5MS column was used. This column was 30 m long and had a 0.25 mm I.D. and a film thickness of 0.25 µm. The GC program started at 40°C with a 3 minutes hold. The temperature was then programmed at a rate of 10°C/min to 325°C. An HP5972 mass selective detector (MSD) was used in the full scan mode scanning from 40-400 amu at a speed of 2.2 scans/s.

5.1.4.4 Sampling Program

Details of the precise procedure for loading the water sample, drying and transfer of the components to the GC column are listed in **Table 2**. At the start of the sampling program, the TDS-2 unit contains an empty glass tube. At this time, the TDS on-line rack contains a PDMS filled tube. First, the PDMS cartridge is conditioned with 10 mL of HPLC grade water. Then, the water sample is loaded at a flow rate between 1 and 10 mL/min. Next, the cartridge is washed with HPLC grade water to remove interfering substances. Now, the PDMS cartridge has to be dried. It is very important that the cartridge is dried to full dryness. Failure to do so can result in distorted analyses. The first part of the drying step is carried out outside the TDS thermal desorption oven while the cartridge is still in the TDS on-line rack (external drying). During this step, the cartridge is purged in backflush with nitrogen at ambient temperature to remove most of the water. After 12.5 minutes external drying, when water can no longer be visually observed in the cartridge, the cartridge is automatically transferred to the TDS-2. Inside the TDS-2, the cartridge is dried to total dryness (internal drying) under a flow of helium at a slightly elevated temperature. During the internal drying step, the CIS-4 and the transfer line are backflushed to prevent water from entering the analytical column. When internal drying is complete, the CIS-4 is cooled down to the initial temperature (-100°C) and the thermal desorption program is started. Upon completion of the thermal desorption program, the PDMS tube inside the TDS-2 is exchanged for the empty tube and the GC and MSD programs are started.

Table 2 Sample preparation program of the automated sorptive extraction/thermal desorption procedure. Steps 1-4 (26.5 min) are carried out outside the thermal desorption system during the GC run, steps 5-9 (15.5 min) are carried out inside the thermal desorption system prior to the next GC run (40 min).

No	Step	Action	Time (min)
1	Condition cartridge	Flush cartridge with 10 mL HPLC grade water (5 mL/min)	2
2	Load sample	Load the water sample, 10 mL, 1 mL/min	12
3	Wash cartridge	Flush cartridge with 10 mL HPLC grade water (5 mL/min)	14
4	External drying	Purge cartridge with N_2, 800 mL/min, 12.5 min	26.5

5	Insert cartridge	Insert cartridge into TDS-2, backflush valve is switched on	27
6	Internal drying	Purge cartridge with He, 250 ml/min, 5 min, 50°C	32
7	Cryotrap cooldown	CIS-4 is cooled to the initial temperature (-100°C). Backflush valve is switched off	33
8	Thermal desorption	TDS-2 thermal desorption program is started: 50°C - 1°C/s - 225°C (5min)	41
9	Thermal desorption end	TDS-2 is cooled to 50°C, PDMS cartridge is removed	42
10	Sample injection	CIS-4 is ramped from -100°C to 300°C at 10°C/s GC and MSD are started	42
11	GC program	Initial 40°C (3 min) then at 10°C/min to 325°C	82

5.1.5 Results and Discussions

Freshly prepared PDMS traps were conditioned by pumping 50 mL of methanol through the trap. The trap was subsequently dried and processed as indicated in **Table 2**, omitting steps 1 through 3. If, after completion of this procedure, non-siloxane components are found in the blank chromatogram, the cartridge is also thermally conditioned at 250°C for 2 hours. A conditioned cartridge can in principle be stored in the autosampler. If a cartridge is to be stored outside of the autosampler, metal end-caps are used to prevent the trapping of contaminants from air onto the sorbent.

The first experiments concerned the blank chromatograms generated by the PDMS sorbent. After thorough conditioning, 10 mL of HPLC grade water was passed through the PDMS cartridge. The chromatogram obtained from this analysis is shown in **Figure 3**. Although this chromatogram contains several distinct peaks, these do not interfere in the analysis of target solutes, because from their mass spectra they are all readily identified as siloxane breakdown products. This is one of the powerful aspects of PDMS: the risk of inadvertently identifying a sorbent degradation peak as an actually sampled analyte is minimal.

In **Figure 4** the chromatogram obtained after preconcentration of 10 mL of the spiked water sample (**Table 1**) is shown. Recoveries determined versus a 1 µl cold splitless injection are also listed in **Table 1**. During initial experiments also concentration levels of 10 and 100 times those listed in **Table 1** were used. For these, more concentrated samples, identical recoveries were found as those listed in **Table 1**, only solutes 43, 44 and 45 were found in considerably higher recovery. For most components a recovery between 70 and 130% was observed, which is adequate for quantitation purposes.

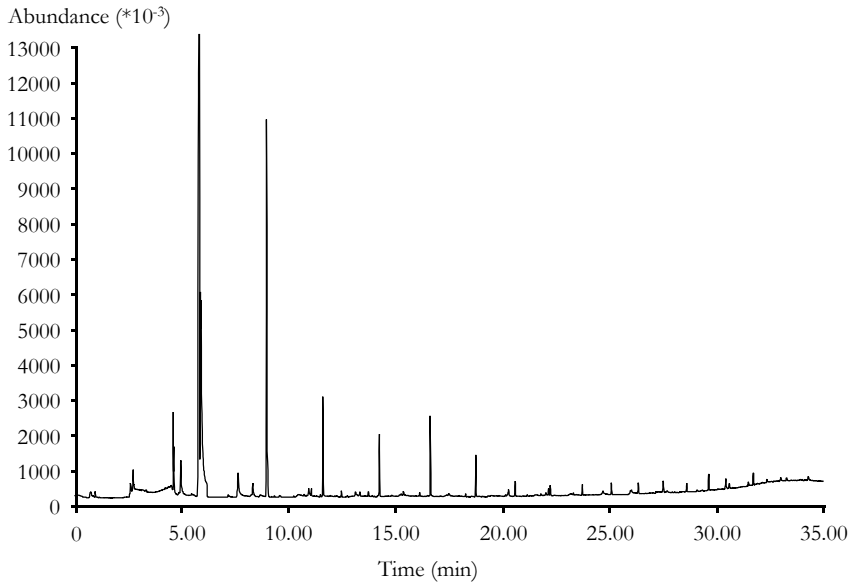

Figure 3 Chromatogram of 10 mL HPLC grade water. Conditions as in **Table 2**. All peaks present in the blank are siloxane degradation products. Major peaks are a series of cyclic siloxane breakdown products.

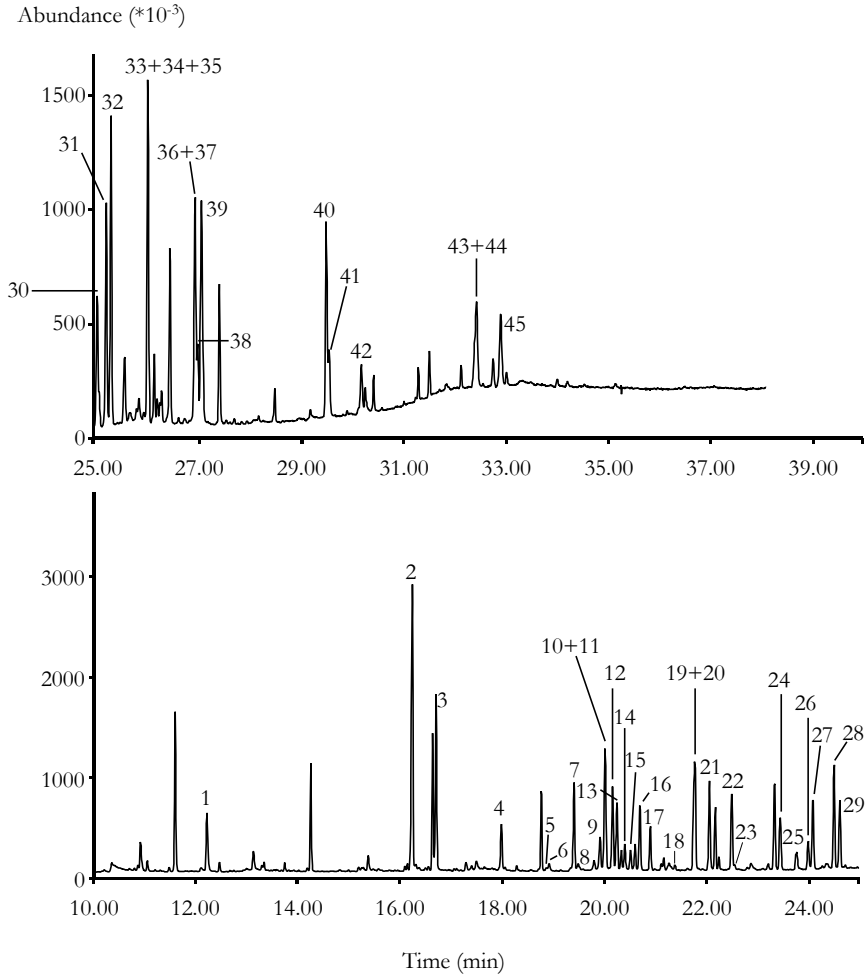

Figure 4 Chromatogram of the 45 analytes in tap water at a level of 0.4-8 μg/L. (**Table 1**). Other conditions as in **Table 2**.

However, for seven solutes poor recoveries ranging from 0 to 25% were observed. The solutes lost are three PAHs (indeno[123cd]pyrene, dibenz[ah]anthracene and benz[ghi]perylene) and four triazines (desethyl- atrazine, deisopropylatrazine, metribuzin and cyanazine). Losses of solutes are probably not because of volatility, since the most volatile solute (naphthalene) is quantitatively retained. The two groups of (partially) lost solutes, however, have very different characteristics concerning polarity. The three PAHs are the most apolar solutes present in the test mixture. Since the PDMS phase is also apolar, affinity of the PAHs for this phase is expected to be very high. Losses of these solutes are therefore unlikely to occur due to incomplete

trapping by the PDMS material. Most probably, the PAHs are lost due to adsorption in tubing, valves, HPLC pumps *etc.* which is supported by the fact that at higher concentrations higher recoveries were found for these solutes, this despite the fact that 5% methanol was added to suppress adsorption. Unfortunately, however, it was found that increasing the methanol concentration to values in excess of 5% resulted in additional losses of the polar solutes. Therefore it was decided not to change the amount of methanol.

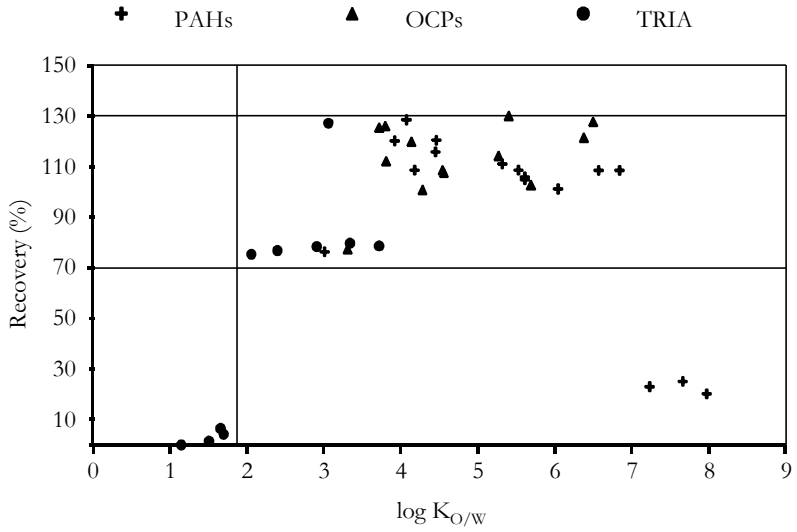

Figure 5 Recovery of the 45 analytes used versus their octanol water partitioning coefficient. Line at log $K_{O/W}$ = 1.77 is the theoretical limit above which all solutes should be quantitatively retained. The three most apolar PAHs are lost due to adsorption in the water sampling system.

The other group of lost analytes are the most polar triazines. These solutes are very polar and are therefore expected to exhibit only a very moderate affinity for the apolar PDMS phase. The poor recoveries observed for these solutes are hence most likely caused by incomplete trapping of the solutes by the PDMS material rather than by adsorption somewhere in the system. This loss on the 'polar end' can be explained using the theory described in **Section 5.1.3**. For the PDMS trap used here, the estimated plate number is 5.1[17,20]. The sample volume, V_S, is 20 mL (10 mL sample and 10 mL wash). Substitution of these values and the PDMS trap parameters in **Equation 3** result in a $(K_{O/W})_{req}$ of 60 and a log $(K_{O/W})_{req}$ of 1.77. Solutes with a log $K_{O/W}$ in excess of 1.77 should be quantitatively retained. In **Figure 5** recoveries of the test solutes are plotted versus their octanol water partitioning coefficient to show the losses of solutes at both ends of the scale. A vertical line is drawn at log $K_{O/W}$ 1.77. From **Figure 5** it is clear that all solutes with a log $K_{O/W}$ in excess of 1.77 are quantitatively retained (except the three most apolar PAHs). On the polar end (low $K_{O/W}$) four solutes are lost. The most polar solute that is quantitatively retained is

simazine which has a log $K_{O/W}$ of 2.06. This indicates that there is a very good agreement between the theoretically calculated required $K_{O/W}$ and the actual $K_{O/W}$ value above which quantitative retention is realized. For solutes with log $K_{O/W}$ above 7, problems might occur due to system adsorption effects. For practical purposes an application range of 2-7 in log $K_{O/W}$ can be used. Repeated experiments showed that the PDMS extraction cartridge could be re-used for up to at least 150 experiments. Relative standard deviations (n=3) were between 10-25% for all solutes under investigation.

Extension of the polarity range to values below a log $K_{O/W}$ of 2 is desired since there are also interesting solutes in this range. With the PDMS material this is, in principle, only possible by reducing the sample volume (or water wash steps) which of course has clear drawbacks such as a reduced sensitivity and a higher change of cartridge and system contamination. A better approach is to investigate more polar phases with a higher affinity for polar analytes.

5.1.6 Conclusion

The results presented in this part indicate that packed PDMS extraction cartridges are excellent enrichment devices for the preconcentration of a large number of pesticides and PAHs from aqueous samples. The procedure described closely resembles solid phase extraction with thermal desorption (SPETD), however, with some important differences. Retention on the PDMS sorbent is based on sorption (partitioning) while all SPE methods employ adsorbents which adsorb molecules onto their surface. Advantages of sorption were addressed, the most important ones being: improved inertness, well known retention properties and good blanks.

Degradation peaks of the PDMS sorbent can be readily identified as siloxane breakdown products by the use of the mass spectrometric detection. A fully automated set-up allowing automatic sample loading, drying, thermal desorption and GC-MS analysis was described. For most solutes investigated, quantitative recoveries were found; only some of the polar triazines and the most apolar PAHs were (partially) lost. Losses of apolar solutes is due to adsorption in the system which can only be prevented by adding an organic modifier, *e.g.* methanol, to the water sample. Methanol was used as modifier at a fixed concentration of 5%.

A theory model was derived which allows calculation of breakthrough volumes and recoveries from octanol/water partitioning coefficients ($K_{O/W}$). Alternatively, the $K_{O/W}$ value required for quantitative trapping can be calculated from the sample volume. The application ranges roughly from log $K_{O/W}$ 2 to log $K_{O/W}$ 7 where the high end is restricted by system adsorption effects. With the set-up used here and using mass spectrometric detection in the scan mode, detection limits are in the order of 10 ng/L.

5.2 Automated Sorptive Extraction-Thermal Desorption-GC-MS Analysis: Determination of Phenols in Water Samples*

5.2.1 Summary

A recently developed method for the automated analysis of micropollutants in water samples has been evaluated for the determination of phenols in aqueous samples. Several phenols were selected from the priority lists to represent the entire range of these priority pollutants. The phenols are derivatized off-line with acetic anhydride which is added directly to the water sample. After derivatization is complete, the sample is transferred to the analytical system where automated sample processing takes place. 10 mL of the samples is loaded onto a cartridge packed with polydimethylsiloxane particles which extracts the analytes from the water. After sample loading, the cartridge is dried with nitrogen to eliminate water and derivatization agent. The cartridge is then transferred to the analytical system in which thermal desorption and chromatographic analysis takes place. Using mass spectrometric detection in the selected ion monitoring mode (SIM), detection limits are in the order of 1-5 ng/L.

5.2.2 Introduction

Phenols occur widely in our environment, in nature as building blocks of plants and have several industrial applications[22]. Because of their toxicity and persistency, monitoring of this class of pollutants in aqueous samples is required at or below the μg/L level. Adequate enrichment from the water sample followed by chromatographic analysis with sensitive and selective detection is needed.

Many enrichment techniques are available for the preconcentration of the analytes in question before the actual analytical quantification by gas or liquid chromatography. Classical liquid/liquid extraction (LLE) has been used which is a simple and straightforward technique[23]. However, because of well-known drawbacks like large consumption of organic solvents, LLE is more and more being replaced by solid phase extraction (SPE). For the latter technique, a variety of adsorbent phases is available including C_8 and C_{18} modified silicas[24,25,26], styrene-divinylbenzene copolymers[27], graphitized carbon blacks[28] and XAD resins[29,30]. Though preconcentration of the phenols as such is possible with good recoveries and low concentration detection limits[31,32], it can sometimes be problematic due to the high polarity of this class of solutes. Additionally, the lower polarity of derivatized phenols and the insensitivity of

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these derivatives to pH variations is bound to result is lower detection limits, however, at the expense of a derivatization step. Combining this with the easier chromatography of phenol derivatives has led many authors to rely on the conversion of the phenols into less polar solutes.

Chromatographic analysis can be done by either gas (GC) or liquid chromatography (LC). GC is the method of choice due to its superior separation efficiency. Additionally, it allows much lower detection limits by using electron capture detection (ECD)[30] or mass spectroscopy (MS)[33]. For routine GC, derivatization is preferred because the polar phenols adsorb onto the column resulting in broad and tailing peaks. Phenols are easily acylated with acetic acid anhydride[33] facilitating both extraction and GC-MS analysis at low concentration levels. Alternatively, a pentafluorobenzoyl group can be introduced for electron capture detection (ECD).

In this contribution, the coupling of automated sorptive extraction/thermal desorption (SE/TD) to capillary GC/MS is described for the determination of acylated phenols in aqueous samples. This approach was used previously for the analysis of pesticides and PAHs in water samples (**Section 5.1**). In short, it consists of enrichment of acylated phenols, derivatized in situ in the water sample, onto a cartridge packed with 100 % polydimethylsiloxane (PDMS) particles. The PDMS phase behaves as a liquid in which the derivatized solutes can dissolve (partition). After sampling, the retained analytes are thermally desorbed onto the GC column.

5.2.3 Experimental

5.2.3.1 Chemicals and Materials

The phenols were obtained from Supelco (Bellefonte, PA, USA). A 35 ng/μL standard solution was prepared in ethyl acetate (Biosolve, Valkenswaard, the Netherlands). Spiked water samples were prepared in HPLC grade water (Biosolve) by addition of the appropriate amount of the ethyl acetate solution.

The PDMS cartridges were prepared as described in **Section 5.1** . The PDMS particles were homemade according to the procedure described and were sieved in the range 125-250 μm before use. Conditioning was performed by washing the cartridge with *ca.* 10 mL of methanol (Biosolve) and subsequently thermally conditioning of the cartridge at 250ºC for 24 hours under a flow of helium. Before sampling, the PDMS cartridge is washed with 10 mL pure water.

5.2.3.2 Instrumentation and Experimental Procedure

The instrumentation used was the same as described in **Section 5.1** and consists of an autosampler for automated sample pretreatment (TDS-OL, Gerstel, Müllheim a/d Ruhr, Germany), a thermal desorption unit (TDS-2, Gerstel) and an HP 6890 GC coupled to a HP 5972 MSD (Hewlett Packard, Little Falls, DE, USA). A CIS-4 PTV injector (Gerstel) was used as a cryotrap. The GC column was 30 m long, with an inner diameter of 0.25 mm and was coated with 0.25 μm of HP-5MS (Hewlett Packard). An important feature of the system is a backflush adapter that is installed at the bottom of the cryotrap. Activating the backflush line allows backflushing of the cryotrap and a part of the sample introduction system and can thus prevent water vapor from entering the analytical column as was described in **Section 5.1.4.3**.

The procedure starts with derivatization of the phenols in the water sample. Hereto, an existing procedure[34] was slightly modified. To a 20 mL water sample 1 mL acetic acid anhydride and 1 g sodium hydrogen carbonate were added. After brief shaking, the mixture was allowed to stand for 15 minutes to complete reaction. Subsequently, 10 mL of the sample was pumped through the PDMS cartridge. After sampling is complete, the cartridge is washed with 10 mL pure water to remove excess reagent, solubilized salts and other undesired matrix compounds. Prior to thermal desorption, the cartridge is dried at ambient temperature for 25 minutes and at 50ºC for 5 minutes. Both steps are carried out under a nitrogen flow of 300 mL/min. Finally the phenols are thermally desorbed at 225ºC for 5 minutes, cryofocussed at -150ºC and splitless injected onto the capillary GC column. The oven temperature program started at 40ºC which was maintained for 2 minutes and was then ramped at 15ºC/min to 300ºC. The mass selective detector was operated either in the full scan mode (scan) by scanning from 40 to 300 amu or in the time scheduled selected ion monitoring mode (SIM) by monitoring 2 ions per component as indicated in **Table 3**.

Table 3 Ions monitored during SIM analysis.

No	Component	Ion 1	Ion 2	Group
1	Phenol	94	136	1
2	4-Methylphenol	108	150	2
3	2-Chlorophenol	128	170	3
4	2,6-Dimethylphenol	122	164	3
5	2-Ethylphenol	122	164	3
6	4-Isopropylphenol	136	178	4
7	2,4-Dichlorophenol	162	204	5
8	2,3,5-Trimethylphenol	136	178	5
9	2,4,6-Trichlorophenol	196	238	6
10	Pentachlorophenol	264	306	7

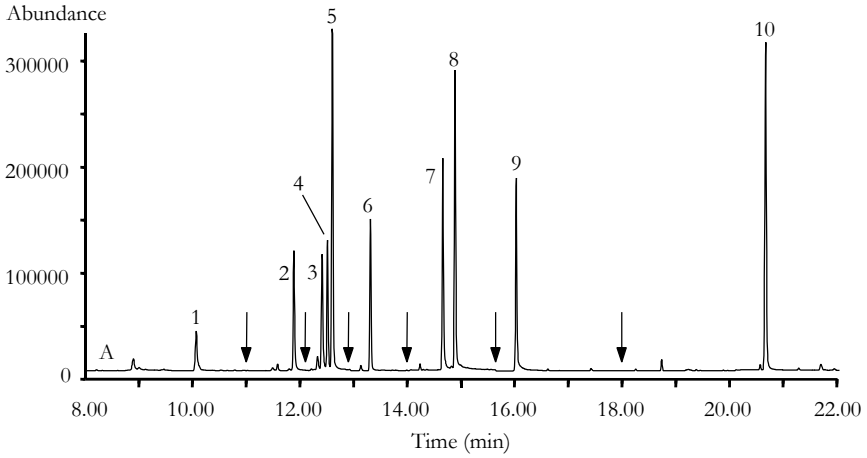

Figure 6 Chromatogram of the analysis of an acylated phenol standard recorded in the full scan mode. 35 ng was injected per component. Arrows indicate the switch points selected for SIM analysis. For peak identification see **Table 3**.

5.2.4 Results and Discussion

Initial experiments concerned the derivatization and the establishing of a good chromatographic separation. To this extent, 1 mL of the 35 ppm phenol standard in ethylacetate was mixed with 1 mL acetic anhydride. A reference standard of acylated phenols was thus obtained. The chromatogram from the analysis of 2 μL of this standard is shown in **Figure 6**. Completion of the reaction was confirmed by the absence of free phenols. The arrows in **Figure 6** represent the switch points which were used for further SIM experiments.

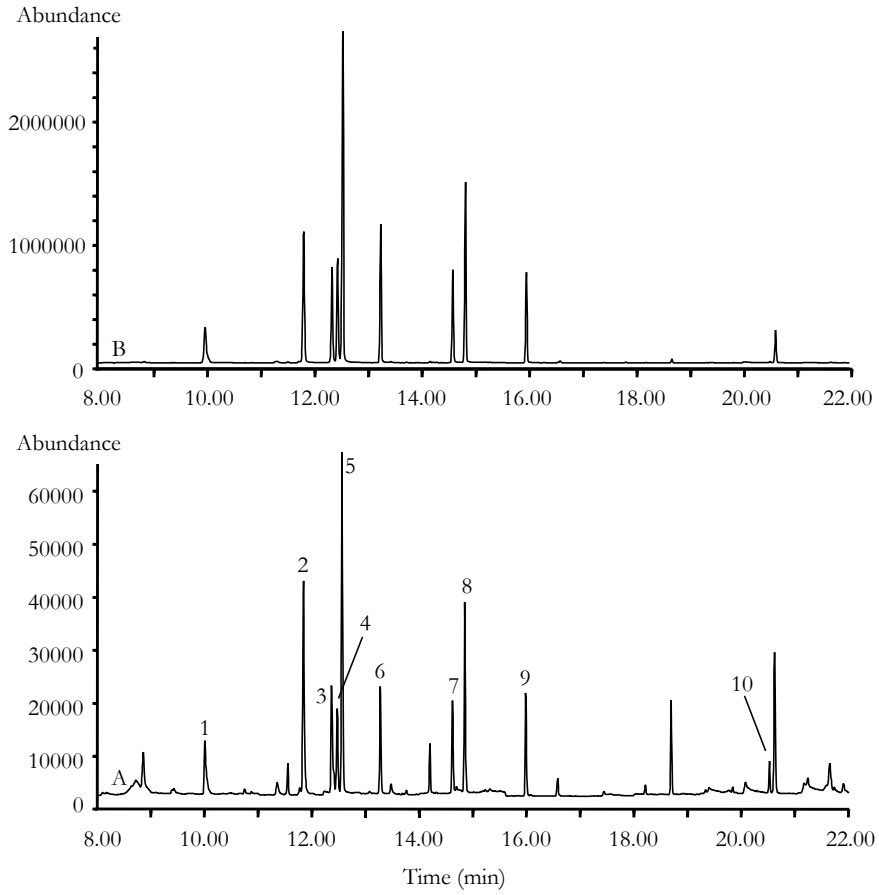

Figure 7 SIM chromatograms of the analysis of A, 10 mL of a spiked tap water sample (0.1 μg/L) and B, a standard injection (35 ng/component).

Following these initial experiments, a tap water sample was spiked at a level of 0.1 ng/mL with the underivatized phenols. 20 mL of the spiked tap water sample was derivatized as described above and 10 mL was enriched onto a conditioned PDMS cartridge. A total amount of 1 ng was injected. **Figure 7A** shows the result of the SIM analysis and **Figure 7B** the SIM analysis of a standard injection of acylated phenols corresponding to an amount of 35 ng per analyte. **Table 4** shows the recoveries of the test analytes versus the 2 μL direct injection.

Table 4 Recovery and relative standard deviation (RSD, n=3) from the analysis of tap water samples spiked to a level of 0.1 µg/L with the phenols.

No	Component	Recovery (%)	RSD (%)
1	Phenol	72	5
2	4-Methylphenol	64	16
3	2-Chlorophenol	95	11
4	2,6-Dimethylphenol	107	7
5	2-Ethylphenol	101	2
6	4-Isopropylphenol	109	15
7	2,4-Dichlorophenol	103	5
8	2,3,5-Trimethylphenol	97	3
9	2,4,6-Trichlorophenol	94	9
10	Pentachlorophenol	98	5

From **Table 4** it is clear that most analytes were quantitatively enriched on the PDMS material. Only the first two analytes (phenol and 4-methylphenol) are partially lost. This can be due to either breakthrough during sampling or during the water wash step after sampling, or due to the drying step. The latter was tested by spiking 35 ng of the acylated phenols directly onto the PDMS material and then subjecting it to the drying steps. In this case only minor losses of the solutes occurred and it can therefore be concluded that the observed losses are due to elution out of the PDMS cartridge by the water phase. The sensitivity of the method is very good as can be deduced from the abundances in the SIM trace for 0.1 ng/mL. For a signal to noise ratio of 8, LOD values are between 1 and 10 ng/L.

Instead of the in situ derivatization approach described above, an alternative method was also investigated. This involved the preparation of a PDMS cartridge impregnated with acetic anhydride through which the water sample was then applied. To this extent, 5 mL of acetic anhydride was pumped through the PDMS trap at a flow rate of 0.5 mL/min to soak the PDMS particles with the reagent. After this step a brief drying step was inserted (10 seconds) to eliminate the liquid acetic anhydride still present in the trap. After this, 0.5 mL of a water sample spiked to a level of 70 ng/mL with the phenols was passed through the trap at a flow rate of 0.5 mL/min. Following water sampling, the cartridge was subjected to the external and internal drying steps described above and was finally thermally desorbed onto the column. The chromatogram obtained from this analysis is shown in **Figure 8**.

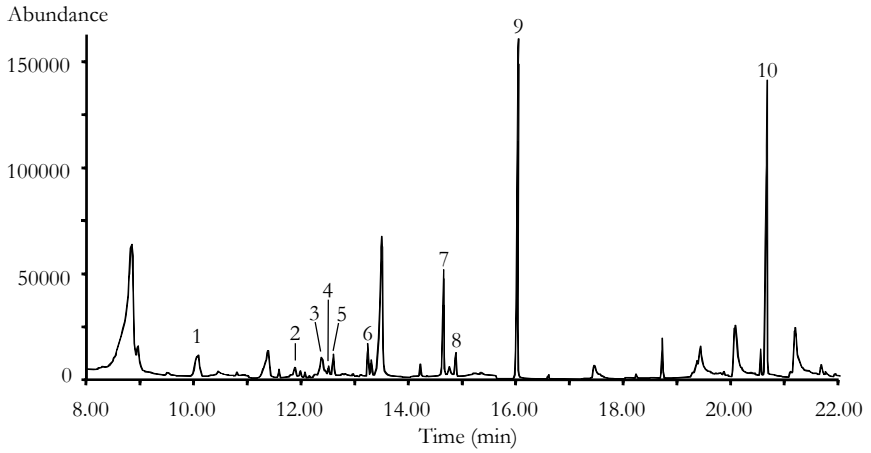

Figure 8 Chromatogram of the analysis of 0.5 mL of a water sample spiked to 70 ng/mL with underivatized phenols. Sample was preconcentrated on a PDMS cartridge impregnated with acetic anhydride. For peak identification see Table 5.

