

Analytische Chemie

**Metal Ion Containing Liquid Chromatographic  
Stationary Phases for the Analysis of Polycyclic  
Aromatic Sulfur Heterocycles in Fossil Fuels**

Inaugural-Dissertation  
zur Erlangung des Doktorgrades  
der Naturwissenschaften im Fachbereich Chemie und Pharmazie  
der Mathematisch-Naturwissenschaftlichen Fakultät  
der Westfälischen Wilhelms-Universität Münster

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Tag der mündlichen Prüfungen: .....

Tag der Promotion: .....

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*To my parents*



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# 1 Introduction

## 1.1 Fossil fuels

Fossil fuels – coal, petroleum and natural gas are the world’s primary source of energy. Besides, petroleum has a multitude of industrial uses, including providing the base ingredients for such varied products as plastics, fertilizers and fabrics. In 2001, three countries – the United States, Russia and China, with a combined population of 1.71 billion out of the total population of the world of 6.30 billion were the leading producers and consumers of world energy. They together produced 38 % and consumed 41 % of the world’s total energy. The United States is the global leader in energy consumption. The U.S. comprises of 5 % of the World’s population and consumes 25 % of the energy. The future projections of the U.S. energy consumption show an increasing demand of petroleum (see figure 1.1) [1].

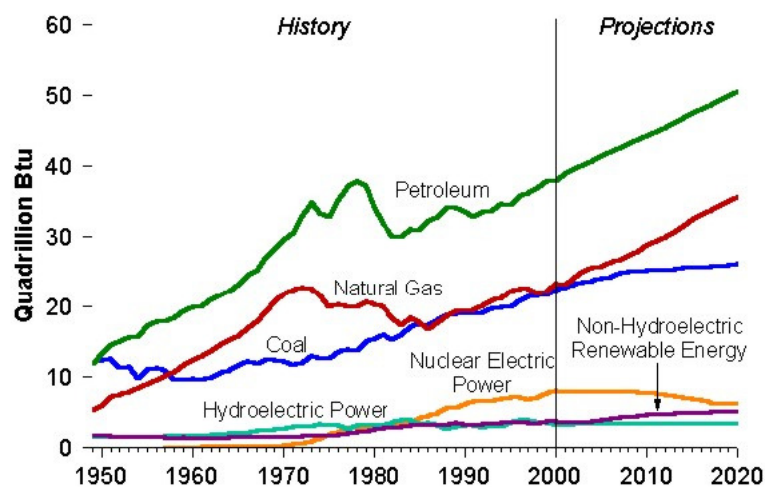


Figure 1.1: Graph showing the history and projections of the U.S. energy consumption in British thermal units (Btu) [1]. The increasing demand for petroleum can be seen in the projections.

## 1.2 Sulfur in fossil fuels

The combustion of fossil fuels not only allows us to heat our homes, fuel our industries, and transport people and goods, but also has a negative effect on the

quality of our environment. Sulfur in crude oil and the products derived from it, is perhaps the most talked about subject in public since it has a pivotal bearing on the environment on one side and constitutes a tough challenge to the refiner on the other side. It has reached such a proportion that refiners have to resort to desulfurizing even residues before these are put to use. It is one of the most energy intensive processes of the refinery. Crude oils containing high amounts of sulfur ( $> 1\%$ ) are termed “sour crudes” and those containing low sulfur amounts are termed “sweet crudes”. Sulfur dioxide ( $\text{SO}_2$ ) gas and other sulfur compounds are emitted during combustion of fossil fuels that contain sulfur. These sulfur compounds have a detrimental effect on human health, wildlife, agricultural productivity, quality of life and are a major contributor to acid rain. Sulfur compounds also reduce catalyst efficiency, thereby increasing nitrogen oxides ( $\text{NO}_x$ ) and hydrocarbon emissions from automobile engines. These negative environmental impacts have prompted the development of regulations that limit sulfur compound emissions from some sources and the sulfur content of transportation fuels. These regulations have evolved over time and have become more strict with respect to both sulfur content and sulfur compound emissions.

Sulfur in fossil fuels also affects the quality of a number of products. For example, catalysts for low-emissions vehicles are sensitive to the sulfur content of gasoline and diesel fuel. Similarly, the catalysts used in petroleum processing can be “poisoned” by sulfur. Sulfur affects the technical quality of other petroleum products as well. Fuel oils used in heat-treating metals or in firing glass-melting furnaces must be low in sulfur to avoid damaging the product. The sulfur content of coke has an impact on the quality of the steel it is used to produce.

Because sulfur has a negative effect on both the environment and on the quality of products, low-sulfur fuels are more desirable than high-sulfur fuels. However, because low-sulfur fuels are scarce and removing sulfur from fossil fuels is expensive, low-sulfur fuels are more valuable than high-sulfur fuels. The sulfur content of fossil fuels has become increasingly important to the value of these fuels as environmental regulations gradually lower the sulfur content limits for fossil fuels and restrict the emission of sulfur from fossil fuel combustion. These regulations have encouraged the development of technologies that remove sulfur from fossil fuels and

the design of transportation and power generation equipment that operate on low-sulfur fuel.

### 1.3 Origin of sulfur in crude oils

Sulfur is the third most abundant element in crude oils. Sulfur content in crude oils range from 0.05 to 13.95 wt % [2]. The identification of several organo sulfur compounds (OSC) has led to a number of hypotheses regarding their origin and interaction of the sulfur and carbon cycle in the geosphere. *Cyr* and *Payzant* [3, 4] suggested a biosynthetic origin for the bicyclic, tetracyclic and hopane sulfides present in petroleum. However, none of the reported OSC or their functional precursors have been reported to occur in biota. Sulfur represents a ubiquitous element, which occurs in all living organisms, for example in some amino acids. However, the origin of high amounts of sulfur in crude oils cannot be explained entirely by sulfur from biota since it is not present in such high concentrations in living organisms.

*Schmid* suggested that 2,5-di-n-alkylthiolanes present in petroleum might originate from reactions of the n-alkanes present in the oil with elemental sulfur during early maturation [5]. This hypothesis was partly supported by simulation experiments. Heating of n-octadecane in the presence of elemental sulfur at high temperatures produced a mixture of 2,5-dialkylthiophenes [5]. Similarly, heating of cholestane with elemental sulfur yielded number of sulfur containing steranes [5]. A theory assumes that the origin of sulfur lies in the sulfate ions in sea water. Microorganisms like *Desulfovibrio* and *Desulfobacter* reduce sulfate to sulfide under anaerobic conditions [6].



This reduced sulfur can be oxidized by other microbes e.g. *Thiobacillus* to elemental sulfur which then undergoes anaerobic incorporation into plant or animal derived organic material [6]. Thus formed aliphatic sulfur compounds can be converted by condensation reaction and aromatization into complex ring structures. Similarly, elemental sulfur can also aromatize cycloalkanes by hydrogen abstraction.

*Brassell et al.* suggested an incorporation of inorganic sulfur species ( $\text{HS}^-$ ,  $\text{HS}_x^- \dots$ ) into chlorophyll derivatives [7]. *Damste et al.* [8] assumed that sulfur incorporation reactions on an intramolecular basis with suitable functionalized precursors at the early stage of diagenesis are probably the major origin of organo sulfur compounds (see figure 1.2). These sulfur incorporation reactions also take place intermolecularly, giving rise to the formation of sulfur-containing high molecular weight substances. These reactions may explain the relatively high amount of organic sulfur in asphaltenes and hetero fractions of crude oils and kerogens.

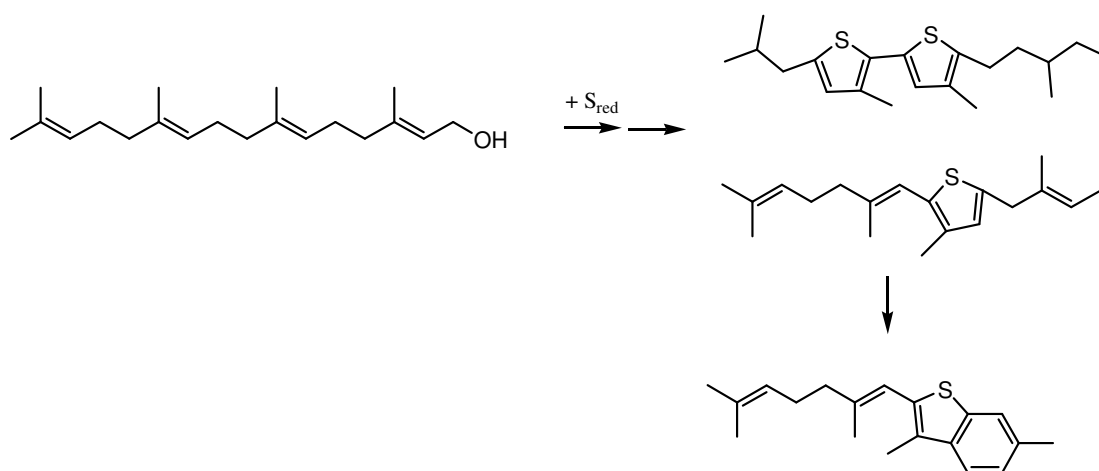


Figure 1.2: Example showing the incorporation of sulfur in functionalized hydrocarbons during diagenesis. Picture shows the formation of isoprenoid thiophene, bithiophene and benzothiophene by the incorporation of sulfur in phytol [8].

OSC are usually present in almost all fractions of crude oil distillation. Higher boiling fractions contain relatively more sulfur and the compounds are of higher molecular weight. The low boiling crude oil fractions contain mainly the aliphatic organosulfur compounds as shown in figure 1.3. For instance, fractions boiling below 150 °C were reported to contain alkane and cycloalkanethiols, dialkylsulfides, disulfides and thiophenes with one or two short side chains [2].

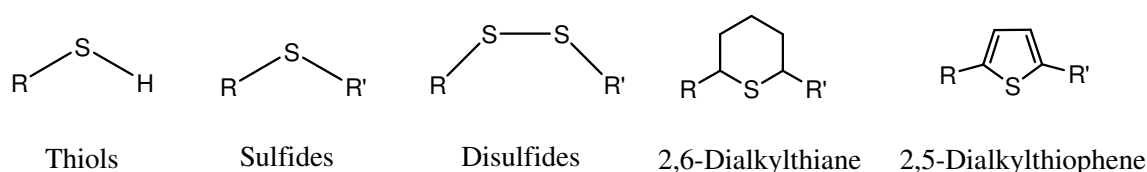


Figure 1.3: OSC present in the low boiling crude oil fractions.

The OSC in higher boiling crude oil fractions boiling above 250 °C predominantly contain thiophenic rings as shown in figure 1.4. Compounds containing thiophene and thiophene condensed with other aromatic rings such as benzothiophene, dibenzothiophene and their alkylated derivatives were reported to be present in higher boiling fractions of oil. Several OSC parent structures of petroleum origin are reviewed by *Czogalla and Boberg* [2].

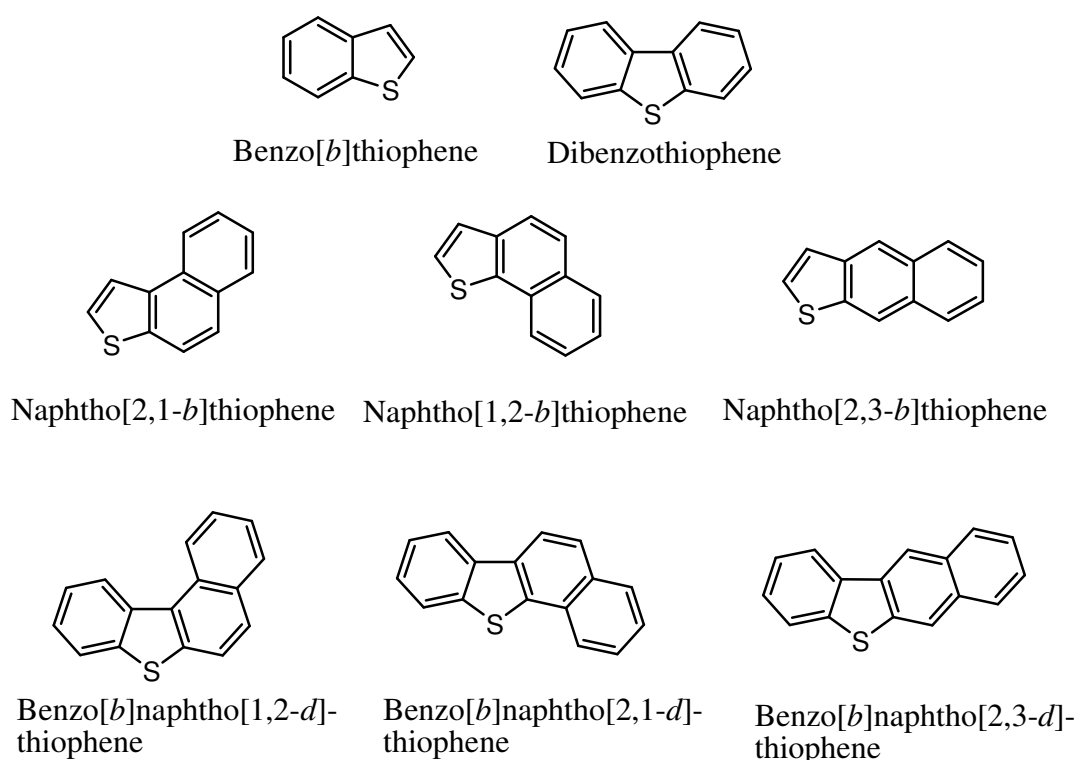


Figure 1.4: Parent structures of PASHs with two to four condensed rings present in high boiling crude oil fractions.

## 1.4 Refining process

The industrial practice of oil refining is continually changing. These changes can be either due to quality of the feeds, or due to standards to which the products are manufactured. A modern refinery is a highly integrated industrial plant which employs different physical and chemical processes such as distillation, extraction, reforming, hydrogenation, cracking and blending to convert crude oil to higher value products. A schematic diagram of the refining process is shown in figure 1.5. The

main products are liquid petroleum gas, gasoline, jet and diesel fuels, wax, lubricants, bitumen and petrochemicals.

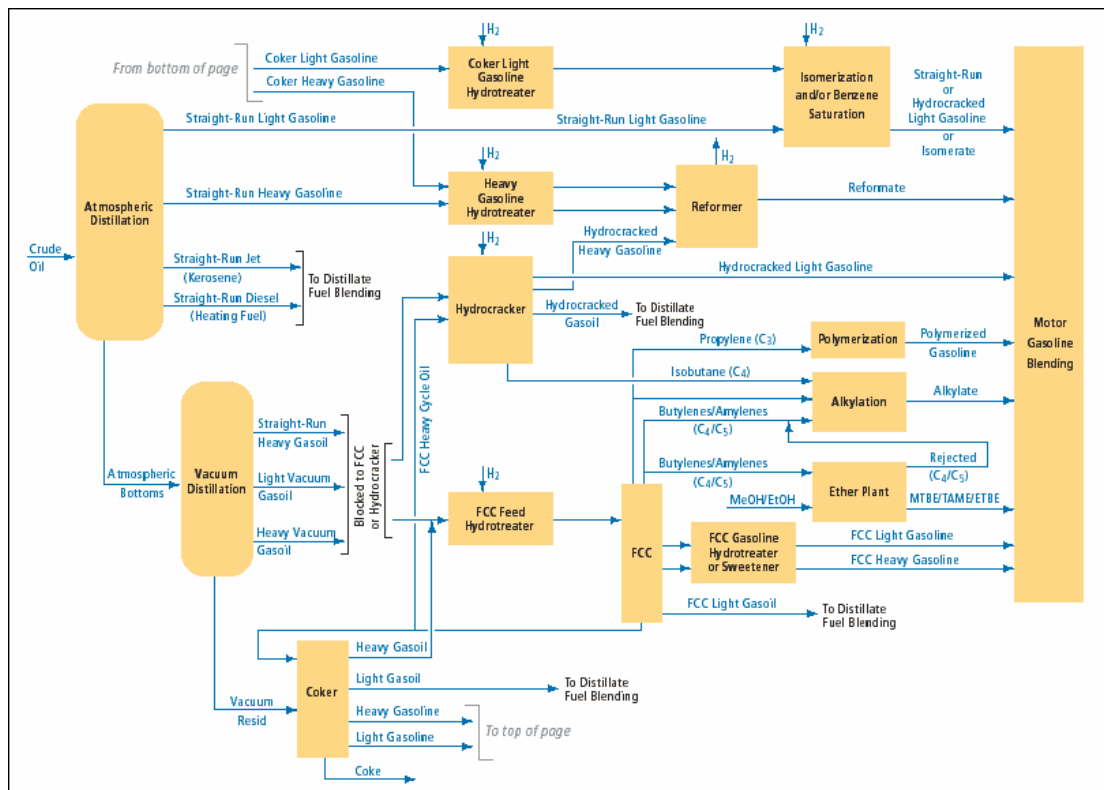


Figure 1.5: A schematic diagram of refining process [9].

The refining process separates crude oil into its constituent hydrocarbons and removes impurities such as sulfur, nitrogen and heavy metals. The first step is fractional distillation, a process based on fundamental physical characteristics: different hydrocarbons boil at different temperatures. In general the more carbon atoms in the hydrocarbon molecule, the higher the temperature at which it boils and vaporizes. Typical characteristics of different distillation fractions obtained from a crude oil are shown in table 1.1.

Table 1.1 Boiling ranges for the classification of refinery products, their uses and number of carbon atoms per molecule.

Fraction	Boiling range	C-atoms per molecule	Uses
Gases		1-4	Domestic fuel (Bottled gas) Motor fuel (LPG)
Light Gasoline	< 65 °C	5-6	Petrol
Naphtha	65-175 °C	7-10	Petrol, white spirit
Kerosene	175-330 °C	11-16	Jet fuel, paraffin
Gas oil	260-550 °C	17-25	Diesel, central heating oil, cracked to make petrol and alkenes
Residue	>550 °C	Above 25	Lubricants, waxes, greases, bitumen for road surfacing, fuel for ships and power stations

The residue from the atmospheric distillation unit is further fractionated under reduced pressure to obtain light and heavy vacuum gas oils. Cracking processes break down heavier hydrocarbon molecules in high boiling fractions into lighter products such as petrol and diesel. These processes include catalytic cracking, thermal cracking and hydrocracking. Catalytic cracking is used to convert heavy hydrocarbon fractions obtained by vacuum distillation into a mixture of more useful products such as petrol and light fuel oil. In this process, the feedstock undergoes a chemical breakdown, under controlled heat (450-500 °C) and pressure in presence of a catalyst. Small pellets of silica-alumina or silica-magnesia have proved to be the most effective catalysts. Fluid Catalytic Cracking (FCC) uses a catalyst in the form of a very fine powder which flows like a liquid when agitated by steam, air or vapor. The catalyst is usually a mixture of aluminium oxide and silica. Recently, the introduction of synthetic zeolite catalysts has allowed much shorter reaction times and improved yields and octane numbers of the cracked gasolines [17]. Thermal cracking uses heat to break down the residues from vacuum distillation. Hydrocracking is catalytic cracking in the presence of hydrogen. Reforming is a process which uses heat, pressure and a catalyst (usually containing platinum) to bring about chemical reactions which upgrade naphthas into high octane petrol and petrochemical feedstock.

## 1.5 Environmental legislations

Due to the worldwide environmental mandates, refiners are facing the challenge of producing increasingly cleaner fuels. In 1998, the European Union first mandated new sulfur specifications for drastically reduced levels that started to be phased in from the year 2000. In 2003 German legislation went even further by rising taxes on transportation fuels by 1.53 cents per litre for gasolines exceeding 10 ppm sulfur. Similar regulations were legislated in the U.S. and elsewhere soon after. The EPA Tier II regulations require reduction of sulfur in highway diesel from 500 ppmw to 15 ppmw by June 2006 and that in gasoline from 350 ppmw to 30 ppmw by January 2005 [10]. The regulations are likely to become more stringent as governments continue to study sulfur emission sources around the globe.

## 1.6 Hydrodesulfurization

Removal of sulfur-containing compounds is currently achieved by Hydrodesulfurization (HDS), a catalytic process operated at elevated temperatures (300-340 °C) and pressures (20-100 atm of H<sub>2</sub>) by using a Co-Mo/Al<sub>2</sub>O<sub>3</sub> or Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The primary phenomena involved in conventional heterogeneous hydrodesulfurization are summarized as follows but the sequence of these phenomena may not necessarily occur in the order shown [11].

1. Adsorption (coordination) of the sulfur compound to the active site
2. Hydrogenation of unsaturated C=C bonds
3. Cleavage of two carbon-sulfur bonds (sequential or simultaneous)
4. Addition of hydrogen to the broken bonds of both sulfur and carbon
5. Release of the hydrocarbon product from the catalytic site
6. Release of the H<sub>2</sub>S from the site

The reactivity of organosulfur compounds varies widely depending on their structure and local sulfur atom environment. *Givens* and *Venuto* clearly showed that the position and number of substituents present on benzothiophene had a strong influence on both the overall reactivity and the degree of desulfurization [12]. In case



of dibenzothiophenes, the work of *Houalla* [13] showed that ring substitution in positions such as the 2 and 3 positions did little to reduce the reactivity. It has been proposed that steric inhibition of adsorption on the catalyst surface is the major cause of such reduced reactivity [13]. For molecules such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), it was clearly shown that the methyl groups interfere with catalyst-molecule interactions as the sulfur atom adsorbs primarily through a one point attachment and the dibenzothiophene system is nearly perpendicular to the catalyst surface [15].

The reaction rates for the HDS reaction vary for different sulfur containing compounds as demonstrated in the figure 1.6.

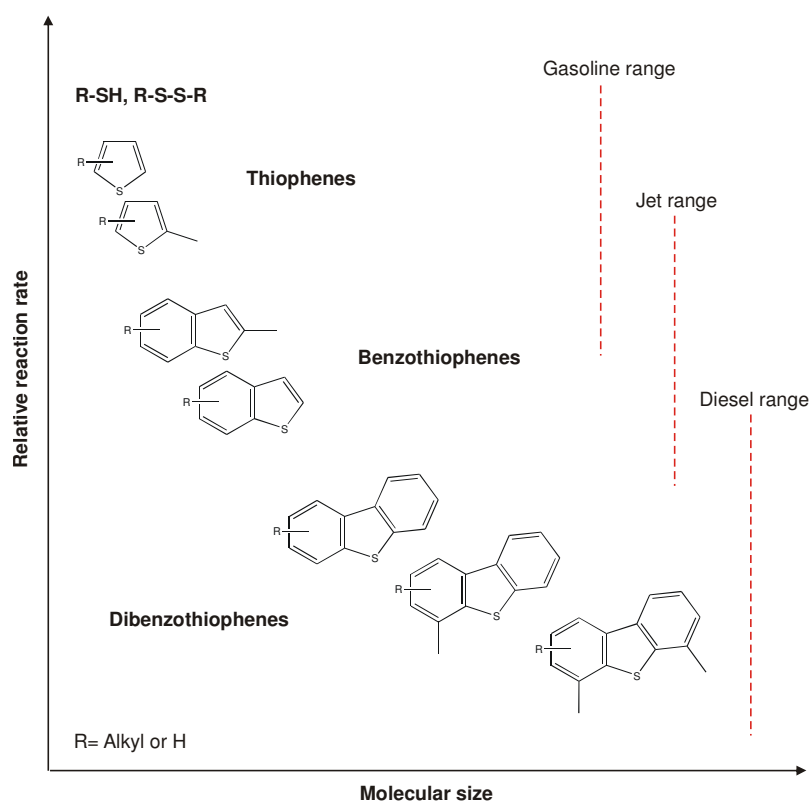


Figure 1.6: Graph showing the effect of molecular size on the reactivity of organosulfur molecules. As the size increases, the reactivity of molecules decreases and they become more difficult to remove using desulfurization reactions [14].

HDS is highly efficient in removing thiols, sulfides, and disulfides but is less effective for some Polycyclic Aromatic Sulfur Heterocycles (PASHs), especially

those containing functional groups that hinder the sulfur atom (e.g. 4,6-dimethyldibenzothiophene). Because of this problem, the sulfur compounds that remain in the transportation fuels are mainly benzothiophenes, dibenzothiophenes and their alkylated derivatives.

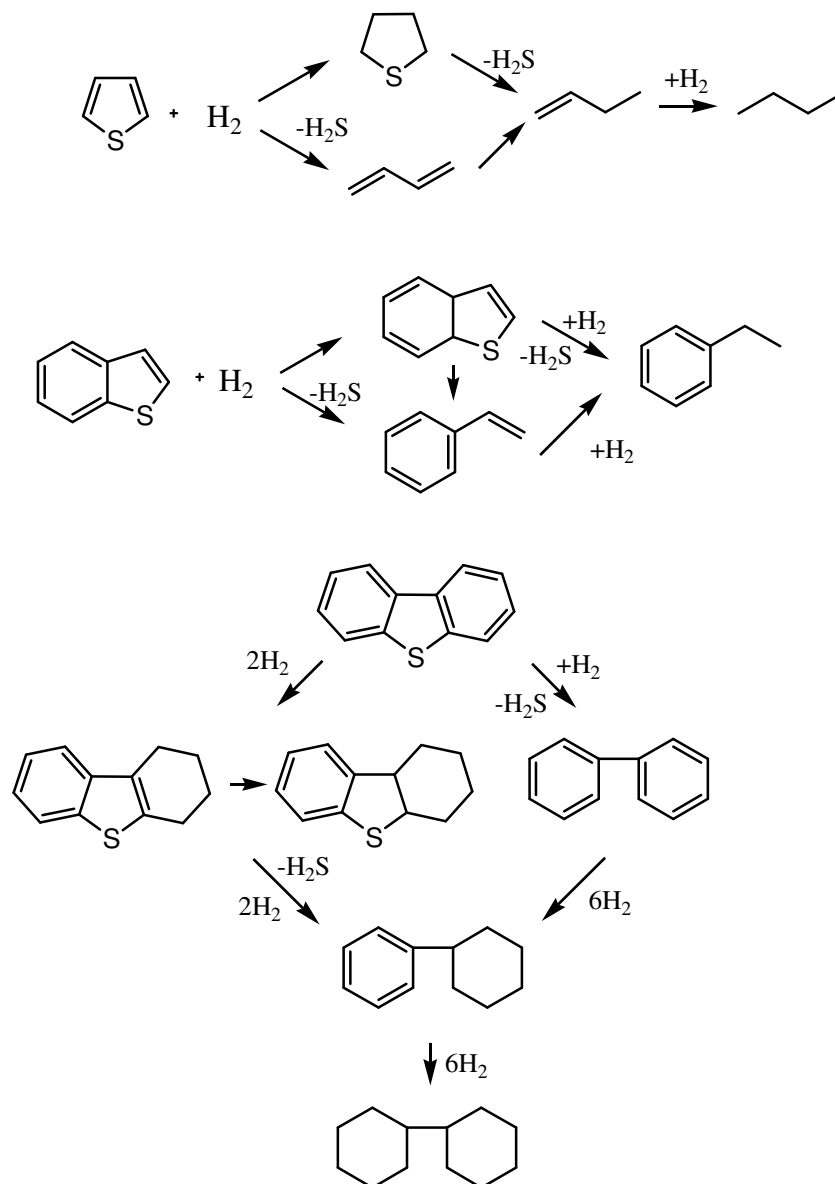


Figure 1.7: Hydrotreating reaction pathways for thiophene, benzothiophene and dibenzothiophene [17].

