

Full Length Article

Acid-selective mass spectrometric analysis of petroleum fractions

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ABSTRACT

Naphthenic acids are cycloaliphatic carboxylic acids that are naturally-occurring constituents of petroleum. Analytical mass spectrometric methods aimed at carboxylic acids tend to involve deprotonation to generate carboxylate anions, but also produce detectable ions of every acidic component of the mixture. A charged tag carbodiimide is able to facilitate detection of model naphthenic acids as well as low levels of naphthenic acids in petroleum fractions via tandem electrospray ionization mass spectrometry. This approach exhibits greater selectivity than deprotonation, and a picture of the acidic components of a petroleum fraction emerges after a quick derivatization step and without the use of chromatographic separation. The method may prove useful in the context of characterizing the naphthenic acid components of complicated matrices.

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1. Introduction

Petroleum is a highly complex matrix, typically composed of hydrocarbons as well as a wide variety of polar molecules. The hydrocarbons constitute about 90% whereas the polar species form a small fraction of about 10%, incorporating nitrogen, oxygen and sulphur heteroatoms as well as heavy metals (vanadium, iron and nickel) [1]. These polar components have been a major concern in the petroleum industry, given their ability to corrode refinery units, inhibit catalytic activities in refinery processes and as well, pollute the environment [2,3].

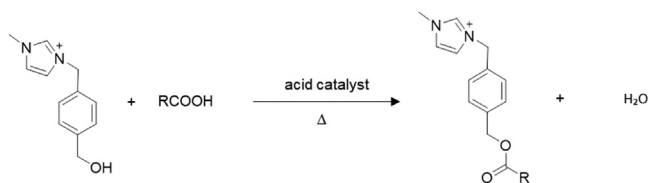
Naphthenic acids are a fraction of oxygen-containing cyclic compounds in petroleum that have recently gained attention, owing to their corrosiveness in refinery units [4]. Naphthenic acid comprises cyclohexyl, cyclopentyl and phenyl groups with long chain hydrocarbon backbone attached to a carboxylic acid group or long chain hydrocarbons attached to a carboxylic group, which is formed as a result of the oxidation of naphtha in petroleum [5,6]. They are described with the chemical formula: $C_nH_{2n+z}O_2$, where n is the number of carbons and z can be zero or a negative integer to indicate the hydrogen deficiency due to the presence of multiple rings [7]. Naphthenic acids are present in petroleum in a considerable amount of up to 4% by weight [8]. The acidity of petroleum is evaluated by measuring the total acid number (TAN), which is referred to as, the mass of potassium hydroxide required to neutralize a given mass of petroleum. However [9], Turnbull and

co-workers reported that the size and structure of naphthenic acids play a significant role in their corrosiveness [10]. Thus, the TAN method of addressing corrosiveness in crude oil is not a reliable method. In view of this, it is imperative to investigate other characterization techniques to account for the acid fraction of petroleum.

Various analytical techniques have been developed to enhance characterization of naphthenic acids in petroleum. These include: Fourier transform infrared (FTIR) spectroscopic analysis, gas chromatography (GC) and high performance liquid chromatography (HPLC) [11–13]. These techniques are generally employed to determine the total naphthenic acid concentration [14,15]. Unfortunately, considering only the acid concentration in assessing corrosiveness of naphthenic acids in petroleum is not sufficient; but employing techniques that will also determine the size and structure of naphthenic acids would be a better approach. In order to determine the size and structure of naphthenic acids in petroleum, several studies have been conducted using state-of-the-art mass spectrometry methods. Electron ionization (EI) was employed to characterize naphthenic acids which detected about 1500 naphthenic acids [16]. As well, chemical ionization (CI) [17,18], fast atom bombardment (FAB) [19,20], atmospheric pressure chemical ionization (APCI) [21] and electrospray ionisation (ESI) methods were compared to determine the molecular distribution of naphthenic acids extracted from petroleum [22,23]. However, for the study of complex mixtures, soft ionization techniques, such as ESI are preferred over hard ionization techniques, such as EI [24–27]. The latter would yield similar fragments leading to a complicated mass spectrum; whereas the former would simplify the mass spectrum by preserving the molecular ion of the species of interest in a complex mixture [28].