From this chromatogram, recoveries were calculated versus the 2 μL splitless injection (35 ng/component). The results are listed in **Table 5**. As is clear from this table, poor recoveries attained which can be attributed to several reasons. First, the polar phenols do not partition well into the PDMS phase and therefore are not derivatized by the reagent present in PDMS. Second, since the solubility of acetic acid anhydride in water is very high, the acetic anhydride may be eluted out of the PDMS bed. Third, though the reaction is fast, it may that the contact time between analytes and reagent is too short.

Table 5 Recovery of phenols from a 0.5 mL, 70 μg/L spiked water sample. Enrichment was on an acetic acid anhydride impregnated trap. (# : no mass spectrum match)

No	Component	Recovery (%)
1	Phenol	5 (#)
2	4-Methylphenol	0.4 (#)
3	2-Chlorophenol	0.3 (#)
4	2,6-Dimethylphenol	0.5 (#)
5	2-Ethylphenol	0.2 (#)
6	4-Isopropylphenol	1.5
7	2,4-Dichlorophenol	5.4
8	2,3,5-Trimethylphenol	0.6 (#)
9	2,4,6-Trichlorophenol	17.5
10	Pentachlorophenol	44.5

5.2.5 Conclusion

The viability of sorptive PDMS preconcentration for the analysis of phenols from water samples was demonstrated. Recoveries and relative standard deviations were determined at the 0.1 ppb level. All solutes were quantitatively trapped except phenol and 4-methylphenol, which are partially lost in the sampling process. Using 10 mL samples and mass spectrometric detection in the SIM mode, detection limits were in the 1-10 ng/L range. In this initial study, tap water was the only sample used. Subsequent studies are required to extent the applicability of the described approach to more contaminated samples such as surface and waste waters.

5.3 Capillary GC Determination of Amines in Aqueous Samples Using Sorptive Preconcentration on Polydimethylsiloxane and Polyacrylate Phases*

5.3.1 Summary

The use of sorptive extraction/thermal desorption (SE/TD) for the enrichment of amines from aqueous samples was investigated. The amines were in situ derivatized in the water sample by pentafluorobenzoylchloride and are subsequently enriched onto the SE cartridge. Two SE/TD cartridges were used, a commercially available polydimethylsiloxane (PDMS) packed cartridge and a newly synthesized polybutyl-acrylate (PBA). Blank profiles of PBA were not as good as those obtained from the PDMS phase. A complex chromatogram was obtained using mass spectrometric detection. Fortunately, the use of a nitrogen-phosphorous detector (NPD) resulted in clean blanks. The PBA phase showed superior performance for the enrichment of the polar amine derivatives from water samples compared to the PDMS material. Using a CGC-NPD set-up and only 1 mL samples, detection limits are in the sub-µg/L range.

5.3.2 Introduction

Short chain aliphatic amines, such as ethylamine, dimethylamine, *etc.* are components of important concern since they occur in various environmental matrices. Some of these amines are produced in vast quantities (exceeding one million tons per year) and are thus likely to be encountered in environmental samples. Moreover, amines can be formed as secondary pollutants from the biodegradation of nitrogen containing compounds such as amino acids and proteins. Many amines are hazardous and are associated with bad smell[35]. Additionally, they can be the source for the formation of N-nitrosamines[36]. These and other factors stress the importance for monitoring of amines in aqueous samples.

The high water solubility and very high polarity of the amines renders analysis difficult since the solutes are not easily extracted from the (polar) water matrix and analysis of these polar solutes is difficult with common analytical techniques[37]. In order to reliably determine amines at low concentration levels, chromatographic analysis coupled to sensitive and selective detection is the best option to use. The use of liquid chromatography (LC) requires the analytes to be derivatized since the amines have no chromophore and can therefore not be sensitively detected as such. With

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fluram as the derivatization agent detection limits in LC-fluorescence in the pg/L range were reported[38].

Nevertheless, determination of amines by capillary gas chromatography (CGC) is often to be preferred over LC due to its superior separating power and the availability of a wide range of selective and sensitive detectors. Though separation and detection of the underivatized amines is possible, it does generally not provide good chromatography or low detection limits[39,40]. Derivatization is also required, on the one hand, for easier sample enrichment and, on the other hand, for improved chromatographic performance. The derivatization reactions for amines have recently been reviewed by Kataoka[41].

Though most hyphenated chromatographic systems provide high sensitivity, aqueous samples still have to be concentrated to meet the desired detection limits. This can be performed by well known techniques such as liquid/liquid extraction (LLE)[42,43] and solid phase extraction (SPE)[38,44]. Recently, a relatively new approach for the preconcentration of amines using solid-phase microextraction (SPME) was described by Pan *et al.* [45]. Here, the analytes were sorbed into a thin layer of a liquid phase bonded onto a fused silica fiber. The extraction mechanism is similar to that in LLE, namely dissolution (partitioning) of the analytes into the extractant phase. We recently introduced a new extraction method, Gum Phase Extraction (GPE) which is also based on the use of a cross-linked liquid phase, similar to the one used in SPME. In this new approach, cartridges are packed with particles *e.g.* 100% polydimethyl-siloxane (PDMS) and the operation is similar to solid phase extraction. These cartridges can be applied for air[20] or water[16] sampling. For water sampling, the sample is applied by means of a vacuum pump, the retained analytes are thermally desorbed (TD) and analyzed by CGC[17].

Until now, only polydimethylsiloxane (PDMS) was available for GPE. In this investigation a polybutylacrylate (PBA) phase was synthesized as well. It is known from SPME that PBA performs better for more polar compounds compared to the PDMS phase. In the present contribution the viability of preconcentration of amines by GPE on both PDMS and PBA materials was evaluated. The analytes were derivatized in the water phase by pentafluorobenzoylchloride. Selective detectors such as the mass spectrometer (MS) and the nitrogen-phosphorous detector (NPD) were used.

5.3.3 Experimental

5.3.3.1 Preparation of the Sorptive Phases

For this investigation, two sorptive phases, polydimethylsiloxane (PDMS) and polybutylacrylate (PBA), were prepared and evaluated. PDMS packed extraction tubes (6 mm O.D. x 4 mm I.D.) were obtained from Gerstel (Müllheim a/d Ruhr, Germany) which are designed according to specifications described previously[17]. The PDMS tubes were conditioned at 325ºC for 1 hour and subsequently at 225ºC for 4 hours prior to use.

PBA was synthesized from butylacrylate (BA) and 10 % vinylacrylate (VA). 9 grams of BA and 1 gram of VA were placed in a 50 mL round bottom two-neck flask. To this mixture, 10 mg of dicumylperoxide was added to initiate polymerization. The flask was fitted with a reflux condenser and an argon inlet. After purging with argon for 2 minutes, the flask was heated to *ca.* 120ºC and the reaction was allowed to proceed for 1 hour. After completion of the reaction, the flask was cooled down and the polymerized material was removed. The raw polymer was washed with subsequently ethylacetate, isopropanol and tetrahydrofurane. The resulting material was cryogenically grinded and sieved into the range 125-250 μm and then put in thermal desorption tubes (Gerstel). PBA tubes were conditioned at 225ºC for 24 hours prior to use.

5.3.3.2 Experimental Set-Up

For this investigation an experimental set-up similar to the one described previously[16,20] was used. It consists of a thermodesorption unit (TDS-2, Gerstel), in which the thermal desorption tubes are desorbed and a PTV injector (CIS-3, Gerstel) where the desorbed analytes are cryotrapped and subsequently injected onto the CGC column. The system was interfaced to an HP 5890 Gas Chromatograph (Hewlett Packard, Little Falls, DE, USA) equipped with a nitrogen-phosphorous detector (NPD). The NPD detector was operated in the nitrogen selective mode with a hydrogen flow of 3 mL/min and an air flow of 110 mL/min. The GC was fitted with a 15 m L x 150 μm I.D. column coated with a 2 μm film of CP SIL5CB (Chrompack, Middelburg, the Netherlands). The carrier gas was helium at a pressure of 145 kPa. Both thermal desorption and cryotrap reinjection were performed in the splitless mode.

An HP 6890 GC (Hewlett Packard) equipped with an HP 5972 Mass Selective Detector (MSD) was used for characterization of the blank profiles of both the PDMS and the PBA sorptive phases. This system was also equipped with a Gerstel Thermodesorption system but here a CIS-4 PTV injector was used for focussing of the thermally released analytes. This system was equipped with a 30 m L x 250 μm I.D. GC

column coated with a 0.25 μm film of HP-5MS (Hewlett Packard). The carrier gas was helium at a pressure of 50 kPa and the system was operated in the splitless mode.

5.3.3.3 Experimental Procedure

The registration of blank profiles by GC-MS was done in the following way. The PDMS and PBA cartridges were thermally desorbed at 225ºC for 5 minutes. Thermally released solutes were cryotrapped in the CIS injector at -150ºC. After thermal desorption was complete, the CIS was balistically programmed to 325ºC. The splitless time was set at 1.5 minutes. The GC program started at 40ºC which was kept for 2 minutes and then the temperature was ramped at 15ºC/min to 325ºC.

The experimental procedure for preconcentration of water samples and analysis by GC-NPD started with derivatization of the analytes in the water sample. 100 μL of pyridine and 100 μL of 10M NaOH were added to a 10 mL water sample after which the sample was briefly mixed. Subsequently, 50 μL pentafluorobenzoylchloride (PFBOC) was added to the aqueous sample and the reaction was allowed to proceed for 10 minutes under sonnication. The PFBOC, which is not mixable with the water phase, is present as small droplets during sonnication. After sonnication is stopped, the PFBOC particles quickly clog together and can easily be separated from the water phase with a pipette. In this way the amount of reagent entering the system and the analytical column can be minimized. Conditioning of the PDMS or PBA cartridge was done with 1 mL of distilled water. This was sampled through the cartridge by means of a vacuum pump. Subsequently, 1 mL of the derivatized water sample was loaded on the cartridge by means of the same vacuum pump. In order to dry the cartridge, it was connected to a nitrogen source (grade 7.0) for 25 minutes at a flow of 300 mL/min. Now, the cartridge is ready for thermal desorption and is inserted into the TDS-2 unit of the GC/NPD system. Desorption and CGC analyses were performed according to the conditions described for recording the blank profiles.

5.3.4 Results and Discussion

5.3.4.1 Characterization of Blank Profiles

After thorough conditioning of the PDMS and PBA sorptive phases, initial experiments focused on the blank levels of these materials. Both materials were subjected to thermal desorption at 225ºC and blank profiles were recorded on the 6890/5972 GC-MS instrument. The blank runs are shown in **Figure 9**. It is immediately clear that both blank chromatograms contain distinct peaks. In the case of PDMS, these were identified as the cyclic siloxanes D_3, D_4, *etc.* Though the presence of these solutes might

interfere with the analysis of the target solutes, the siloxane degradation products can easily be distinguished on the basis of their mass spectra. Unfortunately, the situation is much worse in the case of the PBA phase. Here, a large number of intense peaks is encountered which block most of the chromatogram and leave little opportunity for the elucidation of unknowns. The use of the PBA phase prohibits the application of universal detectors such as the mass spectrometer. Therefore, for all other work, the GC/NPD system was used. Since both the PDMS and the PBA phases do not contain nitrogen, very clean blank chromatograms were obtained on this system. Therefore, both materials can be used for the sensitive and selective determination of nitrogen containing components.

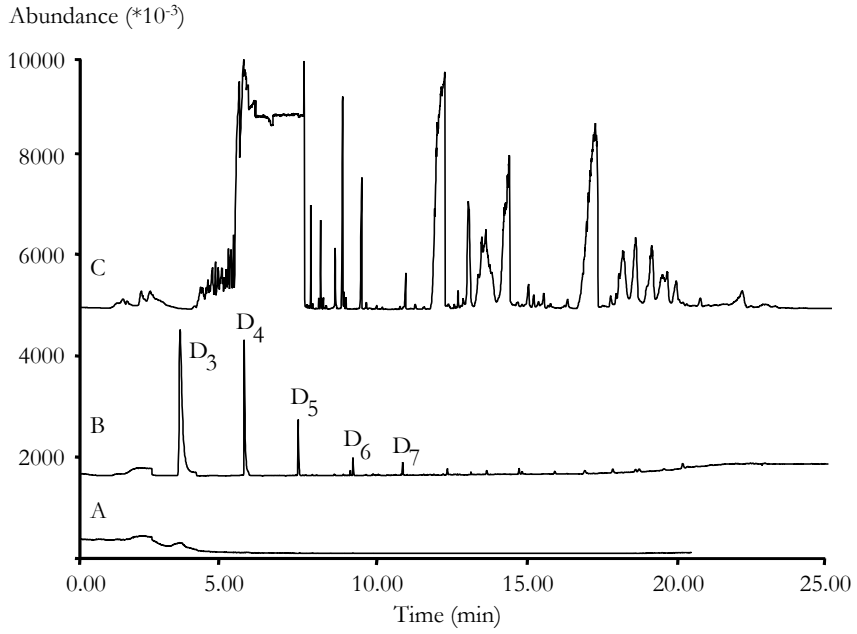

Figure 9 Blank chromatograms of the sorptive extraction phases. A is a system blank. B is a blank chromatogram of the PDMS material; peaks labeled D were identified as cyclic siloxanes. Chromatogram C is the result of a blank run on the PBA phase.

5.3.4.2 Determination of Amines in Tap Water

In order to test the performance of the analytical procedure, recoveries from water samples of 5 amines were determined on both the PDMS and the PBA phase at a concentration level of 10 μg/L. The results are listed, together with relative standard deviations (RSD in %, n=3), in **Table 6**. From this table it is clear that on the PDMS phase losses occur for the more polar and volatile solutes (*i.e.* dimethylamine and

ethylamine). This can be caused by either breakthrough during sampling or evaporation during drying. This was tested by repeating the procedure but now with a drying step of 50 minutes instead of 25 minutes. Under these changed conditions identical recoveries were encountered which led to the conclusion that the analytes were lost during the sampling of water through the PDMS bed.

Table 6 Recoveries (REC, %) and relative standard deviations (RSD, %) of amines, determined as their pentafluorobenzoylchloride derivatives. Concentration level is 10 μg/L in water samples.

	PMDS		PBA	
	REC	RSD	REC	RSD
Dimethylamine	26	30	98	9
Ethylamine	73	19	110	7
Dipropylamine	86	11	106	11
Pentylamine	107	4	93	6
Hexylamine	97	6	101	8

On the PBA phase none of the analytes are lost and quantitative recoveries are established. Compared to the PDMS phase, PBA is a more polar sorbent. Therefore it was already suspected to exhibit a stronger retention for the derivatized amines which is confirmed by these experimental results. Low RSDs (6-11 %) illustrate the repeatability of the procedure. A typical chromatogram of a 1 mL tap water sample spiked at 1 μg/L is shown in **Figure 10**. This chromatogram is very clean and reveals hardly any peaks in addition to the test solutes. This is primarily due to the selectivity of the NPD detector. Both the blank peaks of the PBA phase and the derivatization agent do not contain nitrogen and do therefore not show up.

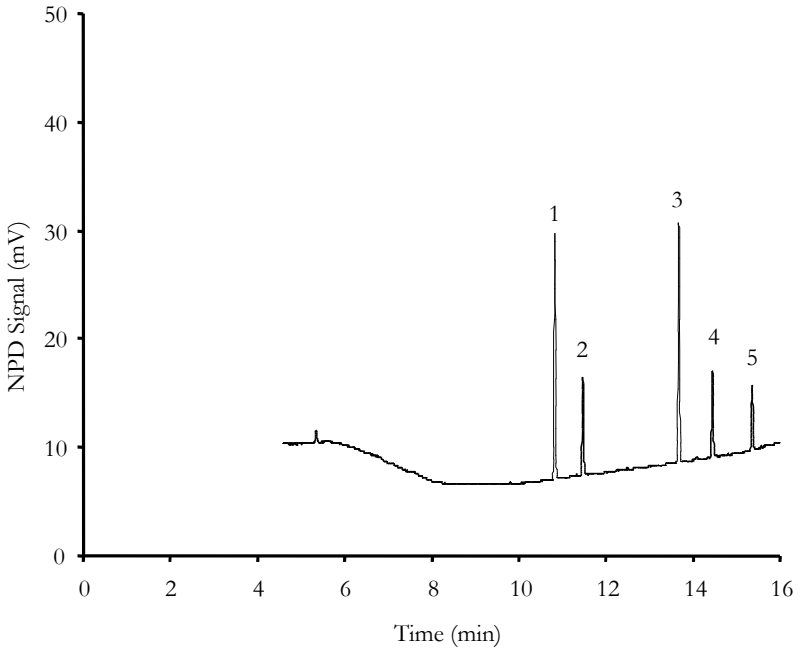

Figure 10 Chromatogram of 1 mL of a water sample spiked to a level of 1 μg/L (solutes 2, 4 and 5) or 2 μg/L (solutes 1 and 3). Solutes were derivatized in the water matrix and preconcentrated on the polybutylacrylate (PBA) phase. Peak identification: 1, dimethylamine; 2, ethylamine; 3, dipropylamine: 4, pentylamine; 5, hexylamine

5.3.5 Conclusion

The preconcentration and analysis of in situ derivatized amines using sorptive extraction is described. Next to the already available polydimethylsiloxane (PDMS) phase, a novel (experimental) polybutylacrylate (PBA) material was synthesized. This more polar sorbent shows a higher affinity for the polar derivatized amines and allows to trap these analytes quantitatively. This was not possible on the apolar PDMS phase. Though the blank level of the PBA phase is rather poor, clean chromatograms were obtained when the NPD was used. With this detector and using 1 mL water samples, detection limits are in the sub-μg/L range.

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6 Equilibrium Gum Phase Extraction

6.1 Summary*

A novel approach for sample enrichment, namely equilibrium gum phase extraction (EGPE), is presented. Though in principle it can be applied to both aqueous and gaseous samples, only gaseous samples are discussed. A packed bed of sorption (or partitioning) material is used to enrich volatiles from gaseous samples. Normally, air sampling is stopped before breakthrough occurs but in EGPE sampling is continued until all compounds of interest are in equilibrium with the sorptive material. Because of the nature of the sorption mechanism which is basically dissolution, all compounds partition independently into the sorbent (stationary phase) and displacement effects do not occur. This is a great advantage over adsorption materials. Additionally, theory allows the calculation of enrichment factors from literature retention index data. Moreover, EGPE also benefits from the features of sorption materials like very high inertness and interference free blanks. The performance of EGPE is illustrated with the analysis of several analytes including the epoxides ethylene oxide and epichlorohydrin in real-life air sampling.

6.2 Introduction

Most of the techniques presently used for the preconcentration of volatile organic compounds (VOCs) in air and gaseous samples are based on adsorption of the analytes of interest on a suitable preconcentration material followed by either liquid or thermal desorption[1,2,3]. Commonly used adsorbents include carbon-based materials like activated carbon and carbon molecular sieves[4,5] and porous organic polymers like Tenax and Chromosorb[6]. Thermal desorption is increasingly being used as a sensitive alternative to liquid desorption. Here, the trapping material is heated and the analytes released at high temperatures (typically 200-300°C) are transported to the analytical

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column by the carrier gas. Thermal desorption allows the rapid and complete transfer of the entire sample to the GC column resulting in maximum sensitivity. Therefore, the performance of thermal desorption procedures are in many cases superior to liquid desorption. Unfortunately, thermal desorption embraces some typical problems. Where in liquid desorption, blank levels are almost solely determined by the purity of the solvent, in thermal desorption, blanks are caused by the adsorbent itself. At the high temperatures used, adsorbents tend to breakdown (especially polymeric ones) resulting in characteristic degradation peaks[7]. Additionally, at elevated temperatures during thermal desorption, the adsorbent might react with the analytes to form artifacts[8,9] as was recently observed for sulfur compounds[10] or might permanently bond them to the surface. These are of course highly undesirable effects. Moreover, the unpredictable nature of adsorbents (dependence on sample humidity, sample concentration, *etc.*) makes these two effects very tedious in practice.

The performance of traps packed with polydimethylsiloxane (PDMS) as an alternative to adsorbents was recently evaluated[11]. PDMS is very inert as known from gas chromatography. Permanent adsorption and reactions on PDMS are negligible. The performance of PDMS for the enrichment of a number of analytes was compared to that of the adsorbents Chromosorb, Carbotrap and Tenax. For many polar (and/or reactive) compounds much better performance in terms of recoveries was observed on PDMS. A marked disadvantage of PDMS, however, is the low capacity for volatile compounds, *e.g. n*-heptane has a breakthrough volume of less than 250 mL for 300 mg PDMS at room temperature. This not only results in diminished sensitivity compared to sampling on adsorbents but also renders sampling difficult. Firstly, timing a short sampling period can be difficult also with respect to start-up effects. Secondly, temperature becomes a very important factor as it has an exponential influence on the breakthrough volume.

In this contribution, a novel approach for PDMS sample enrichment is proposed. Whereas sampling is normally stopped when the first compound starts to be lost from the trap (breakthrough sampling), sampling is stopped when all analytes are in equilibrium with the PDMS sorbent. This approach is referred to as equilibrium gum phase extraction (EGPE). In EGPE, analyte enrichment factors are no longer dependent on the sample volume but solely on the partitioning equilibrium constant (K), sample pressure and temperature. These dependencies will be described in the theory section. EGPE also benefits from the features of PDMS sorption like high inertness, fast desorption and relies on the predictability of equilibrium constants. Several applications illustrate the use of EGPE for the enrichment of volatile and instable compounds from gaseous samples.

6.3 Theory of Equilibrium Gum Phase Extraction

6.3.1 Calculation of Enrichment Factors

In EGPE, the gaseous sample is sampled until the compounds of interest are in equilibrium with the sorbent. Sampling is thus stopped (far) beyond the breakthrough point for (most) compounds. This also means that calibration cannot be performed with a simple liquid calibration solution as described previously[11]. Instead, a continuous stream of calibration gas coming from a gas cylinder or a headspace device is necessary. One of the advantages of PDMS sorption is, as mentioned above, that it was already extensively studied in the past because PDMS is the most commonly applied GC stationary phase. Literature data on the retention of many compounds are available as Kováts retention indices[12]. In a previous publication[13] a simple approach was presented to calculate equilibrium constants (K) from retention indices (RI). In the equilibrium sorption mode, the gas phase is in full equilibrium with the PDMS sorbent and the sorbed volume of air is equivalent to the retention volume of the trap. The concentration of a compound in the gas phase, C (in kg/m^3) can be calculated by:

Equation 1

$$C = \frac{m_{sorbed}}{V_r} = \frac{m_{sorbed}}{V_0 \times \left(1 + \frac{K}{\beta}\right)} \approx \frac{m_{sorbed}}{V_{PDMS} \times K} \quad \text{for } K >> 1$$

where: m_{sorbed} is the sorbed amount of the compound under investigation (in kg), V_r is the retention volume of the trap (in m^3), V_0 is the dead volume of the trap (in m^3), V_{PDMS} is the volume of PDMS (in m^3) in the trap and ß is the phase ratio. For practical purposes, the approximation can be used. V_{PDMS} is determined by weighing the amount of PDMS present and conversion with it's density of 825 kg/m^3. K is calculated from retention indices and m_{sorbed} is determined from a calibration curve.

6.3.2 Influence of Pressure Drop

Calculation of the equilibrium sorbed amount of a compound using **Equation 1** is only valid when the composition of the sampled gas is constant over the length of the trap. This requirement is often met. When the sampling flow rate is set too high this, however, is no longer the case. As a consequence of the sorption mechanism, at lower sampling pressures (where the gas phase concentration, expressed as kg/m^3 is lower), the amount of analyte sorbed into the sorbent (m_{sorbed}) will be proportionally lower. The pressure profile inside the trap has therefore to be known from which an average pressure over the trap length can be calculated. The packed bed can be either under turbulent or laminar flow conditions but most often it will be in an intermediate flow

regime. The parameter expressing the degree of turbulence is the Reynolds number (Re):

Equation 2

$$Re = \frac{\rho v_0 d_p}{\mu}$$

where: ? is the gas phase density (in kg/m^3), v_0 the superficial velocity (in m/s), d_p the particle diameter (in m) and μ the viscosity (in kg/ms). Under normal conditions, *i.e.* sampling with a vacuum pump, the gas pressure will decrease through the bed whereas the superficial velocity will increase. Since μ and d_p are independent of pressure and ? v_0 is a constant throughout the bed, Re is a constant through the bed and thus the degree of turbulence is also constant. It can be noted that whereas in an open tubular column the transition from laminar to turbulent is abrupt at a Re of *ca.* 2300, in a packed bed this transition is much more gradual with a fully laminar flow at Re<1 and a fully turbulent flow at Re>1000. The practical working range for air enrichment traps is Re 1 to 100. The actual pressure drop over a small piece of packed bed is given by[14] :

Equation 3

$$\frac{\partial p}{\partial x} = \frac{150\mu v_0}{d_p^2}\frac{(1-\varepsilon)^2}{\varepsilon^3} + \frac{1.75 G v_0}{d_p}\frac{1-\varepsilon}{\varepsilon^3}$$

where: p is the pressure in the bed (in kg/ms^2), x the length coordinate through the bed (in m), G the mass flow through the section of the bed (equal to ? v_0, in kg/m^{2}s) and e the porosity. The first part of **Equation 3** describes the behavior of the packed bed under laminar flow conditions whereas the latter part describes the turbulent flow regime. Since all parameters in **Equation 3** are independent over the bed except v_0, **Equation 3** can be reduced to:

Equation 4

$$\frac{\partial p}{\partial x} = A v_0$$

where: A is a constant. Since v_0 is inversely proportional with p, **Equation 4** leads to:

Equation 5

$$\int p \partial p = \int A' \partial x$$

where A' is a second constant. **Equation 5** can be integrated to lead to the average pressure over the bed:

Equation 6

$$f = \frac{2}{3}\frac{P^3 - 1}{P^2 - 1} P_{in} \quad \text{with} \quad P = \frac{P_{in}}{P_{uit}}$$

where: P_{in} and P_{uit} are the trap in and outlet pressures. The true equilibrium sorbed amount of a compound is now given by $m_{sorbed}f/P_{in}$. Where m_{sorbed} is the amount of compound partitioned into the PDMS phase without pressure drop effects.

6.4 Experimental Section

6.4.1 Thermal Desorption Cartridges

Prepacked (crosslinked) PDMS traps were obtained from Gerstel (Müllheim a/d Ruhr, Germany) and conditioned for 1 hour at 300°C and then for 4 hours at 250°C. After this procedure, no peaks appeared in the blank chromatogram with the exception of cyclic siloxanes.

6.4.2 Experimental Set-Up

The experimental set-up used was described previously[11]. In short, it consists of a TDS-2 thermodesorption unit (Gerstel) mounted on a HP 6980/5973 GC/MSD system (Hewlett Packard, Little Falls, DE, USA) also equipped with a flame ionization detector (FID). A CIS-4 PTV injector (Hewlett Packard) is used for cryofocusing the analytes prior to transfer onto the analytical column. Two analytical columns were used, a 30 m L x 320 μm I.D. x 4 μm d_f CP-SIL 5 CB column (Chrompack, Middelburg, the Netherlands) and a 30 m L x 320 μm I.D. x 10 μm d_f Porabond Q (Chrompack). The GC was programmed from 35°C (4 min) at 15°C/min to 275°C. The temperature during sampling was kept at 22.5 ± 0.1°C.

6.4.3 Chemical Standards

The BTX gas mixture was obtained from BOC specialty gases (Guildford, Surrey, UK). This sample contained benzene, toluene and p-xylene at a concentration of 25 mg/m^3 in helium. Other gaseous samples were generated in situ in a home-made headspace device previously described[15]. A small amount of liquid, present in a vial, is placed inside a small glass bulb. A continuous nitrogen stream is supplied which causes a steady evaporation of the liquid forming a stable (spiked) concentration in the outgoing nitrogen stream. By measuring the flow rate of the gas used and the weight loss of the vial, the outgoing concentration can be calculated.

6.5 Results and Discussion

6.5.1 Prediction of Enrichment Factor

Using the 25 mg/m^3 BTX standard gas mixture, the accuracy of the enriched concentration, predicted by **Equation 1**, was investigated. A stream of 1 L nitrogen (grade 5.0) per minute was supplied to the home-made headspace device. To this, a flow from the BTX cylinder was added to generate a final concentration of 0.1 mg/m^3. From this gas stream, 6 L was sampled through a PDMS tube containing 0.45 mL material at a flow rate of 100 mL/min to ensure full equilibration between the PDMS phase and the gas sample without pressure drop effects. A chromatogram from an enriched BTX sample, shown in **Figure 1** illustrates the principle of EGPE quite effectively. Though in the original sample all compounds were present in equal concentration in EGPE compounds with increasing partitioning constant (*e.g.* p-xylene) are enriched in higher amounts than compounds with lower partitioning constants, *e.g.* benzene.

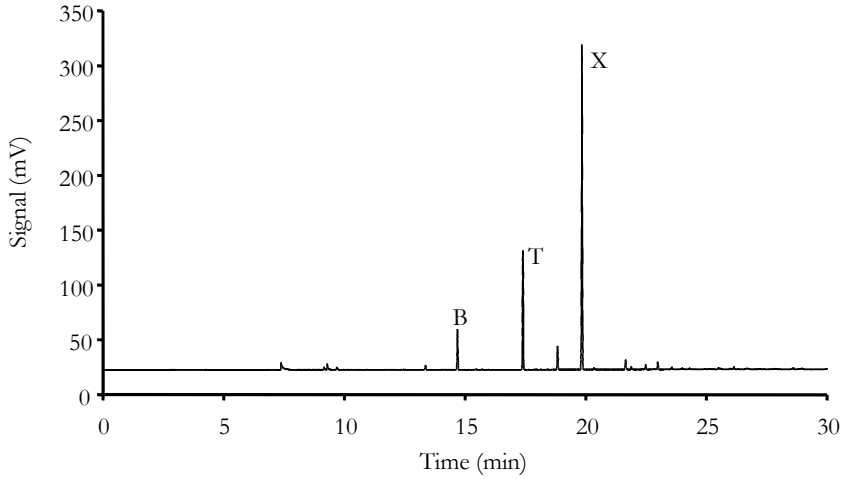

Figure 1 Chromatogram of the enrichment of a 0.1 mg/m^3 mixture containing benzene (B), toluene (T) and p-xylene (X) on a tube containing 0.45 mL PDMS. Sample volume: 6 L, sampling flow rate: 0.1 L/min. Temperature during sampling 22.5 ± 0.1°C. Column: 30 m L x 320 µm I.D. x 4 µm d_f CP-SIL5CB. Detection: FID.

