



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

Naphthenate deposits are a major obstacle in ensuring an economic and successful flow in the production and processing of crude oil. The formation of these deposits depends mainly on a specific group of high molecular weight tetrameric acids, sometimes called ARN. Among the challenges of identifying and characterizing the ARN of this complex matrix, we propose the use of a new analysis methodology for identifying these species in oil samples and naphthenate deposits with minimal sample preparation. Such methodology is based on an unconventional approach to the negative-mode electrospray ionization technique, combined with high resolution and precision mass spectrometry. The methodology proved to be promising and advantageous, since it requires a simpler sample preparation and a reduced consumption of reagents and analysis time. With good feasibility of application to identify the nature of deposits and to estimate, in an initial phase, the potential for inorganic scale and the need for oil treatment in production units.

Keywords ARN · Naphthenates · Sample preparation · ESI-FT-ICR MS · Rapid detection · Unconventional ionization electrospray

Introduction

In crude oil production, ensuring an economic and successful flow (Simon et al. 2015) is critical. However, calcium naphthenate deposits can precipitate and build up in surface facilities causing flow irregularities and equipment clogging (Sjöblom et al. 2014).

These deposits are formed at the oil/water interface, due to a specific group of high molecular weight tetrameric naphthenic acids (Simon et al. 2019), sometimes called ARN (Norwegian term for eagle) (Mediaas et al. 2005), capable of crosslinking with calcium ions (Simon et al. 2020a) upon changes in pH in the co-produced water (Mediaas et al. 2005; Simon et al. 2020b) and precipitating as an insoluble salt (calcium naphthenate) capable of constraining oil production systems.

In this context, identifying ARN in the oil helps identify the nature of the deposit and assess fouling potential and the need for early treatment (Sjöblom et al. 2014).

However, the ARN content in crude oils is very small, being in undetectable concentrations at levels of a few tens of parts per million (Simon et al. 2020a), which hinders measurement from the matrix, due to its great complexity and varied composition (Subramanian et al. 2017).

The literature reports some analytical strategies that involve measuring ARN from crude oil (Albuquerque et al. 2016; Barros et al. 2022a; Marshall et al. 2011; Mediaas et al. 2003, 2014; Paek and Mennito 2017), which require laborious sample pre-preparation and extraction methods, a significant

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consumption of solvents and, sometimes, extra care due to the toxicity of chemical reagents in the process (Barros et al. 2022a; Marshall et al. 2011; Mediaas et al. 2003; Nordgård et al. 2012).

Nonetheless, a varied analytical instrumentation greatly contributes to characterizing naphthenic acids, which includes ARN, in petroleum and its derivatives (Barros et al. 2022a). Even so, the widespread use of modern instrumental techniques for determining these species does not eliminate the need for preparation methods, which are 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) is an important analytical tool in characterizing naphthenic acids (Barros et al. 2022b; Li et al. 2022; Juyal et al. 2015; Marshall et al. 2011; Mediaas et al. 2005; Mapolelo et al. 2009, 2011; Orrego-Ruiz et al. 2016; Putman and Marshall 2016) and with good prospects for identifying ARN directly in petroleum and derivatives, with a simple preparation and minimal consumption of sample and reagents.

Ionization in the ESI involves protonation or deprotonation of the analytes in the aqueous and gaseous phases, thus, the pKa of functional groups is important in their ionization response at the ESI source. For an analyte to be protonated with the ESI, it must be basic in the solution or in the gaseous phase. This is also true for acid analytes and deprotonation. In addition, ESI analysis of basic analytes generally works best at low pH, whereas acid analytes analysis works best at higher pH (Wang and Cole 1997). However, this is not always true, since protonated ions are observed when the ESI-MS analysis is performed with basic solutions (when the pH is higher than the analyte pKa) (Kelly et al. 1992; Wang and Cole 1994; Zhou and Cook 2000) and, likewise, deprotonated ions can be observed in ESI analysis of acid solutions (Wang and Cole 1994; Zhou and Cook, 2000). Therefore, we propose a new methodology that comprises the identification and characterization of ARN in petroleum samples and, with minimal sample preparation, calcium naphthenates deposits, by an unconventional approach of the electrospray ionization technique in negative mode [ESI(-)], combined with FT-ICR MS. The solubilization of naphthenate deposits and their conversion into their mono and doubly charged forms was performed by shifting the chemical balance by adding formic acid. Thus, these compounds were accessible to analysis by ESI(-) MS using this unconventional ionization strategy.

