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Analysis of Naphthenic Acids in Water and Petroleum Products

Introduction

Naphthenic acids are organic acids comprised of one or more rings and at least one carboxyl group. Cyclohexananoic acid ($C_7H_{12}O_2$) is an example of the simplest member of this group. The rings are usually saturated (ie. not aromatic).

Naphthenic acids are found in crude oil and are particularly prevalent in crudes prepared from oil sands bitumen. As they are surface active, they can cause a range of problems for oil refiners. Not the least of which is their corrosivity to steel. The following list summarizes some of the key features:

1. Contain 7-30 carbon atoms.
2. One or more ring structures, usually saturated.
3. May contain hydroxyl or amino groups.
4. Soluble in crude oil.
5. Soluble in water at pH 9 or more.
6. Surface active.
7. Corrosive to steel.
8. Extremely toxic to fish at concentrations of about 1 mg/L.

Methods

There are several ways of measuring naphthenic acids in water and oil, including FTIR and GC/MS. In our lab, we employ a liquid-liquid extraction to isolate the acids from water or oil, then use GC/MS combined with a derivatizing agent, developed by St. John et al (J. Chromatography., 807: 241-251, 1998) to detect them.

Extraction from water and oil relies on the fact that naphthenic acids are soluble in dichloromethane when in their –COOH form, but are soluble in water when in the COO^- form. Thus, by a series of extractions at different pHs, the naphthenic acids can be separated from neutral oils and other organic material.

Once the acids are purified and concentrated in dichloromethane, they are converted into the t-Butyldimethylsilyl derivative (t-BDMS for short). To quantify the acids, the GC/MS is calibrated with standards containing known amounts of naphthenic acids.

How the Naphthenics are detected

Figure 1 shows what a typical chromatogram of derivatized naphthenic acids looks like. The size of the acids in this example range from 7 to about 20 carbons. Compounds such as the C8 and C9 indicated, are sharp spikes a they tend to represent single compounds, like methyl cyclohexanoic acid. Larger material tends to elute as unresolved humps because they are a mix of many compounds having the same number of carbons.

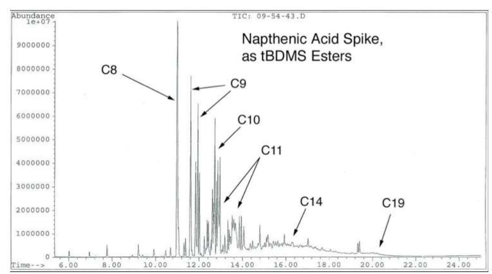

Figure 1; Chromatogram of Naphthenic Acid standard as tBDMS derivative.

The mass spectrometer takes a scan every second or so, giving rise to mass spectra like that shown in Figure 2, from which structural information can be obtained.

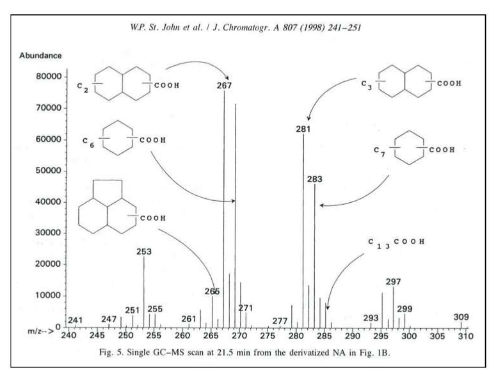

Figure 2; Naphthenic Acid Mass Spectrum and associated structures.
Taken from St. John et al (1998).

Watson's Notes

Innovative Solutions for Difficult Problems

You have recently been in Afghanistan, I perceive"

With these words was born the most famous team in detective fiction; Sherlock Holmes and his trusted comrade and biographer, Dr. John H. Watson.

In the spirit of Watson, who chronicled the exploits of Holmes, we have created this newsletter named "Watson's Notes".

In the pages of "Watson's Notes", modern day scribes document the discoveries, unusual cases and other news of Investigative Science Incorporated, our scientific consulting firm in Burlington, Ontario, Canada.

Please contact us if you have comments, and please read on.

