Diplomarbeit

Development and Application of Test Methods for the Characterisation of Selective Enrichment Properties of Silica Based Sol-Gel Materials for Organic Trace Pollutants

Ausgeführt am Institut für Chemische Technologie und Analytik der Technischen Universität Wien

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Datum Unterschrift

Abstract

The aim of the diploma thesis was the development of a test method for the kinetic and thermodynamic adsorption behaviour of sol-gel derived substrates. The production of sol-gel derived silica materials with selective enrichment properties for organic compounds is a contribution to the EU project MISPEC (Multiparametric in-situ spectroscopic measuring system for coastal monitoring) in which these materials are to be used as selective SERS (surface enhanced RAMAN spectroscopy) sensor layers.

For the synthesis of the sol-gel substrates, various organically modified silica alkoxy precursors were used. In addition to the substrates, several polymers and SPE materials were also investigated for comparison.

Due to their hydrophobic character and their macroporosity, the wetting of the substrates in monolithic form proved to be nearly impossible. It was therefore decided to grain the monolithic materials and to investigate all materials in particulate form.

Various procedures were developed to characterize the kinetics and thermodynamics of the adsorption of different organic compounds to these materials:

The first approach was to apply SPME/GC (solid phase micro extraction/gas chromatography) with FID (flame ionisation detector) detection for the determination of the adsorption properties of the substrates. For this purpose, a certain amount of substrate was suspended in water, then the suspension was spiked with several volatile test analytes such as chlorobenzene and n-nonane. Compared to a blank sample, a decrease of the analyte concentration in solution could be observed, depending on the affinity of the substrates for the analytes. The time resolution of this method was 20 min, which was not enough to follow the extraction kinetics.

Next, HPLC/DAD (high performance liquid chromatography/diode array detector) analysis was applied for the investigation of the adsorption properties of the substrates. Samples of 1 ml volume were taken and filtered with syringe filters immediately thereafter. This method allowed a time resolution of 1 min. Two different sets of test analytes were used for this method. Several substituted aromatic compounds were used in the first series. Again, the substrates were suspended and the suspension spiked with various aromatic compounds (propylbenzene and benzonitrile as example). The

extraction kinetics could be observed with a variation of less then 1 to about 15 min for the equilibrium time.

For the next experiment series several PAHs were used as test analytes. The final analyte concentration was reduced due to the limited solubility. Here the time needed for an equilibrium varied from 10 min to 80 min.

A third experimental strategy was developed to investigate the reversibility of the adsorption. Therefore the substrates in particulate form were used as SPE columns. The substituted aromatic compounds as well as the PAHs were used as test analytes. A certain amount of spiked solution was applied on the SPE columns for adsorption. The desorption was achieved with n-hexane. The recovery rates ranging from 80-120 % show that the adsorption is reversible, so the substrates can in principle be regenerated.

The capacity of the substrates correlates with their specific surface area as well as with their polarity. The adsorption kinetics can not be derived from the pore size distribution of the substrates, thus a chemical screening method is absolutely necessary to determine this parameter.

Zusammenfassung

Ziel dieser Diplomarbeit war es, verschiedene Testmethoden für das Adsorptionsverhalten von mit Sol-Gel Chemie synthetisierten Substraten zu entwickeln und anzuwenden.

Die Herstellung von Sol-Gel Materialien mit selektiven Anreicherungseigenschaften für organische Verbindungen ist der Beitrag dieser Arbeitsgruppe zum EU-Projekt MISPEC (Multiparametric In-situ Spectroscopic Measuring System for Coastal Monitoring). Die Materialien sollen dabei als SERS aktive (Surface Enhanced RAMAN Spectroscopy) Sensorschichten dienen.

Die Substrate wurden dabei mit Sol-Gel-Chemie aus organisch modifizierten Siliciumalkoxyedukten hergestellt. Zusätzlich wurden verschiedene Polymere und SPE Materialien zu Vergleichszwecken mit denselben Methoden untersucht.

In den Vorversuchen stellte sich heraus, dass die monolithischen Materialien sehr schlecht benetzbar waren. Um diese Materialien in einer annehmbaren Zeitspanne mit den jeweiligen Probelösungen zu benetzen, wurde beschlossen, diese zu mahlen und somit alle Materialien als Partikel zu untersuchen.

Zuerst wurde SPME/GC (Festphasenextraktion/Gaschromatographie) mit FID (Flammenionisationsdetektion) als Untersuchungsmethode angewandt. Dazu wurden die Substrate in Wasser suspendiert und die Suspension anschließend mit den Testanalyten, wie z.B. Chlorbenzen oder n-Nonan gespikt. Im Vergleich zu einer Leerprobe konnte eine deutliche Abnahme der Analytkonzentration in Lösung beobachtet werden, abhängig von den Adsorptionseigenschaften der Substrate. Die Zeitauflösung dieser Methode betrug 20 min, was nicht ausreichte, um die Kinetik der Adsorption zu verfolgen.

Als nächster Ansatz wurde HPLC/DAD (Flüssigkeitschromatographie mit Diaodenarray Detektor) als Untersuchungsmethode der Adsorptionseigenschaften der Materialien angewendet. Wie zuvor wurden die Substrate suspendiert. Als Testanalyten dienten verschiedene substituierte aromatische Verbindungen, wie z.B. Propylbenzen oder Benzonitril. Nach dem Spiken der Lösung wurden zu verschiedenen Zeitpunkten Proben gezogen, das Probenvolumen betrug dabei 1 ml, wobei weitere Anreicherung der Analyten durch den Feststoff durch Filtration mit einem Spritzenfilter gestoppt wurde. Mit dieser Methode konnte eine zeitliche Auflösung von 1 min erzielt werden. Die

Extraktionskinetik konnte verfolgt werden, wobei die Zeit bis zum Erreichen des Gleichgewichts von unter 1 min bis 15 min variierte.

Für die nächste Messserie wurden PAHs als Testanalyten verwendet, der Versuchsaufbau wurde für diese Messungen beibehalten. Die Analytkonzentration musste aufgrund der begrenzten Löslichkeit der Analyten reduziert werden. Bei diesen Messungen konnte ebenfalls die Kinetik der Extraktion verfolgt werden, dabei dauerte die Einstellung des Gleichgewichts zwischen 10 min und 80 min.

Die letzte Versuchsreihe diente dazu, die Reversibilität der Adsorption zu untersuchen. Zur Anreicherung wurden die Substrate in SPE Kartuschen gefüllt. Als Testanalyten dienten sowohl die substituierten aromatischen Verbindungen als auch die PAHs. Zur Adsorption wurde eine gespikte wässrige Lösung auf die Säulen aufgebracht. Die Desorption wurde mit n-Hexan durchgeführt. Die gemessenen Wiederfindungsraten zwischen 80 und 120% zeigen, dass die Adsorption prinzipiell reversibel verläuft, die Substrate können also mit einem Lösungsmittel regeneriert werden.

Die Kapazität der Materialien für die Adsorption korreliert gut mit der spezifischen Oberfläche und der Polarität der Materialien. Die Adsorptionskinetik lässt sich dagegen nicht aus der Porengrößenverteilung ableiten. Um diesen Parameter zu erhalten sind also chemische Adsorptionsversuche aus flüssiger Phase unerläßlich.

Acknowledgements:

My parents who supported my students life financially and also encouraged me to proceed with my university studies in times of low spirits (which were fortunately few).

Ao.Prof. Dr. Erwin Rosenberg for the possibility to realise my diploma thesis at the Institute for Chemical Technology and Analysis. Apart from his guidance he allowed me to work very independently.

My colleges from the group of Organic Trace Analysis, Michael, Samer and Manuel who always provided some help when needed.

The MISPEC project group for the support they provided for my work and for four splendid days in Dublin

The European Commission that enabled this work through funding of the MISPEC (Multiparametric in-situ spectroscopic measuring system for coastal monitoring), proj. Nr. EVK3-CT-2 under the program “Environment and Climate”.

1) Introduction

1.1 The MISPEC project

Pollution is a growing problem for coastal zones in Europe since they are highly populated and ship transportation is also growing. For an efficient pollution monitoring, in-situ measurements are required. No truly in-situ operating methods for the determination of chemical pollution are existing so far. The project for a "Multiparametric in-situ spectroscopic measuring system for coastal monitoring" (MISPEC) has thus been funded by the EU with the aim to develop a cheap, permanent in-situ monitoring system for the maritime environment. Central to this approach are optical sensors sharing an underwater multichannel spectrometer. A central data merger will collect the data of the individual sensors / optodes and send them through the underwater cable to the data acquisition unit on board the research ship, as well as provide on-line data pretreatment as well as the possibility of incorporating additional sensors to the platform. Parameters monitored by the newly developed sensor are oxygen, turbidity, salinity, temperature, pressure as well as the concentrations of trace organic pollutants like polyaromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs). The sensor for the organic compounds is based on sensitive detection by surface enhanced Raman spectroscopy (SERS). One essential contribution for the successful development of these sensors is to provide substrates which show SERS activity and enrich the apolar pollutants efficiently.

1.2 Aim of the diploma thesis

The distribution coefficient and the capacity of the substrate determine the enrichment factor and thus - together with the achievable surface enhancement of the Raman signal - the sensitivity of the sensor. The adsorption and desorption kinetics affect the response time and the reversibility of the sensor. An investigation of the adsorption and desorption behaviour of the substrates is thus essential to determine the suitability of the sol-gel materials particularly synthesised for sensor application. The aim of this diploma thesis was to develop and apply a screening method to investigate the sorption behaviour of the

synthesized sol-gel materials. This method would provide the data to decide which material has the desired enrichment properties for the use as chemical sensing layer for the optical sensor.

1.3 Sol-Gel Chemistry – an Overview[1]

A sol is per definition a colloidal suspension of solid particles in a liquid. A gel is a quasi continuous network of a solid in a liquid, where the gel network can reach a mm to cm size A gel network can be derived from a sol when interactions between the particles become so strong that they merge. These interactions can be covalent bonds, hydrogen bridges, electrostatic attraction or even van der Waals interactions.

1.3.1 Precursors

Inorganic sol-gels can start from various precursors. The most important ones shall be discussed in the following.

Silica: One possibility how silica sol-gels can be synthesized is the use of silica salts like Na_2SiO_3 as precursors. These silicates are compared to other precursors very cheap and are mainly used in industry for the synthesis of silica based sol-gels. The disadvantage is that these precursors are hard to purify, and that precursors based on silicates pose limitations concerning the possibility of modifying the synthesis parameters and thus the properties of the resulting sol-gel network.

Another possibility how silica based sol-gels can be synthesized is the use of alkoxy precursors $Si-(OR)_4$. However, these precursors are expensive and therefore their use on industrial scale is not very common. There are certain advantages alkoxy based precursors offer. They are easy to refine by distillation. The kinetics of the synthesis can be modified by the alkoxy residue, with methanol, ethanol and propanol being mostly used. Based on the fact that silica can form very stable Si-C bonds, there are many variations how precursors can be modified. A simple alkyl chain would make the final network hydrophobic, unsaturated organic residues could be incorporated into an organic polymer, organic residues with amino groups could coordinate metal cations later on, etc. There are numerous examples how precursors can be modified with organic radicals.

Transition metals: As for silica, metal salts like chlorides and nitrates (for example VCl_5) can be used as precursors for sol-gel synthesis. The only way to modify the reactivity or the final structure of the network is the counter ion, so precursors based on metal salts lack the flexibility that alkoxy precursors have. Like for silica, alkoxy precursors are also available for transition metals. Since the coordination number of transition metals is usually larger than their charge, precursors based on transition metals tend to form oligomers in solution. So the degree of oligomerisation is a very important quality criterion for these precursors. Since Me-C bonds of transition metals are not stable there is no way to incorporate organic functionalities by a direct covalent bond. However, alkoxy precursors can be modified when using organic molecules with chelating residues like carboxyles, amines, etc., which form coordinative bonds with the metal centres. However, one has to be aware that these bonds are not as stable as covalent bonds when considering organically modified alkoxides of transition metals. Furthermore, alkoxide precursors are not available for all transition metals and they are much more expensive than metal salts. Examples are $Ti\text{-}(OPr)_4$, $Zr\text{-}(OPr)_4$

1.3.2 Synthesis

The first step in the synthesis of a sol-gel synthesized from alkoxy precursors is the hydrolysis of the alkoxy bond which results in the formation of the corresponding alcohol and a hydroxy group. The resulting hydroxy group can either condense with another hydroxy group or an alkoxy group, thus forming a dimer.

$$Si\text{-}OH + Si\text{-}OR(H) \rightarrow Si\text{-}O\text{-}Si + R(H)\text{-}OH$$

As polycondensation takes place, first a colloids and later on particles are formed. The emerging particles may further grow or aggregate, where the favoured reaction is determined by the reaction conditions. However, the reactivity of the alkoxides strongly varies with the central atom. The hydrolysis of silica alkoxides is very slow at neutral pH, so either bases or acids are needed as catalysts to ensure a reasonable gelation time. The reactivity of transition metals is usually much higher compared to silica precursors, and it depends mainly on the electrophility of the metal centre. Metal centres whose valances are already saturated, e.g., by the formation of alkoxy oligomers, are hydrolysed slower than unsaturated metal centres. Usually it is necessary to add chelating agents to the

reaction mixture in order to slow down the reaction of transition metal alkoxides, otherwise it becomes impossible to control the synthesis.
When referring to acidic conditions, it has to be taken into account that basic or acidic conditions always is related to the pKa of SiOH bonds, so acidic conditions are for silica pH < 2.5. When acids are used as catalysts for the synthesis of silica based sol-gels, the hydrolysis is faster than the condensation and due to the mechanism terminal hydroxy groups condense preferably so the sol-gel grows polymer like. The emerging clusters tend to aggregate when they are very small, this growth mechanism is called reaction limited cluster aggregation.

Under basic conditions the condensation is faster than the hydrolysis. Particle growth is more likely than aggregation of the particles. Under basic conditions particles are also dissolved according to their size (the smaller the faster) and the emerging monomers condense immediately on larger particles. So a sol-gel network derived by basic catalysis is in theory formed by rather large particles with a uniform size. These particles are porous because remaining alkoxy groups react more slowly compared to hydroxy groups, so the particles do not grow evenly. This growth mechanism is called the reaction limited monomer cluster path.

When transition metal salts are used for the synthesis of sol-gels, the first step is the formation of an aquo complex. According to the pH and the cation, also hydroxo and oxo complexes are formed in the solution as well as intermediate complexes. The network is formed by a condensation of these complexes, which can happen by two different mechanisms: either by nucleophilic addition

$$M\text{-}OX + M\text{-}OY \rightarrow M\text{-}OX\text{-}M\text{-}OY$$

or by nucleophilic substitution with M-OX-M + OY as outcome.

These bridges can either be hydroxy groups (Olation) or oxo groups (Oxolation). The pH window where this synthesis leads to a network is very narrow, this synthesis requires usually a very high pH, depending on the metal cation. The anions may also complex and influence therefore the synthesis. Usually the anions are also incorporated in the network.

1.3.3 Ageing Process

Ageing is per definition the time between the formation of the network and the drying process. Since the sol-gel synthesis is mainly a kinetically controlled process, the network contains places with a high surface energy. There are also monomers and oligomers which are not incorporated in the sol-gel network. During the aging process these remaining oligomers condense on the existing network. There is a continuous process of dissolving and condensing during the aging process (Ostwald ripening), so the whole network changes to a formation which is energetically more favourable. This process usually leads to an increased mechanical stability of the network. The ageing process is induced by acidic conditions or by basic conditions with the possibility to additionally increase the temperature to shorten ageing time. In general the specific surface area of the materials decreases during this process.

1.3.4 Drying Process

The drying process is very important in order to preserve the initial network thus leading to an aerogel. The drying process can also lead to a shrunk network, a so called xerogel or to a simple powder. During the drying process first unbound water evaporates. Then the water trapped in the pores starts to evaporate, depending on the pore size. The surface tension of the liquid phase creates capillary forces, also depending on the size of the pores. These forces can exceed the mechanical stability of the network and therefore destroy the initial sol-gel network, leading to a powder. If the network can withstand the capillary forces they force the network to shrink. Remaining hydroxy groups may condense and make this shrinkage permanent, so usually a xerogel is formed when drying a sol-gel. There are several possibilities to preserve the initial network. First the capillary forces can be eliminated by removing water by supercritical fluid extraction. Since the conditions under which a supercritical fluid is formed can be very extreme for most solvents, this approach is only suitable when using supercritical CO_2 to extract water or solvents from the network. The second possibility is to reduce capillary forces and the presence of free hydroxy bonds on the surface of the sol-gel. This can be realised by a derivatisation with trimethylchlorsilane or analogue reagents. The network will shrink

during the drying process, but it will also expand afterwards since no new Si-O-Si bridges can be formed. The same effect can be achieved by using organically modified precursors. This approach is called ambient drying.

1.3.5 Possibilities to Modify the Sol-Gel Network

Porosity is a very important feature of a sol-gel. Pore sizes are classified in three different categories. Micropores range up to 2 nm, mesopores from 2 nm to 50 nm and macropores are larger than 50 nm. Micropores are an immanent feature of most solid materials and emerge because of the linkage of primary building units like tetraeders for silica and aluminium or octaeders in case of titanium. Micropores are mainly influenced by the conditions of the synthesis. Sol-gel networks automatically have mesopores. The solvent used to dilute the reactionary solution is one factor that influences the mesoporosity of the gel network. Additional mesoporosity can be gained by the use of detergents and other bipolar molecules which form micelles in the solution. Here the sol-gel network condenses around these micelles. After the synthesis these porogens have to be removed either by calcination or by extraction. One approach to synthesize macroporous sol-gels is to add organic particles in the desired size of the pores which have to be removed by calcinations. H_2O_2 can also be used as porogen, since its decomposition forms O_2 bubbles around which the network is formed.

Surface polarity is a very important property. There are several possible ways to modify the surface polarity. One approach is to derivatise the existing hydroxy groups with trialkylchlorosilanes or similar reagents. The problem with this approach is that the procedure has to be repeated several times in order to cover a majority of the surface. A second approach is to use alkylated precursors for the synthesis. When using a base catalysed synthesis the alkylated precursors are less reactive than tetraalkoxy precursors, so the surface of the network will automatically show an increased concentration of organic functionalities whereas the core will consist mainly of mechanically more stable pure SiO_2.

1.4 Characterisation Methods[2]

1.4.1 Electron Microscopy

Electron microscopy uses the interaction of an electron beam with a sample for the generation of the signal. There are two important techniques based on this principle, that is, scanning electron microscopy and transmission electron microscopy. The lateral resolution strongly depends on the nature of the evaluated signal and lies between ca. 50 nm for the secondary electron picture of a standard SEM and 0.x nm for the transmitted electrons of a high end TEM. The morphology of materials can thus easily be evaluated with these techniques, although the resolution of SEM may not be sufficient to observe mesopores. Newly developed techniques like the record of stereotopical picture, where two pictures are recorded alternating from slightly different angles and thus allows to visualise the object three dimensional, enable even a spatial resolution, which otherwise is difficult to obtain. The intensity of backscattered electrons mainly depends on the average atomic number, thus giving the possibility to observe microphases with a different average atomic number. The analysis of the X-rays produced allows the determination of the elemental composition of the sample with a resolution in the low µm range for components >0.1 %. The evaluation of X-rays has the restriction that elements with a low atomic number show a very poor sensitivity. Electron energy loss spectroscopy used in conjunction with a TEM has a similar information contents with a better sensitivity for small nuclei and a better lateral resolution.

1.4.2 Atomic Force Microscopy

In atomic force microscopy the attractive or repulsive force between a tip and the surface of a sample is used for the generation of a signal. Since the tip is mounted on a cantilever, the deflection of the cantilever directly correlates with the occurring force. The angle of deflection is usually detected by the reflection of a laser beam on the back of the cantilever. The position of the cantilever is controlled by a small piezo electric crystal. The resolution of this method approaches the atomic level for ideal surfaces. Information that possibly can be gained with atomic force microscopy is for instance the structure of the material on an atomic level with a direct evaluation of pore sizes, surface roughness, etc. Another possibility is the recording of force/distance plots which allow a

determination of the elasticity modules at different domains of the sample. By using chemically surface-modified tips it is even possible to gain information on the hydrophobicity of the sample.

1.4.3 Hg Porosimetry

The basic principle of mercury porosimetry is rather simple. Since mercury is non wetting for most solids, pressure has to be applied in order to force it into the pores of a material to be characterised. Pressures up to 4 kbar can be applied, allowing the analysis of the pore size distribution in the range from 500 μm down to 3.5 nm. Common porosimeters simply apply pressure and record the volume of mercury intruded into the material. Entrapped gas is considered negligible in the evaluation. The data evaluation is very simple. By knowing the surface angle and the surface tension of mercury, the corresponding pore diameter can be calculated from the pressure by a simple mathematically transformation. When a cavity is filled with mercury, the pressure that has to be applied is related to the diameter of the largest entrance to this cavity, so the whole cavity volume appears in the region of the diameter of this entrance. Pore size distributions are therefore always shifted towards smaller diameters compared to microscopic investigation methods. Hysteresis loops in the intrusion / extrusion plot indicate the presence of such cavities, where mercury stays trapped during the extrusion process. The second outcome of mercury porosimetry is information on the bulk density as well as on the skeletal density of the solid material. For a valid result, temperature has to be controlled rigidly and the compressibility of the solid has to be taken into account. Under the assumption of a defined pore geometry even the specific surface area can be calculated.

1.4.4 Adsorption from the Gas Phase

Adsorption experiments form the gas phase are a common approach in the investigation of solid materials. One possibility to apply adsorption from the gas phase as characterization method is the recording of so called adsorption isotherms. In this case the solid is exposed to a gas which is adsorbed on its surface. When the applied pressure is increased, the adsorbed amount also increases, depending on certain properties of the solid, like affinity to the gas, porosity and surface area. The determination of adsorption

isotherms is made at a constant temperature. The usual plot is adsorbed amount vs. applied pressure relative to the vapour pressure at the constant temperature. One possibility to record adsorption isotherms is to make a point by point determination, which means that after a certain pressure is applied the equilibrium is awaited. Another approach are continuous measurements where the isotherm is not recorded at the equilibrium. Here the isotherm strongly depends on the applied mass flow. There are also two approaches in determining the adsorbed amount. In the gas adsorption manometry approach, the adsorbed amount is computed with the difference between the applied pressure and the equilibrium pressure for each point. Here the volume of the sample cavity has to be calibrated before. In the gas adsorption gravimetry technique the adsorbed amount is determined by weighing the sample. Here it is more difficult to ensure a good thermal contact between cooling reservoir and sample. A usual approach to evaluate the obtained isotherms is to apply the so called BET (Brunauer, Emmett, Teller) model for isotherms. This model is a multilayer extension of the Langmiur model. The assumptions made for this model is that the adsorption energy does not depend on the surface coverage and the adsorption takes place layer by layer. Since the affinity of the solid surface for the gas is considered larger than the affinity of an adsorbed layer to the gas, the point where a monolayer is adsorbed should clearly be visible. Together with the required space of one gas molecule when adsorbed (σ), the relative surface area is accessible from the measurement of adsorption isotherms. One has to realise, though, that σ depends on the adsorbent as well as on the temperature, so there is always a certain degree of uncertainty in the determination of the surface area. The occurrence of hysteresis loops in the adsorption/desorption isotherms indicates the presence of mesopores in the solid material, where capillary condensation takes place. By evaluating these hysteresis loops by the so-called BJH evaluation (Barrett, Joyner, Halenda), the size distribution and the volume of these mesopores can be determined. Other data that can be gained by the adsorption from the gas phase is the adsorption enthalpy by using the so called adsorption calorimetry.

1.4.5 Adsorption from the liquid phase

Adsorption experiments with liquids are also applied as investigation methods for solid materials. The simplest way to use adsorption experiments with a liquid is the determination of the immersion enthalpy. Of course there are two different approaches in the measuring setup, one for wetting and another one for non-wetting systems, but the principle is clear. A solid is exposed to the liquid and the change of temperature of the system is measured. With a known c_p (thermal coefficient) for the system the immersion enthalpy can easily be determined. However, this approach gives only the enthalpy for an average interaction between solid and liquid, but an estimation of some properties of the surface can be made with this approach, using solvents with different polarities and functionalities. It is necessary to use absolutely water free solvents for the determination of the immersion enthalpy. When a solid of the same material is available with a known specific surface area, the surface area of a sample can be determined with the assumption that the immersion enthalpy is proportional to the exposed surface area. Other experiments rely on the interaction of already dissolved molecules with the surface of the solid. Surface area estimations can be made with the use of surfactants or dyes that are adsorbed on the solid surface under the condition that the adsorbed layer is monomolecular. When several of these experiments are executed with molecules of different sizes, the pore size distribution can also be estimated (molecular sieving effect). Contrary to the adsorption experiments from the gas phase, molecules with a more specific interaction with the surface are used, so that a chemical characterization can be made. When executing these experiments, one has to consider that the interactions with the surface may strongly rely on the pH or on the amount of already physisorbed solvents, so the experimental conditions have to be controlled rather strictly in order to obtain valid results.

1.4.6 NMR

Nuclear magnetic resonance spectroscopy is a widespread method in chemistry. Due to their quantum structure, certain isotopes have a magnetic spin, which can occupy two or more different quantum states which are without the presence of a magnetic field energetically equal. When applying a magnetic field, these energy levels are no longer equal and it is possible to excite nuclei which occupy the ground state with

electromagnetic radiation. Since the strength of the magnetic field on the place of the nucleus is influenced by the shielding effect of the electronic shell, the difference of the energetic states also depends on it. So NMR offers the possibility to differentiate between nuclei with a different chemical environment (oxidational state, bonded groups). Several nuclei important for the investigation of solid materials are accessible for NMR. ^{29}Si NMR is a very important investigation method for silica derived solid materials. With ^{29}Si NMR it is possible to determine how and to which neighbours (e.g. Si-O-Si, Si-O-Al, Si-OR, Si-OH, Si-R,… a ^{29}Si nucleus is bonded. So it is possible to control if the Si-R bonds remain unaffected by the synthesis conditions, or how many Si-OR groups remain in the network not hydrolysed. The formation of certain intermediates during the synthesis can also be made visible with this method. The ^{1}H NMR is mainly used to determine the acidity of siloxane groups which is a very important factor for catalytic applications of silica derived solids. Of course, physisorbed water has to be removed previously, since the ^{1}H signals of water would conceal the ^{1}H signals of siloxane groups. ^{13}C NMR may be important to determine if a calcination process has been successful or if introduced organic sidegroups remain unaffected by synthesis. In general, NMR is a very useful tool for the analysis of solid materials.

1.4.7 Chromatography

Chromatography can also be applied as investigation method for solid materials by using them as stationary phase. Since the process of chromatography relies on the interaction of molecules with a stationary phase which can be a solid, it can be applied to investigate solids. In gas chromatography the mobile phase is a gas, usually He or N_2. Of course only volatile analytes are accessible to gas chromatography. The retention of the analytes is mainly based on their volatility and their interaction with the surface, the mobile phase is considered as inert. When applying different analytes with specific functionalities, the polarity of the surface as well as the strength of different interactions can be determined with gas chromatography. However, this method is limited by the volatility of the analytes, very polar or even ionic analytes cannot be used for the characterization of solid materials with GC.