Materials and methods

Materials

All chemical products used were of analytical grade (purity greater than 99.5%). Toluene was supplied by Vetec Química Fina Ltda, Duque de Caxias, Brazil. Methanol by Dinâmica Química Contemporânea Ltda, Indaítuba, Brazil. Formic acid and ammonium hydroxide were purchased from Sigma-Aldrich, St. Louis, USA.

Samples

A calcium naphthenate deposit sample and two petroleum samples (referenced as oil 1 and oil 2, which had reports of naphthenate deposition) from a production field located in the sedimentary basin off the Brazilian coast, were studied. All samples were provided by the Petrobras Research, Development and Innovation Center (CENPES, Rio de Janeiro Brazil), as well as the characteristics of samples of oils 1 and 2 (Table S-1), being the method for determining the total acidity number (TAN) was in accordance with ASTM D664 (2017), API gravity and density at 20 °C with ISO 12,185 and water content, determined by Karl Fischer potentiometric titration, in accordance with ASTM E-203/01 (2001).

Methods

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 oil samples were diluted to 1 mg mL⁻¹ in toluene:methanol (1:1) containing 0.1% v/v of ammonium hydroxide (NH₄OH) for ESI(-) and to 0.1% v/v formic acid (CH₂O₂) for ESI(±).

The naphthenate deposit, free of residual oil as reported in the literature (Barros et al. 2022b), 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(-) with the addition of formic acid was discriminated by the representation ESI(-)_{FA} throughout the discussions. Table 1 shows the different conditions for spectra acquisition.

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 (~ m/z 980–1300, ARN ion region) and thus increase mass accuracy. Before the acquisitions, the equipment was externally

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

Parameters	ESI(+)	ESI(-)	ESI(-) _{FA}
Injection flow (mL min ⁻¹)	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

calibrated using an optimized calibrant solution of L-arginine and tuning mix (m/z 200–1500).

Mass spectra were acquired with 200 sweeps of transient signals in the 4 M (mega-dot) time domain, resulting in an FID of 2.25 s.

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

Results and discussion

Depending on the type and amount of the naphthenic acids and the calcium content in the produced water the naphthenate deposit formed could be very severe. In the case of north portion of Campos Basin (Brazil), the naphthenate deposition potential is high due to the commingled production in the Floating Production Storage and Offloading (FPSO) of crudes and formation waters from different fields. In this case, a presalt light crude co-produced with a CO₂ and calcium-rich formation water that come from a carbonate reservoir, and a postsalt high total acid number crude co-produced with a formation water that presents a lower calcium concentration that comes from a sandstone reservoir. CO₂ degassing and the mix of these two incompatible formation waters also contribute to increase the naphthenate deposition and calcium carbonate scale can be also co-precipitated. Figure S-1 shows collect aliquots rich in oil/water/sediments accumulated in electrostatic separator vessel of the FPSO.

Solid state Nuclear Magnetic Resonance (NMR) experiment of the solids in Figure S-1b demonstrates that this sample is rich in naphthenates (signals from ~190 to 170 and ~55 to 5 ppm), aromatic hydrocarbons probably from crude oil (signal from ~155 to 105 ppm) and chemicals (signal from ~78 to 70 ppm), Figure S-2. On the other hand, the detailed speciation of the deposit can be used to identify its origin, based on the composition of classes and number of carbons (Mapolelo et al. 2009), as for example, in the

works of Juyal et al. (2015); Barros et al. (2022b) who identified ARN species with low molecular weight (with C_{60–77} hydrocarbon backbones) in field deposits in South America, indicating molecular similarity between ARN species found in West African deposits (Mapolelo et al. 2009), attributing genetic relatedness between field deposits on both sides of the Atlantic Ocean.

