Solventless Extraction and Enrichment Methods for Compound-Specific Isotope Analysis

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Die Natur und der Wahnsinn finden immer einen Weg.

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Table of Contents

Abbreviations and Symbols

$Amp^{total}_{(mass\ 44)}$	-	total amplitude of mass 44 for 100 % extraction
$Amp^{t}_{(mass\ 44)}$	-	amplitude of mass 44 at a specified time *t*
BSTFA	-	bis(trimethylsilyl)acetamide
Carbowax®	-	polyethylenglycol PEG
CME	-	capillary micrroextraction
DAI	-	direct aqueous injection
DCCC	-	droplet countercurrent chromatography
DI	-	direct immersion
ESD	-	equilibrium sampling device
f	-	degree of freedom
f_{air}	-	fraction in air
Film	-	film thickness
FTD	-	flame thermal detection
G	-	purge gas flow rate
GC	-	gas chromatography
HPLC	-	high performance liquid chromatography
HRGC	-	high resolution gas chromatography
HS	-	headspace
HSME	-	headspace solvent microextraction
i.d.	-	internal diameter
INCAT	-	inside needle capillary adsorption trap
In-tube SPME	-	in-tube solid-phase microextraction
ISD	-	in situ derivatisation
ISyD	-	in-syringe derivatisation
ITE	-	in-tube extraction ·
ITEX	-	in-tube extraction device
ITS	-	in-tube silylation
ITSPME	-	in-tube solid-phase microextraction
K_{aw}	-	air-water partitioning constant
$K_{o/w}$	-	octanol-water partitioning coefficient
K^s	-	Setschenow constant in $Lmol^{-1}$
K_{sa}	-	sorbent-air partitioning coefficient
kV	-	kilo volts
LC	-	liquid chromatography
LD	-	liquid desorption
LLE	-	liquid-liquid extraction
LOD	-	limit of detection
LOQ	-	limit of quantification
LPME	-	liquid-phase micro extraction
LVI	-	large volume injection
m/z	-	mass to charge ratio
MASE	-	membrane-assisted solvent extraction
MDL	-	method detection limit
MEPS	-	microextraction in packed syringes
micro-SPE	-	micro- solid-phase extraction
MS	-	mass spectrometry
NT	-	needle trap
o.d.	-	outer diameter
OTME	-	open-tubular microextraction

OTT	-	open tubular trapping
P&T	-	purge and trap
PA	-	peak area
PDMS	-	polymdimethylsiloxane
PDMS/AC	-	polymdimethylsiloxane + 10 % active charcoal
PTV	-	programmable temperature vaporizer
PVOCs	-	polar volatile organic compounds
RAM	-	restricted access material
R_s	-	chromatographic resolution
RT	-	room temperature
SBSE	-	stir-bar-sorptive extraction
s_d	-	standard deviation
SD	-	standard deviation
SDE	-	single drop extraction
SDME	-	single drop microextraction
SME	-	solvent microextraction
Sol-gel CME	-	sol-gel capillary microextraction
Sol-gel OTME	-	sol-gel open-tubular microextraction
SPDE	-	solid-phase dynamic extraction
SPE	-	solid-phase extraction
SPME	-	solid-phase microextraction
staticHS	-	static headspace
t	-	student *t*-factor
t	-	time
TD	-	thermal desorption
V_w	-	volume of the aqueous sample
$\dot{V}$	-	extraction flow rate
w/w	-	weight percent

Summary

Contamination of groundwater with polar and volatile organic compounds such as fuel enhancers, aromatic and chlorinated hydrocarbons is a serious problem in industrialized countries. Due to their adverse environmental effects, legal threshold values for most of these contaminants are in the low µg/L range. A very useful tool for the assessment of contaminant sources, tracking of contaminant flow paths and determination of degradation processes at contaminated sites is compound specific isotope analysis (CSIA). Unfortunately, compound specific isotope analysis with gas chromatography isotope ratio mass spectrometry (GC/IRMS) systems is less sensitive compared with gas chromatography mass spectrometry (GC/MS) systems and its applicability outside the source area of contaminated sites is often limited. To extend the fields of CSIA application to lower contaminant sites, it was the goal of this work to develop suitable enrichment and extraction techniques for various polar and volatile groundwater contaminants. To this end solventless, microextraction approaches such as headspace solid-phase dynamic extraction (HS-SPDE) and in-tube extraction (ITEX) were validated by GC/MS for the enrichment of volatile groundwater contaminants such as ethers, alcohols, halogenated methanes, ethanes and ethenes.

A HS-SPDE method was evaluated for three ethers and twelve alcohols. In this evaluation four different SPDE needle coatings with different phase polarities and sorption properties (WAX, 1701, PDMS, PDMS/AC) were tested. Lowest method detection limits (MDLs) in ng/L range were obtained with the WAX and the PDMS/AC phase. The second investigated HS-SPDE method was evaluated for halogenated hydrocarbons such as halomethanes and halogenated ethylenes. The method was thoroughly validated with method detection limits in ng/L range and precisions between 3.1-16 % for the investigated analytes were obtained. An ITEX method was evaluated and optimized for the determination of nineteen priority groundwater contaminants including halogenated volatiles and monoaromatic compounds. Method detection limits for monoaromatic compounds were between 28 ng/L (ethylbenzene) and 68 ng/L (1,2,4-trimethylbenzene). For halogenated volatile organic compounds MDLs between 48 ng/L (chloroform) and 799 ng/L (dichloromethane) were obtained. The precision of the method was between 3.1 % (toluene) and 7.4 % (1,2,3-TMB). Both investigated microextraction methods provide high sensitivities, short sample preparation and extraction times and a high sample throughput. For the HS-SPME methods the applicability to real samples was shown. For both methods the MDLs were determined by GC/MS and an evaluation of these two methods by GC/IRMS will be done in future works.

Finally, a commercially available purge and trap system was modified for the extraction of higher sample volumes to reach lower detection limits. The method was evaluated for twenty halogenated hydrocarbons and BTEX groundwater contaminants. Method detection limits for monoaromatic compounds between 0.07 and 0.35 µg/L are, the lowest MDLs reported so far for continuous-flow isotope ratio measurements using an automated system. MDLs for halogenated hydrocarbons were between 0.76 and 27 µg/L. The environmental applicability of the P&T-GC/IRMS method in the low µg/L range was shown in a case study on groundwater samples from a VOC contaminated former military air field. In connection with the purge and trap method validation a new approach to determine method detection limits in GC/IRMS based on an iterative moving mean method is presented. The results show that P&T offers the lowest method detection limits for volatile organic compounds in combination with P&T. Headspace solid-phase dynamic extraction as well as HS-ITEX in combination with GC/IRMS will be in the range between HS-SPME-GC/IRMS and P&T-GC/IRMS.

Zusammenfassung

Die Kontamination von Grundwasser mit polaren und flüchtigen Verbindungen wie Antiklopfmitteln, aromatischen- und chlorierten Kohlenwasserstoffen stellt ein ernstzunehmendes Problem in industrialisierten Ländern dar. Wegen ihrer nachteiligen Wirkung auf die Umwelt wurden für die meisten dieser Stoffe, Grenzwerte in µg/L Bereich festgesetzt. Als besonders nützliches Hilfsmittel bei der Erkundung kontaminierter Standorte in Bezug auf die Identifikation von Kontaminationsquellen, der Bestimmung von Fliesspfaden und Abbauprozessen im Aquifer hat sich die komponentenspezifische Isotopenanalyse erwiesen. Unglücklicherweise ist die komponentenspezifische Isotopenanalyse mittels Gaschromatographie Isotopenverhältniss Massenspektrometrie (GC/IRMS) im Vergleich mit Gaschromatographie Massenspektrometrie (GC/MS) Methoden wenig sensitiv, was die Anwendung auf hoch kontaminierte Standorte beschränkt. Um das Gebiet der komponentenspezifischen Isotopenanalytik auch auf gering kontaminierte Standorte zu erweitern, war es das Ziel dieser Arbeit neue, geeignete Anreicherungs- und Extraktionsmethoden für unterschiedlichste polare- und flüchtige polare Grundwasserkontaminanten zu entwickeln. Zu diesem Zweck wurden lösungsmittelfreie, Mikroextraktionsmethoden wie dynamische Gasraum Festphasenextraktion (SPDE) und die In-tube Extraktion (ITEX) für die Anreicherung polarer Grundwasserkontaminanten wie Ether, Alkohole, halogenierte Methane, Ethane and Ethene mittels GC/MS validiert.

Die erste HS-SPDE Methode wurde für drei Ether und zwölf Alkohole evaluiert, wobei vier verschiedene Extraktionsphasen unterschiedlicher Polarität (WAX, 1701, PDMS, PDMS/AK) und Sorbtionseigenschaften getestet wurden. Die geringsten Nachweisgrenzen in ng/L Bereich wurden mit der WAX und der PDMS/AK Phase erreicht. Die zweite hier untersuchte HS-SPDE Methode wurde für halogenierte Kohlenwasserstoffe wie Halomethane und halogenierte Ethylene durchgeführt. Die Methode wurde eingehend validiert, wobei die Nachweisgrenzen in ng/L Bereich, und die Präzision der Methode zwischen 3.1 und 16 % lagen.

In-tube Extraktion wurde für 19 leichtflüchtige halogenierte Kohlenwasserstoffe und monoaromatische Benzolderivate evaluiert und optimiert. Für die aromatischen Verbindungen wurden Nachweisgrenzen zwischen 28 ng/L (ethylbenzene) und 30 ng/L (1,2,3-Trimethylbenzol) erreicht. Für die leichtflüchtigen halogenierten Verbindungen wurden Nachweisgrenzen zwischen 48 ng/L (Chloroform) und 799 ng/L (Dichlormethan) ermittelt. Alle Untersuchten Methoden liefern hohe Sensitivität kurze Probenvorbereitungs- und Extraktionszeiten sowie einen hohen Probendurchsatz. Für die HS-SPDE Methoden wurde die Anwendbarkeit anhand von Realproben gezeigt. Sowohl die Evaluierung der SPDE Methoden als auch der ITEX Methode wurden Am GC/MS durchgeführt und anschließende Arbeiten sind nötig um die Methoden am GC/IRMS zu evaluieren.

Zusätzlich zur Evaluation dieser Methoden wurde ein kommerziell erhältliches Purge und Trap System so modifiziert, dass damit die Extraktion größerer Probenvolumina möglich wurde, um eine höhere Extraktionsausbeute zu erreichen. Die Methode wurde für zwanzig monoaromatische und halogenierte Kohlenwasserstoffe evaluiert. Die für monoaromatische Verbindungen erhaltenen Nachweisgrenzen liegen zwischen 0.07 und 0.35 µg/L und sind die bis jetzt niedrigsten erhaltenen Nachweisgrenzen für die Kombination von P&T und GC/IRMS. Für die halogenierten Kohlenwasserstoffe wurden Nachweisgrenzen zwischen 0.76 µg/L und 27 µg/L ermittelt. Die Anwendbarkeit der Methode wurde an realen, kontaminierten Grundwasserproben eines stillgelegten Militärflugplatzes getestet. Im Zusammenhang mit der Purge und Trap Methode wurde ein neurer Ansatz zur Ermittlung der Nachweisgrenze für GC/IRMS Methoden, beruhend auf einem iterativen

Mittelwert Verfahren verwendet. Die dynamische Festphasenextraktion sowie ITEX werden in Bezug auf die Nachweisgrenze im Bereich zwischen SPME-GC/IRMS und P&T-GC/IRMS anzusiedeln sein.

1 General Introduction and Theory

1.1 Compound Specific Isotope Analysis (CSIA)

Compound specific isotope analysis (CSIA) by using on-line continuous flow gas chromatography isotope ratio mass spectrometry (GC/IRMS) has found a wide application range in different disciplines such as geochemistry, environmental chemistry, archaeology, forensic-, bio- and food sciences.[1-4]

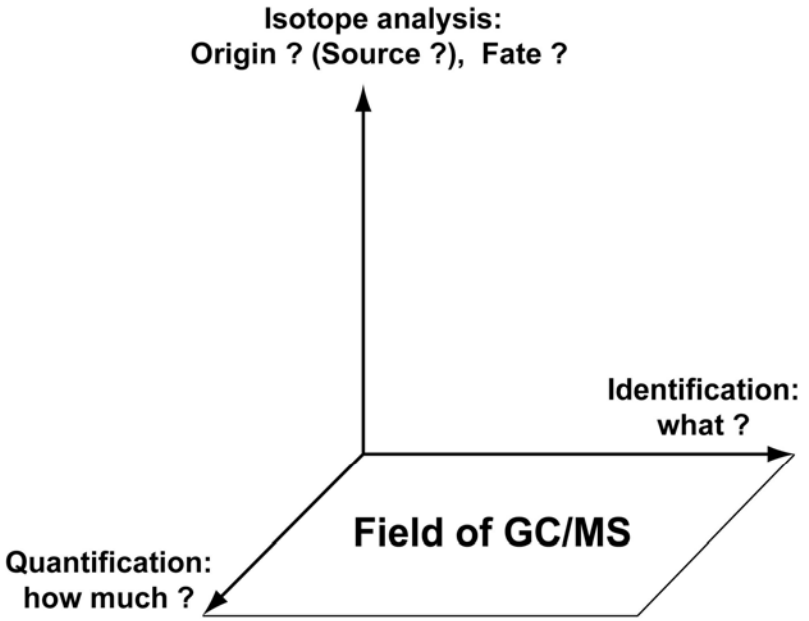

Figure 1.1 The compound specific isotope analysis (CSIA) by GC/IRMS gives additional information on origin and fate of analysed compounds.

In the last years CSIA has become a useful tool also in contaminant hydrology. Supplementary to qualitative and quantitative GC/MS analysis, compound specific isotope analysis opens another dimension (Figure 1.1) in the assessment of contaminated sites due to (i) identification of contaminant sources, (ii) tracking of contamination pathways[5], (iii) identification[6, 7] and quantification of chemical or biological remediation processes[8]. Especially, the determination of natural remediation processes in an aquifer is of high economic interest, because a time consuming and expensive technical remediation of contaminated sites is often not necessary. Thus, CSIA in combination with other hydrogeochemical parameters is the most promissing tool to characterise and quantify such natural remediation processes.[3, 9] Compound specific isotope analysis employs the determination of the ratio R_x between two stable isotopes of an element E (e.g. $^{13}C/^{12}C$, $^{2}H/^{1}H$, $^{18}O/^{16}O$, $^{15}N/^{14}N$) in a single compound x. The δ-notation and the system of differential measurements were introduced in the late 1940 by Urey and his collaborators to report comparable stable isotope data.[10, 11] In equation 1.1 it is defined as the relative difference in parts per thousand (per mil, ‰) between the compound's isotope ratio R_x and the isotope ratio of an international reference standard, $R_{reference}$.

$$\delta E_x = \left(\frac{R_x - R_{reference}}{R_{reference}} \right) \times 1000 \ [\text{per mil}] \qquad \textbf{(1.1)}$$

In case of carbon isotope measurements, Vienna Peedee Belemnite (VPDB) is used as international reference standard. For VPDB an internationally accepted $^{13}C/^{12}C$ ratio of 0.0111802 has been reported.[12] The measurement of relative differences in isotopic ratios instead of absolute ratios is used, because systematic errors can be eliminated, more precise values can be obtained and mass-discriminating effects in a single instrument can be corrected[3, 4]. More detailed information on referencing strategies in stable isotope ratio mass spectrometry is given in the literature. [4, 12]

1.2 Compound Specific Isotope Analysis Instrumentation

The hyphenation of gas chromatographic separation to an isotope ratio mass spectrometer was introduced by Matthews and Hayes in 1978[13]. In Figure 1.2, a schematic setup and a description of a gas chromatography-combustion-isotope ratio mass spectrometer GC/C/IRMS for carbon isotope ratio determination is shown.

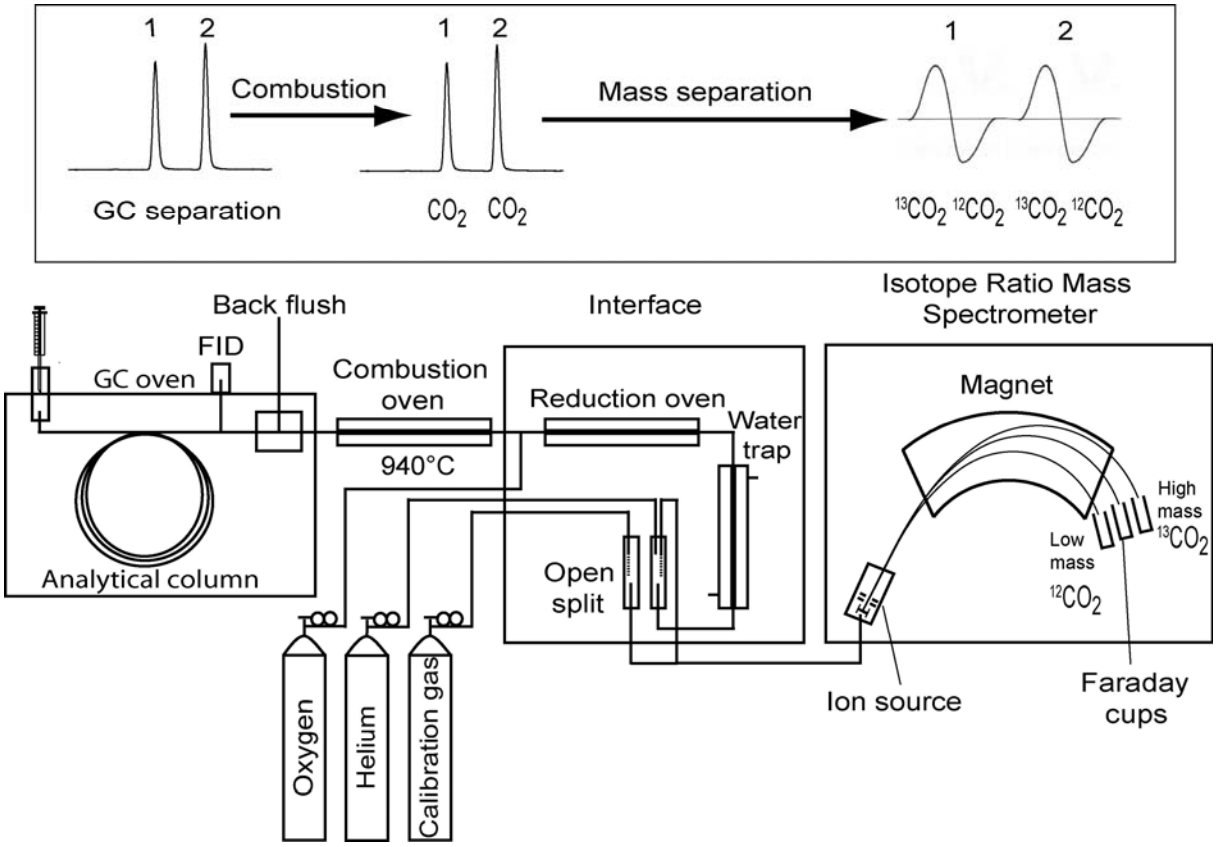

Figure 1.2 Schematic overview of a GC/C/IRMS for determination of $\delta^{13}C$ values. After injection, chromatographic separation of the analytes in a gas chromatograph takes place. After separation the analytes are completely combusted in a 940 °C hot catalytical reactor to CO_2 and H_2O. The catalyst in the reactor consists of PT/NiO/CuO wires. Nitrogen oxides that are formed during the combustion of nitrogen containing compounds are reduced to N_2 in the following reduction oven. Disturbing water is removed by a Nafion™ membrane. The water is removed to prevent formation of $^{12}CO_2H^+$ (m/z 45) during ionisation. Following combustion the CO_2 is ionized in the ion source of the mass spectrometer. After ionisation the formed isotopologues $^{12}CO_2$ (m/z 44), $^{13}CO_2$ (m/z 45) and $^{12}C^{18}O^{16}O$ (m/z 46) are diverted according to their masses in the magnetic field and detected in separate faraday cups. The amplification of the faraday cups is adapted to the natural isotope abundances of the detected isotopes. Mass 46 is used for correction of the relative abundance of ^{17}O by determination of ^{18}O in the mass 46 isotopologue.

Since the first commercially available system for carbon isotope ratio determination in 1988 the method was extended in 1992 to $^{15}N/^{14}N$ ratio measurements and more recently in 1996 to $^{18}O/^{16}O$ ratio determination.[4] In Table 1.1 an overview of the elements measureable by on-line GC-IRMS is given.

Table 1.1 With GC/IRMS measurable stable isotope ratios.[a)]

Stable isotope	Natural abundance of the heavier isotope (%)	Conversion gas	Measured m/z	Detection limits (nmol of element on-column)	Precision (%)
$^{2}H/^{1}H$	0.015	H_2	2,3	8 – 10	5
$^{13}C/^{12}C$	1.11	CO_2	44, 45, 46	1	0.2
$^{15}N/^{14}N$	0.366	N_2	28, 29, 30	0.8 – 1.5	0.5
$^{18}O/^{16}O$	0.204	CO	28, 29, 30	5	0.8

a) Values adapted from Ref.: [3]

However, GC measurements are limited to GC compatible substances, i.e. compounds establishing relatively low boiling points, mass to charge ratios lower than about 350 and sufficient stability against thermal decomposition. Other important points are that for accurate and precise GC/IRMS measurements a base line separation (chromatographic resolution $R_s > 1.5$) and a low chromatographic background noise are required.[4] Base line separation is required because integration over the entire peak from baseline to baseline gives the isotopic signature of one compound. If peaks are not baseline separated, a part of the later eluting lighter isotopologue form the first compound is mixed with a part of the earlier eluting heavier isotopologue of the following compound and a wrong isotopic ratio for both compounds is the result. The second point is that a high background noise caused by unresolved organic matter or column bleeding leads to a dilution of the isotopic signal.
Anoter restriction is that a derivatisation may lead not reproducible $\delta^{13}C$ values.[1] An extended discussion on derivatisation in GC/IRMS is given in chapter 1.5.1. To overcome some of these problems and to expand the field of CSIA to compounds not amenable to GC, several attempts to hyphenate liquid chromatography with isotope ratio mass spectrometry (LC/IRMS) have been reported.[14-17] More recently, a commercially available LC/IRMS was introduced.[18] The method applies wet chemical combustion of the analytes by an oxidizing agent such as ammonium peroxodisulfate at elevated temperatures. The CO_2 is separated from the liquid phase by a membrane and introduced by a Helium stream into the source of an IRMS. The method is restricted though to carbon isotopic measurements and water as eluent. In this study, only the separation by gas chromatography should be emphasized.
A major drawback of compound-specific stable isotope analysis in environmental applications is its rather poor sensitivity. [3] For a precise isotopic measurement, this represents at least ~1 nmol carbon of a given compound on-column for commercially available 3 kV GC/IRMS instruments. [19] That means that, e.g. 66 mg/L TCE have to be injected in 1 µL solvent. [3] However, environmental concentrations of interest are frequently lower, even at contaminated sites. For this reason the method is restricted to laboratory experiments or highly contaminated sites. This shows clearly that it is necessary to hyphenate efficient extraction and enrichment techniques with GC/IRMS in order to fully exploit the potential of the method. Unfortunately all extraction and enrichment methods involve the danger of isotopic fractionation and this caused by phase transfer processes. [19] Therefore it is necessary to evaluate these methods thoroughly. Table C 1.1 in the appendix gives an overview of the extraction and injection techniques for common groundwater contaminants used prior to GC/IRMS determination.

1.3 Extraction and Enrichment

Extraction and enrichment is one of the most important and often the most time consuming step in an analytical procedure.[20] Compared with sophisticated separation and detection techniques, extraction is often neglected or considered as analytical step of minor importance.[21] Nevertheless, the importance of extraction can not be overemphasised because all errors that occur in this step of the analytical process can not be corrected for by the best subsequent separation or detection method. Before a successful application of chromatographic methods, extraction is typically necessary in order to separate analytes from interfering matrix components and enrich them. A separation from matrix is especially important if non-specific detectors (e.g. flame ionisation detector FID, thermal conductivity detector TCD etc.) are used. As pointed out in chapter 1.2, a special and delicate example is GC/IRMS; here all mentioned factors are of importance. (i) A very good separation of analytes from matrix components to get accurate and precise isotope values is compelling [1, 22, 23], and (ii) for field applications enrichment and clean up is necessary. [3] In particular, the extraction of polar contaminants from aqueous matrices is often a challenge. Their environmental behaviour and fate is more difficult to evaluate and extraction is complicate because of their additional molecular interactions and high affinity to the aqueous matrix. Furthermore, polar organic compounds are becoming more important in the water cycle. Especially in the last years, a shift in focus in environmental chemistry towards polar compounds can be observed. [24] Reasons for this shift are (i) their importance in industrial production and wide application as functional additives (ii) their environmental formation during the degradation of non-polar precursors, (iii) their high environmental mobility as well as their persistence, and (iv) adverse effects for human beings and ecosystems. [25]
Here, the classification for non-polar and polar compounds according to Goss and Schwarzenbach will be used. [26] After this classification organic compounds can be categorized by their interaction forces in three groups. The first group contains apolar compounds such as alkanes and PCBs that interact only by van der Waals interactions. The second group, the monopolar compounds such as BTEX and chlorinated hydrocarbons interact by van der Waals forces and either as H-acceptors or H-donors. The third group, the bipolar compounds are able to interact by van der Waals interactions as well as H-donors and H-acceptors. Compounds that can be assigned to the last group are e.g. alcohols (phenols), carboxylic acids and amines. In this review the focus is set to monopolar and bipolar compounds. Another criterion, applied here for the reviewed compounds is an octanol-water partitioning coefficient, $K_{o/w}$ of less than 1000 ($log\ K_{o/w} \leq 3$).

1.4 Established Extraction and Enrichment Approaches; their Advantages and Limitations

1.4.1 Static Headspace

For PVOCs the method of choice used to be static headspace gas chromatography (staticHS/GC). [27] The method has the advantages, that a clean-up can be avoided because disturbing matrix components remain in the solution and the method is completely solventless. A major disadvantage is the often rather low sensitivity caused by low air-water partitioning constants (K_{aw}) of the target analytes. In combination with GC/IRMS, staticHS analysis was applied in different studies.[28-33]
As pointed out in Table 1.2, headspace injection does not fractionate significantly for MTBE [28, 29] BTEX [30-32] and chlorinated ethylenes. [32] Hunkeler et al., however, found significant isotopic fractionation between 1.03 to 1.29 ‰ for chlorinated methanes.[33] Method detection limits for $\delta^{13}C$ staticHS-GC/IRMS applications are between 100 to 500 µg/L for BTEX [30-32], 4000-5000 µg/L for MTBE[28, 29], 800-3300 µg/L for chlorinated methanes[33] and 400 µg/L for chlorinated ethylenes.[32] For $\delta^{2}H$ measurements, staticHS-GC/IRMS with about ten times higher method detection limits were obtained.[28]

1.4.2 Purge and Trap

To overcome the relatively low sensitivity of staticHS, exhaustive dynamic headspace methods, e.g. purge and trap (P&T) were developed. P&T was developed thirty years ago[34], and in combination with GC/MS it is nowadays a routine method for trace analysis of volatile organic compounds (VOCs) in water samples. Especially in the US, several EPA protocols for the determination of volatiles in drinking, waste and hazardous waste water rely on it. [35] Static headspace as well as P&T can be easily automated. Neither P&T nor static headspace can be used directly for an extraction in the field but a more recent development is a continuous on-line purge and trap method.[36]
Application of P&T-GC/IRMS has been reported several times [19, 37-41] and showed lowest detection limits in CSIA for VOCs by achieving highly reproducible compound-specific isotope enrichments (0.2-0.9 ‰).[3, 19] A more detailed overview of P&T as enrichment method for CSIA is given in section 5.1.
The extraction of analytes from aqueous matrices can be subdivided in traditional and non-traditional techniques (microextraction approaches).[42] The most common traditional and widespread method is liquid-liquid extraction (LLE). It is based on analyte partitioning between water and an immiscible organic solvent. LLE is simple, and many US-EPA protocols for environmental analysis still rely on LLE.[43, 44] These methods typically need large volumes of sample and organic solvent (100-250 mL or even more) as well as repeated extraction for sufficient enrichment yields, clean-up and concentrating by evaporation or distillation are necessary. These multiple working steps make the methods laborious and time consuming. Other drawbacks of LLE include possible formation of emulsions, errors by repetitive manual operations and potential losses during the procedure.[21, 45] Additionally, LLE can hardly be automated and used for field analysis.[44, 46] The organic high purity solvents used are usually toxic, harmful for the environment and not negligible quantities of solvent waste have to be handled. A problem that especially occurs in the extraction of polar organics is that the used polar solvents dissolve to a certain content in the water phase. At the latest, since the Montreal Protocol´ treaty and the limited use of ozone layer destroying chlorinated solvents, e.g. chloroform and dichloromethane (often used in LLE), the analytical chemists developed alternative extraction methods.[21, 42, 47] One group of these alternatives is solid phase extraction (SPE). In water analysis, SPE is nowadays the most widely used sample preparation technique for non-polar compounds.[44] It offers a wide field with a lot of applications and was often subject of detailed reviews[48-50], and monographs.[51] An aqueous sample passes through a solid sorbent bed, packed inside a disk or cartridge, in which the analytes are trapped on an immobilised phase and later re-extracted by organic solvents. Advantages of SPE are often lower (but not negligible) amounts of organic solvents, suitability for field sampling and automation of the sampling process. [44, 45] SPE with subsequent thermal desorption was applied by Vreuls et al. [52, 53] and Mol et al. .[54] In these methods a liner, filled with a sorbent material was used as SPE extraction device. After extraction it was inserted directly into a programmable thermal vaporizer (PTV). Water was removed through the split vent of the injector by evaporation in the carrier gas stream whereby analytes stay trapped in the coating and were subsequently thermally desorbed into the GC column for separation. This technique is strongly related to large volume injection (LVI) and direct aqueous injection (DAI) [55, 56] into GC, combined with previous separation of water and was reviewed several times in this context. [57-60] Limited efficiencies by insufficient retention (low breakthrough volumes) can be observed for volatiles and very polar compounds. [43, 61] More recently, micro-SPE methods were introduced with the aim of sample and sorbent reduction. [62, 63] SPE as well as micro-SPE uses breakthrough sampling for enrichment, what means that the analyte is trapped as long as the capacity of the sorbent in suffient. Gum-phase extraction (GPE) is very similar to SPE but as trapping material a bed of polydimethylsiloxane (PDMS) is used instead of an adsorptive solid package. [64-66]

1.5 Microextraction approaches and techniques

A dominant trend in sample preparation is miniaturisation and over the last 15 years different solvent-less or solvent-reduced extraction methods on a micro scale approach were developed. After Lord and Pawliszyn, microextraction is defined as a technique where the volume of the extraction phase is very small in relation to the sample volume. [67] Another criterion for microextractions, in contrast to exhaustive methods is that only a fraction of the analytes is extracted.[24] Because of this, microextraction devices can be used as equilibrium sampling devices (ESDs) that have a negligible impact to the sample.[68] Miniaturized extraction has several advantages. (i) The devices can be used directly in the field without long preparation and with less equipment. (ii) It is often easier to implement miniaturized devices in already existing systems and a connection with GC or HPLC is often straightforward. (iii) Miniaturized devices or techniques have lower operating costs and are less laborious and time consuming. (iv) Another dominant point is that these methods can be partly or fully automated, which leads to higher sample throughput, better reproducibility and simple on-line hyphenation. A detailed overview of automation of solid-phase microextraction was given by O´Reilly et al. .[69] Here, an overview over recent developments in microextraction techniques and new developments in solid-phase microextraction (SPME) should be given. SPME will be discussed in much less detail and the reader is referred to monographs [44, 70] and reviews [42, 61, 71-73] for more detailed information.
All extraction methods whether they base on large scale extraction or on a microextration approach have in common, that one or more compounds are depleted in a sample and enriched in an extraction phase. The sample matrix can be manifold. Here the focus is set on water as sample phase or the headspace above the water phase, respectively. The extraction phases used for analyte enrichment from aqueous matrices are usually organic solvents, solid adsorbents, liquid state polymers or mixtures of the latter two materials. Two fundamental extraction processes can be distinguished. In case of the liquid coatings partitioning into the extraction phase with additional solvation of the molecules by the liquid coating takes place. Analyte molecules can diffuse in the whole liquid coating within the extraction time by diffusion. Solid sorbents have a defined crystalline structure and due to very low diffusion coefficients in solids, in an adequate timescale only adsorption on the sorbent surface takes place. Because only a limited space is available, a competition of analytes for free adsorption sites at higher concentrations can occur. This causes displacement (competition effects) of analytes with lower affinity to the sorption phase.[19]

1.5.1 Solid-Phase Microextraction (SPME)

Solid-phase microextraction (SPME) was the first microextraction method that was introduced by Pawliszyn and co-workers in the early 1990s[74, 75] and it is nowadays the most prominent and widely used microextration method with a wide range of applications and hundreds of publications. The method combines several steps such as sampling, enrichment and sample clean-up. A thin fused silica fiber coated with extraction phase is utilized for the extraction of analytes from aqueous samples. This fragile fiber is fitted in a special syringe holder for its protection during penetration of vial and GC injector septa. Fibers are used in two application modes. One mode is the direct immersion of the fiber (DI-SPME) into the sample, the other one is analyte extraction from headspace above the sample as shown in Figure 1.3 a and b. Different extraction phases are commercially available. The classical absorption coating for non-polar compounds is liquid phase polydimethylsiloxane (PDMS). For polar and volatile polar compounds, polyacrylate (PA), polyethylenglycole (Carbowax) or mixed phase coatings, with embedded sorbent particles in the liquid extraction phase such as carboxen™/polydimethylsiloxane (CAR/PDMS) can be used. Two approaches are followed to expand the application range for polar analytes. One approach is the development of derivatisation techniques for polar compounds. A review of derivatisation for polar compounds and SPME was given by Quintana and Rodriguez. [24] Two derivatisation strategies were used; the first is on-fibre and the second in-port derivatisation. In the first case, the derivatisation reaction occurs before or during

the extraction. In the second case polar analytes with acid-base properties are extracted as ion pairs, which are thermally decomposed in the GC injector. [24] However, derivatisation prior to GC/IRMS is not recommended because of ^{13}C dilution by carbon added during derivatisation, kinetic isotope effects during the derivatisation reaction and changes in the isotopic signature. [1] A second approach to expand SPME to more polar compounds is the development of polar extraction coatings. The use of sol-gel reactions seems to be a promising approach. By sol-gel processes the extraction phase can be chemically bonded to the silica rod and highly cross-linked phase networks can be synthesised. As a result, higher thermal stabilities and surface areas can be obtained.[76] Higher mechanical and pH stabilities were reached with surface-bonded sol-gel titania hybrid organic-inorganic[77] and zirconium based materials. [78] Other types of coating materials are electrochemically polymerised polyaniline for the extraction of phenols[79] and aliphatic alcohols [80] from water and anodized zinc[81], aluminium [82] or copper wires. [83] A more detailed discussion of customary SPME coatings for polar analytes can be found elsewhere. [24, 84]

Main drawbacks of SPME are limited lifetimes of relatively expensive fibers. Several problems result from the technical construction of the SPME device itself. The most common practical problems facing SPME are mechanical damage of the coating due to scraping, needle bending and fiber ruption caused by the fragility of the fused silica support. Several attempts to overcome these mechanical related drawbacks were done, such as the introduction of bendable StableFlex fibers with an alloy core. [24] Because of these drawbacks and the limited applicability to polar compounds, several new microextraction approaches were developed to overcome such problems (see below).

1.5.2 Solid-Phase Microextraction and CSIA

Solid-phase microextraction was used in direct immersion[19, 33, 85] as well as headspace extraction[28, 86] mode. As shown in Table 1.2 direct immersion SPME reached method detection limits between 9-22 µg/L and showed no significant isotopic fractionation for BTEX compounds. [19, 85] For MTBE, headspace SPME showed slight fractionation for $\delta^{13}C$ measurements (-0.9 ‰[28] and -0.67 ‰ [86]) and method detection limits between 11-350 µg/L. For MTBE extraction by direct immersion SPME no significant isotopic fractionation was observed. [19] Hunkeler et al. found a significant negative deviation for SPME analysis of TBA (-1.18 ‰) [86]. Because of this, Hunkeler et al. used corrections in order to allow a comparison with data generated by different methods.[8] If fractionation is observed it tends to yield negative deviations from pure phase standards, i.e., the lighter compound partitions stronger into the fiber. This is in principle the same isotope type of effect as found in gas chromatography. Although this effect is often quite small, for highly chlorinated compounds Zwank et al. [19] found substantial deviations (-7.3 ‰) using direct immersion SPME, which could not be explained. However SPME is a useful tool in combination with GC/IRMS when all parameters are hold constant and a previous evaluation for possible isotopic fractionation has been carried out.

1.5.3 Stir Bar Sorptive Extraction (SBSE), High Capacity Headspace Extraction (HSSE) and Rod Extraction

Stir bar sorptive extraction (SBSE) utilizes a glass incorporated magnetic stir bar coated with a polydimethylsiloxane (PDMS) extraction phase as shown in Figure 1.3 d. The method was introduced by Sandra et al. [87] and is based on the same principle as solid-phase microextraction but exhibits a bigger extraction phase volume and due to this a higher sorption capacity. As example, a 100 µm PDMS fiber with a length of 1 cm has a volume of about 0.6 µL compared with volumes between 24-126 µL for the commercially available PDMS stir bar coatings. PDMS coated stir bars were commercialised under the brand name "Twister™" by Gerstel (Mülheim a.d. Ruhr, Germany). In various studies, a correlation between the PDMS/water partitioning coefficent ($K_{PDMS/w}$) and the octanol-water partitioning coefficient ($K_{o/w}$) was made, according to the following equation:

$$K_{o/w} \approx K_{PDMS/w} = \beta(m_{PDMS} / m_w) \quad \textbf{(1.2)}$$

where, β is the phase ratio between the volume of the aqueous sample and the volume of the PDMS phase and m_{PDMS}, m_w are the masses of the solute in the PDMS phase, and the solute in the water phase, respectively. With this estimation it is also possible to calculate theoretical recoveries:

$$m_{PDMS}/m_o = \frac{\left(\frac{K_{o/w}}{\beta}\right)}{1+\left(\frac{K_{o/w}}{\beta}\right)} \quad \textbf{(1.3)}$$

where, m_0 is the original amount of solute in the aqueous phase. According to equation 1.3 low recoveries (under 50 %) are expacted for compounds with $K_{o/w}$ values <10000 (log $K_{o/w}$ < 4) for a 0.5 µL PDMS SPME fiber and a 10 mL sample. With coated stir bars of a volume ranging from 25-125 µL PDMS, theoretical recoveries close to 100 % are achieved under the same conditions for solutes with $K_{o/w}$ values larger than 500 (log $K_{o/w}$ > 2.7). Due to these considerations, quantitative extraction can be obtained for more polar analytes with much lower $K_{o/w}$ in SBSE and HSSE compared with a PDMS SPME fiber.[87, 88]

As shown in Figure 1.3 c and d, the stir bar is either placed directly into the sample or in case of high-capacity headspace sorptive extraction (HSSE), in the headspace above the sample. In case of direct immersion into the sample, the bar is stirred for a fixed time with a fixed stirring speed. Typical stirring times are between 30 and 60 minutes.[89] After extraction, the bar is removed from the sample solution with tweezers and dried with a lint-free tissue. After this, thermal desorption (SBSE-TD) or desorption with a solvent, followed by large volume injection (SBSE-LVI) [90] into a GC is carried out. For thermal desorption, the bar is transferred into a glass thermal desorption tube and introduced automatically into a thermal desorption module. Desorbed compounds are transported under helium flow and cryofocused with liquid nitrogen in a programmed temperature vaporizer (PTV). Different studies dealing with extraction of priority water contaminants by SBSE[88, 91] and off-flavour compounds.[92-96] The analyte spectrum includes polar compounds such as pesticides[97-102], endocrine disruptors[90, 103-105], as well as polar phenols [106-111] and bisphenol A.[112] An overview of SBSE extraction for polar compounds is given in appendix C (Table C 1.1). For liquid desorption of stir bars and subsequent large volume injection, the bar is introduced in a low volume of an organic solvent (e.g. isooctane) for a certain time under stirring at room temperature. An aliquot of up to 250 µL is than introduced in a LVI capable GC injector. Serôdio et al. used this combination for screening of more than 60 endocrine disrupting chemicals, including herbicides, organochlorines and organophosphorous pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, biocides, phthalates and alkylphenols in water samples. [105] As in SPME, in-situ derivatisation was applied several times to convert analytes into GC amenable compounds and to lower polarity by transformation of polar functional groups. Derivatisation leads often to sharper peaks, better separation and higher sensitivity. [113, 114] In situ-derivatisation of phenols and chlorophenols [113] with acetic acid anhydride was perforemed has been reported several times.

A special derivatisation method, named in-tube silylation was used by Kawaguchi et al. .[108] The derivatisation takes place in the thermal desorption unit. For this a glass capillary tube is placed behind the PDMS stir bar and the derivatisation reagent (*N*,*O*-bis(trimethylsilyl)acetamide, BSTFA) is transported in the gas stream to the bar, where the derivatisation takes place.

High-capacity headspace sorptive extraction (HSSE) was described by Tienpont et al. for extraction of 45 volatiles from aqueous solutions as well as flavour aroma compounds of coffee and bananas. [115] As shown in Figure 1.3 c, headspace bars consist of a glass rod of ca. 5 cm length with a PDMS tubing over the last cm and are very similar to SPME fibers. These rods are mounted in the screw caps of headspace vials or Erlenmeyer flasks. After extraction, the rods are manually put in an empty glass tube for thermal desorption as used for SBSE extraction. Headspace bars with 50 and 100 mg PDMS coating are available (Gerstel, Mühlheim a.d. Ruhr, Germany). Tienpont et al. compared in their

work, HSSE rods (50 mg, 51.5 µL PDMS) with SPME (100 µm, ~0.6 µL PDMS) for hydrocarbon, aromatic hydrocarbon, chlorinated hydrocarbon and ester model compounds (with log $K_{o/w}$ between 1.1 and 6.7) under identical extraction conditions. Limits of detections (0.02-0.150 ng/L) obtained for HSSE with a 51.5 µL extraction phase, were in the same order of magnitude as for SBSE with a 55 µL phase in the liquid phase (0.01-0.5 ng/L) for similar compounds. [87, 115] Montero et al. used an ordinary PDMS rod (see Figure1 e) for the extraction of unpolar chlorinated aromatic compounds and PCE by shaking those over head in sample bottle. [116] With subsequent thermal desorption he this overcomes high costs for coated stir bars with comparable results, and thus could be a viable alternative.

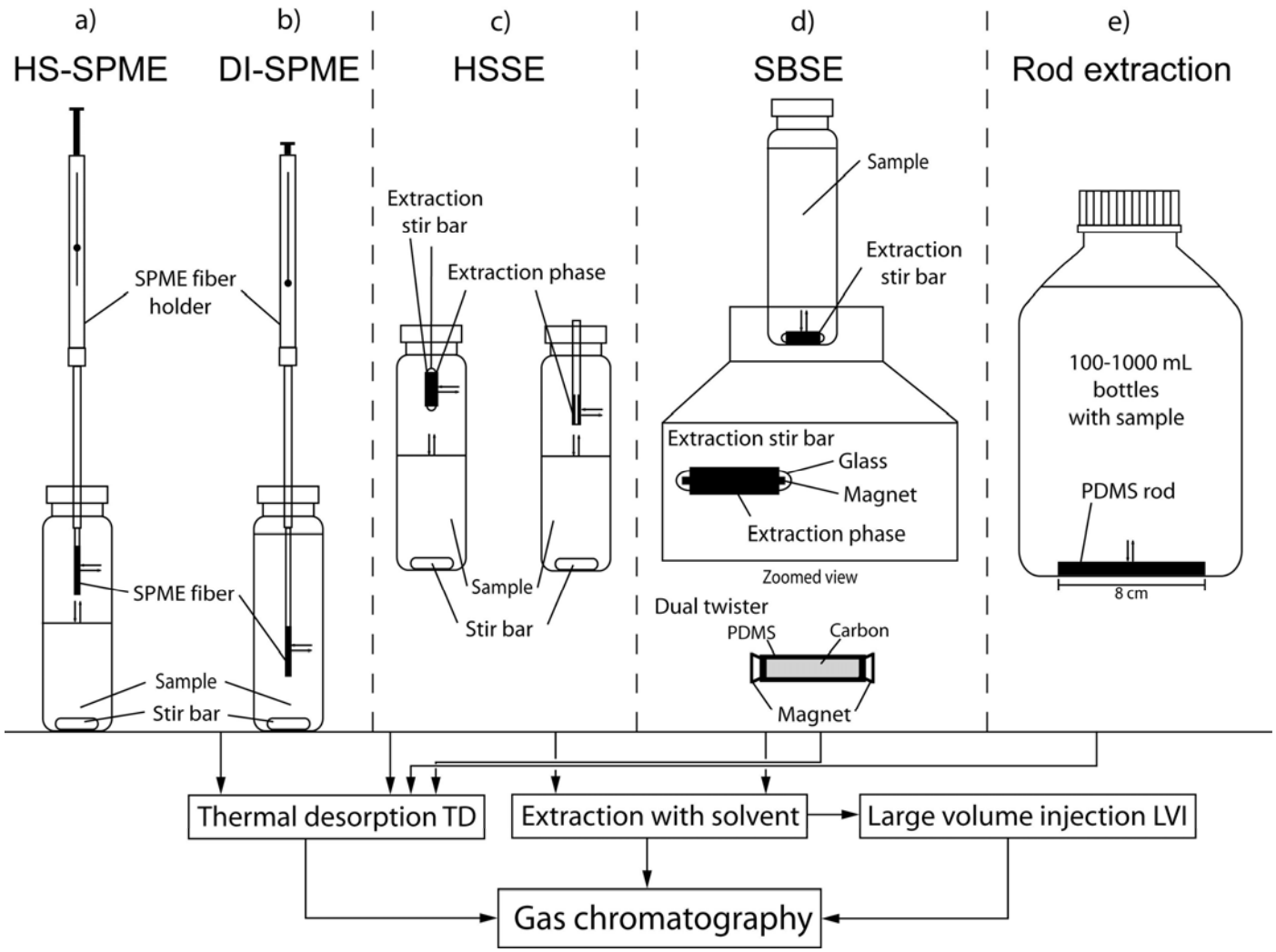

Figure 1.3 Various microextraction methods and applied desorption techniques : a) Headspace solid-phase microextraction (HS-SPME) drawn after Ref. [73]; b) Direct immersion solid-phase microextraction (DI-SPME) drawn after Ref. [73]; c) High capacity headspace sorptive extraction (HSSE) drawn after Ref.: [115] and [117]; d) Stir bar sorptive extraction (SBSE) drawn after Ref.:[89]and Dual twister after Ref.: [118]; e) Rod extraction re-drawn according to Ref.: [116]

As alternative methods, SBSE, HSSE and rod extraction have also some drawbacks. A major one is that a few laborious manual steps such as removing of the stir bar (or PDMS rod) with tweezers, rinsing and drying are necessary and can lead to errors.[119] Because of these drawbacks, procedures with less intermediate steps for minimizing errors and higher sample throughput were developed. An automated high-capacity sorption probe that utilizes a PDMS rubber tubing mounted on a rod was presented by Pettersson et al.. [119] The PDMS phase volume is with 120 µL comparable with a stir bar of 2 cm length and a 1000 µm film thickness (126 µL). The sampling procedure was completely carried out by a robotic autosampler and the system was evaluated for 44 environmentally harzardous compounds (amines, chlorinated aromatics, nitro aromatics, PAHs). The extraction efficiencies for compounds with a log $K_{o/w} \leq 3$ were between 5.2 and 14.4 % for one hour extractions with RSD between 4.7-6.2 % (n = 5). It was shown that the increased volume and surface area of the extraction phase leads to high extraction rates at the initial state of the extraction, indicated by fast increasing sorption profiles. Although higher recoveries for polar compounds can be achieved with bigger PDMS sorption phase volumes, limits in effectiveness and extraction yields of these methods for polar organic compounds were observed. [115] Recently, Bicchi et al. introduced a dual-phase twister. [118] This twister consists of a short PDMS tube closed at both ends with two magnets (Figure 1.3 c). The inner volume is filled with an activated carbon packing material. In a preliminary study he investigated the applicability of this twister for volatiles from coffee, whiskey and atrazine spiked water. They observed for atrazine a 80 % increase in absolute percent recovery for a dual-phase twister compared with a conventional SBSE twister. So far, SBSE-TD-GC/IRMS was applied only one time for the determination of MTBE, TBA and TBF by Veld and coworkers but so far no published results are available. [120]

1.5.4 In-needle, in-tube microextraction techniques

Different in-needle or in-tube extraction (ITE) techniques were developed to overcome, fiber related drawbacks such as fragility, low sorption capacity[121] and bleeding from thick film coatings.[122] In-tube techniques can be used either in a static or a dynamic mode. In the static mode, analytes are transferred to the sorbent only by diffusion. In dynamic mode the analytes are transferred actively by pumping or under gravitational flow of sample phase through the needles or tubes. [73] The techniques can be divided in methods that apply either a coating as internal extraction phase immobilized in the needle or capillary wall and methods that use a sorbent packing material as extraction phase.

1.5.4.1 Methods with Extraction Coatings

In-tube SPME is a sample preparation technique that uses, open tubular fused silica GC capillaries with stationary phase coatings instead of externally coated fibers. Eisert and Pawliszyn developed in-tube SPME for hyphenation with HPLC because fiber-SPME hardly can withstand aggressive HPLC solvent conditions.[73, 123] They placed a PEG wax coating between the autosampler needle and the injection valve. In their work they described the theoretical aspects of in-tube SPME and demonstrated the applicability of this method for six phenylurea pesticides. [123] The method was subject of several reviews. [72, 89, 124]

In-tube solid-phase microextraction was also coupled with gas chromatography. Although this approach was named in-tube SPME, it is basically similar to open tubular trapping (OTT).[124] In OTT, a short capillary GC column is also used for the extraction of analytes from water. The method was developed as alternative to solid phase extraction and the main advantage of the method was the easy removal of water by purging a short gas plug through the column.[125] Desorption of the trapped analytes is done either with a small amount of solvent or by thermal desorption. OTT or In-tube SPME overcomes mechanical instability problems inherent in conventional SPME, but this approach suffered

from complex instrumental setups and unfavourable sampling conditions as high pressure drops for long traps and limited sample flow rates. [115]

A method that applies only a short piece of coated column is sol-gel capillary microextraction (solgel-CME). It was used for extraction of phenols, alcohols and amines from water samples. [121] For the extraction, a special in-house-assembled-gravity-fed sample dispensing unit as illustrated in Figure 1.4 c, was used. An aqueous sample of 25 mL was filled in the dispenser and was allowed to flow through the extraction capillary under gravity. After extraction, the capillary was purged with helium gas and connected to the injection port of a GC. The method offers very low detection limits in the low ppt range (see appendix C, Table C 1.2) for GC-FID measurements. The authors reported for polar and non-polar analytes run to run RSD values for GC peak areas smaller than 6 % and 4%. For desorption, they connected the capillary with the extracted analytes to the inlet end of the GC column by using a two-way press fit fused silica connector inside the GC injector. This procedure can not be automated, is time consuming and seems to be a real drawback to the method. Nevertheless, the sol-gel approach seems to be promising, perhaps if it is used in combination with easier automatable methods. Other methods that use inside coated needles, are capillary adsorption trap (INCAT) by McComb[126] and Shojania [127, 128] and solid-phase dynamic extraction(SPDE) that has been evaluated in this work. Shojania et al. used the INCAT device as passive and active sampler for BTEX from air samples by using colloidal graphite paint as extraction phase. They reported reproducibility's for mixed BETX solutions and active sampling between 6.3-9.3 % RSD. [128] In another study, they used the device for fingerprint analysis of different fuels, paint thinners and lighter fluids with a detection limit of 65 ppb for benzene and a reproducibility for GC fingerprints with an average RSD of 9.8 %.[127] In case of SPDE, syringes with PDMS (polymdimethylsiloxane), PDMS/AC (polymdimethylsiloxane+10% active charcoal), CT-5 (5% diphenyl / 95% dimethyl polysiloxan, Carbowax™ (polyethylenglycol PEG), CT-1701 (14% cyanopropyl / 86% dimethylpolysiloxan), CT-225 (50% cyanopropyl / 59% polysiloxane) and custom made coatings are commercially available. SPDE needle coatings possess around 4-6 times larger extraction phase volumes compared to a 100-µm PDMS SPME fiber. [129 130] The first SPDE paper dealing with pesticides in water samples was published by Lipinski et al. [131] in 2001 and since this time only a few papers and application notes appeared. Lipinski used an ordinary steel GC capillary for extraction of pesticides from water samples. Recently, SPDE has been applied in forensic, food and environmental analysis for various analytes. Forensic applications were reported for cannabinoids [132], amphetamines [133] and synthetic designer drugs in hair samples.[129] Bicchi et al. used HS-SPDE for the analysis of volatile flavors in aromatic plants and food matrices.[130]

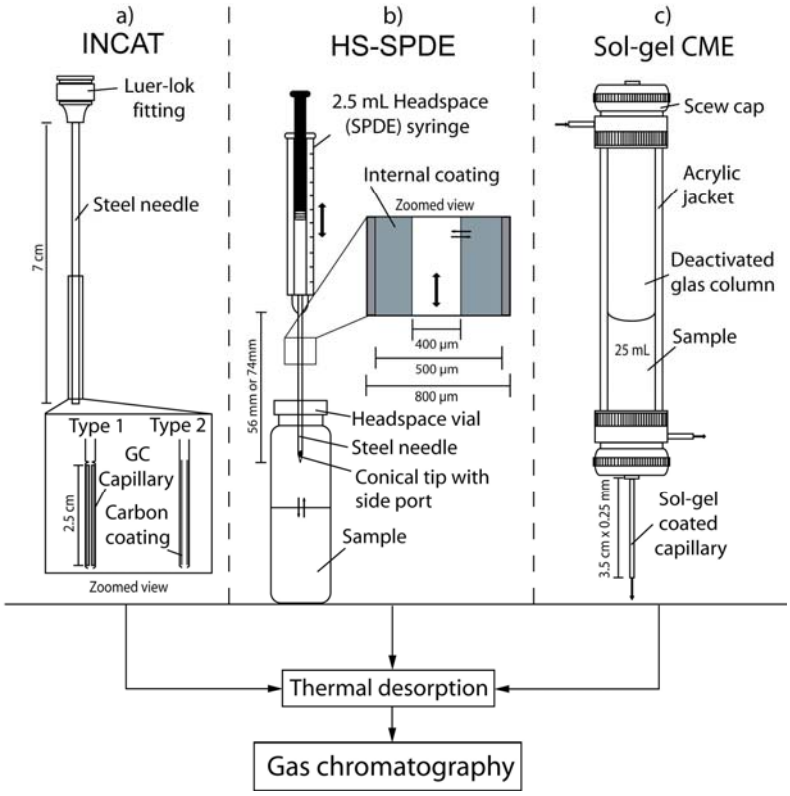

Figure 1.4 In-needle and in-tube techniques with internal coatings as extraction phase. a) Inside needle capillary adsorption trap (INCAT) re-drawn after Ref.:[126]. Type 1 utilizes a 2.5 cm long GC capillary (DB-5) as extraction phase. In Type 2 a carbon coating (colloidal graphit paint was used as sorbent). b) Solid-phase dynamic extraction (SPDE) c) Sol-gel CME gravity extraction device re-drawn after Ref.:[121].

