Journal of Chromatography A, 1218 (2011) 3208–3216

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

# Chemical characterization of aromatic compounds in extra heavy gas oil by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry

Bárbara M.F. Ávila[a], Ricardo Pereira[a], Alexandre O. Gomes[b], Débora A. Azevedo[a,*]

[a] Universidade Federal do Rio de Janeiro, Instituto de Química, Ilha do Fundão, Rio de Janeiro, RJ 21941-909, Brazil
[b] Petrobras,CENPES/PDP/TPAP, Ilha do Fundão, Rio de Janeiro, RJ 21941-909, Brazil

ARTICLE INFO

*Article history:*
Available online 8 October 2010

*Keywords:*
Aromatic hydrocarbons
Sulfur compounds
Extra heavy gas oil
Comprehensive two-dimensional gas chromatography
Time-of-flight mass spectrometry

## ABSTRACT

Comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC-TOFMS) was used for the characterization of aromatic compounds present in extra heavy gas oil (EHGO) from Brazil. Individual identification of EHGO compounds was successfully achieved in addition to group-type separation on the chromatographic plane. Many aromatic hydrocarbons, especially polycyclic aromatic hydrocarbons and sulfur compounds, were detected and identified, such as chrysenes, phenanthrenes, perylenes, benzonaphthothiophenes and alkylbenzonaphthothiophenes. In addition, triaromatic steroids, methyl-triaromatic steroids, tetrahydrochrysenes and tetraromatic pentacyclic compounds were present in the EHGO aromatic fractions. Considering the roof-tile effect observed for many of these compound classes and the high number of individual compounds identified, GC × GC-TOFMS is an excellent technique to characterize the molecular composition of the aromatic fraction from EHGO samples. Moreover, data processing allowed the quantification of aromatic compounds, in class and individually, using external standards. EHGO data were obtained in $\mu g\,g^{-1}$, e.g., benzo[a]pyrene were in the range 351 to 1164 $\mu g\,g^{-1}$. Thus, GC × GC-TOFMS was successfully applied in EHGO quantitative analysis.

## 1. Introduction

Petrochemical products contain a large and diverse number of chemical classes, such as paraffins, naphthenes, aromatic and unsaturated hydrocarbons, as well as sulfur, oxygen and nitrogen compounds [1]. There are a great number of individual components within these classes, making these samples extremely complex. For analysis of these mixtures, Blomberg et al. [2] demonstrated the applicability of comprehensive two-dimensional gas chromatography (GC × GC) to the characterization of a complex petrochemical mixture and several aromatic hydrocarbons and sulfur compounds were identified in samples. Similarly, in extra heavy gas oil (EHGO) samples, the number of individual components is vast, and no single chromatographic technique is able to separate and characterize these complex mixtures completely. So, comprehensive two-dimensional gas chromatography (GC × GC) could be particularly useful in solving this problem [1,3,4].

EHGO samples are obtained by molecular distillation, a procedure usually used for the distillation of thermally unstable material, which is the most economically feasible method of purification [5]. This technique is widely applied in fine chemistry, petrochemistry, pharmaceutical chemistry and oil and grease analysis, as well as in scientific research to concentrate and purify organic chemicals of high molecular weight, high boiling point, high viscosity or poor heat stability [5]. Moreover, since petroleum sources are progressively decreasing, the demand for upgrading heavy fractions is increasing.

Molecular distillation has been used for heavy petroleum processing and characterization [6,7]. In this way, GC × GC coupled to time-of-flight mass spectrometry (GC × GC-TOFMS) could be used for detailed chemical characterization of EHGO obtained by molecular distillation. The results regarding the chemical composition of EHGO is very important to petrochemical industries, giving information about the nature, chemical makeup and applicability of these materials.

Concerning aromatic compounds, there are few studies reporting the analysis of such substances in petrochemical samples by GC × GC. Table 1 shows some of the most important results obtained [3,8–13,14–20]. In particular, there is no work regarding EHGO analysis by the mentioned technique. Furthermore, the literature points to only one paper concerning the characterization of saturated biomarkers in Brazilian EHGO samples using GC × GC coupled to time-of-flight mass spectrometry [21].

---

* Corresponding author. Tel.: +55 21 25627488; fax: +55 21 22603967.
*E-mail addresses:* debora@iq.ufrj.br, debora_quim@hotmail.com (D.A. Azevedo).

0021-9673/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2010.09.051

**Table 1**
Important works regarding aromatic compound analyses in petrochemical samples by GC × GC.

| Sample | Detector used | Characterized molecules | Reference |
|---|---|---|---|
| BTEX | FID | Benzene, toluene, xylenes, alkylbenzenes, naphthalenes, methylnaphthalenes | [8] |
| Crude oils | FID | Naphthalenes, biphenyls, fluorenes, phenanthrenes, chrysenes, dibenzothiophenes, benzonaphthothiophenes, steranes, triterpanes, triaromatic steranes | [9] |
| Jet fuel | FID | Alkylbenzenes | [10] |
| Kerosene | TOF | Monoaromatic compounds and alkylbenzothiophenes | [11] |
| Naphtha | FID | Aromatic compounds | [12] |
| Crude oils and FCC products | TOF, AED | Aromatic thiols, alkylated benzothiophenes, dibenzothiphenes, benzonaphthothiophenes, phenanthrene, pyrene and methylpyrene, chrysene, carbazoles | [13] |
| Naphtha | FID | Mono- and diaromatics | [3] |
| Diesel | FID | Mono-, di- and triaromatics, naphthenic-diaromatics | [14] |
| Gasoline | FID, TOF | Benzene and alkylbenzenes, toluene, naphthalene, styrene, benzothiophenes | [15] |
| Gasoline | FID | Benzene, toluene, ethylbenzene, naphthalene, xylenes | [16] |
| Diesel | FID | Mono- and diaromatics | [17] |
| Source rocks | FID, SCD | Aromatic compounds, benzothiophenes, dibenzothiophenes | [18] |
| Downhole fluid | FID, TOF | Naphthalenes, phenanthrenes, alkylbenzenes | [19] |
| Heavy oil | TOF | Alkylbenzenes and polycyclic aromatic hydrocarbons (PAHs) | [20] |