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

Despite having typical Gaussian petroleum profiles, with the m/z range of 200–1200 and mean molecular weight (M_w) with similar values (around 659 and 680 Da), the profiles spectra were altered in both oils as a function of the ionization mode, but with a greater amplitude for the ESI(-)_{FA}-MS, which is ionized with formic acid.

The graphs of oil classes from the data obtained by ESI(+) and ESI(-)_{FA} (Fig. 1c, d, respectively) showed that the most abundant species identified by FT-ICR MS in ESI(+) were N[H] and O₃[H] classes. Alternatively, in ESI(-)_{FA}, the O₂[H], N[H], N₂[H], O₃[H], and O₄[H] classes stood out. The O₈[H] class was observed in both oils by ESI(-)_{FA}, which can be correlated with ARN, as electro-spray ionization in the negative mode provides the most acidic polar species composition in its deprotonated forms [M-H]⁻ forms, whereas in positive mode only the polar and basic components are provided (Palacio Lozano et al. 2020).

Figure 2 shows the FTIR MS spectra of oil samples 1 and 2 ionized in negative mode by adding ammonium hydroxide (ESI(-)) and formic acid (ESI(-)_{FA}) at concentrations of 0.1, 0.5, and 1.0% v/v. In the conventional ESI(-) mode of ionization, with addition of the base, oils 1 and 2 showed Gaussian profiles, with m/z between 200 and 1000, depending on the concentration of ammonium hydroxide added (Fig. 2a–f).

According to this study, 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 (Fig. 2h, i and k L) showed only typical signs of clusters. This guided the experiments in using the 0.1% v/v concentration of formic acid in ESI(-)_{FA} for identifying ARN in the samples.

The class plots obtained from FT-ICR MS by ESI(-)_{FA} (Fig. 2n) indicated that the major classes are O₄[H], O₂[H], and N[H] in oils 1 and 2, with differences in the variation and abundance of the classes compared to ESI(-) (Fig. 2m). 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.

Figure 3 shows the reproducibility of the results, regarding the ionization of oil samples by adding formic acid in the

