Determination of naphthenic acids in crude oil by chemical ionization mass spectrometry *

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Abstract  Naphthenic acids in petroleum are considered a class of biological markers. Their potential use in source correlation and as an indicator of biodegradation was reported in the past (Dzidic et al., 1988; Behar and Albrecht, 1984). Due to their highly complicated properties, detailed characterization of the acids is difficult.

A method based on positive ion CI (chemical ionization) mass spectrometry using isobutane reagent gas to produce (M + 15)⁺ ions was applied to the analysis of naphthenic acid esters. Since the complex mixture of naphthenic acids cannot be separated into individual components, only the determination of relative distribution of acids classified in terms of hydrogen deficiency was possible. The identities and relative distribution of fatty and mono-, di-, tri-, and higher polycyclic acids were obtained from the intensities of the (M + 15)⁺ ions according to z-series formula CₙH₂ₙ₊₂O₂ of naphthenic acids. The components are characterized on the basis of group type and carbon number distributions. A comparison of the FAB and CI results showed that the group type distributions obtained by both methods agree surprisingly well. The results indicated this method is simple, rapid and easy to operate. The geochemical implication of naphthenic acids was investigated by using a set of well-characterized crude oil samples. It is found that the naphthenic acid distribution can be used as a fingerprint for oil-oil and oil-source correlations.

Key words  CI-MS; naphthenic acid; distribution; z-series

1 Introduction

Carboxylic acids present in petroleum or crude oils are often called naphthenic or petroleum acids. Their contents in crude oils vary from 0% to 4%. The naphthenic acids are extremely complicated mixtures and contain predominant compounds with cyclic or polycyclic backbone compounds that are not possible to separate into individual components, even by high resolution GC (gas chromatography) (Dzidic et al., 1988; Behar and Albrecht, 1984). GC characteristics of the saturated hydrocarbon fraction of crude oils and the characteristics of their biomarkers have been reported (Yin Wei et al., 2003). The interest in naphthenic acids is twofold. One is they are a class of biological markers for the studies of geochemical correlations, as well as biodegradation mechanisms; the other is their presence in the refinery streams causes corrosion problems and hazardous wastewaters would lead to fish toxicity (Behar and Albrecht, 1984; Cranwell, 1984).

In the past, many different methods and analytical techniques were used to analyze naphthenic acids. Some employed extensive sample preparation such as extraction, separation and chemical reaction prior to determination by spectroscopic techniques. Some of the published work has relied on the GC/MS (mass spectrometry) technique with EI (electron impact) and positive ion CI. These techniques allowed rapid analysis of several specific acid types. The EI spectra, however, do not provide sufficient information for the identification of all acids, since the fragmentation patterns are obscured by ions from many other different acids, and in the course of EI analysis lots of fragment ions can be formed and most acids cannot show molecular ion peaks. GC/MS can only be used to identify volatile or low molecular weight or weak polar acids and is not suitable for heavy components with low volatility or strong polar acids (Cranwell, 1984).

Positive ion CI mass spectrometry is not suitable for the analysis of naphthenic acids either, because the spectra of the acids generally exhibit the (MH-H₂O)⁺ fragment ions, indicative of the loss of water from the
protonated molecular ions. These fragment ions also make it complicated the molecular weight determination and the identification of acid types.

Two MS methods have been newly developed. One involves negative ion CI analysis using NF₃ as reagent gas and the other method employs negative ion fast atom bombardment MS (FAB-MS) (Dzidic et al., 1988; Behar and Albrecht, 1984; Cranwell, 1984). Although negative CI-MS and FAB-MS can make petroleum acids produce single charged carboxylic ions (M-1)⁻, but these techniques are very complicated and cannot be performed on many bench-top MS instruments commonly found in analytical laboratories. Therefore, there is a continuing demand for improved methods for the analysis of acids in petroleum-related samples.

The goal of the present study is to develop positive ion CI conditions for the probe MS. We can solve the problem above by esterifying the naphthenic acids as the esters of naphthenic acid can be produced in a variety of ways. Some of these methods involve the use of hydrochloric acid-methanol, boron tri-fluoride-methanol, sulfuric acid-methanol and diazomethane to form methyl esters. Using isobutane as reagent gas to form the characteristic ion (M+15)⁺ of esters. The extent of molecular fragmentation is greatly decreased and strong base peaks representing the un-fragmented naphthenic acid constituents are obtained in the CI spectra. It is possible to obtain molecular weight and structural information about naphthenic acid components from the prominent (M+15)⁺ ion peaks, and the relative distribution of naphthenic acids was also determined.

2 Experimental

The properties of the samples are presented in Table 1.

<table>
<thead>
<tr>
<th>API Density g/cm³, 20°C</th>
<th>Viscosity m²/s, 15.6°C</th>
<th>Pour point (°C)</th>
<th>S content (wt%)</th>
<th>Carbon residue (wt%)</th>
<th>Acidity mg KOH/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.4</td>
<td>0.9231</td>
<td>142.42</td>
<td>-17.8</td>
<td>1.06</td>
<td>4.40</td>
</tr>
</tbody>
</table>

2.1 Extraction of the acids

Many methods to extract acids from crude oils have been described, such as column chromatography with silica gel, anion-exchange resin based on acidity by using solvents of increasing polarity, repeated extraction with alkaline ethanolic and Freon 113 solvents (Dzidic et al., 1988).

The crude oil under investigation was deposited at the top of the adsorbent and eluted with diethyl ether. After 7 h, neutral, basic and weakly acidic compounds were recovered. The fraction containing naphthenic acids was eluted with a 20% solution of formic acid in diethyl ether, followed by two hours of ether recycling.

After evaporation of the solvents in a rotary evaporator, the acids were converted to their corresponding methyl esters. The methyl esters were obtained by reaction with a methanol-boron tri-fluoride solution at room temperature for 12 h, the esters were extracted with chloroform after addition of water. A purification step permitted their separation from a very polar resin by recycling liquid chromatography over a second column of potassium hydroxide-treated silica. After separation according to increasing polarity by thin-layer chromatography, the purified methyl esters are separated by using cyclohexane-dichloromethane.

**Table 1. Properties of crude oil**

![Fig. 1. Procedure for extracting petroleum acids from crude oils.](image-url)