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

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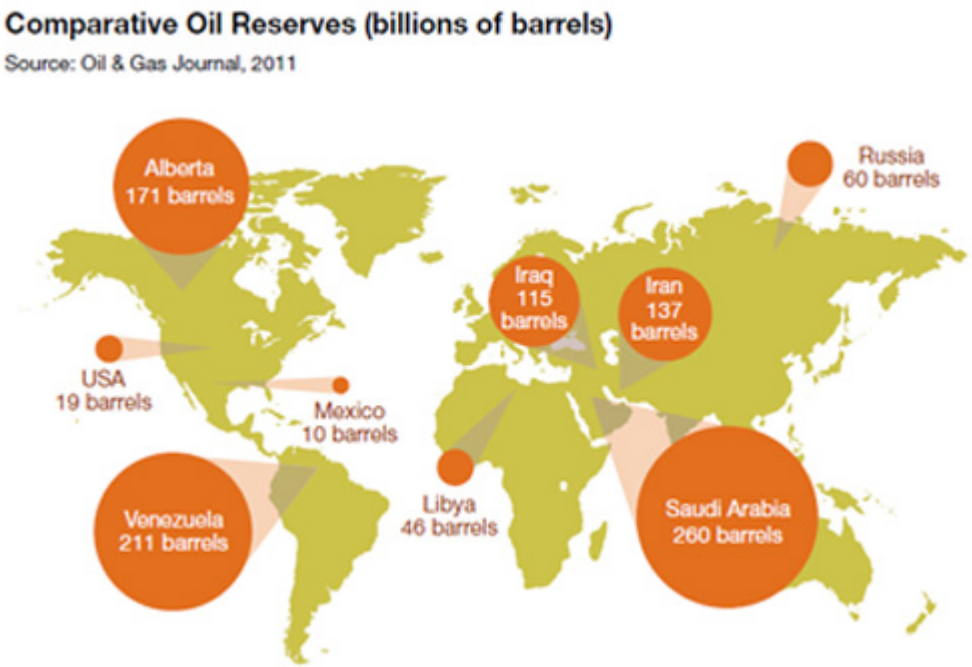
Edmonton, May 26, 2015