1.5.4.2 Methods with Extraction Fillings

All previously discussed in-tube or in-needle techniques, employ stationary phase films coated inside on the tube wall. The following in-needle techniques make use of different types of sorbent particle beds inside the needle. These methods show particularly similarities to SPE. A method that is very similar to SPE, is a cartridge filled with PDMS particles introduced by Baltussen et al.. [64] The method was used for retention modelling of pesticides, PAHs and for the determination of acetylated phenols from water samples. [65] For the determination, 10 mL sample containing derivatized phenols were enriched onto such a PDMS cartridge and then thermodesorbed in a thermodesorber unit as it is used for SBSE or HSSE. Limits of detections were between 1–5 ng/l (S/N: 8/1) with recoveries between 72-109 % (RSD: 2-16 %, 0.1 ppb standard, n = 3). An in-needle trap was developed by Berezkin and Kubinec. [134] A similar method by Kubinec utilizes a 5 mL glas syringe connected via a micro valve to a 9 cm long stainless steal needle. The needle is filled as shown in Figure 1.5 with Porapak Q and aluminium oxide. The syringe needle is immersed directly into the sample which is then aspirated into the syringe. By passing the Porapak Q and the aluminium oxide bed, analytes were adsorbed. The device is then flushed with air to remove residual water. After valve closing, analytes were thermally desorbed into the hot injector. Aluminium oxide functions as water reservoir. During the thermal desorption this water evaporate and transports the analytes with the vapour stream out of the needle. These techniques are easy to implement in existing autosampler systems. A disadvantage of all these direct immersion in-needle techniques is that even very tiny particles are able to block the needles and tubes, which requires very clean samples or headspace extraction. All inside needle techniques have in common, that have not yet found such a wide acceptance as SPME.

Another device, that uses a filling inside a stainless steel needle is the needle trap (NT) by Wang and Pawliszyn. [135] This needle trap is either filled with Carboxen 1000™ or with a mixed packing of PDMS, DVB and Carboxen particles. Wang et al. reported detection limits between 0.23 ng/L – 2.10 ng/L for benzene gas samples. By Saito et al, a needle extraction device for GC/MS analysis of VOCs (Toluene, ethyl acetate) was presented[136]. As extraction phase a copolymer bed of methacrylic acid and ethylene glycol dimethacrylate was used.
All in-tube or in-needle microextraction techniques provide low method detection limits and relatively good precision. So far no application of these methods in combination with CSIA has been reported.

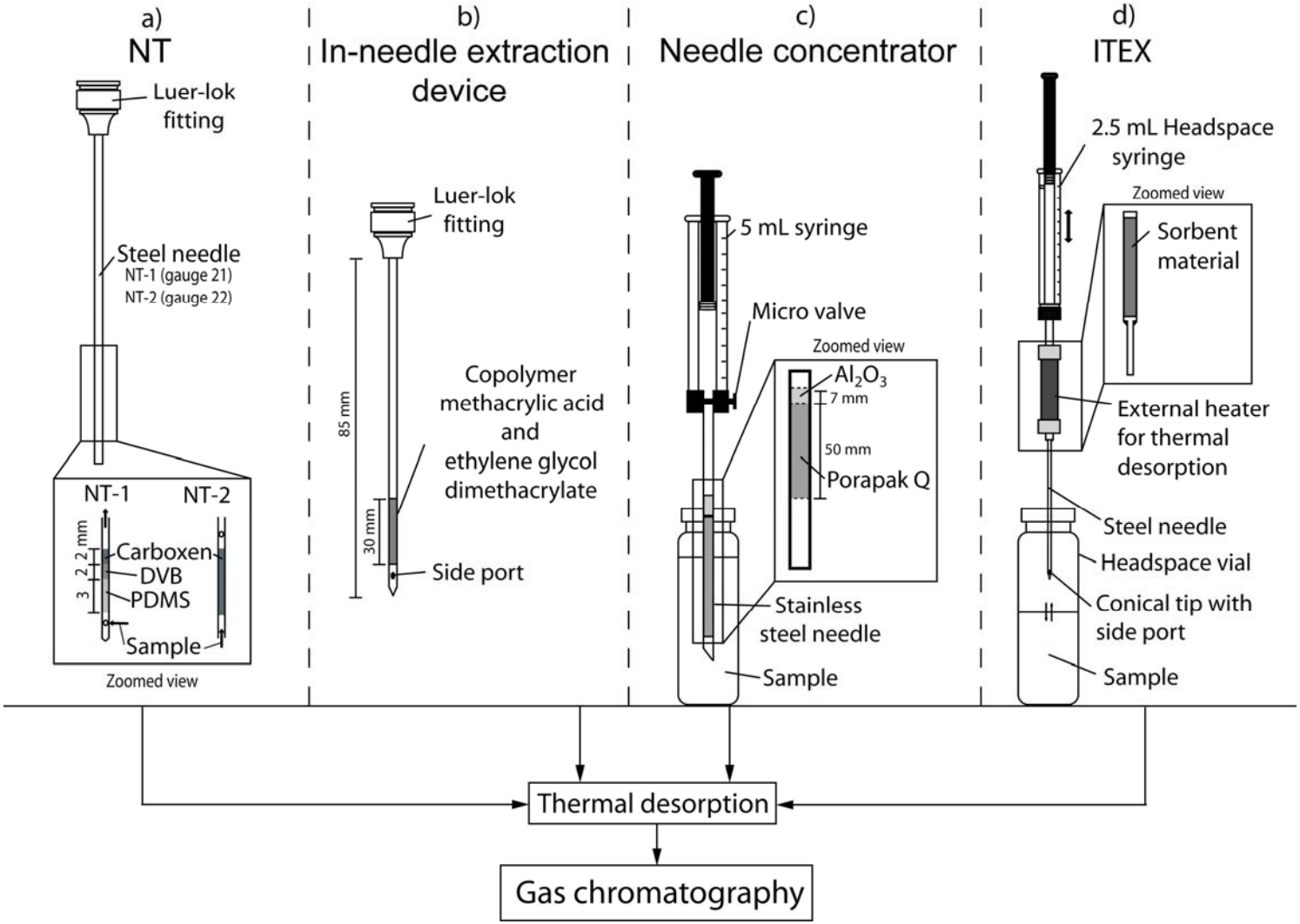

Figure 1.5 In-needle and in-tube techniques utilizing sorbent packing material as extraction phase. a) Needle trap device re-drawn from Ref.:[135]. NT-1 is filled with three different types of sorbent particles. NT-2 is filled with Carboxen 1000 as sorbent packing material. b) In-needle extraction device re-drawn after Ref.:[136] c) Needle concentrator re-drawn after Ref.:[137] d) In tube extraction device (ITEX) from BGB-Analytik.

1.5.5 Liquid-Phase Microextraction Techniques

Liquid-phase microextraction (LPME) is a simple extraction approach that combines classical liquid-liquid extraction with microextraction by greatly reducing the solvent to sample phase ratio. For extraction, a very small drop of a water immiscible solvent or in case of headspace measurements, a high boiling solvent is applied for analyte extraction from water samples. Drop volumes are in the micro- to picoliter range, and the technique can be categorized by the used sample volumes. Here only microdrop-LPME is included considered. The method was introduced by Jeannot and Cantwell in 1996 with detailed theoretical considerations about mass-transfer in the extraction process. [138] The target analyte (4-methylacetophenone) was extracted by an 8 µL organic solvent drop (n-octane) containing an internal standard by direct immersion into the sample. [139] The drop was located at the top of a teflon rod, which was screwed in a 1 mL vial, as shown in Figure 1.6 a. After extraction, the rod with the solvent drop was withdrawn from the sample solution and a 1 µL aliquot of the organic extract was injected by a microsyringe into a GC injector. The method was later simplified by suspending a drop directly from the tip of a microsyringe needle that is either immersed inside the sample [139] solution or in the headspace above the sample (Figure 1.6 a-b). [140, 141] Different reviews about drop extraction techniques were published. [24, 44, 84, 142-144] In literature, synonymously used terms for liquid phase microextraction are single-drop microextraction (SDME), single drop extraction (SDE), solvent microextraction (SME), liquid-liquid microextraction (LLME), micro liquid-liquid extraction (mLLE) or in case of headspace sampling headspace solvent microextraction (HSME) and headspace liquid-phase microextraction (HS-LPME).[142] An overview of the techniques is given in appendix C (Table C 1.3). Different requirements for the used solvent have to be taken into account: (i) the solvent should extract the analytes efficiently and has to be adjusted for the analytes, (ii) for headspace extraction, the vapour pressure of the solvent should be low to minimize losses during extraction, and for direct immersion the water solubility of the solvent should be as low as possible. Another physicochemical aspect is that the solvent should have (iii) a high surface tension for a stable drop formation and especially for unspecific detection it is necessary that the solvent peak should be readily separated from the analyte peak. As extraction solvents for direct immersion, n-hexane, n-octane, isooctane, cyclohexane, n-hexadecane, toluene, chloroform, butylacetate and diisopropyl ether were reported. For headspace analysis, n-octane, n-decane, n-hexadecane, toluene, *o*-xylene, cyclohexane, 1-octanol, benzyl alcohol, ethylene alcohole, diethylphthalate were utilized. [142] Due to the substantial water solubility of polar solvents, the direct immersion method is restricted to non-polar solvents. Another problem of the direct immersion sampling is the formation of emulsions, especially when dealing with Complex sample matrices.[24] Considerations about the used drop size and volume lead to the result, that a bigger organic drop results in higher extraction efficiencies but makes manipulation more elaborate and less reliable. [145] It was observed that drops with volumes larger 5 µL became buoyant and could not be withdrawn back into the syringe.[145] Therefore, solvent volumes between 1-3 µL are commonly used. As shown in the zoomed view in Figure 1.6 b, an agitation in the drop ($\geq$ 1µL) is introduced by convection in the stirred sample, which leads to higher extraction rates. [44, 138]

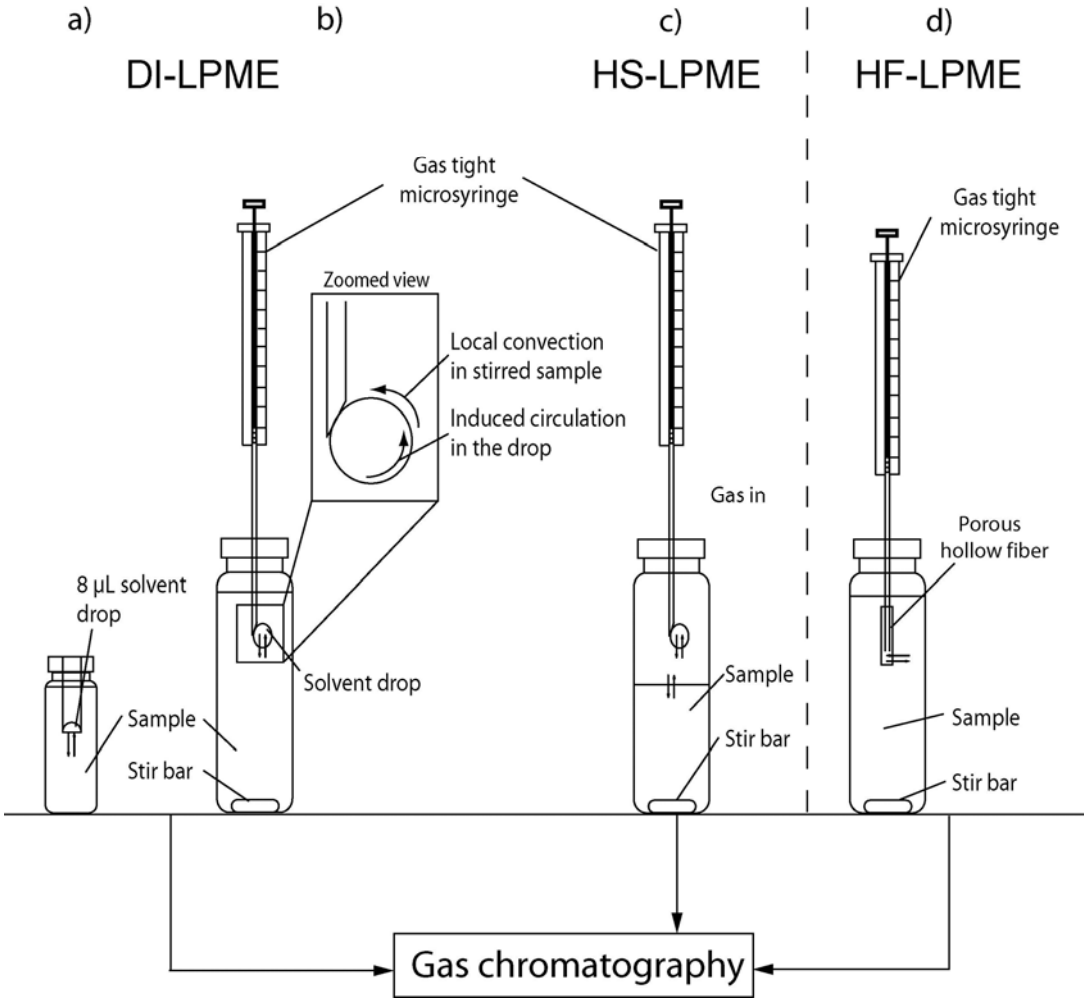

Figure 1.6 Liquid-phase microextraction techniques. a) Microdrop extraction device re-drawn after Ref. :[139] b) Microdrop extraction at a needle tip re-drawn after Ref.: [139, 140] c) d)Hollow fiber liquid-phase microextraction re-drawn according to Ref.: [146]

The reported applications of microdrop-LPME for polar compounds from aqueous matrices (see Table 1.5), include alcohols [141], chlorobenzenes, halogenated hydrocarbons, BTEX, fuel oxygenates such as MTBE [147], nitroaromatic explosive [148], warfare agents. [149] Apart from headspace and direct immersion, another modes for LPME are possible. This approach is dynamic-LPME. In dynamic-LPME, 1 µL of solvent is withdrawn into a 10 µL microsyringe. Than the syringe tip is inserted into the sample. In the next step 3 µL of sample are withdrawn in a time of 2s (dwell time) in the syringe and left there the next 3s for extraction. After this extraction step, the withdrawn 3 µL sample are pushed out within 2s. This process is repeated several times. At the end of the process, the organic solvent with the enriched target compounds is injected into the GC injector. [145] Simply said, the glas body of the syringe is used as micro separation funnel. [148] In dynamic LPME, an organic solvent film is formed on the inner surface of the syringe by withdrawing the plunger. Mass transfer occurs between this organic film and the aqueous sample plug. Film formation is controlled by solvent characteristics as surface tension and solvent viscosity. He and Lee introduced this method for chlorobenzenes. [145] In their work they considered a theoretical model on mass transfer and kinetics of the system, and compared static-LPME with dynamic-LPME.
LPME with its very low solvent amounts is compared with SPME, SBSE and other microextraction techniques extremely inexpensive. In case of thermal desorption into the GC injector, the method does not lead to peak broadening and tailing by slow analyte desorption as it mightbe the case for desorption from polymer coatings and no carry over effects can occur. Another advantage is that the method can be completely automated with an ordinary autosampler. In contrast, if these methods are carried out manually, drop sizes in static-LPME and withdrawing volumes and dwell times in dynamic-LPME are hardly reproducible. Saraji derivatised phenols with N,O-bis(trimethylsilyl)acetamide inside the syringe barrel after liquid-phase microextraction.[150] In case of in syringe derivatisation (ISyD) it is not possible to automate the complete method, because the needle has to be closed with a septum, to prevent losses by evaporation during reaction at higher temperature.
Another LPME approach is strongly related to membrane extraction techniques. Hollow fiber liquid-phase microextraction (HF-LPME) as shown in Figure 1.6 d utilizes a short piece of membrane tube as support for the solvent at the tip of the syringe. An automation of the method is hardly possible, because the membrane has to be removed from the needle tip before injection. Because of their simplicity, low costs and low solvent consumption, LPME could have a high potential for future developments and a combination with GC/IRMS seems possible but was so far not reported.

1.6 Scope of the present work

As described in the previous sections, the determination of isotope ratios by CSIA for environmental applications is restricted by the low sensitivity of the used isotope ratio mass spectrometers. To overcome this problem, two approaches can be taken. One path is the development of improved isotope ratio mass spectrometers; the other is the development of extraction, enrichment and clean-up methods to achieve sufficiently high analyte concentrations for precise isotope measurements. The latter approach seems to be the easier and more likely to succeed. Thus, the main goal of this work was the development and evaluation of potential extraction and enrichment techniques for the compound specific isotope analysis and the improvement of existing extraction methods for common polar and polar volatile groundwater contaminants. As main target compounds in this work, ethers, alcohols, halogenated methanes, ethylenes, and BTEX compounds were continued. As pointed out in the previous sections, a special focus was set on microextraction approaches. Reasons for this are advantages including absence of toxic solvents, simplicity for automatization, high throughput). Especially the advantages of in-needle techniques such as low fragility, easy implementation in existing systems and higher sorption capacities initiated their evaluation and application for polar groundwater contaminants. Therefore, two different commercially emerging methods were investigated while were commercially available. The first one, SPDE, applies an internal polymer coating as extraction phase and the second one, ITEX, uses a packed sorbent for extraction.

In chapter two, a SPDE method was developed and evaluated for alcohols and ethers. The varius extraction phases were compared and method related parameters were investigated. Chapter three addresses the development of a SPDE method for chlorinated hydrocarbons. Chapter four deals with the development of an ITEX method for nineteen common groundwater contaminants. As for SPDE methods the method was thoroughly validated.
Finally, in chapter 5 a new approach to determine method detection limits in the µg/L range for CSIA was developed and applied for a modified P&T method. The P&T was modified to allow extraction of larger sample volumes in order to reduce method detection limits. All method parameters have been evaluated for potential isotopic fractionation.

2 Solid-Phase Dynamic Extraction for the Enrichment of Polar Volatile Organic Compounds from Water

2.1 Introduction

Over the last decade, several solvent-free microextraction techniques based on a compound's partitioning between a liquid or gas phase and a fixed stationary extraction phase have been introduced in gas chromatography for many different matrices and analytes [151]. All these techniques have in common the absence of toxic organic solvents, simplicity and ease of automation. Solid-phase micro extraction (SPME), has become the most prominent and widely used solventless micro extraction technique for organic compounds in aqueous samples [75, 152]. However, different variations adopted from SPME, such as stir bar sorptive extraction (SBSE) and headspace sorptive extraction (HSSE), have been developed to increase sorption capacity and to overcome some drawbacks of SPME, such as fiber fragility [87, 115]. Other approaches utilize flow through techniques where the stationary phase is coated or packed inside a fused silica capillary column or stainless steel needle, including open-tubular trapping (OTT) [125], inside needle capillary adsorption trap (INCAT) [126], in-tube-SPME coupled to LC [123] and GC [153], capillary microextraction (CME) [121], and needle trap (NT) [135]. A recently commercialized technique based on the same principle is solid-phase dynamic extraction (SPDE). As seen in Figure 1, SPDE utilizes a 2.5 mL headspace syringe with a needle that is coated on the inside similar to a fused silica GC column with an immobilized extraction phase. SPDE needle coatings possess around 4-6 times larger extraction phase volumes compared with a 100-µm SPME fiber [154]. For the extraction, the needle can be immersed directly into the sample or in the headspace above it. The syringe plunger is moved up and down several times for a dynamic extraction of the sample, and the analytes are sorbed in the internal coating. After several extraction cycles (aspirating and dispensing) the analytes are thermally desorbed from the coating in the GC injector.

So far, there have been very few systematic investigations on extraction parameters and applications of SPDE, restricted to chlorinated pesticides in water [131], volatile flavours in plants and food [117], and cannabinoids, amphetamines and synthetic designer drugs in hair samples [129, 132, 133]. In this work, we aimed at the analysis of polar volatile organic compounds (PVOC) such as ethers and alcohols as probe compounds since these are more difficult to extract from water than nonpolar compounds. In the case of ethers, 1,4-dioxane, methyl *tert*-butyl ether (MTBE) and tetrahydrofuran (THF) were selected because of their frequent occurrence in environmental aqueous matrices (rain, surface and groundwater) [155-157]. Some of the small chain alcohols are also used as fuel oxygenates [158] or are present in fuel at low concentrations [159], are used as partitioning tracers for the characterization of residual nonaqueous phase liquids [160, 161], and are important analytes in food science, e.g., because of their presence in alcoholic beverages ("fusel oils"). The occurrence of 2-ethylhexanol in drinking water has been reported, probably from its presence in polymers as a by-product of 2-ethylhexyl phthalate synthesis [162]. Some of the investigated compounds, e.g., MTBE, tetrahydrofuran, and 2-ethylhexanol have been selected as candidates for further investigations in the OECD Screening Information Data Sets (SIDS) because of their high production rates, toxicity and physicochemical behavior [163].

The main objective of this work was to provide a sensitive, robust and fast method for determination of PVOC in aqueous matrices using SPDE. To this end, we (i) studied in detail the effects of the most important extraction parameters on partitioning of the target compounds (i.e., extraction temperature, ionic strength, and number of extraction cycles), (ii) compared different extraction phases for the

probe compounds with regard to achievable method detection limits (MDLs), and (iii) demonstrated the application of SPDE for the determination of fusel oils in alcoholic beverages and of salting out constants (Setschenow constants).

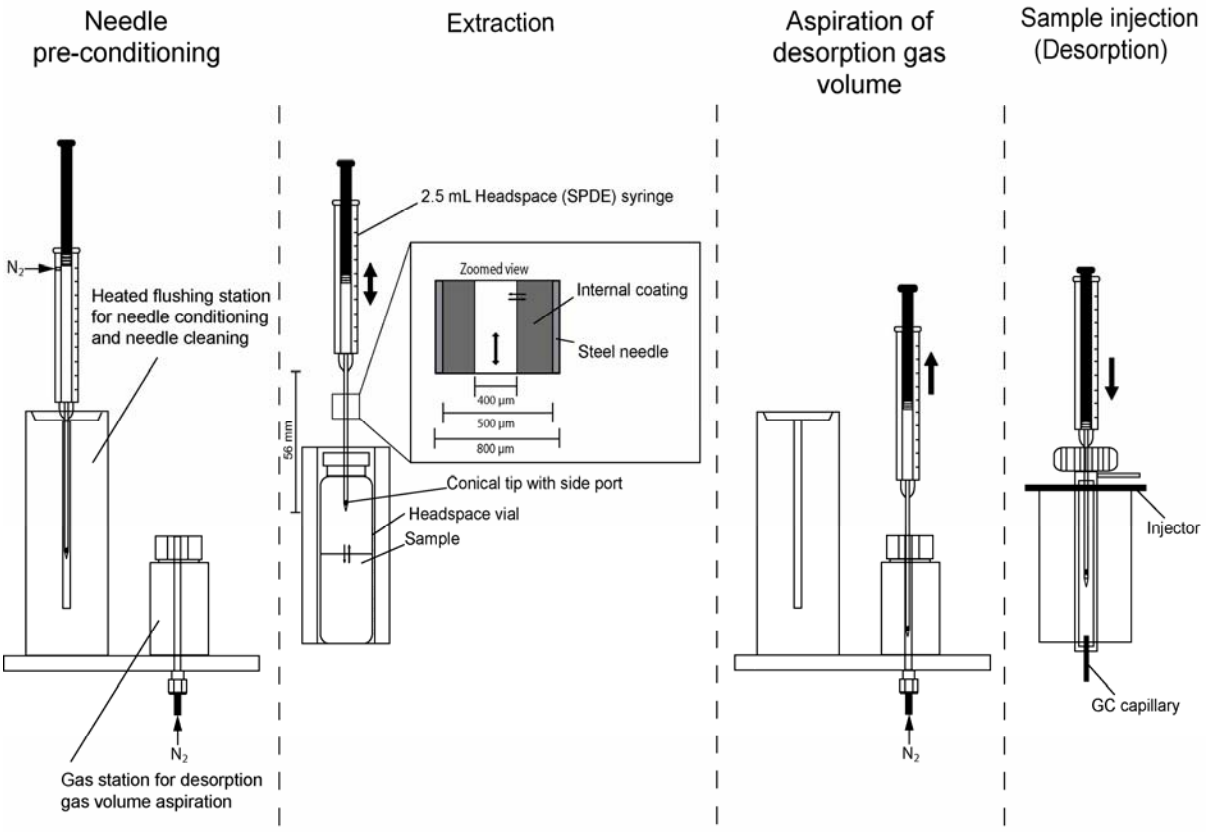

Figure 2.1 Schematic overview of the various steps in a HS-SPDE procedure. The left part shows the conditioning of a needle in the flush station before first use and after each analysis. In the middle part, the dynamic extraction of the headspace is shown. The right part describes the aspiration of a desorption volume at the gas station and subsequent thermal desorption in the injector.

2.2 Experimental

2.2.1 Chemicals and Reagents

Methanol (99.9 %) from Merck (Darmstadt, Germany) was used to prepare stock solutions. The methanol was checked by GC-MS for its purity and the absence of the investigated low chain alcohols. As solvent for the preparation of standard solutions, Milli-Q water was used from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA). Ethanol (99 %) and tetrahydrofuran (99.9 %) were obtained from Merck (Darmstadt, Germany), *tert*-butanol (99.5 %), 2-butanol (99.5 %), 1-pentanol (99+ %), 1-propanol (99+ %), 3-methyl-1-pentanol (99 %), 1-hexanol (98 %) and 2-ethylhexanol (99.6 %) from Aldrich (Steinheim, Germany), isopropanol (99.5 %), isobutanol (99 %), methyl *tert*-butyl ether were purchased from Acros Organics (Geel, Belgium) and 1-butanol (99.5 %), 3-pentanol (99.5 %), 1,4-dioxane (99.5 %) were purchased from Fluka (Buchs, Switzerland). *Tert*-butanol-d_{10} (99 %) from Acros Organics (Geel, Belgium) and 1,4-dioxane-d_8 (99+ %) from Aldrich (Steinheim, Germany) were used as internal standards. Table 2.1 shows the physico-chemical

properties of the investigated analytes. Sodium chloride (> 99.5%) purchased from Fluka (Buchs, Switzerland) was used to vary the ionic strength of the water samples.

2.2.2 Stock Solutions and Standard Mixtures

Methanolic stock solutions with a concentration of 1000 mg/L were prepared with a 100 µL gastight glas syringe in 10 mL volumetric flasks. These primary stock solutions were transferred for storage in 10 mL brown screw cap glass bottles without headspace, sealed with PTFE septa and kept in the refrigerator at 4 °C in the dark and were prepared monthly. Standard solution mixtures of 1 ppm_v were prepared from individual stock solutions in Milli-Q water and discarded weekly. Lower concentrated solutions for calibration and MDL determination were prepared likewise by volumetric dilution to the required concentration level.

Table 2.1 Physicochemical properties of target compounds

Compound	CAS-no.	Density (kg/L) [a,b]	Boiling point (°C) [a,b]	Vapor pressure (kPa) [b]	Dimensionless air-water partitioning constant K_{aw} x 10^4	Constants for temperature dependent air-water partitioning constant K_{aw}		Water solubility (g/L) [b]	Target ions used for quantification (m/z)
						A	B		
methyl *tert*-butyl ether	1634-04-4	0.74	55	33	240	4745[c]	12.6[c]	51	73
tetrahydrofuran	109-99-9	0.87	66	22	28.8	n.a.	n.a.	miscible	42
1,4-dioxane	123-91-1	1.0	101	27	1.96	n.a.	n.a.	miscible	88
ethanol	64-17-5	0.79	78	7.9	0.90	6349[d]	12.8[d]	miscible	45
1-propanol	71-23-8	0.80	97	15	3.03	7192[d]	16[d]	miscible	31
Isopropanol	67-63-0	0.79	83	33	3.31	n.a.	n.a.	miscible	45
1-butanol	71-36-3	0.81	118	4	3.60	n.a.	n.a.	63	56
2-butanol	78-92-2	0.81	99.5	2.4	3.70	6929[d]	15.2[d]	180	45
Isobutanol	78-83-1	0.80	108	9	4.00	6980[d]	15.6[d]	85	43
tert-butanol	75-65-0	0.79	83	5.6	0.45	8030[c]	19.5[c]	miscible	59
1-pentanol	71-41-0	0.82	138	1.2	5.31	n.a.	n.a.	22	42
3-pentanol	584-02-1	0.82	116	2	8.09	n.a.	n.a.	52	59
2-methyl-1-butanol	137-32-6	0.82	129	n.a.	5.76	n.a.	n.a.	30	57
3-methyl-1-butanol	123-51-3	0.81	131	2	5.76	n.a.	n.a.	27	55
1-hexanol	111-27-3	0.82	156	0.7	6.99	n.a.	n.a.	5.9	56
3-methyl-1-pentanol	589-35-5	0.82	151	n.a.	n.a.	n.a.	n.a.	4.3	56
2-ethylhexanol	104-76-7	0.83	183	0.4	10.8	n.a.	n.a.	0.88	57

[a] Specification from manufacturer
[b] Data from SRC Phys Prop Database (http://esc.syrrees.com)
[c] Ref. [164]
[d] adapted from Ref. [165]
n.a.: not available

2.2.3 Instrumentation

All samples were measured using a TraceGC 2000 (ThermoFinnigan, Milano, Italy) gaschromatograph coupled to a TraceDSQ (ThermoFinnigan, Austin TX, US) single quadrupole mass spectrometric detector. SPDE was performed with a CTC-CombiPAL autosampler supplied by Chromtech (Idstein, Germany). Data acquisition, processing and evaluation were carried out using Xcalibur Data System Version 1.3 (ThermoFinnigan, Austin TX, US). The analytes were separated on a Restek Stabilwax fused-silica capillary column (60 m x 0.32 mm ID, 0.5 µm film thickness, Restek Corp., Bellefonte PA, US). The temperature program used to obtain separation of the target compounds was as follows: 1 min at 40 °C, 7 °C/min to 110 °C, 3°C/min to 130 °C, 7 °C/min to 180 °C, at 180 °C hold for 8 min. The temperatures for the transfer line and the ion source were set to 250 and 220 °C, respectively. The initial GC oven temperature was held at 40 °C to trap the analytes before separation in order to prevent peak broadening. The GC was equipped with a programmable temperature vaporizer BEST PTV (ThermoQuest, Austin TX, US) that was used in the splitless mode at an injection port base temperature of 200 °C and a splitless time of 1.5 min. A 2 mm I.D. deactivated silcosteel liner (BGB, Anwil, Switzerland) was used, and the transfer time was adjusted to 20 s. Carrier gas was Helium 5.0 (Messer, Griesheim, Germany) with a constant flow rate of 1.5 mL/min. The MS was in the electron impact ionization mode (EI) at 70 eV. Full-scan mode (m/z = 30-150) was used for all measurements, including the real samples. The obtained chromatogram under optimized conditions is shown in Figure 2.2. 1,4-dioxane (RT: 12.78 min) was later included in the investigation and was evaluated separately under the same GC and SPDE conditions. 2.2.4 SPDE equipment and evaluation

The autosampler was supplied with a heatable CTC agitator (Chromtech, Idstein, Germany) for incubation and shaking, an additional gas station (Chromtech, Idstein, Germany) to aspire desorption gas, and a heated flushing station for conditioning of the SPDE needles and reconditioning after each analysis to prevent carryover. The gas station and the syringe body were flushed with nitrogen (purity 5.0). The syringe body was held at a temperature of 35°C in the syringe adapter heater. All steps of SPDE were fully controlled by the CTC-CombiPAL with custom-made software macros.

Four different commercially available SPDE needle coatings with different polarities ranging from a polar WAX to a non-polar PDMS were tested for their efficiency for alcohol and ether extraction. The four SPDE coatings were: (1) a polar polyethylene glycol WAX phase (50 µm film thickness and 56 mm film length), (2) a cyanopropylphenyl / polydimethylsiloxane 1701 phase (50 µm film thickness and 56 mm film length), (3) a non-polar polydimethylsiloxane PDMS phase (50 µm film thickness and 56 mm film length), and (4) a polydimethylsiloxane with 10% embedded activated carbon PDMS/AC phase (50 µm film thickness and 56 mm film length). All needles were obtained from Chromtech (Idstein, Germany). The needles were pre-conditioned in the flush station. The WAX, PDMS and 1701 were conditioned for 30 min at 220 °C, 250 °C and 250 °C, respectively and the PDMS/AC for 60 min at 280 °C. During the pre-conditioning, the syringe was flushed with nitrogen gas through the needle side port. The pre-extraction time for establishing of headspace-sample partition equilibrium in the vial was tested at 70 °C between 2 and 40 min. No significant changes in the obtained peak areas were observed and a pre-extraction time of 5 min was generally used. Investigated parameters using a WAX phase included extraction temperature (30, 40, 50, 60, 70 °C), number of extraction cycles (1, 2, 5, 10, 30, 50), and ionic strength (0, 5, 10, 15, 25 % (w/w) sodium chloride). During evaluation of these parameters, all measurements have been carried out in triplicate using 1 ppm_v standard solution mixtures.

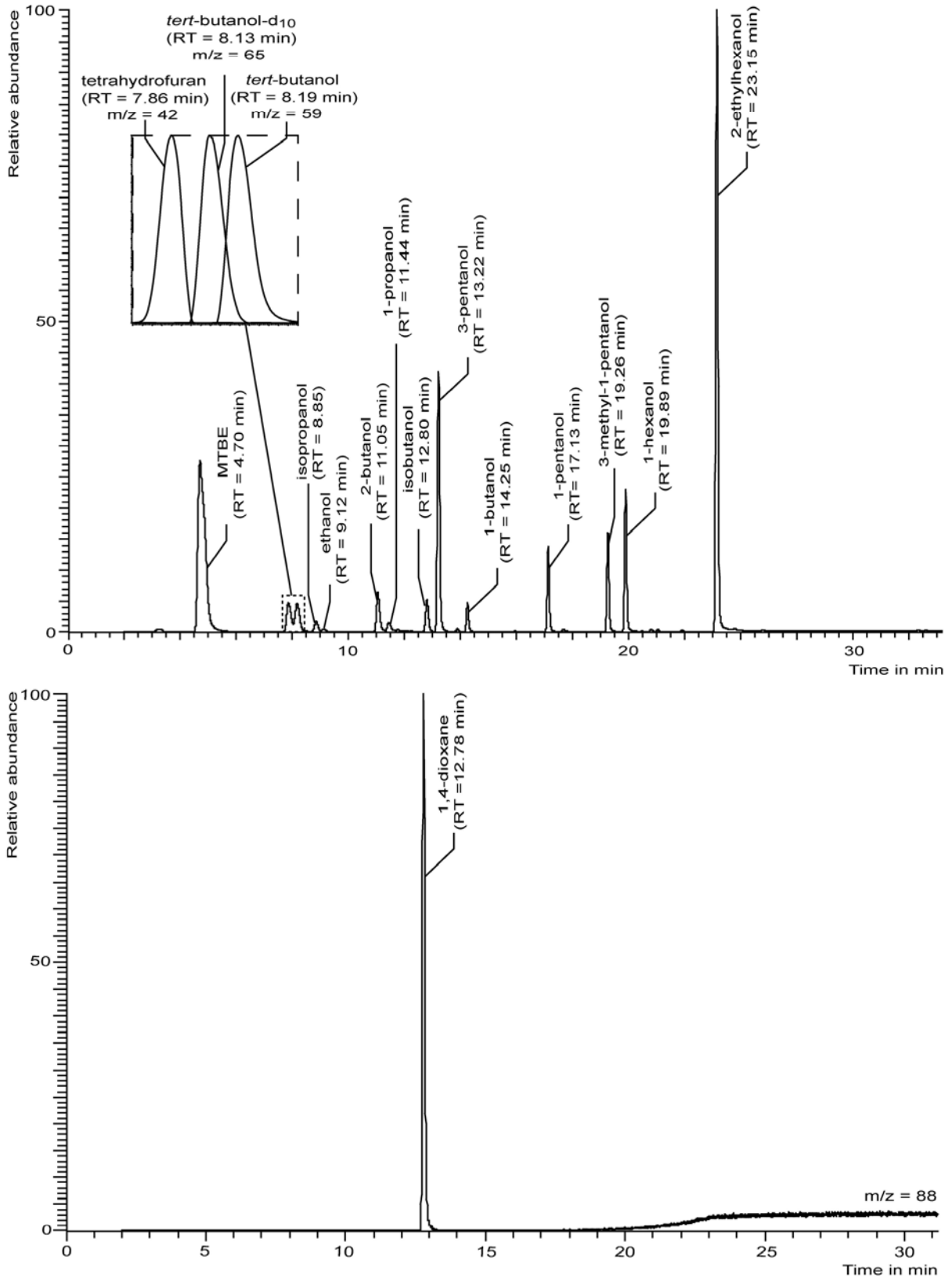

Figure 2.2 Upper chromatogram shows target compound separation with a combination of reconstructed ion chromatograms of a 1 ppm_v standard solution of alcohols and ethers (without 1,4-Dioxane). M/z values used for the upper chromatogram are given in Table 1. The lower chromatogram shows a 1 ppm_v standard solution of 1,4-dioxane.

2.2.5 HS-SPDE parameters for MDL determination and quantitative analysis

Twenty-mL screw cap headspace vials were filled with 3.33 g sodium chloride. In case of alcoholic beverage samples, the samples were diluted by a factor of 50 with Milli-Q water in a 25-mL volumetric flask to prevent possible matrix and co-solvent effects. 10 mL standard solution mixture or diluted real sample were transferred to the vials that were sealed with PTFE coated silicone septa and magnetic screw caps. It was necessary to shake the vials at least for ten minutes in order to ensure complete dissolution of the salt. The samples were placed on a heatable tray (Chromtech, Idstein, Germany), which was set to a constant temperature of 50 °C. Before measuring, the samples were shaken for 5 min at 70 °C in the agitator at a speed of 500 rounds per minute (agitator on time: 5 s, agitator off time: 2 s). Afterwards, the SPDE needle was inserted 20 mm through the septum into the vial for dynamic extraction of the headspace. Fifty 2.5-mL extraction strokes with an extraction flow rate of 125 µL/s were done. After the extraction, a desorption volume of 1 mL nitrogen gas was aspirated into the syringe at the gas station before thermal desorption into the injector with a desorption flow rate of 50 µL/s, i.e. total desorption time was 20 s. Following desorption, the needle removed from the injector and was flushed with nitrogen for 5 min in the needle flush station at a temperature of 200°C, in order to prevent carry-over effects.

2.3 Results and Discussion

2.3.1 Extraction Temperature

In this study, a temperature range between 30 °C and 70 °C was investigated. Experimental extraction data for each compound could be fitted well by exponential functions, as shown in Table 2 und exemplary for six compounds in Figure 2.3. As shown in Figure 2.3, the highest peak area was always observed at a temperature of 70 °C and all compounds showed a similar behavior. In order to compare the increase in extraction efficiency between the compounds, the ratios between the highest and the lowest peak areas were calculated (Table 2.2). The highest increase of extraction efficiency was observed for 3-pentanol with a factor of ~ 9 and the lowest for MTBE with an increase of ~ 4. According to the calculated ratios of obtained peak areas, a stronger temperature dependency was observed for the alcohols than for the ether. Similar to HS-SPME, there are two major processes involved in the SPDE extraction. The first one is the partitioning of the analytes between headspace and water, the second the partitioning between the analytes in the headspace and the sorbent.

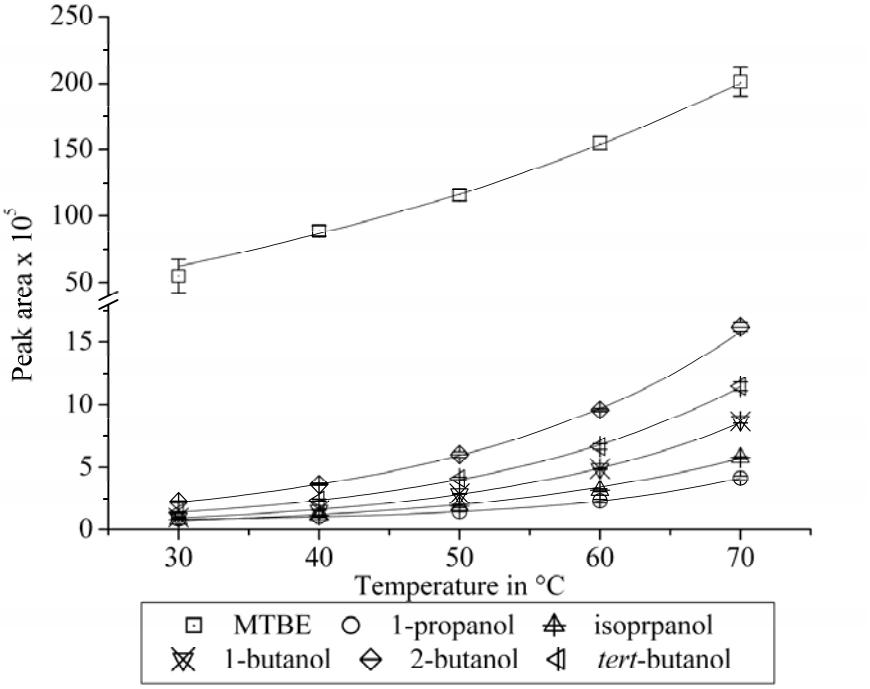

Figure 2.3 Dependency of peak areas on temperature. Triplicate measurements were carried out for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

Table 2.2 Obtained exponential curve fits, their correlation coefficients and ratios of the peak area between highest and lowest investigated temperature for each compound.

Compound	Exponential curve fit	Correlation coeff. (R^2)	Peak area at 70 °C/ peak area at 30 °C
methyl *tert*-butyl ether	$y = 2\times10^{6} e^{3.1\times10^{-2}x}$	0.982	3.7
tetrahydrofuran	$y = 2.29\times10^{6} e^{3.55\times10^{-2}x}$	0.997	4.3
1,4-dioxane	$y = 1.73\times10^{5} e^{3.76\times10^{-2}x}$	0.999	4.5
ethanol	$y = 9.17\times10^{1} e^{9.67\times10^{-2}x}$	0.988	7.0
1-propanol	$y = 2.25\times10^{4} e^{3.97\times10^{-2}x}$	0.971	5.0
Isopropanol	$y = 1.69\times10^{4} e^{4.94\times10^{-2}x}$	0.994	7.3
1-butanol	$y = 1.85\times10^{4} e^{5.45\times10^{-2}x}$	0.999	8.9
2-butanol	$y = 5.28\times10^{4} e^{4.84\times10^{-2}x}$	0.999	7.1
isobutanol	$y = 2.80\times10^{4} e^{4.87\times10^{-2}x}$	0.999	7.1
tert-butanol	$y = 2.99\times10^{4} e^{5.18\times10^{-2}x}$	0.999	8.2
1-pentanol	$y = 4.45\times10^{4} e^{4.94\times10^{-2}x}$	0.999	7.3
3-pentanol	$y = 1.26\times10^{5} e^{5.44\times10^{-2}x}$	0.999	9.0
3-methylpentanol	$y = 1.04\times10^{5} e^{4.84\times10^{-2}x}$	0.999	7.0
1-hexanol	$y = 1.11\times10^{5} e^{4.96\times10^{-2}x}$	0.999	7.3
2-ethylhexanol	$y = 8.06\times10^{5} e^{4.35\times10^{-2}x}$	0.995	5.8

The temperature influences not only the air-water partitioning, but also the partitioning between headspace and sorbent. To evaluate the influence of the temperature on the air- sorbent partitioning, the ratio of the measured peak area of four analytes to their analyte fraction in the headspace was plotted against temperature (Figure 2.4). The initial analyte fraction in air, f_{air}, was calculated by equation 2.1:

$$f_{air} = \frac{1}{1 + \frac{V_{sample}}{K_{aw} \cdot V_{hs}}} \quad \textbf{(2.1)}$$

where K_{aw} is the air-water partitioning constant, V_{sample} the sample volume and V_{hs} the headspace volume. This calculation was done for all compounds for which temperature dependent K_{aw} were available from literature or could be calculated by the van´t Hoff-type equation:

$$\ln K_{aw} \cong -\frac{A}{T} + B \quad \textbf{(2.2)}$$

where A and B are compound-specific constants. Values for A and B are given in Table 2.1. Figure 2.4 shows that the extracted amount on the extraction phase *relative to the concentration in the headspace* decreases with increasing temperature. This indicates that the increase in the headspace concentration at higher temperatures due to a higher K_{aw} is partially offset by a lower sorbent-air partition constant K_{sa}. Higher sorbent temperatures decrease K_{sa} because sorption is an exothermic process. This might also explain previous findings of maximum extraction yields at intermediate temperatures with a decrease at higher temperatures [117, 166]. In order to maximize extraction efficiency, the extraction phase was held as cool as possible by keeping the syringe body temperature at 35 °C. Other authors used higher temperatures to prevent a condensation of water vapor in the syringe body [131] but in our system such a condensation was not observed and reproducibility was not affected.

2.3.2 Number of Extraction Cycles

In SPDE, the number of extraction cycles (aspirating and dispensing of the syringe) is directly correlated with the extraction time. The volume of the aspirated headspace in each cycle was kept constant at 2.5 mL to exchange the highest possible headspace volume. The volume flow rate was held constant at 125 µL/s because literature data suggests that the volume flow for the extraction of volatile compounds did not show a substantial influence on the extraction yield [117]. Before the first extraction cycle, equilibrium between air and water was established. One to 50 extraction cycles, corresponding to extraction times between 0.66 and 33.3 minutes, were tested. Exemplary extraction profiles are shown in Figure 2.5.

Experimental data could be fitted with sigmoidal functions and show similarities with typical SPME equilibration time profiles. All analytes show stable responses after 50 cycles, meaning that additional cycles do not further increase peak areas. However, the differences in individual extraction profiles are relatively high, especially for the first 10 aspiration cycles. Since with the chosen experimental settings a laminar flow in the needle is obtained (Reynolds number R_e of around 22), the equilibration time increases linearly with the sorbent-air partitioning coefficient K_{sa} [167]. The rapid equilibration for MTBE compared with the low chain alcohols shown in Figure 5 thus seems to be caused by a rather low K_{sa} value.

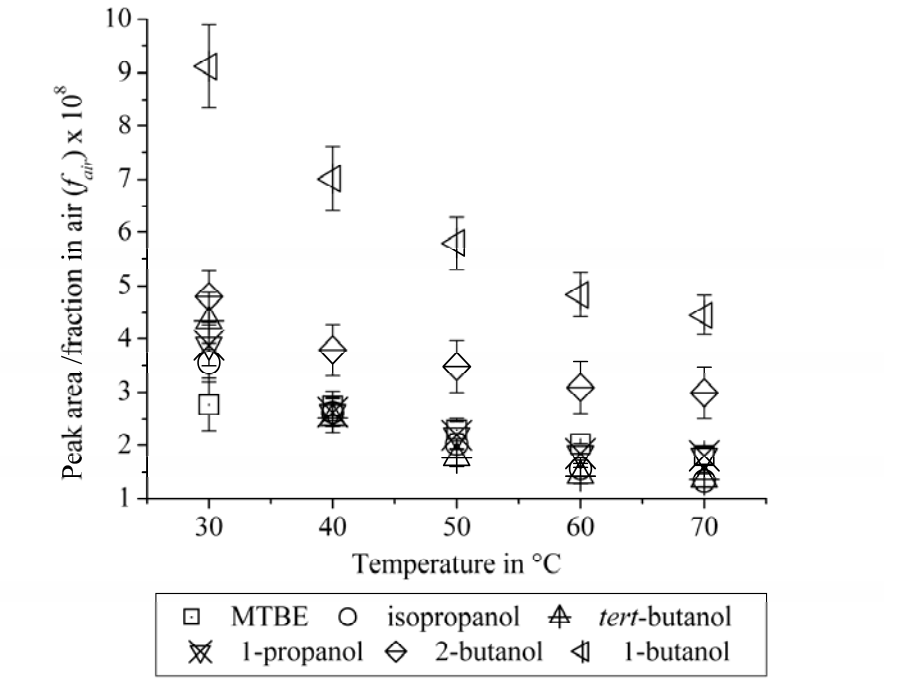

Figure 2.4 Ratio of peak area (extracted amount) of a given analyte over analyte fraction in air (fr_{air}) depending on temperature. Error bars indicate the estimated uncertainty from error propagation.

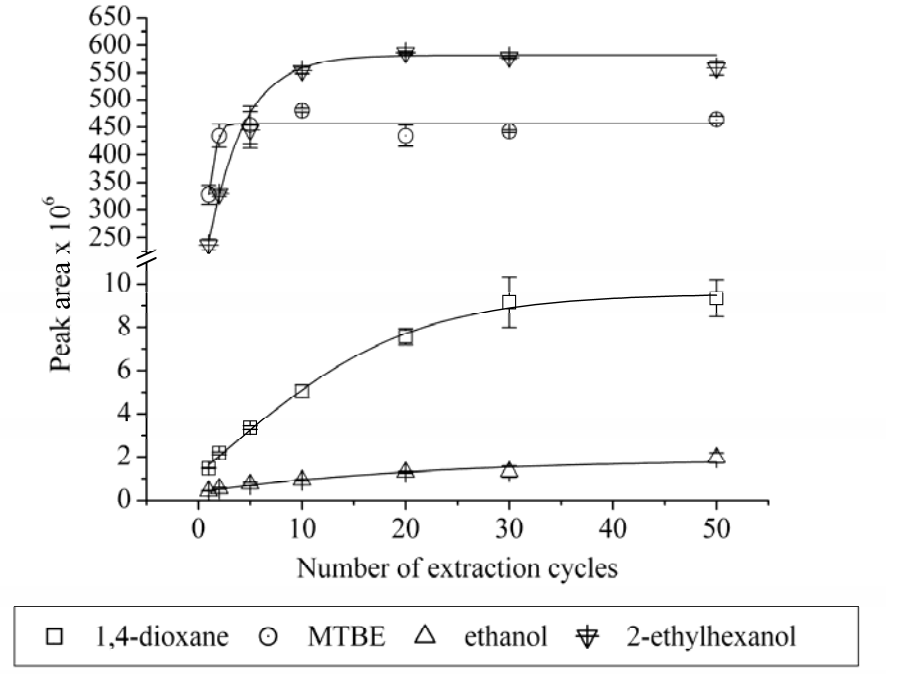

Figure 2.5 Exemplary extraction profiles for four of the investigated compounds. Triplicate measurements were done for each point; error bars indicate the standard deviation. Lines give fitted extraction profiles using a sigmoidal function.

2.3.3 Addition of Salt and Determination of Setschenow Constants

The influence of electrolyte addition (sodium chloride) to the sample solution on extraction yield was tested by using 50 extraction cycles and an extraction temperature of 70 °C. Five different concentration levels from 0 % to 25 % NaCl (w/w) were used. Higher concentration levels were not

used because of (i) approaching the sodium chloride water solubility and inadequately long dissolving times, and (ii) previous reports of decreased sensitivities for MTBE and no substantial increase in sensitivity for ethanol, *tert*-butanol and isopropanol for salt concentrations above 25 % (w/w) [168, 169]. The addition of salt increases the sample volume and therefore volume correction factors were determined experimentally for the tested salt concentrations and applied in all subsequent calculations. Figure 2.6 shows that salt addition leads to significantly higher extraction efficiencies for all the investigated compounds and internal standards. Peak areas for all compounds increased by factors between 2.4 and 3.7 (Table 2.3). Note that for ethanol and MTBE ratios are given for 15 % NaCl (w/w) because at 25 % smaller peak areas were obtained. Apart from these two compounds, best results were generally obtained for the highest salt concentration. For ethanol, isopropanol, TBA, and MTBE our results are in good agreement with previous studies using SPME for extraction [168, 169].

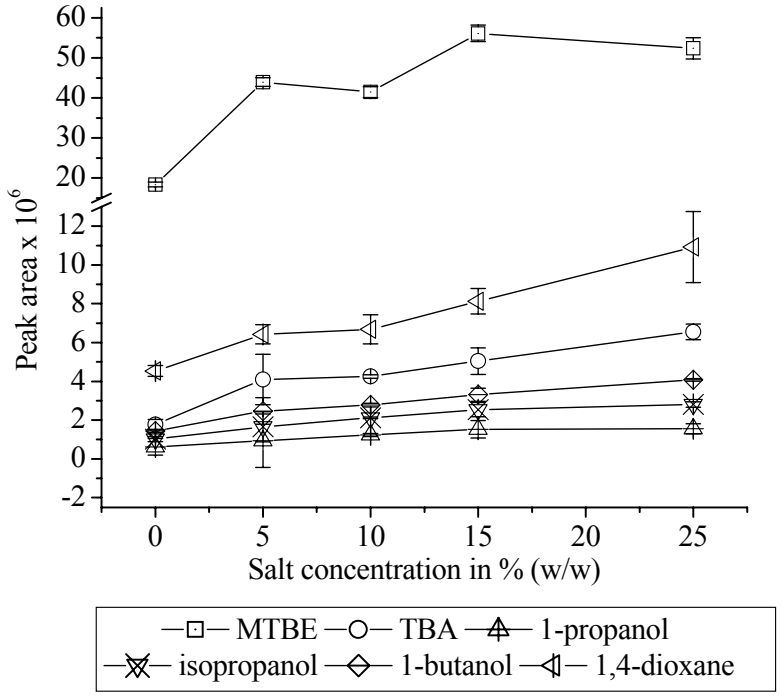

Figure 2.6 Effect of ionic strength on extraction yield for six exemplary compounds. Triplicate measurements were done for each point, error bars indicate the standard deviation.

