# Chemical characterization of N-methylpyrrolidone fractions of asphaltenes by ESI FT-ICR MS.

**Verônica V. Carvalho[1] (PG), Géssica A. Vasconcelos[1] (PG), Carla S. de Freitas[1] (PG), Lilian V. Tose[2] (PG), Felipe P. Fleming (PQ)[3], Felipe M. R. Cardoso(PQ)[3]  Wanderson Romão[2] (PQ), Boniek G. Vaz[1] (PQ)***

[1] *Federal University of Goiás, Goiânia – GO, Brazil.  *boniek@ufg.br*
[2] *Federal  University of Espírito Santo, Vitória – ES, Brazil.*
[3] *Petróleo Brasileiro S.A -CENPES- Rio de Janeiro, RJ, Brazil.*
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## Abstract

Asphaltenes, when dissolved in NMP, generate two fractions, a soluble (NS) and an insoluble (NI). Ascanius[1] reported that the insoluble fraction did not absorb fluorescence or UV-Vis, indicating the aliphatic presence and opening new horizons about asphaltenes composition. Therefore, these fractions were characterized fluorescence, IR and ESI (±) FT-ICR MS.

## Introduction

Asphaltenes form two fractions (NS and NI) when placed in NMP. Ascanius[1] characterized these fractions using fluorescence, IR, and UV-Vis to revealing that NI fraction did not have active absorption suggesting that these fractions have a low proportion of aromatic compounds. This fact opened a new debate on the composition of asphaltenes, which are widely discussed in the literature because they are composed mainly of highly aromatic and polar molecules. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) have the highest available mass resolution, resolving power, and mass accuracy to perform the analysis of complex petroleum mixtures at the molecular level. Here, we describe a detailed characterization of NS and NI asphaltenes NMP fractions by ESI FT-ICR MS to fulfills the lack of information about the composition of NMP asphaltenes fractions.

## Results and Discussion

The insoluble fraction (NI) and the soluble fraction (NS) of asphaltenes were obtained after the addition of 20 mL of NMP in asphaltene sample followed by filtration. NS fraction was removed from NMP by liquid-liquid extraction in a water/toluene system. NS and NI fractions and the original asphaltene were characterized by infrared spectroscopy, fluorescence spectroscopy, and ESI (±) FT-ICR MS. Figure 1 illustrates the mass spectra obtained for all samples. In both positive and negative mass spectra, NS fraction shows a wide number of detected compounds. On the other hand, NI fraction, in both positive and negative mode, shows mass spectra with a very reduced number of detected compounds.  These findings corroborate with results of IR and fluorescence analysis.  To display the similarities or differences between fractions and the original asphaltene patterns we construct certain types of plots such as class distribution  and DBE versus carbon number (CN) plot, which are routinely used in petroleomics studies.
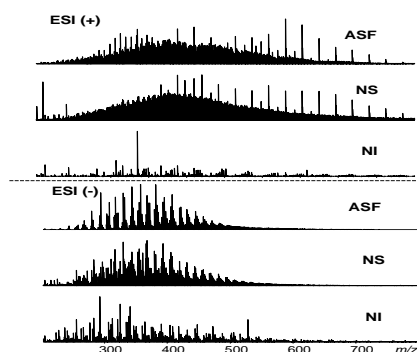


**Figure 1.** ESI (±) FT-ICR MS spectra.

Figure 2 shows the class distribution and DBE vs CN plots of N class for NS, NI, and the original asphaltene. Note that the NS fraction is composed mostly by compounds that belong to N and N2 classes while HC class was the most abundant in NI fraction. For the N class, NS fraction showed higher DBE values varying from 15-50, and 15-20, in positive and negative mode respectively. CN varies 20-80 and 20-50 to NS in positive and negative mode, respectively. NI fraction does not exhibit any N-compound detected.
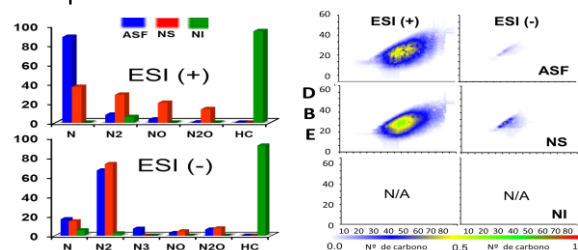


**Figure 2.** Class diagram and carbon number vs. DBE graphics.

## Conclusions

FT-ICR MS data revealed that the NS fraction are composed mainly of polar compounds while NI presents only nonpolar compounds, corroborating with IR, fluorescence and UV-Vis data.

## Acknowledgment

[1]Ascanius, B. E.; Garcia, D. M.; Andersen S. I. *Energy & Fuels,* 2004, 18, 1827-1831.