Oil Sands - Alberta



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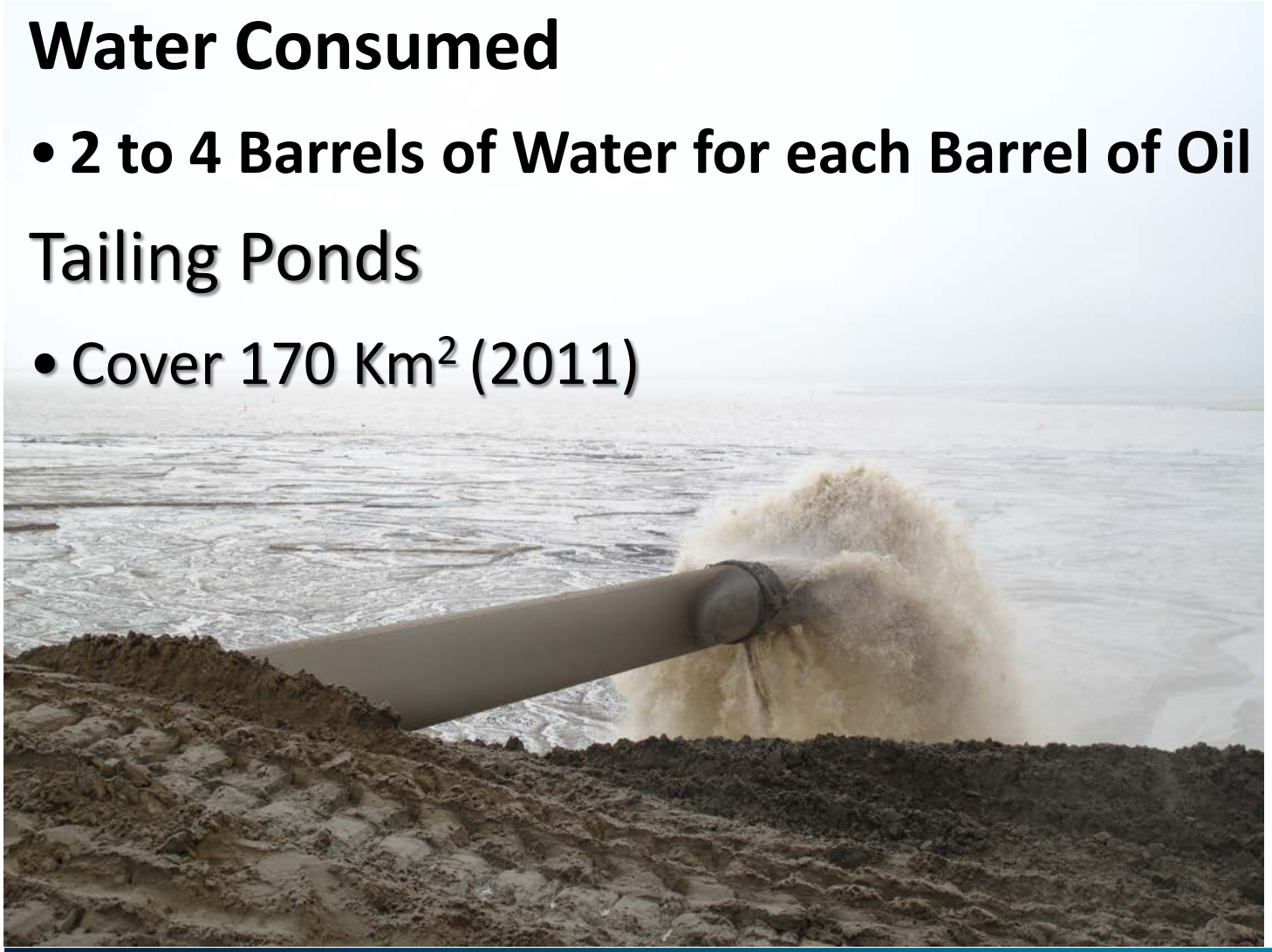
Oil Sands – Water Use

Water Consumed

- **2 to 4 Barrels of Water for each Barrel of Oil**

Tailing Ponds

- Cover 170 Km^2 (2011)



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Oil Sands Affected Water (OSPW) – Toxicity

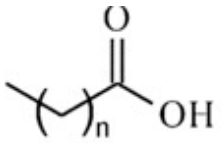
It is known that the dissolved organics are the toxic fraction.

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

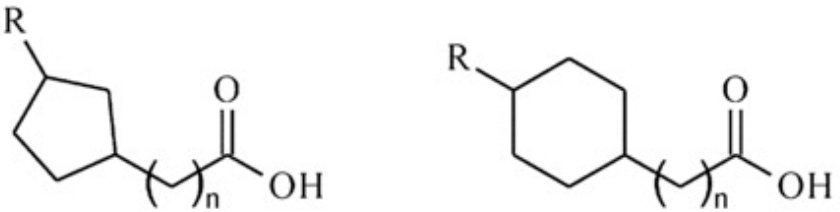
Unspecific mixture of several carboxylic acids with molecular weight of 120 to well over 700 Da obtained by naphtha fraction of crude oil.

Naphthenic acids – ($C_nH_{2n+Z}O_2$)

