Petroleomic Analysis by use of FT-ICR MS

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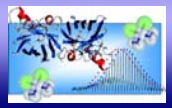
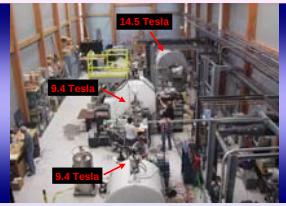
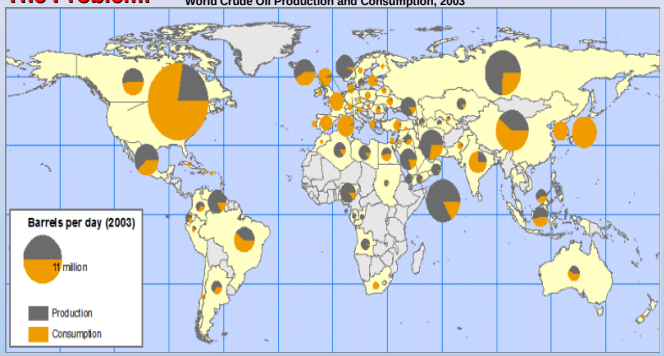




The Problem:

World Crude Oil Production and Consumption, 2003



In 2003, the global oil production was 70 million barrels per day. Oil production is marginal or non-existent in a large amount of countries, notably in Africa. Eight producers, Saudi Arabia, the United States, Russia, Iran, China, Venezuela, Mexico and Norway accounted for 55% of the global production. The global oil demand in 2003 was 77 million barrels per day. Oil demand is roughly a function of population and level of development. Seven countries, the United States, Japan, China, Germany, Russia, Italy and France, accounted for 52% of the global oil demand. It is essential that methods in petroleum production continue to improve in order to meet global demand.

With the "easy" oil reserves diminishing, oil companies are being forced to drill heavy oils to meet world demand. It is imperative to understand the chemical composition of these more difficult to retrieve oils.

What is Petroleomics?

Petroleomics[1, 2] is the term used to describe the study of all components of crude oil (petroleum) and how these components affect the properties and reactivity of that specific crude oil. This idea is not new to the industry. The composition of crude oil is the cornerstone of molecular based management of refinery processes. Simply stated, petroleum companies sell molecules and consequently, an oil's composition determines its economic value. Therefore, compositional knowledge equals power and enables the company to produce oil reserves more efficiently, to predict production problems and prevent pipe fouling, to reduce refining byproducts and waste, to use the oil reserves more efficiently and finally to make money. This need to determine and understand a crude oil's composition is the force behind all crude oil analysis.

Petroleum varies dramatically in color, odor, composition and flow properties that reflect the diversity of its origin. The terms light or heavy are often used to describe different types of crude oils. Although not derived from composition, light petroleum (sweet crude oil) is usually rich in low-boiling constituents, whereas heavy petroleum (sour crude oil) is composed of more aromatic, heteroatom-containing constituents with higher boiling points. The decrease in light oil reserves around the world has led to the production of petroleum based products from the heavy crude oils that are more readily available.

COVER STORY

PITTCON 2003

FINE LOOK AT CRUDE OIL

Analytical techniques could lead to new understanding of petroleum

As recently as a few years ago, who would have thought that we could have a detailed picture of the components of petroleum?

At one time, scientists thought that the

tion for scientists, but that changed with the development of deepwater facilities. "We don't want to put in 50 miles of pipeline and then have it clog up."

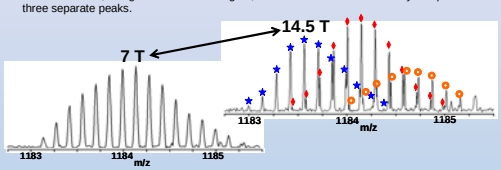
Mullins uses fluorescence depolarization, which measures the rotational diffu-

The topic is relatively new. Oil samples have only been analyzed at the Magnetics lab for the past few years. The article to the left shows how recent and important the science of petroleomics is.

"We don't want to put in 50 miles of pipeline and then have it clog up."