The reactivity of thiophenes fused to more condensed aromatic rings might be suspected to be less than those of dibenzothiophenes, however, it has been observed that the more condensed ring systems are in fact more easily desulfurized than dibenzothiophenes, particularly when Ni-Mo catalyst are used [15, 16]. HDS of thiophenic compounds proceeds via two reaction pathways as shown in the figure 1.7.

In the first pathway, the sulfur atom is directly removed from the molecule (hydrogenolysis pathway). In the second pathway, the aromatic ring is hydrogenated and sulfur is subsequently removed (hydrogenation pathway). Both pathways occur in parallel employing different active sites of the catalyst surface. Which reaction pathway predominates depends on the nature of the sulfur compounds, the reaction conditions, and the catalyst used. At the same reaction conditions, DBT reacts preferably via the hydrogenolysis pathway whereas for DBT alkylated at the 4 and 6 positions both the hydrogenation and hydrogenolysis routes are significant [17].

Conventional hydrodesulfurization (HDS) processes cannot currently produce zero sulfur level fuels, while maintaining other fuel requirements such as oxygen content, vapor pressure, benzene content, overall aromatics content, boiling range and olefin content for gasoline, and cetane number, density, polynuclear aromatic content, and distillation 95 % point for diesel fuel [17]. Future fuel cells will also require deeply desulfurized fuels, if at all possible with “zero” sulfur content. For example, methanol based fuels for on-board fuel cell applications required the use of a fuel with sulfur content less than 1 ppmw in order to avoid poisoning and deactivation of the reformer catalyst.

## 2 Separation methods for the analysis of polycyclic aromatic sulfur heterocycles in fossil fuels

PASHs are part of a tremendously complex mixture, each one present in minute quantities. The usual work-up schemes employed for the analysis of the aromatic compounds of petroleum products involves separating the aromatic fraction from aliphatic and resin compounds by column chromatography on silica gel. This results in a mixture of PASHs together with polycyclic aromatic hydrocarbons (PAHs). Gas Chromatography coupled with a sulfur selective detector [e.g. Atomic Emission Detector (AED)] can be used to analyze sulfur aromatics in low boiling petroleum fractions like diesel fuel but the selectivity of this detector is not sufficient for heavily desulfurized diesel samples. Additionally, gas chromatographic techniques cannot be used for the analysis of PASHs in high boiling fractions like vacuum residues. A group separation of PASHs from PAHs is highly desirable. In several respects the separation methods are still under development, although considerable progress has been accomplished in identification of sulphur-containing materials. This chapter gives an overview of several separation methods already reported in the literature.

### 2.1 Separation by adsorption liquid chromatography

Identification of sulfur compounds in higher boiling and residual materials has been carried out by a wide range of methods. The most commonly used separation procedures have been based on a variety of liquid chromatographic methods with the analysis by mass spectrometry. *Snyder* initiated petroleum separations by a relatively high performance liquid chromatography [18]. In the 1960s, an application of this approach was shown in a routine method for sulfur compounds in 400 °F range samples. In this procedure, estimates of total alkylthiophenes, alkylmonosulfides, and aromatic sulfides were determined in chromatographic fractions. Analysis was based on dual wavelength ultraviolet spectra and iodine complex measurement [18].

In further work on 400 to 1000 °F petroleum distillate fractions, a liquid chromatographic procedure using alumina as adsorbent was developed to produce five functional class groupings [19]. These ranged from saturated hydrocarbons to polar oxygen plus nitrogen compounds. Diaromatics were obtained mixed with aliphatic monosulfides, and polyaromatic hydrocarbons were mixed with polyfunctional sulfides. Thiophenes were apparently mixed throughout the aromatic classes and were not clearly identified. While hydrocarbon classes were well separated at the selected cut points, sulfur compound types were distributed across the fractions. Subsequent development of the separation and characterization procedure utilized removal of sulphide by mercury-loaded cation exchange resin [20]. This was applied primarily to polar cuts obtained from ion exchange and alumina adsorption chromatography. It was not possible to recover sulfides from the mercury adduct.

Several other procedures have been developed for isolation of sulfur class fractions by adsorption liquid chromatography. *Poirier* and *Smiley* [21] described a procedure for the isolation of a sulfur class based on the dual-packed silica and alumina column technique developed under the API 60 program by *Hirsch, et al.* [22]. The sulfur class cut consisted of alkyl and arylsulfides and of thiophenes from thiophene to dibenzothiophene. It was obtained by washing the column with pentane containing 5% ethyl acetate after saturates had been eluted with pure heptane. Analysis of fractions from a crude oil by gas chromatography showed mostly cyclic alkyl sulfides and alkyl-benzothiophenes. Lesser amounts of noncyclic sulfides and dibenzothiophenes were also found. Only a slight contamination of the sulfur class fraction by aromatic hydrocarbons was encountered.

In the original development of the dual packed silica alumina column [22], alkylthiophenes were found to elute throughout the collection range of the monoaromatic hydrocarbons and noncyclic sulfides somewhat overlapped monoaromatics. Also, benzothiophenes, cyclic sulfides, thiaindanes and thiatetralins appeared throughout the diaromatic collection range. In view of this it is not clear how the separation of *Poirier* and *Smiley* [21] was achieved.

A related procedure was used by *Mel'nikova, et al.* in the study of distillates of a crude oil that contained significant amounts of mercaptans and other sulfur

compound types [23]. Mercaptans were removed by basic extraction, and sulfides were removed by sulphuric acid extraction. Each of these compound classes was recovered for further examination. The extracted distillates were then processed on dual packed alumina and silica columns to obtain a saturate fraction, an intermediate aromatic cut, and three aromatic sulfur concentrates. The sulfur containing fractions were characterized by mass spectrometry (MS). Compound types identified included noncyclic and cyclic sulfides, thiaindanes, and alkyl and aromatic thiophenes containing upto four rings.

## 2.2 Separation by derivatization

Another procedure that has been developed is derivatization of sulfur compounds as an aid in isolation. In some cases this has been used in combination with the adsorption chromatographic methods described earlier. Oxidation of the sulfur compounds to sulfones and sulfoxides is the most common procedure. This is usually followed by liquid chromatography to isolate the oxidised sulfur compounds as a polar class. An early application of this procedure was developed by *O'Donnell* [24]. Mono and diaromatic fractions isolated from asphaltenes by silica and alumina column chromatography were oxidised by hydrogen peroxide in acetic acid to convert sulfur compounds to sulfones [24].

Oxidation procedures were further developed by *Drushel* [25, 26]. Reaction routes for both preparation of sulfones and for selective oxidation of sulfur compounds to sulfoxides were described. Both procedures yielded products that could be reduced to sulphide and thiophene materials corresponding to the original sample components. The sulfoxide route was preferred because there appeared to be less oxidation of the aromatic hydrocarbons in the original fractions. However it appears that in the repeated oxidation procedures required to obtain complete conversion of the thiophenes, a substantial amount of these thiophenes would have been oxidised to sulfones. Several characterization procedures were applied to the products with low and high resolution MS supplying the definitive analysis. In the petroleum fractions examined, small amount of cycloalkyl sulfides were found while the dominant sulfur compounds were benzothiophenes and dibenzothiophenes and their naphtheno derivatives. Some thiophenes of higher aromatic ring numbers were found. The level

of alkylthiophenes and naphthenothiophenes seemed rather low when compared to the amounts of higher aromatic thiophenes.

An attempt was made to characterize the sulfoxides directly by gas chromatography and MS [27]. The sulfoxides proved to be unstable at the temperatures required. Sulfur dioxide (SO<sub>2</sub>) is known to be easily removed in pyrolytic preparative organic synthesis and therefore the instability of sulfoxides must be expected. However, the sulfone dibenzothiophene dioxide has been determined successfully by gas chromatography [28].

The further development of procedures based on oxidation of sulfur compounds to sulfones was done by *Willey et al.* [28] and *Kong et al.* [29]. These studies concentrated on the methods and problems encountered for the thiophene class. The procedures used for conversion to sulfones, isolation of sulfones, and reduction back to the parent sulfur compounds were essentially those of *Drushel and Sommers* [26]. *Willey* [28] applied the method to aromatic fractions obtained by solvent extraction of coal liquids and shale oils with dimethylsulfoxide. Analysis and identification were assisted by reference of the GC and MS results of 32 model thiophenic compounds. In this set, the aryl ring number including the thiophene ring ranged from two to five, and the thiophene ring was bonded to other rings on one, two or three sides. The coal liquid and shale oil aromatic fractions contained thiophenes ranging from benzothiophene and its alkyl derivatives all showed extensive reduction to the 2,3-dihydro form because of the severity of the lithium aluminium hydride reduction procedures.

The oxidation-isolation procedure was included in a complex liquid and gas chromatographic treatment of a coal liquid by *Kong et al.* [30]. Following the recovery of the sulfur heterocycle fraction, it was separated by liquid chromatography on Bondapak NH<sub>2</sub> to produce ring number fractions. These were then analysed by several polar and non-polar GC columns. A number of thiophenes of three to six rings were identified. This oxidation procedure was also made part of a broader class separation method for synthetic fuels [31].

*Kong, et al.* [29] examined the oxidation isolation method in detail on selected model thiophenes. Those with aryl rings fused to both the b and d sides of the thiophene ring such as dibenzothiophene gave recoveries of about 70 percent when carried through the oxidation and reduction procedures. Benzophenanthro[4,5-*bcd*]thiophene was recovered in 13 % yield, and five thiophenes fused on the b side only had recoveries of 0-4 %. From this it is clear that the thiophene class characterization may be seriously distorted by failure to detect many possible types of thiophenes. The oxidation isolation procedure was again applied to the aromatic fractions from coal liquids and shale oils. Thiophenes ranging from C1-benzothiophene to a group of five ring thiophenes were identified. The great bulk of thiophenic material had aryl fusion on both side of the thiophene ring.

More recently, *Andersson* has extensively investigated the oxidation/reduction procedure with hydrogen peroxide in acetic acid, recommended for the isolation of a PASH fraction from complex mixture by *Willey et al.* [28]. Several side-reactions which can lead to massive loss of many analytes and possibly to the formation of new PASHs were reported [32].

### 2.3 Separation by complexing methods

*Rall et al.* described extraction procedures based on  $ZnCl_2$  solutions. They determined that the method was selective for cyclic sulfides that were free from steric hindrance from substitution on the carbon adjacent to the sulfur [33]. More recent procedures have generally combined metal ion complexing with column chromatographic separation. *Orr* used mercury acetate or zinc chloride in aqueous acetic acid solution supported on silica gel in liquid chromatography of model compounds [34, 35]. Lower molecular weight sulfides were well retained, but retention fell off with increasing carbon number as would be expected from reduced solubility in aqueous acetic acid. As mentioned above, *Snyder* [20] developed a procedure based on a mercury-loaded, sulfonic acid type cation exchange resin. This resin held sulfur compounds quite strongly.



*Vogh* and *Dooley* developed a method for ligand exchange chromatography based on a copper loaded, carboxylic-type cation exchange resin [36]. Both acyclic and cyclic sulfides were well retained relative to aromatic hydrocarbons. Aryl sulfides were retained somewhat less than alkyl sulfides but resolved well from aromatic hydrocarbons. Thiophenes showed no useful retention and were eluted with aromatic hydrocarbons. Sulfides were removed from the aromatic concentrates of a 370-535 °F distillate of a crude oil. Detailed mass spectral examination of the sulfide fraction showed high concentrations of multi-ring cyclic sulfides, aryl sulfides and diphenyl disulfides. The sulphide free hydrocarbon fractions from these separations gave little indication of thiophenes.

More effective methods for the separation of thiophenes from aromatic hydrocarbons have been developed using silver- or palladium- based ligand exchange chromatography. *Joyce* and *Uden* used silver nitrate – loaded silica to demonstrate effective separation of model compounds and got nearly complete separation of thiophenes from aromatic concentrates containing mono- and diaromatic classes [37]. Benzothiophenes were determined to have been enriched by about 96 percent in comparison with naphthalenes for a shale oil sample. *Gundermann et al.* separated alkyl and aryl sulfides from hydrocarbons on  $\text{CuCl}_2$  loaded silica and dibenzothiophenes from phenanthrene on  $\text{PdCl}_2$  loaded silica [38]. The  $\text{PdCl}_2$  column showed substantial retention difference of the two compounds but gave rather poor column efficiency. A separation scheme for complex samples was outlined, but no results were presented.

The palladium ligand exchange method has been applied extensively to separation of thiophenes from petroleum, coal liquid, and shale oil aromatic fractions. *Nishioka et al.* further evaluated the procedure in terms of operating conditions, mobile phase composition, and representative model compounds [39]. Thiophenes of two to five rings were found to be generally well separated from aromatic hydrocarbons and furans. Recoveries of thiophenes ranged from 35 to 90 percent with naphtho[2,3-*b*]thiophene showing lowest recovery. The nature of the reactivity of thiophenes with the adsorbent was not determined. Thiophene fractions isolated from coal liquid aromatic fractions were shown to be nearly free of aromatic hydrocarbons. In a detailed study of the method [40], the thiophenes from coal-derived products

were analyzed in relation to a set of 57 pure model thiophene compounds. Analysis was based on gas chromatography on two types of shape selective, liquid crystalline capillary columns. Identification was achieved by reference to model compounds and by GC-MS. Most of the thiophenic compounds were identified and were shown to be rather highly condensed with a low level of alkylation. Further modification of this method was developed for characterization of a catalytically cracked petroleum vacuum residue [41]. Following the isolation of thiophenes from aromatic concentrates by the PdCl<sub>2</sub> isolation procedure, the sulfur heterocycles were further split to three, four and five ring subclasses by supercritical chromatography on an aminosilane column. These fractions were then analysed by gas chromatography-flame photometric detection (GC-FPD) and gas chromatography-mass Spectrometry (GC-MS) procedures.

A more critical review of the palladium chloride silica isolation procedure was carried out by *Andersson* [42]. The technique was changed to include aminopropano bonded silica in the same or in a following column. This removed palladium that was complexed to the thiophenes. Recoveries of thiophenes was examined for a set of five model compounds of which two were fused to aryl rings on only one side of the thiophene ring. The recovery of these compounds in the entire eluate ranged from 98 to 106 percent and was considered to indicate no loss on the column, contrary to the apparent loss reported by *Nishioka et al* [39]. It was found that some benzo- and naphthothiophenes were weakly retained on the PdCl<sub>2</sub> column and would elute with di- and triaromatic hydrocarbons. Similarly, phenanthro[3,4-*b*]thiophene and chrysene have nearly the same retention factors. Alkyl substitution increases retention, particularly if it is on the thiophene ring. The conclusion was made that the PdCl<sub>2</sub> method could be used for efficient separation of only polycyclic aromatic hydrocarbons from sulfur heterocycles that contain internal thiophene rings or carry several alkyl groups. However, the method was not destructive for thiophenes.

## 2.4 Direct characterization methods

A number of procedures have been described for identification of sulfur compounds in complex mixtures that do not require their isolation. Many of these methods were developed for volatile samples that could be resolved into individual

compounds by gas chromatography and could not be applied to high boiling and residual materials. *Burchill et al.* analyzed unfractionated coal products by capillary gas chromatography with flame ionisation detector (FID) and sulfur sensitive flame photometric detection (FPD) [43]. Selected compounds were identified by GC-MS. Selected ion monitoring assisted in the identification by drawing single ion chromatograms corresponding to sulfur heterocyclic compounds. Thiophenes of two to five rings were identified. The smaller thiophenes were extensively alkylated while the higher ring compounds had few or no alkyl groups.

Mass spectrometry has been utilized as a sulfur-sensitive detector through collision activated dissociation by *Hunt and Shabanowitz* [44]. This procedure was evaluated using several types of sulfur compounds. Thiophenes through dibenzothiophene (all with low level of alkylation) failed to give any response. The method monitored the ionic species that lost the SH fragment in the collision activation process. Three petroleum crude distillation fractions were examined by this procedure. The results for these samples were similar and somewhat unusual in that few or no members of the benzothiophene and dibenzothiophene classes were found. Instead, phenylthiophenes, naphthylthiophenes, phenylbenzothiophenes, and/or naphthenobenzothiophenes were found. More recently with the development of equipment and methods that respond directly to sulfur, gas chromatographic and mass spectrometry procedures have been developed. Selective detectors of importance for PASH analysis include Flame Photometric Detector (FPD), the Electrolytic Detector (ELD), the Sulfur Chemoluminescence Detector (SCD) and the Atomic Emission Detector (AED) [45]. Gas Chromatography-Atomic Emission Detector (GC-AED) is described briefly as it is used in this work.

The strength of GC-AED lies in the detectors ability to simultaneously determine the atomic emissions of several elements present in the analytes in one chromatographic run. The AED is thus a multi-element selective detector. Figure 2.1 shows a schematic diagram of the AED. In the AED, the analytes exiting the GC column are fed into microwave induced helium plasma and atomized. Some of the atoms gain enough energy to become excited and when giving off this excess energy, light at certain wavelengths that are characteristic for the element is emitted. Sulfur is an element with an excellent minimum detectable quantity in atomic emission

detection, namely in the picogram range. Furthermore, the selectivity versus carbon is very high, ca  $3.5 \times 10^4$  and the linear range independent of sulfur species, is on the order of  $10^4$  [46].

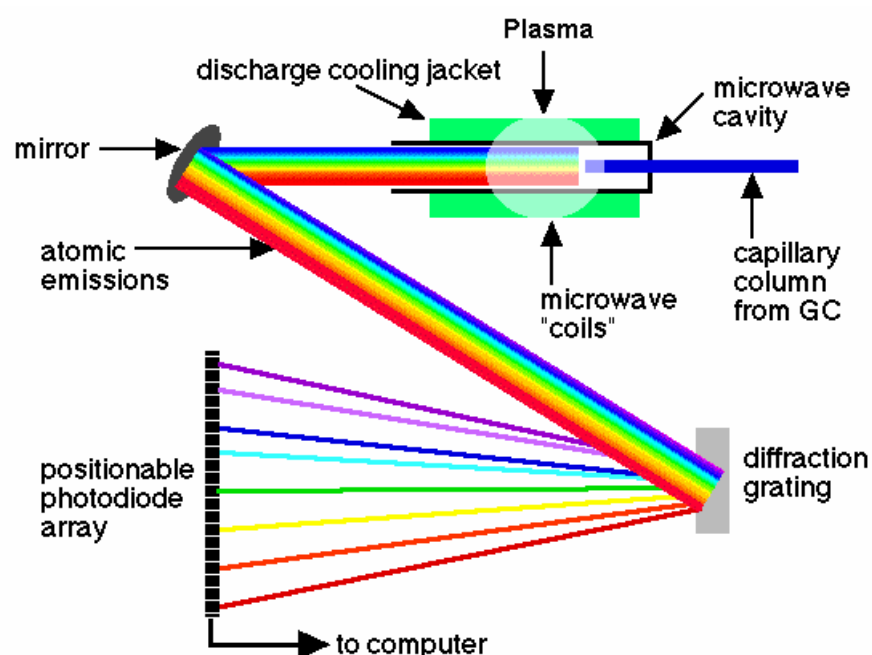


Figure 2.1: Schematic diagram of an atomic emission detector [47].

## 2.5 Summary

No completely satisfactory procedure has been developed for the isolation of the sulfur compounds present in high-boiling and residual fractions of crude oil. Liquid chromatographic procedures based on metal ion-loaded columns have been the most satisfactory of the methods previously examined. Various problems were encountered, such as incomplete separation and bleeding of the metal ion. Several modifications were examined to produce an improved technique for sulfide isolation. These included improved stationary support, choice of metal ion, and composition of mobile phase. Separations by complexing methods have received most attention in recent years and have produced good sulfide and fair thiophene fractions by ligand exchange procedures. This approach offers the greatest promise of further improvement in thiophene class isolation.

### 3 Objectives

The efforts in many countries to reduce the sulfur level in transportation fuel to something on the order of 10 ppm mean that refineries worldwide have put major efforts into the reduction of sulfur from approximately 1 % in crude oils. In future it is expected that crude oils as well as higher-boiling fractions of higher sulfur content will need to be used to cover the demands for petroleum products. Such materials often are more difficult to hydrodesulfurize to the levels desired [17]. In order to develop better HDS catalysts and improve process conditions, it is highly desirable to gain more insight into the structure of those high-boiling compounds that are particularly recalcitrant. The very high complexity of such mixtures necessitates a fractionation of the sample into smaller subsets according to characterized criteria.

For characterizing these sulfur compounds, it is desirable to separate them from the PAHs before applying any techniques for structural elucidation. A stationary phase containing a palladium(II) complex of 2-Amino-1-Cyclopentene-1-Dithiocarboxylic Acid (ACDA) was previously shown to be efficient for the separation of PASHs in lighter petroleum fractions [50]. However, when the phase was used for the separation of sulfur aromatics from a vacuum residue, considerable amounts of sulfur were found in the first fraction [51]. The objective here is to gain information on the correlation between structure and retention of the sulfur aromatics on the Pd(II) column to better understand which compound classes can be expected in the two fractions from that column. For this purpose we should synthesize several model compounds and individually chromatograph them to reveal clear patterns of retentivity.

Our next objective is to synthesize a stationary phase incorporated with maximum possible amount of various polyvalent metal ions by using the Sol-gel process. After the synthesis of the desired silica gel, it is intended to study the retention properties of various PASHs on the gel, especially the monoalkylated and dialkylated dibenzothiophenes. A chromatographic method should be developed for the isolation of PASHs from various petroleum fractions. The gel should be able to separate PASHs from real world samples like crude oil and diesel with minimum

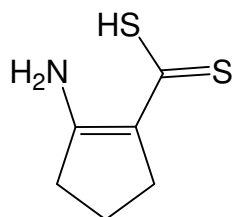
separation time. The gel has to be tested for its reusability and it should be characterized by its separation efficiency, reproducibility, capacity, longevity, temperature effects, mass balance etc. The efficiency of separation and the amount of sulfur present in the sample can be analyzed using a gas chromatograph with an Atomic Emission Detector or Flame Ionization Detector (GC-AED or GC-FID), mass spectrometry can be used for the characterization of PASHs in high boiling fractions like vacuum residues.

## 4 Liquid chromatographic properties of aromatic sulfur heterocycles on Pd(II)-ACDA silica gel

### 4.1 The Pd(II)-ACDA silica gel

The usual workup schemes employed for the analysis of the aromatic compounds of petroleum products involve separating the aromatic fraction from components of lower and higher polarity by column chromatography on silica gel. This results in a mixture of the PASHs together with the polycyclic aromatic hydrocarbons (PAHs). For characterizing these sulfur compounds, it is desirable to separate them from the PAHs before applying any techniques for structural elucidation.

A bonded silica gel material developed for sulfide isolation designed specifically to support palladium in a form suitable for this purpose was already reported [48]. This material was developed to be somewhat analogous to the PdCl<sub>2</sub> technique developed by *Nishioka et al.* [39] and *Andersson* [42] for isolation of polycyclic aromatic sulfur heterocycles from oil fractions. A compound used in the calorimetric determination of several metals and capable of being bonded to silica [49], 2-amino-1-cyclopentene-dithiocarboxylic acid (ACDA), was chosen for its unique chemical properties. Its structure shows four possible binding sites that may form a chelate.



2-Amino-1-cyclopentene-  
1-dithiocarboxylic acid  
(ACDA)

Figure 4.1: Structure of ACDA.

The overall electronic effect of this compound would tend to make it a soft base which can chelate with large, polyvalent metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pt}^{2+}$ , etc.) resulting in a functional group with enough residual lewis acidity to form ligand complexes with electron pair donors (PASHs and sulfides) in solvents of low polarity, yet retain the chelated metal ion in the highly polar solvents used to break the ligand complex. The Pd(II)-ACDA-silica phase was previously used for the separation of PAHs and PASHs in twelve desulfurized diesel samples [50], and subsequent gas chromatographic analysis of the hydrocarbon fraction with sulfur selective detection (GC-AED) did not show any trace of sulfur. Similarly, every peak in the sulfur fraction was detected both in the carbon- and the sulfur-selective mode, inferring a complete separation of PAHs and PASHs [50]. However, when the phase was used for the separation of sulfur aromatics from a vacuum residue, considerable amounts of sulfur were found in the first fraction [51]. The present work was undertaken to gain information on the correlation between structure and retention of the sulfur aromatics on the Pd(II) column to better understand which compound classes can be expected in the two fractions from that sample. A series of model compounds was synthesized and individually chromatographed to reveal clear patterns of retentivity.

