

International Masters Programme
Applied Environmental Measurement Techniques

**Removal of Organic Contaminants from Landfill Leachate by Natural
And Rest Product Adsorbents**

Masters Thesis
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Abstract

This Master thesis was requested by Nexans IKO Sweden AB, cable company, with the purpose to investigate adsorption capacity of natural and rest product adsorbents for removal of organic contaminants in a landfill leachate. Two sets of batch experiments were performed at laboratory with artificial solutions of organic contaminants. In the first set, fiber ash, bark, raw and ground peat moss were tested as adsorbents for removal of diesel oil. Fiber ash, sand and ground peat were tested in a second test to determine the removal capacity of n-Hexadecane (C_{16}) and n-Dodecane (C_{12}).

High percentage removal of diesel hydrocarbons was obtained by ash and ground peat, 98% and 97% respectively, and 83% by bark. In the second series of the batch tests two extraction methodologies were applied, solid-phase extraction (SPE) and solid-phase microextraction (SPME) prior to gas chromatographic analysis with flame ionization detector (FID). Two methods gave different results with a high variance in concentrations of specific hydrocarbons. The SPME methodology gave a broad range of percentage removal of C_{12} and C_{16} thus making the results difficult to interpret. The SPE technique used was proven to be more reliable and sensitive, therefore, conclusions were mainly made based on the results of this technique. The removal percentage were 91% for C_{12} and 97% for C_{16} on ash; 78% for C_{12} and 76% for C_{16} on sand, and 92% for C_{16} on ground peat. Regarding the high adsorption capacity of ash and ground peat in removal of organic hydrocarbons in both batch tests, these materials are recommended to be used as good and cheap adsorbents.

Column experiments were also carried out in the field with real leachate from the Nexans company landfill. However the concentrations of organic contaminants in the inlet water were too low to be worth working with in the column study. Hence, only adsorbents behavior in the columns and analyses of outlet waters from the columns are presented. Despite ash showed a good adsorption capacity in the batch tests, it cannot be used as an adsorbent alone in the columns due to its low permeability, channeling and cementing properties. It is therefore recommended to investigate a possibility of addition of ash to the ground peat. Ground peat is concluded to be preferably used as a main adsorbent for remediation of the landfill leachate, due to its high potential in removal of organic hydrocarbons and due to the superior behavior as an adsorbent. Further recommendations are given for laboratory scale research and for treatment of the landfill leachate in a full-scale peat moss filter bed.

Table of content

Abstract	ii
Chapter 1: INTRODUCTION	1
1.1. Description of the problem	1
1.2. Objectives	1
Chapter 2: STUDY BACKGROUND	2
2.1. Nexans Company	2
2.2. Landfill contamination	2
Chapter 3: THEORETICAL BACKGROUND	6
3.1. Organic pollutants in the environment	6
3.2. Adsorption, batch and column experiments	9
Chapter 4. Experimental	12
4.1. Characteristics of the adsorbents	12
4.2. Batch experiment I	13
4.3. Column experiments	14
4.4. Batch experiment II	16
4.5. Measurement techniques	17
Chapter 5. Results and discussion	21
5.1. Batch experiment I, with diesel oil	21
5.2. Batch experiment II, with C ₁₂ and C ₁₆	23
5.3. SPME versus SPE	31
5.4. Landfill leachate analysis and column experiments	32
Chapter 6. Conclusions	35
Chapter 7. Further recommendations	36
References	38
Appendix 1	41
Appendix 2	42
Appendix 3	43
Appendix 4	45
Appendix 5	46

Chapter 1: INTRODUCTION

1.1. Description of the problem

A landfill, which had been in use by Nexans IKO, Sweden AB from 1948 until 2000, is reported to be highly contaminated with oil, dioxins and heavy metals (EnviroVision HB, 2002). The pollution is mainly a result from dumping of oil and residuals from the production of PVC-plastic electricity cables. The landfill is ranked as a high-risk waste area and needs to be treated to prevent further pollution of ground water and surrounding areas. Also the contaminated land needs to be restored by reducing contaminant concentrations to acceptable levels. The environmental consultant, EnviroVision HB, is planning to carry out a remediation of the groundwater by extracting dug wells, and treat the contaminated water above-ground via adsorption.

Different artificial adsorbent materials have been used, such as activated carbon and zeolites, to remove organic contaminants from water (Calace, 2001, Gupta et al., 2000, Wong 1997, Cheremisinoff, 1979). They have been efficient, but due to their relatively high cost, there is a need to utilize low cost, preferably natural occurring adsorbents to remove both metals and organic contaminants in a sustainable way.

A work was done to investigate the adsorption capacity of six cheap and natural products: fiber ash, bark, saw dust, peat moss, seaweed and shrimp shale, in batch tests for metal removal (Chauvet, 2003). Peat moss and fiber ash showed the highest efficiencies of metals removal from contaminated leachates. The fiber ash adsorbed 78% of Cr (VI) and 99.9% of Cu; peat 80% of Zn, Pb, followed in efficiency by bark, sawdust, shrimps and sea weed.

A number of works have been carried out to investigate different adsorbents for removal of organic pollutants (Ratola *et al.*, 2003; Gupta *et al.*, 2000; Bras *et al.*, 1999). It was found that pine bark and fly ash display a high capacity in removing organochlorine pesticides, which are defined as organic pollutants with high level of persistence and toxicity.

Thus the high potential of bark, fiber ash and peat moss in removal of metals, and previous findings of high efficiency of these adsorbents in removal of organics, motivated this study.

The work was aimed to test above-mentioned adsorbents for metal and organic contaminants. This thesis work was focused on organic contaminants. Results and discussion of metal removal in column tests can be found in the Master thesis report “Metal ions sorption from industrial leachate onto natural and rest products materials” (Kalmykova, 2004).

1.2. Objectives

The aims and goals with this thesis work was to:

- Test adsorption capacities of fiber ash, bark and peat in batch experiments.
- Design fixed-bed columns for adsorption testing.
- Develop a methodology for extraction and analysis of organic contaminants in leachate from the tests.
- Compare results obtained from solid phase extraction and solid phase microextraction extraction methodologies.

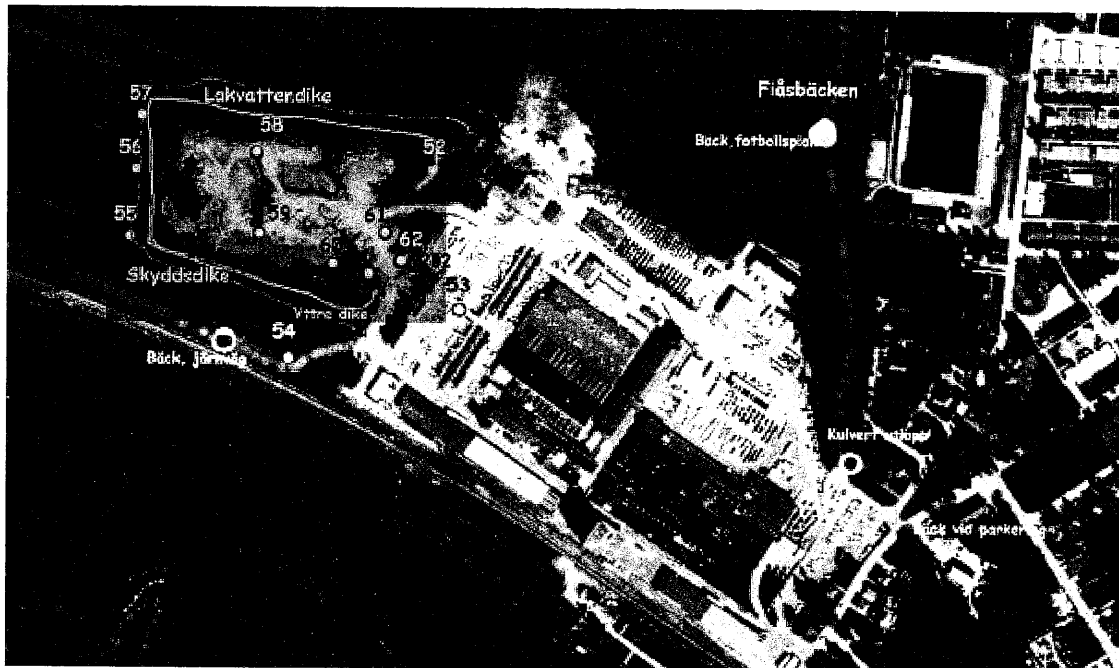


Figure 1. Airplane picture of Nexans IKO Sweden AB (1990).

Chapter 2: STUDY BACKGROUND

2.1. Nexans Company

Nexans IKO Sweden AB produces cables and is situated in Grimsås, Västra Götaland. Nexans was founded in 1948 as a small family company, IKO Kabel AB. In 1968 the company was sold to American ITT, then in 1987 it merged with French Alcatel Cables & Components. By 2000, there was reorganization within the company, and the bigger part became a separate company named Nexans IKO Sweden AB.

Nexans is the third largest producer of cables with 450 employees. It produces power, machinery and telecommunication cables. The latter include optical and access network copper cables. At the moment, wastes from cable production are recycled or sent for proper destruction except for PVC, which are stored due to their low demand in recycling.

2.2. Landfill contamination

In 1999, the concern about landfill pollution arose, and the first hydrological and chemical investigations were performed by the consultant company KM in 2000, then by EnviroVision HB in 2002.

The landfill has a total area 33 600 m² and confined from two sided by small ditches. In Figure 1, the landfill area is highlighted in red. The presence of a stream Flåsbäcken in the vicinity makes the risk for environmental pollution high.

Table 1. Concentration of organic contaminants at three locations of the landfill (Hargelius, 2002)

Element	Units	Spot 202	Spot 216	Spot S38	Guideline values ^a
oil	mg/kg d.w.	58000	----		
Aliphatic>C ₁₆ -C ₃₅	µg/l	160	----		100 ^b
Aromatic>C ₈ -C ₁₀	µg/l	1870	----	<4.0	100 ^c
Total xylen	µg/l		----	<0.2	20
Cancerogen PAH	µg/l		----	0.58	0.2
Dioxins	ng/kg d.w.	----	38000	----	250

^a-Swedish guideline values or equivalents for levels in polluted groundwater and soil

^b- sum of total extractable aliphatic hydrocarbons

^c- sum of total extractable aromatic hydrocarbons

*Level in relation to guideline or corresponding value:

Not very serious < guideline value

Moderately serious 1-3 x guideline value

Very serious > 10 x guideline value

History and sources of wastes

From 1948 to 1960, the landfill was in use by Daltorps' commune. During this period peat moss from exploitation, toxic wastes, barrels polluted with oil were deposited in the landfill. From 1948 until 2000, residuals from the cable production, including copper and lead wastes, PVC, oil and neon lamps were dumped there, and from 1948 until 1967, PVC rests were burned at the landfill (Figure 1, point 54). Currently the landfill is not in use.

Landfill pollution

The pollution investigation in 2003 revealed high concentrations of metals and organic pollutants in the groundwater and in the landfill soil. Metals such as arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc were present in extremely high concentrations. In Figure 2, different colors indicate contamination by different metals and organic pollutants.

Table 1 presents concentrations of organic pollutants at different spots. At the location 216, the concentration of dioxins exceeds the guideline value by 152 times. Location 202 is highly polluted with aliphatic, aromatic, polyaromatic hydrocarbons and xylenes. Location S38 is mainly contaminated with aliphatic hydrocarbons.

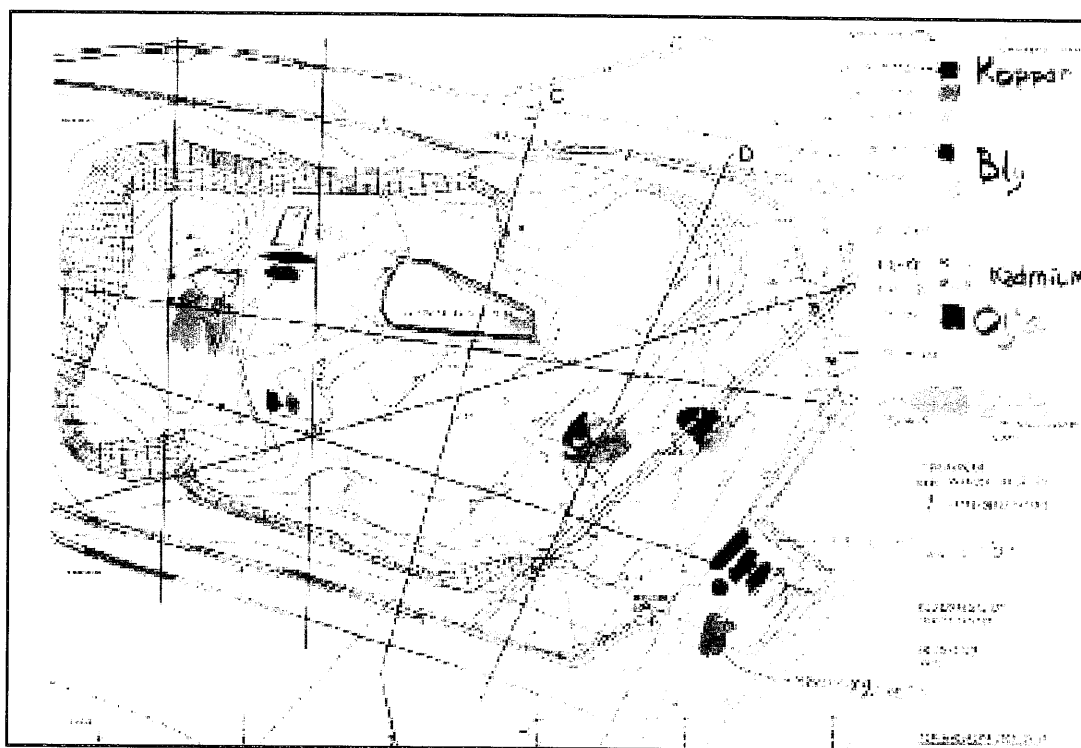


Figure 2. Pollution by metals and organic contaminants at different locations of the landfill (Hargelius, 2002).

Figure 3 presents chromatograms of oil analyses at these two locations. In chromatogram A, a high number of peaks at the beginning of the chromatogram indicates high contamination by low molecular weight volatile hydrocarbons, probably from lighter fuels as gasoline. Peaks with higher retention times at the end of the chromatogram are distributed in a typical pattern of fresh diesel oil. In chromatogram B, low molecular weight compounds (peaks in the beginning of the chromatogram) are also present, but in lower concentrations than in chromatogram A. Spot S38 (chromatogram B) is mainly contaminated with higher molecular weight and potentially persistent hydrocarbons, which appear at the end of the chromatogram with higher retention times. The hump in the middle of the chromatogram is an indication of incomplete biological degradation of hydrocarbons (Püttmann, 1988). The high peaks at the end of the chromatogram may indicate occurrence of natural organic degradation products from peat moss, as it was explained by the commercial laboratory. However, presence of PCBs, nonylphenols and phtalates could not be excluded, and therefore further analyses for these compounds are recommended. More detailed analysis at spots 202 and S38 are given in Appendix 1.