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Scheme 1. Representation of esterification reaction between naphthenic acids and a charged tag alcohol (R = alkyl or aryl group).

The use of Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been a preferred technique for petroleum characterization given its ultra-high resolution and ultra-high mass accuracy [29–32]. Qian and co-workers combined HPLC with ESI-FT-ICR-MS to characterize acid fractions in crude oil and this technique was able to identify fifteen different chemical formulas of naphthenic acids [33]. Barrow et al. employed FT-ICR-MS to conduct a study on the degradation of naphthenic acids in the environment [34]. Clingenpeel et al. also employed FT-ICR-MS for characterization of naphthenic acids; and reported that during the petroleum refining process, naphthenic acids could contribute to the formation of stable emulsions [35]. In addition, Rowland and co-workers used modified aminopropyl silica (MAPS) chromatography coupled with negative ion electrospray ultrahigh resolution mass spectrometry to characterize naphthenic acids in a petroleum mixture [36].

Herein, we employ a rapid, simple and inexpensive method by means of ESI-MS to characterize naphthenic acids in petroleum fractions as well as model naphthenic acids. ESI is a soft ionisation technique which is able to generate positively charged ions when basic species are protonated with a weak acid. ESI also generates negatively charged ions when acidic species are deprotonated with a weak base [37]. Hence, ESI-MS does not detect neutral species. Alternatively, derivatization methods could be used to promote the detection of species of interest in ESI-MS [38].

In this study, we use a charge-tagging technique which has been successful in detecting thiols and phenols in petroleum fractions [38,39]. A charged tag alcohol (3-[4-(hydroxymethyl)benzyl]-1-methylimidazolium hexafluorophosphate) and a charged tag carbodiimide compound (1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide methiodide) are employed in this study for naphthenic acid derivatization reactions. Derivatization of naphthenic acid with a charged tag alcohol mimics Fischer esterification of carboxylic acids, which is a simple and prominent reaction of carboxylic acids (Scheme 1).

The role of the charged tag alcohol and carbodiimide compounds is basically to facilitate detection of the naphthenic acid derivatives. Carbodiimide is a functional group with the chemical formula, $RN=C=NR$ [40]. Compounds containing the carbodiimide functional group are prevalently used as a dehydrating agent to activate carboxylic acids for coupling with primary amines to yield amide compounds [41]. Carbodiimide is also a well-known tool in the field of bioconjugation, peptide synthesis and modification of polysaccharides [42–44]. In addition; the charge-tagging technique will be compared with a deprotonation method. The deprotonation method involves the use of ammonium hydroxide to deprotonate naphthenic acids present in the petroleum fractions and the commercial naphthenic acid mixture.

2. Experimental

2.1. Chemicals and samples

All chemicals and solvents employed were purchased from Sigma-Aldrich or Alfa Aesar. The petroleum fractions used in this

study are distillates of crude oil supplied by Imperial Oil, Ontario, Canada.

2.2. NMR

A Bruker Avance 300 MHz spectrometer was used to obtain 1H NMR spectra with solutions prepared in $CDCl_3$ and CD_3OD .

