Complex Mixture Analysis & Environmental Petroleomics

Ion Cyclotron Resonance Facility
National High Magnetic Field Laboratory
Florida State University
National High Magnetic Field Laboratory

FT-ICR
Global Oil Reserves

- Heavy Oil: 15%
- Conventional Crude Oil: 30%
- Extra Heavy Oil: 25%
- Oil Sands Bitumen: 30%

http://www.eia.gov/
Shift in World Oil Production from Light to Heavy Crudes
Shift in World Oil Production from Light to Heavy Crudes
Pain at the PUMP...
“Petroleomics” : The Challenge

Prediction of Chemical and Physical Properties from Molecular Composition
We Measure the Mass of Molecules

~$10^6$ Molecules in a Single Crude!
We Measure the Mass of Molecules

~10^6 Molecules in a Single Crude!
Organic Sulfur Compounds in Crude Oil

Cyclic Sulfides

Thiophene

Benzothiophene

Dibenzothiophene

Naphthobenzothiophene

H — S — R
Thiols (Mercaptans)

R — S — R
Sulfides

R — S — S — R₁
Disulfides

CORROSIVE (33%)
Organic Sulfur Compounds in Crude Oil

- Cyclic Sulfides
- Thiophene
- Benzothiophene
- Dibenzothiophene
- Naphthobenzothiophene

Chemical structures:
- 
- 
- 
- 

H — S — R
Thiols (Mercaptans)

R — S — R
Sulfides

R — S — S — R₁
Disulfides

DIFFICULT TO REMOVE
(67%)
Organic Nitrogen Compounds in Crude Oil

"Acidic" (nonbasic)

Pyrrole
Indole
Carbazole
Benzo(a)carbazole

Basic

Pyridine
Quinoline
Benzo(f)quinoline
Indoline
Organic Nitrogen Compounds in Crude Oil

CATALYTIC FOULING

Acidic (nonbasic)
- Pyrrole
- Carbazole
- Benzo(a)carbazole

Basic
- Pyridine
- Quinoline
- Benzo(f)quinoline
- Indoline
Organic Nitrogen Compounds in Crude Oil

