

Naphthenic Acids

*An Overview of Their
Contributions to Corrosion Effects*

Crude Oil Quality Group

January 27, 2005

Corrosion Has Many Sources

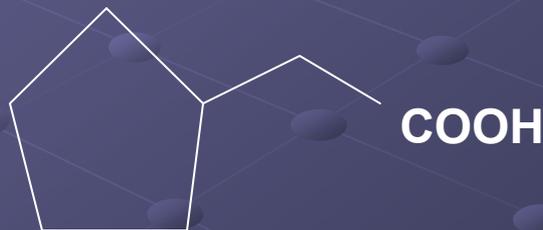
Naphthenic acids are just one source of the corrosive properties of crude or crude fractions.

Other naturally found crude components that can contribute to corrosion in the refining process are mineral acids, phenols, hydrogen sulfide, mercaptans, and carbon dioxide.

Exactly What are Naphthenic Acids?

General term for all organic acids found naturally in crude oils.

GENERAL structure is believed to be



What Makes Them Special?

Naphthenic acid corrosion is characterized by deep pitting and metal impingement.

These effects can be seen even in highly alloyed metallurgies which are normally resistant to corrosive attack from sulfidic species.

How is Naphthenic Acid Concentration related to TAN?

There is no direct correlation. TAN is a measurement of all acidic species present in the crude.

Many crudes with high TAN numbers can have a low naphthenic acid content, and vice-versa.

How is Naphthenic Acid Concentration Related to Corrosive Potential?

It's tricky.

The corrosive potential from naphthenic acids are a function not only of concentration, but also of temperature and wall shear stress (along with Reynold's number).

And this means.....?

Naphthenic acid concentration may be a serious source of corrosion for one process and have relatively benign effects for another.

The density and viscosity of the liquid and the vapor in the pipe, the degree of vaporization in the pipe, and the pipe diameter are all factors affecting the corrosive activity of naphthenic acids.

Furnace Tubes and Transfer Lines

Vaporization and flow rates are very high.

Small amounts of Nap acids are activated and corrosion is significantly increased.

Turbulence is also a significant factor.

Vacuum Column

Nap acids are preferentially vaporized and condensed. This increases the TAN of the condensed material.

Relatively low velocity. This means that corrosion is almost all in the liquid phase at the point of condensation.

And this Means?

There is not a one-size-fits-all rule of thumb for how naphthenic acids will affect a given metallurgy in a given process.

Depending on process conditions even a small amount of naphthenic acids can greatly accelerate corrosion in specific areas of the refinery.

A Fast Summary

Naphthenic acids are responsible for a specific type of corrosion in specific areas of the refining process.

Naphthenic acid concentration is not necessarily a function of TAN magnitude.

Naphthenic Acid Analysis

It's not as easy as it may appear.

Naphthenic Acid Analysis

TAN- Already Discussed. Correlations not that great.

UOP 565 and 587. Sulfur compounds are removed prior to potentiometric or color-indicator titration. Not very sensitive, and is not very specific to naphthenic acids.

Mobil Method- LC extraction and IR quantification. Much more specific, but wt% is based on a generic calibration standard.

Naphthenic Acid Analysis

Fast Atom Bombardment –Mass Spec

Very specific to naphthenic acids, and provides a very good profile of the MW distribution of the species that are present.

Not a very easy technique/instrumentation is significant.

Energy and Fuels, 1991, Vol 5, pp371-375

Naphthenic Acid Analysis

Negative-Ion Microelectrospray High-Field
Fourier Transform Ion Cyclotron
Resonance Mass Spectroscopy

Energy and Fuels 2001, Vol 15, pp.1505-1511

Naphthenic Acid Analysis

Electrospray Ionization High-Field Asymmetric
Waveform Ion Mobility Spectrometry-Mass
Spectrometry

VERY little sample prep/No loss of volatile
components such as formic or acetic acid.