In liquid chromatography the retention of an analyte is determined by its interaction with the stationary phase as well as with the mobile phase. Even polar or charged molecules

can be separated with this analytical method, so more different interactions of the surface with probe molecules can be investigated. So the retention time depends on the interaction of the stationary phase with the analyte molecules (the stronger the interaction the longer the retention time) and the interaction of the analyte molecules with the mobile phase (the better the solubility of the analytes in the mobile phase, the shorter the retention time). So the retention time reflects the distributional coefficient of the analyte molecule between the stationary and the mobile phase. However there are certain restrictions of this method considering the solid sample. The specific flow resistance of the investigated solid must not be too high so that the column can be made long enough for a considerable retention of the selected analytes. Furthermore, the solid used as stationary phase must not be compressible. A last possibility is the use of size exclusion chromatography for the characterization of porous solids. In size exclusion chromatography the retention of the analytes does not rely on interactions with the solid phase or the liquid phase but rather on the total accessible volume these analytes can enter within the solid phase. With a mixture of differently sized analytes the pore size distribution can be estimated with this method. [3]

1.5 Applications of Silica based Sol-gel Materials in Analytical Chemistry

1.5.1 Chemical sensors

A chemical sensor is defined as an independent platform for the determination of a specific parameter which either employs a chemical for the detection of a certain parameter or the detected parameter itself is the presence of a specific molecule. In general, the presence of an analyte generates a detectable signal. The generated signal can be of optical or electrical nature. One way to use sol-gel materials for sensor construction is as pure enrichment phases for the analyte molecules. In this case the enrichment phase has to be selective to reduce crosstalk, which is a frequently occurring problem in sensor technology. The second possibility how sol-gel derived layers can be exploited is their use as host matrix for probe molecules which interact specific with the analyte molecule. These could be enzymes which react with the analyte molecule or dyes which change their optical features in the presence of the analyte. In both cases the pore structure of the

layer plays a very important role since it determines the diffusion paths and therefore the response time of the sensor as well as the occurrence of bleeding of guest molecules since they are in most cases not covalently linked to the host matrix.

One feature of silica based sol-gel materials which makes them suitable for optical sensors is their optical transparency ranging from the UV (above 200 nm) up to the mid IR. This is of vital importance for an optical sensor which generates a change in its optical properties in the presence of the analyte. This could be either a change of absorption, fluorescence or even the refractive index of the sensor layer. Bleeding has always been the problem when using dyes as probe molecules, but it can be overcome by using organically modified precursors which lead to a more hydrophobic network where dyes are adsorbed more efficiently or by covalently linking the dyes to the network. Enzymes are also used in the field of optical sensors as selective molecules. One approach is for instance to use glucose oxidase for the analysis of glucose.[4,5] Cholinesterase has been applied for the detection of organophosphorus biosensors with a change of fluorescence as detected signal.[6] Another example is the use of an antibody as selective molecule which has been done in the case of isoproturon as analyte.[7] A sensor for halogen anions has been developed with the use of a fluorescent probe molecule: The halogenides are quenching the fluorescence of the probe molecule.[8] Simple pH indicating dyes can also be incorporated in a sol-gel network in order to fabricate optical pH sensors.[9] Another possibility is to employ the formation of a complex as specific reaction as was done for NO_2 where a Ru complex has been incorporated in a sol-gel matrix.[10] The simplest possibility is to generate a hydrophobic sol-gel coating where apolar gaseous analytes are adsorbed and to use the change of the refractive index as optical signal. [11]

Amperometric sensors detect the current generated by a chemical reaction as signal. Since the generated current has to be transported to an electrode, the sol-gel matrix has to be conducting. This is either achieved by using vanadium based networks or by incorporating conducting particles (mainly carbon or gold) into a non-conducting sol-gel network. Based on this principle, glucose sensors have been developed, using the enzyme glucoseoxidase which oxidizes glucose in the presence of oxygen.[12,13] Other enzymes

which perform redox reactions can also be used and enable an amperometric detection of organic and inorganic peroxides[14] or of phenols.[15]

1.5.2 SPME

Solid phase micro extraction is a recently developed sample preparation technique which allows the enrichment and the desorption of analyte molecules without the use of further solvents.[16,17] In SPME an enrichment layer on a fused silica fibre is used which adsorbs analytes from the gas or the liquid phase. In GC the desorption is achieved thermally in the heated injector block, in HPLC the desorption is achieved by flushing the fibre with a small solvent volume on line directly to the separation column. Usually PDMS coatings or carboxen/PDMS coatings are used. Sol-gel chemistry offers the possibility of synthesising coatings with enhanced thermal stability and solvent resistance. With the use of organically modified precursors the polarity of the fibre can be adjusted to the requirements. An increased coating thickness can also be achieved, leading to an increased capacity of the fibre. However, an optimised porosity is again essential for reasonable equilibrium times.[18,19]

1.5.3 GC

Conventional capillary GC columns have polymer coatings which may, from the physico-chemical point of view, be classifed as liquids. However, there is always the problem that these columns are bleeding and have a limited temperature stability. Therefore the deactivation of the remaining silanol groups of the capillary wall may also decrease with time with the result of asymmetric peaks for polar molecules. Sol-gel chemistry can be even performed in a capillary column thus allowing to employ the advantage of sol-gel derived coatings for gas chromatography. Although the used coatings are mainly based on silica derived materials, the synthesis parameters can be adjusted to completely remove silanol groups. In addition, the synthesis can be performed in one step.[20] Polar organic molecules like crown ethers can for instance be incorporated and allow excellent peak shapes for polar molecules.[21]

1.5.4 HPLC

Commonly used packed columns use particulates in the low µm range as stationary phase for separation. A great disadvantage of these columns is that the plate numbers, which determine the separation performance, depend on the particle size as does the specific flow resistance. So packed columns a high amount of plate numbers require small particles and have therfore a high specific flow resistance. These columns do not allow a high flow of the mobile phase in order to not exceed the pressure limitation of the instrument. Considering monolithic columns the plate number is determined by the thickness of the skeletal structure, whereas the backpressure of the system is determined by the pore structure. Both features can be modified independently with sol-gel chemistry, allowing high performance columns which can be operated at a high flow of the mobile phase, and thus reducing the runtime without significantly reducing the separation efficiency. For these reasons recent developments focus on the synthesis of monolithic separation columns. The macroporous structure can either be achieved by adding polymers like PEG to the reaction solution[30,31,32,35,36] as well as by adding H_2O_2 which decomposes to O_2 during the synthesis.[28] The separation efficiency of monolithic columns is usually comparable with commonly used packed columns as has been shown in several publications.[22,26,27] Flow rates up to 9 ml/min have been achieved with monolithic columns.[32,24,25] Another possibility is to perform capillary LC, either in the form of open-tubular LC where the wall coating is sol-gel derived or with a capillary that is filled with a monolithic material.[29,33,34]

1.5.5 Electrophoresis and Electrochromatography

In capillary electrophoresis and electrochromatography the flow of the mobile phase is not achieved by pressure but by electroosmotic flow. Both techniques are performed in a capillary. In case of capillary electrophoresis the separation of molecules is achieved by their different electroosmotic mobility. The analytes that can be separated with this technique have to be charged. A common problem in capillary electrophoresis is the adsorption of proteins and other molecules with basic functionalities on the silanol groups of the capillary surface. One way how sol-gel chemistry is applied in the field of electrophoresis is the coating of the capillary with organically modified precursors. This method is preferable since it can be performed in one step. Usually this procedure

decreases the affinity of the surface for molecules with basic functionalities, but one has to consider that the electroosmotic flow is also modified. Sometimes it is desired to modify the electroosmotic flow or even to reverse it.[37,38] In electrochromatography the separation is like at HPLC achieved by the interaction of analytes with a stationary phase, whereas the necessary flow of the mobile phase results from a gradient of the electric potential instead of a pressure gradient. Sol-gel derived materials are used as modifiers for the electroosmotical flow as well as for the synthesis of a separation phase which can be either a coating[39,40,42,45,46] or a monolith.[44] These monoliths may also be synthesized from particles which are linked with a sol-gel network.[41,43]

1.5.6 Analytical Techniques based on Immunoaffinity

Immunoaffinity is the summary of all methods which rely on the interaction of an antigen (=analyte) with an antibody. Applied techniques in analytical chemistry are immunoassays, immunoaffinity extraction and immunochromatography. Biomolecules tolerate only a small variance from their natural environment (T, pH, solvent concentration) in order to maintain their natural conformation and therefore their functionality. If the deviation from these conditions is too large, this change in conformation might become irreversible. Sol-gel chemistry is one possibility to achieve the immobilization without damaging the biomolecules irreversibly since it can be carried out under very mild conditions. Since the molecules are not only physisorbed on a surface but in fact entrapped in cages in the network, bleeding should not occur. Physisorbed molecules can be removed by a washing step. Several investigations have shown that the encaging of these biomolecules preserves their natural conformation and makes them more tolerant towards temperature and solvents. These advantages have lead to a widespread use of sol-gel chemistry in the field of immunoaffinity techniques.[47]

Immunoassays offer fast, semi-quantitative analysis. The detection of an analyte is very specific with a very low detection limit. This technique offers a possibility for the screening of a large number of samples. Immunoassays are usually not regenerable. Immunoassays which use sol-gel materials as hosts for the biomolecules have been so far developed for atrazines[48] and trinitrotoluene.[49] These immunoassays are also not regenerable but they offer an improved storability.

Solid phase extraction is a very common method for sample cleanup and the preconcentration of analytes. With the incorporation of antigens an almost specific preconcentration of analytes is possible, although the sol-gel matrix and the cartridge may show low unspecific retention. This technique is mainly used in environmental analysis, where the matrix of a sample may cause problems and the analyte concentrations are usually very low. For the desorption the antibody has to change its conformation to decrease the specific retention for the analyte. Since antibodies can be very expensive, a reversible change of conformation is desired. Since the sol-gel network stabilizes the antibody, it is possible to regenerate immunoaffinity extraction columns without significant loss of activity. Immunoaffinity-extraction columns for PAHs[50,51,52] , nitroaromatic compounds[53,54], atrazine[55], triazine and phenylurea derivates[56,57,58] have been developed for environmental analysis.

Immunochromatography uses the antigen-antibody affinity for the specific retention for a specific analyte. It may be considered as further development of immunoaffinity SPE. Since the adsorption has a slow kinetics, the flow of the mobile phase through the column has to be kept low. The peaks tend to be very broad because the biomolecules do not allow a high concentration of solvent and the desorption is also a slow process. Therefore immunoaffinity columns are often used as precolumns for a conventional HPLC. [59,60,61]

2) Experimental Section

2.1 Investigated Materials

The investigated sol-gel materials were specially synthesized for the subsequent characterisation experiments. The synthesis is based on using either tetraalkoxysilanes or trialkoxysilanes with one different functionality (= organically modified precursors). The organically modified silanes ("ormosils") used in this work were carrying either methyl, octyl or 3-aminopropyl functionalities. For some materials tetraalkoxy silanes were additionally used as educts for the synthesis. The alkoxy residues were either methothoxy or ethoxy groups. To allow a mixing of the hydrophobic silica precursors with the catalyst in water necessary for the hydrolysis, a solvent is required Ist die Funktion des Lösungsmittels wirklich die, gegenseitige Löslichkeit herzustellen, oder nicht eher die eines Porogens ?. Methanol, ethanol and isopropanol were used for the synthesis of the investigated materials. Aqueous 3 N NaOH was used as catalyst.. To achieve a macroporous structure for the sol-gels, 30% H_2O_2 was added simultaneously with the NaOH. The mechanism of the synthesis has not been elucidated yet. However, it seems that gas formation is essential , since it can be seen that the peroxide decays during the reaction and forms oxygen bubbles. The materials were further aged under basic conditions in 1 M NH_4OH at 57°C and finally dried at 110°C. The aging initiates structural changes and terminates the condensation. It is an absolutely essential procedure to improve the mechanical stability of the monolithic materials. The detailed composition of the starting materials for the synthesis of the sol-gel materials is given in Table 2.1.1.

Sol Gel Materials					
No.	**Substance Name**	**Si-Precursor**	**Solvent**	**3N NaOH**	**30% H_2O_2**
1	MTMOS/MeOH	10 ml MTMOS	10 ml MeOH	500 µl	10 ml
2	ETEOS/MeOH	10 ml ETEOS	10 ml MeOH	500 µl	10 ml
3	MTMOS/iPrOH 0.5	10 ml MTMOS	10 ml i-PrOH	500 µl	10 ml
4	MTMOS/iPrOH 1.0	10 ml MTMOS	10 ml i-PrOH	1000 µl	10 ml
5	10% C8-TEOS	3,6 ml MTMOS + 0,4 ml C8-TMOS	4 ml MeOH	200 µl	4 ml
6	10% APTES	12 ml MTMOS + 1,5 ml 3-Aminopropyl TEOS	14 ml MeOH	700 µl	14 ml
7	MTEOS/TEOS	5 ml MTEOS + 5 ml TEOS	10 ml i-PrOH	500 µl	10 ml
8	MTMOS/TMOS	5 ml MTMOS + 5 ml TMOS	10 ml i-PrOH	500 µl	10 ml

Tab. 2.1.1 Composition of the reaction mixtures for the synthesis of the investigated sol-gel materials

Substances 1, 3, and 4 form monolithic, macroporous materials.

The reactionmixture of substance 2 did not become homogenous. However, after 1.5 h, were formed in the solution (without visible macroporosity), so this material was not investigated further.
The reaction mixtures of substances 5 and 6 were homogenous, but no monoliths were produced under these conditions but instead porous particles.

Substances 7 and 8 formed a sol-gel within 2 minutes. The formed monoliths were transparent without visible macroporosity.

For the purpose of a better comparison several SPE materials and polymers were investigated together with the sol-gel materials. These were:

C8 Spe-Ed (Applied Separations) }
C18 Spe-Ed (Applied Separations) } silica-based SPE materials
LiChrolut (Merck) } polymeric SPE material

Carboxylated PVC (Scientific Polymer Products Inc.)
Polyacrylicacid (Scientific Polymer Products Inc.)
Polyethylene / 5% Polyacrylicacid Copolymer(Scientific Polymer Products Inc.)

The most important physical properties of the synthesised sol-gel materials as well as of the commercial SPE and polymer materials are given in Table 2.1.2 where known.These measurements were carried out by Michael Sulyok in the skope of his Ph.D. thesis.[62]

Physical Properties				
Substance	**Specific Surface (with N_2 BET) m^2/g**	**Density (g/cm^3)**	**BJH Pore diameter**	**REM pore diameter**
MTMOS/MeOH	11.36	0.211	5.7 nm	0.69 µm
MTMOS/iPrOH 0.5	293.06	0.254	4.2 nm	0.41 µm
MTMOS/iPrOH 1.0	206.00	0.213	3.5 nm	0.71 µm
10% C8-TEOS	0.59	0.276		0.83 µm
10% 3-APrTEOS	201.21	0.198	6.5 nm	0.69 µm
MTEOS/TEOS				
MTMOS/TMOS	556.16		8.8 nm	
C8 Spe-Ed				
C18 Spe-Ed				
LiChrolut				
Carboxylated PVC		1.40		
Polyacrylicacid		1.23		
Polyethylene / 5% Polyacrylicacid Copolymer		0.91		

Tab 2.1.2 Physical properties of the investigated materials where available.

2.2 Immersion Experiments

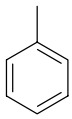
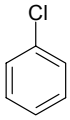
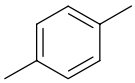
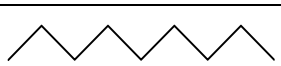
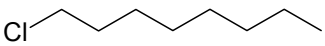
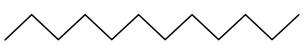
Before starting with the investigation of the substrates, the immersion behaviour had to be tested. The chosen material for this purpose was a monolithic MTMOS/MeOH. This monolith had a bulk density of 0.211 g cm^{-3} and it was found to be hydrophobic. When simply immersing it into a water filled beaker, it would float on the surface. In the next attempt, the monolith was immersed in water by placing a weight on top of it. After one week the monolith was investigated and only the outermost mm of the material proved to be wetted. After that the decision was made to grain all monoliths to a fine powder. By this approach the time needed for wetting could be reduced to a maximum of 2 hours which was in our opinion acceptable.

2.3 Measurement of Analyte Profiles by SPME/GC

The general idea behind all measurements was to bring the substrates into contact with a solution, which is spiked with test analytes. These analytes would be adsorbed on the immersed substrates, and as a consequence their concentration in the liquid phase would decrease. The affinity of the substrates to certain analytes would reveal some of their chemical properties. By determining the concentration of the test analytes in the liquid phase, the adsorption process could be made observable. For the analysis of the more volatile test analytes, gas chromatography was chosen as analysis method. Sampling and enrichment of the test analytes was performed by solid-phase microextraction (SPME) from the headspace above the suspension of the sol-gel materials in the solution fortified with the analytes. According to theory[17], there should be an equilibrium between the gas phase and the liquid phase related to the volatility of the compound. As there should also be an equilibrium between the SPME fibre and the gas phase, the concentration measured with the SPME fibre is related to the concentration of the analytes in the liquid phase.

2.3.1 Test Analytes

A variety of apolar test analytes was chosen. Their enrichment on the hydrophobic solid phase should be sufficient to observe a decrease of the analyte concentration in solution. Standards with analyte concentrations of 10 mg/g, 0.1 mg/g were prepared in MeOH, the standard with a concentration of 1 µg/g each analyte was prepared in water.

Physical Properties				
Name	**Structure**	**Bp (°C)**	**logKow**	**Water Solubility (mg/l)**
Toluene		110.6	2.73	526
Chlorobenzene		131.7	2.84	498
p-Xylene		138.3	3.15	162
N-Nonane		150.8	4.76	220
1-Chlorooctane		181.5	4.52	4.89
N-Dodecane		216.3	6.10	0.0037

Tab. 2.3.1 Physical properties of the test analytes investigated with SPME/GC

2.3.2 Experimental Setup

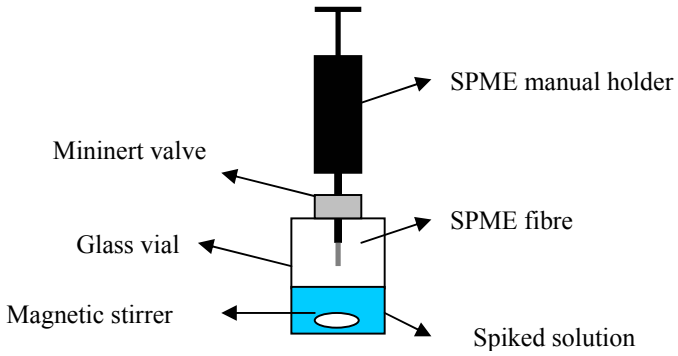


Fig. 2.3.1 Sketch of the experimental setup applied for SPME-GC

A 40 ml screw-cap vial was filled with ca. 18 ml water (exact volumes were obtained by measuring the weight. Then the solid material to be investigated was added. The mixture was stirred magnetically until the solid was suspended evenly. After spiking the solution with a final analyte concentration of 0.5 ppm, the vial was immediately closed with a Mininert valve to prevent a loss of the volatile analytes. The sample mixture was stirred magnetically during the whole process. The extraction was made with a CX/PDMS fibre for 20 minutes at room temperature. After extraction, the fibre was injected manually in the GC injection port.

SPME: Supelco SPME fibre assembly for manual holder, 75 µm Carboxen/PDMS coating, Supelco SPME holder (manual)

GC: HP 5890 Series II
Column: 2x J&W DB5HT 30 m x 0.25 mm x 0.1 µm
Gas flow (He):1 ml/min at 35°C, constant pressure
Injector temperature: 250 °C

MS: HP 59827 A

Source temperature: 200°C

Quad temperature: 100°C

Injection: splitless

Scan range: 30-400, 0.8 s/scan

HED/EI mode, no solvent delay

FID: supplied with the HP 5890 II GC

N_2: 3.05 bar; H_2: 1.1 bar; synth. air: 2.0 bar

Injection: split 1:10

Temperature program for MS and FID measurements: 35°C (5 min), then with 20°C/min to 250°C, hold for 4.25 min (total run time: 20 min)

Retention times (FID)	
Analyte	**RT (min)**
MeOH	1.073
Toluene	2.309
Chlorobenzene	3.645
p-Xylene	4.352
N-Nonane	5.491
1-Chlorooctane	8.060
N-Dodecane	9.577

Tab 2.3.2 Retention of the used analytes under given experimental conditions

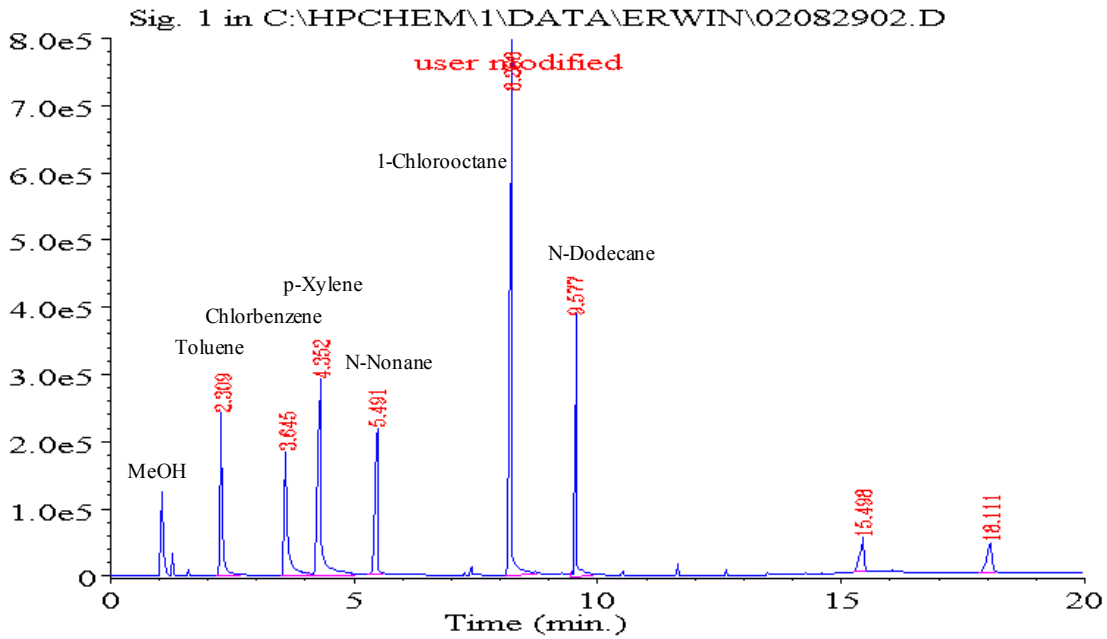


Fig. 2.3.2-2 Typical FID-chromatogram of the test analytes, 0.5 ppm analyte concentration in solution. The peaks at RT 15.498 min and 18.111 min do not belong to the standard.

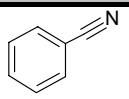
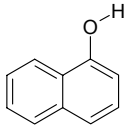
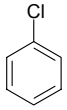
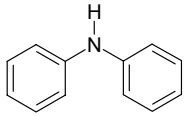
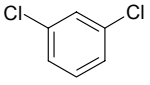
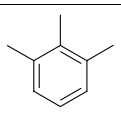
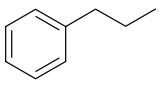
2.4 Measurement of Enrichment Profiles of Substituted Aromatic Compounds by HPLC-DAD

The next step in our experiments was to measure the concentration of the analytes directly in the solution to avoid problems caused by the previous setup as discussed in chapter 3.5. Furthermore, the time resolution of the SPME method is insufficient to observe the extraction kinetics. The direct measurement of the analyte concentration in solution allows to take samples at any deliberate moment. However, to stop the extraction process, the solid particles have to be removed from the spiked solution. Since the concentration in the liquid phase should be directly determined, it was necessary to use HPLC instead of GC, because the injection of aqueous samples would damage the GC columns. For the following measurements nylon syringe filters with 13 mm diameter and

0.2 µm pore size were chosen to remove the solid particles and additionally to protect the HPLC column. The nylon material should show little affinity towards apolar analytes.

2.4.1 Model Analytes

The use of HPLC with diode array detection which measures the absorption spectra of the analytes in the UV-VIS range, restricted the range of analytes to (UV absorbing) aromatic compounds. The following table 2.4.1 lists the analytes that were finally used to investigate the sol-gel materials. Other aromatic compounds had to be removed from the initial set of compounds to achieve a baseline separation for all peaks. Standards with the concentrations of 10 mg/g, 1 mg/g and 0.1 mg/g each analyte were prepared in acetonitrile.

Physical Properties				
Name	**Structure**	**Bp (°C)**	**logKow**	**Water Solubility (mg/l)**
Benzonitrile		191.1	1.56	2000
1-Naphthol		288	2.85	866
Chlorobenzene		131.7	2.84	498
Diphenylamine		302	3.5	53
1,3-Dichlorobenzene		173	3.53	125
1,2,3-Trimethylbenzene		176.1	3.66	75.2
N-Proplybenzene		159.2	3.69	52.2

Tab. 2.4.1 Physical properties of the selected model analytes

2.4.2 Experimental Setup

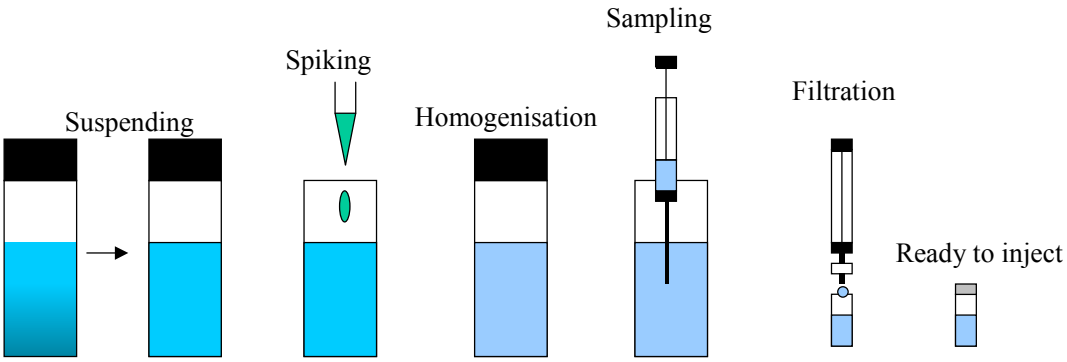


Fig. 2.4.1 Sketch of the applied sample preparation procedure

The grained, powdery substances were weighed into 40 ml glass vials and then suspended with a magnetic stirrer in approximately 20 ml water. After the particles were evenly suspended, which took up to 1.5 hours, the solution was spiked with a mixed standard. 1 ml samples were taken with a 2.5 ml luer-lock syringe at defined times after spiking. These samples were immediately thereafter filtered with nylon syringe filters into HPLC vials and were then ready to inject.

Syringe filters: SGE, Nylon, 13 mm diameter, 0.2 µm pore size

HPLC: HP 1090 Series II

Column:	Kromasil 100-5C18 15 cm x 4mm, 5 µm particle size
Temperature:	35 °C
Flow:	1 ml/min
Injection Volume:	20 µl

HPLC Separation	
Time (min)	**%ACN**
0-1	50
1-11	50-80 (Gradient)
11-13	80
13-15	80-50 (Gradient)

Tab. 2.4.2 Acetonitrile/water gradient of the HPLC separation

UV/VIS Detection: integrated diode array detector

Measurement: 200 nm / 16 nm BW

Reference: 400 nm / 40 nm BW

Retention Times	
Analyte	**RT (min)**
Benzonitrile	4.239
1-Naphthol	4.800
Chlorbenzene	7.223
Diphenylamine	7.864
1,3 Dichlorbenzene	9.332
1,2,3 Trimethylbenzene	9.860
N-Proplybenzene	10.300

Tab. 2.4.3 Retention times of the model analytes under the given experimental conditions for substituted aromatic compounds.