## 4.2 Experimental section

All the compounds shown in table 4.1 are synthesized in our laboratory [52]. The syntheses of some of the compounds synthesized for the above mentioned purpose are explained. For extensive experimental details see chapter 10.

### 4.2.1 Liquid chromatography

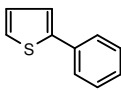
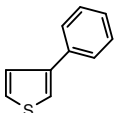
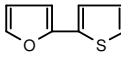
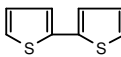
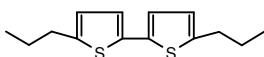
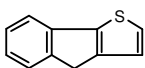
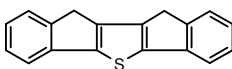
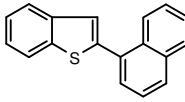
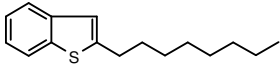
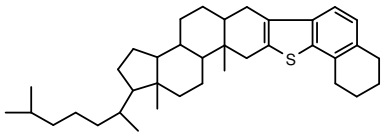
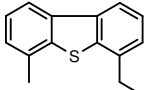
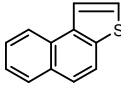
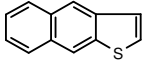
The Pd-ACDA column (4.6 x 150 mm) was prepared as described in References [50, 53]. Fraction 1 was eluted with cyclohexane:dichloromethane (7:3) as mobile phase for 15 min and then the eluent was made more polar by adding 0.3 % isopropanol to elute fraction 2. The fraction volume was reduced to 1 mL by rotary evaporation before the gas chromatographic analysis (GC-FID).

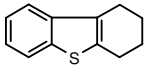
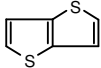
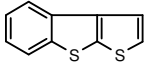
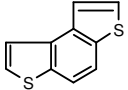
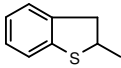
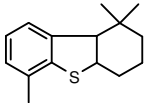
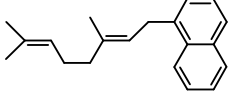


#### 4.2.2 Syntheses of model compounds

- **2,3-Dihydro-2-methylbenzo[*b*]thiophene** was synthesized by the reduction of 2-methylbenzothiophene as described in the literature [54].
- **2- and 3-Octylbenzothiophenes** were synthesized as a mixture (20 % of the 2-isomer and 80 % of the 3-isomer) through acylation of benzothiophene with octanoyl chloride/ $\text{AlCl}_3$  followed by Wolff-Kishner reduction.
- **4H-Indeno[1,2-*b*]thiophene** was synthesized as described in References [55, 56].
- **5,5'-Dipropyl-2,2'-bithiophene** was synthesized through an adoption of the method described in References [57, 58].
- **1-[(2E)-3,7-dimethyl-2,6-octadienyl]naphthalene** was synthesized as described in the literature [59].

Table 4.1: Model compounds – structures, names, eluting in which fraction from the Pd(II)-ACDA phase, double bond equivalent and examples of occurrence in fossil materials.

No.	Model Compound	Name	Fraction	DBE	Occurrence in fossil materials
1		2-Phenylthiophene	1	7	Shale oil [60, 61]
2		3-Phenylthiophene	1	7	Shale oil [60, 61]
3		2-(2-Thienyl)furan	1	6	
4		2,2'-Bithiophene	1	6	Coal [62]
5		5,5'-Dipropyl-2,2'-bithiophene	1	6	Shale oil [63]
6		4H-indeno[1,2- <i>b</i> ]thiophene	1	8	Shale oil [63]
7		Diindenothiophene	1	13	
8		2-(1-Naphthalenyl)benzo[ <i>b</i> ]thiophene	2	13	Lignite [64] Coal tar [65]
9		2 and 3-Octylbenzo[ <i>b</i> ]thiophene	2	6	Gas oil [66] Light cycle oil [67] Shale oil [63] Vacuum gas oil [68]
10		Cholestano[2,3- <i>b</i> ]-5,6,7,8-tetrahydro naphtho[2,1- <i>d</i> ]thiophene	2	11	
11		4-Ethyl-6-methyl dibenzothiophene	2	9	Desulfurised diesel oil [50]
12		Naphtho[2,1- <i>b</i> ]thiophene	1	9	Shale oil [60,61,63] Coal liquids [28] Light cycle oil [67] Lubricating oil [69]
13		Naphtho[2,3- <i>b</i> ]thiophene	2	9	Shale oil [60,61,63] Coal liquids [28] Light cycle oil [67] Lubricating oil [69]

14		1,2,3,4-Tetrahydrodibenzothiophene	2	7	Coal extract and SRC-I <sup>a</sup> [70]
15		Thieno[3,2- <i>b</i> ]thiophene	2	5	Coal[62] Shale oil[61]
16		Thieno[2,3- <i>b</i> ]benzothiophene	2	8	Coal[62]
17		Benzo[1,2- <i>b</i> : 4,3- <i>b'</i> ]dithiophene	2	8	
18		2,3-Dihydro-2-methylbenzothiophene	b)	5	Coal liquids [28] Hydrotreated light cycle oil [67] Coal extract and SRC-I [70]
19		1,1,6-Trimethyl-1,2,3,4,4a,9b-hexahydrodibenzo[ <i>b,d</i> ]thiophene	b)	6	Coal [71] Desulfurised diesel fuel <sup>c</sup> [72]
20		1-[(2E)-3,7-dimethyl-2,6-octadienyl]naphthalene	1	9	

DBE = Double Bond Equivalent

a) SRC = solvent refined coal

b) this compound does not elute from the phase even with an eluent of 100 % methanol

c) found in desulfurized diesel fuel are 1,1,4a,6-tetramethyl-9-alkyl-1,2,3,4,4a,9b-hexahydrodibenzothiophenes

### 4.3 Results and discussion

The sulfur aromatic compounds in higher-boiling petroleum fractions like vacuum residues (here with a boiling point above 466 °C) show a different behavior toward complexation with the Pd(II) than the PASHs in lighter fractions do. These lighter fractions mainly consist of alkylated benzothiophenes and dibenzothiophenes which have been shown in separate experiments to be well retained by the Pd(II) phase and therefore elute in fraction 2 (see Experimental section) [50]. However, the vacuum residue sulfur aromatic compounds were recovered in both fractions, leading to sulfur content of 2.0 % (fraction 1) and of 2.8 % (fraction 2), respectively [51].

This is probably not due to steric hindrance to complexation, since PASHs in distilled petroleum fractions, including sterically hindered sulfur aromatic compounds like 4-ethyl-6-methyldibenzothiophene, strictly elute in fraction 2. [50] Figure 4.2 shows the liquid chromatogram obtained for a vacuum residue.

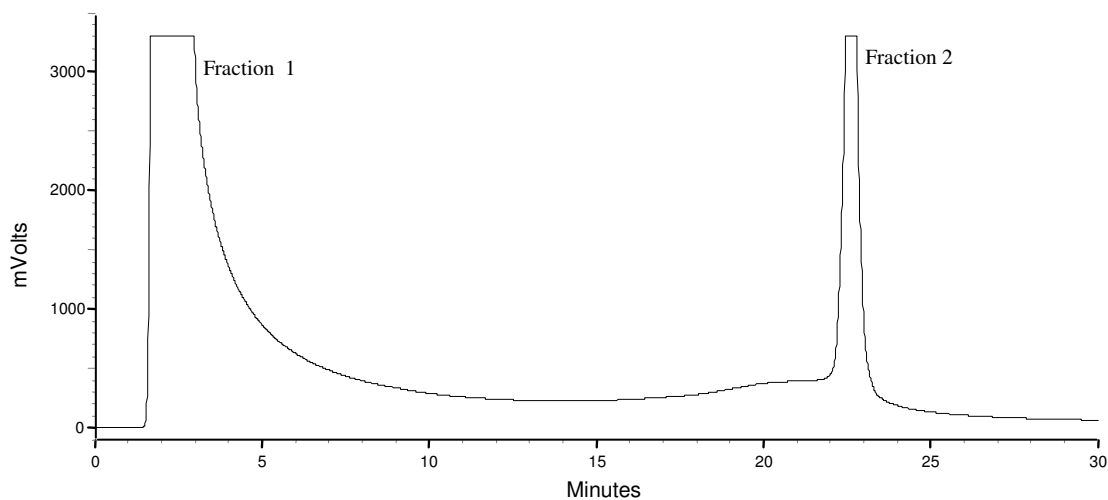


Figure 4.2: The aromatic fraction of a vacuum residue on the Pd(II)-ACDA column. Fraction 1 was eluted with cyclohexane:dichloromethane (7:3) as mobile phase for 15 min, and then the eluent was made more polar by adding 0.3 % isopropanol to elute fraction 2 at a flow rate of 1mL/min.

It has been demonstrated that the strength of the interactions between Pd(II) and thiophenes is correlated with the Hückel pi electron density on the sulfur atom so that both of them diminish in the order dibenzothiophene > benzo[*b*]naphtho[2,1-*d*]thiophene > benzothiophene [70]. Thiophene has an even lower electron density and is thus expected to be very weakly retained by Pd(II) complexation, in agreement with experimental results. Alkyl substitution increases this electron density; therefore alkyl derivatives are more strongly retained than parent compounds unless a steric effect is in operation for compounds with alkyl groups in close proximity to the sulfur atom. It has been reported that 2- and 3-methyldibenzothiophenes are more strongly retained when compared to 4-Methyldibenzothiophene by Pd(II) column [70]. Sulfides in which the sulfur atom is not part of an aromatic system should have a higher tendency to interact with Pd(II) due to their higher Lewis basicity. Since it was recently reported that 1,1,4a,6-tetramethyl-9-alkyl-1,2,3,4,4a,9b-hexahydrodibenzothiophenes are quite resistant to desulfurization [72], we included some examples of similar

cyclic sulfides here. These types of cyclic sulfides were shown to be present in desulfurized diesel samples [72]. However, such compounds were never seen in the PASH fraction when a Pd(II) column was used for the isolation of PASHs. Our assumption is that the sulfur aromatics of the vacuum residue that elute in fraction 1 contain a thiophene ring that is not condensed with further aromatic rings. A great variety of such systems has been described from fossil materials, e.g. from shale oils (see the references in the table 4.1).

To better understand the behavior of different classes of sulfur aromatic compounds on the Pd(II) phase, we have synthesized a series of substituted thiophenes and investigated their retention on this phase. The test compounds contain the sulfur atom either in a thiophene, a benzothiophene, or an indenothiophene ring. Furthermore, two dihydrobenzothiophenes were included to study the retention of sulfidic compounds, and lastly a specially synthesized olefin was used to see if the (soft) Lewis basic character of a carbon-carbon double bond leads to strong interactions with the soft Lewis acid Pd(II). A list of the compounds used is found in the table 4.1.

#### **4.3.1 Non-annealed thiophenes**

Thiophene and the two methylthiophenes elute with very short retention times and are found in fraction 1. Thiophenes substituted with aromatic rings behave identically: The phenylthiophenes, thienylfuran and bithiophene also elute in Fraction 1, demonstrating that an oxygen heterocycle does not interact strongly with Pd(II) and that two thiophene rings which conceivably could form a five-membered complex with Pd(II) are likewise fairly weakly complexed. To see if this is true also for alkyl substituted derivatives, 5,5'-dipropyl-2,2'-bithiophene was synthesized and found to behave as its parent. Thiophenes not condensed with further rings can thus be expected generally to elute in fraction 1.

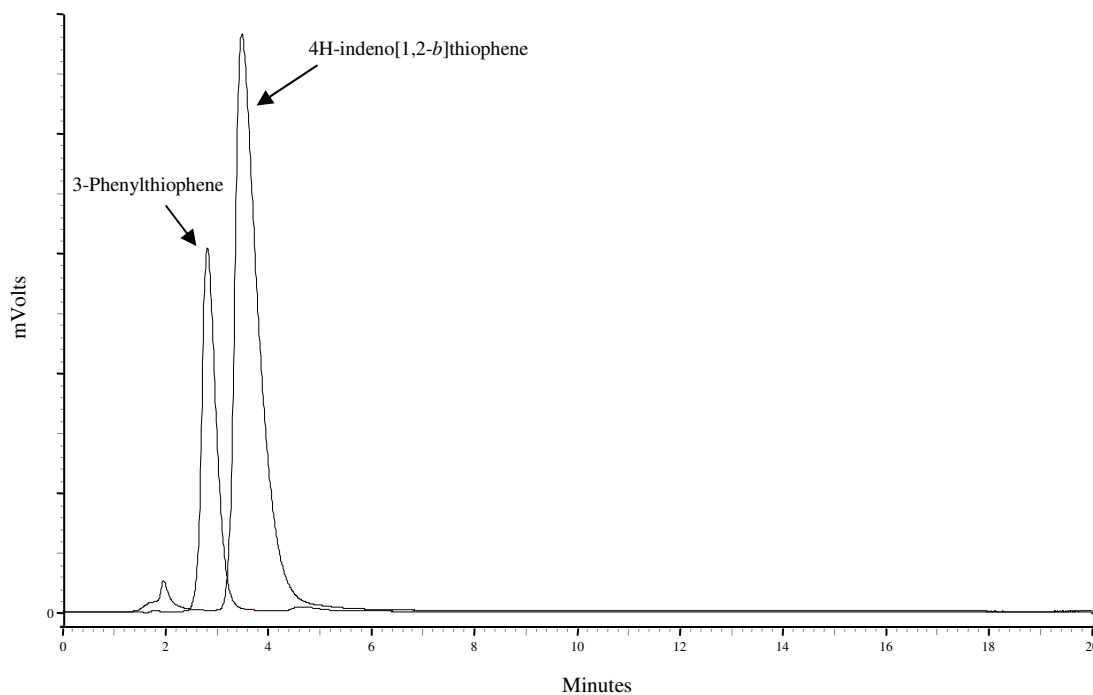


Figure 4.3: Chromatogram showing the elution of 3-phenylthiophene and 4H-indeno[1,2-*b*]thiophene from the Pd(II)-ACDA column. Mobile phase CH:DCM (7:3) for 10 min and then CH:DCM(7:3) + 0.3 % IP at a flow rate of 1 mL/min.

### 4.3.2 Thiophenes annealed with a non-aromatic ring

A thiophene annealed on one or more sides with non-aromatic rings can be viewed as an alkylated or bridged arylated thiophene and is thus not expected to form strong complexes with Pd(II). This is borne out by the indenothiophene studied that is about as strongly retained as phenylthiophene plus an alkyl substituent. Figure 4.3 shows the elution of 3-phenylthiophene and indenothiophene on the Pd(II) column. The diindenothiophene isomers are more strongly retained but using the normal criteria for a cutting point between Fraction 1 and 2, they would still elute in Fraction 1. In the table only one isomer is listed but despite small differences in retention, the same conclusion can be drawn for other two isomers.

### 4.3.3 Benzothiophenes

Benzothiophenes are more strongly retained than thiophenes and they can be separated from PAHs containing several aromatic rings. Methyl groups in any position except for the 7-position increases the retention somewhat.

1,2,3,4-Tetrahydrodibenzothiophene is a disubstituted benzothiophene and consequently shows good complexation. One example of a benzothiophene with an aromatic substituent was used, in this case the bulky naphthalenyl group in the 2-position of the benzothiophene where it is expected to exert a considerable amount of steric hindrance to the interaction between the sulfur atom and the palladium ion. Despite this, the retention was strong enough to allow the bulk of it to be collected in Fraction 2. The same holds true for the two isomers of benzothiophene substituted with a naphthalenyl group in position 3. Long-chain substituted benzothiophenes of a type that can be expected in higher-boiling petroleum fractions are represented by a mixture of 2- and 3-octylbenzothiophene. A very complex benzothiophene is cholestanol[2,3-*b*]-5,6,7,8-tetrahydronaphtho[2,1-*d*]thiophene (entry 10 in the table 4.1) in which the sulfur atom is situated in a crowded position. Despite this, these three compounds eluted in Fraction 2.

#### 4.3.4 Dihydrobenzothiophenes

Two dihydrobenzothiophenes which contain the sulfur in a non-aromatic ring were tested. Both compounds were completely retained by Pd(II) and could not be washed off the column, even after prolonged elution with pure methanol. Since some similar compounds have been demonstrated to be quite recalcitrant to hydrodesulfurization [72]. Their determination may be of major interest which would not be possible if the Pd(II) column is used during sample preparation. However, in most analytical work a polycyclic aromatic fraction is first isolated on silica, and monoaromatic sulfides would be expected to elute in an earlier fraction. Thus if such sulfides are to be determined, a specially-designed sample preparation needs to be devised.

#### 4.3.5 Compounds with three condensed aromatic rings, one of them a thiophene ring

Three aromatic rings are displayed by dibenzothiophenes and the three naphthothiophenes. Dibenzothiophenes (DBT) are normally abundant in fossil materials, naphthothiophenes much less so. As shown by entry 11, alkylation in the 4- and 6-position of a dibenzothiophene does not hinder the complexation and all DBTs

that we have investigated elute in Fraction 2. Alkylation in any other position than 4 increases the strength of the interactions with Pd(II), alkylation in the 4-position weakens them somewhat but the compounds still elute comfortably in Fraction 2. Naphthothiophenes are a more complex case in that the two parents naphtho[1,2-*b*]- and naphtho[2,1-*b*]thiophene are found in Fraction 1 and naphtho[2,3-*b*]thiophene in Fraction 2 as shown by entries 12 and 13. Alkylation would presumably strengthen the interactions with Pd(II) but this has not been investigated so far.

#### 4.3.6 Compounds with two sulfur atoms in aromatic rings

Especially in higher-boiling materials or in immature fossil material, aromatic compounds containing two thiophene rings can be expected. A thienothiophene, a thienobenzothiophene and a benzodithiophene were used to model the behavior of such condensed aromatic compounds. They are all well retained by Pd(II) and elute in Fraction 2. The two sulfur atoms can also occur in non-condensed rings in thioanalogues of biphenyl as was discussed under "Non-annealed thiophenes".

#### 4.3.7 Nitrogen heterocycles

In a separate work, the nitrogen heterocycles acridine and carbazole were tested on the Pd(II) phase [73]. Their interactions with the phase were so strong that they could not be eluted from it even using pure methanol as eluent. Since it is expected that the higher polarity of nitrogen heterocycles makes them retained by the silica used in the initial chromatographic fractionation of a petroleum sample, their removal from the PAHs and PASHs should be guaranteed already at this early stage.

#### 4.3.8 Olefins

Since the olefinic double bond is considered to be a soft Lewis base, it could well be imagined to interact with the (soft) Lewis acid Pd(II) as is well-known in many situations, e.g. the industrial Wacker process. We synthesized 1-[(2E)-3,7-dimethyl-2,6-octadienyl]naphthalene in order to study whether the two double bonds in the side chain can interact strongly with the stationary phase; this would mean that such sulfur-free compounds would elute not with the PAHs in Fraction 1 but with



condensed sulfur aromatics. However, the compound elutes in Fraction 1, implying that olefinic interactions with Pd(II) are not very strong under the present conditions.

The results obtained here are of immediate interest to research into the identity of the sulfur compounds in high-boiling petroleum fractions and will thus be used to investigate recalcitrant compounds in hydrodesulfurized materials. The Pd(II) column fractionates the sulfur aromatics into three groups as indicated in table-4.1. (The third group would encompass such compounds that are too strongly bonded to elute.) We have shown that when the two fractions are individually methylated to form the methylthiophenium ions of the sulfur aromatics and subjected to Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS), hundreds or thousands of exact masses will be obtained from a real-world sample [51]. From the exact masses the molecular composition can be calculated. However, especially when the parent ring systems grow larger, as expected in higher-boiling materials, a large number of isomers is possible. FT-ICR-MS will not differentiate between isomers since only  $M^+$  ions are formed and these obviously have the same  $m/z$  value for isomers. Therefore other methods are needed that will allow a differentiation between parental structures and the Pd(II) may be useful in such circumstances.

Consider the isomeric indenothiophenes and cyclopentadienebenzothiophene. Such compounds and their alkylated derivatives have been reported to occur in crude oils, syncrude and shale oil [2, 61] but mass spectrometry does not help in identifying the parent systems. However, these compounds and their alkyl derivatives are expected to behave differently on the Pd(II) phase, indenothiophenes eluting in Fraction 1 and cyclopentadienebenzothiophene, being a substituted benzothiophene, in Fraction 2. FT-ICR-MS on the individual fractions should now be helpful in determining whether these compounds are contained in the sample.

A somewhat more complex situation arises when the parent compounds are not isomeric but their alkyl derivatives are. When the elemental composition of an ion is known from high-resolution MS, its double bond equivalent (DBE) can be calculated which is defined as the sum of the number of double bonds and rings in the molecule [51]. Alkyl derivatives derived from different parents (of different molecular weights) with the same double bond equivalent can have the same

molecular composition and thus be indistinguishable in mass spectrometry. For instance, a benzothiophene with a naphthenic ring annealed onto it, whether a five- or a six-membered ring, (e.g. tetrahydrodibenzothiophene, entry 14) and phenylthiophenes have the same DBE of 7. Although the parent compounds have different molar masses, namely 188 for tetrahydrodibenzothiophene and 160 for phenylthiophene, and these compounds therefore can be easily distinguished by mass spectrometry, higher alkylated derivatives will have the same molar mass. A tetrahydrodibenzothiophene substituted with a total of 10 carbon atoms in side chains will have the molecular formula  $C_{22}H_{32}S$  which is identical to the formula of a phenylthiophene with a total of 12 carbon atoms in the side chains. Being isomeric, these derivatives cannot be distinguished by mass spectrometry (without fragmentation). However, as the results in this work shows, these compounds are expected to be separated on the Pd(II) column so that phenylthiophenes elute in Fraction 1 and tetrahydrobenzothiophenes in Fraction 2. Thus, if the exact mass for  $C_{22}H_{32}S$  is found in Fraction 2, it cannot be a substituted phenylthiophene. It is still not unambiguously identified since various possibilities exist, for instance a  $C_{10}H_{21}$ -substituted tetrahydrodibenzothiophene or a  $C_{11}H_{23}$ -substituted cyclopenteno-benzothiophene. A similar situation arises with several other parent compounds.

#### 4.4 Summary

This study reveals the chromatographic behavior of a large number of sulfur-containing ring systems on a Pd(II)-based stationary phase and is a necessary first step for the application of this phase to fossil fuel analysis, especially for heavy compounds which cannot be analyzed easily by gas chromatography. The separation of the very complex mixture of such compounds into groups depending on the parent structure will considerably facilitate the identification of the sample components. The results here delineate the principles of retention in that compounds found in Fraction 1 generally are thiophenes without condensed aromatic rings whereas the more strongly retained compounds in Fraction 2 all contain this motif. This separation is coupled with high-resolution mass spectrometric investigations to elucidate the structure of high-molecular weight sulfur aromatic compounds recalcitrant to hydrodesulfurization (chapter 8).

## 5 Development of a stationary phase for the isolation of PASHs from fossil fuels

### 5.1 Limitations of Pd-ACDA silica gel

The disadvantages of Pd-ACDA silica gel include:

- (i) Incomplete separation of PASHs. As already explained in the previous chapter 4, if sulfur is present in a non-aromatic ring, the compounds bind to the phase irreversibly and cannot be eluted out even with pure methanol. So an important class of compounds (aromatic sulfides) is lost during the sample preparation. Such compounds are reported to be present in desulfurized diesel fuels [72].
- (ii) It is quite cumbersome to synthesize the ligand, which makes the synthesis of this bonded phase more difficult and expensive.
- (iii) The ligand ACDA is quite bulky, so the amount of ACDA which can be bonded onto the silica gel is low and consequently, the amount of palladium ions loaded onto the phase is lower than desired.

An ideal solution for this problem of group separation of PASHs from PAHs would be to synthesize a silica gel which is incorporated with the maximum possible amount of suitable metal ions. Besides this, the gel should be easily synthesized and commercially viable. In order to achieve this goal several attempts have been made which are described in this chapter.

The initial idea was to synthesize a silica gel incorporated with maximum possible amount of palladium(II) ions by the sol-gel process. The sol-gel process involves the synthesis of inorganic matrices through the formation of a colloidal suspension (sol) and the gelation of the sol to form a wet gel, which after drying forms the “dry gel” (xerogel).

## 5.2 Theory of sol-gel process [74]

### 5.2.1 Hydrolysis and condensation

The sol-gel technique uses water and low molecular weight alkoxy silanes such as tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), or an equivalent organometallic alkoxide (such as tetrakisopropoxytitanium or tetrakispropoxy aluminium) as sol-gel precursors. Because alkoxy silanes are not miscible with water, a common solvent is used for homogenization, although in some cases (especially when sonication is used) the released alcohol can provide sufficient homogenization. The polycondensation of alkoxy silanes can be summarized in terms of three reactions: hydrolysis of the ester, silanol-silanol condensation, and silanol-ester condensation as shown in figure 5.1.

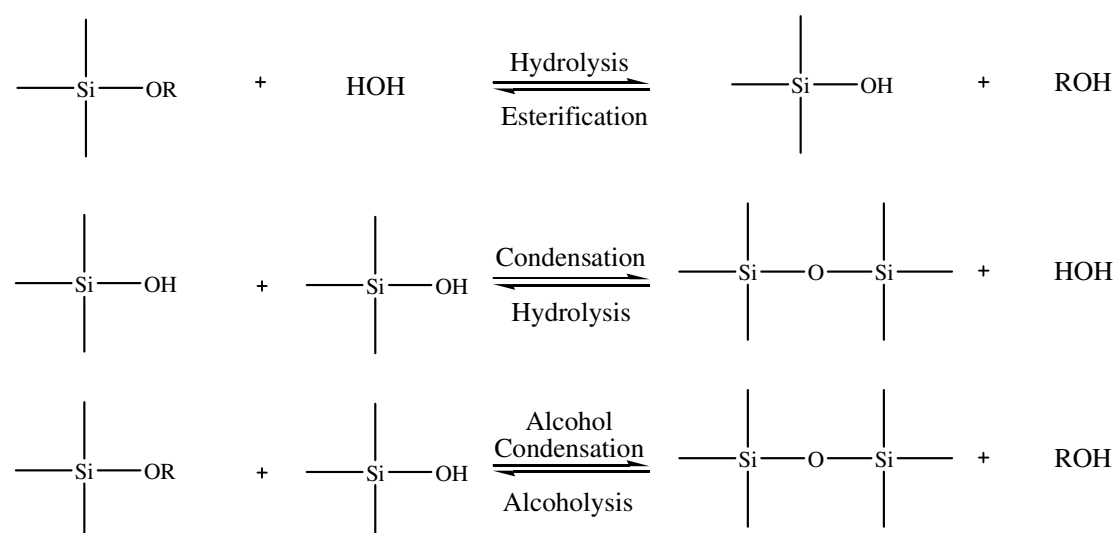


Figure 5.1: Sol-gel reaction scheme.