For a quantification of the effect of salt concentration on extraction, salting out or Setschenow constants K^s were determined according to equation 2.3 using measurements at various salt concentrations [170]:

$$\log\left(\frac{\gamma_{w,salt}}{\gamma_w}\right) = K^s \left[salt\right]_{total} \qquad \textbf{(2.3)}$$

where γ_w is the activity coefficient of the compound in pure water, $\gamma_{w,salt}$ is the activity coefficient in the saline aqueous solution, and $[salt]_{total}$ is the total molar salt concentration. Note that K^s values are salt-specific, thus the given values are strictly valid only for sodium chloride. The ratio of γ_w to $\gamma_{w,salt}$ can be calculated with equation 2.45 using the known air-water partitioning constant K_{aw} [171]:

$$\frac{\gamma_{w,salt}}{\gamma_w} = \frac{r}{1+(1-r)K_{aw}} \qquad \textbf{(2.4)}$$

The parameter $r = C_{g,salt}/C_g$, the ratio of the analyte concentrations in the gas phase with salt addition and without, is equal to the ratio of measured peak areas, *PA*, obtained with salt addition and without: $r = PA_{salt}/PA$. Using the calculated K^s the modified air-water partitioning constant K_{aw}^{salt} can be calculated by equation 2.5:

$$K_{aw}^{salt} = K_{aw} 10^{K^s [salt]_{total}} \quad \textbf{(2.5)}$$

For the determination of the Setschenow constants total salt concentrations up to 3 mol/L (15% (w/w)) were used. As discussed above, at higher salt concentrations than 15 % (w/w) considerable deviations from the behavior described by equation 2.5 were observed (i.e., decreasing peak areas at higher salt concentrations). Therefore, values at 25 % (w/w) were not considered for K^s calculation. The obtained correlation coefficients (n = 3-4 points) were between 0.962 (isopropanol) and 0.999 (1,4-dioxane). As shown in Table 2.3, Setschenow constants in the range 0.08 to 0.17 L/mol were obtained.

Table 2.3 Obtained ratios of the peak area between highest and lowest investigated salt concentration for each compound and determined Setschenow constants.

Compound	Peak area (25% NaCl)/ peak area (0% NaCl)	Setschenow constant, K^s [L/mol]	Corr. coeff. R for K^s determination
methyl *tert*-butyl ether	3.1[a]	0.17	0.995
tetrahydrofuran	2.9	0.16	0.988
1,4-dioxane	2.4	0.08	0.999
ethanol	2.4[a]	0.13	0.992
1-propanol	2.5	0.13	0.980
isopropanol	2.8	0.13	0.962
1-butanol	2.8	0.12	0.985
2-butanol	3.4	0.15	0.978
isobutanol	3.2	0.15	0.982
tert-butanol	3.7	0.16	0.976
1-pentanol	3.2	0.14	0.982
3-pentanol	3.5	0.14	0.973
3-methylpentanol	3.2	n.a.	n.a.
1-hexanol	3.4	0.14	0.974
2-ethylhexanol	3.4	0.15	0.976

With 0.08 L/mol, 1,4-dioxane showed an exceptionally low salting-out constant. Except for MTBE (Setschenow constant of 0.11 L/mol) [171], no data are available in the literature for comparison. However, the values agree rather well with values for other polar compounds such as phenol (0.13 ± 0.02) whereas higher values have been reported for less polar compounds such as BTEX, chlorinated hydrocarbons and PAHs [170]. Contradicting these observations, in SPME and static headspace literature it was reported that the salting out effect is much more pronounced for polar than for nonpolar compounds [27, 152] Finally, the Setschenow constants given in Table 2.3 have been determined at 70 °C. Although the temperature effect on K^s is probably not very high, there is no data available in literature to corroborate this assumption. The salting out effect is important both in analytical chemistry (as utilized in this study to enhance air-water partitioning) and environmental chemistry (e.g., air-sea water partitioning) but surprisingly little systematic work on it has been carried out so far.
Thus, further investigations in this field are much needed to foster our understanding of salt effects in air-water systems.

2.3.4 Method Detection Limits and Precision

Method detection limits (MDLs) were determined according to the U.S. Environmental Protection Agency procedure [172] using the optimized conditions indicated in the experimental section. To this end, seven replicates were measured at an approximate signal:noise ratio of 5:1, and standard deviations for these were calculated. For each compound, three point calibrations bracketing the test level were used for quantification, Finally, MDLs were calculated according to equation 2.6 by multiplying the standard deviation s_d with the student t-factor:

$$MDL = t_{N-1,\,0.99} \times s_d \qquad \textbf{(2.6)}$$

The MDLs for the probe compounds using each of the four phases were calculated and are summarized in Table 2.4. In general, lowest MDLs were achieved with the WAX and the PDMS/AC phase. Such a result was expected for the WAX phase due to its polarity. The comparison between the PDMS and the PDMS/AC shows that the adsorption on the embedded char coal particles has a pronounced effect on the extraction yield. On all phases, 1-propanol and ethanol showed the highest MDLs. A comparison with MDLs obtained by other enrichment techniques are given in Table 4. Note that the given values depend on the procedure used for the determination of MDLs as has been discussed recently for fuel oxygenates [173]. For MTBE, reported methods using SPME give within one order of magnitude comparable results. For some alcohols no other studies indicating MDLs are available. The rather high MDL for 2-ethyl-1-hexanol in comparison with the smaller chain alcohols was due to an ubiquitous background signal that might be caused by 2-ethylhexyl phthalate from the GC injector septa or other sources in the lab.
The achievable precision of the overall method was estimated for the WAX phase by averaging the relative standard deviations of all triplicate measurements (1 ppm_v) that had been carried out during SPDE evaluation over several weeks under different conditions. The average RSDs ranged from 2% (THF, 1-pentanol, 1-hexanol, 2-ethylhexanol) to 14% (ethanol). This indicates a good repeatability of measurements over extended usage times.

2.3.5 Application to Real Samples

The applicability of SPDE in the analysis of real samples was tested with different kinds of alcoholic beverages such as beer, wine, brandy, and rum. In Figure 2.7, the chromatogram for a white wine sample is shown. In this sample, 45.8 mg/L 1-propanol, 91.7 mg/L isobutanol, 2.25 mg/L 1-butanol and 6.4 mg/L 1-hexanol have been found. Because of the high sensitivity of the method, the samples can be diluted with water to suppress matrix and cosolvent effects. As can be seen in Figure 2.7, in addition to the target analytes investigated here, HS-SPDE is also applicable to the analysis of small chain ester aroma components in such a matrix. The esters were not included in the evaluation, but an adaptation of the HS-SPDE method to this compound class should be rather straightforward.

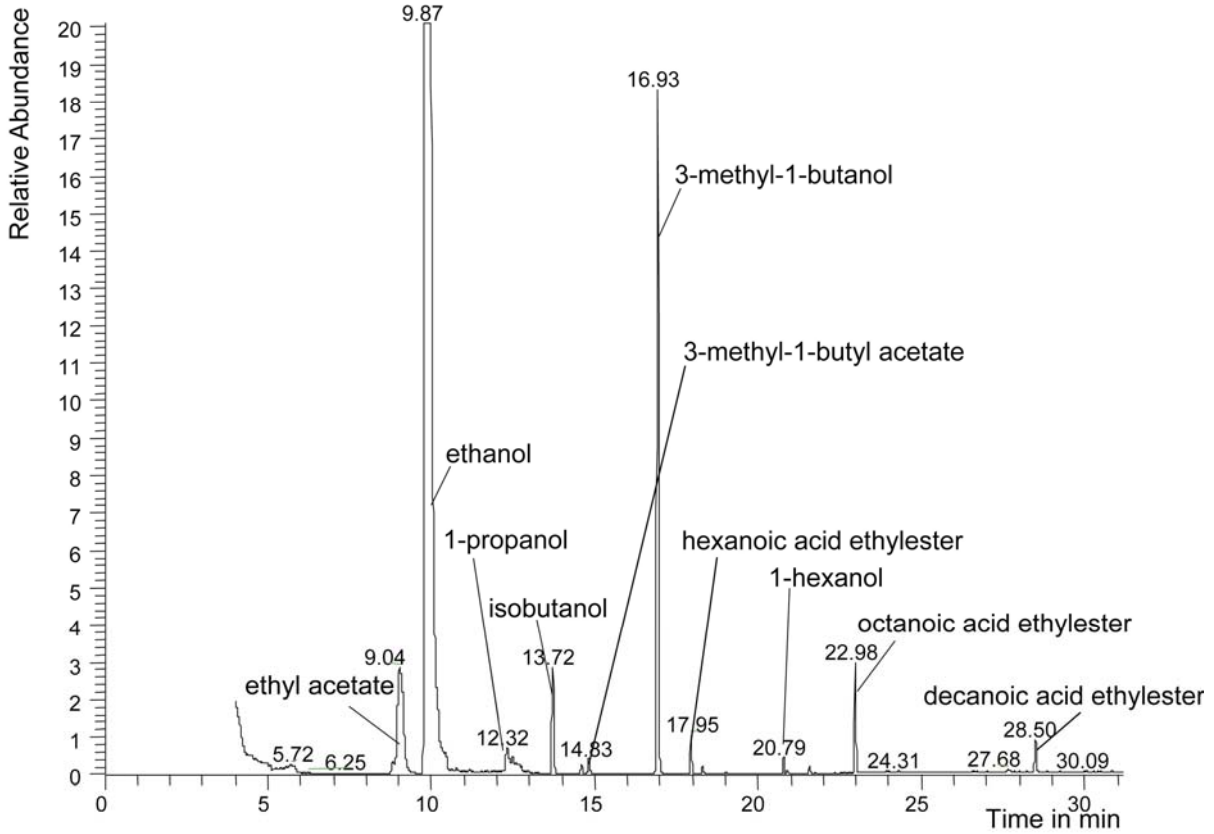

Figure 2.7 Full-scan chromatogram of a white wine sample (diluted 50 times) obtained under standard conditions described in the experimental part using a WAX coating (without internal standard).

2.4 Conclusions

The results reported here show that HS-SPDE is suitable for the trace determination of polar volatile organic compounds (PVOC) in aqueous matrices. The adjustment of parameters such as salt concentration, temperature, sorption and desorption conditions has a significant influence on the extraction yields. The comparison of MDLs for four coatings has shown that the most efficient materials are the polar WAX and the nonpolar polydimethylsiloxane with embedded activated carbon particles (PDMS/AC). The needle showed a lower fragility than SPME fibers and a longer lifetime: With only one WAX coated needle more than 500 headspace measurements (the whole method evaluation) have been carried out without noticeable adverse effects on extraction efficiency. In particular for polar WAX phases this is a significant improvement in comparison with SPME Carbowax coatings. Furthermore, except for MTBE, the obtained MDLs with SPDE are comparable or even better than with other injection/enrichment techniques.

Table 2.4 HS-SPDE method detection limits for target analytes in µg/L using four different coatings in comparison with literature data. Bold values indicate lowest MDLs within a 30% range.

Compound	WAX	PDMS/AC	PDMS	1701	Comparison with MDLs from literature	
methyl *tert*-butyl ether	**0.06**	**0.07**	0.32	0.08	0.10	(direct aqueous injection, GC-MS)[159]
					0.008	(SPME, GC-MS) [168]
					0.001	(purge & trap, GC-MS) [174]
					2	(static headspace, GC-MS) [175]
					0.21	(static headspace, GC-MS) [176]
tetrahydrofuran	0.48	0.94	0.55	**0.32**	76	(static headspace, GC-FID) [177]
1,4-dioxane	**0.8**	1.2	0.95	**0.91**	2	(direct aqueous injection, GC-MS) [178]
					0.16	(LLE, GC-MS) [178]
					816	(static headspace, GC-FID) [177]
ethanol	**2.3**	4.9	8.9	3.1	15	(SPME, GC-MS) [168]
					360	(static headspace, GC-FID) [177]
					18	(static headspace, GC-MS [176]
					67	(HSME, GC-MS) [150]
1-propanol	**3.5**	4.4	**2.9**	6.3	20	(HSME, GC-MS) [150]
isopropanol	0.3	**0.15**	0.33	0.19	40	(direct aqueous injection, GC-MS) [179]
					89	(static headspace, GC-FID) [177]
					5.5	(static headspace, GC-MS) [176]
1-butanol	**0.34**	0.57	0.97	0.53	5	(HSME, GC-MS) [150]
2-butanol	0.2	**0.11**	0.16	0.16	3	(HSME, GC-MS) [150]
isobutanol	1.9	**0.09**	0.8	2.0	n.a.	
tert-butanol	**0.15**	**0.15**	0.47	0.35	1.1	(direct aqueous injection, GC-MS) [159]
					0.11	(purge & trap, GC-MS) [174]
					1.8	(SPME, GC-MS) [168]
					0.79	(static headspace, GC-MS) [176]
					5	(HSME, GC-MS) [150]
1-pentanol	0.15	0.17	0.29	**0.1**	3.7	(SPME, GC-FID) [180]
3-pentanol	**0.06**	0.11	0.1	**0.06**	2	(HSME, GC-MS) [150]
2-methyl-1-butanol	0.45	**0.19**	0.64	**0.16**	n.a.	
3-methyl-1-butanol	0.52	**0.02**	0.43	0.81	n.a.	
3-methyl-1-pentanol	0.02	**0.004**	0.21	0.09	n.a.	
1-hexanol	0.03	**0.004**	0.17	0.23	0.4	(direct aqueous injection, GC-MS) [181]
					3.2	(SPME, GC-MS) [182]
2-ethylhexanol	**0.18**	**0.13**	0.48	0.34	0.5	(closed loop stripping, GC-FID) [162]

n.a.: no literature data available, HSME: headspace solvent microextraction, SPME: solid-phase microextraction, LLE: liquid-liquid extraction

3 Determination of Halogenated Volatile Organic Hydrocarbons in Water Samples by Solid-Phase Dynamic Extraction

3.1 Introduction

Contamination of groundwater with chlorinated solvents and benzene is a widespread environmental problem due to the toxicity, suspected carcinogenity and persistence of these compounds.[183, 184] Chlorinated solvents such as perchloroethylene (PCE) and trichloroethylene (TCE) are used in dry cleaning and electronic industry as degreasers, as extraction solvents in chemical processes and as heat-exchange fluids. [185] TCE, cis-1,2-dichloroethylene (*cis*-1,2-DCE) and vinyl chloride (VC) are frequently found as degradation products in contaminated groundwater aquifers. [8, 186] Halomethanes such as chloroform, bromoform, and dichloromethane (DCM) are used as industrial solvents and are formed as disinfection by-products when chlorine reacts with natural organic matter and bromides in drinking water.[187]

Several methods using liquid-liquid extraction (LLE), solid-phase extraction (SPE), headspace (HS) [27], purge and trap (P&T) and solid-phase microextraction [185, 188-194] have been reported in the literature for the analysis of halogenated VOCs in water. [195-197] P&T is the pre-concentration method for VOCs from water most frequently used in routine analysis in the US. Several EPA protocols in the 500, 600 and 8000 series, e.g. EPA method 524.4 for measurement of purgeable organic compounds in water, rely on P&T.[198] Due to higher sample volumes, exhaustive extraction and higher sorption capacities of the trap, lowest MDLs can be obtained with P&T. [19] An inter-laboratory study which compared SPME with P&T and static HS was done by Nilsson and co-workers. [191] SPME and other microextraction techniques offer several advantages over other analytical methods such as the absence of toxic organic solvents, short preparation times, capability of field sampling [193] and the opportunity for complete automation. [69, 193]

In the last few years, different types of in-needle or in-capillary microextraction methods and devices were developed to overcome some SPME related drawbacks such as fiber fragility and low sorption capacities.[121] These methods utilize two different approaches. One approach uses an immobilized coating on the walls inside a needle [128] or capillary [46, 121, 125] as extraction phase. The other approach uses packings or fillings with sorbent material for extraction. [199, 200]

Enrichment by solid-phase dynamic extraction (SPDE) utilizes a 2.5 mL headspace syringe with a needle that is coated on the inside walls with an immobilized extraction phase. For extraction, the syringe plunger is moved up and down several times for a dynamic extraction of the sample headspace; thereby the analytes are sorbed in the internal coating. After several extraction cycles (aspirating and dispensing) the analytes are thermally desorbed from the coating in the hot GC injector. A schematic overview of the procedure is given in Figure 2.1 and in the literature. [129, 201] SPDE needle coatings possess around 4-6 times larger extraction phase volumes compared with a 100-µm SPME fiber [129] and nowadays all coating types that have been commercialized in SPME are available for SPDE as well. The applicability of HS-SPDE has been demonstrated for a limited number of analytes in environmental [131], food [130, 201] and forensic analysis.[129]

In this work, we aimed at the analysis of volatile halogenated hydrocarbons such as halomethanes (dichloromethane (DCM), chloroform, carbon tetrachloride (CT), bromoform), and halogenated ethanes and ethylenes (1,2-dichloroethane, 1,2-dibromoethane, *cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene (trans-1,2-DCE), trichloroethylen, tetrachloroethylene) in groundwater samples. The main objective was to provide a sensitive, robust, fully automated method with the lowest expenditure in sample preparation. SPDE can be easily implemented in an existing autosampler system and is an alternative to a P&T system with relatively high purchasing costs. Compared with SPME, the method offers higher sorption capacities and a higher stability of the used extraction phase with regard to bending and breaking of fibers. Additionally, the applicability of a dynamic headspace extraction technique for volatile compounds should be tested. To this end, we (i) studied in detail the effects of the most important extraction and desorption parameters of the target compounds, (ii) determined

method detection limits and precision as well as (iii) showed the applicability for determination of VOCs in groundwater samples from a contaminated field site.

3.2 Experimental

3.2.1 Chemicals and Reagents

Methanol (99.9 %) from Merck (Darmstadt, Germany) was used to prepare stock solutions. As solvent for the preparation of standard solutions, millipore water was used from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA).
Trichloroethylene (99.5 %) and dichloromethane (≥99.9 %) were obtained from Merck (Darmstadt, Germany), cis-1,2-dichloroethylene (97%), trans-1,2-dichloroethylene (98%), tetrachloroethylene (99.9+ %), bromoform (99+ %), carbon tetrachloride (99+ %) from Aldrich (Steinheim, Germany), and chloroform (99.5 %) and benzene (99,5%) from Fluka (Buchs, Switzerland). Vinyl chloride was obtained as methanolic standard (2000 µg/mL) from Supelco (Bellefonte, PA, US). The physico-chemical properties of the investigated analytes are summarized in Table 1. Sodium chloride (>99.5%) purchased from Fluka (Buchs, Switzerland) was used to vary the ionic strength of the water samples. The salt was pulverized in a mortar and heated over night at 180°C in an incubator to remove possible organic residues.

3.2.2 GC/MS Equipment and Method

All measurements were carried out with a TraceGC 2000 (ThermoFinnigan, Milano, Italy) gaschromatograph coupled with a TraceDSQ (ThermoFinnigan, Austin TX, US) single quadrupole mass spectrometric detector. SPDE was performed with a CTC-CombiPAL autosampler supplied by Chromtech (Idstein, Germany). Data acquisition, processing and evaluation were carried out using the standard software Xcalibur Data System Version 1.3 (ThermoFinnigan, Austin TX, US). The analytes were separated on a RTX-VMS capillary column (60 m x 0.32 mm ID, 1.8 µm film thickness, Restek Corp., Bellefonte PA, US). The temperature program used to obtain separation of the target compounds was as follows: 10 min at 40 °C, 4 °C/min to 100 °C, 10 °C/min to 170 °C. Total GC runtime was 34 min. The temperatures for the transfer line and the ion source were set to 250 and 220 °C, respectively. The initial GC oven temperature was held at 40 °C to trap the analytes before separation in order to minimize peak broadening. The GC was equipped with a programmable temperature vaporiser BEST PTV (ThermoQuest, Austin TX, US) that was used in the splitless mode at an injection port base temperature of 300°C and a splitless time of 2 min. A 2 mm I.D. deactivated silcosteel liner (Restek Corp., Bellefonte PA, US) was used. Highest desorption efficiency was observed with an injector temperature of 300°C. Higher temperatures than 300 °C were not used to prevent degradation of the extraction phase and thus prolong its lifetime. Carrier gas was Helium 5.0 (Messer, Griesheim, Germany) with a constant flow rate of 1.5 mL/min. The MS was in the electron impact ionization mode at 70 eV. Full-scan mode (m/z = 49-300) was used for all measurements, including the real samples. A chromatogram under optimized conditions is shown in Figure 3.1.

Table 3.1 Physicochemical properties of target compounds

Compounds in elution order	Abbrev.	CAS-no.	MW (g·mol-1) a)	Density (kg·L-1) a)	Boiling point (°C) a)	Vapor pressure (kPa) a)	Calculated air-water partitioning constant Kaw d)	Constants for temperature dependent air-water partitioning constants Kaw b)		Water solubility (g/L) a)	Log Ko/w a)
								A	B		
vinyl chloride	VC	75-01-4	62.5	0.91 [c)]	-13.7	355	1.04	4.119	1223	1.1	1.27
dichloromethane	DCM	75-09-2	84.9	1.33	40.1	57.5	0.11	4.561	1644	13	1.31
trans-1,2-dichloroethylene	*trans*-DCE	156-60-5	96.9	1.27	48.0	40.7	0.45	5.247	1669	6.3	2.09
cis-1,2-dichloroethylene	*cis*-DCE	156-59-2	96.9	1.27	60.0	28.2	0.17	4.464	1559	0.8	1.86
chloroform		67-66-3	119.4	1.48	61.4	25.1	0.16	5.343	1830	8.0	1.95
carbon tetrachloride	CT	56-23-5	153.8	1.62	76.7	14.5	1.18	5.736	1689	0.8	2.77
benzene	benz	71-43-2	78.1	0.88	80.1	12.6	0.24	5.053	1693	1.8	2.17
trichloroethylene	TCE	79-01-6	131.4	1.46	87.0	10.0	0.40	5.874	1871	1.1	2.42
tetrachloroethylene	PCE	127-18-4	165.8	1.62	121.1	2.51	0.69	6.394	1955	0.2	2.88
bromoform		75-25-2	252.8	2.89	149.6	0.72	0.02	5.476	2120	3.0	2.67

a) Ref.: [202]
b) Ref.: [165]
c) liquid phase
d) Values calculated for 25 °C with van't Hoff type equation $\log K_{aw} = A - B/T$
n.a. : not available

3.2.3 SPDE Equipment and Method

The autosampler was additionally equipped with a single magnet mixer, a gas station to aspire desorption gas, and a heated flushing station for conditioning and reconditioning of the SPDE needles (all from Chromtech, Idstein, Germany). The gas station and the syringe body were connected via the autosampler to a nitrogen gas cylinder (purity 5.0). The syringe body was held at a temperature of 35 °C in the syringe adapter heater. All steps of the SPDE method were fully controlled by the CTC-CombiPAL with custom-made software macros.
A needle coated with a PDMS/AC phase (polydimethylsiloxane with 10% embedded activated carbon) with 50 µm film thickness and 56 mm film length was used. Needles were obtained from Chromtech (Idstein, Germany). The needles were pre-conditioned in the flush station for 90 min at 280 °C. During the pre-conditioning, the syringe was flushed with nitrogen gas through the syringe side port. Samples were placed on a heatable tray (Chromtech, Idstein, Germany), which was set to a constant temperature of 60 °C. Before measuring, the samples were stirred for 5 min at 60 °C in the single magnet mixer at 700 rounds per minute to establish equilibrium between headspace and water phase. Afterwards, the SPDE needle was inserted 12 mm through the septum into the vial for dynamic extraction of the headspace under continuous stirring. Fifteen 1-mL extraction strokes with an extraction flow rate of 50 µL/s corresponding to an extraction time of 10 min were done. After extraction, a desorption volume of 1 mL nitrogen gas was aspirated into the syringe at the gas station before thermal desorption into the injector with a desorption flow rate of 10 µL/s. Following desorption, the needle was removed from the injector and flushed with nitrogen for 2 min in the needle flush station at a temperature of 280°C, in order to prevent carry-over effects.

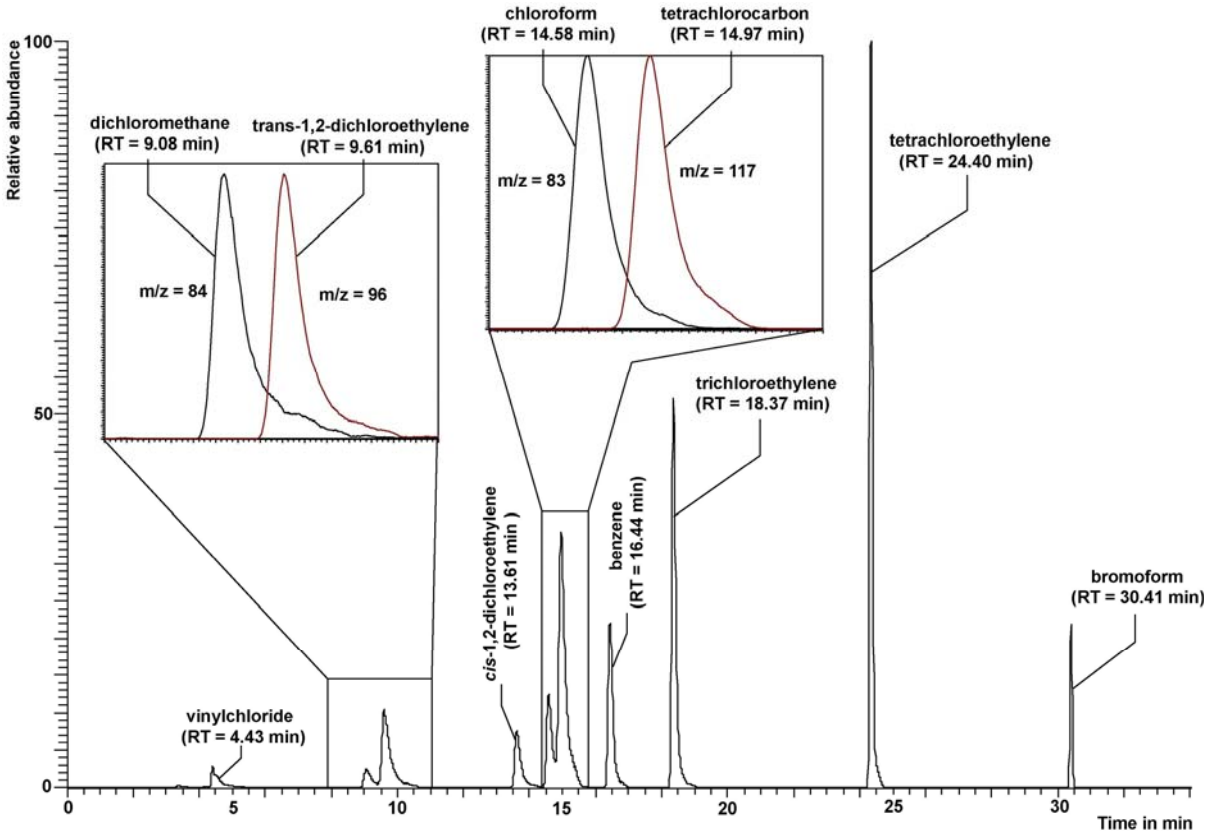

Figure 3.1 Full-scan chromatogram of the ten VOC target compounds with a combination of reconstructed ion chromatograms of a 100 µg/L standard solution under optimized conditions. m/z values used for quantification are given in Table 3.2.

3.2.4 Stock Solutions and Standard Mixture

Mixed methanolic stock solutions with a concentration of 2000 mg/L were prepared weekly and were stored at 4 °C in the dark refrigerator. Vinyl chloride was available as 2000 mg/L standard methanolic solution. Standard solutions were prepared before each experiment from these primary stock solutions in millipore water. Lower concentrated solutions for calibrations, MDL determination and optimization were prepared likewise by volumetric dilution to the required concentration levels. During evaluation of method parameters, all measurements have been carried out in triplicate using 100 µg/L standard solution mixtures.

3.2.5 Preparation of Standards and Groundwater Samples

A 20-mL screw cap headspace vial (BGBAnalytik, Anwil, Switzerland) was filled with 0.52 g (5 % (w/w)) sodium chloride and a 8 mm glass coated stir bar (FisherScientific, Ulm, Germany). Then, 10 mL of standard solution mixture or real sample were transferred immediately with a 10-mL gastight Hamilton syringe (BGBAnalytik, Anwil, Switzerland) to the vial that was sealed immediately with a PTFE coated silicone septum and a magnetic screw cap. It was necessary to shake the vials for at least ten minutes in order to ensure complete dissolution of the salt.
Groundwater samples from a former waste oil recycling facility were stored without headspace in 1 L brown glass bottles in a dark cool storage room (4 °C). Ten mL aliquots of groundwater were processed as described above. Quantification was carried out by an external standard calibration, therefore identical sample and headspace volumes were used in the standards and the samples.

3.3 Results and Discussion

3.3.1 Evaluation of Extraction Parameters for SPDE

As for other microextraction methods, desorption and extraction parameters including desorption temperature, extraction time and temperature, as well as salting out have to be optimized for highest extraction yields. In case of solid-phase dynamic extraction additional parameters originating in the dynamic process have to be optimized. These additional parameters are pre-desorption time, desorption flow rate, desorption volume, and extraction flow rate.

3.3.2 Extraction Cycles

In solid-phase dynamic extraction the number of extraction cycles correlates directly with the extraction time. One to fifty extraction cycles, corresponding to extraction times between 0.66 and 33.3 min, were investigated. During the extraction process the temperature was held at 25 °C and before extraction the samples were equilibrated for 2 h in the heated tray. The extraction flow rate and volume were set to 50 µL/s and 1 mL, respectively. Fig. 3.2 shows that a stable response could be observed after 15 cycles (10 min), i.e., additional cycles led to no further increase in peak areas for most of the target analytes. Bromoform shows a lower slope in the extraction profile, especially for the first extraction cycles and does not reach equilibrium within fifty cycles.

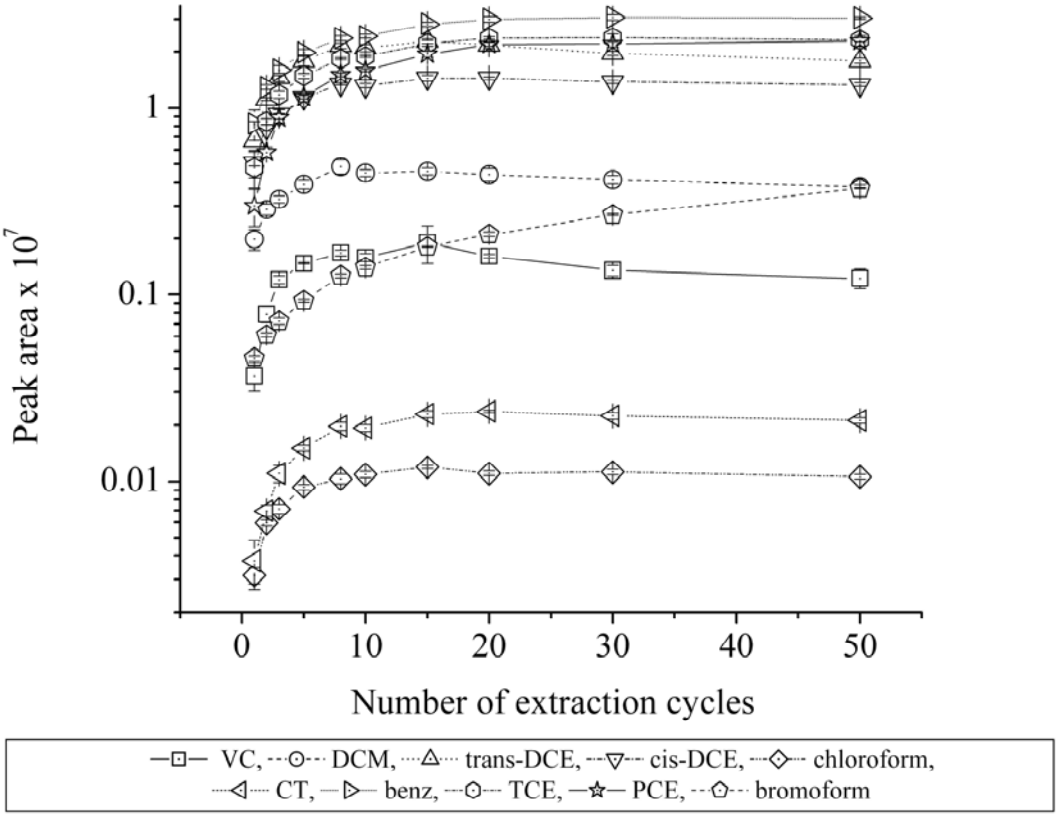

Figure 3.2 Extraction profiles for the investigated compounds at 25 °C. Triplicate measurements were done for each point , error bars indicate the standard deviation. The logarithmic scale for peak areas was chosen for a better interpretation of the curves over the large peak area range for the different analytes

The large difference for bromoform compared with the other compounds is due to its ten times smaller air-water partitioning coefficient. In contrast to bromoform, vinyl chloride has the highest air-water partitioning coefficient and shows the highest slope and fastest extraction. This indicates that the limiting factor in the extraction process is the air-water partitioning coefficient. Similar results are known for HS-SPME [203, 204] For VC, *trans*-DCE and dichloromethane decreases in peak areas can be observed for more than 15 extraction cycles. This decrease could either be explained by a competition with other compounds, or by evaporation through the hole in the septum along the SPDE needle. The latter explanation was given by Nilsson et al., who found the same slightly decreasing peak areas for light VOCs. [193] The former result was reported by Shojania et al. during active sampling of BTEX compounds with the INCAT device. In their study, active sampling of all BTEX compounds simultaneously led to a distinct competition trend, preferring the heavier compounds. [128] The curves obtained here for chloroform, CT, TCE and benzene are comparable with extraction time profiles found for HS-SPME. [205] For the optimized method, 15 extraction cycles were used.

3.3.3 Extraction Temperature

A temperature range between 20 °C and 70 °C was investigated in this study. For the evaluation, the extraction flow rate was held at 50 µL/s, extraction volume at 1 mL, and 15 extraction cycles were done. In Figure 3.3a, the extraction temperature is plotted against the peak area. In this plot, a maximum peak area was observed for most of the components.

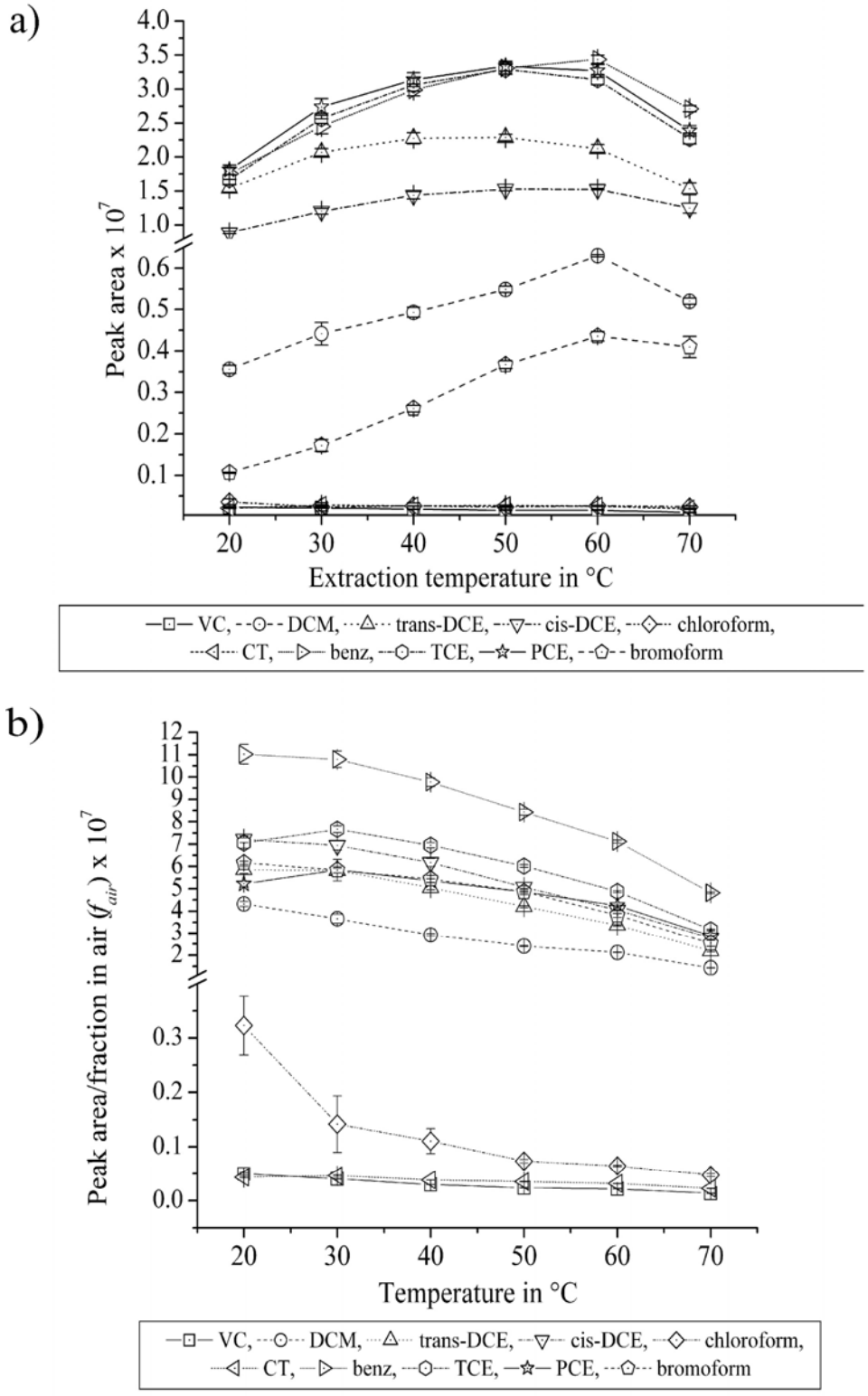

Figure 3.3 a) Effect of the extraction temperature on extraction yield. Measurements were carried out in triplicate for each point. Error bars indicate the standard deviation but are often smaller than the symbol size. **b)** Ratio of peak area (extracted amount) of a given analyte over analyte fraction in air (f_{air}) depending on temperature. Error bars indicate the estimated uncertainty from error propagation.

This behavior is well known and a similar maximum could be observed in SPME for a variety of volatile and semivolatile compounds. [185, 206, 207] As in SPME, two counteracting processes play a role. First, the air-water partitioning constant K_{aw} increases with increasing temperature but at the same time the sorbent-air partitioning coefficient K_{sa} decreases with increasing temperature, because the molar change in enthalpy for the sorption process is positive and the sorption process is exothermic. In this work, the extraction phase was held as cool as possible, therefore the syringe body was set to 35 °C. During extraction one fifth of the needle was introduced in the vial headspace. The rest of the steel needle is in contact with room temperature which was held at 20 °C. Nevertheless, with increasing temperature in the vial the temperature of the steel needle and the coating increases. For a better evaluation of temperature influence on the air-sorbent partitioning, the ratio of measured peak areas to the analyte fraction in air f_{air} was plotted in Fig. 3.3b against the temperature. The fraction in air was calculated according to literature [201, 202] by using the air-water partitioning coefficients in Table 1. Figure 3.3b shows that the extracted amount in the coating decreases with increasing temperature relative to the concentration in the headspace and the higher K_{aw} is partially compensated by the lower K_{sa}. Most compounds show a decrease of K_{sa} with temperature, while TCE and PCE have a maximum for K_{sa} at a vial incubation temperature of 30 °C. Another factor that could decrease K_{sa} is the humidity in the system that increases with temperature. [206]

3.3.4 Extraction Flow Rate

Fig. 3.4 shows the effect of extraction flow rate on peak areas for the investigated compounds. With decreasing extraction flow rate an increase in the extraction yield can be observed.
Obviously, the diffusion into the extraction phase is reduced by a higher flow rate. The best fit for this trend was achieved by potential functions of the type $PA = a\dot{V}^{-b}$, were PA is the peak area, $\dot{V}$ the extraction flow rate and a, b are fitting parameters. The fitting parameters for the extraction flow rate are given in Table 3.2. For very volatile compounds such as VC the effect is not as pronounced as for compounds with lower air-water partitioning constants. A possible explanation for the observed trend is a higher diffusion coefficient into the coating for the very volatile compounds. For adequate extraction times an extraction flow rate of 50 µL/s was used for the optimized method with a constant extraction volume of 1 mL.

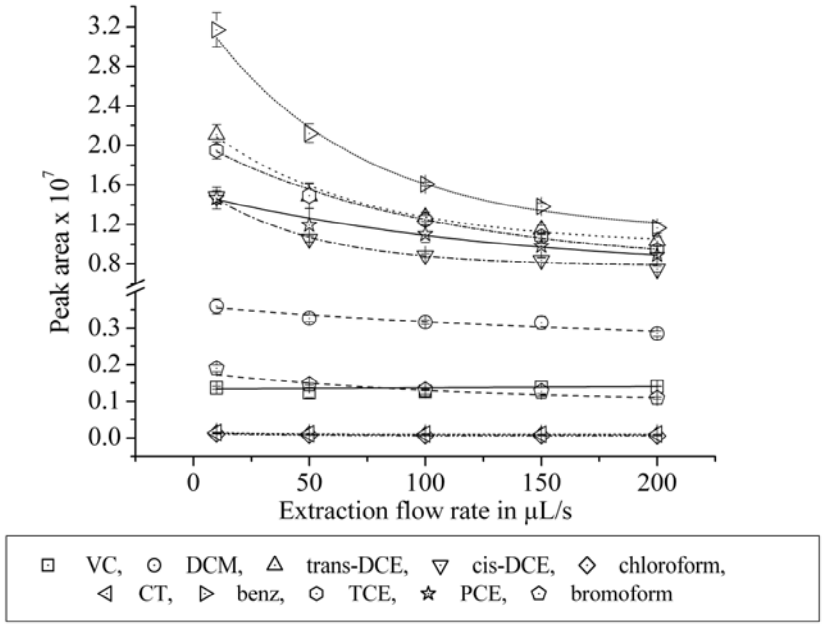

Figure 3.4 Dependency of peak areas on extraction flow rate. Measurements were carried out in triplicate for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

3.3.5 Effect of Ionic Strength and Determination of Setschenow Constants

The influence of salt addition to the sample solutions on extraction yields was tested by using 15 extraction cycles at an extraction temperature of 25 °C. Six different electrolyte concentrations, ranging from 0% to 25% NaCl (w/w) were used. Higher salt concentration levels were not used because of approaching the sodium chloride water solubility and inadequately long dissolving times. The addition of salt increases the sample volume and therefore volume correction factors were determined experimentally for the tested salt concentrations and applied in all subsequent calculations. Figure 3.5 shows that salt addition leads to higher extraction efficiencies for most investigated compounds.

Comparing peak areas at a concentration of 25% (w/w) NaCl with 0% (w/w) NaCl shows that extraction yields for all compounds increase by factors between 1.0 and 3.0. The values are in rather good agreement with literature data obtained at full saturation [185] but smaller than reported in a previous study for a 7.5 % (w/w) NaCl solution. [208] To quantify the effect of salt concentration on extraction, salting-out constants (Setschenow constants) K^s were determined exemplarily for some of the investigated compounds. [189, 202, 209]

For the determination of Setschenow constants, total salt concentrations up to 1.9 mol/L (10 % (w/w)) were used. Higher salt concentrations lead to considerable deviations that could not be described by the used equations. [171, 201] The obtained correlation coefficients (n = 3 points) were between 0.987 and 0.999. As shown in Table 2, Setschenow constants range between 0.152 and 0.213 L/mol. For benzene a somewhat lower constant than in literature was obtained, and for TCE and PCE a good agreement with a previous report [209] was found. For the optimized method 5 % (w/w) NaCl (0.52 g) was used. As shown in Figure 3.5, higher salt concentrations lead to higher standard deviations and lower reproducibility.

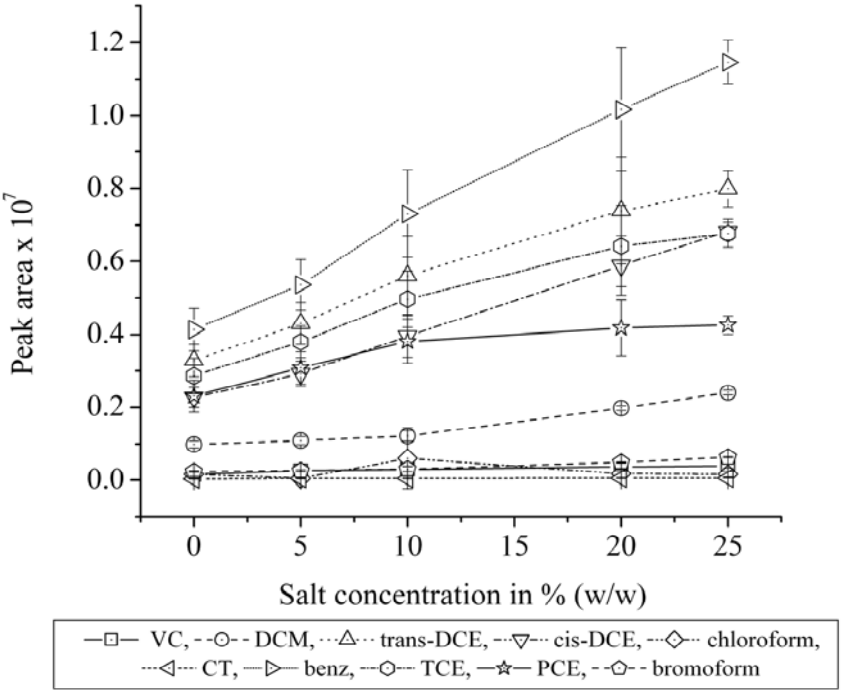

Figure 3.5 Effect of ionic strength on extraction yield of the target analytes. Measurements were carried out in triplicate for each point at 25°C. Error bars indicate the standard deviation but are often smaller than the symbol size.

Table 3.2 Fitting parameters for desorption and extraction flow rates as well as obtained ratios between highest and lowest investigated salt concentration, and determined Setschenow constants compared with constants reported in literature

Compounds in elution order	**Extraction flow rate**			**Desorption flow rate**			**Peak area (25 % NaCl) / peak area 0 % NaCl)**	**Determined Setschenow constants** [c]		**Setschenow constants from literature K^s in L mol^{-1}**			
										Gosset et al. [a]		**Dewulf et al.** [b]	
	A	**b**	**R^2**	**a**	**b**	**R^2**		**K^s (L mol^{-1})**	**R^2**	**K^s (L mol^{-1})**	**R^2**	**K^s (L mol^{-1})**	**R^2**
vinyl chloride	-[*)]	-[*)]	-[*)]	3 x 10^7	-0.7894	0.9878	2.5	-	-	n.a.	n.a.	n.a.	n.a.
dichloromethane	4 x 10^6	0.06480	0.8644	2 x 10^7	-0.4467	0.9853	2.4	-	-	0.107	0.998	n.a.	n.a.
trans-1,2-dichloroethylene	4 x 10^7	0.23180	0.9946	8 x 10^7	-0.4941	0.93	2.4	0.179	0.999	n.a.	n.a.	n.a.	n.a.
cis-1,2-dichloroethylene	2 x 10^7	0.22260	0.9948	5 x 10^7	-0.4570	0.9872	3.0	0.137	0.999	n.a.	n.a.	n.a.	n.a.
chloroform	2 x 10^6	0.20020	0.9854	1 x 10^6	-0.4032	0.5589	1.0	-	-	0.107	0.998	0.153	0.976
carbon tetrachloride	2 x 10^4	0.06390	0.0337	225470	-0.7830	0.8565	1.7	-	-	n.a.	n.a.	0.185	0.999
benzene	7 x 10^7	0.32510	0.9774	1 x 10^8	-0.4777	0.9953	2.8	0.152	0.999	n.a.	n.a.	0.173	0.982
trichloroethylene	3 x 10^7	0.23360	0.9595	1 x 10^8	-0.4191	0.9859	2.4	0.178	0.997	0.187	0.999	0.182	0.991
tetrachloroethylene	2 x 10^7	0.15660	0.9553	1 x 10^8	-0.4176	0.9846	1.8	0.213	0.987	0.213	0.994	0.150	0.962
bromoform	3 x 10^6	0.17080	0.9679	335624	-0.4456	0.6878	2.7	-	-	n.a.	n.a.	n.a.	n.a.

[a] Ref.: [209]

[b] Ref.: [189]

[c] Determined at 25 °C at salt concentrations between 0 – 10 % NaCl (w/w)

-: could not be fitted with a linear function

-[*)]: could not be fitted by exponential function

n.a. : not available

3.3.6 Desorption Temperature and Pre-desorption Time

The pre-desorption time, is the time, in which the needle is inserted into the hot injector to achieve thermal equilibrium of the extraction phase, before the syringe plunger is moved down for desorption. For the evaluation, three different pre-desorption times (0, 5, 10 s) were investigated. As in a previous study [201], the pre-desorption time showed no significant influence on the sensitivity. A longer pre-desorption time leads to peak tailing and splitting, as described previously in literature. [129] Wang et al. observed the same phenomenon during the needle trap evaluation and suggested that the air volume in the needle expands significantly due to the high injector temperature. Parts of the analytes are then swept with expanded air into the GC column, which leads to peak splitting and broadening. [135] Corroborating these results no pre-desorption time was used further, i.e., the plunger was moved down immediately after needle injection into the injector.

3.3.7 Desorption Flow Rate

The desorption flow rate was varied between 10 µL/s and 1000 µL/s with a constant desorption volume of 1000 µL. These desorption flow rates correlate with desorption times between 100 s and 1 s. In Figure 3.6 the peak area of the analytes is plotted vs. the desorption flow rate. Fig. 3.6 shows that the sensitivity is significantly influenced by the nitrogen flow rate during desorption. The obtained results could be fitted by the same expression as for the extraction flow rate. The fitting parameters are reported in Table 3.2. The explanation for inverse proportional relationship between peak area and desorption flow rate is that the analytes need time to diffuse from the coating into the nitrogen gas stream. These results agree with previous reports for other compounds on highest sensitivities at low desorption flow rates. [129] In the optimized method a flow rate of 10 µL/s was therefore used.

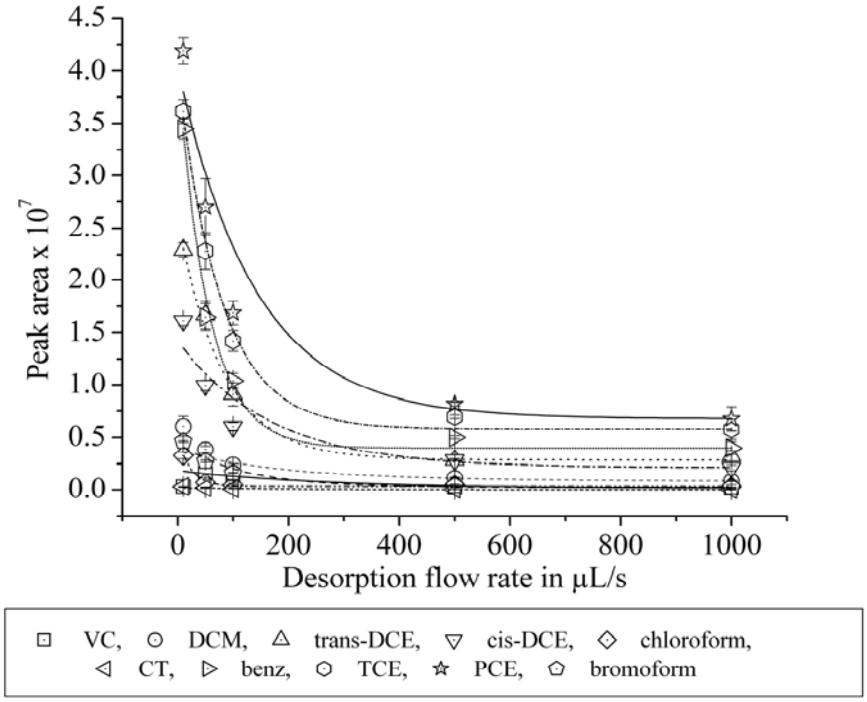

Figure 3.6 Dependency of peak areas on desorption flow rate. Triplicate measurements were carried out for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

3.3.8 Desorption Volume

The desorption volume has, according to literature a significant influence on the desoption process. [129, 130] Musshoff et al. found the highest efficiency with the highest possible syringe desorption volume of 2.5 mL. [129] Bicchi et al. found that no significant change in peak areas occurred for desorption volumes higher 1 mL for volatile food aromatics. [130] In disagreement with these results, we found in this study that significant changes of peak areas did not occur for desorption volumes between 0.5 mL and 1 mL for any component (Fig . 7). From 1 mL to 2.5 mL a decrease in the peak areas was observed with peak tailing and even peak splitting at higher desorption volumes. The reason for this seems to be the slow transfer of the analytes to the capillary column in the injector at higher desorption volumes. Therefore, a desorption volume of 1 mL was used in the optimized method. Using a column cryofocusing unit should prevent this phenomenon and would also lead to sharper peaks.

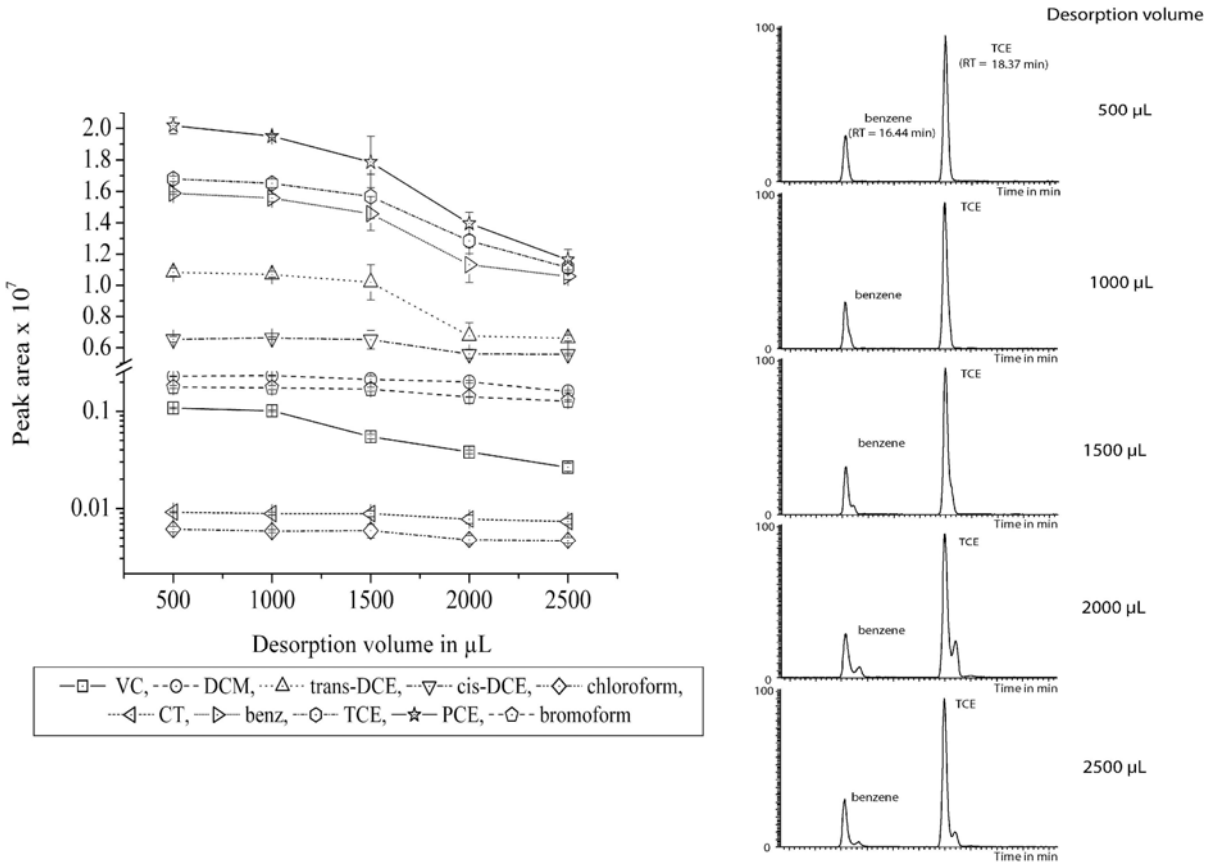

Figure 3.7 On the left hand side, the dependency of peak areas on desorption flow rate is shown. Triplicate measurements were carried out for each point. Error bars indicate the standard deviation but are often smaller than the symbol size. On the right hand side the splitting of the peaks by increasing the desorption volume is shown exemplarily for benzene and trichloroethylene.