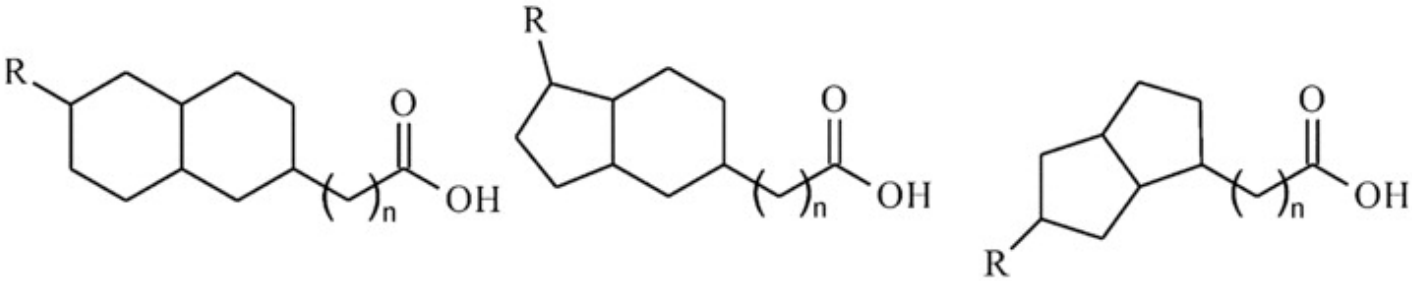
Z = 0



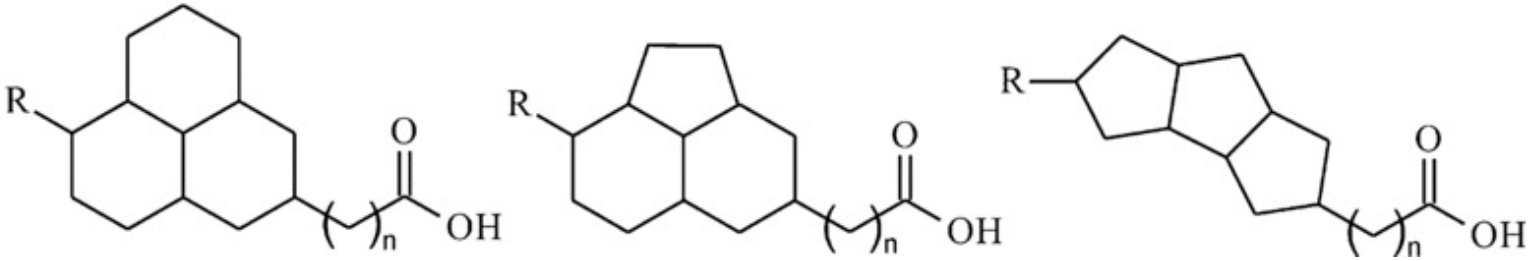
Z = -2



Z = -4



Z = -6

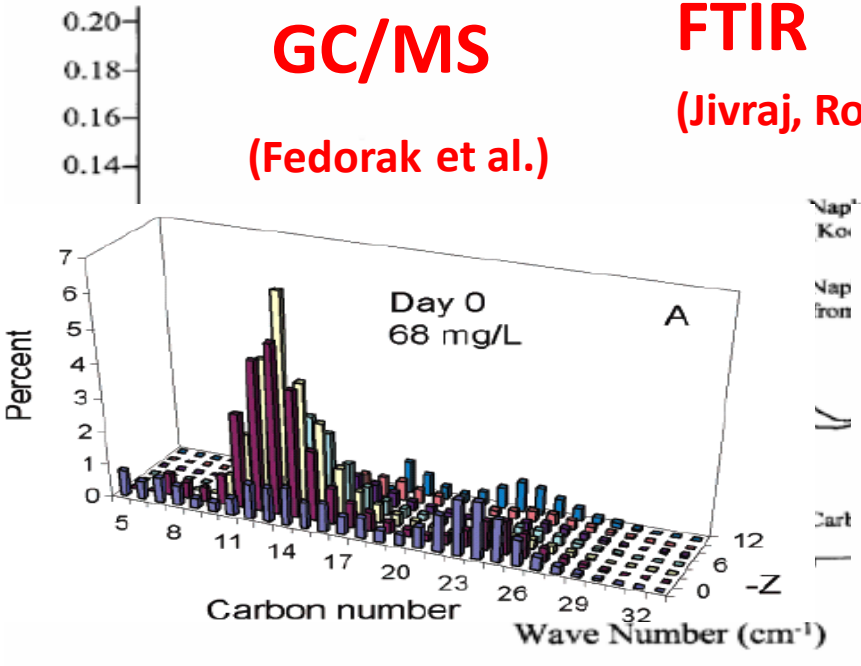


Naphthenic acids Analysis

Low Resolution Mass Spectrometry

GC/MS

(Fedorak et al.)