The hydrolytic ability of the Si-O-Si bond is responsible for the differences between organic and inorganic polycondensation. Organic polymers evolve through the formation of dimers, trimers, and linear chains, which cross-link to form the gel state. Inorganic particles, however, evolve either through the aggregation of small colloids or by addition of low molecular weight particles to larger ones. Because silica particles can dissolve, particularly under basic conditions, a source of low molecular weight silica monomers or oligomers is available even at advanced stages of polymerization. This, and the fact that high molecular weight silica oligomers are more stable than smaller ones, provides excellent conditions for “necrophilic” growth

of large particles by feeding on low molecular weight dissociated fragments (the Ostwald ripening mechanism).

### **5.2.2 Gelation**

The gel point is defined as the point at which the entire solid mass becomes interconnected. At the initial stages of polymerization, the silanol functional groups at the surface of the growing particles are partly deprotonated, and their negative charge provides a repulsion barrier that stabilizes the sol. Later, solvent evaporation and water consumption by alkoxy silane hydrolysis concentrate the solution and destabilize the suspension.

### **5.2.3 Drying, aging and fracture**

During the last stage of gelation, water and the organic solvent evaporate from the glass cavities and the volume of the solid matrix shrinks gradually. In some cases, the final volume of the xerogel is < 10 % of the initial volume of the gel. During the drying phase, some of the larger pores are emptied while smaller pores remain wetted by the solvent creating large internal pressure gradients. This stress causes cracks in large monoliths and is also responsible for fractures in dry monolithic sensors upon immersion in water. A xerogel is the desirable end product for HPLC applications. Although a final high temperature step can be used for densification, organically modified sol-gel matrices seldom withstand the high temperatures that are needed for these purposes.

### **5.2.4 Effect of process parameters [74]**

A large number of process variables can be used to control average pore size and the distribution of pore sizes, specific surface area, mass fractal dimension, concentration of silanol groups, and other structural characteristics of xerogels. However, the quantitative relationship between the properties of the xerogels and the preparation variables is by no means straight forward; non monotonic functions and interdependencies among different properties are common. Delicate manipulation of

one variable is simple, whereas tuning a set of specifications is more demanding and often requires a tedious trial and error process.

The pH and the H<sub>2</sub>O:Si molar ratio are the most significant process parameters. Higher pH accelerates the hydrolysis and the condensation steps, increases dissolution of silica particles, and thus provides a continuous source of low molecular weight silicon species that promote particle ripening. These conditions also increase deprotonation and surface charges, thereby postponing the aggregation and gelation steps. High pH preparations therefore yield monoliths constructed of denser and larger building blocks that exhibit larger void fraction, average pore diameter, and specific surface area. Under very low pH (< 2) the dissolution of silica particles becomes negligible, gelation is hindered by the positively charged protonated surface, and the hydrolysis of the alkoxide monomers and the condensation rate are increased because of acid catalysis. Polycondensation in low pH conditions thus resembles the polycondensation of organic polymers and yields dense and low surface area materials. Such conditions are used to prepare narrow pore gas separating membranes.

Large H<sub>2</sub>O:Si ratios accelerate the rate of alkoxide hydrolysis, decrease the rate of aggregation, and thus increase the porosity and the specific surface area of the silica xerogel. However when this ratio becomes < 4 (the stoichiometric ratio), the polymerization becomes increasingly controlled by the rate of condensation. The rate of hydrolysis is slowed down and the Ostwald ripening mechanism becomes negligible. Low H<sub>2</sub>O:Si ratios yield chain like polymeric structures with a large excess of residual organic material because of the presence of unhydrolysed alkoxy groups. Low pH and low H<sub>2</sub>O:Si ratios provide adequate viscosity for fibre drawing.

Numerous other process parameters can also be used to control the properties of the xerogels. For example, excess solvents decrease the tendency for aggregation and thus increase the porosity of the final product. Ammonia, amines, fluoride ions, and other catalysts are used to accelerate the hydrolysis and condensation steps and alter the specific surface area. Surfactants are often used to reduce surface tension, stabilize the smaller particles, and increase the specific surface area (in addition to their function in fracture prevention). Longer and bulkier alkoxysilane monomers decrease the rate of hydrolysis and condensation. Higher temperatures increase the

solubility of silicon oligomers, sol stability, porosity and specific surface area of the xerogels.

### 5.2.5 Physical configuration

The sol-gel process can be used for molding different configurations porous ceramics, including monolith blocks, films, fibers, and spherical monodispersions. Application of high pH and high H<sub>2</sub>O:Si ratio, particularly when accompanied with low ionic strength conditions, provides ideal conditions for the Ostwald ripening mechanism. Indeed, the Stöber process [77] for the production of spherical, micrometer-sized, monodispersions of silica particles uses bubbling of ammonia gas, low ionic strength conditions, a dilute solution, and a high H<sub>2</sub>O:Si ratio. In addition, irregular powders can, of course, be obtained from monoliths by conventional crushing and milling techniques.

### 5.2.6 Immobilization methods

Traditionally, organic reagents have been immobilized in silica gel matrices by impregnation or by using the high reactivity of surface silanol groups to anchor the reagents by covalent bonding. The sol-gel process has led to two additional ways of immobilizing organic and inorganic compounds: Sol-gel doping and polycondensation of appropriately derivatized organically modified silicon-containing precursors.

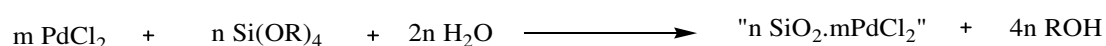
### 5.2.7 Sol-gel doping

*Avnir, Levy and Reisfeld* [75] were the first to realize that moderate or even ambient temperature sol-gel processing opens a way for immobilization of heat sensitive compounds by incorporation of the modifiers in the sol-gel precursors, a method which was thought to be exclusively reserved for the modification of organic polymers. This so called “sol-gel doping” method gained popularity as a result of its generality and simplicity, and a variety of photometric reagents for the detection of anions, cations, redox species, and airborne pollutants have been successfully

immobilized on silica, titania and other xerogels [76]. This concept is intermediate between impregnation and covalent bonding techniques and provides a general, inexpensive route for the immobilization of reagents.

### 5.3 Silica gels doped with Pd(II) ions synthesized from TEOS precursor

In order to incorporate Pd(II) ions into the gel, one of the initial attempts was to dissolve the palladium salts in the hydrolyzing agent or the common solvent.



Both acid catalysed and base catalysed hydrolysis of the TEOS precursor were used for the synthesis of several silica gels. In a typical experiment a solution of palladium salt in alcohol or water was added to precursor TEOS. Following which a known amount acid (HCl) or base (aq. NH<sub>3</sub>) was added and a homogeneous solution is formed. This mixture was stirred for an hour at room temperature and dried in an oven at 60 °C. Compositions for some of the starting solutions and the gelation times are shown in the table 5.1. In order to find the right parameters, some gels were synthesized initially without the addition of palladium salts.

Table 5.1: Relative molar ratios of the precursors used for the synthesis of silica gels doped with Pd(II) ions.

Gel No.	TEOS (mol)	Alcohol (mol)	H <sub>2</sub> O (mol)	HCl (mol)	aq. NH <sub>3</sub> (mol)	PdCl <sub>2</sub> (mol)	t <sub>Gel</sub> /h
1	1	1.88 <sup>a)</sup>	10	0.05	-	-	24
2	1	1.88 <sup>a)</sup>	10	0.05	-	0.016	24
3	1	8.50 <sup>b)</sup>	5	-	1	-	2
4	1	8.50 <sup>b)</sup>	5	-	1	0.016	2

a) Methanol and b) Isopropanol

After the synthesis of silica gels, the next important task was to modify them to fit the conditions of an HPLC column. Silica gels used in HPLC columns frequently have spherical particles with particle size ranging from 5-10 μm and high



surface area. To meet these requirements, the gels were synthesized by Stöber process (entries 3 and 4 in table 5.1) that leads to spherical particles of a defined diameter [77], in some cases hydrolysed silica sols were spray dried with a mini spray drier. The larger particles obtained by acid hydrolysis were powdered by a ball mill to give particles of required size. The powdered gels were dry packed into a HPLC column and tested for their efficiency with standard compound like phenanthrene (10 ng/ $\mu$ L) and dibenzothiophene (10 ng/ $\mu$ L).

Several gels were synthesized using the precursor TEOS. Only one of the gels synthesized by acid catalyzed hydrolysis showed interesting properties. This gel retained dibenzothiophene more strongly than phenanthrene. This column has shown high back pressures on the HPLC pumps, which can be ascribed to the fact that the gels were powdered manually which may lead to a large distribution of particle sizes with a lot of fines that would lead to a high resistance in flow. Atomic absorption spectroscopic studies were done on this silica gel by dissolving the gel in hydrofluoric acid to determine the amount of palladium ions incorporated in the gel. These studies have shown that 0.1 % of palladium ions were incorporated in the gel, which is much less than the desired goal. Even though this phase could in principle be used for the desired separations, the poor reproducibility of the synthesis, manifested in the varying retention properties of the gels prepared under identical conditions, makes it obvious that an in-depth study of the synthesis and the factors leading to the desirable material would be necessary.

The main drawbacks of this method are

- (i) Poor solubility of palladium salts in the hydrolysing agents like water, methanol and ethanol.
- (ii) Conversion of palladium salts into complexes in presence of acid or base used as a catalyst for hydrolysis.
- (iii) High degree of leaching is observed when the gels were washed with methanol which led to the depletion of Pd(II) ions incorporated in the gel.

## 5.4 Organic modification of sol-gel matrices

The problems faced with the attempts to synthesize silica gels using the TEOS precursor showed the need for an organic modification of the silica gels. As mentioned earlier, one of the disadvantages of the bonded phase Pd-ACDA silica gel is the bulky ligand ACDA, so by synthesizing silica gels with simple ligand systems like aminopropano one can incorporate a greater amount of palladium ions into the gel.

Organic modification is usually used to reduce the degree of crosslinking, improve film adhesion to its support, reduce the concentration of the surface silanol groups and the ion exchange capacity, alter partition coefficients, or introduces reactive functional groups that can be subsequently used for anchoring of molecular recognition species on pre-prepared xerogels. The traditional method for the organic modification of silica is based on condensation of the surface silanol groups and organochlorosilane or organoalkoxysilane modifiers. The sol-gel process provides a convenient method for the production of organically modified surfaces by incorporating alkoxysilane monomers that contain desirable functional groups in the starting polymerization mixture [78]. Ormosils (organically modified silica) and Ormocers (organically modified ceramics) can be tailored from commercially available organofunctional alkoxysilanes. The ratio of tetraalkoxysilane and organotrialkoxysilane can be used to control the cation exchange capacity and polarity of the porous surface. Monomers containing a Si-C bond and an easily derivatized radical such as an amino-, vinyl-, epoxy-, or mercapto- group can be used to prepare readily derivatized xerogels. These can be subsequently used as covalent anchors for specific chelating agents, redox mediators, or photometric reagents.

### 5.4.1 Copolymerization of modified reagents

This form of immobilization involves the synthesis of an alkoxysilane monomer containing covalently bound organic reagent and the subsequent use of the precursor in the sol-gel process. For example, *Avnir* and *coworkers* have synthesized a trimethoxysilane derivative of methyl red and used it to prepare a pH sensor [79]. Following this concept, precursors like 3-(2-aminoethanoamino)propano trimethoxy

silane (AS) or methylamino-propanotrimethoxy silane (MATS), which are commercially available were combined with TEOS during the sol-gel process. The amino groups present in the side chain of the precursors would be expected to chelate the palladium salts.

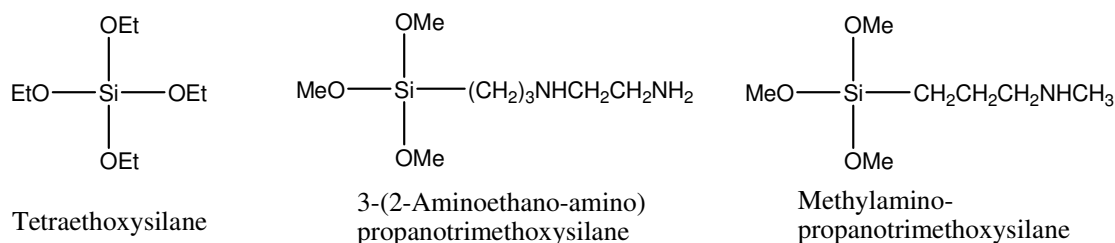


Figure 5.2: Structures of some sol-gel precursors.

Several gels were synthesized, packed into HPLC columns and tested for their ability to separate aromatic hydrocarbons and thiophenic compounds. Only a few representative starting solutions are shown in table 5.2. Further variations of the copolymerisation of TEOS with precursors AS and MATS were also tested but the resulting gels did not display useful properties and are thus not discussed further.

Table 5.2: Relative molar ratios of the precursors used for the synthesis of silica gels doped with Pd(II) ions.

Entry	TEOS	AS	MATS	H <sub>2</sub> O	MeOH	HCl	PdCl <sub>2</sub>	t <sub>gel</sub> /h
1	1	0.2	-	5.47	3.00	0.02	0.016	0.5
2	1	1	-	5.47	3.00	0.02	0.016	
3	1	-	0.5	5.16	5.00	0.02	0.016	1
4	1	-	1	5.16	5.00	0.02	0.016	1

All the gels synthesized were brown in color, clearly showing the incorporation of palladium salts in the silica gels. Despite of this fact, when used as stationary phase in HPLC, palladium(II) ions immobilized on the gel did not interact with the compound classes (PAHs and PASHs) with cyclohexane as mobile phase. In this context, it appears that the skeletal unit  $\text{H}_2\text{N}-\text{C}=\text{C}-\text{C} \begin{array}{l} \text{S} \\ \diagup \\ \text{S} \end{array}$  in ACDA plays an important role in binding Pd(II) in such a way that there is a free coordination site to form ligand complexes with sulfur aromatics. Since no promising leads were found using this approach despite a large number of attempts it was abandoned in favour of other systems.

## 5.5 Incorporation of metal ions on commercially available cation exchange resins

Initial modification of commercially available silica gels for isolation of PASHs involved metal loading of propanosulfonic acid bonded silica (Excil SCX 100). This bonded phase was loaded with 0.01 M solutions of palladium(II) chloride, palladium(II) acetate, copper(I) chloride, copper(II) chloride and silver nitrate. Each metal ion was loaded onto the silica gel by stirring the gel in a solution of the metal salt. Palladium(II) acetate was dissolved in toluene and the other salts in distilled water. These metal bonded silica gels were filtered off, washed with methanol, dried in vacuo and were slurry packed into stainless steel columns. Columns prepared in this manner were evaluated in a preliminary study with standard solutions of phenanthrene (10 ng/ $\mu$ L) and dibenzothiophene (10 ng/ $\mu$ L) to select the most effective metal ion for the hydrocarbon-thiophene separation. The palladium acetate loaded sulfonic acid silica column has a stronger retention for both aromatic hydrocarbons and thiophenes than does the corresponding palladium chloride column. Several solvent systems were used to elute the aromatic compounds out of the palladium acetate column. Nevertheless, the compounds were bound to the column irreversibly. By using solvents like methanol, acetonitrile and acetone, leaching of palladium salts was observed. The aromatic hydrocarbons and the sulfur aromatics eluted out without any retention of the copper(I) and copper(II) loaded columns. The silver(I)-loaded silica gel also did not show any separation efficiency.

Another commercially available cation exchange silica gel column Luna SCX 100 (benzene sulfonic acid bound silica gel) was contacted with a solution of palladium acetate in toluene using the apparatus shown in figure 5.2. This special apparatus was developed by Frank Michel [80].

The advantages of using this device are

- (i) There is no contact of the reagent solution (Palladium acetate in toluene) with the HPLC pumps or any other parts of the HPLC system.
- (ii) No corrosion of the device as it is made up of borosilicate glass and Teflon pistons.

- (iii) Exact amount of reagent solutions can be injected onto the column as the device does not have any significant dead volume.
- (iv) There is no mixing of reagent solution and the HPLC solvent so the reagent solution is not diluted and various reagent solutions can be used.
- (v) Visual control of the pumping process.
- (vi) Automatic shut down of HPLC pumps at the end of the pumping process.
- (vii) Easy handling and easy cleaning.

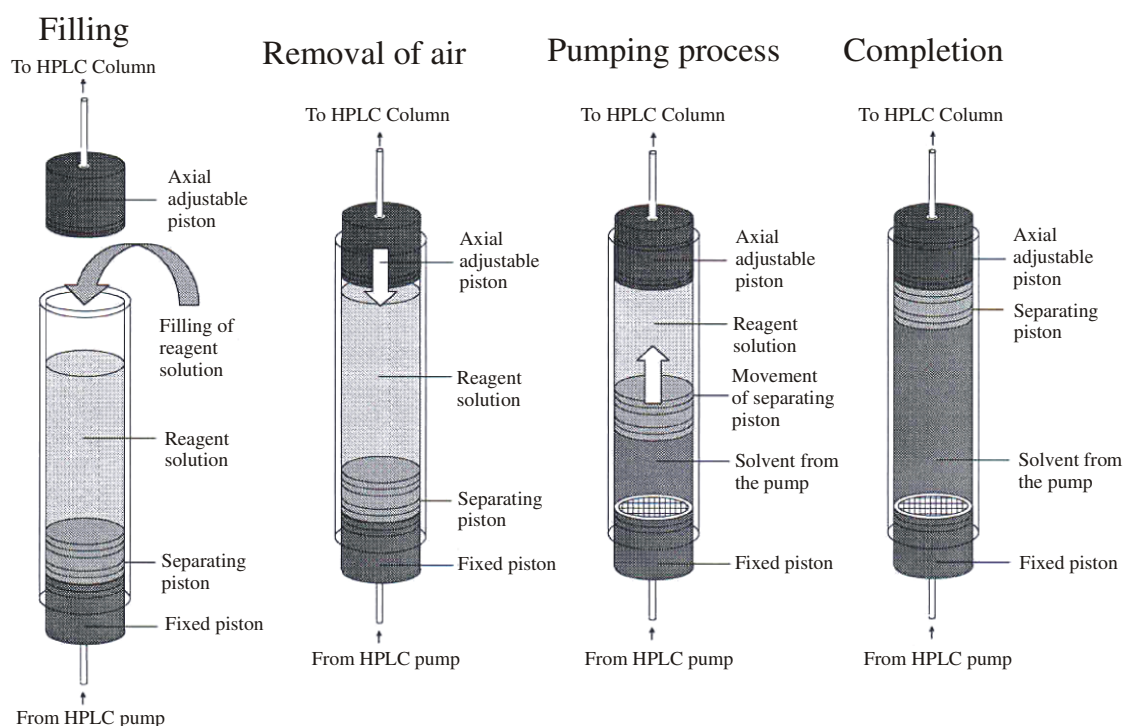


Figure 5.2: Schematic diagram of pumping process. From left to right: filling the tube with the reagent solution, removal of air by inserting the axial adjustable piston, the pumping process and its completion [80].

At first the palladium acetate solution was filled into the reagent tube. During the filling process the separating piston and the fixed piston are in contact with each other as shown in figure 5.2. The reagent solution is just above the separating piston. After that the axial adjustable piston is inserted into the reagent tube whereby remaining air was removed.

Then the reagent tube is fixed to the HPLC pump on the inlet side and the outlet side is connected to the HPLC column as shown in the figure 5.2. The separating piston is moved by the hydraulic pressure created by the solvent from the HPLC pump which further drives the reagent solution onto the HPLC column. This procedure was repeated till the column was saturated with palladium ions. The Pd(II) ion incorporated Luna SCX column was tested for its separation efficiency with naphthalene (10 ng/ $\mu$ L) and phenanthrene (10 ng/ $\mu$ L). Both the compounds eluted with similar retention times with cyclohexane as eluant. Thus this phase cannot be used for the isolation of PASHs.

## 6 Isolation of PASHs using Pd(II)-loaded mercaptopropano silica gel

### 6.1 Complexation of Pd(II) with ACDA

Many attempts have been made to incorporate metal ions [especially palladium(II) ions] into the stationary phase in order to take advantage of their Lewis acid properties in complexing with different organic sulfur compounds. The ions were either deposited as salts onto the gel, electrostatically bound by e.g. ion-exchange phases or complexing groups of a modified gel. Overall, Pd-ACDA silica gel showed a better separation of thiophenic compounds from aromatic hydrocarbons. A better understanding of the complexation properties of Pd(II) with ACDA is essential in order to develop new and efficient stationary phases for the isolation of PASHs.

In principle there can be six possible forms of ACDA [81]. *Takeshima et al.* [82] proposed structure I, while *Bordas et al.* [83] assigned III as the structure for ACDA from nmr spectra in  $\text{CDCl}_3$ . The results obtained by *Nag and Jordar* [81] were in agreement with *Takeshima et al.* [82].

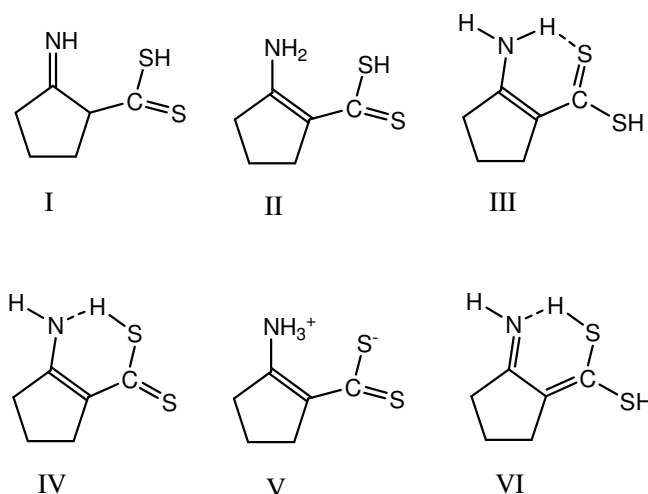


Figure 6.1: Six possible forms of ACDA [81].

The metal complexes of 2-amino-1-cyclopentene-dithiocarboxylic acid (ACDA) and some of its N-alkyl and S-alkyl derivatives were already examined

extensively. This interest was mainly related to the antifungal behavior [83], ascribed to some transition metal complexes of ACDA, but different applications have been found for its coordination properties. For example, ACDA and its metal complexes have been used as model compounds of redox-active enzymes [84]. Despite of intensive investigations, the coordination chemistry of ACDA remains poorly understood. The question about the coordination of the ligands to the metal ion, which can be established either by nitrogen and sulfur (N,S) or whether the coordination is made exclusively by sulfur (S,S) is of great importance.

Crystallographic studies represent a suitable method to answer this question. The low solubility of these complexes in organic solvents makes breeding of suitable crystals for X-ray crystallographic studies extremely difficult. So far only a few reports are available on crystallographic studies of ACDA complexes. A crystallographic study on the Co(III).(ACDA)<sub>3</sub> complex has been reported for which an (S,S) coordination mode was observed [85]. Similarly an (S,S) coordination was observed in several organo(IV) derivatives of ACDA of the type  $\text{ph}_n\text{SnCl}_3 \cdot n(\text{ACDA})$ ;  $n=2,3$  and  $\text{R}_2\text{Sn}(\text{ACDA})_2$ ;  $\text{R}=\text{Ph}/\text{Bu}$  [85]. Besides this, the crystal structures for several complexes of di- and tribenzyltin and the N-ethyl and N-benzyl derivatives of ACDA showed that tin(IV) is bound asymmetrically to the dithiocarboxylato ligand through two sulfur atoms (S,S) [86]. Based on spectroscopic studies, *Nag* and *Jordar* [81] claimed an (N,S) coordination mode for the complexes of Ni(II), Pd(II) and Pt(II). However, the Raman evidences reported by *Cappa de Oliveira* and *Santos* [87] suggest in turn an (S,S) coordination mode for the same metal complexes. In addition to this controversy is the fact that, depending on the preparation procedure, more than one differently colored complex, with the same molecular composition, has been obtained for each metal ion [81]. This observation has been tentatively correlated with different geometrical isomers (cis/trans) of the same complex [81].

Recently, *Amado* and *Riberio Claro* [84] reported an extensive ab initio study on the square planar complexes of Ni(II), Pd(II) and Pt(II) with ACDA and concluded that an (S,S) coordination was preferred. In addition, the experimental observation of differently colored species with the same molecular formula is explained by the low energy difference between cis and trans isomers.



Based on the conclusion that an (S,S) coordination was preferred for transition metal complexes of ACDA, we tried to replace the bulky ligand ACDA with a mercaptopropano group to overcome the limitations of Pd(II)-ACDA silica gel which were already described in chapter 5 (Pg. No. 39). Palladium(II) ions were incorporated onto mercaptopropano silica gel which is known to be a palladium scavenger. This chapter shows the initial results obtained for the isolation of PASHs on Pd(II)-MP-SG and a comparison of retention behavior of sulfur aromatics on Pd(II)-ACDA silica gel and Pd(II)-MP silica gel.