**Acidic** (nonbasic)

- Pyrrole
- Indole
- Carbazole

- Benzo(a)carbazole

**Basic**

- Pyridine
- Quinoline
- Benzo(f)quinolone
- Indoline

DIFFICULT TO UPGRADE → COKE
Several Classes of Weak Acids are Found in Petroleum

Benzoic acid
pKa 12.6
DBE = 5

Decanoic acid
pKa 12.6
DBE = 1

Thiophenol
pKa 10.3
DBE = 4

Naphthol
pKa 17.2
DBE = 7

Carbazole
pKa 19.9
DBE = 9

Cyclopentadiene
pKa 18.0
DBE = 3

Indene
pKa 20.1
DBE = 6

Fluorene
pKa 22.6
DBE = 9

Bordwell pKa Table (Acidity in DMSO)
Modified APS Mass Spectra

Traditional NAP Acid Isolation (APS)
~4,400 Peaks Assigned

(-)ESI 9.4T FT-ICR MS w/ NH₄OH
Modified APS Mass Spectra

Traditional NAP Acid Isolation (APS)
~4,400 Peaks Assigned

(70/30) MeOH:H₂O 5% FA
~1,200 Peaks Assigned

(-)ESI 9.4T FT-ICR MS w/ NH₄OH
Modified APS Mass Spectra

Traditional NAP Acid Isolation (APS)
~4,400 Peaks Assigned

(80/20) MeOH:H₂O 5% FA
~1,300 Peaks Assigned

(-)ESI 9.4T FT-ICR MS w/ NH₄OH
Modified APS Mass Spectra

Traditional NAP Acid Isolation (APS)
~4,400 Peaks Assigned

(90/10) MeOH:H₂O 5% FA
~1,900 Peaks Assigned

(-)ESI 9.4T FT-ICR MS w/ NH₄OH
Modified APS Mass Spectra

Traditional NAP Acid Isolation (APS)
~4,400 Peaks Assigned

MeOH 5% FA
~4,200 Peaks Assigned
Modified APS Mass Spectra

Traditional NAP Acid Isolation (APS)
~4,400 Peaks Assigned

(5/95) DCM:MeOH 5% FA
~7,000 Peaks Assigned

(-)ESI 9.4T FT-ICR MS w/ NH$_4$OH
Modified APS Mass Spectra

Traditional NAP Acid Isolation (APS)
~4,400 Peaks Assigned

(20/80) DCM:MeOH 5% FA
~5,500 Peaks Assigned

m/z

(-)ESI 9.4T FT-ICR MS w/ No Modifier
Modified APS Mass Spectra

Traditional NAP Acid Isolation (APS)
~4,400 Peaks Assigned

~13,500 Unique Assignments for fractions 1-6

200% > Traditional Characterization

(-)ESI 9.4T FT-ICR MS w/ No Modifier
APS vs MAPS Fractionation

MAPS: $O_2$ Class

MAPS: $O_2S_1$ Class

MAPS: $O_2S_2$ Class

Double Bond Equivalents vs Carbon Number

Relative Abundance (% Total)
Eagle Ford Shale Play
Western Gulf Basin
South Texas

The Economics

- Largest oil & gas development in the world ($30 billion in 2013)

- $60 billion impact on S. Texas economy in 2012 (116,000 jobs)
Eagle Ford Shale Play

Geology

6000 ft
Oil

Wet gas/condensate

14,000 ft
Gas

The HC’s

Light, high quality fluids
Stabilized (topped)
What is the composition of Eagle Ford Shale Oil?
May 2010

Deepwater Horizon
Macondo Well Blowout

How does it compare to Macondo Well Oil?

~4.8 - 5 million barrels released over 87 days
Petroleum Requires Ultrahigh Resolution Mass Spectrometry

Planar PAH Stability Limit

FT-ICR MS
No volatility limitation

GC-FID of Macondo Well Oil

Light, sweet crude
High % light distillates
Low asphaltene content

Aeppli et al., ES&T, 46.16 (2012)
Light, sweet crude
High % light distillates
Paraffinic
Low asphaltene content
Deepwater Horizon
24,598 peaks > 6σ

Eagle Ford Shale Oil
44,539 peaks > 6σ
Positive-Ion APPI FT-ICR MS
Unstabilized Whole Shale Oil Eagle Ford

44,539 peaks > 6σ
12 peaks $> 6\sigma$
60 mDa

3.4 mDa

$\text{C}_3 / \text{SH}_4$

$[\text{C}_{32}\text{H}_{36}\text{N}_4\overset{58}{\text{Ni}}]^+\quad m/z\ 534.22845$
-200 ppb
DBE 17

$[\text{C}_{42}\text{H}_{30}]^+\quad m/z\ 534.23394$
-400 ppb

$[\text{C}_{39}\text{H}_{34}\text{S}_1]^+\quad m/z\ 534.23394$
-500 ppb

$m/\Delta m_{50\%} = 1,100,000$
What are Petroporphyrins?

• Metal containing compounds
• First compounds to link petroleum to its biologic origin (1930s)
• Concentrate in heavy oil
• Two main types: Ni, VO

Maturity Index
More mature crudes:

↑ DPEP
↓ Ni/VO
Structures of Petroporphyrins

Chlorophyll a → Deoxophyllerythropho-etioporphyrin
Heme → Etioporphyrin

http://www.ch.ic.ac.uk
Structures of Petroporphyrins

Etio
\[
\text{C}_{36}\text{H}_{44}\text{N}_{4}\text{O}_{1}\text{V}_{1} \\
599.29480 \text{ Da}
\]

DPEP
\[
\text{C}_{36}\text{H}_{42}\text{N}_{4}\text{O}_{1}\text{V}_{1} \\
597.27923 \text{ Da}
\]

Rhodo - Etio
\[
\text{C}_{36}\text{H}_{38}\text{N}_{4}\text{O}_{1}\text{V}_{1} \\
593.24796 \text{ Da}
\]

Di - DPEP
\[
\text{C}_{36}\text{H}_{40}\text{N}_{4}\text{O}_{1}\text{V}_{1} \\
595.26362 \text{ Da}
\]
Heavy Oil Deposit = Enriched in Vanadyl Porphyrins

DPEP Vanadyl Porphyrins

N N N N O

VO

m/z

300 400 500 600 700
Petroporphyrin Characterization in Whole Asphaltenes

$\text{C}_3\text{S}_2 \text{ vs } \text{N}_3^{58}\text{Ni}$ → $\rightarrow$ 570 $\mu$Da