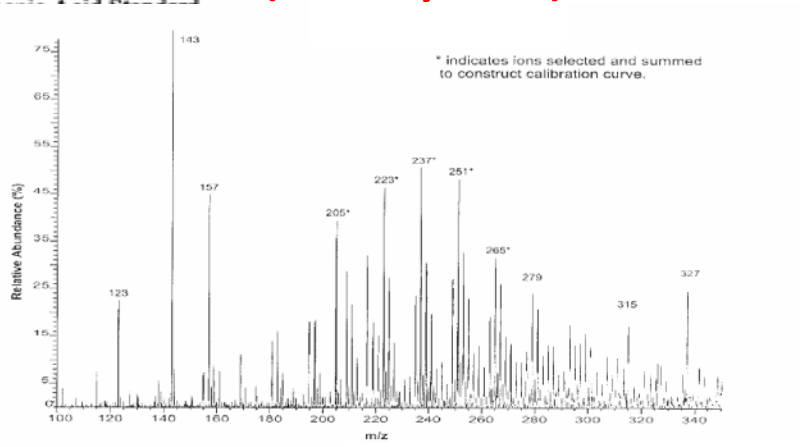


FTIR

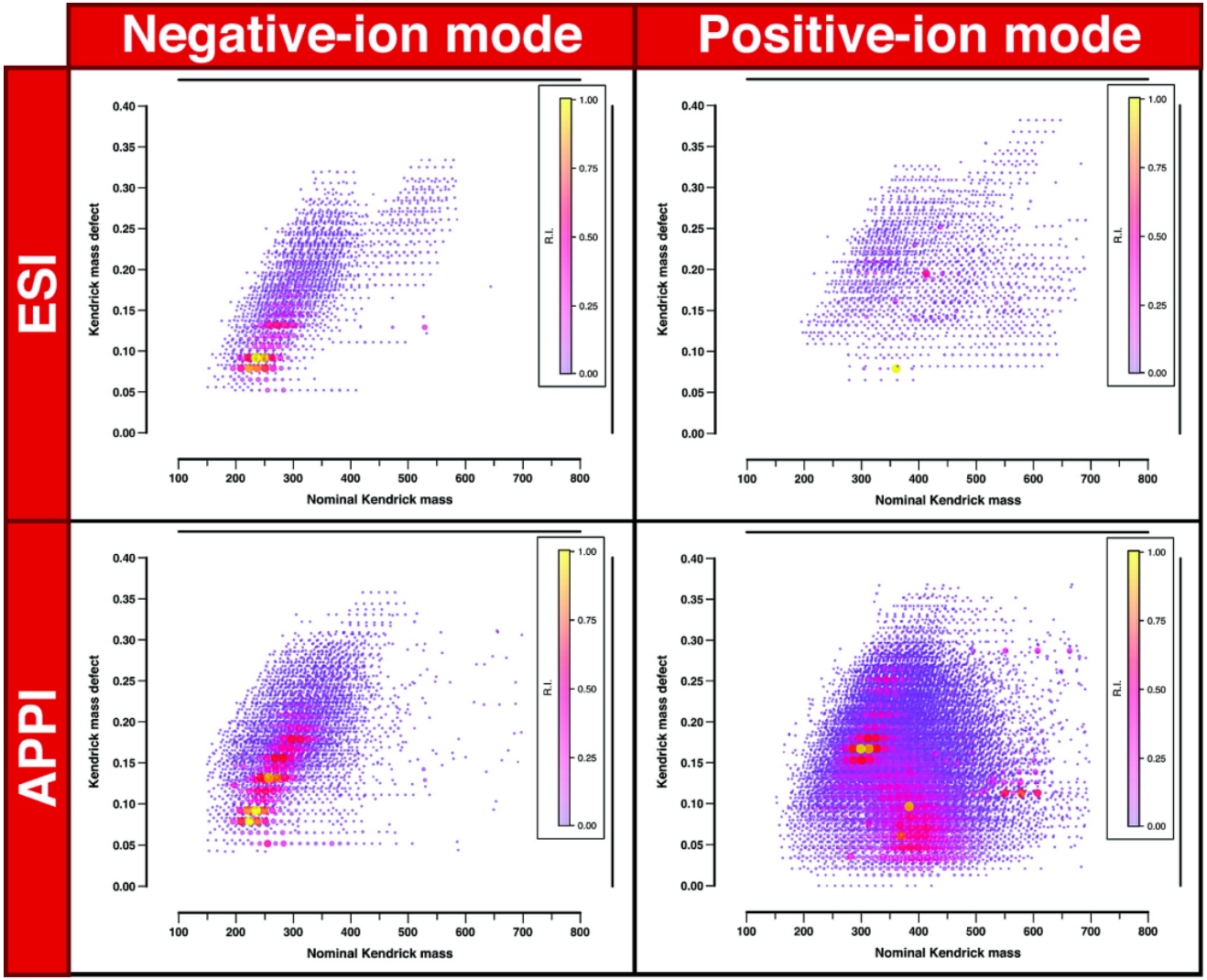
(Jivraj, Rogers et al.)