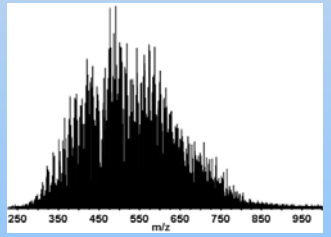
The importance of the magnetic field

The image below is that of the mass spectrometer results for the same sample using two different FT-ICR superconducting magnets. Using the 7 Tesla field magnet, only one peak is found. However, using the 14.5 Tesla magnet, it can be seen that it is actually composed of three separate peaks.



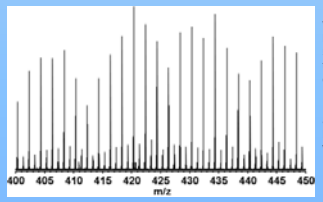
The Accuracy of the Data

Take a look at the graph below, which depicts the MS results of a sample of South American crude oil.



This is a mass spectrum, the type of reading you'll get from any mass spectrometer. Each peak represents a type of molecule. The numbers running across the bottom of the graph – what's called the mass to charge ratio, or m/z – refer to the molecule's atomic mass. The height of the peaks tells us how many there are.
As you can see, these peaks are packed in very tightly. In this example, the range of molecular masses covered starts at about 225 Dalton and goes up to 1,000 Dalton – and there's an awful lot happening in between. The crude oil is complex; it's hard to differentiate the molecules.

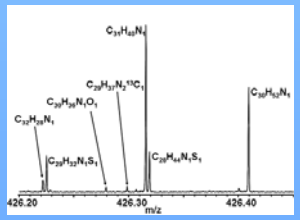
So here is a close up of the peaks between 400 and 450 dalton.



We've honed in significantly on the sample here, covering not a range of 775 Dalton but of 50. It becomes clear that the blur we saw in the above spectrum actually can be broken down into individual, discernible peaks.

However, the lines are still pretty fuzzy. To be able to tell those peaks apart – or even to know that there is more than one peak there – we need to zoom in even closer.

Here is a close up of the peaks at the 426 dalton area.



What before looked to be a single line is actually several, depicting several separate hydrocarbons. $C_{31}N_{40}N_1$ is the most numerous of the bunch, but the sample also contains (in order of abundance), $C_{30}H_{42}N_1$, $C_{28}H_{44}N_1S_1$ and $C_{29}H_{32}N_1S_1$, among others.
In fact, when you look at this crude oil sample with the help of FT-ICR, you will find upwards of 11,000 different hydrocarbons.

Other machines cannot produce this level of detail. Instead, they essentially lump together several different molecules in a single peak, which represents their weighted average – something quite different than what is truly there.

This capacity is of extreme interest to scientists. In fact, the instruments here hold the world's record in mass resolution. In fact, FT ICR MS was able to differentiate between two distinct molecules that were only about .0005 Dalton apart in atomic mass. That's about as much as an electron weighs, which is extremely close to nothing.

Acknowledgements

Dr. Alan G. Marshall *Professor, Chemistry CR Program Director* CIMAR, ICR
Christopher L. Hendrickson, Director of Instrumentation

References

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2. Rodgers, R. P.; Schaub, T. M.; Marshall, A. G., Petroleomics: MS returns to its roots. *Analytical Chemistry* **2005**, 77, (1), 20A-27A.

Fu, J.M.; Klein, G.C.; Smith, D.F.; Kim, S.; Rodgers, R.P.; Hendrickson, C.L. and Marshall, A.G., *Comprehensive Compositional Analysis of Hydrotreated and Untreated Nitrogen-Concentrated Fractions from Syncrude oil by Electron Ionization, Field Desorption Ionization, and Elecrospray Ionization Ultrahigh-Resolution FT-ICR Mass Spectrometry*, **Energy & Fuels**, **20**, 1235-1241 (2006)

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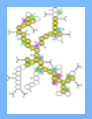
http://keck.med.yale.edu/prochem/fticrfaq.htm

Some challenges with Oil

To you, all crude oil might look, smell and feel the same. And in fact, all crude oil is made up mostly of hydrocarbons, molecules of carbon and hydrogen. But on a molecular level, there can be tremendous differences. There are many types of hydrocarbons, for example. Crude oil contains varying amounts of nitrogen, sulfur, nickel and other elements, as well. The makeup depends on where, and under what pressures and temperature, it was formed, as well as the types of plants that decomposed to make it.
In fact, crude oil is supremely complex – one sample might contain more than 30,000 different chemical substances. Those molecules harbor important information – about the sample's tendency to rust steel pipes or to clog them, for example, or what makes it form an emulsion with water. A close look at the content of sulfur, a pollutant, in the oil would indicate how difficult it would be to get rid of. Having such detailed chemical profiles of crude oil could also help pinpoint the origin of a spill.

