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Determination of aromatic sulphur compounds in heavy gas oil by using (low-)flow modulated comprehensive two-dimensional gas chromatography–triple quadrupole mass spectrometry☆

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ABSTRACT

The present research is focused on the development of a flow-modulated comprehensive two-dimensional gas chromatography–triple quadrupole mass spectrometry (FM GC × GC–MS/MS) method for the determination of classes of aromatic organic sulphur compounds (benzothiophenes, dibenzothiophenes, and benzonaphthothiophene) in heavy gas oil (HGO). The MS/MS instrument was used to provide both full-scan and multiple-reaction-monitoring (MRM) data. Linear retention index (LRI) ranges were used to define the MRM windows for each chemical class. Calibration solutions (internal standard: 1-fluoronaphthalene) were prepared by using an HGO sample, depleted of S compounds. Calibration information was also derived for the thiophene class (along with MRM and LRI data), even though such constituents were not present in the HGO. Linearity was satisfactory over the analyzed concentration range (1–100 mg/L); intra-day precision for the lowest calibration point was always below 17%. Accuracy was also satisfactory, with a maximum percentage error of 3.5% (absolute value) found among the S classes subjected to (semi-)quantification. The highest limit of quantification was calculated to be 299 μg/L (for the C1-benzothiophene class), while the lowest was 21 μg/L (for the C4-benzothiophene class).

1. Introduction

Crude oil is formed predominantly of a great number of hydrocarbons [i.e., paraffins, naphthenes, mono- and polyaromatic hydrocarbons (PAHs)] along with smaller amounts of compounds containing heteroatoms such as sulphur, oxygen or nitrogen [1]. The resulting mixture is of extreme complexity, and hence, very challenging in analytical terms.

Sulphur is the most abundant heteroatom in crude oils, with concentrations increasing in the heavy petroleum fractions [1,2]. The combustion process of petroleum derivatives releases SO_x to the atmosphere (SO_2 and SO_3), causing a series of problems to the environment and human health [2]. For such a reason, the S content of various petroleum products has been subjected to stringent regulations [2,3].

The S compounds contained in crude oil belong to the following main classes: sulphides, disulphides, thiols, and thiophene-based compounds [4,5]. The thiophene-based compounds are aromatic sulphur heterocycles (thiophene, benzothiophene, dibenzothiophene, benzonaphthothiophene, *etc.*, and their alkylated derivatives) and are more concentrated in the high-boiling oil fractions [1,6]. The number of possible alkylated isomers is very high, especially in the classes of polyaromatic sulphur heterocycles (PASHs).

The relatively-low concentrations of sulphur heterocyclic species in petroleum products (*e.g.*, 1–2%), in addition to matrix complexity, in particular co-elution with a variety of PAHs, makes the gas chromatographic determination of such target compounds a very difficult task. Even so, the development of effective analytical methods for the monitoring of S compounds in petroleum products

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is of high importance. Gas chromatography (GC) approaches based on pre- fractionation [7–10], the use of selective detectors [10–13], and comprehensive two-dimensional GC (GC × GC) [9,14–16], have been employed in this research field.

Specifically, the use of GC with atomic emission, flame photometric or sulphur chemiluminescence detection (SCD) has been widely used for the determination of S components in fossil fuels [10–13]. However, even though such detectors can give a uniform response for S-containing compounds they do not provide structural information. The use of mass spectrometry (MS) is an obvious choice for structural elucidation, even though the presence of matrix interferences can still represent a problem [17]. Selected-ion-monitoring has been often exploited [17–21], even though such an approach can yield incorrect quantification results [17,21]. In fact, many PAHs and PASHs not only have a similar GC retention behavior, but are also characterized by the same significant fragmentation ions [10]. Such an analytical problem can be circumvented, for example, by separating the PASHs from the interfering PAHs, through complexation with $PdCl_2$ deposited on silica gel [8,22,23]. A major drawback of $PdCl_2$-based sample preparation is that PASHs with an internal thiophene ring can be easily lost. On the basis of the aforementioned considerations, both a powerful GC and selective MS step would appear to be desirable in such an application type.

The use of GC × GC for the detailed characterization of organic S compounds in fossil fuels has proved to be a valid option [24]. Cryogenically modulated GC × GC coupled with time-of-flight mass-spectrometry (ToF MS), has been employed for the analysis of PASHs in fossil fuels [9,14–16,25,26]. For example, Machado and co-workers compared GC × GC-ToF MS with GC–MS (single quadrupole) in the analysis of PASHs in coal tar and bitumen [25,26]. Additionally, the same research group found that the use of two fractionation steps, prior to GC × GC-ToF MS analysis, increased the number of identified PASHs in heavy gas oil (HGO) [16]. Mahé and co-workers used GC × GC-ToF MS (along with GC × GC-SCD) for the analysis of PASH classes in HGO, following a Pd-based fractionation process [9]. The focus of the authors was on specific classes of S compounds, rather than on analyte-to-analyte identification. Even though GC × GC-ToF MS is a very powerful method, many of the problems related to both co-elution and ions in common between PASHs and PAHs still remain.