ESI/MS

(Headley et al.)



Application of HRMS to OSPW



Barrow, M.P., *et al.*, (2010) *Analytical Chemistry*, 82 (9), 3727-3735.

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AITF Ultra High Resolution Method

1. **NO EXTRACTION**

   (100 µL injection after centrifugation)

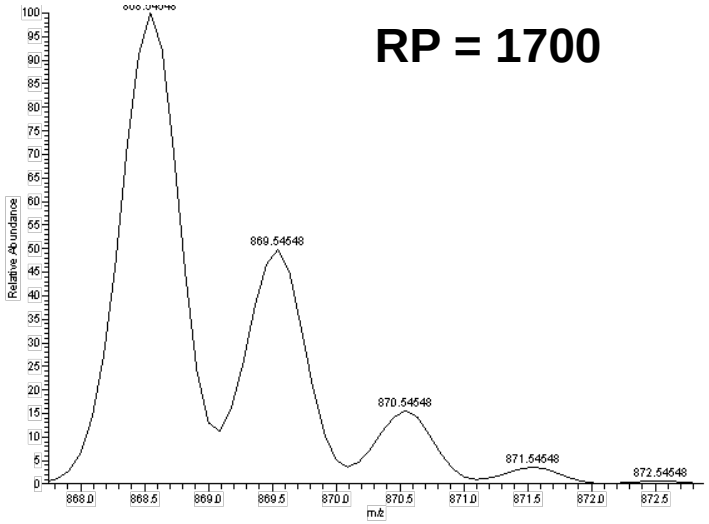
2. **HPLC C_{18} column**

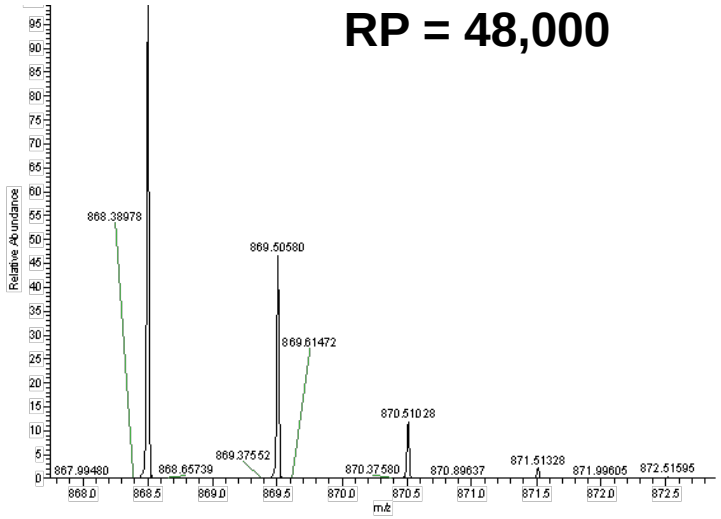
3. **ESI (negative mode)**

4. **MDL 0.03 mg/L**

Why Ultra High Resolution?

