

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231275502>

# Naphthenic Acids in Crude Oils Characterized by Mass Spectrometry

ARTICLE *in* ENERGY & FUELS · DECEMBER 1999

Impact Factor: 2.79 · DOI: 10.1021/ef9901746

---

CITATIONS

142

---

READS

135

4 AUTHORS, INCLUDING:



Chang S Hsu

Florida State University

151 PUBLICATIONS 1,673 CITATIONS

SEE PROFILE

# Naphthenic Acids in Crude Oils Characterized by Mass Spectrometry

Chang S. Hsu,<sup>\*,†</sup> G. J. Dechert,<sup>†</sup> W. K. Robbins,<sup>†</sup> and E. K. Fukuda<sup>‡</sup>

Exxon Research & Engineering Co., Annandale, New Jersey 08801, and Rutgers University, New Brunswick, New Jersey 08901

Received August 9, 1999. Revised Manuscript Received October 17, 1999

The presence of naphthenic acids in crude oils is of concern in the petroleum industry due to their corrosivity to refinery units. It is desirable to determine the ring type and carbon number distributions because the corrosivity of naphthenic acids is dependent on the sizes and structures. The characterization of naphthenic acids is also of interest to geochemical studies, particularly migration and biodegradation, and to refinery wastewater treatment for environmental compliance. We have evaluated chemical ionization, liquid secondary ion mass spectrometry (fast ion bombardment), atmospheric pressure chemical ionization (APCI), and electrospray ionization in both positive and negative ion modes for the determination of molecular distribution of acids without derivatization. Negative-ion APCI using acetonitrile as a mobile phase yields the cleanest spectra with good sensitivity among the ionization techniques evaluated. The selectivity of negative-ion APCI for naphthenic acids has also been demonstrated by comparing results for a whole crude oil with those for the isolated acid fraction. APCI also holds a great potential for on-line liquid chromatography–mass spectrometric (LC/MS) to separate acids by high-performance liquid chromatography (HPLC) followed by mass spectrometric characterization of acids.

## Introduction

Naphthenic acids, originally identified as carboxylic acids in crude oils with single or multiple saturated rings, is the phrase loosely used to include all acidic components in crude oils that may even contain aromatic functionality. Their presence in crude oils is of concern due to their corrosivity to refinery units.<sup>1–3</sup> It is highly desirable to determine the ring-type distribution and the carbon number distribution of each ring type because the corrosivity of naphthenic acids is dependent on the sizes and structures.<sup>4</sup> The characterization of naphthenic acids is also of interest to geochemical studies, particularly migration and biodegradation,<sup>5–7</sup> and to refinery wastewater treatment for environmental compliance.<sup>8</sup>

Mass spectrometry is well suited for characterizing acidic components at the molecular level. Due to their polarity, acids are commonly derivatized to correspond-

ing esters for detailed gas chromatography/mass spectrometric (GC/MS) analysis.<sup>9,10</sup> However, direct acid analysis is more desirable because it can provide rapid analysis without the concern of losing material through derivatization. Several methods have previously been developed for such purposes, including fluoride-ion chemical ionization<sup>11</sup> and negative-ion fast-atom bombardment.<sup>12</sup> We have evaluated alternative soft ionization techniques, including chemical ionization (CI), liquid secondary-ion mass spectrometry (LSIMS), atmospheric pressure chemical ionization (APCI), and electrospray ionization (ESI), that would yield molecular or pseudo-molecular ions for the determination of molecular distribution of naphthenic acids.

## Experimental Section

For CI experiments a Finnigan TSQ-46B tandem quadrupole mass spectrometer that was operated at a single-stage mode was used. Only the most commonly used reagent gases, methane, isobutane, and ammonia, were used for the evaluation. In isobutane CI, for example, an excess amount of isobutane was introduced into a CI source until the forepump pressure reading was at 0.4 Torr and the ion gauge reading was  $2 \times 10^{-5}$  Torr. At this pressure, isobutane generates *tert*-butyl ions (57 Da) predominantly to react with sample molecules. A small amount (less than 1 mg) of the sample was deposited into a capillary quartz tube that was then inserted

\* Corresponding author: Fax: (908) 730–3314. E-mail: cshsu@erenj.com.

<sup>†</sup> Exxon Research & Engineering Co.

<sup>‡</sup> Rutgers University.

(1) Derungs, W. A. *Corrosion* 1956, 12, 617t–622t.

(2) Gutzeit, J. *Mater. Perform.* 1977, 16, 24–35.

(3) Piehl, R. L. NACE Conference, *Corrosion/87*, 1987, Paper No. 196.

(4) Slavcheva, E.; Shone, B.; Turnbull, A. NACE Conference *Corrosion/98*, 1998, Paper No. 579.

(5) Ahsan, A.; Kalsen, D. A.; Patience, R. L. *Mar. Pet. Geol.* 1997, 14, 55–64.

(6) Jaffe, R.; Albrecht, P.; Oudin, J. L. *Geochim Cosmochim. Acta* 1988, 52, 2599–2607.

(7) Koike, L.; Reboucas, L. M. C.; Reis, F. De A. M.; Marsaioli, A. J.; Richnow, H. H.; Michaelis, W. *Org. Geochem.* 1992, 18, 851–860.

(8) Lai, J. W. S.; Pinto, L. J.; Kiehlmann, E.; Bendell-Young, L. I.; Moore, M. M. *Environ. Toxicol. Chem.* 1996, 15, 1482–1491.

(9) Schmitter, J. M.; Arpino, P.; Guiochon, G. *J. Chromatogr.* 1978, 167, 149–158.

(10) Green, J. B.; Stierwalt, B. K.; Thomson, J. S.; Treese, C. A. *Anal. Chem.* 1985, 57, 2207–2211.