2.3. ESI-MS

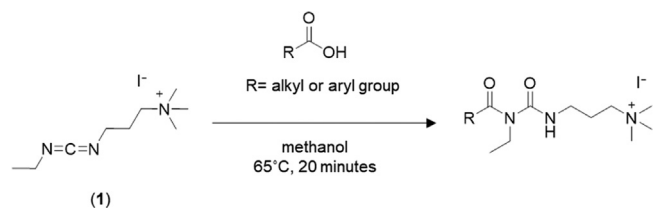
ESI-MS of the synthesized product as well as the charged-tag reactions with the naphthenic acid models, a commercial naphthenic acid mixture and petroleum fractions were conducted in the positive ion mode on a Waters Acquity TQ Detector mass spectrometer. The parameters used were: capillary voltage, 3 kV; cone voltage, 15 V; extraction voltage, 2 V; source temperature, 70 °C; desolvation temperature, 170 °C; cone gas flow rate, 100 L/h; desolvation gas flow rate, 200 L/h. Scan time was set to 1 s. Also, ESI-MS of the deprotonated naphthenic acid mixture and petroleum fractions were conducted in the negative ion mode using the same instrument parameters. Pressurized sample infusion (PSI) experiments using ESI-MS (+) were employed for the derivatization reactions. The PSI experiments involved derivatization reactions at 65 °C in methanol, in a Schlenk flask. The derivatized material was fed into the ESI source by means of PEEK tubing and 3 psi of argon gas. The derivatization reactions included: reaction between charged tag carbodiimide (1) (1 mmol, 1 eq) and naphthenic acid model compounds (10 mmol, 10 eq); reaction between charged tag carbodiimide (1 mM) and a commercial naphthenic acid mixture (10% v/v) as well as petroleum fractions (10% v/v). After the PSI experiment for the petroleum fraction, the reaction solution was further diluted to 10 ppm using HPLC grade methanol. An Exactive Plus Orbitrap Mass Spectrometer from Thermo Fisher Scientific (Waltham, MA, USA) was used to analyse the diluted reaction solution in the positive ion mode. The capillary temperature of the Orbitrap Mass Spectrometer was set to 250 °C, the spray voltage was set to 3.5 kV, sheath gas flow rate was set to 30, auxiliary gas flow rate was set to 10 and the auxiliary gas temperature was set to 175 °C. A mass accuracy of less than 2 ppm and a resolving power of 100,000 (at m/z 400) assisted in data collection over the mass range of m/z 140–2000 in the full scan mode. An integrated syringe pump was used whereby the flow rate was set to 50–100 $\mu l \text{ min}^{-1}$.

Offline experiments were also carried out prior to characterization. These involved: deprotonation of petroleum fractions (10% v/v); and a commercial naphthenic acid mixture (10% v/v) in methanol with ammonium hydroxide (30 μl , 2% v/v in methanol). In addition, a charged tag alcohol (1 mmol, 1 eq) was used to derivatize a naphthenic acid model compound, 2-methoxyphenylacetic acid (10 mmol, 10 eq). A concentrated sulphuric acid served as a catalyst through gentle reflux under argon for about 3 h in 50 ml of dichloromethane in the presence of activated 4 Å molecular sieves. All solutions after the offline experiments were fed into the ESI source by means of a syringe pump and an analytical syringe connected to PEEK tubing.

MS/MS experiments were carried out with a Waters Acquity TQ Detector to obtain structural information using the parameters as follows: collision voltage, 10 V; high mass and low mass resolution at 15 V each. Interpretation of the mass spectra was facilitated using chemcalc.org [45].

2.4. Synthesis of 3-(4-(bromomethyl)benzyl)-1-methylimidazolium hexafluorophosphate

1-methylimidazole (0.46 ml, 5.77 mmol) reacted with excess α, α' -dibromo-p-xylene (2.049 g, 7.76 mmol) through gentle reflux under argon for about 16 h in 50 ml of THF, a synthesis based



Scheme 2. Representation of a derivatization reaction between naphthenic acids and a charged tag carbodiimide (1).

on a standard laboratory preparation of imidazolium-based ionic liquids [[46]]. A white powder was recovered from acetonitrile through vacuum filtration which was vacuum dried for 24 h. The 3-(4-bromomethyl)benzyl-1-methylimidazolium bromide (0.220 g) was dissolved in 25 ml of 50% v/v aqueous methanol, followed by the addition of sodium hexafluorophosphate (0.330 g). The solution was stirred for 12 h. A white powder was recovered from the reaction solution via vacuum filtration (28.9% yield).