Resolving Power and Mass Accuracy (sub 2 ppm)





http://fiehnlab.ucdavis.edu

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

Quadrupole
- **GC-MS**
- **ESI-MS**

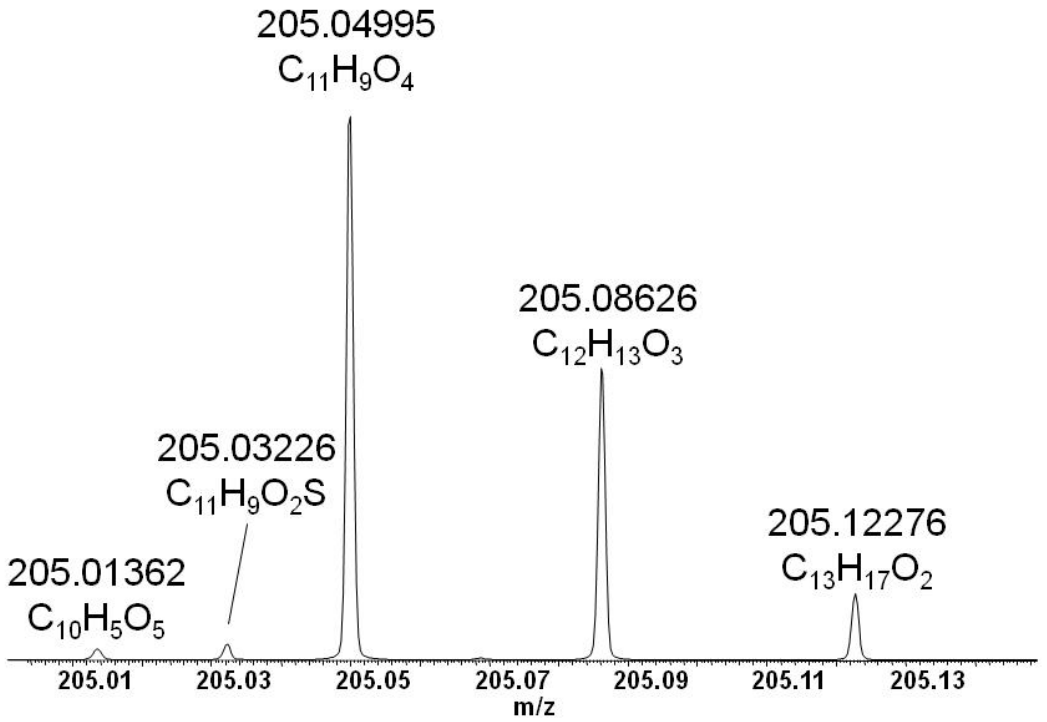
TOF

Orbitrap

H_4S = 36.0034
C_3 = 36.0000

FTICR

Orbitrap Mass Spectrometer



Main Feature:
Ultra High-resolution (> 100.000)

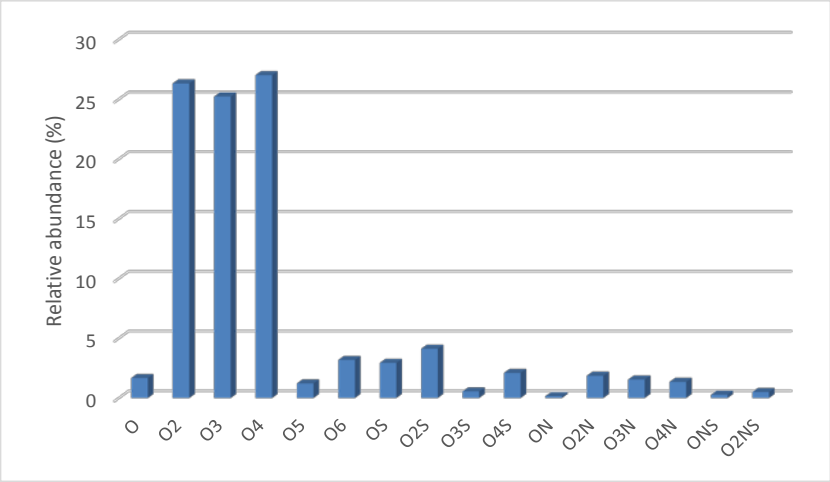
http://planetorbitrap.com/

Why Chromatography?