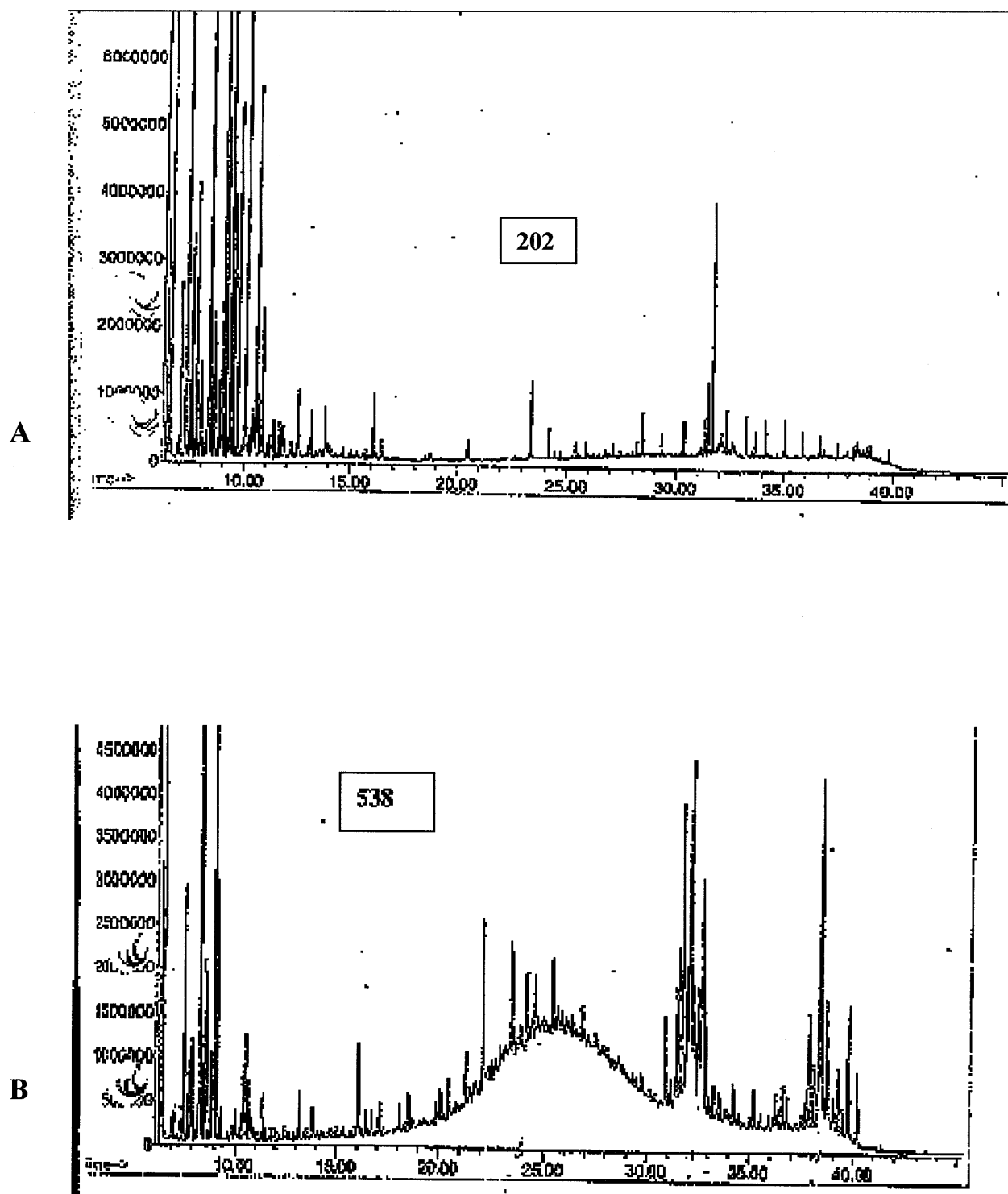


Figure 3. Chromatograms from oil analyses with GC/MS (Analytica AB) at two spots:
A- spot 202, B – spot S38 (Hargelius, 2002).

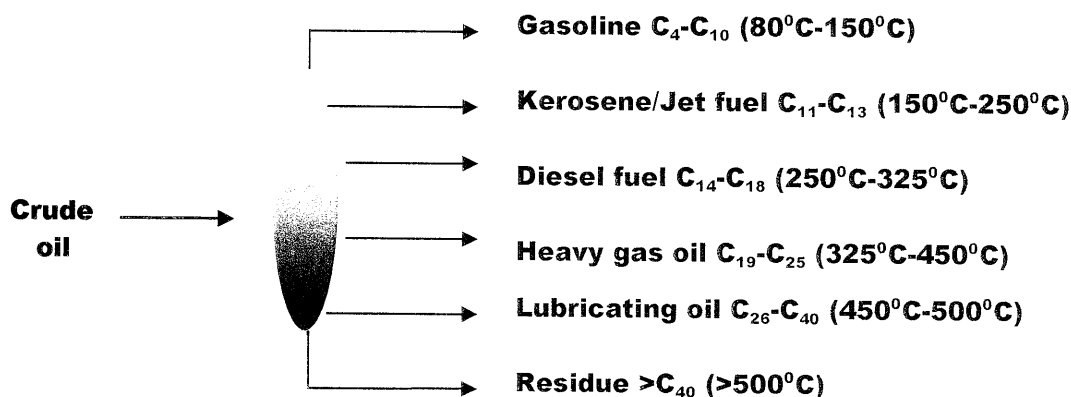


Figure 4. Hydrocarbon products from crude oil refining (CSI, 2003).

Chapter 3: THEORETICAL BACKGROUND

3.1. Organic pollutants in the environment

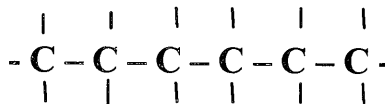
Petroleum hydrocarbons

Crude oil and petroleum products are complex mixtures of hydrocarbons that can be graded by their carbon chain length and boiling points into various forms with different characteristics and industrial applications (Spiro, 2003), Figure 4.

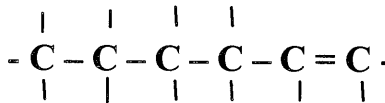
Main component groups of petroleum are aliphatic, aromatic hydrocarbons, and sulphur, nitrogen and oxygen containing compounds.

Aliphatic hydrocarbons - are the main components of the lighter fuels/oils although they can be produced by the breakdown of the more complex long chain hydrocarbons. They are good solvents, highly volatile and act as a good medium for heavier hydrocarbon migration. Aliphatic hydrocarbons can be:

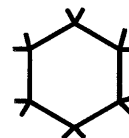
Saturated (alkanes) with no double or triple bonds,
e.g. hexane.



Unsaturated (alkenes, alkynes) with
double or triple bonds, e.g. hexene.



Cyclical (cycloalkanes). They are saturated hydrocarbons with ring structures, e.g. cyclohexane.



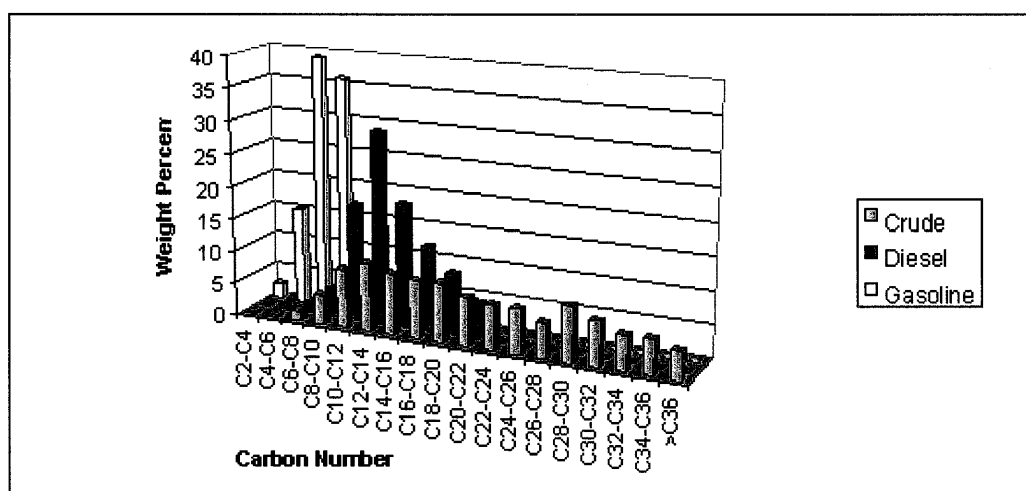
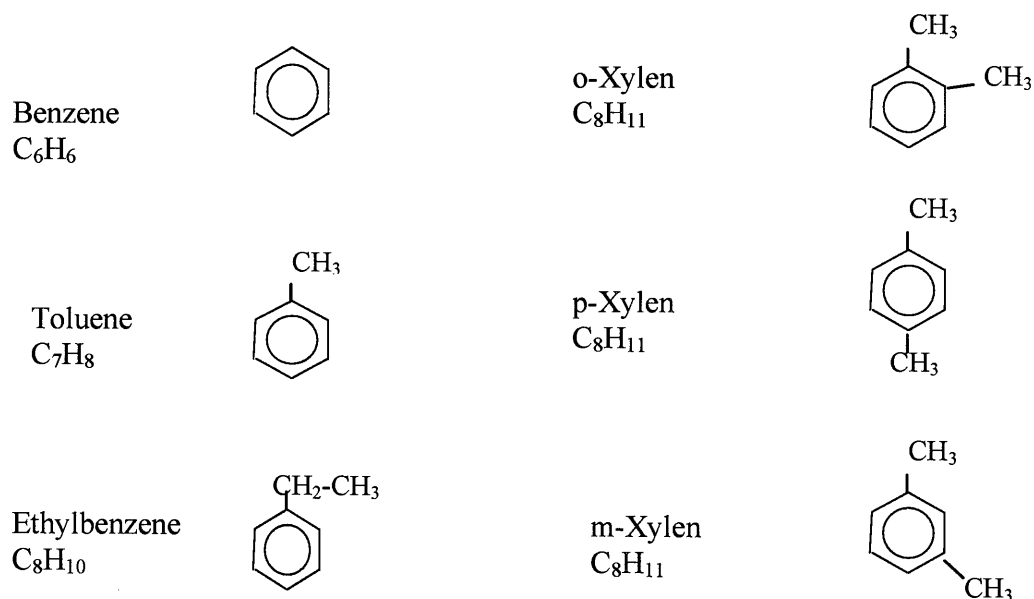


Figure 5. Relative distribution of hydrocarbons in crude oil, diesel and gasoline (CSI, 2003).

Figure 5 shows an example of the relative distribution of hydrocarbons in crude oil and petroleum products.

Aromatic hydrocarbons - there are two important types: BTEX and PAHs.

BTEX, Benzene, Toluene, Ethylbenzene and three isomers of Xylene, are the most soluble in water. These hydrocarbons are toxic to human health and could easily evaporate into volatile organic vapors (CSI, 2003).

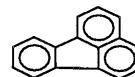


Polycyclic Aromatic Hydrocarbons (PAHs). These are organic compounds that contain two or more benzene rings:

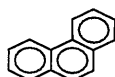
Naphthalene
 $C_{10}H_8$



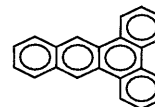
Benzo(a)Pyren
 $C_{20}H_{12}$



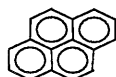
Phenanthrene
 $C_{14}H_{10}$



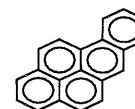
Dibenzo(a,h)Anthracene
 $C_{22}H_{14}$



Pyrene
 $C_{16}H_{10}$



Fluoranthene
 $C_{16}H_{10}$



NSO compounds – nitrogen, sulphur and oxygen containing compounds. These can be in the form of "polar components" or "asphaltenes", and various forms of complex hydrocarbons in association with inorganic elements.

Humans can be exposed to hydrocarbon contamination in a number of ways: ingestion, dermal contact and inhalation; effects can be either acute and/or chronic.

Acute effects arise from short-term exposure and effects include contact dermatitis, respiratory difficulties and anaphylactic shock.

Chronic effects build up over extended periods, e.g. kidney damage, neurological conditions or carcinogenic effects (Connel, 1997).

The aromatic components of petroleum are the most toxic compounds present: BTEX compounds due to their toxicity and vapors; PAHs due to their potential carcinogenicity and relative persistence. These substances are usually lethal to larvae and juveniles in the range 0.1 to 10 mg/L, and adults in the range 0.1 to 100 mg/L (Spiro, 2003).

Hydrocarbon behavior in the soil

When oil is spilled on the ground, it moves vertically downwards into the unsaturated zone towards the surface of groundwater. The movement of oil in a horizontal direction depends on properties of the soil. The more fine-grained the soil, the more strongly capillary forces move the oil (Wong, 1997).

All petroleum products contain components, which are to a certain extent, soluble in water. These components dissolve and move in the direction of the flow of groundwater, though not as freely as water itself since they adsorb into the soil particles. Biological processes also influence degradation of petroleum components.

Petroleum hydrocarbons that are leached or spilled into the subsurface can be present in several forms:

- Non-aqueous phase liquid (NAPL)
- Adsorbed phase
- Vapor phase
- Dissolved phase

NAPL are present as free-flowing liquid hydrocarbons in the pore or interstitial spaces between the soil particles. They migrate downward due to the force of gravity. When a substantial amount of contaminant is released, it may reach the water table and accumulate on the top of water surface.

In the adsorbed phase contaminants become sorbed to the soil particles and colloids. Concentration equilibrium will eventually be reached between the contaminant molecules dissolved in the liquid phase and the contaminant molecules that is attached to the soil particle. When concentration equilibrium changes, the soil may adsorb more organic molecules or release them.

A part of hydrocarbons exist in vapor phase, and dispersion occurs from areas of higher concentration to areas of lower concentration. Eventually, the equilibrium will be established near the source of contamination. Air movements result in disturbance of equilibrium promoting volatilization, however air movements in the vadose zone are very slow under natural conditions. Finally, some of hydrocarbons will dissolve in the soil moisture and exist in soluble state.

Dioxins

Dioxins are compounds that are not deliberately produced as environmental contaminants, but are produced by combustion and in synthesis of some commercial chemicals. In the environment, dioxins are persistent and tend to accumulate in food chains. The most toxic dioxin is 2,3,7,8-TCDD. The dioxins always occur as a mixtures and toxicity usually estimated in 2,3,7,8-TCDD equivalents described as International Toxic Equivalence Factors (I-TEFs) (Spiro, 2003).

Effects of dioxins on human health. Short-term exposure of human to high levels of dioxins may result in skin damages, such as patchy darkening of the skin, and altered liver function. Long-term exposure is linked to impairment of the immune system, the nervous system, the endocrine system and reproductive functions (WHO, 1999).

3.2. Adsorption, batch and column experiments

Adsorption

Adsorption is a phenomenon where molecules of the contaminants dissolved in water attach themselves to the surface of an individual soil particles (McKay, 1996). This surface attachment can be physical, chemical, or exchange adsorption. Physical adsorption is caused by Van der Waals forces and is the easiest to separate. Chemical adsorption is formed by chemical bonding and requires significant efforts to separate. Exchange adsorption is caused by the electrical attraction between adsorbate and the surface.

Batch experiments

Batch tests are carried out in order to determine capacity of different adsorbents to adsorb pollutants in question. After batch experiments adsorption coefficients are obtained, and then their comparison allows to select the most effective materials. Usually batch tests are carried out before column experiments as it is a rapid technique to obtain results.

The main principle of batch experiments is to blend in a beaker certain proportions of known concentrations of adsorbents and adsorbates until the adsorption equilibrium is reached. After separation of liquids from solids analyte concentrations in the liquid phase are determined.

Column experiments

In column experiments, a solution with known concentrations of analytes is fed into a column packed with a given adsorbent. The effluent concentration is monitored as a function of time. The resulting data is plotted as a breakthrough curve (Christensen, 2002). Column tests better mimic field condition than batch experiments because of the dynamic conditions. Changing different parameters, flow rate, packing density, pH, height, inlet concentration results in a filter-bed design where optimal conditions for pollutant removal are reached with reasonable maintenance and operation costs.

Mass Transfer Zone (MTZ) and breakthrough

To understand the dynamics of the adsorption process within the fixed bed the concept of mass transfer zone (MTZ) must be understood. The MTZ is the area within the column bed where adsorption takes place (McKay, 1996). The MTZ moves through the bed in the direction of flow. Breakthrough occurs when the MTZ reaches the effluent zone of bed (Figure 6). If the process flow contains multiple adsorbates, each may have its own MTZ.

