



ESI-FT-ICR MS in the identification and characterization of tetrameric acids (ARN) in petroleum and naphthenates with minimal sample preparation

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Abstract

Among the challenges of identifying and characterizing the ARN of its complex matrix, we propose the use of a new analysis methodology for the identification of these species in oil samples and naphthenate deposits *in situ*. Such a methodology is based on an unconventional approach to the negative-mode electrospray ionization technique, ESI(-), combined with high resolution and precision mass spectrometry (FT-ICR MS). The methodology proved to be promising and advantageous, as it requires simpler sample preparation, reduced consumption of reagents and analysis time. With good feasibility of application to identify the nature of deposits and also to estimate, in an initial phase, the potential for incrustation and the need for oil treatment in production units.

Keywords

ARN; sample preparation; ESI-FT-ICR MS.

Introduction

During crude oil production, calcium naphthenate deposits can precipitate and build up in surface facilities causing flow irregularities and equipment clogging [1].

These deposits are formed at the oil/water interface, due to the presence of a specific group of high molecular weight tetrameric naphthenic acids [2], sometimes called ARN (Norwegian term for eagle) [3].

In this context, identifying the presence of ARN in the oil is useful to identify the nature of the deposit, assess the fouling potential and the need for early treatment [1].

However, the ARN content in crude oils is very small, being in undetectable concentrations at levels of a few tens of parts per million [4], which makes it difficult to measure from its matrix, which has great complexity and varied composition.

The literature reports some analytical strategies that involve the measurement of ARN from crude oil [5], which require laborious sample preparation and extraction methods, a significant consumption of solvents and, sometimes, an extra care due to toxicity of chemical reagents involved in the process [5].

However, there is a diversity in analytical instrumentation that greatly contributes to the characterization of naphthenic acids, which

includes ARN, in petroleum and its derivatives [5]. Even so, the widespread use of modern instrumental techniques for the determination of these species does not eliminate the need for preparation methods, which is one of the critical steps in the analytical process and can be an obstacle to obtaining reliable results.

In this sense, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has proved to be an important analytical tool in the characterization of naphthenic acids [5] and with good prospects for the identification of ARN directly in petroleum and derivatives, with simplicity in preparation and minimal consumption of sample and reagents.

Therefore, in the present study, we propose a new methodology that comprises the identification and characterization of ARN in petroleum samples and, *in situ*, calcium naphthenates deposits, by an unconventional approach of the electrospray ionization technique in negative mode, ESI(-), combined with FT-ICR MS.

Methodology

Materials

All chemical products used were of analytical grade (purity greater than 99.5%). Toluene supplied by Vetec Química Fina Ltda, Duque de Caxias, Brazil.

Methanol by Dinâmica Química Contemporânea Ltda, Indaiatuba, Brazil. Formic acid and ammonium hydroxide were purchased from Sigma-Aldrich, St. Louis, USA.

A sample of calcium naphthenate deposit and two oil samples (referenced as oil 1 and oil 2, which had reports of naphthenate deposition), were studied. All samples were provided by the Petrobras Research Center (CENPES, Rio de Janeiro Brazil).

Experimental Procedure

FT-ICR MS analysis was performed using a 9.4T Q-FT-ICR MS hybrid (Solarix, Bruker Daltonics Bremen, Germany) equipped with a commercially available ESI source (Bruker Daltonics).

The mass spectra were acquired using 200 scans of time-domain transient signals of 4M (mega-point).

The data were processed by the Composer software (Sierra Analytics, Modesto, CA, USA) and the elemental compositions were determined through the m/z values.

The equipment was externally calibrated using an optimized calibrating solution, which was used to obtain a greater number of signals in the region of interest ($\sim m/z$ 980 – 1300, ARN ion region) and thus increase the mass accuracy. Thus, before the acquisitions, the equipment was externally calibrated using an optimized calibrant solution of L-arginine and tunnig mix (m/z 200-1500).

The oil samples were diluted to 1 mg mL⁻¹ in toluene: methanol (1:1) containing 0.1% v/v of NH₄OH for ESI(-) e to 0.1% v/v formic acid for ESI(±).

The naphthenate deposit (free of residual oil as reported in the literature [6]) was diluted to 0.5 mg mL⁻¹ in toluene:methanol (1:1) containing 0.1% v/v formic acid for measurements in ESI(-).