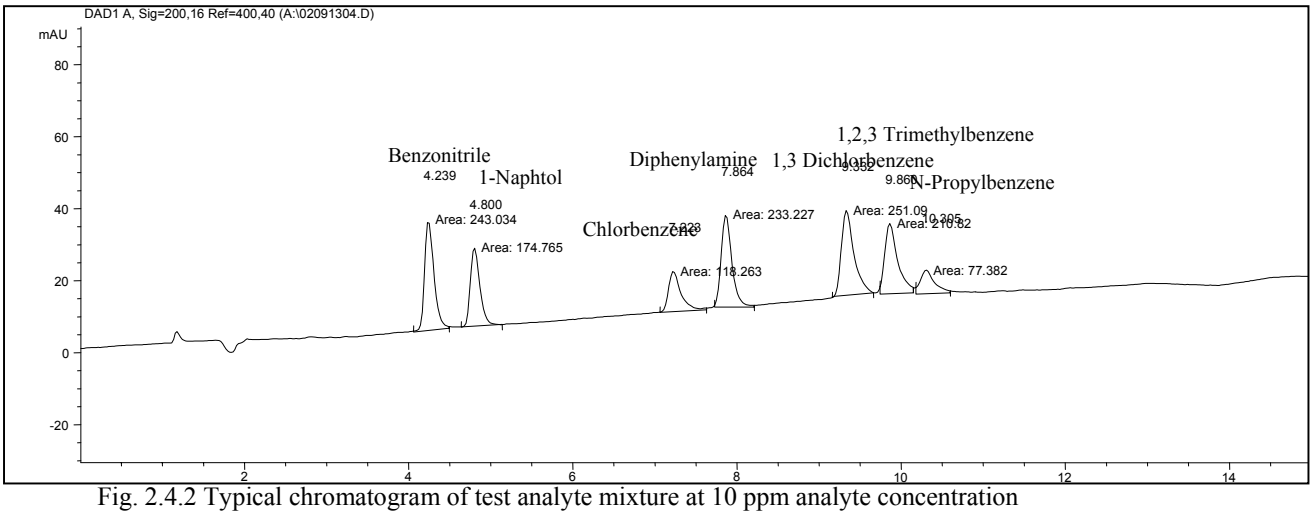
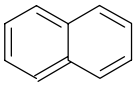
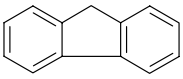
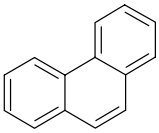
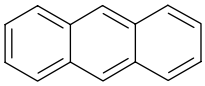
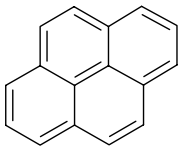
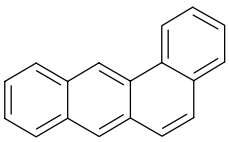


Fig. 2.4.2 Typical chromatogram of test analyte mixture at 10 ppm analyte concentration

2.5 Measurement of Enrichment Profiles by HPLC/DAD of Polycyclic Aromatic Hydrocarbons (PAHs)

2.5.1 Model Analytes

The selection of test analytes was done with the intention to cover a representative range of two-, three- and four-ring systems, but also with respect to avoiding problems with their chromatographic separation. To this aim, test chromatograms in the Agilent supply materials and consumables catalogue were considered. A second consideration in the selection of compounds was that higher PAHs (more than four condensed rings) would not only be very expensive but also lead to very long HPLC runs. The additional information would probably be poor in comparison to the additional costs and the additional time consumption. The PAHs have in general a poor solubility, so the first stock solution had a concentration of only 1 mg/g and was prepared in acetone, the final standard had a concentration of 0.1 mg/g for each analyte and was prepared in acetonitrile.

Physical Properties				
	Structure	**Bp (°C)**	**pKow**	**Water Solubility (mg/l)**
Naphthalene		217.9	3.30	31
Fluorene		295.0	4,18	1.89
Phenanthrene		340.0	4.46	1.15
Anthracene		339.9	4,45	0.0434
Pyrene		404.0	4,88	0.135
Chrysene		448.0	5.81	0.002

Tab. 2.5.1 Pysical properties of the used model analytes

2.5.2 Experimental Setup

The experimental setup was the same as described in chapter 2.4 for enrichment profiles of substituted aromatic compounds. Since the previously used nylon filters showed little recovery for the PAHs (as discussed in chapter 3.3), a change of the filter type was decided. Also, a modified gradient was used for the separation.

Syringe filters: Agilent, Regenerated Cellulose, Housing: Polypropylene, 0.2 µm pore size, 13 mm disc diameter

HPLC: HP 1090 Series II

Column: Kromasil 100-5C18 15 cm x 4mm, 5 µm particle size

Temperature: 35 °C

Flow: 1 ml/min

Injection Volume: 20 µl

HPLC Separation	
Time (min)	**%ACN**
0-1	60
1-11	60-100
11-13	100
13-15	100-60

Tab. 2.5.2 Acetonitrile/water gradient of the HPLC separation for PAHs.

UV/VIS Detection: integrated diodearray detector

Due to different absorption maxima of the PAHs, chromatograms were recorded at two different wavelengths to achieve a similar sensitivity for all analytes.

Measurement: 200 nm / 16 nm BW

254 nm / 16 nm BW

Reference: 400 nm / 40 nm BW

Detection		
	RT (min)	**Wavelength**
Naphthalene	7.532	200 nm
Fluorene	9.229	200 nm
Phenanthrene	9.715	254 nm
Anthracene	10.073	254 nm
Pyrene	11.276	200 nm
Chrysene	12.051	254 nm

Tab. 2.5.3 Retention times and detection wavelengths of the model analytes

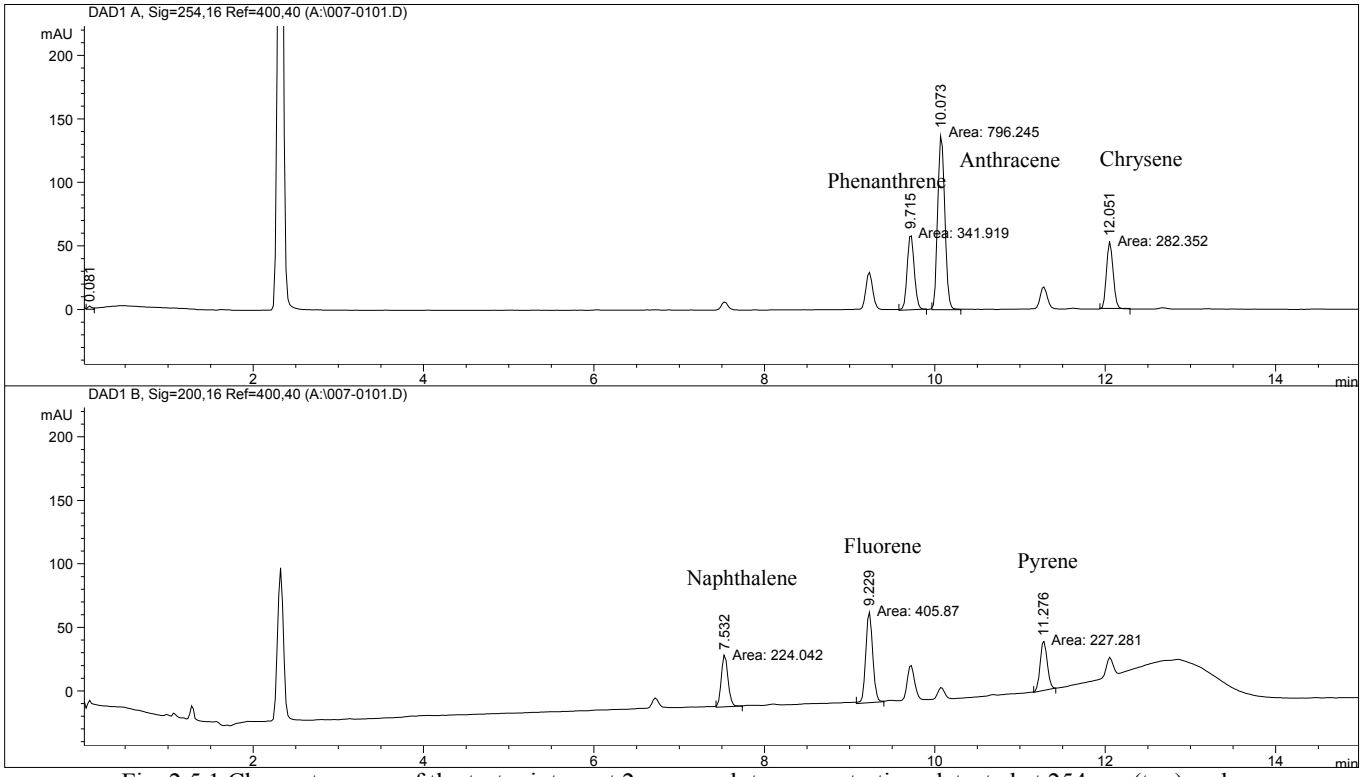


Fig. 2.5.1 Chromatograms of the test mixture at 2 ppm analyte concentration, detected at 254 nm (top) and 200 nm (bottom).

2.6 Desorption Studies

2.6.1 Model Analytes

For these studies, the same set of substituted aromatic compounds and PAHs as described in chapter 2.4.1 and 2.5.1 was investigated. The $4*10^{-4}$ g/g standard was prepared in acetone. The $4*10^{-6}$ g/g calibration standard was prepared in n-hexane.

2.6.2 Experimental Setup

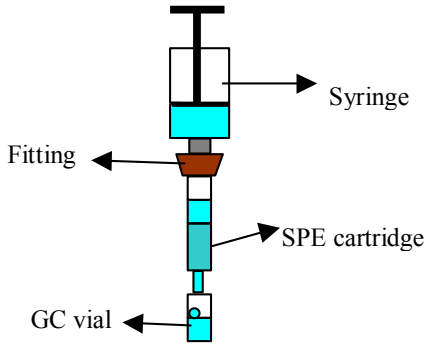


Fig. 2.6.1 Sketch of the experimental setup used for the determination of desorption efficiency

The sample solutions were prepared by spiking water with the $4*10^{-4}$ g/g standard to produce a final analyte concentration of $2*10^{-6}$ g/g in the test solution. For the adsorption, 10 ml of spiked solution were filled into a glass syringe and then pressed through the SPE cartridges manually with the help of a gas tight syringe adapter. Then the cartridges were blown dry. To determine the amount of analytes that was not extracted by the investigated materials in the first step, the percolate of the first extraction was applied to 0.2 g LiChrolut SPE cartridges. These cartridges were then eluted and analysed as the other SPE cartridges which allowed to assess whether breakthrough occurs for the different analytes and SPE materials and if yes, to what extent. For the desorption n-hexane was used, since this solvent is also used in environmental analyis for the desorption of PAHs and it will also be suited for the desorption of hydrophobic analytes. The extract was collected in GC vials and then directly injected without further preconcentration step. To determine the recoveries, the volume of the extract was determined indirectly from its weight and its density at room temperature. The absolute amount of substance was determined then from the extract concentration and volume.

To determine the optimal volume for the elution of the analytes, three elution steps were made with approximately 1.5 ml n-hexane each for MTMOS/MeOH and the 0.2g LiChrolut cartridges which were used for the determination of breakthrough. The analyte

concentrations in the second and third fraction were less than 5% compared to the first fraction for both materials, so one elution step with 1.5 ml n-hexane was considered as sufficient for the following measurements. The desorption experiments were made in triplicate, each time using a new cartridge. It was tried to obtain a constant flow of approximately 2 ml/min for all adsorption and desorption experiments

GC-MS Analysis

GC:	HP 5890 Series II
Column:	2x J&W DB5HT 30 m x 0.25 mm x 0.1 µm
Gas flow (He):	1 ml/min at 35°C, constant pressure
Injector temperature:	300 °C
Injection:	splitless

Temperature program:
The temperature program was optimised step-wise with the $4*10^{-4}$ g/g standard. The final parameters were 35 °C start temperature for three minutes, then 10 °C/ min ramp to 280 °C then hold for 2.5 min given a total run time of 30 min.

MS: HP 59827 A

Source temperature:	200°C
Quad temperature:	100°C
Scan range:	30-400, 0.8 s/scan

HED/EI mode, solvent delay 2 min

To assign the chromatographic peaks to the test compounds, the $4*10^{-4}$ g/g standard was measured in the scan mode. The dominant ions of all analytes were also determined with the GC-MS operated in the scan mode. After that the MS measurements were made in the selected ion monitoring (SIM) mode, since the detection limit can be decreased by at least one order of magnitude compared to the scan mode.

Analyte	Retention time (min)	Selected Ions (Amu)	SIM Mode: Time Window (min)	SIM Mode: Monitored Mases (Amu)
Chlorobenzene	3.60	112, 77	2 - 4.5	112, 77
Propylbenzene	5.52	120, 91	4.5 - 6	120, 91
Benzonitrile	6.12	103	6 - 8.5	103, 146, 105
1,3 Dichlorobenzene	6.40	146		
1,2,3 Trimethylbenzene	6.71	105		
Naphthalene	9.31	128	8.5 - 13	128
1-Naphthol	14.19	144	13 – 15.5	144, 166, 169
Fluorene	14.55	166		
Diphenylamine	15.21	169		
Phenanthrene	16.68	178, 152	15.5 - 19	178, 152
Anthracene	16.80	178, 152		
Pyrene	19.85	202	19 - 21.5	202
Chrysene	23.12	228	21.5 - 25	228

Tab. 2.6.2: Parameters of the measurements executed in the SIM mode and retention times of the selected model analytes

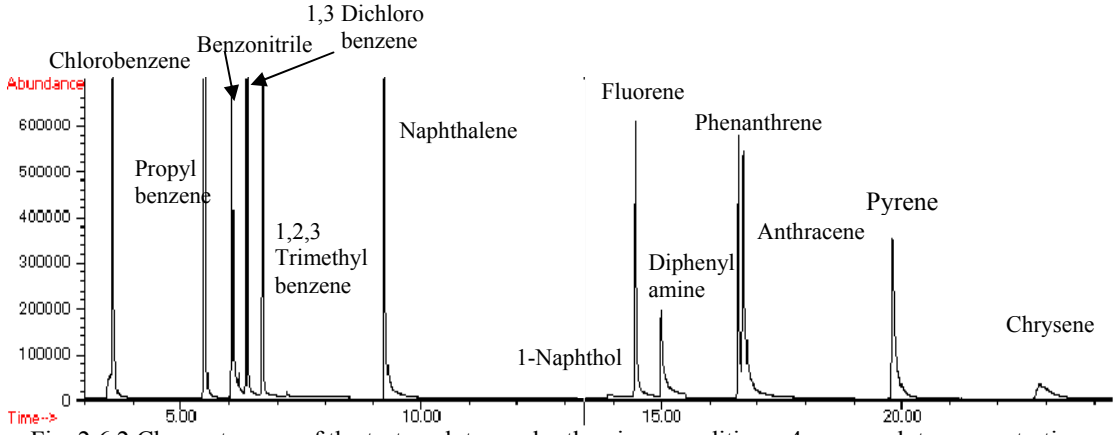


Fig. 2.6.2 Chromatogram of the test analytes under the given conditions, 4 ppm analyte concentration

2.7 Data Evaluation

2.7.1 Evaluation of the SPME-GC and HPLC-DAD Experiments

The peaks were evaluated by their area. The chromatograms were integrated with the HP Chemstation software. The resulting peak areas had to be divided by the concentration of the analytes (computed with the weights of the aqueous solution and the spiked standard) to receive the so-called specific peak area. This is necessary to be able to compare the results of different experiments within a series.

Specific PA= PA / analyte mass (1)

The specific peak areas of the measurements with a suspended solid were normalized by dividing them by the specific peak areas of a spiked solution without a suspended solid (= reference). This operation leads to the so-called normalized peak area.

Normalised PA = specific PA (sample) / specific PA (reference) (2)

All concentrations refer to the solution. That means, that for a material with a high affinity for the analytes, a low concentration of these compounds was observed in the solution and vice versa

2.7.2 Evaluation of the Desorption Experments

The relative sensitivity of the GC-MS measurements is obtained by dividing the peak area of the calibration solution with the computed concentration.

Relative Sensitivity [counts*s/(g/g)] = Peak Area (standard)/Concentration (standard) (3)

The concentration of the extracts is obtained by dividing the relative sensitivity with the peak area of the extracts.

Concentration (extract) [g/g] = Peak Area (extract) / Relative Sensitivity (4)

The eluted amount of analyte can be determined with the concentration and the weight of the extract.

Mass (analyte) [g] = Concentration (analyte) * Mass (extract) (5)

The recovery rates can be determined from the used and the recovered amount of analyte.

Recovery Rate = Analyte Mass (extract) / Analyte Mass (spiked solution) (6)

Finally the mean and the standard deviation of the three experiments were calculated.

3)Results

3.1 Extraction Profiles by SPME-GC

3.1.1 Preliminary Experiments

In preliminary experiments the tightness of the used Mininert valves and screwcaps was checked. All used vessels proved to be tight. The suspended amount of sample was found suitable with 0.2 g in 20 ml of water, the analyte concentration was 0.5 ppm each analyte. The next step was to determine the kinetics of the extraction. For this purpose a sample was prepared with suspended substrate and several subsequent extractions were made with the SPME fibre, allowing a temporal resolution of ½ hour. A parallel experiment was executed with a blank sample without suspended substrate. In both cases the detected amount of analyte decreased. It was assumed that for this range of analytes the equilibrium between the gas and liquid phase was reached since both samples were stirred intensively. The SPME extraction was in all cases carried out for 20 min, so theoretically the extraction yield should be the same for all experiments. Since the vessels used for these experiments were proven tight, the only explanation of the occurring decrease of analyte concentration even for the blank sample was that the SPME fibre had been extracting a major part of the analytes. Therefore it was decided to make only one measurement per sample at what we considered to be the equilibrium. For the final measurements the substrates were suspended until they were evenly distributed. Then the samples were spiked with a final analyte concentration of 0.5 ppm and stirred for another hour until equilibrium was established between the solid and the liquid phase. (Later measurements showed that the equilibrium concentrations should be reached for these analytes after this time) The SPME was carried out at room temperature for 20 min. Detailed results of the preliminary experiments are given in the appendix.

3.1.2 Equilibrium Concentrations

The equilibrium concentrations as determined from the SPME measurements are presented in the Table 3.1.1 and 3.1.2 and in Figure 3.1.1 and are subsequently discussed for each material individually.

Norm. PA at the Equilibrium						
	MTMOS/ MeOH	**MTMOS/ iPrOH 0.5**	**MTMOS/ iPrOH 1.0**	**10% C8-TEOS**	**10% APTES**	**C8 Spe-Ed**
Toluene	0.431	0.092	0.101	0.604	0.238	0.615
Chlorobenzene	0.164	0.028	0.005	0.230	0.070	0.322
p-Xylene	0.116	0.004	0.015	0.157	0.028	0.139
N-Nonane	0.716	0.001	0.008	0.791	0.026	0.086
1-Chlorooctane	0.046	0.002	0.002	0.051	0.002	0.004
N-Dodecane	0.412	0.013	0.011	0.064	0.009	0.019

Tab. 3.1.1 Normalised PA at the equilibrium 0.5 ppm initial analyte concentration

Norm. PA at the Equilibrium					
	C18 Spe-Ed	**LiChrolut**	**Polyacrylic acid**	**PE/ 5% Polyacrylicacid Copolymer**	**Carboxylated PVC**
Toluene	0.484	0.002	0.854	0.648	0.471
Chlorobenzene	0.258	< l.o.d.	0.721	0.369	0.155
p-Xylene	0.119	< l.o.d.	0.796	0.255	0.261
N-Nonane	0.067	< l.o.d.	0.560	0.196	0.720
1-Chlorooctane	0.003	< l.o.d.	0.779	0.040	0.386
N-Dodecane	0.008	< l.o.d.	0.961	0.089	0.738

Tab. 3.1.2 (continued) Normalised PA at the equilibrium 0.5 ppm initial analyte concentration
l.o.d.: limit of detection; for a better visability of the differences between the substrates the extraction efficiency is given as remaining normalised concentration in solution

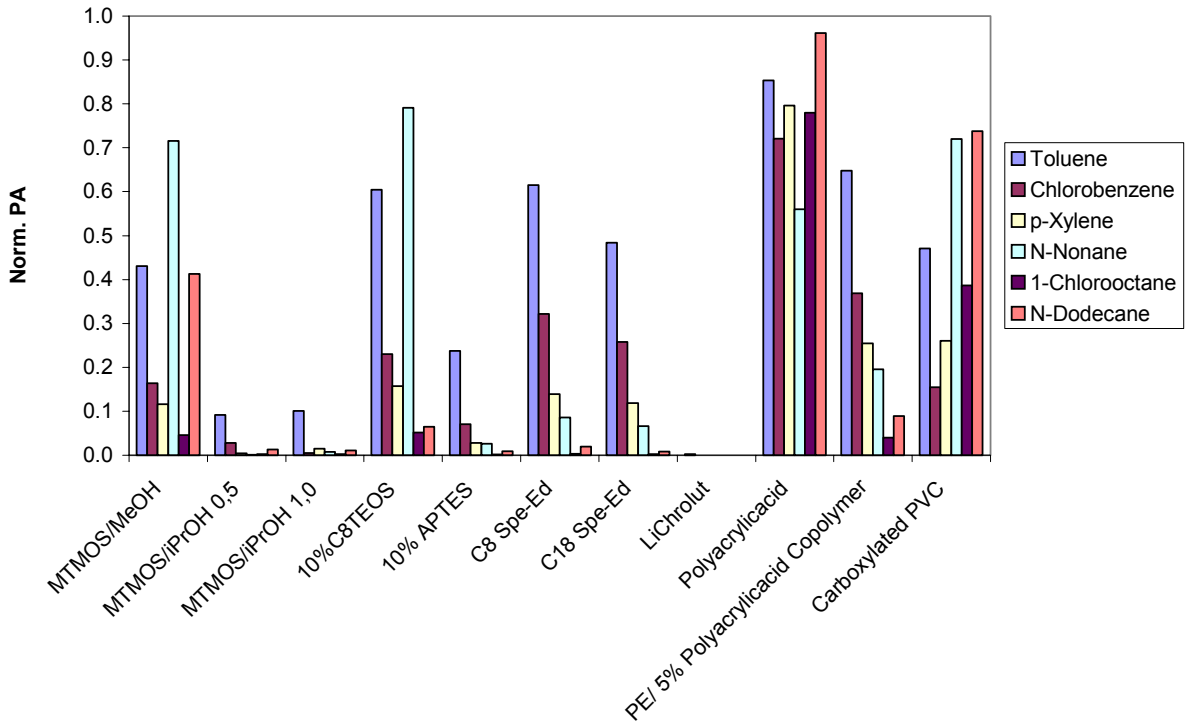


Fig. 3.1.1 Normalised. PA at the equilibrium, 0.5 ppm initial analyte concentration

MTMOS/MeOH particles were suspended evenly after ½ hour. With the exception of both n-alkanes the equilibrium concentrations of the analytes in solution correspond to their pKow. So this material shows a certain selectivity in the adsorption between the n-alkanes and the aromatic analytes as well as 1-chlorooctane

MTMOS/iPrOH 0.5 and MTMOS/iPrOH 1.0 were suspended evenly only after 1 ½ hours. Some of the larger particles still floated on the surface of the liquid phase, which means that they probably were not wetted completely. Both substrates extract the model analytes more efficiently than the previous material. Both sol-gel materials show a similar selectivity for all analytes, the equilibrium concentrations reflect the trend of the pKow of the analytes.

10% C8-TEOS was easily suspended in the aqueous phase. The remaining concentrations of the analytes at the equilibrium are similar to the MTMOS/MeOH material with the exception of n-dodecane, which is extracted much better from the solution.

10% APTES was also readily suspended. It shows a high affinity to the analytes, but not as high as that of both MTMOS/iPrOH materials. Since the specific surface area is comparably large(see Tab. 2.1.2), the distribution koefficient of the test analytes between liquid and solid phase is not as favourable as for both MTMOS/iPrOH materials. This is believed to be caused by a more polar surface which enriches the apolar analytes not as goos as the more apolar surfaces of the MTMOS derived sol-gel substrates.

C8 Spe-Ed and the C18 Spe-Ed are very much alike. Both materials are very apolar, but the affinity towards the analytes is not as good as expected. Since the remaining concentration of the analytes again correlates with their pKow, both materials have no particular (compound-class) selectivity. The particles of the C18 Spe-Ed agglomerated during the suspension process and were not distributed evenly. Since these materials were only investigated for comparison, and they are very similar, it was decided that the investigation of C18 Spe-Ed was of no further use.

LiChrolut is suspended very well after several minutes. Only a very small amount of toluene could be detected after the extraction, which means that only insignificant amounts (less than 1%) of all other analytes remained in the solution.

Polyacrylic acid dissolved in the water. The liqiuid phase became viscous with a gel-like character. It showed little affinity to the apolar analytes due to its high polarity. This material was not investigated further.

PE / 5% Polyacrylic acid copolymer could not be suspended properly, the particles floated on the surface of the solution. Obviously as a consequence of its hydrophobic nature, the particles could not be wetted by the test solution.. The affinity for the analytes

is comparable to both Spe-Ed materials. Due to the problems of suspending this material adequately, it was not investigated further in the following expariments.

Carboxylated PVC is suspended very well. It has a low affinity for the analytes. It extracts the aromatic compounds and the 1-chlorooctane better than the n-alkanes which correlates with the results for MTMOS/MeOH and 10% C8-TEOS.

In general, one can say that the absorption of the analytes strongly correlates with their pKow, which is not very surprising since most of the solid materials are very apolar. Exceptions are n-nonane and n-dodecane for the MTMOS/MeOH and n-nonane for the 10% C8-TEOS material. (See Fig. 3.1.1) This trend does not occur for the polar solids polyacrylicacid and carboxylated PVC. The design of the experiments includes several distriution equilibria which have to be established, and the use of the SPME fibre for the measurements may itself affect one or more of the solid phase/liquid phase, liquid phase/gaseous phase and gaseous phase/SPME fibre equilibria.

3.2 Enrichment Profiles of Substituted Aromatic Compounds by HPLC-DAD

3.2.1 Preliminary Experiments

After choosing the test analytes, the influence of the nylon filter was tested by determining the recovery rates at several different concentration levels. For this purpose, a spiked solution was filtered at various concentration levels. As it turned out, the hydrophilic analytes 1-naphthol and diphenylamine were more or less completely adsorbed by the nylon filters. Also the apolar analytes were adsorbed in the range of 10-50%, which was still considered acceptable to make valid conclusions about the observed trends. The concentration dependency of the adsorbed amount seemed to be small, so the recovery rates of the filter were not used for acorrection. Due to a lack of alternatives at that moment, it was decided to use the nylon syringe filters. In the next step the optimal ratio of analyte to solid substrate was determined. For this purpose equilibrium

concentrations were measured at four different concentration levels with a test substrate. At an analyte concentration of 10 ppm and 0.02 g/g suspended solid all analytes could be detected at the equilibrium, so finally these parameters were found suitable for our experiments. Finally the suitable times of sampling had to be chosen. For this purpose, the rough time dependence of the extraction was determined by taking several samples over half an hour after spiking the suspension. Since the equilibrium seemed to be reached after roughly 20 min, it was decided to take samples at 1, 5, 10, 15 and 30 min after spiking. So the final parameters for these experiments were 0.4 g solid suspended in 20 ml water, spiking with 200 µl of a 1 mg/g stock solution in acetonitrile leading to a final analyte concentration of 10 ppm and taking samples at 1, 5, 10, 15 and 30 min with a volume of 1 ml. Detailed results of the experiments are given in the appendix.