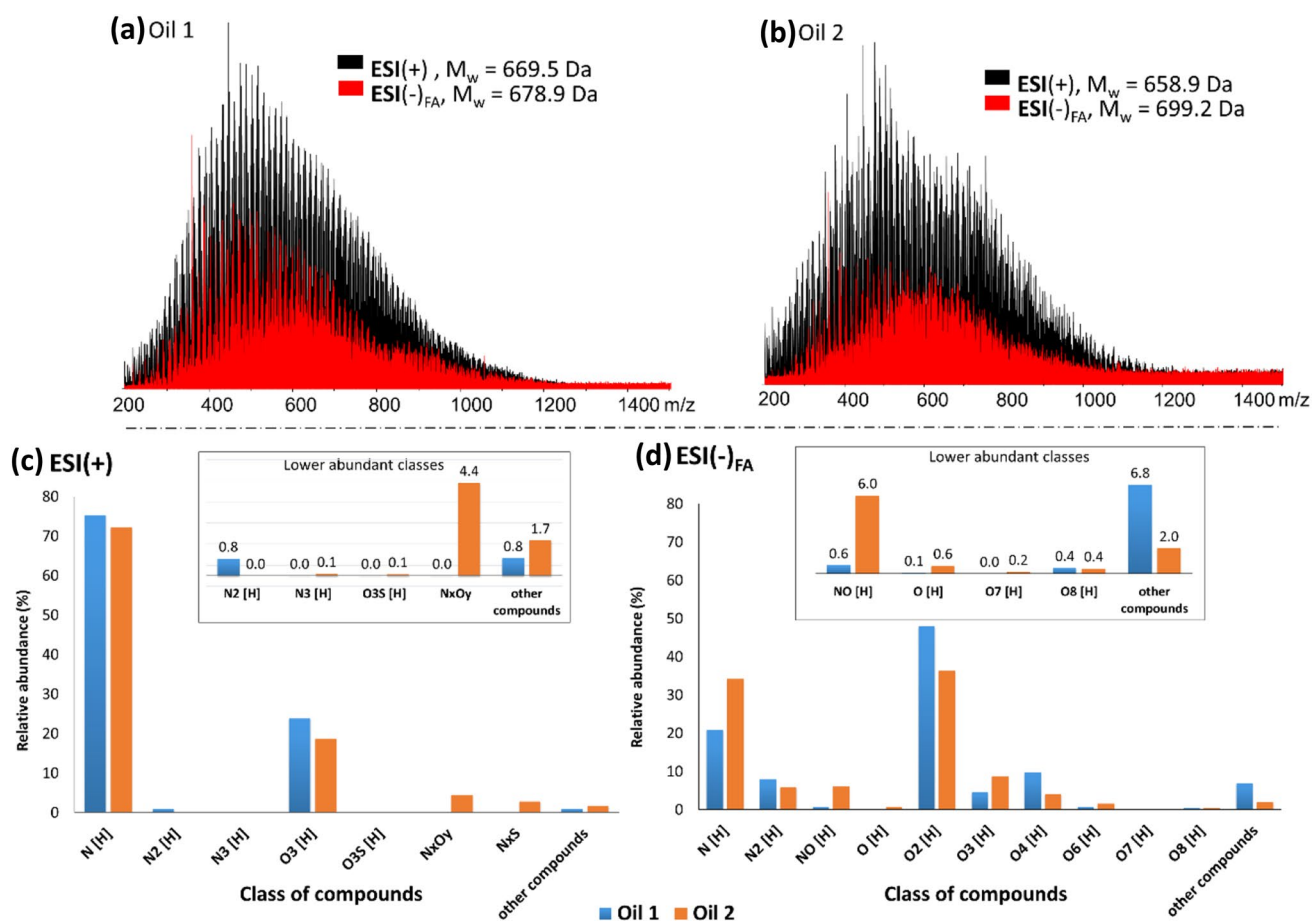


Fig. 1 FT-ICR MS spectra obtained in ESI(+) and ESI(-)_{FA} obtained for samples of **a** oil 1 and **b** oil 2, respectively; distribution graphs of classes of heteroatoms containing compounds in oil 1 and 2, obtained from FT-ICR MS data combined with ESI(+)

(c) and ESI(-)_{FA} (d), respectively. Inserted in the figure, highlighted, are the enlarged graphs for the classes of compounds with lower abundances

negative electrospray (ESI(-)_{FA}). It shows the FT MS spectra in the ESI(-)_{FA} of oils 1 and 2, in triplicate (Fig. 3a–f), and the graph of the mean of the classes with their relative standard deviations (Fig. 3g). The mean of triplicate FT-ICR MS by ESI(-)_{FA} of the oils showed the identification of a total of around 2780 molecular formulas in oil 1, of which about 24 corresponded to the O₈[H] class. For oil 2, a mean of around 2,192 compounds were identified, among which 11 belong to the O₈ class (ARN class).

In general, ions can be produced by many mechanisms, depending on the ionization source and polarity (Palacio Lozano et al. 2020). 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), adding 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. The response of analytes in negative mode decreases gradually with the increase of formic acid concentration. This response confirms that acidic conditions decrease the ESI response of negative ions, that is, low pH conditions do not favor the formation of the deprotonated analyte. However, similarly to that observed in this study, the weaker acids (i.e., acetic acid, propionic acid, and n-butyric acids) increased the ESI negative ion response at concentrations ranging from 10 μ M to 10 mM (Wu et al. 2004).