(11) Dzidic, I.; Somerville, A. C.; Raia, J. C.; Hart, H. V. *Anal. Chem.* 1988, 60, 1318–1323.

(12) Fan, T.-P. *Anal. Chem.* 1991, 65, 371–375.

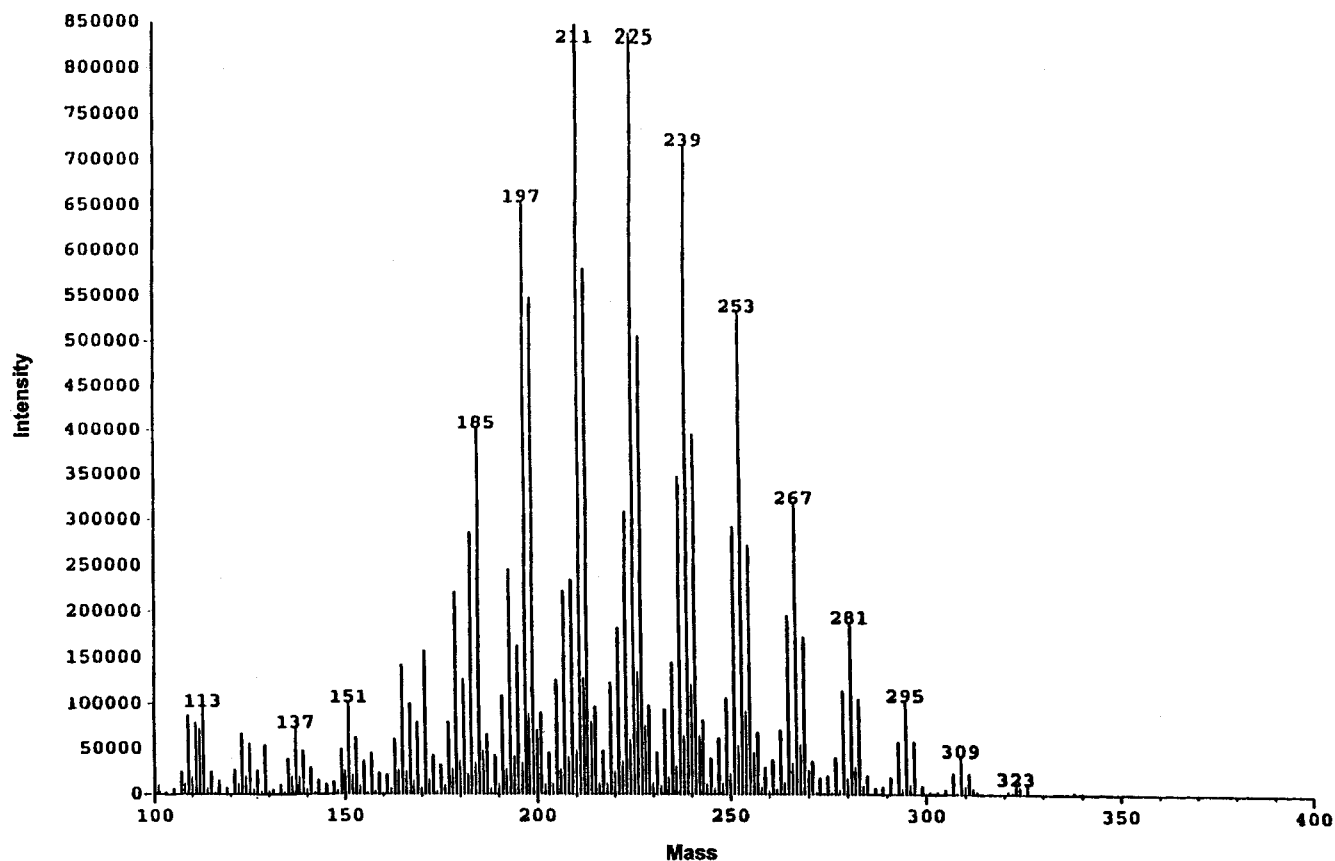


Figure 1. Positive-ion isobutane chemical ionization mass spectrum of the TCI Acid.