From this chromatogram absolute detected amounts were determined using a calibration line constructed from several direct injections of a liquid calibration solution onto the PDMS material. Absolute detected amounts (m_{sorbed}) are listed in

Table 1 as well as the corresponding concentrations calculated using **Equation 1**. The determined concentrations are somewhat smaller than the 0.1 mg/m^3 level from the reference gas. Apparently, compounds seem to partition slightly less into the PDMS particles than predicted by **Equation 1**. This can have numerous causes of which the most obvious are erroneous literature RI data or a slightly higher temperature during sampling. This deviation is acceptable for practical work, especially since the reproducibility of EGPE analyses is very good, typically better than 5% RSD. Detection limits for BTX with FID detection are listed in the last column of **Table 1** for a signal to noise level of 8. Detection limits are sub-μg/m^3 for all compounds and are, due to the nature of EGPE, lowest for p-xylene which has the highest partitioning constant. In real-life samples, detection limits can be higher because of the presence of chemical interferences. Lower detection limits can be achieved by using either a more sensitive (and/or selective) detector like the mass spectrometer in the ion monitoring mode or the use of lower trapping temperatures.

Table 1 Enrichment of the BTX mixture on a trap containing 0.45 mL PDMS phase. Listed are literature data on retention indices (RI) from which K values were determined on the PDMS trap. The detected amount of each component (m_{sorbed}) was calculated using a liquid calibration solution spiked on the PDMS trap. Detection limits are specified for a signal to noise ratio of 8.

Component	RI[12]	K[13]	m_{sorbed} (ng)	C (μg/m^3)	Detection limit (μg/m^3)
Benzene	654.13	419	17.2	91	0.5
Toluene	756.49	1106	40.9	82	0.2
p-Xylene	857.45	2891	125	96	0.08

6.5.2 Equilibrium Sorption Profile

The nature of the EGPE sorption profile was investigated in the following way. A solution containing 1% of 5 alkanes, namely n-pentane through n-nonane, was prepared in methanol. 5 mL of this solution was placed in a 10 mL vial inside the home-made headspace device and a continuous flow of 0.5 L/min clean air (grade 4.5) was introduced. From the outlet of the head-space device, gas was sampled at a flow of 50 mL/min using a constant flow sampler (Gillian Instrument Corporation, West Caldwell, NJ, USA) avoiding in this way pressure drop effects. Sampling times from 1 to 90 min were used to follow the saturation of the 0.45 mL of PDMS phase. The temperature was 22.5°C during these experiments. Results of the analyses are summarized in **Figure 2**. Peak areas were normalized to the peak areas found (or suspected) at infinite sampling time. The sample volume (V) was divided by the retention volume (V_r) to obtain the relative sample volume. In this way, similar sorption profiles are obtained for all compounds.

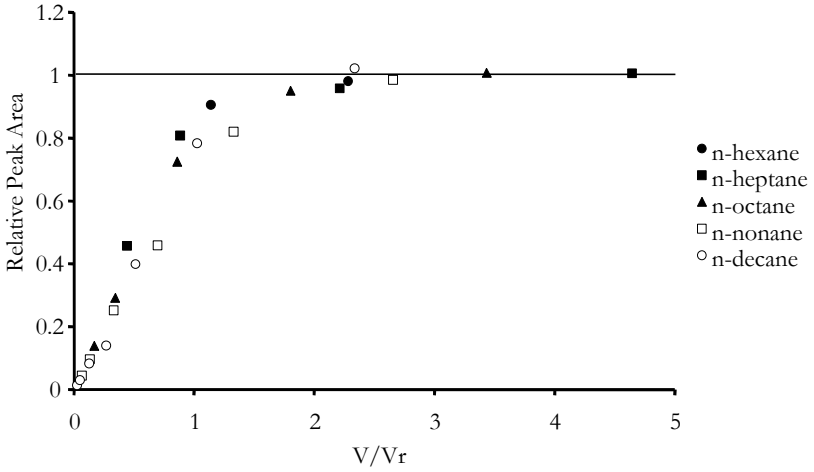

Figure 2 Enrichment of an air sample spiked with 5 alkanes (n-pentane though n-nonane). Different volumes were sampled at a flow rate of 50 mL/min. Peak areas are expressed relative to the peak areas obtained for infinite sampling time and sampling volume is expressed relative to a compound's retention volume. Data are based on a 0.45 mL PDMS trap.

In the sorption profiles two interesting parts can be distinguished. The part of the curve for which $V/V_r < 0.5$ is linear and represents 'normal' breakthrough sampling. Here, the peak area is directly proportional to the sampled volume. The part of the curve for which $V/V_r > 2$ represents the equilibrium enrichment region where the sorbed amount of compound is no longer dependent on the sampled volume. For (V/V_r) values in excess of 5 (not shown in **Figure 2**), relative standard deviations become very small as will be shown later. This is of course ideal for quantitative sampling. However, in cases where sampling times need to be minimized, it is acceptable to sample only until V/V_r equals 2. Additionally, the required (minimum) equilibrium sampling volume depends on the flow rate at which sampling is performed. This is illustrated in **Figure 3** where sorption profiles for n-hexane on 0.45 mL PDMS are shown at flow rates between 50 and 500 mL/min. At higher flow rates, a larger volume has to be sampled to reach equilibrium. At a flow rate of 50 mL/min, V/V_r is roughly 1.6 at 95% of the equilibrium whereas at a flow rate of 500 mL/min this point is only reached at a V/V_r of 3.4. A doubled sample volume at a ten times increased flow rate, however, still implies a reduction in sampling time by a factor of 5. Therefore high flow rates are, in general, to be preferred as long as pressure drop effects do not occur.

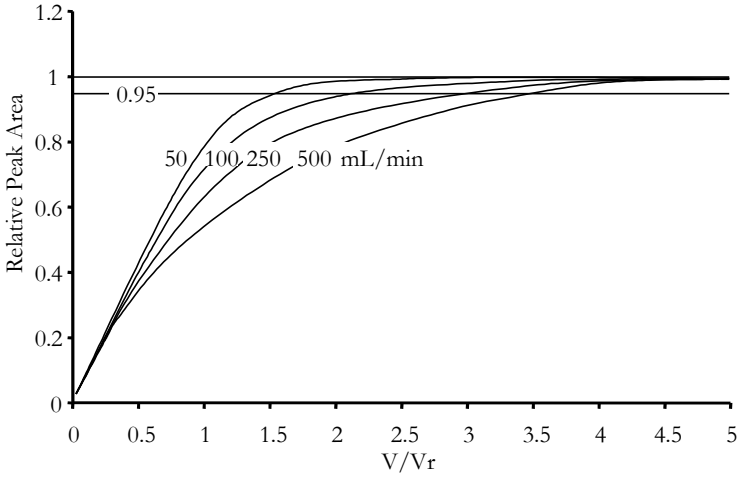

Figure 3 Sorption profiles of n-hexane on a 0.45 mL PDMS trap at room temperature (22.5°C). Sampling flow rate was varied between 50 and 500 mL/min.

6.5.3 Displacement Effects

One of the most important advantages of enrichment by sorption is the absence of displacement effects. Normally when employing adsorbent phases, a compound present in a very high concentration tends to push others off from the active sites of the surface of the adsorbent. In EGPE, the equilibrium mechanism, in principle, allows independent partitioning of all solutes. This was investigated by using a gas stream spiked with a constant concentration of n-hexane. Additionally, a certain amount of acetone was added and the amount of n-hexane sorbed was followed. The results of these experiments are listed in **Table 2**. Displacement only occurs at acetone concentrations of *ca.* 5000 mg/m^3 which is very unrealistic to occur in practice. Consequently displacement can be assumed to be negligible.

Table 2 EGPE of a gas sample spiked with n-hexane at 2 mg/m^3 and different concentrations of acetone. Each entry is the average of 4 sequential experiments. Flow rate during sampling was 50 mL/min. PDMS trap of 0.45 mL.

Concentration acetone (mg/m^3)	Peak area n-hexane	Displacement (%)
0	488	0
5	489	0
50	488	0
500	486	0.4
5000	461	5

6.5.4 High Flow Sampling - Influence of Pressure Drop

The influence of a pressure gradient through a PDMS sorption cartridge under EGPE conditions was theoretically investigated in the theory section. Using **Equation 6** it can be concluded that the maximum theoretical analyte loss due to a pressure drop is 33% which is too much to ignore. Using the 2 mg/m^3 n-hexane standard in air, the influence of pressure drop was investigated. Using different flow rates, different pressure drops were generated and the amount of n-hexane on the PDMS trap was determined. In- and outlet pressures were measured using digital pressure gauges (Gerstel, Müllheim a/d Ruhr, Germany) which were calibrated to an accuracy of 1 mbar. The results are listed in **Table 3**. Both the theoretical f factor from **Equation 6**, which is calculated solely on the basis of the in- and outlet pressure, and the experimentally determined recovery relative to the situation without pressure drop are given in **Table 3**. The experimentally determined pressure drop loss is slightly higher than that experimentally determined. This error can have several causes including inaccurate pressure measurements (not likely as the instrumentation used was carefully calibrated), slight temperature deviations or slight concentration variations form the headspace device. A 5% loss in analyte occurs at a flow rate of *ca.* 200 mL/min and a 10% loss at *ca.* 500 mL/min. In most cases, a 10% loss is still acceptable. Therefore, it is recommended to work at flow rates below 500 mL/min but if this results in unacceptably long sampling times higher flow rates can be used, however, only with the use of a correction for the pressure drop.

Table 3 Influence of a pressure drop on the enrichment of *n*-hexane spiked at 2 mg/m^3 in air. PDMS trap of 0.45 mL.

Flow (mL/min)	P_{in} (mbar)	P_{out} (mbar)	f/P_{in} (theoretical)	Peak area hexane	Recovery
50	1024	1015	0.995	332	1
150	1024	988	0.983	329	0.988
300	1024	912	0.946	306	0.922
620	1024	839	0.912	289	0.870
1000	1024	755	0.856	265	0.798
1250	1024	603	0.798	237	0.713
1450	1024	524	0.770	231	0.696

6.5.5 EGPE Determination of Epichlorohydrin

After the theoretical studies, some challenging compounds in air were sampled by EGPE to illustrate its performance, inertness and favorable characteristics of PDMS. Epichlorohydrin, a not too volatile solute (RI = 696.3), is not easily enriched on classical adsorption materials because of destruction and reactions of the epoxide.

On a PDMS trap of 0.45 mL, epichlorohydrin has an equilibrium volume of 280 mL as calculated from the equations described by Baltussen *et al.*[13] Therefore, 1000 mL air was sampled at 100 mL/min to guarantee equilibrium under absence of a pressure drop. Analyses were accomplished on the GC/MSD system using selective ion monitoring (SIM) in the positive chemical ionization (PCI) mode with methane as reagent gas. The latter was selected for enhanced selectivity since PCI allows quantification on the MH^+ ion which is more specific than the lower m/z fragment ions generated under EI conditions. **Figure 4** shows the chromatogram for m/z 93, 65 and 63 obtained from the enrichment of an air sample containing 0.2 μg/m^3 epichlorohydrin. 56 pg epichlorohydrin was collected on the PDMS trap. Epichlorohydrin is clearly detected without interferences. Detection limits are around 10 ng/m^3 (ppt).

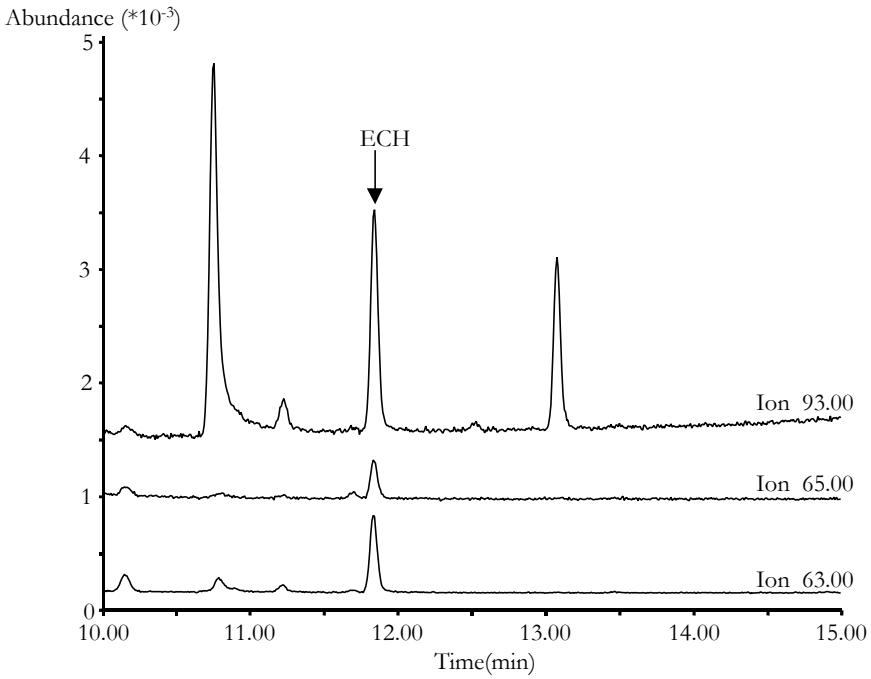

Figure 4 EGPE enrichment of epichlorohydrin spiked at 0.2 μg/m^3 in air. Column: 30 m x 320 μm I.D. x 4 μm d_f CP-SIL5CB. Detection: MSD operated in the PCI-SIM mode.

6.5.6 Monitoring Ethylene Oxide in Air

Ethylene oxide (EO) is another important air contaminant difficult to monitor at trace levels in work places. It is a highly volatile (RI=424.4) and unstable compound. Enrichment of EO from air samples is normally done using HBr impregnated silica

cartridges to convert the analyte into 2-bromoethanol. This compound is subsequently eluted from the cartridge with acetone and an aliquot is injected into a GC-ECD instrument. Disadvantages of this approach include a reduced sensitivity (only an aliquot is injected) and many manual handling steps. For enrichment by EGPE an equilibrium sorption volume of 15 mL was calculated from the retention index for EO. Measurements of the air in our laboratory showed that it did not contain EO, at least not at the detection limits of our instrument. Therefore it was decided to spike laboratory air at a level of 0.5 mg/m^3. During 10 minutes air spiked at the 0.5 mg/m^3 level was sampled at a flow rate of 50 mL/min to ensure complete equilibrium of a PDMS trap containing 0.45 mL material. **Figure 5** shows the chromatogram obtained on the Porabond Q column. Detection was done on the MSD in the electron-impact (EI)-scan mode, scanning from 10-200 amu. Ions 29 and 44 were extracted from the total ion current. EO is clearly identified, however, one interference was present corresponding to acetaldehyde. Both compounds generate the same mass spectrum and can thus not selectively be detected with MS. Detection limits are around 20 μg/m^3 but in real life samples this level may not be reached if large quantities of acetaldehyde are present. Lower detectability can be reached on a more selective column in combination with SIM detection.

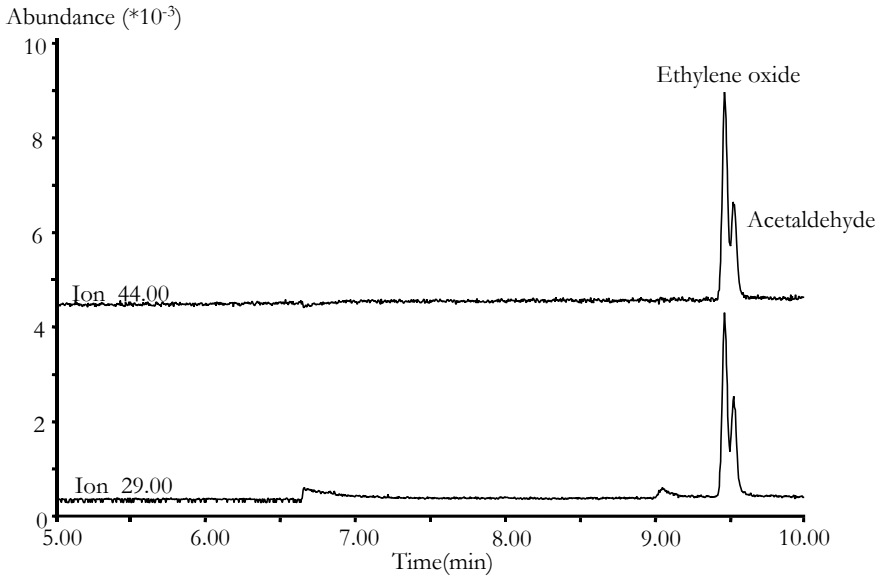

Figure 5 EGPE enrichment of EO from a spiked air sample (0.5 mg/m^3). First peak is EO, second peak is acetaldehyde. Detection: MSD operated in the EI-scan mode. Specific ions were extracted from the total ion current. Column: 30 m L x 320 μm I.D. x 10 μm d_f Porabond Q.

6.6 Conclusion

Equilibrium Gum Phase Extraction (EGPE) is a valuable extension on the volatile side of the PDMS working range. It has been shown that displacement effects are absent due to the sorption mechanism of the PDMS phase so that highly reliable sampling is guaranteed. The equilibrium nature of the sampling process ensures a high reproducibility of typically 5% RSD. For quantitation purposes enrichment factors can be calculated from literature retention indices and gaseous standards are not required for routine analysis. Enrichment of volatile and reactive compounds is possible without degradative losses because of high inertness of the PDMS sorbent. Recommended flow rates are below 500 mL/min to avoid pressure drop effects and V/V_r should be at least 2.

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7 Stir Bar Sorptive Extraction

Another novel approach for sorptive sample enrichment, stir bar sorptive extraction (SBSE) is introduced in this chapter. First, the path that lead to the discovery of this innovative technique is outlined followed by the theoretical description and several real-life applications.

7.1 Study into the Equilibrium Mechanism Between Water and PDMS for Very Apolar Solutes: Adsorption or Sorption ?*

7.1.1 Summary

Recently several publications appeared correlating octanol-water partitioning coefficients ($K_{O/W}$) with solid phase microextraction (SPME) extraction coefficients on polydimethylsiloxane (PDMS) fibers. This correlation seems very good for medium-polar to polar compounds but cannot explain the observations for apolar compounds. It is shown that for polychlorinated biphenyls (PCBs) the published data are erroneous, because of system adsorption effects. PCB concentrations up to 10 times were measured on the Teflon coated stir bar, applied in SPME, compared to the SPME fiber. This artifact explains the low partitioning constants for the analytes under investigation. Using a short packed PDMS trap it is shown that the true PDMS-water equilibrium constant is indeed proportional to literature $K_{O/W}$ data.

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7.1.2 Introduction

In SPME the knowledge of an accurate value for the equilibrium partitioning coefficients ($K_{PDMS/W}$) of all compounds under investigation is most helpful. It would be very convenient if these coefficients could be directly deduced from octanol-water partitioning coefficients ($K_{O/W}$) which are tabulated for numerous compounds[1]. In a number of publications $K_{PDMS/W}$ values have been correlated with $K_{O/W}$ literature data[2,3,4]. It was found that over a certain polarity range $K_{O/W}$ and $K_{PDMS/W}$ data correlate very well, especially for low molecular weight (MW) analytes such as the BTXs[5,6] (benzene, toluene, xylene and related compounds). This correlation is rather obvious as the $K_{O/W}$ value is a measure of analyte polarity, *e.g.* very apolar analytes have a very high $K_{O/W}$ and are consequently almost exclusively present in the octanol phase. In the PDMS-water equilibrium the same mechanism occurs, namely very apolar analytes will partition virtually exclusively into the apolar PDMS phase and will thus consequently have a very high $K_{PDMS/W}$ value. The agreement between $K_{O/W}$ and $K_{PDMS/W}$ data illustrate that the behavior of both PDMS and 1-octanol behave similarly as extracting liquid.

Although this correlation seems to hold for a wide range of solutes, for high MW and very apolar solutes like polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)[7] the correlation between $K_{O/W}$ and $K_{PDMS/W}$ seemed to be no longer valid. For PCBs it was found[8] that with decreasing polarity (increasing $K_{O/W}$ of a factor of $4*10^4$), the measured $K_{PDMS/W}$ decreased by a factor of 40 which would mean a misprediction in $K_{PDMS/W}$ of a factor $2*10^6$. The authors explained their data by assuming surface adsorption on the PDMS fibers instead of bulk partitioning (sorption) and emphasized by comparison of data from two PDMS fibers (7 μm and 100 μm) the validity of this model. Despite their seemingly convincing results, we had serious doubts about this surface adsorption model and investigated the PDMS-water equilibrium of PCBs in more detail.

PCBs (and also PAHs) are among the compounds with lowest water solubility[9], often in the ng/L range and are known to easily adsorb on glass or other surfaces (*e.g.* the stir bars used in SPME). We suspected this to be occurring in the experiments and data presented by Yang *et al.*[8]. With increasing apolarity, compounds will adsorb more strongly on active surfaces and will increasingly be lost, which should explain the observed effect. It was already mentioned by Yang *et al.*[8] that the stir bars could not be re-used since that causes contamination problems (by the adsorbed PCBs ?). Other surfaces accessible for PCB adsorption are the walls of the glass vial and the septum. Though these were deactivated glass and Teflon, respectively, this can certainly not fully eliminate the adsorption of apolar solutes like PCBs.

Recently an alternative set-up to SPME using cartridges packed with 100% PDMS particles for the extraction of compounds from water was presented[10]. The data using this approach were correlated with literature $K_{O/W}$ data and good

relationships were noted for a range of pesticides and PAHs. Only the highest MW (6-ring) PAHs were found to perform poorly because of system adsorption effects caused by adsorption in the HPLC pump and tubing used to pump the sample through the cartridge. The PCBs under investigation are even more apolar than the 6-ring PAHs and the system as it was described[10] will certainly not be directly applicable to the problem at hand. Instead of preparing a water sample containing the PCBs which will certainly result in adsorption problems, a small amount of PCB standard was injected with a syringe directly on the PDMS trap followed by pumping a certain volume of water through the trap. The analyte recovery as a function of sampled water volume allows to determine the amount of analyte eluted out of the PDMS trap and thereby the $K_{PDMS/W}$ constant. Since pure PDMS particles have too much retention for PCBs, fused silica particles with different PDMS loading were used. The SPME experiment of Yang *et al.*[8] was repeated and not only the SPME fiber but also the stir bar were thermally desorbed.

7.1.3 Experimental

7.1.3.1 Test Solutions

A mixture of 7 PCBs (composition shown in **Table 1**) ranging from the trichloro- to heptachlorobiphenyls was obtained from NSI Environmental Solutions Inc. (RTP, NC, USA). This 10 μg/mL mixture in dichloromethane was diluted to 10 times in methanol for spiking the packed PDMS traps. For SPME experiments, the 10 μg/mL standard was diluted to 0.1 μg/L in methanol and 5 μL was used to spike 10 mL of bidistilled water to a concentration of 50 ng/L.

7.1.3.2 PDMS traps

For the work described in this report it was impossible to use 100% PDMS particles since these exhibit too much retention for the high MW PCBs. Instead of the pure PDMS phase, two GC stationary phases were used. These were either 5% or 20% PDMS coated on 100 μm fused silica beads (Restek, Bellefonte, PA, USA). These two materials were packed in OPTIC-2 (Atas, Veldhoven, the Netherlands) liners with the following dimensions: length 81 mm, inner diameter 3 mm. 50 mg of PDMS packing was placed on a glass frit positioned 15 mm from the bottom of the injector and was kept in place by a small plug of deactivated glass wool on top. The PDMS traps were conditioned up till 300°C until no peaks are detected in blank chromatograms applying the PCI-SIM mode.

7.1.3.3 Experimental Set-Up

The experimental set-up consists of an HP 6890/5973 GC/MSD system (Hewlett Packard, Little Falls, DE, USA). The MS was operated in the positive chemical ionization (PCI) mode using methane as reagent gas. The electron multiplier voltage was set at a value 200 V above that recommended by the auto tune program. The MSD was operated in the time-scheduled selected ion monitoring mode using 3 ions/component. The GC was fitted with a 25 m long, 250 μm inner diameter column coated with a film of 0.25 μm HP-5MS (Hewlett Packard). The oven was programmed from 40°C at 20°C/min to 325°C.

For desorption of the PDMS traps, an OPTIC-2 (Atas) programmable temperature vaporizing (PTV) injector was used. The initial temperature was 40°C which was kept for 0.1 min. Subsequently the injector was programmed at 12°C/s to 310°C which was kept for 10 minutes. The split vent was continuously open at a flow of 25 mL/min, this was required for sharp injection bands as this inlet was not equipped with a cryogenic concentration device.

SPME fibers coated with 100 μm PDMS (Supelco, Bellefonte, PA, USA) were desorbed in a Gerstel CIS-4 PTV injector (Müllheim a/d Ruhr, Germany). The initial temperature of 40°C was programmed to 325°C at 12°C/s. Desorption was done in the splitless mode with the valve closed for 1.5 min.

Teflon coated stir bars were desorbed in a Gerstel TDS-2 thermodesorption instrument for 5 minutes at 300°C under a helium flow of 200 mL/min. Thermally released analytes were splitlessly transferred to a cold trap kept at -150°C and were re-injected onto the analytical column in the splitless mode. Blank analysis of the stir bars confirmed the absence of PCBs prior to the experiments described below.

7.1.3.4 Analytical Procedure

The short packed PDMS traps were used in the following way. First, the cartridges were spiked with 1 μl of the 1 ppm standard to introduce an amount of 1 ng of the PCBs. Subsequently, the trap was briefly purged with air to remove the solvent (dichloromethane) after which a certain volume of water was sampled (up to 10 liters) by means of a vacuum pump to simulate the sampling of an actual water sample. Drying of the trap was performed by flushing with nitrogen for 25 minutes at a flow of 500 mL/min. Recoveries were calculated relative to a 1 μL direct injection.

SPME experiments were performed as outlined by Yang *et al.*[8]. SPME fibers were desorbed directly into the PTV injector. The stir bars were first briefly dried with a piece of tissue paper and then put in an empty thermal desorption tube (17.8 cm length, 4 mm I.D., Gerstel) which was inserted into the thermodesorption instrument.

Table 1 Ions monitored for the 7 PCB congeners. Systematic numbering according to Ballschmitter *et al.*[11].

Compound	MS ion 1	MS ion 2	MS ion 3
PCB 28	259	261	287
PCB 52	291	293	319
PCB 101	291	293	319
PCB 118	327	329	353
PCB 138	327	329	353
PCB 153	361	365	389
PCB 180	395	397	399

7.1.4 Results and Discussion

After establishing proper operation of the analytical instrumentation, recovery experiments were started with the PDMS traps. Sample volumes were between 25 mL and 10 L which were loaded at a rate of 100 mL/min by means of a vacuum pump. Recovery of the analytes was calculated relative to a 1 μL direct injection. The ions selected for time-scheduled SIM are listed in **Table 1**. **Figure 1A** shows the recovery of the 7 PCBs from water as a function of the sampled volume for the 5% PDMS material and **B** for the 20% PDMS material. As is clear from this figure, at higher sample volumes, PCBs are increasingly lost because of breakthrough from the PDMS trap. In principle, the shape of this curve is that of an error function (integrated Gaussian peak) of which the center corresponds to the retention volume (V_r), which in turn can be calculated to a $K_{PDMS/W}$ value by the formula:

Equation 1 $$V_r = K_{PDMS/W} \times V_{PDMS} \quad \text{or} \quad K_{PDMS/W} = \frac{V_r}{V_{PDMS}}$$

where: V_r and V_{PDMS} are the retention volume and the volumes of PDMS material in the trap, respectively. V_r was determined as the volume at which the recovery is exactly 50 %. For clarity, 50 mg of the 5% PDMS material contains 2.5 mg of PDMS which converts to (density 825 g/L) 2.06 μL. 50 mg of the 20% PDMS material contains 8.25 μL of PDMS liquid phase. **Table 2** shows the data calculated from **Figure 1A** and **1B** and the resulting estimates for $K_{PDMS/W}$.

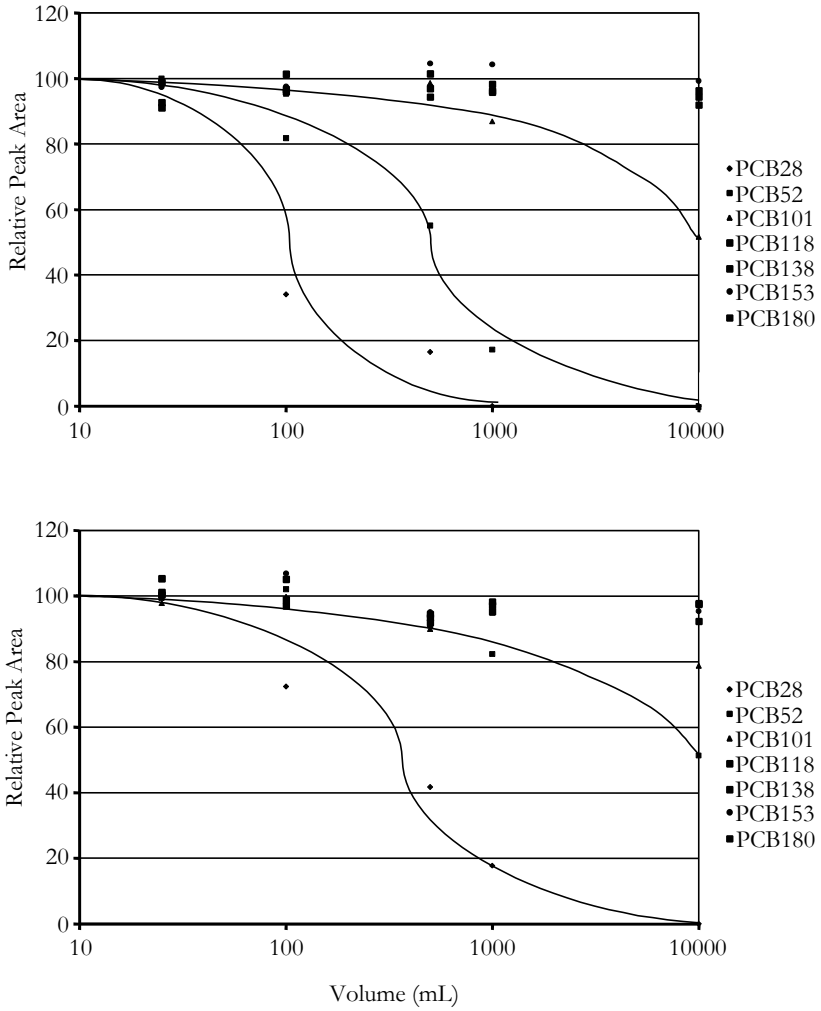

Figure 1 A. Recovery of the PCBs as a function of the sampled water volume. Trap was filled with 50 mg of 5% PDMS on fused silica. Amount of PCBs was 1 ng in all cases. B. Recovery of the PCBs as a function of the sampled water volume. Trap was filled with 50 mg of 20% PDMS on fused silica. Amount of PCBs was 1 ng in all cases.