Obtaining an excessive load on the droplets by an electrochemical reaction that occurs at the spray tip is necessary to perform a successful ESI analysis. In negative mode, the dominant reaction is reduction. Within unmodified proton solutions derived from protic solvents or analytes are reduced to hydrogen gas, the additional protons, provided by an acid modifier, help the reduction and excessive negative charge increase in spray droplets. This excess negative charge probably accumulates on the droplet surface due to

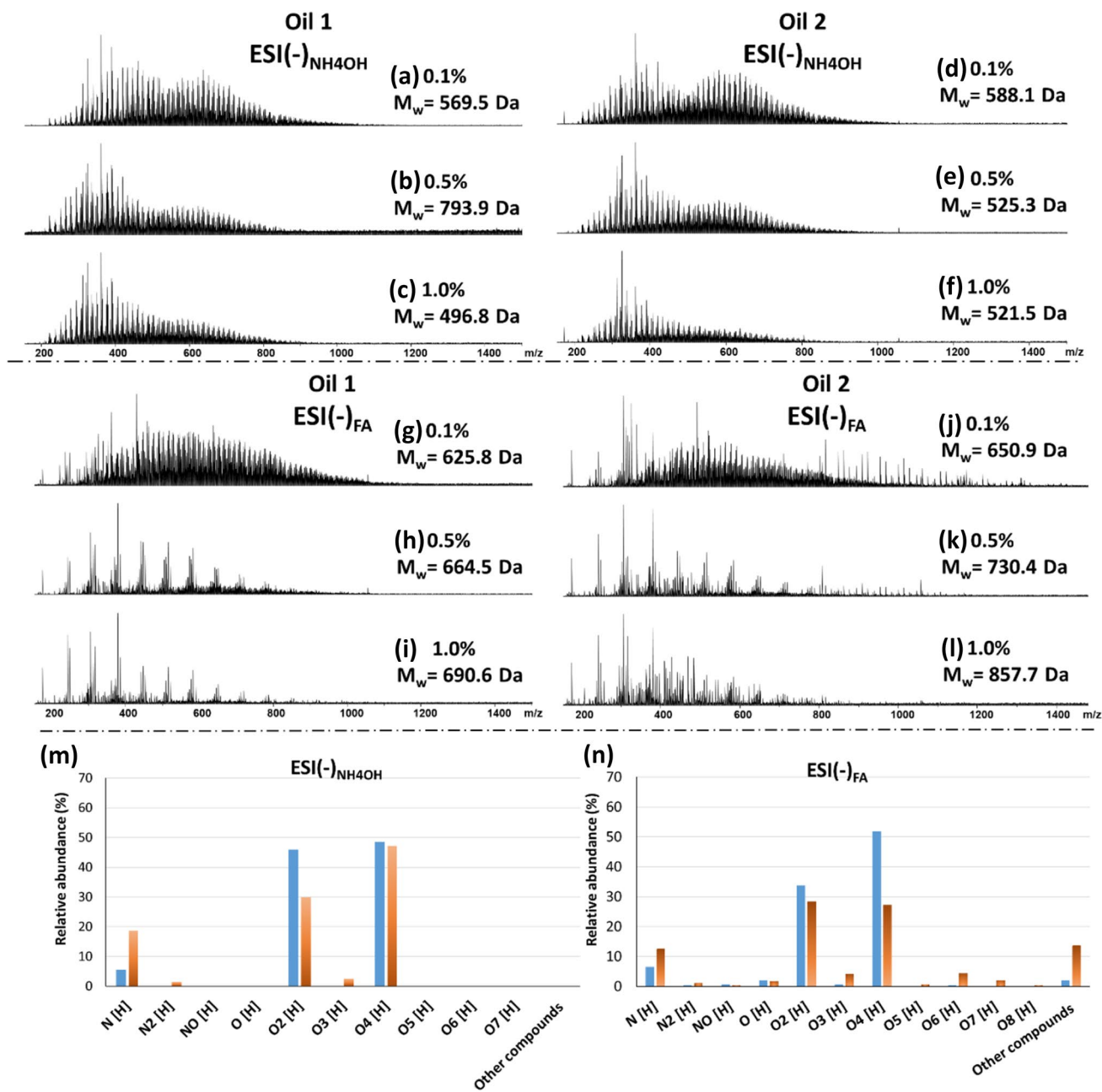


Fig. 2 FTIR MS spectra of oil samples 1 and 2 ionized in negative mode by adding ammonium hydroxide (ESI(-)) (a–f) and formic acid (ESI(-)_{FA}) (g–l) at concentrations of 0.1, 0.5, 1.0% v/v; and

distribution graphs of classes of heteroatoms of compounds present in oils 1 and 2 revealed from FT-ICR MS data by ESI(-) (m) and ESI(-)_{FA} (n)

electrical repulsion in negative mode ESI, increasing the pH on the droplet surface and providing a local environment in which the deprotonation of the analytes occurs more easily than inside the solution.