## 6.2 Experimental section

The mercaptopropano silica gel synthesis is described in detail in chapter 10. 2 g of this bonded phase was contacted with 100 mL of aqueous palladium chloride solution (0.01 M) for 12 h, filtered off, washed with water and methanol, dried in vacuo at room temperature. Approximately 1 g of Pd(II)-loaded silica gel was packed into a stainless steel column (4.6 x 150 mm) according to slurry method using methanol and a Knauer pneumatic pump. Fraction 1 was eluted with cyclohexane:dichloromethane (7:3) as mobile phase for 15 min and then the eluent was made more polar by adding 0.5 % isopropanol to elute fraction 2 at a flow rate of 1 mL/min.

### 6.2.1 Testing with standards

The retention of a compound on a HPLC column is described by a parameter called retention factor (k). The retention factor is a measure of the time the analyte resides in the stationary phase relative to the time it resides in the mobile phase. The definition of retention factor is shown in the equation below

$$k = \frac{t_r - t_m}{t_m}$$

Where,  $t_r$  = Retention time of the analyte.

$t_m$  = The dead time or the retention time of a substance that is unretained on the column.

Retention factors were calculated for several PAHs and PASHs on Pd(II)-MP-SG. A comparison of retention factors obtained for both Pd(II)-ACDA silica gel and Pd(II)-MP silica gel are shown in table 6.3.

### 6.2.2 CHNS analyses

A comparison of the elemental analyses of both Pd(II)-ACDA silica gel and Pd(II)-MP silica gel is as shown in table 6.1.

Table 6.1: Elemental analyses of Pd(II)-ACDA silica gel and Pd(II)-MP silica gel. Three measurements as well as the mean values in mmol/g for each element are shown.

	Pd(II)-ACDA-SG	Pd(II)-MP-SG
C [%]	5.77	3.85
	5.87	3.87
	5.86	3.87
C [mmol/g]	4.86	3.21
H [%]	1.16	0.54
	1.32	0.56
	1.29	0.49
H [mmol/g]	1.26	1.59
N [%]	1.22	-
	1.25	-
	1.26	-
N [mmol/g]	0.89	-
S [%]	1.40	3.22
	1.52	3.20
	1.50	3.18
S [mmol/g]	0.46	1.00

### 6.2.3 Metal loading

The amount of Pd(II) loaded on both Pd(II)-ACDA silica gel and Pd(II)-MP silica gel were determined by atomic absorption spectroscopy (AAS).

Table 6.2: Amount of palladium(II) ions loaded on Pd-ACDA silica gel and Pd(II)-MP silica gel.

Silica gel	Amount of silica gel (mg)	Amount of Pd(II) found (mg)	Metal loading mmol/g
Pd(II)-ACDA-SG	104	10	0.94
Pd(II)-MPS-SG	101	11	1.07

Table 6.3: Retention factors of some PAHs and PASHs on both Pd(II)-ACDA silica gel and Pd(II)-ACDA silica gel. Fraction 1 was eluted with cyclohexane:dichloromethane (7:3) as mobile phase for 10 min and then the eluent was made more polar by adding 0.5 % isopropanol to elute fraction 2.

Compound	Retention factors on Pd(II)-ACDA silica gel	Retention factors on Pd-MP silica gel	Fraction
Toluene	0.04	0.02	1
Naphthalene	0.09	0.08	1
Phenanthrene	0.12	0.11	1
Fluorene	0.14	0.06	1
Thiophene	0.11	0.93	1
2-Phenylthiophene	0.20	0.22	1
3-Phenylthiophene	0.50	1.91	1
4H-Indeno[1,2- <i>b</i> ]thiophene	0.90	3.01	1
Benzothiophene	>6.8	> 6.8	2
Dibenzothiophene	>6.8	> 6.8	2
Benzonaphthothiophene	>6.8	> 6.8	2
4-Methylthiophene	>6.8	> 6.8	2
4,6-Dimethylthiophene	>6.8	> 6.8	2

#### 6.2.4 Crude oil

The aromatic fraction of a crude oil (Kirkuk) was obtained by fractionating 80  $\mu$ L of the crude oil on 5 g activated silica (heated to 450  $^{\circ}$ C for 12 hr, 5 % water added and then stored for at least 12 hr at 150  $^{\circ}$ C), column dimension 8\*90 mm. The aliphatics were eluted with 30 mL cyclohexane and then the aromatics with 25 mL cyclohexane/dichloromethane (7:3, v/v). The aromatic fraction obtained was reduced to 200  $\mu$ L by rotary evaporation. 50  $\mu$ L of this aromatic fraction was injected onto Pd(II)-MP-SG and the liquid chromatogram obtained is shown in figure 6.2.

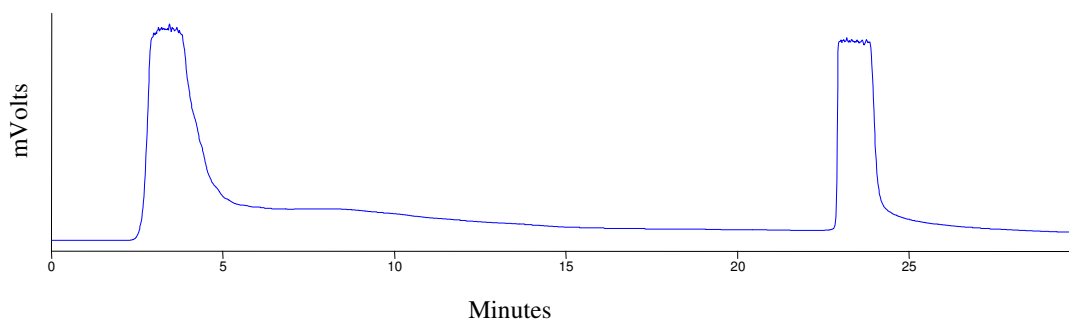


Figure 6.2: Liquid chromatogram showing the elution of PAH and PASH fraction of a crude oil on a Pd(II)-MP-Silica gel.

### 6.3 Results and discussion

The one ring, two ring and three ring PAHs (see toluene, naphthalene and phenanthrene in table 6.3) have similar retention properties on both Pd(II)-ACDA silica gel and Pd(II)-MP silica gel. Thiophene and 4H-Indeno[1,2-*b*]thiophene are retarded more strongly on Pd(II)-MP silica gel when compared to Pd(II)-ACDA silica gel but they would still elute in fraction 1. Benzothiophenes, dibenzothiophenes and their alkylated derivatives showed similar properties on both Pd(II)-ACDA column and Pd(II)-MP column and elute in fraction 2. The initial results obtained by determining the retention factors for some PAHs and PASHs (see table 6.3) show that the bonded phases Pd(II)-ACDA silica gel and Pd(II)-MP silica gel have similar retention properties and Pd(II)-MP-silica gel in principle can be used to separate PASHs from PAHs. The limitations of Pd(II)-ACDA silica gel were already described (chapter 5, Pg. No. 39). It is quite cumbersome to synthesize the ligand ACDA which makes the synthesis of the bonded phase Pd(II)-ACDA silica difficult and costly. The advantage of Pd(II)-MP silica gel over Pd(II)-ACDA silica gel is its easy synthesis.

In order to test the separation efficiency of Pd(II)-MP silica gel, the aromatic fraction of a crude oil was injected onto the Pd(II)-MP silica gel and the obtained fractions were tested with GC-FID and GC-AED. There were no sulfur containing compounds in the PAH fraction (see figure 6.3) and figure 6.4 shows the GC-AED chromatogram of PASH fraction. Every peak in the PASH fraction was detected in both the carbon and sulfur selective modes which show that in this fraction all compounds contain sulfur. Thus at least for this kind of sample, it has been

demonstrated that this phase can be used for an efficient and clear separation of PASHs from PAHs.

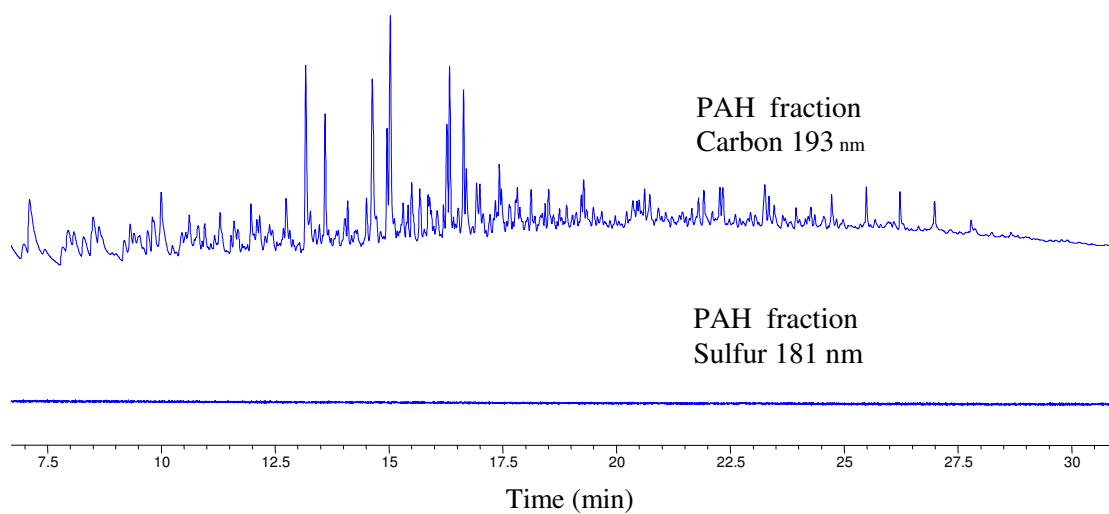


Figure 6.3: GC-AED chromatogram for the PAH fraction of the Kirkuk crude oil after LEC separation on Pd(II)-MP silica gel.

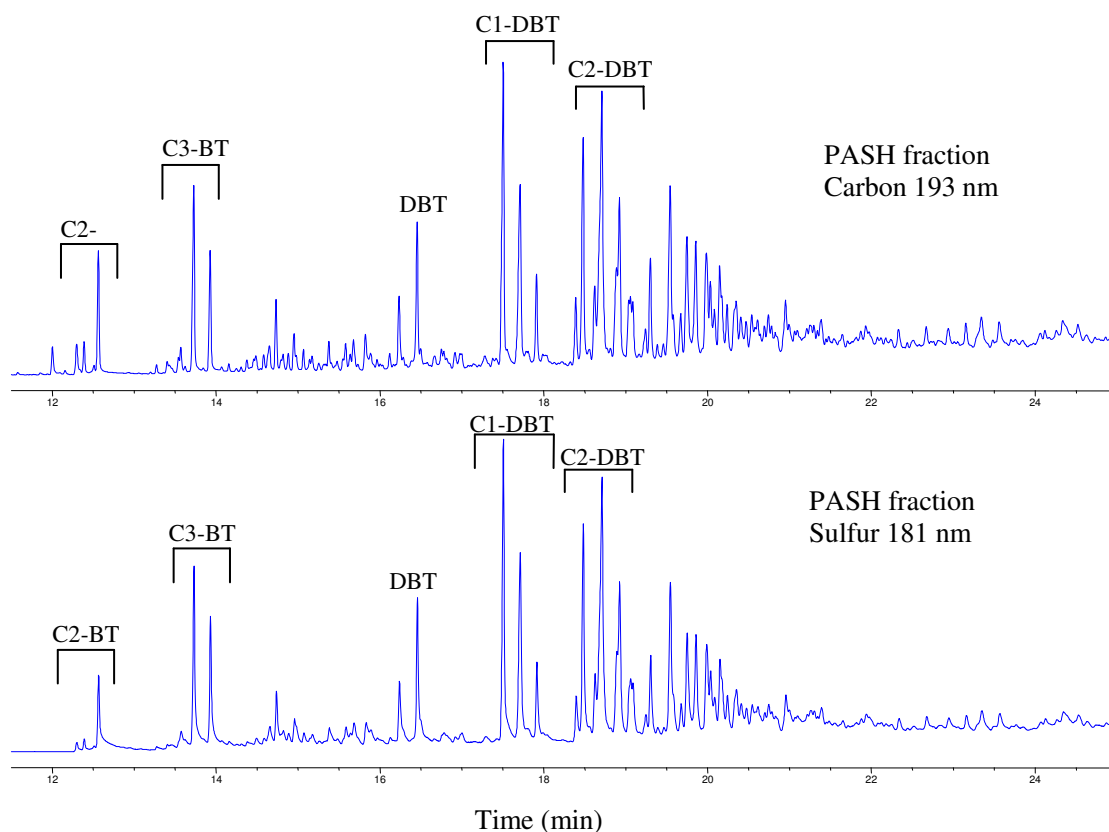


Figure 6.4: GC-AED chromatogram for the PASH fraction of the Kirkuk crude oil after LEC separation on Pd(II)-MP silica gel.

## 6.4 Summary

The coordination chemistry of various metal complexes of ACDA ligand is discussed. Based on the conclusion that a (S,S) coordination was preferred for transition metal complexes of ACDA, an attempt was made to replace the bulky ligand ACDA with a mercaptopropano group. This chapter briefly describes the preliminary results obtained for the isolation of PASHs from a crude oil using Pd(II) loaded mercaptopropano silica gel. A comparison of the retention behavior of several PASHs on Pd(II)-ACDA silica gel and Pd(II)-MP silica gel is presented. The results obtained here show that the Pd(II)-MP silica gel can be used in principle to separate PASHs from petroleum samples. The advantage of Pd(II)-MP silica gel over Pd(II)-ACDA silica gel is its easy synthesis and the somewhat higher metal loading.

## 7 Argentation liquid chromatography of PASHs on a silver(I) loaded mercaptopropano silica gel

### 7.1 Argentation chromatography

An interesting and useful subset of LEC is argentation chromatography, where silver(I) is the metal ion employed. The relative merits of incorporating the silver ion in the stationary phase versus including it in the mobile phase are already reported [88]. The major disadvantages of the mobile phase approach seem to be possible column deterioration and the build-up of metallic silver on the chromatographic system. Silver containing stationary phases have been used in liquid chromatography to improve the separation of isomeric olefins [89, 90] and heterocyclic aromatic hydrocarbons [91] for analytical and preparative purposes and also for the determination of thermodynamic data relating to  $\text{Ag}^+$  complexation [92, 93]. These data provide information on position and/or configuration of a double bond, on the substitution in the vicinity of a double bond and of its conjugation with other  $\pi$  electrons via their influence on complexation. For heterocyclic hydrocarbons one can ascertain from the complexation constants whether the lone pair of electrons is participating in aromatic electron systems and whether their intermolecular interaction with  $\text{Ag}^+$  is especially hindered by shielding substituents.

*Frei and coworkers* [94] deposited insoluble silver halides onto silica gel and obtained some good separation of nitrogen-containing species, but interaction with unsaturated species was too weak to be useful due to the low coverage by the silver halide. *Jezorek et al.* reported the argentation liquid chromatography of polynuclear aromatic hydrocarbons on a silver(I) loaded mercaptopropano silica gel stationary phase [95]. In that study they presented their initial results with mercaptopropano silica gel as a stationary phase for argentation chromatography. They reported the separation of five PAH standards namely acenaphthene, anthracene, pyrene, chrysene and perylene, in a normal phase mode [95].

## 7.2 Argentation liquid chromatography of PASHs

Unlike olefins and nitrogen heterocycles, dibenzothiophene did not elute faster from a C-18 column when silver ions were included in the mobile phase which means that a complexation interaction between the PASH and the silver ions was not observed [88]. However, if the sulfur atoms are not part of an aromatic system, e.g. in thianthrene, a considerable complexation effect was found and the compound showed a much reduced retention time. Ligand exchange chromatography of polycyclic aromatic sulfur heterocycles on silica gel modified with silver nitrate was also reported [96]. In that study silica gel containing 20 % silver nitrate was used to study the retention behavior of PAHs and PASHs. Sulfur heterocycles were shown to be about as strongly retained as the corresponding PAHs [96]. One- and two-ring aromatics from a shale oil fraction were reported to be separated into fractions enriched in the sulfur heterocycles by using a silver nitrate coated silica column. In the present work, we studied the retention behavior of several PASHs on silver(I)-loaded mercaptopropano silica gel stationary phase.

## 7.3 Experimental section

The **silver(I)-mercaptopropano silica gel** was synthesized as described in the literature [95]. This bonded silica phase was packed into a stainless steel column (4.6 x 150 mm) at a pressure of 450 bar using a Knauer pneumatic pump. Isocratic elution was used with 5 % isopropanol in cyclohexane as solvent.

### 7.3.1 Metal loading

The amount of silver(I) ions loaded onto the gel was determined by atomic absorption spectroscopy (AAS). The AAS studies showed a metal loading of 0.71 mmol/g.

### 7.3.2 Testing with standards

A standard mixture of several dibenzothiophenes [dibenzothiophene (DBT), 2-fluorodibenzothiophene (2FDBT), 2-methyldibenzothiophene (2MDBT), 4-methyldibenzothiophene (4MDBT), 1,3-dimethyldibenzothiophene (13DMDBT),



4,6-dimethyldibenzothiophene (46DMDBT), 6-ethyl-2,4-dimethyldibenzothiophene (6E24DMDBT), 2,4,7-trimethyldibenzothiophene (247TMDBT), 2,4,6,8-tetramethyldibenzothiophene (2468TMDBT)] was injected onto the Ag(I)-phase and the obtained liquid chromatogram is shown in the figure 7.1(a).

### 7.3.3 Testing with real world samples

The Ag(I) containing stationary phase was tested with the aromatic fraction of a diesel fuel, a crude oil and a vacuum gas oil.

**Diesel Fuel:** 100  $\mu$ L of a diesel fuel (B-328/99) was fractionated into aliphatics and aromatics on an open tubular column (8 x 90 mm) filled with 5 g activated alumina. Aliphatics were eluted with 30 mL cyclohexane and the aromatic fraction with 25 mL cyclohexane/dichloromethane (3:1, v/v). The volume of the obtained aromatic fraction was reduced to 200  $\mu$ L and it was further fractionated on Pd(II)-ACDA-silica gel into PAHs and PASHs. The volume of the PASH fraction thus obtained was reduced to 100  $\mu$ L and was injected onto the Ag-MPS-silica gel. Figure 7.1(b) shows the liquid chromatogram obtained.

**Crude oil:** 80  $\mu$ L of crude oil (Kirkuk) was also fractionated as described above and the obtained PASH fraction was injected onto the Ag-MP-silica gel and the fractions collected are shown in the liquid chromatogram figure 7.1(c).

**Vacuum gas oil:** 0.95 g of vacuum gas oil (Iranian Light) was fractionated into aliphatics, aromatics and resin compounds as described in the SARA method [97]. The PASH fraction obtained after fractionation over Pd-ACDA-silica gel was also injected onto the Ag(I)-MP-silica gel. Figure 7.1(d) shows the liquid chromatogram obtained.

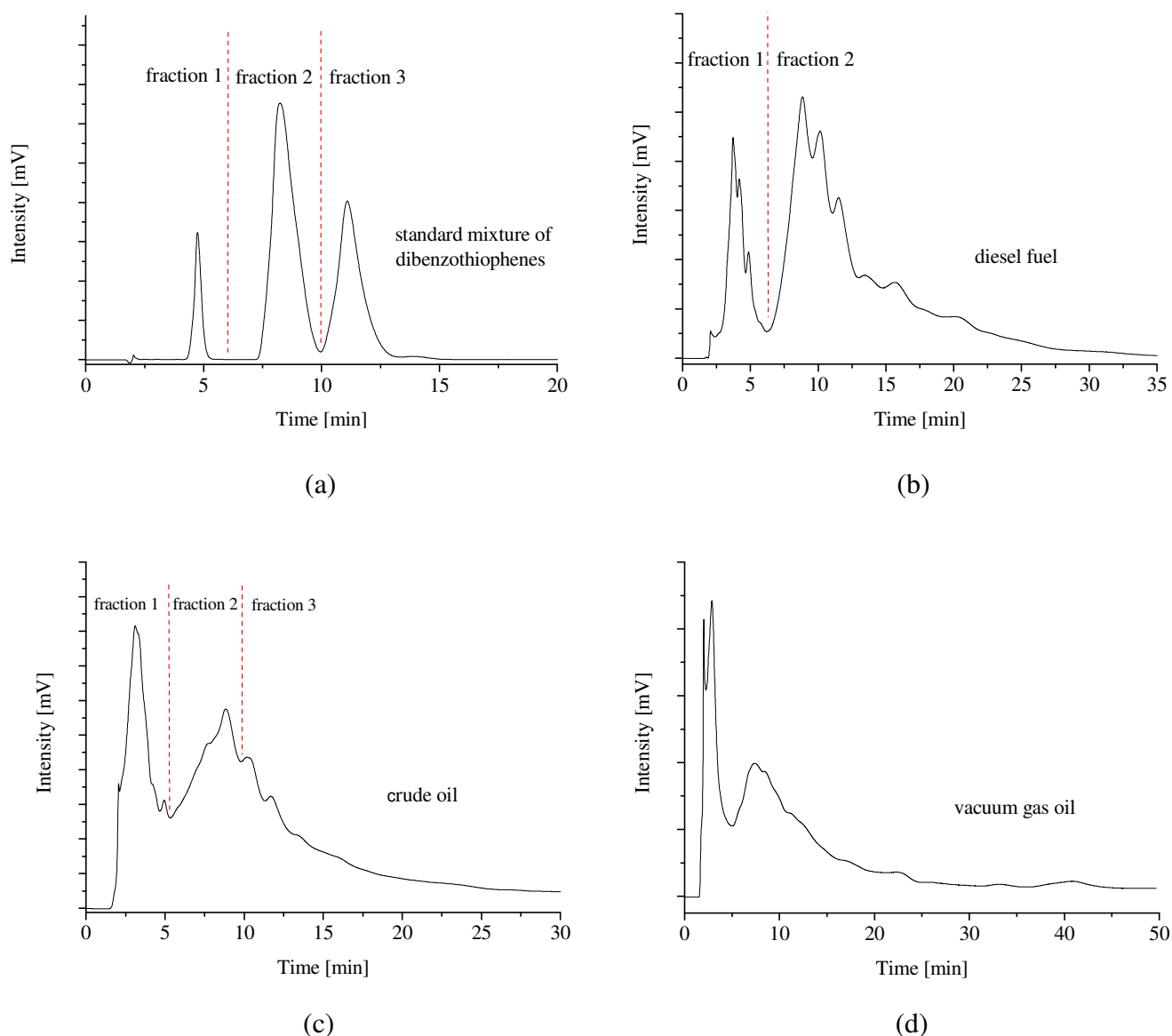


Figure 7.1: Liquid chromatograms of (a) standard mixture of dibenzothiophenes, (b) PASH fraction of a diesel fuel, (c) PASH fraction of the Kirkuk crude oil, (d) PASH fraction of a vacuum gas oil on Ag(I)-MP-Silica gel with 5 % isopropanol in cyclohexane as solvent system at a flow rate of 1 mL/min.

## 7.4 Results and discussion

Argentation liquid chromatography is based on the ability of Ag(I) to form weak, reversible charge-transfer complexes with unsaturated organic compounds, in this instance polycyclic aromatic compounds and their alkylated derivatives. The accepted model supposes the formation of a  $\sigma$ -type bond between the occupied  $2p\pi$

orbitals of the olefinic bond and the free 5s and 5p orbitals of the Ag(I), and the formation of (probably weaker)  $\pi$ -acceptor backbond between the occupied 4d orbitals of Ag(I) and the free antibonding  $2p\pi^*$  orbitals of the olefinic bond [98].

In order to study the retention behavior of several aromatics, their retention factors were determined. The retention factors for some PAHs and several PASHs are shown in table 7.1.

Table 7.1: Retention factors for some PAHs and several PASHs on Ag(I)-MP silica gel. The mobile phase is cyclohexane containing 5 % of isopropanol.

Entry	Compound	Retention factor
1	Toluene	0.22
2	Thiophene	0.26
3	Naphthalene	0.90
4	Benzothiophene	1.27
5	Phenanthrene	5.15
6	Dibenzothiophene	5.34
7	2-Methylthiophene	0.26
8	3-Methylthiophene	0.28
9	2-Phenylthiophene	1.23
10	3-Phenylthiophene	1.41
11	2-Methylbenzothiophene	1.47
12	3-Methylbenzothiophene	1.26
13	5-Methylbenzothiophene	1.45
14	6-Methylbenzothiophene	1.01
15	2,5-Dimethylbenzothiophene	1.82
16	2,6-Dimethylbenzothiophene	1.71
17	2,3,4,7-Tetramethylbenzothiophene	1.47
18	1,2,3,4-Tetrahydrodibenzothiophene	2.46
19	2-Methyldibenzothiophene	7.04
20	4-Methyldibenzothiophene	5.05
21	2-Octyldibenzothiophene	5.57
22	2,4-Dimethyldibenzothiophene	6.27
23	4,6-Dimethyldibenzothiophene	4.85
24	4,6-Diethyldibenzothiophene	4.88
25	1,3,7-Trimethyldibenzothiophene	5.40
26	1,4,6-Trimethyldibenzothiophene	5.97
27	1,4,8-Trimethyldibenzothiophene	6.46
28	2,4,6-Trimethyldibenzothiophene	5.43
29	3,4,7-Trimethyldibenzothiophene	7.33
30	2,4-Dimethyl-6-ethyl-dibenzothiophene	4.66
31	2,4,6,8-Tetramethyldibenzothiophene	6.53
32	Methyl phenyl sulfide	6.36
33	Benzo[ <i>b</i> ]naphtho[1,2- <i>d</i> ]thiophene	23.16
33	2-Fluorodibenzothiophene	2.04

The similar retention factors of the compound pairs thiophene/toluene, benzothiophene/naphthalene, dibenzothiophene/phenanthrene (see table 7.1, entries 1 to 6) show that the retention properties are mostly based on the number of pi electrons present in the compounds. A strong complexation interaction between the sulfur atom in the PASHs and the silver ions was not observed. The linear dependence of  $\ln k$  ( $k$  = retention factor) on the number of  $\pi$  electrons present in various PASHs is shown in figure 7.2.