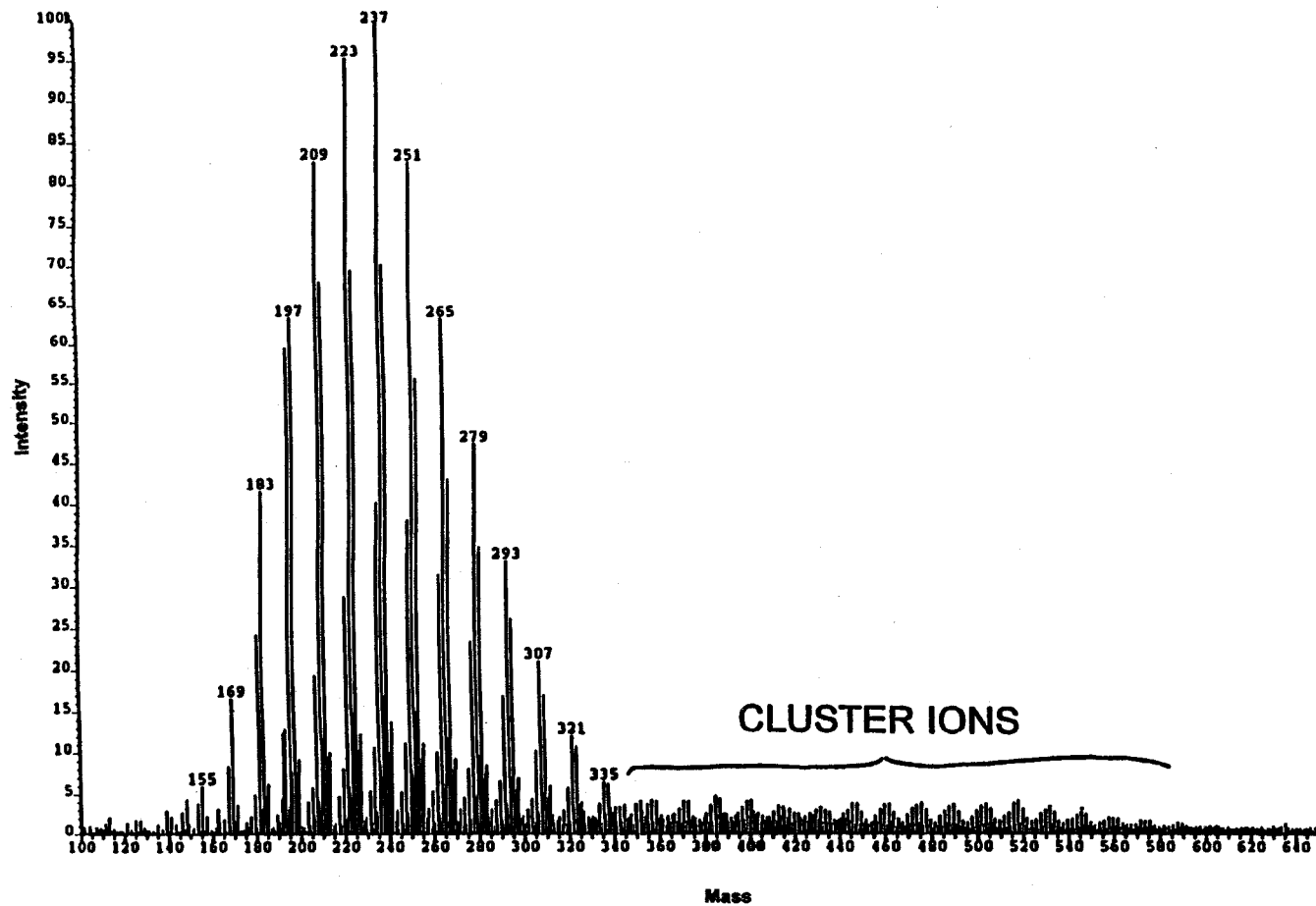
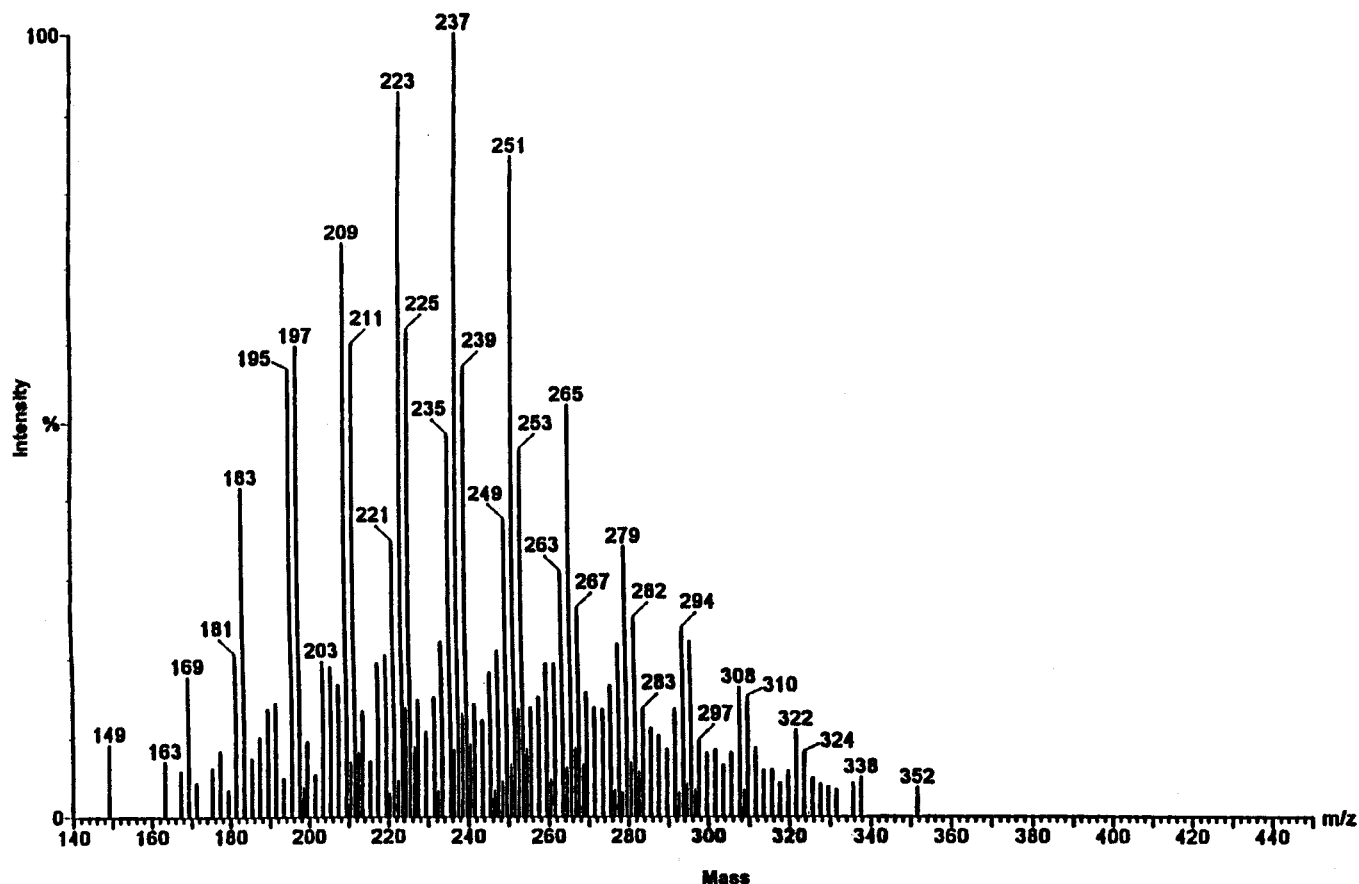


Figure 2. Negative-ion fast iodide anion bombardment mass spectrum of the TCI Acid.