The MTZ is called the adsorption zone or critical bed depth. The MTZ is generally a band, between the spent and the fresh adsorbent, where contaminants are removed. The length of the MTZ can be defined as L_{MTZ} . When L_{MTZ} = bed depth, it becomes L_{CRIT} , or the theoretical minimum bed depth necessary to obtain the desired removal. Thus, when designing fixed-bed absorbers it is important that the bed depth of adsorbents exceeds L_{MTZ} . As well if the flow rate increases significantly, the MTZ can lengthen and exceed the depth of the adsorbent bed, thus providing insufficient residual time for complete removal of the target adsorbate.

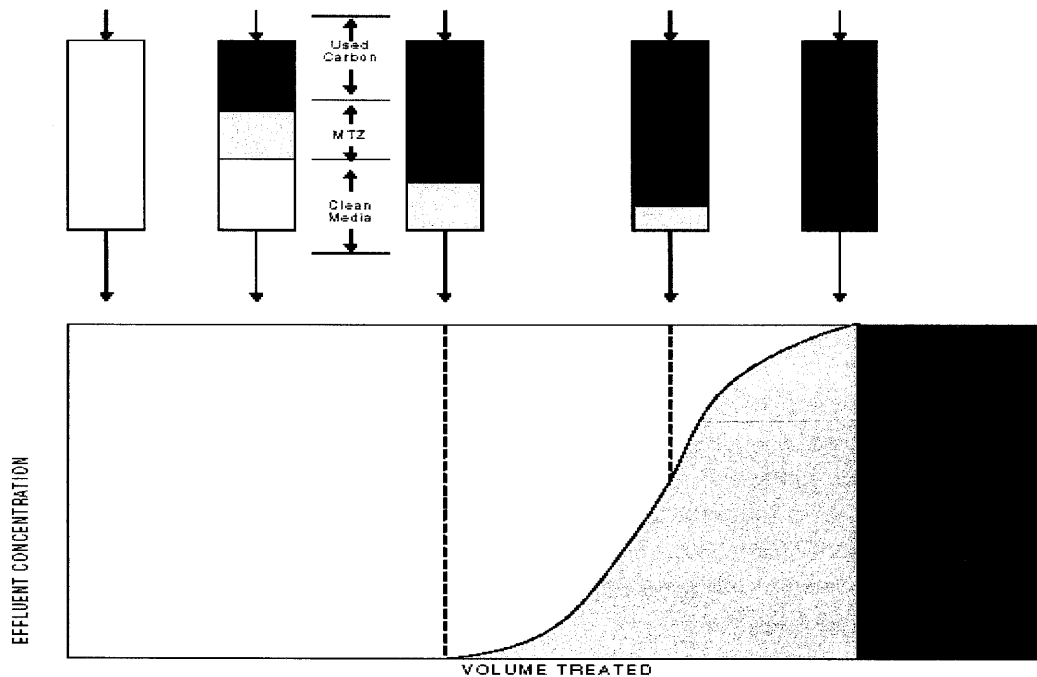


Figure 6. Adsorption column mass transfer and idealized breakthrough zone (Henning, 1990).

Empty Bed Contact Time (EBCT)

To normalize bed depth for different loading rates, the concept of empty bed contact time (EBCT) is often used. EBCT or retention time is the time that the liquid would take to fill the volume of adsorbent rate, and it is a direct function of liquid flow rate and adsorbent volume (McKay, 1996). Equations for EBCT are as follows:

$$EBCT = V/Q = L_{bed}/(Q/A) = L_{bed}/\text{Loading rate} \quad (1)$$

Where: V – volume of bed occupied by the adsorbent

L_{bed} – length of adsorbent bed

Q – flow rate

A – area of bed

The EBCT affects costs and performance of adsorbent systems. Too small EBCT results in frequent adsorbent replacement resulting in higher operation and maintenance costs, too high EBCT is unnecessary as adsorbent exhaustion rates, e.g. mass of adsorbent per volume of liquid treated, reach a constant value (McKay, 1996). From the pilot testing with different bed heights and flow rates EBCT can be obtained.

Table 2. Main constituents of fiber and fly ash.

Components	Fiber ash	Fly ash*
	% TS	% TS
SiO ₂	28.9	44.9
Al ₂ O ₃	20.7	22.0
CaO	43.7	5.7

*(Rio, 2002)

Chapter 4. Experimental

4.1. Characteristics of the adsorbents

Bark. Pine bark has a very complex organic structure consisting only of 0.5% of inorganic compounds. It includes 39.3% of soluble materials in polar solvents, mainly dye compounds, and 59.7% of aromatic contents among others. It also contains fatty matter, carbohydrates, starch, lighnin, phenolic structures, pectines, suberin and hydrolyzable tannins. Inorganic materials include metals such as calcium, potassium, magnesium and sodium, with calcium being most representative. (Bras *et al.*, 1999). This large variety of functional group attracted attention to this adsorbent for removal of metals and good results have been obtained (Palma, 2003, Seki, 1997). Pine bark has a very porous structure, and it is considered as a good adsorbent in removal of organic contaminants due to its high affinity of hydrophobic compounds to them (Ratola *et al.*, 2002).

The pine bark used in this study, “Ecobark”, was from the Swedish company Sydkraft Värme Syd AB. It is modified to make the material more lipophilic, and applied for removal of oil spills. The bark has fraction sizes ranging from 0.074 until 5.6 mm, and mainly from 0.8 to 1.5 mm. More detailed size distribution of the bark is shown in Appendix 3.

For the batch test I, with diesel oil, the bark was used without preliminary drying and grinding. For the batch test II, with C₁₂, C₁₆, and for the column, bark was ground and dried at 105⁰C for 24h.

Fiber ash. The fiber ash used in this study is a residual product of the production of toilet tissues, household towels, facial tissues and napkins of the company SCA Hygien Products AB. The main constituents are SiO₂ (30%), Al₂O₃ (21%) and CaO (44%) (see Table 2). More detailed composition of the fiber ash can be found in Appendix 4. The company initiated the study of the fiber ash composition in order to investigate recycling and disposal possibilities of this residual product.

Fiber ash is a strong alkaline material, with pH 12.6 and its surface charged negatively. Hence, removal of metals is believed to be due to electrostatic adsorption and precipitation (Chauvet, 2003). The adsorption capacity of fly ash has been found to be high in removal of organochlorine pesticides (Gupta *et al.*, 2001). The main mechanism that governs adsorption onto ashes is not fully understood. The major constituents of fly ash are also SiO₂, Al₂O₃ and CaO but in different percentage proportions (Table 2). About 50% of the fiber ashes had particle sizes up to 0.074 µm (more details in Appendix 4).

In batch test I, with the diesel oil, the fiber ash was used untreated. For the column and batch test II with C₁₂ and C₁₆, the fiber ash was dried at 500⁰C to remove any adhering organic matter.

Peat moss. Peat moss is the decaying sphagnum moss in the water column; the detritus above the wetland sediment and the dissolved and colloidal organic material incorporated into the sediments. It is mainly composed of lignin and hemicellulose, which is partly broken down to humic substances (Chauvet, 2003). Physical and chemical properties of peat vary significantly depending on the age, depth, and type of moss. The most abundant and effective surface-active peat components for metal binding are phenols, hydroxyls, carboxyls and ketones. High percentage of organic content can be an explanation for the organic pollutant adsorption.

The peat moss used in this study was delivered from the moss area close to Nexans. In the experiments, raw peat and ground dry peat were used. The characteristic of the peat is given in Appendix 3. Humic acid content of the peat was not evaluated in this study.

Sand. Silty sand was used in the column experiments to provide filtration of the influent and the effluent leachate water from suspended solids. It was also tested for adsorption capacity in the batch test II along with the other adsorbents. Sand is reported to have low adsorption capacity for organic pollutants due to its low affinity to organic compounds, and previous experiments showed that sorption of organics is directly related to the organic matter content (Loffredo, 1999).

4.2. Batch experiment I

The purpose of this beaker experiment was to compare effectiveness of different absorbents for organic pollutant removal from water solutions with known concentrations of oil and adsorbents. In this beaker experiment the following adsorbents were studied: fiber ashes, bark, raw and dry ground peat moss. The diesel oil was chosen to imitate the petroleum contamination in the landfill leachates. It was obtained from an oil refining company in Göteborg.

Prior to the experiment, glass beakers, filters and the other glass equipment, which had contact with the solution, were rinsed with heptane and then with methanol. Thereafter the equipment were readily rinsed with hot tap water, nanopurewater, and in the last step - oven-dried for > 2h at 105⁰C. Paddles and plastic containers were kept for 1 hour in hot water and then dried.



Figure 7. Batch experiment I with diesel oil.

To get 800 ml solution spiked with 50 mg/L diesel oil, a stock solution was prepared in propanol as diesel oil is highly insoluble in water. 2.5 g of diesel were dissolved into 50 ml of isopropanol (50 000 mg/L). Then 800 ml of this solution was transferred into the 6 separate beakers and pH was adjusted with 1M of HCl

Then, 40g of the different adsorbents were introduced into the beakers. A blank beaker was used without adding any adsorbents to figure out the quantity of the diesel oil, which may be lost during filtration and adsorption on the glass and paddles.

The system was agitated with plastic paddles for 48 hours. Then, filtration with glass fiber filter (0.45 μm) was used to separate the solid phase from the liquid. Before filtration the beakers were left to let the adsorbents settle down.

After filtration weighted amounts of solids were transferred to glass containers, measured volumes of the liquids - to the plastic containers; and the samples were kept frozen, at -15°C for 1 month. Plastic containers were chosen for the liquid to allow freezing.

4.3. Column experiments

Four plastic columns (60 x 490 mm) were rinsed with hot tap water and then with nanopure water before packing the adsorbents. Ash, raw peat, ground peat and bark were the adsorbents to be tested. The decided flow rate was 2 ml/min with EBCT 7h, and it was applied in upflow-mode.

Ash. It was tried several times to pack the column with ash but due to its cementing properties, low permeability and channeling problems it was decided to give in with the idea of using ash alone as an adsorbent. It was attempted to mix ash with sand in different proportions (from 10/90 to 50/50 sand and ash respectively), and with different sand size. When ash was mixed with courser sand, segregation of ash from sand was noted as the water was applied to the column. Heavier than ash, sand particles tended to settle down, whereas lighter ash particles were directed by water flow to the top of the column. When finer sand was mixed with ash, channeling and low permeability remained. Thus, to use sand in proportion more than 60% by mass was not considered as an appropriate option, since the column with low dry weight of the effective adsorbent content could imply its frequent replacement. However due to high ash capacity in metal removal, it was decided to add it to ground peat, and test two columns: one with ground peat only; second with ground peat mixed with ash.

Ground peat+ash. Visually, the texture of the adsorbent material of ground peat with ash looked more cemented and more plastic than the material of ground peat alone. Though no channeling and low permeability were noted. The amount of ash added was 5 % by weight.

Raw peat. The column with raw peat was the most troublesome. While running the column, the content of the column swelled and it reached the outlet tubes and resulted in clogging. The column were repacked several times with different moisture content of raw peat before packing but the result was the same. Even removing several times swollen part of peat from the column during the run, i.e. resulting in very low dry mass content inside the column, did not give desirable results, because the peat did not let the water pass through. Then it was decided to change the flow rate from 2 to 1 ml/min. Still the problem remained, inlet tubes periodically slipped from the inlet glass tube or from the place where they were jointed together.

Thus to overcome above mentioned problems for future investigations with raw peat, flow rate less than 1 ml/min, and construction of a big filter bed could be a solution (more discussed in Chapter 6).

Bark and ground peat. Both these adsorbents did cause any problem neither during packing nor during the column run: there were not channeling, swelling and clogging of the inlet and outlet tubes.

Thus to summarize, 4 columns were packed with following adsorbents: bark, ground peat, ground peat+ash, and raw peat. Characteristics of the adsorbents and column parameters are given in Appendix 3. All the adsorbents were weighted and kept in nanopurewater before packing the columns. Thereafter the columns were feed with nanopurewater in order to remove the air as it hinders uniform distribution of flow throughout the area of the column. It should be noted that the packing procedure took place in the laboratory and thereafter the columns were transferred to the landfill. But during transportation and the installation of the columns, the adsorbents in the columns dried out, and when the leachate was applied, adsorbent materials inside the columns were fractured. Hence columns should not let stay without feeding with the water. All the columns were repacked again at the working place and filled with nanopurewater, and then the landfill leachate was applied immediately. On the bottom and on the top (above the adsorbents) of the columns, sand was placed in order to provide the clean influent and effluent waters from suspended solids.

3000 L of the landfill leachate was kept prior to the filtration in a storage tank during 2-3 weeks. As some parts of organic contaminants are lighter than water and tend to float on the surface, it was decided to stir the leachate prior applying to the columns. The stirring procedure would provide uniform distribution of organic contaminants in the water column, that is, avoid the fluctuating their concentration in inlet waters. Different inlet concentration leads to problems associated with interpreting the results. The landfill leachate was pumped from the storage tank into glass flask (20 L), and after the stirring procedure was applied into 4 columns. The scheme of the total process is presented in Figure 8.

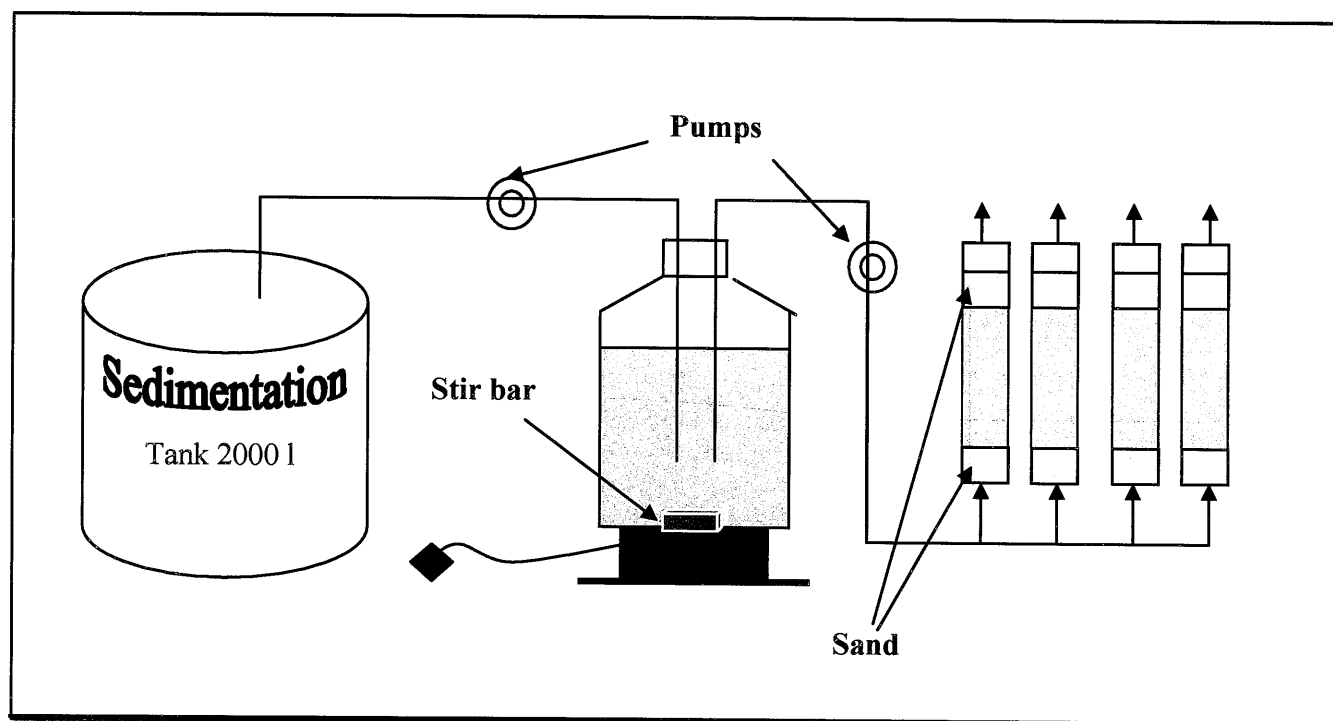


Figure 8. Schematic process of the landfill leachate treatment.