The ESI MS is strongly governed by the chemistry in the droplet surface layer. As such, the greater pH change on the droplet surface compared with the solution can increase the ESI response in negative mode when moderate concentrations of acid modifiers are used. However, this phenomenon

is suppressed at higher concentrations of the acid modifier due to the decrease in the pH gradient within the spray droplet. Therefore, analyte deprotonation is suppressed in these analytic conditions in the negative mode of ionization.

In fact, adding organic acids to inhibit the formation of naphthenate is already used in the oil field by the injection of organic acids Bretherton et al. (2005).

Furthermore, conventionally, ARN are recovered from their matrix by acidified extraction, by using chemical

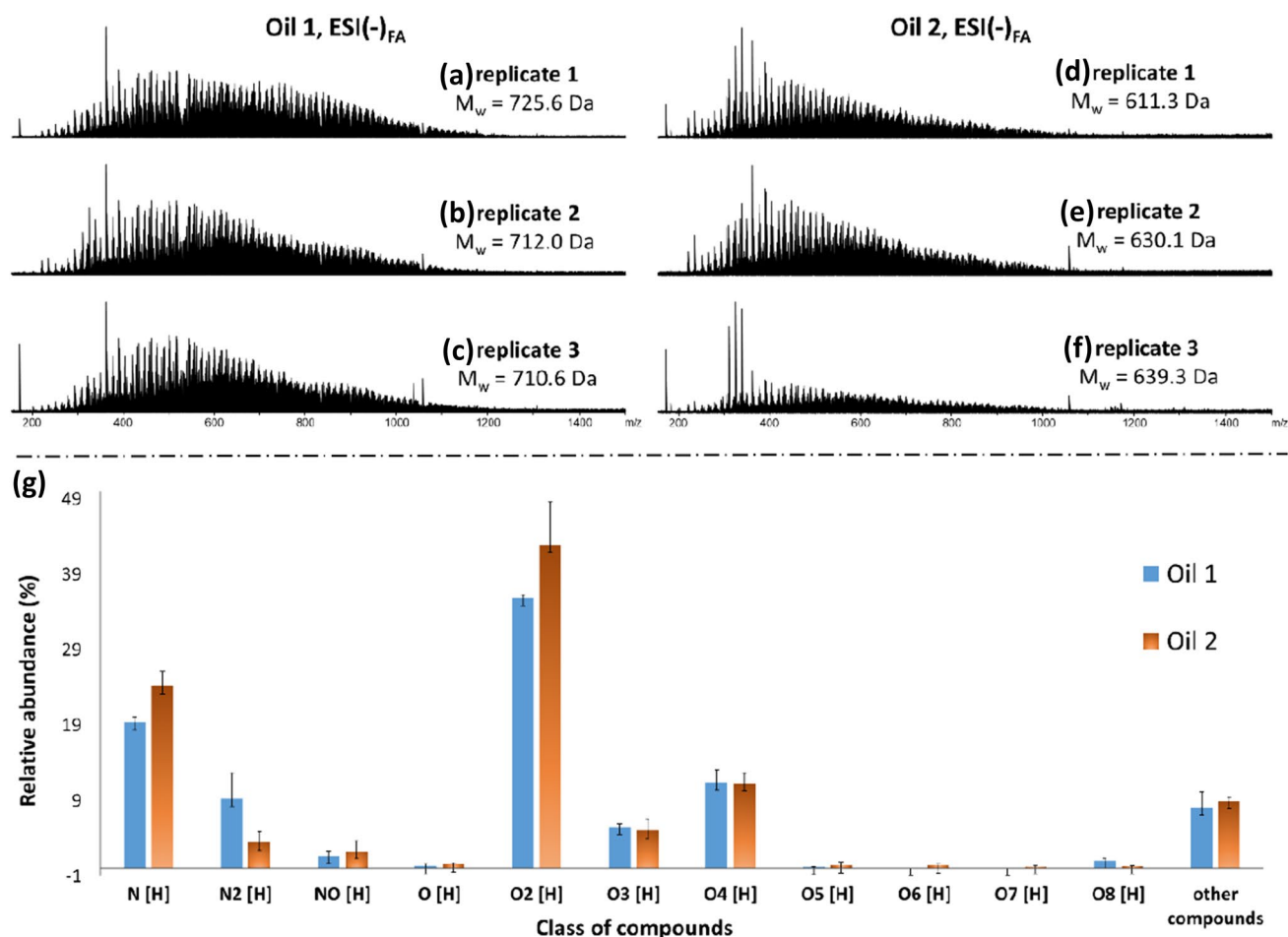


Fig. 3 FT-ICR MS spectra ionized in negative mode by FA addition from oils 1 (a–c) and 2 (d–f); graph of mean distribution of the classes of heteroatoms of the compounds (g)

equilibrium manipulation for ARN salt extraction and purification (Barros et al. 2022b). Thus, ARN chemically linked as naphthenates are converted into free acid monomers, according to the following equation (Barros et al. 2022b).