U of Alberta Research

<http://www.osern.rr.ualberta.ca/Downloads/conradsymp03/fedorak.pdf>

Naphthenic Acid Analysis

SPE cartridge Extraction/Esterification/Mass Spec

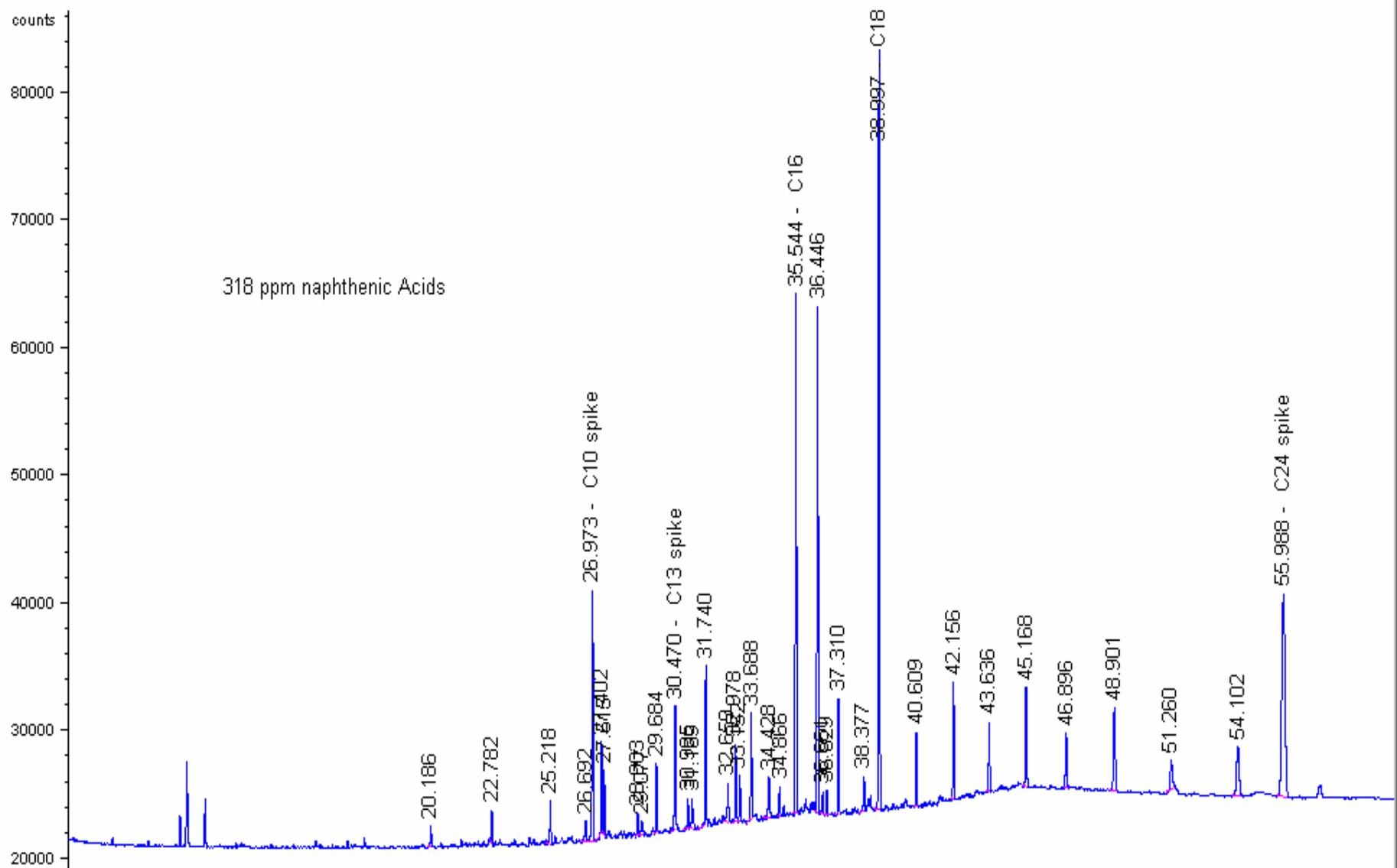
Provides a very solid analysis of C10+ naphthenic acids.

Lighter acids can be lost in the esterification step.

Analytical Chem, 2001, Vol 73, pp 703-707.

Data Analysis 5245-1B.D NACIDS.M Calibration Short

FID1 A, (M:\HPCHEM\3\DATA\N101104\5245-1B.D)



Vertical toolbar with icons for zoom, pan, and other analysis functions.