$^1\text{H NMR}$ (300 MHz, CD_3OD): δ (ppm) = 3.93 (s, 3 H), 4.59 (s, 2 H), 5.41 (s, 2 H), 7.61–7.40 (m, 6 H), 8.95 (s, 1 H). QTOF ESI (+): $[\text{M}]^+ m/z$ 265.1; ESI (-): $[\text{M}]^- m/z$ 145.1.

Synthesis of 3-[4-(hydroxymethyl) benzyl]-1-methylimidazolium hexafluorophosphate (charged tag alcohol).

3-(4-(bromomethyl)benzyl)-1-methylimidazolium hexafluorophosphate (0.65 g, 1.59 mmol) was reacted with NaOH (6 g, 0.15 mol) solution in 50 ml distilled water at 70 °C. The solution was mechanically stirred for 10 h. The reaction solution was filtered and the filtrate was vacuum dried. The powder was redissolved in a minimum amount of methanol and a white precipitate was formed after leaving the solution at 4 °C overnight. The white precipitate was recovered from the reaction solution through vacuum filtration (15% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 3.90 (s, 3 H), 5.05 (s, 2 H), 5.29 (s, 2 H), 7.50–7.29 (m, 6 H), 8.64 (s, 1 H). QTOF ESI (+): $[\text{M}]^+ m/z$ 202.1; ESI (-): $[\text{M}]^- m/z$ 145.1.

3. Results and discussion

3.1. Derivatization with a charged tag alcohol

After synthesis of the charged tag alcohol (see Figure S1, supporting information), the charged tag mixture contained impurities such as sodium bromide which has similar solubility as the charged tag alcohol so purification was a challenge. Nevertheless, the efficiency of the charged tag alcohol was tested in an esterification reaction with a model naphthenic acid, 2-methoxyphenylacetic acid. The charged tag alcohol unexpectedly decomposed during esterification and the derivatized product with m/z 351, was not of sufficient intensity to be easily identified (see Figure S2, supporting information). The inefficiency of this method of analysis could be attributed to low efficiency of the charged tag alcohol, long reaction time, solvent restrictions (both charged tag and analyte need to be soluble); and harsh reaction conditions of esterification and purification problems. Thus, a charged tag carbodiimide (1) was employed as an alternative for derivatization.

3.2. Derivatization of model naphthenic acids

The reactivity of a charged tag carbodiimide (1) was studied via online reaction monitoring in positive ion mode ESI-MS (Scheme 2).

This derivatization was conducted by adding a mixture of different model naphthenic acids (cyclopentanecarboxylic acid, cyclohexanepentanoic acid and cyclohexaneacetic acid in the same molar amount) to a solution containing the charged tag carbodiimide (1) at 65 °C (Fig. 1). The limit of detection and limit of

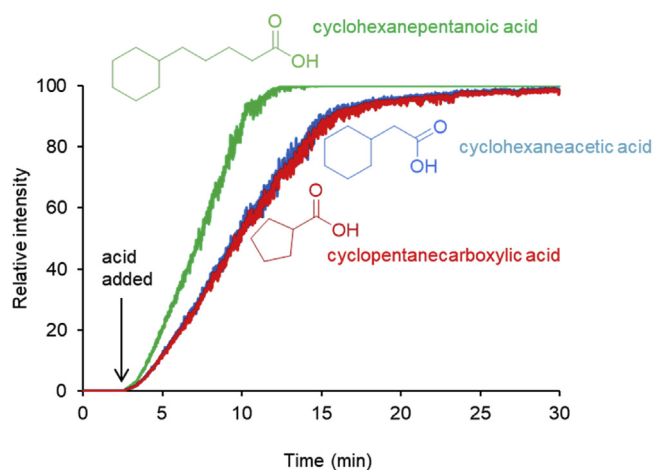


Fig. 1. Positive ion mode ESI-MS of an online reaction monitoring between (1) and a mixture of three naphthenic acid model compounds (cyclopentanecarboxylic acid, cyclohexanepentanoic acid and cyclohexaneacetic acid) at 65 °C in methanol.

