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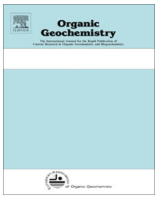

Characterization of unusual tetracyclic compounds and possible novel maturity parameters for Brazilian crude oils using comprehensive two-dimensional gas chromatography-time of flight mass spectrometry

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ABSTRACT

Eleven Brazilian oil samples from different sources, biodegradation and maturity levels were analyzed by comprehensive two-dimensional gas chromatography-time of flight mass spectrometry (GC×GC-TOFMS). Geochemical characterization associated with principal component analysis (PCA) allowed the identification of the three most mature oils. The GC×GC chromatographic conditions used in this study allowed us to perform group-type (or chemical class) separation in the following second dimension (^{2}D) order: (i) tricyclic terpanes; followed by (ii) steranes with 3 rings containing 6 carbon atoms and 1 ring containing 5 carbon atoms; (iii) tetracyclic terpanes with 4 rings containing 6 carbon atoms; (iv) pentacyclic terpanes with 4 rings containing 6 carbon atoms and 1 ring containing 5 carbon atoms; and finally (v) pentacyclic terpanes with 5 rings containing 6 carbon atoms. This information was used to tentatively identify the ring structure of eight unusual compounds found in the saturated fraction of the oils. These compounds had the double bond equivalent (DBE) value four, which was calculated based on molecular ions $M^{+\cdot}$ at m/z 274, 288 and 316, indicating possible tetracyclic structures. Two of them presented a diagnostic peak at m/z 191 and six at m/z 203. A trend between the ratios of two of these unusual compounds and the C_{24} tetracyclic terpane versus 4,6/1,4 dimethyldibenzothiophene ratio shows promise as a maturation parameter. Thus, these unusual compounds are prone to respond to the maturation on a scale from mature to overmature, when compared with traditional maturation parameters.

1. Introduction

Gas Chromatography (GC) coupled to Mass Spectrometry (MS) has been one of the most important techniques used to assess structural information of the large amounts of compounds observed in complex crude oil samples. Historically, one dimensional GC–qMS-instruments were used for single ion monitoring (SIM) because the full scan mode acquisition rate was not always fast enough to analyze a wide range of ions during GC runs (Sparkman et al., 2011). Nowadays, GC–MS-quadrupole combinations have achieved a sufficient acquisition rate for the monitoring of multiple fragment ions while superior sensitivity and selectivity have been provided by GC–MS/MS-triple quadrupoles performing MS/MS tandem experiments. In spite of progress in GC–MS technology, a great number of chromatographic co-elution problems in complex sample analyses remain unsolved. Many of these co-elution issues can be addressed by multiple ion monitoring or by applying deconvolution algorithms, which separate overlapping peaks and reconstruct clean chromatograms and mass spectra for each component (Lu et al., 2008). However, this is ineffective when two co-eluting compounds have similar mass spectra and/or the same diagnostic ion.

One key instrumental setup that has the potential to address such issues is comprehensive two-dimensional gas chromatography-time of flight mass spectrometry (GC×GC-TOFMS) (Aguiar et al., 2010). Unlike GC–MS analyses, GC×GC instrumentation produces full mass spectrum data with a high acquisition rate, which assures reliable qualitative and quantitative

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results. In GC×GC, the increase in signal-to-noise ratio is achieved due to the focusing of the chromatographic peaks by a modulator, which generates narrow peaks. In addition, the chemical background of the column, which is typical for one dimensional ^{1}D GC, generates a characteristic bleeding that increases the baseline with the temperature program. In GC×GC, this bleeding is constantly modulated and separated as any analyte compound in each ^{1}D fraction. Therefore, some compounds with low abundances, which are commonly lost in the background noise in one dimensional ^{1}D GC, are more easily resolved in GC×GC-TOFMS. An example of how this technique is effective in displaying compounds hitherto unobservable due to problems of resolution and/or co-elution is found in Oliveira et al. (2012a) and Kiepper et al. (2014) where four isomers for C_{19}–C_{24} tricyclic terpanes and C_{31} 3β-methylhopane were identified respectively. Recently, Araújo and Azevedo (2016) also used GC×GC-TOFMS to identify unusual steranes in branched-cyclic hydrocarbon fractions of crude oils from the Sergipe-Alagoas Basin, Brazil.

Moreover, ^{2}D separation improves the quality of mass spectra, making peaks purer by separating mass fragments of co-eluting compounds. A clear example in crude oil research can be seen in the investigation of C_{27} 17α(H)-22,29,30-trisnorhopane (Tm) and C_{27} 18α(H)-22,29,30-trisnorneohopane (Ts), which are commonly used for maturity evaluations (Seifert, 1978). Even though these two compounds are separated and analyzed in ^{1}D GC, a source dependence which can affect the maturity interpretation of the Ts/Tm ratio has previously been reported (Moldowan et al., 1986). This apparent source dependence can be explained by Ts co-eluting with the C_{30} tetracyclic terpane (TeT_{30}) (Rullkötter and Wendisch, 1982). Furthermore, the concentration of Tm could also be influenced by the C_{30} tricyclic terpane (Tr_{30}), which co-elutes with Tm on ^{1}D (Aguiar et al., 2010). It is well established that the abundance of TeT_{30} and Tr_{30} can be influenced by this kind of organic matter input (Aquino Neto et al., 1983; Moldowan et al., 1983; Peters et al., 2005a). Since the majority of studies using Ts/Tm are conducted with ^{1}D GC, it is difficult to rule out that co-eluting compounds do not cause problems in interpretation. Therefore, the common solution in geochemical studies based only on one dimensional GC has been to use parallel biomarker parameters (Peters et al., 2005a).