Table 2 Experimentally determined retention volumes and calculated $K_{PDMS/W}$ values. Additionally $K_{O/W}$ literature data are included.

	5% PDMS on fused silica		20% PDMS on fused silica		Literature data	
Compound[11]	V_r (mL)	$K_{PDMS/W}$	V_r (mL)	$K_{PDMS/W}$	$K_{PDMS/W}$ (SPME)[7]	$K_{O/W}$[1]
PCB 28	79	$3.9*10^4$	$3.9*10^2$	$4.7*10^4$	$8.7*10^3$	$5.5*10^5$
PCB 52	$5.7*10^2$	$2.8*10^5$	$1.0*10^4$	$1.3*10^5$	$7.3*10^3$	$1.8*10^6$
PCB 101	$1.0*10^4$	$5.1*10^6$	$>10^4$	$>10^6$	$3.8*10^3$	$7.1*10^6$
PCB 118	$>10^4$	$>10^7$	$>10^4$	$>10^6$	$3.3*10^3$	$2.5*10^6$
PCB 138	$>10^4$	$>10^7$	$>10^4$	$>10^6$	$2.3*10^3$	$1.0*10^7$
PCB 153	$>10^4$	$>10^7$	$>10^4$	$>10^6$	$2.5*10^3$	$2.8*10^7$
PCB 180	$>10^4$	$>10^7$	$>10^4$	$>10^6$	$8.7*10^2$	

From **Table 2** it can be deduced that calculated $K_{PDMS/W}$ data are in good agreement between 5% and 20% PDMS. This is a first (but strong) indication that PCB retention is a bulk, dissolution process (sorption) rather than a surface adsorption phenomenon. The $K_{PDMS/W}$ values increase with increasing $K_{O/W}$, or in other words, more apolar analytes are partitioned more strongly into the (apolar) PDMS phase which is exactly what is expected. Comparing these results with the $K_{PDMS/W}$ data reported by Yang *et al.*[8] (**Table 2**) a remarkable dissimilarity is noted. The data show a decrease of $K_{PDMS/W}$ with increasing apolarity what is the opposite as observed from our experiments. In order to find the cause of these findings, the SPME experiment was repeated and not only the analysis of the SPME fiber itself was carried out but also of the Teflon stir bar.

10 mL water samples were prepared as described in **Section 7.1.3.1**. SPME fibers were exposed to the water sample for 1 hour under stirring at a speed of 1000 rpm. After this, the fiber was retracted and desorbed in the PTV injector. The stir bar was dried and inserted into an empty thermal desorption tube which was desorbed after completion of the SPME run. **Table 3** lists the results of these analyses and the recoveries on both the SPME fiber and on the stir bar expressed as the amount present relative to the totally introduced amount are given. From these data it is clear that a significant amount of PCBs is present on the stir bar. In fact, all PCBs are present in higher amounts on the stir bar than on the SPME fiber. Additionally, it is clear that compounds with a high PCB number (more apolar) are present in lower amounts on the SPME fiber than those with a lower PCB number (more polar) which is the same effect as observed by Yang *et al.*[8]. This is, however, counteracted by the amount of PCB present on the stir bar so that the most apolar solutes are still extracted in the highest amount (overall). It has to be noted that in addition to the stir bar and the SPME fiber, PCBs can also be present adsorbed on the glass wall. This was not investigated in this study.

Table 3 Recovery of the PCBs from the SPME experiments at an extraction time of one hour.

Compound[11]	SPME fiber	Stir bar	Total
PCB 28	16 %	40 %	56 %
PCB 52	18 %	52 %	70 %
PCB 101	16 %	57 %	73 %
PCB 118	5 %	83 %	88 %
PCB 138	9 %	59 %	68 %
PCB 153	9 %	80 %	89 %
PCB 180	8 %	75 %	83 %

7.1.5 Conclusion

It is shown that published $K_{PDMS/W}$ data are erroneous because of system adsorption effects. It is biased by adsorption onto stir bars used in the SPME procedure and probably the glass vial. Ten times more compound can be present on stir bars than on the SPME fiber itself. Using a short packed PDMS trap, it was shown that the true PDMS-water equilibrium constant is indeed proportional to literature $K_{O/W}$ data. It can be concluded that the water-PDMS contact is definitely a sorption mechanism instead of an adsorption effect.

From the data presented in this section the idea arose to actually use a stir bar, coated with a suitable sorbent layer, for sample enrichment. This is described in **Section 7.2.**

7.2 Stir Bar Sorptive Extraction (SBSE), a Novel Extraction Technique for Aqueous Samples. Theory and Principles*

7.2.1 Summary

The theory and practice of a novel approach for sample enrichment namely the application of stir bars coated with the sorbent polydimethylsiloxane (PDMS) and referred to as stir bar sorptive extraction (SBSE) is presented. Stir bars with a length of 10 and 40 mm coated with 55 and 219 μL of PDMS liquid phase, respectively were applied. 10 mm stir bars are best suited for stirring sample volumes from 10 up to 50 mL whereas 40 mm stir bars are more ideal for sample volumes up to 250 mL. Depending on sample volume and the stirring speed, typical stirring times for equilibration are between 30 and 60 minutes. The performance of SBSE is illustrated with the analysis of volatile and semivolatile micropollutants from aqueous samples. Detection limits using mass selective detection are in the low ng/L range for a wide selection of analytes from the EPA priority pollutant lists including analytes ranging in volatility from 1,1,1-trichloroethane to chrysene. For the extraction of selected compounds from 200 mL samples, detection limits below 0.1 ng/L are reached in the ion monitoring mode (SIM). A comparison between SBSE and solid phase microextraction (SPME) is made.

7.2.2 Introduction

The use of polydimethylsiloxane (PDMS) as extraction medium for analytes from both liquid and gaseous samples has been described, in different set-ups, by numerous groups. Owing to the specific characteristics of PDMS, superior performance is encountered and this for the following reasons. Firstly, analytes are not retained on an active surface as is the case with adsorbents but are partitioned (or sorbed) into the bulk of the PDMS phase and retained within the bulk of the sorbent. Since sorption is a much weaker process than adsorption, degradation of unstable analytes is significantly less or absent on PDMS compared to adsorbents. Secondly, due to the weaker interaction with the analytes, compounds can be desorbed at lower temperatures thus minimizing the losses of thermolabile solutes. Thirdly, the retaining capacity of PDMS for a certain compound is not influenced by the presence of high amounts of water or other analytes since all solutes have their own partitioning equilibrium into the PDMS phase and displacement does not occur. Fourthly, degradation fragments of the PDMS sorbent all contain characteristic silicone mass fragments which can easily be discerned with the use of a mass selective detector. Organic adsorbents, on the other hand, give

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rise to organic breakdown products which can interfere with the elucidation of unknowns.

One of the first approaches exploring the properties of PDMS for sample enrichment was open tubular trapping[12,13,14,15,16,17,18,19]. In principle, a PDMS open tubular trap (OTT) is similar to a capillary GC column with a layer of PDMS coated onto the wall. Most often 320-530 μm I.D. capillaries were used coated with a layer of typically 5-20 μm of PDMS[13,14] although coatings of 100 μm have been applied[20,21]. The sample (water, air) is pumped/sucked through the open tubular trap and sampling is normally stopped when the first analyte of interest is no longer fully retained by the PDMS (breakthrough sampling). Analytes can either be released from the OTT by heating (thermal desorption) or with an organic solvent (liquid desorption). Thermal desorption is to be preferred as it generally ensures the highest sensitivity. Despite the clear advantages of OTT over adsorbents, the principle never gained widespread acceptance because of several limitations. OTT have a limited sample capacity as only a small amount of stationary phase is present per trap length. For adequate retention, long traps are necessary (up to several meters). This strongly limits the allowable sampling flow rate, especially in those cases where the sample has to be sucked through the column (gases). The excessively long sampling times and the need for a second oven for thermal desorption renders OTT rather unattractive in practice. In an attempt to overcome the problems associated with OTT's, Ortner and Rohwer[22] designed a multi-channel OTT. This short trap contains several channels in parallel and should tolerate significantly higher flow rates since the pressure drop over the trap is very small. Unfortunately, this device allows flow rates up to only 15 mL/min. Due to the unfavorable geometry of the trap, at higher flow rates the number of plates generated by the trap becomes too low to ensure quantitative trapping. On the instrumental side, the multi-channel OTT has the advantage that it can be desorbed in a standard GC injector.

Some ten years ago a new approach to PDMS sample preparation, namely solid phase micro extraction (SPME), was introduced by Arthur and Pawliszyn[23]. Instead of a layer of PDMS present inside an open tubular column, the PDMS layer was coated onto the outside of a needle of a syringe-like device. The needle can be inserted directly into the sample and into the analytical instrument for thermal desorption. SPME is by nature an equilibrium extraction technique and relies, similar to OTT, on the partitioning of the analytes between the sample and the PDMS phase. This requires that the sample should be in a closed and confined space for accurate definition of the volume and that it should be thoroughly mixed (stirred) for rapid equilibration. This is rather simple in the case of liquid samples but is not straightforward for gaseous samples. Equilibration times are typically in the order of 10-30 minutes which is sufficiently fast in most cases. Though SPME is a simple and rapid technique, the applicability of SPME is limited by the small amount of PDMS on the needle (typically less than 0.5 μL) which results in low extraction efficiencies. This demands the use of very sensitive and selective detectors. Two approaches for the

increasing the sensitivity of SPME techniques have been followed, the internal cooling of the SPME fiber[24] and the use of very strong (adsorbing) coatings or the. Though internally cooled fibers are able to extract significantly higher amounts of analytes, the simplicity of the SPME extraction method is largely lost. The use of strong adsorptive coatings is rather tricky pathway as these materials are likely to show strong matrix effects and poor linearity in static extraction systems (see **Chapter 2**).

Recently, a novel approach, namely a short bed packed with 100% PDMS particles, was introduced[25,26]. The enrichment device used resembles commonly applied adsorption tubes. However, the advantages of sorption listed above apply. The packed PDMS bed contains *ca.* 300 μL of PDMS which is a marked increase compared to the amount present in OTT or SPME. Moreover, the total bed length is around 6 cm with a particle diameter of *ca.* 350 μm which means that high flow rates, up to 2.5 L/min for gases or 100 mL/min for liquids, can be reached. Sampling of large volumes for ultimate sensitivity can be performed in a relatively short time. For strongly retained compounds, sampling is performed in the breakthrough mode whereas for weakly retained analytes or in those cases where maximum sensitivity is desired, sampling is continued until all analytes are in equilibrium with the sorbent[27]. Generally, sampling times can be kept within 30 minutes while still yielding adequate sensitivity. Desorption is accomplished thermally for maximum sensitivity but the analytes may also be desorbed by a liquid, *e.g.* for on-line coupling to liquid chromatography. For many compounds the superior performance of PDMS compared to classical adsorbents was shown including sulfur compounds[28] and epoxides[27]. For gaseous samples packed PDMS beds work very well but for liquid (aqueous) samples, where drying after sampling is essential, the packed PDMS approach fails for volatile analytes. These compounds are totally lost during the drying process.

A procedure for the sorptive enrichment of water samples with the sensitivity of packed PDMS beds but with the application range (in terms of volatility) of SPME was developed. Stir bars were incorporated in a glass tube giving an outer diameter of 1.2 mm and coated with a layer of 1 mm PDMS which represents a total thickness of the stir bars of 3.2 mm O.D. The stir bars are introduced in the aqueous samples and extraction takes place during stirring. The amount of PDMS can be varied with the length, typically 10 mm (55 μL PDMS) to 40 mm (219 μL PDMS) long coatings are applied to small and large volumes, respectively. After a certain stirring time, the stir bar is removed from the water sample, introduced in a glass tube and transferred to a thermal desorption instrument where the analytes are thermally released and transferred to the GC-MS instrument. With this novel approach, the enrichment factors of packed PDMS beds can be combined with the simplicity of SPME. In this contribution, the theory and principles of SBSE are presented and its performance illustrated.

7.2.3 Theory

The theory of SBSE is rather straightforward and similar to that of SPME[29]. With the approximation that the partitioning coefficients between PDMS and water ($K_{PDMS/W}$) are proportional to octanol-water partitioning coefficients ($K_{O/W}$) it can be stated that:

Equation 2

$$K_{O/W} \approx K_{PDMS/W} = \frac{C_{SBSE}}{C_W} = \frac{m_{SBSE}}{m_W} \times \frac{V_W}{V_{SBSE}}$$

where C_{SBSE} and C_W are the analyte concentration in the SBSE and water phase respectively, m_{SBSE} and m_W are the mass of analyte in the SBSE and water phase respectively and V_{SBSE} and V_W are the volume of the SBSE and water phase, respectively. With the phase ratio ß, which equals V_W/V_{SBSE}, **Equation 2** can be rewritten in:

Equation 3

$$\frac{K_{O/W}}{\beta} = \frac{m_{SBSE}}{m_W} = \frac{m_{SBSE}}{m_0 - m_{SBSE}}$$

where m_0 is the total amount of analyte originally present in the water sample. Finally **Equation 3** is transformed to the extraction efficiency or recovery from the water sample giving:

Equation 4

$$\frac{m_{SBSE}}{m_0} = \frac{\left(\frac{K_{O/W}}{\beta}\right)}{1+\left(\frac{K_{O/W}}{\beta}\right)}$$

The only parameter governing the recovery of an analyte from the sample is the ratio of the partitioning constant and the phase ratio between the PDMS on the stir bar and the water sample. **Figure 2** illustrates the extraction recovery of an analyte as function of $K_{O/W}/ß$ ratio. At $K_{O/W}/ß=1$, the recovery is 50%. At low $K_{O/W}/ß$ values the recovery is approximately proportional to $K_{O/W}/ß$ where at $K_{O/W}/ß$ values in excess of 5, extraction is essentially quantitative.

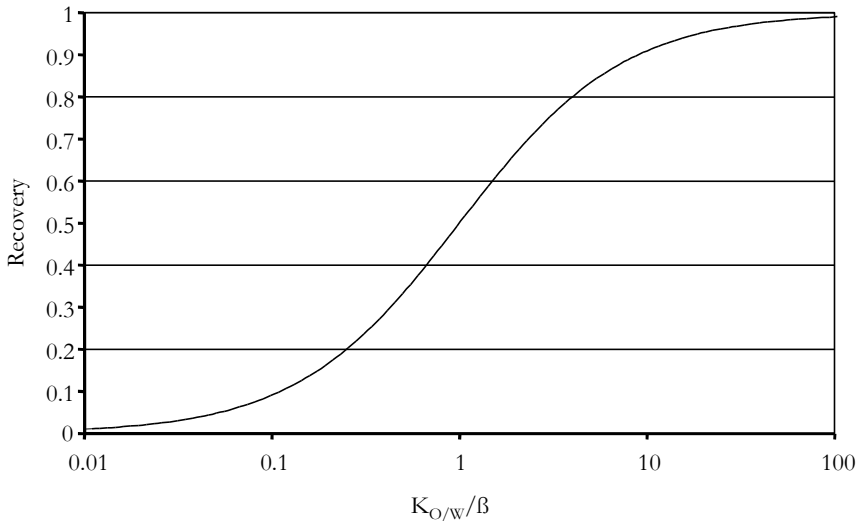

Figure 2 Recovery as a function of the ratio of octanol-water partitioning constant and phase ratio ($K_{O/W}/ß$) for SBSE and SPME extraction.

In SPME, the maximum volume of PDMS coated onto the fiber is *ca.* 0.5 µL (100 µm film thickness). For a typical sample volume of 10 mL the phase ratio equals $2 \cdot 10^4$. This implies that quantitative extraction is only obtained for compounds with a $K_{O/W}$ in excess of 10^5. Only a very limited number of analytes exhibit such high $K_{O/W}$ values and, moreover, it was recently shown that this type of apolar solutes strongly adsorb onto the stir bar and glass vial as used in SPME[30]. In conclusion, in SPME there is no real opportunity to realize quantitative extraction. In SBSE, on the other hand, the situation is much more favorable. A stir bar coated with 100 µL PDMS can easily be used to extract 10 mL of water leading to a ß of 100 which implies that solutes with a $K_{O/W}$ in excess of 500 are extracted quantitatively into the PDMS coated stir bar. This not only renders quantification straightforward but also ensures a significantly increased sensitivity for those compounds with a $K_{O/W}$ below 10^5. In **Figure 3**, the extraction recovery of analytes from a 10 mL water sample is shown for SPME and SBSE. It is clear that quantitative extraction is obtained at a much lower $K_{O/W}$ in SBSE compared to SPME which is caused solely by the much lower phase ratio. In case of incomplete extraction in SBSE, calibration is still possible and done in a way similar to SPME, *i.e.* using water samples of known concentration of target solutes.

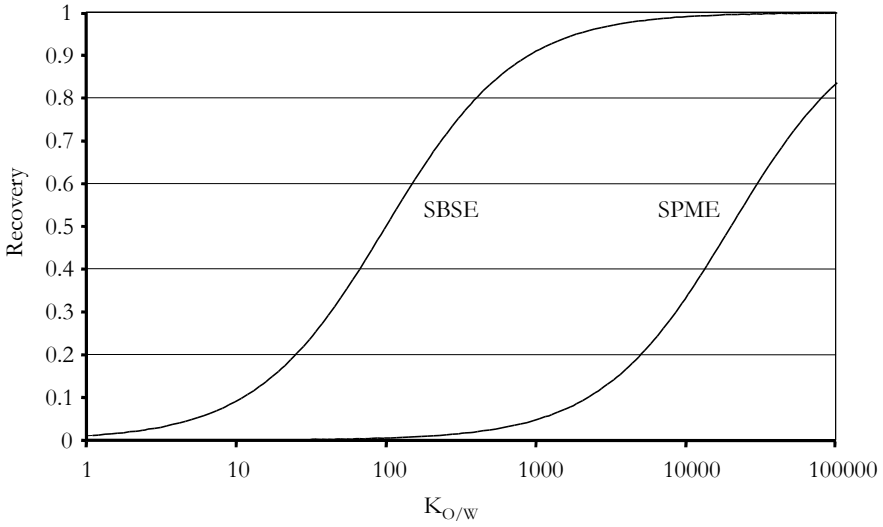

Figure 3 Theoretical recovery of analytes in SBSE and SPME from a 10 mL water sample as a function of their octanol-water partitioning constant. Volume of PDMS on SPME fiber: 0.5 µL, volume of PDMS on SBSE stir bar: 100 µL.

So far, the discussion has been largely limited to the equilibrium conditions of SBSE. However, considering the thickness of the coating (1 mm) used here, the speed of extraction (or the required equilibration time) is also an important factor to consider. Due to the thickness of the coating, it is assumed that all resistance to mass transfer is in the coating and that the sample is perfectly stirred. For this situation we use the equation described by Pawliszyn[31]:

Equation 5

$$t_{95\%} = \frac{d_{PDMS}^2}{2D_{PDMS}}$$

where: $t_{95\%}$ is the time required to reach 95% extraction, d_{PDMS} is the thickness of the PDMS layer used, in m and D_{PDMS} is the diffusion coefficient of the analyte under investigation in PDMS, in m^2/s. For benzene ($D_{PDMS} = 2.5*10^{-10}$ m^2/s[31]) an equilibration time of 30 minutes is found. This equilibration time is quite acceptable as normal GC runs including thermal desorption typically require 30-60 min. Sample extraction can therefore be performed in parallel with the chromatographic analysis.

7.2.4 Experimental

7.2.4.1 PDMS Coated Stir Bars

The first stir bars were prepared by removing the Teflon coating of existing stir bars, reducing the O.D. of the magnet and enveloping the magnet with a glass tube to give a 1.2 mm O.D. Silicone tubing with an I.D. of 1 mm and an O.D. of 3 mm from Dow Corning (Midland, MI, USA) was slided over the magnetic glass tube. However, as a stir plate is itself magnetic it is not required to use a magnetic stir bar. Non-magnetic stir bars were prepared from stainless steel rods with an outer diameter of 0.8 mm and a length of 40 mm. The total amount of PDMS material present on the 10 and 40 mm stir bars was 75.7 and 300.9 mg, respectively, which converts with the density of 0.825 g/mL to volumes of 92 and 365 µL. As the PDMS tubing contains *ca.* 40 % (v/v) of fumed silica as filling material (determined with solid-state NMR and thermo-gravimetric analysis), the effective volumes of PDMS are 55 and 219 µL respectively. PDMS coated stir bars are also available from Gerstel GmbH, under the trade name Twister™. The coated stir bars showed good mechanical stability and were not damaged by either collisions with glassware during stirring or due to thermal desorption. Stir bars can be easily handled by means of a pair of tweezers or a piece of metal wire with which it can be retrieved from the sample upon extraction. After removing the PDMS coated stir bar from the liquid sample it is transferred into an empty glass tube and inserted into the thermal desorption instrument. This might be considered laborious for certain applications, therefore an SBSE-autosampler is currently being designed. In order to prevent contamination by analyte carry-over the stir bars should be used only once, however, re-use of a single stir bar up to 100 times was demonstrated. Due to the thickness of the PDMS coating, no losses of (volatile) solutes were encountered during the transfer processes.

7.2.4.2 Experimental Set-Up

The experimental set-up is based on the Gerstel TDS-2 thermodesorption system (Gerstel GmbH, Müllheim a/d Ruhr, Germany) which is mounted on an HP 6980/5973 GC/MSD system (Hewlett Packard, Little Falls, DE, USA). A CIS-4 PTV injector (Gerstel) is used for cryofocusing the analytes prior to transfer onto the analytical column. Liquid nitrogen was used to cool the CIS down to –150°C during thermal desorption. For analytes more volatile than n-nonane, the CIS-4 liner was filled with Tenax and a 1 µm CP-SIL5CB column (Chrompack, Middelburg, the Netherlands) with an inner diameter of 250 µm and a length of 25 m was used. For semi-volatiles, the CIS liner was left empty to promote fast release upon heating of the cryotrap and a 0.25 µm HP 5MS column (Hewlett Packard) with an inner diameter of 250 µm and a length of 25 m was used. For very volatile compounds, cryocooling of the oven was employed. In all cases a column head pressure of 0.5 bar helium was applied.

7.2.5 Results and Discussion

In a first series of experiments, the performance of stir bar sorptive extraction (SBSE) was compared to that of a standard SPME procedure for the extraction of PAHs from aqueous samples. 60 mL water samples containing 5% methanol to prevent adsorption onto glassware were spiked with a PAH standard (Supelco, Bellefonte, PA, USA) and put in 100 mL Erlenmeyer flasks. For the SBSE extraction experiments, the sample was spiked at the 30 ng/L (ppt) level and for the SPME experiments the water sample was spiked at the 3 μg/L (ppb) level. A higher concentration level was chosen for SPME since a lower extraction efficiency was expected especially for the lower PAHs. For SBSE extraction the 10 mm stir bar containing 55 μL PDMS was employed whereas for the SPME experiments a 100 μm PDMS fiber containing 0.5 μL PDMS was used. In both cases an equilibration time of 30 minutes while stirring at 1400 rpm was chosen. Though this will generally be sufficient for equilibration in SPME, SBSE may require an additional stirring period for full equilibration. SBSE desorption was performed at 250°C for 5 minutes under a flow of 150 mL/min helium whereas SPME fibers were desorbed at 300°C in the split/splitless port of the GC with a splitless time of 2 minutes. Analyses were performed on the HP 5MS column and the column was programmed from 50°C (2 min isothermal) to 325°C at 15°C/min.

Figure 4 shows the chromatograms obtained from the SBSE and SPME extractions. Though the extraction principle and phase are identical for both techniques a striking difference in the recoveries can be observed. In the SBSE experiments all compounds are extracted to a similar extent whereas in SPME the more apolar compounds are extracted in significantly higher amounts than the least apolar ones. This can be entirely attributed to the phase ratio between the PDMS extraction phase and the water sample. In the case of SBSE, the phase ratio is *ca.* 100 times higher than in SPME, therefore SBSE operates in the flat regime of **Figure 3** for $K_{O/W}$ values in excess of 1000. SPME on the other hand, only enters the flat region for extremely high $K_{O/W}$ values. **Table 4** shows the recoveries of the individual PAHs. It can be noted that the recoveries for the SBSE extraction are all between 60 and 70 % which accounts for the fact that full equilibration is still not achieved. This is further illustrated in **Table 5** in which the average SBSE recovery at different stirring times is listed. Extending the stirring period to 120 minutes ensures a close to 100% recovery for all compounds.

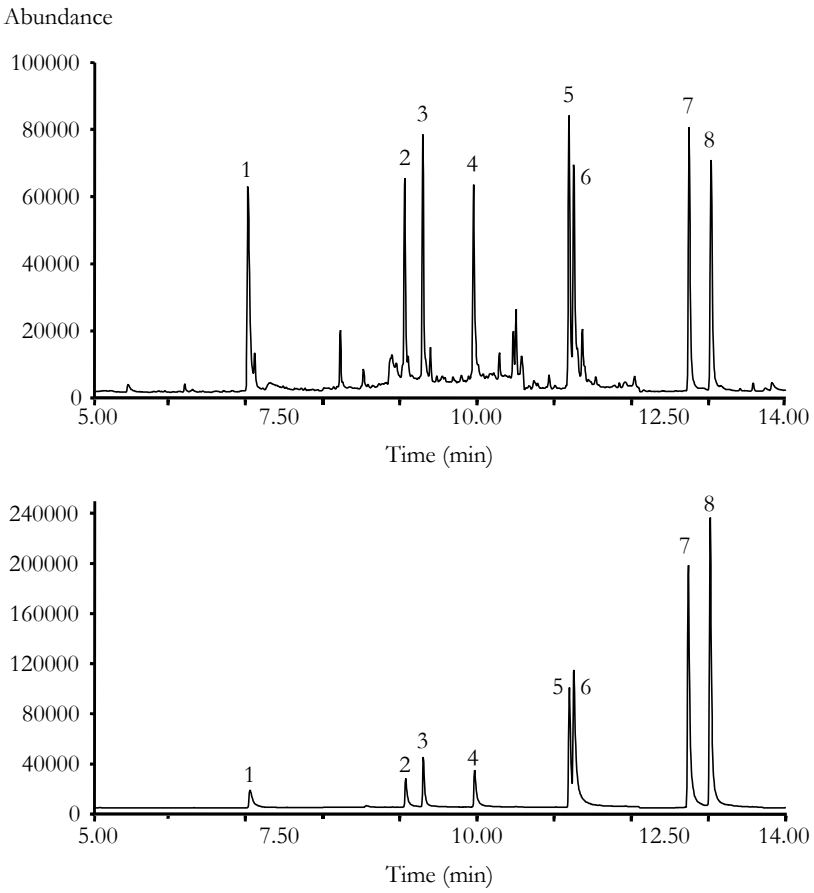

Figure 4 Analysis of a 60 mL water sample spiked with PAHs using SBSE (upper chromatogram) and SPME (lower chromatogram). In both cases an equilibration time of 30 minutes was used. In the SBSE experiment a spiking level of 30 ng/L was used whereas in the SPME experiment a 3 μg/L level was used. Conditions: see text. For solute identification see **Table 4**.

Table 4 Recoveries of PAHs from a 60 mL water sample for 30 min extraction time. For detailed conditions see text.

Nr.	Compound	Log $K_{O/W}$[1]	Recovery SBSE (%)	Recovery SPME (%)
1	Naphthalene	3.01	62	1.2
2	Acenaphthylene	4.07	61	2.4
3	Acenaphthene	3.92	63	3.3
4	Fluorene	4.18	61	3.4
5	Phenanthrene	4.46	67	8.0
6	Anthracene	4.45	66	15
7	Fluoranthene	5.53	69	21
8	Pyrene	5.32	67	24

Table 5 Recoveries of PAHs from a 60 mL as a function of the stirring time in SBSE. Listed is the average recovery of the PAHs from **Table 4**.

Stirring time (minutes)	Recovery (%)
15	37
30	66
60	89
120	96

SBSE has been evaluated for a typical environmental mixture containing a selection of semi-volatile priority pollutants ranging from apolar to polar solutes. A test mixture containing 35 compounds, the composition of which is listed in **Table 6**, was obtained from Hewlett-Packard. In a first experiment a sample volume of 10 mL was selected since this can be regarded as a typical volume in SPME and thus a good comparison is possible. The water sample, to which 5% methanol was added, was contained in a 25 mL vial. An SBSE stir bar containing 55 μL PDMS was used. In a second experiment, a stir bar coated with 219 μL PDMS was used to extract a 200 mL water sample placed in a 250 mL flask. The spiking levels were 1 μg/L and 50 ng/L for the first and second experiment, respectively.

Table 6 Compounds in the semi-volatile mixture and mass ions used for. E1, SBSE of a 10 mL sample with a stir bar coated with 55 µL PDMS. Stirring for 40 minutes at 1400 rpm. Concentration after spiking: 1 µg/L. E2, SBSE of a 200 mL sample with a stir bar coated with 219 µL PDMS. Stirring for 75 minutes at 1000 rpm. Concentration after spiking: 0.05 µg/L. Both E1 and E2 are the average recoveries of three experiments. * No value listed due to high blank levels.