quantitation for cyclohexaneacetic acid were determined to be 0.7 μM and 2.3 μM respectively; these are only approximations and will differ between samples and matrices (see Figure S7, supporting information for details). Fig. 1 shows a pseudo zero-order reaction whereby derivatization of cyclohexanepentanoic acid (green) was faster than cyclohexaneacetic acid (blue) and cyclopentanecarboxylic acid (red). This could be explained by steric hindrance of the cyclohexyl and cyclopentyl groups in cyclohexaneacetic acid and cyclopentanecarboxylic acid respectively; since both groups are close to the carboxyl group. Hence, the reaction rate decreased. In the case of cyclohexanepentanoic acid, the steric effect was relatively less due to the presence of four CH_2 groups keeping the bulky group away from the carboxyl group; therefore, the rate of reaction increased correspondingly. The pseudo zero-order nature of each trace points to a reaction insensitive to the concentration of the carbodiimide (1).

3.3. Derivatization and deprotonation of naphthenic acids in a commercial naphthenic acid mixture

A commercial naphthenic acid mixture was examined to evaluate the usefulness of the charged tag carbodiimide (1). The commercial acid mixture served as a model petroleum fraction given that it is composed of isolated naphthenic acids from petroleum [47,48]. Fig. 2 displays a homologous series of naphthenic acid derivatives with m/z from 300 ($\text{C}_{16}\text{H}_{34}\text{N}_3\text{O}_2$) to 784 ($\text{C}_{52}\text{H}_{96}\text{N}_3\text{O}_2$); within this range, species with between zero and five double bond equivalents (DBE) were observed.

Constituents of the commercial naphthenic acid mixture were also determined via deprotonation. Deprotonated naphthenic acid species were detected as $[\text{M}-\text{H}]^-$ (Fig. 3). The ESI (-) MS spectrum of Fig. 3 depicts a homologous series of naphthenic acids with m/z from 101 ($\text{C}_4\text{H}_7\text{O}_2$) to 613 ($\text{C}_{43}\text{H}_{75}\text{O}_2$). Within this series, naphthenic acids with m/z from 101 to 339 were identified as species with 0 DBE and naphthenic acids with m/z greater than 339 were identified as 5 DBE species.

In a direct comparison between the derivatized and deprotonated commercial naphthenic acid mixture (Fig. 4), we observed naphthenic acid derivatives of relatively low intensities at m/z from 500 to 784; whereas the deprotonated acid species of same distribution were more conspicuous. It is possible that the higher mass carboxylates are exhibiting considerably higher surface activity than their lower mass counterparts, and are hence overrepresented, whereas the relative abundance of the charged tag variants are

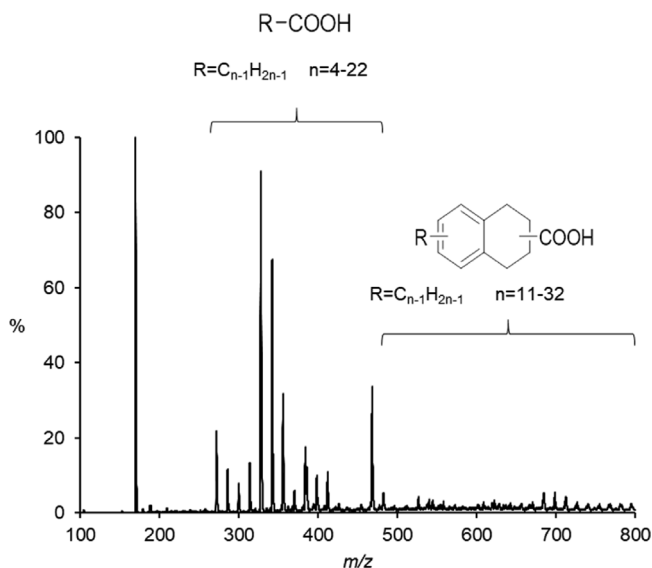


Fig. 2. Positive ion mode ESI-MS spectrum of naphthenic acids in a commercial naphthenic acid mixture which were derivatized with (1) in methanol at 65 °C.

