Fuel 220 (2018) 379–388

Contents lists available at ScienceDirect

Fuel

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

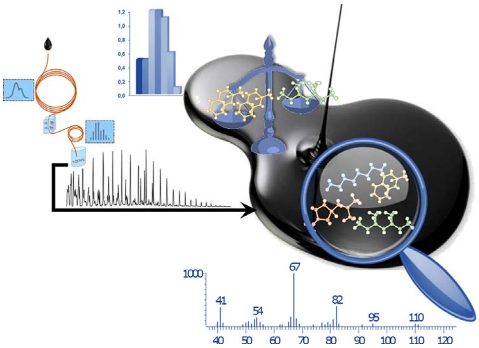
Full Length Article

Rapid hydrocarbon group-type semi-quantification in crude oils by comprehensive two-dimensional gas chromatography

Dayane M. Coutinho[a,*], Daniela França[a], Gabriela Vanini[a], Luiz André N. Mendes[b], Alexandre O. Gomes[b], Vinícius B. Pereira[a], Bárbara M.F. Ávila[a], 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 R&D Centre, Ilha do Fundão, Rio de Janeiro, RJ 21941-915, Brazil*

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Group-type semi-quantification
Hydrocarbon classes
Comprehensive two-dimensional gas chromatography
n-Alkanes
Branched alkanes

ABSTRACT

Petroleum is the main source of energy used in the world. The oil industry faces challenges in trying to understand the chemical composition of crude oils, quantitatively and qualitatively. The application of specific and sophisticated techniques allows a detailed characterization and provides important information that impacts from the exploration to production, transportation, and crude oil refining. A set of twelve crude oil samples with different API gravity were analyzed via comprehensive two-dimensional (2D) gas chromatography coupled to time-of-flight mass spectrometry (GC × GC-TOFMS) aimed at the detection, identification and semi-quantification of hydrocarbon classes using extracted ion chromatogram (EIC) and total ion chromatogram (TIC). The use of the polar/non-polar column configuration provided better separation between the hydrocarbon classes which allowed the identification and semi-quantification of the same. Therefore, series of *n*- and *iso*-alkanes, alkyl-cyclohexanes, alkyl-cyclopentanes, alkyl-decalines, alkyl-naphthalenes, alkyl-phenanthrenes and alkyl-9H-fluorenes were characterized. In the present study, a semi-quantification approach to data assessment using TIC is proposed. Comprehensive evaluation provided the chromatographic fingerprint of each sample in a single analysis followed by the semi-quantification of the hydrocarbon classes. The oil samples presented completely different hydrocarbon class data, even when presenting similar API gravity values. Branched alkanes and *n*-alkanes were the major semi-quantified compounds, and branched alkane concentrations were higher than *n*-alkanes in the majority of samples. These results afford valuable information for the petrochemical industry.

---

[*] Corresponding authors.
E-mail addresses: dmc@pos.iq.ufrj.br (D.M. Coutinho), debora@iq.ufrj.br (D.A. Azevedo).

https://doi.org/10.1016/j.fuel.2018.02.009
Received 9 October 2017; Received in revised form 1 February 2018; Accepted 2 February 2018

GC × GC-TOFMS was applied for speciation and group-type semi-quantification using a single oil drop without a fractionation or clean up step.

1. Introduction

The compositional analysis of petroleum via separation of classes provides valuable information to understand the behavior between different types of crude oils. Petroleum can be qualitatively and quantitatively characterized by various separation techniques. Group-type separation is an essential, traditional approach used to separate and classify crude oil, based on oil components' solubility, which involves separation into saturate hydrocarbon (saturates), aromatic hydrocarbon (aromatics), resins, and asphaltenes (SARA) fractions [1–3]. Although a large number of procedures for SARA separation have been developed and applied for decades, including gravimetric adsorption chromatography, an American Society for Testing and Materials standard test method [4,5], most shows inadequacies, such as extensive cross-contamination, poor analytical precision [6], diversity of the methods and lack of uniformity. High performance liquid chromatography (HPLC) has been applied in petroleum products and samples [7–10]. However, this technique presents limitations, such as the difficulty of quantifying isolated fractions [11]. In addition, thin-layer chromatography with flame ionization detection (Iatroscan TLC-FID) is a fast method for SARA analysis applied in petrochemical industries. This instrument offers accurate method for quantifying SARA fractions in solvent extracts [12]. However, latroscan TLC-FID provides only the amount of the four major classes, not a group type characterization.