4.4. Batch experiment II

In this batch test, it was decided to choose known organic compounds, n-Hexadecane (C_{16}), n-Dodecane (C_{12}), and n-Eicosane (C_{20}) (further in the text C_{12} and C_{16}). They are a group of n-alkanes, which are the main constituents of diesel oil. The concentrations of C_{12} , C_{16} and C_{20} were 200, 100, 100 ppm respectively. Due to their lipophilic nature, C_{12} , C_{15} and C_{20} were dissolved in mixture of ether and metanol before it was introduced into beakers. After mixing with water C_{20} returned to its solid state, therefore in the experiment only C_{12} and C_{16} were used. However these compounds were not uniformly distributed in the water, oily slicks could be noticed on the surface of the water.

Thereafter 40 g of the prepared adsorbents (ash, sand, ground peat) were introduced into the beakers. To be able to figure out losses of C_{12} and C_{16} during agitation and following filtration, a blank beaker without addition of any adsorbents was used. The system was agitated during 48 hours. After agitation, the mixtures were filtrated through the glass wool to separate the solids from the liquids prior to the extraction techniques. For solid phase microextraction, 18 ml of filtrate was taken into glass containers; the remained waters were kept for solid phase extraction.

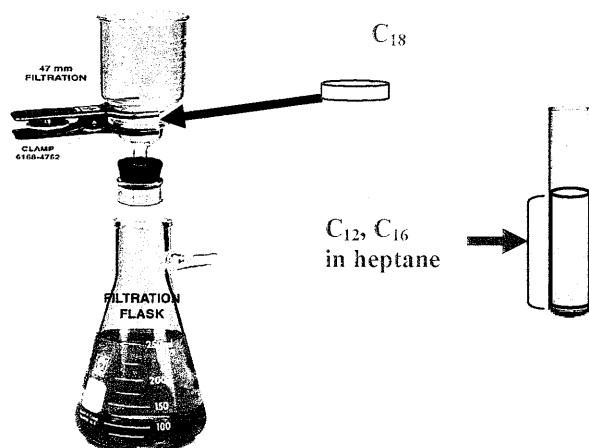


Figure 9. Solid phase extraction

4.5. Measurement techniques

Solid phase extraction procedures (SPE) are used to extract trace of organic compounds from environmental samples prior to chromatographic analysis (Pichon, 2000). The main principle is a liquid sample passes through a SPE disc, and the analytes are “extracted” from the sample onto the sorbent material (Figure 9). Finally, the desired analytes may be selectively recovered from the disc by an elution solvent. Modified silica with a C_{18} reversed-phase sorbent has been usually applied, which is very effective in adsorption of hydrophobic species from aqueous solutions (Ferrer *et al.*, 1999). The mechanism of interaction depends on Van der Waals forces (Ferrer *et al.*, 1999).

Basically, the procedure involves three steps: extraction disc conditioning, sample extraction and sample elution, more detailed procedure and extraction disc characteristics are given in Appendix 5. In this experiment hexane was chosen as an elution solvent, and vacuum was applied to speed up the percolation of the filtrates through the disc.

During solid phase extraction of the adsorbate solutions, there were problems with ground peat filtrate, which did not percolate through the disc. It contained high amount of suspended solid, which clogged the pores of the extraction disc, so that no extraction procedure could be carried out. Thus it was decided to conduct one more batch test with the same procedure but only for ground peat and blank. The latter was run with the same procedure. After agitating the adsorbate solutions were filtrated: first, with glass wool, to separate the solids; second, with glass filter, to make cleaner ground peat filtrate.

After filtration, an internal standard, 2-fluorobiphenyl, was added to the liquids in order to be able to calculate recovery of the analytes. The final decided concentration of IS was 100 mg/L. To prepare solution with this concentration, stock solutions of IS was made: 0.5g of 2-fluorobiphenyl was added into 50 ml of isopropanol (10 000 mg/l). Since the volumes of the filtrates obtained after the filtration were different, the volume of stock solution of IS added were also different.

After the solid phase extraction procedure, the final volume of the analytes extracts in heptane was 20 ml. Samples were stored in the refrigerator prior to gas chromatographic analysis.

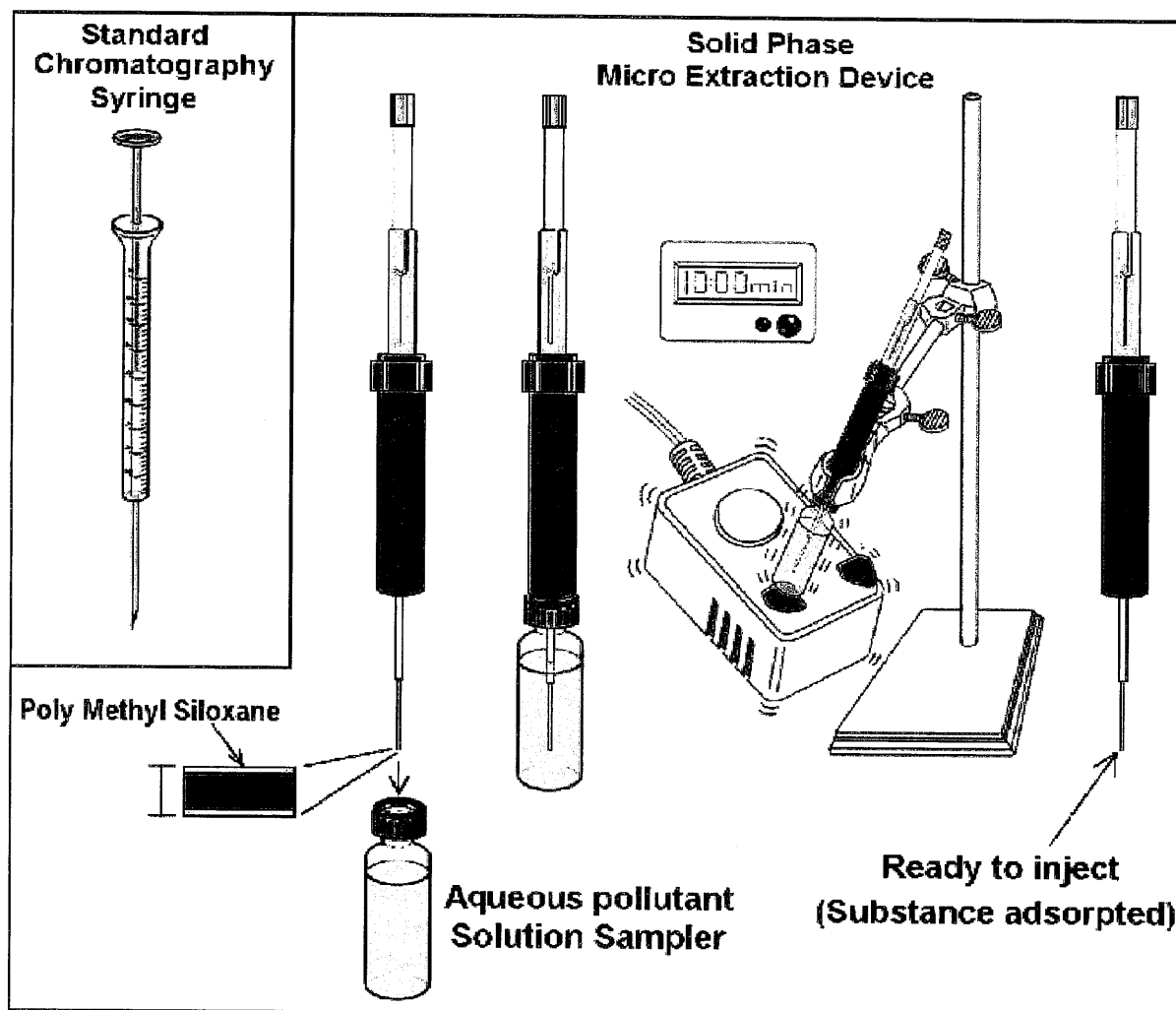


Figure 10. Solid phase microextraction device and standard chromatography syringe (Lozano, 2002).

Solid phase microextraction (SPME) is a relatively new solventless extraction technique (Pawliszyn, 1997). The procedure starts when a syringe with a small diameter fiber on the top of plunger is introduced headspace (above liquid of the sample) or into liquid portion of the sample under a standard set of conditions: sample volume, mixing and temperature.

The SPME device is shown in Figure 10, with the stirring procedure and comparison with a standard chromatographic syringe. SPME is an equilibrium process where analytes partition between water/air and polymeric extraction phase, which is polydimethylsiloxane coated onto a fused silica fiber for extraction of semi-volatile hydrocarbons. Coating thickness ranges from 7 to 100 μm (Langenfeld, 1996). After the extraction, the fiber is retracted and directly introduced into a gas chromatograph.

After Batch test I, for SPME, the volume of the samples was 150 ml, and the stirring equipment were used. The SPME procedure took 20 minutes. After each procedure, the stirring bars were washed with hot tap water. After Batch test II and column tests, the samples were transferred into vials, 8 ml, and stirring of the samples were carried out as shown in Figure 9, without stirring bars but under vibration during 20 minutes.

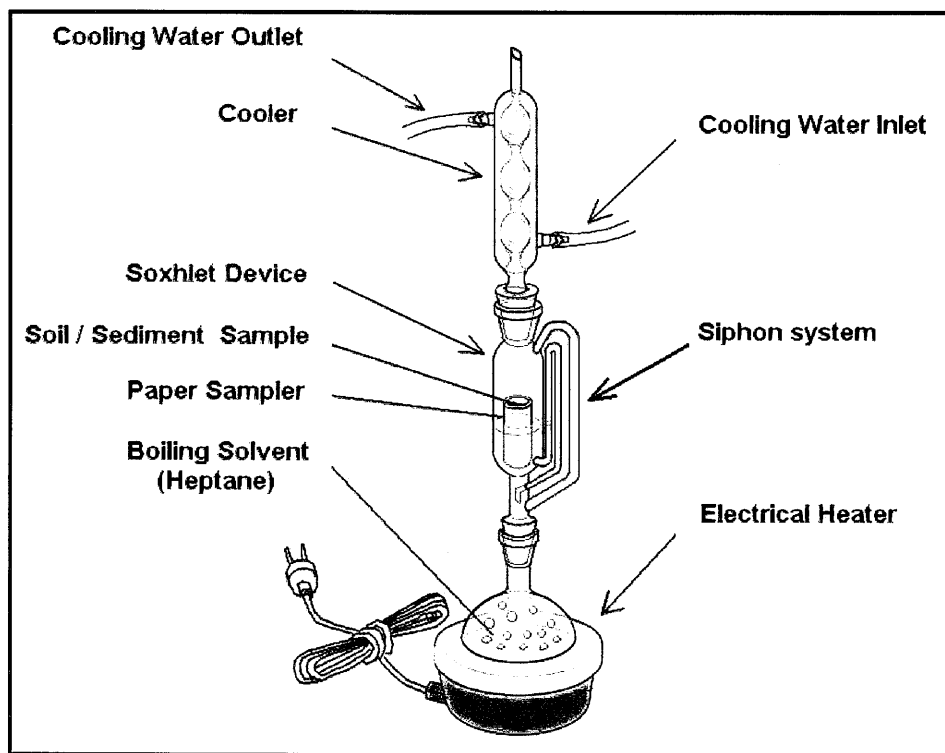


Figure 11. Soxhlet extraction apparatus (Lozano, 2002)

Soxhlet extraction. The main principle of the Soxhlet extraction is the partition process (liquid-solid), where a target analyte is extracted with a solvent from the soil or adsorbent material. The apparatus is shown in Figure 11. During the extraction, solvent is boiled, and then its vapors are condensed in a cooler and drop into a porous thimble with the sample. The process is repeated every 10 minutes, and the whole extraction takes 12 - 24 hours. The net effect is continuous extraction by the solvent.

In this work 450 ml of a mixture of n-Heptane and acetone was used as a solvent. Twenty grams of the adsorbents were extracted during 24 h. Before extraction all equipment was cleaned with n-heptane and acetone. After the Soxhlet extraction, solvent extracts (≈ 400 ml) were evaporated in a steam rotary evaporator. In this equipment the extract was evaporated in a hot water bath in a vacuum-sealed system until a volume of 10 ml, normally process takes 40-50 min.

Next step included evaporation of the extract with a direct contact with a flow of nitrogen on the liquid surface. The extracts were evaporated until a volume of 2 ml (8 min).

GC/FID. General scheme of a gas chromatograph with a flame ionization detector is shown in Figure 12. Chromatographic separation of a mixture occurs by the differential retention of the components between a stationary phase and a mobile phase (Reeve, 1998). A capillary GC column was used (stationary phase: DB5; film thickness: $0.25\ \mu\text{m}$; inner diameter: $0.2\ \text{mm}$; length: $30\ \text{m}$). The temperature program for batch test 1 was: injector temperature $280\ ^\circ\text{C}$, detector temperature $280\ ^\circ\text{C}$, oven temperature $50\ ^\circ\text{C}$, $+7\ ^\circ\text{C}/\text{min}$ to $200\ ^\circ\text{C}$, $15\ ^\circ\text{C}/\text{min}$ to $280\ ^\circ\text{C}$. The total running time was 30 min.

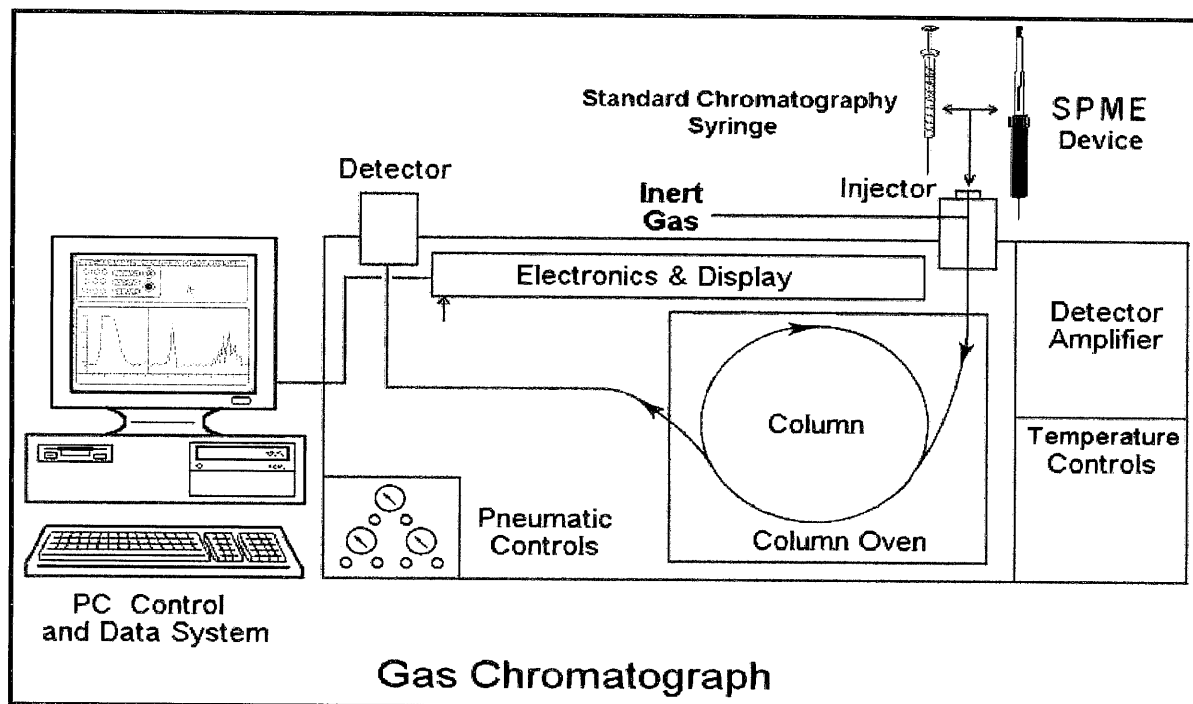


Figure 12. Gas chromatographic equipment used (Lozano, 2002).