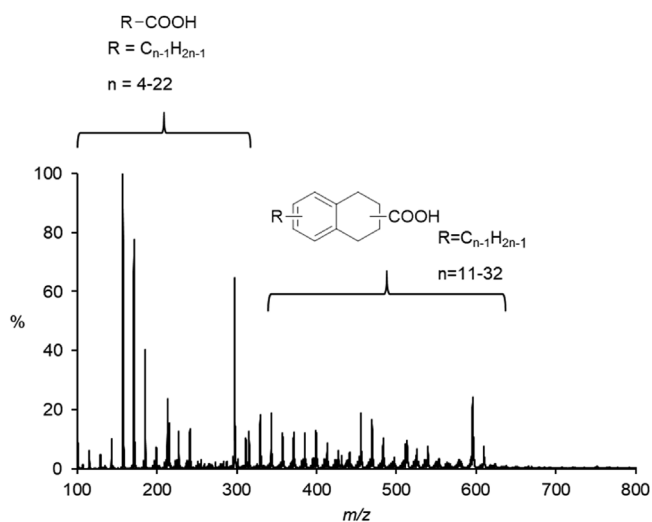


Fig. 3. Negative ion mode ESI-MS spectrum of naphthenic acids in a commercial naphthenic acid mixture which were deprotonated with ammonium hydroxide in methanol at room temperature.

dependent more on the nature of the charged tag itself (note the masses of the latter span $\sim m/z$ 300–700, whereas the former are $\sim m/z$ 100–500).

3.4. Derivatization and deprotonation of naphthenic acids in petroleum fractions

In order to determine various naphthenic acids present in petroleum fractions, the charged tag carbodiimide (1) was employed to assess its performance with regard to selectivity in highly complex matrices. Upon addition of the complex matrices to the charged tag (1), acid derivatives were detected from m/z 328 ($C_{18}H_{38}N_3O_2$) to 600 ($C_{38}H_{70}N_3O_2$); but with relatively low intensities (Fig. 5 and Figure S3, supporting information). An explanation to this observation could be low concentration of naphthenic acids present in the petroleum fractions; thus, the naphthenic acids exhibited poor signal to noise ratio.

However, a better approach to facilitate assignment of these derivatized species was via tandem mass spectrometry; whereby

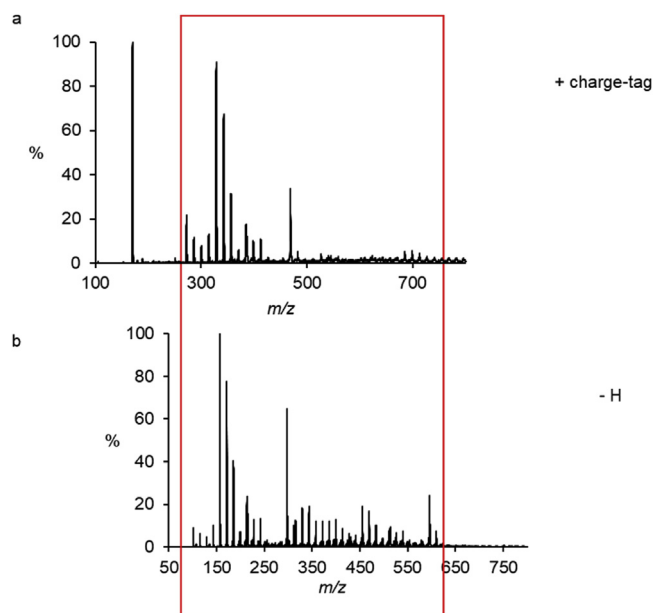


Fig. 4. Comparison between: a) Derivatized naphthenic acid species; and b) Deprotonated naphthenic acid species of a commercial naphthenic acid mixture.