In the present study, the aromatic fractions of EHGO samples were analyzed using GC × GC-TOFMS and their molecular compositions characterized, providing a detailed report on the classes of compounds present in these samples. Moreover, the data processing allowed for a quantitative analysis of the aromatic extra heavy gas oil fractions, another objective of this work. Because of the limited information on the chemical constituents of EHGO, this study also enhanced the understanding of these samples and continued the study initiated by our group on Brazilian EHGO samples.

## 2. Experimental

### 2.1. Sampling and sample preparation

Three extra heavy gas oil (EHGO) samples were supplied by CENPES/PDP/TPAP, Petrobras (Brazil), and named RO-59, RO-82 and AL-35. Each of these EHGO samples was obtained by molecular distillation ($10^{-3}$ mmHg) of the vacuum residue (ASTM D 5236). Molecular distillation is a process used to separate the fractions of different molecular weight in the vacuum residue at the lowest possible temperature to avoid damage. The EHGO samples were then fractioned into saturated (*n*-hexane), aromatic [*n*-hexane: $CH_2Cl_2$ (8:2)] and polar compounds [$CH_2Cl_2$:MeOH (9:1)] by liquid chromatography, using activated silica gel (Merck) [22,23].

### 2.2. GC × GC-TOFMS

The GC × GC-TOFMS system was a Pegasus 4D (Leco, St. Joseph, MI, USA), which is an Agilent Technologies 6890 GC (Palo Alto, CA, USA) equipped with a secondary oven and a non-moving quad-jet dual-stage modulator. Data acquisition and processing was carried out using ChromaTOF software version 4.0 (LECO Corp., St. Joseph, MI). The GC column set consisted of a HP-5 ms, 5%-phenyl–95%-methylsiloxane (30 m, 0.25 mm i.d., 0.25 μm $d_f$) as the first dimension ($^1$D) and a BPX-50 (Austin, Texas, USA), 50%-phenyl–50%-methylsiloxane (1.5 m, 0.1 mm i.d., 0.1 μm $d_f$) as the second dimension ($^2$D). The second column was connected to the TOFMS by an empty deactivated capillary (0.5 m × 0.25 mm i.d.). The columns and the empty deactivated capillary were connected by SGE unions using SilTite metal ferrules (Austin, Texas, USA) for 0.10–0.25 mm i.d. GC columns.

GC conditions followed published experimental settings [21]. Briefly, the primary oven temperature program was 70 °C for 1 min, ramp at 20 °C $min^{-1}$ to 170 °C, and then ramp at 2 °C $min^{-1}$ to 325 °C. The secondary oven temperature program had a temperature 10 °C higher than that of the primary one. Carrier gas flow rate was 1.5 mL $min^{-1}$ using helium. A previous analysis was made using the same modulation period for saturated hydrocarbons (8 s), but several wrap around peaks were observed. Therefore, the modulation period was altered for 10 s with a 2.5 s hot pulse duration and a 30 °C modulator temperature offset versus the primary oven temperature.

The MS transfer line was held at 280 °C, and the TOFMS was operated in the electron ionization mode with a collected mass range of 50-600 *m*/*z*. The ion source temperature was 230 °C, the detector was operated at 1650 V, the applied electron energy was 70 eV, and the acquisition rate was 100 spectra $s^{-1}$.

### 2.3. Data processing

GC × GC-TOFMS data acquisition and processing were performed by ChromaTOF software version 4.0 (Leco, St. Joseph, MI, USA). After data acquisition, samples were submitted to a data processing method where the individual peaks were automatically detected on the basis of a 10:1 signal to noise ratio. Individual peak areas were automatically acquired, and compound identification was performed by examination and comparison with literature mass spectra, retention time, authentic standards and elution order.

A standard mixture solution of PAHs (EPA 610) was acquired from Supelco (Bellefonte, USA). After dilution, the injected solution contained 1.6 ng μ$L^{-1}$ of anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[k]fluoranthene, chrysene, indene[1,2,3-cd]pyrene, phenanthrene and pyrene; 3.2 ng μ$L^{-1}$ of benzo[b]fluoranthene, benzo[g,h,i]perylene, dibenzo[a,h]anthracene, fluoranthene and fluorene; and 32 ng μ$L^{-1}$ of acenaphthene, acenaphthylene and naphthalene. These compounds were used as external standards for compound identification and external quantification, and were analyzed applying the same analytical conditions used for extra heavy gas oil samples. Any response factor was used, being the quantification relative to the respective external standards.

Quantification of identified compounds was achieved from the relation between the sum of peak areas in respect to the PAH standards and its concentration in the external standard mixture. For example, triaromatic steroid compounds and alkylbenzonaphthothiophenes were quantified relative to pyrene and chrysene standards, respectively. Therefore, it was possible to calculate the relative concentrations (ng μ$L^{-1}$) of each compound identified by the relationship between its peak area and the peak area of the external standard of known concentration. Later, this concentration was corrected to the initial EHGO mass (μg $g^{-1}$).