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Research article

A novel capped Pd nano-particle GC–MS technique for the identification of terpenoid sulfoxides in petroleum condensates

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ABSTRACT

Capped palladium (Pd) nano-particle column chromatography was first used to separate a novel series of high molecular weight terpenoid sulfoxides (HMTSs) from petroleum condensate oil within the heterocyclic polyaromatic sulfur compound (S-PAH) fraction. The separation technique was based on complex formation between nano-sized heavy charged Pd^{2+} ions and sulfoxide ligands. HMTSs were identified by interpretation of GC–MS fragmentation patterns. The infrared spectra of the pre-isolated S-PAH fraction confirmed the presence of sulfoxide groups with an absorption band at 1264 cm^{-1}. The novel HMTS series included three members with the general formula $C_{20}H_{34}OSR$ (main compound $C_{25}H_{44}OS$). The mass spectra of these three compounds were characterized by a major fragment ion at *m/z* 322. We identified a relationship between oil emergence and HTMS structure, indicating a base cross-linked macromolecular structure for the tested petroleum condensates and volatile oils. Atomic emission detection (AED) was unable to detect HMTS in spite of its sulfur atoms, most likely due to the high carbon to sulfur atom ratio producing quenching.

1. Introduction

Thiols, sulfides, disulfides, thiophenes, and benzothiophenes are the most common sulfur-containing moieties in petroleum fractions (Fig. 1). These common sulfur configurations have been investigated in a number of quantitative and qualitative analytical studies due to their known toxic and corrosive properties and the pollutant effect of SOx emissions [1,2]. Although high molecular weight terpenoid sulfoxides (HMTSs) are an interesting and unexpected sulfur configuration in petroleum fractions and naturally occurring biomarkers, there are relatively few studies on these unusual sulfur configurations. Unrecognized until 1983 [3,4], these compounds are of interest because of their unexpected structure, rarity depending on petroleum oil maturity, and irreversible adsorption on chromatography due to their high molecular weight and polarity.

There are three main categories of sulfoxide and sulfone studies. The first represents a small number of studies that have identified natural occurring C_{20}, C_{25}, and C_{30}HMTSs in oils and sediments as novel biomarkers. These can be divided into biogenic and abiogenic studies on petroleum fractions. In the abiogenic studies, sulfoxides were identified in crude oil as weak bases as early as 1967, their existence attributed to mild oxidation of crude oil during storage, consistent with their absence in virgin crude oil [3]. With respect to biogenic production, it has recently been confirmed that biodegrading bacteria or algae can grow on sulfur-containing compounds in the petroleum fraction, e.g., dibenzothiophene (DBT), leading to sulfoxide formation [4–7]. HMTSs have been identified in Athabasca asphalts by infrared spectroscopy [6], and small amounts of isoprenoid compounds have been detected in black sea sediment extracts [7,8]. Tricyclic hexaprenoids C_{20}–C_{30} were also identified in Northern Alberta heavy oils as the most abundant configurations [8–10,4].

The second and largest group of studies concerns the chemical oxidation of sulfur atoms to sulfoxides and sulfones for a model compound, e.g., benzothiophenes (BTs) and DBTs, with the aim of testing the oxidation selectivity of each technique [11]. The third category represents laboratory-based biodegradation of model sulfur compounds by pre-isolated bacterial strains, e.g., DBT derivatives, to study the oxidation pathways of sulfur compounds and the most suitable bio-desulfurization method for petroleum oil [12–13]. Several studies have been published for different model compounds, e.g., 2,3,4-tetrahydrodibenzothiophene (THDBT), DBT and benzo[*b*]naphto[2,1-*d*]thiophene (BNT) and also for different bacterial strains. Sulfoxides, sulfones, sulfites, and sulfides were the products of these bacterial degradation pathways [14–16].

The most common chromatographic analysis of HMTS in petroleum fractions is based on indirect analysis and consists of four main steps: (i) column (silica or alumina) separation of the polar fraction; (ii) chemical reduction of sulfoxide by $LiAlH_4$ to sulfides; (iii) column separation of