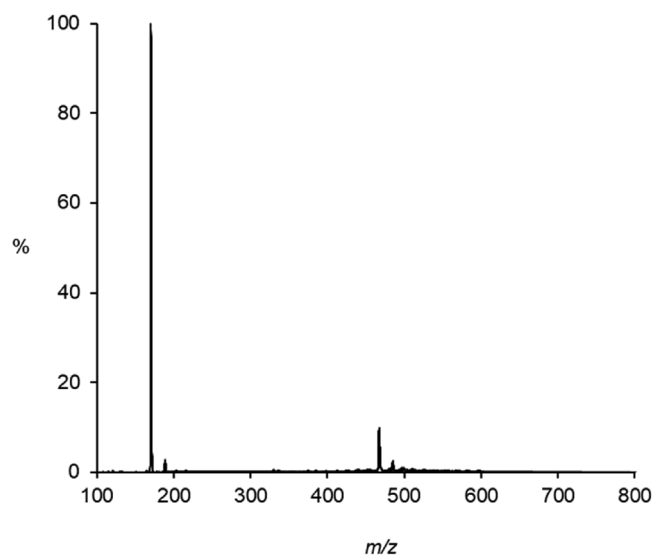


Fig. 5. Positive-ion ESI-MS of naphthenic acids in petroleum fraction (A) which were derivatized with (1) in methanol at 65 °C (note: m/z 328–466 and m/z 468–600 are acid derivatives; but species at m/z 467 with $\sim 10\%$ relative intensity is an aggregate of the charged tag).

product and precursor ions of species in a complex matrix could be deduced. In view of this, a product ion experiment was conducted after a full MS scan as shown in Fig. 5, to determine a common product ion of the naphthenic acid derivatives in the petroleum fraction. The common product ion was determined as the base peak at m/z 170 (Fig. 6).

With this established, a precursor ion experiment was conducted to determine the precursor ions of the common product ion in the complex matrix. A significant feature of this experiment is the improved signal to noise ratio of species of interest. This was apparent after the precursor ion experiment by which a variety of acid derivatives from m/z 328 ($C_{18}H_{38}O_2N_3$) to 600 ($C_{38}H_{70}O_2N_3$) with 0 to 7 DBE were detected (Fig. 7). However, after conducting an orbitrap mass spectrometric analysis, naphthenic acid species of similar nominal mass were identified with the

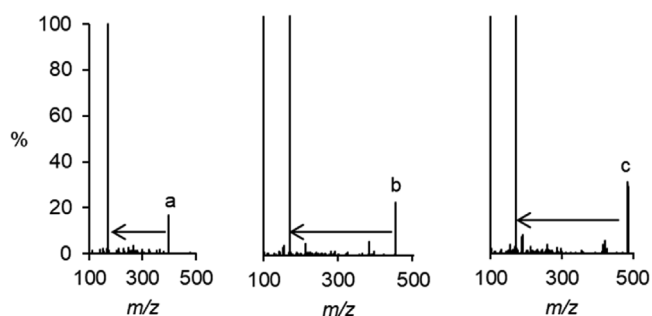


Fig. 6. Representation of product ions of derivatized naphthenic acids at (a) m/z 398; (b) m/z 454; (c) m/z 498; and a common product ion at m/z 170.