The analysis of the samples in the unconventional ESI(-) that occurs by the addition of formic acid, we discriminated by the representation ESI(-)_{FA}, throughout the discussions.

Table 1 shows the different conditions for acquiring the spectra.

Table 1. Parameters used in the acquisition of FT-ICR MS spectra of the investigated samples.

Parameters	ESI(+)	ESI(-)	ESI(-) _{FA}
Injection flow (mL min)	12.0	7.0	12.0
Capillary voltage (kV)	4.5	3.7	3.7
Nebulizer gas pressure (bar)	2.0	1.5	1.5
TOF (ms)	1.0	1.0	1.0
Ion transfer temperature (°C)	250	250	250
Skimmer (V)	50.0	-35.0	-50.0
Collision voltage (V)	-45.0	30.0	45.0
Time of accumulation of ions in the hexapole (s)	0.050	0.060	0.150

Results and Discussion

Figure 1 shows the mass spectra of the oil samples with reports of calcium naphthenate precipitation, called oils 1 and 2, obtained by FT-ICR MS combined with ESI(+) (Figure 1a) and ESI(-) of unconventional way, which we discriminated by the ESI(-)_{FA} representation (Figure 1b).

It is possible to observe that in both oils, despite having typical gaussian profile of petroleum, with the m/z range of 200-1200 and average molecular weight (M_w) with similar values (between \sim 659 and 680 Da), the profiles spectra were altered as a function of the ionization mode, but with a greater amplitude for the ESI(-)_{FA}-MS, that is ionized with formic acid.

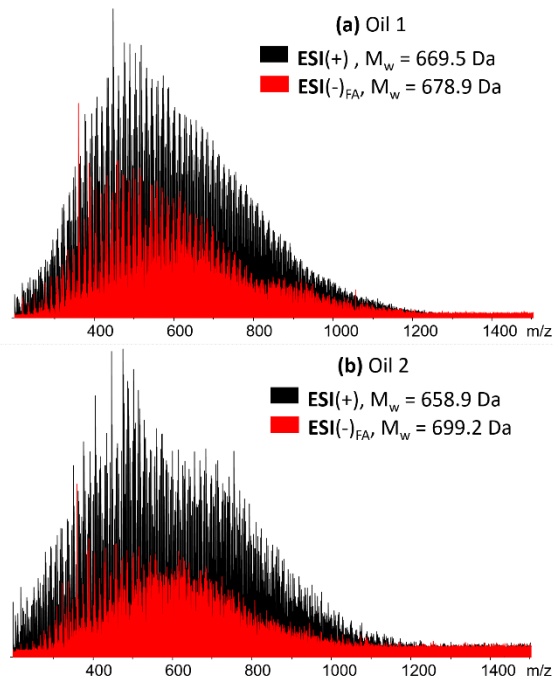


Figure 1. FT-ICR MS spectra of oils (a) 1 and (b) 2 obtained by ESI(+) and ESI(-)_{FA}.

The graphs of oil classes from the data obtained by ESI(+) and ESI(-)_{FA} (Figure 2a and 2b, respectively), revealed that the most abundant species identified by FT-ICR MS in ES(+) were N [H] and O₃[H] classes. Alternatively, in the ESI(-)_{FA}, the O₂[H], N[H], N₂[H], O₃[H] and O₄[H] classes stood out. It is important to note that the O₈[H] class was observed in oil 2 by ESI(+) and in both oils by ESI(-)_{FA}, but only the one indicated in the negative mode can be correlated with ARN. Because electrospray ionization in negative mode provides the composition of more acidic polar species in their deprotonated [M-H]⁻ forms, while in positive mode only the polar and basic component.

In our study, we observed that the mass spectra of oils 1 and 2 by ESI(-)_{FA} showed mass spectra with typical petroleum gaussian profiles only for 0.1 %v/v of formic acid. At higher concentrations, the mass spectra (which are not shown here) showed only signals of formate agglomeration. This guided the experiments in using the 0.1 %v/v concentration of formic acid in the ESI(-)_{FA} for the identification of ARN in the samples.