The temperature program for the rest experiments was: injector temperature 300 °C, detector temperature 300 °C, oven temperature 50 °C, +7 °C/min to 200 °C, 15 °C/min to 300 °C. The total running time was 40 min. The volume injected after SPE was 0.5 µm.

Table 3. Percentage removal of diesel hydrocarbons in the Batch test I.

	Peak area of diesel oil	Removal, (%)	Mass of dry adsorbent, (g)
Blank	54408		
Bark	9647	83,0	34,3
Ash	1155	97,8	39,8
Ground peat	1690	96,9	35,2

Chapter 5. Results and discussion

5.1. Batch experiment I, with diesel oil

Diesel oil content in the filtrates (SPME-GC)

The diesel oil used in this batch experiment is a mixture of hydrocarbons. The chromatographic methodology using GC/FID gives a number of peaks in the chromatograms but does not identify the specific organic compounds of the oil. Thus in the blank chromatogram (Figure 12), the fourteen highest peaks of hydrocarbons from the diesel oil were identified by their retention time and their peak areas were calculated. Retention time ranges of the chosen peaks were within 14 and 30 min. Then the total peak area of the hydrocarbons in the diesel oil blank was compared with the total peak areas of the hydrocarbons in ash, bark, raw peat and ground peat chromatograms. As it can be seen from these representative chromatograms in Figure 11, a high removal was reached by ash, ground peat and bark. Peaks with high retention times in the chromatograms for ground peat and bark indicate occurrence of more high molecular weight natural organic compounds. Raw peat chromatogram was not evaluated due to impossibility to distinguish the peaks of natural organic compounds from those of diesel oil.

As no Internal standard was added, no quantifications were made but the relative total areas of the peaks were calculated. In Table 3, the removal of the diesel hydrocarbons is expressed as percentage. Ashes and ground peat were the most effective in removing the diesel oil by 98% and 97% respectively. Less percentage removal by bark may be attributed to the less dry bark mass and the larger size of the adsorbent material used.

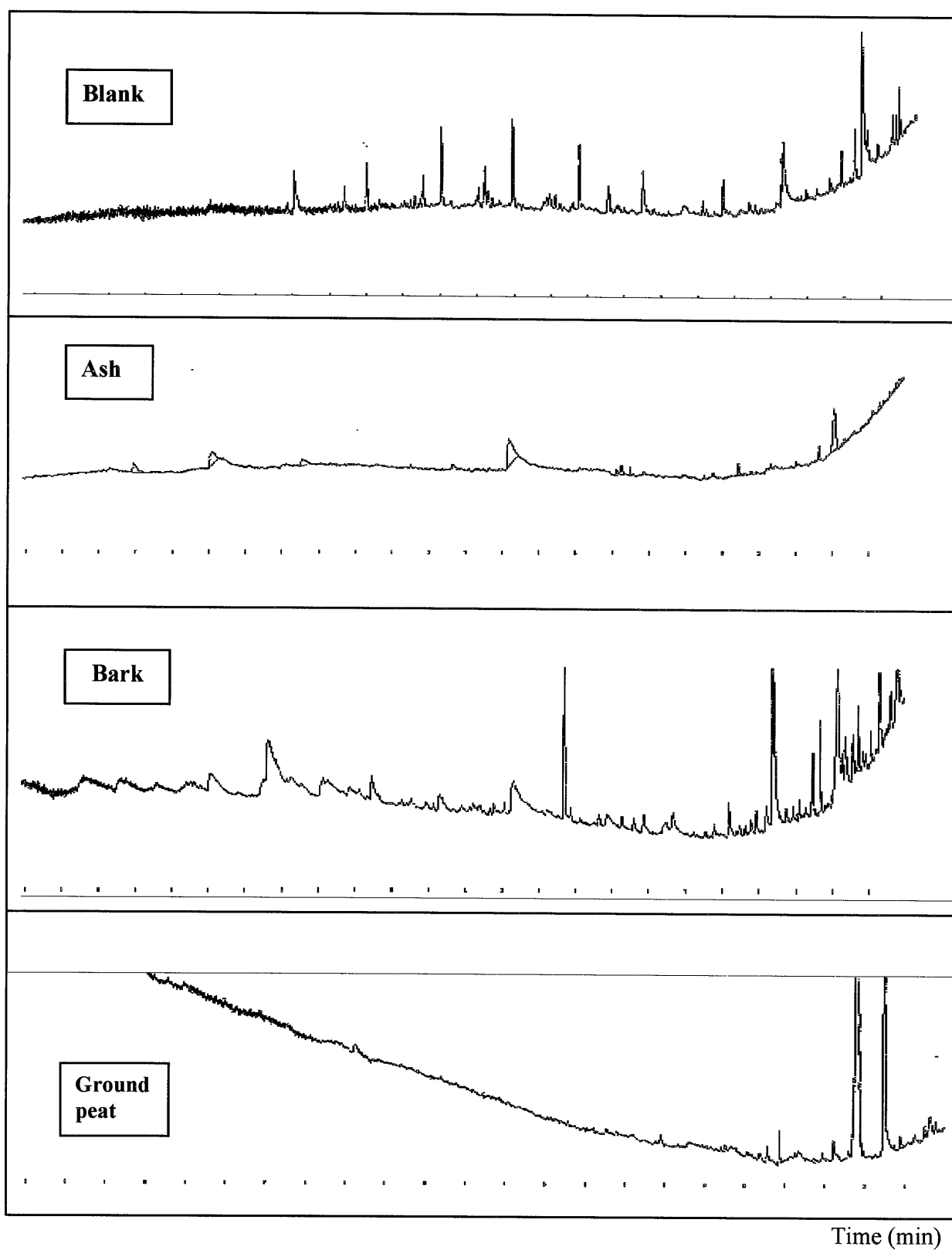


Figure 13. Representative chromatograms with hydrocarbons from batch test II, with the diesel oil (SPME).

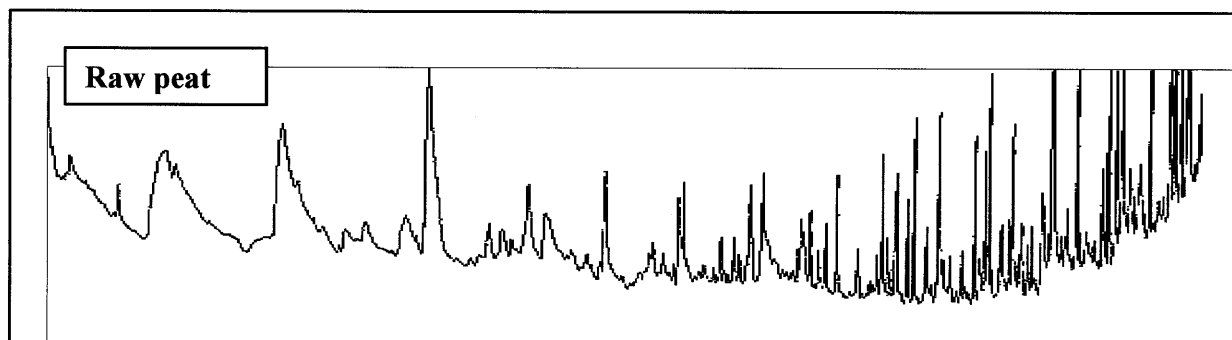


Figure 13. (Continued).

Diesel oil content in the adsorbents, Soxhlet-SPME-GC

To be able to evaluate the amount of the diesel oil that was really adsorbed, extraction of the adsorbent material used in the batch test I was made by Soxhlet extraction. Unfortunately, along with diesel oil in the extraction solvent, there were natural occurring organic substances, dissolved from bark and peat that made it impossible to distinguish and evaluate the peaks in the chromatograms. Selected chromatograms are presented in Appendix 3.

5.2. Batch experiment II, with C₁₂ and C₁₆

With the use of C₁₂ and C₁₆ with known retention time and in high concentration, in this batch experiment, it became easier to identify peaks in the chromatograms and interpret the results compared with Batch test I.

This paragraph discusses results obtained after applying two extraction methodologies: solid-phase extraction (SPE) and solid-phase microextraction (SPME), and the problems associated with them.

SPE/FID

As it was described in the experimental part, there were difficulties related to peat filtrate percolation through the extraction disc, which made it impossible to carry out SPE. Hence a more careful clean-up filtration was needed (2-step filtration of ground peat will be discussed later). The results reported here concern only ash and sand.

Internal standard in batch test II was added after filtration to be able to calculate recovery of C₁₂ and C₁₆ during SPE. Table 4 shows the results of the chromatographic analysis of ash and sand filtrates.

Table 4. Removal in percentage of C₁₂ and C₁₆ in batch test II with SPE.

	Area, C ₁₂	Area, IS	Area, C ₁₆	A _{C12} /A _{IS}	A _{C16} /A _{IS}	C ₁₂ removal,%	C ₁₆ removal,%
Blank I	1167730	8775212	2611613	0.133	0.298		
Ash	127083	10853781	101667	0.012	0.009	91	97
Sand	313455	10710454	772602	0.029	0.072	78	76

*To determine percent of C₁₂ and C₁₆ removal, following equation was applied:

$$C_{12/16} \text{ removal, \%} = 100 - \frac{\frac{\text{Peak area } C_{12/16} (\text{Adsorbent})}{\text{Peak area of IS (Adsorbent)}} - \frac{\text{Peak area } C_{12/16} (\text{Blank})}{\text{Peak area of IS (Blank)}}}{x 100\%} \quad (2)$$

As it can be seen from Table 4 the peak area of C₁₆ is about 2 times higher than C₁₂. It assumes great losses of C₁₂ via evaporation during agitation, filtration and the extraction procedure. Comparison of the ash and sand chromatograms (Figure 14) with the blank shows high adsorption capacity for both materials. The mechanism that governs adsorption on ash and sand is not fully understood here. In some previous works with dyes, high capacity of fly ash) is due to alumina (Al₂O₃), silica (SiO₂) and calcium oxides (CaO), which adsorb the ionic forms of dyes (Kumar *et al.*, 1987).

Sand was known to have low adsorption capacity in removing nonionic organic compounds due to its low affinity to organics. However sand surface is not smooth but consist of irregularities such as ridges and cavities. These surface irregularities may provide sites capable of retaining high concentrations of contaminant creating high organic matter regions into which petroleum contaminants may partition (Bhandari *et al.*, 2000). Thus some more investigation should be done related to adsorption mechanisms by ash and sand.

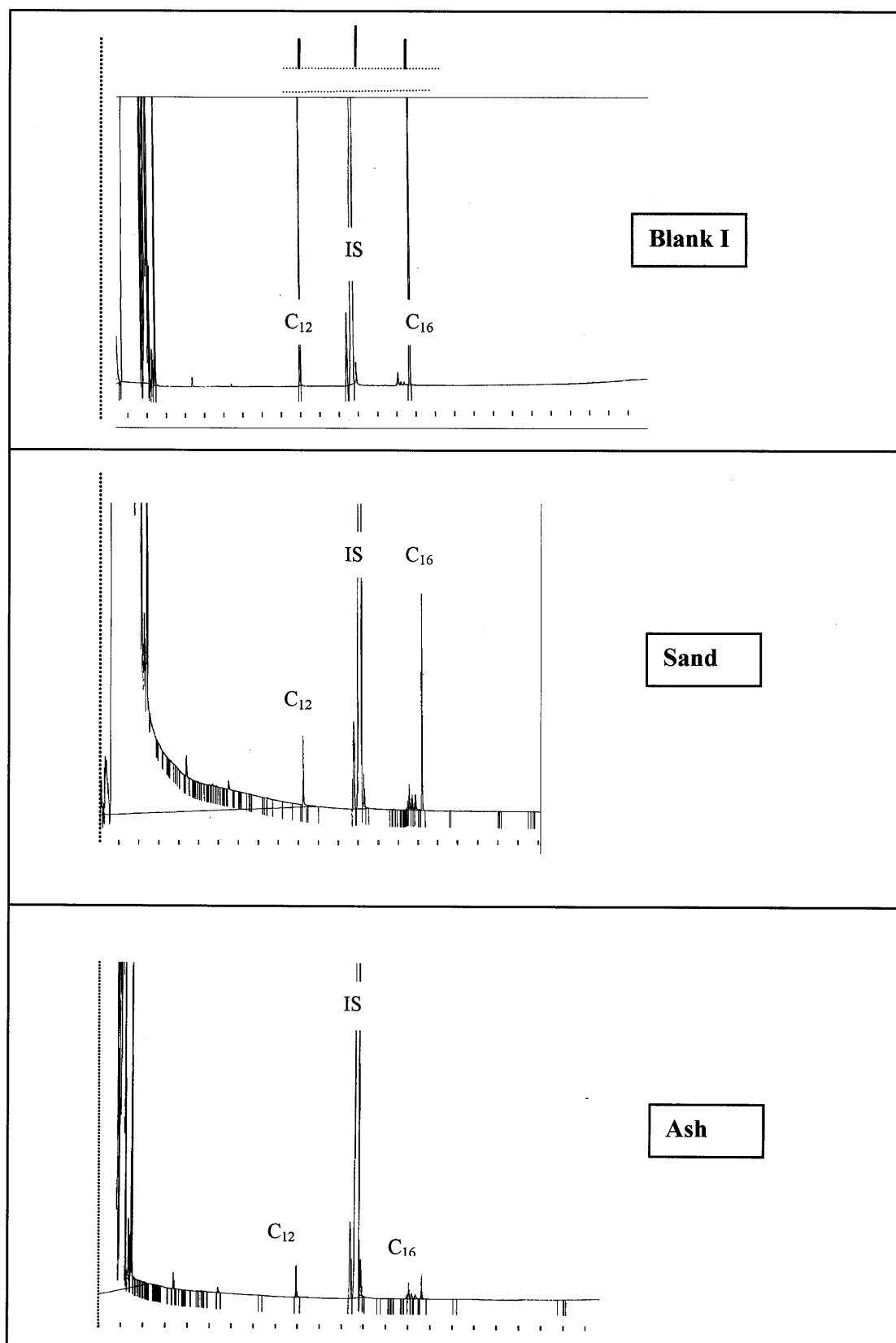


Figure 14. Representative chromatograms from batch test II, with C_{12} and C_{16} , SPE.

Table 5. Percentage removal of C₁₂ and C₁₆ in batch test II with SPE.

	Area C ₁₂	Area IS	Area C ₁₆	A _{C12} /IS	A _{C16} /IS	C ₁₂ removal, %	C ₁₆ removal , %
Blank II	57726	11 364357	2 711109	0.005	0.238	----	----
Ground peat	59700	1 976903	42369	0.03	0.02	----	92

A two-step filtration for the ground peat filtrate was done twice, using glass wool and glass filter. Blank solution was filtrated with the same procedure to be able to compare with the peat moss results.

Comparison of both the blank and ground peat chromatograms (Figure 15) shows a good removal of C₁₆. Concerning C₁₂, its peak area in the ground peat chromatogram is slightly higher then in the blank (peak areas can be compared from Table 5), which can be attributed to a less recovery of C₁₂ of blank during SPE.