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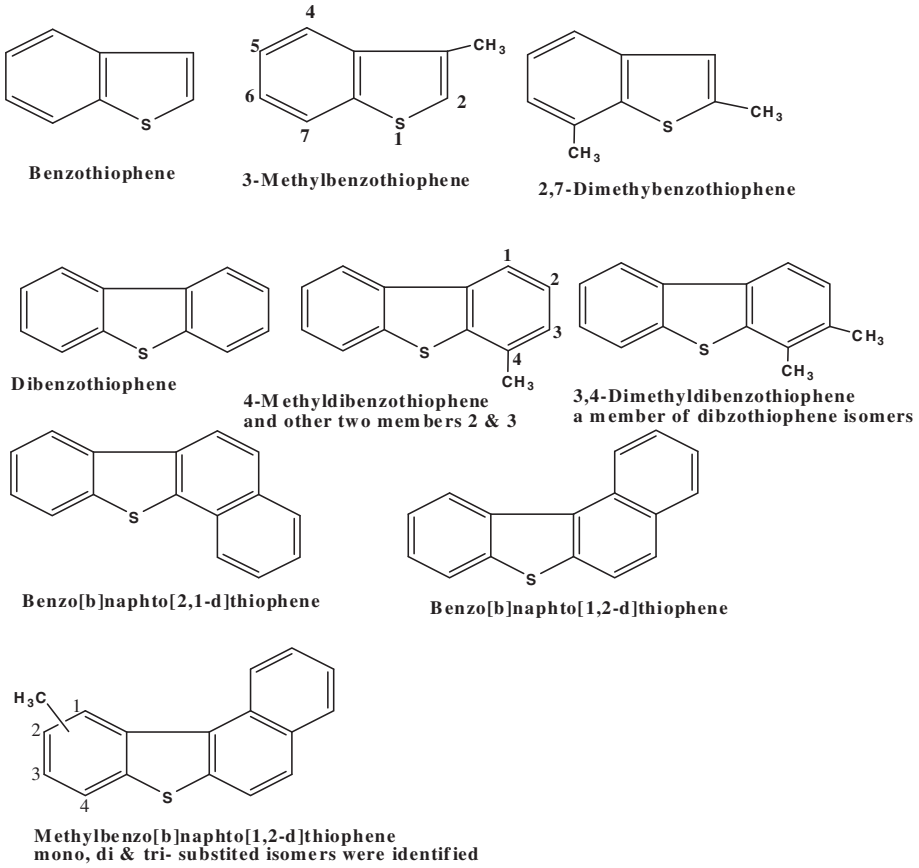

Fig. 1. Structures for the general S-PAHs isomers in the investigated petroleum samples [2].

the reduced, highly branched sulfoxides from low molecular weight sulfides; and (iv) GC-mass spectrometric identification (GC–MS) [3–10]. Methanol has been used in the eluent to separate sulfoxides and sulfones from the given fraction on silica columns. Of note, these GC–MS studies identified the reduced forms of highly polar sulfoxide and sulfone molecules but without identification of the original compounds [3–10]. These high molecular weight sulfoxides were initially reduced to low molecular weight compounds to render them amenable to separation from other functional compounds by column chromatography, particularly for the non-routine analysis of highly polar and branched sulfoxides by GC–MS [3–10]. Regardless of the presence of low molecular weight biodegradable products, e.g., BTs and DBTs, sulfoxides have been directly analyzed using common analytical techniques including GC-atomic emission detection (GC-AED) [11], GC–MS [2–10], positive-ion electrospray Fourier transform ion cyclotron resonance MS [17], GC-Fourier transform infrared spectroscopy (GC-FTIR) [18], and liquid chromatography time-of-flight mass spectrometry (LC–ToF–MS) [19–21].

Sripada and Andersson [22] showed that heavy polycyclic aromatic sulfur heterocyclics, but not nitrogen compounds, eluted on a Pd(II) stationary phase. Although early petroleum sulfoxides were used as a good extract for Pd(II) from acidic media due to complex formation between electron donor sulfoxide [23,24] and heavy-charged metal ions, there have yet to be any studies on Pd column chromatographic separation of sulfoxides from petroleum fractions. Therefore, the aims of this study were to: (i) identify HMTS in condensate oil by GC–MS and IR; (ii) examine the ability of nano-Pd aggregates [1] to separate HMTSs from petroleum condensate oil based on nano-Pd(II) sulfoxide complex formation; (iii) test the elution of heavy sulfoxides on a Pd(II) stationary phase; (v) draw attention to the relationship between HMTS structure and the emergence of the oil; and (iv) interpret the inability of AED to detect such hetero-atom-containing molecules.

2. Materials and methods

2.1. Petroleum samples

Petroleum condensate samples were collected directly from the separator at the well head. Condensate oil samples were kindly provided by different Egyptian companies: Khalada, Centurion, Petrobel, Wapeco, El-Hamara, and Bedr Eldien. Volatile oil samples were from VE-gas and Phobis petroleum companies.

2.2. Nano-Pd(II)-mercaptopropano silica gel synthesis

Briefly (see [2]), dried silica gel (60 mesh) was refluxed with 5 mL 3-mercaptopropanotrimethoxysilane (3-trimethoxysilyl-1-propanethiol) in 20 mL dry toluene for 5 h. The obtained mercaptopropano silica gel (MPS) was further treated with 250 mL aqueous palladium chloride solution (0.01 M) for 12 h.

2.3. Column chromatography

Briefly (see [2]), a 20 × 0.8 cm glass column was filled to about 3 cm with 2 g silica gel. The bulk of the oil was eluted with 40 mL cyclohexane and then cyclohexane:dichloromethane (3:1). The cyclohexane fraction was used for the next step. Separation of PAHs and S-PAHs: 1.5 g Pd(II)-MPS gel was packed into a 20 × 0.8 cm glass column. A sulfur-free fraction was eluted with 40 mL cyclohexane:dichloromethane(9:1), and S-PAHs were eluted with 40 mL cyclohexane:dichloromethane