3.4 Validation of the Method

Method detection limits (MDLs) were determined according to the U.S. Environmental Protection Agency procedure. [210] The first step was to find individual test level concentrations in preliminary measurements for all compounds at a signal to noise ratio of about 5:1. Nine replicates were measured at this concentration and standard deviations for these measurements were calculated. For each compound, six point calibrations (each point in triplicate) bracketing the test level was used for

quantification. Finally, MDLs were calculated by multiplying the standard deviation s_d with the student *t*-factor for a degree of freedom f = 8. MDLs for all target compounds were determined accordingly, and are presented in Table 3.3. The MDL were between 12 ng/L for *trans*-DCE and *cis*-DCE and 870 ng/L for VC. These method detection limits are comparable with reported detection limits for SPME-GC/ITMS methods. [204, 211] However, reported MDL values are difficult to compare because of different methods to determine or calculate these values.

The precision of the method was determined with nine replicates each at two concentration levels: once from the replicates used for MDL determination, once at a higher concentration level of 100µg/L. Relative standard deviations at the low concentration level were between 1.0 % for bromoform and 16 % chloroform. At the higher concentration level relative standard deviations between 3.2 % for benzene and 7.5 % for vinyl chloride were observed. Precisions are comparable with precisions reported in literature for SPME methods. [206, 208, 211]

Table 3.3 Validation data for the SPDE-GC/MS method

Compounds in elution order	Target ions used for quantification (m/z)[a)]	Retention times (min)	Minimum linear range (µg/L)[b)]	Correlation coefficient R^2	Method detection limit (ng/L)	Precision at low concentration (%)[c)]	Precision at high concentration (%)[d)]
vinyl chloride	62, 64	4.43	0. 870 - 83	0.993	870	4.0	7.5
dichloromethane	84, 49	9.08	0.119 -23	0.991	119	5.0	6.6
trans-1,2-dichloroethylene	96, 61	9.61	0.012 -23	0.999	12	3.1	5.1
cis-1,2-dichloroethylene	96, 61	13.61	0.012 - 24	0.998	12	1.5	5.1
chloroform	83, 119	14.58	0.018 - 25	0.998	176	16	3.7
carbon tetrachloride	117, 119	14.97	0.019 - 27	0.997	19	4.8	6.8
benzene	78, 51	16.44	0.013 - 15	0.998	13	3.7	3.2
trichloroethylene	130, 95	18.37	0.013 - 28	0.997	13	3.6	4.9
tetrachloroethylene	166, 131	24.40	0.028 - 29	0.990	28	5.7	5.0
bromoform	173, 252	30.41	0.022 - 60	0.996	22	1.0	6.8

[a)] Base peak used for quantification is underlined.
[b)] Linear range measured for MDL determination
[c)] Relative standard deviations (n = 9, fortification level approx. five times higher than MDL for individual compounds)
[d)] Relative standard deviations (n = 9, fortification level 100 µg/L)

3.5 Analysis of Groundwater Samples

The SPDE-GC/MS method was applied to the analysis of several groundwater samples from a former oil recycling facility. Samples from eight different wells of the contaminated site were investigated for the target compounds. The quantification was based on a six point external standard calibration curve that was generated by spiking Milli-Q water samples with the target analytes. Calibration and real water samples were analyzed using the optimized method parameters described above. Each sample was analyzed three times using the optimized SPDE method. The determined concentrations are reported in Table 3.4. In Figure 3.8, a typical chromatogram of a real sample is shown. It should be emphasized here that the method is also applicable for the determination of other BTEX compounds than benzene and even low molecular weight PAHs such as acenaphtene as can be seen in the chromatogram. The concentrations given in Table 3.4 agree rather well with those measured by a commercial laboratory two months before using a standardized method for BTEX determination.

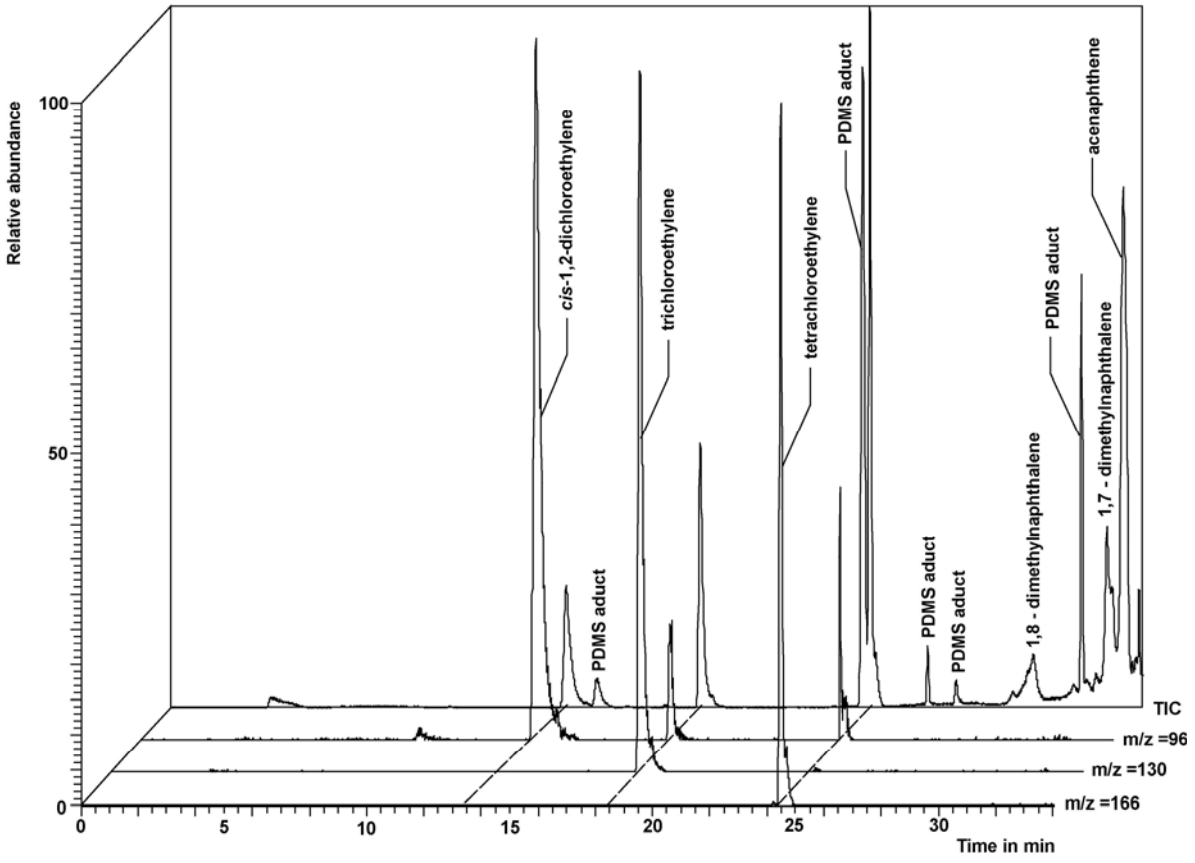

Figure 3.8 Full-scan chromatogram with a combination of reconstructed ion chromatograms for the quantification masses of chlorinated ethylenes from well B 6 obtained under optimized conditions described in the experimental part. PDMS fragments from the SPDE coating occur in the chromatogram. At retention times longer than 30 min, dimethyl naphthalenes and acenaphthene occur in the chromatogram.

Table 3.4 Detected VOCs in groundwater samples from a former oil recycling facility

Compounds	**Concentration in examined groundwater wells (µg/L)**							
	B 1	**B 2**	**B 3**	**B 4**	**B 5**	**B 6**	**B 7**	**B 8**
trans-1,2-dichloroethylene	-	-	3.6 ± 0.7	0.9 ± 0.3	-	0.5 ± 0.1	-	-
cis-1,2-dichloroethylene	2.5 ± 0.8	-	22 ± 6	28 ± 5	0.8 ± 0.4	119 ± 12	44 ± 1.3	0.5 ± 0.3
benzene			30 ± 7	21 ± 2	-	-	-	-
trichloroethylene	1.3 ± 0.1	-	0.11 ± 0.01	0.1 ± 0.08	0.6 ± 0.09	60 ± 6	14 ± 0.8	1.2 ± 0.06
tetrachloroethylene	21 ± 1	-	-	-	73 ± 13	72 ± 5	1052 ± 17	464 ± 22

-: not detected

4 In-tube Extraction (ITEX) for Extraction of Volatile Organic Hydrocarbons from Groundwater

4.1 Introduction

Around 15 years ago solid-phase micro-extraction (SPME) was introduced as solventless equilibrium microextraction method. Since this time, other related micro-extraction methods such as stir bar sorptive extraction (SBSE), liquid-phase micro-extraction (LPME) and several in-tube or in-needle extraction techniques were developed to overcome some fiber related drawbacks such as fiber fragility, diminished lifetimes of polar coating materials and low sorption capacities. [24] In-tube or in-needle extraction techniques roughly can be divided in methods that either apply a coating on the inner surface or a sorbent material packed inside a tube or a needle. Methods with sorbent packings, such as ITEX offers the advantage that a variety of commercial available sorbent materials and higher amounts of sorbent material can be used to obtain higer extraction yields than possible with coated extraction phases. Early approaches used gas chromatography capillary columns such as so called open tubular traps (OTT). [125] A very similar method is known as in-tube SPME, which was originally developed in combination with HPLC, [123] for the determination of chlorinated hydrocarbons[212] and pesticides. [122] A shorter capillary with a sol-gel coating (sol-gel CME) was used by Bigham et al. for determination of compounds such as PAHs, aldehydes and ketones as well as for more polar compounds such as phenols, alcohols and amines. [121] Other in-tube techniques such as in - capillary extraction (INCAT) [127] or solid-phase dynamic extraction (SPDE) [201, 213, 214] use a needle as support for the extraction phase. These needle based methods have the advantage that thermal desorption can be carried out directly in the injection port of a gas chromatograph and the whole process can easily be implemented in an auto-sampler. To achieve higher extraction yields, efforts were made to increase the amount of extraction phase by applying packed sorbent materials. A method to determine BTEX compounds that applies a sorbent bed was developed by Berezkin and Kubinek. [215] Another needle based device that uses a packed sorbent is the needle trap (NT) by Wang and Pawliszyn. [135] This needle trap is either filled with Carboxen 1000 or with a mixed packing of PDMS, DVB and Carboxen particles. A similar needle extraction device for GC/MS analysis of VOCs (toluene, ethyl acetate) was presented by Saito and co-workers, by using a copolymer bed of methacrylic acid and ethylene glycol dimethacrylate. [136]

ITEX enhances the advantages of previous needle-based methods by applying a stainless steel needle that is divided into two parts. Compared with SPME, the method offers a higher roubustnes with regard to bending and breaking of fibers. As shown in the schematic illustration of the ITEX procedure in Figure 4.1, the lower part consists of an ordinary needle canula with a hole on the side for vial and septum penetration. The upper part with a bigger diameter contains the sorbent material. The upper part of the ITEX needle is surrounded by a heater for thermal desorption after the extraction process. Compared with other in-needle techniques the thermal desorption occurs outside the GC injector, which makes the method independent from the injector temperature profile and offers a gradient free desorption. After thermal desorption, the sorbent material is flushed with nitrogen at elevated temperature for cleaning. In this study, Tenax TA® was used as packing material for extraction of the target analytes. The ability to apply relatively high amounts of a variety of packing materials, e.g. as used in P&T, is a special advantage of the method and opens a wide range of applications to various compound classes with different polarities.

In this work, in-tube extraction (ITEX) was evaluated for the determination of nineteen priority groundwater pollutants [183, 216] such as volatile halogenated hydrocarbons (dichloromethane, chloroform, carbon tetrachloride, bromoform, 1,2-dichloroethane, 1,2-dibromoethane, *cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene, trichloroethylene, tetrachloroethylene) and BTEX compounds (toluene, ethylbenzene, propylbenzene, 1,2,4-trimethylbenzene, benzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, *para*-xylene). All these compounds have adverse effects to environmental systems and human health and most of the components are known or probable human carcinogens. [184]

The main objective was to evaluate a sensitive, robust method that applies a solid sorbent material as extraction phase, with the ability to use the wide range of sorbent materials that were available for purge and trap and air sampling.To this end, in this work the evaluation of (i) the most important extraction and desorption parameters, as well as the (ii) determination of validation parameters such as method detection limits and precisions for volatile organic compounds was done.

4.2 Experimental

4.2.1. Reagents

Methanol (99.9 %) from Merck (Darmstadt, Germany) was used to prepare stock solutions. As solvent for the preparation of standard solutions, Milli-Q water from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA) was used. Trichloroethylene (99.5 %), dichloromethane (≥99.9 %) and toluene (99.9 %) were obtained from Merck (Darmstadt, Germany). *Cis*-1,2-dichloroethylene (97%), *trans*-1,2-dichloroethylene (98%), tetrachloroethylene (99.9+ %), bromoform (99+ %), 1,2-dichloroethane (99.8%), 1,2-dibromomethane (99 %), carbon tetrachloride (99+ %), isopropylbenzene (99 %), *para*-xylene (99 %), ethylbenzene (99.8 %), propylbenzene (98 %), 1,2,4-trimethylbenzene (98 %) were purchased from Aldrich (Steinheim, Germany) and chloroform (99.5 %), benzene (99.5 %), 1,3,5-trimethylbenzene (99 %), 1,2,3-trimethylbenzene (90-95 %) from Fluka (Buchs, Switzerland). Fluorobenzene (99 %) from Aldrich (Steinheim, Germany) was used as internal standard. Sodium chloride (>99.5%) purchased from Fluka (Buchs, Switzerland) was used to vary the ionic strength of the water samples. Sodium chloride was pulverized for a faster dissolution in a mortar and heated over night at 180°C in an incubator to remove possibly existing organic residues. Abbreviations used for the compounds were explained in Table 5.1 in section 5.1.

4.2.2 GC/MS Equipment and Method

All samples were measured using a TraceGC 2000 (ThermoFinnigan, Milano, Italy) gaschromatograph coupled with a TraceDSQ (ThermoFinnigan, Austin TX, US) single quadrupole mass spectrometer. ITEX was performed with a CTC-CombiPAL autosampler supplied by Chromtech (Idstein, Germany). Data acquisition, processing and evaluation were carried out using the standard software Xcalibur Data System Version 1.3 (ThermoFinnigan, Austin TX, US). The analytes were separated on a RTX-VMS capillary column (60 m x 0.32 mm ID, 1.8 µm film thickness, Restek Corp., Bellefonte PA, US). To obtain sharper peaks, especially for the early eluting chlorinated hydrocarbons, 1 m of a 0.53 i.d. deactivated capillary column was used as retention gap between the injector and the analytical column. The temperature program used to obtain separation of the target compounds was as follows: 14 min at 40 °C, 4 °C/min to 100 °C, hold for 2 min, 10°C/min to 170 °C and hold for 5 min. The total runtime of the GC program was 36 minutes and the temperatures for the transfer line and the ion source were set to 250 °C and 220 °C, respectively.

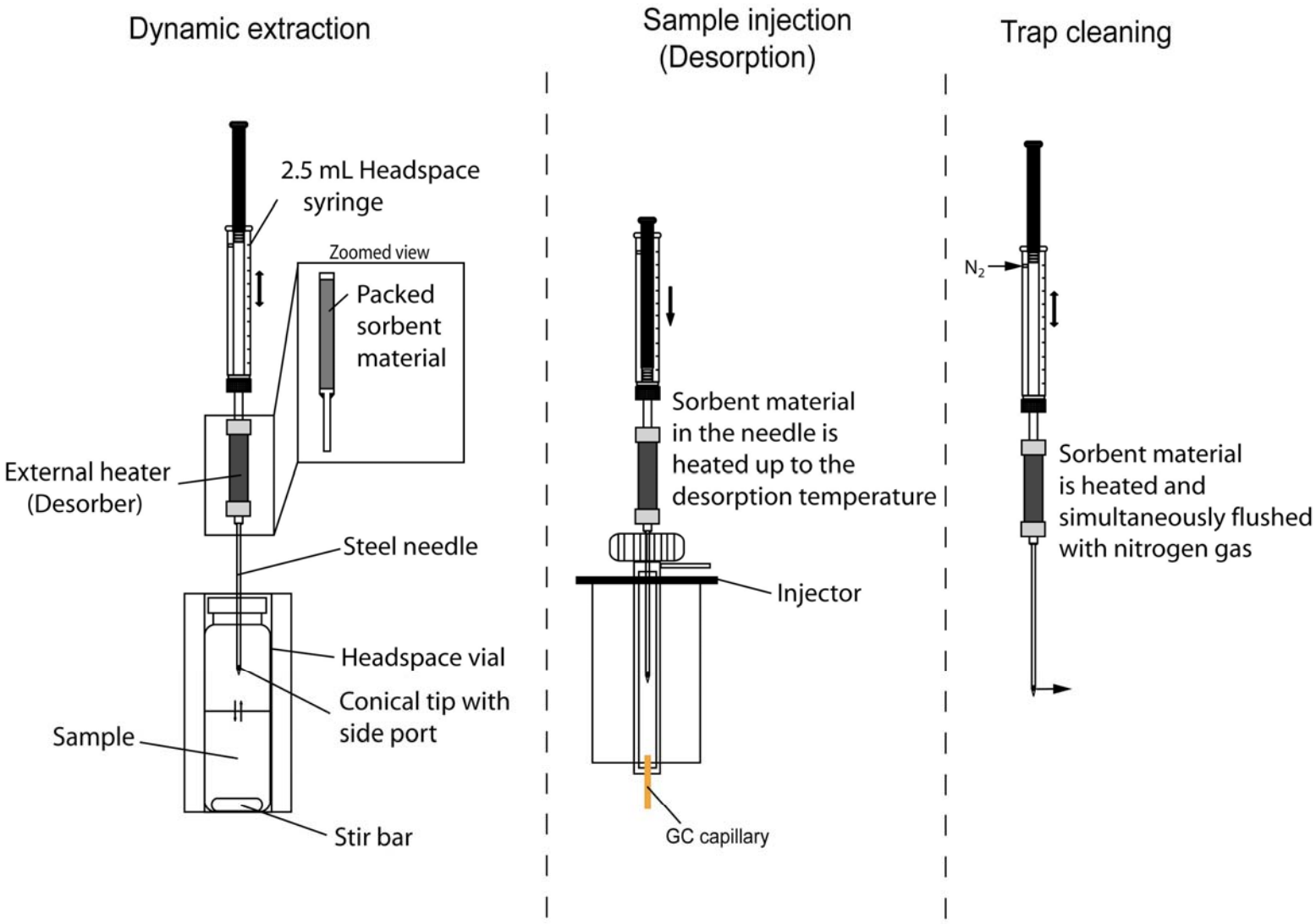

Figure 4.1 Schematic overview of the different operation steps of the ITEX method. The left part shows the dynamic extraction of the sample headspace. In the middle part, the thermal desorption into the injector by heating the desorber is shown. In the right part, the trap is cleaned by flushing the heated trap

The initial GC oven temperature was held at 40 °C to trap the analytes before separation in order to prevent peak broadening.
The GC was equipped with a programmable temperature vaporiser BEST PTV (ThermoQuest, Austin TX, US) that was used in the splitless mode at an injection port base temperature of 170 °C and a splitless time of 2 min to compensate pressure caused by the gas injection. The PTV was programmed such that during the injection phase the column flow was set to 1mL/min to minimize the pressure during injection of the gas volume. After 2 min it was set to a constant column flow of 1.5 mL/min for the rest of the chromatographic separation. A 1 mm I.D. deactivated silcosteel liner (Restek Corp., Bellefonte PA, US) was used. As carrier gas Helium 5.0 (AirLiquide, Düsseldorf, Germany) was used. The MS was in the electron impact ionization mode (EI) at 70 eV. Full-scan mode (m/z = 49-300) was used for all measurements, including the real samples. A chromatogram of a 5 µg/L standard obtained under optimized conditions is shown in Figure 4.2.

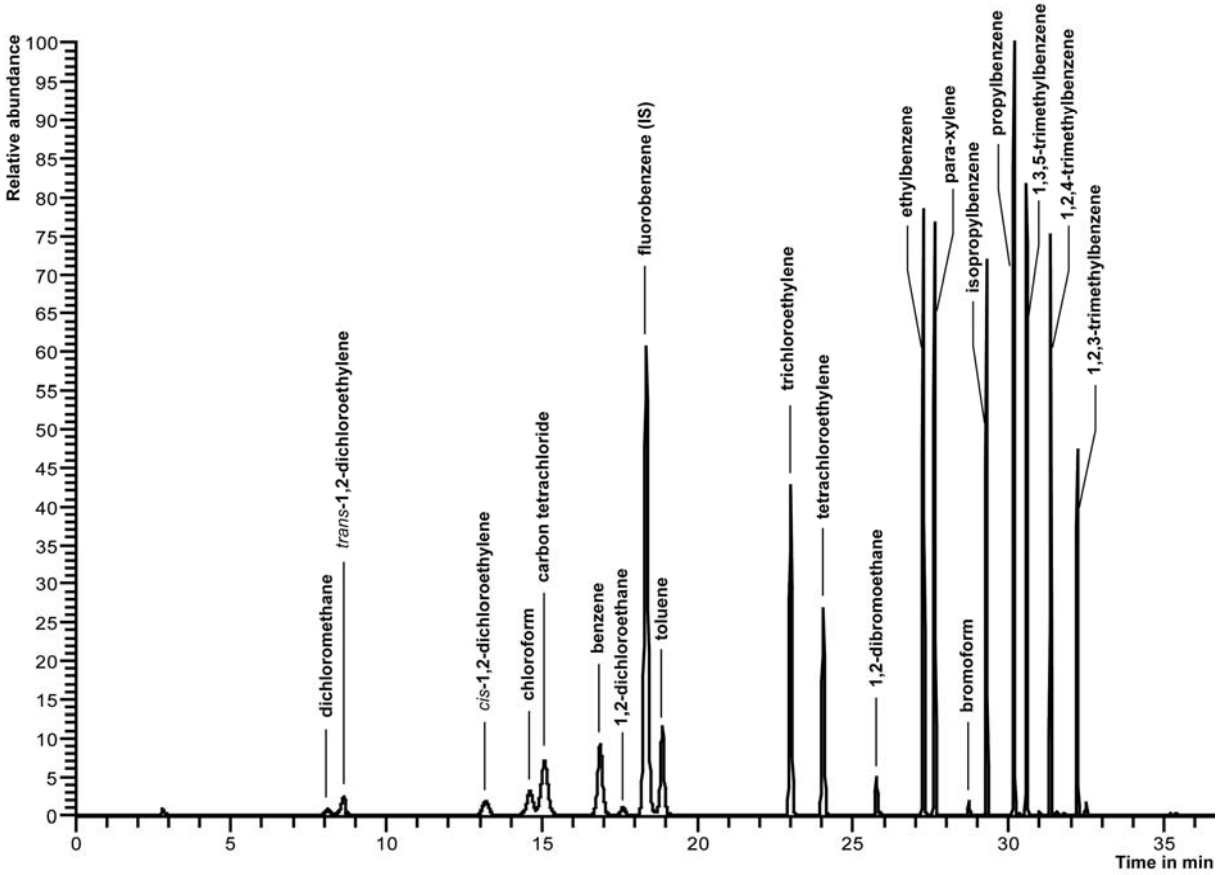

Figure 4.2 Full-scan chromatogram of the 19 chlorinated volatile hydrocarbons and BTEX target compounds with a combination of reconstructed ion chromatograms of a 5 µg/L standard solution under optimized conditions. Quantifier m/z and retention times are given in Table 4.2.
Internal standard (IS) fluorobenzene with a retention time of 18.35 min (m/z = 96 and 70).

4.2.3 ITEX - Equipment and Procedure

The autosampler was equipped with a single magnet mixer (Chromtech, Idstein, Germany) and a temperature controlled tray holder (Chromtech, Idstein, Germany). The samples were placed in the thermostated tray holder (45 °C). Before extraction the sample was stirred for 15 min in the single magnet mixer at an incubation temperature of 50 °C to establish equilibrium distribution of the analytes between aqueous and gas phase in the vial before extraction. The extraction volume of the gas phase was set to 1000 µL and 20 extraction cycles were used for the optimized method. The plunger speed during the extraction was set to 100 µL/s. For thermal desorption, the desober was heated up to 170 °C and 700 µL of the sample were transferred by a desorption flow rate of 10 µL/s into the hot injector. After desorption, the ITEX device was flushed with nitrogen gas at a desorber temperature of 210 °C for 20 min.

4.2.4 Stock Solutions and Standard Mixture

Mixed methanolic stock solutions with a concentration of 2000 mg/L were prepared weekly and were stored at 4 °C in the dark refrigerator. Standard solutions were prepared before each experiment from these primary stock solutions in Milli-Q water. Lower concentrated solutions for calibrations, MDL determination and optimization were prepared likewise by volumetric dilution to the required concentration levels. During evaluation of optimized parameters, all measurements have been carried out in triplicates using 100 µg/L standard solution mixtures.

4.2.5 Preparation of Stock and Standard Solutions

Twenty-mL screw cap headspace vials (BGBAnalytik, Anwil, Switzerland) were filled with 0.52 g (5 % (w/w)) sodium chloride, 8 mm glass coated stir bars (FisherScientific, Ulm, Germany) and 10 mL of standard solution mixture were transferred immediately with a 10 mL gastight Hamilton syringe (BGBAnalytik, Anwil, Switzerland) into the vials that were sealed immediately with PTFE coated silicone septa and magnetic screw caps. It was necessary to shake the vials for at least ten minutes in order to ensure complete dissolution of the salt.

4.2.6 Method detection limits, Precision

Method detection limits (MDLs) were determined according to the U.S. Environmental Protection Agency procedure [210] by using the optimized conditions indicated in the experimental section. To this end, seven replicates were measured at an approximate signal to noise ratio of 5:1, and standard deviations for these were calculated. For each compound, six point calibrations curves bracketing the test level were used for quantification. Finally, MDLs were calculated by multiplying the standard deviation s_d with the student *t*-factor for the corresponding degree of freedom ($f = 6$). The precision was determined at the fortification level concentration used for MDL determination as well as at the end of the determined linear range.

4.3 Results and Discussion

4.3.1 Evaluation of Extraction and Desorption Parameters for ITEX

The optimization of polymer based microextraction methods include various extraction and desorption parameters. Such parameters are the extraction temperature and time as well as the influence of the ionic strength and the desorption temperature. To obtain highest extraction yields for dynamic in-needle extraction methods additional parameters concerning the dynamic headspace extraction process have to be optimized, i.e., desorption flow rate, desorption volume, extraction flow rate as well as the extraction volume.

4.3.2 Number of Extraction Cycles

As shown in Figure 4.3, one to fifty extraction cycles corresponding to extraction times of 0.66 to 33.3 min were evaluated. During the extraction process the temperature was held at 30 °C and before extraction the samples were equilibrated for 2 h in the 25 °C heated tray to establish equilibrium before starting the extraction. The extraction flow rate and volume were set to 40 µL/s and 1000 µL, respectively. The desorption flow rate and extraction volume were held constant at 50 µL/S and 700 µL, respectively. Figure 4.3 shows that a state of equilibrium could not be observed for most of the investigated compounds after 50 cycles. Only for PCE equilibrium was established after 30 cycles (20 min). Compared to HS-SPDE in section 3.3.2, a longer time is needed to attain equilibrium. This can be explained by different chemical and physical properties (e.g., porosity, tortuosity) of the different extraction phases used as well as by differences in sorbent to extraction volume ratio or the geometric design of the extraction chamber. However, as an adequate extraction time, a fixed value of 20 extraction cycles was chosen for the optimized method.

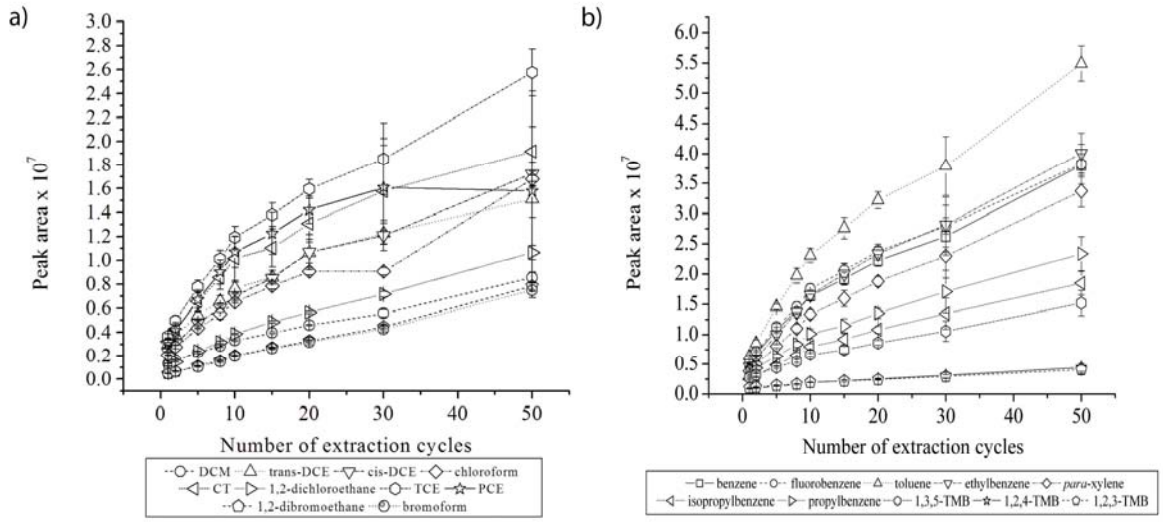

Figure 4. 3 Extraction profiles for the investigated compounds at 30 °C for a) chlorinated hydrocarbons and b) aromatic hydrocarbons as a function of extraction time (i.e., extraction cycles) . Triplicate measurements were done for each point; error bars indicate the standard deviation.

4.3.3 Extraction Temperature and Ionic Strength

The effect of extraction temperature on extraction efficiency was studied within a range between 30 °C and 60 °C. For this evaluation, the extraction flow rate was held constant at 50 µL/s and the extraction volume for each extraction cycle at 1000 µL. Twenty extraction cycles corresponding to an extraction time of 13.3 min and a total extraction volume of 20 mL were carried out. The desorption volume was set to700 µL and a desorption flow rate of 10 µL/s was used. As shown in Figure 4.4, most BTEX compounds show optimum extraction yields at 50 °C with a slight decrease at 60 °C. Only the trimethylbenzene isomers showed highest extraction yields at 60°C. For the halogenated compounds an increase up to 60°C was observed for most compounds, only CT, TCE and PCE showed a slight decrease at the highest temperature. However, the extraction yields for BTEX as well as chlorinated hydrocarbons increase between 30°C to 50°C on average by a factor of 1.6 and for the optimized method an extraction temperature of 50 °C was used.

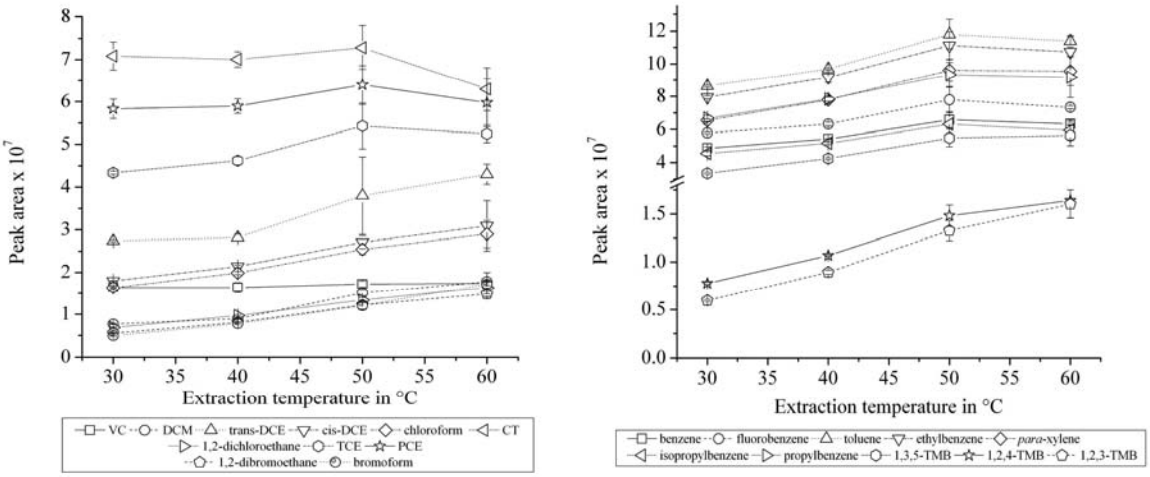

Figure 4. 4 Dependency of extraction yield on extraction temperature for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

Compared with extraction temperature profiles for HS-SPME [217] the optimum extraction temperature was about 20 °C higher both for HS-ITEX as well as for HS-SPDE [218] (see section 3.3.3). This may be rationalized as follows. In HS-SPME, the entire extraction phase is immersed completely into the heated headspace of the sample during extraction while in HS-SPDE the tip of the needle with a short part of extraction phase and in HS-ITEX only the needle is in direct contact with the heated headspace, and the lower temperature of the extraction chamber of SPDE and ITEX allows a more efficient extraction due to the exothermic nature of the gas phase to solid sorption processes. Thus, higher temperatures for promoting the air-water partitioning (endothermic processes) can be applied in SPDE and ITEX without compromising the extraction yields by lowering the air-sorbent partitioning coefficients.
According to the results obtained in section 3.3.5 for SPDE, a salt concentration of 5 % (w/w) NaCl (0.52 g) was used for the final method.

4.3.4 Extraction Flow Rate and Volume

Figure 4.5 shows the effect of the extraction flow rate on the extraction yields (signified by peak areas) of the investigated compounds. The extraction flow rate was has been varied between 10 µL/s and 150 µL/s at otherwise constant method parameters (desorption volume: 1 mL; 15 extraction cycles; desorption flow rate: 50 µL/s). Under these conditions the corresponding extraction times were between 3.3 and 50 minutes. The peak areas increased by a factor of 1.3 for 1,3,5-TMB to 2.6 for

DCM. With decreasing extraction flow rate an increase in the extraction yield occurred indicating a higher degree of non-equilibrium sorption due to rate limiting diffusion into the extraction phase at higher extraction flow rates. Variations of the extraction volume were examined in a range from 500 – 2500 µL at an extraction flow rate of 50 µL/s, an incubation temperature of 30 °C and at 15 extraction cycles. As shown in Figure 4.6 an almost linear increase of extraction yields with extraction volume occurred, the maximum increase depended on the analytes and ranged from a factor of 1.8 (*trans*-DCE) to 4.8 (bromoform). An extraction flow rate of 50 µL/s was used for the optimized method with a constant extraction volume of 1 mL.

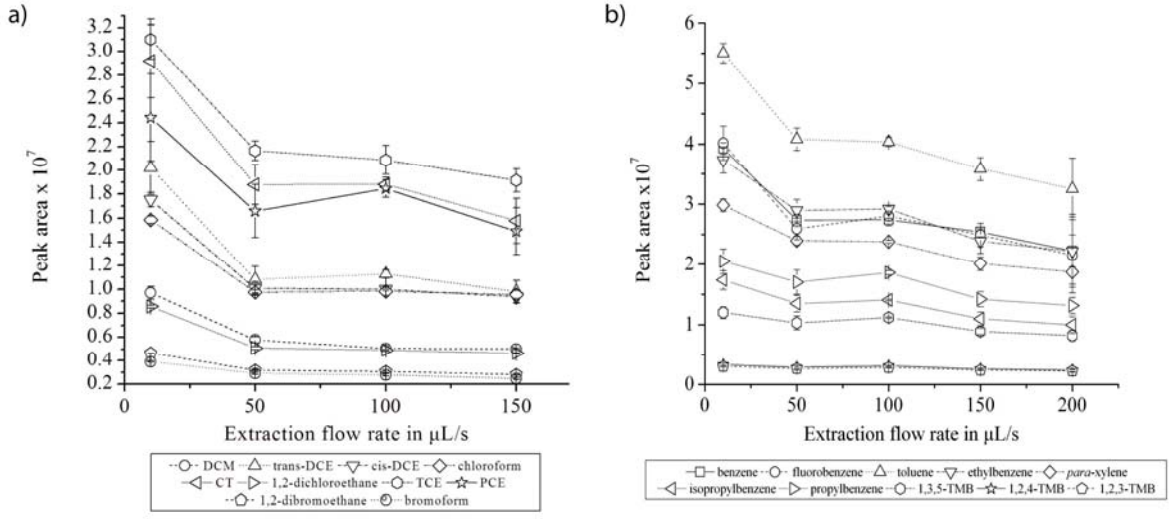

Figure 4. 5 Dependency the extraction yield on extraction flow rate for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

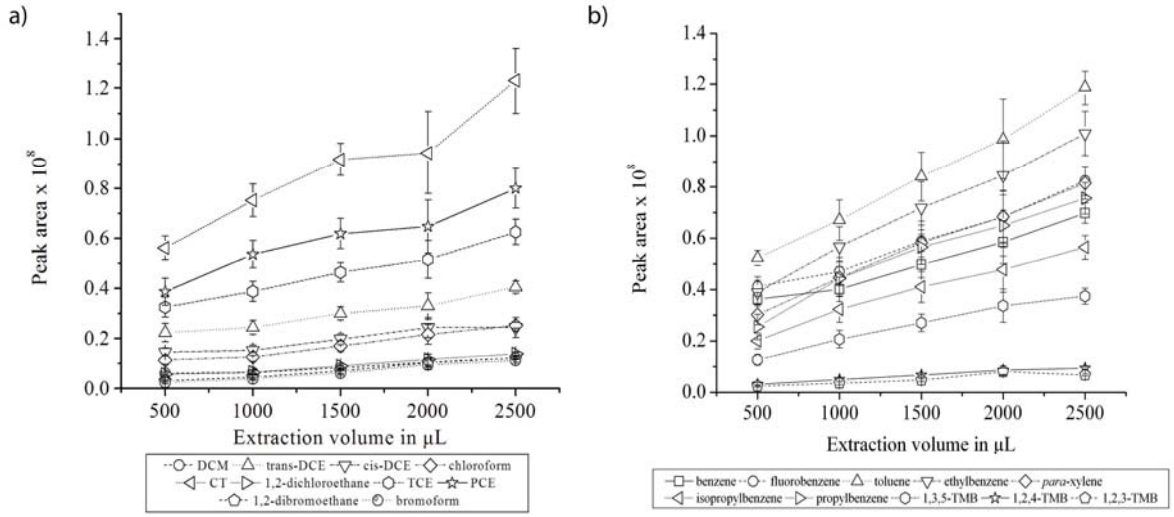

Figure 4. 6 Dependency of extraction extraction yield on extraction volume for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

4.3.5 Conditions for the Desorption Step: Temperature, Flow Rate, Volume

As presented in Figure 4.7 the desorption flow rate showed a strong influence on the extraction yield. The desorption flow rate was varied from 10 - 500 µL/s at a constant desorption volume of 1 mL, which correlates to desorption times between 1 s and 100 s. During the evaluation of this parameter, the extraction volume as well as the extraction flow rate were kept constant at 1000 µL and 50 µL/s, respectively. For desorption flow rates of 10 µL/s, a factor of 4 (DCM) to 26 times higher peak areas (ethylbenzene) than for 100µL/s were obtained indicating a rate limiting diffusion of the analytes from the coating into the nitrogen gas stream during the desorption step. These results agree with results for the HS-SPDE method evaluated in section 3.3.7 of this work and and also with similar results reported in the literature. [129] Thus, in the parameter set of the optimized method a desorption flow rate of 10 µL/s was used.

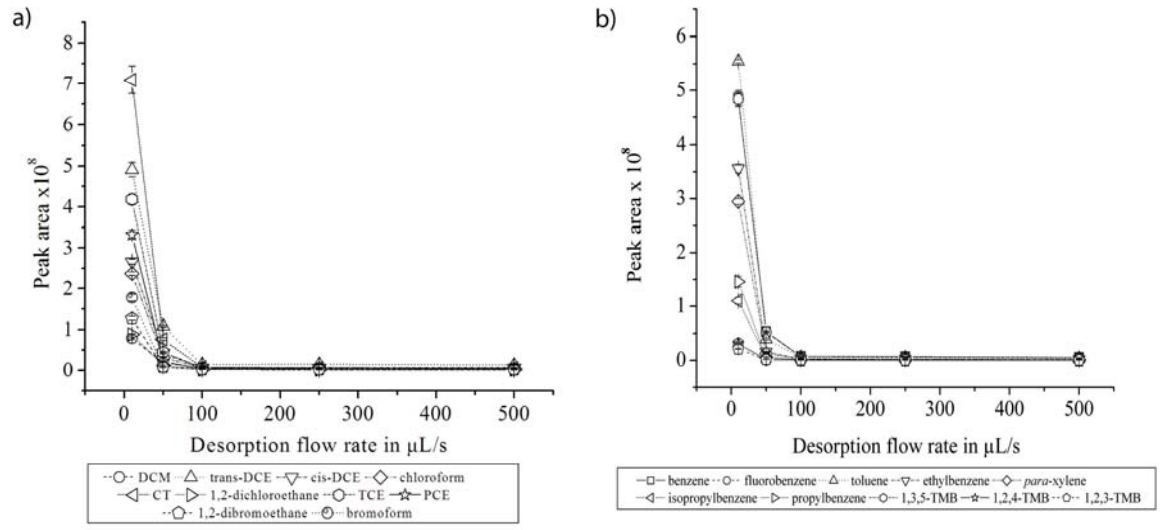

Figure 4.7 Dependency of peak areas on desorption flow rate for a)chlorinated hydrocarbons and b) monoaromatic hydrocarbons. Triplicate measurements were carried out for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

A fixed desorption temperature of 170 °C was used during the evaluation of other method parameters as well as in the parapeter st of the optimized method. Although higher desorption temperatures might increase desorption rates, this temperature was chosen to assure a prolonged lifetime of the extraction phase and thus unchanged properties of the fibre over extended use times.
The effect of the desorption volume on peak areas was investigated between 500 µL and 1000 µL, but no significant influence on the extraction yield was observed (Figure 4.8). This observation is in agreement with results obtained for a solid-phase dynamic extraction method for chlorinated hydrocarbons [218] and alcohols.[201] In this study only a slight peak area increase was observed for desorption volumes of 700 µL compared with 500 µL. For some compounds such as *trans*-DCE and benzene a decrease in the peak area can be observed when using 1000 µL. At a desorption flow rate of 500 µL the standard deviation for some compounds, e.g. carbon tetrachloride is relatively high. A desorption volume of 700 µL was used in the parameter set of the optimized method.

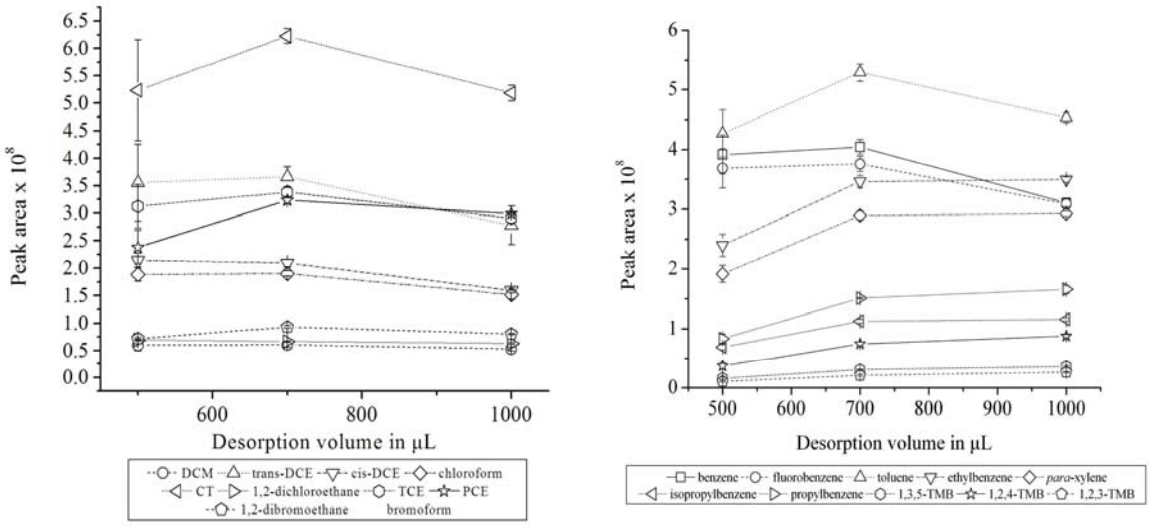

Figure 4.8 The diagrams show the dependency of desorption volume on extraction yield for a) chlorinated and b) monoaromatic hydrocarbons. Measurements were carried out in triplicates for each point. Error bars indicate the standard deviation but are often smaller than the symbol size.

4.4 Validation of the Method

The linear dynamic range of the ITEX method was investigated over six orders of magnitude between 0.028 – 1218 µg/L and linear correlation coefficients between 0.990 and 0.998 were obtained.
Method detection limits (MDLs) were determined as described in the experimental part according to the U.S. Environmental Protection Agency procedure. [210] Method detection limits for all target compounds were determined with and without fluorobenzene as internal standard.

Table 4.2 Validation data of the ITEX-GC/MS method

Compounds in elution order	Target ions used for quantification (m/z)[a)]	Retention times (min)	Linear dynamic range (µg/L) without IS	R^2	MDL (ng/L) without IS [b)]	MDL (ng/L) with IS [b)]	Precision without IS (%)[c)]	Precision without IS (%)[d)]
DCM	84, 49	8.13	0.799 - 618	0.991	799	413	50	18
trans-DCE	96, 61	8.63	0.365 - 523	0.993	365	261	31	3.9
cis-DCE	96, 61	13.20	0.061 - 521	0.992	61	116	4.6	1.2
chloroform	83, 119	14.64	0.048 - 611	0.993	48	242	3.1	3.2
CT	117, 119	15.11	0.072 - 676	0.992	72	124	4.3	1.4
benzene	78, 51	16.88	0.036 - 360	0.992	36	44	4.0	1.3
DCA	62, 98	17.61	0.071 - 510	0.990	71	157	5.6	1.0
TCE	130, 95	18.83	0.049 - 602	0.990	49	71	3.2	2.0
toluene	92, 91	23.00	0.035 - 364	0.998	35	19	3.8	2.4
PCE	166, 131	24.04	0.057 - 683	0.992	57	67	3.3	3.1
EDB	107, 188	25.76	0.081 - 920	0.991	81	327	3.6	3.4
ethylbenzene	106, 91	27.25	0.028 - 360	0.998	28	24	3.1	1.9
para-xylene	106, 91	27.62	0.029 - 360	0.998	29	24	3.2	2.0
bromoform	173, 252	28.67	0.129 - 1218	0.992	129	418	4.3	4.2
isopropylbenzene	105, 120	29.30	0.041 - 362	0.990	41	50	4.4	2.7
propylbenzene	91, 120	30.14	0.048 - 361	0.992	48	62	5.5	2.1
1,3,5-TMB	120, 105	30.57	0.180 - 369	0.992	47	71	5.7	1.8
1,2,4-TMB	120, 119	31.35	0.047 - 359	0.991	47	67	5.2	2.0
1,2,3-TMB	120, 77	32.24	0.068 - 369	0.991	68	75	7.4	2.6

[a)] Base peak used for quantification is underlined.
[b)] (n = 7, fortification level 0.4 µg/L)
[c)] RSD at fortification level (n=7)
[d)] Relative standard deviation (n=3) at highest calibration level
IS: internal standard fluorobenzene with a retention time of 18.35 min (m/z = 96)

By using fluorobenzene as internal standard higher MDLs (Table 4.2) as well as lower precisions (Figure 4.9) especially for the chlorinated compounds were obtained. This observation is in agreement with results found for HS-SPDE. Especially for the chlorinated compounds (e.g., EDB), fluorobenzene is not an ideal internal standard. DCM and *trans*-DCE deviate from this trend. These two very volatile and early eluting compounds are very susceptible to the desorption parameters. We expect improved precisions and MDLs for such compounds by using a cryofocus unit .
The method detection limits for the BTEX compounds without internal standard ranged between 28 ng/L for ethylbenzene and 68 ng/L for 1,2,3-TMB. MDLs for chlorinated hydrocarbons without internal standard were between 48 ng/L for chloroform and 799 ng/L for dichloromethane.
All MDL values given refer to concentrations of the analytes in the water phase.

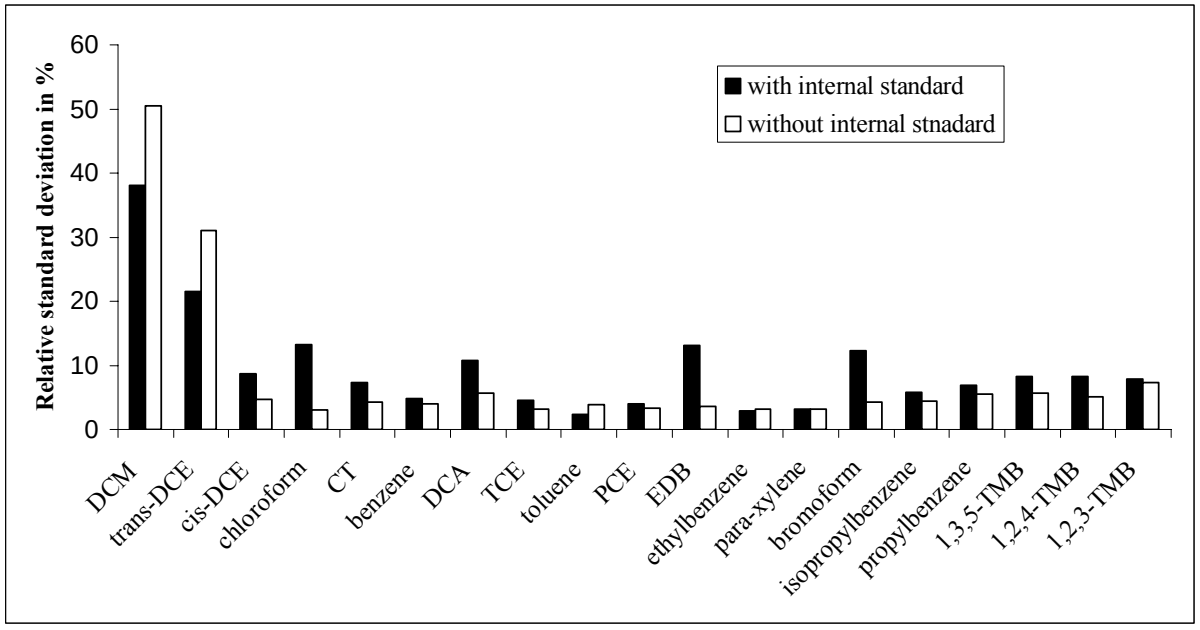

Figure 4.9 Comparison of the relative standard deviations obtained at a 0.4 µg/L fortification level with and without fluorobenzene as internal standard.

In Table 4.1 a comparison between the HS-ITEX-GC/MS method, the HS-SPDE-GC/MS method evaluated in section 3 and other extraction methods as HS-SPME and P&T is shown. When comparing the obtained data one needs to take into account that different extraction phases and different methods for MDL determination were used. It can be seen from Table 4.1. that with mixed extraction phases such as Carboxen/polydimethylsiloxane (CAR/PDMS) lower MDLs can be obtained than with pure partitioning phases as polydimethylsiloxane (PDMS). This trend can also be observed for benzene, determined by the HS-SPDE/MS method in section 3.4 compared with the HS-SPDE method evaluated by Ridgway et al. . [214] Here a 30 times lower method detection limit was found with the PDMS/AC coating compared with PDMS in their study. Another important point is that MDLs for an enrichment method obtained using an electron capture detector (ECD) are not comparable with data obtained by an MS because of the much higher sensitivity of the former one for polyhalogenated compounds. The HS-SPDE-GC/MS method showed a factor of 2 to 30 times lower MDLs than the HS-ITEX-GC/MS method by using a PDMS/AC extraction phase. However, the method showed one order of magnitude lower detection limits than the comparable HS-SPME/MS method by Wypych et al. [208], which used the same MDL determination method as used in this study. Compared with a P&T-GC/MS method by Martinez et al. [219] two to three orders of magnitude higher MDLs were obtained by HS-SPDE/MS.

The precision was determined as relative standard deviation at around five times higher concentrations than the method detection limit for (n=7) measurements. Good precisions between 3.1 % (ethylbenzene) and 7.4 % (1,2,3-TMB) were obtained for most of the compounds. The first two eluting compounds dichloromethane and *trans*-DCE show very high relative standard deviations of 50 % and 31 %. These poor precisions can be explained by the low response factor of these compounds in a quadropol MS detector as well as the broad shape of their peaks caused by not optimal desorption conditions (lack of cryo focusing). The precisions for the other analytes were comparable to those obtained for the SPDE-GC/MS method for chlorinated hydrocarbons in Table 3.3 in section 3.4. The precisions for high concentrations of analytes were determined by calculating the relative standard deviations (n=3) at the highest concentration level of the linear range. The obtained precisions without internal standard were in the range 1.0 % (DCA) to 18 % (DCM). These results are also comparable with results obtained by the HS-SPDE method in section 3.4. Except the low precisions for dichloromethane and *trans*-DCE the precisions are comparable with other microextraction methods. [208]

Table 4.1 Comparison between MDLs of HS-ITEX-GC/MS and other micro enrichment methods. Note that different extraction phases as well as different MDL determination methods were used.