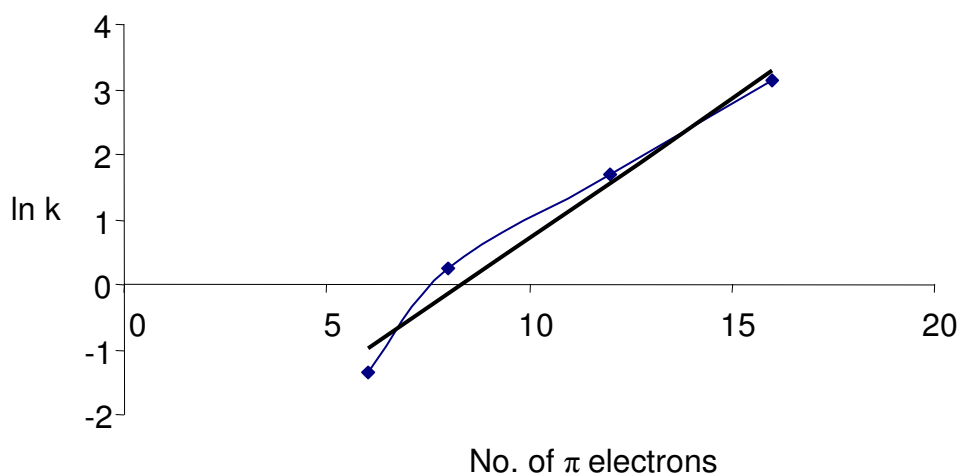


Figure 7.2:  $\ln k$  for thiophene, benzothiophene, dibenzothiophene and benzonaphthothiophene on Ag(I)-MP silica gel with cyclohexane containing 5 % isopropanol (1 mL/min) as eluent.

As sulfur atom increases the electron density of the aromatic ring, PASHs are retarded strongly than corresponding PAHs but the difference is not very large. A surprising behavior is seen with dibenzothiophenes with a methyl substituent in the 2-position. Such compounds are more strongly retained when compared to the other alkylated dibenzothiophenes. The retention behavior of 2-fluorodibenzothiophene was also studied since fluorinated PASHs are used as internal standards for the analysis of sulfur aromatics in petroleum samples.

To study the effect of alkylation, a standard mixture containing several alkylated dibenzothiophenes was injected onto the silver(I)-loaded mercaptopropano silica gel column and the collected fractions as shown in figure 7.1(a) were tested with GC-FID. The gas chromatograms obtained are shown in figure 7.3. As expected,

2FDBT eluted faster than dibenzothiophene on the Ag(I) column. Fraction 1 in figure 7.1[I(a)] shows only the presence of 2-FDBT. Dibenzothiophenes (except 6-ethyl-2,4-dimethyldibenzothiophene) with a methyl group in the 2-position are retained more strongly than other alkylated dibenzothiophenes and elute in the fraction 3 [see figure 7.3 and figure 7.1(a)]. Noteworthy is that also long alkyl side chains such as octyl group are eluted together with the methyl derivatives and not, as is often the case in normal-phase liquid chromatography, lower retention factor.

As expected, methyl phenyl sulfide in which the sulfur atom is not part of the aromatic system is retained more strongly than benzothiophene in accordance with its higher Lewis basicity. As explained before, the position of a methyl group influences the retention. For dibenzothiophene, a methyl group in the 2-position contributes to an exceptionally long retention time. Based on the retention factors of several benzothiophenes, dibenzothiophenes and benzonaphthothiophene (see table 7.1) it is expected that this phase can be used for the fractionation of PASHs obtained from real world samples into several compound classes.

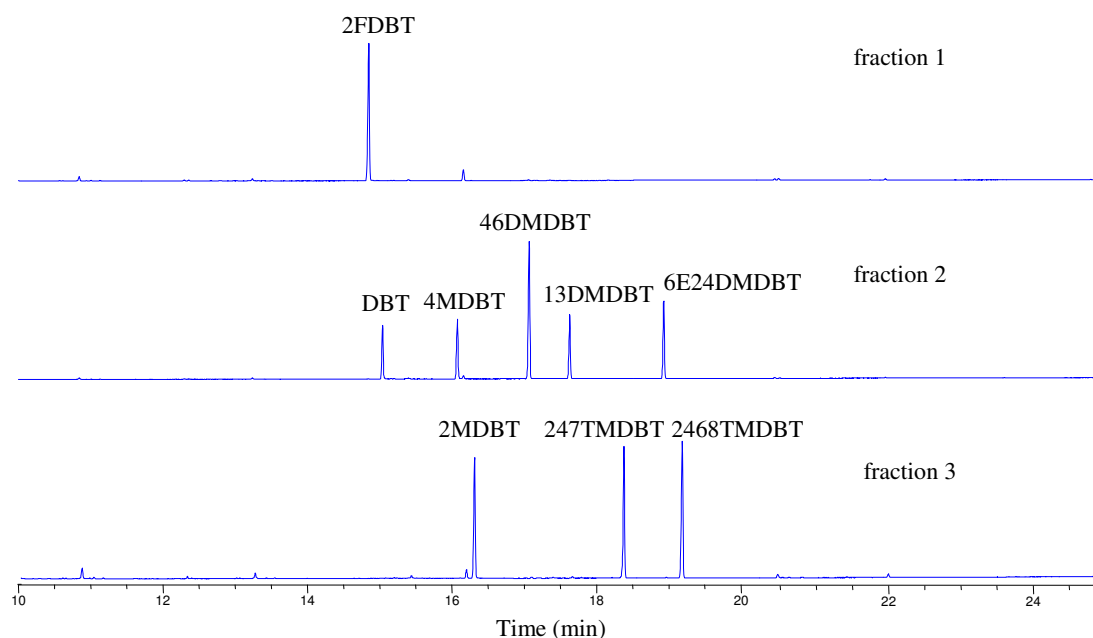


Figure 7.3: GC-FID chromatogram for the fractions obtained when a standard mixture of several dibenzothiophenes was injected onto Ag(I)-MP-silica phase [see figure 7.1(a) for the liquid chromatogram].

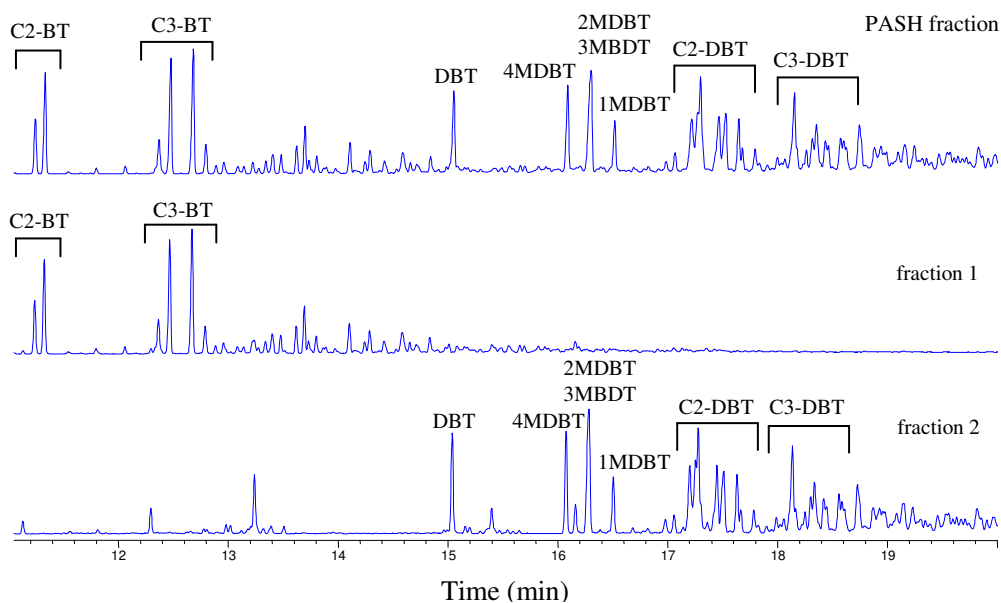


Figure 7.4: GC-FID chromatogram for the fractions obtained from a PASH fraction of a diesel on Ag(I)-MP-SG [see figure 7.1(b) for the liquid chromatogram] (Peaks in fraction 2 trace at 12.25 min and 13.21 min are impurities).

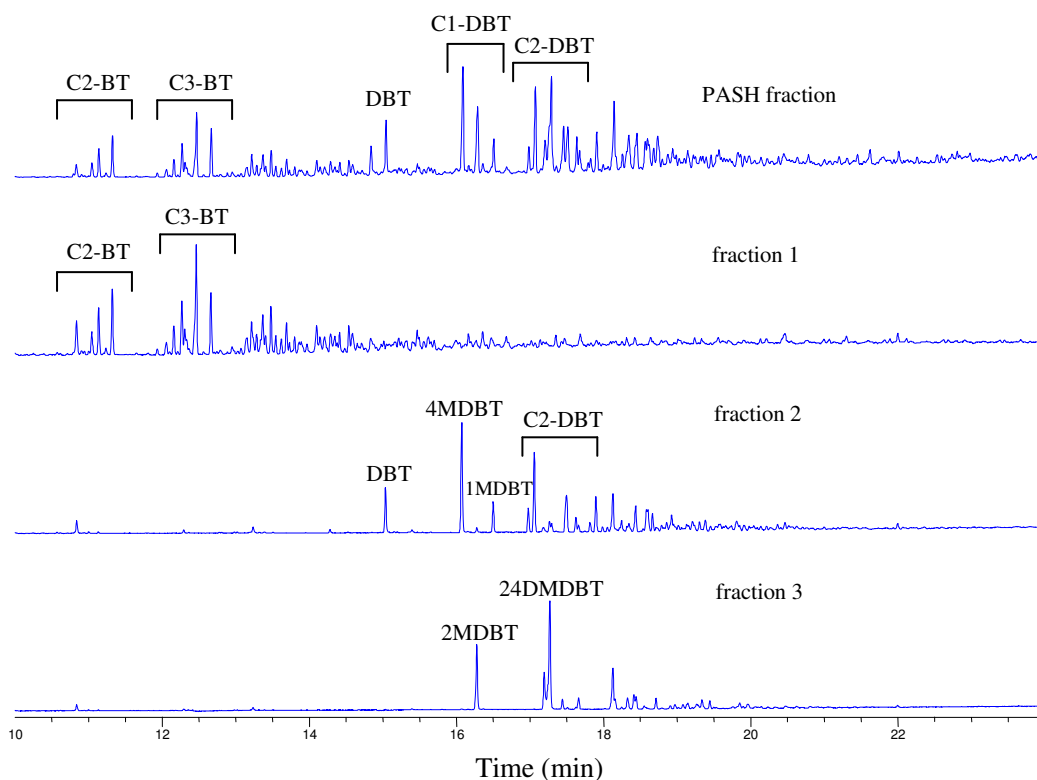


Figure 7.5: GC-FID chromatogram for the fractions obtained from a PASH fraction of Kirkuk crude oil on Ag(I)-MP-SG [see figure 7.1(c) for the liquid chromatogram].

When the PASH fraction of a diesel fuel was injected onto the Ag(I) phase, two fractions were collected as shown in the liquid chromatogram [figure 7.1(b)]. Figure 7.4 shows the gas chromatograms for the collected fractions. Gas chromatographic studies of these fractions show an enrichment of alkylated benzothiophenes in fraction 1 and dibenzothiophenes in fraction 2. Fraction 1 shows the elution of di-, tri- and higher alkylated benzothiophenes. There were no benzothiophenes present in fraction 2. Similar fractionation was also observed for the PASH fraction of a crude oil [figure 7.1(C)] and a vacuum gas oil [figure 7.1(d)] on the Ag(I) phase. Gas chromatograms obtained for the crude oil fractions are shown in the figure 7.5. A clear separation of benzothiophenes in fraction 1 and dibenzothiophenes in fractions 2 & 3 can be seen. Grouping of aromatic sulfur fractions by the number of rings is highly desirable prior to MS characterization for unambiguous interpretation of MS data.

## 7.5 Summary

The retention properties of polycyclic aromatic sulfur heterocycles on a silver(I)-loaded mercaptopropano silica gel was described. Polycyclic aromatic sulfur heterocycles (PASHs) and polycyclic aromatic hydrocarbons (PAHs) elute according to the number of pi electrons and therefore there is no particular effect of Ag(I)-S interactions. As sulfur increases the electron density of the aromatic ring, PASHs are retained more strongly than the corresponding PAHs but the difference is not very large. The effect of alkyl substituents on the retention of dibenzothiophenes was studied. This bonded phase was tested with the sulfur aromatic fraction from several real world samples for their separation into various compound classes. As group separation of PASHs from PAHs is not enough for complete analysis of PASHs because of large number of isomers. Further fractionation of PASHs into compound classes like benzothiophenes, dibenzothiophenes and benzonaphthothiophenes and so on will allow us to simplify the enormously complex samples so that high resolution mass spectrometry can be applied to a great advantage.

## 8 Mass spectrometric characterization of a vacuum residue

### 8.1 Mass spectrometry

Mass spectrometry is one of the basic analytical tools for identification, quantification and structure elucidation of organic compounds. It is a technique in which atoms or molecules from a sample are ionized, separated according to their mass to charge ratio ( $m/z$ ), and then recorded. The important components of a mass spectrometer are the inlet system, ion source, mass analyzer, detector, recorder and the vacuum system. Mass spectrometry (without fragmentation) is well suited for complex mixture analysis, because unlike other types of spectroscopy, the number of mass spectral peaks per analyte is of order one. Mass spectrometers with resolution higher than 10,000 are considered to be high resolution instruments. High resolution mass spectrometers are necessary to distinguish between ions with the same nominal (integer mass) but a different exact mass (due to different elemental compositions). This chapter briefly describes Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) used for identification of sulfur aromatics in a vacuum residue.

The recent success of FT-ICR-MS in the petroleum characterization derives to a large extent from recent advances in ion-source technology. Generation of odd-electron molecular ions from both electron impact and field desorption/field ionization (FD/FI) sustained petroleum mass spectral analysis for decades [99-102] and those techniques have been successfully coupled to FT-ICR mass spectrometers [103-106]. However, extensive fragmentation of aliphatic hydrocarbon chains and the need for highly volatile analytes severely limit application of electron ionization to petroleum samples. Fragmentation is deleterious, because generation of more than one signal per analyte ion can greatly complicate an already crowded mass spectrum. The generation of quasimolecular ions e.g.,  $(M+H)^+$  and  $(M-H)^-$  by Chemical Ionization (CI), Electrospray Ionization (ESI), Laser Desorption (LD) and MALDI has enabled the detailed characterization of previously inaccessible low-volatile high-molecular weight species. *Fenn* and *Zhan* first attempted to apply ESI to a range of petroleum products, including gasolines, jet fuels, diesels and crude oils [107]. Although the



quadrupole mass spectrometer applied in the study did not have sufficient mass resolution to separate isobaric molecules and determine their composition, it clearly demonstrated that petroleum products contain many polar molecules that can be ionized by ESI.

## 8.2 Electrospray ionization (ESI)

This is the softest ionization method. Ionization is produced by spraying a sample solution through a conducting capillary tube at a high potential. An electrospray (ES) is produced by applying a strong electric field to a liquid passing through a capillary tube with a weak flux ( $1-10 \mu\text{L min}^{-1}$ ). The electric field is obtained by applying a potential difference of 3-6 kV between this capillary and the counter electrode, which are separated by 0.3-2.0 cm. This field induces a charge accumulation at the liquid surface located at the end of the capillary, which will then break up to form highly charged droplets. As the solvent contained in these droplets evaporates, they shrink to the point where the repelling coulombic forces come close to their cohesion forces, thereby causing their explosion. Eventually after a cascade of further explosions the highly charged ions desorb. Electrospray mass spectra normally correspond to a statistical distribution of multiply charged molecular ions obtained from protonation  $(M + nH)^{n+}$ , while avoiding the contributions from dissociations or from fragmentations.

## 8.3 Fourier transform ion cyclotron resonance mass spectrometry

Ion cyclotron resonance mass spectrometry is a technique in which ions are subjected to a simultaneous radiofrequency electric field and a uniform magnetic field, causing them to follow spiral paths in an analyzer chamber. By scanning the radiofrequency or magnetic field, the ions can be detected sequentially.

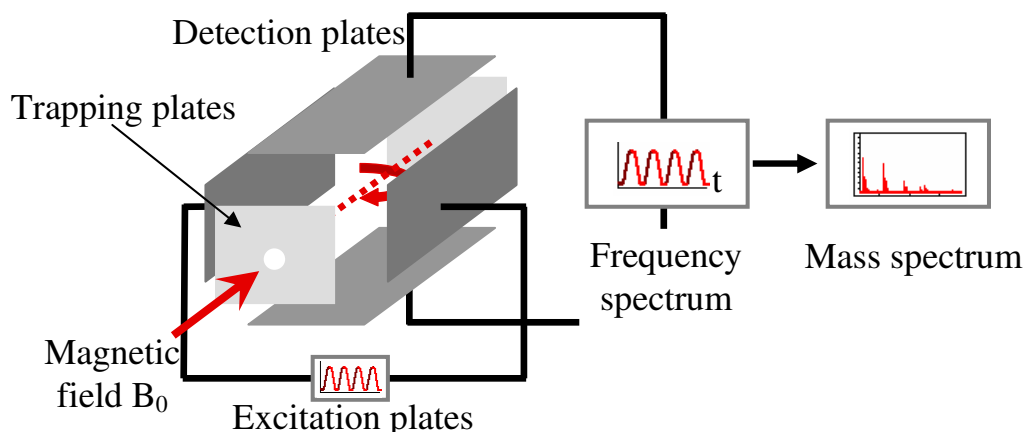


Figure 8.1: Schematic representation of a cubic FT-ICR cell.

In an FT-ICR spectrometer (figure 8.1) ions are trapped electrostatically within a cubic cell in a constant magnetic field. A covalent orbital (“cyclotron”) motion is induced by the application of a radio-frequency pulse between excitation plates. The orbiting ions generate a faint signal in the detection plates of the cell. The frequency of the signal from each ion is equal to its orbital frequency, which in turn is inversely related to its  $m/z$  value. The signal intensity of each frequency is proportional to the number of ions having that  $m/z$  value. The signal is amplified and all the frequency components are determined, yielding the mass spectrum. If the pressure in the cell is very low, the ion orbital motion can be maintained over many cycles and the frequency can be measured with high precision. However, that trapping potential perturbs the relationship of the ICR frequency to  $m/z$  [109]. To obtain subparts-per-million mass accuracy needed for petrochemical analysis, the frequency-to- $m/z$  conversion must be determined from the measured ICR frequencies and known masses of calibrant ions of at least two different  $m/z$  values in the same mass spectrum [108]. The FT-ICR instrument can therefore be used to generate very high resolution spectra for complex petroleum fractions.

#### 8.4 Mass resolution and mass accuracy

For complex mixture analysis, the high mass resolving power of FT-ICR can separate signals from ions of very similar masses (e.g., the 0.0034 Da split between isobars differing in elemental composition by  $\text{SH}_4$  vs  $\text{C}_3$ , both with a nominal mass of 36 Da). Resolution of such isobars allows speciation of chemical classes that, for the same mixture, are not observed with other MS techniques [109]. Of the several

figures of merit for ICR performance that improve linearly or quadratically as a function of magnetic field strength, two that are especially significant for complex mixture analysis are the maximum number of trapped ions (which limits the dynamic range) and the decreased tendency for coalescence of closely spaced peaks [110, 111]. Considerable improvement in those respects has been realized with the advent of high-field ( $> 7$  T) superconducting solenoid ICR magnets that provide high temporal stability ( $< 50$  ppb/h field drift) and spatial homogeneity ( $< 10$  ppm peak-to-peak variation within the measurement volume), both of which enable highly accurate mass measurement. Finally, the ability to measure ICR frequencies with parts-per-billion accuracy imparts potentially the same accuracy to the measurement of  $m/z$ . FTICR mass accuracy is best at low trapping potential. Thus few ions are in the trap and the signal to noise ratio (S/N) is relatively low. However, the dynamic concentration range (ratio of strongest to weakest signal) and the need for accurate relative abundances for petroleum samples require a high S/N. To reconcile these contradictory requirements, high-resolution, high-mass-accuracy FT-ICR mass spectra of petrochemicals are usually generated by ensemble-averaging numerous ( $\sim 50$ - $100$ ) scans, each acquired at a low ( $\sim 0.5$  V) trapping potential. In order to study the importance of liquid chromatographic steps involved in the sample preparation for PASHs, we have performed the mass spectrometric studies of the vacuum residue itself and of the LEC fractions obtained after liquid chromatographic separations.

## 8.5 Experimental section

### 8.5.1 Vacuum residue sample

The vacuum residue sample investigated in this study was provided by the Institut Francais du Petrole, Vernaison, France. It is a deeply hydrodesulfurized vacuum residue with a sulfur content of 0.39 wt %.

### 8.5.2 Chromatographic separations

Using column chromatography, the vacuum residue sample was fractionated into saturate, aromatic and resin compounds according to the SARA method [97]. Ligand exchange chromatographic separation of polycyclic aromatic sulfur

heterocycles was performed on a Pd(II)-ACDA-silica gel to obtain two fractions (LEC fraction 1 and LEC fraction 2) as explained in the previous chapter 4 .

### 8.5.3 ESI FT-ICR-MS analysis

The ionization of aromatic compounds with electrospray techniques is not very efficient [112, 113]. For PASHs, Pd(II) has been used as a sensitivity enhancing reagent in standard resolution experiments with an ESI ion trap MS [113]. This technique, however may show problems with samples of unknown sulfur content, as concentration ratios of Pd(II) and sulfur are crucial. A derivatization of organic sulfur to methylsulfonium salts to achieve selectivity toward sulfur aromatics for ESI-FT-ICR mass spectrometric analysis of a vacuum residue was recently reported [114]. The vacuum residue, LEC fraction 1 and LEC fraction 2 were methylated at the sulfur atom as described by *Acheson and Harrison* [115]. Approximately 1 mmol of sulfur compound and 1 mmol of iodomethane were dissolved in 3 mL of dry 1,2-dichloroethane (DCE). To this solution 1 mmol silver tetrafluoroborate in 2 mL DCE was added and yellow silver iodide precipitated immediately. The mixture was allowed to react for 48 h followed by filtration of the precipitate. The precipitate was washed with DCE and the combined extracts were rotavapoured before mass spectrometric analysis. Figure 8.2 shows the high resolution mass spectra of the vacuum residue.

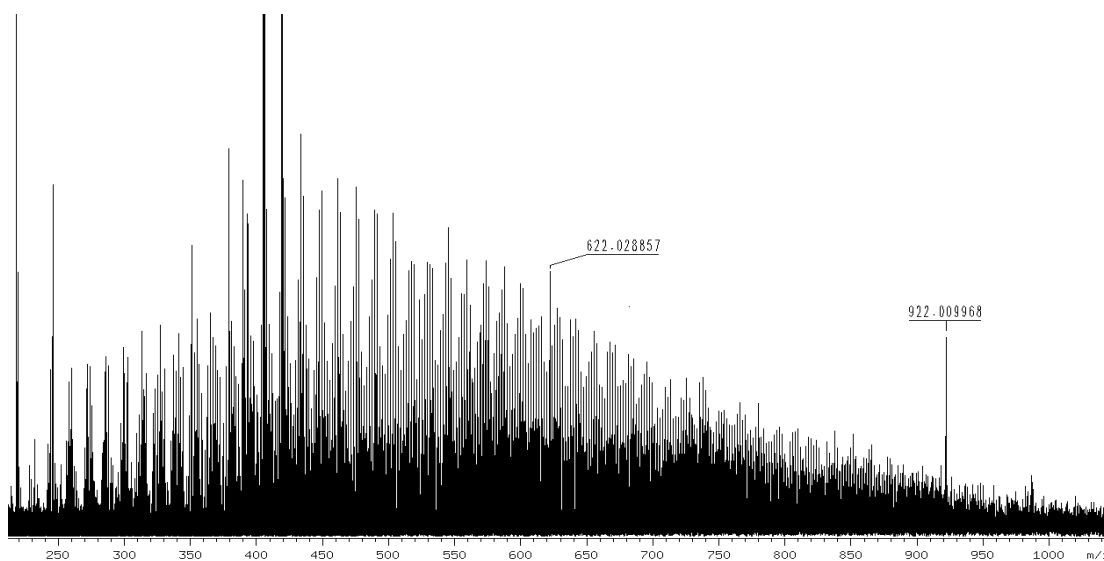


Figure 8.2: High resolution mass spectra of the vacuum residue. Two internal calibrants are identified by their exact masses.

## 8.6 Data analysis

Due to the high resolution power of FT-ICR instruments of below 1 ppm, the accuracy of the measured signals is sufficiently precise to calculate the underlying elemental compositions [104]. A common misconception is that mass accuracy alone provides the elemental composition assignments. However, even with subparts-per-million mass accuracy and knowledge of the ionic charge state, elemental compositions may be unambiguously assigned only up to ~ 400 Da. Elemental compositions for higher-mass ions required data reduction based on the Kendrick mass scale and helpful spacings in the mass spectrum [116, 117].

### 8.6.1 Kendrick mass scale

For ultrahigh-resolution measurements, it is useful to convert measured mass to the Kendrick mass [118], which sorts compounds into homologous series according to alkylation, classes (number of heteroatoms), and types (rings plus double bonds). For example, the IUPAC mass of CH<sub>2</sub>, 14.0157 Da, becomes a Kendrick mass of 14.0000 Da. So,

$$\text{Kendrick mass} = \text{IUPAC mass} \times (14.00000/14.01565)$$

Compounds with the same nitrogen, oxygen, and sulfur composition and the same number of rings plus double bonds but different number of CH<sub>2</sub> units will differ in Kendrick mass by integer multiples of 14.0000 Da. These compounds are thus identified as members of homologous series. Stated another way, members of a homologous series will have same Kendrick mass defect (KMD) defined as [Kendrick nearest-integer (nominal) mass - Kendrick exact mass] x 1000, which is unique to that series. For example, the alkylation series of simple alcohols (methanol, ethanol, propanol, butanol, etc.) share the same heteroatom composition (O1) and number of rings plus double bonds but differ simply in the number of CH<sub>2</sub> units. Therefore, Kendrick normalization yields a series with an identical mass defect that appears as a horizontal row in a plot of KMD versus Kendrick nominal mass (KNM). This series is easily distinguished from species of other classes and types. Most notably, unambiguous assignment of a single elemental composition for a low-mass member

of a homologous series serves to identify all other members of that series. In this way, Kendrick mass sorting extends elemental composition assignment to masses up to three times higher than would be possible based on mass-measurement-accuracy alone. Therefore a Kendrick mass plot represents a compact display of all the data. An efficient data reduction procedure based on the Kendrick mass scale has already been reported [116]. We employed this approach for the data analysis of the thousands of mass signals obtained from FT-ICR-MS measurements. The work flow of this procedure is shown in figure 8.3.