Data Analysis

1156-12.D

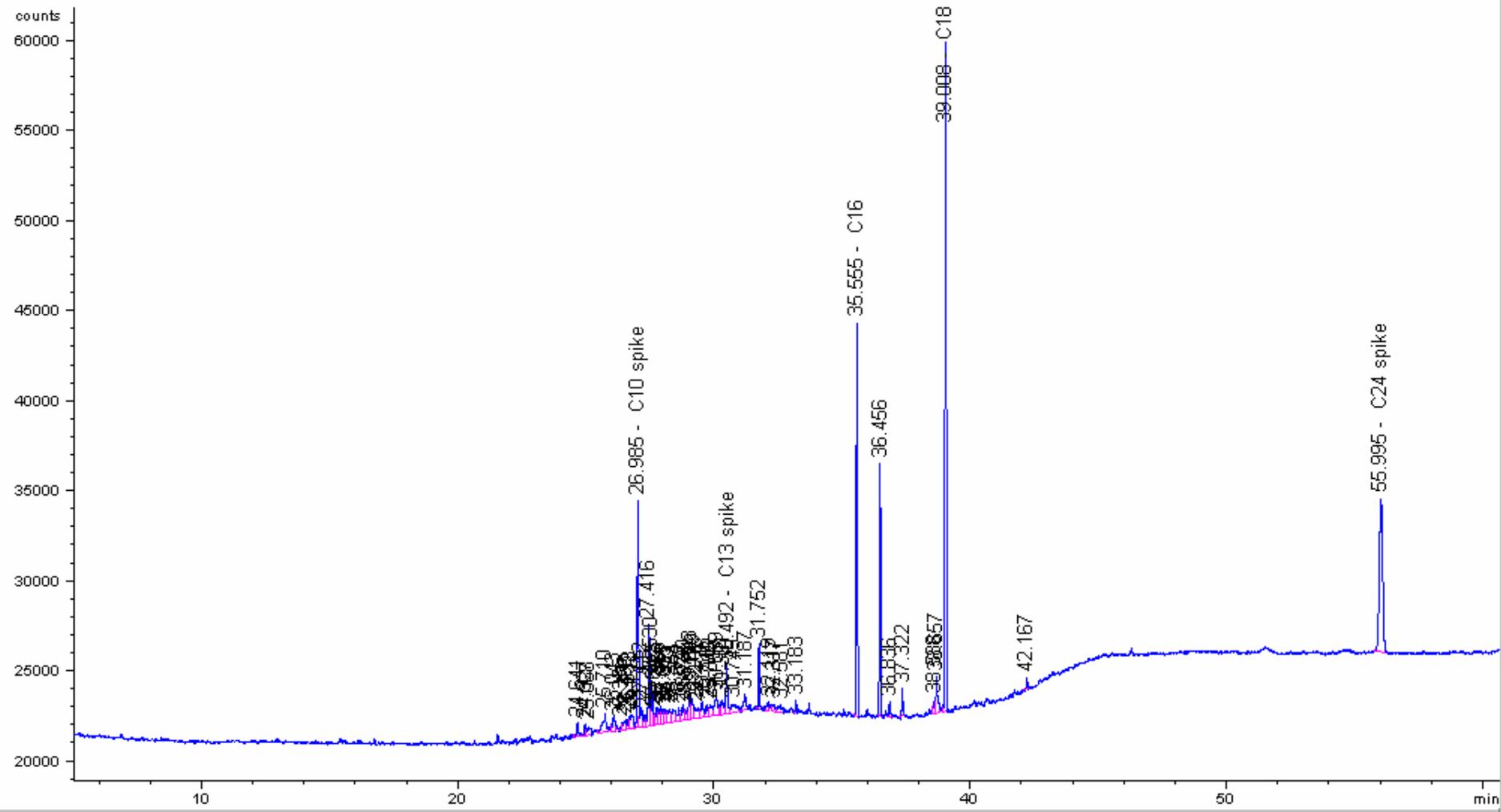
NACIDS.M

Calibration

Short



FID1 A, (N092804\1156-12.D)



Integration done.