Recently, Bissada et al. [6,13] reported a novel automated multidimensional high performance liquid chromatography (AMD-HPLC) for SARA separation and quantification. The AMD-HPLC system is fully automated and uses a set of two columns; it is based on a combination of adsorption and partition chromatography and separates SARA fractions and *n*-paraffins, *iso*-paraffins and naphthenic (PIN) fractions. Although the system shows good performance, further attention should be paid to the use of other chromatographic techniques to evaluate the purity of the fractions obtained by this method. Another technique that has become widely used to characterize polar compounds in crude oils and petroleum fractions is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) [14–16]. The ultrahigh resolution and mass accuracy allows the assignment of the elemental composition and classification considering the number of heteroatoms of oxygen, nitrogen and others [17].

On the other hand, Vendeuvre et al. [18] previously noted that group-type separation by comprehensive 2D gas chromatography (GC × GC) provides detailed information about samples when compared to other methods. In numerous previous studies, GC × GC has been reported in the quantitative analysis of environments [19,20], foods [21], petrochemicals [22–26], cosmetics [27] and bio-oils [28,29]. However, most studies use GC × GC with flame ionization detector (FID) for quantitative analysis. The combination of GC × GC and time-of-flight mass spectrometry (TOFMS) has been much employed in qualitative analysis and offers a detailed characterization about the chemical composition of complex mixtures, such as petroleum, but the quantitative approach is still much less commonly used in complex matrices [30,31]. In complex matrices such as petroleum, coelutions still can occur, thus the coupling of the TOFMS as the detection system can be considered a third dimension, providing a reliable identification through the mass spectrum and an additional separation capacity by the spectral deconvolution algorithm. The deconvolution procedure consists of a data treatment used for the mathematical separation of coeluted peaks chromatographically showing minor differences in retention time in the Gaussian distribution of the ions within the signal for the total ions. Thus, it is possible to discriminate and obtain the mass spectra of the substances [32]. The spectral deconvolution process allows the choice of a selective ion for the EIC, where through this it is possible to obtain area information and retention time of substances classes that elute in the same region in the chromatographic plane. There is why TOFMS is so important in complex samples analyses because even with two dimensions there are classes superpositions in the chromatogram.

Quantitative analysis using GC × GC-TOFMS is more complex than one-dimensional gas chromatography (1D-GC). Due to the modulation process, a single peak is sliced into several small peaks, and its quantification requires the integration of each of these peaks to obtain the total area of the target compound [33]. Additionally, despite the high peak capacity, coelution between interferers and the target compound may occur [34], therefore, it is necessary to verify the mass spectra of each slice. Ávila et al. [35] presented a group-type separation and identification of several individual compounds and a quantitative analysis after data processing using GC × GC-TOFMS. This study was performed on extra heavy gas oil (EHGO) samples obtained by molecular distillation. Series of aromatic hydrocarbons, especially polycyclic aromatic hydrocarbons and sulfur compounds, were quantified. Further, triaromatic steroids, methyl-triaromatic steroids, tetrahydrochrysenes and tetraromatic pentacyclic compounds were present in EHGO samples. Jennerwein et al. [31] showed the combination of mass spectral data and retention times in both dimensions within the automated scripts. This approach provides not only the details of the 2D chromatogram, but also avoids false classifications. Most recently, Silva et al. [29] applied GC × GC-TOFMS for the individual quantification of products in bio-oil samples obtained from three different processes: real thermal, catalytic and hydrodeoxygenated bio-oil. Quantification was performed with reliability using the analytical curves of oxygenated standards, hydrocarbons and deuterated internal standards. Also, in the study, a semi-quantification by classification was performed as a preliminary evaluation regarding the composition of the samples.

The characterization of organic compounds in oil samples is difficult to accomplish due to variety of chemical classes, each with different characteristics of volatility, polarity, and concentration. Currently, the petroleum industry has a great interest in connecting the effect of hydrocarbon class concentrations with the different properties of crude oils, as the traditional physical-chemical parameters alone are insufficient to understand petroleum behavior and application in transport and refining. The available analytical tools do not allow to know its composition completely because to the complexity of petroleum samples. The use of GC × GC-TOFMS has been considered valuable, especially in relation to the generated image because, with this technique, it is possible to obtain the structured chromatogram that distinguishes compounds of the same class, which interact differently in the second column, in specific chromatographic regions.

Thus, the present study aims the qualitative and semi-quantitative chemical composition characterization of individual compounds and main hydrocarbon classes in twelve Brazilian crude oils with different API gravities. Additionally, GC × GC-TOFMS was also applied in a single chromatographic analysis without a fractionation step to obtain the total area of the main hydrocarbon classes.