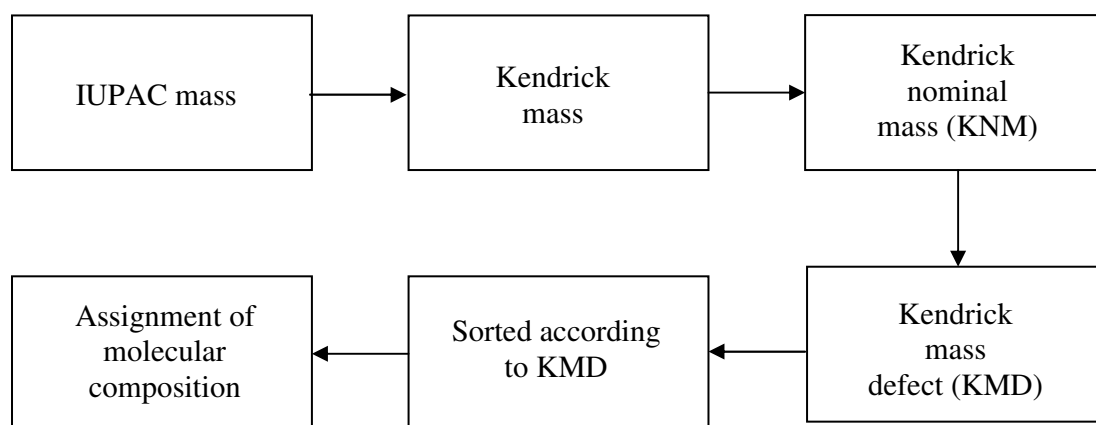


Figure 8.3: Flow diagram of the data analysis.

The mass peaks are divided into 14 nominal mass series, followed by sorting homologous series according to their Kendrick mass defects (KMDs). Identification of compound type series is based on the averaged KMD of each series, thus eliminating time-consuming procedures for the determination of elemental composition of individual peaks. The Kendrick mass defects are related to the hydrogen deficiency index  $Z$  which is defined as the number of hydrogen atoms less than a completely saturated compound with the same number of carbon atoms and without rings. For a given elemental composition  $^{12}\text{C}_{(c-x)}^{13}\text{C}_x\text{H}_h\text{S}_s$ , is  $Z=h-2c$ . However,  $Z$  being negative and attaining the value  $-2$  for a compound with no rings or double bonds, this definition is inconvenient in the present discussions and therefore, the sum of rings and double bonds is defined as Double Bond Equivalent (DBE).

## 8.7 Results and discussion

### 8.7.1 Vacuum residue without prefractionation

The methylation reaction used derivatized both sulfur compounds and nitrogen heterocycles present in the vacuum residue. Therefore, we have found several nitrogen heterocycles and sulfur compounds in our analysis.

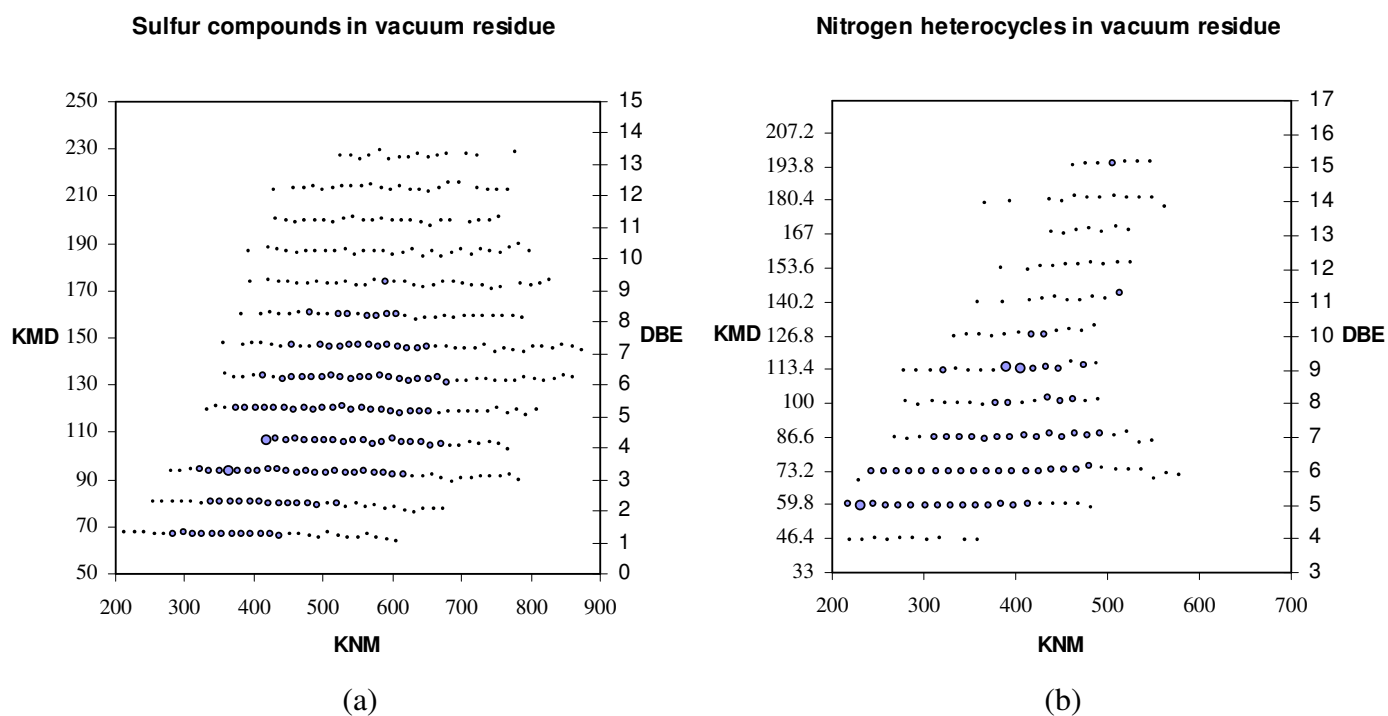

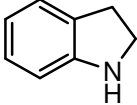
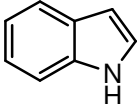
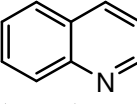
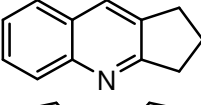
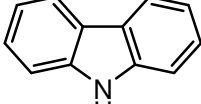
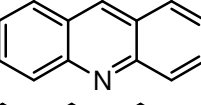
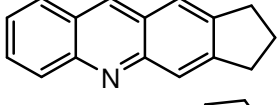
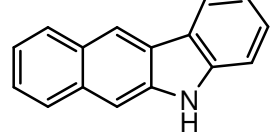
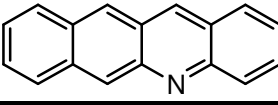


Figure 8.4: Kendrick mass defect (KMD) plots of signals from the vacuum residue (a) for sulfur compounds (b) for nitrogen heterocycles.

The Kendrick mass plot obtained for the sulfur aromatics and the nitrogen heterocycles present in the vacuum residue is shown in figure 8.4. As explained above, the KMDs on the y-axis are related to the sum of rings and double bonds, defined as DBE of the compounds.

Table 8.1: Possible parent structures of nitrogen heterocycles which can be assigned to the obtained KMD values from high resolution mass spectral data.

Possible Parent Structures	Name	Double Bond Equivalent (DBE)	Kendrick Mass Defect (KMD)
	Pyridines	4	46.06
	Indolines	5	59.46
	Indoles	6	72.86
	Quinolines	7	86.26
	Naphthoquinolines	8	99.66
	Carbazoles	9	113.06
	Acridines	10	126.46
	Naphthenobenzoquinolines	11	139.86
	Benzocarbazoles	12	153.26
	Benzacridines	13	166.66

The possible parent structures for the nitrogen heterocycles are shown in the table 8.1. The poisoning effect of nitrogen compounds on thiophene hydrodesulfurization is described elsewhere [119]. The sample preparation for the analysis of nitrogen heterocycles in crude oils using FT-ICR-MS done by dissolving the oil samples in known amount of acetic acid was already reported [120]. As the focus of this study is on PASHs, their parent structures are discussed in detail. The



majority of compounds show a DBE value between 1, which corresponds to one double bond or an aliphatic ring and 13 which allows for the existence of up to four condensed aromatic rings. Compounds with a KMD of approximately 64 represent aliphatic sulfur compounds with a DBE of 1, i.e. they contain one aliphatic ring or one double bond and a single sulfur atom. A KMD of approximately 77 translates into a DBE of 2 which could represent parent structures like dihydrothiophene. Thiophenes with increasing alkyl chain lengths are seen in the figure 8.4 (a) with a KMD of 90 and a DBE of 3. A Kendrick mass defect of approximately 130.6 which translates into  $DBE = 6$  for the compounds containing one sulfur atom could represent benzothiophenes with an increasing number of carbon atoms in the side chains toward higher Kendrick nominal masses.

The number of possible isomers increases as more rings are added. For instance, several sulfur aromatic parent structures that can be visualized for compounds with a KMD of 144 and  $DBE = 7$  are 2- and 3-phenylthiophenes, tetrahydrodibenzothiophenes and cyclopentabenzothiophenes. Similarly, compounds with KMD of 157.4 and  $DBE = 8$  could represent parent structures like indenothiophenes, indanylthiophenes and cyclopentadienylbenzothiophenes. All these parent structures were already reported to be present in an Austrian shale oil [60, 61, 63]. As mass spectrometry can not distinguish between isomers, it is difficult to determine the exact parent structures of the sulfur aromatics present in high boiling fractions like vacuum residue only by identifying them based on their class (number of heteroatoms) and type (KMD).

## 8.8 LEC fractions of vacuum residue

Chromatographic methods often provide the most powerful approach for the analysis and separation of complex mixtures of wide range of compounds. Using column chromatography the nonpolar polycyclic aromatic compounds were isolated from the vacuum residue as described in the SARA method [97]. These aromatic compounds were further fractionated on a Pd(II)-containing stationary phase (as explained in previous chapter 4) to obtain LEC fraction 1 and LEC fraction 2. The Kendrick mass plots obtained for these fractions are shown in figure 8.5.

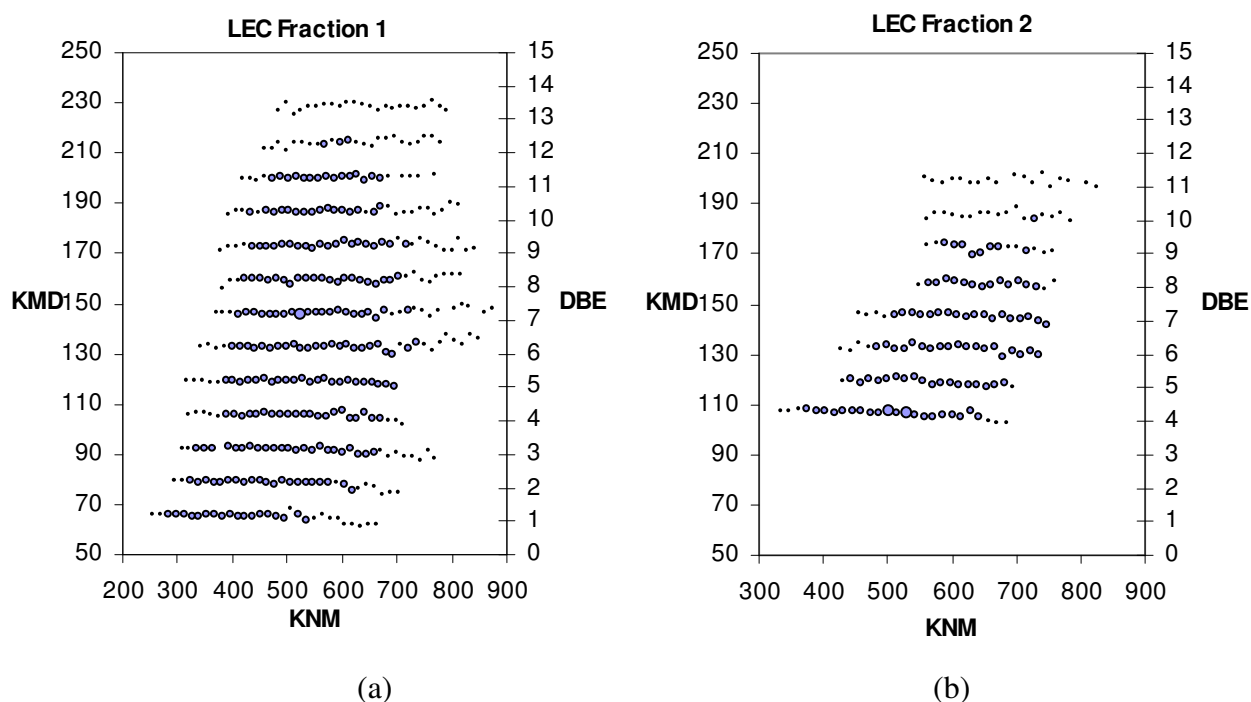


Figure 8.5: Kendrick mass defect plots of (a) LEC fraction 1 and (b) LEC fraction 2 of a highly desulfurized vacuum residue.

In general, compounds containing thiophene rings that are not condensed with other aromatic systems are weakly retained on the Pd(II) column and elute in fraction 1 but as shown in figure 8.5 (b) there are some compounds with DBE of 4 and 5. In this context, it is not yet clear about the type of thiophene isomers that elute in LEC fraction 2. Thiophenes rings condensed with other aromatic rings are more strongly retained and elute in fraction 2 with a more polar solvent. The enormous number of sulfur aromatic compounds present in LEC fraction 1 compared to LEC fraction 2, show that the deeply desulfurized vacuum residue has a higher concentration of compounds containing thiophene rings that are not condensed with other aromatic rings. Isomers of aromatic sulfur compounds with similar KMDs are found in both the LEC fractions as shown in figure 8.6.

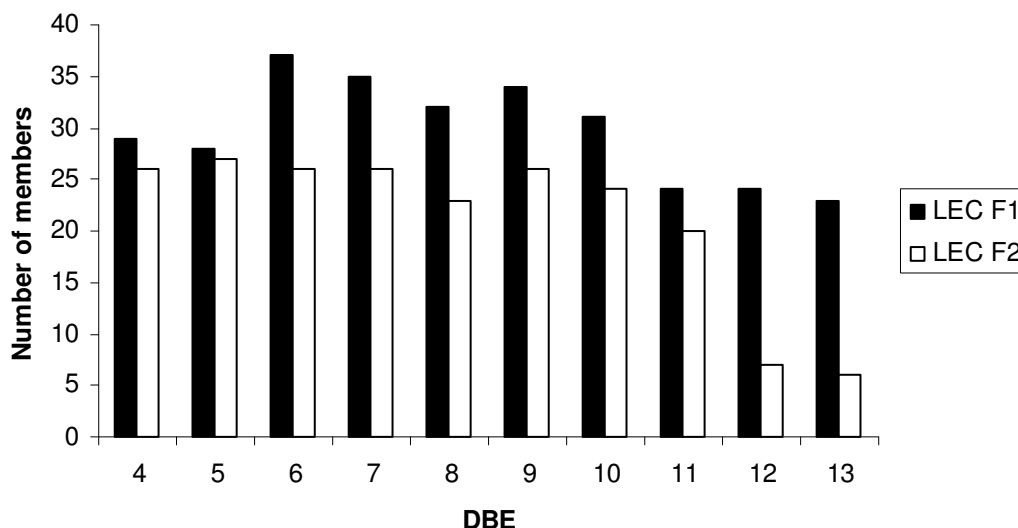



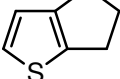
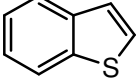
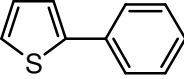
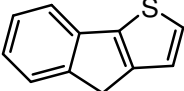
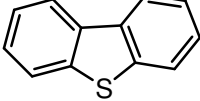
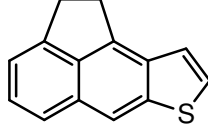
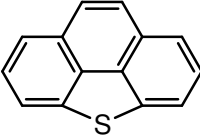
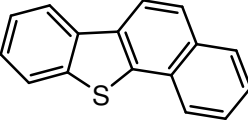


Figure 8.6: Bar diagram showing the number of isomeric pairs of aromatic sulfur compounds having the same KMDs present in both LEC fraction 1 (black) and LEC fraction 2 (white).

Based on the retention properties of several polycyclic aromatic sulfur heterocycle model compounds (discussed in chapter 4.) and high resolution mass spectral data obtained for the LEC fractions, we were able to delineate some structural properties of several recalcitrant PASHs in both the LEC fractions. The possible parent structures found in both the LEC fractions are shown in the table 8.2. Benzothiophenes are retained by the Pd(II) column so they elute in LEC fraction 2. Compounds with a KMD of approximately 130.6 and DBE = 6 in the LEC fraction 2 could represent benzothiophenes. Compounds with a KMD of 144.0 and DBE = 7, present in the LEC fraction 1 represent phenylthiophenes as these parent structures are known to elute in fraction 1. Other conceivable structures for DBE = 7 are tetrahydrodibenzothiophenes and cyclopentabenzothiophenes. However these compounds elute in fraction 2 and appear in figure 8.5 (b). Compound classes with DBE = 8 include indenothiophenes and indanylthiophenes. Indenothiophenes behave similar to phenylthiophenes on the Pd(II) column and elute in fraction 1. Indanylthiophenes are substituted thiophenes and are also expected to elute in fraction 1. A group of compounds appearing at DBE of 9 in figure 8.5 (b) could be dibenzothiophenes or naphthothiophenes as these compounds elute in fraction 2.

Table 8.2: Possible parent structures of aromatic sulfur heterocycles present in the LEC fractions.

Possible Parent Structures	Name	DBE	KMD in mmu	LEC fraction
	Tetrahydrothiophenes	1	63.63	1
	Dihydrothiophenes	2	77.03	1
	Thiophenes	3	90.43	1
	Naphthenothiophenes	4	103.83	1
	Benzothiophenes	6	130.60	2
	Phenylthiophenes	7	144.00	1
	Indenothiophenes	8	157.42	1
	Dibenzothiophenes	9	170.82	2
	Acenaphthenothiophenes	10	184.22	2
	Phenanthro- [4,5- <i>bcd</i> ]thiophene	11	197.6	2
	Benzo[ <i>b</i> ]naphtho- [2,1- <i>d</i> ]thiophene	12	211.0	2

## 8.9 Summary

Polycyclic aromatic sulfur heterocycles (PASHs) show very poor reactivity in catalytic hydrodesulfurization processes in refineries, especially those in high-boiling fractions and distillation residues. This chapter briefly describes FT-ICR-MS employed for the analysis of sulfur aromatics in a vacuum residue. To study the importance of liquid chromatographic steps involved in the sample preparation for PASHs, we have performed the mass spectrometric studies of the vacuum residue itself and of the LEC fractions obtained after liquid chromatographic separations. A comparative study of mass spectral data obtained from a vacuum residue without prefractionation and its LEC fractions (fractions 1 and 2) is presented. As mass spectrometric data (without fragmentation) cannot distinguish between isomers, the chromatographic separation of sulfur aromatics from vacuum residue on the Pd(II)-ACDA phase was highly useful in identifying the parent structures of the compounds obtained in the fractions unambiguously.

## 9 Summary

Refiners worldwide are facing a tough challenge to produce increasingly cleaner fuels to comply with current low legal limits for sulfur in fuels. Various technologies are used but dominating is the catalytic hydrodesulfurization (HDS) process which is operated at elevated temperatures (300-350 °C) and hydrogen pressures (50-100 bar). The catalytic hydrodesulfurization (HDS) is highly efficient in removing the sulfur in thiols, sulfides and disulfides. Thiophenic compounds can be more difficult to desulfurize and thus some polycyclic aromatic sulfur heterocycles (PASHs) survive the reaction. Such compounds are present in considerable amounts in crude oils and often exhibit very complex patterns of alkylated derivatives. The objective of this work is to develop metal ion containing stationary phases for the isolation and identification of PASHs from various petroleum fractions to define the structural features of those PASHs which are recalcitrant to the desulfurization process. Such information is of great help in the development of new catalysts and improved refinery processes.

The very high complexity of petroleum fractions demands a prefractionation of the recalcitrant PASHs prior to mass spectrometric characterization. Here we investigated the liquid chromatographic properties of several sulfur aromatic model compounds on stationary phases containing Pd(II) and Ag(I) ions. A stationary phase containing a palladium(II)-complex was previously shown to be efficient for the separation of PASHs in lighter petroleum fractions. In this work, we characterized this ligand exchange chromatographic phase using a large number of sulfur aromatic model compounds that were synthesized for the purpose. In general, compounds containing thiophene rings that are not condensed with other aromatic systems are weakly retained and elute in a first fraction with the polycyclic aromatic hydrocarbons. Thiophene rings condensed with other aromatic rings are more strongly retained and elute in a later fraction with a more polar eluent. If the sulfur is in a non-aromatic ring, the compound is irreversibly retained by the Pd(II) ions. Some steric effects are seen in compounds with alkyl or aryl substituents close to the sulfur atom but in general they do not interfere strongly with the complexation. Thus it seems

possible to separate groups of aromatic sulfur compounds according to their complexation properties.

Even though Pd-ACDA silica gel is used for the isolation of PASHs from petroleum samples, it is not without its limitations. Several attempts have been made to develop new stationary phases by incorporating metal ions [especially palladium(II) ions] onto the silica gels, in order to take the advantage of their Lewis acid properties in complexing with different organic sulfur compounds.

The ions were either deposited as salts onto the gel, electrostatically bound by e.g. ion-exchange phases (Luna SCX and Excil SCX) or complexing groups of a modified gel (aminopropano silica gel). The sol-gel process was also used to incorporate palladium ions into silica gels. None of these gels incorporated with Pd(II) ions were able to separate PASHs from PAHs.

Recent studies have shown that an (S,S) coordination was preferred for transition metal complexes of ACDA. An attempt was made to replace the bulky ligand ACDA with a mercaptopropano group. A Pd(II) loaded mercaptopropano silica gel [Pd(II)-MP silica gel] was shown to have similar retention properties as the Pd(II)-ACDA silica gel and therefore it can be used for the isolation of sulfur aromatics from petroleum fractions. The advantage of Pd(II)-MP silica gel over Pd(II)-ACDA silica gel is its easy synthesis.

A comparable Ag(I)-loaded stationary phase was similarly investigated. It shows that PASHs are retained based on the number of  $\pi$ -electrons in the aromatic rings. The interaction of Ag(I) with sulfur in PASHs is weaker than that of Pd(II). However, the degree of alkylation plays a certain role for the retention properties. This phase was used for further separation of PASHs into compound classes like benzothiophenes, dibenzothiophenes, benzonaphthothiophenes and related compounds. The several fractionations according to defined criteria allow us to simplify the enormously complex samples so that high-resolution mass spectrometric analysis can be applied to great advantage.

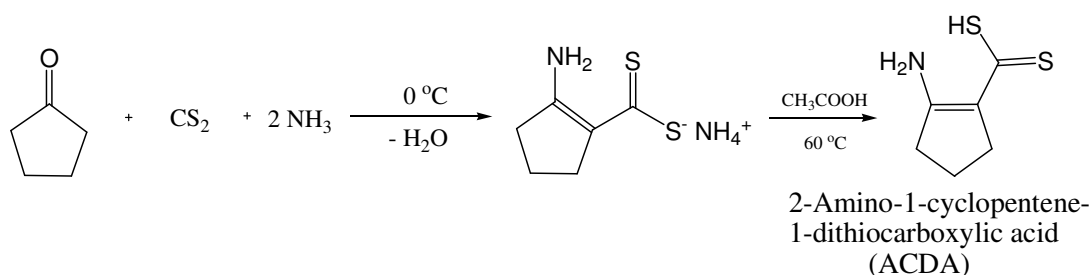
## 10 Appendix

### 10.1 Synthesis of Pd(II)-ACDA silica gel [49,50,53]

#### 10.1.1 Synthesis of aminopropano silica gel

4 g of LiChrosorb Si 100 (10  $\mu\text{m}$ , dried at 160  $^{\circ}\text{C}$  for 24 h) was refluxed in a solution of 5 mL 3-aminopropanotrimethoxysilane in 20 mL dry toluene. The reaction product was filtered off and washed successively with toluene and methanol. The obtained aminopropano silica gel was dried at 50  $^{\circ}\text{C}$  in an oven.

#### 10.1.2 Synthesis of 2-Amino-1-cyclopentene-dithiocarboxylic acid (ACDA)



A mixture of cyclopentanone (12.5 g, 150 mmol), carbon disulfide (15 g, 195 mmol) and 150 mL of aqueous ammonia (25 %) was stirred below 0  $^{\circ}\text{C}$  for 12 h. The yellow solid product was collected, washed with ether and dried. The crude product was recrystallized from ethanol. 4 g (0.022 mol) of the ammonium salt of ACDA was dissolved in 50 ml of acetic acid at 70  $^{\circ}\text{C}$ . The obtained orange colored solution was cooled to room temperature and 100 ml of water was added and stirred for 2 h. The yellow solid material which separated from the solution was collected and recrystallized from methanol (yield 40 %).