Nr.	Compound	Ion 1	Ion 2	log $K_{O/W}$[1]	E1	E2
1	n-Nitrosodimethylamine	74	42		0.88	1.4
2	Bis-(2-chloroethyl)ether	93	63	1.12	5.3	3.9
3	1,2-Dichlorobenzene	146	148	3.38	59	37
4	1,3-Dichlorobenzene	146	148	3.38	66	37
5	1,4-Dichlorobenzene	146	148	3.39	61	28
6	Bis-(2-chloroisopropyl)ether	121	123		24	5.5
7	n-Nitrosodipropylamine	130	70		9.3	1.9
8	Nitrobenzene	123	77	1.88	14	2.5
9	Hexachloroethane	201	203	3.40	52	25
10	Isophorone	138	82	1.67	9.7	3.3
11	Bis-(2-chloroethoxy)ether	93	63		6.0	1.3
12	1,2,4-Trichlorobenzene	180	182	3.97	68	36
13	Naphthalene	128	102	3.01	59	28
14	Hexachlorobutadiene	225	260	4.78	43	34
15	Dimethylphthalate	162	127		69	43
16	2,6-Dinitrotoluene	163	77	1.89	6.7	3.2
17	Acenaphthylene	152	76	4.07	60	34
18	Acenaphthene	153	154	3.92	78	54
19	2,4-Dinitrotoluene	165	89	1.98	12	4.4
20	Diethylphthalate	149	177	2.7	33	*
21	4-Chlorophenylphenylether	204	141		73	48
22	Fluorene	166	165	4.18	86	54
23	n-Nitrosodiphenylamine	169	168	3.13	67	56
24	Azobenzene	182	77		67	54
25	4-Bromophenylphenylether	248	250		81	56
26	Hexachlorobenzene	284	286	6.18	70	54
27	Phenanthrene	178	152	4.46	73	65
28	Anthracene	178	152	4.45	72	63
29	Dibutylphthalate	149	223	4.57	70	*
30	Fluoranthene	202	101	5.53	73	42
31	Pyrene	202	101	5.32	74	50
32	Butylbenzylphthalate	149	206		*	53
33	Dioctylphthalate	149	167		*	*
34	Benz[b]anthracene	228	114	5.61	76	57
35	Chrysene	228	114	5.61	67	47

The mass selective detector was operated in the scan mode from 40 to 400 amu at 2.5 scans/s. From the total ion current two compound specific ions listed in **Table 6** were selected per compound for quantitation. Analysis was performed on the 1 μm d_f CP-SIL5CB column. The GC oven was programmed from 5°C which was kept for 2 minutes at 13°C/min to 325°C. Subambient operation was performed with liquid nitrogen cooling to guarantee good peak shapes for the first eluting analytes under splitless conditions.

Table 6 lists the compounds present in the test mixture and the mass spectral ions selected for identification and quantification of the individual compounds. Additionally for many compounds the $P_{O/W}$ ($^{10}\log K_{O/W}$) is listed indicating the polarity of the solutes. The last two columns give the recovery of the analytes from the 10 mL (E1) and 200 mL (E2) sample, respectively.

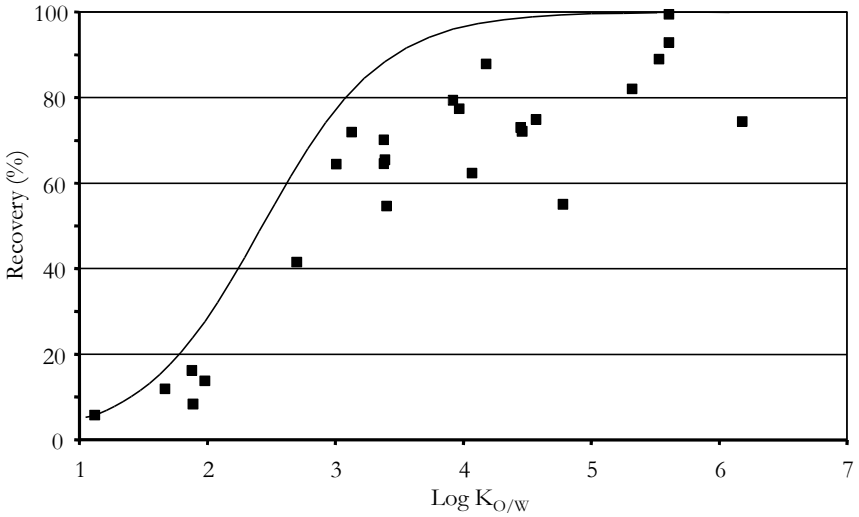

Figure 5 Recovery versus $K_{O/W}$ for extraction of semi-volatiles (**Table 6**) from a 10 mL water sample with a stir bar coated with 55 μL of PDMS. Line represents the theoretical equilibrium recovery after an infinite stirring time.

For recovery of the 10 mL sample, it is clear that strong differences occur with recoveries ranging between 1% (n-nitrosodimethylamine) and 86% (fluorene). Based on the presented theory, these differences can be attributed to the difference in octanol-water partitioning coefficient between these compounds. **Figure 5** shows a plot of the recoveries of the test solutes as a function of their octanol-water partitioning coefficients. Additionally, the equilibrium theoretical line for the SBSE extraction of a 10 mL sample with a stir bar coated with 55 μL PDMS is drawn. The general trend that compounds with a low $K_{O/W}$ exhibit a low recovery can clearly be observed, however, it

should be noted that in all cases the measured recovery is lower than the theoretical equilibrium recovery. At the low end of the $K_{O/W}$ scale, recoveries are close to the theoretical line but at log $K_{O/W}$ data in excess of 2 to 3 a rather large scattering below the theoretical line occurs. This can be due to several reasons. Firstly, though $K_{O/W}$ is generally a good approximation of the PDMS-water distribution constant this does not always have to be the case. Secondly, for very apolar solutes (log $K_{O/W}$ in excess 6.5) it was shown in a previous publication that adsorption onto glass and other surfaces can be a very important process causing analyte loss and reduced recoveries. Thirdly, the conditions chosen here with a stirring time of 40 minutes are not sufficient for full equilibration leading to recoveries less than the equilibrium extraction data.

Table 7 Extraction of the semi-volatile mixture of **Table 6** at different equilibration times. Shown is the average extraction level (the average over the 35 test compounds) relative to the extraction achieved after 5 hours stirring (equilibrium conditions). Each table entry is the average over three sequential extractions.

Sample Volume (mL)	RPM (min^{-1})	Time (min)	Average Relative Extraction Level (%)	RSD (%, n=3)
10	1400	15	52	7.9
10	1400	40	90	10
10	1400	75	98	8
200	1000	15	35	18
200	1000	40	63	13
200	1000	75	82	14

Table 7 shows the average recovery relative to the recovery obtained at full equilibration (5 hours). For the extraction of the 10 mL sample with the small stir bar, equilibrium is achieved significantly faster than for the 200 mL sample with the large stir bar. This is partly due to the fact that for the 200 mL sample a maximum stirring speed of only 1000 rpm can be used whereas for the 10 mL sample (and in fact for samples up to *ca.* 50 mL) the maximum speed of the stirring plate can be applied. In practice, full equilibration is not essential for accurate quantification. A timed stirring period can also be used for calibration, as is done in SPME. However, it is desired to at least approach the equilibrium extractable amount to maximize sensitivity and to remove strains from the actual timing of the stirring period. In **Figure 6** the chromatogram of the analysis of the 10 mL water sample spiked to a level of 1 μg/L (corresponding to extraction procedure E1 from **Table 6**) is shown. Most compounds (with the exception of the most polar ones) can easily be discerned from the background even with the mass spectrometer in the scanning mode. Detection limits using ion extraction from the total ion current are in the order of 0.5 μg/L for the most polar analytes to 10 ng/L for the most apolar ones. Switching the MS to the selected ion monitoring mode can lower these limits to 0.01 μg/L and 0.5 ng/L respectively.

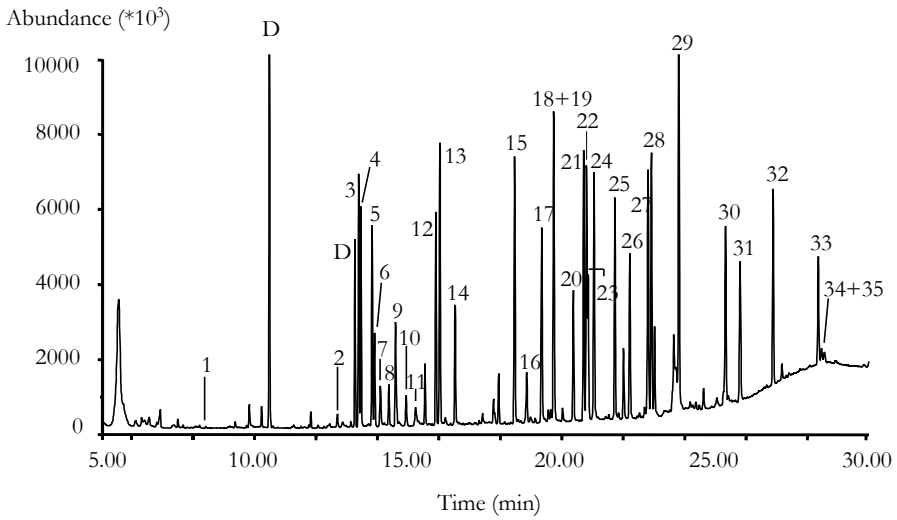

Figure 6 Chromatogram of the semi-volatile mixture (**Table 6**) at the 1 μg/L level extracted from a 10 mL water sample with the 55 μL PDMS stir bar.

Table 8 Compounds in the volatile mixture.

Nr.	Compound	Nr.	Compound
1	1,1,1-Trichloroethane	23	1,1,2,2-Tetrachloroethane
2	1,1-Dichloropropene	24	o-Xylene
3	Benzene	25	1,2,3-Trichloropropane
4	Carbon tetrachloride	26	Isopropylbenzene
5	Cychlohexane	27	Bromobenzene
6	Dibromomethane	28	2-Chlorotoluene
7	1,2-Dichloroethane	29	Propylbenzene
8	Bromodichloromethane	30	4-Chlorotoluene
9	Trichloroethene	31	1,3,5-Trimethylbenzene
10	Cis-1,3-dichloropropene	32	t-Butylbenzene
11	Trans-1,3-dichloropropene	33	1,2,4-Trimethylbenzene
12	1,1,2-Trichloroethane	34	1,3-dichlorobenzene
13	Toluene	35	1,4-dichlorobenzene
14	Dibromochloromethane	36	sec-Butylbenzene
15	1,2-Dibromoethane	37	Isopropyltoluene
16	Tetrachloroethene	38	1,2-Dichlorobenzene
17	1,1,1,2-Tetrachloroethane	39	Butylbenzene
18	Chlorobenzene	40	1,2-Dibromo-3-chloropropane
19	Ethylbenzene	41	1,2,4-Trichlorobenzene

20	m-Xylene	42	Hexachlorobutadiene
21	p-Xylene	43	Naphthalene
22	Bromoform	44	1,2,3-Trichlorobenzene

To illustrate the potential of SBSE for volatile analytes, a test mixture containing volatile EPA priority compounds, listed in **Table 8** was used to spike a water sample. Conditions for the volatile test mixture were identical to those used for the semivolatile mixture with the exception of the GC oven programming rate which was set at 10°C/min and instead of an empty CIS liner the Tenax packed liner was used. The chromatogram obtained is shown in **Figure 7** and clearly illustrates the excellent performance for volatile compounds which appear as sharp and symmetrical peaks allowing accurate quantification and assuring low detection limits. A 10 mL water sample containing 4 of the volatile compounds at the 1 ng/L level was prepared and analyzed with the presented SBSE method. The mass selective detector was operated in the selected ion monitoring mode (SIM) for maximum sensitivity. **Figure 8** shows the chromatogram obtained for this analysis. The four spiked compounds are clearly observed despite the very low spiking level. Detection limits are around 0.3 ng/L for the dichloropropenes and 0.08 ng/L for 1,2,4-trichlorobenzene. Additionally, ion monitoring analysis at ion m/z 91 was used to illustrate the sensitivity of the SBSE procedure. **Figure 9** shows the performance of the 219 μL SBSE stir bar for the extraction of a 200 mL water sample spiked to a level of 5 ng/L with the test compounds. Very high sensitivity is attained while still achieving a low background. Detection limits are in the order of 0.01-0.1 ng/L.

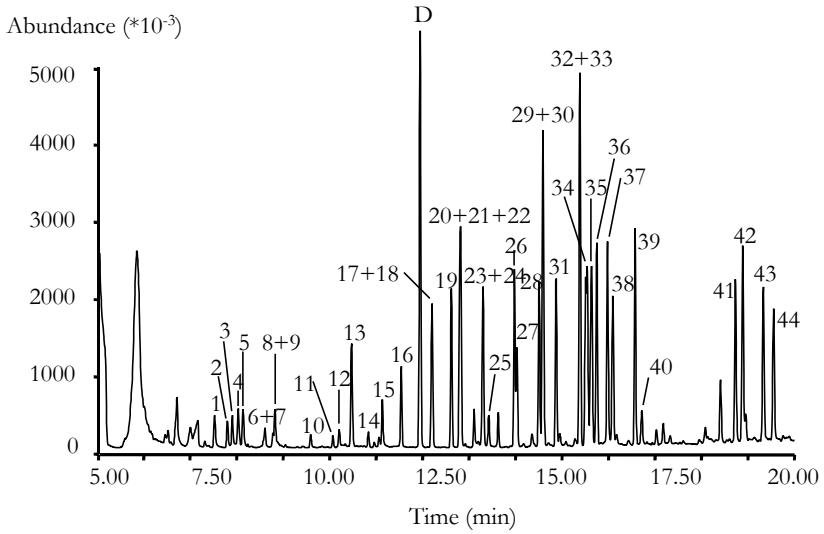

Figure 7 Chromatogram of the volatile mixture (**Table 8**) spiked at the 2 μg/L (ppb) level in a 10 mL water sample and extracted with the 55 μL PDMS stir bar.

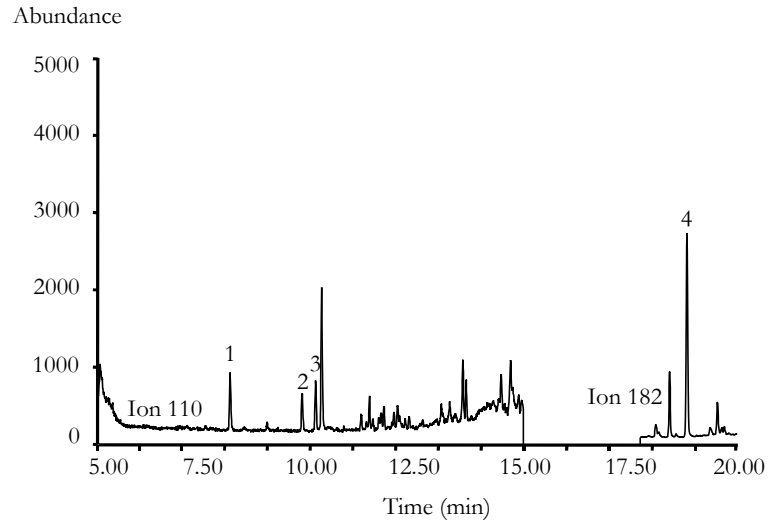

Figure 8 Selected ion monitoring (SIM) analysis of four selected compounds from the volatile mixture spiked at a level of 1 ng/L in a 10 mL water sample. Peak identification: 1; 1,1-dichloropropene, 2; cis-1,3-dichloropropene, 3; trans-1,3-dichloropropene, 4; 1,2,4-tichlorobenzene.

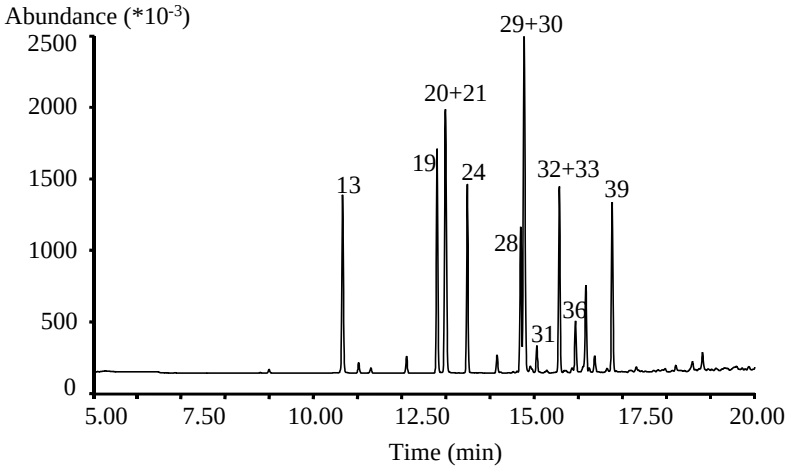

Figure 9 SIM analysis at m/z 91 of the volatiles mixture (selective monitoring of alkylated mono-aromatics) at the 5 ng/L in a 200 mL sample. Extraction with a stir bar coated with 219 µL PDMS.

7.2.6 Conclusion

A new technique for enrichment of volatiles and semi-volatiles from aqueous samples is described. Analytes are sorbed into a PDMS layer coated onto a stir bar followed by thermal desorption. Due to the increased amount of PDMS in stir bar sorptive extraction (SBSE) compared to SPME up to a 500 fold increase in sensitivity can be attained with stirring times between 30 to 60 minutes. Additionally, as drying of the stir bars is not required, volatile compounds can also be conveniently handled. The results presented in this report indicate that these stir bars are excellent enrichment devices for the preconcentration of a wide variety of compounds from aqueous samples. The PDMS sorbent generates good blanks and moreover, degradation peaks of the sorbent can be readily identified as siloxane breakdown products by the use of mass spectrometric detection. The detection limits obtained were in the low to even sub-ppt range. PDMS coated stir bars showed no deterioration after 100 extractions. For further validation of the SBSE concept, however, the preferable approach is to use the coated stir bars only once, to prevent contamination by analyte carryover. This strategy is also often chosen for validated SPE methods. Due to the very low price of the commercial stir bars, which is comparable to an SPE cartridge, this will not be a drawback. SBSE can be a rapid and sensitive alternative to commonly applied techniques, such as SPME, SPE and purge and trap. SBSE has been applied to the analysis of volatiles and semi-volatiles in other aqueous samples like beverages, biological fluids *etc.* These results are described in **Chapter 8**. Future contributions related with SBSE will include its application to gaseous samples, liquid instead of thermal desorption followed by large volume injection and the development of stir bars coated with polar sorbents.

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8 Applications of Stir Bar Sorptive Extraction

8.1 Summary*

The principle of a novel and simple approach for sorptive extraction of organic solutes from aqueous samples, namely the application of stir bars coated with a thick layer of a sorbent like polydimethylsiloxane (PDMS), is presented. The PDMS layer (0.3 to 1 mm) is coated on a glass tube in which a magnet is incorporated. The amount of PDMS present can be varied with the coating thickness and with the stir bar length so that typically 20 – 350 μL PDMS is present. In comparison to SPME, which employs a maximum of 0.5 μL PDMS, this is a large increase which results in a proportional sensitivity increase, as discussed in **Chapter 7**. After a certain stirring time, the stir bar is removed from the sample and transferred to a thermal desorption instrument where the analytes are thermally released and analyzed by capillary GC-MS, capillary GC-AED or capillary GC-PFPD. Stir bar sorptive extraction (SBSE) was evaluated for the enrichment of volatile and semivolatile compounds at the mg/L to ng/L level from aqueous samples like surface water, beverages (tea, coffee, wine, orange juices), and yogurt.

8.2 Introduction

The analysis of organic compounds from aqueous samples such as, environmental, biomedical, food and other samples, normally starts by the extraction and enrichment of the solutes from their original matrix. Sample preparation methods are based on liquid-gas extraction like in purge and trap (P&T) or liquid-gas equilibrium like in headspace (HS), on liquid-liquid extraction (LLE) or on solid phase extraction (SPE)[1]. During the past years, miniaturization has become a dominant trend in analytical chemistry. Typical examples of miniaturisation in sample preparation techniques are in-vial LLE (or micro-LLE), ambient static HS, disk cartridge SPE and solid phase micro extraction (SPME)[1] as was discussed in **Chapter 2**. In combination with state-of-the art

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analytical instrumentation, this results in faster analysis, higher sample throughput, lower solvent consumption and less manpower per sample compared to conventional sample preparation methods while maintaining or even improving the sensitivity.

Extraction of organic compounds from an aqueous or gas phase with the sorbent polydimethylsiloxane (PDMS) was described by different groups in the mid 80s using open tubular traps coated with thick PDMS films[2,345678,9,10,11,12,13,14]. Practical limitations (low sample capacity, low breakthrough volumes, *etc.*), however, limited the applicability of PDMS coated open tubular traps. Some 10 years ago, a micro-extraction method based on PDMS sorption was developed by Arthur and Pawliszyn[15], namely solid phase micro-extraction (SPME). Due to its simplicity and performance, SPME created a lot of interest in sorptive extraction techniques. The applicability of sorptive extraction has recently been broadened by the development of PDMS particles which can be used for extraction of organic solutes from gaseous samples in the breakthrough[16,17,18] or equilibrium mode[19] and from aqueous samples[20,21,22].

Features of sorptive extraction include predictable enrichment, the absence of displacement effects, inertness and rapid desorption at mild temperatures. Sorptive extraction is by nature an equilibrium technique and for water samples based on the partitioning of analytes between the silicone and the aqueous phase. Recent studies[23,24,25] have correlated this equilibrium with the octanol/water distribution coefficients ($K_{O/W}$). It is important in this respect to realize that the sorption equilibrium is directly related with the phase ratio and thus the amount of PDMS applied. In SPME, for example, this is only in the order of 0.5 μL or less, thereby limiting the enrichment on the PDMS fiber. This results in low recoveries for solutes with low $K_{O/W}$ values, *e.g.* less than 10.000. In order to enhance the enrichment factor, a new approach namely using stir bars coated with a thick PDMS layer was recently developed[26]. In stir bar sorptive extraction (SBSE), 20-350 μL PDMS coatings can be used. Consequently, the sensitivity is increased by a factor of 40 to 700. It was shown in **Chapter 7** that total extraction is possible for solutes with $K_{O/W}$ values larger than 500. For solutes with $K_{O/W}$ less than 500 calibration, as done in SPME, should be applied.

In this contribution, the principle of SBSE is further explained and its performance is illustrated with the analysis of flavor compounds in tea, coffee and yogurt, and with the analysis of traces of contaminants like pesticides in wine and orange juice, endocrine disrupters in wine, an off-flavor in beer, and organic micropollutants down to the ng/L (ppt) level in a surface water.

8.3 Experimental

8.3.1 Stir Bars

Initial experiments were performed on PDMS coated stir bars prepared in-house. These stir bars are build up of three essential parts. The first part is a magnetic stirring rod, necessary for transferring the rotating movement of a stirring plate to the sample liquid. The second part of the stir bar is a thin glass layer which is deposited on the magnetic stirring rod. The third and outer part is a layer of PDMS into which the analytes are sorbed. Though the PDMS coated stir bar is a rather simple device, the glass layer is essential in the construction of high quality stir bars. It effectively prevents catalytic decomposition of the PDMS layer by the metal of the magnetic rod. PDMS coated stir bars are commercially available under the trade name Twister™ from Gerstel GmbH (Müllheim a/d Ruhr, Germany).

For practical applications, stir bars coated with a PDMS layer with a thickness between 0.3 and 1 mm are used. The stir bar length is varied between 10 and 40 mm. In this contribution, 10 mm L x 3.2 mm O.D. (containing 55 μL PDMS) and 40 mm L x 3.2 mm O.D. (containing 220 μL PDMS) stir-bars were used. These stir bars are applied for different sample volumes, the 10 mm stir bars for 1 to 50 mL sample volumes and the 40 mm stir bars for 100 to 250 mL sample volumes.

8.3.2 Extraction Procedure

Stir bar sorptive extraction of a liquid sample is performed by placing a suitable amount of sample in a vial or other piece of glassware, *e.g.* an Erlenmeyer flask, depending on the chosen volume. A PDMS coated stir bar is added and the sample is stirred during 30 to 120 min. The thinner PDMS coatings require only a short equilibration time whereas the 1 mm PDMS coating may require an equilibration time as long as two hours for full equilibration, depending also on the chosen stirring speed. It has to be noted, however, that full equilibration is often not necessary as described in **Chapter 7**.

After extraction, the stir bar is removed by means of a short piece of metal wire and introduced in an empty glass thermal desorption tube (187 mm L x 4 mm I.D.) and transferred to a thermal desorption unit. Desorption temperatures depend primarily on the volatility of the analytes of interest, and are between 150-300°C at which the stir bar is desorbed for 5-15 min under a flow of helium. As an alternative to thermal desorption, liquid desorption may also be used, but this is not described here.

8.3.3 Instrumentation

The instrumental set-up consisted of a TDS-2 thermodesorption system (Gerstel) mounted on an HP 6890 GC (Hewlett-Packard, Little Falls, DE, USA) equipped with a CIS-4 PTV inlet. The PTV injector is operated as a cryotrap for cryogenic refocusing of the thermally desorbed analytes. Temperatures down to -150°C are used employing liquid nitrogen cooling.

Detection was done using either a quadrupole mass spectrometer (MSD, HP 5973), an atomic emission detector (AED, HP G2350A) or a pulsed flame photometric detector (OI PPD-5380, Gerstel) operated in the sulfur mode.

Several chromatographic columns were used including a 30 m L x 0.25 mm I.D. x 0.25 μm HP-5 MS column (Hewlett-Packard), a 30 m L x 0.25 mm I.D. x 1 μm CP Sil 5CB column (Chrompack, Middelburg, The Netherlands) and a 30 m L x 0.25 mm I.D. x 0. 25 μm Stabilwax column (Restek, Bellefonte, PA, USA). The carrier gas was helium in all cases. Additional details on chromatographic and other operational conditions are described in the text for each application.

8.4 Results and Discussion

The applications described in this chapter are divided in two classes; those dealing with relatively high concentrations of wanted solutes (quality control analysis, **Section 8.4.1**) and those related with the analysis of traces and ultra-traces of undesired contaminants (**Section 8.4.2**). It is not the aim here to present too many details and to discuss the data on all applications. Rather, these applications are intended as an illustration of the versatility and performance of SBSE.

8.4.1 Quality Control

8.4.1.1 Coffee Samples

Coffee was prepared from different brands and the aroma profiles were compared by placing 10 mL samples in head space vials. SBSE extraction was performed on 10 mm stir bars during 90 minutes. The stir bars were then thermally desorbed by programming the thermodesorption unit from its initial temperature, 20°C, at 60°C/min to a final temperature of 240°C at which the stir bar was desorbed for 10 minutes. During thermal desorption the TDS-2 was operated in the splitless mode so that the entire amount of desorbed analytes flows towards the cryotrap. The desorbed solutes were cryofocussed at -150°C using liquid nitrogen in an empty glass tube. After desorption, the PTV was programmed to 280°C for re-injection of the trapped compounds. Since

the coffee samples were found to be rather concentrated, PTV reinjection was performed in the split mode at a split ratio of 1:20. The analytical column applied for the coffee samples was the Stabilwax column, which was operated in the constant flow mode at a flow of 1 mL/min. The GC oven temperature was programmed from 40°C, which was kept for 1 min, at a rate of 5°C/min to 240°C. The detector used was the mass spectrometer.

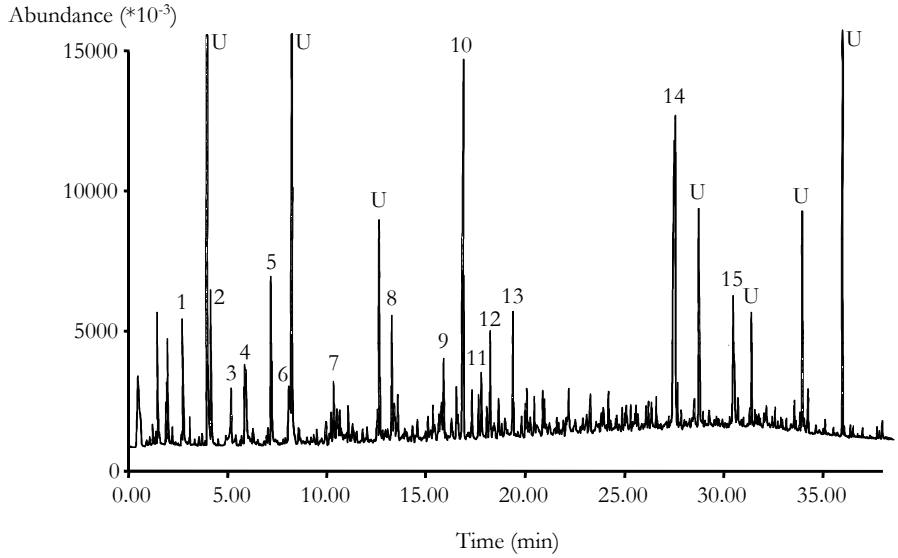


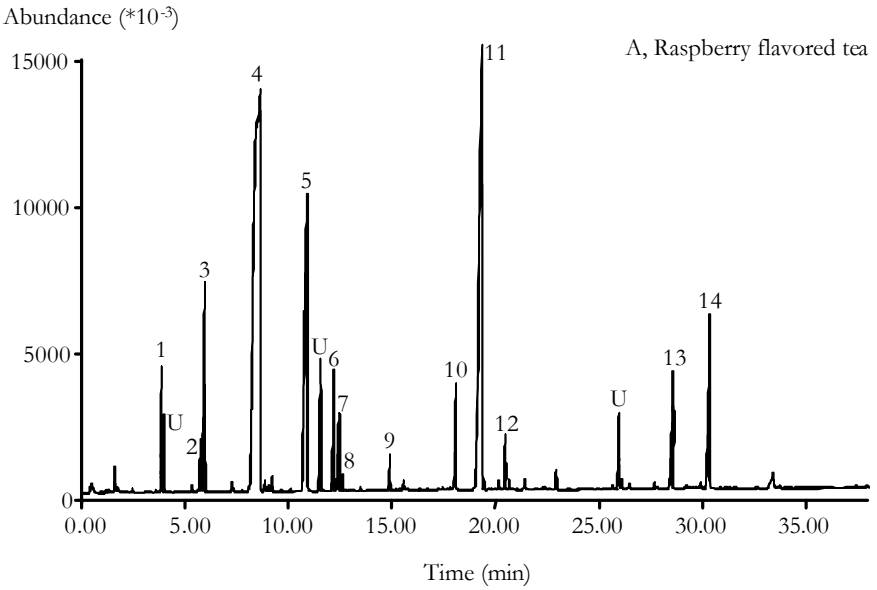
Figure 1 SBSE-TD-CGC-MS of Coffee. Conditions: 10 mm stir bar coated with 55 μL of PDMS, 90 min extraction at 1400 rpm. Identified compounds: 1, pyridine; 2, furfural; 3, furfurylalcohol; 4, 2,6-dimethylpyrazine and ethylpyrazine; 5, 5-methylfurfural; 6, 2-ethyl-6-methylpyrazine; 7, 2,6-diethylpyrazine; 8, furfurylpyrrole; 9, 4-ethylguaiacol; 10, 4-vinyl-2-methoxyphenol; 11, 2-(2'-furyl)-5-methylpyrazine; 12, eugenol; 13, 1-furfuryl-2-formylpyrrole; 14, caffeine; 15, linoleic acid; U, unknown.