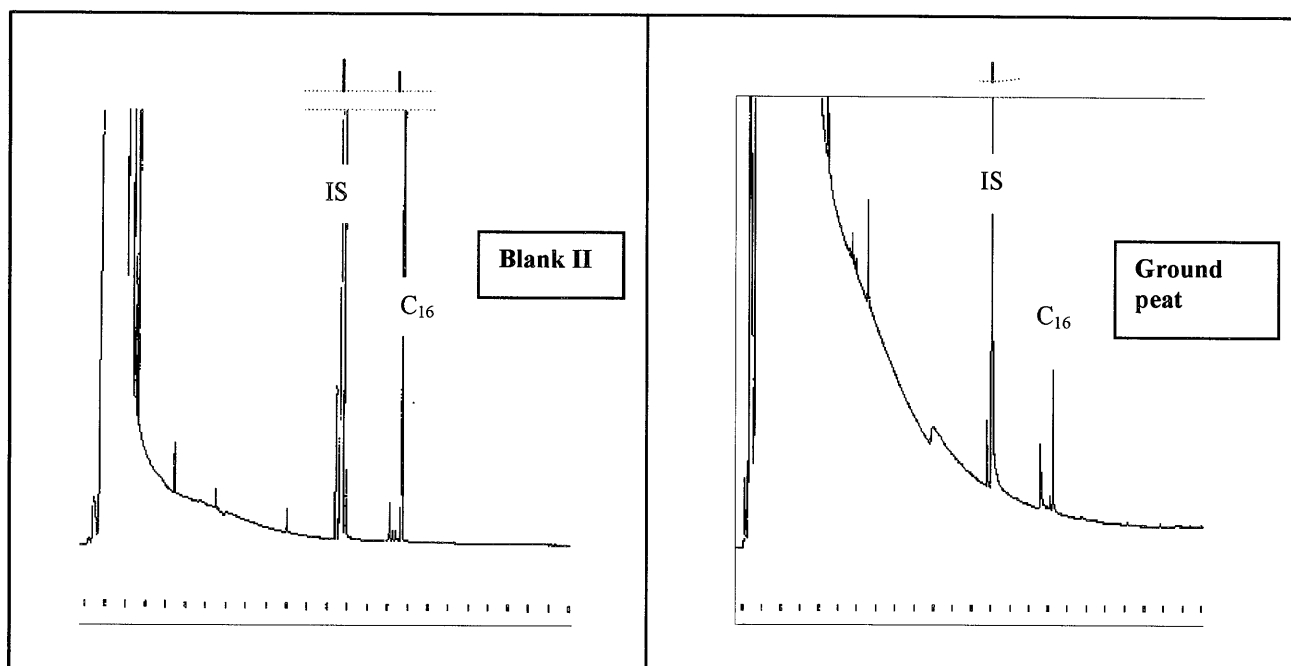


Figure 15. Representative chromatograms after batch test II, with C₁₂ and C₁₆, 2-step filtration, SPE.

Table 6. Percentage removal of C₁₂ and C₁₆ in batch test II

	Area C ₁₂	Area C ₁₆	C ₁₂ removal, %	C ₁₆ removal, %
Blank Ia	336099	4446521	-----	-----
Blank Ib	11977	761639	-----	-----
G. peat	28946	226111	0 - 91.4	70.4 - 95
Ash	1249	38762	89.6 – 99.6	94.9 – 99.1
Sand	9443	32567	22 – 97.2	95.7 – 99.3

SPME/FID

Analyses by SPME-GC of the same adsorbate solutions give results with a much broader range of uncertainties, due to the fact that no IS was used, and because obtained blank chromatograms differed greatly from one injection to another. In Figure 16, blank Ia and blank Ib are the chromatograms of the same blank sample but taken at different time with the span of 2 weeks (their peak areas can be seen from the Table 6). Such difference can possibly be explained by degradation of C₁₂ and C₁₆ or evaporation during the storage. However contamination of blank Ia during the GC analysis may not be excluded as some other peaks of organic compounds appeared in the chromatogram (Figure 16). Thus the analyte peak areas of all the chromatograms were compared with the both blank chromatograms, and results are reported with the range of removal calculated (Table 6).

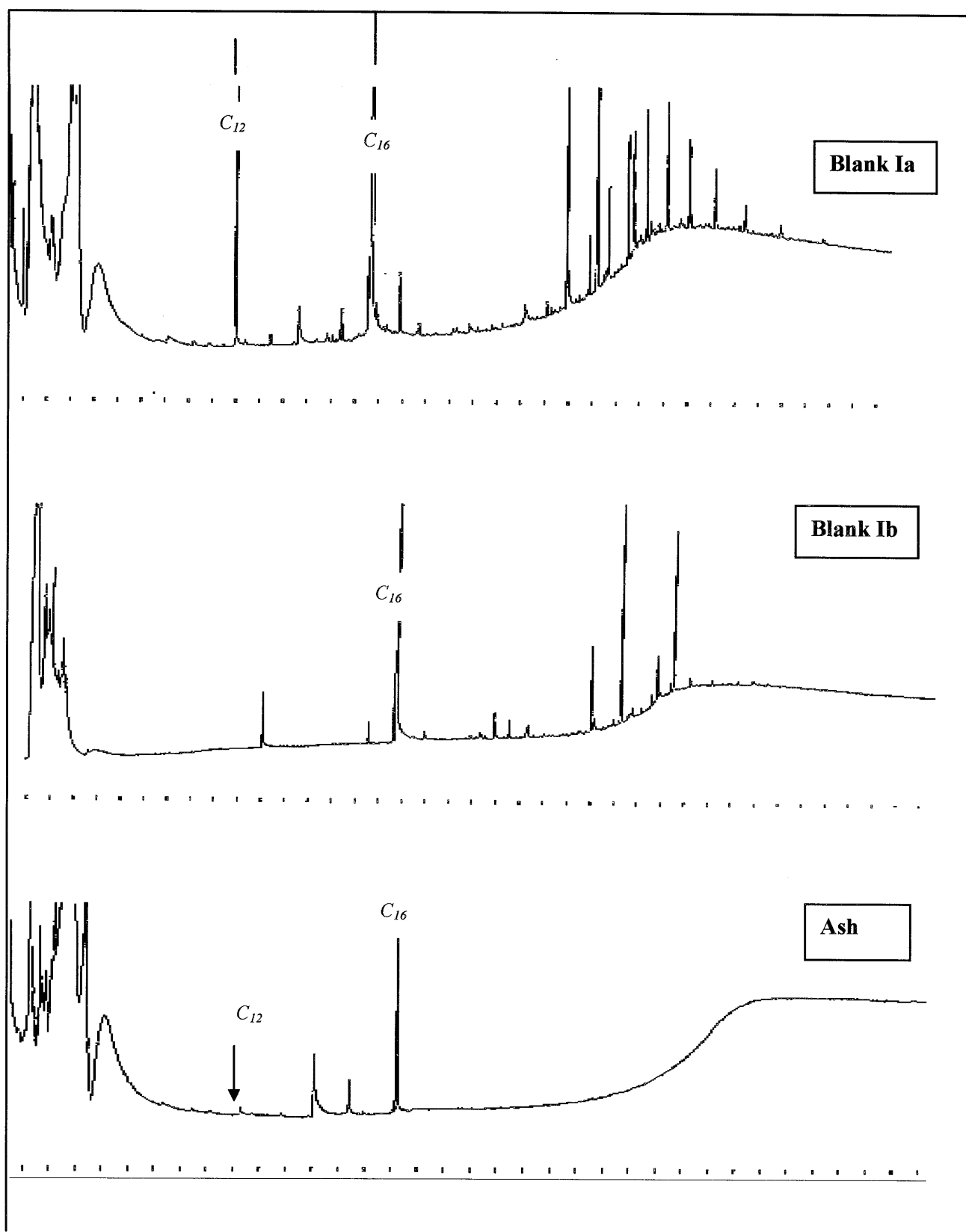


Figure 16. Representative chromatograms after batch test II, with C_{12} and C_{16} , SPME.

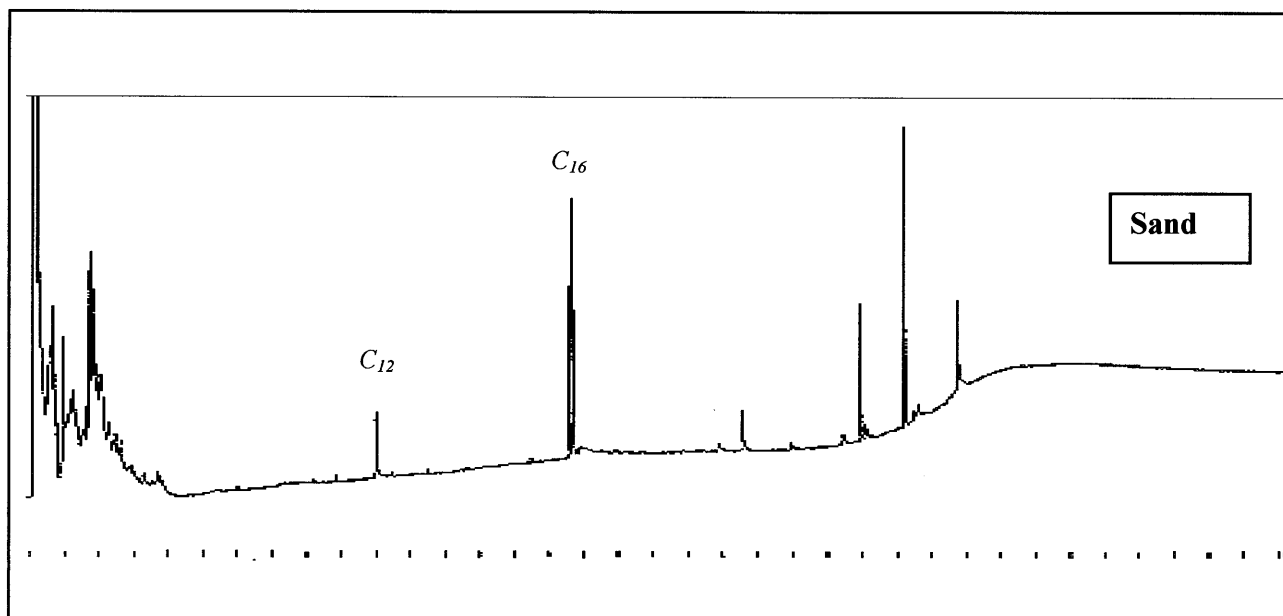


Figure 16. (Continued).

Table 7. Percentage removal of C_{12} and C_{16} in the batch test II with 2-step filtration, SPME.

	Area C_{12}	Area C_{16}	C_{12} removal, %	C_{16} removal, %
Blank II	1989	169040	----	----
Ground peat	4244	86044	----	49

Based on these results it is difficult to assess C_{12} adsorption of ground peat and sand. However, with more certain extent it can be concluded that the degree of C_{16} removal by ash and sand is significant.

Table 7 presents the results of the chromatographic analyses of ground peat after 2-step filtration. Five replicates of ground peat sample with SPME-GC were taken in order to obtain chromatograms with approximately the same peak areas. The C_{12} peak was either not detected or the peak areas were higher than that of the blank. Thus it was not possible to calculate the C_{12} percentage removal. C_{16} removal with 2-step filtration and SPME was much lower compared with SPE and SPME without filtration.

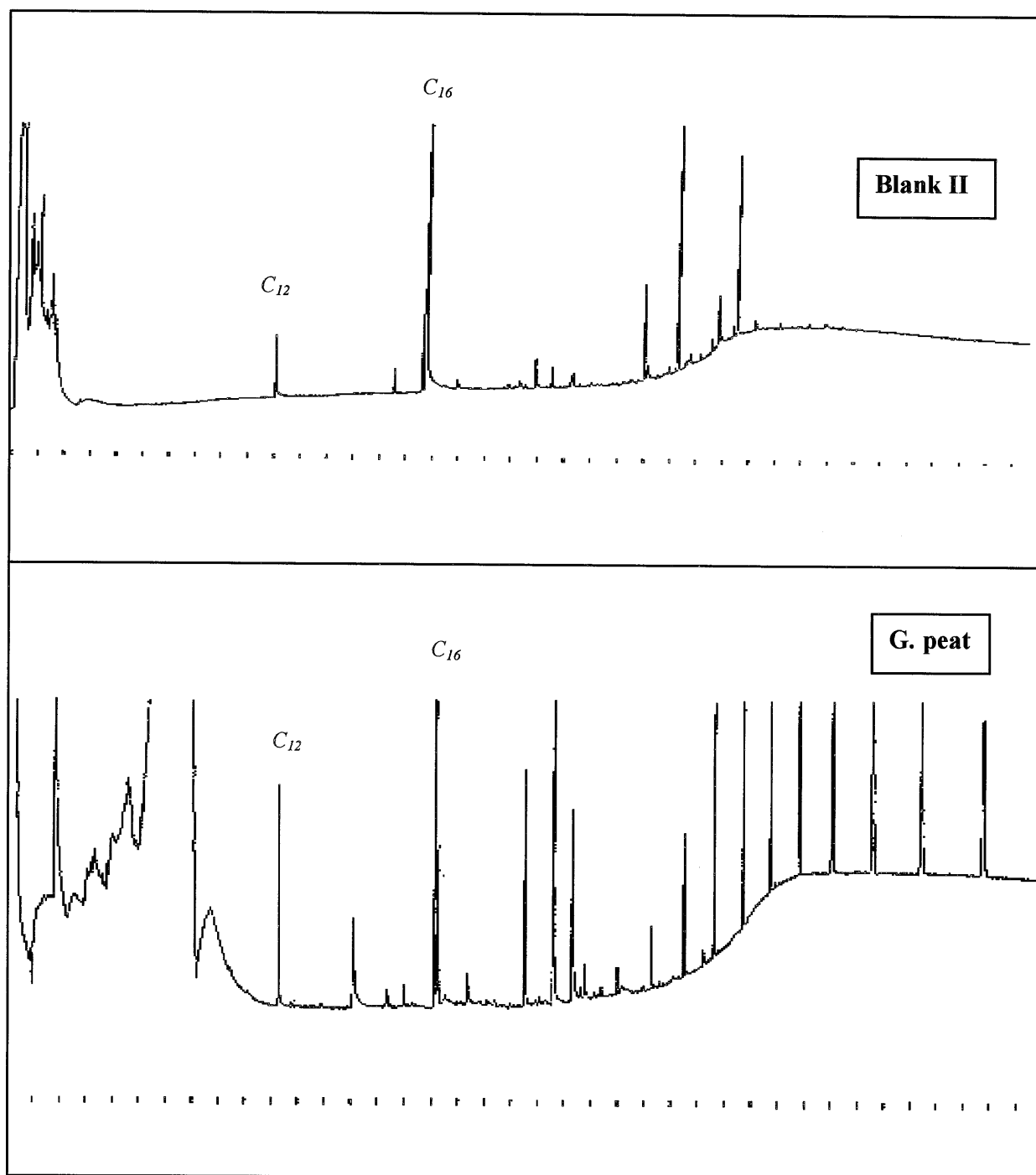


Figure 17. Representative chromatograms after batch test II, with C_{12} and C_{16} 2-step filtration, SPME.

Table 8. Comparison of extraction methods, SPE and SPME, after batch test II.

Adsorbent	SPE-GC Percent removal, %		SPME-GC Percent removal, %	
	C ₁₂	C ₁₆	C ₁₂	C ₁₆
Ash	91	97	90 – 99	95 – 99
Sand	78	76	22 – 97	95 - 99
Ground peat	----	----	0 - 91	70 - 95
Ground peat (2-step f.)	----	92	----	49

5.3. SPME versus SPE

The results obtained with SPE-GC and SPME-GC are different from each other. Except for ash where the percentage removal of C₁₂ and C₁₆, with both extraction methods was steady high, 90% - 99%. Results of analyses of sand obtained with SPE-GC show less adsorption capacity of C₁₆ than with SPME-GC. However it is vice versa with ground peat with considerably high difference in the results.

Basically, all the results obtained with the SPME technique showed a broad range of percentage removal of the analytes, especially C₁₂ thus making it difficult to interpret the results. Despite of some advantages of SPME over SPE, such as short extraction time, elimination of solvents and bulky glassware, the main drawback proved to be in susceptibility to contamination during subsequent chromatographic analysis. Significant time was required to run samples again and again in attempt to obtain chromatograms with approximately the same peak areas of the analytes. The differences in the peaks may be attributed to some contamination during GC/FID analysis from the injection port septum and leaching problem during injection. Also some processes during the storage of aqueous solutions such as degradation of the analytes, or their partition onto suspended solids present in the solution might be important.