3.2.2 MTMOS/MeOH

MTMOS/MeOH					
	1 min	**5 min**	**10 min**	**15 min**	**30 min**
Benzonitrile	0.648	0.450	0.335	0.294	0.271
Chlorobenzene	0.138	0.114	0.065	0.059	0.070
1,3 Dichlorobenzene	0.095	0.034	0.000	0.000	0.000
1,2,3 Trimethylbenzene	0.467	0.261	0.205	0.159	0.137
N-Proplybenzene	0.121	0.052	0.000	0.000	0.000

Tab. 3.2.2 MTMOS/MeOH: Time dependence of the extraction process (given as normalised analyte concentration in solution)

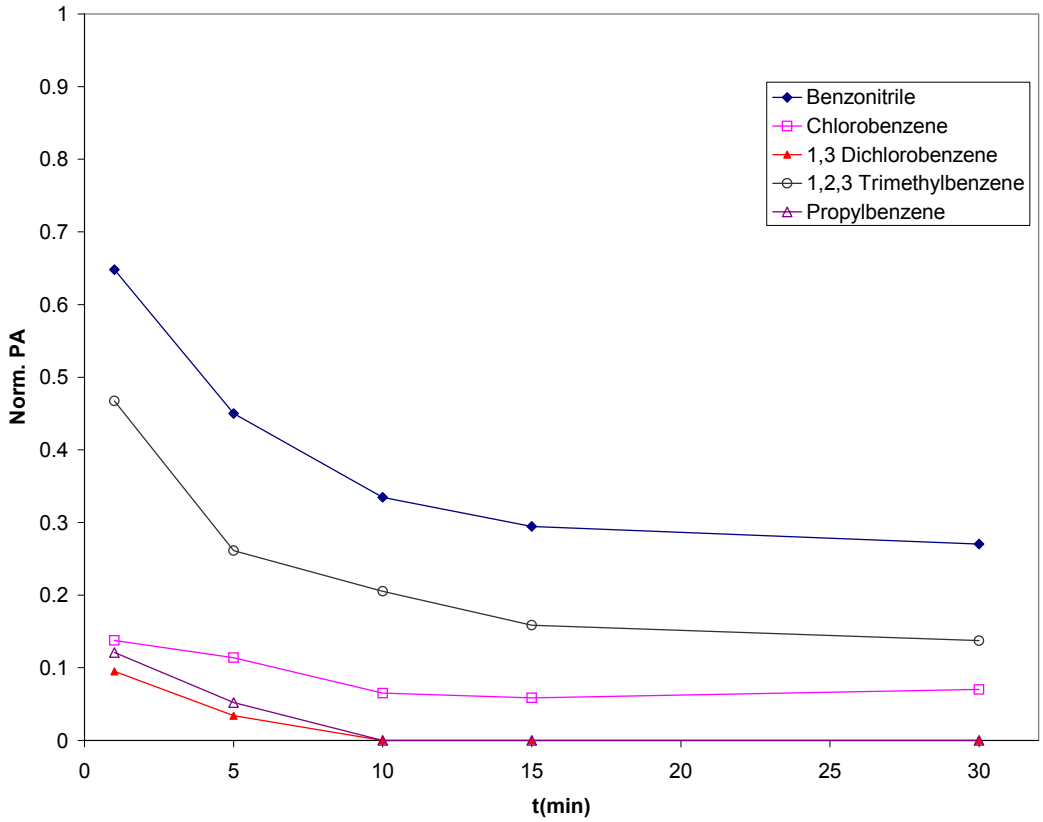


Fig. 3.2.2 MTMOS/MeOH: Time dependence of the extraction process (given as normalised analyte concentration in solution)

As can be seen, the concentration of the analytes is decreasing with time. N-propylbenzene and 1,3-dichlorobenzene are both extracted completely from the solution. Surprisingly a rather large amount of 1,2,3-trimethylbenzene remains in the solution, although it has a similar pKow as n-propylbenzene. This could be caused by the fact that most likely 1,2,3 trimethylbenzene is larger than propylbenzene and its adsorption is sterically hindered by the morphology of the material. The kinetics of the extraction are roughly the same for all analytes.

3.2.3 MTMOS/iPrOH 0.5

MTMOS/iPrOH 0.5					
	1 min	**5 min**	**10 min**	**15 min**	**30 min**
Benzonitrile	0.188	0.155	0.145	0.136	0.128
Chlorobenzene	0.055	0.067	0.035	0.040	0.000
1,3 Dichlorobenzene	0.000	0.000	0.000	0.000	0.000
1,2,3 Trimethylbenzene	0.028	0.008	0.000	0.000	0.000
N-Proplybenzene	0.000	0.000	0.000	0.000	0.000

Tab. 3.2.3 MTMOS/iPrOH 0.5: Time dependence of the extraction process (given as normalised analyte concentration in solution)

This material has a higher affinity for the analytes than the MTMOS/MeOH. It is hard to tell if the extraction is faster, since only benzonitrile and chlorobenzene are still detectable after 10 minutes. The results for benzonitrile suggest that the kinetics are similar to the kinetics of the MTMOS/MeOH. The higher affinity to the analytes is explainable by the large specific surface of the MTMOS/iPrOH 0.5 (293 m^2/g compared to 11 m^2/g).

3.2.4 MTMOS/iPrOH 1.0

MTMOS/iPrOH 1.0					
	1 min	**5 min**	**10 min**	**15 min**	**30 min**
Benzonitrile	0.196	0.155	0.151	0.127	0.118
Chlorbenzene	0.039	0.047	0.036	0.022	0.032
1,3 Dichlorbenzene	0.000	0.000	0.000	0.000	0.000
1,2,3 Trimethylbenzene	0.000	0.000	0.000	0.000	0.000
N-Proplybenzene	0.000	0.000	0.000	0.000	0.000

Tab. 3.2.4 MTMOS/iPrOH 1.0: Time dependence of the extraction process (given as normalised analyte concentration in solution)

The MTMOS/iPrOH 1.0 is very similar to the MTMOS/iPrOH 0.5. It shows an increased affinity to 1,2,3 trimethylbenzene and a somewhat smaller affinity to chlorobenzene, but as these concentrations are near the detection limit, particularities or problems with the data evaluation may obscure the results: In fact, in such a case the peak could be still integrated as peak and in the other case not. The results of benzonitrile are more or less

the same for both materials. Again, the large inner surface correlates with a high affinity for the analytes.

3.2.5 10% C8-TEOS

10% C8-TEOS					
	1 min	**5 min**	**10 min**	**15 min**	**30 min**
Benzonitrile	0.828	0.757	0.708	0.660	0.591
Chlorobenzene	0.573	0.292	0.216	0.179	0.114
1,3 Dichlorobenzene	0.309	0.140	0.089	0.061	0.046
1,2,3 Trimethylbenzene	0.518	0.334	0.210	0.157	0.118
N-Proplybenzene	0.401	0.145	0.100	0.054	0.048

Tab. 3.2.5 10% C8-TEOS: Time dependence of the extraction process (given as normalised analyte concentration in solution)

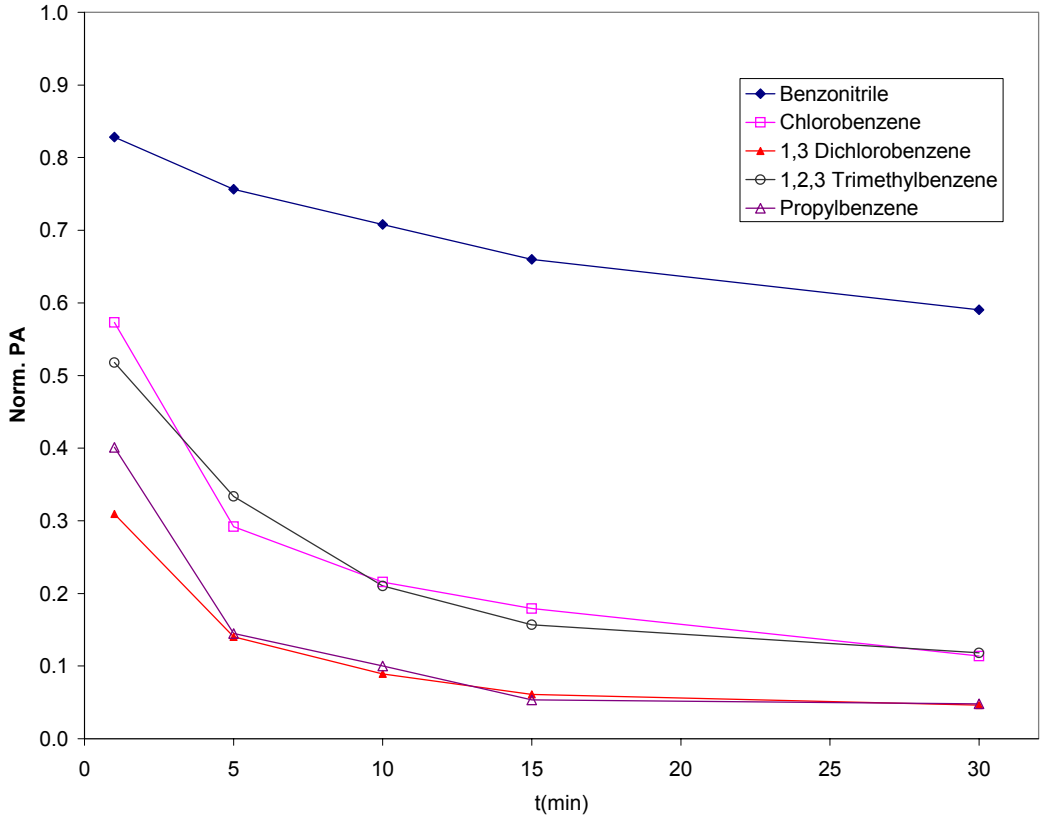


Fig. 3.2.5 10% C8-TEOS: Time dependence of the extraction process (given as normalised analyte concentration in solution)

Remarkable for this material is its very low affinity for benzonitrile: About 60% of this compound remain in the solution after 30 min of extraction. The extraction yield of the other analytes corresponds to their pKow except for 1,2,3-trimethylbenzene, where an equilibrium concentration similar to n-propylbenzene could be expected. Compared to MTMOS/MeOH the extraction kinetics are slower, one reason could be that the C8 chains form a micelle like structure within the material and that the diffusion into these micelles is slower than the diffusion through free pores.

3.2.6 10% APTES

10% APTES					
	1 min	**5 min**	**10 min**	**15 min**	**30 min**
Benzonitrile	0.245	0.264	0.237	0.229	0.221
Chlorobenzene	0.030	0.042	0.037	0.041	0.045
1,3 Dichlorobenzene	0.000	0.000	0.000	0.000	0.000
1,2,3 Trimethylbenzene	0.000	0.000	0.000	0.000	0.000
N-Proplybenzene	0.000	0.000	0.000	0.000	0.000

Tab. 3.2.6 10% APTES: Time dependence of the extraction process (given as normalised analyte concentration in solution)

The extraction kinetics are comparatively fast, the equilibrium state seems to be reached after 5 min. The affinity of the substrate for benzonitrile is smaller than that of both MTMOS/iPrOH sol-gel materials, but almost equal for all other analytes.

3.2.7 C8 Spe-Ed

C8 Spe-Ed					
	1 min	**5 min**	**10 min**	**15 min**	**30 min**
Benzonitrile	0.394	0.413	0.401	0.418	0.415
Chlorobenzene	0.139	0.115	0.118	0.124	0.152
1,3 Dichlorobenzene	0.000	0.000	0.000	0.000	0.000
1,2,3 Trimethylbenzene	0.027	0.019	0.026	0.027	0.022
N-Proplybenzene	0.000	0.000	0.000	0.000	0.000

Tab. 3.2.7 C8 Spe-Ed: Time dependence of the extraction process (given as normalised analyte concentration in solution)

The analyte concentrations remain constant after the first measurement at 1 min. The extraction kinetics seems to be very fast for all analytes. Again, the hydrophobicity of the analyte determines the extraction yield. And similar to e.g. the 10% C8-TEOS or the MTMOS/MeOH material, 1,2,3-trimethylbenzene is not extracted completely. The adsorption of 1,2,3 trimethylbenzene seems to be sterically hindered by its size.

3.2.8 LiChrolut

LiChrolut					
	1 min	**5 min**	**10 min**	**15 min**	**30 min**
Benzonitrile	0.004	0.004	0.004	0.004	0.004
Chlorobenzene	0.000	0.000	0.000	0.000	0.000
1,3 Dichlorobenzene	0.000	0.000	0.000	0.000	0.000
1,2,3 Trimethylbenzene	0.000	0.000	0.000	0.000	0.000
N-Proplybenzene	0.000	0.000	0.000	0.000	0.000

Tab. 3.2.8 LiChrolut: Time dependence of the extraction process (given as normalised analyte concentration in solution)

This material has a very strong affinity to all of the analytes, even to the polar benzonitrile. The extraction is already finished after 1 min.

3.2.9 Carboxylated PVC

Carboxylated PVC					
	1 min	**5 min**	**10 min**	**15 min**	**30 min**
Benzonitrile	0.808	0.758	0.738	0.668	0.619
Chlorobenzene	0.475	0.324	0.229	0.169	0.150
1,3 Dichlorobenzene	0.163	0.106	0.074	0.051	0.053
1,2,3 Trimethylbenzene	0.199	0.163	0.130	0.121	0.121
N-Proplybenzene	0.198	0.130	0.110	0.106	0.113

Tab. 3.2.9 Carboxylated PVC: Time dependence of the extraction process (given as normalised analyte concentration in solution)

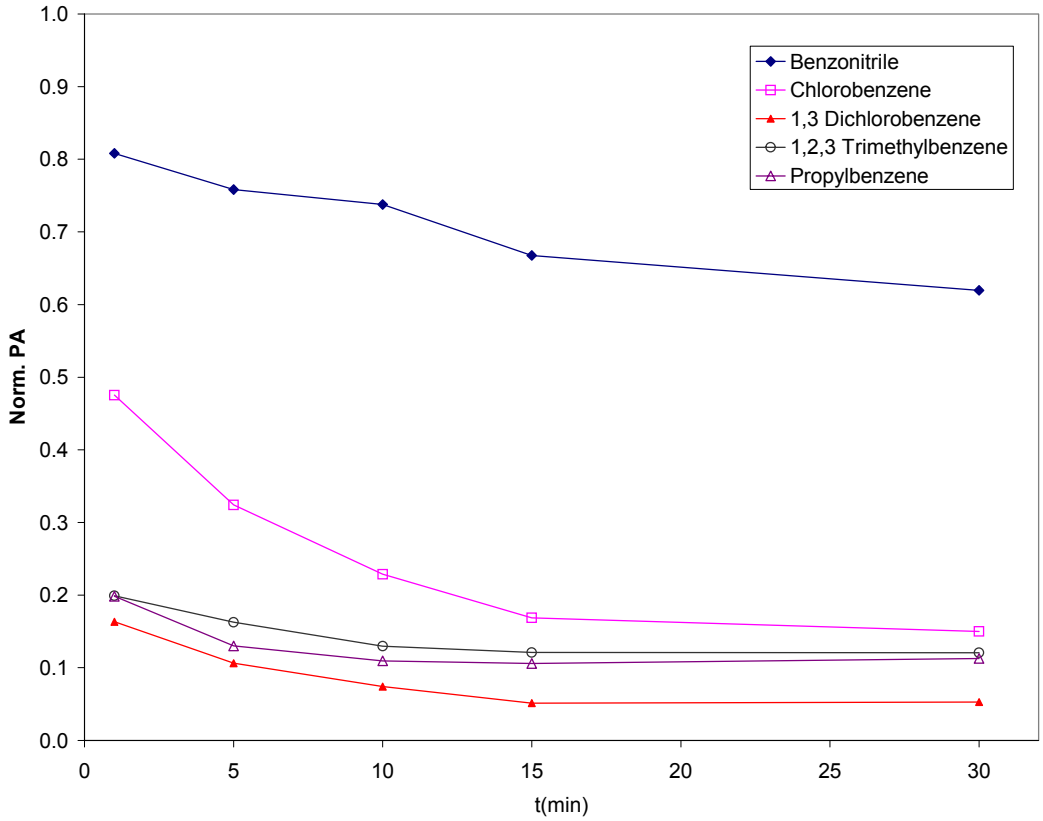


Fig.. 3.2.9 Carboxylated PVC: Time dependence of the extraction process (given as normalised analyte concentration in solution)

The adsorption behaviour of carboxylated PVC is similar to that of the 10% C8-TEOS. It has generally a low affinity to the analytes. The extraction seems to be finished after 15 min. The affinity to the chlorinated benzene derivatives is higher than expected from the pKow which might be explained by the fact that this solid material itself is a highly chlorinated polymer and thus exhibits selective interaction with the chlorinated hydrocarbons.

3.2.10 Comparison of the Equilibrium Concentrations

Equilibrium				
	MTMOS/ MeOH	**MTMOS/ PrOH 0.5**	**MTMOS/ PrOH 1.0**	**10% C8-TEOS**
Benzonitrile	0.271	0.128	0.118	0.591
Chlorobenzene	0.070	< l.o.d.	0.032	0.114
1,3 Dichlorobenzene	< l.o.d.	< l.o.d.	< l.o.d.	0.046
1,2,3 Trimethylbenzene	0.137	< l.o.d.	< l.o.d.	0.118
N-Proplybenzene	< l.o.d.	< l.o.d.	< l.o.d.	0.048
	10% APTES	**C8 SPE-ED**	**LiChrolut**	**PVC Carbox.**
Benzonitrile	0.221	0.415	0.004	0.619
Chlorobenzene	0.045	0.152	< l.o.d.	0.15
1,3 Dichlorobenzene	< l.o.d.	< l.o.d.	< l.o.d.	0.053
1,2,3 Trimethylbenzene	< l.o.d.	0.022	< l.o.d.	0.121
N-Proplybenzene	< l.o.d.	< l.o.d.	< l.o.d.	0.113

Tab. 3.2.10 Overview of the extraction efficiencies reached after an equilibration time of 30 min (expressed as normalised PA of the concentration of the analytes remaining in solution)

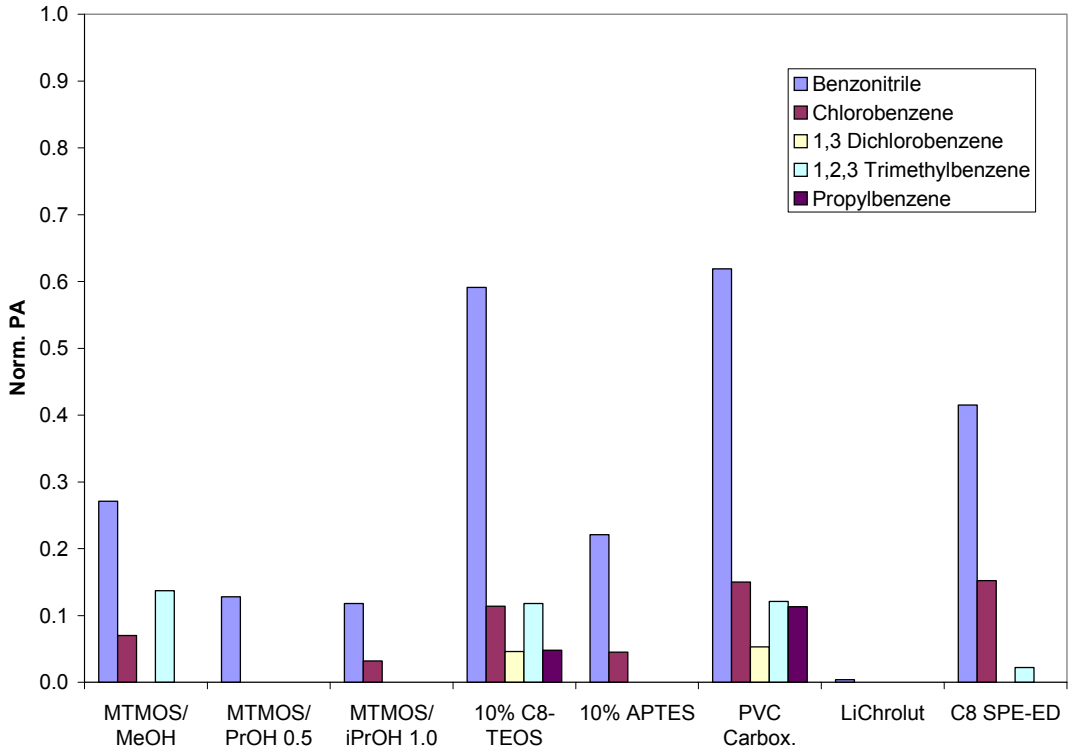


Fig. 3.2.10 Overview of the extraction efficiencies reached after an equilibration time of 30 min (expressed as normalised PA of the concentration of the analytes remaining in solution)

MTMOS/MeOH extracts the analytes comparatively well. 1,2,3-trimethylbenzene is extracted by the substrate with a small yield, which could be caused by steric hindrance of the adsorption process.

MTMOS/iPrOH 0.5 and **MTMOS/iPrOH 1.0** show an increased affinity to the analytes. Only small amounts of benzonitrile remain in the solution. Their high specific surface areas provide a high capacity for adsorption.

10% C8-TEOS and **Carboxylated PVC** behave very similar. The equilibrium concentrations of the analytes remaining in the solution are rather high. The concentration of 1,2,3-trimethylbenzene is in both cases higher than expected. The only difference is that the Carboxylated PVC shows a lower affinity to n-propylbenzene.

The **10% APTES** substrate extracts the analytes comparatively well. There seems to be no steric hindrance for the adsorption of 1,2,3 trimethylbenzene.

LiChrolut has an excellent extraction behaviour, only very small amounts of benzonitrile could be detected even after 1 min of extraction.

C8 Spe-Ed extracts the analytes compared to the other materials moderately well. The equilibrium concentrations in solution correlate with the pKow of the analytes.

3.3 Enrichment Profiles of PAHs

3.3.1 Preliminary Experiments

For the determination of the extraction profiles of PAHs the same experimental setup was used as for the extraction profiles of substituted aromatic compounds. As a modification to previous experiments, alternatives to the nylon filters were looked for, since these have shown almost complete loss of 1-naphthol and diphenylamine, obviously due to irreversible adsorption . Filters made of regenerated cellulose should be a suitable substitute for the nylon filters. For a comparison of their performance samples with three

different concentrations were measured unfiltered and filtered by both filter materials. The nylon filters adsorbed all PAHs except naphthalene at concentrations above 1 ppm. In comparison the RC filters adsorbed up to 60% for pyrene. The recovery rates increase with the initial analyte concentration, so it was decided to spike the samples with the maximum concentration possible, which proved to be 2 ppm (at higher concentrations the solution became turbid which means that the analyte concentration exceeded the solubility). In order to maintain the ratio of suspended amount of solid to analyte concentration, the suspended amount of solid was reduced to 0.01 g/g. Again the kinetics were studied in a preliminary experiment to decide upon the sampling times. The parameters of the final measurements were 2 ppm analyte concentration and 0.01 g/g suspended substrate in 20 ml water and sampling times at 1, 5, 10, 15, 30 and 90 min with 1 ml sample volume. Detailed results of the preliminary experiments are given in the appendix.

3.3.2 MTMOS/MeOH

MTMOS/MeOH							
t (min)	**1**	**5**	**10**	**15**	**30**	**45**	**90**
Naphthalene	0.843	0.695	0.560	0.465	0.342	0.243	0.186
Fluorene	0.827	0.719	0.600	0.575	0.458	0.329	0.256
Phenanthrene	0.760	0.806	0.679	0.694	0.549	0.498	0.404
Anthracene	0.599	0.412	0.370	0.304	0.217	0.191	0.123
Pyrene	0.359	0.301	0.162	0.221	0.140	0.107	0.209
Chrysene	0.644	0.608	0.520	0.406	0.280	0.247	0.144

Tab. 3.3.2 MTMOS/MeOH: Time dependence of the extraction process (given as normalised analyte concentration in solution)

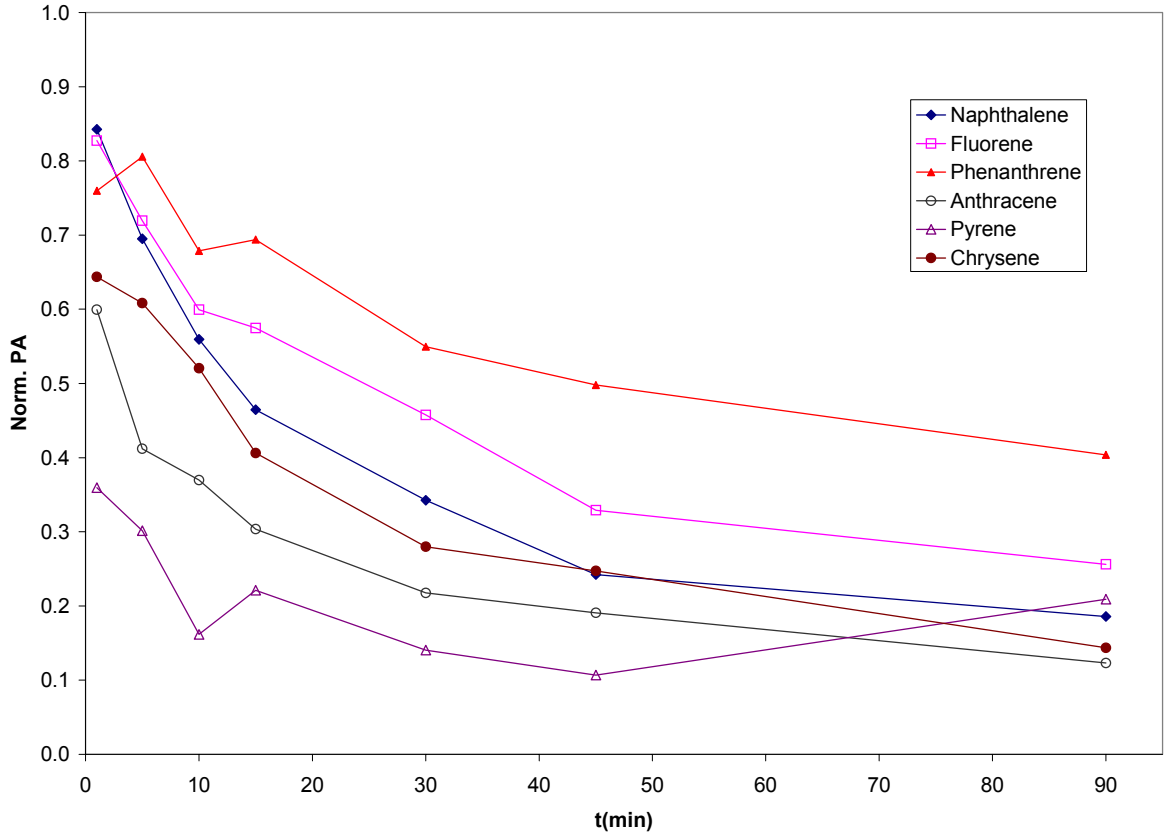


Fig. 3.3.2 MTMOS/MeOH: Time dependence of the extraction process (given as normalised analyte concentration in solution)

As can be seen, all analytes are extracted from the solution with roughly the same kinetics. About 40% of phenanthrene remain in the liquid phase, which is somewhat surprising, because the pKow is the same as for anthracene. One explanation could be that there occurs steric hindrance for phenanthrene to be adsorbed due to its angled shape.