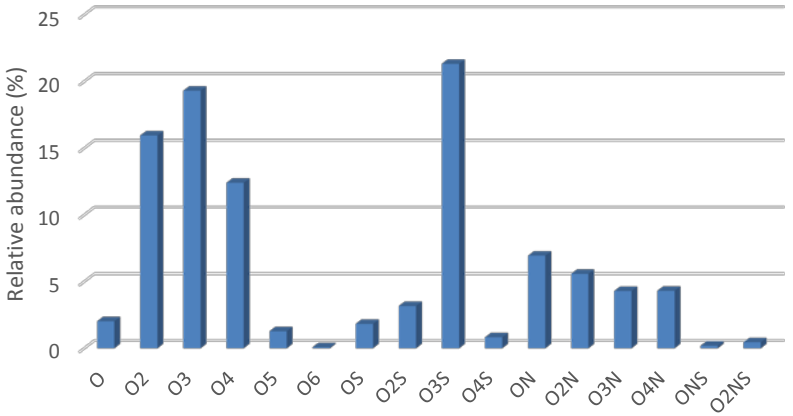
1. **Reduce *matrix effect***
   - Nyakis et al. (ES&T 2013 p4471)
     - direct infusion FTICR-MS to analyze OSPW AEOs
     - **973** peaks by analysis of whole extract
     - **2231** peaks when pre-fractionated into 8 subsamples by UPLC
   - Headley et al. (Anal. Chem. 2007 p6222)
     - Same extract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

The Challenge: OSPW is super complex!

NEGATIVE ESI

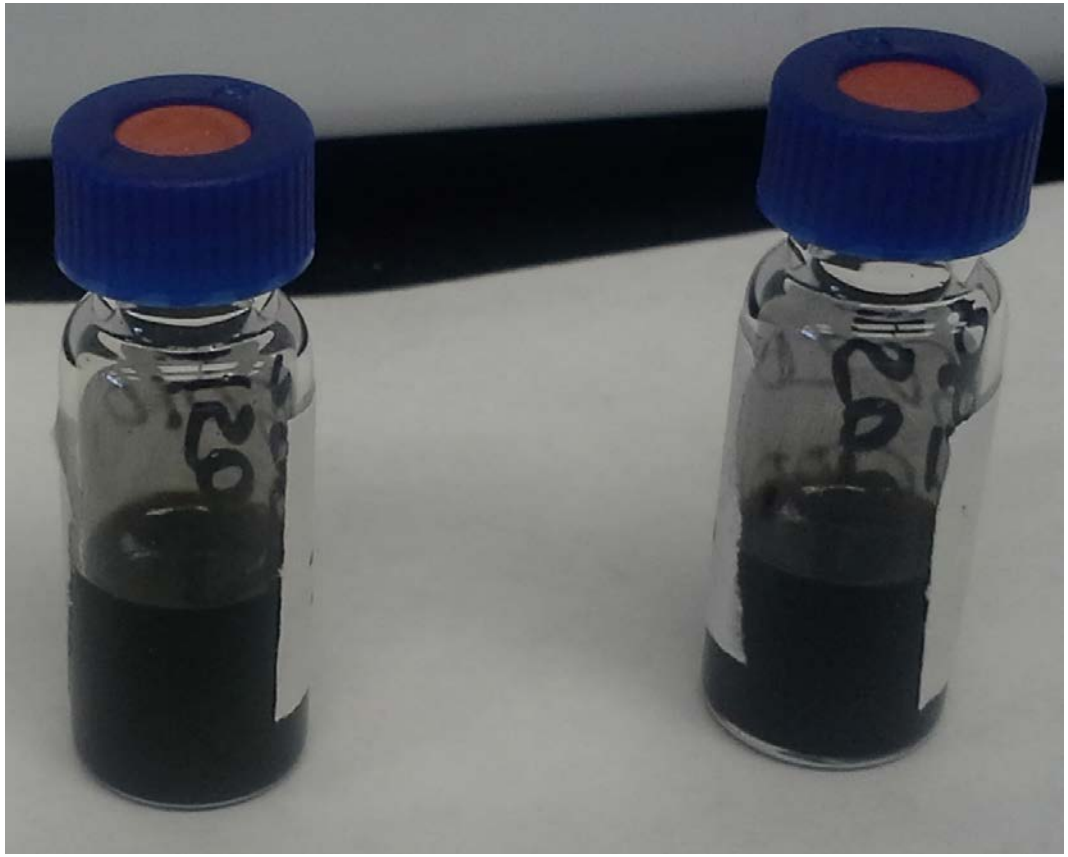


POSITIVE ESI



Around 20% of the extractable organic compounds are the classical NAs (BML Sample).