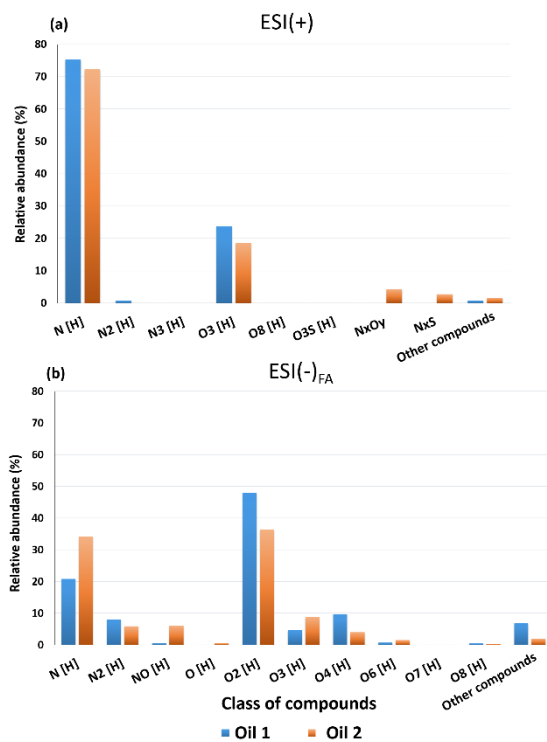


Figure 2. Distribution graphs of classes of heteroatoms containing compounds present in oils 1 and 2, obtained from FT-ICR MS data combined with (a) ESI(+) and (b) ESI(-)_{FA}.

The class plots obtained from FT-ICR MS by ESI(-)_{FA} (Figure 3a) indicated that the major classes are O₄[H], O₂[H] and N[H] in oils 1 and 2, with differences important in the variation and abundance of the classes in relation to the ESI(-) (Figure 3b). The O₈[H] class observed only with ESI(-)_{FA} stands out, due to the possible conversion of conjugated salts (naphthenates) into ARN acids by the addition of formic acid.

The average of triplicate FT-ICR MS by ESI(-)_{FA} averages of the oils revealed the identification of a total of ~2780 molecular formulas in oil 1, of which about 24 corresponded to the O₈[H] class. For oil 2, an average of ~2192 compounds were identified, among which 11 belong to the O₈ class (ARN class).

In general, ions can be produced through several different mechanisms, depending on the ionization source and polarity [7]. Conventionally in ESI, acid addition favors protonation mechanisms that generate [M+H]⁺ species, which are only observed in the positive mode. However, for oil samples with reports of calcium naphthenate precipitation (oils 1 and 2), the addition of formic acid caused the conversion of the conjugated salts (naphthenates) to their acids, ARN. In other words, the salts of these acids were immediately converted to ions of the [M-H]⁻ type, with the addition of acid in the ESI(-)_{FA} that allowed the detection of ARN in the FT-ICR MS.

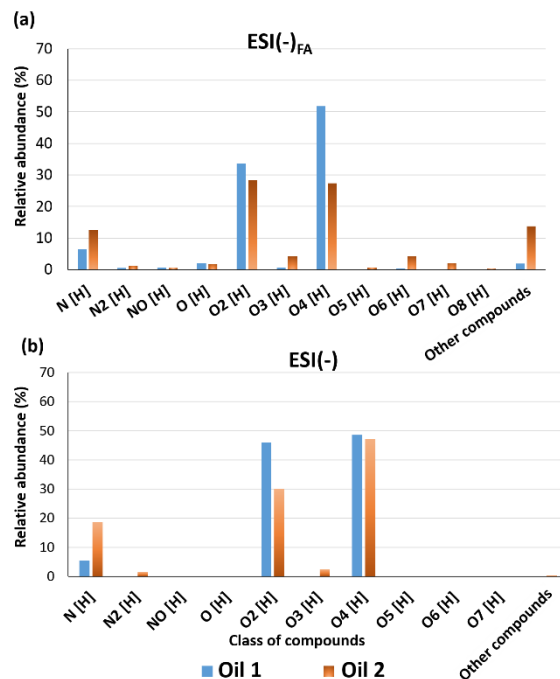


Figure 3. Distribution graphs of classes of heteroatoms containing compounds present in oils 1 and 2 revealed from FT-ICR MS data by (a) ESI(-) and (b) ESI(-)_{FA}.

In fact, the methodology of adding organic acids to inhibit the formation of naphthenate is already used in the oil field through the injection of organic acids [8]. Furthermore, conventionally, ARN are recovered from their matrix by acidified extraction, so that chemical equilibrium manipulation for ARN salt extraction and purification [5]. Thus, ARN chemically linked as naphthenates are converted into free acid monomers [5]. Therefore, we have seen that the *in situ* conversion of the ARN salt to its acid form is pertinent, with subsequent direct analysis of the sample, without any type of extraction or fractionation.