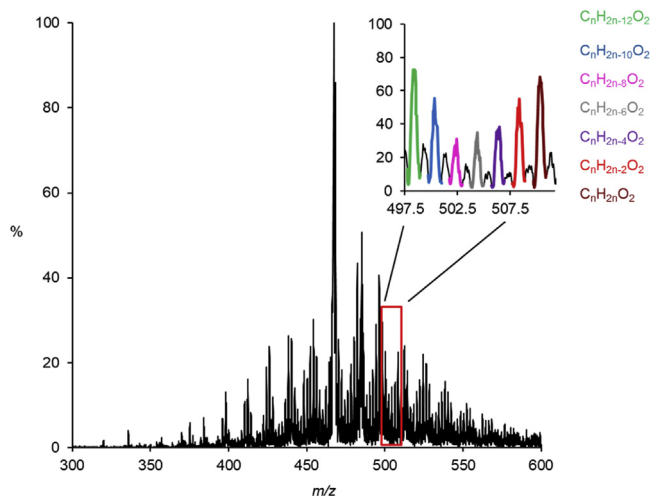


Fig. 7. Representation of precursor ions of derivatized naphthenic acids in petroleum fraction (A) with colour-coded acid species from m/z 498 to 510.

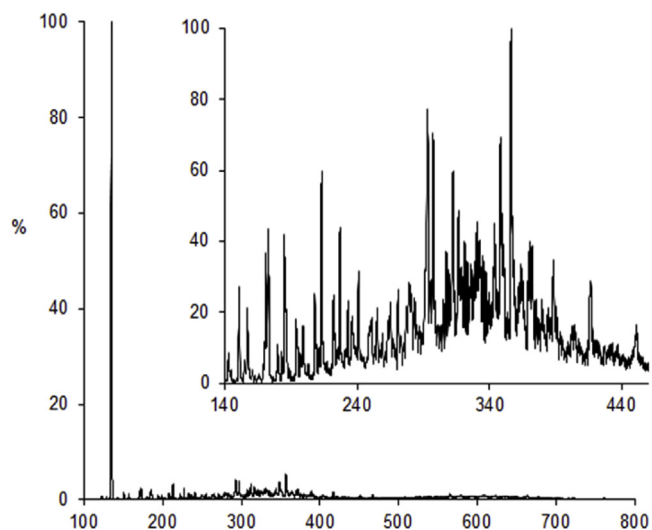


Fig. 8. Negative ion mode ESI-MS spectrum of naphthenic acids in petroleum fraction (A), which were deprotonated with ammonium hydroxide in methanol at room temperature. Inset: expansion of the m/z 140–440 range.

formulae $C_nH_{2n+2}O_2N_3$ ($n = 26-29$) and $C_nH_{2n-12}O_2N_3$ ($n = 27-30$); interpreted as 0 and 8 DBE species respectively (Table S1, supporting information).

Petroleum fractions were also deprotonated in a similar fashion as the commercial acid mixture; but a complex spectrum was produced (Fig. 8 and Figure S4, supporting information). As a result,

assignment of naphthenic acids in petroleum fraction (A) was not as simple as the commercial naphthenic acid mixture, in that after deprotonation, all protic species present could be detected. Nevertheless, we were able to identify a range of various naphthenic acids from m/z 157 ($C_9H_{17}O_2$) to 429 ($C_{29}H_{49}O_2$) with 0 to 8 DBE which were in agreement with results obtained by Dalmaschio and coworkers [3]. This trend was akin to the mass spectrum of petroleum fraction (B) (Figure S4, supporting information).

4. Conclusions

Charge-tagging is a simple and selective methodology which facilitates detection of desired species through ESI-MS; but considering the performance of the charged tag alcohol in this study, we infer that, Fischer esterification of naphthenic acids with a charged tag alcohol is problematic given the harsh conditions and solvent restrictions involved. However, charged tag carbodiimide enhances detection of model naphthenic acids; and as well, offers rapid and selective analysis of naphthenic acids in petroleum fractions which is useful for qualitative studies. The results of this study have also proved that deprotonation is relatively sensitive; but the complexity of mass spectrum involved, in relation to petroleum fractions, gives the charge-tagging technique an advantage of selectivity in characterizing naphthenic acids.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ijms.2018.10.029>.

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