**Figure 3.** Negative-ion atmospheric pressure chemical ionization (APCI) mass spectrum of the TCI Acid.

into the cavity of a probe. The probe was then inserted into the ion source of the mass spectrometer through a vacuum lock. The sample was heated ballistically from ambient temperature to 400 °C via a heating coil around the cavity of the probe. In the CI experiments, both positive -ion and negative-ion mass spectra of the sample were acquired. A Finnigan INCOS data system was used for instrumental control and data acquisition.

For LSIMS experiments a VG-ZAB reverse-geometry double-focusing mass spectrometer was used. A cesium iodide pellet is heated to produce  $\text{Cs}^+$  and  $\text{I}^-$  ions with an emission current reading at 2 A. For naphthenic acids the negative-ion mode was found to be more effective than the positive-ion mode. In the negative-ion mode, the sample was mixed with triethanolamine (TEA) and bombarded by fast iodide anions with a kinetic energy of 25 keV. The sample ions generated from fast iodide anion bombardment (FIAB) were extracted and accelerated out of the ion source at 8 kV. A VG SIOS data system was used for the instrument control and data acquisition.

The APCI and ESI experiments were carried out at Rutgers University using Micromass Platform II mass spectrometer (an instrument for liquid chromatography-mass spectrometry) equipped with a DECpc computer running on a Version 2.2 of the MasslynxNT software. The single quadrupole instrument can be operated in either the APCI or ESI mode. The sample was dissolved in acetonitrile and introduced through a loop injector onto the tip of a heated APCI nebulizer probe where the mobile phase containing the sample was pneumatically converted into an aerosol and rapidly heated to 450 °C into vapor phase at the probe tip. A corona discharge pin at 3 kV was used to ionize the vapor from the nebulizer. The source temperature was maintained at 150 °C. The sample and reagent ions passed through a counter electrode prior to being expanded through a sample cone and skimmer assembly into the mass spectrometer.

**Table 1. Conversion of Nominal  $z^*$  Series to Corresponding  $\text{O}_2$   $z$ -Series**

$z^*$	$z(\text{O}_2)$
-10	0
-12	-2
-14	-4
-2	-6
-4	-8
-6	-10
-8	-12

Multiple-scan carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were acquired with a Varian Unity+ 500 MHz NMR spectrometer. Samples are diluted in deuterated chloroform ( $\text{CDCl}_3$ ) to 30% solution containing 25 mg of chromium acetoacetate ( $\text{CrAcAc}$ ) as a relaxation agent per milliliter of the solution.

The commercial samples of naphthenic acids for MS evaluation were purchased from Kodak, Fluka, Pfaltz & Bauer (P&B), and TCI America. For the APCI selectivity studies, naphthenic acids were isolated from an acidic Californian crude oil with TAN (total acid number) of 4.06 mg KOH/g sample by solid-phase extraction with aminopropyl silica.<sup>13</sup>

## Results and Discussions

CI (low-pressure CI or conventional CI) has evolved into a routine mass spectrometric operation.<sup>14,15</sup> Commonly used reagent gases are methane, isobutane, and ammonia, although other gases can also be used. For

(13) Morrison, B.; DeAngelis, D.; Bonnette, L.; Wood, S. PittCon/92, New Orleans, March, 1992.

(14) Harrison, A. G. *Chemical Ionization Mass Spectrometry*, 2nd ed.; CRC Press: Boca Raton, FL, 1992.

(15) Munson, B. *Anal. Chem.* **1977**, *49*, 772A-778A.

