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Analysis of naphthenic acids by matrix assisted laser desorption ionization time of flight mass spectrometry

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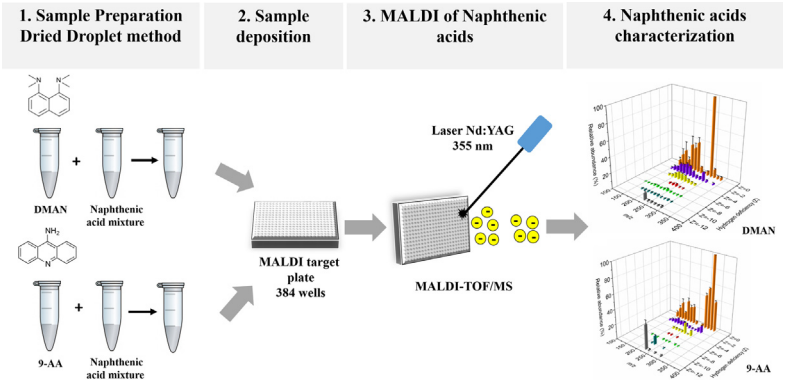
GRAPHICAL ABSTRACT



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ABSTRACT

We report on a matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF) method to analyze naphthenic acids (NAs), from petrochemical samples, using 9-aminoacridine (9-AA) and a proton sponge 1,8-bis(dimethylamino) naphthalene (DMAN), as matrices. Singly charged deprotonated molecules of NAs, $[M-H]^-$, dominated the negative ion MALDI mass spectra. The negative ions were pre-formed in solution through an acid/base Brönsted-Lowry reaction promoted by the highly basic matrices (9-AA and DMAN). The DMAN afforded cleaner spectra with absence of clusters, aggregates or matrix interferences at low m/z; in addition, it provides molecular weight distributions similar to those observed with negative ion electrospray ionization (ESI). In contrast, MALDI spectra obtained with 9-AA exhibits matrix interferences at low mass, and bias towards aliphatic NAs. Finally, we observe the presence of monomeric species in the low mass region and non-covalent aggregates at higher masses in the negative mode MALDI spectra with both matrices, much like with negative mode ESI. We demonstrate that MALDI-TOF/MS is a viable tool for NAs analyses with added advantages such as high throughput and exceptional tolerance to the presence of impurities and salts in the samples, when compared with ESI.

1. Introduction

Naphthenic acids (NAs) are possibly originated from the microbial oxidation of hydrocarbons, and are commonly found in immature and biodegraded heavy crude oils together with other polar compounds such as carbazoles and phenols. Some NAs have been used as biomarkers by geochemists to indicate crude oil sources of origin [1].

NAs are complex mixtures of mono alkyl-substituted cyclic and acyclic compounds existing in various isomeric forms for a particular elemental composition. The formula $C_nH_{2n+z}O_2$ typically

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defines NAs, where Z (an even negative integer) refers to the hydrogen deficiency and its modulus divided by two indicates the number of rings present in the acid structure. NAs and other polar molecules constitute around 3–5%w of the crude oil and, despite their low content, they are responsible for many problems in production and processing schemes. For instance, flow assurance problems during recovery of heavy crude oil occur when pressure reduction in the well induces water degassing and release of dissolved carbon dioxide. This phenomenon causes an increase in pH and dissociation of NAs to form carboxylate ions. These anionic species readily react with inorganic cations (Na^+, Ca^{2+}) present in water, to form salts known as naphthenates [2–5]. Sodium naphthenates, in particular, are known to stabilize water in oil emulsions; while calcium naphthenates are generally sticky or solid deposits formed mostly of tetra acids known as ARNs [6–9]. These compounds, found across the whole oil production system (wellheads, electrostatic coalescers, oil/water separators, heat exchangers tubes and storage tanks) are responsible for unexpected refineries shutdowns and lengthily clean-up procedures that affect productivity [9]. Additionally, because of their amphiphilic properties, naphthenates can stabilize water in oil (w/o) emulsions causing severe flow assurance problems related mainly to an increase in fluid viscosity [10–14]. Thus, characterization of NAs is fundamental to better understand the stabilization mechanisms of w/o emulsions and to provide useful information to design new and effective demulsifying processes for heavy crude oils. In addition, NAs identification is useful to establish correlations between undesirable NA-induced corrosion and the chemical nature of NAs [15–17].

NAs are considered a complex mixture and their characterization by mass spectrometry has been reported using different ionization techniques and a wide variety of analyzers [18]. For instance, electron ionization (EI) [19], chemical ionization (CI), electrospray ionization [20], nano-electrospray ionization (ESI) [21], fast atom bombardment ionization (FAB) [22], atmospheric pressure chemical ionization (APCI) [23] and atmospheric pressure photoionization (APPI) [24] have been employed to analyze NAs in crude oil, distillates, bitumen, oil sands, process water [25] and even natural water. Nowadays, ESI coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR) [26–29], is also widely used to characterize NAs. Soft ionization methods for NAs analysis offer not only high selectivity and sensitivity without fragmentation, but also solve problems related with GC/EI-MS approaches that required long extraction procedures and derivatization, resulting in an incomplete detection and extensive fragmentation of these species [19,30].