Mass e$^-$ 548 $\mu$Da

$[\text{C}_{27}\text{H}_{24}\text{N}_4^{58}\text{Ni}]^{++}$
Positive-ion Electrospray FT-ICR MS at 9.4 Tesla

Il Duomo
Whole Sample

21,972 peaks > 6σ

Vanadyl Fraction

14.01565 Da

DPEP
Vanadyl Porphyrins

15,479 peaks > 6σ
Nickel Porphyrin Structural Distribution *Il Duomo*

![Graph showing the distribution of nickel porphyrins with carbon number and DBE axes, indicating relative abundance (% total).]
Sulfur-Containing Vanadyl Porphyrins

Relative Abundance (% total)

Carbon Number
Viscosity-Density Relationship

- **Light Crude Oil**
  - Viscosity, cP: 10 - 100
  - Density, kg/m³: 884
  - Gravity, API°: 35

- **Heavy Crude Oil**
  - Viscosity, cP: 100 - 10,000
  - Density, kg/m³: 934 - 1000
  - Gravity, API°: 20 - 10

- **Bitumen**
  - Viscosity, cP: 10,000 - 1,000,000
  - Density, kg/m³: 966 - 1000
  - Gravity, API°: 15 - 10

Deepwater Horizon Crude Oil

- **“Sweet”**
- **“Sour”**
“Petroleomics” : The Challenge

Land $0.5 MM
SubSea $3 MM
“Petroleomics” : The Challenge

Lost Production $1.2 MM/Day
Refinery: “Asphaltenes”

Environment: “Tar Balls”
Deepwater Horizon Blowout April 2010

~ 5 million barrels of Light, Sweet Crude Released into the Gulf of Mexico over 87 days
“Who are the toughest kids on the block?”
Establish “Molecular Fingerprint” of the Released Oil

Deepwater Horizon Crude

$\text{N}_1 \quad \text{HC}^{13}\text{C}$

$\text{HC}^{13}\text{C}$

$\text{O}_1$

$\text{N}_1$

$\text{HC}$

$m/z$

300 400 500 600 700 800 900

m/z
Right Tool for the Job

Measure the Mass of Molecules
Why FT-ICR Mass Spectrometry for Crude Oil?

- Ultrahigh Mass Accuracy (10-200 ppb)
- Ultrahigh Mass Resolving Power
Theoretical Mass Resolving Power

\[
\frac{m}{\Delta m_{50\%}} = 1.274 \times 10^7 \frac{z B_0}{m} T_{acq'n}
\]

- 9.4 T 6s
- 14.5 T 6s

1.1 mDa
(SH\textsubscript{3}\textsuperscript{13}C\textsubscript{1} vs C\textsubscript{4})

3.4 mDa
(SH\textsubscript{4} vs C\textsubscript{3})
NHMFL Instrumentation Development

Quadrupole Mass Filter

External Accumulation
Efficient Ion Ejection

Ionization

Transfer Octopole

Open ICR Cell
Absorption Mode Spectra

Simultaneous ECD/IRMPD

Ionization

760 2 3×10⁻³ 5×10⁻⁶ 2×10⁻⁸ 8×10⁻¹⁰ 3×10⁻¹⁰ Torr
Once the ion is trapped, the magnet bends it into a circular path. We measure cyclotron frequency:

\[ \omega = \frac{qB}{m} \]

So we can calculate the mass of the ion. We know the magnetic field.

“Light” Ions have a High frequency

“Heavy” Ions have a Low frequency
Resolving Power

Next Highest Resolution Mass Spectrometer

High B-Field FT-ICR MS
Petroleum Requires High Magnetic Field FT-ICR MS
Molecular “Fingerprint”
Petroleum Demands the Best Performance of FT-ICR MS

**BUT....**

*only if all ion packets maintain coherence throughout the entire detection period*
Petroleum Demands the Best Performance of FT-ICR MS

Electric & Magnetic Field Inhomogeneities
Ion-Neutral Collisions
Ion Cloud Interactions
Most Complex Mixture Resolved and Identified

25 peaks at a single nominal mass

\[ m_2 - m_1 = 3.4 \text{ mDa} \]

11,127 peaks >3\( \sigma \) baseline rms noise

55 Elemental Compositions at a Single Nominal Mass

$m/\Delta m_{50\%} = 350,000$

World Record 2013 Most Complex Mixture Resolved and Identified in a Single Mass Spectrum