Some previous works demonstrated higher sensitivity of SPME with increasing of sample volumes (Langenfeld, 1996), but as long as the water volume is measured with reasonable accuracy and applied for all samples, small sample sizes (1-2 ml) could be used without a great loss in sensitivity. In this work 150 ml in the batch test I and 1.8 ml in batch test II were used. Smaller volumes are more advantageous than larger ones as they do not require stirrings bars, which are mainly covered with plastic, and this in turn can be a source of contamination of the sample.

Unlike the SPME-GC/FID technique there was no difficulties related to chromatographic analysis of samples obtained with SPE-GC/FID. The analytes peak areas did not differ much from each other thus avoiding multiple runs of GC. Moreover with time, no degradation or losses of extracts of the analytes in the solvent were noticed.

The main disadvantages of this technique appear at different steps of SPE sequence. Firstly, SPE is a laborious and time-consuming procedure. As said before, bulky glassware is required to conduct SPE with large volumes of samples (about 1L). C₁₂ and C₁₆ had a tendency to adsorb on the flask walls and connecting tubes.

From Table 4 it can be seen that the C₁₆ peak is twice as high as C₁₂ but initial concentration was 100 versus 200 ppm respectively. Thus C₁₂ losses during SPE were almost 4 times higher than C₁₆. This assumes that C₁₈ extraction disc may not be accurate enough for the extraction of the compounds with less molecular weight due to evaporation processes.

The main problem of SPE seems to be the extraction of the analytes from complex environmental matrices. Ash and sand filtrates did not cause any problem during the percolation step, as all particles were removed prior extraction and the water was relatively clean. But when it came to more complex peat water, without several-step filtration, to obtain solution free of suspended solids and humic acids filtrate was not possible. These additional steps lead to a very low recovery of analytes. That could be seen if we compare the chromatograms of the blanks I and II (Figure 14, 15, Table 4, 5), with and without additional filtrations, keeping in mind the high concentrations of C₁₂ and C₁₆ used. Thus more effective extraction of analytes should be developed further.

Despite of all numerous problems arisen during SPE, it seems that this method is more sensitive than SPME. Since after all losses of the analyses during the procedure, the peaks of analytes were easily identified on blank chromatogram, which made it possible to compare with the other chromatograms (except for C₁₂ in the ground peat chromatogram), and the most important, the peaks of the analytes of a given sample did not differ from each other as with the use of SPME.

Further possible suggestions about how to overcome and improve these two techniques are discussed later in chapter 6.

5.4. Landfill leachate analysis and column experiments

Chromatograms in Figure 18 represent an inlet sample taken in the first day of running of the columns and outlet samples after the bark and ground peat columns. Surprisingly, peaks of organics detected were very small. The purpose of this column experiment was to test the adsorption capacity of the adsorbents with time. Yet if this inlet chromatogram to be compared with the chromatograms of bark and ground peat, it would be clear that further column experiment was no sense to continue. The concentrations of organic compounds in outlet samples were higher than in the inlet samples. However the columns were let to run until obtaining results from the analytical laboratory (Analytica AB), and also to test the adsorption of metals (Kalmykova, 2004).

Report from Analytica AB confirmed the low concentrations of organic contaminants (Table 9). The more detailed results of these analyses are given in Appendix 2. All values of contaminants are below Swedish guideline values (Swedish EPA, 2004). This implies that the majority of organic contaminants was degraded, partitioned onto sediment particles or evaporated during the sedimentation (2 weeks in the tank) and during the constant stirring in the glass flask.

Table 9. Organic contaminants in the leachates from the columns analyzed by Analytica AB.

ELEMENT		INLET	AFTER BARK COLUMN	AFTER G.PEAT COLUMN	GUIDLINE VALUES*
Aliphatic >C ₁₀ -C ₁₂	µg/l	<10	<10	15	Sum of
Aliphatic >C ₁₂ -C ₁₆	µg/l	<10	<10	15	aliphatic HC
Aliphatic >C ₁₆ -C ₃₅	µg/l	14	13	<10	100
Naftalen	µg/l	0.14	0.21	<0,1	
sum 16 EPA-PAH	µg/l	0.14	0.21	<0,8	
*PAH cancerogen	µg/l	<0,4	<0,4	<0,4	0.2
Other PAH	µg/l	0.14	0.21	<0,4	10

*Swedish EPA, Guideline values for levels in polluted groundwater

This fact should be taken into consideration for further implementation of remediation steps for organic pollutants.

Since there was no point to continue the column experiment, all following work was transferred into the laboratory and dealt with the batch experiments, which were described in previous paragraphs. Thus a discussion that follows further mainly concerns analyses of the inlet leachate and after the columns with bark and ground peat.

Bark. In attempt to obtain the adsorption capacity of the bark at least after one day of the column run, inlet concentration can be compared with outlet (Table 9). The results show no adsorption but enrichment of outlet water with organics, probably partly natural components from bark. Aliphatic hydrocarbons, with higher carbon chain, which are an indication of diesel oil, were presented at almost the same concentration in inlet and outlet samples. This may be explained by either contamination from the column itself (it was plastic and washed with just hot water) or contamination from the adsorbent. In Figure 16, it could be seen that some peaks in the bark chromatogram have an oil-like pattern unlikely being natural. The findings indicate that the Ecobark could be contaminated by diesel hydrocarbons during the treatment processes or transportation. Due to these facts the bark was excluded from the batch tests II with C₁₂ and C₁₆. Nevertheless, since some previous works reported high adsorption capacity of bark in removal of organic contaminants further investigation of bark should be done.

Ground peat. In contrast to bark, ground peat effectively removed high molecular weight aliphatic hydrocarbons (C₁₆-C₃₅) after first day of the run, but enriched outlet water with lower molecular weight aliphatics (C₁₀-C₁₆). Either contamination from the column or from peat or both could be the explanation. Naphthalene and other PAH:s seems to be well removed in the peat moss column. No channeling, clogging of the tubes and swelling of the adsorbent were noted.

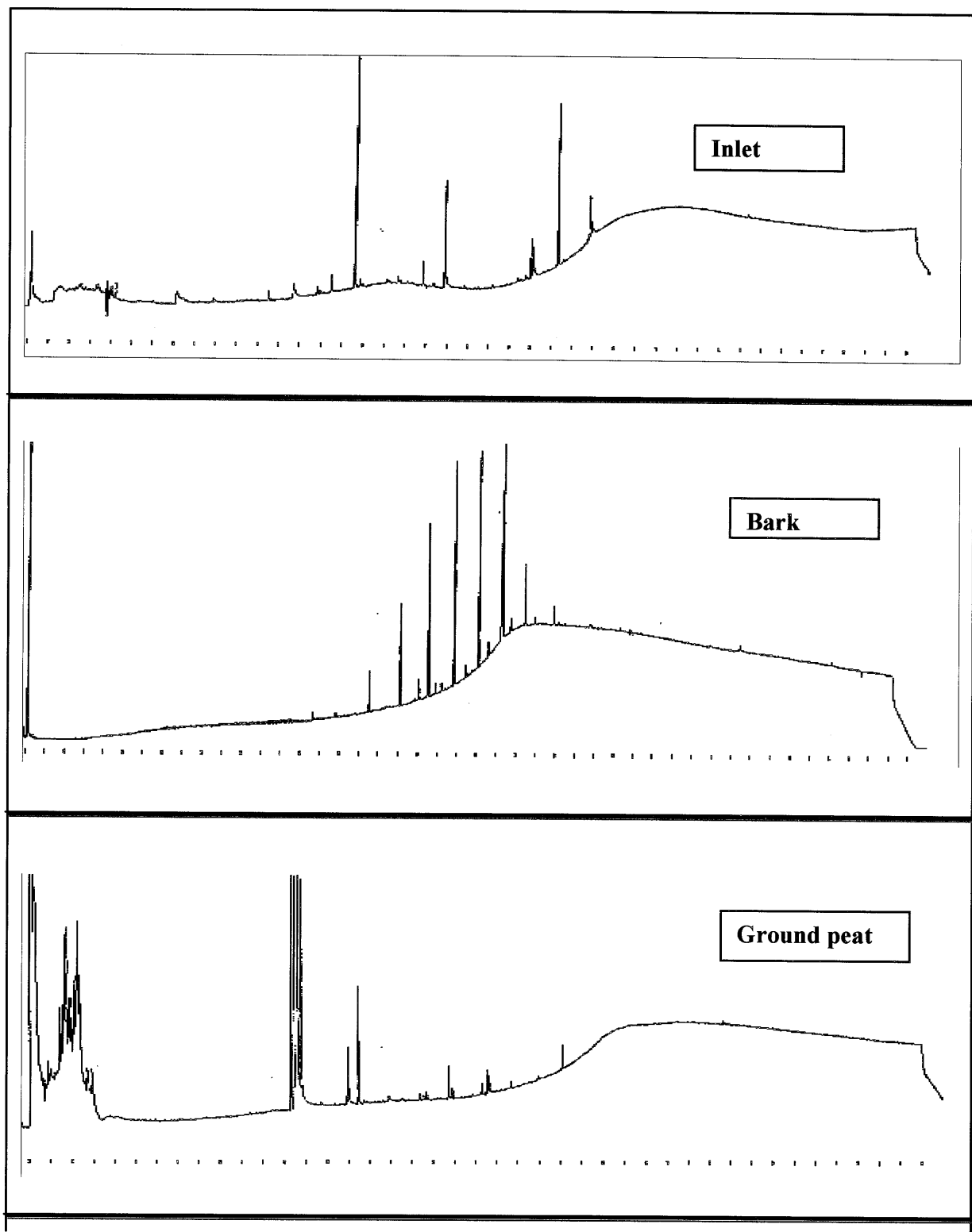


Figure 18: Chromatograms of oil analyses on the landfill leachate (inlet) and after columns with bark and ground peat (outlet).

Chapter 6. Conclusions

Of all tested adsorbents in the batch experiments, fiber ash was proven to be the most effective in adsorption of diesel oil, C₁₂ and C₁₆ (91-99%). Due to difficulties related to the extraction and analytical procedure of the organic contaminants adsorption by sand and ground peat is given with broader range of percentage removal. Sand was effective in removing C₁₆ (78-99%) but it was difficult to determine the efficiency in removing C₁₂ (22-97%). Ground peat showed good removal capacity in the batch test I with diesel oil (97%) and removal of C₁₆ with SPE-GC/FID (92%). It is impossible to interpret C₁₂ due the high uncertainty level (0-91%).

In this work SPE methodology seems to be more sensitive and reliable than SPME. Despite of numerous problems during extraction steps, peaks were well detected and interpreted in contrast to SPME methodology. In this perspective, if based only on SPE technique, ash and peat could be qualified as good natural cheap adsorbents as an alternative to activated carbon or other synthetic materials. However the SPME technique should be developed further as it has the potential to overcome many difficulties associated with SPE for the extraction of organics from complex environmental matrices.

This conclusion is fully based on the batch tests. Continuous flow experiments using packed columns should be considered as necessity to simulate more closely real treatment of the landfill leachate. Despite columns to treat real leachate were constructed, concentrations of organic contaminants in it were too low to evaluate analysis data. Only suggestions about behavior of the adsorbents are given.

Fiber ash appeared to be very effective in removing organic contaminants, but it could be used only as an additive due to its cementing nature. Ground dry peat, with or without ash, is preferably to be used as a main adsorbent for further adsorbent tests on landfill leachate, as it is a cheap and available raw material.

Chapter 7. Further recommendations

Laboratory scale.

For further analyses of organic contaminants it is recommended to focus on laboratory scale research. Column experiments will be a better solution rather than batch experiments. First reason is that agitation during batch experiments seems to enrich the water phase with natural organic components from the peat or bark, thus making the analytical procedure complicated. On the contrary, the column effluents were relatively clean (visually it was seen) from solids with almost no color that indicates less natural organic content. Secondly, columns will ensure simulation of real treatment environment. Important factors such as temperature, pH and flow rate should be investigated in further analysis.

Choice of the adsorbents

Ground peat is preferably to be used as an adsorbent during remediation of the landfill leachate. Even if the raw peat bed shows good performance, using a ground dry peat bed will provide higher volumes of the landfill leachate to be treated due to rapid draining through the dry peat bed in contrast to low percolation through raw peat. Addition of ash to the peat should be investigated further due to its high potential in removal of organic contaminants.

As addition of ash into peat resulted in worse performance of the column for metal removal (Kalmykova, 2004), column in series can be set up. It means that the leachate can pass through both columns: first column with ground peat where removal of metals is maximum, the second one with ground peat and ash where removal of organic contaminants is maximum, or vice versa.

Treatment of the landfill leachate

If a big peat fixed bed will be installed for the treatment of the landfill leachate, some consideration should be taken into account.

Pretreatment before adsorption is necessary. Keeping the leachate in open storage tank provided high degradation and evaporation rates for organic contaminants. Many remediation systems for soil contaminated with volatile organic compounds and petroleum hydrocarbons include in-situ aeration (or soil vapor extraction), which enhance volatilization and it is relatively low-cost remediation technology (Lim, 1997). This application could be considered as a pretreatment of the leachate before filtration, although installation and energy expenses should be calculated.

Also another pretreatment alternative is to pretreat the leachate in an agitation tank with ash. This will avoid all problems related to channeling and cementing. But as well some thoughts should be given in terms of energy and installation costs.

Considering design of the peat bed, it could be constructed in such way that the container tank could be raised from the ground in order to collect effluent for the analysis. Leachate could be applied in downflow mode. The bottom of the bed should be made of grid.

On the grid a stone drainage layer should be placed to ensure free drainage of leachate and filtration of the effluent from suspended solids from the peat. Graduated layers of increasing stone size to the bottom and upper layer could be sand.

Analytical procedure

SPE is the best to be used as a main extraction procedure. The columns with adsorbents in laboratory, if to be investigated for organic pollutant removal, should be run for several days with deionized water in order to provide cleaner effluent. This prestep will facilitate percolation through extraction disc (C18).

SPME should be developed further. To increase sensitivity of the method in analysis of more volatile organic compound, the fiber could be hold headspace (above the surface), instead of the water phase. Less volume of sample containers is preferable in order to avoid use of stirring bars.