Therefore, 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 consolidated when we obtained a FT-ICR MS spectrum (Fig. 4) 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 (Fig. 4) show that the O_8 class (ARN class) is majoritarian in the deposit (86.8%), with a mean M_w distribution of 1185.5 Da and signals concentrated in the three specific regions, emphasized between m/z 475–650 and 950–1300, which correspond to doubly (ARN^{2-}) and monocharged (ARN^{1-}) tetrameric acids, respectively.

The high resolution and mass accuracy of the FT-ICR MS combined with the $ESI(-)_{FA}$ showed that the main

species in the deposit comprise ARN with hydrocarbon skeletons with carbon numbers between C_{60-83} , and that among the most abundant are the monocharged ones, $[C_{71}H_{124}O_8-H]^-$ and $[C_{81}H_{142}O_8-H]^-$ of respective m/z of 1103.92404 and 1242.06619, with emphasis on the ion $[C_{80}H_{142}O_8-H]^-$, of m/z 1230.06537, which corresponds to a natural ARN (C_{80} hexacyclic acid, $M_w = 1230$ g mol^{-1}), described by Lutnaes et al. 2006, whereas the doubly charged ions, $[C_{80}H_{140}O_8-H]^{2-}$, $[C_{80}H_{144}O_8-2H]^{2-}$, and $[C_{81}H_{142}O_8-H]^{2-}$, have the respective m/z 613.52104, 615.53667, and 620.52893.

Table S-2 shows the assignments of the molecular formulas, double bond equivalents (DBE) and the mass error of the ARN^- species in the deposit, obtained from the FT-ICR MS data with ionization by the addition of formic acid in the $ESI(-)$.

We could 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 $ESI(-)_{FA}$ with the data assignments.