The present research is focused on the use of flow-modulation (FM) GC × GC combined with triple-quadrupole mass spectrometry (MS/MS) for the semi-quantification of PASHs in HGO. Five classes of benzothiophenes (BT – from no C substituent, to C4 substituents), five classes of dibenzothiophenes (DBT – from no C substituent, to C4 substituents), and the single tetra-aromatic compound benzo[b]naphtho[2,1-d]thiophene (BNT), were subjected to analysis. Multiple reaction monitoring (MRM) information on four classes of thiophenes (T – C1 to C4 substituents) is also reported, even though these compounds were not present in the HGO sample. A wide-bore column (0.32 mm ID) was used in the second dimension. The flow modulator was operated using reduced gas flows and a long accumulation loop as described in recent research [27,28].

To the best of the authors' knowledge, only a single MS/MS (with 1D GC) study involving the analysis of S compounds (in crude oil) has been reported [29]. A single PASH class, namely DBT, was subjected to quantification.

2. Materials and methods

2.1. Samples, standard compounds and sample preparation

The sample of Arabic heavy gas oil (boiling point: 400 °C) was provided by the "Centro de Pesquisas e Desenvolvimento da Petrobras" (CENPES), Petrobras (Brazil). The heavy gas oil was diluted using dichloromethane to a final concentration of 40 mg/mL.

The EPA 610 Polynuclear Aromatic Hydrocarbons Mixture standard solution was used as source of PAHs (Sigma–Aldrich/Supelco, Bellefonte, PA, USA).

Standards of 3-methylthiophene, 2,5-dimethylthiophene, 2-propylthiophene, 3-butylthiophene, benzothiophene, 2-methylbenzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene, 4,6-diethyldibenzothiophene and benzo[b]naphtho[2,1-d]thiophene were purchased from Sigma–Aldrich/Supelco. Standards of 2,5-dimethylbenzothiophene, mixture of 2,3,4- and 2,3,6-trimethylbenzothiophene, 2,3,4,7-tetramethylbenzothiophene, 3-methyldibenzothiophene, 1,4,7-trimethyldibenzothiophene were purchased from Prof. J. Andersson (University of Münster, Münster, Germany).

A sample of HGO, without the S compounds, was prepared as follows: an open glass column (250 mm × 30 mm ID) was packed with 10 g of silica gel (Sigma–Aldrich/Supelco, 35–60 mesh). The silica gel was previously activated at 120 °C for 16 h. One hundred mg of HGO were eluted with 40 mL of hexane, to isolate the hydrocarbons from the more-polar S compounds. The fraction collected was reduced in volume with a rotary evaporator, and solubilized with dichloromethane.

Calibration solutions were prepared at the final concentrations of 1, 5, 10, 25, 50, 100 mg/L by using the HGO sample depleted of S compounds. The internal standard, 1-fluoronaphthalene, was also purchased from Sigma–Aldrich/Supelco and was present in the solutions at a concentration of 10 mg/L.

2.2. FM GC × GC–MS/MS analyses

All comprehensive two-dimensional GC–MS/MS applications were carried out on a system consisting of two Shimadzu GC2010 instruments (GC1 and GC2), and a TQ8040 triple quadrupole mass spectrometer (Shimadzu, Kyoto, Japan). Data were acquired by using the GCMSsolution software ver. 4.0 (Shimadzu). Bidimensional chromatograms were generated by using the ChromSquare software ver. 2.0 (Shimadzu). The MS database employed was the NIST11. The first GC was equipped with an AOC-20i auto-injector, and a split-splitless injector (310 °C).

The primary column (D1), an SLB-5 ms [(silphenylene polymer, practically equivalent in polarity to poly(5% diphenyl/95% methylsiloxane)] 20 m × 0.18 mm ID × 0.18 μm d_f, was connected to position 1 of a 7-port wafer chip modulator (SGE, Ringwood, Victoria, Australia). The secondary column (D2), an SPB-50 [poly(50% diphenyl/50% dimethyl siloxane)] 10 m × 0.32 mm ID × 0.20 μm d_f, was connected to position 6 of the interface, and to the MS/MS system. First and second dimension columns were kindly supplied by Sigma-Aldrich/Supelco. The seventh port was blocked using an adequate nut. A 99.8-μL accumulation loop (47 cm × 0.53 mm ID stainless steel tube) was employed. Modulation period was 8200 ms, with a 500 ms flushing pulse.

GC1 temperature program: 80–310 °C at 3 °C/min. The second GC oven was mantained at a +40 °C positive temperature offset. Initial He head pressure: 118.6 kPa. Initial auxiliary (APC: advanced pressure control) He pressure: 64.2 kPa. In both dimensions the constant average linear velocity (ALV) mode was applied. Injection volume and mode: 0.5 μL (split ratio: 20:1). A summary of the GC × GC conditions is listed in Table 1.

Triple quadrupole MS conditions: ionization mode: electron ionization (70 eV). Interface and ion source temperatures: 250 °C and 230 °C. Collision gas and pressure: Ar (200 kPa).

Acquisition mode: simultaneous full scan/MRM; MS cycle time: 0.04 s corresponding to 25 Hz spectral production frequency.