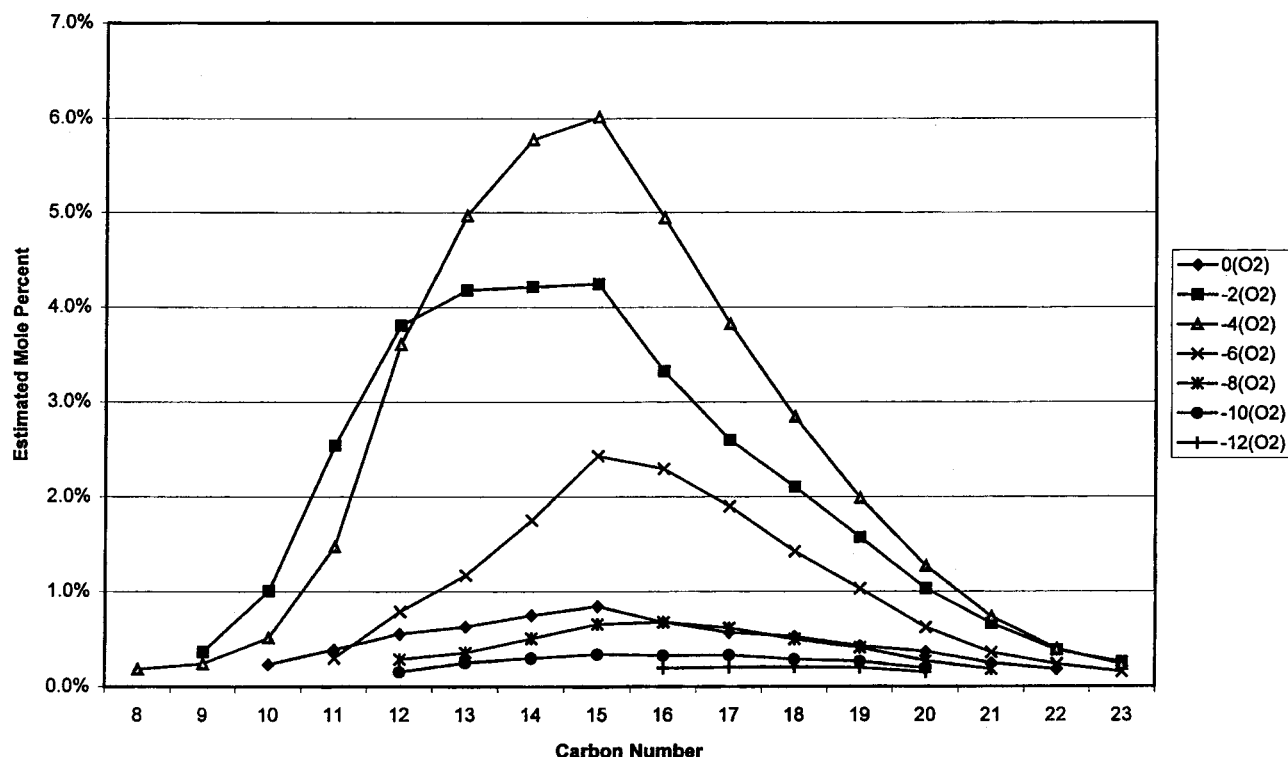


Figure 4. Carbon number distribution of individual ring type in the TCI Acid.

naphthenic acids, the use of  $F^-$ ,  $Cl^-$ , or  $OH^-$  would be expected to yield useful negative-ion CI (NICI) spectra, but these reagent gases are not conveniently used without safety and operational concerns. In our evaluation, both positive- and negative-ion modes were applied using common reagent gases individually. When methane and isobutane are used for NICI, near-zero-energy thermal electrons are generated, resulting in resonance electron capture or dissociative electron capture. In the case of alicyclic naphthenic acids electron capture is not an efficient process. In addition, electron capture can be very efficient for certain polycyclic aromatic hydrocarbons that are not naphthenic acids. When ammonia is used for NICI, very basic  $NH_2^-$  reactant ions are generated. The  $NH_2^-$  ions can abstract not only a proton from an acid but also a proton from the benzylic position of aralkyl compounds. Thus, ammonia NICI is not suitable for selective ionization of naphthenic acids in crude oils either.

In the positive-ion mode, methane CI yields excess amounts of fragment ions. Ammonia CI yields both protonated and ammonium-adduct molecular ions with overall lower sensitivity. The best CI spectra were obtained with positive-ion CI using isobutane as a reagent gas in which naphthenic acids yield primarily protonated molecular ions with minimal fragmentation.

FIAB is a specific type of mass spectrometric technique generally known as LSIMS.<sup>16–18</sup> In LSIMS, a cesium iodide pellet is heated to produce  $Cs^+$  and  $I^-$  ions. Depending on the polarity of the sample ions to be analyzed, either  $Cs^+$  or  $I^-$  ions are accelerated by a potential drop of 25 kV to bombard the target containing

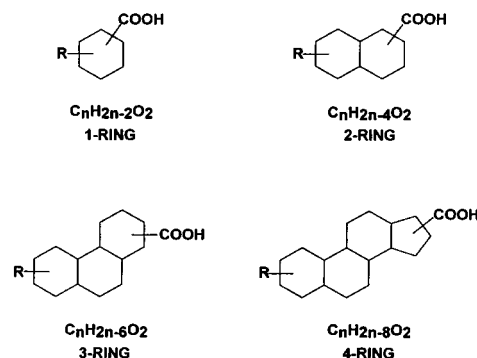


Figure 5. Typical naphthenic acids.

the sample in a liquid matrix. For the characterization of acids, the negative-ion mode was found to be more effective than the positive-ion mode because it gave cleaner spectra with very good sensitivity. In the negative-ion mode, the sample was mixed with triethanolamine (TEA) that is used as a liquid matrix and bombarded by fast iodide anions. This would produce deprotonated molecular anions of the sample by proton transfer from the sample to TEA. Although the sample was bombarded by iodide ion with high kinetic energies (25 keV), the internal energies of the deprotonated molecular anions are low, resulting in minimal fragmentation.

APCI and ESI are commonly used in liquid chromatography/mass spectrometric (LC/MS) experiments.<sup>19,20</sup> We have found that ESI is an order of magnitude less sensitive than APCI using relatively nonpolar solvents that are normally used for hydrocarbon mixtures (unless we analyze water samples containing small amounts of