3.3.3 MTMOS/iPrOH 0.5

MTMOS/iPrOH 0.5						
t (min)	1	5	10	15	30	90
Naphthalene	0.081	0.046	0.050	0.036	0.043	0.030
Fluorene	0.024	0.019	0.015	0.020	0.013	0.022
Phenanthrene	0.000	0.000	0.000	0.000	0.000	0.000
Anthracene	0.044	0.017	0.011	0.010	0.006	0.000
Pyrene	0.000	0.000	0.000	0.000	0.000	0.000
Chrysene	0.464	0.165	0.051	0.023	0.000	0.000

Tab. 3.3.3 MTMOS/iPrOH 0.5: Time dependence of the extraction process (given as normalised analyte concentration in solution)

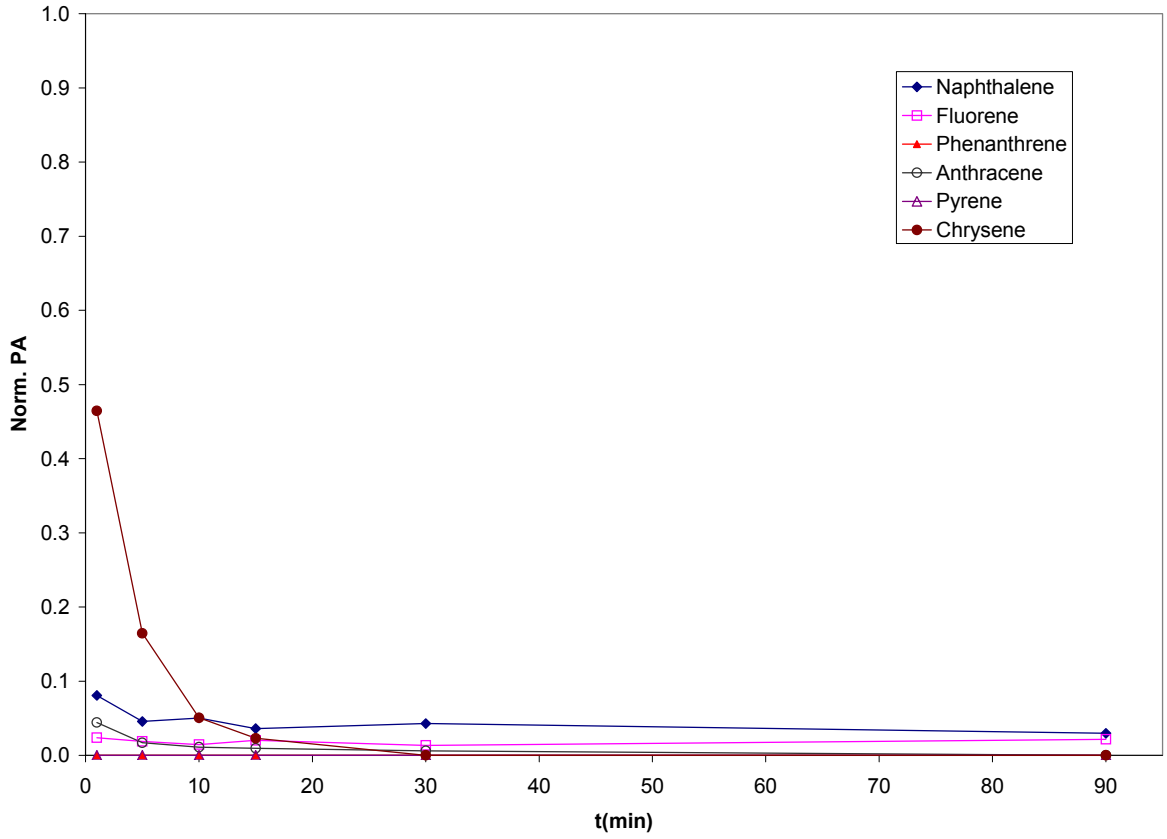


Fig. 3.3.3 MTMOS/iPrOH 0.5: Time dependence of the extraction process (given as normalised analyte concentration in solution)

This material extracts the analytes very quickly. The kinetics for chrysene is significantly slower than for the other analytes. This effect could be explained by the size of the analyte molecules. One has to be aware that the largest part of the surface of this material

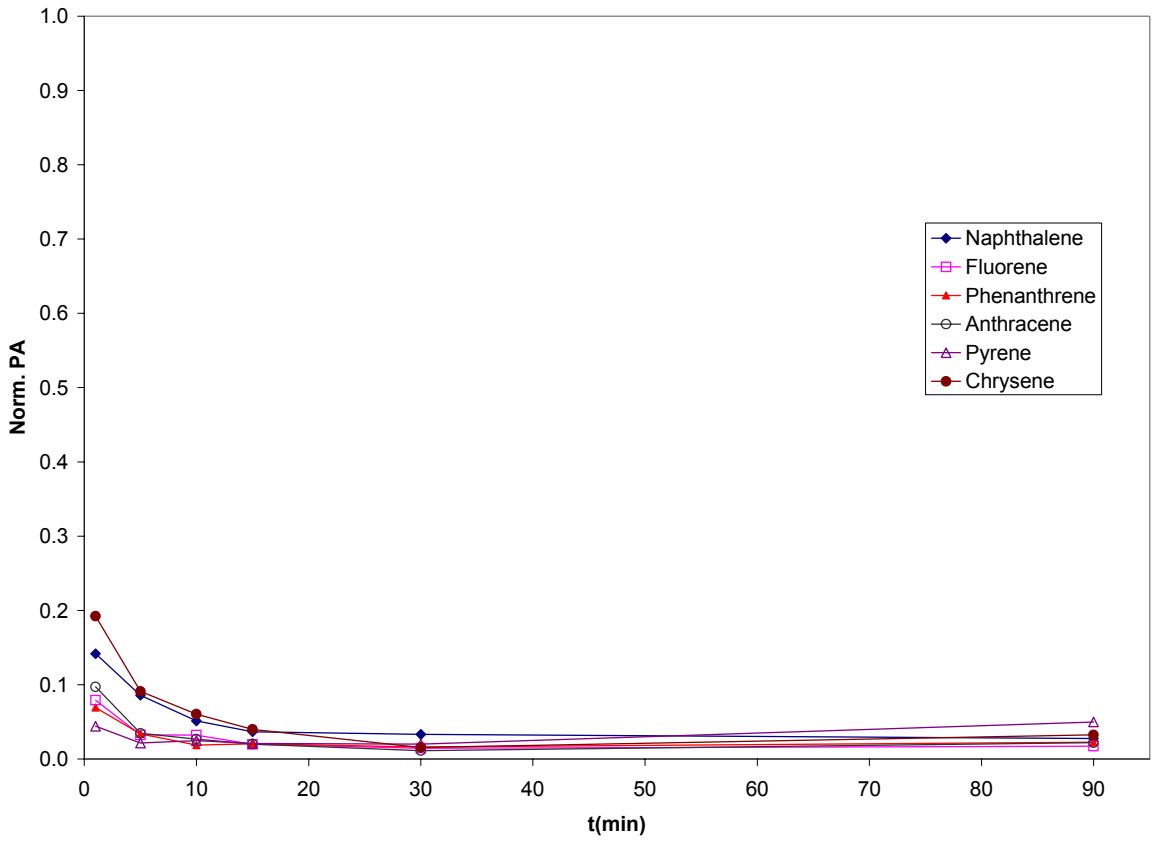
is the internal one in its pores. The pore size distribution of the sol-gel is probably represents a more significant hindrance to the diffusion of chrysene in comparison to the other, smaller PAHs. After 90 min of extraction only naphthalene and fluorene can still be detected in the solution. They have the smallest pKow and can therefore be expected to have the highest concentration in the aqueous solution at the equilibrium.

3.2.4 MTMOS/iPrOH 1.0

MTMOS/iPrOH 1.0						
t (min)	**1**	**5**	**10**	**15**	**30**	**90**
Naphthalene	0.142	0.086	0.051	0.037	0.033	0.028
Fluorene	0.079	0.032	0.032	0.020	0.015	0.017
Phenanthrene	0.069	0.034	0.019	0.021	0.016	0.023
Anthracene	0.097	0.035	0.027	0.020	0.011	0.022
Pyrene	0.044	0.021	0.025	0.021	0.020	0.050
Chrysene	0.192	0.091	0.060	0.040	0.016	0.032

Tab. 3.3.4 MTMOS/iPrOH 1.0: Time dependence of the extraction process (given as normalised analyte concentration in solution)

Fig. 3.3.4 MTMOS/iPrOH 1.0: Time dependence of the extraction process (given as normalised analyte



concentration in solution)

All analytes are extracted with very similar kinetics, the equilibrium is reached after 15 minutes of extraction. Compared to the MTMOS/iPrOH 0.5 the kinetics are slower, but this material shows approximately the same rate of extraction chrysene as for the other PAHs, which means that its adsorption is not hindered for steric reasons. Only about 5% of the analytes remain in the solution, the extraction yields are roughly the same for all analytes.

3.3.5 10% C8-TEOS

10% C8-TEOS						
t (min)	1	5	10	15	30	90
Naphthalene	0.820	0.657	0.583	0.551	0.411	0.252
Fluorene	0.766	0.595	0.535	0.455	0.314	0.152
Phenanthrene	0.790	0.624	0.556	0.486	0.346	0.160
Anthracene	0.797	0.676	0.742	0.647	0.597	0.311
Pyrene	0.457	0.257	0.240	0.182	0.191	0.169
Chrysene	0.835	0.814	0.864	0.833	0.689	0.473

Tab. 3.3.5 10% C8-TEOS: Time dependence of the extraction process (given as normalised analyte concentration in solution)

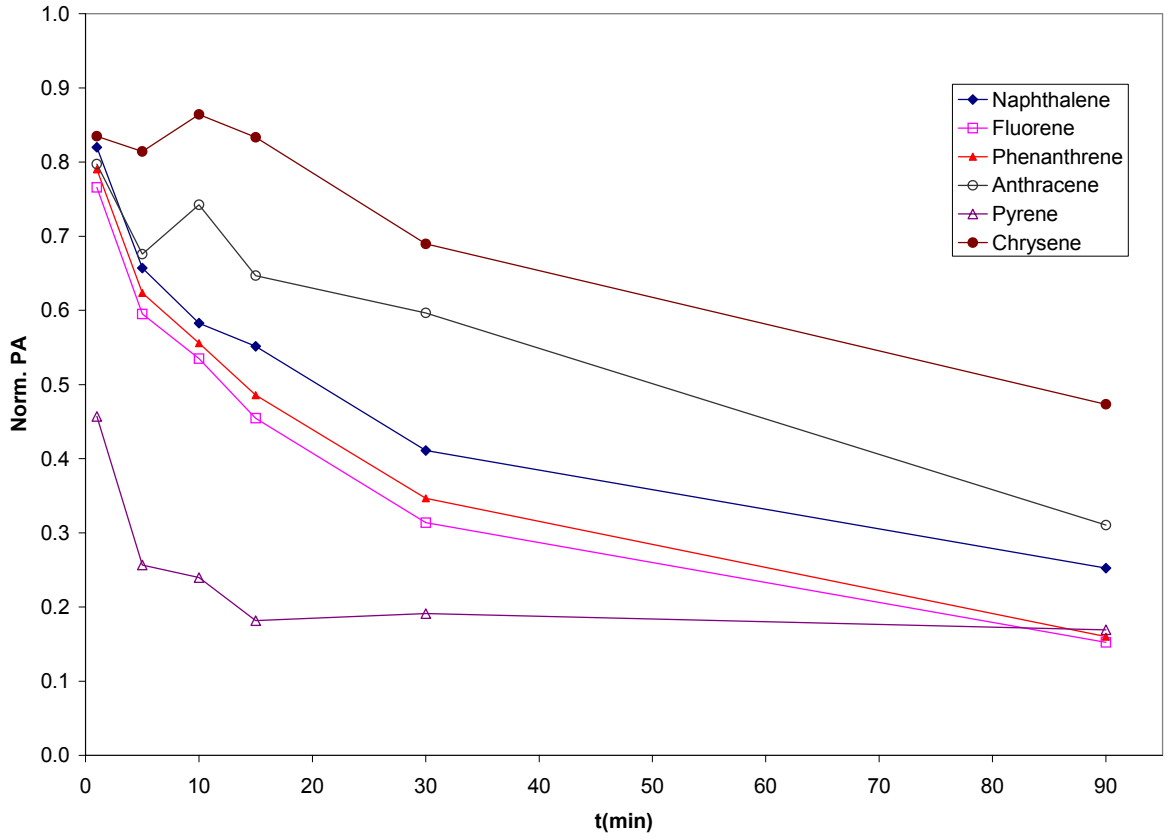


Fig. 3.3.5 10% C8-TEOS: Time dependence of the extraction process (given as normalised analyte concentration in solution)

Compared to the other materials, this sol-gel extracts the analytes very slowly. The equilibrium is not reached even after 90 min of extraction with the exception of pyrene.

This could be caused by the comparatively small inner surface of the 10% C8-TEOS material. One explanation could be the presence of hydrophobic micelles formed by the C8 residues into which the analytes can diffuse but at a significantly lower rate than into free pores.

3.3.6 10% APTES

10% APTES						
t (min)	**1**	**5**	**10**	**15**	**30**	**90**
Naphthalene	0.166	0.100	0.093	0.083	0.082	0.086
Fluorene	0.114	0.043	0.037	0.035	0.018	0.014
Phenanthrene	0.112	0.042	0.035	0.023	0.038	0.014
Anthracene	0.053	0.033	0.023	0.015	0.009	0.009
Pyrene	0.162	0.068	0.048	0.055	0.045	0.015
Chrysene	0.000	0.000	0.000	0.000	0.000	0.000

Tab. 3.3.6 10% APTES: Time dependence of the extraction process (given as normalised analyte concentration in solution)

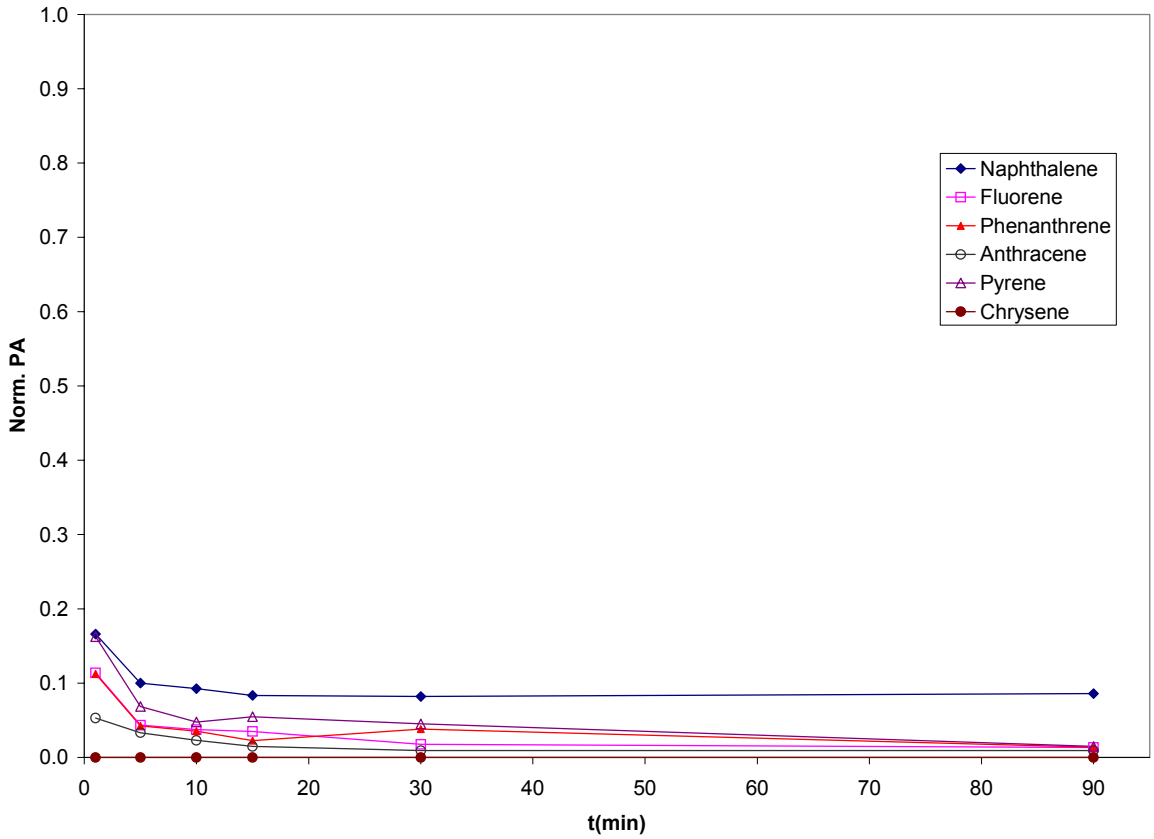


Fig. 3.3.6 10% APTES: Time dependence of the extraction process (given as normalised analyte concentration in solution)

The 10% APTES substrate extracts the analytes very fast, the concentrations remain constant after 15 min. Naphthalene, the smallest PAH with the smallest pKow value is extracted with the poorest efficiency, but even then only 9% of naphthalene remain in the liquid phase. The extraction kinetics is comparable for all analytes. The extraction yield only depends on the pKow, so the material has no additional selectivity for one of the analytes caused by its morphology. Compared with MTMOS/iPrOH 0.5, 10% APTES has a more polar character which explains the higher equilibrium concentrations of the analytes.

3.3.7 MTEOS/TEOS

MTEOS/TEOS						
t (min)	1	5	10	15	30	90
Naphthalene	0.139	0.107	0.073	0.070	0.063	0.056
Fluorene	0.042	0.036	0.036	0.042	0.011	0.011
Phenanthrene	0.022	0.026	0.016	0.030	0.017	0.021
Anthracene	0.032	0.021	0.018	0.011	0.017	0.012
Pyrene	0.024	0.011	0.024	0.020	0.020	0.035
Chrysene	0.091	0.028	0.017	0.011	0.008	0.012

Tab. 3.3.7 MTEOS/TEOS: Time dependence of the extraction process (given as normalised analyte concentration in solution)

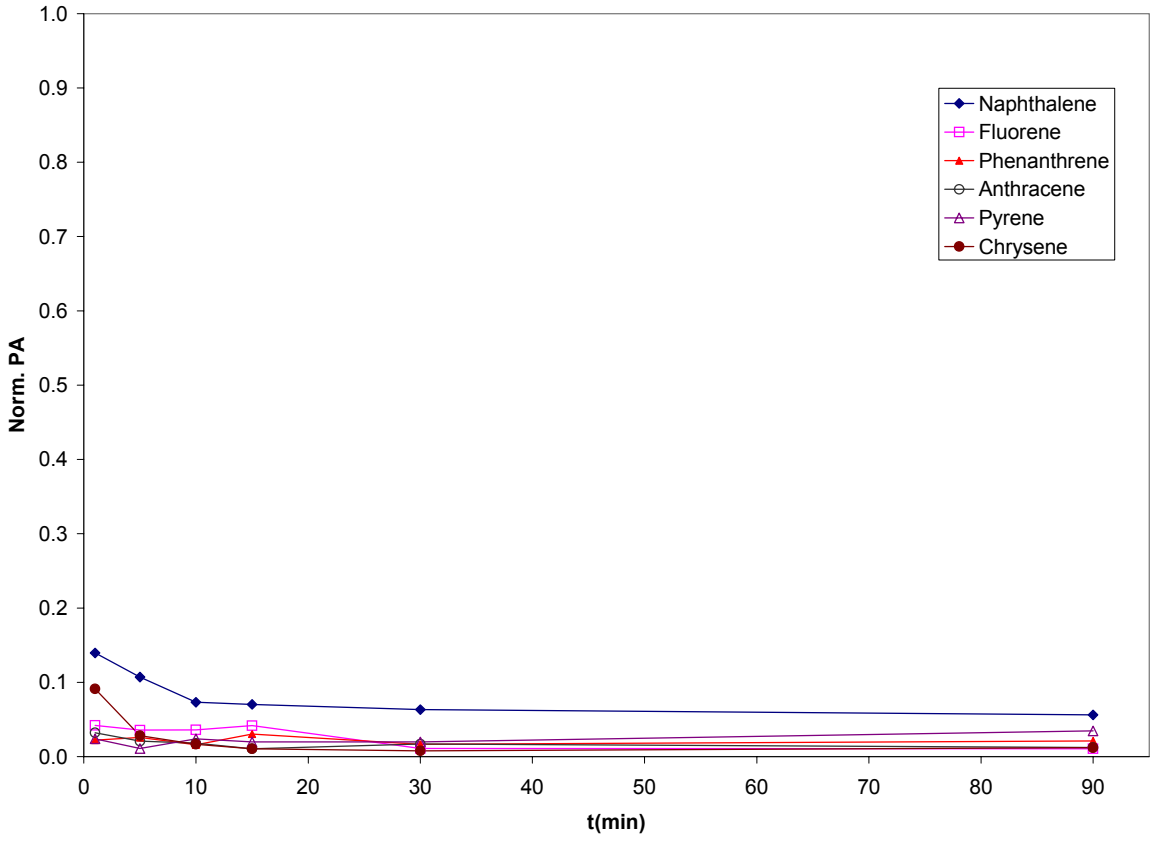


Fig. 3.3.7 MTEOS/TEOS: Time dependence of the extraction process (given as normalised analyte concentration in solution)

MTEOS/TEOS has a similar behaviour as 10% APTES. The extraction is essentially completed after 10-15 min, the analytes are extracted very well. Naphthalene remains to

6% in the solution, indicating that this material perhaps is a little more apolar than the 10% APTES material.

3.3.8 MTMOS/TMOS

MTMOS/TMOS						
t (min)	1	5	10	15	30	90
Naphthalene	0.175	0.074	0.063	0.060	0.039	0.000
Fluorene	0.073	0.040	0.036	0.025	0.020	0.000
Phenanthrene	0.089	0.039	0.029	0.019	0.026	0.000
Anthracene	0.274	0.043	0.033	0.021	0.017	0.000
Pyrene	0.129	0.023	0.063	0.049	0.029	0.000
Chrysene	0.495	0.355	0.254	0.193	0.079	0.000

Tab. 3.3.8 MTMOS/TMOS: Time dependence of the extraction process (given as normalised analyte concentration in solution)

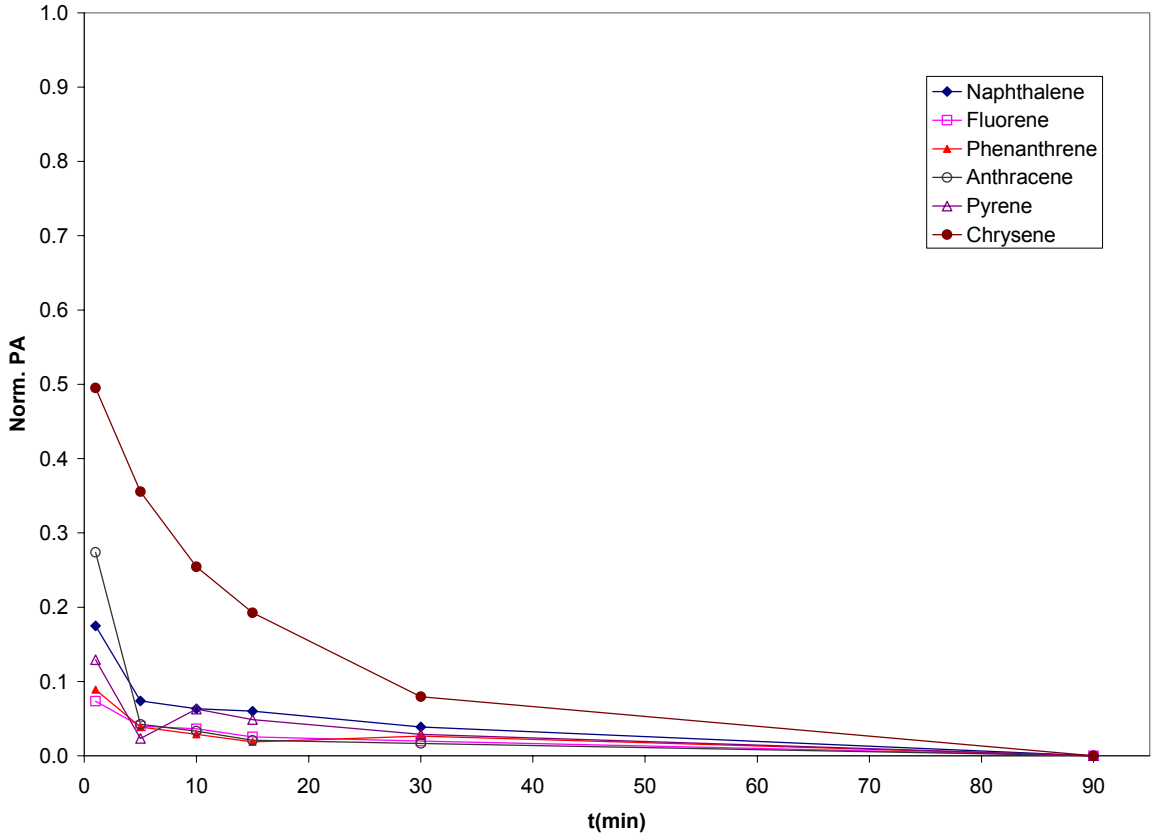


Fig. 3.3.8 MTMOS/TMOS: Time dependence of the extraction process (given as normalised analyte concentration in solution)

The extraction kinetics of the MTMOS/TMOS is very slow compared to the MTEOS/TEOS substrate. Again a kinetic discrimination of the extraction of chrysene occurs like for the MTMOS/iPrOH 0.5 material. The explanation of this phenomenon may be the same: the pores are too small to let the chrysene diffuse without hindrance. After 90 min no analytes could be detected any more in the solution. This material has a very high affinity to the PAHs. It probably has a very large inner surface and therefore a large number of binding sites for the PAHs.