Method	**ITEX-GC/MS**	**SPDE-GC/MS**		**HS-SPME-GC/MS**				**HS-SPME-GC/ECD**	**P&T-GC/MS**
Extraction phase	**Tenax TA** [b]	**PDMS/AC**[b] [218]	**PDMS** [214]	**CAR/PDMS**[a] [220]	**PDMS**[b] [208]	**PDMS** [205]	**PDMS** [206]	**CAR/PDMS**[a] [217]	**Tenax**[a] [219]
DCM	799	119		1237					62
trans-DCE	365	12							
cis-DCE	61	12		38					
chloroform	48	176		15	670	2960	1332	1.4	2
CT	72	19		632	450	2754	162		2
benzene	36	13	400	8.8	200	528			2
DCA	71							3.7	2
TCE	49	13		73	280		730	1..3	10
toluene	35		480	8.7		174			7
PCE	57	28		16			16.2	0.08	14
EDB	81			22					
ethylbenzene	28			8.6					14
para-xylene	29								
bromoform	129	22					86.7	0.3	27
isopropylbenzene	41								58
propylbenzene	48								
1,3,5-TMB	180			8.8					
1,2,4-TMB	47			8.8					
1,2,3-TMB	68								

[a] Signal to Noise ratio (S/N ≥ 3/1)

[b] $MDL = s_d \times t_{(0.99,\, f=6)}$

4.5 Conclusions

The here reported results show that the ITEX-GC/MS method is suitable for the trace determination of volatile organic compounds in aqueous matrices. The effects of the governing parameters for the method optimization of ITEX is very similar to the SPDE method discussed in section 3. The obtained method detection limits and precisions for ITEX are comparable to values achieved by SPDE-GC/MS. Thus, the ITEX method is a very suitable alternative to solid-phase microextraction (SPME) because it provides lower fragility and longer extraction phase lifetimes as well as lower MDLs. A special advantage to the otherwise similar SPDE method is the external desorber around the needle body, which makes the ITEX method independent of the injector temperature profile (gradient between the hot injector and the oven interior), whereby a cooling of the injector would be possible to further enhance peak shapes, extraction yields and detection limits.
A cooling of the needle packing during the extraction, e.g. by using electrical Peltier cooling would be a future improvement for this method because of the negative sorption enthalpies. Further investigations with other extraction phases such as Carboxen would most likely lead to lower method detection limits, comparable those of HS-SPDE/MS.

5 A New Approach to Determine Method Detection Limits in the µg/L Range for Compound Specific Isotope Analysis

5.1 Introduction

Halogenated hydrocarbons such as chlorinated solvents and monoaromatic hydrocarbons represent some of the most common groundwater contaminants.[183] Halogenated solvents, e.g. tetrachloroethylene, trichloroethylene and dichloromethane have been used as dry cleaning agents, degreasers in electronic and metal industry and as solvents in the chemical industry. Therefore these compounds are often found in groundwater at commercial and production sites.[39] Other, very persistent halogenated organics such as DCA and EDB (for abbreviations see Table 5.1) were used as fuel additives and reach the groundwater table often together with fuel derived contaminants such as benzene and its monoaromatic derivatives.[216] All these compounds show adverse effects to the ecosystem and some are carcinogenic.[221] Due to environmental concerns, threshold values in OECD countries are in the low µg/L range and the assessment and remediation of such contaminated sites is often mandatory. In the case of chlorinated ethylenes, remediation is often hampered by the fact that these compounds are present as dense non aqueous phase liquids (DNAPLs) rendering conventional pump-and-treat remedial strategies ineffective.[40] For these reasons, in situ bioremediation of such pollutants has become an inexpensive alternative remedial method. CSIA has become a useful tool in contaminant hydrology and environmental forensics for the assessment of in situ degradation processes at such contaminated sites.[3] Additionally, the spectrum of applications in this field has grown enormously and include, nowadays, tracking of contaminant flow paths[5], allocation of contaminant sources in groundwater, identification and quantification of pollutant degradation[9] as well as determination of the involved reaction mechanisms.[6, 7] The major drawback of CSIA with GC/IRMS for environmental applications is its rather poor sensitivity.[3] To overcome this problem and to increase the sensitivity injection methods such as headspace injection[32] and extraction methods such as solid-phase microextraction[33, 85, 221-223] and P&T[19, 38, 39, 41, 224] have been used. All enrichment and extraction processes involve a potential for isotopic fractionation. [19] Particularly chromatography, as well as evaporation and discrimination of analytes in the GC injector, are possible sources of artifacts due to isotopic fractionation.[225, 226] Thus, a detailed evaluation of extraction or enrichment methods for possible fractionation is mandatory.[19, 32, 226]

Extraction with purge and trap (P&T) was developed thirty years ago[34], and in combination with GC/MS it has become a routine method for trace analysis of volatile organic compounds (VOCs) in water samples.[227] Especially in the US, several EPA protocols for the determination of volatiles in drinking, waste and hazardous waste water, e.g. EPA method 524.4 for measurement of purgeable organic compounds in water, rely on P&T.[198] P&T has been applied previously in combination with GC/IRMS for compound specific isotope analysis. Often the used apparatus was custom-made and automated on-line measurement was not possible. Extraction of chlorinated ethenes and ethanes from groundwater samples for $\delta^{13}C$ [224,39,40] and $\delta^{37}Cl$ [39] analyses at contaminated sites was performed several times.[39] Isotopic values of fuel enhancers and their degradation products such as methyl *tert*-buthyl ether (MTBE)[38] and *tert*-butanol (TBA) were determined by P&T-GC/IRMS with method detection limits of 5 µg/L and ~60 µg/L, respectively.[228] More detailed evaluations that emphasize the necessity of a closer reflection on the method and method detection limits were done by Kelley et al., Zwank et al. and Morrill and co-workers. [19, 41, 229] Kelley et al. used a P&T connected to a GC ion trap MS and a GC/IRMS for the determination of concentration and isotope ratios of BTEX compounds in gasoline contaminated groundwater.[229] Reported standard deviations for duplicate or triplicate measurements were less than 0.5 ‰. The variability of the $\delta^{13}C$ values of BTEX standards over one year showed deviations between ±0.5 ‰ (*para*- and *meta*-xylenes) and ±1.9 ‰ (ethylbenzene) for mass 44 amplitudes lower than 1 volt (V). Smaller standard deviations were observed for mass 44 amplitudes higher than 1 V which corresponds to BTEX concentrations between 200 and 300 ppb. An on-line dynamic headspace method was evaluated by Morrill and co-workers.[41] The difference between this and other P&T methods is a dynamic extraction of the headspace above the sample. This

method obtained reproducible $\delta^{13}C$ values for TCE and *cis*-DCE at concentrations of 50 and 75 µg/L. Conservative limits of quantitation were calculated based on an operational limit of mass 44 peak amplitude >0.2 V and the assumption that there is an inversely linear relationship between concentration and trapping time. Zwank et al. evaluated in a comparative study the performance and applicability of on-column, split/splitless injections as well as SPME and P&T for monoaromatic compounds, chlorinated hydrocarbons and MTBE.[19] A fully automated commercially available P&T concentrator connected to a GC/IRMS was used. In this study it was pointed out that P&T in combination with GC/IRMS showed the most efficient pre-concentration with the lowest method detection limits between 0.25 µg/L for toluene and 5 µg/L for carbon tetrachloride. A threshold value of 500 mV was used for setting the method detection limit. Another interesting finding of this study was that P&T showed high reproducibility and a smaller isotopic fractionation than extraction methods such as SPME.

Because of its potential for low detection limits, minimal isotopic fractionation and high reproducibility, one objective of this study was to enhance the sensitivity of the P&T method. Therefore a commercially available P&T was modified in a way that made it possible to purge larger sample volumes to achieve lower detection limits for CSIA measurements. Another objective was a detailed evaluation of the influence of extraction parameters on $\delta^{13}C$ values and the development of a new approach to determine MDLs for CSIA.

Table 5.1 Pysicochemical properties of the investigated compounds

Compounds in elution order	**Abbrev**	**CAS-no.**	**MW ($g \cdot mol^{-1}$)** [a]	**Density ($kg \cdot L^{-1}$)** [a]	**Calculated air-water partitioning constant K_{aw}** [c]
dichloromethane	DCM	75-09-2	84.9	1.33	0.09
trans-1,2-dichloroethylene	*trans*-DCE	156-60-5	96.9	1.27	0.36
Cis-1,2-dichloroethylene	*cis*-DCE	156-59-2	96.9	1.27	0.14
chloroform		67-66-3	119.4	1.48	0.13
carbon tetrachloride	CT	56-23-5	153.8	1.62	0.94
benzene		71-43-2	78.1	0.88	0.19
1,2-dichloroethane	DCA	107-06-2	99.0	1.25	0.04
fluorobenzene		462-06-6	96.1 [b]	1.02 [b]	0.24
trichloroethylene	TCE	79-01-6	131.4	1.46	0.31
toluene		108-88-3	92.2	0.87	0.21
tetrachloroethylene	PCE	127-18-4	165.8	1.62	0.53
1,2-dibromoethane	EDB	106-93-4	187.9	2.18	0.02
ethylbenzene		100-41-4	106.2	0.86	0.24
para-xylene		106-42-3	106.2	0.86	0.25
bromoform		75-25-2	252.8	2.89	0.02
isopropoylbenzene (cumene)		98-82-8	120.2	0.86	0.29
propylbenzene		103-65-1	120.2	0.86	0.37
1,3,5-trimethylbenzene (mesitylene)	1,3,5-TMB	108-67-8	120.2	0.88	0.25
1,2,4-trimethylbenzene	1,2,4-TMB	95-63-6	120.2	0.88	0.22
1,2,3-trimethylbenzene	1,2,3-TMB	526-73-8	120.2	0.89	n.a.

[a] Ref.: [202]

[b] Data from SRC Phys Prop Database (http://esc.syrrees.com)

[c] Values calculated for 20 °C with van't Hoff type equation $\log K_{aw} = A - B/T$ according to Ref.: [165] [230]

n.a.: not available

5.2 Experimental

5.2.1 Chemicals and Reagents

As a solvent for the preparation of standard solutions, millipore water from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA) was used.
Trichloroethylene (99.5 %), dichloromethane (≥99.9 %), toluene (99.9 %) were obtained from Merck (Darmstadt, Germany), cis-1,2-dichloroethylene (97%), trans-1,2-dichloroethylene (98%), tetrachloroethylene (99.9+ %), bromoform (99+ %), 1,2-dichloroethane (99.8%), 1,2-dibromomethane (99 %), carbon tetrachloride (99+ %), isopropylbenzene (99 %), *para*-xylene (99 %), ethylbenzene (99.8 %), propylbenzene (98 %), 1,2,4-trimethylbenzene, fluorobenzene (99 %) from Aldrich (Steinheim, Germany) and chloroform (99.5 %), benzene (99.5 %), 1,3,5-trimethylbenzene (99 %), 1,2,3-trimethylbenzene (90-95 %) from Fluka (Buchs, Switzerland). The physico-chemical properties of the investigated analytes are summarized in Table 5.1.

5.2.2 Gas Chromatography Isotope Ratio Mass Spectrometry

The compound specific isotope ratios were determined using a Trace GC (Thermo Finnigan, Milan, Italy) coupled to an isotope ratio mass spectrometer (Delta^{PLUS} XP, Thermo Finnigan MAT, Bremen, Germany) via a combustion interface (GC Combustion III, Thermo Finnigan MAT, Bremen, Germany) maintained at 940 °C. The GC was equipped with a programmable temperature vaporizer (PTV) injector (Optic 3, ATAS GL International B.V., Veldhoven, Netherlands). Injector and transfer line temperatures of the purge and trap were held at 250 °C. Analytes were trapped in a deactivated pre-column (0.4 m x 0.53 mm; BGB, Anwil, Switzerland) with cooled nitrogen gas by an on-column cryo-focusing unit (ATAS GL International B.V., Veldhoven, Netherlands), which was held at -100°C during analyte transfer from the P&T. For the thermal desorption process, the cryofocusing unit was heated with a ramp rate of 30 °C/s to 240°C. The analytical separation was carried out with a Rtx-VMS capillary column (60 m x 0.32 mm, 1.8 µm film thickness; Restek Corp., Bellefonte, PA). Helium 5.0 (Air Liquide, Düsseldorf, Germany) at a constant flow of 1 mL/min was used as carrier gas. In addition to the IRMS, the GC was equipped with a flame ionization detector (FID) that received 10% of the eluting carrier gas. The temperature program used to obtain baseline separation of the target analytes was as follows: 10 min at 40 °C, then to 100 °C at 4 °C/min, 2 min at 100 °C, then to 170 °C at 10 °C/min, 2 min at 170 °C, then to 200 °C at 10 °C/min and hold 2 min at 200 °C. The isotopic signatures of all compounds relative to VPDB were obtained using CO_2 that was calibrated against a referenced CO_2 standard. The IRMS was tuned to maximum linearity. Similar to findings by Zwank et al.[19], it was necessary to oxidize the NiO-CuO-Pt catalyst frequently, particularly for the measurement of halogenated compounds. The reoxidation frequency was between 35-40 samples.

5.2.3 $\delta^{13}C$ Determination of Pure Liquid Phase

$\delta^{13}C$ values are defined in equation 1.1, where R_{sample} and $R_{reference}$ are the ratios of the heavy isotope to the light isotope (here, $^{13}C/^{12}C$) in the sample and an international standard material, respectively. For determination of elemental analyzer values, an aliquot of the pure liquid standards was introduced into the combustion furnace of an elemental analyzer (EA) (NC2500, Thermoquest, San Jose, CA) coupled to an IRMS (Delta XL, Thermo, Bremen). The isotopic signatures of the analytes were corrected in order to obtain $\delta^{13}C$ values relative to Vienna Pee Dee Belemnite (VPDB). The correction was obtained using a linear regression derived from the $\delta^{13}C$ determination of a solid reference material

measured with the same instrumental setting and the same internal reference CO_2. EA values as reported in Table 5.2 are measured in triplicate.

5.2.4 Purge and Trap System

A purge and trap concentrator Tekmar VelocityXPT™ together with an autosampler TekmarAQUATek 70 (Tekmar-Dohrmann, Mason, OH) were coupled online to the PTV injector of the GC/IRMS system. The autosampler tray holder was modified to carry twenty 100-mL amber glass bottles. The bottle positions were placed in a way that corresponded to predefined positions by the software. To purge higher sample volumes (up to 100 mL), a commercially available 25-mL fritted sparger was modified as shown schematically in Figure 5.1. The standard 25-mL sample loop was replaced by a 50 m x 1.6 mm ID (3.2 mm OD) Teflon sample loop to hold up to 100-mL of aqueous sample. A modified tray holder, a frit sparger and the sample loop were purchased from PAS Analytik (Magdala, Germany). The aqueous samples were filled without headspace into the 100-mL glass bottles sealed with PTFE coated, silicone septa screw caps. Unfortunately, it was not possible to lower the transfer needle of the autosampler deeper than the value predefined by the manufacturer. Because of this, a 76-mL aliquot of the water samples was transferred by the autosampler into the fritted glassware sparger. The purge time for the optimized method was 15 min. As a purge gas, helium with a purity of 6.0 (Air Liquid, Düsseldorf, Germany) was used with a purge gas flow rate of 50 mL/min. The loop transfer time was optimised to 2.80 min and the sample transfer time to the sparger was set to 3.20 min.

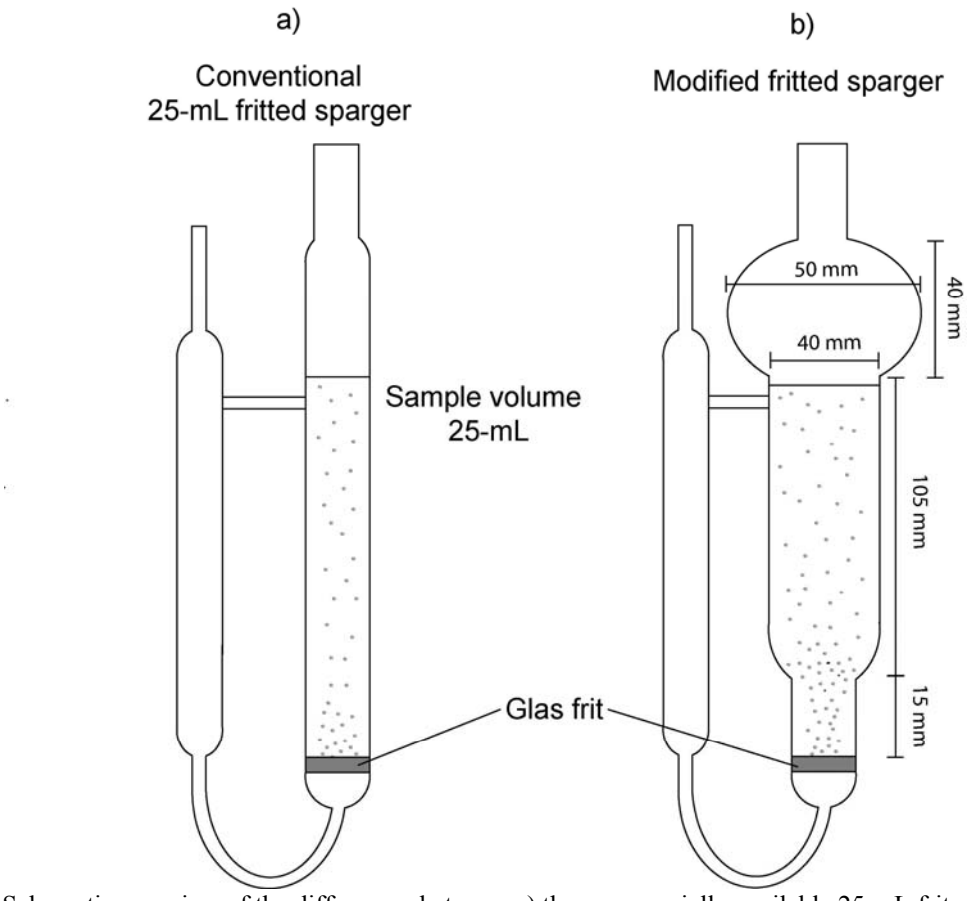

Figure 5.1 Schematic overview of the differences between a) the commercially available 25-mL frit sparger and b) the applied modified frit sparger for higher sample volumes.

The analytes were trapped on a *Vocarb™ 3000 Trap* (Supelco, Bellefonte, PA, US) at room temperature. The dry purge time of the trap was set to 4.0 min with a dry purge flow of 200 mL/min. The desorbtion pre-heating temperature was set to 220°C. By heating the trap to 240 °C for 2 min, the analytes were thermally desorbed and transferred to the cryofocusing unit maintained at -100 °C. The transfer line temperature was held at 250°C during desorption. The GC temperature program began with the heating of the cryofocusing unit. After desorption the analyte trap was baked out at 270 °C for 20 min at a bake flow of 400 mL/min to prevent possible carry over. After each extraction the sample loop and the sparger were rinsed with 90°C hot Milli-Q water also to prevent carry over.

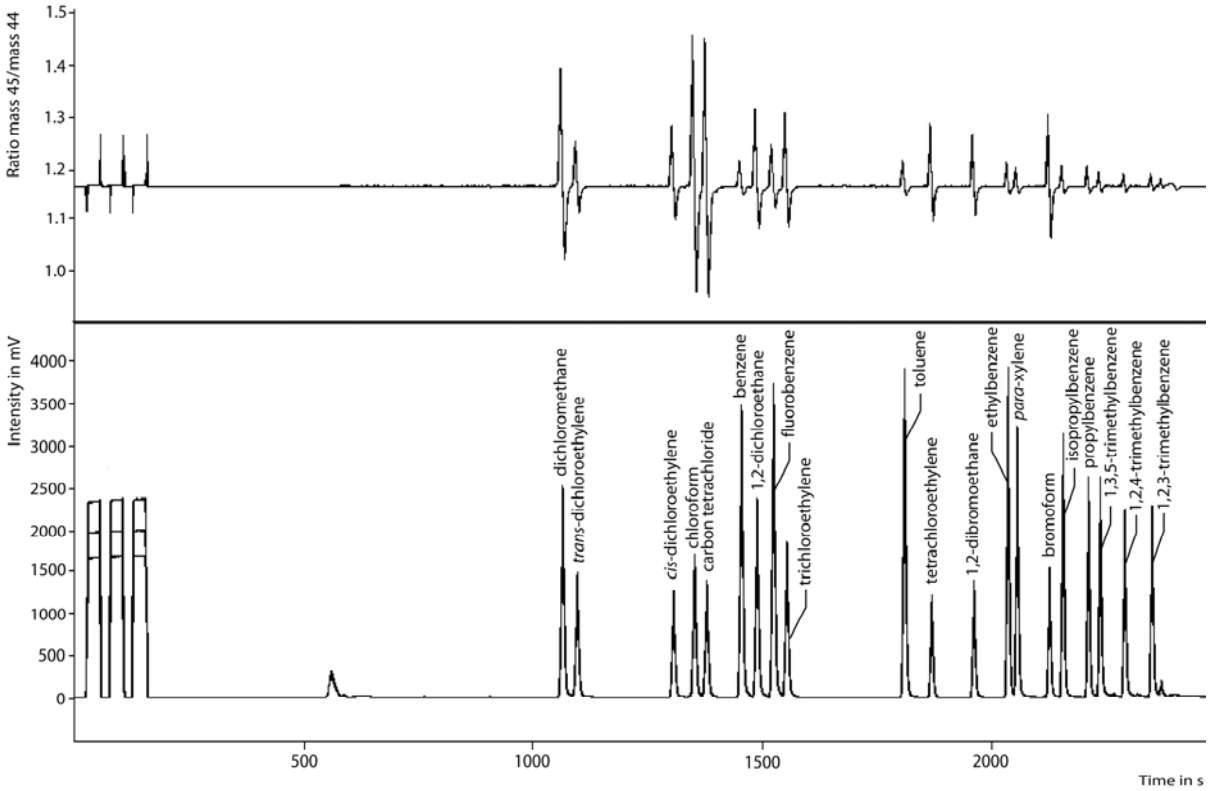

Figure 5.2 P&T-GC/IRMS chromatogram.The lower graph shows an on-line P&T-GC/IRMS chromatogram of an aqueous standard mixture. The concentrations of the different analytes were adjusted to achieve similar signal intensities. In the upper graph, the isotopic swings expressing the ratios of mass 45 ($^{13}CO_2$) to mass 44 ($^{12}CO_2$) are shown. The first three peaks correspond to the reference CO_2 gas. The second reference peak was used for calculation.

5.2.5 Preparation of Stock Solutions, Standards and Environmental Samples

Aqueous stock solutions of the volatile organic compounds were prepared by injection of pure organic substance aliquots by a 10-µL gastight Hamilton syringe through a PTFE/silicone septum into a 1-L amber Schott screw cap glass bottle (FisherScientific, Ulm, Germany). The bottles were shaken for 24 hrs with an overhead shaker to dissolve all compound completely. Stock solutions were prepared daily, before preparation of standard solutions, for the GC/IRMS experiments. Standard solutions for method optimisation were prepared by injecting aliquots of the stock solution into a known volume of Milli-Q water in 100-mL amber screw cap bottles (BGB Analytik, Anwil, Switzerland) sealed with PTFE/silicone septa.

5.2.6 Determination of Method Detection Limits

To quantify method detection limits, the mean $\delta^{13}C$ values of the three highest concentration levels were determined. A ±0.5 ‰ interval was set around the calculated mean value. This interval incorporates the total analytical error including the internal reproducibility on triplicate measurements as well as the accuracy of the measurement with respect to international standards.[5, 32] This moving mean procedure was repeated consecutively by including the $\delta^{13}C$ value of the next lower concentration level into the mean value calculation. The last concentration for which the $\delta^{13}C$ value was within this iterative interval or for which the standard deviation was lower ±0.5 ‰ for triplicate measurements was defined as the method detection limit.

5.3 Results and discussion

5.3.1 Chromatographic Conditions

As shown in Fig. 5.2, baseline separation for all twenty investigated compounds was achieved with a cryofocusing temperature of -100 °C. Especially for early eluting analytes such as *trans*-DCE, *cis*-DCE, CT, and chloroform, a pronounced tailing and tendency to overlap of peaks was observed for higher cryofocusing temperatures. Preliminary experiments indicated that for vinyl chloride even a temperature of -130 °C was necessary to reach adequate peak shapes (data not shown). Another prerequisite to obtain sharp peaks was to heat the trap rapidly with a temperature rate of 30°C/s to 240 °C. In every chromatogram unidentified peak was observed after a retention time of ~550 s (see Fig. 5.2). The peak height depended on extraction time and flow rate. This peak was not detected during a full GC/MS scan of the standards headspace under the same chromatographic conditions thus identification failed. The stability of the retention times of all analytes is shown in Table 5.2 Improved relative standard deviations and retention time stabilities can be observed for later eluting compounds.

5.3.2 Optimization of Purge & Trap Parameters

Three different groups of P&T parameters can be adjusted. The first group influences the sample transfer to the sparger (time for transferring the sample into the loop, transfer time of the sample to the sparger). Both times were optimized manually by visual investigation of the sample loop and the sparger. For the loop transfer time a value of 2.80 minutes was evaluated and for the sample transfer time to the sparger a time of 3.20 min was used to ensure a complete transfer.

5.3.3 Purge Flow Evaluation

The second group includes the actual parameters of the P&T process such as purge gas flow rate and purge time. Because these parameters determine the phase-transfer process and could potentially cause isotopic fractionation[41, 231], a more detailed evaluation was carried out. In Fig. 5.4 the evaluation of the purge flow rate on extraction yields (here expressed as amplitude of mass 44 in mV) and on $\delta^{13}C$ values (in ‰) is shown for four representative compounds. Four different purge gas flow rates between 40 mL/min and 80 mL/min were investigated. As in the work of Zwank et al., the purge time for this experiment was held constant for 11 min.[19] The results show a maximum peak height for mass 44 at a purge flow rate of 50 mL/min for most of the compounds. For compounds with very low dimensionless air-water partitioning constants K_{aw} such as bromoform (0.02) and EDB (0.02) and DCA (0.4) an increase in the extraction yield was observed up to a flow rate of 80 mL/min. The carbon isotope values did not vary with purge flow rate as shown in Figure 5.3.

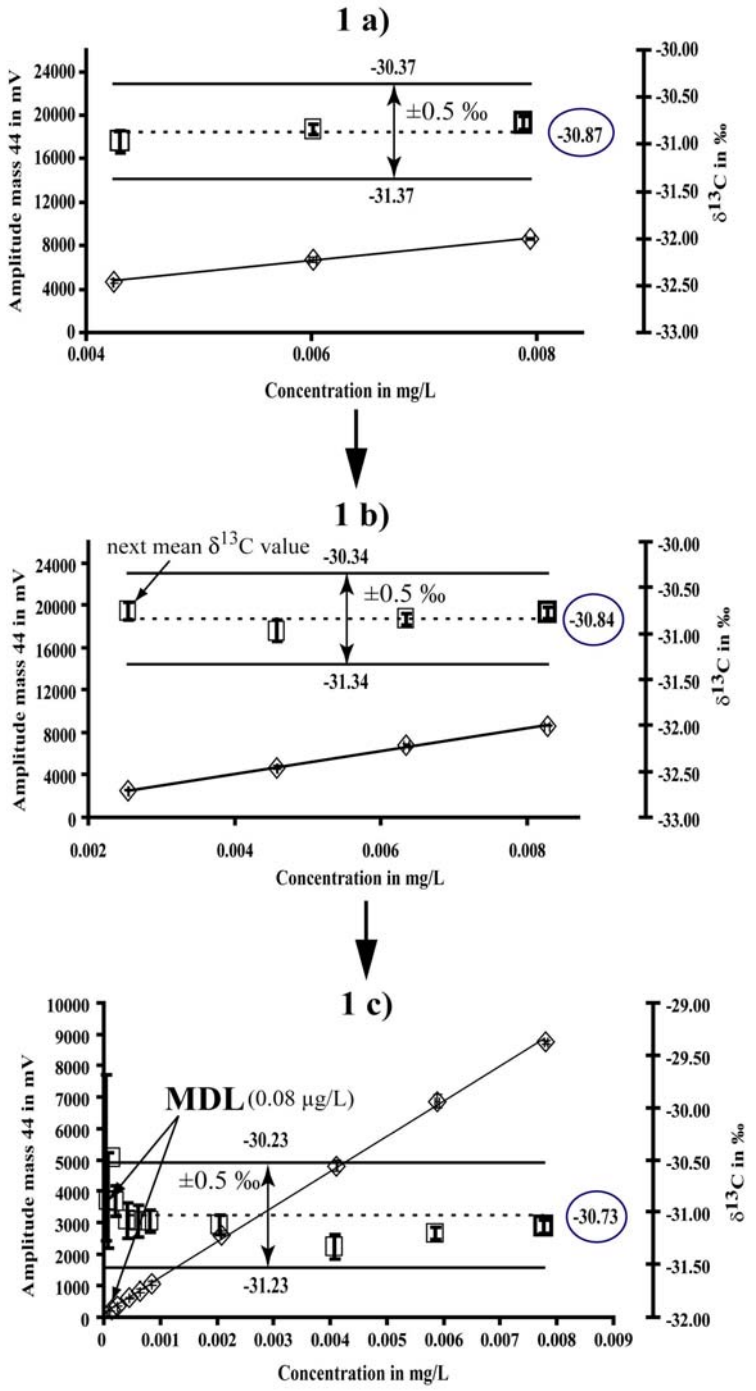

Figure 5.3 Schematic illustration of MDL determination for fluorobenzene. In 1a) the determination of the moving mean of mean $\delta^{13}C$ values (each n=3) for the first three concentration levels is shown. A ±0.5 ‰ interval was set around this moving mean value. All $\delta^{13}C$ mean values are within this interval. Because of this, in 1b), the next moving mean value with the next lower $\delta^{13}C$ value mean was calculated. This procedure was iterated as long as either the first $\delta^{13}C$ value was outside the ±0.5 ‰ interval around the moving mean or the standard deviation of a mean $\delta^{13}C$ value was higher ±0.5 ‰. In 1. c), both abort criteria can be observed. The MDL is then defined as the last concentration with a $\delta^{13}C$ mean value that fits both criteria.

5.3.4 Evaluation of purge time

In the lower graphs of Figure 5.5, theoretical purge extraction efficiency (solid curve) is compared with measured extraction yields. The theoretical purge efficiency was determined by the following equation, adjusted from the literature:[202]

$$\frac{Amp^{total}_{(mass\ 44)}}{Amp^{t}_{(mass\ 44)}} = 1 - e^{(-K_{aw}G/V_w)t} \times 100\% \qquad \textbf{(5.1)}$$

where $Amp^{total}_{(mass\ 44)}$ and $Amp^{t}_{(mass\ 44)}$ are peak amplitudes, the former a total amplitude for 100 % extraction and the latter an amplitude at a specified time, *t*, before reaching 100 % extraction for a compound. V_w is the volume of the aqueous sample (e.g. 76 mL/min), *G* the purge gas flow rate (e.g. 50 mL/min), and K_{aw} the dimensionless air-water partitioning constant. Calculated K_{aw} values for 20 °C are compiled in Table 5.1. For the determination of the theoretical curve, the mass 44 amplitudes were normalized with respect to the highest amplitude that was set to 100 %. As shown in Figure 5.5, experimental extraction efficiencies could be predicted quite well for the chlorinated compounds such as CT. For the BTEX compounds the measured values reach 100 % extraction efficiency faster than predicted by the dynamic phase equilibrium model. As can be seen in Figure 5.5, the amplitude of mass 44 decreases for purge times longer than 15 min for CT and 25 min for benzene. This decrease indicates analyte breakthrough through the trap, which was also observed by Zwank et al. .[19] The shift to a lower carbon isotope ratio for CT at 60 min purge time could be a result of this breakthrough. Generally, after 15 min purge time stable carbon isotope ratios were observed for all of the compounds. Compounds with low air-water partitioning constants, e.g. bromoform, EDB and DCA do not reach 100 % extraction efficiency within 60 min but show stable carbon isotope values after 15 min. Longer purge times lead also to an unacceptable high water content in the source. As an example, mass 18 amplitude of 7000 mV was observed after 18 measurements obtained for this evaluation. For 18 measurements at a purge time of 15 min and a purge flow of 50 mL/min, the value was stable at around 1000 mV. In Table 3, $\delta^{13}C$-values for all compounds at 15 min and a purge flow rate of 50 mL/min (optimized conditions) are presented. A comparison of this values with EA values of the pure liquid phase showed no significant deviations (<0.5 ‰) except for chloroform with a deviation of -1.48 ‰. The third group of parameters that can be optimized include the dry purge time to remove water from the trap and prevent high water content in the mass spectrometer as well as the desorption temperature for analyte desorption from the analyte trap. The desorption temperature was adapted from literature but the time was prolonged by 1 min.[19]
The remaining parameters are mentioned in the experimental section.

Table 5.2 Retention times of the target compounds for the optimized method and equations of the linear curve fits as well as correlation coefficients from the consecutive dilution steps from method detection limit determination.

Compounds in elution order	Retention time (s) ± RSD[a)]	Linear fit of calibration curve	Correlation coeff. (R^2)
DCM	1104 ± 11	y = 1.0e6x - 162	0.999
trans-DCE	1133 ± 12	y = 3.6e6x - 146	0.998
cis-DCE	1328 ± 5.8	y = 3.5e6x + 23	0.998
chloroform	1371 ± 5.8	y = 9.4e5x + 41	0.998
CT	1396 ± 5.5	y = 7.6e5x + 11	0.999
benzene	1468 ± 4.5	y = 2.0e6x + 110	0.998
DCA	1500 ± 5.4	y = 1.54e6x + 43	0.999
fluorobenzene	1531 ± 4.9	y = 1.0e6x + 57	0.999
TCE	1562 ± 5.5	y = 2.0e6x + 37	0.999
toluene	1810 ± 3.9	y = 1.0e6x + 80	0.999
PCE	1870 ± 3.5	y = 1.1e6x + 70	0.999
EDB	1960 ± 3.8	y = 5.8e6x + 20	0.999
ethylbenzene	2033 ± 3.0	y = 1.0e6x + 76	0.999
para-xylene	2053 ± 3.1	y = 2.0e6x + 115	0.999
bromoform	2122 ± 4.4	y = 1.8e6x + 25	0.999
isopropylbenzene	2151 ± 2.9	y = 1.0e6x + 75	0.999
propylbenzene	2206 ± 3.2	y = 9.4e6x + 64	0.999
1,3,5-TMB	2232 ± 2.8	y = 9.0e6x + 20	0.999
1,2,4-TMB	2285 ± 2.8	y = 7.7e6x + 15	0.999
1,2,3-TMB	2344 ± 2.8	y = 7.2e6x + 30	0.999

[a)] RSD: relative standard deviations for (n = 12-33)

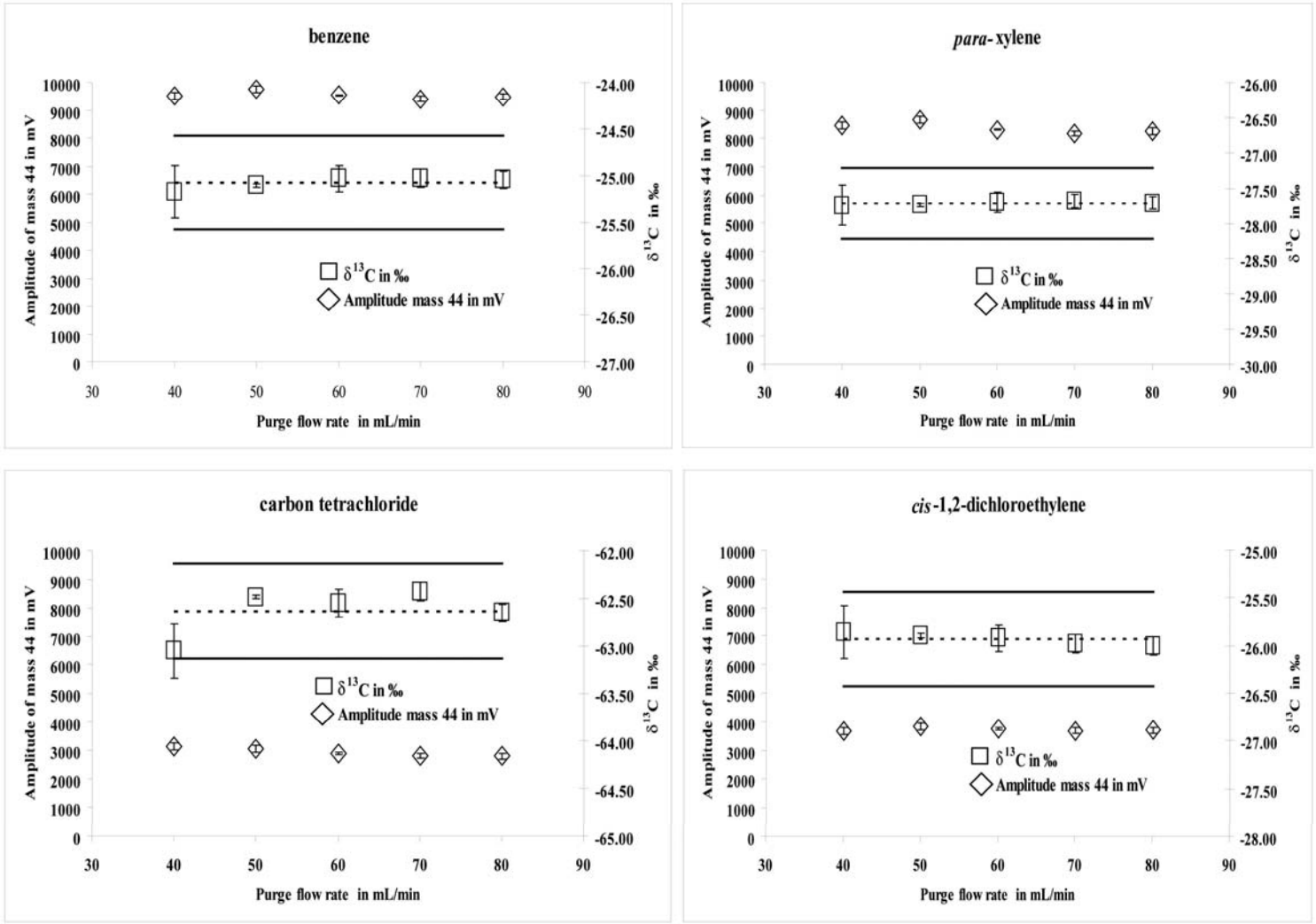

Figure 5.4 Evaluation of the purge flow rate and its influence on $\delta^{13}C$ values. Here the evaluation of four of the twenty investigated compounds is shown exemplarily. The squares represent the $\delta^{13}C$ values in per mil and the diamonds show the amplitude of mass 44 in mV. Triplicate measurements were done for each point; error bars indicate the standard deviation.

5.3.5 Determination of method detection limits

For the determination of method detection limits, consecutive dilutions were prepared from the aqueous stock solution. Within the tested concentration range the relationship between peak amplitude of mass 44 and the concentration showed very good linear correlations for all the investigated compounds (Table 5.2) that may be used even for a quantification of the analytes.
The method detection limit was determined according to a new methodology described in the experimental part. For the four compounds in Figure 5.6, detection limits are for benzene 0.20 µg/L (0.16 nmol C), *para*-xylene 0.07 µg/L (0.04 nmol C), CT 19µg/L (0.72 nmol C) and *cis*-DCE 0.76 µg/L (0.14 nmol C). These points are highlighted by arrows in Figure 5.6.
In Table 5.3 method detection limits for the P&T method are listed with their corresponding carbon isotope values and mass 44 amplitudes. As pointed out by Zwank et al., [19] even lower peak amplitudes may yield reliable isotope data because of the absence of a solvent and the use of cryofocusing. Figure 5.6 and Table 5.3 show that stable isotope values for BTEX compounds can be obtained down to amass 44 amplitude of ~200 mV. For chlorinated methanes but not for chlorinated ethanes and ethylenes, this value is approximately ten times higher. So far, there is no convincing explanation for this behaviour but it seems likely that conversion processes in the combustion oven are responsible. The reproducibility (Table 5.3) was determined by measuring and then calculating of the mean and standard deviation of all $\delta^{13}C$ values from the highest concentration to the defined MDL concentration (n = 12-33).

5.3.6 Application to environmental samples at trace level concentration

The method applicability for the determination of carbon isotope values at low µg/L levels of monoaromatic and halogenated volatile organic compounds was tested with jet fuel contaminated groundwater from a former military air field in eastern Germany. The groundwater at this contaminated site contains BTEX as well as chlorinated volatile organic compounds. In Figure 5.7, a P&T-GC/IRMS chromatogram of a well with BTEX concentrations smaller 4 µg/L (TCE) and 6mg/L (PCE) is shown. The achieved MDLs with P&T-GC/IRMS allow the reliable analysis of $^{13}C/^{12}C$ ratios at these low contaminant concentrations.

5.4 Conclusions

In this paper, we present the applicability of a modified P&T concentrator combined with GC/IRMS for the determination of $^{13}C/^{12}C$ ratios. For BTEX compounds and chlorinated ethylenes, fractionation effects caused by the analytical method are negligible relative to chemical and microbiological transformation processes.[3] P&T as a pre-concentration method may also be a useful tool when lower analyte concentrations needed for the isotope ratio determination of other elements ($^{2}H/^{1}H$, $^{15}N/^{14}N$, $^{18}O/^{16}O$).

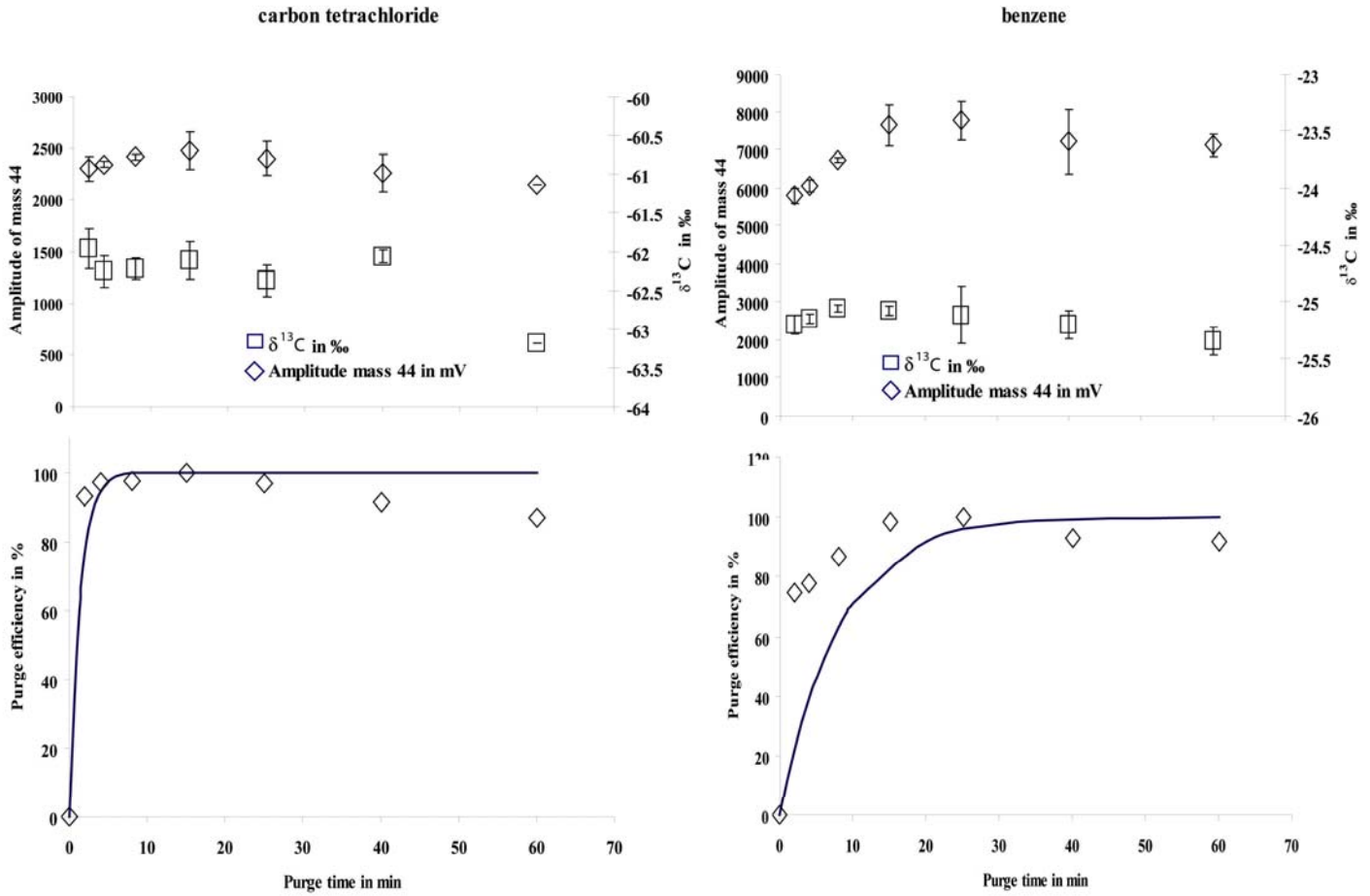

Figure 5.5 Evaluation of purge time. In the upper part, the influence of purge time on $\delta^{13}C$ values is shown exemplarily for carbon tetrachloride and benzene. The squares represent $\delta^{13}C$ values in ‰ and the diamonds show the amplitude of mass 44 in mV. Triplicate measurements were done for each point and vertical bars indicate the standard deviation. The lower part shows the influence of purge time on extraction efficiency compared with theoretically predicted extraction efficiency using eq 2 with K_{aw} values calculated for 20 °C (Table 1).The purge gas flow rate and the sample volume was 50 mL/min and 76 mL, respectively.

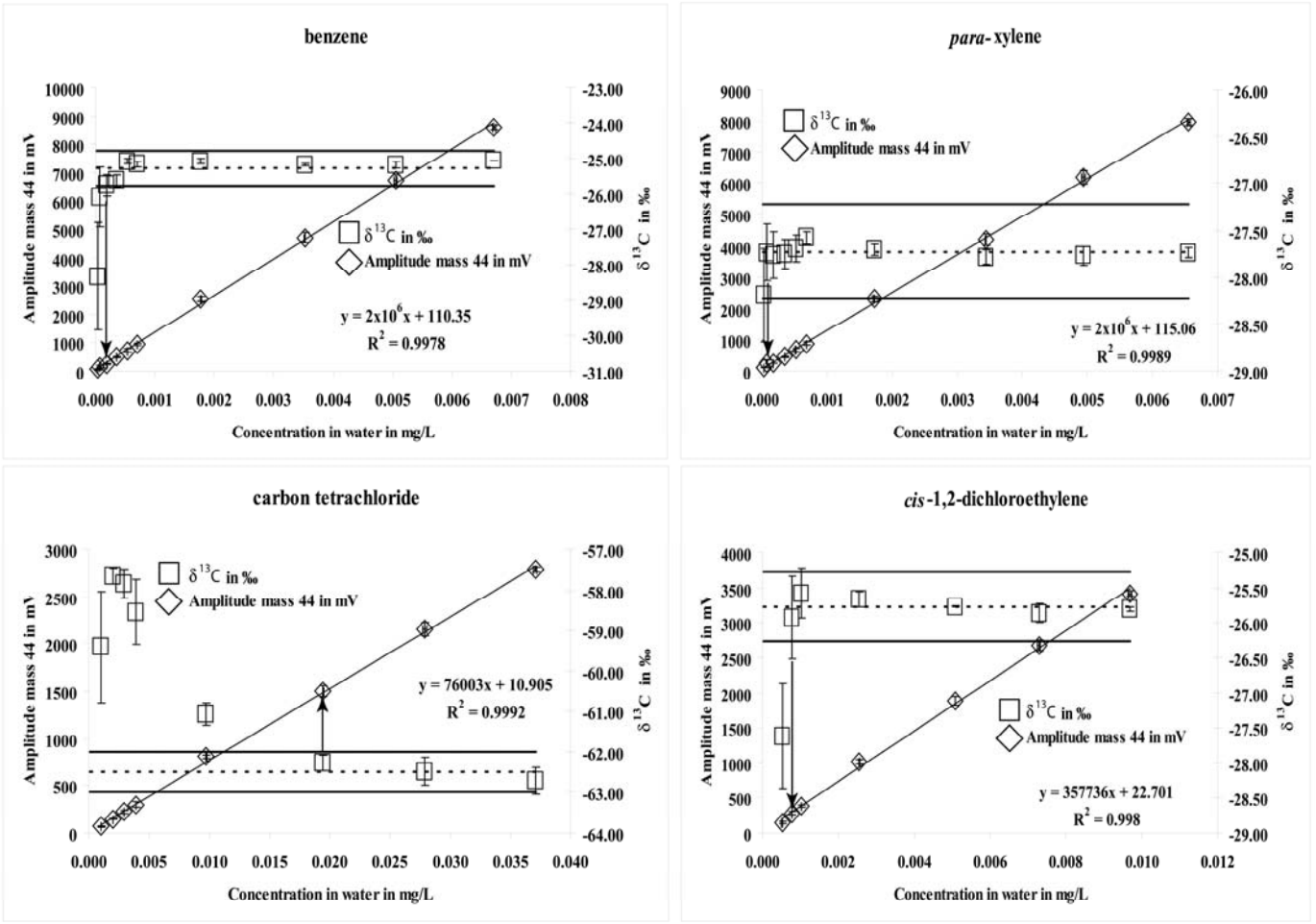

Figure 5.6 Evaluation of method detection limits (MDLs) for four exemplary compounds. The squares represent the $\delta^{13}C$ values in per mil and the diamonds show the amplitude of mass 44 in mV. The linear curve fit and the correlation coefficient are shown in each graph. Triplicate measurements were done for each point; error bars indicate the standard deviation. The horizontal broken lines represent the iteratively calculated mean value. The solid lines around the mean value represent the ±0.5 ‰ interval including the total analytical error that incorporates the internal reproducibility on triplicate duplicate measurements as well as the accuracy of the measurement with respect to international standards.

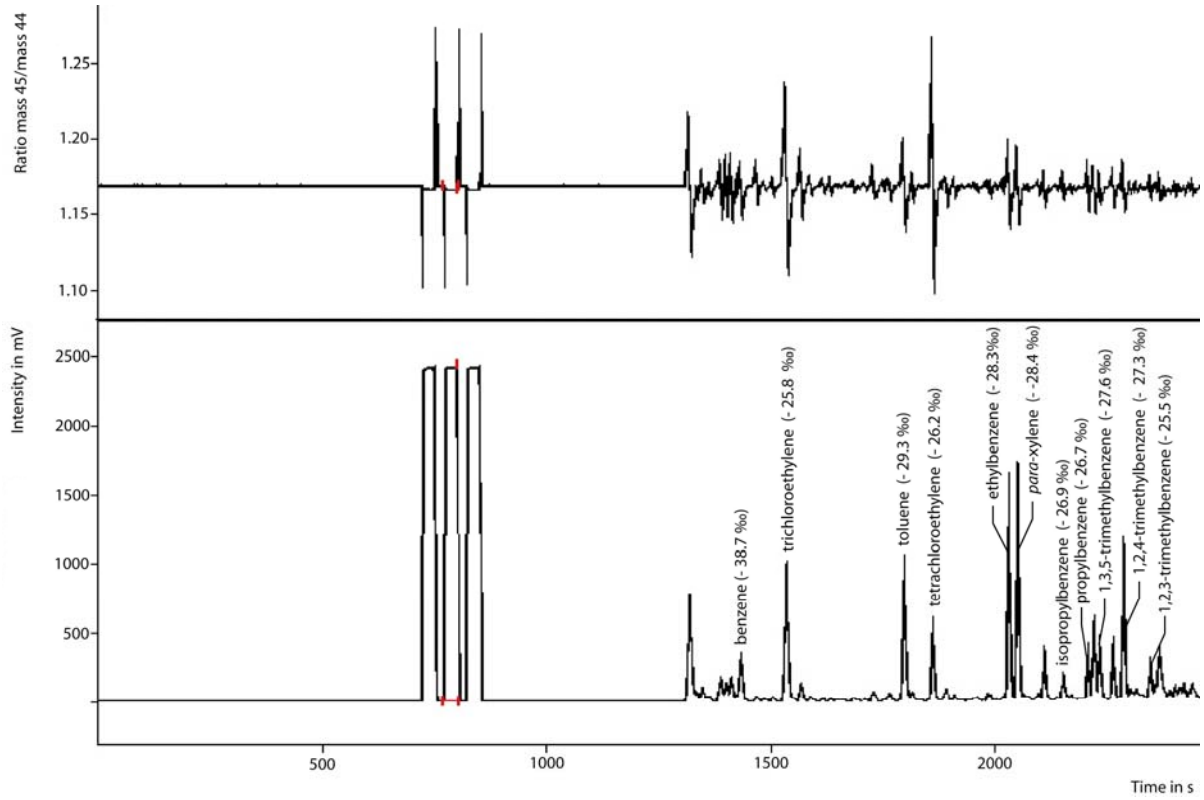

Figure 5.7 P&T-GC/IRMS chromatogram of a jet fuel contaminated groundwater sample from a former military air field in eastern Germany. The first three peaks correspond to the reference CO_2 gas. The second reference peak was used for evaluation of each compound.

