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Short communication

Application of liquid-phase microextraction for the determination of sulfur compounds in crude oil and diesel

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ABSTRACT

A liquid-phase microextraction (LPME) method was for the first time developed for the determination of sulfur compounds in Arabian crude oil and diesel. A wide range of sulfur compounds, which included benzothiophene, dibenzothiophene and their derivatives, was used for model compounds. The analyses were performed by a gas chromatography equipped with a sulfur chemiluminescence detector (GC-SCD). Under optimum conditions, a linearity was achieved for the extraction sulfur compounds between 0.10 and 250 $\mu g\,mL^{-1}$ with the correlation of determination ranging from 0.98 to 0.99. Applying the same optimum conditions, the extraction of 77–91% of the sulfur compounds in the Arabian light, Arabian medium and Arabian heavy, and diesel was achieved.

1. Introduction

Crude oil consists of more than two hundred sulfur compounds including the derivatives of thiophenes and benzothiophenes, which constitute a total sulfur content in the crude oil of about 0.01–3% [1–6]. The amount of sulfur in the petroleum products increases along with the boiling point of the distillate fractions [7,8]. The sulfur compounds damage the environment drastically and also lead to adverse effects in the petroleum refining process [9,10]. The sulfur compounds generate SO_x during the combustion process causing the acid rain [11–16]. To improve the quality of the air, environmental regulations have been implemented in many parts of the world to reduce the emission of the SO_x through the restriction of the emissions level <10 $mg\,L^{-1}$ [17–20].

A quantitative determination of the sulfur compounds in the crude oil is a challenging task because of the presence of a complicated matrix. As the American Petroleum Institute (API) gravity and viscosity are higher for the crude oil and diesel, the traditional methods of sample preparation are ineffective. Based on the gas chromatography (GC), the American Society for Testing and Materials (ASTMs) methods have been reported for the quantitative measurement of the sulfur compounds [21]. Generally, crude oil was simply diluted with organic solvents (20 times), avoiding sample preparation prior to the GC analysis [22]. The metal constituents such as nickel (Ni) and vanadium (V) as high as 1000 $\mu g\,g^{-1}$ in the crude oil are a cause of concern for the GC analysis [23]. The selectivity in the sulfur analysis using ASTM methods relies on the instrumental conditions. For instance, ASTM D5623, ASTM D3328, ASTM D6228 methods were reported for the sulfur analysis in the petrochemical matrices using the GC with pulsed flame photometric detector (PFPD) whereas the ASTM D5504 method was reported for the GC with the sulfur chemiluminescence detection [24–28]. In all these ASTM methods, the samples were directly analyzed by a series of dilutions, which caused the poor quantitation and contamination of the GC injection port due to a large volume of the solvent used in the dilution [29].

Liquid–liquid extraction techniques have been used to remove sulfur compounds form fuel oil (not directly from crude oils) with various organic solvents such as acetone, ethanol and formic acid. The extraction performance of these solvents was poor due to simultaneous removal of hydrocarbons [29].

More environmental friendly methods, including a solid-phase microextraction (SPME), a dispersive liquid–liquid microextraction and a solid-phase extraction, have also been reported in the literature [30–32]. SPE and micro-SPE have been applied for determination of sulfur compounds in crude oil [33,34]. For prior extraction, more complex pretreatment steps are required for these techniques. Recently, a hollow fiber membrane supported liquid-phase micro-extraction (HFM-LPME) has been used for the analysis of several analytes that have complex matrices like beverages, urine, soil, wastewater, and oil spills in the sediment samples