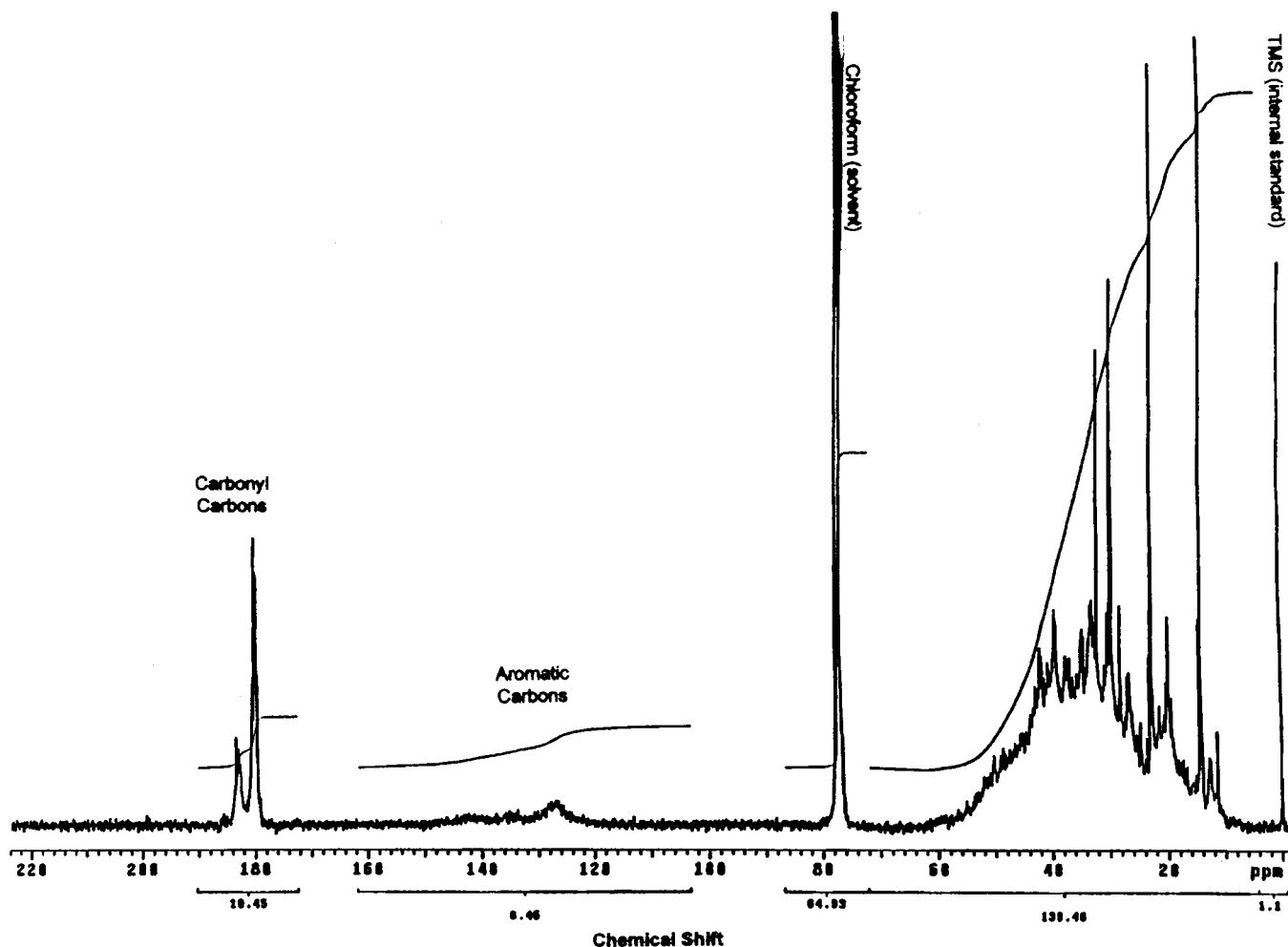
(16) Barber, M.; Bordoli, R. S.; Elliott, G. J.; Sedgwick, R. D.; Tyler, A. N. *Anal. Chem.* **1982**, *54*, 645A–657A.

(17) Pachuta, S.; Cooks, R. G. *Anal. Chem.* **1987**, *59*, 647–669.

(18) Benninghoven, A. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 459–462.

(19) Bruins, A. P. (a) *Mass Spectrom. Rev.* **1991**, *10*, 53–78. (b) *Trend Anal. Chem.* **1994**, *13*, 37–43.

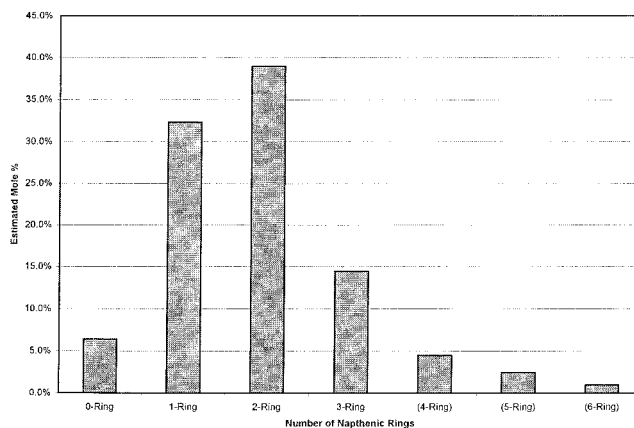
(20) Garcia, D. M.; Huang, S. K.; Stansbury, W. F. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 59–65.



**Figure 6.**  $^{13}\text{C}$  Nuclear magnetic resonance spectrum of the TCI Acid.

oils. In that case, we can add a base to deprotonate the acids for enhanced ionization). For example, using acetonitrile as a mobile phase the acid will be in a neutral form that would yield weak signals in ESI. In addition, ESI is more susceptible to signal suppression by matrix materials. In APCI, the sample is dissolved in a solvent and injected onto a liquid chromatograph or a loop injector to transfer the sample molecules to the tip of a heated nebulizer. The mixture of solvent and sample vapor is then ionized by corona discharge at 3–5 kV. For naphthenic acids, acetonitrile has been found to be a good solvent and reagent gas. Acetonitrile is deprotonated to form the acetonitrile anion,  $\text{CH}_2\text{CN}^-$ , under the APCI conditions. The acid molecules are then ionized by proton transfer to  $\text{CH}_2\text{CN}^-$ , yielding deprotonated molecular ions with minimum fragmentation and high sensitivity.

