

Analyses of bicyclic and tricyclic acids biomarkers in Potiguar Basin – Brazil Oils by ESI- and APCI-TOF MS

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Introduction

Naphthenic acids comprise a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids. They are found in petroleum because either the deposit has not undergone sufficient catagenesis or it has been biodegraded by bacteria (Peter et al., 2005). Working with marine evaporitic oils from Fazenda Belem, Potiguar Basin, Lopes et al. (2005) found a good correlation between acidic and neutral biomarkers. However the acidic fraction requires laborious techniques of separation, purification and derivatization which considerably delay the analysis of these compounds.

This study compared ESI and APCI methods in determining the molecular distribution of naphthenic acids (n-alkanes, bicyclic and tricyclic) in crude oil and in acidic fraction, resulting from the liquid-liquid extraction.

Experimental

Studied oils: Oil samples used in this study were obtained from Fazenda Belém field, in northwestern part of Potiguar Basin. More detailed geological information on this Basin was presented by Lopes *et al.* (1999).

Liquid-liquid Extraction: About 500 mg of oil sample was dissolved in dichloromethane and extracted with 5% sodium bicarbonate solution.

ESI and APCI MS TOF Analysis: The acidic fractions and crude oil were analyzed in a high resolution micrOTOF-Q II (BRUKER), small amount of sample was

dissolved in 500 µL toluene:methanol (1:1) and then, 20 µL of concentrated NH₄OH was added. Electro-spray ionization (ESI) source was optimized as follows: negative ionization mode, capillary voltage 3.0 kV, nitrogen was used as nebulizing gas with a flow rate of 5 L/min and a temperature of 200 °C at 0.3 bar. The atmospheric pressure chemical ionization (APCI) source was optimized as follows: negative ionization mode, capillary voltage 4.0 kV, nitrogen was used as nebulizing gas with a flow rate of 4 L/min, temperature of dry gas of 200 °C and temperature of vaporizer of 450 °C at 2.0 bar.

GC/MS Analysis: The analyses were performed using a Thermo Scientific TSQ Quantum XLS Ultra Triple Quadrupole GC-MS instrument. Capillary chromatographic column (Equity TM-1, 30 m, 0.25 mm ID). Initial temperature of 70 °C (4 min hold), followed by a ramp of 2 °C/min up to a final temperature of 300 °C (20 min hold). The carrier gas was helium at a constant flow rate of 1.0 mL/min. Transfer line temperature was 310 °C. The quadrupole mass spectrometer was operated in full scan mode over the mass range 50–650 Da (EI mode at 70 eV).

Results and Discussion

Hydrocarbons were detected by GC/MS, and carboxylic acids were obtained by liquid-liquid extraction and then detected by ESI-TOF MS and APCI-TOF MS. The GC-MS analyses showed low hopane/sterane ratios, high gammacerane (>60) and bisnorhopane (>10). Ts/Tm, C₃₅/C₃₄ indices of the oils allowed their classification as marine evaporitic type. Biodegradation was confirmed by

the presence of 25-norhopane and the total loss of *n*-alkanes and isoprenoids.

Naphthenic acids were also evaluated in crude oil by both ESI and APCI MS techniques to simplify the analytical procedures, preserving the relative composition of compounds in the oils samples and detecting higher homologues. The acidic oil fractions were analyzed in a high resolution ESI- and APCI-TOF MS by direct infusion (Figure 1). Working with negative Electrospray Ionization-ESI, we detected a series of bicyclic (C_{15} - C_{20}) and tricyclic acids (C_{20} - C_{26}).

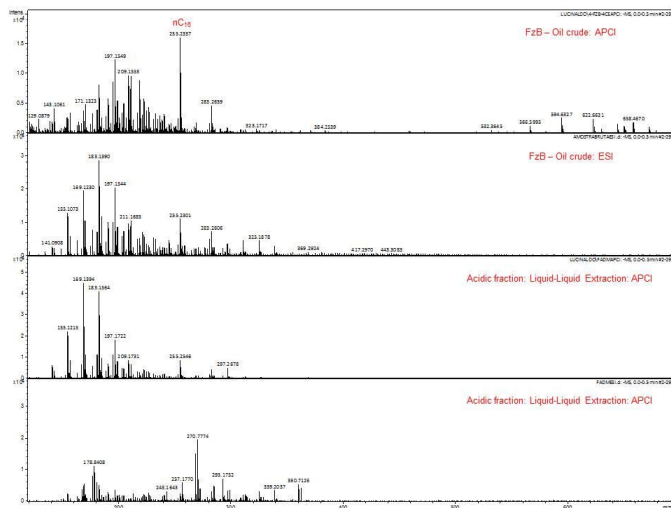


Figure 1. Comparison of ESI vs APCI results (Full scan negative ion mode, scan range 100 – 1000 m/z).

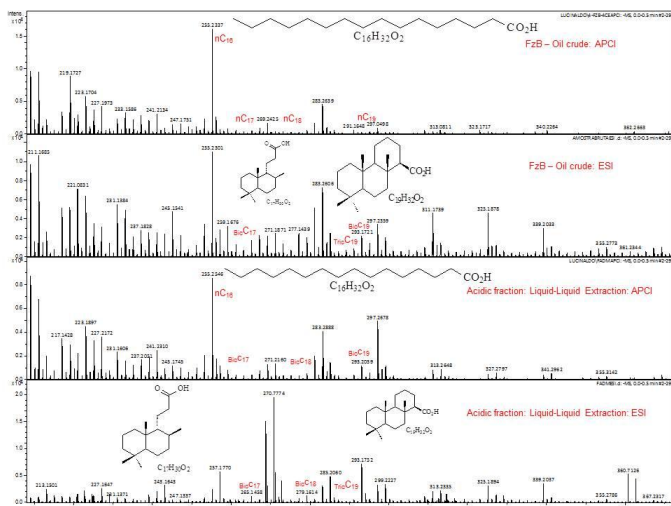


Figure 2. Expansion of highlighted region from previous Fig. 1.

Soft ionization methods (APCI- and ESI-TOF) produce one major ion from each compound, with little further fragmentation, and it avoids extraction, purification and derivatization steps, required for the analysis of naphthenic acids. Atmospheric pressure

chemical ionization is a supplementary technique to electrospray. It is a soft ionization technique but not as soft as ESI. Because charged ions are not generated in APCI and it operates at high temperatures this technique is used to analyze smaller, thermally stable polar and non-polar compounds. Signal suppression due to unknown matrix interferences is a common problem in quantitative analysis, especially in ESI, so this is a limitation.

Analyses by both methods showed that It was possible to evaluate the distribution of n-alkane, bicyclic and tricyclic acidic biomarkers without laborious processes of purification and derivatization of oil sample, for high to moderate level of biodegradation.

Conclusions

LC-MS (ESI and APCI) is an analytical method for the sensitive characterization of “molecular fossil” in crude oil. In general naphthenic acids are known to be difficult to analyze; some respond well in ESI, and others respond better in APCI mode. ESI and APCI - MS methods were evaluated for naphthenic acids analyses. Based on analyses of n-alkanoics, mono and sesquiterpenoids carboxylic acids, ESI in the negative ion mode was found to be superior, however both techniques have their specificity.

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