A typical chromatogram of a coffee sample is shown in **Figure 1** which features the same excellent peak shapes and resolution of a typical capillary gas chromatogram. Apparently, stir bar thermal desorption injection does not compromise the chromatographic run in any way. Also note the good peak shapes of the volatiles which is due to the split injection. In the chromatogram of **Figure 1**, compounds ranging from highly volatile solutes such as pyridine and furfural to semivolatiles such as caffeine and linoleic acid are observed. This effectively illustrates the wide application area of SBSE in terms of analyte volatility. Moreover this volatility range can be handled in a single analysis. Important flavor compounds include the pyrazines, furan and pyrrol derivatives, and some monoterpenoids. Also note that in addition to neutral analytes, both acidic (*e.g.* linoleic acid) and basic (*e.g.* pyridine) compounds are extracted and

released by the PDMS coated stir bar which illustrates not only the power and versatility of the sorption mechanism but also the inertness of PDMS.

8.4.1.2 Tea Samples

The second application of SBSE concerns the analysis of several tea samples with different aroma's, *i.e.* raspberry flavored tea (**Figure 2A**), "herb-mix" flavored tea (**Figure 2B**), fruit flavored tea (**Figure 2C**) and tropical fruit flavored tea (**Figure 2D**). The SBSE extraction times are listed in the legend of **Figure 2**. The same conditions as for the coffee sample were used except that the column was the apolar HP-5 MS and that the oven was programmed to a final temperature of 300°C. The raspberry tea is characterized by high concentrations of amyl propionate, cis-3-hexenyl propionate and ß-ionone. Surprisingly, *iso*- and *n*-butylphthalate are present in relatively high concentrations as well. The herb-mix tea contains several terpenoids with anethole as main compound, while phthalates are absent in this sample. The fruit tea is composed of several esters and ketones, together with a- and ß-ionone. The phthalates, on the other hand, are present at unacceptable high levels. In the tropical fruit tea, limonene is the main compound and the presence of ?-decalactone and ?-undecalactone are worthwhile mentioning. In this sample, only *n*-butylphthalate is present but another synthetic product namely triacetin has been identified. The occurrence of the phthalates and of triacetin is not so strange because they are known as aroma keepers *i.e.* they are responsible for a slower release of the aroma solutes.


Abundance (*10-3)
A, Raspberry flavored tea
15000
10000
5000
0
1
U
2
3
4
5
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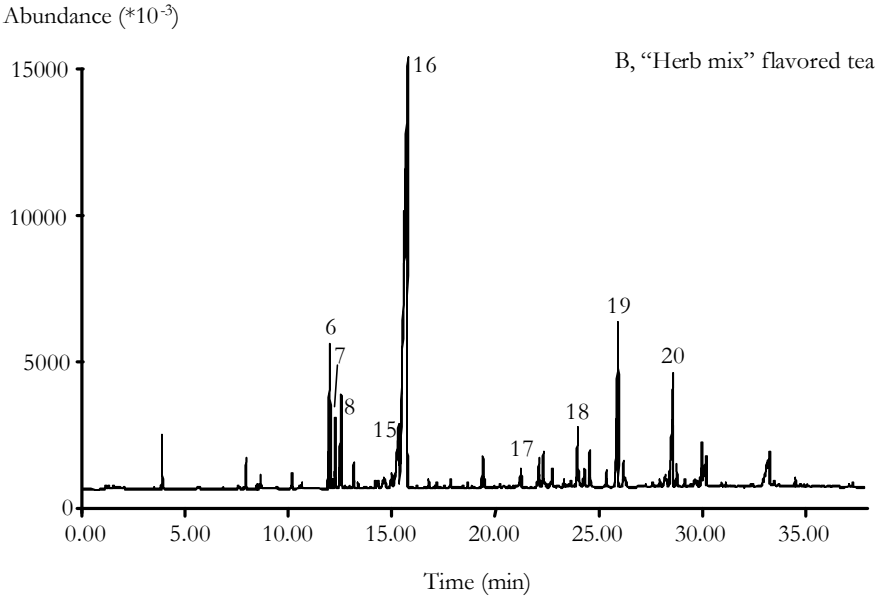
6
7
8
9
10
11
12
U
13
14
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
Time (min)


Abundance (*10-3)
B, "Herb mix" flavored tea
15000
10000
5000
0
16
6
7
8
15
17
18
19
20
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
Time (min)

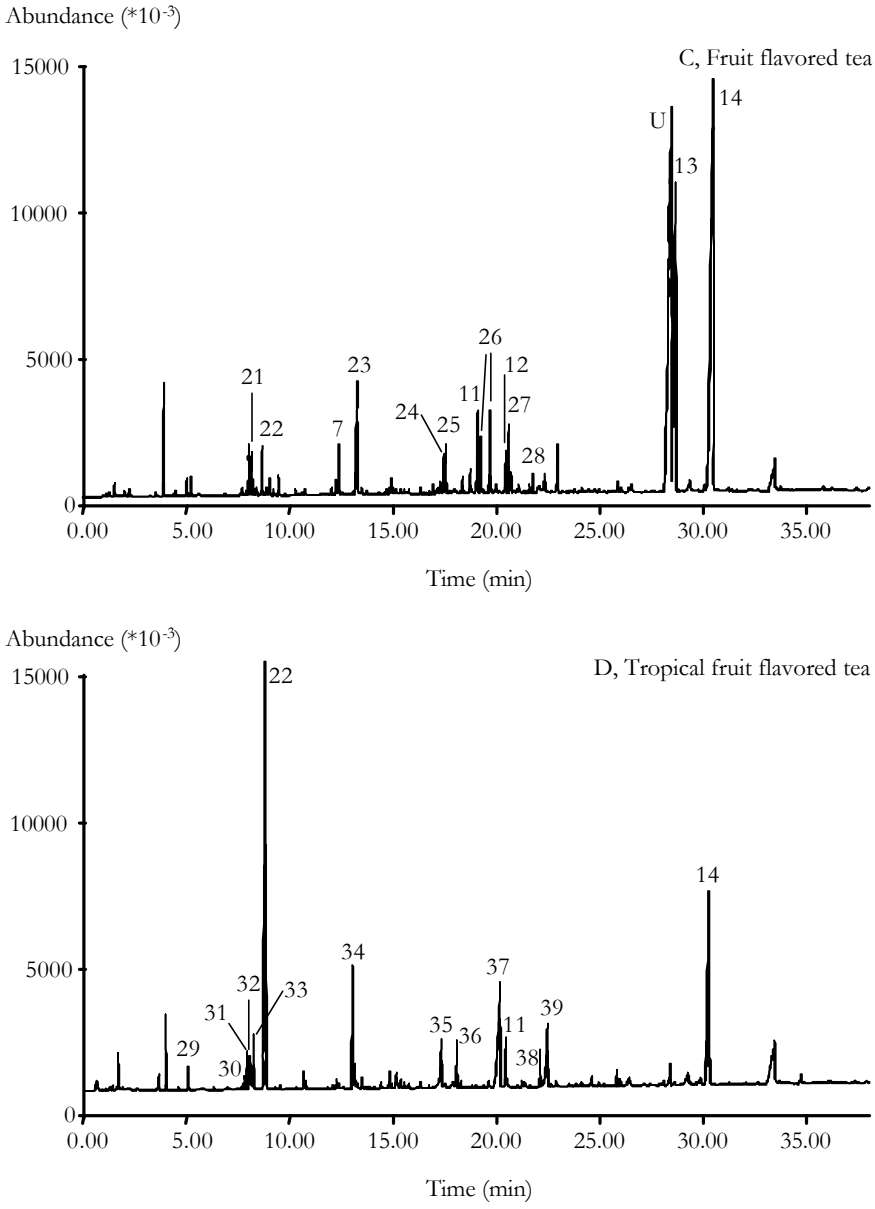


Figure 2 SBSE-TD-CGC-MS of raspberry flavored tea. A 10 mm stir bar was used at a stirring speed of 1400 rpm. A: Raspberry flavored, 60 min stirring. B: Herb-mix flavored, 360 min stirring. C: Fruit flavored, 180 min stirring. D: Tropical fruit flavored, 240 min stirring. Identified compounds: 1, butyl acetate; 2, butyl propionate; 3, amyl acetate; 4, amyl propionate; 5, *cis*-3-hexenyl propionate; 6, menthone; 7, *iso*-menthone and benzyl acetate; 8, menthol; 9, benzyl propionate; 10, damascone; 11, a-ionone; 12, ß-ionone; 13, di-isobutylphthalate; 14, dibutylphthalate; 15, cinnamic aldehyde; 16,

anethole; 17, p-methoxy cinnamic aldehyde; 18, bisabolol oxide B; 19, bisabolol oxide A; 20, en-in dicycloether; 21, *cis*-hexenyl acetate; 22, limonene; 23, styrallyl acetate; 24, megastigma-4,6(E),8(E)-triene; 25, neryl acetate; 26, neryl, geranyl acetone; 27, phenylethyl isovalerate; 28, benzyl hexanoate; 29, *iso*-amylacetate; 30, myrcene; 31, butyl butyrate; 32, ethyl hexanoate; 33, *cis*-3-hexenyl acetate; 34, *cis*-3-hexenyl butyrate; 35, triacetin; 36, hexyl caproate; 37, ?-decalactone; 38, geranyl butyrate; 39, ?-undecalactone; U, unknown.

8.4.1.3 Yogurt

Also fatty matrices (milk, fresh cheese, yogurt, *etc.*) have been analyzed with SBSE. A typical example is shown in **Figure 3** presenting the profile for yogurt flavored with strawberries. For this application, the yogurt sample was diluted 1:1 with distilled water and extracted. Other conditions were the same as for the coffee sample. Compounds responsible for the strawberry flavor namely ethyl-3-methyl butyrate and ?-decalactone are clearly present. It is surprising that the lipid matrix did not disturb the SBSE enrichment for this quality control application.

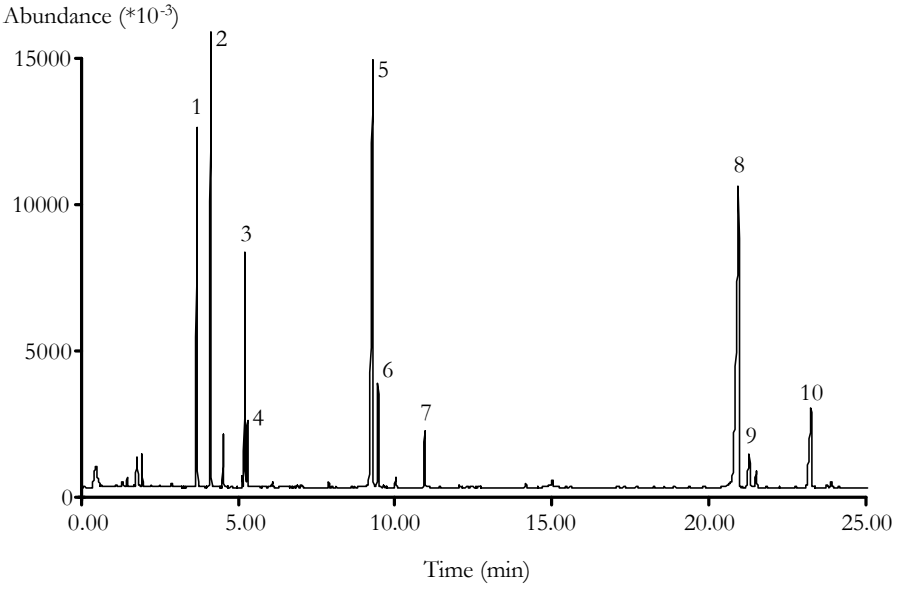


Figure 3 Analysis of a strawberry flavored Yogurt by SBSE-TD-CGC-MS. The sample was first diluted 1:1 in water and then extracted with a 10 mm stir bar for 60 min at 1400 rpm. Identified compounds: 1, methyl-2-methylbutyrate; 2, ethylbutyrate; 3, ethyl-3-methylbutyrate; 4, *cis*-3-hexenol; 5, ethyl caproate; 6, *cis*-3-hexenyl acetate; 7, isoamyl butyrate; 8, methyl cinnamate; 9, vanilline; 10, ?-decalactone.

8.4.2 Trace analysis

8.4.2.1 Surface water

To illustrate the potential of SBSE for volatile analytes, a 200 mL surface water sample collected from a nearby pond was placed in a 300 mL Erlenmeyer flask and extracted with a 40 mm stir bar coated with 220 μL PDMS. Stirring was performed for 60 minutes at 1000 rpm. TD-CGC-MS analysis was done on the 1 μm CPSil-5 column in the scan mode scanning from 40 to 500 amu at 2.5 scans/s. Desorption was performed in the splitless mode at 250°C for 5 min. The PTV was cooled down to -150°C during thermal desorption and the liner was packed with 20 mg Tenax to retain the highly volatiles[26]. The trapped compounds were transferred from the CIS-4 to the analytical column in the spitless mode for maximum sensitivity. The GC oven program started at 10°C (2 min) to 300°C at 10°C/min. The obtained chromatogram is shown in **Figure 4**. The largest peaks in the total ion chromatogram (TIC) correspond with the PDMS degradation products D3, D4 and D5 (cyclic siloxane oligomers). As can be seen, the breakdown signals are very low for the high amount of PDMS applied. Additionally, a series of aldehydes (n-hexanal A6 to n-decanal A10) is present. From the TIC, several priority pollutants could be elucidated by ion extraction. The upper traces in **Figure 4** show the ion traces for benzene (m/z 78), toluene, ethylbenzene, and the xylenes (m/z 91) and the 1,3- and 1,4-dichlorobenzenes (m/z 146). Quantification was done by spiking bidistilled water with 25 ng/L of an EPA volatiles mixture (Supelco, Bellefonte, PA, USA) containing these compounds and analyzing the spiked sample with identical SBSE conditions. The concentrations in the surface water were 5.1 ng/L benzene, 3.9 ng/L toluene, 0.4 ng/L ethylbenzene, 0.7 ng/L m+p-xylene, 0.5 ng/L o-xylene, 2.9 ng/L 1,3-dichlorobenzene and 1.4 ng/L 1,4-dichlorobenzene.

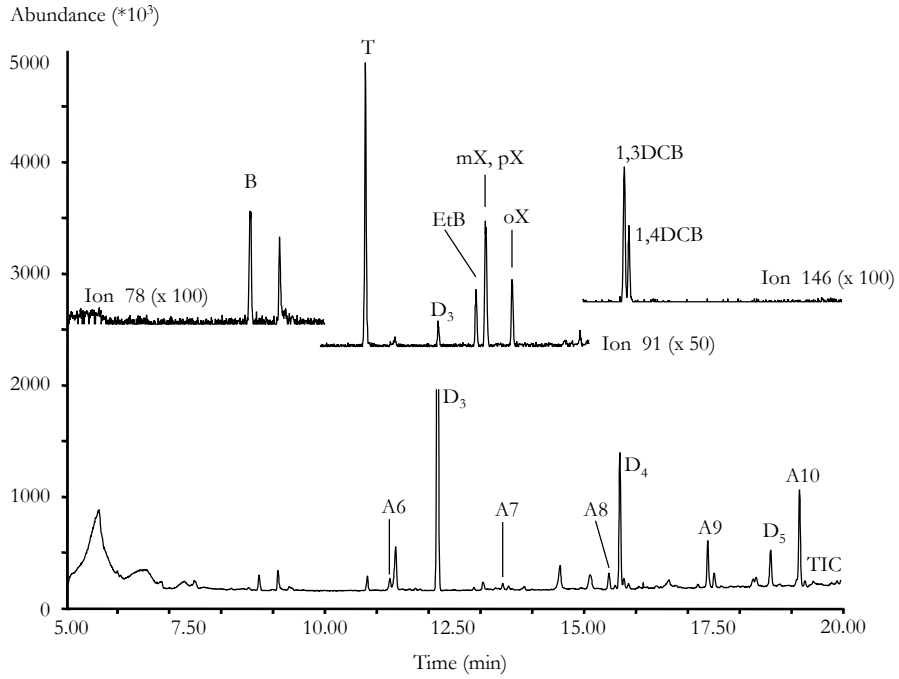


Figure 4 SBSE-TD-CGC-MS of surface water. Bottom chromatogram shows the total ion current, upper traces are selected ion chromatograms at specific ion masses. Abbreviations: A6 to A10, the linear aldehydes hexanal to decanal; D_x, cyclic siloxane degradation products; B, benzene; T, toluene; EtB, ethylbenzene; oX, mX and pX, ortho-, para- and meta-xylene; DCB, dichlorobenzene.

8.4.2.2 Wine analysis

Different white and red wines were analyzed under the following conditions. A 25 mL sample is placed in a 40 mL vial and extracted with a 10 mm stir bar containing 55 µL of PDMS during 40 min while stirring at 1400 rpm. The stir bars were then thermally desorbed at 300°C during 10 min. The solutes were cryofocussed in the PTV inlet at -150°C. Chromatographic separation was performed on the HP-5 MS column. The oven was programmed from 70°C (2min) to 150°C at 25°C/min, to 200°C at 3°C/min and to 280°C at 8°C/min. The chromatographic instrument was operated under retention time locking (RTL) conditions for pesticides. This allowed matching of pesticide retention times with those present in the library supplied by HP.

For the wine samples presented here, the AED was used for its ability to selectively monitor the presence of compounds containing specific elements eluting from the GC column. Unfortunately, the AED is not capable of monitoring all elements simultaneously, because only a short wavelength range can be selected. Here the AED

is operated in the range around 830 nm, allowing the simultaneous determination of the chlorine (837 nm), bromine (827 nm) and carbon (834 nm) emission lines. The carbon channel yields an "universal" response, similar to that of an FID or mass spectrometer in the scanning mode, whereas the chlorine and bromine channels show only response for compounds containing these elements. A pesticide-free white and red wine were selected for spiking experiments. **Figure 5** shows the AED chromatogram of the blank dry white wine. Only some response on the chlorine channel before 10 min was detected but these peaks do not have retention times corresponding to those of pesticides.

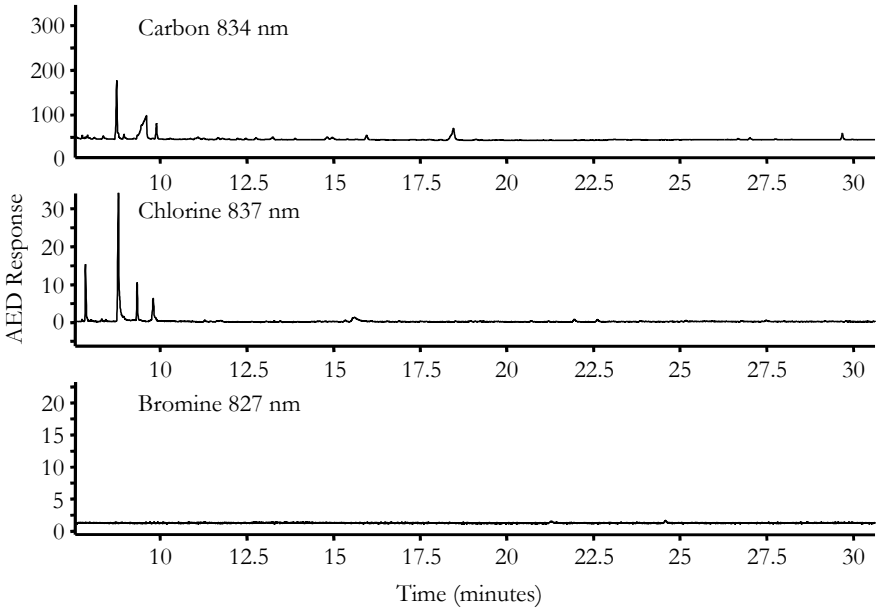


Figure 5 SBSE-TD-CGC-AED chromatogram of a blank white wine. Shown are the carbon channel (top), chlorine channel (middle) and bromine channel (bottom).

After recording blank chromatograms, the blank white and red wine were selected for further spiking experiments at the 1, 10 and 100 μg/L level. The composition of the pesticide mixture used for spiking is given in **Table 1**. **Figure 6** shows a blank red wine spiked at the 1 μg/L level with the 19 pesticides. All pesticides are easily detected with good peak shapes at concentration levels far below the allowable concentrations.

Table 1 Chlorine and bromine containing pesticides under investigation.

Nr.	Compound	Nr.	Compound
1	a-BHC	11	DDE
2	ß-BHC	12	endrin
3	?-BHC	13	endosulfan II
4	d-BHC	14	DDD
5	heptachlor	15	endrin aldehyde
6	aldrin	16	endosulfan sulfate
7	heptachlorepoxide	17	DDT
8	procymidone	18	methidathion
9	endosulfan I	19	bromopropylate
10	dieldrin		

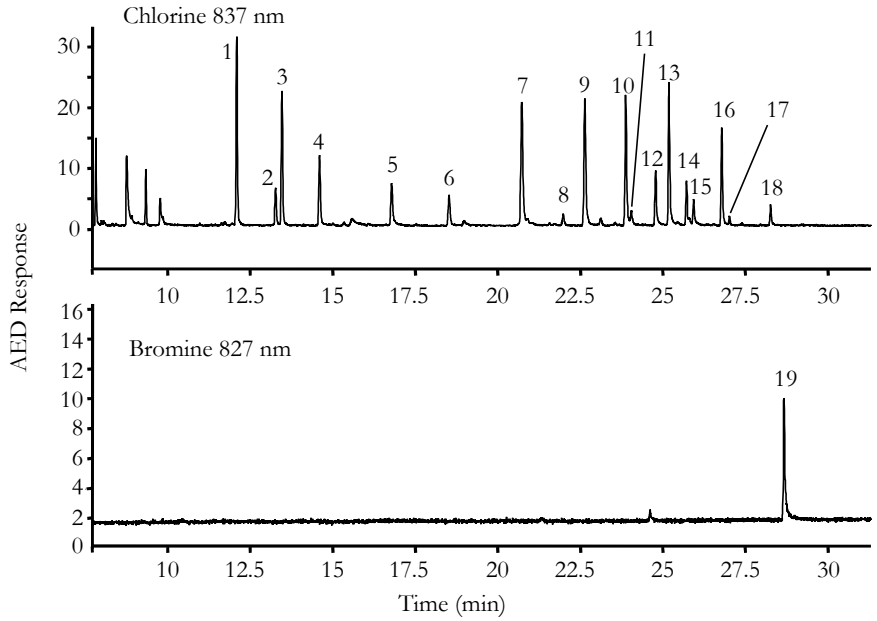


Figure 6 SBSE-TD-CGC-AED of a blank red wine spiked at the 1 µg/L level. For peak identification, see **Table 1**.

During the spiking experiments it was noted that the response of the pesticides for the white and red wines were different. Calibration graphs in the 1 to 100 μg/L level were constructed for all compounds. All calibration curves are linear but the slopes for the white wines are much steeper than for the red wines. This is illustrated in **Figure 7** for endosulfan I. The recoveries from white wines are substantially higher than from red wines. This is a typical matrix effect playing a significant role in the partitioning process. Red wine contains, for instance, small particles and polyphenolic polymers on which pesticides may be adsorbed. Within the two categories of white and red wines calibration differences are virtually absent.

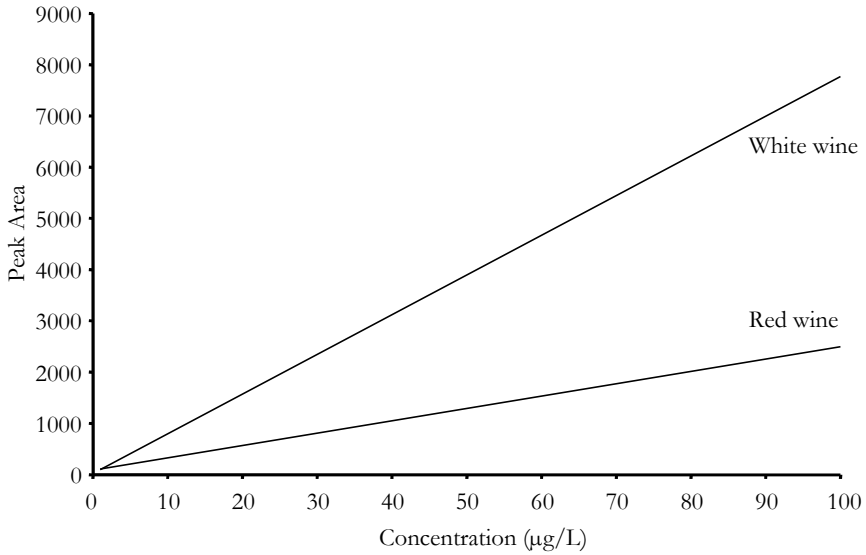


Figure 7 Calibration graphs for endosulfan I spiked at the 1, 10 and 100 ppb level in white and red wine.

During this wine monitoring study several contaminants were detected in some wine samples and two specific cases are presented. **Figure 8A** shows the chlorine-trace of a French dry white wine in which four chlorine containing compounds were detected at the μg/L and sub-μg/L level. The main compound (22.1m) was identified via the RTL pesticide library as procymidone. This was confirmed by analyzing the same sample by CGC-MS, also under RTL conditions. The corresponding spectrum (**Figure 8B**) with the library search (**Figure 8C**) is also shown. The concentration was determined by internal standard addition and was found to be 21 μg/L. The repeatability of SBSE for this particular pesticide was 6.1 RSD% for n=6.

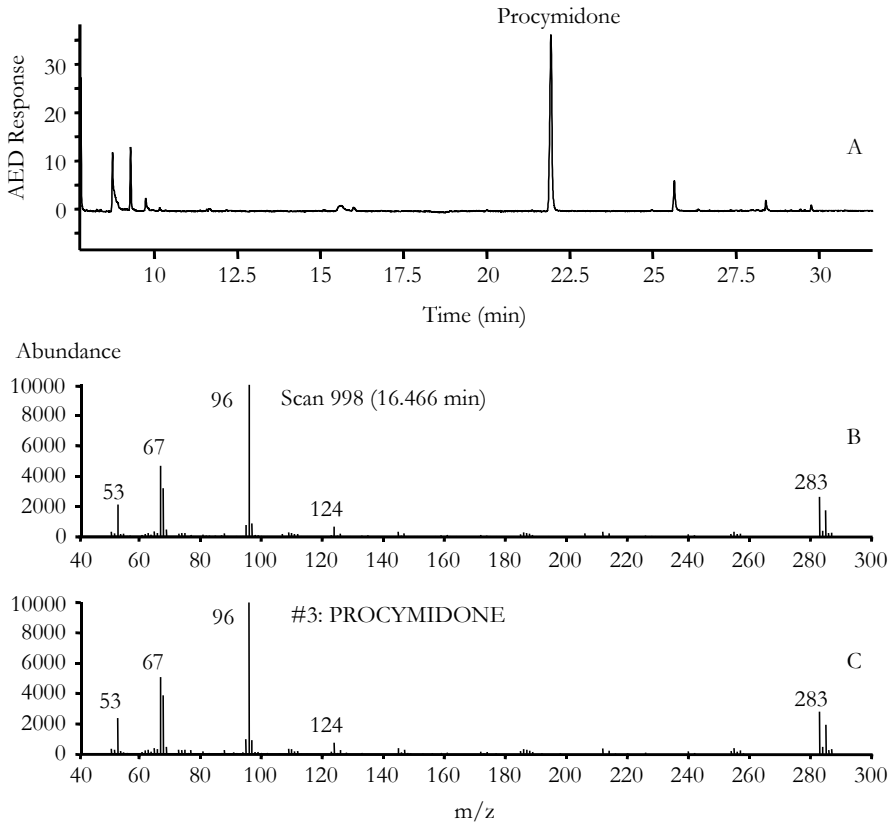


Figure 8 Identification of Procymidone in a French White Wine. A. SBSE-TD-CGC-AED Chromatogram on the chlorine emission line. B. Spectrum of the procymidone peak obtained from a separate SBSE-TD-CGC-MS analysis. C. Library spectrum of procymidone.

A South African red wine sample with a screw stopper contained a series of alkylated phenols at the μg/L level, the origin of which was definitely not natural. The extracted ion profiles shown in **Figure 9** indicated the presence of nonyl phenols, well-known endocrine disrupters. The profile perfectly fits with that of a technical nonyl phenol standard and moreover, each peak between 13 and 13.40 min gave a mass spectrum match with the Wiley database. The origin of this contamination was the plastic sheet in the screw stopper as ascertained by direct thermal desorption capillary GC-MS analysis of the sheet. It has to be noted that a slight discrepancy in retention times exist between sample and standard which is due to the fact that the standard was analyzed 3 months before the sample (for a different project).