3.3.9 C8 Spe-Ed

C8 SPE-ED						
t (min)	**1**	**5**	**10**	**15**	**30**	**90**
Naphthalene	0.221	0.136	0.178	0.149	0.174	0.141
Fluorene	0.079	0.064	0.031	0.050	0.048	0.041
Phenanthrene	0.063	0.038	0.028	0.029	0.043	0.035
Anthracene	0.153	0.034	0.029	0.030	0.022	0.019
Pyrene	0.037	0.025	0.014	0.034	0.029	0.033
Chrysene	0.405	0.238	0.190	0.169	0.068	0.009

Tab. 3.3.9 C8 Spe-Ed: Time dependence of the extraction process (given as normalised analyte concentration in solution)

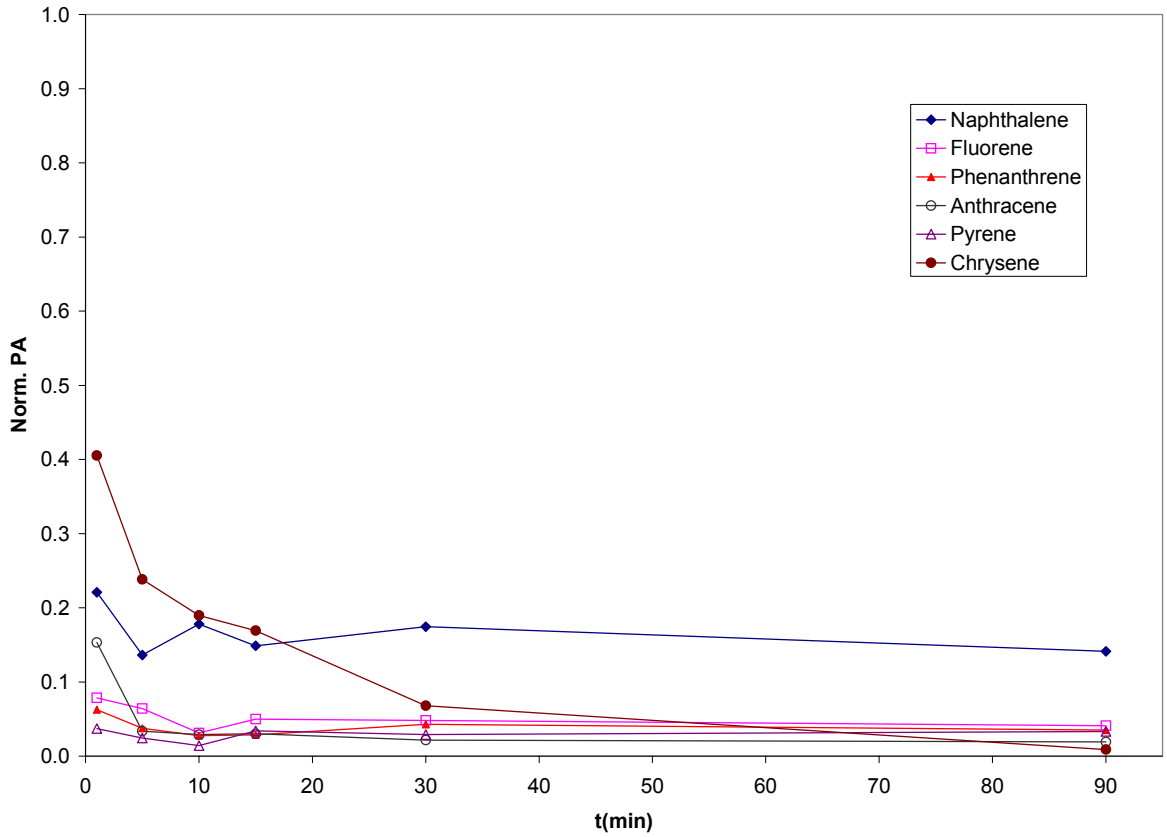


Fig. 3.3.9 C8 Spe-Ed: Time dependence of the extraction process (given as normalised analyte concentration in solution)

The equilibrium is reached after 30 min for chrysene, all other concentrations are constant after 10 min. Again the extraction kinetics of chrysene is the slowest. The equilibrium concentrations are, compared to the other investigated materials, quite high, particularly as this material is commercially used as SPE material. Since this material has like most of the other materials an apolar character, the high analyte concentrations remaining in the liquid phase at equilibrium indicate a low capacity compared with other materials.

3.3.10 LiChrolut

LiChrolut						
t (min)	1	5	10	15	30	90
Naphthalene	0.000	0.000	0.000	0.000	0.000	0.000
Fluorene	0.033	0.000	0.000	0.000	0.000	0.000
Phenanthrene	0.000	0.000	0.000	0.000	0.000	0.000
Anthracene	0.055	0.000	0.000	0.000	0.000	0.000
Pyrene	0.000	0.000	0.000	0.000	0.000	0.000
Chrysene	0.582	0.134	0.011	0.000	0.000	0.000

Tab. 3.2.10 LiChrolut: Time dependence of the extraction process (given as normalised analyte concentration in solution)

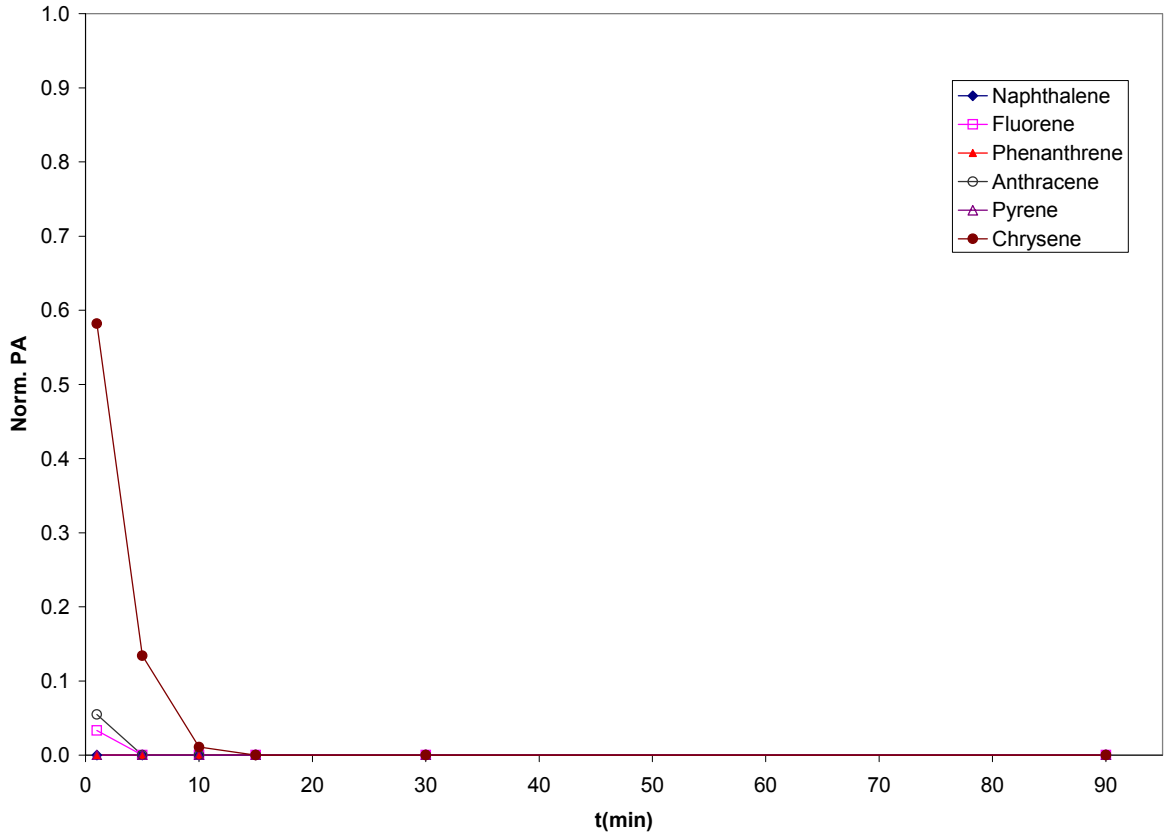


Fig. 3.3.10 LiChrolut: Time dependence of the extraction process (given as normalised analyte concentration in solution)

LiChrolut extracts the analytes very fast. Only chrysene, fluorene and anthracene can still be detected after 1 min. Again chrysene is extracted slowest as was also observed for MTMOS/iPrOH, MTMOS/TeMOS, 10% C8-TEOS and C8 Spe-Ed. The LiChrolut has a

high affinity for the analytes, but again the pore size is believed to cause steric problems for the extraction of chrysene.

3.3.11 Carboxylated PVC

Carboxylated PVC						
t (min)	1	5	10	15	30	90
Naphthalene	0.383	0.315	0.265	0.455	0.369	0.208
Fluorene	0.176	0.107	0.117	0.183	0.144	0.107
Phenanthrene	0.083	0.070	0.248	0.107	0.068	0.052
Anthracene	0.449	0.260	0.174	0.262	0.120	0.070
Pyrene	0.040	0.032	0.055	0.076	0.044	0.112
Chrysene	0.429	0.278	0.250	0.334	0.234	0.162

Tab. 3.3.11 Carboxylated PVC: Time dependence of the extraction process (given as normalised analyte concentration in solution)

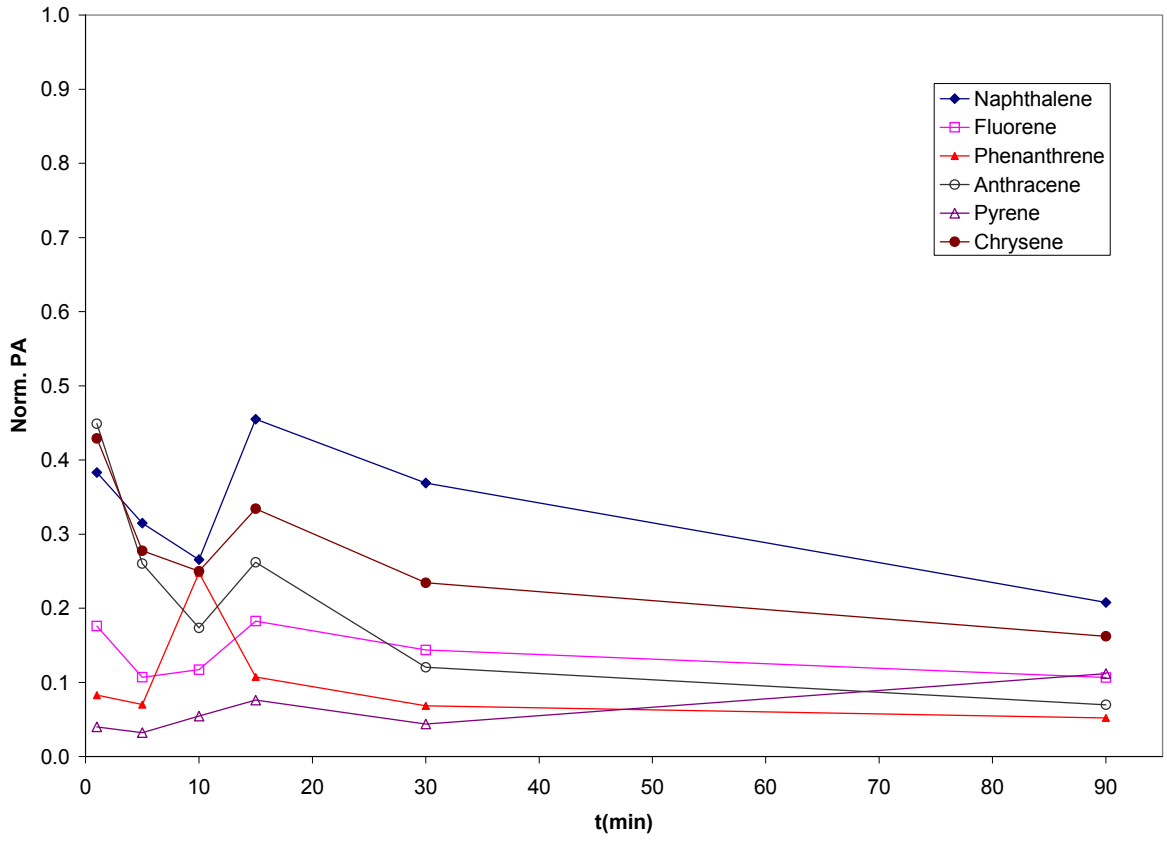


Fig. 3.3.11 Carboxylated PVC: Time dependence of the extraction process (given as normalised analyte concentration in solution)

During this experiment, some problems with the HPLC analysis occured which are reflected in the discontinuities of the concentrations as function of enrichment time. (the column blocked during the measurements, and as the backpressure was too high the column had to be backflushed). But for the measurements after 15 min the equipment was fully functional again, and the data from this point on may be evaluated without restrictions. The Carboxylated PVC has a very low affinity for the PAHs. After 90 min of extraction large amounts of the analytes still remain in the liquid phase. The equilibrium is not yet reached after 90 min.

3.3.12 Comparison of the Equilibrium Concentrations

Equilibrium (90 min)					
	MTMOS/ MeOH	**MTMOS/ iPrOH 0,5**	**MTMOS/ iPrOH 1,0**	**10% C8-TEOS**	**10% 3-APrTEOS**
Naphthalene	0.186	0.030	0.028	0.252	0.086
Fluorene	0.256	0.022	0.017	0.152	0.014
Phenanthrene	0.404	< l.o.d.	0.023	0.160	0.014
Anthracene	0.123	< l.o.d.	0.022	0.311	0.009
Pyrene	0.209	< l.o.d.	0.050	0.169	0.015
Chrysene	0.144	< l.o.d.	0.032	0.473	0.000
	MTEOS/ TEOS	**MTMOS/ TMOS**	**C8 SPE-ED**	**Carbox. PVC**	**LiChrolut**
Naphthalene	0.056	< l.o.d.	0.141	0.208	< l.o.d.
Fluorene	0.011	< l.o.d.	0.041	0.107	< l.o.d.
Phenanthrene	0.021	< l.o.d.	0.035	0.052	< l.o.d.
Anthracene	0.012	< l.o.d.	0.019	0.070	< l.o.d.
Pyrene	0.035	< l.o.d.	0.033	0.112	< l.o.d.
Chrysene	0.012	< l.o.d.	0.009	0.162	< l.o.d.

Tab. 3.3.12 Overview of the extraction efficiencies reached after an equilibration time of 90 min (expressed as normalised PA of the concentration of the analytes remaining in solution)

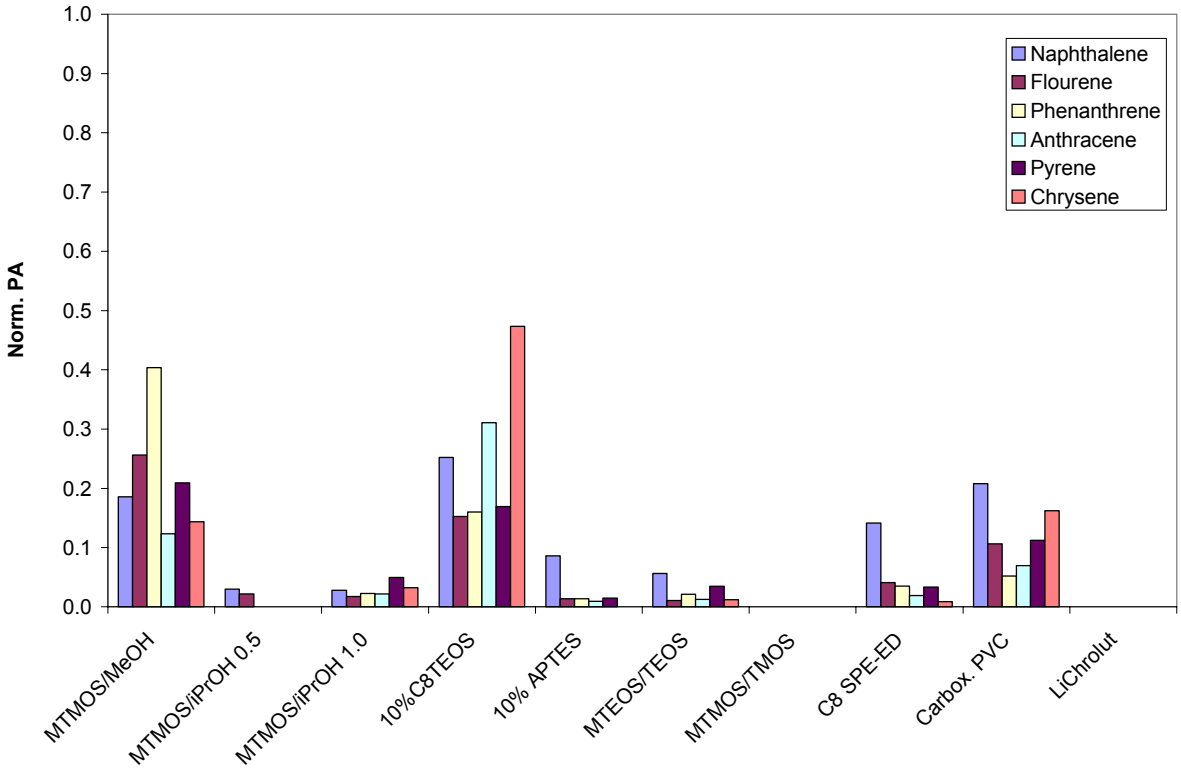


Fig. 3.3.12 Overview of the extraction efficiencies reached after an equilibration time of 90 min (expressed as normalised PA of the concentration of the analytes remaining in solution)

The materials **MTMOS/MeOH** and **10% C8-TEOS** leave large amounts of analytes in the solution after 90 min. As the extraction kinetics of these materials have shown, the equilibrium is not yet reached after 90 min.

MTMOS/iPrOH 0.5 extracts the analytes very well, after 90 min only naphthalene and fluorene can be detected.

MTMOS/iPrOH 1.0 depletes the analytes equally well from the solution. The equilibrium concentrations are a little bit higher than for the MTMOS/iPrOH 0.5.

10% APTES and **MTEOS/TEOS** behave in a very similar way. The extraction is equally fast and the equilibrium concentrations are more or less the same. The concentration of naphthalene is a little bit higher with the 10% APTES material since this sol-gel is more polar than MTEOS/TEOS.

MTMOS/TMOS and **LiChrolut** show similar properties. The extraction kinetics for chrysene is in both cases significantly slower than for the other analytes, and all analyte concentrations are below the detection limit after 90 min.

C8 Spe-Ed extracts the analytes not in a satisfactory way. The extraction efficiency for the investigated compounds is roughly half of that of the 10% 3-APTES. The equilibrium concentrations seem to be determined by the pKow of the analytes.

Carboxylated PVC proves to be less / not suitable for extraction. The extraction is very slow, so the equilibrium is not yet reached after 90 min, the kinetics indicate that the equilibrium would be reached after about 150 min.

3.4 Desorption Studies

The results of the desorption studies are summarised in tables 3.4.1.-3.4.3 which give the recovery rates (R), the breakthrough (B), and the absolute standard deviation (D) of the recovery rates (R).

	MTMOS/MeOH			MTMOS/iPrOH 0.5			MTMOS/iPrOH 1.0		
	R %	B %	D %	R %	B %	D %	R %	B %	D %
Chlorobenzene	62.9	2.9	45.4	73.5	0.9	37.5	74.8	0.7	4.3
Propylbenzene	84.2	0.8	23.8	76.2	0.4	31.4	80.2	0.2	2.8
Benzonitrile	12.1	6.4	6.4	120.8	1.2	53.9	108.7	1.1	2.9
1,3 Dichlorobenzene	80.1	36.6	32.9	89.9	0.8	31.5	97.8	0.4	11.4
1,2,3 Trimethylbenzene	82.6	2.1	29.0	87.0	0.5	34.9	94.3	0.3	4.8
Naphthalene	90.1	5.6	32.0	102.2	0.2	27.6	110.6	0.1	9.1
1-Naphthol	13.0	9.7	2.0	138.8	7.6	73.0	167.5	5.8	64.4
Fluorene	117.8	2.8	38.3	136.6	0.8	103.0	129.7	0.7	83.8
Diphenylamine	91.2	6.2	28.4	256.8	1.4	183.2	245.8	1.1	160.5
Phenanthrene	231.0	1.0	96.1	253.8	0.1	168.7	270.9	0.1	173.6
Anthracene	100.8	0.5	9.7	104.6	0.1	64.2	111.6	0.1	59.4
Pyrene	107.3	0.6	23.7	137.8	0.1	96.0	146.5	0.1	96.2
Chrysene	109.9	1.3	31.6	153.0	0.2	115.6	207.7	0.0	173.4

Tab. 3.4.1: Recovery rates (R), breakthrough (B) and absolute standard deviation (D) of the investigates substrates

	10% C8-TEOS			10% APTES			MTEOS/TEOS		
	R %	B %	D %	R %	B %	D %	R %	B %	D %
Chlorobenzene	20	23.1	8.6	53.5	0.7	6.8	19	3.8	2.6
Propylbenzene	40	19.9	8.6	76.8	0.2	7.9	25.7	0.5	8.1
Benzonitrile	3.2	6.7	0.9	34.9	1.2	5.6	12.8	1.7	9.1
1,3 Dichlorobenzene	35.7	14.6	7.3	80.1	0.5	12.5	27.3	2.2	8.9
1,2,3 Trimethylbenzene	40.4	23.7	10.7	75	0.4	11.1	28.1	0.4	9.2
Naphthalene	44.8	12.2	10.5	93.5	0.2	10.4	33.1	0.6	12
1-Naphthol	6.9	24.5	9.4	49.1	5.6	37	15.8	9.2	16.3
Fluorene	54.6	0.6	15	93.6	0.6	31	39.3	0.9	16.1
Diphenylamine	33.8	4.2	16.3	155.9	1.1	85.7	28.5	1.3	5.1
Phenanthrene	51.2	1.7	13.3	180.4	0.1	75.5	47.8	0.1	23.4
Anthracene	33.2	2.6	12.7	85.2	0	33.2	33.2	0.2	9.9
Pyrene	23.7	3	16	108.7	0.1	54.9	35.5	0.2	19.4
Chrysene	11.5	0.3	11.9	97.7	0.1	50.5	27.1	0.2	20.6

Tab. 3.4.2: Recovery rates (R), breakthrough (B) and absolute standard deviation (D) of the investigates substrates

	MTMOS/TMOS			C8 SPE-ED			LiChrolut		
	R %	B %	D %	R %	B %	D %	R %	B %	D %
Chlorobenzene	29.9	9.5	6.5	80.1	1.3	4.9	72.2	1.5	1.2
Propylbenzene	45.4	1.8	5	65.6	0.5	1.8	63.5	0.5	6.1
Benzonitrile	13.2	2.9	10.9	99.5	1.3	20.7	28.4	1.6	7.2
1,3 Dichlorobenzene	45.1	2.8	5.6	91.2	1.4	13.1	69.5	1.3	7.1
1,2,3 Trimethylbenzene	49.2	3.4	5.3	89.7	0.5	4.7	80.9	0.7	3.2
Naphthalene	55	1.8	8.2	124.1	0.3	15.6	81.8	0.3	22.2
1-Naphthol	10	5.6	4.8	349.7	6.5	49.2	6.1	7.0	1.3
Fluorene	59.4	0.6	7.9	106.0	0.7	44.7	48.8	0.9	24.6
Diphenylamine	60.5	0.9	32	288.8	1.3	146.2	6.3	1.4	4.2
Phenanthrene	58.8	0.3	20.9	185.3	0.1	87.8	49.8	0.1	28.8
Anthracene	53.9	0.1	47.4	73.8	0.1	6.3	39.2	0.0	11.7
Pyrene	25.1	0.7	22.3	61.8	0.2	10.5	29.4	0.9	14.2
Chrysene	21.1	0.5	28	42.5	0.3	17.2	18.1	0.4	17.0

Tab. 3.4.3: Recovery rates (R), breakthrough (B) and absolute standard deviation (D) of the investigates substrates

3.4.1 MTMOS/MeOH

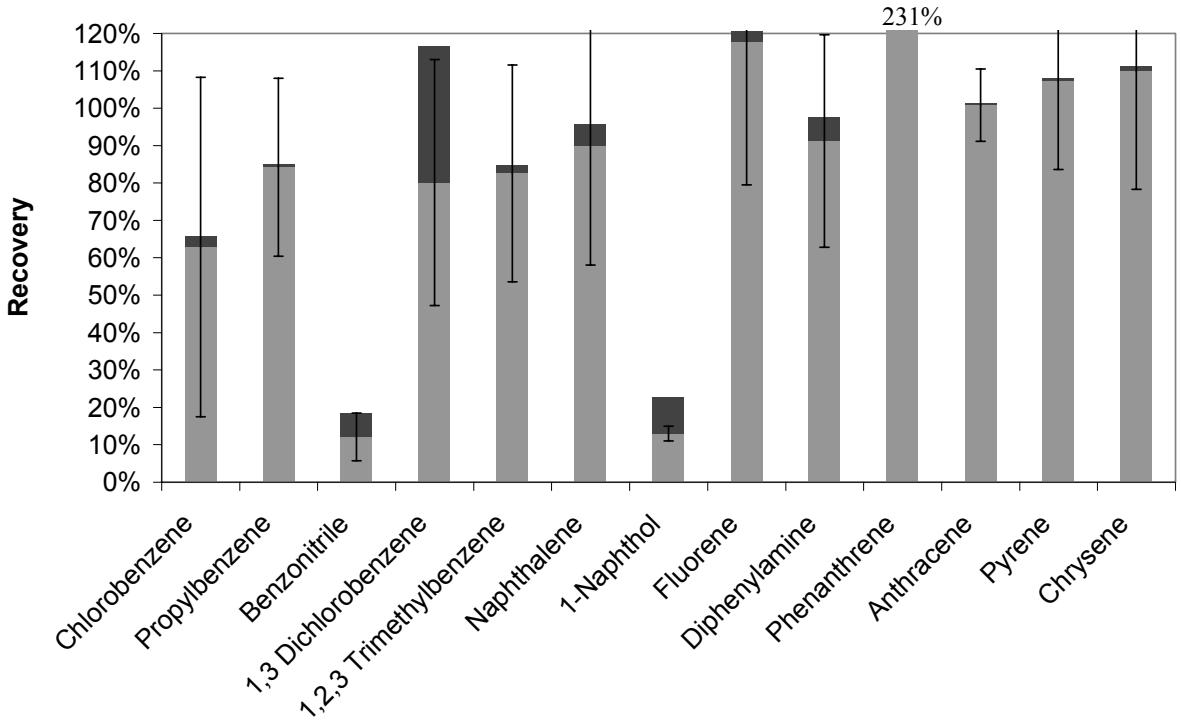


Fig.3.4.1 Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with MTMOS/MeOH

This material showed a high flow resistance during the sample enrichment. As can be seen, the recovery rates for all hydrophobic analytes range from 63% for chlorobenzene to 118% for fluorene. The recovery rate for phenanthrene is 231%. This extreme overestimation will be discussed in section 3.5.4. The recovery rates for benzonitrile and 1-naphthol are 13%, these analytes exhibits, even when compared to the results obtained with the other substrates, a significant breakthrough, which means that they are probably not adsorbed to a highextent.

