



Analysis of polycyclic aromatic sulfur heterocycles in Egyptian petroleum condensate and volatile oils by gas chromatography with atomic emission detection

Nagy E. Moustafa*, Jan T. Andersson

Institute of Inorganic and Analytical Chemistry, University of Münster, Corrensstrasse 30, 48149 Münster, Germany

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ABSTRACT

Eight Egyptian petroleum condensates and two volatile oils were analyzed by gas chromatography. The condensate oils range in color from colorless to yellow and brown. The samples are composed mainly of saturates hydrocarbons (C_3 to C_{35}). The polycyclic aromatic sulfur heterocycles (PASH) were isolated through use of a silica bonded palladium(II)-complex and their distribution investigated by gas chromatography (GC) with atomic emission detection (AED) in the sulfur-selective mode. The condensate oils show distinctly different distributions of the PASHs, some containing mainly benzothiophenes, and others both benzo- and dibenzothiophenes and a third group in which the dibenzothiophenes strongly dominate. The alkyl substituted sulfur compounds are quantified. The distribution patterns of the PASHs are correlated to the type of reservoir source rocks.

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1. Introduction

There are five types of petroleum materials: dry gas, wet gas, condensate oil, volatile oil and crude oil. The volatile oil is similar to crude oil in its appearance and color, whereas its bulk composition is similar to condensate oil. Petroleum condensate is single phase gas in the subsurface but produces both liquid and gaseous phases when it is brought to the surface and the pressure and temperature are reduced to near ambient conditions. The liquid phase is known as condensate or natural gas liquid (NGL) and is a commercially important raw material for refineries in Egypt and other countries. The condensate oil is a fraction of petroleum comprising hundreds of hydrocarbon compounds, with a distillation range usually from 30 to 330 °C, and has been used to substitute naphtha in the petrochemical industry for producing a wide range of chemical products [1]. The most important parameter describing gas condensate phase behavior is the dew point (or saturation) pressure. At a given temperature, this is the pressure at which a gas condensate will turn into a two-phase system in response to a reduction in pressure. Gas and liquid samples are taken at the head of the condensate reservoir by a test separator using a Welker cylinder for PVT studies and to determine how much condensate is produced from a given volume of subsurface gas. Compared to crude oil, the condensate oil shows an abnormal behavior in PVT studies since the one gaseous phase turns into two phases on pressure release, and forms the so-called retrograde condensate oil [2]. This can

be analyzed to give an indication about the relative amounts of the constituents in the condensate oil matrix.

Sulfur compounds in petroleum products are often associated with adverse effects such as catalyst poisoning, corrosion or pollution through acid rain on combustion and thus hydrodesulfurization (HDS) has become a major industrial process. The current specification in Europe calls for a maximum sulfur content of 10 ppm in transportation fuels. The polycyclic aromatic sulfur heterocycles (PASH) constitute a major class of sulfur compounds in petroleum and can be particularly difficult to desulfurize catalytically. The two- and four-ring PASHs, benzothiophenes (BT) and benzonaphthothiophenes (BNT), occur in considerable amounts in petroleum but are somewhat easier to desulfurize than the three-ring PASH dibenzothiophene (DBT). The recalcitrance of DBTs to HDS is strongly influenced by the position of the alkyl substituents. Alkyl-DBTs can be divided into three groups with respect to their HDS reactivity: those without 4- and 6-substituents have the highest activity, followed by DBTs with one substituent in the 4- or 6-positions, and DBTs with both 4- and 6-positions substituted. The latter are generally recognized as the least reactive sulfur species [3–5] although at least one tetramethyl-DBT with one free 4-position has been found to be recalcitrant [6]. The speciation of alkyl-PASHs in material that is intended to be hydrodesulfurized can therefore give information on the ease of the reaction [7,8].

Condensates seem to be a fossil material that has not received much attention by analytical chemists yet and we know of no studies of the sulfur compounds in them. The discovery of condensate reservoirs in Egypt occurs at a faster pace than that of crude oils and will thus contribute importantly to the supply of fossil-fuel based energy in that country as well as in many others that have access to

* Corresponding author. Permanent address: Egyptian Petroleum Research Institute, 11727 Nasr City, Cairo, Egypt.

E-mail address: nemoustaf@yahoo.com (N.E. Moustafa).

condensate oils. If the condensates are going to be industrially desulfurized, analytical information on the sulfur species is necessary. Condensates associated oil fall largely in the gasoline and diesel boiling range and the aliphatics range from C_2 to C_{36+} . Gas chromatography is therefore suitable as a convenient and high-resolution technique for the analysis of sulfur compounds. The predominance of hydrocarbons requires selective detectors but analytical problems such as shifts in retention times, interference in MS detection [9] and maybe changes in peak heights may be traceable to the presence of a large excess of hydrocarbons. Therefore it is preferable to separate the sulfur compounds from the hydrocarbons as a first step in the analysis.

PASHs have long been investigated as conveyors of geochemical information in fossil materials. Abundant BTs and DBTs in petroleum are regarded as indicators of a carbonate-evaporate source environment. The types and the concentrations of BTs and DBTs and the ratio of DBT to phenanthrene have been related to the type of reservoir source rocks [10,11]. DBTs were found to be more abundant in oils derived from marine carbonates than in those from freshwater environments [12]. The relative abundance of dimethyl- and trimethyl-DBTs in total PASHs of oils from freshwater environments were lower than those of saline and hypersaline oils.