Table 5.8 Evaluated parameters (‰ vs VPDB)[a)]

Compounds in elution order	EA-IRMS	P&T-GC-IRMS				
	Pure liquid phase (‰)	δ^{13}C-value *under optimized conditions (‰)* [b) c)]	Reproducibility (‰)[d)]	Mean of ±0.5 ‰ interval for MDL determination	MDL in water (µg/L)	Amplitude mass 44 at MDL (mV)[b)]
DCM	n.d.	-35.95 ± 0.07	-36.49 ± 0.43	-36.49	27	2646 ± 126
trans-DCE	-25.54 ± 0.03	-25.98 ± 0.06	-26.18 ± 0.43	-26.10	5.1	1699 ± 95
cis-DCE	-25.81 ± 0.08	-25.68 ± 0.09	-25.76 ± 0.28	-25.77	0.76	270 ± 24
chloroform	-57.72 ± 0.05	-59.20± 0.10	-59.16 ± 0.26	-59.16	18	1761 ± 63
CT	-61.91 ± 0.11	-62.11 ± 0.25	-62.49 ± 0.32	-62.49	19	1503 ± 59
benzene	n.d.	-25.08 ± 0.04	-25.27 ± 0.28	-25.27	0.20	252 ± 4
DCA	n.d.	-27.96 ± 0.11	-28.50 ± 0.33	-28.54	2.3	362 ± 18
fluorobenzene	n.d.	-30.83 ± 0.03	-30.76 ± 0.15	-30.73	0.08	121 ± 60
TCE	-26.69 ± 0.11	-26.40 ± 0.19	-26.55 ± 0.27	-26.47	1.2	256 ± 10
toluene	-26.82 ± 0.06	-27.19 ± 0.08	-27.15 ± 0.08	-27.12	0.07	185 ± 53
PCE	n.d.	-27.19 ± 0.08	- 27.17 ± 0.28	-27.08	1.3	178 ± 5
EDB	n.d.	-29.94 ± 0.08	-29.72 ± 0.28	-29.72	3.9	228 ± 10
ethylbenzene	-25.72 ± 0.06	-25.53 ± 0.03	-25.24 ± 0.09	-25.44	0.35	507 ± 17
para-xylene	n.d.	-27.70 ± 0.07	-27.73 ± 0.12	-27.73	0.07	233 ± 111
bromoform	n.d.	-49.46 ± 0.10	-49.48 ± 0.32	-49.48	14	257 ± 10
propylbenzene	-26.10 ± 0.17	-25.56 ± 0.04	-25.48 ± 0.18	-25.49	0.07	197 ± 135
isopropylbenzene	n.d.	-26.98 ± 0.07	-26.71 ± 0.32	-26.71	0.17	225 ± 2
1,3,5-TMB	-26.89 ± 0.12	-26.49 ± 0.08	- 26. 54 ± 0.22	-26.54	0.07	167 ± 97
1,2,4-TMB	-27.36 ± 0.12	-26.87 ± 0.02	-26.88 ± 0.19	-26.88	0.18	161 ± 4
1,2,3-TMB	n.d.	-25.00 ± 0.04	-25.07 ± 0.20	-25.07	0.18	143 ± 2

[a)] Uncertainties correspond to standard deviations of replicate measurements, [b)] (n = 3), [c)] value at a purge gas flow rate of 50 mL/min and purge time of 15 min,[d)] (n=12-33)
n.d.: not determined

6 General Conclusions and Outlook

As evaluated in the previous chapters, the in-needle extraction techniques, SPDE as well as ITEX, provide high sensitivities with method detection limits in the ng/L range for GC/MS. The methods are robust and provide high throughput analysis by relatively low sample preparation times. Both systems have the potential to overcome GC/IRMS related sensitivity problems and should be evaluated for possible isotopic fractionation in future studies. Preliminary results, which are not presented in this thesis, showed that no significant fractionation can be expacted for BTEX compounds, but more work on this topic has to be done. The SPDE method for ethers and alcohols is not restricted to groundwater but can be applied in food science as well in investigations of adulteration on alcoholic beverages by using the method in combination with isotopic fingerprinting. A special advantage of the ITEX method is the independence from the injector temperature profile during thermal desorption into the injector. Because of this a cryofocusing inside the injector is possible. Preliminary results during the optimization showed that even a determination of vinyl chloride by ITEX at room temperature was possible but leads to adverse peak shapes. In future studies and especially for the evaluation of ITEX with CSIA a cool trap for the syringe body is recommended.

Due to the fact that so far, no general rules on the determination of method detection limits for CSIA exists, an attempt for the definition of MDLs was presented in this work.

By enhancing the sensitivity of GC/IRMS to the low µg/L or ng/L range, a distinction between contaminant emission by point or diffusive sources into the groundwater could be achieved. As in previous studies it could be confirmed, that P&T showed lowest detection limits and low isotopic fractionation for carbon isotope measurements of volatile organic compounds. Future work in the field of P&T-GC/IRMS will be the development of water removal traps to allow for purging of higher sample volumes and the applicability of this method for other elements in CSIA. A drawback in this work was the limitation of the autosampler needle penetration depth, so that not the complete sample volume could be used. This software related problem should also be solved in cooperation with the supplier of the P&T system.

As discussed in the introduction, many microextraction methods have been developed and used prior to gas chromatographic separation. Not much work has been dedicated to the use of these methods in conjunction with GC/IRMS. In the future, it would for example be also interesting to evaluate liquid-phase microextraction techniques. Especially the combination of dynamic-liquid phase microextraction in bigger syringes with subsequent large volume injection could be an interesting approach. However, as it was shown in this work the here investigated methods have potential for GC/IRMS measurements and should be investigated more detailed for this purpose.

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Appendix A

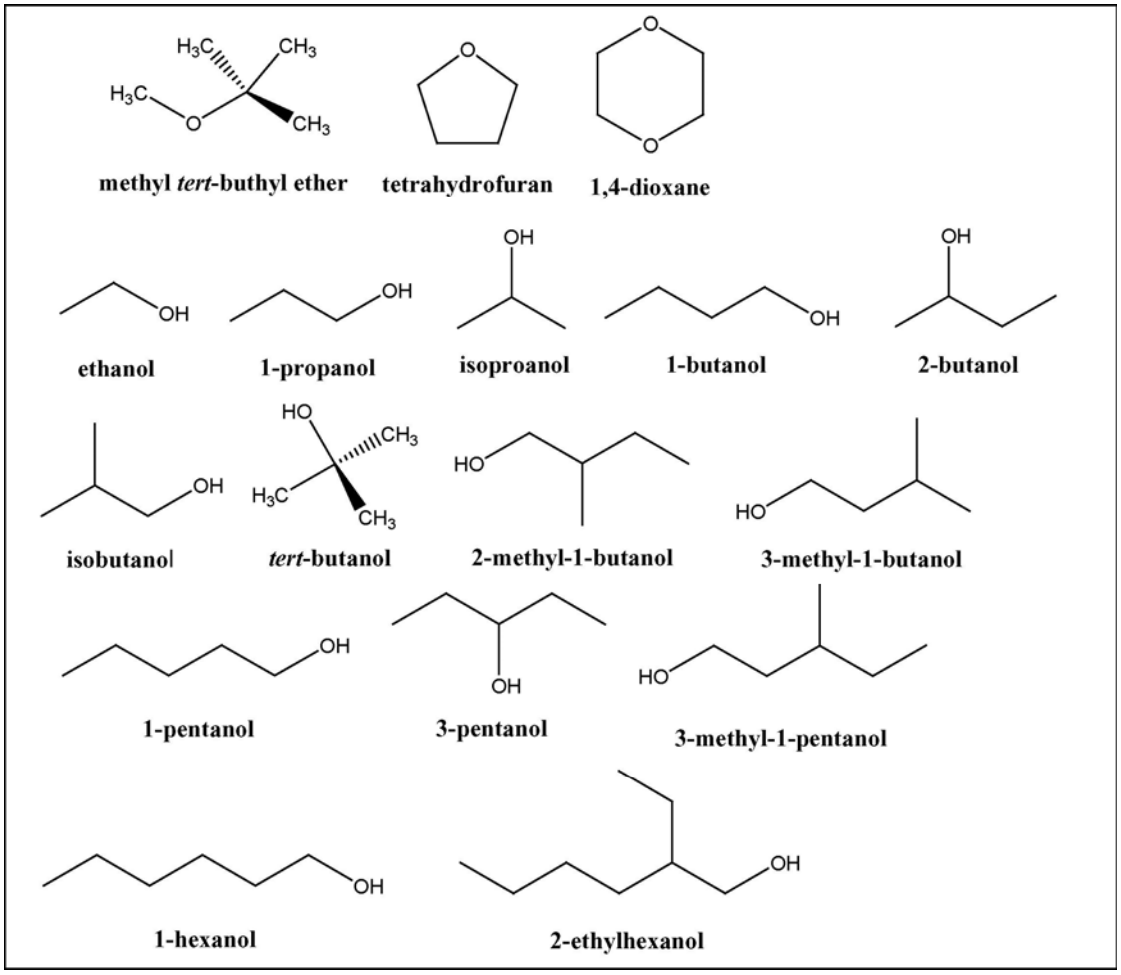
Physicochemical properties

A 1 Structures of the investigated compounds

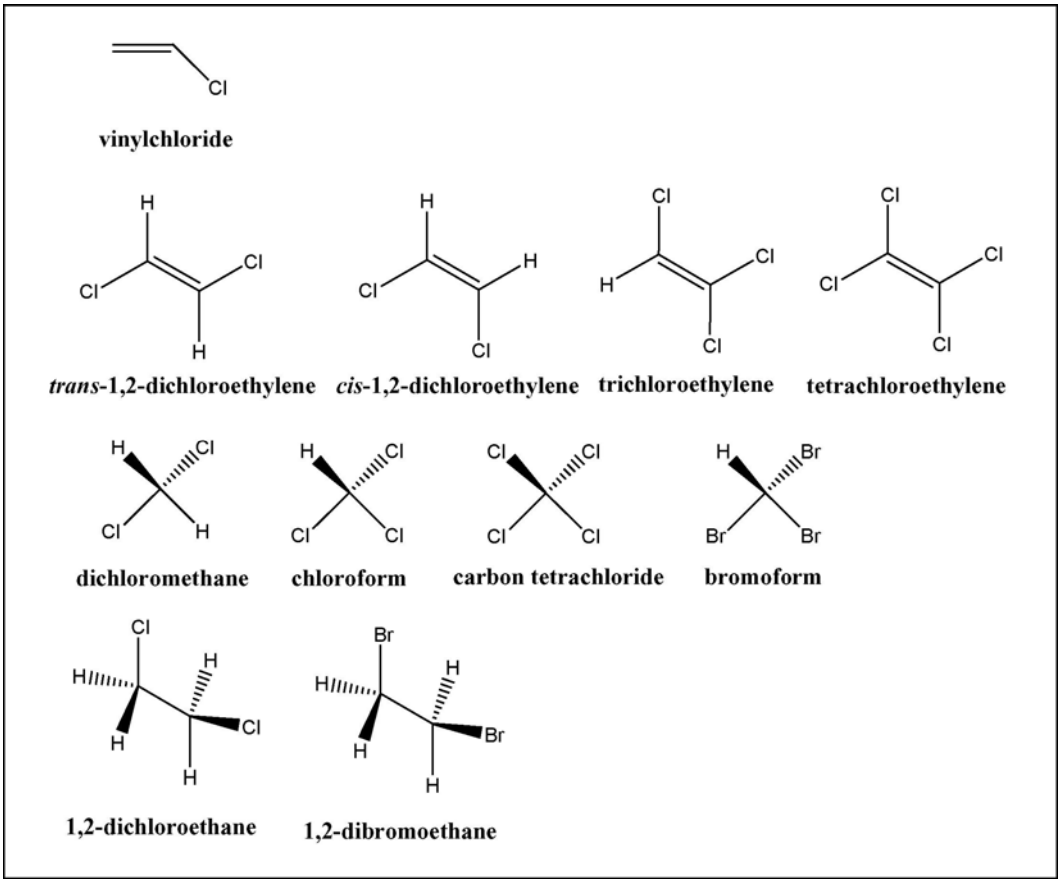
A 2 Physicochemical properties

A 1 Structures of the investigated compounds

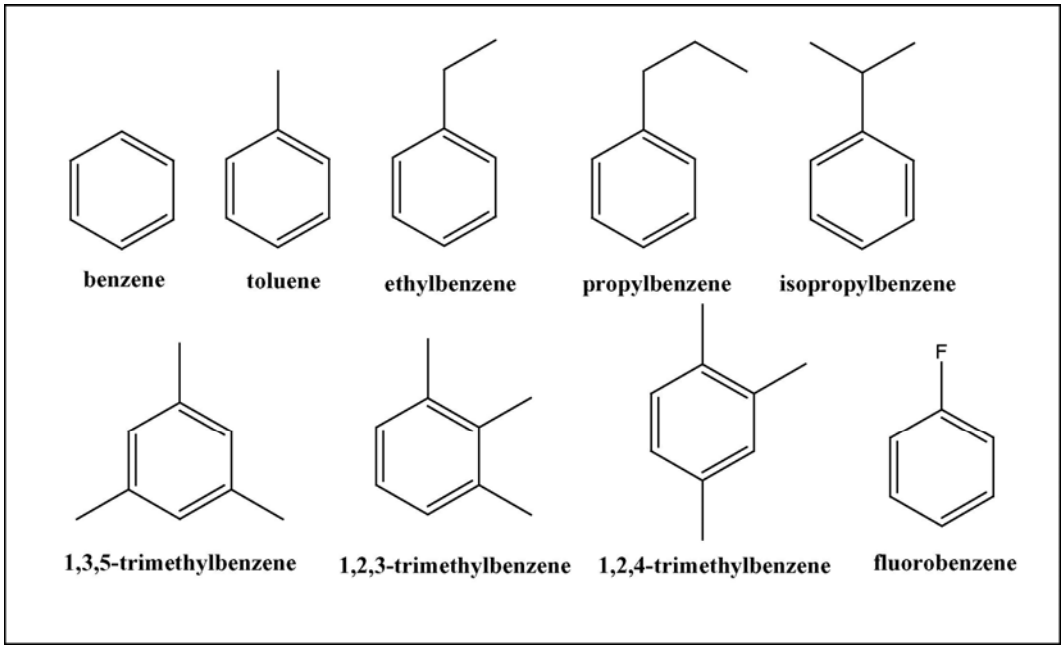
A 1.2 Structures of ethers and alcohols



A 1.3 Structures of chlorinated hydrocarbons



A 1.4 Structures of monoaromatic hydrocarbons



A 2.1 Physicochemical properties of ethers and alcohols

Compound	Abbrev.	CAS-no.	MW ($g \cdot mol^{-1}$) [a]	Density (kg/L) [a),b]	Boiling point (°C) [a),b]	Vapor pressure (kPa) [b]	Calculated air-water partitioning constant K_{aw} x 10^4 [e]	Constants for temperature dependent air-water partitioning constant K_{aw}		Water solubility (g/L) [b]	Log $K_{o/w}$ [b]
								A	B		
methyl *tert*-butyl ether	MTBE	1634-04-4		0.74	55	33	240	4745[c]	12.6 [c]	51	0.94
tetrahydrofuran	THF	109-99-9		0.87	66	22	28.8	n.a.	n.a.	miscible	0.46
1,4-dioxane		123-91-1		1.0	101	27	1.96	n.a.	n.a.	miscible	-0.27
Ethanol	EtOH	64-17-5		0.79	78	7.9	0.90	6349[d]	12.8 [d]	miscible	n.a.
1-propanol		71-23-8		0.80	97	15	3.03	7192 [d]	16 [d]	miscible	n.a.
isopropanol		67-63-0		0.79	83	33	3.31	n.a.	n.a.	miscible	n.a.
1-butanol		71-36-3		0.81	118	4	3.60	n.a.	n.a.	63	n.a.
2-butanol		78-92-2		0.81	99.5	2.4	3.70	6929 [d]	15.2 [d]	180	n.a.
isobutanol		78-83-1		0.80	108	9	4.00	6980 [d]	15.6 [d]	85	n.a.
tert-butanol	TBA	75-65-0		0.79	83	5.6	0.45	8030 [c]	19.5 [c]	miscible	n.a.
1-pentanol		71-41-0		0.82	138	1.2	5.31	n.a.	n.a.	22	n.a.
3-pentanol		584-02-1		0.82	116	2	8.09	n.a.	n.a.	52	n.a.
2-methyl-1-butanol		137-32-6		0.82	129	n.a.	5.76	n.a.	n.a.	30	n.a.
3-methyl-1-butanol		123-51-3		0.81	131	2	5.76	n.a.	n.a.	27	n.a.
1-hexanol		111-27-3		0.82	156	0.7	6.99	n.a.	n.a.	5.9	n.a.
3-methyl-1-pentanol		589-35-5		0.82	151	n.a.	n.a.	n.a.	n.a.	4.3	n.a.
2-ethylhexanol		104-76-7		0.83	183	0.4	10.8	n.a.	n.a.	0.88	n.a.

[a] Specification from manufacturer
[b] Data from SRC Phys Prop Database (http://esc.syrrees.com)
[c] Adapted from: [1]
[d] Adapted from: [2]
[e] Values calculated for 25 °C with van't Hoff type equation $\log K_{aw} = A - B/T$
n.a.: not available

A 2.2 Physicochemical properties of chlorinated hydrocarbons

Compound	Abbrev.	CAS-no.	MW ($g \cdot mol^{-1}$) [a]	Density ($kg \cdot L^{-1}$) [a]	Boiling point (°C) [a]	Vapor pressure (kPa) [a]	Calculated air-water partitioning constant K_{aw} [c]	Constants for temperature dependent air-water partitioning constants K_{aw} [b]		Water solubility (g/L) [a]	Log $K_{o/w}$ [a]
								A	B		
vinyl chloride	VC	75-01-4	62.5	0.91 [d]	-13.7	355	1.04	4.119	1223	1.1	1.27
dichloromethane	DCM	75-09-2	84.9	1.33	40.1	57.5	0.11	4.561	1644	13	1.31
trans-1,2-dichloroethylene	*trans*-DCE	156-60-5	96.9	1.27	48.0	40.7	0.45	5.247	1669	6.3	2.09
cis-1,2-dichloroethylene	*cis*-DCE	156-59-2	96.9	1.27	60.0	28.2	0.17	4.464	1559	0.8	1.86
chloroform		67-66-3	119.4	1.48	61.4	25.1	0.16	5.343	1830	8.0	1.95
carbon tetrachloride	CT	56-23-5	153.8	1.62	76.7	14.5	1.18	5.736	1689	0.8	2.77
1,2-dichloroethane	DCA	107-06-2	99.0	1.25	83.6	11.2	0.05	4.434	1705	n.a.	1.46
trichloroethylene	TCE	79-01-6	131.4	1.46	87.0	10.0	0.40	5.874	1871	1.1	2.42
tetrachloroethylene	PCE	127-18-4	165.8	1.62	121.1	2.51	0.69	6.394	1955	0.2	2.88
1,2-dibromoethane	EDB	106-93-4	187.9	2.18	131.5	1.62	0.03	3.661	1556	n.a.	1.96
bromoform		75-25-2	252.8	2.89	149.6	0.72	0.02	5.476	2120	3.0	2.67

[a] Adapted from: [3]

[b] Adapted from: [2]

[d] liquid phase

[c] Values calculated for 25 °C with van't Hoff type equation $\log K_{aw} = A - B/T$

n.a. : not available

A 2.3 Physicochemical properties of monoaromatic hydrocarbons

Compound	Abbrev.	CAS-no.	MW ($g \cdot mol^{-1}$) [a]	Density ($kg \cdot L^{-1}$) [a]	Boiling point (°C) [a]	Vapor pressure (kPa) [a]	Calculated air-water partitioning constant K_{aw} [e]	Constants for temperature dependent air-water partitioning constants K_{aw} [c]		Water solubility (g/L) [a]	Log $K_{o/w}$ [a]
								A	B		
benzene		71-43-2	78.1	0.88	80.1	12.6	0.24	5.053	1693	1.75	2.17
fluorobenzene		462-06-6	96.1 [b]	1.02 [b]	85.1 [b]	n.a.	0.30	5.251	1723	n.a.	n.a.
toluene		108-88-3	92.2	0.87	110.6	3.71	0.30	5.271	1745	0.56	2.69
ethylbenzene		100-41-4	106.2	0.86	136.2	1.23	0.31	6.541	2100	0.17	3.20
para-xylene		106-42-3	106.2	0.86	138.1	3.72	0.30	4.900	1615	0.18	3.27
isopropoylbenzene		98-82-8	120.2	0.86	154.2	1.23	0.34	3.774	1265	0.06	3.66
propylbenzene		103-65-1	120.2	0.86	159.2	1.17	0.45	4.587	1471	0.05	3.69
1,3,5-trimethylbenzene	1,3,5-TMB	108-67-8	120.2	0.88	164.7	0.62	0.30	4.329	1448	0.05	3.42
1,2,4-trimethylbenzene	1,2,4-TMB	95-63-6	120.2	0.88	169.4	0.45	0.27	5.125	1697	0.06	3.65
1,2,3-trimethylbenzene	1,2,3-TMB	526-73-8	120.2	0.89	176.1	0.33	n.a.	n.a.	n.a.	0.07	3.60

[a] Adapted from: Schwarzenbach[3]

[b] Data from SRC Phys Prop Database (http://esc.syrrees.com)

[c] Values calculated for 20 °C with van't Hoff type equation $\log K_{aw} = A - B/T$ according to Ref.: [2, 4]

n.a.: not available

Appendix B

Data

B 1 Parameter of Solid-Phase Dynamic Extraction evaluation for ethers and alcohols

B 1.1 Evaluation of extraction temperatures for ethers and alcohols
B 1.2 Salting out effect for ethers and alcohols
B 1.3 Number of extraction cycles for ethers and alcohols

B 2 Parameter of Solid-Phase Dynamic Extraction evaluation for VOCs

B 2.1 Injector temperature
B 2.2 Pre-desorption time
B 2.3 Desorption flow rate
B 2.4 Extreaction flow rate
B 2.5 Applicability of SPDE-GC/MS for real groundwater samples

B 3 Parameter of In-tube Extraction (ITEX) evaluation for VOCs

B 3.1 Desorption temperature
B 3.2 Desorption flow rate
B 3.3 Desorption volume
B 3.4 Number of extraction cycles
B 3.5 Extraction volume
B 3.6 Extraction flow rate
B 3.7 Extraction temperature

B 1 Parameter of Solid-Phase Dynamic Extraction evaluation for ethers and alcohols

B 1.2 Evaluation of extraction temperatures for ethers and alcohols

methyl *tert*-butyl ether		**Peak area**			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	4084846	6472522	5925575	5494314	1250895
40	9096846	9110742	8404921	8870836	403554
50	12094297	11178112	11558149	11610186	460304
60	15499985	15968618	14976315	15481639	496406
70	18887040	20505731	20972636	20121802	1094522

tetrahydrofuran		**Peak area**			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	635034	676149	631515	647566	24816
40	1018548	945821	969678	978016	37073
50	1486749	1393704	1269337	1383263	109081
60	1955077	1871282	1896249	1907536	43023
70	2782061	2735592	2880347	2799333	73907

1,4-dioxane		**Peak area**			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30		543978	545994	544986	1426
40	766083	753469	769544	763032	8461
50	1138067	1125185	1145174	1136142	10133
60	1627721	1594270	1670632	1630874	38279
70	2516290	2493792	2315295	2441792	110126

1,4-dioxane-d_8		**Peak area**			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	outlier	466764	456918		
40	645436	631355	656377	644389	12544
50	917661	968997	942874	943177	25669
60	1368293	1341926	1435117	1381779	48037
70	2120145	2067551	1931265	2039654	97481

ethanol		**Peak area**			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30					
40					
50	9580	12164	15480	12408	2958
60	32126	14851	34035	27004	10568
70	96758	78793	86671	87407	9005

1-propanol		**Peak area**			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	92710	79490	78650	83617	7886
40	108821	96785	104981	103529	6148
50	149519	146012	144417	146649	2610
60	247598	223444	229674	233572	12540
70	431150	415913	396913	414659	17153

isopropanol	Peak area				
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	77670	78204	82622	79499	2718
40	109367	117711	116682	114587	4550
50	182384	190958	208947	194096	13557
60	318599	305217	327295	317037	11122
70	575408	585039	572748	577732	6467

1-butanol	Peak area				
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	98598	93041	99502	97047	3499
40	157790	163096	155941	158942	3714
50	287798	292531	288262	289530	2609
60	492313	482641	489307	488087	4950
70	881930	869853	848207	866663	17086

2-butanol	Peak area				
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	221392	234964	226286	227547	6873
40	367639	354346	372436	364807	9372
50	617633	610816	574145	600865	23390
60	970932	945673	955846	957484	12709
70	1622253	1653624	1584647	1620175	34535

isobutanol	Peak area				
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	120963	122182	117822	120322	2249
40	183993	200952	197419	194121	8948
50	324451	328303	331583	328112	3570
60	535495	528339	533790	532541	3738
70	872071	842974	830917	848654	21157

tert-butanol	Peak area				
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	139137	145902	134526	139855	5722
40	232797	240912	248880	240863	8042
50	419449	396911	413655	410005	11704
60	641019	688196	666304	665173	23609
70	1116114	1184360	1149035	1149836	34130

tert-butanol-d_{10}	Peak area				
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	11547965	1123830	outlier		
40	19542931	18215476	18526521	18761643	694259
50	32189615	31652110	32182200	32007975	308210
60	51617057	50999430	51614975	51410487	355988
70	99783821	92869105	90685119	94446015	4749903

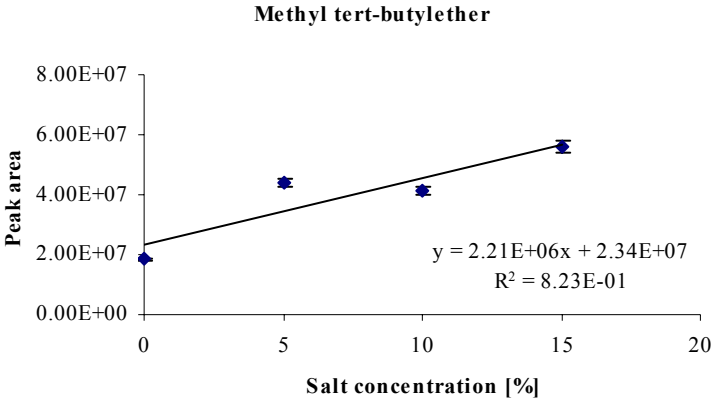
3-pentanol		Peak area			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	643252	641504	643374	642710	1046
40	1110248	1096338	1104410	1103665	6985
50	1976712	2012108	1993674	1994165	17703
60	3337609	3238479	3286109	3287399	49578
70	5841966	5804817	5696347	5781043	75664

3-methyl-1-pentanol		Peak area			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	460661	447166	436820	448216	11955
40	696820	707727	711676	705408	7695
50	1200043	1245947	1232457	1226149	23593
60	1912750	1911118	1951999	1925289	23146
70	3123716	3204101	3067771	3131863	68529

1-hexanol		Peak area			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	511528	493663	491391	498861	11029
40	792617	783387	796034	790679	6542
50	1350052	1375790	1376964	1367602	15210
60	2183875	2182866	2200261	2189001	9765
70	3644161	3748332	3599397	3663963	76417

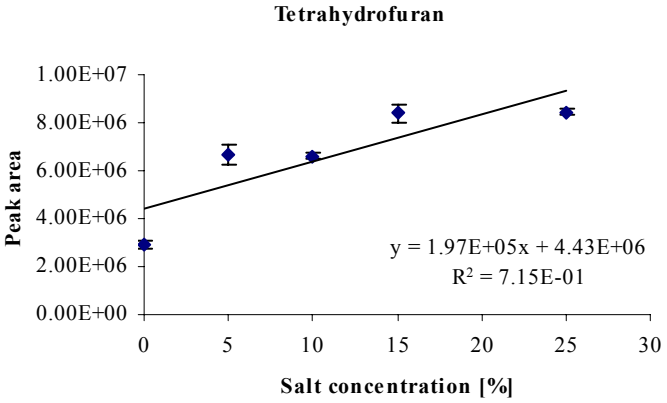
2-ethyl-1-hexanol		Peak area			
Temperature in °C	**Measurement 1**	**Measurement 2**	**Measurement 3**	**Mean**	**STDV**
30	2921201	2854012	2797397	2857537	61977
40	4552020	4593508	4746796	4630775	102596
50	7555262	7696131	7807443	7686279	126379
60	11268503	10990689	11163671	11140954	140293
70	16442693	17014039	16435017	16630583	332105

B 1.2 Salting out ether and alcohols

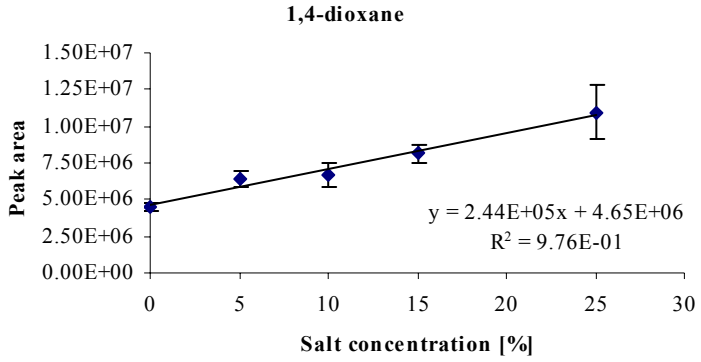


MTBE	0%	5%	10%	15%	25%
Peak area	18938822	47634867	47628493	65000211	51171462
	19420370	47978143	46091019	67918080	50526681
	18253342	45969473	44889805	64013647	55395556
Average	18386499	43943582	41441104	56106832.4	52364566
STDV	586476.15	1074409.2	1372780.2	2030265.38	2644637.9
Normalized	0.3277052	0.7832127	0.7386106	1	0.9333011
Coeff. of variation	0.0318971	0.0244497	0.0331261	0.03618571	0.0505043

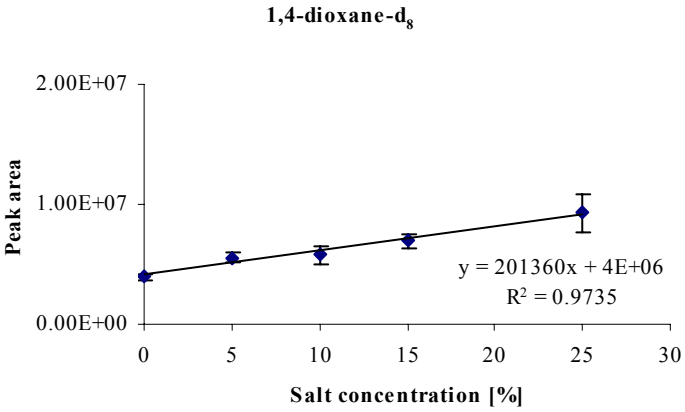
25% was outlier in T-test



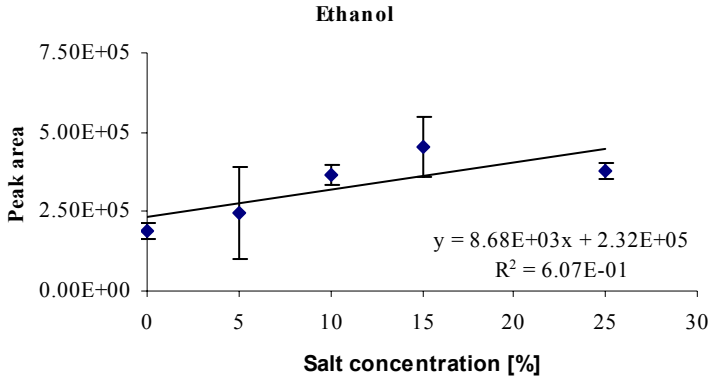
THF	0%	5%	10%	15%	25%
Peak area	3070796	6668255	7392835	9518638	11274521
	3121418	7342864	7480688	9739751	11207846
	2784718	7388731	7266543	10241424	11038459
Average	2915509	6641966.1	6619387.4	8404635.03	8423483.4
STDV	181553.53	403378.8	107645.95	370357.116	121698.25
Normalized	0.3461168	0.7885059	0.7858254	0.9977624	1
Coeff. of variation	0.0622716	0.0607318	0.0162622	0.04406582	0.0144475



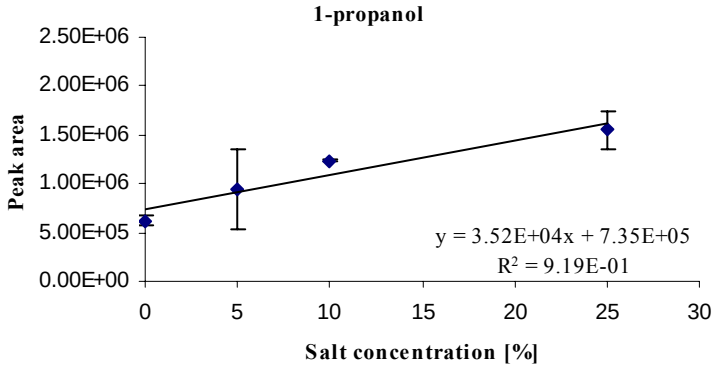
1,4-dioxane	0%	5%	10%	15%	25%
Peak area	4621658	6612283	6640013	10265921	15744664
	4386901	6607883	8126418	9199109	12388159
	4949701	7482502	7585163	9063954	15347870
Average	4533334	6425579	6682630	8128041.29	10926309
STDV	282685.6	503696.1	752292.6	658417.217	1834096.5
Normalized	0.414901	0.588083	0.611609	0.74389636	1
Coeff. of variation	0.062357	0.078389	0.112574	0.08100564	0.1678606



1,4-dioxane-d_8	0%	5%	10%	15%	25%
Peak area	3989332	5759719	5692781	8790432	13524187
	3893095	5825930	7096604	7871921	10597002
	4359112	6381700	6466857	7732914	12732025
Average	3975781	5576606	5757188	6950325.94	9260882.7
STDV	246025.3	341595.4	703147	574649.128	1514059.4
Normalized	0.429309	0.602168	0.621667	0.75050362	1
Coeff. of variation	0.061881	0.061255	0.122134	0.08267945	0.1634898

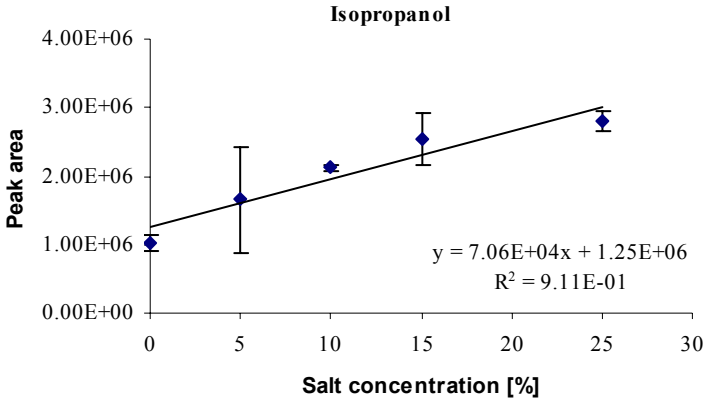


Ethanol	0%	5%	10%	15%	25%
Peak area	225450	109800	432522	432480	523374
	175856	279649	413330	543928	474485
	184354	402608	371199	620758	514646
Average	190209.42	245834.23	363871.19	455040.081	380078.96
STDV	26522.513	147028.41	31368.414	94667.938	26074.311
Normalized	0.4180059	0.5402474	0.7996465	1	0.8352648
Coeff. of variation	0.1394385	0.5980795	0.0862075	0.20804308	0.0686024

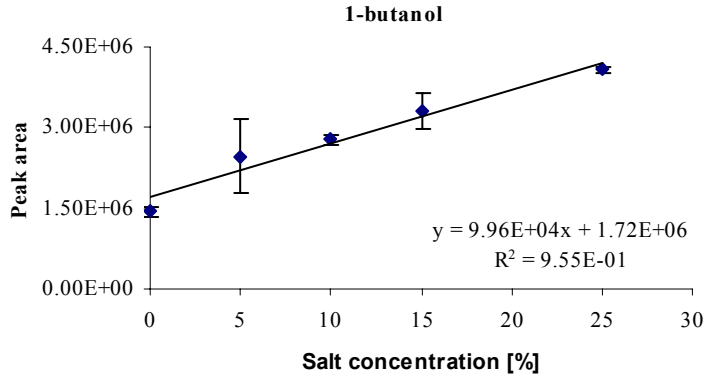


1-propanol	0%	5%	10%	15%	25%
Peak area	697586	556468	1374443	1565056	1959216
	595939	1124293	1363258	1843098	2096458
	625793	1351706	1382018	1935083	2115893
Average	623352.05	941200.2	1231704.4	1522313.27	1550859.5
STDV	52245.588	409582.18	9437.712	192651.92	85401.764
Normalized	0.4019397	0.6068894	0.7942076	0.98159327	1
Coeff. of variation	0.0838139	0.4351701	0.0076623	0.12655209	0.0550674

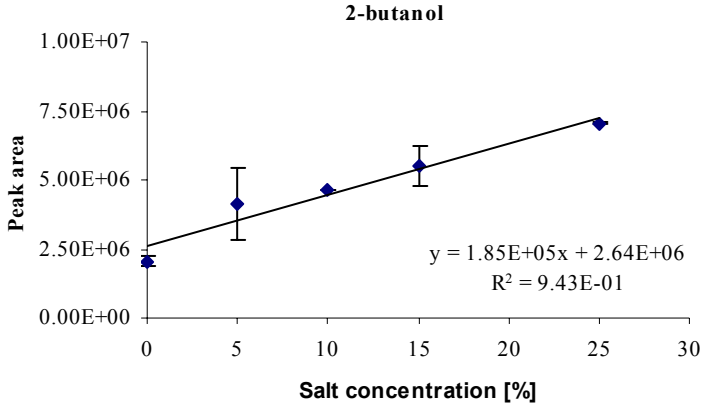
15% was outlier in T-test



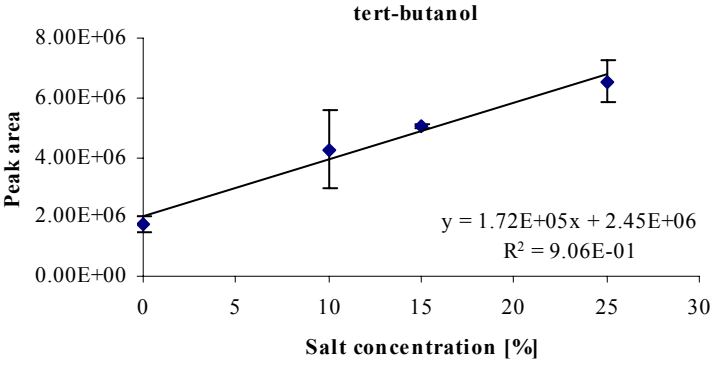
IPA	0%	5%	10%	15%	25%
Peak area	1192990	940829	2320096	2567181	3645007
	944942	1934527	2410534	3049931	3641069
	1007530	2466982	2369598	3289747	3874405
Average	1021576.5	1658125.1	2122810.3	2537605.89	2804528.9
STDV	128996.43	774606.03	45286.562	368026.471	133594.31
Normalized	0.3642596	0.5912312	0.7569222	0.90482428	1
Coeff. of variation	0.1262719	0.4671578	0.0213333	0.14502901	0.0476352



1-butanol	0%	5%	10%	15%	25%
Peak area	1531749	1856467	3025192	3481130	5482727
	1514976	3014460	3063012	4003314	5344911
	1381704	3083154	3196349	4131544	5385943
Average	1438255.8	2468743.3	2775874.9	3309449.44	4074327.7
STDV	82215.43	689254.14	89910.906	344518.368	70762.534
Normalized	0.3530044	0.6059265	0.6813087	0.81226884	1
Coeff. of variation	0.0571633	0.2791923	0.0323901	0.10410141	0.0173679

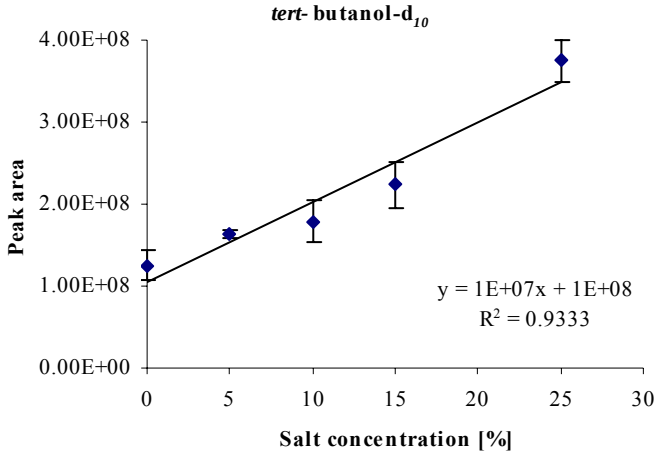


2-butanol	0%	5%	10%	15%	25%
Peak area	2284490	3010396	5172546	5595064	9308406
	2069019	4842061	5176619	6793974	9332461
	1943193	5506368	5163764	6960014	9380241
Average	2045029.6	4146237.6	4638020.8	5512635.63	7041453.5
STDV	172599.53	1292683	6569.6763	744764.277	36564.643
Normalized	0.2904272	0.5888326	0.6586738	0.78288319	1
Coeff. of variation	0.0843995	0.3117725	0.0014165	0.13510131	0.0051928

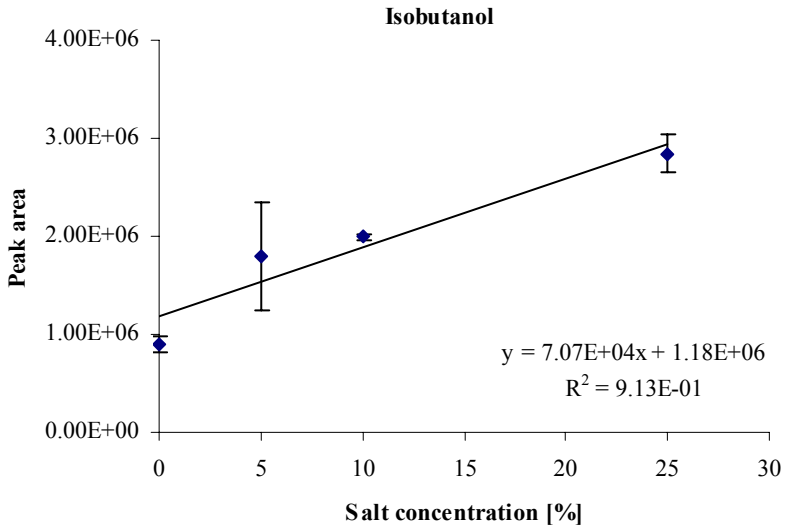


TBA	0%	5%	10%	15%	25%
Peak area	2114574	3005084	4634988	5122633	8447138
	1689973	4625674	4754742	6180494	8463857
	1633811	5571625	4824328	6402276	9149077
Average	1766258.4	4097682	4249687.3	5044352.32	6548662.7
STDV	262860.31	1297964.3	95771.314	683830.31	400525.56
Normalized	0.2697128	0.6257281	0.6489397	0.77028739	1
Coeff. of variation	0.1488232	0.3167557	0.0225361	0.13556355	0.0611614

5% was outlier in T-test

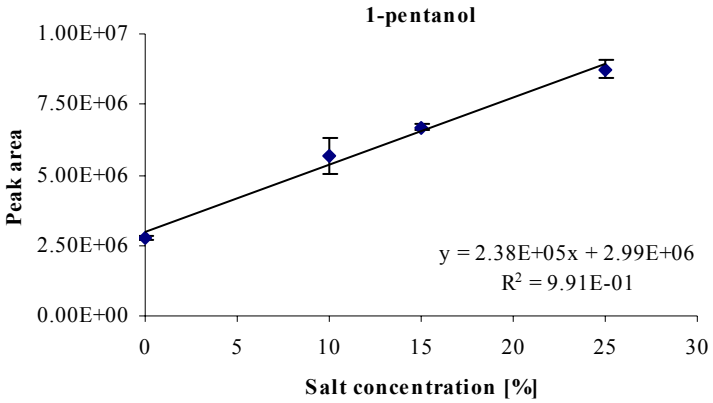


TBA-d_{10}	0%	5%	10%	15%	25%
Peak area	145482306	170076205	170321575	229770910	487006973
	130287069	174610257	212468660	273618977	477823836
	110594975	179144304	214968527	280972041	526969825
Average	125482597	162583672	178716578	223468391	374876141
STDV	17491901	4534049.5	25086439	27683558.1	26130084
Normalized	0.3347308	0.4336997	0.476735	0.5961126	1
Coeff. of variation	0.139397	0.0278875	0.14037	0.12388132	0.0697032



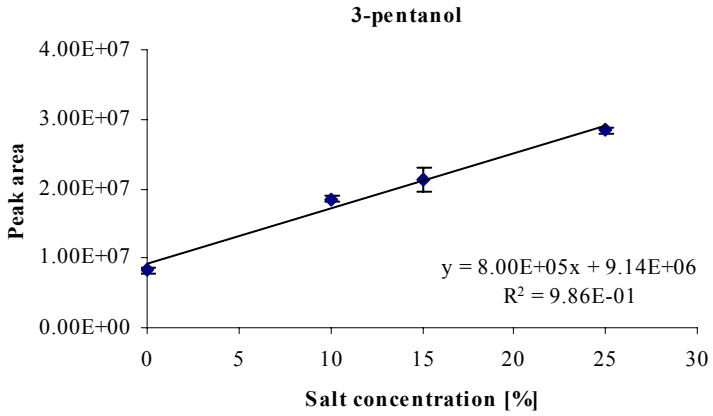
Isobutanol	0%	5%	10%	15%	25%
Peak area	1022233	1312093	2187684	2595832	3845083
	899319	2088576	2252993	2918662	3740656
	845287	2376135	2219692	2955776	3740216
Average	898608.13	1792972.2	1991302.2	2413219.63	2846111.1
STDV	90680.019	550424.29	32656.633	197971.522	60418.374
Normalized	0.3157319	0.6299727	0.6996572	0.84790072	1
Coeff. of variation	0.1009116	0.3069899	0.0163996	0.08203626	0.0212284

15% was outlier in T-test



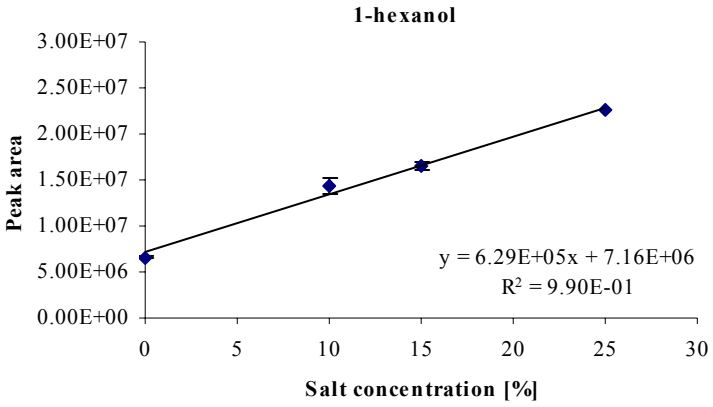
1-pentanol	0%	5%	10%	15%	25%
Peak area	2919581	5752969	6213729	7474945	11910761
	2849862	7033296	6228485	8038545	11456396
	2773611	6516812	6436261	8007893	11488170
Average	2774595	5991181.4	5644244.2	6701352.29	8758831.6
STDV	73009.354	644133.67	124438.14	316916.939	253653.4
Normalized	0.3167768	0.6840161	0.6444061	0.7650966	1
Coeff. of variation	0.0263135	0.1075136	0.0220469	0.04729149	0.0289597

5% was outlier in T-test



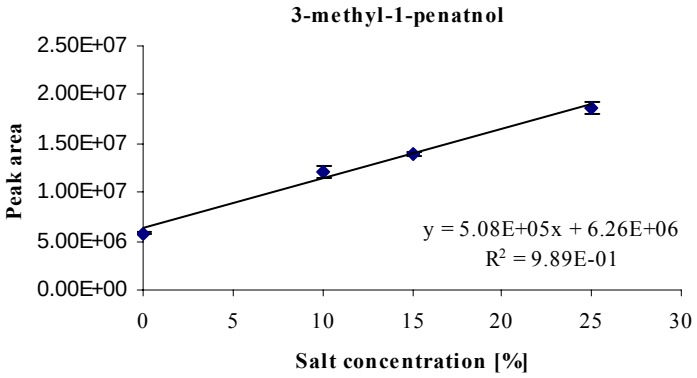
3-pentanol	0%	5%	10%	15%	25%
Peak area	8870818	17186493	20449828	23209753	38227244
	8532860	22215834	20283116	25151796	37775813
	8057513	21781127	21054670	26479898	37363135
Average	8269231.8	18989779	18473123	21322679.1	28487909
STDV	408581.98	2786691.7	405980.77	1644649.62	432199.31
Normalized	0.2902716	0.6665908	0.6484548	0.74848172	1
Coeff. of variation	0.0494099	0.1467469	0.0219768	0.07713147	0.0151713

5% was outlier in T-test



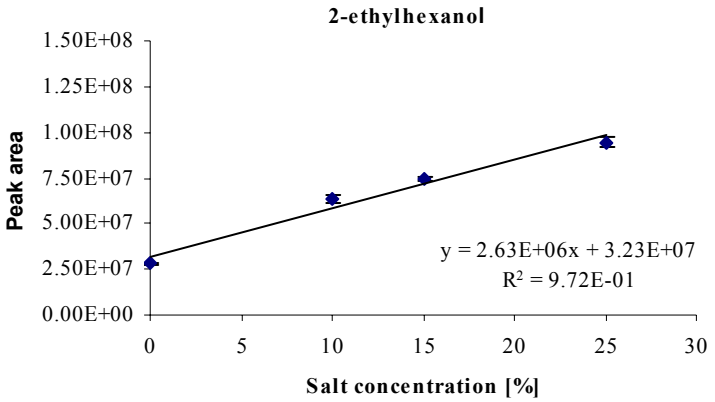
1-hexanol	0%	5%	10%	15%	25%
Peak area	6927505	17684175	16080994	18478620	30397869
	6772266	18856699	15895851	19730899	29442503
	6684296	17611422	16061790	19938094	29781678
Average	6620294.2	16807488	14362484	16566527.6	22521219
STDV	123145.23	698906.33	101802.49	789640.933	484330.33
Normalized	0.2939581	0.7462957	0.6377312	0.73559641	1
Coeff. of variation	0.0186012	0.041583	0.0070881	0.04766484	0.0215055

5% was outlier in T-test



3-methyl-1-pentanol	0%	5%	10%	15%	25%
Peak area	6046643	14483264	13365093	15668813	24987256
	5932417	15568876	13316550	16714234	24494933
	5818672	14651015	13759876	16677020	24585700
Average	5780309.8	13874716	12091115	13977443.1	18612597
STDV	113985.58	584403.2	243155.64	593123.273	262001.21
Normalized	0.310559	0.7454476	0.64962	0.75096683	1
Coeff. of variation	0.0197196	0.04212	0.0201103	0.04243432	0.0140766

5% was outlier in T-test



2-ethylhexanol	0%	5%	10%	15%	25%
Peak area	29710814	79322473	72000740	86429554	127230001
	28184877	81376698	69725712	85433827	121254761
	28529364	76596457	70846234	90534096	126548660
Average	28068947	73650494	63554506	74758271.4	94242541
STDV	800310.27	2397975.1	1137556.3	2703438.59	3270909.3
Normalized	0.2978373	0.7814994	0.6743717	0.79325399	1
Coeff. of variation	0.0285123	0.0325588	0.0178989	0.0361624	0.0347074

5% was outlier in T-test

Compound	$PA_{highest\ conc.}/PA_{without\ salt}$
Methyl *tert*-buthyl ether	3.05
Tertahydrofuran	2.89
1,4-Dioxane	2.41
1,4-Dioxane-d_8	2.33
Ethanol	2.00
1-propanol	2.49
Isopropanol	2.75
1-butanol	2.83
2-butanol	3.44
tert-butanol	3.71
tert-butanol-d_{10}	2.99
Isobutanol	3.17
1-pentanol	3.16
3-pentanol	3.45
1-hexanol	3.40
3-methyl-pentanol	3.22
2-ethylhexanol	3.36

B 1.3 Number of extraction cycles for ethers and alcohols

methyl tert-butyl ether	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	314878534	457840196	416138218	484216403	443587130	439576799	471038364
	347227466	417174359	481602965	478783772	447753084	444127161	461438417
	320919987	428350297	463596346	477158054	412150952	444060357	458556329
Mean	327675329	434454951	453779176	480052743	434497055	442588106	463677703
STDV	17199981	21008990	33818499	3696321	19464071	2608082	6535373

tetrahydrofuran	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	19475285	30167192	37854841	53554744	57420569	55911449	55680930
	19512902	29608436	41385697	50368472	57689531	59807176	56352343
	20065678	28521394	40343304	52297129	57775074	55029851	56026729
Mean	19684622	29432341	39861281	52073448	57628391	56916159	56020001
STDV	330540	836911	1814110	1604870	184992	2542202	335757

tert-butanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	19934752	27477393	27567719	34003521	38548503	38041800	40825347
	21114782	27442264	29715489	32669302	37958580	42848728	50794041
	20417082	27446392	29468430	35232286	39697622	35778007	46365860
Mean	20488872	27455350	28917213	33968370	38734902	38889512	45995083
STDV	593282	19201	1175206	1281854	884378	3610780	4994679

isopropanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	4773255	6417227	7224310	9037434	11224117	10469189	13052770
	4848622	6235697	8303727	8695141	10757960	12885880	17297204
	4900249	6285539	7380552	9122295	11650485	9751334	15519774
Mean	4840709	6312821	7636196	8951623	11210854	11035468	15289916
STDV	63866	93790	583353	226137	446410	1642208	2131533

Ethanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	447962	565441	733338	897647	1329588	1239675	1716291
	427079	509630	818386	894583	1313048	1631191	2165614
	426869	572997	686244	987844	1251977	1125777	2003669
Mean	433970	549356	745989	926691	1298204	1332214	1961858
STDV	12118	34611	66973	52982	40879	265110	227561

2-butanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	11974191	17954968	23194043	31173307	36265930	33229472	37460762
	13277037	17752919	23957095	29139769	34365303	38360926	40789827
	13033486	17887753	23816131	30685995	36455158	33562062	40099447
Mean	12761571	17865213	23655756	30333024	35695464	35050820	39450012
STDV	692680	102893	406020	1061725	1155832	2871455	1756984

1-propanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	2176037	3497820	4486681	5843741	7133638	6422649	7925730
	2805100	3301166	4708109	5549063	6562147	7951872	8832518
	2778437	3355201	4571285	5654029	7136294	5896294	8577123
Mean	2586525	3384729	4588692	5682278	6944026	6756938	8445124
STDV	355743	101598	111736	149356	330720	1067784	467583

isobutanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	6113356	9891892	13519082	19724617	22574421	21346640	22998199
	6669166	9713370	14949038	18763756	21443306	24334549	24371253
	6649460	9462141	14098927	18955852	2288501	20907095	23269789
Mean	6477327	9689134	14189016	19148075	15435409	22196095	23546414
STDV	315362	215898	719222	508454	11399594	1864950	727125

3-pentanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	58322906	95607027	122067739	189520563	236012090	239059663	259801219
	66603428	91811522	138294831	184506480	232086753	260379857	255426612
	65974423	90400538	130455352	183749359	235441223	234374959	252444875
Mean	63633586	92606362	130272641	185925467	234513355	244604826	255890902
STDV	4609924	2692714	8115089	3136374	2120795	13860927	3700084