Most heavy oils contain a substance know as Asphaltene. Asphaltene can be thought of as the "Cholestrerol" of oil. It is responsible for the clogging of pipes.

Asphaltene



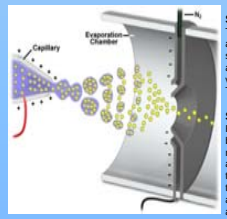
Sulfur containing compounds are detrimental to the environment and the refining process. The effort continues to reduced greenhouse gas producing sulfur species in refined fuels. The identification of these sulfur species and their fate in commonly used refining processes is paramount in the future removal of hard to deal with species resistant to conventional removal methods.

Highlighted by the recent pipeline rupture in Prudhoe Bay, the corrosion of production, transport (as in this case) and refining equipment threatens domestic as well as worldwide petroleum production. Most commonly encountered in refining, corrosion is a multi-billion dollar problem that will only get worse in the future as lower grade, acid rich reservoirs are tapped to meet worldwide energy demands. Compositional information on acidic species present in crude oil is essential in refinery and production risk assessments, equipment design / modifications and ultimately the prediction of corrosion.

The Current Strategy

Electrospray Ionization

Electrospray ionization (ESI) is a popular technique in mass spectroscopy for ionizing samples before they are measured. ESI works well with heavier compounds and is therefore often used in petroleomics.

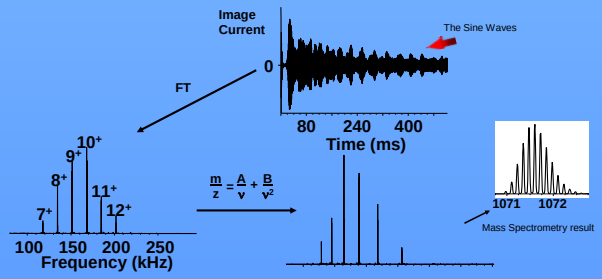


Stage 1
The sample is mixed with a solvent and introduced into a vessel, called a capillary, that ends in a very fine tip. A very high voltage is applied to this tip, which charges the molecules in the solvent. Because they are highly charged with the same charge, these molecules, once they are pushed through the nozzle into the Evaporation Chamber, repel one another almost violently. When the charged liquid first exits the tip, it briefly forms a cone shape (known as a Taylor cone) before the droplets burst away from each other into a fine spray.

Stage 2
Released from the nozzle, the droplets in the spray go through a series of divisions. This occurs because the solvent within these droplets gradually evaporates, forcing the charges in the molecules within these droplets (which, again, are identical) closer together. When these ions are pushed close enough together, they will repel each other, causing the droplets to divide into two smaller droplets. This process repeats itself until the solvent is completely evaporated and the droplets have split up to the point that each is a single, charged molecule. One of the advantages of this ionization method is that the molecules remain intact and will not be broken apart.

Into the Penning Trap and analyzed

After the molecules are ionized, they are funneled by an ion guide into the Penning trap, which is located in the center, or bore, of a superconducting magnet. This whole set-up, by the way, is connected to a vacuum pump system that keeps unwanted outside molecules from straying into the sample. This allows ions to spin in circles more than 100,000 times without colliding into another particle. Then the signal reader and computer will translate everything that happened in the cell into usable data.

How it Works

Fourier transform ion cyclotron resonance mass spectrometry is a type of mass spectrometer for determining the mass-to-charge ratio (m/z) of ions based on the cyclotron frequency of the ions in a fixed magnetic field. The ions are trapped in a Penning trap (a magnetic field with electric trapping plates) where they are excited to a larger cyclotron radius by an oscillating electric field. The resulting signal consists of a superposition of sine waves. The useful signal is extracted from this data by performing a Fourier transform to give a mass spectrum.