85,920 peaks > 6σ

2013
World Record 2013 Most Complex Mixture Resolved and Identified in a Single Mass Spectrum

171 peaks > 6σ (400 mDa)

85,920 peaks > 6σ

2013
Exact Mass = 39 Da

\[ C_1 N_1 ^{13} C_1 \text{ vs } H_5 ^{34} S_1 \]

\[ \Delta m = 530 \, \mu\text{Da} \]

\[ [C_{34}H_{35}N_1S_2^{13}C]^+ \quad \text{+80 ppb S/N 46} \]

\[ [C_{33}H_{40}S_2^{34}S]^+ \quad \text{+50 ppb S/N 51} \]

Mass e$^-\ 548 \, \mu\text{Da}
Macondo Well Petroleum
APPI FT-ICR MS at 9.4 Tesla

~ 28,000 mass spectral peaks > 6σ
RMS error 122 ppb
Assigned Mass Spectral Peaks In a Single Mass Spectrum

Deepwater Horizon Blowout 2010
Assigned Mass Spectral Peaks In a Single Mass Spectrum

Weathered Oil

Refinery Residue 593° C
Assigned Mass Spectral Peaks In a Single Mass Spectrum

- Weathered Oil
- Refinery Residue 593+ °C
- McKenna Joined NHMFL
Assigned Mass Spectral Peaks In a Single Mass Spectrum

# Assigned Mass Spectral Peaks ($10^4$)

Weathered Oil

Refinery Residue $593^\circ C$

McKenna Joined NHMFL
Enhanced Complexity

Nondistillable Fraction

Average 244 peaks across 450 mDa

\[ \frac{m}{\Delta m_{50\%}} > 1,300,000 \]

S/N 50

450 mDa

450 mDa
Compositional Diversity :

Mother Nature vs. Big Oil
Middle Eastern Heavy Crude Residue from Vacuum Distillation (593+ °C)

30,727 peaks $> 6\sigma$

Tar Ball from *Deepwater Horizon*
04-05-11 Gulf Shores, AL

60,597 peaks $> 6\sigma$

~80 peaks per 1 Da window
$m/\Delta m_{50\%} = 600,000$ at m/z 649
Mother Nature is the Best Organic Chemist

http://www.incidentnews.gov
Elemental Analysis of Deepwater Horizon Crude

**Axes:**
- Y-axis: % Relative Abundance
- X-axis: Elements (C, H, N, S, O)

**Graph Details:**
- Two categories: Whole Crude and Tarball
- C: Whole Crude is significantly higher than Tarball.
- H: Both categories have similar values.
- N, S, O: Low abundance, with variations in Whole Crude and Tarball.
Weathered Oil Requires FT-ICR MS

Wellhead  surface slick  sand patty  rock scraping

Pensacola Beach, Florida

Professor Markus Huettel
Department of Oceanography
Florida State University

30°19'32.08"N
87°10'30.55"W
Intertidal Zone
Deepwater Horizon
Pre-Spill Crude

28,721 Peaks > 6σ
Deepwater Horizon
Wellhead Crude

28,721 Peaks > 6σ

Gulf Shores, AL
11/28/11

60,072 Peaks > 6σ
Deepwater Horizon Crude Oil
~17 peaks

C$_3$/SH$_4$ $\rightarrow$ $\leftarrow$ 3.4 mDa

549.2  549.3  549.4  549.5
m/z

$N_1^{13}C_1$
HC

$S_2$

$O_1$

$N_1^{13}C_1$
HC

$O_1$

$N_1^{13}C_1$
HC
Mother Nature is the Best Organic Chemist

Deepwater Horizon Crude Oil
~17 peaks > 6σ

Tar Ball
Cocodrie, LA May 2010
~40 peaks > 6σ
Weathered Petroleum Requires *Even Higher* Magnetic Field
FT-ICR MS

21 Tesla
Advantages of High Magnetic Field

Mass Resolving Power
Acquisition Speed

B (tesla)

0 25

9.4 T 12 T 14.5 T 21 T

Mass Accuracy
Dynamic Range
Kinetic Energy
Peak (Non)Coalescence

B (tesla)

0 25

7 T 9.4 T 12 T 14.5 T 21 T

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