Recently, laser desorption ionization (LDI) in negative ion mode coupled to FT-ICR [31] was used to assign oxygenated compounds in three crude oils with different total acid number (TAN) values. This report concluded that the O_2 compound class readily forms negative ions due to the oxygen electronegativity and the acidity of the OH group that helps to stabilize the ion's charge. In addition, detection of non-aromatic O_x (x = 1, 2) compound classes, as deprotonated molecules $[M-H]^-$, with DBE values from 1 to 3 supports this conclusion. However, as the DBE values increase NAs radical anions become more abundant than the deprotonated molecules in the LDI spectrum. This suggests that as the analyte's aromaticity increases, electron capture becomes the dominant mechanism in negative ion mode ionization due to the high electron affinity of polyaromatic species. Consequently, in a complex mixture, non-aromatic NAs tend to exhibit low abundances and S/N ratios in LDI. This disadvantage could be addressed using a suitable matrix able not only to stabilize deprotonated molecules but also to absorb energy (337 or 355 nm) and promote efficient desorption of both non-aromatic and aromatic species. For example, several strong and weakly acidic metabolites such as fatty acids, amino acids, hormones and lipids were ionized in negative ion mode using 1,8-bis(dimethylamino) naphthalene (DMAN) as MALDI matrix [32]. This highly basic matrix allowed the identification of the analytes directly in complex biological samples such as leaves (*Arabidopsis thaliana*), insects bodies (*melanogaster* males and females) and even human blood, with detection limits as low as pico- and femto-moles [33]. DMAN is particularly suitable for analysis of low molecular weight metabolites due to the absence of interfering matrix signals or clusters in the low mass range; for this reason it is also called an ion-less matrix.

Another matrix, 9-aminoacridine, has also been successfully employed to detect small metabolites such as aliphatic and aromatic carboxylic acids, phytohormones and amino acids in complex biological matrices with detection limits in the femto-mole range [34,35]. On the other hand, high molecular weight matrices are alternatives to overcome the problem of interfering ions in the low mass region, common when using traditional matrices such as 2,5-dihidroxy benzoic acid (DHB), α-cyano-4-hydroxycinnamic acid (CHCA) and sinapinic acidic to analyze acidic compounds. The matrix meso-tetrakis-pentafluorophenyl-porphyrin (M_r - ~ 974 Da) does not show clusters or matrix ions in the low mass region and has been employed to characterize, by MALDI-TOF/MS, low molecular weight compounds particularly saturated fatty acids (<1000 Da) [36]. In addition, some high molecular weight metal phthalocyanines (Al, Ga, In) have also been used as a MALDI matrices to ionize, in negative ion mode, small molecules such as citric acid, stearic acid, salicylic acid, cholic acid, palmitic acid and gibberellic acid, without interference matrix peaks at low mass [37].

In this contribution we explore the versatility of UV-MALDI for the analysis of NAs from petrochemical samples using 9-aminoacridine and 1,8-bis(dimethylamino) naphthalene (DMAN, "proton sponge") as basic matrices. To the best of our knowledge there are no reports in literature related to the characterization of NAs by MALDI, which is surprising considering that the technique is commonly used for the characterization of polar analytes such as proteins, peptides, carbohydrates and polymers and, more recently, for the analysis of low molecular weight metabolites (including carboxylic acids). MALDI-TOF analyses have the advantage of high throughput and exceptional tolerance to the presence of impurities and salts in the samples in contrast with ESI, routinely used for NAs analysis by MS.

2. Experimental section

2.1. Materials

1,8-Bis(dimethylamino) naphthalene (DMAN), 9-aminoacridine (9-AA) and a mixture of naphthenic acids (Fluka 70340) were acquired from Sigma Aldrich (St. Louis, MO, USA). HPLC grade acetonitrile (ACN) and methanol (MeOH) were purchased from Merck (Germany). All chemicals are commercially available and were used as supplied. All aqueous solutions were prepared using deionized water with resistivity <18 MΩ/cm. The ion exchange sugar (poly-1,6-glucose) based resin QAE-Sephadex® A-25 (Chloride form) was acquired from Sigma-Aldrich (St. Louis, MO).

2.2. Sample preparation

For MALDI analysis, stock solutions of DMAN and 9-AA were prepared in ACN:H_2O (1:1) at 0.5 mM and 2 mM, respectively. A stock solution (2 mM) of the NAs standard mixture was also prepared in ACN:H_2O (1:1). NAs molar concentrations were calculated using an average molecular weight of 240 g/mol previously reported for the same NA standard mixture [38]. The NA stock