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ELEMENTARY MY DEAR WATSON

How did Holmes know Watson had been in fghanistan anyway?

! This is explained in the first chapters of "A Study of Scarlet". According to the story, on their first meeting, Holmes observed that Watson was a physician with a "military bearing". He also observed that he was well tanned, had suffered some health hardships and had an injured arm, which he held in an awkward manner. Holmes asked himself, where would a military doctor have been injured in the tropics. At the time, England had troops in Afghanistan, leading Holmes to deduce: "You have recently been in Afghanistan, I perceive".

The ions in Figure 2 provide information about the size and shape of the individual naphthenic acids. These ions, which are particularly strong with the tBDMS derivative, arise from the loss of the t-butyl group from the tBDMS derivative. As a result, the fragments weight 57 mass units less than the total weight. The fragmentation process is illustrated in Figure 3.

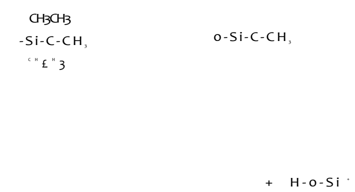

Figure 3; The origin of the Key Mass Spectral Ions Used in this Analysis. Taken from St. John et al (1998).

Using this approach, it is assumed that each ion with a mass greater than 200 mass units represents the molecular weight (minus 57) of each individual component of the naphthenic acid mixture, each having the formula; $C_nH_{2n-z}O_2$, where "Z" represents two times the number of rings in the molecule. The general formula applies to any cyclic monocarboxylic acid; meaning one acid group and at least one cyclic structure in each molecule.

Figure 2 shows that an ion with a mass of 267, for example, represents a molecule having a single carboxyl group, two rings and a 2 carbon side chain. It contains 13 carbons and would have a "Z" value of 4. The actual molecular weight of such a molecule would be 210 mass units ($C_{13}H_{22}O_2$). The weight of 267 comes from the additional 114 mass units from the t-BDMS derivative minus 57; a fragmentation that happens inside the mass spectrometer.

The method has some limitations which should be discussed here. First, other neutral oils can interfere by contributing mass spectral ions in the region of interest. To counteract this effect, we use several purification steps to ensure that oil contamination is minimized. As well, we use other mass spectral ions to confirm the identity of the naphthenic acid fraction. For extremely oily samples, a method proposed by Scott et al (Chemosphere 73: 1258-1264, 2008), focusses only on the mass spectral ion at 267. This ion represents a 13-carbon acid and tends to be found only in naphthenic acids, not in other contaminating oils. The drawback with this approach is that it cannot detect fatty acids and gives no information on the weight distribution of naphthenic acids.

Second, because only the masses greater than 200 are used, it is not possible to determine the species of smaller molecules unless they happen to occur in pure form in the chromatogram. This means that molecules lighter than about C8, Z=0 are ignored.

Molecular Species Profile

As explained earlier, each ion in the 200+ molecular weight range represents the naphthenic acids with a particular number of carbons and ring systems. If the ion intensity is tabulated along with the theoretical carbon and ring number, the size and shape of the naphthenic acids can be summarized graphically. A typical plot from Canadian crude is shown in Figure 4.

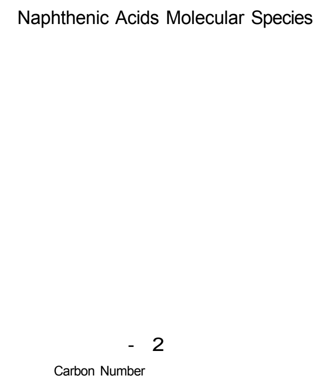

Figure 4; Molecular Species Chart of Naphthenic Acids from Canadian Crude.

The carbon number is across the x-axis, the percent occurrence is on the y-axis and the number of rings, or "z" is shown on the z-axis.

This type of analysis provides a useful fingerprint of the acids found in given crude oil or water samples.

Applications

In the ISI laboratory, we currently have methods available for the determination of the amount and molecular species of naphthenic acids in surface waters, refinery process waters and crude oils. These analyses are useful for toxicity identification studies, refinery process optimizations and identification of the source of crudes in spill situations.

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