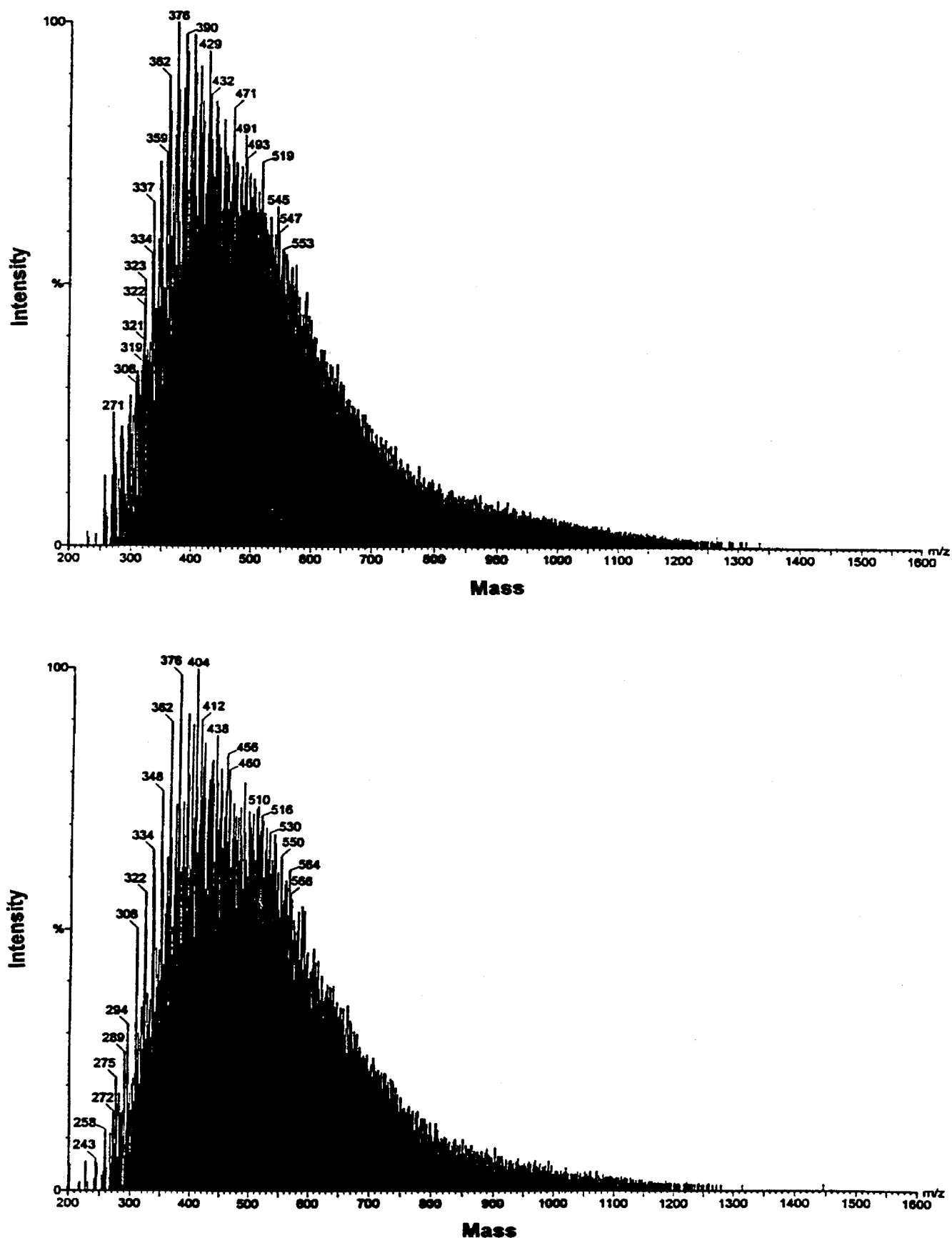
Four commercial samples of naphthenic acids from Kodak, Fluka, Pfaltz & Bauer (P&B), and TCI were used for the evaluation. These acid mixtures represent acids isolated from petroleum fractions (typically gas oils) from different sources. Although several MS techniques show similar results for each acid sample, the acid distributions among these commercial samples differ.<sup>21</sup> The acid sample from TCI (i.e., "TCI Acid") are used



**Figure 7.** Ring-type distribution of the TCI Acid.

below to illustrate the characteristics of  $i\text{C}_4\text{-CI}$ , FIAB, and APCI. Figures 1–3 exhibit the positive-ion  $i\text{C}_4\text{-CI}$ , negative-ion FIAB, and negative-ion APCI mass spectra, respectively, of the TCI Acid. Note that positive-ion  $i\text{C}_4\text{-CI}$  yields protonated molecular cation,  $(\text{M} + \text{H})^+$ , while negative-ion FIAB and APCI yields deprotonated molecular anion,  $(\text{M} - \text{H})^-$ . The molecular ion profiles in the mass spectra are similar. However,  $i\text{C}_4\text{-CI}$  gives slightly lower carbon number distributions than FIAB and APCI MS due to low volatility of higher-molecular-weight species. Since  $i\text{C}_4\text{-CI}$  requires vaporization of the sample by direct heating, decarboxylation (thermal decomposition) of acids is also possible. The low-mass

(21) Hsu, C. S.; Dechert, G. J.; Robbins, W. K.; Fukuda, E.; Roussis, S. G. *Prepr. Pap.-Am. Chem. Soc., Div. Petrol. Chem.* **1998**, 43, 127–130.



**Figure 8.** Comparison of APCI mass spectra of the isolated acidic fraction (top trace) and the whole Californian crude oil from which the acids are isolated (bottom trace).

ions (<150 Da) observed in *i*C<sub>4</sub>-CI are believed to be fragment ions produced in the chemical ionization processes. FIAB and APCI yield almost identical mass

spectra. However, FIAB also yields acid dimer clusters (>350 Da) due to ionization in a liquid matrix needed for analysis. Hence, APCI gives the cleanest mass



spectra among the techniques evaluated, it does not yield fragment and dimer cluster ions.