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Appendix 1

Concentration of organic contaminants at spot 202 and S38, after sedimentation.
Report from environmental chemistry laboratory, Analytica AB (March, 2003)

<i>Organic compounds</i>	<i>Concentration at spot S38, (µg/L)**</i>	<i>Concentration at spot 202, (µg/L)</i>
Aliphatic>C5-C8	<10	<10
Aliphatic>C8-C10	<10	43
Aliphatic>C10-C12	<10	<10
Aliphatic>C12-C16	74	<10
Aliphatic>C5-C16	74	43
Aliphatic>C16-C35	1200	160
Aromatic>C8-C10	<4.0	1870
Aromatic>C10-C35	1.4	0.8
Benzene	<0.2	0.5
Toluene	0.2	1.7
Ethylbenzene	<0.2	34
Total Xylen	<0.2	130
Naphthalen	<0.1	1.3
Acenaftylen	<0.1	0.11
Acenaften	<0.1	0.24
Fluoren	<0.1	0.22
Fenanthren	0.53	0.60
Antracen	<0.1	0.19
Fluoranthen	0.42	0.67
Pyren	0.36	0.53
*Benzo(a)antrathen	0.11	0.27
*Krysen	0.16	0.24
*Benzob)fluoranthen	0.20	0.34
*Benzo(k)fluoranthen	<0.1	0.13
*Benzo(a)pyren	0.11	0.23
*Dibenzo(ah)antracen	<0.1	<0.1
Benzo(ghi)perylene	<0.1	0.14
Indeno(123cd)pyren	<0.1	0.15
Sum 16 EPA-PAH	1.9	5.4
*PAH Carcinogenic	0.58	1.4
Other PAH	1.3	4.0

* Carcinogenic compounds

Appendix 2

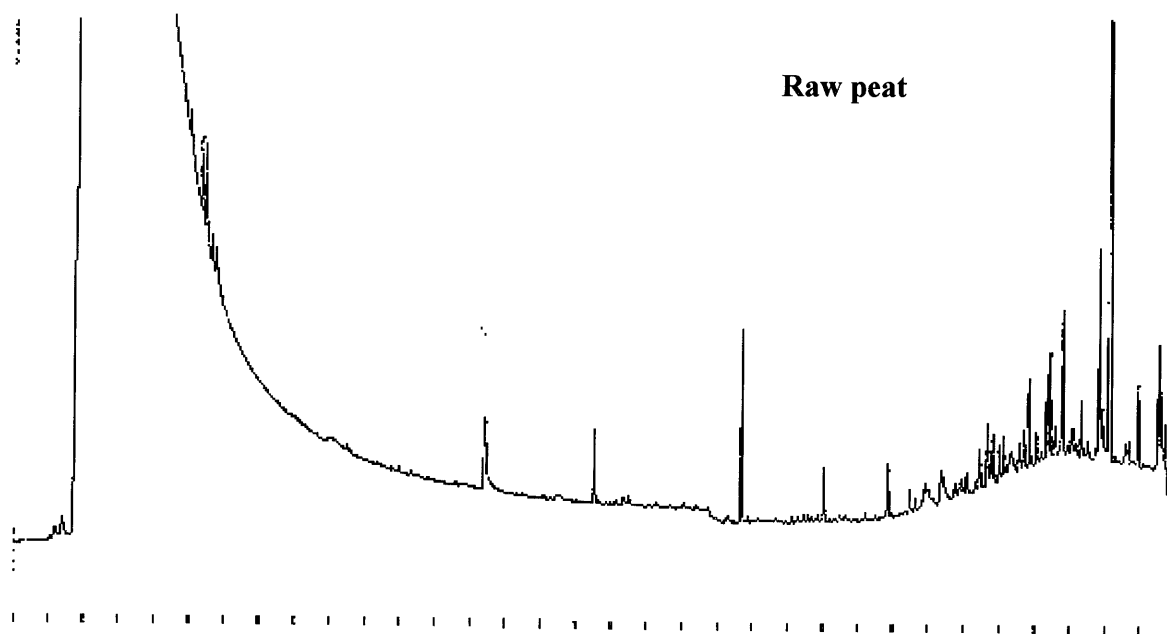
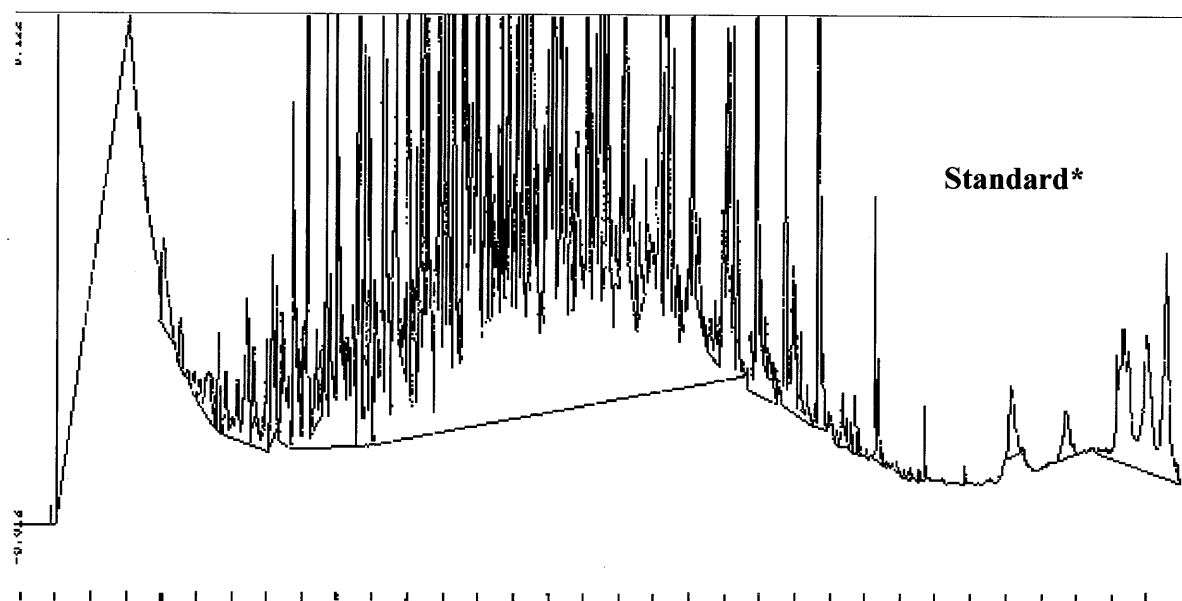
Concentration of organic contaminants in the leachate after sedimentation in inlet, and in the effluent after bark and ground peat columns. Report from environmental chemistry laboratory, Analytica AB (Nov., 2003)

<i>Organic compounds</i>	<i>Ground water</i>	<i>After bark column, (µg/L)**</i>	<i>After ground peat column, (µg/L)**</i>
Aliphatic >C10-C12	<10	<10	15
Aliphatic >C12-C16	<10	<10	15
Aliphatic >C16-C35	14	13	<10
Chlorbenzene	<1	<1	<1
Total PCB	<1	<1	<1
Total phenols	<2	<2	<2
Naphtalene	0.14	0.21	<0,1
Acenaftülen	<0,1	<0,1	<0,1
Acenaften	<0,1	<0,1	<0,1
Fluoren	<0,1	<0,1	<0,1
Fenanthren	<0,1	<0,1	<0,1
Antracen	<0,1	<0,1	<0,1
Fluoranthen	<0,1	<0,1	<0,1
Pyren	<0,1	<0,1	<0,1
*Benze(a)antracen	<0,1	<0,1	<0,1
*Crysene	<0,1	<0,1	<0,1
*Benzo(b)fluoranthen	<0,1	<0,1	<0,1
*Benzo(k)fluoranthen	<0,1	<0,1	<0,1
*Benzo(a)pyren	<0,1	<0,1	<0,1
*Dibenzo(ah)antracen	<0,1	<0,1	<0,1
Benzo(ghi)perylene	<0,1	<0,1	<0,1
*Indeno(123cd)pyren	<0,1	<0,1	<0,1
Total 16 EPA-PAH	0.14	0.21	<0,8
*PAH carcinogenic	<0,4	<0,4	<0,4
Other PAH	0.14	0.21	<0,4
Other compounds	detekt	ej detk	ej detk

* Carcinogenic compounds

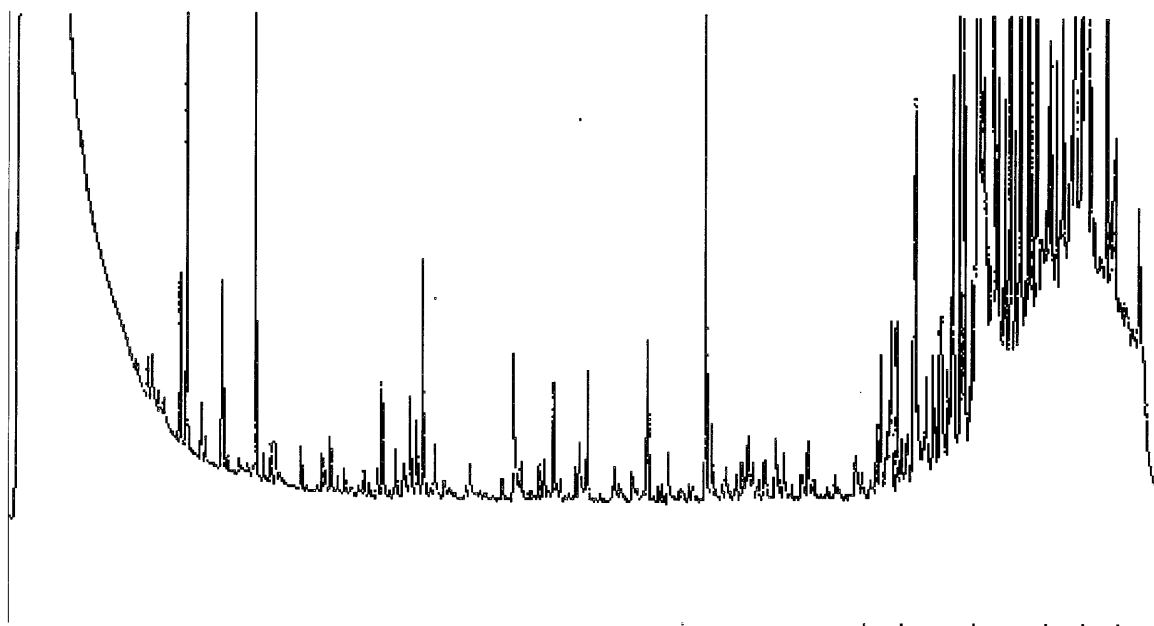
Appendix 3

Chromatograms of the diesel oil analyses in bark, raw and ground peat adsorbent materials after Soxhlet extraction

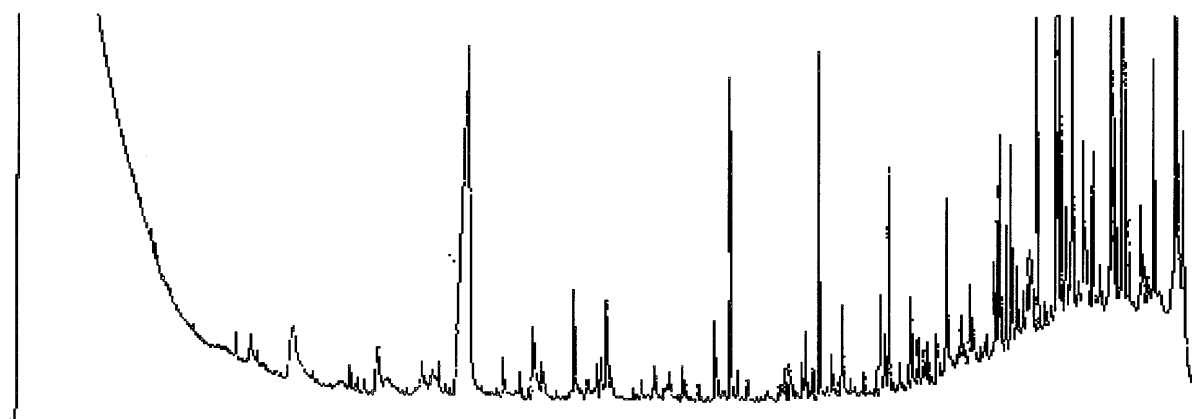


Appendix 3 (continued)

Bark



Ground peat



Appendix 4

Characteristics of the adsorbents and design of the column tests.

Table 1. Adsorbent characteristics.

Adsorbent	Moisture content, %	Org. content, d.w., %
Bark	14.3	96.5
Ash	0.5	0.5
Raw peat	61.3	43.9

Table 2. Grain size distribution of the adsorbents.

Sieve pore diameter (mm)	Material passed through the holes, %		
	Peat moss	Ash	Bark
8	100.0	100.0	100.0
5.6	100.0	100.0	99.9
4	100.0	100.0	94.2
2	99.68	100.0	54.7
1	97.45	100.0	18.6
0.5	90.13	99.8	4.8
0.25	66.56	95.5	2.2
0.125	46.18	78.3	2.0
0.074	27.71	57.6	1.9
Bottom	---	---	---

Table 3. Design of the column experiments.

	Row peat	Peat moss/ash	Ground peat	Bark
Mass of adsorbent (g)	645	779	870	821.3
Dry mass of adsorbent (g)	116	235,8	255,6	281
Water content (%)	82	70	71	66
Height (cm)	30	30	30	30
Internal diameter (cm)	6	6	6	6
Volume of adsorbent (ml)	848	848	848	848
Packing density (g/ml)	0.12	0.25	0.27	0.3
Average flow (ml/min)	1	2	2	2
EBCT, min	848	424	424	424

Appendix 5

Characteristics of the extraction disc (C18) and analytical procedure of SPE.

3M

Empore™

Extraction Disks for Environmental Analysis

with Octadecyl (C₁₈) for use with
47 mm and 90 mm extraction apparatus

Instructions for Use

General Product Characteristics

Description:

3M™ Empore™ Extraction Disks are a unique extraction product that effectively replaces liquid/liquid extraction. A patented 3M process is used to entrap adsorbent particles into a matrix of inert PTFE to create a mechanically stable sorbent disk.

Formulation:

90% ± 2% adsorbent particle
10% ± 2% PTFE

Product Characteristics:

Thickness: 0.50 mm ± 0.05 mm
SPE Flow rate: < 10 min/L DI H₂O @ 25°C @ 20 in. Hg (47 mm disk)
Solvents: Compatible with all organic solvents
pH: Stable between 2-12. Range may be extended by short contact times.

3M Empore Sample Preparation Products are intended for solid phase extraction during scientific research only. These products are not intended for use in medical devices or in assessment and treatment of clinical patients. 3M does not warrant the use of these products for any application outside the products intended use.

Suggested Application Procedures

General: Water Analysis

3M™ Empore™ Extraction Disks provide a rapid, efficient alternative to liquid/liquid extraction for sample preparation. The disks can be used for purification and concentration of samples prior to final analysis. Advantages of Empore Extraction Disks include: enriched solvent usage, rapid sample throughput and reduced analytical interferences. The enclosed instructions are general guidelines for use. Sample volume, solvent type and conditioning may be changed to adapt to specific methods and analytes as needed.

Extraction Equipment

- 47 mm or 90 mm Empore C18 extraction disks
- 47 mm or 90 mm glass filtration apparatus or multi-stage extraction apparatus
- Vacuum source (0-20 in. Hg)

Sample Preparation

- Microbiological growth can be retarded by lowering sample pH to 2.
- 3M™ Filter Aid 100 and/or prefiltration may be helpful if the sample contains excessive suspended solids.

Extraction Disk Conditioning

Disk conditioning is critical for a successful extraction. Conditioning provides a good interface between the sorbent and the sample matrix. **FAILURE TO CONDITION THE EXTRACTION DISKS PROPERLY WILL RESULT IN ERRATIC AND LOW RECOVERIES.**

1. Center the extraction disk on the base of the filtration apparatus and clamp the reservoir in place on top of the disk.
2. Wash the disk with 10 mL of elution solvent.^{**}
3. Apply vacuum to dry the disk.
2. Add 10 mL^{**} methanol to the disk. Apply vacuum and pull approximately 1 mL through the disk. Vent the vacuum and allow the disk to soak for 30-60 seconds.
3. Apply vacuum and pull methanol through the disk until the methanol surface is 3-5 mm above the disk surface.
6. *Optional:* Add 10 mL reagent grade water to the reservoir, apply vacuum and pull the water through the disk until the water surface is 3-5 mm above the disk surface.

If disk should become dry while conditioning with methanol or water, repeat steps 4 through 6.

****If desired, place a vial in the vacuum apparatus to collect and dispose of wash and conditioning solvents. Remove vial prior to sample extraction.**

Sample Extraction

- Pour the sample into the reservoir and apply vacuum. Recoveries are not affected by flow rate. Flow rate is dependent on vacuum source and particulate content of the sample. Flow rates through individual extraction disks may vary.
- After sample extraction is complete, remove as much residual water as possible from the disk by applying vacuum to dry the disk for 5-20 minutes.

Sample Elution

Eluting twice with 10 mL solvent is recommended. Smaller volumes of solvent may be used if the elution techniques have been perfected.^{**}

- Place tip of filter base into the collection vessel (see diagram).
- Add 10 mL elution solvent to sample container, rinsing down the sides. Transfer solvent from sample container to reservoir with a pipet, washing the walls of the reservoir in the process.
- Apply vacuum and pull approximately 1 mL elution solvent through the disk. Vent the vacuum and allow the disk to soak 30-60 seconds before applying vacuum to dry the disk.
- Repeat this process with a second aliquot of eluting solvent.
- A third aliquot of elution solvent may be used as a final rinse of the reservoir and disk to enhance recoveries.

^{**}Note: Suggested solvent volumes will vary according to the disk diameter and the amount of filter aid material. A general guide for solvent volumes is to completely cover the disk and bed of filter aid, such that 1-3 mm of solvent is above the surface. Repeat with second aliquot.