1-butanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	5052908	8180432	12108493	18783184	25098631	25536594	29354933
	5633348	8074977	13375973	18310608	24436964	28668346	29227505
	5551255	7884470	12119900	18343868	25868444	24975117	28827075
Mean	5412504	8046626	12534789	18479220	25134680	26393352	29136504
STDV	314112	150004	728509	263765	716421	1990103	275444

1-pentanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	8616774	14384916	19323453	29762915	39110931	44452176	55169342
	9662874	13965557	21855602	28231457	38823950	46306823	53869926
	9401372	13468080	20790012	29182400	40603158	46006224	52795154
Mean	9227007	13939518	20656356	29058924	39512680	45588408	53944807
STDV	544411	458972	1271355	773160	955221	995418	1188864

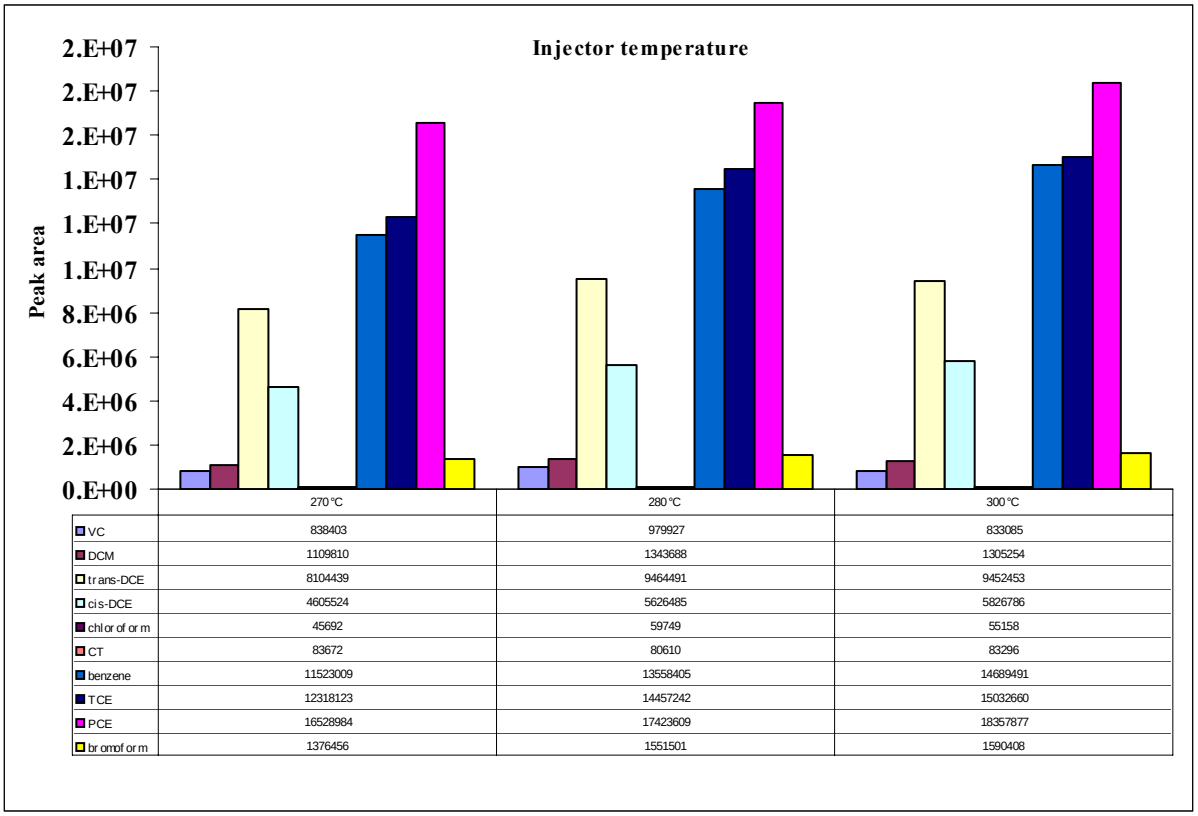
3-methyl-1-pentanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	26238256	40567008	54731662	81647547	99301270	109342222	126556244
	27136529	39484470	62408031	79205233	100045810	113256518	128289358
	26800329	38278753	60215750	80699654	101881333	112759880	123580763
Mean	26725038	39443410	59118481	80517478	100409471	111786207	126142122
STDV	453845	1144680	3954069	1231306	1327919	2131070	2381457

1-hexanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	35622553	56906455	77924678	119467264	141950225	156479675	174603688
	37605316	55388203	87986819	113220959	141891720	158837155	179065337
	36960158	54028793	85277848	117622752	148143193	161927355	172062747
Mean	36729342	55441150	83729782	116770325	143995046	159081395	175243924
STDV	1011333	1439561	5206635	3209214	3592520	2732040	3544925

2-ethylhexanol	Number of extraction cycles						
	1	2	5	10	20	30	50
Peak area	228586473	333860291	408110022	552966901	583667678	575042976	549134891
	247619845	330047329	471303161	549142406	588508725	579681571	572616200
	234123530	324117100	454812669	560144669	586099119	579574984	554218350
Mean	236776616	329341573	444741951	554084659	586091841	578099844	558656480
STDV	9790121	4909787	32778159	5585650	2420532	2647861	12353773

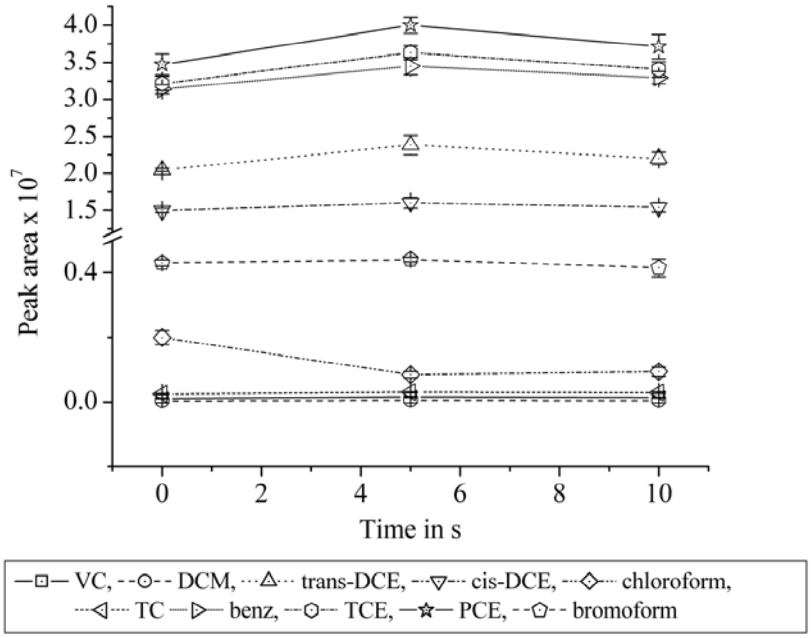
B 2 Parameter of Solid-Phase Dynamic Extraction evaluation for VOCs

B 2.1 Injector temperature



	270 °C	280 °C	300 °C
VC	838403	979927	833085
DCM	1109810	1343688	1305254
trans-DCE	8104439	9464491	9452453
cis-DCE	4605524	5626485	5826786
chloroform	45692	59749	55158
CT	83672	80610	83296
benzene	11523009	13558405	14689491
TCE	12318123	14457242	15032660
PCE	16528984	17423609	18357877
bromoform	1376456	1551501	1590408

B 2.2 Pre-desorption time



	DCM		
	Time in s		
	0	**5**	**10**
	6213036	5618953	5652823
	6736073	6035860	5689852
	6632245	6001200	5927940
Mean	6527118	5885338	5756872
STDV	276913	231346	149302

	***trans*-DCE**		
	Time in s		
	0	**5**	**10**
	20643423	25043041	22897107
	20464082	23995230	21241024
	20246402	22444081	21888036
Mean	20451302	23827451	22008722
STDV	198819	1307578	834612

	***cis*-DCE**		
	Time in s		
	0	**5**	**10**
	15180486	16820511	16098338
	15088834	15941076	14776453
	14647117	15323980	15350516
Mean	14972146	16028522	15408436
STDV	285189	752088	662843

	Chloroform		
	Time in s		
	0	5	10
	6121474	738981	793036
	2142676	925352	954325
	1842557	873769	1072868
Mean	3368902	846034	940076
STDV	2388515	96231	140459

	CT		
	Time in s		
	0	5	10
	264893	312889	313144
	245255	300147	267898
	233295	287731	290566
Mean	247814	300256	290536
Standard deviation	15954	12580	22623

	Benzene		
	Time in s		
	0	5	10
	31536490	35522148	33747444
	31904664	34702065	32080838
	30688149	33217032	32993526
Mean	31376434	34480415	32940603
STDV	623852	1168433	834563

	TCE		
	Time in s		
	0	5	10
	32578238	37356176	35230668
	32816517	35945902	33463200
	31049381	35597201	33437360
Mean	32148045	36299759	34043743
STDV	958901	931348	1027989

	PCE		
	Time in s		
	0	5	10
	35731556	41210805	38938921
	35307571	39694803	36555932
	33113494	39039702	35827827
Mean	34717540	39981770	37107560
STDV	1405228	1113636	1627251

	Bromoform		
	Time in s		
	0	5	10
	4279112	4378371	4466650
	4411904	4490603	3957588
	4217755	4359145	4029337
Mean	4302924	4409373	4151192
STDV	99240	71001	275541

B 2.3 Desorption flow rate

Compound	Desorption flow rate in µL/s				
VC	**10**	**50**	**100**	**500**	**1000**
Peak area	336729	1562685	663404	201006	208329
	251651	1563308	640705	228050	115154
	278563	1566777	864748	191053	113048
Mean	288981	1564257	722952	206703	145510
STDV	43486	2205	123322	19145	54413

Compound	Desorption flow rate in µL/s				
DCM	**10**	**50**	**100**	**500**	**1000**
Peak area	7152347	3493782	2507316	1192731	841485
	5533618	4038105	2286453	1109277	804167
	5471490	4051074	2357068	1128522	831668
Mean	6052485	3860987	2383612	1143510	825773
STDV	953015	318075	112799	43699	19344

Compound	Desorption flow rate in µL/s				
trans-DCE	**10**	**50**	**100**	**500**	**1000**
Peak area	23500561	17403328	8193318	2835253	3659154
	22197740	17484785	8813261	2782373	2688263
	23053454	15138622	10333424	2958632	3339512
Mean	22917252	16675578	9113334	2858753	3228976
STDV	662004	1331666	1101157	90449	494794

Compound	Desorption flow rate in µL/s				
cis-DCE	**10**	**50**	**100**	**500**	**1000**
Peak area	16588248	10119587	6237313	2854884	2327219
	15659688	10357780	5580299	2804693	1834858
	16143964	9382930	6243245	2922056	2172302
Mean	16130633	9953432	6020286	2860544	2111460
STDV	464423	508221	381051	58886	251757

Compound	Desorption flow rate in µL/s				
chloroform	**10**	**50**	**100**	**500**	**1000**
Peak area	3143230	339378	492921	395935	194609
	3630762	579944	590840	531035	476984
	3058271	1178954	276913	495941	304600
Mean	3277421	699425	453558	474304	325398
STDV	308937	432353	160623	70101	142332

Compound	Desorption flow rate in µL/s				
CT	**10**	**50**	**100**	**500**	**1000**
Peak area	318154	195765	87822	17077	10544
	269894	187907	77963	18517	8114
	277801	165277	97262	18010	10719
Mean	288617	182983	87682	17868	9793

STDV	25884	15829	9650	731	1456
Compound	**Desorption flow rate in µL/s**				
Benzene					
	10	**50**	**100**	**500**	**1000**
Peak area	35406202	22881901	13981582	6741503	5881914
	33424049	22551385	13121428	6514321	4679335
	34545334	20489110	14535639	6803505	5398296
Mean	34458528	16480611	10409687	5014957	3990136
STDV	993923	1296641	712605	152252	605115

Compound	**Desorption flow rate in µL/s**				
TCE					
	10	**50**	**100**	**500**	**1000**
Peak area	36805797	24157156	14489239	7116350	6629683
	34811276	23408692	13120686	6765301	4776361
	36759650	20823588	15021394	6973578	5922046
Mean	36125575	22796479	14210439	6951743	5776030
STDV	1138449	1749078	980546	176540	935250

Compound	**Desorption flow rate in µL/s**				
PCE					
	10	**50**	**100**	**500**	**1000**
Peak area	43245447	29171009	17148146	8374107	7850358
	40729015	27800856	15639350	8037447	5540439
	41689025	24007352	17851845	8162807	6901317
Mean	41887829	26993072	16879781	8191454	6764038
STDV	1269941	2674925	1130398	170148	1161062

Compound	**Desorption flow rate in µL/s**				
bromoform					
	10	**50**	**100**	**500**	**1000**
Peak area	4711177	2802457	1605432	369505	246438
	4630528	2821013	1579512	388299	205262
	4542102	2627339	1676773	383867	240058
Mean	4627936	2750270	1620572	380557	230586
STDV	84568	106865	50367	9825	22162

B 2.4 Exreaction flow rate

Compound	Extraction flow rate in µL/s				
VC	**10**	**50**	**100**	**150**	**200**
Peak area	1341425	1337597	1290906	1445564	1401154
	1346411	1304705	1323569	1494251	1402139
	1418823	1090994	1192897	1186861	1407456
Mean	1368886	1244432	1269124	1375559	1403583
STDV	43318	133895	68005	165220	3390

Compound	Extraction flow rate in µL/s				
DCM	**10**	**50**	**100**	**150**	**200**
Peak area	3412768	3374944	3227997	3029389	2886030
	3554090	3187723	3161723	3076809	2896455
	3816133	3261360	3119573	3355109	2768437
Mean	3594331	3274676	3169764	3153769	2850307
STDV	204671	94318	54658	175970	71093

Compound	Extraction flow rate in µL/s				
trans-DCE	**10**	**50**	**100**	**150**	**200**
Peak area	20310510	15614504	12916348	11784239	10849576
	20679330	15540558	13143534	11610089	10081394
	22223311	13423167	12213552	11009849	10058734
Mean	21071050	14859410	12757811	11468059	10329901
STDV	1014783	1244372	484837	406262	450194

Compound	Extraction flow rate in µL/s				
cis-DCE	**10**	**50**	**100**	**150**	**200**
Peak area	**14885583**	**10765660**	**8982338**	**8244806**	**7777460**
	14180982	10613272	8911458	8233587	7446939
	15350577	10208127	8657601	8621553	7178362
Mean	14805714	10529020	8850466	8366649	7467587
STDV	588874	288157	170744	220825	300083

Compound	Extraction flow rate in µL/s				
chloroform	**10**	**50**	**100**	**150**	**200**
Peak area	118455	84006	74289	74496	67574
	121868	85555	78351	67271	67002
	124526	87156	67091	76896	62882
Mean	121616	85572	73244	72888	65819
STDV	3044	1575	5702	5010	2560

Compound	Extraction flow rate in µL/s				
CT	**10**	**50**	**100**	**150**	**200**
Peak area	146150	123950	121254	110126	100260
	137748	123100	108679	104304	111302
	160021	88399	87816	83055	98534
Mean	147973	111816	105916	99162	103365
STDV	11248	20284	16889	14250	6928

Compound	Extraction flow rate in µL/s				
Benzene	**10**	**50**	**100**	**150**	**200**
Peak area	31175040	21507357	16291204	13714179	12192075
	30222066	21965593	15956408	13492912	11595707
	33551512	20183880	15924310	14259289	11129604
Mean	31649539	21218943	16057307	13822127	11639129
STDV	1714691	925209	203195	394427	532565

Compound	Extraction flow rate in µL/s				
TCE	**10**	**50**	**100**	**150**	**200**
Peak area	19195866	15550406	12791689	11036245	9783272
	18819936	15764699	12630008	10905109	9410467
	20483376	13453160	11904328	10315020	9083497
Mean	19499726	14922755	12442008	10752125	9425745
STDV	872357	1277209	472610	384180	350138

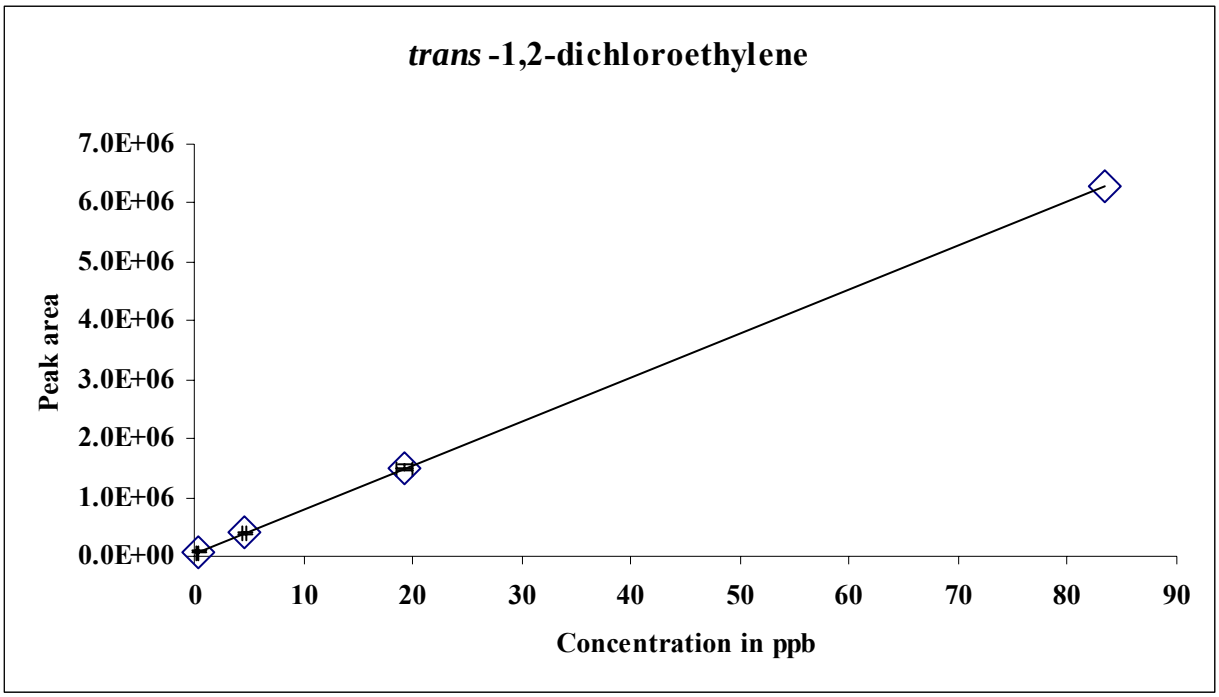
Compound	Extraction flow rate in µL/s				
PCE	**10**	**50**	**100**	**150**	**200**
Peak area	14155107	12875650	11503593	10617335	9127777
	13923196	12941493	11468927	10350932	8912764
	15904928	9998551	10078435	8491729	8667574
Mean	14661077	11938565	11016985	9819999	8902705
STDV	1083430	1680424	812993	1158002	230267

Compound	Extraction flow rate in µL/s				
bromroform	**10**	**50**	**100**	**150**	**200**
Peak	1886649	1457041	1299033	1212607	1129125
	1819858	1453983	1313050	1198976	1063995
	2004677	1493072	1319515	1398712	1080278
Mean	1903728	1468032	1310533	1270098	1091133
STDV	93586	21739	10471	111591	33895

B 2.6 Applicability of SPDE-GC/MS for real groundwater samples

***trans*-1,2-dichloroethylene**	**Peak area of calibration levels**				
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**
	outlier	1521693	416430	90380	-
	6451553	1444403	409720	84016	-
	6136238	1543330	388522	outlier	-
Mean	6293896	1503142	404890	79312	-
Standard deviation		52007	14567	14025	-

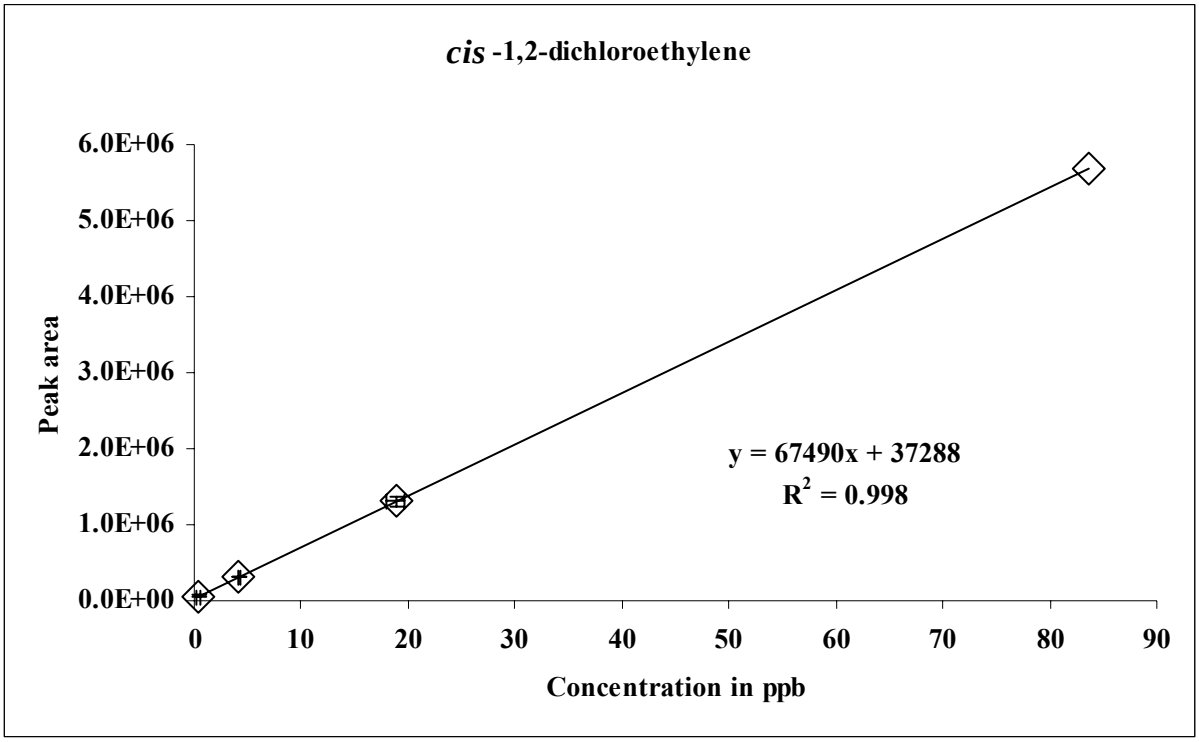
	Concentration in ppb				
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**
	outlier	20	4.7	0.348	-
	86	18	4.6	0.262	-
	81	20	4.3	outlier	-
Mean	84	19	4.6	0.3	-
Standard deviation		0.70	0.20	0.06	-



***trans*-1,2-dichloroethylene**	**Sampling wells**							
	B 25 Epple	**B 28 Epple**	**B 34 Epple**	**B 45 Epple**	**B 54 Epple**	**B 1 Eck**	**B 1 Mahle**	**B 836**
Measurement 1 in ppb	-	-	2.4	0.9	-	0.5	-	-
Measurement 2 in ppb	-	-	2.7	0.4	-	0.4	-	-
Measuremnet 3 in ppb	-	-	3.4	0.7	-	0.3	-	-
Concnetration mean in ppb (05.05.2006)	-	-	2.9 ± 0.5	0.7 ± 0.2	-	0.4 ± 0.1	-	-
Concnetration mean in µg/L (05.05.2006)	-	-	3.6 ± 0.7	0.9 ± 0..3	-	0.5 ± 0.1	-	-
Concnetration mean in µg/L (Amt für Umweltschutz 09.02.2006)	< 5	< 5	8	< 5	< 5	< 5	< 5	< 5

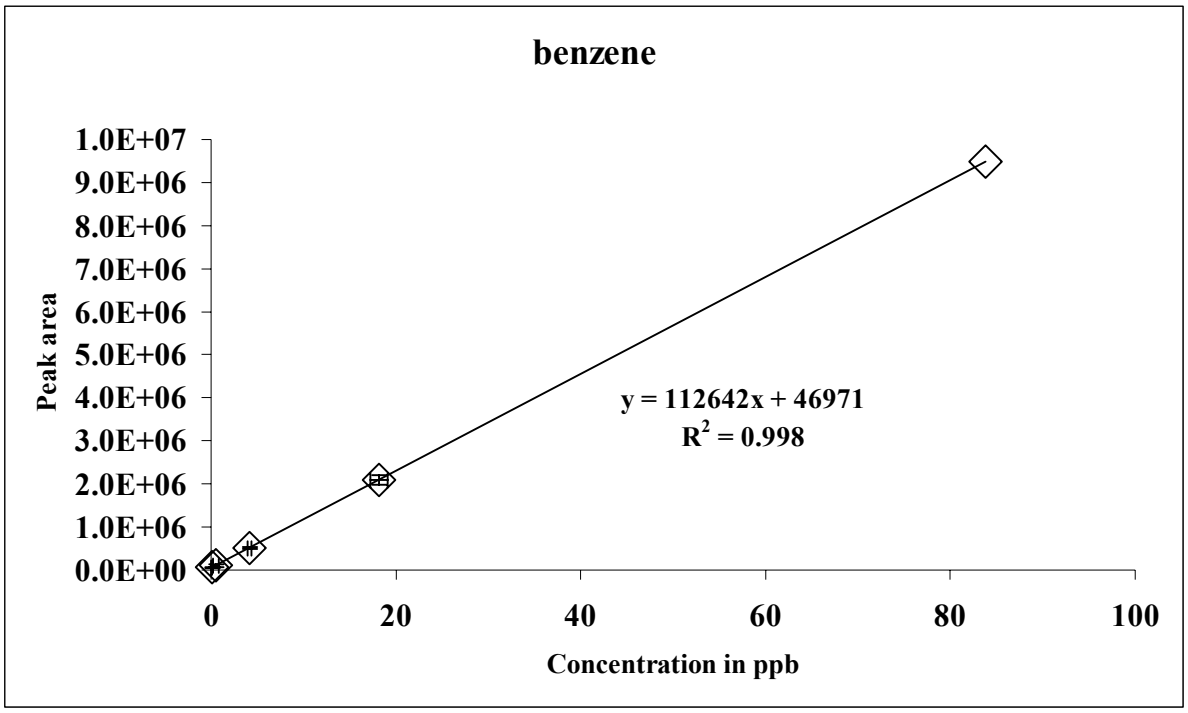
***cis*-1,2-dichloroethylene**	**Peak area of calibration levels**				
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**
	outlier	1369953	321816	70779	-
	5816505	1246918	327287	64511	-
	5547625	1306497	314199	48214	-
Mean	5682065	1307789	321101	61168	-
Standard deviation		61528	6573	11648	-

	Concentration in ppb				
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**
	outlier	20	4.2	0.5	-
	86	18	4.3	0.4	-
	82	19	4.1	0.2	-
Mean	84	19	4.2	0.4	-
Standard deviation		1	0.1	0.2	-



***cis*-1,2-dichloroethylene**	**Sampling wells**							
	B 25 Epple	**B 28 Epple**	**B 34 Epple**	**B 45 Epple**	**B 54 Epple**	**B 1 Eck**	**B 1 Mahle**	**B 836**
Measurement 1 in ppb	1.3	-	14	26	0.9	105	33	0.7
Measurement 2 in ppb	2.1	-	15	18	0.7	88	35	0.2
Measuremnet 3 in ppb	2.5	-	22	23	0.3	87	35	0.3
Concnetration mean in ppb (05.05.2006)	2.0 ± 0.6	-	17 ± 5	22 ± 4	0.6 ± 0.3	93 ± 10	34 ± 1.0	0.4 ± 0.2
Concnetration mean in µg/L (05.05.2006)	2.5 ± 0.8	-	22 ± 6	28 ± 5	0.8 ± 0.4	119 ± 12	44 ± 1.3	0.5 ± 0.3
Concnetration mean in µg/L (Amt für Umweltschutz 09.02.2006)	< 5	< 5	28	26	< 5	66	57	< 5

benzene					
	Peak area of calibration levels				
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**
	outlier	2210020	520124	139404	61718
	9808220	2017436	529976	110850	56929
	9173555	2048860	488624	72588	52929
Mean	9490888	2092105	512908	107614	57192
Standard deviation	-	103318	21600	33525	4401
	Concentration in ppb				
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**
	outlier	19	4.2	0.8	0.1
	87	18	4.3	0.6	0.1
	81	18	3.9	0.2	0.1
Mean	84	18	4.1	0.5	0.1
Standard deviation	-	0.92	0.19	0.30	0.04



benzene								
	Sampling wells							
	B 25 Epple	**B 28 Epple**	**B 34 Epple**	**B 45 Epple**	**B 54 Epple**	**B 1 Eck**	**B 1 Mahle**	**B 836**
Measurement 1 in ppb	-	-	26	24	-	-	-	-
Measurement 2 in ppb	-	-	32	21	-	-	-	-#
Measuremnet 3 in ppb	-	-	43	25	-	-	-	-
Concnetration mean in ppb (05.05.2006)	-	-	34 ± 8	23 ± 2	-	-	-	-
Concnetration mean in µg/L (05.05.2006)	-	-	30 ± 7	21 ± 2	-	-	-	-
Concnetration mean in µg/L (Amt für Umweltschutz 09.02.2006)	< 1	< 1	78	120	< 1	< 1	< 1	< 1

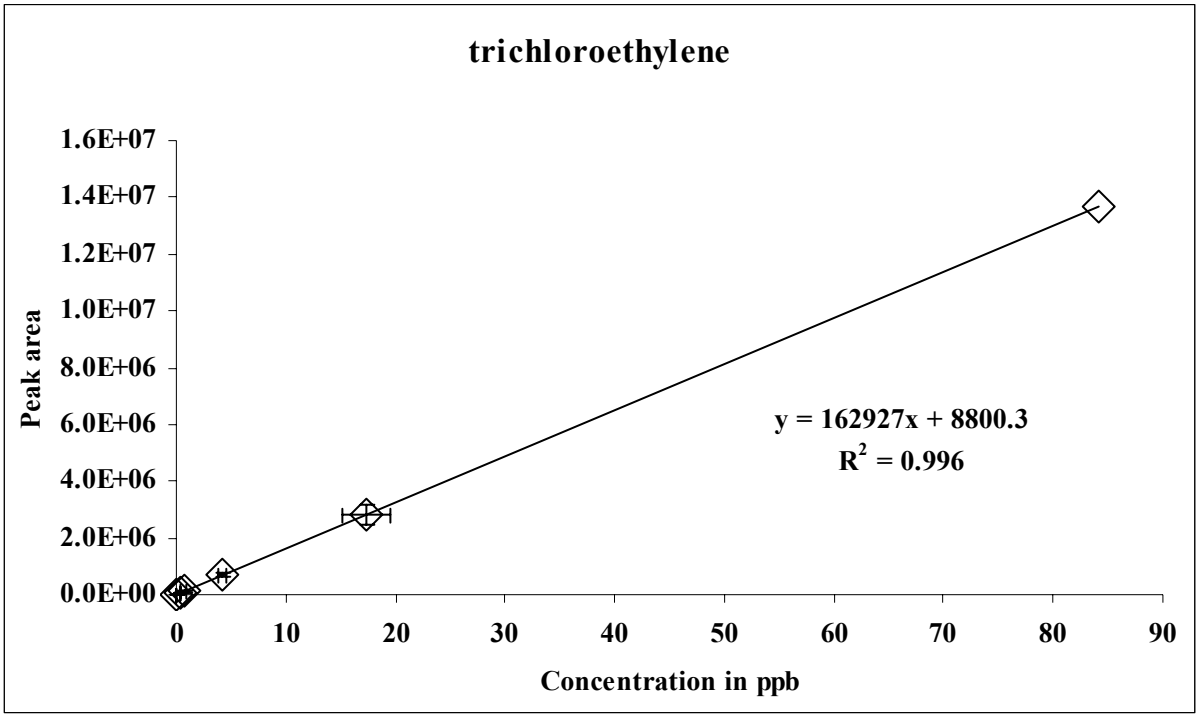
trichloroethylene

Peak area of calibration levels

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
	outlier	19	4.6	0.9	0.3	0.08
	88	18	3.9	0.7	0.3	0.05
	80	15	4.0	0.4	0.3	0.03
Mean	84	17	4.2	0.7	0.3	0.05
Standard deviation		2	0.4	0.2	0.0	0.03

Concentration in ppb

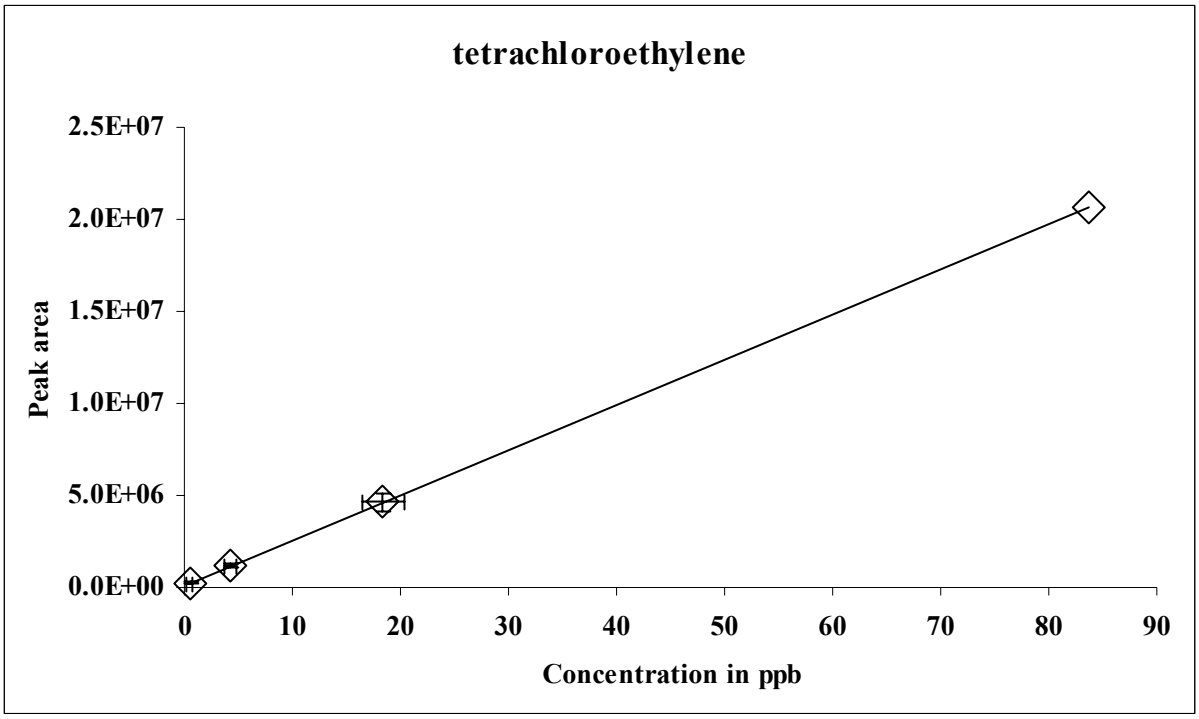
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
		3159427	762115	151987	59770	22300
	14366909	2892424	643460	125914	57557	16719
	13049548	2439614	664624	79648	56429	13830
Mean	13708228	2830488	690067	119183	57918	17616
Standard deviation		363882	63287	36636	1700	4306



trichloroethylene

	Sampling wells							
	B 25 Epple	B 28 Epple	B 34 Epple	B 45 Epple	B 54 Epple	B 1 Eck	B 1 Mahle	B 836
Measurement 1 in ppb	0.7	-	0.08	0.2	0.4	45	9.0	0.8
Measurement 2 in ppb	0.9	-	0.06	0.1	0.4	37	10	0.8
Measuremnet 3 in ppb	0.9	-	0.08	0.1	0.3	41	9.5	0.8
Concnetration mean in ppb (05.05.2006)	0.9 ± 0.1	-	0.07 ± 0.01	0.1 ± 0.05	0.4 ± 0.06	41 ± 4	9.6 ± 0.6	0.8 ± 0.04
Concnetration mean in µg/L (05.05.2006)	1.3 ± 0.1	-	0.11 ± 0.01	0.1 ± 0.08	0.6 ± 0.09	60 ± 6	14 ± 0.8	1.2 ± 0.06
Concnetration mean in µg/L (Amt für Umweltschutz 09.02.2006)	1.4	0.3	0.4	0.2	0.9	56	22	1.9

tetrachloroethylene					
	Peak area of calibration levels				
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**
		5136849	1301294	308967	-
	22553811	4635316	1066098	273857	-
	18799674	4157610	1145281	163699	-
Mean	20676742	4643258	1170891	248841	-
Standard deviation		489668	119671	75796	-
	Concentration in ppb				
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**
	outlier	20	4.8	0.7	-
	91	18	3.8	0.6	-
	76	16	4.2	0.2	-
Mean	84	19	4.6	0.3	-
Standard deviation		0.7	0.2	0.06	-



tetrachloroethylene								
	Sampling wells							
	B 25 Epple	**B 28 Epple**	**B 34 Epple**	**B 45 Epple**	**B 54 Epple**	**B 1 Eck**	**B 1 Mahle**	**B 836**
Measurement 1 in ppb	12	-	-	-	48	48	643	291
Measurement 2 in ppb	12	-	-	-	52	42	662	297
Measuremnet 3 in ppb	13	-	-	-	36	43	644	272
Concnetration mean in ppb (05.05.2006)	13 ± 1	-	-	-	45 ± 8	45 ± 3	649 ± 11	287 ± 13
Concnetration mean in µg/L (05.05.2006)	21 ± 1	-	-	-	73 ± 13	72 ± 5	1052 ± 17	464 ± 22
Concnetration mean in µg/L (Amt für Umweltschutz 09.02.2006)	28	0.6	0.8	0.9	100	79	2300	930

B 3.1 Desorption temperature

Compound	Temperature in °C		
	150	**170**	**180**
DCM			
Peak area	94440263	102219589	88994427
	99031917	95634636	89769854
	96784756	95628921	95736504
Mean	96752312	97827715	91500262
STDV	2295999	3803475	3689123
***trans*-DCE**			
Peak area	520173417	595611063	533249037
	545461620	579921126	530283457
	534213102	561945036	545748852
Mean	533282713	579159075	536427115
STDV	12669749	16845946	8207907
***cis*-DCE**			
Peak area	242784122	276073617	258638593
	251475840	280265341	248522650
	244418494	269192881	259659871
Mean	246226152	275177280	255607038
STDV	4619222	5590385	6156474
chloroform			
Peak area	156766479	187782088	172072769
	163880649	181870274	168992483
	173915603	180553862	174323845
Mean	164854243	183402075	171796366
STDV	8615917	3849886	2676407
CT			
Peak area	843271582	1059835914	954846733
	949129013	1020317993	978398876
	788884060	991527758	974139703
Mean	860428218	1023893889	969128437
STDV	81488489	34294188	12550316
benzene			
Peak area	417529020	523389957	487051718
	462842792	514835847	482447808
	410993692	503379478	492987179
Mean	430455168	513868427	487495569
STDV	28238206	10040256	5283686

DCA			
Peak area	100316973	107336388	100556862
	97466370	104558822	99107148
	88528581	102428659	98527406
Mean	95437308	104774623	99397139
STDV	6150558	2460971	1045344

fluorobenzene			
Peak area	483427812	582415871	530712599
	523519485	575376818	520568612
	441391061	549893294	536103052
Mean	482779453	569228661	529128087
STDV	41068050	17110797	7887504

TCE			
Peak area	447461599	532756036	480866758
	489269012	526092300	474981351
	387155880	491570900	484597933
Mean	441295497	516806412	480148681
STDV	51335062	22107118	4848339

toluene			
Peak area	563475374	667531717	601137314
	626751704	654909796	596485636
	460801518	636258004	614999846
Mean	550342865	652899839	604207599
STDV	83750900	15733443	9631406

PCE			
Peak area	329989226	433908853	383166047
	375758869	436520311	387544562
	282478628	414025336	398541587
Mean	329408907	428151500	389750732
STDV	46642828	12303102	7921628

EDB			
Peak area	148553351	163375489	148071922
	143024210	160752205	148572556
	100304738	156157632	138171590
Mean	130627433	160095109	144938689
STDV	26405344	3653518	5865823

ethylbenzene			
Peak area	288746105	410444799	378266323
	343337235	404012447	368394254
	260430820	393785510	383568128
Mean	297504720	402747585	376742902
STDV	42141469	8401362	7700794

para-xylene			
Peak area	231714716	336001430	311311493
	279212344	334194425	300439665
	207942672	328365703	315542154
Mean	239623244	332853852	309097771
STDV	36287052	3990480	7790810
bromoform			
Peak area	174760720	218586661	204768402
	169536219	213738440	202733957
	118670149	206851160	199311626
Mean	154322363	213058754	202271328
STDV	30986031	5897200	2757648
isopropylbenzene			
Peak area	78684951	135047017	127105217
	95002487	137233228	120783789
	75299809	130660049	134235230
Mean	82995749	134313432	127374745
STDV	10534995	3347429	6729770
propylbenzene			
Peak area	91410721	164699660	164099374
	114630598	167328217	154806186
	88934459	162538475	172677111
Mean	98325259	164855451	163860890
STDV	14175014	2398668	8937849
1,3,5-TMB			
Peak area	18903951	34039491	34484701
	22859689	35012119	31576072
	18836382	33573976	36089248
Mean	20200007	34208529	34050007
STDV	2303600	733822	2287774
1,2,4-TMB			
Peak area	47355200	80902350	83611687
	57328404	83373235	76570187
	45969299	80683521	85878509
Mean	50217634	81653035	82020128
STDV	6196972	1493749	4853968
1,2,3-TMB			
Peak area	13093689	22544481	23222397
	16451921	23519236	21454791
	13279376	22620146	24228314
Mean	14274996	22894621	22968501
STDV	1887558	542254	1404085

B 3.2 Desorption flow rate

	Desorption flow rate in µL/s				
VC	**10**	**50**	**100**	**250**	**500**
Peak area	6242424	9117	12347	11846	13407
	6730620	4113	9808	7841	14531
	5585783	7581	10597	15034	10380
Mean	6186276	6937	10917	11574	12773
STDV	574480	2564	1299	3604	2147
DCM					
Peak area	80865770	21333537	3062452	2717434	2694497
	79222702	20285745	2914739	2996310	2658856
	75459474	20184362	2310136	2863760	2609394
Mean	78515982	20601214	2762442	2859168	2654249
STDV	2771570	636232	398611	139494	42739
trans-DCE					
Peak area	488029954	110172498	15690701	13423867	12796856
	510422501	106065061	15388397	14922312	12083736
	475316689	106483018	10362009	15047374	12405596
Mean	491256381	107573525	13813702	14464518	12428729
STDV	17773910	2260457	2993073	903397	357123
cis-DCE					
Peak area	273309221	43152686	6672393	5713581	5401461
	261685970	41488194	6537127	6340832	5280408
	262693364	40629801	5025445	6196614	5217781
Mean	265896185	41756894	6078321	6083675	5299883
STDV	6439607	1282726	914323	328523	93376
chloroform					
Peak area	241182372	33050732	5241021	4244069	3936642
	233715790	31630603	5085316	4760729	3877578
	233782399	31449285	3975099	4676510	3861551
Mean	236226854	32043540	4767145	4560436	3891924
STDV	4291734	876953	690336	277199	39548
CT					
Peak area	670995769	79148352	8002871	5332824	4563903
	729360581	75481666	7599206	5951024	4104120
	729304950	73129658	4722735	5696236	4299324
Mean	709887100	75919892	6774937	5660028	4322449
STDV	33680892	3033183	1788683	310687	230762

benzene					
Peak area	491670372	55157671	7861234	6423056	5508187
	495921362	53232830	8066995	7010548	5394159
	469633382	52305409	6021556	6922885	5407608
Mean	485741706	53565303	7316595	6785496	5436651
STDV	14111212	1454907	1126245	316928	62315

DCA					
Peak area	89843336	12093338	1804548	1516196	1417835
	88433946	11642893	1738556	1637279	1427980
	86623048	11283892	1543427	1620668	1368911
Mean	88300110	11673374	1695510	1591381	1404909
STDV	1614310	405583	135778	65640	31585

fluorobenzene					
Peak area	499444000	54460990	7512918	5762307	5004265
	472645074	51601828	7477951	6398845	4827374
	478031297	50907761	5500242	6440496	4938937
Mean	483373457	52323526	6830370	6200549	4923525
STDV	14175670	1883347	1152058	380100	89447

TCE					
Peak area	420800086	46571451	6647212	5390164	4518473
	430043327	43872532	6582500	5780436	4293176
	404347801	43533338	4560874	5794943	4535910
Mean	418397071	44659107	5930195	5655181	4449187
STDV	13015217	1664800	1186309	229626	135390

toluene					
Peak area	558002345	41134945	5628493	4207760	3511500
	553544331	38934130	5711289	4626650	3333234
	551588741	38172002	4344237	4810182	3298392
Mean	554378473	39413692	5228006	4548197	3381042
STDV	3287160	1538585	766486	308779	114315

PCE					
Peak area	320070741	23179803	3357822	2434863	1896597
	338469805	21803301	3415094	2609540	1727853
	338563876	20828479	2134894	2641601	1736751
Mean	332368141	21937194	2969270	2562002	1787067
STDV	10649965	1181367	723158	111266	94960

EDB					
Peak area	132662503	7851905	1360932	1057776	889556
	123770765	7450655	1360736	1134983	865172
	124258626	7126338	1241117	1133867	842914
Mean	126897298	7476300	1320928	1108875	865881
STDV	4998769	363463	69119	44257	23329

ethylbenzene					
Peak area	347079221	16797883	2738834	1973284	1515527
	361219681	15412822	2828215	2233655	1463096
	360002931	15302070	2071581	2235833	1381598
Mean	356100611	15837591	2546210	2147591	1453407
STDV	7836404	833478	413463	150958	67489

Para-xylene					
Peak area	288561052	13421238	2346151	1716983	1300865
	298700002	12480057	2415011	1907935	1250500
	296974872	12375921	1796283	1864045	1181566
Mean	294745309	12759072	2185815	1829654	1244310
STDV	5424739	575811	339097	100013	59889

bromoform					
Peak area	187524853	7976922	1638162	1170470	857407
	170638374	7169765	1605413	1189866	845727
	175468254	6654443	1474869	1153197	800230
Mean	177877160	7267043	1572815	1171177	834455
STDV	8697149	666585	86389	18345	30209

isopropylbenzene					
Peak area	103258810	5673709	1282920	1054488	774190
	114707639	5320665	1306990	1081364	753047
	112854842	5240693	951923	1119072	684058
Mean	110273764	5411689	1180611	1084975	737098
STDV	6145356	230412	198415	32443	47135

propylbenzene					
Peak area	134377336	5960415	1607093	1244631	835126
	150666475	5549364	1616982	1272992	869365
	152187627	5334555	1165370	1337160	727425
Mean	145743813	5614778	1463148	1284928	810639
STDV	9872997	318016	257931	47405	74071

1,3,5-TMB					
Peak area	28926226	1753294	587220	454728	323803
	31678213	1642541	598467	454754	326923
	31978383	1647323	447374	483406	279063
Mean	30860941	1681053	544353	464296	309930
STDV	1682220	62609	84175	16550	26777

1,2,4-TMB					
Peak area	28926226	1753294	587220	454728	323803
	31678213	1642541	598467	454754	326923
	31978383	1647323	447374	483406	279063
Mean	30860941	1681053	544353	464296	309930
STDV	1682220	62609	84175	16550	26777

1,2,3-TMB					
Peak area	20529629	1845587	836398	596844	409893
	21801301	1674799	843219	569967	432722
	21996070	1712442	714256	563320	353366
Mean	21442333	1744276	797958	576710	398660
STDV	796402	89734	72568	17750	40853

B 3.3 Desorption volume

Compound	**Desorption volume in µL**			
	500	**700**	**850**	**1000**
VC				
Peak area	12884179	14298707	2431670	3611601
	15619789	14809383	12128423	3610288
	14938446	14088755	11211480	3395956
Mean	14480805	14398948	8590524	3539282
STDV	1424067	370624	5353392	124125
dichloromethane				
Peak area	49122660	66192836	27151692	55864591
	59988123	58364912	53283007	48930038
	70041533	57714327	57400698	53981727
Mean	59717439	60757358	45945132	52925452
STDV	10462063	4718488	16405301	3585916
***trans*-dichloroethene**				
Peak area	275717027	386406507	118694433	311552148
	382364676	355791681	314372989	279749839
	407621723	355646154	304359326	241639272
Mean	355234476	365948114	245808916	277647087
STDV	70012485	17717637	110198172	35003839
cis-dichloroethane				
Peak area	199645219	216868822	79677713	158760252
	219056820	206686812	181457977	163733202
	223894658	204095201	178800139	155085641
Mean	214198899	209216945	146645276	159193032
STDV	12833876	6752224	58010835	4339994
chloroform				
Peak area	174209619	194979612	77127144	148075036
	196090535	185268663	168856316	160277397
	194678202	190205239	178578761	145896790
Mean	188326118	190151171	141520740	151416408
STDV	12245626	4855700	55977968	7750744

CT				
Peak area	417049090	638097799	170967823	517386957
	569820688	615575803	568153233	532716964
	583595883	614075134	548279318	504630039
Mean	523488554	622582912	429133458	518244653
STDV	92436240	13457221	223798714	14063093

benzene				
Peak area	354027964	418549543	156699785	310238924
	408546059	394964596	356630747	317133251
	411943196	399367737	340307013	304547585
Mean	391505740	404293959	284545848	310639920
STDV	32501122	12540461	111018368	6302408

1,2-dichloroethane				
Peak area	67991812	67702405	39965471	62705103
	71104978	67121839	68682794	64552891
	69355300	65530944	69340116	62030239
Mean	69484030	66785062	59329460	63096078
STDV	1560570	1124222	16772927	1305983

fluorobenzene				
Peak area	330517985	390664892	149776877	306246183
	385775194	366822378	351727075	318283520
	389358527	369891857	337055839	302264457
Mean	368550569	375793042	279519931	308931386
STDV	32985878	12970519	112599983	8340284

TCE				
Peak area	266629594	347781269	116075078	285804574
	334592891	330453686	323905407	301452712
	335778211	335282314	306830138	285735538
Mean	312333565	337839090	248936874	290997608
STDV	39585237	8942265	115378004	9054452

toluene				
Peak area	381588856	540719501	227841926	450838132
	445020511	512076912	498814173	462548602
	453833140	533624786	481673756	446462323
Mean	426814169	528807067	402776618	453283019
STDV	39413352	14916678	151740101	8317163

PCE				
Peak area	203163478	327643770	113315583	297329176
	251726060	316347852	325988442	302721897
	259224261	326605286	301616043	298429614
Mean	238037933	323532303	246973356	299493563
STDV	30433969	6243545	116390737	2849447

1,2-dibromoethane				
Peak area	70788649	95834169	59172975	80333815
	71162646	91583137	91030319	81813992
	74335067	91664213	87447005	79421628
Mean	72095454	93027173	79216766	80523145
STDV	1948555	2431267	17450651	1207367

ethylbenzene				
Peak area	218916944	353772802	160135727	346180944
	245345747	334777622	359546268	354523996
	254691288	349693374	336745680	347294460
Mean	239651326	346081266	285475892	349333134
STDV	18554534	9999486	109144786	4529765

***para*-xylene**				
Peak area	176412958	296118334	131843334	290611150
	194360694	280962638	298602181	297556198
	204391379	291831391	282590675	289398186
Mean	191721677	289637454	237678730	292521844
STDV	14174672	7812413	92005111	4401858

bromoform				
Peak area	65676007	109472095	84075112	130418352
	60739266	111110057	131559019	132458197
	67613097	109353750	126956308	131182428
Mean	64676123	109978634	114196813	131352992
STDV	3544322	981626	26187476	1030563

isopropylbenzene				
Peak area	65637297	115998237	45377824	114917360
	67527075	109495142	118864520	118189423
	74539663	112680608	107695010	113639039
Mean	69234678	112724662	90645784	115581941
STDV	4690412	3251771	39598999	2346860

propylbenzene				
Peak area	85323515	151573285	63791897	166062909
	74833396	149829785	166141932	172089991
	90451473	151423571	147971940	158598232
Mean	83536128	150942213	125968590	165583711
STDV	7960977	966296	54607628	6758632

1,3,5-TMB				
Peak area	15998724	29680091	13697997	34679950
	13627674	29750420	34765922	37253805
	17154261	30978352	29607634	34338859
Mean	15593553	30136288	26023851	35424205
STDV	1797867	730097	10981666	1593632

1,2,4-TMB				
Peak area	39274222	71255385	36741295	85835905
	30373087	75790123	87126269	90650833
	39528801	77179819	72479821	86684333
Mean	36392037	74741776	65449128	87723690
STDV	5214118	3098226	25917839	2570230

1,2,3-TMB				
Peak area	11120399	18984588	10787028	25394615
	8863514	21422385	25171860	26656462
	11026867	21709368	20370390	25354414
Mean	10336927	20705447	18776426	25801830
STDV	1276870	1497199	7323687	740406

B 3.4 Number of extraction cycles

Compound	**Number of extraction cycles**								
	1	**2**	**5**	**8**	**10**	**15**	**20**	**30**	**50**
VC									
Peak area	2264010	2721336	2957692	3062225	3573606	3237516	3223443	4437367	423578
	2328018	2333777	2824387	3305244	3352956	2628343	3860320	4988948	3924460
	2078398	2273913	2422085	2638542	2501291	2537737	3179790	2535253	3378794
Mean	2223475	2443009	2734721	3002004	3142618	2801199	3421185	3987189	2575611
STDV	129653	242890	278835	337406	566257	380568	380929	1287303	1883579

DCM	**1**	**2**	**5**	**8**	**10**	**15**	**20**	**30**	**50**
Peak area	1292932	1671771	2296980	2736570	3365777	4010736	4559948	5667044	8113047
	1325911	1620827	2396320	2909822	3336590	3839580	4667947	5822413	9011113
	1287886	1647797	2226720	2848683	3202540	3965815	4557653	5203515	8556130
Mean	1302243	1646799	2306673	2831692	3301636	3938710	4595183	5564324	8560097
STDV	20652	25487	85215	87867	87051	88739	63026	321982	449046

***trans*-DCE**	**1**	**2**	**5**	**8**	**10**	**15**	**20**	**30**	**50**
Peak area	3003873	4038183	5622251	6471163	8059448	9230468	9829081	12453490	13544798
	3089151	3601395	5573730	7087152	7802430	8276942	10532963	13001202	16559151
	2831734	3529350	5028191	6254040	7071132	8202906	11578830	11298946	15160369
Mean	2974920	3722976	5408057	6604118	7644337	8570105	10646958	12251213	15088106
STDV	131128	275343	329868	432177	512774	573088	880427	868968	1508475