3.4.2 MTMOS/iPrOH 0.5

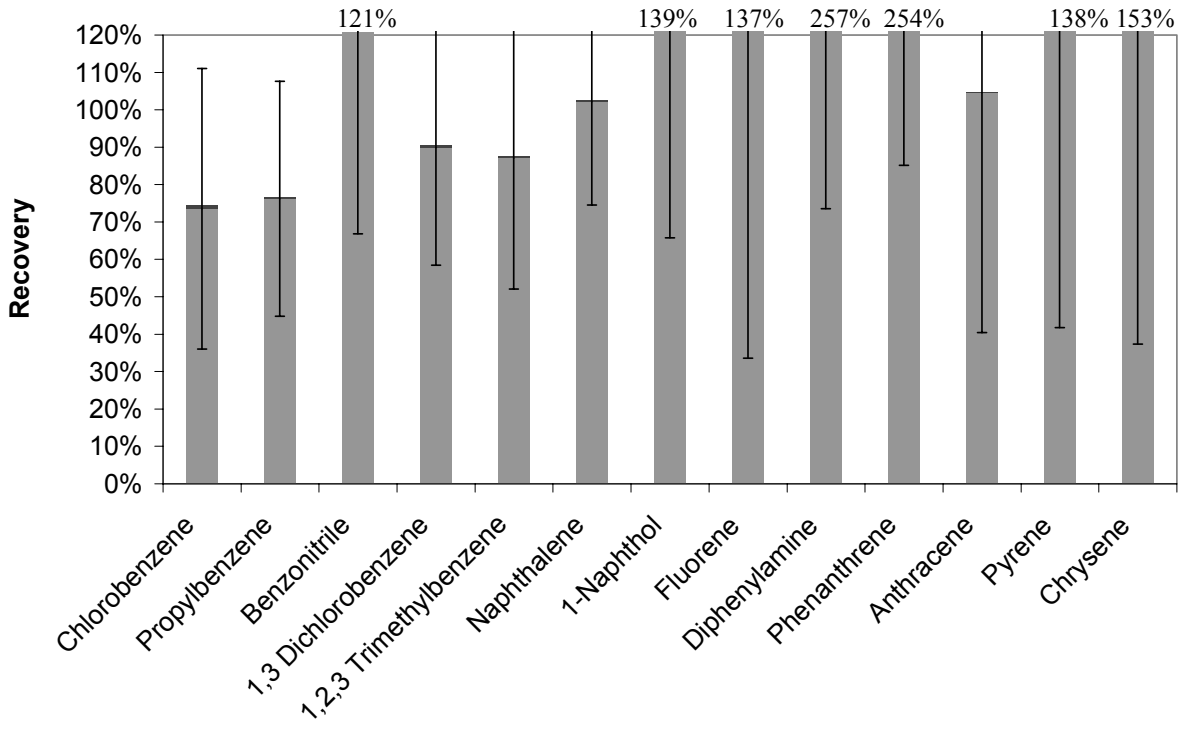


Fig.3.4.2: Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with MTMOS/iPrOH 0.5

This material also showed a high flow resistance during all experiments. The recoveries for all analytes are excellent, chlorobenzene with 73% is the analyte with the lowest recovery. Even the hydrophilic analytes are adsorbed and desorbed to a large extent. The recovery rates for most PAHs, 1-naphthol and diphenylamine exceed 140%, and in two cases even 250% which will be discussed later. However, the recovery rates for

naphthalene and anthracene as well as the recovery rates of the hydrophobic substituted aromatic compounds show in no case this extreme overestimation, so they can be viewed as valid.

3.4.3 MTMOS/iPrOH 1.0

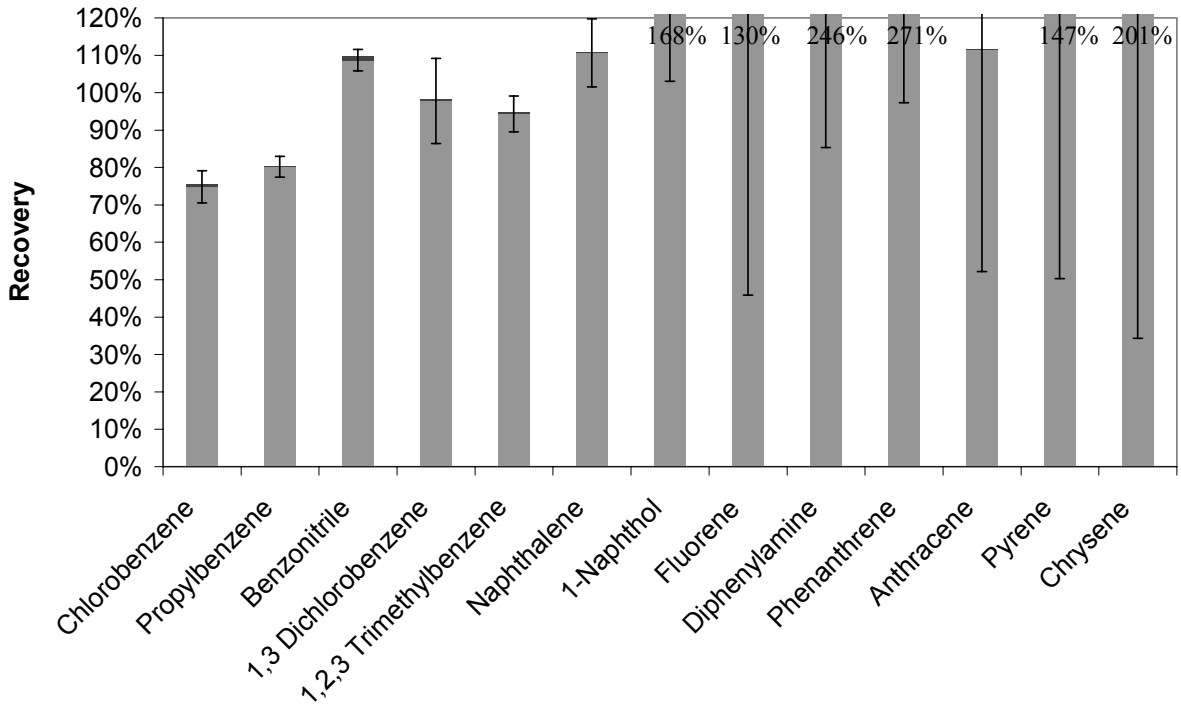


Fig.3.4.3: Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with MTMOS/iPrOH 1.0

Like the two previous materials, MTMOS/iPrOH 1.0 also presented a high flow resistance. With the exception of benzonitrile, fluorene and diphenylamine, the recovery rates for all analytes are slightly higher than the recovery rates obtained for the MTMOS/iPrOH 0.5 material. Chlorobenzene is recovered the least with a rate of 75%, diphenylamine shows the highest recovery rate with 246%. For none of the analytes a significant breakthrough is observed.

3.4.4 10% C8-TEOS

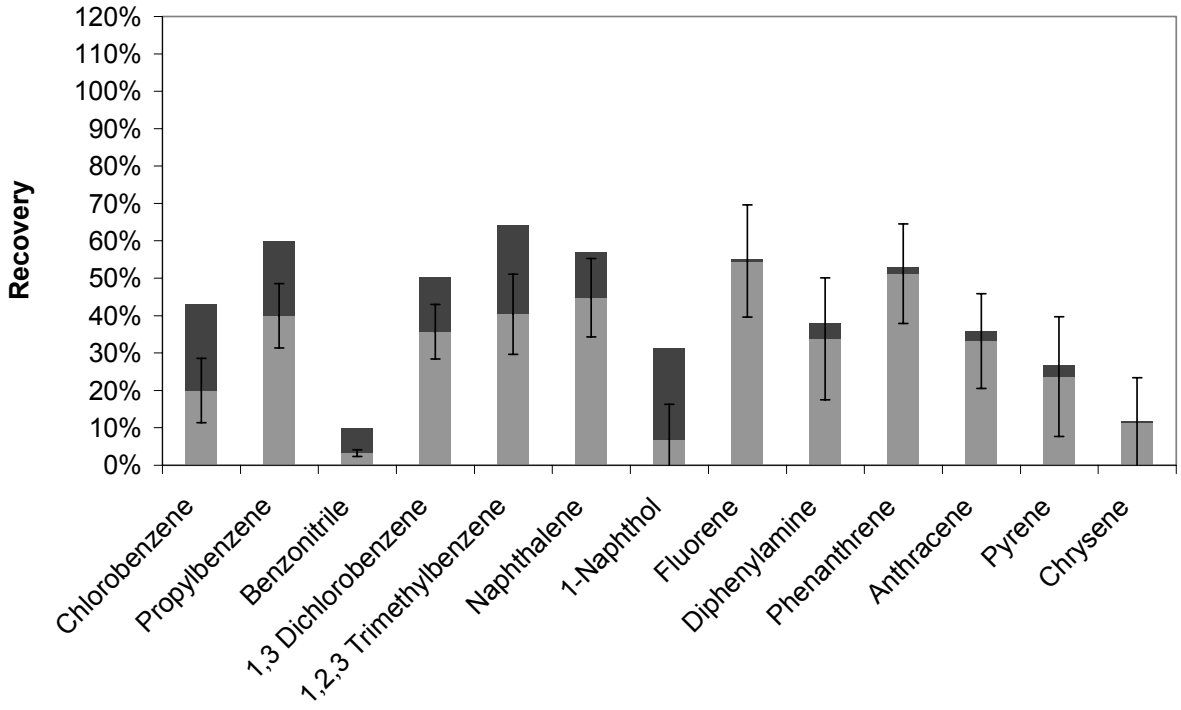


Fig.3.4.4 Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with 10% C8-TEOS

This material showed no significant flow resistance, it was not necessary to apply pressure in order to press the spiked solution through the SPE column. Compared to all other materials, the recovery rates of all analytes are very low. Benzonitrile and 1-naphthol are recovered the least with rates of 3.2% and 6.9%, , but even the hydrophobic PAHs are recovered with only low rates between 11% for chrysene and 55% for fluorene. The previous measurements indicate that this material does not have a sufficiently large specific surface to achieve a fast adsorption and a high capacity. The low flow resistance could also mean that due to the rather large particles fractions of the sample could channel through the SPE column bed with insufficient interaction for a succesful adsorption.The breakthrough is significant for all analytes except the PAHs with 24.5% for 1-naphthol as highest value.

3.4.5 10% APTES

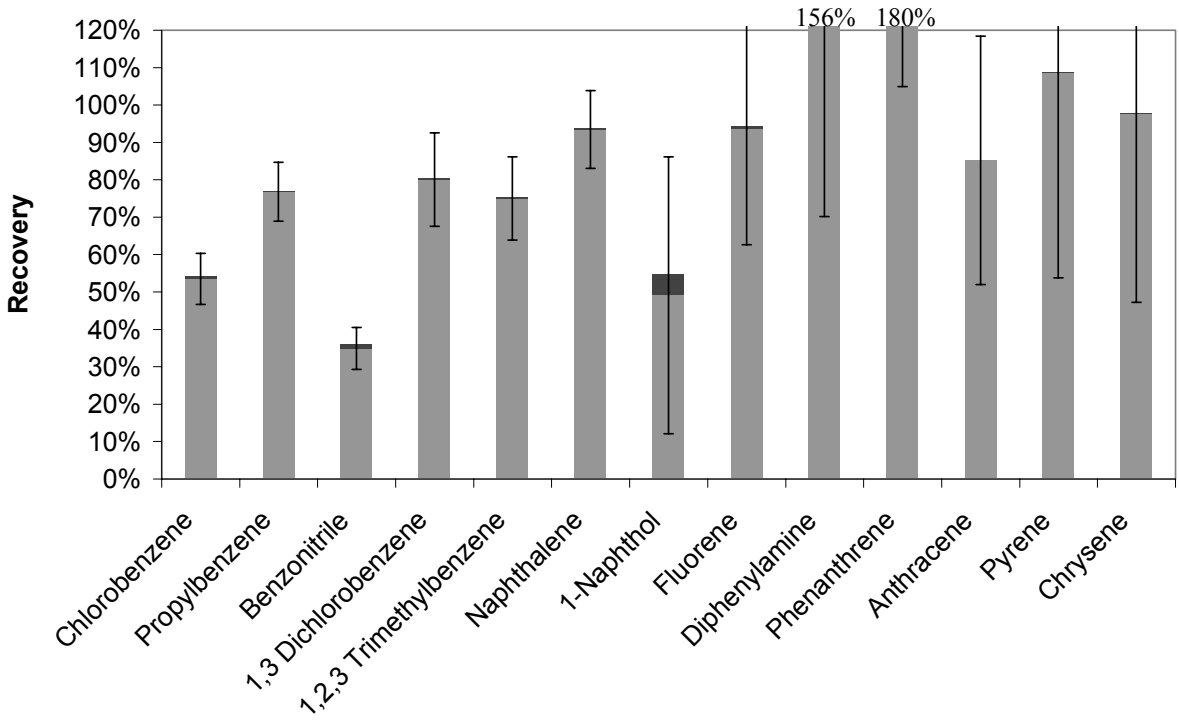


Fig.3.4.5: Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with 10% APTES

This material had the highest flow resistance of all investigated sol-gel materials. The recovery rates are low compared to the previous materials. The polar compounds benzonitrile and 1-naphthol are recovered with rates of only 35% and 49%, which is surprising because this material should be more hydrophilic than both MTMOS/iPrOH materials. Phenanthrene has the highest recovery rate with 180%, in general all PAHs have high recoveries.

3.4.6 MTEOS/TEOS

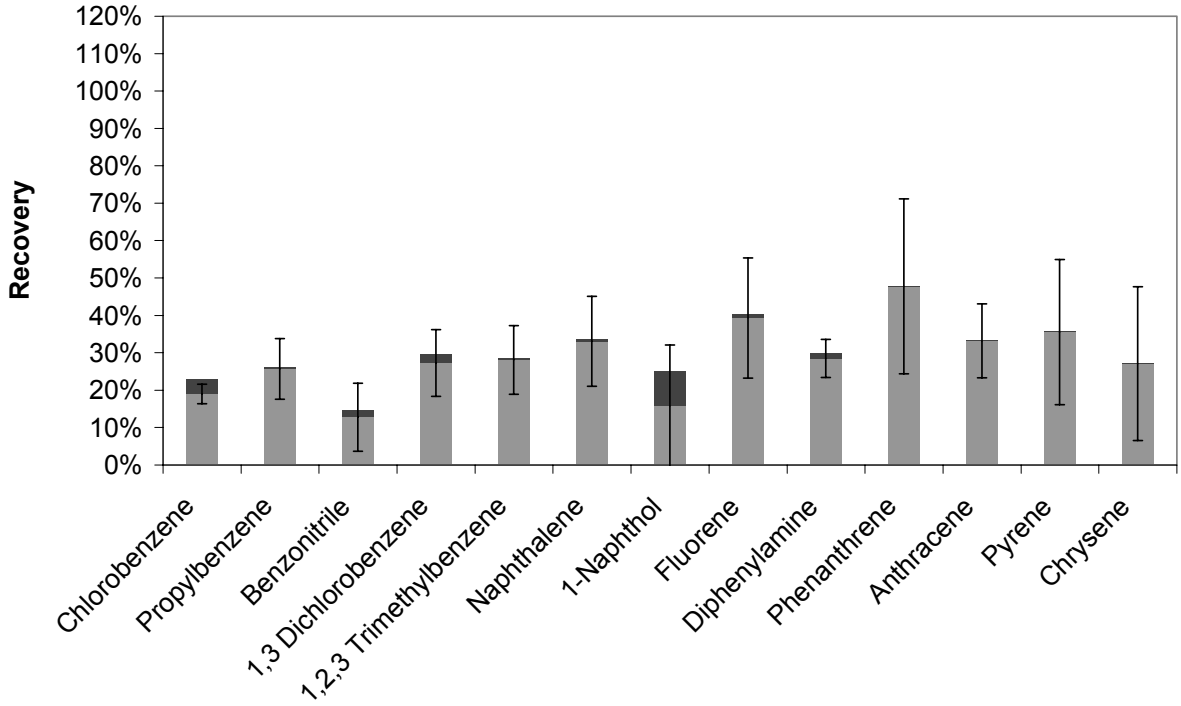


Fig.3.4.6: Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with MTEOS/TEOS

This material showed only low flow resistance for the sorption processes. Again, the hydrophilic analytes benzonitrile and 1-naphthol have the lowest recovery rates with 13% and 10%. The hydrophobic aromatic compounds and the PAHs have comparable recovery rates, reaching from 21% for chrysene to 59% for fluorene. All substituted aromatic compounds exhibit a certain extent of breakthrough, chlorobenzene has the largest degree of breakthrough with 9.5%.

3.4.7 MTMOS/TMOS

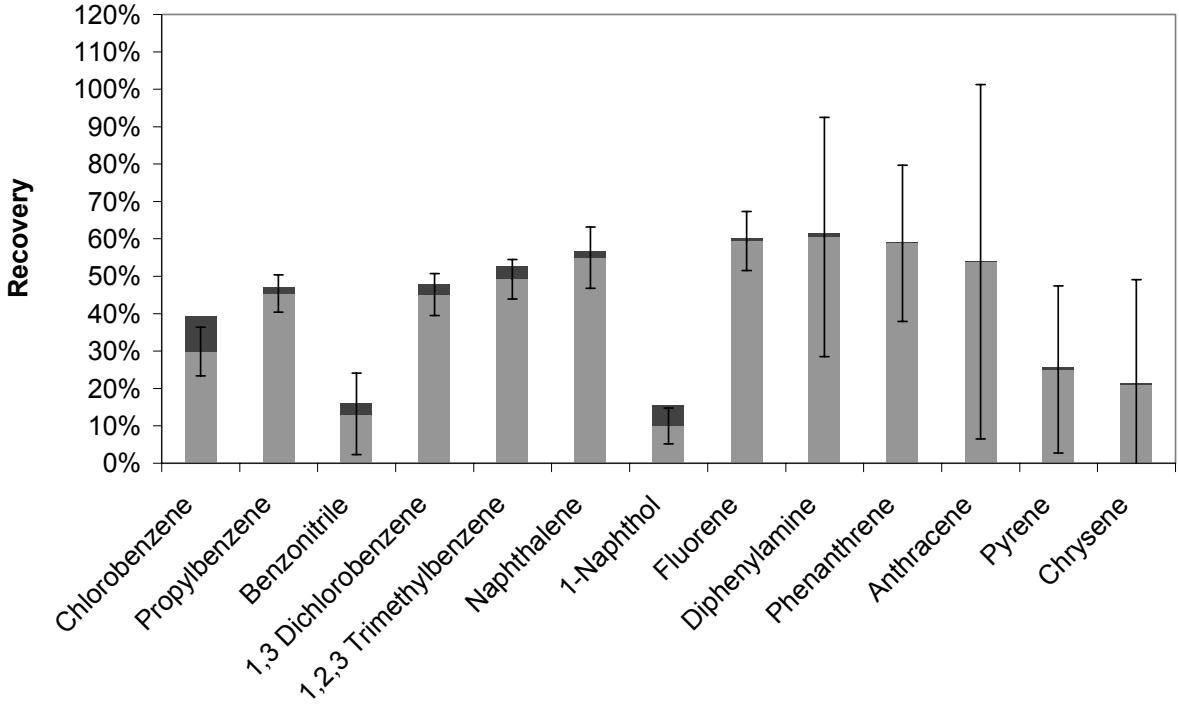
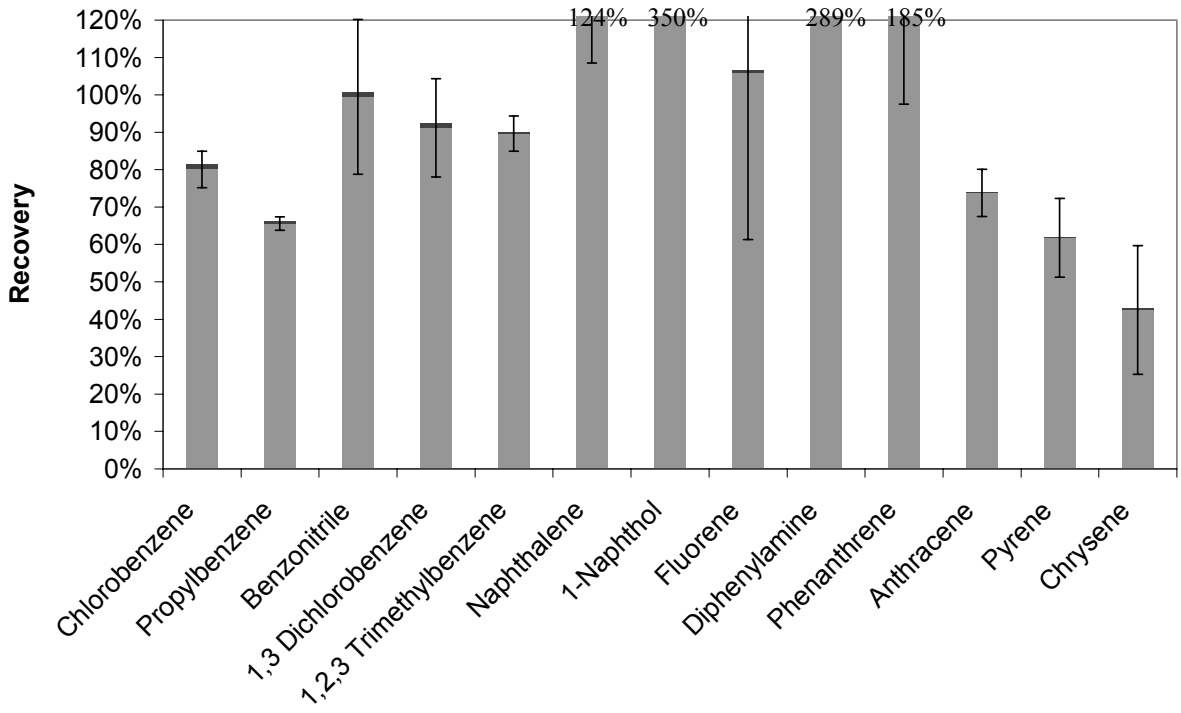


Fig.3.4.7: Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with MTMOS/TMOS

This sol-gel material also had only a negligible flow resistance. The recovery rates are in general low, reaching from 12.8% for benzonitrile to 47.8% for phenanthrene. Only chlorobenzene and 1-naphthol show a significant breakthrough with 3.8% and 9.2%. The differences between the recovery rates of hydrophobic and hydrophilic compounds is smaller than for the MTMOS/TMOS material, it seems that MTEOS/TEOS is less selective.

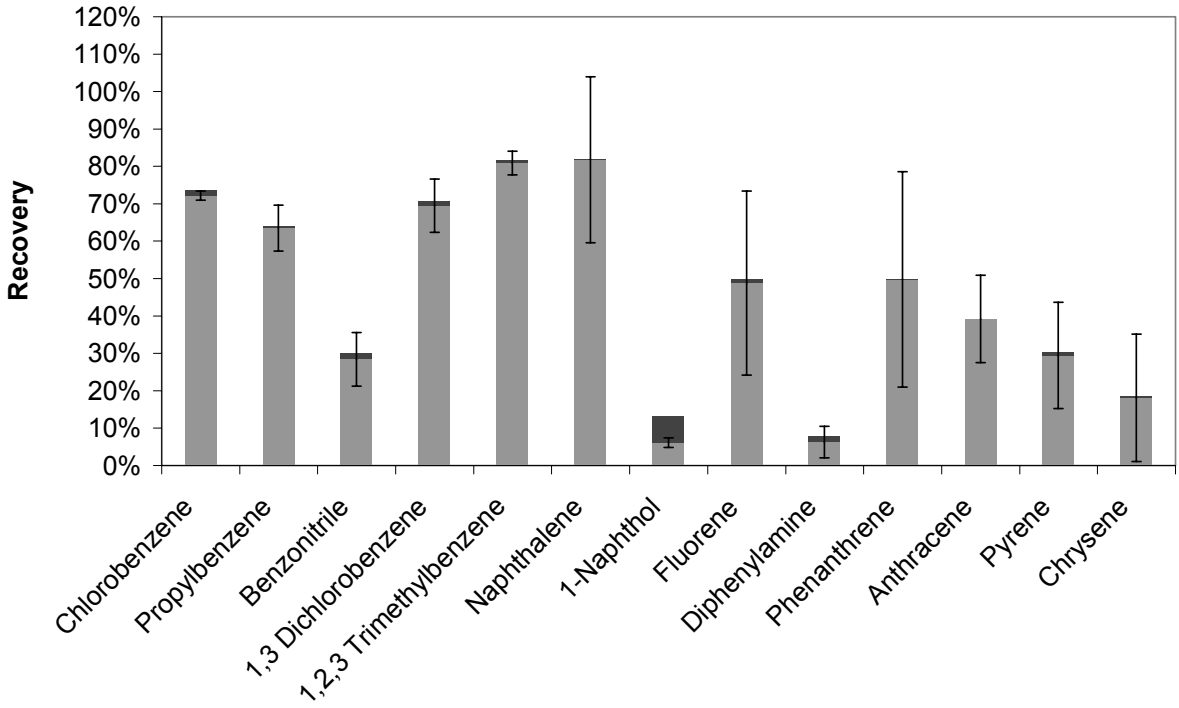
3.4.8 C8 Spe-Ed



Tab. 3.4.8: Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with C8 Spe-Ed

This commonly used SPE material showed no significant flow resistance. The recovery rates are overall high. Chrysene has the lowest recovery rate with 42.5%, 1-naphthol has the highest recovery rate with 350%. 1-naphthol has also the highest breakthrough value with 6.5%, all other breakthrough values are below 2% and therefore not significant.

3.4.9 LiChrolut



Tab. 3.4.9: Recovery rates (light gray), breakthrough (dark gray) and absolute standard deviation (error bars) of the recovery experiments performed with of LiChrolut

Similar to the C8 Spe-Ed cartridge this SPE material also showed no appreciable flow resistance. The recovery rates for all hydrophobic aromatic analytes and naphthalene are comparatively high with 63.5% for propylbenzene and 81.8% for naphthalene. The polar compounds have very low recovery rates, with 28% for benzonitrile, 6% for 1-naphthol and diphenylamine. This SPE material is very polar and therefore the polar analytes can probably not be eluted with the apolar n-hexane. The breakthrough value for 1-naphthol is the highest with 7%, all other breakthrough values are not significant. The reason for these comparatively low recovery rates is probably the choice of n-hexane as solvent, which will be discussed in 3.5.4.

4) Discussion

4.1 Discussion of Analytical Methods

4.1.1 SPME/GC Investigations

The SPME/GC method for characterising the solid substrates is rather limited in its applicability. In the experiments it was observed that the measured analyte concentrations decrease with the number of extractions, even when using a blank sample without substrate. This prevents the method from being used for the determination of enrichment kinetics. The used glass vessels are not likely to have a high affinity for the applied apolar test analytes. Since the tightness of the used vessels has been confirmed in preliminary experiments, the most plausible explanation is that the SPME fibre itself influences the equilibrium between solid and liquid phase. Sicne SPME is a consumptive (although not exhaustive) extraction technique, it will remove significant amounts of analytes from the solution and thus shift the equilibrium between the substrate abd the sample solution. A second explanation could be that, although the liquid phase has been firmly stirred, the equilibrium between gas and liquid phase has not been reached for all but the first extractions in a series. Another drawback of this method is the long extraction time of 20 min. As has been shown in the later measurements the enrichment on the solid substrates takes place in the first 10-15 min, so there is no chance to observe the extraction kinetics with this setup. So the only chance to perform these measurements is to make a one point analysis at the equilibrium and to get a semi-quantitative overview of the affinity of the substrates to the applied analytes.

4.1.2 Enrichment Profiles by HPLC-DAD

The material of the syringe filter (nylon) proved to be a factor with significant influence on the results. Its affinity to polar analytes like 1-naphthol and diphaenylamine prohibited to obtain results for these compounds. The apolar analytes were adsorbed by the filter material at a ratio of only 10-50%, nearly independent from the initial concentration. So the extraction kinetics could be measured for the apolar analytes. The time resolution of roughly 1 min proved to be enough to follow the extraction kinetics for some substrates,

since in general the extraction is completed to a large degree within the first 5 minutes. The disadvantage of this setup is the rather time consuming manual sampling. The HPLC-DAD measurements themselves could be performed with an autosampler.