The molar masses of acid components can be easily obtained from the dalton values of the protonated or deprotonated molecular ions. From the molar masses, the ring-type distribution of acids and the carbon number distribution in each ring type can be determined. For example, the deprotonated molecular ion of 237 Da shown in Figure 3 corresponds to an acidic species of molar mass of 238. Using the approach suggested by Hsu et al., the nominal mass series,  $z^*$ , of the 238 Da acid can be determined to be  $-14$  by the remainder of the nominal mass divided by 14, i.e., the modulus of  $(\text{nominal mass}/14) - 14$ .<sup>22</sup> The nominal mass series can then be converted into corresponding  $z$ -series in the general formula of  $C_nH_{2n+z}O_2$  for acids, according to the Table 1.

The 239 Da acid is in the  $z = -4(O_2)$  series that is belonged to 2-ring naphthenic acid (see below). Once the  $z$ -value is determined, the carbon number of this specific acidic species can be easily determined to be 15.

As for hydrocarbons, the distribution of acids determined by mass spectrometric analysis can be conveniently expressed by  $z$ -series where  $z$  represents hydrogen deficiency in the molecular formula of  $C_nH_{2n+z}O_2$ . For example, acyclic (0-ring) aliphatic acids have a general formula of  $C_nH_{2n}O_2$ . The whole series can be expressed as  $z = 0 (O_2)$  series. One-ring naphthenic acids have a formula of  $C_nH_{2n-2}O_2$ . Hence, they can be expressed as a  $z = -2(O_2)$  series. Figure 4 shows the carbon number distribution of seven acid series in the TCI Acid.

Figure 5 shows typical 1- to 4-ring naphthenic acids with  $z$ -values of  $-2 (O_2)$  to  $-8 (O_2)$ , respectively. Note that 4-ring naphthenes share identical molecular formula as benzenes. Hence, the  $z = -8 (O_2)$  series can be either 4-ring naphthenic acids or an acid series containing one phenyl group in their hydrocarbon backbones. Assuming that all of the naphthenic rings are five-membered, the minimum number of carbon atoms for 4-ring naphthenic acids would be 14. However, the  $z = -8 (O_2)$  acids start at carbon number of 12 as shown in Figure 4. This suggests that these are not 4-ring naphthenic acids, but rather aromatic acids with a phenyl group in the hydrocarbon backbones. Similarly, the acids with  $z = -10(O_2)$  and  $-12(O_2)$  start with carbon numbers much less than the smallest naphthenic acids with 5- and/or six-membered rings, suggesting that they are aromatic acids as well. The presence of aromatic acids in the TCI Acid was confirmed by  $^{13}C$  NMR analysis, shown in Figure 7. The chemical shifts in the 120–150 ppm region indicate the presence of aromatic carbons.

From the carbon number distributions shown in Figure 4, the carbonyl carbons are calculated to be 6.8 mol % that agrees quite well with 6.5% determined by  $^{13}C$  NMR. However, the aromatic carbon estimated by MS is 3.1%, compared to 5.4% determined by  $^{13}C$  NMR.

The higher aromatic number by  $^{13}C$  NMR is probably due to the presence of nonacidic aromatic hydrocarbons that are not detected by the selective negative ion FIAB and APCI techniques. Figure 7 exhibits the ring-type distribution of the TCI Acid, which shows that the most abundant naphthenic acids have two saturated rings. As discussed above, the 4-, 5-, and 6-ring "naphthenic acids" are actually acids containing aromatic rings. The total amount of aromatic acids is less than 10%.

To evaluate the selectivity of APCI to the whole range of acidic components in a crude oil, we have isolated an acid fraction from a Californian crude oil with high acid content. The whole crude oil and its acid fraction were separately introduced into the LC/MS through a loop injector without chromatographic separations. Figure 8 compares the negative-ion APCI spectrum of the isolated acid fraction (top spectrum) with that of whole crude oil (bottom spectrum). The similarity of these two spectra indicates that only the acidic components in the crude oils yield negative APCI ions, leaving other components largely un-ionized. The TAN (total acid number, i.e., mg KOH/g oil for neutralization<sup>23</sup>) of the crude oil is 4.06, which is equivalent to 0.0725 mmol acid/g oil. With an average molar mass around 500 shown in Figure 8 the acids would account for about 3.6% of the crude oil by mass, consistent with the amount of acids actually isolated (3.9 mass %). Hence, the selectivity of the APCI technique to the acids in crude oils is demonstrated.

## Conclusions

For the characterization of naphthenic acids, we found that NICI does not give any advantages over positive-ion CI, regardless of the reagent gas used (methane, isobutane, and ammonia). In addition, the interfering background ions in NICI are difficult to eliminate. For positive-ion CI, isobutane was found to yield the cleanest spectra with good sensitivity over methane and ammonia. For FIAB and APCI, on the other hand, the negative-ion mode was more selective and sensitive to the acids than the positive-ion mode.

Negative-ion APCI using acetonitrile as a solvent and mobile phase appears to yield the cleanest spectra among the mass spectrometric techniques evaluated for the characterization of acids, without the discrimination of heavier ions and the formation of fragment and cluster ions. APCI also holds a great potential for further development of on-line liquid chromatography–mass spectrometric (LC/MS) methods to separate acids by high-performance liquid chromatography followed by mass spectrometric characterization for the determination of acid structures.

**Acknowledgment.** The authors acknowledge the  $^{13}C$  NMR spectrum of the TCI Acid provided by Steve Rucker and A. R. Garcia of Exxon Research & Engineering Co.

EF9901746

(22) Hsu, C. S.; Qian, K.; Chen, Y. C. *Anal. Chim. Acta* **1992**, 264, 79–89.

(23) 1998 Annual Book of ASTM Standards; American Society for Testing and Materials: West Conshohocken, PA.; Vol. 05.01, ASTM D 664/IP 177.