The atomic emission detector (AED) exhibits a sulfur response being compound independent [13] and is an established technique for PASH analysis in petroleum fluids [14–19]. The present study is the first one to investigate PASHs in condensates as possible industrial raw materials for the production of transportation fuel and uses GC-AED to obtain a distribution analysis of BTs and DBTs of six petroleum condensates and two volatile oils and GC-MS to obtain further information on unknown PASHs. An identification of the aromatic parent systems and the degree of alkylation is thus possible for many of the compounds present.

2. Experimental

2.1. Samples and standard compounds

The petroleum condensate samples were collected directly from the separator at the head of the well. The condensate oil samples were kindly provided by different Egyptian companies: Khalada, Centurion, Petrobel, Wapeco, El-Hamara and Bedr Eldien. The volatile oil samples are from VE-gas and Phobis petroleum companies. The physical appearance of different samples is illustrated in Fig. 1. All the condensate samples are from Egyptian Western Desert reservoirs.

The reference compounds used for the identification were all synthesized in our laboratory [20]. The following abbreviations are used to denote the alkyl substituents of the BTs and DBTs: M, methyl, E, ethyl, DM, dimethyl, and TM, trimethyl. The alkylated BT reference

compounds used are as follows: BT, 2-MBT, 2,6-DMBT, 3,5-DMBT, 2,3,4-TMBT, 2,3,6-TMBT, 2,5,7-TMBT and the DBTs are: DBT, 1,4-DMDBT, 1,2,4-TMDBT, 2,3,4-TMDBT, 2,6-DMDBT, 2,8-DMDBT, 3,6-DMDBT, and 4,6-DMDBT. The internal standard used for the quantifications was 2-fluorodibenzothiophene (2-FDBT) (99.9 wt.% purity) and was synthesized in our laboratory [21]. The solvent did not contain any traces of sulfur compounds. Chemicals for synthesis and HPLC grade solvents were from Sigma–Aldrich (Taufkirchen, Germany).

2.2. Instrumentation

Gas chromatographic analyses for sulfur compounds were performed on an HP 5890 II chromatograph with a split/splitless injector at 300 °C with the Agilent atomic emission detector (AED) [6,13] operated at the sulfur wavelength of 181 nm. The column was a Varian VF-5 ms ($30\text{ m} \times 250\ \mu\text{m} \times 0.25\ \mu\text{m}$). The oven temperature was held at 80 °C for 3 min and then programmed at 3 °C min^{-1} to 220 °C, then at 8 °C min^{-1} to 270 °C and finally at 20 °C min^{-1} to 300 °C and held there for 20 min. The injection volume was 2 μL .

Gas chromatographic analyses of the fractions separated on silica were performed on an HP 5890 II chromatograph with a split/splitless injector (260 °C), a flame ionization detector (300 °C) and a similar column as above. The oven temperature was held at 60 °C for 2 min and then programmed at 5 °C min^{-1} to 300 °C, held for 5 min. The injection volume was 1 μL .

2.3. GC-MS

The GC-MS analyses were carried out on a GCQ-Finnigan MAT chromatograph with an ion trap mass analyzer. The conditions were: initial temperature 60 °C for 1 min, ramp at 5 °C min^{-1} to 300 °C, held for 20 min. The capillary column was a DB-5 from J&W ($30\text{ m} \times 250\ \mu\text{m} \times 0.25\ \mu\text{m}$).

2.4. Synthesis of Pd(II)-mercaptopropano silica gel [22]

Silica gel (60 mesh) was dried at 130 °C for 24 h. 3 g of dried silica gel was refluxed with 5 mL 3-mercaptopropanotrimethoxysilane (3-trimethoxysilyl-1-propanethiol) in 20 mL dry toluene for 5 h. The resulting bonded silica gel was filtered off and washed with toluene and methanol successively. The obtained mercaptopropano silica gel (MPS) was dried at 50 °C in an oven. 2.5 g of MPS was further treated with 250 mL aqueous palladium chloride solution (0.01 M) for 12 h. The palladium bonded silica phase was filtered off, washed successively with water, iso-propanol and cyclohexane, and dried *in vacuo* at room temperature.

2.5. Column chromatography

Separation of the higher molecular-weight compounds and filtration: 0.5–1 mL of the sample was separated by column chromatography. A glass column $20\text{ cm} \times 0.8\text{ cm}$ was filled to about 3 cm with 2 g silica gel. The bulk of the oil was eluted with 40 mL cyclohexane and then with cyclohexane:dichloromethane (3:1). The cyclohexane fraction was used for the next step.

Separation of PAHs and PASHs: 1.5 g Pd(II)-mercaptopropano silica gel was packed into a glass column of $20\text{ cm} \times 0.8\text{ cm}$. A sulfur-free fraction eluted with 40 mL cyclohexane:dichloromethane (9:1). The PASHs were eluted with 40 mL cyclohexane:dichloromethane (2:1) containing 1% iso-propanol. The sulfides were eluted with 40 mL of cyclohexane:dichloromethane (2:1) containing 1.5% iso-propanol saturated with NH_3 . Finally the column was washed with 50 mL of cyclohexane:dichloromethane (9:1) for regeneration. The solvent volume was reduced to 1 mL by rotary evaporation before GC-AED analysis. The quantitative analysis was based on 2-fluorodibenzothiophene as



Fig. 1. Variation in color of condensate oils. Left to right: Waxy (BDR Co.); light yellow (Wapco-Ast-2); yellow (Khalada); colorless (Centurion-Azher); light brown (Petrobel-Fayroyz) and brown (Centurion-El-bassant-2).

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