***cis*-DCE**	**1**	**2**	**5**	**8**	**10**	**15**	**20**	**30**	**50**
Peak area	2336953	3263626	4873688	5717778	7164903	8674873	9564166	12542906	16291206
	2334050	2987729	4838503	6421534	7194741	8651447	10163884	13053851	18311947
	2283682	2969386	4532017	5942710	6742036	8227382	12346948	10627950	17106764
Mean	2318229	3073580	4748069	6027341	7033893	8517901	10691666	12074902	17236639
STDV	29953	164840	187932	359430	253196	251869	1464542	1278874	1016611

chloroform	1	2	5	8	10	15	20	30	50
Peak area	2061990	2881615	4319823	5133485	6599819	8026649	8988885	8988885	16265417
	2106760	2643942	4392917	5992721	6527511	8007334	9421100	9421100	17503290
	1999600	2706561	4264526	5431156	6421523	7527255	8807472	8807472	16605698
Mean	2056117	2744039	4325755	5519121	6516284	7853746	9072486	9072486	16791468
STDV	53821	123189	64401	436320	89676	282914	315241	315241	639504

CT	1	2	5	8	10	15	20	30	50
Peak area	3344142	4870495	7358366	8873980	11722443	12676701	13423967	17741563	17748462
	3422532	4065557	6841327	9410483	10576736	10966125	14173757	18927621	21535544
	2874223	3837821	5559464	7448198	8132031	9498456	11613110	10685135	18205150
Mean	3213632	4257958	6586386	8577554	10143737	11047094	13070278	15784773	19163052
STDV	296539	542556	926152	1014171	1833952	1590669	1316454	4456054	2067288

benzene	1	2	5	8	10	15	20	30	50
Peak area	4912805	7201853	11001879	13722901	17053896	20357934	21802253	27627116	36595338
	5025702	6568365	11057202	14699049	16632611	19001416	23385321	28364823	40281984
	4722832	6508127	10242417	13542315	15590994	18284033	21579855	22682584	37150553
Mean	4887113	6759448	10767166	13988088	16425834	19214461	22255809	26224841	38009292
STDV	153061	384316	455287	622295	753053	1053237	984486	3089780	1987691

DCA	1	2	5	8	10	15	20	30	50
Peak area	1078713	1507833	2379897	3023718	3870419	4883821	5566884	7115041	9999654
	1081722	1447974	2422436	3252665	3876993	4922011	5753707	7435430	11168381
	1059885	1479853	2386524	3186742	3798881	4767644	5627034	6950831	10810628
Mean	1073440	1478554	2396286	3154375	3848765	4857825	5649208	7167101	10659554
STDV	11835	29951	22888	117855	43325	80400	95365	246458	598830

fluorobenzene	1	2	5	8	10	15	20	30	50
Peak area	5270847	7566372	11540850	14392722	18177447	21787787	23488449	29189910	35091103
	5211291	6942268	11626283	15467574	17874403	20496575	25105946	30535771	41788721
	4929621	6711007	10588588	13756966	16528762	19451024	22859968	24020161	37790815
Mean	5137253	7073216	11251907	14539087	17526871	20578462	23818121	27915281	38223546
STDV	182264	442462	576038	864646	877567	1170532	1158714	3439739	3369713

TCE	1	2	5	8	10	15	20	30	50
Peak area	3780252	5442493	8099994	10175462	12694794	14832417	16173564	20144314	24282319
	3794020	4838764	8092868	10809940	12153925	13734703	16614212	20394337	28006237
	3436284	4603915	7175684	9430464	10921553	12873671	15078884	15048886	25003105
Mean	3670185	4961724	7789515	10138622	11923424	13813597	15955553	18529179	25763887
STDV	202682	432600	531605	690475	908814	981753	790541	3016613	1975091

toluene	1	2	5	8	10	15	20	30	50
Peak area	6511346	9153636	14960866	19540310	23961941	29499990	32194579	39646815	53012954
	6459558	8426880	14736235	21068111	23533898	27296292	33593564	41722443	58285106
	6204804	8112033	14121343	18619424	21748158	26015771	30820927	32324251	53403293
Mean	6391903	8564183	14606148	19742615	23081332	27604018	32203023	37897836	54900451
STDV	164088	534203	434617	1236816	1174232	1762375	1386338	4937175	2937688

PCE	1	2	5	8	10	15	20	30	50
Peak area	3338584	4729641	7257272	9327781	11725158	14053239	14309373	18208533	20906100
	3212167	3983147	6886470	9831365	11171374	12076972	15301033	18097102	20373660
	2876996	3703581	5951215	7873374	9218633	10593041	13036509	11987260	6080654
Mean	3142583	4138789	6698319	9010840	10705055	12241084	14215639	16097632	15786805
STDV	238532	530441	673050	1016745	1316722	1735927	1135168	3560122	8409988

EDB	1	2	5	8	10	15	20	30	50
Peak area	451733	629021	1098589	1510422	1996031	2696935	3169120	4370809	7489044
	449722	614524	1102633	1636092	2020427	2726611	3274969	4646327	8131025
	453934	618198	1135726	1585087	2024530	2640949	3359584	4318989	7924848
Mean	451796	620581	1112316	1577201	2013663	2688165	3267891	4445375	7848306
STDV	2106	7537	20374	63205	15407	43499	95429	175948	327764

ethylbenzene	1	2	5	8	10	15	20	30	50
Peak area	4717777	6512331	10320790	13654991	17054379	21627646	23154637	29006504	37229596
	4652372	5791013	10043727	14510726	17004061	20151570	24552725	32208947	43774713
	4354781	5646895	9608275	12825416	15604131	18208982	22380928	23256648	39230158
Mean	4574977	5983413	9990931	13663711	16554190	19996066	23362763	28157366	40078156
STDV	193479	463690	359180	842689	823160	1714629	1100756	4536154	3353948

para-xylene	1	2	5	8	10	15	20	30	50
Peak area	3987220	5454045	8394222	11070773	13945963	17203117	18322465	23887079	31074694
	3852488	4920986	8075052	11713742	13617822	16120167	19707860	26073721	36394582
	3713826	4628859	7768770	10275894	12513170	14550049	18312296	18989262	33628521
Mean	3851178	5001297	8079348	11020136	13358985	15957778	18780874	22983354	33699266
STDV	136702	418414	312748	720260	750647	1333968	802810	3627662	2660650

bromoform	1	2	5	8	10	15	20	30	50
Peak area	478398	668673	1023825	1433719	1906937	2696368	2972863	4159743	6797497
	457721	635476	1032692	1529330	1951971	2662824	3204179	4521039	7860545
	488666	612395	1078547	1434652	1988563	2521458	3314861	4114653	7857292
Mean	474928	638848	1045021	1465900	1949157	2626883	3163968	4265145	7505111
STDV	15762	28290	29371	54934	40886	92829	174509	222755	612814

isoprpylbenzene	1	2	5	8	10	15	20	30	50
Peak area	2634516	3497223	5171936	6748777	8289747	10122262	10634788	13986275	16476019
	2474525	3034327	4863008	6916840	8292025	9208217	11450930	15761189	20368369
	2326250	2855155	4594285	5936634	7318920	8325185	10315644	10651355	18642265
Mean	2478430	3128902	4876409	6534084	7966897	9218555	10800454	13466273	18495551
STDV	154170	331317	289059	524186	561166	898583	585493	2594302	1950318

propylbenzene	1	2	5	8	10	15	20	30	50
Peak area	3711653	4835307	6839494	8604529	10514197	12653546	13280949	17479485	20266775
	3499792	4190159	6266315	8731029	10700556	11366773	14479089	20393996	25760342
	3290424	3945617	6001016	7812669	9209867	10356481	12863107	13414466	24078536
Mean	3500623	4323694	6368942	8382742	10141540	11458933	13541048	17095982	23368551
STDV	210616	459631	428556	497733	812215	1151302	838802	3505533	2814761

1,3,5-TMB	1	2	5	8	10	15	20	30	50
Peak area	2924533	3582732	4669576	5520425	6735155	8106969	8310956	10654205	12896701
	2781626	3132604	4469629	5751605	6846958	7435988	9065190	12217485	16955895
	2606808	2982579	4228442	5259685	6329347	6897446	8556106	8839314	15747890
Mean	2770989	3232638	4455882	5510572	6637153	7480135	8644084	10570335	15200162
STDV	159129	312332	220888	246108	272366	605969	384737	1690646	2084291

1,2,4-TMB	1	2	5	8	10	15	20	30	50
Peak area	922073	1130075	1410273	1626906	1931955	2322740	2395159	3089209	3677966
	902560	1006741	1336697	1647171	1999474	2315134	2580220	3640630	4923580
	855534	944104	1287532	1583756	1906511	2038373	2565370	2714630	4677728
Mean	893389	1026973	1344834	1619278	1945980	2225416	2513583	3148156	4426425
STDV	34205	94622	61773	32389	48042	162028	102826	465806	659737

1,2,3-TMB	1	2	5	8	10	15	20	30	50
Peak area	1025394	1229494	1508510	1630235	1976630	2248139	2321834	2857901	3276556
	1008604	1136363	1463020	1729888	2005955	2249131	2513036	3277817	4516351
	994859	1071541	1391585	1628310	1978861	2022122	2430150	2687929	4503396
Mean	1009619	1145799	1454372	1662811	1987149	2173131	2421673	2941215	4098768
STDV	15293	79398	58940	58099	16325	130778	95882	303641	712086

B 3.5 Extraction volume

Compound	Extraction volume in µL				
	500	**1000**	**1500**	**2000**	**2500**
VC					
Peak area	6753896	19688990	21018292	22616976	32117742
	17884878	21353755	23021655	13003679	25685369
	17906770	21562461	22369087	22931343	23993999
Mean	14181848	20868402	22136345	19517332	27265703
STDV	5252363	838312	834263	4607636	3499704

DCM	**500**	**1000**	**1500**	**2000**	**2500**
Peak area	5624927	5269456	7182583	8801952	12766189
	5306785	6355422	8474510	9954075	11938541
	7141088	7428819	9458580	12701172	11927780
Mean	6024267	6351232	8371891	10485733	12210836
STDV	800321	881561	932001	1635639	392718

***trans*-DCE**	**500**	**1000**	**1500**	**2000**	**2500**
Peak area	18463334	20851005	26532538	30590633	43979990
	21388461	24906486	30616738	28018177	38795194
	27230620	27521547	32862483	40291401	38823115
Mean	22360805	24426346	30003920	32966737	40532766
STDV	3644669	2744319	2620269	5284721	2437582

***cis*-DCE**	**500**	**1000**	**1500**	**2000**	**2500**
Peak area	13982085	12962944	17079511	20647052	20647052
	12894831	15076219	19809428	22646436	22646436
	16773179	17994903	22563715	29853341	29853341
Mean	14550031	15344689	19817551	24382276	24382276
STDV	1633466	2063042	2238924	3953800	3953800

chloroform	500	1000	1500	2000	2500
Peak area	10023732	10488138	14502250	17423153	26689376
	10338817	12612269	17171221	20497249	25105888
	13562611	14977303	19372705	26985470	23947154
Mean	11308387	12692570	17015392	21635291	25247473
STDV	1599159	1833573	1991406	3985878	1123975

CT	**500**	**1000**	**1500**	**2000**	**2500**
Peak area	52454948	66384421	83080716	95153088	141299267
	53288270	77271808	93523302	73869272	116484212
	62856899	82085359	98583095	113944462	111342787
Mean	56200039	75247196	91729038	94322274	123042089
STDV	4719389	6567808	6454739	16371172	13079296

benzene	500	1000	1500	2000	2500
Peak area	35181322	34307147	43497552	51310339	75194563
	33686374	40074736	49778768	53867425	68294424
	39797192	45959455	56027934	70263737	65914585
Mean	36221630	40113779	49768085	58480500	69801191
STDV	2600923	4757115	5115513	8397149	3935502

DCA	500	1000	1500	2000	2500
Peak area	5607283	5383109	7775416	9018239	14929072
	5351489	6339865	8880660	11516946	13718658
	6196528	7733999	10267180	14378716	13091382
Mean	5718433	6485658	8974419	11637967	13913037
STDV	353825	965268	1019416	2190078	762721

fluorobenzene	500	1000	1500	2000	2500
Peak area	37822800	40242408	51306783	60405252	90288846
	39309738	46987588	58687065	61670156	80383846
	46528311	53777284	66580297	82901836	76553259
Mean	41220283	47002427	58858048	68325748	82408650
STDV	3802115	5525600	6236558	10319779	5787426

TCE	500	1000	1500	2000	2500
Peak area	27588909	33876760	41781074	47439195	69690650
	32758803	38739720	46359972	45242657	59953202
	37291330	43786915	51129129	62163990	58099546
Mean	32546347	38801132	46423392	51615281	62581132
STDV	3963845	4046037	3816591	7512773	5083827

toluene	500	1000	1500	2000	2500
Peak area	49722784	57125946	73369480	85833914	127724280
	56454769	67646529	82279468	89689158	116857546
	50854529	76451039	96608508	120491142	111673927
Mean	52344028	67074504	84085819	98671405	118751918
STDV	2943225	7899798	9572888	15508953	6688046

PCE	500	1000	1500	2000	2500
Peak area	32197701	46574250	55322914	60773236	90803481
	45244615	54411627	60422848	54092768	77159745
	38624362	59894989	69995768	79369888	72058653
Mean	38688893	53626956	61913844	64745297	80007293
STDV	5326576	5466401	6082240	10694739	7913008

EDB	500	1000	1500	2000	2500
Peak area	3468693	3633200	5771033	7918020	12907476
	3061528	4481639	6836930	10299493	12368609
	2602293	5400442	8423972	12677105	11233772
Mean	3044171	4505094	7010645	10298206	12169952
STDV	353919	721664	1090001	1942889	697576

ethylbenzene	500	1000	1500	2000	2500
Peak area	37098526	46727310	60990037	74360084	111430236
	45333936	57882684	68946949	75486832	100937554
	34223417	65584997	85558931	103612664	90574480
Mean	38885293	56731664	71831973	84486527	100980757
STDV	4708525	7741521	10235564	13532042	8514382

para-xylene	500	1000	1500	2000	2500
Peak area	29917037	36692780	49400430	60186636	89383546
	35329854	45562027	55575856	62573750	80954383
	25536723	51530295	69691318	82445446	74023491
Mean	30261205	44595034	58222535	68401944	81453807
STDV	4005429	6095860	8492495	9977960	6280652

bromoform	500	1000	1500	2000	2500
Peak area	2785325	3185995	5234704	7026299	12140975
	2533011	3830972	5937319	9587175	11305634
	1719369	4640114	7440631	11942798	10149686
Mean	2345902	3885694	6204218	9518757	11198765
STDV	454843	594901	920128	2007735	816445

isopropylbenzene	500	1000	1500	2000	2500
Peak area	17999596	25712409	35234684	41722927	61463153
	24477996	33241019	38590638	41321299	57605789
	17770160	38018474	49362218	60215901	50250147
Mean	20082584	32323967	41062513	47753376	56439697
STDV	3109437	5065606	6026576	8813862	4651359

propylbenzene	500	1000	1500	2000	2500
Peak area	23408065	35250521	49835430	57246891	82012076
	32332765	46245342	54051038	55785567	77348676
	20813982	51497676	65747422	81797699	67362999
Mean	25518271	44331180	56544630	64943385	75574584
STDV	4933580	6769566	6731091	11932722	6110615

1,3,5-TMB	500	1000	1500	2000	2500
Peak area	11470877	16313969	23704309	28306285	40283696
	15736434	21441744	25874595	30037700	38884708
	10913550	24475011	31682949	42775981	33095749
Mean	12706954	20743575	27087284	33706655	37421385
STDV	2154215	3368109	3368248	6451819	3111552

1,2,4-TMB	500	1000	1500	2000	2500
Peak area	2869500	3998348	5858897	7114544	9706599
	3965637	5147126	6414881	7878335	9889345
	2597949	5818734	7812466	10941391	8548991
Mean	3144362	4988069	6695415	8644757	9381645
STDV	591216	751632	821840	1653631	593483

1,2,3-TMB	500	1000	1500	2000	2500
Peak area	2187033	2865233	4257068	5237116	6916275
	2990963	3533957	4550285	6147168	7208352
	2164272	4266256	5496920	8015384	6320665
Mean	2447422	3555149	4768091	8015384	6815097
STDV	384453	572162	529079	1391827	369391

B 3.6 Extraction flow rate

Compound	Extraction flow rate in µL/s				
VC	**10**	**50**	**100**	**150**	**200**
Peak area	4649720	2358197	5140772	3302147	3726282
	6651584	3501327	4064995	4295095	359758
	6739215	3148141	4311743	2752144	3857412
Mean	6013506	3002555	4505837	3449795	2647818
STDV	1181886	585306	563541	782000	1982602

DCM	10	50	100	150	200
Peak area	10250696	5975294	4847381	5074646	5213031
	9686794	5846821	5263229	4944060	650528
	9168213	5494712	5047098	5019271	5239353
Mean	9701901	5772276	5052569	5012659	3700971
STDV	541399	248812	207978	65544	2641794

trans-DCE	10	50	100	150	200
Peak area	17628920	9770879	11591314	9720692	10082846
	21628059	11982763	11332485	10782714	1739424
	21393085	10691747	10905723	8894766	10360040
Mean	20216688	10815130	11276507	9799391	7394103
STDV	2244150	1111092	346207	946431	4899057

cis-DCE	10	50	100	150	200
Peak area	16822284	9675245	9925193	9377724	9373684
	17865006	10737382	10075033	9883438	3306473
	17895669	9805606	9950103	8891013	9871265
Mean	17527653	10072745	9983443	9384058	7517141
STDV	611059	579272	80291	496243	3655022

chloroform	10	50	100	150	200
Peak area	15993073	9641425	9434793	9643571	9572043
	16077778	9975865	10142773	9834521	4414805
	15517707	9692121	9904755	9173371	9824329
Mean	15862853	9769803	9827440	9550488	7937059
STDV	301890	180246	360267	340262	3052968

CT	10	50	100	150	200
Peak area	25871975	17452734	19226844	15460676	15809811
	31947499	20678966	19083280	17780832	9417491
	29720236	18295704	18222426	14062929	15003780
Mean	29179903	18809135	18844183	15768146	13410361
STDV	3073592	1673276	543221	1877926	3481332

benzene	10	50	100	150	200
Peak area	39444623	26859201	26755754	24938548	25877139
	40148455	28515298	28546373	26364215	15274397
	38292922	26645464	26942566	24946119	25645160
Mean	39295333	27339988	27414898	25416294	22265565
STDV	936732	1023444	984328	820932	6055640

DCA	10	50	100	150	200
Peak area	8425860	5040898	4818779	4621267	4519578
	8668351	5243224	4912452	4681912	2438841
	8589590	4990816	4998382	4630220	4622252
Mean	8561267	5091646	4909871	4644466	3860224
STDV	123702	133637	89829	32736	1232024

fluorobenzene	10	50	100	150	200
Peak area	37287413	24166303	28415179	24157821	25035232
	42878934	27729937	27970334	27110977	14298174
	40338862	25875135	27695144	23425305	25408323
Mean	40168403	25923792	28026886	24898034	21580576
STDV	2799655	1782315	363334	1951149	6309503

TCE	10	50	100	150	200
Peak area	30622359	21421125	20556025	18869123	19633139
	32890222	22587051	22237743	20224721	10503503
	29573091	21028752	19876510	18357850	18797936
Mean	31028557	21678976	20890093	19150565	16311526
STDV	1695461	810518	1215548	964733	5047201

toluene	10	50	100	150	200
Peak area	53925408	39016061	39938090	34760709	35795497
	56914636	42731679	41238025	38053689	26618493
	54240111	40666877	39892900	34686928	35175338
Mean	55026718	40804872	40356338	35833775	32529776
STDV	1642539	1861649	763897	1922856	5128703

PCE	10	50	100	150	200
Peak area	20348648	14373954	19189022	14386880	2795906
	27420889	18835277	18497981	17052454	2125186
	25547880	16566087	17730385	13237274	2796106
Mean	24439139	16591773	18472463	14892203	2572399
STDV	3664168	2230772	729653	1957144	387298

EDB	10	50	100	150	200
Peak area	4642428	3148195	2964476	2762092	15034427
	4652796	3234699	3055943	2802005	10211060
	4658036	3142051	3198442	2879547	13890600
Mean	4651087	3174982	3072954	2814548	13045363
STDV	7943	51808	117907	59723	2520325

ethylbenzene	10	50	100	150	200
Peak area	34846158	27208123	28742945	22188752	23902690
	39051535	30857516	29421451	26126481	19155294
	38106335	28768714	29454945	23278261	23684447
Mean	37334676	28944784	29206447	23864498	22247477
STDV	2206330	1831056	401753	2033269	2680131

Para-xylene	10	50	100	150	200
Peak area	28914379	23476470	23559983	19060556	20139503
	30941750	24786249	24000793	21291111	16408132
	29669157	23627014	23840957	19960267	19551053
Mean	29841762	23963244	23800578	20103978	18699563
STDV	1024648	716706	223162	1122200	2006130

bromoform	10	50	100	150	200
Peak area	3966379	2793554	2668059	2375417	2413943
	3812222	2959711	2807046	2517564	2048496
	3920531	2963520	2859845	2524123	2432437
Mean	3899711	2905595	2778317	2472368	2298292
STDV	79159	97049	99068	84026	216527

isoprpylbenzene	10	50	100	150	200
Peak area	15614899	12002051	14139943	10321037	10815743
	18517175	14719244	14150118	12253406	8392604
	17997040	13730331	13942008	10348524	10743009
Mean	17376371	13483875	14077356	10974322	9983785
STDV	1547489	1375260	117325	1107805	1378483

propylbenzene	10	50	100	150	200
Peak area	18085466	14779942	18799235	13530401	13850391
	21938763	18623411	18796802	15637985	11614649
	21436901	17737328	18171230	13459127	14017898
Mean	20487043	17046894	18589089	14209171	13160979
STDV	2094910	2012608	361878	1237902	1341778

1,3,5-TMB	10	50	100	150	200
Peak area	10904802	9014195	11187881	8538353	8658988
	12621471	11028549	11326282	9551494	7216121
	12488127	10918289	11117170	8676237	8826582
Mean	12004800	10320344	11210445	8922028	8233897
STDV	954957	1132501	106366	549476	885394

1,2,4-TMB	10	50	100	150	200
Peak area	3114558	2531846	3103716	2457181	2531677
	3410706	3097146	3143414	2723904	2173620
	3442613	3005203	3113540	2557281	2523741
Mean	3322625	2878065	3120223	2579455	2409679
STDV	180897	303339	20676	134737	204472

1,2,3-TMB	10	50	100	150	200
Peak area	2865804	2360571	2751844	2306635	2341706
	3077191	2761244	2870866	2426123	1990398
	3058973	2807283	2809807	2455213	2412573
Mean	3000656	2643033	2810839	2395991	2248225
STDV	117140	245699	59517	78739	226079

B 3.7 Extraction temperature

Compound	Extraction temperature in °C			
	30	40	50	60
VC				
Peak area	16627642	17705742	16392180	19609840
	16692189	16170722	17712797	17961156
	15921134	15321390	17632424	14579184
Mean	16413655	16399285	17245800	17383393
STDV	427755	1208496	740348	2564612

DCM	30	40	50	60
Peak area	7781843	9068795	15261680	17845000
	7649697	8857262	14300859	17879458
	7611413	8992721	15592662	17685516
Mean	7680985	8972926	15051734	17803325
STDV	89419	107147	671004	103470

trans-DCE	30	40	50	60
Peak area	27508627	28886721	41191638	45434228
	27483143	28256597	27719701	42796802
	27146746	27338857	45003534	40692874
Mean	27379506	28160725	37971624	42974635
STDV	201978	778373	9080699	2375674

***cis*-DCE**	**30**	**40**	**50**	**60**
Peak area	17838505	21692566	26084635	37733309
	18064891	21097980	26271467	27465269
	18077686	21378292	28840526	27504773
Mean	17993694	21389613	27065543	30901117
STDV	134550	297455	1540017	5916885

chloroform	**30**	**40**	**50**	**60**
Peak area	16262131	20292433	24815532	32697992
	16396700	19677895	24618721	27142891
	16532238	19607056	26767746	27139818
Mean	16397023	19859128	25400667	28993567
STDV	135054	376921	1188008	3208126

CT	**30**	**40**	**50**	**60**
Peak area	67038175	72018042	67725431	67487039
	72559505	69732199	72808857	63920430
	72928391	68412274	77914046	57439467
Mean	70842024	70054172	72816111	62948979
STDV	3299389	1824319	5094311	5093742

benzene	**30**	**40**	**50**	**60**
Peak area	47770381	54023959	62310669	62446377
	48554307	54562249	63853139	64420176
	49711690	54083611	71307475	63313622
Mean	48678793	54223273	65823761	63393391
STDV	976623	295073	4811252	989314

DCA	**30**	**40**	**50**	**60**
Peak area	6783525	9458597	13430480	15913227
	6790392	9732053	12734198	16272542
	6994129	9844568	13926343	16975330
Mean	6856015	9678406	13363674	16387033
STDV	119659	198499	598874	540229

fluorobenzene	**30**	**40**	**50**	**60**
Peak area	57279937	64282362	72597427	74242002
	57753374	63567933	74366757	73518719
	58602004	61933814	86738107	72446308
Mean	57878438	63261370	77900764	73402343
STDV	669848	1203913	7704324	903486

TCE	**30**	**40**	**50**	**60**
Peak area	42962487	47268482	50215574	54455683
	43580836	45943735	52270797	52499614
	43548236	45331659	60376762	50331618
Mean	43363853	46181292	54287711	52428972
STDV	347975	990023	5372466	2062940

toluene	30	40	50	60
Peak area	85896049	97325501	110886092	117146555
	86198708	97176967	115107037	114212318
	87029862	96346620	127985071	110200901
Mean	86374873	96949696	117992734	113853258
STDV	587076	527533	8907255	3486720

PCE	30	40	50	60
Peak area	55773252	60787923	60731664	64967855
	60247585	58612108	61900988	60689914
	58877375	57467872	69246172	53728908
Mean	58299404	58955968	63959608	59795559
STDV	2292477	1686524	4615479	5672600

EBD	30	40	50	60
Peak area	5531840	8118737	12182740	14466264
	5433920	8144980	11173241	15560715
	5603403	7975093	13181605	14498173
Mean	5523054	8079603	12179195	14841717
STDV	85082	91455	1004187	622874

ethylbenzene	30	40	50	60
Peak area	78579229	93627858	106674071	116445062
	79525753	93706486	105807549	107933952
	80337435	88162389	120981039	97730422
Mean	79480806	91832244	111154220	107369812
STDV	879964	3178431	8521297	9370066

para-xylene	30	40	50	60
Peak area	64846683	78650543	92646211	104706043
	65161024	79717426	91667281	95310370
	66332403	75590906	104004535	86838524
Mean	65446703	77986292	96106009	95618312
STDV	782975	2141953	6857813	8937739

bromoform	30	40	50	60
Peak area	4863400	7579411	12333851	17721007
	4831874	7979336	11006561	17748070
	5110178	7763882	12759810	16095848
Mean	4935151	7774210	12033407	17188308
STDV	152395	200162	914423	946195

isopropylbenzene	30	40	50	60
Peak area	43876888	52117036	60089329	65564808
	46296899	52191329	60087690	59455989
	46395742	50793489	69357760	53563545
Mean	45523176	51700618	63178260	59528114
STDV	1426584	786474	5351604	6000957

propylbenzene	30	40	50	60
Peak area	64967433	79514968	90212053	104444226
	66611594	78716954	88141617	91771564
	68601448	76909314	101953071	79430539
Mean	66726825	78380412	93435580	91882110
STDV	1819745	1335030	7448652	12507210

1,3,5-TMB	30	40	50	60
Peak area	32762865	43033925	52846376	63014678
	33847578	42136183	50818054	55837983
	34038036	42201841	61036852	50346767
Mean	33549493	42457316	54900427	56399809
STDV	687863	500436	5410203	6352616

1,2,4-TMB	30	40	50	60
Peak area	7661783	10744786	14825624	18267204
	7838097	10734096	13693675	16335372
	7886937	10587514	15933231	14610237
Mean	7795605	10688799	14817510	16404271
STDV	118438	87878	1119800	1829457

1,2,3-TMB	30	40	50	60
Peak area	5831607	8808274	13337143	17516854
	5949626	9211958	12185766	15978068
	6054239	8837738	14322831	14592992
Mean	5945157	8952657	13281913	16029305
STDV	111383	225044	1069602	1462604

Appendix C

Tables of enrichment techniques

C 1 Tables of enrichment techniques

Table C 1.1 Extraction techniques used in combination with CSIA for common groundwater pollutants (adapted and updated from Ref.:[5])

Compound	Injection/ enrichment technique	Isotopic fractionation during analysis	Detection limit definition	Detection limit [µg/L]		Ref.
				$\delta^{13}C$	$\delta^{2}H$	
MTBE	liquid injection[a]	OC[b] <0.3‰; SL[c] ~1‰	Amplitude > 0.5 V	24000	-	[6]
	headspace injection	n.r.[d]	C: < 0.5‰ total error H: < 4‰ total error	5000	50000	[7]
	headspace injection	n.r.[d]	n.r.[d]	4000 (TAME: 6000)	-	[8]
	headspace SPME	C: -0.9‰ H: -17‰ (both with resp. to HS injection)	C: < 0.5‰ total error H: < 4‰ total error	350	1000	[7]
	headspace SPME	Significant but small fractionation (-0.67±0.21‰)	Amplitude > 0.75 V	11	-	[9]
	direct immersion SPME	Reproducible fractionation (<0.5‰), but presence of BTEX concentrations >3 mg/L caused 2‰ deviation.	Amplitude > 0.5 V	16	-	[6]
	P&T	Small shift of $\delta^{13}C$ values (+0.33‰)	n.r.[d]	15	-	[10]
	P&T	n.r.[d]	n.r.[d]	5	-	[11]
	P&T	n.s.f.[e]	Amplitude > 0.5 V	0.63	-	[6]
	P&T	n.r.[d]	< 0.5‰ precision	2.5	20	[12]
benzene	liquid injection[a]	n.s.f.[e]	Amplitude > 0.5 V	19000	-	[6]
	headspace injection	n.r.[d]	< 0.5‰ total error	500	-	[13]
	direct immersion SPME	n.s.f.[e]	Amplitude > 0.5 V	22	-	[6]
	P&T	n.s.f.[e]	Amplitude > 0.5 V	0.30	-	[6]
	P&T	n.r.[d]	Amplitude > 1 V	200-300	-	[14]
	P&T	n.r.[d]	Moving mean within ± 0.5‰ interval and σ < 0.5 ‰	0.20	-	This work
toluene	liquid injection[a]	OC[b] n.s.f.[e] SL[c]~-1‰	Amplitude > 0.5 V	9500	-	[6]
	headspace injection	No deviation from pentane injection of standards	Amplitude > 2 V	-	2000	[15]
	headspace injection	n.s.f.[e]	Amplitude > 0.2 V (at σ < 0.5 ‰)	100	-	[16]
	direct immersion SPME	n.s.f.[e]	Peak area equiv. to 50 pmol CO_2 at the ion source (ca. 0.7 Vs)	45	-	[17]
	direct immersion SPME	n.s.f.[e]	Amplitude > 0.5 V	9	-	[6]
	P&T	n.s.f.[e]	Amplitude > 0.5 V	0.25	-	[6]
	P&T	n.r.[d]	Amplitude > 1 V	200-300	-	[14]
	P&T	n.s.f.[e]	Moving mean within ± 0.5‰ interval and	0.07	-	This work

			σ < 0.5 ‰			
ethylbenzene	P&T	n.r.[d]	Amplitude > 1 V	200-300	-	[14]
***p*+*m*-xylene**	P&T	n.r.[d]	Amplitude > 1 V	200-300	-	[14]
***o*-xylene**	P&T	n.r.[d]	Amplitude > 1 V	200-300	-	[14]
chlorinated methanes	liquid injection[a]	$CHCl_3$, ~-1.5‰	Amplitude > 0.5 V	170000 -	-	[6]
		CCl_4, OC[b] - 3.31±0.34‰		220000		
	direct immersion SPME	$CHCl_3$, -1.8±0.28‰	Amplitude > 0.5 V	170 - 280	-	[6]
		CCl_4, -7.3±0.22‰				
	direct immersion SPME	n.s.f.[e] -0.09 to 0.40 ‰	1.5 nmol C on column	360 - 2200	-	[18]
	headspace injection	1.03 to 1.29 ‰	1.5 nmol C on column	800 - 3300	-	[18]
	P&T	$CHCl_3$ and CCl_4, n.s.f.[e]	Amplitude > 0.5 V	≤5.0	-	[6]
	P&T	$CHCl_3$, ~-1.5‰ CCl_4 and DCM, n.s.f.[e]	Moving mean within ± 0.5‰ interval and σ < 0.5 ‰	18-27	-	This work
chlorinated ethylenes	liquid injection[a]	Small but significant fractionation observed for TCE and cis-DCE	Amplitude > 0.5 V	71000 - 84000	-	[6]
	headspace injection	TCE, n.s.f.[e]	Amplitude > 0.2 V (at σ < 0.5 ‰)	400	-	[16]
	direct immersion SPME	n.s.f.[e]) -0.37 to +0.06‰	1.5 nmol C on column	130-290	-	[18]
	headspace injection	0.21 to 0.69 ‰	1.5 nmol C on column	170 - 1000	-	[18]
	direct immersion SPME	Small (~1‰) but significant fractionation observed for *cis*-DCE only	Amplitude > 0.5 V	66 – 130	-	[6]
	P&T	n.s.f.[e]	Not given	5	-	[19]
	P&T	Small (~0.7‰) but significant fractionation observed for cis-DCE only	Amplitude > 0.5 V	1.4	-	[6]
	P&T	n.s.f.[e]	Moving mean within ± 0.5‰ interval and σ < 0.5 ‰	0.8-5.1	-	This work
	dynamic headspace extraction	n.s.f.[e]	Amplitude > 0.2 V (lower linearity limit of the MAT 252 used)	10-38	-	[20]
misc. compounds						
methylcyclohexane	direct immersion SPME	< 0.5 ‰	Peak area equiv. to 50 pmol CO_2 at the ion source (ca. 0.7 Vs)	24	-	[17]
alkylated benzenes	P&T	n.s.f.[e]	Moving mean within ± 0.5‰ interval and σ < 0.5 ‰	0.07-0.35	-	This work
hexanol	direct immersion SPME	< 0.5 ‰	Peak area equiv. to 50 pmol CO_2 at the ion source (ca. 0.7 Vs)	4200	-	[17]
***tert*-butyl alcohol**	direct immersion SPME	Significant fractionation (-1.18±0.12‰)	Amplitude > 0.75 V	360	-	[9]

***tert*-butyl alcohol**	P&T	n.r.[d]	< 0.5‰ precision	25	-	[12]
bromoform, ethylene dibromide	P&T	n.r.[d]	Moving mean within ± 0.5‰ interval and σ < 0.5 ‰	14, 3.9	-	This work

[a] Analyte dissolved in solvent. [b] On column injection. [c] Splitless injection. [d] Not reported in reference. [e] No significant fractionation (<0.5‰) observed.

Table C 1.2 Application of stir-bar-sorptive extraction (SBSE) and headspace sorptive extraction (HSSE) for aqueous water contaminants

Analyte	Aqueous matrix	Extraction device	Application mode	Determination	Extraction conditions	Analytical validation	Ref.
Stir bar sorptive extraction (SBSE)							
Alkylphenols, bisphenol A	Natural water	PDMS 500 µm film, 10 mm length; (24 µL PDMS)	DI	ISD-TD-GC-MS	Sample volume: 10 mL; Extraction time: 60 min; Stirring speed: 1000 rpm; Extraction temperature: RT; Salt addition: 0.5 g Na_2CO_3; Derivatisation reagent: 0.5 mL acetic acid anhydride	Linear range: 1-1000 ng/L; MDL: 0.1-3.2 ng/L (n = 6, 3 x SD) Recovery: 85.3-105.9 % (RSD: 1.6-11.0%, n = 6)	21
Alkylphenols	River water	PDMS 500 µm film, 10 mm length; (24 µL PDMS)	DI	ITS-TD-GC-MS	Sample volume: 2 mL; Extraction time: 60 min; Stirring speed: 500 rpm; Extraction temperature: RT; Derivatisation reagent: 0.5 µL BSTFA (in the TD tube)	Linear range: 1 - 1000 pg/mL; LOD: 0.2 - 10 pg/mL (S/N: 3/1); LOQ: 1 - 50 pg/mL (S/N: > 10:1); Recovery: 93.1 - 98.6 % (RSD: 3.6 - 14.8 %, n = 6)	22
35 EPA priority compounds, PAHs	Water	(i) PDMS 2000 µm film, 10 mm length; (92µL) (ii) PDMS 2000 µm film, 40 mm length; (365µL)	DI	TD-GC-MS	(i) Sample volume: 10 mL; Extraction time: 40 min; Stirring speed: 1400 rpm; Extraction temperature: RT; (ii) Sample volume: 200 mL; Extraction time: 75 min; Stirring speed: 1000 rpm; Extraction temperature: RT;	(i)MDL: ~0.3 ng/L (dichloropropenes), ~0.08 ng/L (1,2,4-trichlorobenzene); Recovery: 0.88-86 % (ii)MDL: 0.01-1 ng/L	23
Phenols	Natural water (mining lake), ground water	PDMS 500 µm film, thickness, 10 mm length; (24 µL)	DI	TD-GC-MS	Sample volume: 10 mL; Extraction time: 45 min; Stirring speed: 1000 rpm, Extraction temperature: RT; Salt addition: 3.3 g NaCl, 0.5 g Ka_2CO_3; pH: 11 (0.42 g $NaHCO_3$); Derivatisation reagent: 250 µL acetic acid anhydride	Linear range: 1 - 15 µg/L; LOD: 0.1 - 0.4 µg/L (S/N: 3/1); Reproducibility: RSD: 6 - 27 %; Carry over level: 0.15 - 4.25 % of peak area	24
Chlorophenols	River water	PDMS 500 µm film, 10 mm length; (24 µL)	DI	ISD-TD-GC-MS	Sample volume: 10 mL; ; Extraction time: 90 min; Stirring speed: 500 rpm, Extraction temperature: RT Salt addition: 1M Na_2CO_3(1 mL); Derivatisation reagent: 200 µL acetic acid anhydride	Linear range: 5 - 1000 pg/mL; LOD: 1 - 2 pg/mL (S/N: 3/1); LOQ: 5 - 10 pg/mL (S/N: >10:1); Recovery: 98.9 - 103.6 % (RSD: 0.9 - 6.1 %, n = 6)	25
(i) 4-nonylphenol, (ii) 4-*tert*-octylphenol	River water	PDMS 500 µm film, 10 mm length; (24 µL PDMS)	DI	TD-GC-MS	Sample volume: 2 mL; ; Extraction time: 60 min; Stirring speed: 500 rpm, Extraction temperature: RT	Linear range: (i) 0.1 - 10 ng/mL (ii) 0.01 - 10 ng/mL; Detection limits: (i) 0.02 ng/mL (ii) 0.002 ng/mL; Recoveries: <97% (RSD: 3.6-6.2%)	26
Phenolic xenoestrogens, bisphenol A	River water	PDMS 500 µm film, 10 mm length; (24 µL)	DI	ISD-TD-GC-MS	Sample volume: 10 mL; Extraction time: 90 min; Stirring speed: 1000 rpm, Extraction temperature: RT; Salt addition: 0.53 g Na_2CO_3; pH: 10.5 (0.42 g $NaHCO_3$); Derivatisation reagent: 200 µL acetic acid anhydride	Linear range: 2 - 1000 pg/mL; LOD: 0.5 - 5 pg/mL, (S/N: 3:1); LOQ: 2 - 20 pg/mL (S/N: >10:1); Recovery: 93.9-113.0 % (RSD: 3.3-7.2 %, n = 6)	27
Phenols	River water, sewage water	PDMS 1000 µm film, 10 mm length; (63 µL PDMS)	DI	LD-LVI-GC-MS	Sample volume : 10 mL; Extraction time: 30 min; Stirring speed: 1200 rpm, Extraction temperature: 50 °C; Salt addition: 20 g/L NaCl; Methanol addition: 10 %; LD: 0.5 mL isooctane (1000 rpm, 30 min, RT)	Linear range: 0.02 - 5 µg/L; LOD: 0.005 - 0.06 µg/L, (S/N: 3/1); Recovery: 51 - 83 %; Repeatability: 1 - 9 %, n = 3; Reproducibility: 1 - 17 %, n = 3	28

Table C 1.2 continued.

Analyte	Aqueous matrix	Extraction device	Application mode	Determination	Extraction conditions	Analytical validation	Ref.
Pesticides	River water	PDMS 500 µm film, 10 mm length; (24 µL)	DI	TD-GC-MS	Sample volume: 10 mL; Extraction time: 60 min; Stirring speed: 1000 rpm; Extraction temperature: RT; Salt addition: 30 % (w/w) NaCl	Linear range: 5 - 1000 ng/L; MDL: 0.2 - 20 ng/L (S/N: 3/1); Recovery: 58.5 - 132 % (RSD: 1.4 - 20.2 %n = 6)	[29]
Pesticides	River water	PDMS 1000 µm film, 10 mm length; (63 µL PDMS)	DI	LD-LVI-GC-MS	Sample volume: 10 mL; Extraction time: 60 min; Stirring speed: 1200 rpm; Extraction temperature: 50°C; Salt addition: 10 g/L NaCl; LD: 4 mL isooctane (1200 rpm, 30 min, RT)	Linear range: 0.05 - 5 µg/L; LOD: 0.01 - 0.24 µg/L (K = 6)[a]; Recovery: 42 - 96 % (atrazine 9 %); Repeatability: 2 - 13 %, n = 5; Reproducibility: 4 - 23 %, n = 5	[30]
Pesticides, PAHs	Water	PDMS 500 µm film, 20 mm length; (47 µL PDMS)	DI	TD-GC-MS	Sample volume: 100 mL; Extraction time: 14 h; Stirring speed: 900 rpm; Extraction temperature: RT; Salt addition: 20 % (w/w) NaCl	-	[31]
Hydroxy-PAHs	Sea water, puddle water	PDMS 500 µm film, thickness, 10 mm length, (24 µL)	DI	ISD-TD-GC-MS	Sample volume: 10 mL; Extraction time: 360 min; Stirring speed: 1000 rpm, Extraction temperature: RT; Salt addition: 100 mg $NaHCO_3$; Derivatisation reagent: 20 µL acetic acid anhydride	Linear range: 0.01-10 µg/L; LOD: 0.27-25 ng/L, (S/N:3/1); LOQ: 0.92-35 ng/L,(S/N: 10:1); Total recoveries: <50 %	[32]
BTEX	Drinking water	PDMS 500 µm film thickness, 20 mm length, (47 µL	DI	GC-MS	Sample volume: 50 mL; Extraction time: 60 min; Extraction temperature: RT	-	[33]
Off-flavor compounds	Spring water, tap water, drinking water, treatment plant water, distribution network water	PDMS 500 µm film, 20 mm length, (47 µL)	DI	ISD-TD-GC-MS-olfactometry	Sample volume: 100 mL; Extraction time: 2 h; Stirring speed: 1000 rpm; Extraction temperature: RT; Salt addition: 1 g Na_2CO_3; Derivatisation reagent: 0.5 mL acetic acid anhydride	Linear range: 0.1-10 ng/L; LOQ: 0.1-1 ng/L (RSD:7-14.6 %, n = 10)[b]; Repeatability: 1-15 %[b]; Reproducibility: 4-15% (2ng/L standard)[b]	[34]
Off-flavor compounds	Drinking water, raw water, tap water	PDMS 500 µm film, 10 mm length, (24 µL)	DI, (HS tested during evaluation)	TD-GC-MS	Sample volume: 60 mL; Extraction time: 4 h; Stirring speed: 1000 rpm; Extraction temperature: RT; Salt addition: 1 g Na_2CO_3; Derivatisation reagent: 0.5 mL acetic acid anhydride	Linear range: 0.1-100 ng/L; MDL: 0.022-0.16 ng/L (n = 6, 3 x SD) Recovery: 89-109 % (RSD: 0.8-3.7%) (1 ng/L standard; n = 6)	[35]
High capacity headspace sorptive extraction (HSSE)							
Hydrocarbons, chlorinated hydrocarbons, aromatic hydrocarbons, esters	Water	PDMS	HS	TD-GC-MS	Sample volume: 10 & 250 mL; Extraction time: 45 min; Extraction; Stirred; temperature: 21 °C;	LOD: 20-150 ppt (S/N: 3/1); Repeatability: 1-3 ppb (RSD : <10 %, standards, n=6)	[36]

Table C 1.3 In-needle, in-tube and syringe based techniques

Analyte	Aqueous matrix	Extraction device	Application mode	Determination	Extraction conditions	Analytical validation	Ref.
In-tube solid-phase microextraction (In-tube SPME)							
(a) alkanes, (b) chlorinated pesticides, (c) PAHs	Water	5 m x 0.53 mm i.d., 1.2 µm PDMS film	Flow through	(a, c) GC-FID (b) GC-ECD	(a) Extraction volume: 300 mL; Extraction time:40 min; Extraction flowrate: 10 mL/min; Extraction temperature: RT	(a) Linear range: 0.1-100 µg/L; Detection limit: 0.01-0.3 µg/L; Repeatability: RSD 5.8-14.8 % (n =6, 0.5 µg/L standard), RSD 4.3-11.3 % (n=6, 20 µ/L standard)	37
BTEX	Water		Flow through		Extraction volume: 1 mL; Extraction temperature: RT	Determination of siloxane-water partition coefficients for BTEX	38
BTEX	Water	70 cm x 0.474 mm i.d., 0.48 µL PDMS phase volume	Flow through	GC-FID	Extraction volume: 1mL; Extrection temperature: ambient (20-23°C) ; Extraction time: 60-70 s (for each repetetive extraction)	Applicability of capillary extractors for K_d determination by negligible depletion LOD: 0.01-1 ppb	39
Chlorinated hydrocarbones	Water	76 cm x 0.251 mm i.d., 0.3 µm film PDMS	Flow through	GC-FID	Extraction volume: 1mL;	Detection limits : 0.50-8.4 ppb(v/v) 2σ (without NaCl), 0.3-1.6 ppb(v/v) 2σ (with NaCl)	40
Sol-gel capillary microextraction (sol-gel CME)							
(a) phenols, (b) alcohols, (c) amines, (d) PAHs, (e) aldehydes, (f) ketones	Water	(i) 3.5 cm x 0.25 mm i.d., ~0.6 µm film; (ii) 3.5 cm x 0.25 mm i.d. ~0.4 µm film	Flow through (special device, see Fig. 2d)	GC-FID	(i) Sample volume: 25 mL; Extraction time: 30 min; (ii) Sample volume: 25 mL; Extraction time: 30min;	Detection limits: (a) 6.001-16.06 ppt, (b) 1.992-2.009 ppt, (c) 2.318-5.976 ppt (d) 0.31-0.94 ppt, (e) 28.36-103.20 ppt, (f) 32.67-215.70 ppt, (S/N = 3/1);	41
Solid-phase dynamic extraction (SPDE)							
Pesticides	Water	SPDE syringe: 4 cm x 0.53 i.d. , 7 µm film PDMS	DI	GC-ECD/NPD	Sample volume: 10 mL; Extraction temperature: -; Extraction cycles:5; Extraction temperature: 70°C; Extraction time: 40 min ; Extraction flow rate: 125 µL/min	LOD: 0.001-0.1 µg/L (S/N = 3/1);	42
Needle concentrator							
BTEX	Drinking water	5ml glass syringe connected with stainless steel needle (90 mm x 1.3 o.d/1.1 i.d.) filled with 5 mm long bed (0.15-0.18 mm Porapak Q , Specific surface area: 550 m^2g^{-1}) and 7mm long bed 0.2-0.4 mm Al_2O_3	Flow through (special extraction syringe, see Fig. 3b)	GC-FID	Extraction volume: 5ml; Extraction flow rate: 1 mL/min; Extraction temperature: RT; Desorption temperature: 280°C	Linear range: 1.6-200 µg/LRecovery: 86-105 % (RSD: 0.2-21.0 % each calibration concentration included, n = 3); LOD: 0.20-0.39 µg/L, $x_d \cdot 2ts_d$ (n = 10 blank measurement, t(N-1, 1-α = 0.95)s); LOQ: 0.43-0.83 µg/L, $x_d \cdot 10ts_d$ (n = 10 blank measurement, t(N-1, 1-α = 0.95)s)	43

film thickness; i.d.: internal diameter; o.d.: outer diameter; PDMS/AC: Polymdimethylsiloxane + 10 % active charcoal; Carbowax: polyethylenglycol PEG;

Table C 1.4 Liquid-phase microextraction for polar compounds from aqueous samples

Analyte	Aqueous matrix	Extraction device	Application mode	Determination	Extraction conditions	Analytical validation	Ref.
Static liquid phase microextraction (static-LPME)							
Cholrobenzenes	Tap water, well water	2.5 µL toluene drop	HS	GC/MS (SIM)	**Sample volume: 10 mL; Extraction time: 5 min; Stirring speed: 1000 rpm; Extraction temperature: RT; Salt addition: 30 % (w/w) NaCl**	Linear range: 0.02–50 µg/L; Repeatability: 2.1 and 13.2% (n = 5); LOD: 0.003-0.031µg/L (S/N:3/1)	44
Halogenated hydrocarbons	Tap water, municipal treatment plant water	2 µL hexane drop	DI	GC/ECD	**Sample volume: ?; Extraction time: 15 min; Extraction temperature: 25°C ± 0.03 °C; Stirring speed: -; Salt addition: -**	Linear range: 0.5-26.2 µg/L; Reproducibility: 2.5-5.2 % (n=10)	45
Nitroarmatics (explosives)	(i)Tap water, (ii)groundwater	1 µL toluene drop	DI	GC/MS	**Sample volume: 5mL; Extraction time: 15 min; Extraction temperature: 25°C ± 0.03 °C; Stirring speed: 400rpm; Salt addition: -**	Linear range: 20-1000µg/L; LOD: 0.08-1.3 µg/L (S/N: 3/1, 4.3-9.8 %, n=5); (i) Recovery: 82-102 %, (RSD: 6.0-13.1 %, 100 µg/L standard, n=5); (ii) Recovery: 89-100 %, RSD: 9.0-13.0 %, 100 µg/L standard, n=5)	46
MTBE	Tap water, well water, spring water ground water	2 µL benzyl alcohol drop	HS	GC/FID	**Sample volume: 6 mL; Extraction time: 7.5 min; Syringe needle temperature: -6 °C;; Stirring speed: 1000 rpm; Extraction temperature: 35 °C; Salt addition: 4 M NaCl**	Linear range: 0.1-500 µg/L; Detection limit: 0.06 µg/L	47
MTBE	Water	1.8 µL benzyl alcohol drop	HS	GC/FID	**Sample volume: 4 mL; Extraction time: 10 min;** Stirring speed: 300 rpm; Extraction temperature: 35 °C; Salt addition: 0.2g/mL NaCl	Linear range: 0.01-10 mg/L; Detection limit: 7 µg/L, (3 times s_d); (RSD: 5.5 %, 1 mg/L standard	48
Phenols	River water	2.5 mL hexyl acetate drop	DI	ISyD-GC/MS	**Sample volume: 3 mL; Extraction time: 15 min; Stirring speed: 250 rpm; Extraction temperature: 45 °C; Derivatisation reagent: 0.5 µL BSTFA (in the TD tube)**	Linear range: 0.04-51 µg/L; Detection limit: 4-61 ng/L, (S/N: 3/1); Precision: RSD 4.8-12.0 % (2.3-4 µg/L standards, n=5)	49
Warfare agents	Water	1 µL dichloromethane/carbon tetrachloride (3:1 v/v)	DI	GC/MS	**Sample volume: 1.8 mL; Extraction time: 30 min; Stirring speed: 300 rpm; Extraction time 30 min; Extraction temperature: RT;**	Linear range: 0.1-10 mg/L; Precision: RSD 8.9-14.0 %(n=6); LOD: 75 to 10 µg/L (S/N :10/1)	50
Alcohols	Distilled water, beer	1 µL ethylene glycole drop	HS	GC/FID	**Sample volume: 5 mL; Extraction time: 15 min;** Stirring speed: 600 rpm; Extraction temperature: 60 °C; Salt addition: 0.4 g/mL NaCl	Linear range: 1-5 mg/L; Detection limit: 3.8-52 µg/L, Repeatability: 4.5-18.8 % (varying concentrations, n=5)	51
Dynamic liquid phase microextraction (dynamic-LPME)							
Chlorobenzenes	(i)Deionized water, (ii)waste water	1 µL isooctane	DI	GC/MS	Sample volume: 6 µL ; Extraction cycles : 15	Linear range: 1-50 µg/L; Detection limits: 0.02-0.05 µg/l (S/N: 3/1) (i) Recovery: 95.4-101.5 % (RSD: 3.4-7.3 %, 20 µg/L standard), 86.0-104.7 % (RSD: 1.6-5.3 %, 2 µg/L standard); (ii) Recovery: 90.4-99.2 % (RSD: 4.2-17.9 %, 20 µg/L standard), 83.2-101.6 % (RSD: 4.6-11.6 %, 2 µg/L standard)	52
Hollow fiber liquid phase microextraction (HF-LPME)							
Insecticides	Drinking water, River water	Q 3/2 polypropylene hollow fiber, 600 µm i.d., 200 µm wall thickness, 0.2 µm pore size, 1.3 cm length	DI	GC/FTD	Sample volume: 5 mL; Extraction time: 20 min; Stirring speed: 800 rpm; Extraction temperature: RT; Salt addition: 15 % (w/v); pH: 5.5	Linear range 0.010-100 µg/L (R^2 = 0.993-0.997); LOD: 1-72 ng/L (S/N: 3/1); Repeatability: 4.4-11.1 % (0.05-0.300 µg/L standards); Reproducibility: 4.6-12.0 % (0.05-0.300 µg/L standards); Relative recovery: 84-105 %, RSD: 4.5-11.3 %)	53

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Seit 2006-12-05	**Wissenschaftlicher Mitarbeiter am Lehrstuhl für Instrumentelle Analytische Chemie bei Prof. Torsten C. Schmidt an der Universität Duisburg-Essen.**
Akademische Lehrer:	**Prof. Dr. Stefan B. Haderlein** **Prof. Dr. Torsten C. Schmidt**