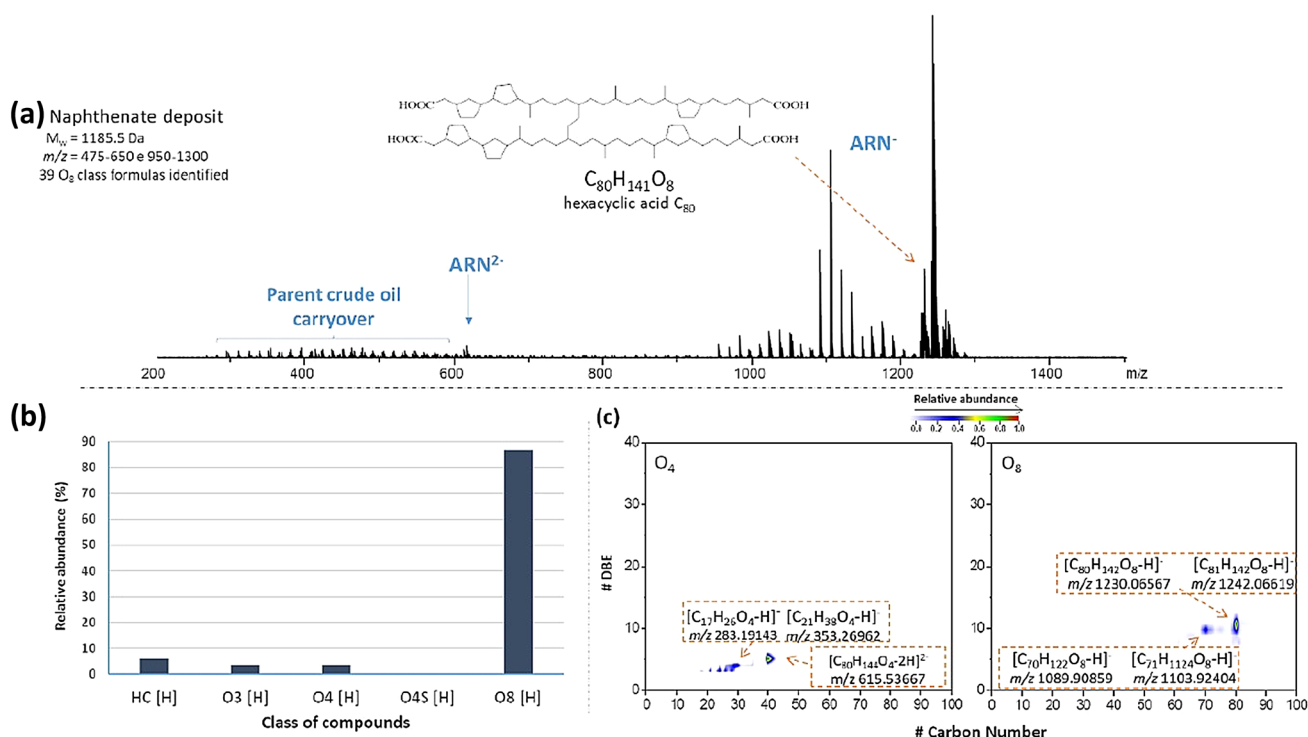


Fig. 4 **a** FT-ICR MS spectrum obtained from direct injection of the naphthenates deposit into the electrospray force, ESI(-)_{FA}; **b** distribution graphs of classes of heteroatoms; and **c** DBE against carbon number plot for the O₄[H] and O₈[H] classes present in the naphthenate deposit

Although naphthenate deposits consist predominantly of ARN (Mapolelo et al. 2009), its detailed speciation can be used to identify its origin, based on class composition and carbon number (Mapolelo et al. 2009).

The results of FT-ICR MS with ESI(-)_{FA} showed the presence of the homologous series C₇₀H₁₂₁O₈, C₇₁H₁₂₃O₈, and C₇₂H₁₂₅O₈, corresponding to low M_w ARN species from C_{60–70} hydrocarbon skeletons, which the literature reported in the characterization of naphthenate deposits from different production fields in the sedimentary basin of the Brazilian coast (Barros et al. 2022b; Juyal et al. 2015) and of West Africa, attributed to the genetic relation between field deposits on both sides of the Atlantic Ocean (Barros et al. 2022b; Juyal et al. 2015).

As such, the methodology of identification and characterization of ARN in oil samples and naphthenate deposits with minimal sample preparation by FT-ICR MS with ionization in ESI(-)_{FA} is very promising since it requires a simpler sample preparation and is advantageous in terms of reagent consumption reduction and analysis time.

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 develop a methodology for identifying and characterizing ARN in petroleum samples and in naphthenates deposits with minimal sample preparation by FT-ICRMS with ionization of samples by adding formic acid in the negative electrospray, ESI(-)_{FA}.

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

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Declarations

Conflict of interest The authors declare competing financial interest.

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