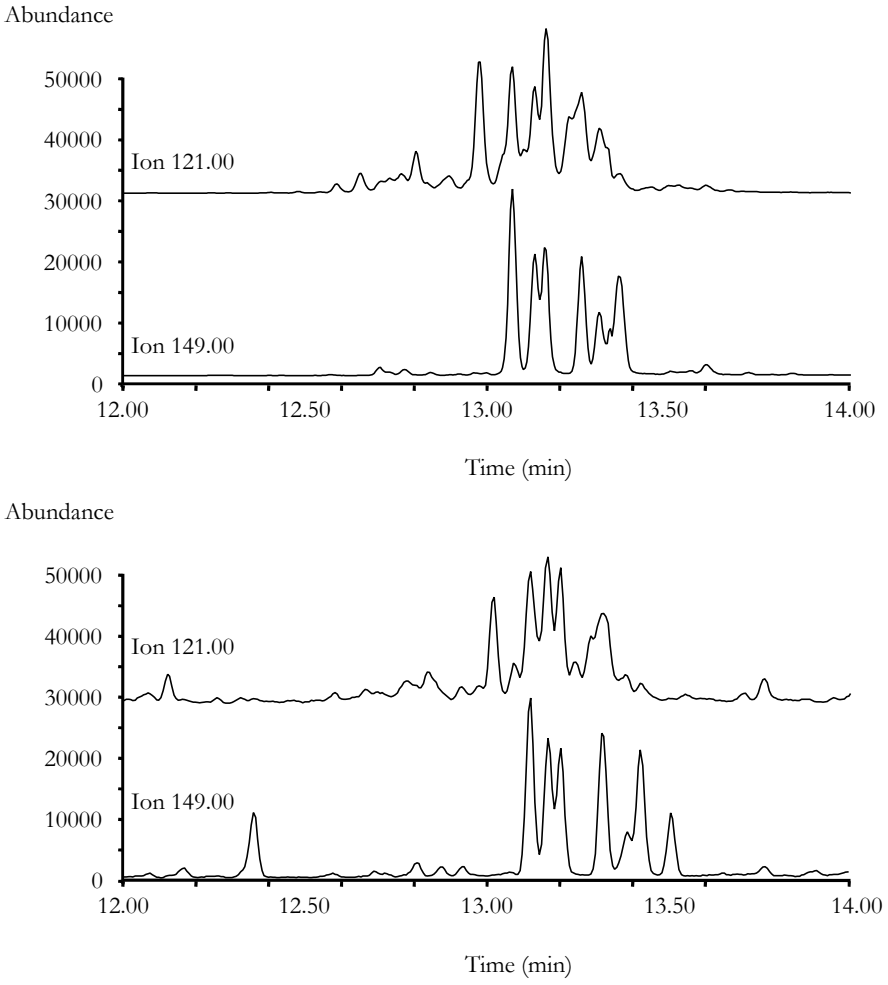


Figure 9 Identification of nonyl phenol in a South African red wine. Shown are extracted ion chromatograms at m/z 121 and 149, two specific ions for nonyl phenol. Top chromatogram was obtained from a South African red wine, bottom chromatogram from a technical nonyl phenol standard. Concentration approximately 5 μg/L.

8.4.2.3 Orange Juice

Several juices were screened on the presence of triazine herbicides including orange, pineapple and apple juices. In total some 10 different brands were taken under investigation and a number of them were found to be positive. This is illustrated in **Figure 10A** , showing the TIC of an orange juice, 50 mL of which was extracted with a 10 mm stir bar during 45 minutes at 1400 rpm. The peak at 14.16 min was identified by the MS library as simazine which is shown in **Figure 10 B** and **10C**.

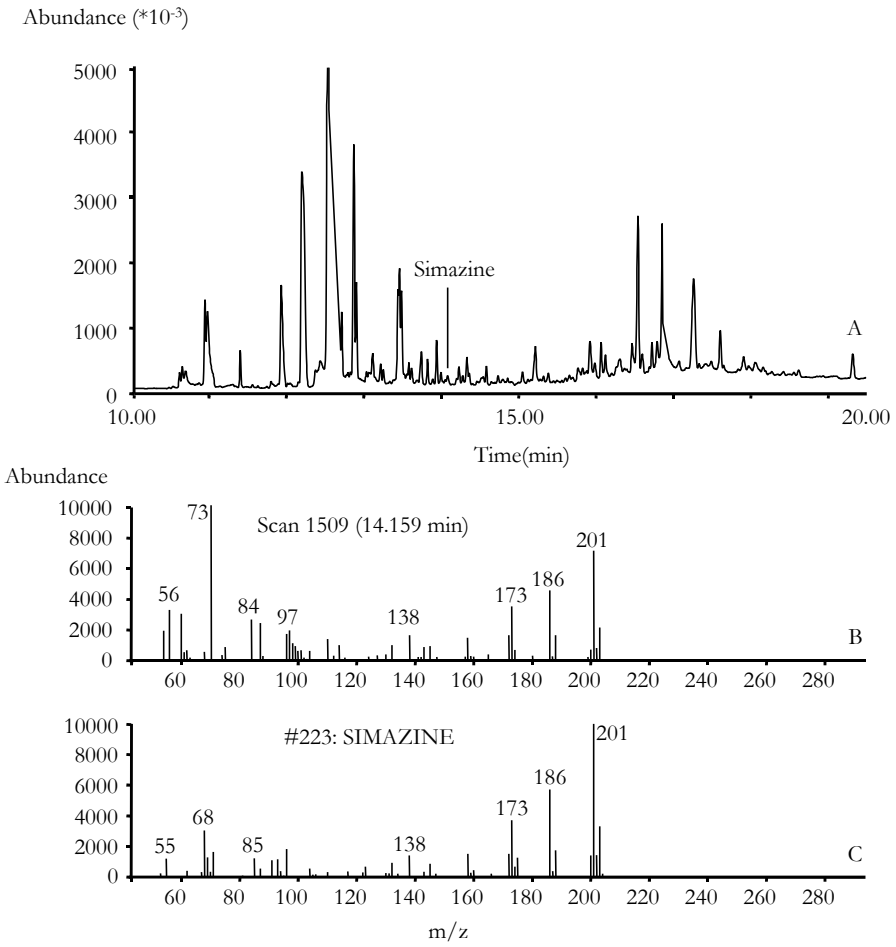


Figure 10 Identification of Simazine in an Orange Juice. A. SBSE-TD-CGC-MS Chromatogram. B. Spectrum retrieved at the location where simazine was suspected to be present. C. Library spectrum

8.4.2.4 Sulfur Compounds in Beer

Sulfur compounds impart a specific aroma to beer and their analysis has always been a real analytical challenge. SBSE can maybe offer a simple and reliable method. 50 mL beer was placed in an aluminum covered vial and extracted with a 10 mm stir bar during 1 hour at 1400 rpm. Thermal desorption was carried out in the splitless mode by programming the TDS from ambient temperature to 240°C (10 min) at 60°C/min. The transfer-line to the PTV was set at 280°C. During desorption, the PTV was cooled to -150°C and then programmed to 280°C (5min) at 12°C/s. Splitless transfer was done on the Stabilwax column which was programmed from 40°C (1 min) to 240°C (30 min) at 5°C/min. The column effluent was split (1:1) to the MSD and PFPD via two 0.6 m L x 0.1 mm I.D. deactivated fused silica capillaries. The MSD was operated in the scan mode while the PFDP was operated in the sulfur mode (6-24 ms). The temperature of the PFPD was set at 250°C and the make-up flows were 11.5 mL/min for hydrogen, 10 mL/min for air flow 1 and 15 mL/min for air flow 2. **Figure 11** shows a profile of a beer sample for which the aluminium coverage of the vial was removed during sampling. In addition to some highly volatile sulfur compounds, several compounds could be identified by the MS. These are listed in the caption of **Figure 11**. Particularly interesting is compound 3 which is known to cause the sunstruck flavor in beer. This compound was absent when the vial was covered with aluminum foil as shown in **Figure 12**. 3-methyl-2-butene-1-thiol is a photo-reaction product between the side chain of the beer bitter acids and sulfur containing amino acids. It causes an off-flavor at the 10 ppt level.

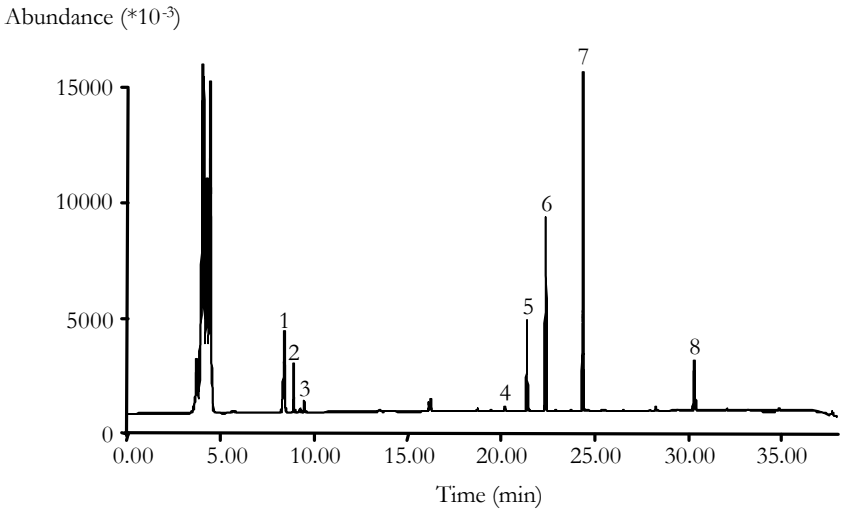


Figure 11 SBSE-TD-CGC-PFPD of beer that has been exposed to light. Peak identification: 1, methylthioacetate; 2, dimethyldisulfide; 3, 3-methyl-2-butene-1-thiol; 4, 4-methylthio-2-butanone; 5, dimethylsulfoxide; 6, 3-(methylthio)-propylacetate; 7, Methionol; 8, 2-(2-furanyl)-thiazole.

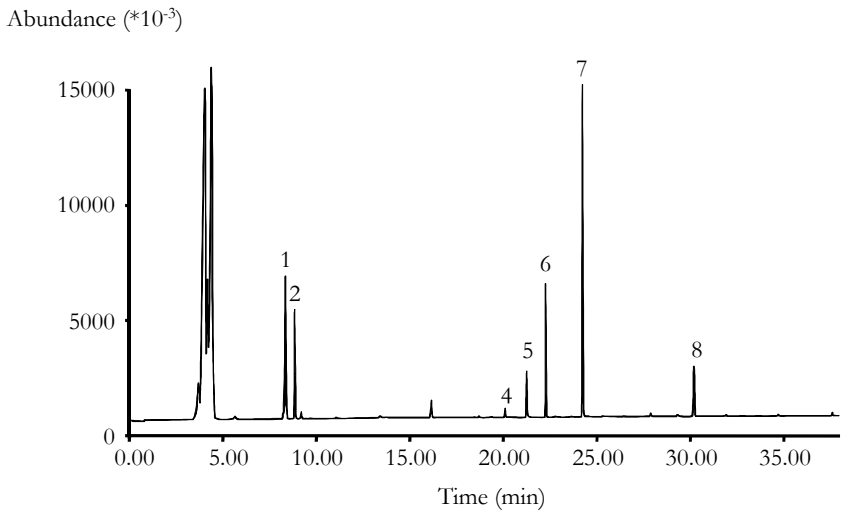


Figure 12 SBSE-TD-CGC-PFPD of beer that has **not** been exposed to light. Peak identification see the caption of **Figure 11**. Note the absence of peak 3.

8.5 Conclusion

Stir bar sorptive extraction (SBSE) is a powerful technique for the extraction of organic compounds from a variety of liquid (aqueous) matrices. Due to the high amount of PDMS coated on the stir bar, high sensitivity can be attained for the pre-concentration of a wide range of compounds. Several typical examples of the performance of SBSE were shown. It was also shown that aroma compounds can be efficiently extracted from a lipid containing yogurt matrix without co-extracting the interfering lipids. Numerous applications in trace analysis were presented including that of endocrine disrupters and pesticides in several beverages.

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9 Concluding Remarks

In this chapter, several conclusions and remarks are made. The three new sorptive sampling concepts that were introduced in this thesis are placed within the context of already existing technologies. Some general comments will be made first, followed by a more detailed description of the preconcentration methods available for liquid samples (**Section 9.1**) and gaseous samples (**Section 9.2**). An overview of analyte/matrix (gaseous/aqueous) combinations is given and the advantages and disadvantages of the listed techniques are highlighted. It is attempted to present a simple framework in order to select the preferred sample preparation procedure for a specific analytical problem. Again, the focus is on modern, efficient and environmental friendly techniques, *e.g.* classical liquid-liquid extraction using 200 mL of dichloromethane is omitted.

Initially, when comparing the new techniques gum phase extraction (GPE), equilibrium gum phase extraction (EGPE) and stir bar sorptive extraction (SBSE) to the already existing sorptive techniques open tubular trapping (OTT) and solid phase microextraction (SPME), several conclusions can be drawn. First, all three new techniques employ a significantly increased amount of sorbent compared to OTT and SPME. As the sensitivity of sorptive enrichment techniques is approximately proportional to the amount of sorbent employed, GPE, EGPE and SBSE exhibit a highly increased sensitivity compared to OTT and SPME. Second, the new sorptive techniques were designed to employ automated thermal desorption equipment that is commercially available from several suppliers, *e.g.* it not necessary to construct home made, and possibly irreproducible and unreliable, instrumentation. Additionally, the availability of autosamplers for thermal desorption allows the analysis of up to at least 20 samples on a routine basis. On-line monitoring systems based on PDMS sorption (GPE and EGPE) have been constructed in the plant volatile project demonstrating the automated and unattended sampling using (E)GPE over longer periods of time. Comparing this with OTT, which relies on complicated instrumentation that is not commercially available, implementation of (E)GPE and SBSE in the analytical laboratory is substantially facilitated. In OTT, the subsequent analysis of multiple samples is possible on a single extraction capillary but experimental conditions should be chosen such as to guarantee complete desorption of the trap and in this way to prevent sample contamination by analyte carryover. Moreover, often samples are taken on-site and transported to the laboratory. This would require a robotized change of the

sampling capillaries for automated sequential OTT analyses and this seems impossible to achieve.

Compared to OTT, SPME can be an attractive technique for routine sampling, provided the demands on detection limits are not too severe. Generally concentration detection limits below 1 μg/L (ppb) are difficult to obtain, even if the highly sensitive ion trap mass spectrometer is used. These low concentration detection limits can only be reached for relatively apolar compounds that partition well into the SPME coating. The attractiveness of SPME stems from its elegant simplicity and the ease with which it can be incorporated in an autosampler that is used for standard liquid injections in a split/splitless, PTV or on-column injector. The rapid equilibration of the SPME-fiber with a sample can be exploited to extract the sample in the SPME autosampler (or manually for that matter) while the previous sample is still running. In this way the analytical instrument can be used in an optimal fashion. On-site sampling and transportation of "loaded" fibers to the laboratory is efficient due to the small size of the SPME assembly and the absence of the need for other equipment such as pumps. However, on-site sampling will require a fresh fiber for each sample and as fiber desorbers with automated fiber change are not (yet) available, manual desorption of the fiber into the gas chromatograph has to be performed. Additional practical problems of SPME are the fragility of the fiber and its high price. This necessitates the re-use of fibers which can be problematic for non-volatile compounds such as PAH's. For these solutes carryover is likely to be observed.

As is clear from the above and from **Chapter 3**, the disadvantages of OTT (low sampling flow rates and low sensitivity) and SPME (low sensitivity) strongly limit the exploitation of the unique properties of sorbents for use in sample preparation. As was described in multiple instances in this thesis, sorptive materials posses typical properties such as a very high inertness, good linearity and the absence of displacement effects, quite contrasting to adsorbent phases where unwanted (*e.g.* too strong) interactions often dominate, particularly in the case of air sampling. The primary objective of the work presented in this thesis was to explore the possibilities of sorptive materials for sample enrichment in new set-ups as an alternative to OTT and SPME. These newly developed techniques combine the good aspects of sorption without the introduction of limitations caused by the geometry in which the sorbent is applied. The successful approaches that are described in this thesis are the use of sorbents in packed beds, GPE and EGPE and the use of sorbents coated on stir bars (SBSE). GPE, EGPE and SBSE show a sensitivity increase up to a factor of 1000 compared to the already existing sorptive techniques OTT and SPME. The new techniques outperform SPME and OTT not only in terms of sensitivity but are also much more cost effective. Two commercial products are already available, namely packed traps filled with 100% PDMS particles and PDMS coated stir bars, which are available under the trade name Twister™. The commercial availability of the disposable parts of (E)GPE and SBSE is certain to facilitate the acceptance of these techniques by the scientific community.

Above a comparison between the techniques introduced in this thesis, (E)GPE and SBSE with SPME and OTT was made. The superior performance of (E)GPE and SBSE was described and illustrated by many examples throughout this thesis. At this place, a comparison with other (non-sorption) techniques is even more important for the simple reason that techniques like solid phase extraction (SPE) and purge and trap (P&T) are much more often applied in practice than OTT and SPME. As has been addressed quite extensively in this thesis the two dynamic sampling techniques GPE and EGPE are particularly useful for gaseous samples. Their application to aqueous samples is restricted to semi-volatiles as volatile compounds will be lost during the drying process. For aqueous samples, stir bar sorptive extraction is an attractive approach as drying processes are not necessary, similar as in SPME. The application limit of SBSE extends from very volatile compounds (*e.g.* C_3-hydrocarbons) to semi-volatiles (*e.g.* PAH's and pesticides). Therefore, in comparing GPE, EGPE and SBSE with classical techniques, a distinction between gaseous and aqueous samples is made.

As was already stated in **Chapter 2**, current analytical techniques for liquid (aqueous) and solid samples are much more developed than those for gaseous samples. One of the reasons for this is the much lower concentration detection limits that are desired in air (ppt range), compared to liquid (ppb range) and solid (ppb to ppm range). Especially at the low concentrations levels of analytes in air, unwanted catalytic breakdown and permanent bonding of analytes is an important problem. This is the area where sorptive sampling can add strongly to currently available technologies. GPE and EGPE have unique applications in air samples, the performance of which can be imitated with OTT or SPME but at unacceptably low detection limits. Non-sorptive techniques such as adsorptive trapping followed by thermal desorption (ATD) show very poor performance compared to (E)GPE for reactive aldehydes, thiols and many other highly relevant compounds.

In the case of solid and liquid samples, the advantages of sorption are smaller. Existing and well-documented techniques such as the innovative SPE for liquid samples and liquid extraction by sonnication for solid or aqueous samples already show very good performance for a wide range of analyte/matrix combinations. Particularly in those cases where the performance of the newly introduced sorptive techniques shows equal or worse performance compared to that of the existing ones, one should best rely on these. However, those cases that can benefit (strongly) from sorption based sample preparation techniques should be highlighted and here the novel (E)GPE and SBSE should be implemented not only to solve real practical analytical problems but also to illustrate the strengths of these techniques. Only by stressing the advantages of new techniques, illustrated by unique applications, these can become accepted. In this context, it is important to realize that no single concept or technique can solve all analytical problems in the best possible way.

In the next two sections, an overview of modern high performance analytical techniques is presented. Since in this thesis, only the application of sorptive sample preparation for liquid and gaseous samples was reviewed, sample preparation techniques for solid samples are omitted here. Techniques employing disposable extraction devices such as packed adsorbent traps in SPE or coated stir bars in SBSE, is to be preferred in order to prevent sample contamination by analyte carryover. However, if this is not critical extraction devices can often be re-used and in this way a more cost-effective working procedure can be obtained.

9.1 Liquid Samples

In **Table 1** an overview of the most important techniques for aqueous samples is given. Depending on the nature of the analytes of interest concerning volatility (volatile/semi-volatile) and polarity (polar/non-polar), different techniques are selected.

Table 1 High sensitivity analytical techniques used for the enrichment of liquid samples sorted on the basis of the analyte properties volatility (volatile/semi-volatile) and polarity (polar/apolar). Techniques shown in *italic* are non-sorptive procedures. Techniques listed in parentheses exhibit medium to low sensitivity.

	Volatile	Semi-volatile
Polar	SBSE SPME	*SPE/μLLE* SBSE
Apolar	*Purge and trap* *(Headspace)* SBSE	*SPE / μLLE* SBSE

For apolar compounds in liquid (aqueous) samples, purge and trap is best used for volatiles and SPE for semi-volatiles. For apolar compounds the classical techniques perform generally quite well and detection limits in the low ng/L range are readily achieved. Application of SBSE or other sorbent based methodologies is often not necessary, though they have certain specific advantages, including the fact of being completely solvent-less. It has to be noted that stir bar sorptive extraction (SBSE) can achieve very low detection limits, *i.e.* at the pg/L level, which is significantly lower than either P&T and SPE without additional concentration or large volume injection. However, this extremely low detection limit is often not required as detection limits defined by regulatory bodies are usually at or above the 0.1 μg/L level.

Purge and trap can be regarded as a high sensitivity technique for the analysis of volatiles from aqueous samples. When for these compounds only medium sensitivity is required, headspace sampling can be a good option, with the advantage of simpler equipment and easier automation. For semi-volatile apolar compounds micro

liquid-liquid extraction (μLLE) can be an interesting alternative to SPE but does not have the versatility of SPE. SPE provides, by careful selection of the adsorbent, wash solvent and desorption solvent the possibility of selective extraction or sample clean-up. μLLE on the other hand, has the advantage that it is very simple and hardly requires any instrumentation. A portion of the sample and the extraction solvent are combined in a closed vial and this effectively prevents sample contamination.

In aqueous samples, the application of SPE and μLLE can be extended relatively far into the range of the more polar compounds, these can also be handled quite successfully. Using SPE, detection limits for polar compounds are often higher than for apolars due to early breakthrough limiting the allowable sample volumes (breakthrough volume). For μLLE the same is true, but here the lower partitioning constant is responsible for poor extraction recoveries. These effects limit the application of SPE and μLLE for the analysis of polar compounds. In these limiting cases, the performance of SBSE becomes interesting. The extremely low detection limit of SBSE, caused by the thermal desorption process, will also be higher for polar analytes but can compare favorably to SPE and μLLE.

The most remarkable part of **Table 1** is that of the volatile and polar compounds which cannot be handled adequately by any conventional technique. Volatile polar compounds are difficult to transfer from the (polar) aqueous phase into the headspace due the well known like-like principle. Therefore purge and trap and headspace sampling are rather ineffective. For volatile compounds, SPE and μLLE cannot be used due to interference of the solvent used in these techniques with the volatile analytes of interest, at least in gas chromatography. In liquid chromatography, polar volatiles cannot easily be analyzed as they often do not possess a UV chromophore due to their low molecular mass. This low molecular mass also makes the use of LC-MS not very straightforward. The one high performance technique for the analysis of polar compounds in aqueous samples is the use of a derivatization reaction to render the compounds both less volatile and less polar in combination with *e.g.* micro liquid-liquid extraction. The disadvantage of derivatization is of course that not all compounds can be converted into suitable derivatives at trace concentration levels in aqueous samples and often the selectivity of derivatization agents is rather poor. However, a strong advantage of this approach is that a functional group can be introduced to facilitate the chromatographic separation and detection. For example, perfluoropropionic anhydride can be used to convert phenols into less acidic compounds for analysis by GC-ECD.

The lack of analytical methods for the analysis of polar volatiles in liquid samples can be filled by the sorption techniques SBSE and SPME. It has to be noted that SBSE is the high sensitivity technique whereas SPME provides low to medium sensitivity. Unfortunately, literature on SPME for polar compounds often employs fibers coated with adsorbent materials. As was pointed out in **Chapter 2**, the use of adsorbent materials in static sampling is very sensitive to matrix effects and likely to

cause irreproducible, unpredictable results. The analytical chemist should be very cautious to circumvent this pitfall. Using SBSE, detection limits at the 0.1 μg/L level are feasible even for polar compounds, particularly if polar (*e.g.* acrylate) coatings become available.

Apart from analyte properties such as volatility and polarity, sorption techniques can also be very successful for particular, "difficult" matrices. This was briefly illustrated in **Chapter 8.4.3.1** with the example of flavor components in yogurt. Yogurt contains suspended fat particles that interfere strongly with the SPE process or can result in foaming in (μ)LLE. The latter effect is often difficult to predict and circumvent in practice. Using SBSE for yogurt samples, good performance was observed without detrimental effects on recoveries or the co-extraction of fatty matrix compounds. The same performance would be difficult, if not impossible, to obtain directly with (μ)LLE or SPE. However, dialysis-SPE can effectively tackle this difficult problem using the clean-up power of membrane dialysis.

9.2 Gaseous Samples

Similarly to **Section 9.1**, in this section the newly introduced sorptive techniques GPE, EGPE and SBSE are compared to classical procedures for gaseous samples. **Table 2** shows appropriate techniques for the analysis of gaseous samples.

Table 2 High sensitivity analytical techniques used for the enrichment of gaseous samples sorted on the basis of the analyte properties volatility (volatile/semi-volatile) and polarity (polar/apolar). Techniques shown in *italic* are the non-sorptive procedures. Techniques listed in parentheses exhibit medium to low sensitivity.

	Volatile	Semi-volatile
Polar	EGPE	GPE
Apolar	*ATD* EGPE	GPE *ATD* *(ALD)*

A remarkable feature of **Table 2** is the minor presence of classical extraction techniques. This is due to the simple fact that in the analysis of gaseous samples, classical techniques often do not perform well. Adsorption with liquid desorption (ALD) often results in very low sensitivity due to the large volumes of organic solvent used for desorption. This organic solvent also precludes the analysis of volatiles as these will be masked by the solvent peak. This limitation might be overcome by analysis on a liquid chromatograph but volatiles very do not posses a UV chromophore and will have a too low molecular mass for LC-mass spectrometry.

Adsorption with thermal desorption (ATD) can provide reasonably high sensitivity but suffers from catalytic degradation effects, permanent adsorption and adsorbent instability as was discussed in **Section 2.2.3**. Moreover, ATD is unsuited for the analysis of polar compounds and to a lesser extent for that of high molecular weight solutes as was pointed out throughout this thesis. If the air analysis literature is reviewed, it can often be noted that only apolar compounds are observed in *e.g.* ambient air. This is certainly not the case in real life, but the polar compounds (acids, thiols, amines, *etc.*) easily degrade during the adsorptive trapping - thermal desorption procedure or are present at too low concentrations. In air analysis there is clearly a need for novel high sensitivity techniques that are applicable not only to apolar compounds!

The sorptive sampling techniques GPE and EGPE have proven to be high sensitivity techniques for the determination of compounds that cannot be handled by classical techniques or only with severe drawbacks such as a low sensitivity or the need for derivatization. Analytes falling into this group include free acids, amines, thiols and many other compounds. This was shown throughout this thesis. In general, GPE is to be preferred due to the simple calibration procedure. It can effectively be applied for a large number of compounds, particularly not too volatile solutes (*i.e.* toluene and less volatile). More volatile compounds will rapidly saturate the sorptive trap so that early breakthrough occurs. This effect is, however, less pronounced at lower flow rates. For volatiles, equilibrium gum phase extraction (EGPE) can be used as it does not suffer from breakthrough effects and takes advantage of the rapid equilibration of the packed sorptive trap. Being an equilibrium technique, EGPE also provides higher sensitivity than GPE, but for less volatile solutes this sensitivity is both not required and will require very long sampling times.

9.3 Conclusion

In this last chapter, the new sorptive sampling concepts introduced in this thesis were placed within the context of already existing technologies. Particularly the analysis of gaseous samples can benefit strongly from the newly introduced sorptive techniques. Air sampling is an interesting application area of GPE and EGPE and allows the high sensitivity enrichment and analysis of polar analytes that are very difficult, or even impossible, to handle with classical techniques. Application of GPE for semi-volatiles and EGPE for volatiles has resulted in numerous examples illustrating the simultaneous speed, sensitivity and the high recoveries that can be obtained with these techniques.

For liquid (aqueous) samples, stir bar sorptive extraction (SBSE) can provide the analyst with extremely low detection limits, but these are in many cases not (yet) needed in practice. More stringent regulations in the future, though, might require ultra high sensitivity techniques such as SBSE. Established techniques for aqueous samples perform very well for the majority of analytes. Interesting, though not fully developed yet, is the application of SBSE for the analysis of polar and volatile analytes

and for difficult matrices such as fatty matrices and biological samples. In some cases described in the text, SBSE outperforms techniques such as SPE, μLLE and P&T.

The sample preparation concepts introduced in this thesis show high potential to result in valuable new analytical tools. Many applications involving difficult analytical problems were described. However, in order for (E)GPE and SBSE to become fully accepted by the scientific community, a large amount of work is necessary by research groups around the world. It is a misunderstanding at this point to think that either (E)GPE or SBSE is as well developed as for example SPE. The reason for this is that several thousands of publications have appeared on SPE whereas this thesis is the first work on (E)GPE and SBSE. Hopefully, somewhere in the future, either (E)GPE and SBSE will be considered established or even conventional techniques.

Summary

Increasingly stringent environmental regulations imposed by governmental organizations require the development of analytical tools that can tackle ever more difficult analytical problems. Not only is there a need for higher sensitivity methods for existing (priority) pollutants but new classes of compounds, especially more polar analytes, are discovered and receive attention as a new generation of pollutants. Of course many of these compounds have always been present but were largely undetected due to inadequacies in old-fashioned analytical techniques. Currently a large number of analyses can be carried out successfully using modern methods such as solid phase extraction (SPE) or micro liquid-liquid extraction (μLLE) but the development of novel approaches, based on new principles, concepts and insights are needed.

In this thesis, three novel sample preparation techniques based on (polydimethylsiloxane, PDMS) sorption were described. Due to the favorable characteristics of sorbents for high sensitivity thermal desorption, primary focus is on the use of these materials in thermal desorption-gas chromatographic systems. Additionally, typical properties of PDMS such as a very high linearity, the absence of displacement effects and catalytic activity and its very high inertness were described in detail. The newly introduced enrichment techniques were compared to existing technologies in order to evaluate if the sorptive sample preparation approaches can provide an extension to the working range of already existing techniques.

Chapter 1 gives a general introduction. Subsequently the principles of adsorption, sorption and their differences are outlined. This chapter ends with the scope of this thesis, the development of novel sorption based sample preparation methods. This is needed as other sorption techniques such as open tubular trapping and solid phase microextraction show too many drawbacks to become widely accepted and used.