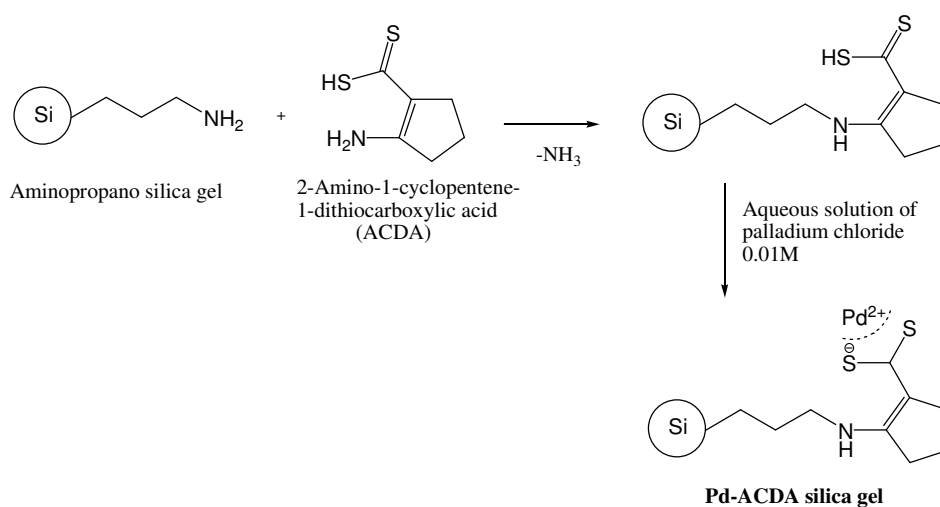
CHNS analyses of ACDA

	C [%]	H [%]	N [%]	S [%]
calculated	45.28	5.70	8.80	40.22
Measurement 1	45.18	5.42	8.78	42.50
Measurement 2	45.24	5.26	8.79	42.10



### 10.1.3 Synthesis of ACDA-functionalised silica gel

2 g of aminopropano silica gel (synthesized as described earlier) was added to a solution of 0.3 g of ACDA dissolved in 5 mL of methanol and refluxed for 5 hr. The apparatus was purged with nitrogen during the reaction. After cooling to room temperature, the ACDA bonded silica was filtered and washed with methanol.



#### CHNS analysis of ACDA-bonded silica gel

Measurement	C (%)	H (%)	N (%)	S (%)
1	12.49	2.16	2.16	2.89
2	12.67	2.28	2.32	3.63
3	12.73	1.99	2.34	3.81
Loading [mmol/g]	1.05	2.14	2.27	3.44

The ACDA-bonded silica was further treated with 150 mL aqueous solution of palladium chloride (0.01 M) in a conical flask to obtain Pd(II)-ACDA silica gel.

## 10.2 Synthesis of silver(I)-loaded mercaptopropano silica gel (Ag-MPSG) [95]

Silica gel (Lichrosorb Si 100, 10  $\mu\text{m}$  particle size) was dried at 160  $^{\circ}\text{C}$  for 24 h. 6 g of dried silica gel was refluxed in a solution of 20 mL 3-mercaptopropanotrimethoxysilane in 80 mL dry toluene for 5 h. The reaction product was filtered off and washed successively with toluene and methanol. The mercaptopropano-silica gel (MPSG) was dried at 50  $^{\circ}\text{C}$  in an oven.

To about 4 g of MPSG 6 mL of 1 M silver nitrate solution and 10-20 mL of water were added and the mixture was stirred for about 30 min. The solid was filtered off and washed with water and methanol.

## 10.3 Synthesis of model compounds

### 10.3.1 Synthesis of 2,3-Dihydro-2-methylbenzo[*b*]thiophene [54]

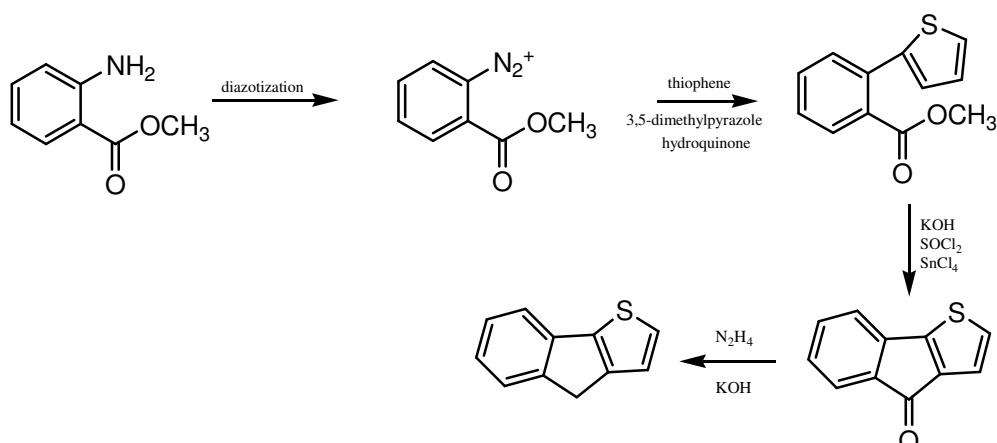
(148mg, 1mmol) of 2-methylbenzothiophene was dissolved in 5 ml of trifluoroacetic acid, (232 mg, 2 mmol) triethylsilane was added and the mixture was stirred at 50  $^{\circ}\text{C}$  for 5 h. The resultant mixture was neutralized with 1 M NaOH and was extracted with ether. The ether extract was washed with water, brine and dried over anhydrous  $\text{MgSO}_4$ . The evaporation of the ether extract yielded 102 mg of 2,3-Dihydro-2-methylbenzo[*b*]thiophene.

Yield: 69 %

Purity: 80 % [(GC-MS) and the rest 20 % was unreacted 2-methylbenzothiophene]

MS: 150 (94 %,  $\text{M}^+$ ), 135 (100 %,  $\text{M}^+ - \text{CH}_3$ )

### 10.3.2 Synthesis of 4H-Indeno[1,2-*b*]thiophene



#### 2-(2-Thienyl)benzoate [55]

To a mixture of 10 g (40 mmol) of 2-(methoxycarbonyl)benzene diazoniumtetrafluoroborate (prepared from diazotization of methyl anthranilate) and 30 mL of thiophene, a solution of 4 g (41 mmol) of 3,5-dimethylpyrazole and 0.5 g (4.5 mmol) of hydroquinone in 30 mL of thiophene was added dropwise. The mixture was stirred at 0 °C for 3 h and then at room temperature (28 °C) for an additional 1 h. The reaction mixture was evaporated in vacuo to remove excess of thiophene and the condensate was column chromatographed on silica gel with toluene as eluant. The toluene fraction was evaporated in vacuo to yield 3.45 g (34.5 %) of 2-(2-thienyl)benzoate.

MS(GC-MS): 218 (100 %, M<sup>+</sup>), 187 (70 %, M<sup>+</sup> - OCH<sub>3</sub>)

#### 4H-Indeno[1,2-*b*]thiophen-4-one [56]

To a three necked 100 mL flask, fitted with a calcium chloride drying tube, containing 2.5 g (12 mmol) of 2-(2-thienyl)benzoic acid (synthesized from the saponification of 2-(2-thienyl)benzoate) dissolved in 25 mL of dry toluene, 0.7 mL dry N,N-dimethylformamide and 1.2 mL thionyl chloride were added. The solution was refluxed for 4 h and toluene was evaporated in vacuo. A brown solution of acid chloride was obtained.

The acid chloride obtained above was dissolved in dry toluene and was cooled to  $-2\text{ }^{\circ}\text{C}$ . A solution of 2 mL anhydrous stannic chloride in 8 mL dry toluene was added at such a rate as to keep the temperature below  $4\text{ }^{\circ}\text{C}$ . After the complete addition, the dark mixture was stirred for 10 min with cooling and for a further 1 h without external cooling. The dark mixture was poured onto a slurry of 75 mL ice and 35 mL 1 M hydrochloric acid. The layers were separated and the aqueous layer was extracted with toluene (100 mL) in three portions. The toluene extract was washed with water, 1 M NaOH, brine and dried over  $\text{MgSO}_4$ . Concentration of this extract gave 1.8 g (yield 75 %) 4H-Indeno[1,2-*b*]thiophen-4-one.

MS(GC-MS): 186 (100 %,  $\text{M}^+$ ), 158 (25 %,  $\text{M}^+ - \text{CO}$ )

#### **4H-Indeno[1,2-*b*]thiophene**

A mixture of 50 mg of 4H-Indeno[1,2-*b*]thiophen-4-one 0.1 mL hydrazine monohydrate, 10 mg potassium hydroxide and 1 mL diethylene glycol in a 10 mL flask fitted with a reflux condenser was heated to  $195\text{ }^{\circ}\text{C}$  over a 1 hr period and was maintained at this temperature another hour. The reaction mixture was cooled, water (3 mL) was added, and distilled. This procedure was repeated until 10 mL distillate was collected. The distillate was extracted with three portions of ether. The combined ether solutions were washed with water, brine and dried over  $\text{MgSO}_4$ . The evaporation of the dried ether extracts yielded 20 mg of 4H-Indeno[1,2-*b*]thiophene. (yield 40 %).

Purity: 97 %

MS (GC-MS): 172 (65 %,  $\text{M}^+$ ), 171 (100 %,  $\text{M}^+ - \text{H}$ )

$^1\text{H-NMR}(\text{CDCl}_3)$ :  $\delta/\text{ppm} = 7\text{--}7.6$  (m, 6H, aromatic H) and 3.61 (s, 2H,  $\text{CH}_2$ )

### **10.3.3 Synthesis of 5,5'-Dipropyl-2,2'-bithiophene**

#### **2-Propyl-5-bromothiophene [57]**

1 g (8 mmol) of 2-propylthiophene was dissolved in 2.5 mL of dry dimethylformamide and a solution of 1 g N-bromosuccinimide in 2.5 mL dry dimethylformamide was added. The mixture was stirred at room temperature for 24 h after which it was poured into 50 mL of water and extracted with diethylether

(3 x 15 mL). The combined ether extracts was washed with water, dried over MgSO<sub>4</sub>, filtered and evaporated under reduced pressure. The crude product 2-propyl-5-bromothiophene obtained was used for further reaction.

MS (EI, 70 eV): 206 (30 %, M<sup>+</sup>), 177 (100 %, M<sup>+</sup>-C<sub>2</sub>H<sub>5</sub>)

### **5,5'-Dipropyl-2,2'-bithiophene [58]**

The crude product 200 mg (1 mmol) 2-propyl-5-bromothiophene was dissolved in dichloromethane and 0.5 g of anhydrous, finely powdered aluminium chloride was added to it. This mixture was stirred for 12 hr and was poured into about 10 mL of water and a little crushed ice contained in a 50 ml flask. Decomposition occurs with the evolution of heat and a dark oil separates out of the solution. The oily layer was collected washed with water, sodium hydroxide solution, again with water and finally dried over anhydrous magnesium sulfate to obtain 102 mg 5,5'-Dipropyl-2,2'-bithiophene (yield: 51 %).

Purity: 60 % (GC-MS)

MS (EI, 70eV): 250 (65 %, M<sup>+</sup>), 221 (100 %, M<sup>+</sup> - C<sub>2</sub>H<sub>5</sub>)

### **10.3.4 Synthesis of 2- and 3-Octylbenzothiophenes**

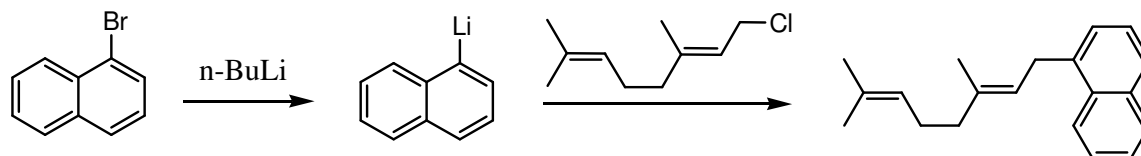
2 – and 3-Octylbenzothiophenes were synthesized as a mixture [20 % of the 2-isomer and 80 % of the 3-isomer (based on the assumption that 3-Octanoylbenezothiophene is the major product obtained from the acylation of benzothiophene)] through acylation of benzothiophene with octanoyl chloride/AlCl<sub>3</sub> followed by Wolff-Kishner reduction.

A 100 ml three necked flask was equipped with a reflux condenser and a dropping funnel protected by a calcium chloride guard-tube. The top of the condenser was connected to a trap for absorbing the hydrogen chloride evolved. 250 mg (~ 2 mmol) of benzothiophene was dissolved in 3 mL dichloromethane and 1 g of anhydrous, finely powdered aluminium chloride was added to it. To this mixture, 300 mg (~ 2 mmol) of octanoyl chloride dissolved in 3 mL dichloromethane was slowly added. When all the Octanoyl chloride was introduced, the mixture was heated on a water bath at 50 °C for 1 hour in order to complete the reaction. This reaction mixture

was cooled and poured into about 15 mL of water and a little crushed ice contained in a 100 mL flask. Decomposition occurs with the evolution of heat and a dark oil separates out of the solution. This mixture was poured into a separatory funnel, the lower layer was collected washed with water, sodium hydroxide solution, again with water and finally dried over magnesium sulfate to obtain a crude product (yield 80 %) which was used for the further reaction. 100 mg (0.4 mmol) of the crude product was mixed with 95 % hydrazine (1 mL), potassium hydroxide (0.5 g), and diethylene glycol (5 mL) at 45 °C in a three necked flask fitted with a condenser arranged for downward distillation. The mixture was heated to 195 °C over a 1 hr period and maintained at this temperature for 0.5 hr. The reaction mixture was cooled, water (10 mL) was added and the mixture was distilled. This procedure was repeated until 30 mL of distillate had collected. The distillate was extracted with three portions of ether. The combined ether solutions were washed twice with water and twice with brine, dried (MgSO<sub>4</sub>) and concentrated to leave 68 mg (yield 68 %) of yellow colored product.

MS (GC-MS): 246 (20 %, M<sup>+</sup>), 147 (100 %, M<sup>+</sup> - C<sub>7</sub>H<sub>16</sub>)

### 10.3.5 Synthesis of 1-[(2E)-3,7-dimethyl-2,6-octadienyl]naphthalene [59]



At 0 °C, 1-bromonaphthalene (100 mg, 0.48 mmol) and geranyl chloride (98 mg, 0.57 mmol) were consecutively added to butyllithium (0.35 mL, 1.6 M in hexanes). After 1 h of stirring at 25 °C, distilled water (5 mL) was added to the mixture followed by extraction with ether [59]. The solvents were stripped off and the residue was chromatographed on silica gel with cyclohexane:dichloromethane (1:1) as eluant to obtain the product.

MS (EI, 70 eV): 264 (40 %, M<sup>+</sup>), 195 (60 %, M<sup>+</sup> - C<sub>5</sub>H<sub>9</sub>), 141 (40 %, M<sup>+</sup> - C<sub>9</sub>H<sub>15</sub>), 123 (45 %, M<sup>+</sup> - C<sub>11</sub>H<sub>9</sub>), 69 (100 %, M<sup>+</sup> - C<sub>15</sub>H<sub>15</sub>)

## 10.4 Instrumental parameters

### 10.4.1 HPLC instrumentation

#### Knauer

Pumps:	2 Knauer HPLC Pump 64
Injector:	Knauer manual injection valve
UV-Detector:	Knauer Variable Wavelength Detector
Detection Wavelength:	254 nm
Flow rate:	1 mL/min
Column Oven:	Gynkoteck STH 585
Software:	Eurochrom 2000, Version 1.5
HPLC-empty columns:	Latek 4.6 mm ID, 150 mm long

#### Hewlett-Packard 1050 HPLC system

Pumps:	Quaternary pumps
Injector:	Manual Injection Valve
Detector:	Diode Array Detector
Detection Wavelength:	200-600 nm
Software:	Chemstation Version 9.3

### 10.4.2 Gas chromatographs

#### GC-AED

Gas Chromatograph:	Agilent 6890N
Atomic Emission Detector:	Agilent G2350A
Autosampler:	Gerstel MPS 2L
Injector:	Gerstel Cold Injection system
Transferline:	300 °C
Carrier gas:	Helium
Capillary column:	VF5ms (Varian), 30 m x 0.25 mm x 0.25 µm
Temperature Program:	60 °C – 2 min – 10 °C/min – 300 °C – 5 min
Injection volume:	1 µL

#### GC-MS

Gas Chromatograph:	Finnegan MAT GCQ
Mass Spectrometer:	Finnegan MAT GCQ Polaris MS
Autosampler:	CTC A200S Liquid Sampler
Injector:	Split / Splitless (60 s)
Injector temperature:	260 °C
Capillary column:	J & W DB17ms, 29.5 m x 0,25 mm x 0.25 µm

Carrier gas:	Helium 6.0
Transferline:	275 °C
Ionization conditions:	EI, 70 eV, Ion source 200 °C
Modus:	Full Scan (50-600 amu)
Temperature Program:	60 °C – 2 min – 10 °C/min – 300 °C – 5 min Filament-Delay: 5 min
Injection volume:	1 µL

### GC-FID

Gas Chromatograph:	Hewlett-Packard 4890 II
Autosampler:	Gerstel MPS 2L
Injector:	Split / Splitless (60 s)
Injector temperature:	280 °C
Detector temperature:	300 °C
Capillary column:	VF5ms (Varian), 30 m x 0.25 mm x 0.25 µm
Carrier gas:	Hydrogen (4.8)
Temperature Program:	60 °C – 2 min – 10 °C/min – 300 °C – 5 min
Injection Volume:	1 µL

### 10.4.3 FT-ICR-MS

High Resolution Mass Spectrometric studies were done using Apex III FT-ICR-MS (Bruker Daltonics, Bremen, Germany), equipped with a 7 T magnet and an Agilent electrospray (ESI) ion source. The methylated samples were introduced as a solution in dichloromethane/acetonitrile mixture 1:1 (v/v) and injected in the infusion mode with a flow rate of 2 µL/min at an electrospray voltage of 4.5 kV. The ions were collected for 0.5 s in a hexapole before release into cyclotron cell. Signals were recorded using 512 k data points and 200 scans were accumulated for each spectrum to improve the signal to noise ratio. Internal and external standards mass calibration was performed using the Agilent electrospray calibration solution, covering the mass range of the sample with the exact masses 322.04812, 622.02896 and 922.00980 Da.

### 10.4.4 Elemental analyses or CHNS analyses

Vario EL III CHNOS Elemental analysis system (Service Department in the Institute of Inorganic and Analytical Chemistry)



**10.4.5 Atomic absorption spectroscopy**

aa/ae spectrophotometer VIDEO 22 (Service Department in the Institute of Inorganic and Analytical Chemistry)

**10.4.6 Spray dryer**

BÜCHI Spray Dryer B-290, Working group of Dr. Hubert Koller, Institute of Physical Chemistry

## 10.5 Abbreviations

AAS	Atomic Absorption Spectroscopy
ACDA	2-Aminocyclopentene-1-dithiocarboxylic acid
AED	Atomic Emission Detector
AS	3-(2-Aminoethano-amino)propanotrimethoxysilane
BT	Benzothiophene
Btu	British thermal units
CH	Cyclohexane
Da	Daltons
DBE	Double Bond Equivalent
DBT	Dibenzothiophene
DCE	Dichloroethane
DCM	Dichloromethane
EI	Electron Ionization
ELD	Electrolytic Detector
EPA	Environmental Protection Agency
ESI	Electrospray Ionization
F	Fahrenheit
FCC	Fluid Catalytic Cracking
FD	Field Desorption
FI	Field Ionization
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
FT-ICR-MS	Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
GC	Gas Chromatography
HDS	Hydrodesulfurization
HPLC	High Performance Liquid Chromatography
ICR	Ion Cyclotron Resonance
IP	Isopropanol
KMD	Kendrick Mass Defect
KNM	Kendrick Nominal Mass
LD	Laser Desorption
LEC	Ligand Exchange Chromatography
LPG	Liquid Petroleum Gas
m/z	Mass to charge ratio
MALDI	Matrix Assisted Laser Desorption Ionization
MATS	Methylamino-propanotrimethoxysilane
min	Minutes
MS	Mass Spectrometry
mV	milli volts
°C	degree centigrade
OSC	Organo Sulfur Compounds
PAH	Polycyclic Aromatic Hydrocarbons
PANH	Polycyclic Aromatic Nitrogen Heterocycles
PASH	Polycyclic Aromatic Sulfur Heterocycles
ppb	Parts per billion
ppm	Parts per million
S/N	Signal to noise ratio
SARA	Saturates Aromatics Resins Asphalts
SCD	Sulfur Chemoluminescence Detector
TEOS	Tetraethoxysilane
UV	Ultra Violet

## 10.6 Materials and devices

Ammonia	25 %	Grüssing
Benzo[ <i>b</i> ]naphtho[2,1- <i>d</i> ]thiophene	98 %	in house
Benzothiophene	95 %	Aldrich
Butyllithium	1.6 M in Hexane	Merck
Cyclohexane	≥ 99.8 %	Fluka
Cyclopentanone	99 %	Aldrich
Dibenzothiophene	98 %	Aldrich
Dichloromethane	99.8 %	Riedel de Haen
Diethylether	p.a.	in house
Acetic acid	96 %	Merck
Ethanol	p.a.	in house
Methyliodide	99 %	Fluka
Isopropanol	≥ 99.8 %	Fluka
Helium	6.0	Institute supply
Helium	He GC BiP	Air products
Magnesium sulfate (water free)	p.a.	in house
Methanol	99.5 %	Grüssing
Sodiumcarbonate	p.a.	in house
Sodiumbicarbonate	p.a.	in house
Sodiumhydroxide	p.a.	Merck
Sodiumnitrite	p.a.	in house
Palladium(II)chloride	59 %	Alfa Aesar
Hydrochloric acid	37 %	Grüssing
Sulfuric acid	p.a.	in house
Toluene	99.8 %	Fluka
1,2,3,4-Tetrahydrodibenzothiophene	> 98 %	Astec
1,2-Dichloroethane	99.5 %	Fluka
2-Methyldibenzothiophene	> 98 %	Astec
2-Octyldibenzothiophene	n.a.	in house
4,6-Dimethyldibenzothiophene	>98 %	Astec
3-Aminopropyltrimethoxysilane	97 %	Aldrich
3-Mercaptopropyltrimethoxysilane	97 %	Aldrich
2-Methylbenzothiophene	98 %	in house
Trifluoroacetic acid	97 %	Aldrich
Methylantranilate	95 %	Aldrich
Thiophene	99 %	Aldrich
3,5-Dimethylpyrazole	95 %	Aldrich
Hydroquinone	n.a.	Aldrich
N,N-dimethylformamide	99.8 %	Aldrich
Diethyleneglycol	99.5 %	KMF
N-bromosuccinimide	n.a.	Fluka
1-bromonaphthalene	99 %	Aldrich
Geranyl chloride	97 %	Aldrich
2,2'-Bithiophene	97 %	Aldrich
2-Propylthiophene	97 %	Aldrich
Carbondisulfide	n.a.	Aldrich
3-(2-Aminoethano-amino)propanotrimethoxysilane	97 %	ABCR
Methylamino-propanotrimethoxysilane	97 %	ABCR
2-(2-Thienyl)furan	97 %	Aldrich

## 10.7 References

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## Acknowledgements

First of all, I would like to thank my principal advisor, Prof. Jan T. Andersson, for his support and enthusiasm over the past few years. Looking back, I was pretty lucky that Jan even let me join his lab in the first place. Jan knew I had little experience in Analytical Chemistry but still decided to take me into his group. He spent enormous amount of time working with me and teaching me how to think like an analytical chemist. Learning chemistry from Jan was certainly one of the most fun and valuable experiences I had in Graduate School. Over the more recent times, Jan has continued to be a mentor and friend to me. Being a part of AK Andersson has been a great honor. Although I am sad to be leaving, I am looking forward to the future and will enjoy watching the lab develop during the upcoming years.

The other mentors of my thesis committee Dr. Hubert Koller and Prof. Günter Haufe have been a true pleasure to interact with. Dr. Hubert Koller, coordinator of NRW Graduate School of Chemistry, could be the most well-organised person I have ever met. He coordinates the graduate school activities, maintains his own research laboratory and, somehow, still finds time to help all the graduate students at the time of need. Prof. Günter Haufe has also been incredibly supportive.

I would like to thank NRW Graduate School of Chemistry for providing the financial aid and for all the support and encouragement.

My undergraduate chemistry teachers also deserve special thanks. My roots as a researcher come from Dr. Anand Solomon at Sri Satya Sai Institute of Higher Learning in India. He was always full of sound advice and was able to foster a great learning environment for undergraduate students.

I would like to thank AK Andersson for making our laboratory a great working environment. There are also a number of people whom I would like to acknowledge individually. The members of the group: Frau. Marianne Lüttmann, Frau. Karin Weißenhorn, Dr. Frank Wasinski, Dr. Hendrik Müller, Claudia Sill, Ansgar Japes, Markus Penassa, Nina Kolbe, Eiman Fathalla, Dr. Abd El-Rahman Hanafy Hegazi and Stefan Trümpler for being a part of the lab. Special thanks to Dr.

Wolfgang Schrader for the FT-ICR-MS measurements, Saroj Kumar Panda for his assistance in mass spectrometric data analysis, Dr. Thomas Schade & Dr. Benedikte Roberz for their corrections and Jens Kü(h)nemeyer for the help in formatting this thesis. I also would like to thank the group members of Dr. Koller.

I would like to collectively thank all the members of NRW Graduate School of Chemistry especially Dr. Stefan Elbers, Uta Bröcker and Christina Bäumer for their help.

This thesis certainly would not have been possible without the love and encouragement of my family and friends. My mom and dad have always been supportive and my sisters have been equally caring.

Hiermit versichere ich, dass ich die vorgelegte Dissertation selbst und ohne unerlaubte Mittel angefertigt, alle in Anspruch genommenen Quellen und Hilfsmittel in der Dissertation angegeben habe und die Dissertation nicht bereits anderweitig als Prüfungsarbeit vorgelegt habe.

Münster, 17. Oktober 2005

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