Quantification of Naphthenic Acids in Water Samples: Challenges from complex matrix?

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Oil Sands - Alberta

Comparative Oil Reserves (billions of barrels)
Source: Oil & Gas Journal, 2011

- Alberta: 171 barrels
- Iraq: 115 barrels
- Iran: 137 barrels
- Venezuela: 211 barrels
- Russia: 60 barrels
- USA: 19 barrels
- Mexico: 10 barrels
- Libya: 46 barrels
- Saudi Arabia: 260 barrels

Edmonton, Calgary, Peace River Oil Sands Area, Cold Lake Oil Sands Area, Athabasca Oil Sands Area, U.S.A., Canada.
Oil Sands – Water Use

Water Consumed

• 2 to 4 Barrels of Water for each Barrel of Oil

Tailing Ponds

• Cover 170 Km² (2011)
Oil Sands Affected Water (OSPW) – Toxicity

It is known that the dissolved organics are the toxic fraction.

Historical belief that naphthenic acids are the source (or main source) of toxicity

**Unspecific mixture** of several carboxylic acids with molecular weight of 120 to well over 700 Da obtained by naphtha fraction of crude oil.
Naphthenic acids – \((C_{n}H_{2n+z}O_{2})\)
Naphthenic acids Analysis

- Spectrophotometry
- FTIR (Jivraj, Rogers et al.)
- GC/MS (Fedorak et al.)
- ESI/MS (Headley et al.)
Application of HRMS to OSPW

1. **NO EXTRACTION**
   
   (100 µL injection after centrifugation)

2. **HPLC C$_{18}$ column**

3. **ESI (negative mode)**

4. **MDL 0.03 mg/L**

**AITF Ultra High Resolution Method**
Why Ultra High Resolution?

Resolving Power and Mass Accuracy (sub 2 ppm)

- RP = 1700
- RP = 48,000

http://fiehnlab.ucdavis.edu

RP = 100  1,000  10,000  100,000  1,000,000

- GC-MS
- ESI-MS

Quadrupole
- TOF
- Orbitrap
- FTICR

H₄S = 36.0034
C₃ = 36.0000
Orbitrap Mass Spectrometer

Main Feature:
Ultra High-resolution (> 100,000)

http://planetorbitrap.com/
Why Chromatography?

1. Reduce *matrix effect*
   - Nyakis et al. (ES&T 2013 p4471)
     - direct infusion FTICR-MS to analyze OSPW AEOs
     - 973 peaks by analysis of whole extract
     - 2231 peaks when pre-fractionated into 8 subsamples by UPLC
   - Headley et al. (Anal. Chem. 2007 p6222)
     - Same extract in different solvents gives different results

2. Cleaner MS/MS
The Challenge: OSPW is super complex!

Around 20% of the extractable organic compounds are the classical NAs (BML Sample).
Complex Samples – GC/MS Results

One liter sample

Extracted with DCM

Concentrate to 1 mL

GC-MS Results:  > 1000 mg/L
GC vs Orbitrap Results for Complex Samples

Merichem oil
at 5 mg/L

Water sample

GC-MS: 1095 mg/L
Orbitrap: 21 mg/L
GC vs Orbitrap

Sample
GC vs Orbitrap

Merichem 5 mg/L

Sample
Advantage of the Ultra High Resolution

Sample 15030016042

m/z 195.1381 ± 0.0007

C_{12}H_{19}O_{2}

Sample 15030108013

Merichem oil 5mg/L

NL: 5.14E5
m/z = 195.13754-195.13884
MS 180320152
4

NL: 3.52E4
m/z = 195.13797-195.13939
MS 180320151
2

NL: 4.13E5
m/z = 195.13785-195.14008
MS 180320150
7
The other “Stuff”?

Too much data: > 2000 signals by sample
Proposed solution for processing the other “stuff”

SIEVE differential expression software makes it easy to define and automate experiments for both control-versus-treatment and trend analyses.
Principal Component Analysis
Automatic deconvolution of the data

Relative Response (%) Sample A

Sample B

Sample C

Sample D
Conclusions

The Ultra High Resolution Method Offer:

- Green (no use of DCM), sensitive, reproducible method for the quantification of Naphthenic acids in complex matrixes.

- Comprehensive non-targeted analysis for the “other compounds” present in the sample.

- Powerful analytical tool for “world class” environmental monitoring programs.
Thank you

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