Chapter 2 presents an overview of current state-of-the art sample preparation techniques. These techniques are presented in separate sections for gaseous (**Section 2.2)**, liquid (**Section 2.3)** and solid samples (**Section 2.4**). Important techniques include adsorbent based trapping for gaseous samples, SPE and μLLE for liquid samples and accelerated solvent extraction (ASE) and micro sonnication for solids. It was concluded that for both solid and liquid (aqueous) samples a variety of

high-performance techniques is available that almost cover the complete range of analytes of interest. Therefore, liquid and solid samples do not require so much the introduction of new techniques. Only in several special cases such as the analysis of polar and volatile compounds from liquid samples and the analysis of specific matrices such as biological, food and beverage samples new technologies are more than welcome. In contrast to liquid and solid samples, the enrichment techniques for gaseous samples is much more difficult. Particularly the analysis of polar compounds in air is an analytical problem that cannot be addressed adequately by conventional techniques. Here significant room for improvement is available and novel analytical techniques are needed.

Chapter 3 addresses two already existing methodologies for sorptive sample enrichment, namely open tubular trapping (OTT) and solid phase microextraction (SPME). OTT uses an open tubular capillary extraction column coated with a layer of sorbent on the inside. The sample (liquid or gaseous) is passed to the OTT column for extraction. Severe drawbacks of OTT are the low sample flow rates that can be applied, leading to long extraction times and the complexity and lack of commercial instrumentation. Additionally, the sensitivity of OTT techniques is often low due to the low amount of sorbent present in typical extraction capillaries. SPME is a technique that uses a sorbent coated fiber for analyte extraction and enrichment. SPME was originally developed for the analysis of liquid samples and is performed by simply dipping the fiber into the liquid phase under stirring. After an equilibrium between the liquid sample and the sorbent coating has been obtained, the fiber is removed and desorbed in the inlet of a gas chromatograph. Extraction of a gaseous sample by SPME is not that straightforward as the gas flow around the SPME fiber should be controlled. Additionally, due to the equilibrium nature of SPME, the often rapid fluctuations in the composition of gaseous samples is difficult to quantitate. Despite the simplicity of SPME, it generally suffers from a poor sensitivity due to the low amount of sorbent that can be coated onto the fiber, typically less than 0.5 μL. **Chapter 3** concludes with the description of several features that newly designed sorptive extraction concepts should exhibit for high sensitivity operation. New high-sensitivity sorptive techniques should incorporate larger amounts of PDMS, preferably more than 50 μL without the introduction of flow rate limitations or other disadvantages. New concepts proposed in this thesis to overcome these limitations are gum phase extraction, described in **Chapter 4** and **5**, equilibrium gum phase extraction, described in **Chapter 6** and stir bar sorptive extraction, described in **Chapter 7** and **8**. Unless otherwise stated, the sorbent used was 100% polydimethylsiloxane (PDMS) in all cases. This material was found to be very stable, inert and showed very favorable thermal desorption characteristics. In addition, the high diffusion constants of analytes in PDMS allow rapid equilibration and/or high sampling flow rates.

Chapter 4 presents the first new sorptive concept in this thesis, namely gum phase extraction (GPE). In this chapter the performance of GPE was evaluated for gaseous samples. GPE is based on a packed bed of PDMS particles, similar to solid

phase extraction (SPE) and air adsorption techniques. GPE typically employs 250 μL of PDMS and in combination with thermal desorption-GC(-MS) this ensures a high sensitivity. In **Section 4.1**, GPE using a packed PDMS cartridge was compared to air enrichment using the popular adsorbents Tenax, Carbotrap 300, Chromosorb and Lichrolut EN. The performance of PDMS was compared to that of the adsorbents for a wide range of compounds including many difficult polar analytes. For many solutes, particularly polar compounds such as organic acids, amines and alcohols, superior performance was observed on PDMS compared to classical enrichment techniques. Many adsorbents, particularly the strong Carbotrap 300, showed low recoveries for a large number of analytes, due to permanent adsorption and/or reactions of adsorbed species. Several applications of GPE in air sampling were illustrated in **Sections 4.1.5.2** through **Section 4.1.5.4**. illustrating detection limits in the low- to sub-ng/m^3 range and the analysis of compounds difficult to handle with classical techniques such as the small organic acid acetic acid. **Section 4.2** describes the reactivity and inertness of the same adsorbent materials as used in **Section 4.1** and PDMS-GPE for the enrichment of sulfur containing compounds from gaseous samples. On the adsorbents Carbotrap and Tenax, low recoveries of most of the sulfur compounds were observed. It was possible to identify the artifacts formed from the original sulfur compounds. The two main artifact forming reactions were H_2S elimination from thiols (R-SH) and dimerization of thiols (two R-SH groups from an R-S-S-R dimer). Another interesting application of PDMS-GPE namely the analysis of volatile compounds emitted by living plants was presented in **Section 4.3**. In this section, GPE was compared against dynamic sampling on Tenax and SPME using both PDMS and acrylate fibers. It was shown that active sampling on PDMS and Tenax resulted in approximately the same results, however, some marked differences were observed. Tenax gave rise to some additional peaks associated with the polymeric structure of this material. Apart from several high molecular weight compounds, which could be assigned quite easily as Tenax degradation products, the presence of low molecular weight interferences was more problematic. As an example, when the same sample was sampled both on Tenax and PDMS, benzaldehyde was found on Tenax at levels ten times higher than on PDMS, due to degradation of Tenax. This presents a real problem as benzaldehyde is, for example, an import flavor compound. Static SPME sampling was also performing reasonably well but in SPME the matching of fiber polarity to the polarity of the analytes to be determined is essential. This complicates analyses in cases such as this one, where unknown compounds are expected. **Section 4.4** describes the rapid analysis of polyaromatic hydrocarbons in air using GPE-PDMS sampling but now followed by on-line liquid desorption and HPLC analysis. Detection limits at the ng/m^3 level were established which is sufficient to monitor a range of priority PAHs in ambient air. The total analysis time, including sampling, was less than 15 minutes.

Chapter 5 describes GPE for the analysis of aqueous samples, similar to the way SPE is used for water samples. An automated system for GPE enrichment-thermodesorption-GC-MS analysis was described in **Section 5.1**. On the basis of octanol water partitioning constants ($K_{O/W}$), which are tabulated for a large number of

compounds in the literature, the maximum allowable sample volume can be calculated. The validity of this model was demonstrated for a range of PAHs, organochlorine pesticides and triazine herbicides. It was found that compounds with a log $K_{O/W}$ value in excess of 1.77 can be trapped from 10 mL samples. For more polar compounds, smaller sample volumes have to be used, which results in a lower sensitivity. Using a 10 mL sample volume detection limits were in the order of 10 ng/L. The same automated system was applied to the analysis of phenols in **Section 5.2**. Phenols as such are too polar to be extracted directly by PDMS. Therefore, in situ derivatization with acetic anhydride was applied to acetylate the phenols into derivatives that could be trapped from 10 mL samples. Detection limits were again in the order of 10 ng/L, similarly to that for PAH's and pesticides. Another in situ derivatization application is presented in **Section 5.3** which describes the determination of amines derivatized with pentafluorobenzoyl chloride. However, it was found that the derivatized amines were still too polar to be trapped efficiently from the water phase onto PDMS. Therefore, a new sorbent, a crosslinked polyacrylate was developed which was able to retain the derivatized amines from 1 mL samples. Unfortunately, the stability of the polyacrylate was not by far as good as that of PDMS and severe bleeding of the acrylate phase was observed. The application of mass spectrometric detection was therefore not possible, instead the nitrogen selective nitrogen phosphorous detector (NPD) was used which showed no signal for the interfering acrylate background peaks. Detection limits in the sub-µg/L range were obtained. The low breakthrough volumes obtained for the derivatized amines are a clear example of the limitation of GPE for the extraction of polar compounds from liquid samples. For these compounds EGPE and especially SBSE are better alternatives.

Chapter 6 introduces equilibrium gum phase extraction (EGPE) which is a modification of breakthrough GPE described in **Chapter 4** and **5**. In EGPE it is not the intention to trap the entire amount of analyte samples but the sample is passed through the sorbent bed until all analytes are in equilibrium between the water and sorbent (PDMS) phase. It was shown that EGPE can achieve better detection limits for all compounds compared to GPE as it is based on the maximum uptake of analyte into the sorbent bed. This is of particular use for compounds that do not partition well into the sorbent bed, *i.e.* volatile compounds in gas analysis and polar compounds in liquid analysis. For these compounds, EGPE shows superior performance compared to GPE. This has, however, to be paid for by a more complicated calibration procedure as the enrichment factors of all analytes have to be known, either from theoretical calculations of from experimental data. Additionally it was shown that many factors have an influence on the experimentally obtained enrichment factors of which the most important are: temperature, pressure and the pressure drop though the bed. Despite the more difficult calibration it was shown that EGPE can effectively extend the application range of GPE. This was illustrated by the trace analysis of the epoxides ethylene oxide and epichlorohydrin in air. For these compounds detection limits of 50 µg/L respectively 20 ng/L were found which are adequate for real-life monitoring

purposes. It has to be noted that these two compounds, particularly ethylene oxide, cannot be analyzed effectively by GPE due to close to zero breakthrough volumes.

Chapter 7 describes the third new sorptive concept, namely that of stir bar sorptive extraction (SBSE). It is based on a sorbent (PDMS) coated stir bar which is used for simultaneous stirring and extraction of aqueous samples. The simplicity of this technique is comparable with that of SPME, however the sensitivity is up to a factor of 1000 higher. SBSE benefits, similar to the other sorptive techniques from the fact that extraction recoveries can be calculated from literature octanol-water partitioning data. This renders methods development rather easy as it does not require experimental data. PDMS coated stir bars were used for the extraction of a large number of volatile and semivolatile EPA-priority pollutants. Detection limits below the 0.1 μg/L range were obtained for all analytes under investigation. Using PDMS coated stir bars with a film thickness of 1 mm, detection limits for aqueous samples in the sub-ng/L range are easily obtained using mass spectrometric detection. This was shown in **Section 7.2** for dichlorinated propenes, trichlorobenzene, a mixture of mono-aromatics and several additional priority pollutants.

Chapter 8 continues with several selected applications of stir bar sorptive extraction. These examples are split into two groups, that deal with relatively high concentrations (quality control, ppm level, **Section 8.4.1**) and those concerning trace level concentrations (μg/L and sub-μg/L level, **Section 8.4.2**). An interesting application in quality control analysis is that of the analysis of a strawberry flavored yogurt sample. From a 1:1 diluted yogurt sample in water, the flavor compounds were captured quite easily and a nice chromatogram could be obtained. Surprisingly, the fatty matrix of the yogurt was not partitioning into the stir bar coating. Several trace and ultra-trace analysis examples are shown, illustrating the performance of SBSE at the low-μg to ng/L level. Interesting applications were developed in the food and beverage area, particularly for several "natural" juices such as orange juice and wine. Surprisingly, in some of the beverage samples, pesticides and endocrine disrupting compound nonyl-phenol were found at the 10-50 μg/L level. Positive identifications included simazine in orange juice and procymidone in wine, both by GC-MS and by GC-AED (atomic emission detection).

Samenvatting

Alsmaar strenger wordende regels omtrent de regulatie van toxische verbindingen in ons milieu vereisen de ontwikkeling van analytische technieken voor steeds complexere analytische problemen. Niet alleen is er behoefte aan gevoeliger meetmethoden voor bekende (prioriteits)verontreinigingen, maar nieuwe klassen van vooral polaire verontreinigingen worden ontdekt en ondervinden versterkte aandacht. Natuurlijk zijn veel van deze verbindingen altijd aanwezig geweest, maar bleven vaak onopgemerkt door tekortkomingen in bestaande analysemethoden. Momenteel worden al veel analyses succesvol uitgevoerd met moderne technieken als vaste fase extractie (SPE) en micro vloeistof-vloeistof extractie (μLLE) maar de ontwikkeling van moderne technieken, gebaseerd op nieuwe principes, concepten en inzichten is noodzakelijk.

In dit proefschrift zijn drie nieuwe monstervoorbewerkingsmethoden beschreven, gebaseerd op basis van (polydimethylsiloxane, PDMS) absorptie. Door de goede geschiktheid van absorbentia voor de zeer gevoelige thermische desorptie ligt de nadruk met name op de toepassing van deze materialen in thermische desorptie-gas chromatografische systemen. De typische eigenschappen van PDMS absorptie, zoals de hoge mate van lineariteit, de afwezigheid van competitieve adsorptie en katalytische activiteit en de zeer hoge inertheid, zijn in detail beschreven. De nieuw geïntroduceerde technieken zijn vergeleken met bestaande technieken om te evalueren, waar deze een uitbreiding kunnen vormen op bestaande technologieën.

Hoofdstuk 1 start met een algemene inleiding, gevolgd door de introductie van de principes van adsorptie en absorptie en de onderlinge verschillen. Dit hoofdstuk eindigt met de beschrijving van het onderwerp van dit proefschrift, de ontwikkeling van nieuwe monstervoorbewerkingsmethoden, gebaseerd op (PDMS) absorptie. Dit is noodzakelijk, omdat reeds bestaande absorptie monstervoorbewerkings technieken zoals capillaire extractie (OTT) en vaste fase micro extractie (SPME) te veel voornamelijk praktische nadelen vertonen om in algemeen gebruik te raken. OTT en SPME bieden onvoldoende mogelijkheden om de gunstige eigenschappen van absorbentia te benutten voor monstervoorbewerking.

Hoofdstuk 2 geeft een overzicht van moderne monstervoorbewerkings technieken voor gasvormige (**Paragraaf 2.2**), vloeibare (**Paragraaf 2.3**) en vaste monsters (**Paragraaf 2.4**). Belangrijke technieken zijn adsorptie bemonstering voor gas monsters, SPE en μLLE voor vloeistoffen en versnelde solvent extractie (ASE) en

micro ultrasoon extractie voor vaste stoffen. De conclusie, die uit deze introductie kan worden getrokken, was, dat voor zowel vaste als vloeibare (waterige) monsters verscheidene zeer goede technieken bestaan, waarmee gezamenlijk de meeste relevante verbindingen aangereikt kunnen worden. Het gevolg hiervan is, dat voor vloeibare en vaste monsters de behoefte aan nieuwe technieken alleen bestaat in een aantal specifieke gevallen. Dit betreft bijvoorbeeld de extractie van zeer polaire, vluchtige verbindingen uit water en de analyse van analieten in complexe matrices zoals biologische monsters en monsters uit de voedingsmiddelen industrie. Betere en vooral eenvoudigere benaderingen zijn hier zeer welkom. Monstervoorbewerking voor gasvormige monsters is, in tegenstelling tot die voor vloeibare en vaste monsters, over het algemeen zeer lastig. Vooral de analyse van polaire verbindingen in lucht is een complex probleem, dat nauwelijks adequaat aangepakt kan worden met bestaande technieken. Vooral dit gebied is gebaat met sterke verbeteringen, die waarschijnlijk alleen bereikt kunnen worden door introductie van nieuwe principes en concepten in monstervoorbewerking. Dit is bijvoorbeeld monstervoorbewerking, gebaseerd op absorptie, beschreven in dit proefschrift.

Hoofdstuk 3 beschrijft de twee reeds bestaande, op absorptie gebaseerde, monstervoorbewerkingstechnieken, namelijk capillaire extractie (OTT) en vaste fase micro extractie (SPME). OTT is gebaseerd op een capillaire kolom die van binnen gecoat is met een absorptie materiaal. Het gasvormige of vloeibare monster wordt door de kolom geleid voor extractie van de componenten. Helaas heeft deze techniek enige belangrijke nadelen zoals een zeer lage maximale bemonsteringssnelheid, lange extractie tijden, hoge mate van complexheid en de niet commercieel verkrijgbare instrumentatie. Misschien belangrijker nog is de vaak slechte gevoeligheid door de kleine hoeveelheid stationaire fase, die in een capillaire kolom aangebracht kan worden. SPME is een tweede absorptie aanreikingstechniek en gebaseerd op een gecoate fiber voor extractie en aanreiking. SPME is origineel ontwikkeld voor de analyse van vloeibare (waterige) monsters door de fiber in het geroerde monster te houden. Nadat er een evenwicht is ingesteld tussen het monster en de SPME coating, wordt de fiber uit het monster gehaald en geïntroduceerd in de inlaat van een gaschromatograaf. Extractie van gasvormige monsters met behulp van SPME is aanzienlijk moeilijker omdat hiervoor de stroming rondom de fiber zeer goed gedefinieerd moet zijn. Ook is door het evenwichtskarakter van SPME de kwantificering van luchtmonsters met vaak snel wisselende concentraties lastig. Ondanks de eenvoud van SPME wordt deze techniek vaak gekenmerkt door een lage gevoeligheid, veroorzaakt door de geringe hoeveelheid absorbent aanwezig op de gecoate fiber, typisch minder dan 0.5 μL. **Hoofdstuk 3** eindigt met de beschrijving van de eisen, waaraan nieuwe hoge gevoeligheid absorptie technieken moeten voldoen. Deze moeten minimaal 50 μL absorbent gebruiken en dit zonder limitaties in bemonsteringssnelheid en andere praktische aspecten. Een aantal nieuwe concepten, om deze limiterende factoren te omzeilen, zijn beschreven in dit proefschrift. **Hoofdstuk 4** en **5** beschrijven gum fase extractie voor gasvormige, respectievelijk vloeibare monsters. In **Hoofdstuk 6** wordt een speciale variant van deze techniek, evenwichts gum fase extractie, beschreven. Een derde absorptie techniek,

gebaseerd op een gecoate roer vlo, is beschreven in **Hoofdstuk 7** en **8**. Tenzij anders vermeld, is het gebruikte absorptiemateriaal steeds 100% puur polydimethylsiloxaan. Dit materiaal is zeer stabiel, inert en vertoont zeer gunstige eigenschappen voor directe thermische desorptie. Door de hoge diffusieconstanten van verbindingen in PDMS is een snelle evenwichtsinstelling of zijn hoge bemonsteringssnelheden mogelijk.

Hoofdstuk 4 presenteert de eerste nieuwe op absorptie gebaseerde monstervoorbewerkingstechniek, gum fase extractie (GPE) en applicaties van deze techniek voor de aanreiking van gasvormige samples. GPE gebruikt typisch 250 µL PDMS, wat in samenwerking met thermische desorptie-GC(-MS) garant staat voor een zeer hoge gevoeligheid. In **Paragraaf 4.1** is GPE, gebaseerd op een gepakte PDMS buisje, vergeleken met lucht bemonstering op de veel gebruikte adsorbentia Tenax, Carbotrap 300, Chromosorb en Lichrolut EN. De werking van PDMS is vergeleken met die van de adsorbentia voor een uitgebreide lijst componenten, waaronder vele moeilijk te analyseren en minder stabiele polaire verbindingen. Voor de meerderheid van verbindingen, vooral voor de polaire zoals organische zuren, amines en alcoholen, werd de superieure werking van PDMS ten opzichte van de klassieke materialen vastgesteld. Veel adsorptie materialen, vooral het sterke Carbotrap 300, vertoonden lage recoveries voor veel analieten door permanente adsorptie en/of reacties van geadsorbeerde componenten.

Een aantal applicaties van GPE in lucht bemonstering zijn beschreven in de **Paragrafen 4.1.5.2** tot en met **4.1.5.4** en illustreren de goede detectiegrenzen in het lage- tot sub-ng/m^3 niveau voor verbindingen, die moeilijk te analyseren zijn met andere technieken, bijvoorbeeld azijn zuur. **Paragraaf 4.2** beschrijft de katalytische activiteit en inertheid van dezelfde adsorbentia als gebruikt in **Paragraaf 4.1** en PDMS-GPE voor de aanreiking van zwavelhoudende verbindingen uit gasvormige monsters. Op de adsorbentia Tenax en Carbotrap werden lage recoveries gevonden voor de meeste zwavelhoudende verbindingen. Het was mogelijk, een aantal artefacten te identificeren, die gevormd werden uit de oorspronkelijk gesamplede verbindingen. De twee belangrijkste artefact vormende reacties waren de eliminatie van H_2S uit thiolen (R-SH) en dimerisatie van thiolen (twee R-SH groepen vormen een R-S-S-R dimeer). Een andere interessante applicatie van PDMS-GPE, de analyse van vluchtige verbindingen geëmitteerd door levende planten, is beschreven in **Paragraaf 4.3**. Voor deze toepassing werd GPE vergeleken met dynamische bemonstering op Tenax en SPME op PDMS en acrylaat fibers. Actieve bemonstering op PDMS en Tenax leidt tot redelijk vergelijkbare resultaten, echter met enkele belangrijke verschillen. Verscheidene degradatie producten, gelijkend op de moleculaire structuur van Tenax, werden aangetroffen. Buiten de aanwezigheid van enkele verbindingen met een relatief hoog moleculair gewicht, die eenvoudig aangewezen konden worden als producten van Tenax degradatie, was de aanwezigheid van laag moleculaire analieten veel problematischer. Indien bijvoorbeeld hetzelfde sample werd bemonsterd op Tenax en PDMS, werd benzaldehyde in circa tien maal hogere concentraties aangetroffen in het Tenax buisje, dit door ontleding van Tenax zelf. Omdat benzaldehyde een belangrijke

geurcomponent is, vormt dit een groot probleem. Statische SPME bemonstering werkte redelijk goed voor de analyse van de vluchtige, door planten geëmitteerde, verbindingen. Hier is alleen wel de overeenkomst tussen de polariteit van de fiber en die van de analieten van groot belang. Dit compliceert de SPME analyse van monsters, waarvan de samenstelling op het moment van bemonstering onbekend is. **Paragraaf 4.4** beschrijft als laatste applicatie de snelle analyse van polyaromatische koolwaterstoffen met behulp van GPE-PDMS, gevolgd door on-line vloeistof desorptie en HPLC analyse. Detectie limieten in het ng/m^3 bereik werden verkregen, voldoende laag om deze verbindingen te analyseren in omgevingslucht. De totale analysetijd, inclusief bemonstering, bedroeg in dit geval 15 minuten.

Hoofdstuk 5 beschrijft GPE voor de analyse van waterige monsters op een analoge wijze met SPE. Een geautomatiseerd systeem voor GPE aanreiking-thermische desorptie-GC-MS analyse is beschreven in **Paragraaf 5.1**. Op basis van octanol water verdelings constanten ($K_{O/W}$), welke in de literatuur voor een groot aantal verbindingen gevonden kunnen worden, kan het maximaal toelaatbare monstervolume berekend worden. De geldigheid van dit model werd gedemonstreerd voor een serie verbindingen waaronder PAHs, organochloor pesticiden en triazine herbiciden. Componenten met een log $K_{O/W}$ waarde van meer dan 1.77 kunnen kwantitatief uit 10 mL samples geabsorbeerd worden. Voor sterkere polaire verbindingen moeten kleinere volumina gebruikt worden. Met gebruik van 10 mL monsters konden detectie grenzen van 10 ng/L voor alle componenten bereikt worden. In **Paragraaf 5.2** is het geautomatiseerde GPE-TD-GC-MS toegepast voor de analyse van fenolen uit waterige monsters. Omdat fenolen als dusdanig te polair zijn om geabsorbeerd te worden door PDMS, werd een acetylerings reactie met azijnzuur anhydride uitgevoerd. De verkregen derivaten konden kwantitatief bemonsterd worden uit 10 mL samples met detectielimieten eveneens in het 10 ng/L bereik. Een tweede in situ derivatizerings applicatie is beschreven in **Paragraaf 5.3** en beschrijft de analyse van amines met behulp van pentafluorobenzoylchloride. Zelfs na deze reactie stap echter bleek het niet mogelijk, de analieten in voldoende mate uit water monsters te absorberen. Daarom werd besloten, een gecrosslinkte acrylaatfase te synthetiseren, welke voldoende retentie vertoonde om de amines uit 1 mL monsters te absorberen. Helaas bleek dat de stabiliteit van deze acrylaat fase veel slechter was dan die van PDMS. Sterke ontleding tijdens de thermische desorptie werd waargenomen. Hierdoor was de toepassing van een massa spectrometer onmogelijk maar, met behulp van de stikstof selectieve stikstof fosfor detector (NPD), kon toch een stabiele basislijn verkregen worden. Detectie limieten onder de µg/L grens werden behaald. De lage doorbraakvolumes voor de gederivatiseerde amines is een goede illustratie van de beperkingen van GPE voor de extractie van polaire verbindingen uit vloeibare monsters. Voor deze verbindingen zijn EGPE, maar met name SBSE, in veel gevallen betere alternatieven.

Hoofdstuk 6 introduceert evenwichts gum fase extractie (EGPE), een variatie op het principe van doorbraak GPE zoals beschreven in **Hoofdstuk 4** en **5**. In tegenstelling tot GPE is EGPE niet gebaseerd op het kwantitatief absorberen van

de totale hoeveelheid van gesamplede analieten maar op het bereiken van evenwicht tussen het monster en de pakking. Omdat EGPE gebaseerd is op de maximale hoeveelheid absorbeerbare componenten, is de gevoeligheid van EGPE voor alle verbindingen beter dan die van GPE. Dit wordt met name toegepast voor de aanreiking van componenten die niet sterk in de absorptie fase partitioneren, zoals vluchtige componenten in lucht analyse en polaire verbindingen uit water. Voor deze verbindingen heeft EGPE duidelijk betere karakteristieken. Dit moet echter wel betaald worden met een complexere calibratie procedure, omdat aanreikingsfactoren voor iedere verbinding bekend dienen te zijn uit ofwel theoretische berekeningen of experimentele data. Tevens is het zo, dat door het evenwichtskarakter van deze techniek vele parameters invloed hebben op de experimenteel verkregen aanreikingsfactoren; de belangrijkste zijn de temperatuur, druk en drukval over de gepakte kolom. Ondanks de moeilijkere calibratie van EGPE kan deze techniek het werkgebeid van GPE significant uitbreiden. Dit werd geïllustreerd met de (sporen)analyse van de epoxides ethyleen oxide en epichloorhydrine in lucht. Voor deze componenten werden detectie limieten van 50 μg/L respectievelijk 20 ng/L gevonden, welke voldoende zijn voor het monitoren van deze verbindingen in omgevingslucht. De analyse van deze verbindingen, met name ethyleen oxide, met GPE is lastig door de zeer lage doorbraakvolumes.

Hoofdstuk 7 beschrijft de derde nieuwe techniek, namelijk roer vlo absorptie extractie (SBSE). Deze techniek is gebaseerd op een met een absorbent (PDMS) gecoate roer vlo, welke gebruikt wordt voor de gelijktijdige menging en extractie van waterige monsters. De eenvoud van deze techniek is vergelijkbaar met die van SPME, echter de gevoeligheid is tot een factor 1000 beter. SBSE extractie heeft het voordeel, dat evenwichts constanten berekend kunnen worden uit octanol water verdelings constanten analoog als voor de andere absorptie technieken. Dit maakt methode ontwikkeling eenvoudig, omdat experimentele data niet vereist is. PDMS gecoate roer vlo's werden gebuikt voor de extractie van een grote serie vluchtige en semi-vluchtige prioriteitsverbindingen van de EPA. Detectie limieten onder de 0.1 μg/L grens werden verkregen voor alle componenten. Gebruik makend van PDMS gecoate roer vlo's met een 1 mm film dikte en massa spectrometrische detectie konden detectie limieten in het sub-ng/L bereik verkregen worden. Dit werd beschreven in **Paragraaf 7.2** voor digechloreerde propenen, trichloor benzeen, een mengsel van mono aromatische verbindingen en verscheidene overige prioriteits verbindingen.

Hoofdstuk 8 beschrijft enkele geselecteerde applicaties van SBSE. Deze voorbeelden zijn gesplitst in twee groepen, die betreffende monsters met relatief hoge concentraties (kwaliteitscontrole, ppm niveau, **Paragraaf 8.4.1**) en die betreffende sporenanalyse (μg/L en sub-μg/L niveau, **Paragraaf 8.4.2**). Een interessante applicatie in kwaliteitscontrole is de analyse van een yoghurt met aardbeiensmaak. Uit een 1:1 in water verdund yoghurtmonster konden de smaakstoffen geabsorbeerd worden en een goed chromatogram werd direct verkregen. De yoghurt matrix, bestaande uit vele vetachtige verbindingen en proteïnen, werd verrassend genoeg niet geabsorbeerd door

de PDMS coating. Verscheidende applicaties van sporen en ultra sporen analyse werden getoond en illustreren de werking van SBSE in het lage μg/L tot ng/L bereik. Interessante applicaties werden ontwikkeld voor de analyse van voedingsmiddelen, zoals vruchtensappen en wijn. Verrassend genoeg werden in enkele monsters pesticiden en de endocriene disruptor nonylphenol aangetoond met concentraties in het 10-50 μg/L gebied. Positieve identificaties van simazine in sinaasappelsap en procymidone in wijn zijn beschreven, zowel met GC-MS als met GC-AED (atomaire emissie detectie).

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Curriculum Vitae

Erik Baltussen werd geboren op 5 juni 1973 te Geldrop. In 1991 behaalde hij het VWO diploma aan de scholengemeenschap Augustinianum te Eindhoven. Aansluitend hierop begon hij met de studie Scheikundige Technologie aan de Technische Universiteit Eindhoven. Tijdens deze studie liep hij gedurende 6 maanden stage bij de groep van prof.dr. H.M.M. McNair te Blacksburg, Virginia in de Verenigde Staten van Amerika voor een onderzoek naar grootvolume injectie voor capillaire gaschromatografie. In 1996 behaalde hij cum laude het ingenieursexamen met een afstudeeronderzoek naar de sporenanalyse van polaire verbindingen in lucht, uitgevoerd bij de vakgroep instrumentele analyse onder leiding van dr.ir. H.-G. Janssen, prof.dr. P.J.F. Sandra en prof.dr.ir. C.A.M.G. Cramers. Aansluitend werd bij dezelfde vakgroep het promotie-onderzoek gestart, waarvan de resultaten in dit proefschrift zijn beschreven. Tijdens dit promotieonderzoek werkte hij gedurende 18 maanden bij het Research Institute for Chromatography te Kortrijk, België en gedurende 2 maanden aan de University of Stellenbosch, Stellenbosch, South Africa. Met ingang van januari 2000 is hij werkzaam in de analytische biotechnologie groep van prof.dr. Th.G.M. Schalkhammer en prof.dr.ir. G.W.K. van Dedem aan de Technische Universiteit Delft.

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