For the extraction profiles of policyclic aromatic hydrocarbons the same experimental setup as for the extraction profiles of substituted aromatic compounds was used. However, the filter material had to be changed to regenerated cellulose. The nylon filters retained over 95% of all analytes except naphthalene, which is of course not acceptable. In comparison to this, the regenerated cellulose filters provided recoveries for the PAHs in the filtration step of at least 50%. The analyte concentrations had to be reduced form 10 to 2 ppm due to a very limited solubility of the higher PAHs. The extraction kinetics could be observed for all substrates since the PAHs are larger than the substituted aromatic compounds and consequently their diffusion coefficients are lower and therefore the extraction kinetics are generally slower. The advantages and disadvantages of this experimental setup are the same as discussed for the extraction profiles of substituted aromatic compounds.

4.1.3 Desorption Studies

As already mentioned, some recovery rates exceed 140%, especially those of 1-naphthol, diphenylamine and all PAHs except naphthalene and anthracene. The cause of this problem is assumed to be the calibration. The calibration standard had 4 ppm analyte concentration. If the recovery rate of an experiment was 100%, the analyte concentration in the eluate would approximately be 12 ppm. So there may be a factor of 3 between the analyte concentration of the calibration standard and the analyte concentration of the eluates. A one point calibration assumes a linear response between injected amount and detected signal with a calibration curve traversing the origin. If this is not the case, the calibration would lead to an overestimation or underestimation of the analyte concentration of samples. A calibration with several standards with different concentration would solve this problem. Since this problem only occurs for four materials and then for a maximum of four analytes, it was decided to refrain from a multilevel calibration. Additionally the desorption yield seems to be a problem especially for polar analytes and polar substrates. The choice of n-hexane was made because the results for

PAHs would be of major value for this project and n-hexane is commonly used for the desorption of PAHs in environmental analysis. However, to improve the desorption of polar analytes and from polar surfaces, the desorbens has to be more polar. Probably acetone or acetonitrile would represent a good compromise for polar as well as for apolar analytes and surfaces.

4.2 Discussion of the Properties of Individual Substrates

4.2.1 MTMOS/MeOH

The BET measurements have shown that this sol-gel material has a very small specific surface area with 11 m^2/g. The BJH evaluation of the BET isotherm gives 5.7 nm as mean mesopore diameter, whereas the REM evaluation gives 0.69 µm as mean macro pore diameter. The density of 0.211 g/cm^3 confirms the high porosity of this material. The equilibrium concentrations of the analytes obtained in the SPME/GC measurements are comparatively high. With the exception of both n-alkanes the measured concentrations correlate with the pKow of the analytes, the equilibrium concentrations of the n-alkanes are higher than expected. This means that the MTMOS/MeOH material has a selectivity in the enrichment between n-alkanes and aromatic compounds which can be caused by steric reasons. The extraction profiles of the substituted aromatic compounds demonstrate that the kinetics of the extraction is similar for all analytes. The equilibrium state is reached at approximately 15 min, the equilibrium concentrations correlate with the pKow of the analytes with the exception of 1,2,3 trimethylbenzene. The adsorption of this analyte seems to be hindered by steric reasons. The corresponding measurements with PAHs as test analytes again show a uniform extraction kinetics for all analytes, this time with approximately 40 min of equilibration time. The equilibrium concentrations in solution are again comparatively high, and they do not follow the pKow, which means that their adsorption is influenced by the morphology of this material. Surprisingly, the desorption studies have as result that the recoveries for all analytes except benzonitrile and 1-naphthol are excellent. Despite the fact that this material showed a high flow resistance, the breakthrough values are high compared to other materials, which means that a large part of the analytes is not adsorbed. Probably the capacity of this material is exceeded by the applied amount of analytes. In summary, this sol-gel material provides

not a high capacity for adsorption. The adsorption kinetics are only moderately fast, and the adsorption of some of the analytes is influenced by steric reasons. This means that this material has neither a high capacity, nor does it show a favourable kinetics and additionally the adsorption is not unspecific. This material is not a suitable substrate for the application as SERS active enrichment layer.

4.2.2 MTMOS/iPrOH 0.5

This sol-gel derived material has a high specific surface area with 293 m^2/g. The mean pore diameter in the mesopore domain is 4.2 nm, the mean macropore diameter is 0.41 µm. This material is also very porous, its density is 0.254 g/cm^3. The equilibrium concentrations obtained in the SPME/GC experiments are very low and indicate that this substrate provides a high capacity for adsorption. The equilibrium concentrations correlate all with the pKow of the analytes, so the adsorption is not influenced by the steric structure of the analytes. The extraction profiles of substituted aromatic compounds have as result that the extraction kinetics are rather fast with 5 min equilibration time. The equilibrium concentrations are very low, only benzonitrile could be detected in the liquid phase at the equilibrium. The extraction profiles of the PAHs show again that the adsorption kinetics are comparatively fast with the exception of chrysene, the largest PAH. The reason for this slower kinetics is probably a diffusion hindrance for chrysene by an unfavourable pore size distribution. The recovery rates obtained during the desorption studies are all larger than 70%, the breakthrough values are negligible for all analytes. This means that the anylytes, including polar substances, are adsorbed as well as desorbed with very good recoveries. As a summary, this material certainly has the desired properties a sensor layer should have: A large surface area which provides a high capacity for adsorption, a fast equilibrium time which would lead to a fast sensor response time and a reversibility of the adsorption, which guarantees that there is an equilibrium between liquid and solid phase and that the sensor can be regenerated after exposure to high concentrations of analyte. The only problem could be that the hydrophobic substrate is not easily wetted and therefore the mass transfer between liquid phase and solid phase is hindered.

4.2.3 MTMOS/iPrOH 1.0

As determined from the BET isotherm, this material has a specific surface area of 206 m^2/g. The obtained mean pore diameter in the mesopore range is 4.2 nm, which is comparable with the MTMOS/iPrOH 0.5. The REM pictures give as a result a mean macro pore diameter of 0.71 µm. The density of this substrate is 0.213 g/cm^3 and confirms its high porosity. The results of the SPME/GC measurements are comparable with the MTMOS/iPrOH 0.5 substrate. The equilibrium concentrations are almost the same and follow the pKow of the test analytes without further steric influence. The extraction profiles of substituted aromatic compounds result in the equilibrium concentrations being reached after 5 min of extraction. The analyte concentrations at the equilibrium are almost the same as for MTMOS/iPrOH 0.5 with the difference that chlorobenzene can still be detected at the equilibrium in the supernatant solution. The extraction profiles of PAHs have as result that the kinetics are the same for all analytes with approximately 15 min as equilibration time. Unlike as observed for MTMOS/iPrOH, chrysene is extracted with the same kinetics as the other analytes. The equilibrium concentrations are very low and almost equal for all analytes. The difference in the pKow of the analytes is not reflected in the equilibrium concentrations. The recovery rates obtained in the desorption studies are even slightly better than the recovery rates obtained for MTMOS/iPrOH 1.0, they are all higher than 75%. So, like with the previously discussed material adsorption and desorption work well. This material seems to be suitable for the application as enrichment layer for sensor application. It has a high capacity, the adsorption has a fast kinetics and the adsorption is reversible. Again, the poor wettability could be a drawback for its application as sensor layer.

4.2.4 10% C8-TEOS

The mean pore diameter in the macropore domain is 0.83 µm, the density of this material is 0.276 g/cm^3, which is slightly more than the density of other macroporous materials. The equilibrium concentrations of the model analytes in the SPME/GC measurements are comparatively high. They follow the pKow of the analytes with the single exception of n-nonane. This is surprising since the equilibrium concentration of the chemically similar n-dodecane seems to fit with its pKow. However, the high concentration of n-nonane

remaining in the sample solution cannot be explained by steric problems of the adsorption. The extraction profiles of substituted aromatic compound have as result that the extraction kinetics are comparatively slow with about 25 min of equilibration time. The equilibrium concentrations of the analytes in the liquid phase themselves are very high and seem to follow their pKow. The corresponding experiments with PAHs as test analytes show similar results. The kinetics are very slow with probably more than 90 min equilibration time, which means that even the concentrations after 90 min do not represent the equilibrium. However, the remaining amounts of analytes after 90 min are comparatively high and do not follow the pKow, but do rather represent the adsorption kinetics of the analytes. The desorption studies show that the recovery rates are very low for polar analytes like benzonitrile and 1-naphthol. Even all apolar analytes are recovered with a rate of less than 60%. The high breakthrough values indicate that probably the capacity of this material is exceeded by the applied amount of analytes. Another explanation for the low recovery rates is that a part of the spiked solution passes the particles without having good contact with the surface, which would be in agreement with the low flow resistance of this material. As a summary, this material is not suited for an application as enrichment phase for a chemical sensor. Its capacity is very limited and its extraction kinetics is very slow. This can be explained by the presence of micelle-like hydrophobic domains formed by C8 residues into which the analytes can diffuse at only a very limited rate.

4.2.5 10% APTES

The BET measurements with this substrate give as a result a specific surface area of 201 m^2/g and a mean pore diameter in the mesopore range of 6.5 nm. The REM measurements show a mean macropore diameter of 0.69 µm. The bulk density of this material is 0.198 g/cm^3. The physical parameters of this material are very similar to the physical parameters of MTMOS/iPrOH 1.0. The equilibrium concentrations obtained for the SPME/GC measurements are roughly twice as high as the equilibrium concentrations of both MTMOS/iPrOH materials, but lower than for MTMOS/MeOH and 10% C8-TEOS. The extraction profiles of substituted aromatic compounds demonstrate that the extraction kinetics are comparatively fast with roughly 5 min equilibration time. At the equilibrium only benzonitrile and chlorobenzene can still be detected in the liquid phase,

their concentration is also higher than observed for both MTMOS/iPrOH substrates. The extraction profiles of PAHs have a similar outcome. The extraction kinetics are uniform for all analytes, with roughly 10 min of equilibrium time. The concentrations at the equilibrium are comparatively low and seem to follow the pKow of the analytes. The recovery rates obtained at the desorption studies are larger than 35% for all analytes, polar analytes are recovered at a lower rate than apolar analytes. Only 1-naphthol has a significant breakthrough value, which means that all other analytes are adsorbed at a very high percentage. The problems of the desorption when using n-hexane as solvent for the desorption of analytes from a polar surface are discussed in chapter 4.1.3. As a summary, this material has an increases polarity compared with pure MTMOS derived materials. Since the physical properties are similar to both MTMOS/iPrOH materials, the reduced affinity to apolar analytes is approximately a result of the increased surface polarity. The increased wettability however may lead to a more favourable adsorption behaviour from an aqueous phase. So this material is well suited for the use as enrichment layer for apolar analytes from an aqueous phase.

4.2.6 MTEOS/TEOS

So far, no BET or REM measurements have been performed on this sol-gel derived substrate. This material was not available for the SPME/GC measurements or the extraction profiles of the substituted aromatic test analytes. The results of the extraction profiles of PAHs are that the extraction kinetics are uniformly fast with about 10 min of equilibration time. The analyte concentrations in the solution at the equilibrium are comparatively low and almost the same as obtained for MTMOS/iPrOH 1.0. The desorption studies show that the desorption step also represents a problem for this material, since it has an increased surface polarity. The recovery rates are all below 55%. This material had a low flow resistance which results from a large particle size. This could cause that an optimal contact between the liquid phase and the surface is not provided. As a result, significant breakthrough occurs for chlorobenzene, benzonitrile and 1-naphthol. As a summary, the experiments indicate that this material has a rather high capacity for adsorption. The extraction kinetics are comparatively fast and this material has a high wettability, which is necessary for a low mass-transfer resistance from the

liquid phase to the inner surface. So this material would be suited for a use as enrichment layer for a chemical sensor.

4.2.7 MTMOS/TMOS

BET measurements were performed with this substrate. Its specific surface area is 556 m^2/g and the meanmeso pore diameter is 8.8 nm. The extraction profiles of PAHs show that this material has very slow extraction kinetics for all analytes with 80-90 min equilibration time. At the equilibrium no analyte could be detected in the liquid phase, so its capacity as well as its affinity to the analytes is high. The desorption studies show similar results for the recovery rates as for MTEOS/TEOS. The recovery rates are comparatively low with 65% for diphenylamine as maximum. Again there are significant breakthrough values for chlorobezene, benzonitrile and 1-naphthol. So the problems with the desorption and the rather large particle size are the same as discussed for MTEOS/TEOS. As a summary, this material had no apparent macroporosity and the particle size could be the limiting factor for the kinetics, but this should then also be the case for MTEOS/TEOS. So the explanation for the slow extraction kinetics is an unfavourable pore size distribution. In spite of the high capacity of this material and its increased wettability, the extraction kinetics make this substrate inapplicable for the use as enrichment layer for a chemical sensor.

4.2.8 C8 Spe-Ed

Physical properties for this commonly used SPE material were not available. The equilibrium concentrations of the analytes as results of SPME/GC measurements are rather high and in the range of the MTMOS/MeOH substrate. The concentrations strictly follow the pKow of the analytes, which means that this material is, as expected, an almost ideal apolar phase. The extraction profiles of substituted aromatic compounds show that the extraction kinetics are very fast and that the equilibrium is reached after approximately 5 min. The equilibrium concentrations are comparatively high and follow roughly the pKow of the analyes. The extraction profiles of PAHs show that the extraction kinetics are fast for all analytes except chrysene, which could also be observed for other substrates. The equilibrium concentrations again correlate with the pKow of the analytes and can be compared with the equilibrium concentrations of 10% APTES. The

recovery rates obtained as a result of the desorption studies are comparatively high even for polar analytes. As a summary this material is very apolar. Its wettability proved to be limited. It is well suited for the use as SPE material, but it seems in comparison to other materials to have a limited capacity for adsorption.

4.2.9 C18 Spe-Ed

This material was also provided by Applied Separations. The SPME/GC measurements show almost identical equilibrium concentrations for all analytes compared to C8 Spe-Ed. The equilibrium concentrations correlate with the pKow of the analytes. However, this material showed an even worse wettability than C8 Spe-Ed, the particles were never fully suspended, somehow they stuck together and formed clusters. Since the results of the SPME/GC measurements were almost identical as for C8 Spe-Ed, it was decided to make no further measurements with this material.

4.2.10 LiChrolut

The LiChrolut material provided by Merck is also commonly used for SPE. The equilibrium concentrations in the SPME/GC measurements were below detection limit with the exception of toluene. The extraction profiles of substituted aromatic compounds have as result that the extraction kinetics of this solid could not be determined since after even one minute of extraction only benzonitrile could be detected just above the limit of detection. However, its concentration was constant during the whole observed period, so probably the equilibrium is reached within the first minute. This material showed the highest affinity for the applied analytes, only benzonitrile could be detected after 30 min of extraction. The extraction profiles of PAHs show that the extraction kinetics are fast for fluorene and anthracene. The equilibrium is reached after 5 min of extraction for these two analytes. Chrysene has a significant slower extraction kinetics with 15 min of equilibrium time. The concentrations of the other analytes were below detection limit after 1 min of extraction, which was also the case at the equilibrium for all analytes. Again, the LiChrolut material proved to have the highest affinity for all analytes. The desorption studies indicate that the recovery rates are surprisingly low for this material. Polar analytes like benzonitrile, 1-naphthol and diphenylamine are only recovered at a rate lower than 30%. However, the reason for the low recovery rates is the choice of n-

hexane as desorbing agent, which has been discussed in chapter 3.5.4. As a summary the affinity of LiChrolut to all applied analytes is unsurpassed. Its use as SPE material is surely justified, although the solvent has to be chosen with respect to the polarity of the SPE material and the analytes.

4.2.11 Polyacrylic acid

This polymer proved to be very hydrophilic. When exposed to water, it simply macerates and forms a gel. Its hydrophility is also represented in the results of the SPME/GC measurement. The relative equilibrium concentrations of all analytes in the liquid phase are almost 100%, which means that they are not retained at all by this polymer. Since this material dissolves in water, it was considered impossible to apply this material for the extraction profiles determined with HPLC-DAD analysis and the desorption studies.

4.2.12 PE/5% Polyacrylic acid copolymer

The PE/5% Polyacrylic acid copolymer proved to be very hydrophobic. There were problems to suspend the particles properly since they tended to float on the water surface. However, SPME/GC measurements were performed with this material. The equilibrium concentrations were almost identical to both Spe-Ed materials. This means that this copolymer is also very apolar and not selective. The problems of suspending this material properly led to the decision that it was of no further use as a comparison for the sol-gel substrates.

4.2.13 Carboxylated PVC

This polymer proved to have comparatively good wettability. The result of the SPME/GC measurements was that the equilibrium concentrations of all analytes in solution were comparatively high. As observed for MTMOS/MeOH the concentrations of n-nonane and n-hexane were higher than expected from their pKow, thus indicating that there are steric reasons which cause this selectivity. The extraction profiles of substituted aromatic compounds show that the extraction kinetics are, compared with other materials, slow. The equilibrium concentrations of all analytes are reached after 15 min. The analyte concentrations at the equilibrium are very high and rather similar to the equilibrium concentrations of 10% C8-TEOS, which means that the concentrations correlate with the

pKow of the analytes. The extraction profiles of PAHs also show slow extraction kinetics for this material. Again all analytes have the same kinetics and reach a state of equilibrium after 70-80 min. The concentrations at the equilibrium are moderate compared to other materials. The flow resistance of this material proved to be too high to execute the desorption studies with this material. As a summary, this material is not an excellent adsorbens. The equilibrium concentrations are in all cases high and the kinetics are comparatively slow.

5) Conclusion and Outlook

The aim of this diploma thesis, the development of screening methods for the characterisation of sol-gel substrates, has been successfully reached. Different experimental setups were developed to study both the kinetics and the thermodynamic equilibrium of the adsorption process of selected organic compounds from the liquid phase to the solid substrates. These setups allowed to characterise the suitability of the different materials developed and synthesised for the purpose of producing selective and sensitive sensor layers at least on a relative basis by the comparison of their response behaviour, adsorption and desorption behaviour.

However, a number of experimental problems were met during the experiments which hampered the characterisation of the materials in absolute terms and called for improvements and modiciations of the method: One major problem for the kinetics experiment was the affinity of the syringe filters for the applied set of analytes which led to a significant loss of analytes. For this reason, syringe filters with a lower affinity to the analytes have to be found, which poses a problem due to the wide range of polarities of the test compounds initially selected. Filters with metal membranes can be expected to be a suitable alternative showing less affinity for organic analytes. Alternatively, the sampling process has to be changed.

The use of substrates which need no graining and suspending in order to decrease the time necessary for wetting would make filtering obsolete. This could be achieved by using substrates in the form of thin films. However, due to the chosen approach for the characterisation of the substrates which is based on the decrease of the concentration in

the solution rather than the determination of the amount of substance adsorbed to the substrate, at least 0.1 g of substrate are necessary to achieve an observable decrease of analyte concentration in solution. To deriveabsolute values for the physico-chemical properties of the substrates, an improved calibration procedure has to be applied for the measurements, capable of actually producingquantitative results. Further automatisation of the sampling process would be important to reduce the standard deviation by eliminating human error.

The developed analytical procedures were successfully applied for the characterisation of various potential sensor substrate materials with respect to affinity, adsorption kinetics and desorption behaviour. It was shown that the capacity of the substrates for adsorption mainly depends on their specific surface area. The polarity of the substrates and therefore the affinity of the substrates can also be estimated with the comparison of substrates with the same surface area and a different chemical composition. The adsorption kinetics could also be followed and showed significant for the investigated materials. However, the dependency of adsorption kinetics on the pore size distribution could not demonstrated clearly. Adsorption experiments are thus essential for the determination of physico-chemical properties of the substrates since they cannot be derived purely by the analysis of morphological parameters, such as the specific surface area and the pore size distribution.

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Appendix I Preliminary Experiments

SPME/GC

Norm. PA Spiked Solution				
	Extraction 1	**Extraction 2**	**Extraction 3**	**Extraction 4**
Toluene	1.000	0.535	0.380	0.328
Chlorobenzene	1.000	0.454	0.347	0.290
p-Xylene	1.000	0.361	0.251	0.203
N-Nonane	1.000	0.406	0.246	0.227
1-Chlorooctane	1.000	0.144	0.094	0.071
N-Dodecane	1.000	0.336	0.328	0.276

Norm. PA of several extractions of a spiked solution without sol-gel Analyte concentration~0.5 ppm

Norm. PA 0.7 g MTMOS/MeOH				
	Extraction 1	**Extraction 2**	**Extraction 3**	**Extraction 4**
Toluene	0.043	0.030	0.036	0.023
Chlorobenzene	0.009	0.009	0.009	0.014
p-Xylene	0.018	0.008	0.014	0.014
N-Nonane	0.008	0.001	0.001	0.001
1-Chlorooctane	0.001	0.004	0.004	0.004
N-Dodecane	0.020	0.015	0.027	0.026

Norm. PA of several extractions of a spiked solution with 0.7 g MTMOS/MeOH added Analyte concentration~0.5 ppm

Norm. PA 0.2 g MTMOS/MeOH					
	Extr. 1	**Extr. 2**	**Extr. 3**	**Extr. 4**	**Extr. 5**
Toluene	0.431	0.165	0.124	0.118	0.109
Chlorobenzene	0.164	0.057	0.045	0.039	0.038
p-Xylene	0.116	0.034	0.020	0.015	0.013
N-Nonane	0.716	0.061	0.014	0.008	0.004
1-Chlorooctane	0.046	0.003	0.001	0.001	0.001
N-Dodecane	0.412	0.010	0.008	0.011	0.006

Norm. PA of several extractions with 0.2 g MTMOS/MeOH added analyte concentration~0.5 ppm

The results of the preliminary experiments for the SPME/GC measurements are discussed in chapter 4.1.1

HPLC/DAD of Substituted Aromatic Compounds

Influence of the Nylon Filter				
	0.5ppm	2ppm	5ppm	10ppm
Benzonitrile	0.786	0.899	0.932	0.883
1-Naphtol	0.083	0.031	0.025	0.062
Chlorobenzene	0.831	0.916	0.758	0.811
Diphenylamine	0,000	0.000	0.000	0.015
1,3 Dichlorobenzene	0.396	0.222	0.344	0.479
1,2,3 Trimethylbenzene	0.257	0.392	0.552	0.597
N-Proplybenzene	0.786	0.612	0.633	0.561

Norm. PA after filtration with nylon filters, experiment conducted at four different concentration levels

Optimal Concentration Levels				
	1ppm	2ppm	5ppm	10ppm
Benzonitrile	0.326	0.280	0.485	0.628
Chlorbenzene	0.000	0.000	0.111	0.190
1,3 Dichlorbenzene	0.000	0.000	0.044	0.101
1,2,3 Trimethylbenzene	0.000	0.000	0.042	0.166
N-Proplybenzene	0.000	0.000	0.139	0.087

Norm. PA of samples taken at the equilibrium at four different concentration levels, 0.4 g MTMOS/MeOH suspended in 20 ml water

Time Dependence of the Extraction								
	1min	5min	10min	15min	25min	35min	45min	60min
Benzonitrile	0.833	0.807	0.667	0.648	0.639	0.643	0.662	0.605
Chlorbenzene	0.344	0.241	0.209	0.256	0.190	0.145	0.162	0.123
1,3 Dichlorbenzene	0.273	0.154	0.098	0.097	0.093	0.098	0.091	0.079
1,2,3 Trimethylbenzene	0.866	0.611	0.391	0.271	0.191	0.183	0.189	0.166
N-Proplybenzene	0.386	0.230	0.116	0.023	0.014	0.000	0.000	0.000

Norm. PA of samples taken at different times after the spiking of the suspension, 0.4 g MTMOS/MeOH in 20 ml water

The results of the preliminary experiments for the HPLC/DAD measurements of substituted aromatic compounds are discussed in chapter 4.1.2

HPLC/DAD of PAHs

Nylon Filter			
	0.5 ppm	**1 ppm**	**2 ppm**
Naphthalene	0.000	0.142	0.199
Fluorene	0.000	0.000	0.000
Phenanthrene	0.000	0.000	0.000
Anthracene	0.000	0.000	0.000
Pyrene	0.000	0.000	0.000
Chrysene	0.000	0.000	0.000

Norm. PA after filtration with nylon filter

RC Filter			
	0.5 ppm	**1 ppm**	**2 ppm**
Naphthalene	1.043	0.975	0.967
Fluorene	0.919	0.758	0.757
Phenanthrene	0.999	0.600	0.612
Anthracene	0.457	0.365	0.512
Pyrene	0.484	0.283	0.519
Chrysene	0.448	0.687	0.915

Norm. PA after filtration with RC filter

MTMOS/MeOH			
	0.5 ppm	**1 ppm**	**2 ppm**
Naphthalene	0.232	0.179	0.186
Fluorene	0.151	0.220	0.256
Phenanthrene	0.196	0.391	0.404
Anthracene	0.197	0.323	0.123
Pyrene	0.483	0.350	0.209
Chrysene	0.349	0.270	0.144

Equilibrium MTMOS/MeOH-water at three different concentration levels

The results of the preliminary experiments for the HPLC/DAD measurements of PAHs are discussed in chapter 4.1.2

Appendix II Chemicals

Precursors		**SPME/GC**		**Substituted aromatics**		**PAHs**		**Misc.**	
MTMOS, pur.	F	Toluene, p.a.	R	1,2,3 Trimethylbenzene, tech.	A	Naphthalene, puriss.	F	NaOH, p.a.	M
TMOS, pur.	F	p-Xylene, tech.	A	Propylbenzene, puriss	F	Fluorene, >90%	F	ACN, p.a.	R
MTEOS, pur.	F	N-Nonane, z.S.	M	1,3 Dichlorobenzene, z.S.	M	Anthracene, >95%	F	Acetone, puriss.	A
TEOS, pur.	F	Chlorooctane, z.S.	M	1-Naphthol, puriss.	F	Phenanthrene, >90%	F	MeOH, p.a.	R
C8-TEOS, pur.	F	Chlorobenzene, z.S.	M	Diphenylamine, 99%	A	Chrysene, pur.	F	iPrOH, p.a.	F
APTEOS, pur.	F	N-Dodecane, z.S.	M	Benzonitrile, z.S	M	Pyrene, >90%	F	30% H_2O_2, p.a.	F
								N-Hexane, p.a.	R

A: Aldritch, F: Fluka, M: Merck, R: Riedl de Haën

All gases were provided by Messer

Appendix III Abbreviations

ACN	Acetonitrile
APTES	3-aminopropyl-trimethoxysilane
BET	Brunauer, Emmett, Teller
BJH	Barrett, Joyner, Halenda
Bp	boiling point
C8-TEOS	octadecyl-trimethoxysilane
CO_2	carbondioxide
CX	carboxen
DAD	diode array detector
EI	electron impact ionisation
ETEOS	ethyl-trimethoxysilane
EU	European union
FID	flame ionisation detector
GC	gas chromatography
H_2O_2	hydrogen peroxide
He	helium
HED	high energy dynode
HP	Hewett Packard
HPLC	high performance liquid chromatography
i-PrOH	isopropanol
IR	infrared
MeOH	methanol
MISPEC	multiparametric in-situ spectroscopic measuring system for coastal monitoring
MS	mass spectrometer
MTMOS	methyl-trimethoxysilane

N_2	nitrogen
NaOH	sodium hydroxyde
NMR	nucleomagnetic resonance
O_2	oxygen
PA	peak area
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxane
PE	polyethylene
PEG	polyethyleneglykol
ppm	parts per million
PVC	polyvinylchloride
REM	raster electron microscope
RC	regenerated cellulose
RT	retention time
SERS	surface enhanced Raman spectroscopy
SIM	selected ion monitoring
SPE	solid phase extraction
SPME	solid phase microextraction
TEOS	tetraethoxysilane
TMOS	tetraethoxysilane
UV	ultra violet
VIS	visible