This discussion became concrete when we obtained a spectrum in the FT-ICR MS (Figure 4a) by the direct injection of a solution of the naphthenate deposit (free of residual oil), diluted only in toluene:methanol (1:1) and 0.1 %v/v formic acid, in the electrospray source in negative mode. The results (Figure 4) attest that the O₈ class is the majority in the deposit, with an average M_w distribution of 1185.5 Da and signals concentrated in the three specific regions, with emphasis on the of between *m/z* 475-650 and 950-1300, which correspond to di (ARN⁻²) and monocharged (ARN⁻¹) tetrameric acids, respectively.

The results of FT-ICR MS allied to ESI(-)_{FA} revealed that the main species present in the deposit are made up of ARN with hydrocarbon skeletons with carbon numbers between C₆₀₋₈₃, and that among the most abundant ions are the monocharged ones, [C₇₁H₁₂₄O₈-H]⁻, [C₈₀H₁₄₂O₈-H]⁻ and [C₈₁H₁₄₂O₈-H]⁻ of respective *m/z* 1103.92404, 1230.06537 and 1242.06619. While the doubly charged ions the doubly charged ions [C₈₀H₁₄₀O₈-H]⁻², [C₈₀H₁₄₄O₈-2H]⁻² and [C₈₁H₁₄₂O₈-H]⁻² have the

respective m/z 613.52104, 615.53667 and 620.52893.

Through the data assignments, it was possible to identify 39 species belonging to the O_8 class (ARN class) among the 80 molecular formulas identified in the deposit by direct ionization in the $ESI(-)_{FA}$.

In consideration of the above, the methodology of identification and characterization of ARN in oil samples and naphthenate deposits *in situ* by FT-ICR MS with ionization in $ESI(-)_{FA}$ shows to be very promising. Since it requires a simpler sample preparation, it is still advantageous in terms of reducing reagent consumption and analysis time.

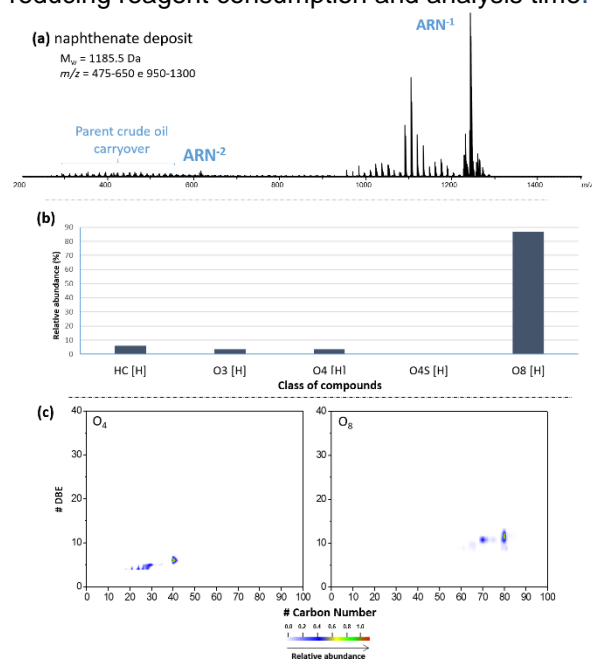


Figure 4. (a) FT-ICR MS spectrum obtained from direct injection of the naphthenates deposit into the electrospray force, $ESI(-)_{FA}$, (b) Distribution graphs of classes of heteroatoms and; (c) DBE versus carbon number plot for the $O_4[H]$ and $O_8[H]$ classes present in the naphthenate deposit.

Conclusions

The articulate and detailed use of the FT-ICR MS allowed us to understand that the ARN species, present in the oil samples with reports of calcium naphthenate precipitation (oils 1 and 2), could be in the form of its conjugated salt (naphthenates). Thus, the study directed us to the development of a methodology for the identification and characterization of ARN in petroleum samples and in naphthenates deposits *in situ* by FT-ICRMS with ionization of samples by the addition of formic acid in the negative electrospray, $ESI(-)_{FA}$.

The methodology proposed here is promising and with good feasibility of application to identify the nature of deposits, estimate the fouling potential and the need for treatment during oil production, with simplicity in sample preparation and minimal consumption of reagents.

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Responsibility Notice

The authors are the only responsible for the paper content.

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