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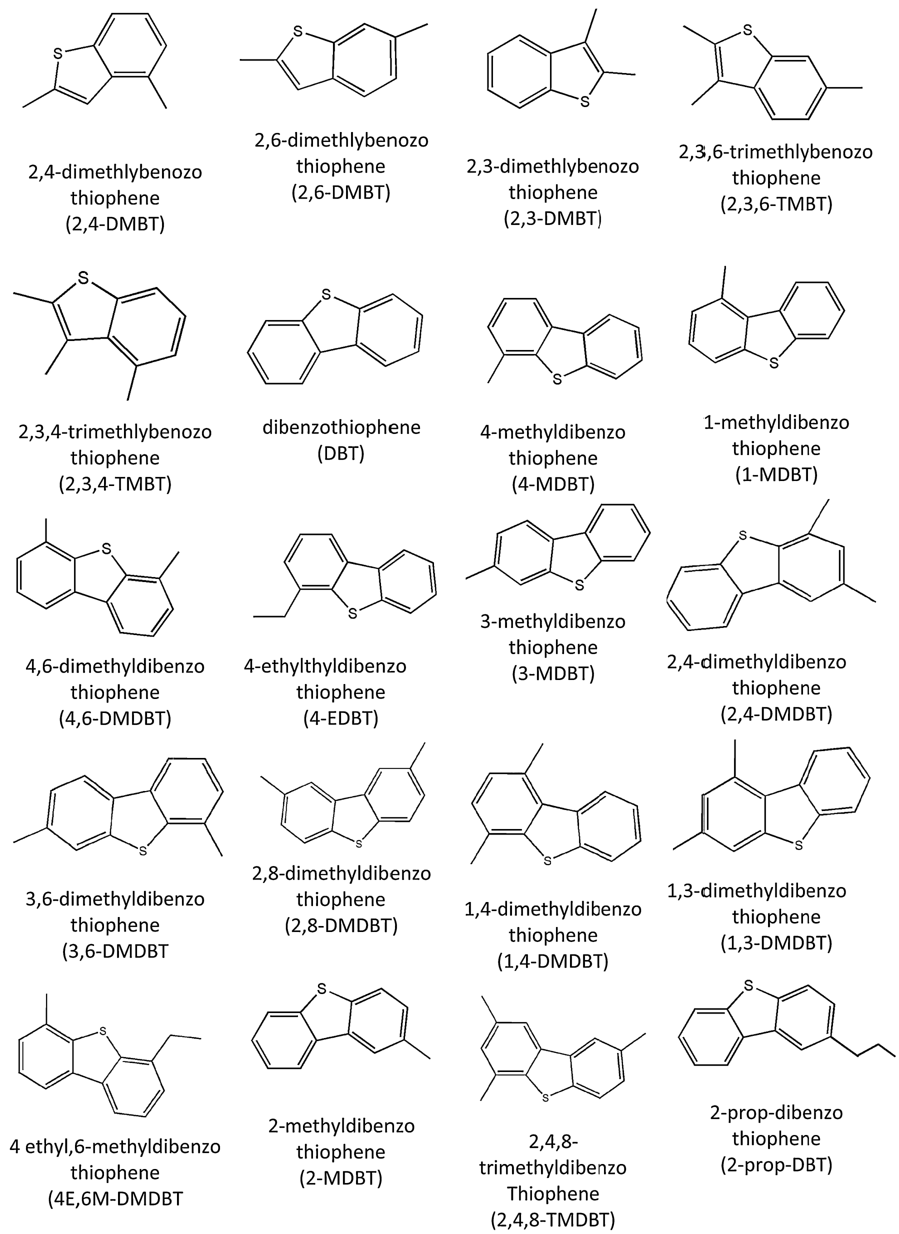

Fig. 1. Molecular structures of sulfur compounds.

[35,36]. The HFM-LPME is a fast, simple and inexpensive sample preparation approach. In the LPME, the extraction, the cleanup of samples and preconcentration is done in a single step. The porous HFM membrane acts as a filter and eliminates interfering particles, producing a clean extract suitable for the direct instrumental analyses. The HFM-LPME has, therefore, received much attention for the selective extraction of analytes from the complex matrices. To the best of our knowledge, no HFM-LPME method has yet been reported for the determination of the sulfur compounds in the complex matrices. Considering the detrimental effect of sulfur and the potential application of the HFM-LPME, it is worth developing a single step HFM-LPME to analyze the amount of sulfur in the crude oil and the diesel.

2. Experimental

2.1. Materials

High purity sulfur compounds were obtained from Sigma–Aldrich in St. Louis, MO, USA, and used as model compounds (Fig. 1). These 19 compounds with a CAS number consisted of the following: 2,4-dimethlybenzo thiophene (2,4-DMBT, CAS 611-01-8); 2,6-dimethlybenzo thiophene (2,6-DMBT, CAS 89816-75-1); 2,3-dimethlybenzo thiophene (2,3-DMBT, CAS 632-16-6); 2,3,6-trimethlybenzo thiophene (2,3,6-TMBT, CAS not available); 2,3,4-trimethlybenzo thiophene (2,3,4-TMBT, CAS 70021-44-2); dibenzothiophene (DBT, CAS 132-65-0); 4-methyldibenzo thiophene (4-MDBT, CAS 31317-07-4); 1-methyldibenzo thiophene (1-MDBT, CAS1455-18-**1**); 4,6-dimethyldibenzo thiophene (4,6-DMDBT, CAS 1207-12-1); 4-ethylthyldibenzo thiophene (4-EDBT, CAS not available); 3-methyldibenzo thiophene (3-MDBT, CAS 1455-18-1); 2,4-dimethyldibenzo thiophene (2,4-DMDBT, CAS 31317-18-7); 3,6-dimethyldibenzo thiophene (3,6-DMDBT, CAS 31613-04-4); 2,8-dimethyldibenzo thiophene (2,8-DMDBT, CAS 1207-15-4); 1,4-dimethyldibenzo thiophene (1,4-DMDBT, CAS 21339-66-2); 1,3-dimethyldibenzo thiophene (1,3-DMDBT, CAS 31317-15-4); 4-ethyl; 6-methyldibenzo thiophene (4E,6M-DMDBT, CAS not available); 2-methyldibenzo thiophene (2-MDBT, CAS 1195-14-8); and 2,4,8-trimethyldibenzo thiophene