GC×GC-TOFMS provides cleaner mass spectra and improves the accuracy of biomarker ratios by resolving co-eluting compounds in ^{2}D. Additionally, the deconvoluted ion current (DIC) in TOFMS analysis can be used for compounds which co-elute in ^{2}D. This is possible due to the fast spectral acquisition rate and absence of concentration skewing (Focant et al., 2004; Mitrevski et al., 2010). Hence, the GC×GC-TOFMS system improves the separation of minor compounds that co-elute in standard GC and GC–MS analyses. It is important to emphasize that the resolution of co-eluting components in GC×GC-TOFMS analyses is a result of an additional dimension for the separation system, which facilitates the identification of new or not often reported (unusual) compounds encountered in complex crude oil samples.

In this study, 11 Brazilian crude oils were examined from differing source rocks and depositional conditions (5 lacustrine, 5 marine and 1 mixture) and with varying biodegradation and maturity levels. The aim was to evaluate the degree of maturation of the oil samples by analyzing saturated and aromatic fractions with conventional and non-conventional biomarker ratios measured by GC×GC-TOFMS. This approach is made possible by the increased capacity of GC×GC-TOFMS in the separation of oil components which can overcome interference in the determination of these parameters caused by their diverse origin and geological history. The enhanced diagnosis capacity enabled by GC×GC-TOFMS leading to High Resolution Molecular Organic Geochemistry (HRMOG), has been previously used for maturation investigations incorporating established parameters (Casilli et al., 2014). An outcome of this current study was the identification of eight unusual tetracyclic biomarkers in the saturated hydrocarbon fractions which may have potential as maturity indicators. The structure and geochemical significance of these tetracyclic compounds are discussed.

2. Material and methods

2.1. Sample preparation

Selected crude oils from the north to the south regions of Brazil were classified by the Research Center of Petrobras (Centro de Pesquisas Leopoldo Américo Miguez de Mello, CENPES, Rio de Janeiro, RJ, Brazil) using proprietary classifying methods (Table 1). These oils were also pre-fractionated by CENPES with medium pressure liquid chromatography (MPLC, model MKW, Margot Köhnen Willsch, Jülich, Germany) into saturated and aromatic fractions (Radke et al., 1980). The saturated fractions were further processed to remove the *n*-alkanes using urea adduction to separate branched and cyclic hydrocarbon fractions (B/C) (Lappas et al., 1997; Netzel and Rovani, 2007). The detailed experimental procedure for urea adduction and chromatographic analysis is described in Marotta et al. (2014) and Casilli et al. (2014), respectively. The B/C and aromatic fractions (total of 22 samples) were dissolved in dichloromethane (TediaBrasil, Rio de Janeiro, RJ, Brazil) with an internal standard of 20 µg/mL of perdeuterated *n*-tetracosane-D_{50} and pyrene-D_{10} (Cambridge Isotope Laboratories, Andover, MA, USA) before chromatographic analyses.

2.2. GC×GC-TOFMS and data processing

Analyses were performed on a Pegasus 4D (Leco, St. Joseph, MI, USA) GC×GC-TOFMS, composed of an Agilent Technologies 6890 GC (Palo Alto, CA, USA) equipped with a secondary oven, a non-moving quad-jet dual-stage modulator and a Pegasus III (Leco, St. Joseph, MI, USA) time of flight mass spectrometer. A DB-5 column (Agilent Technologies, Palo Alto, CA, USA), 5% phenyl–95% methylsiloxane (30 m, 0.25 mm i.d., 0.25 µm d_f) was used as the first dimension column (^{1}D). A BPX-50 column (SGE, Ringwood, VIC, Australia) with 50% phenyl polysilphenylene-siloxane (1.5 m, 0.1 mm i.d., 0.1 µm d_f) was used as the second dimension column (^{2}D). The ^{2}D column was connected to the TOFMS by means of a 0.5 m × 0.25 mm i.d. uncoated deactivated fused silica capillary, using SGE mini-unions and Siltite™ metal ferrules 0.1–0.25 mm i.d. (Ringwood, VIC, Australia) (Silva et al., 2011; Oliveira et al., 2012a).

GC conditions were: splitless mode injection of 1 µL at 290 °C, a purge time of 60 s, and a purge flow of 5 mL/min. Helium was used as the carrier gas at a constant flow rate of 1.5 mL/min. The primary oven temperature program began at 70 °C for 1 min, and was then increased to 170 °C at 20 °C/min, and further to 325 °C at 2 °C/min. The secondary oven temperature program was 10 °C higher than the primary one. The modulation period was 8 s with a 2 s hot pulse duration, and the modulator temperature was 30 °C higher than the primary oven temperature. The transfer line to the MS was set at 280 °C, the electron ionization mode was set at 70 eV, the mass range was 50–600 Da, the ion source temperature was 230 °C, the detector was +50 V above the tune value, and the acquisition rate was 100 spectra/s. Compound identification was performed by mass spectral examination, comparison with literature mass spectra, retention time and elution order, which is extensively reported in previous works (Aguiar et al., 2010, 2011; Oliveira et al., 2012a, 2012b).

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