Complex Samples – GC/MS Results



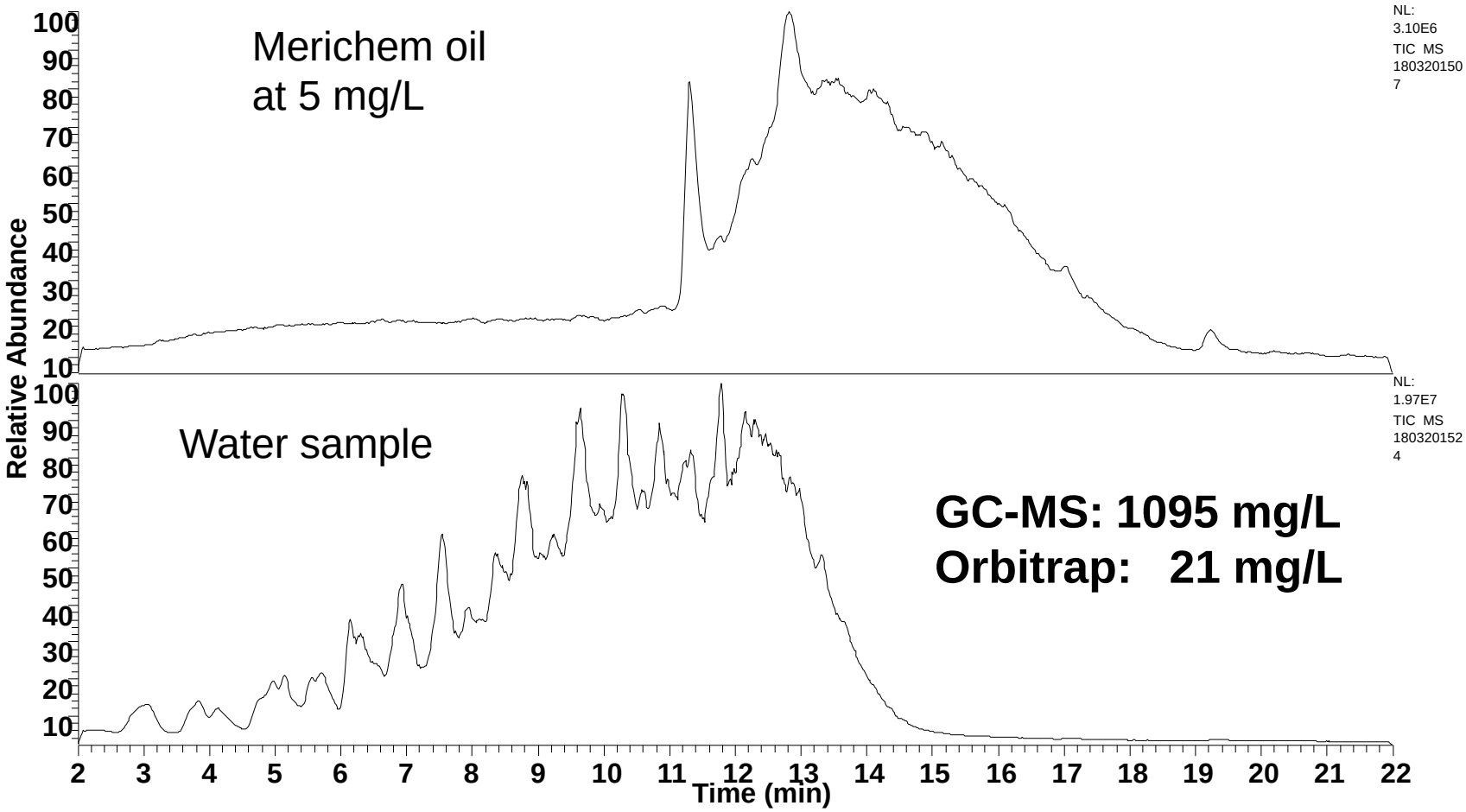
One liter sample

Extracted with DCM

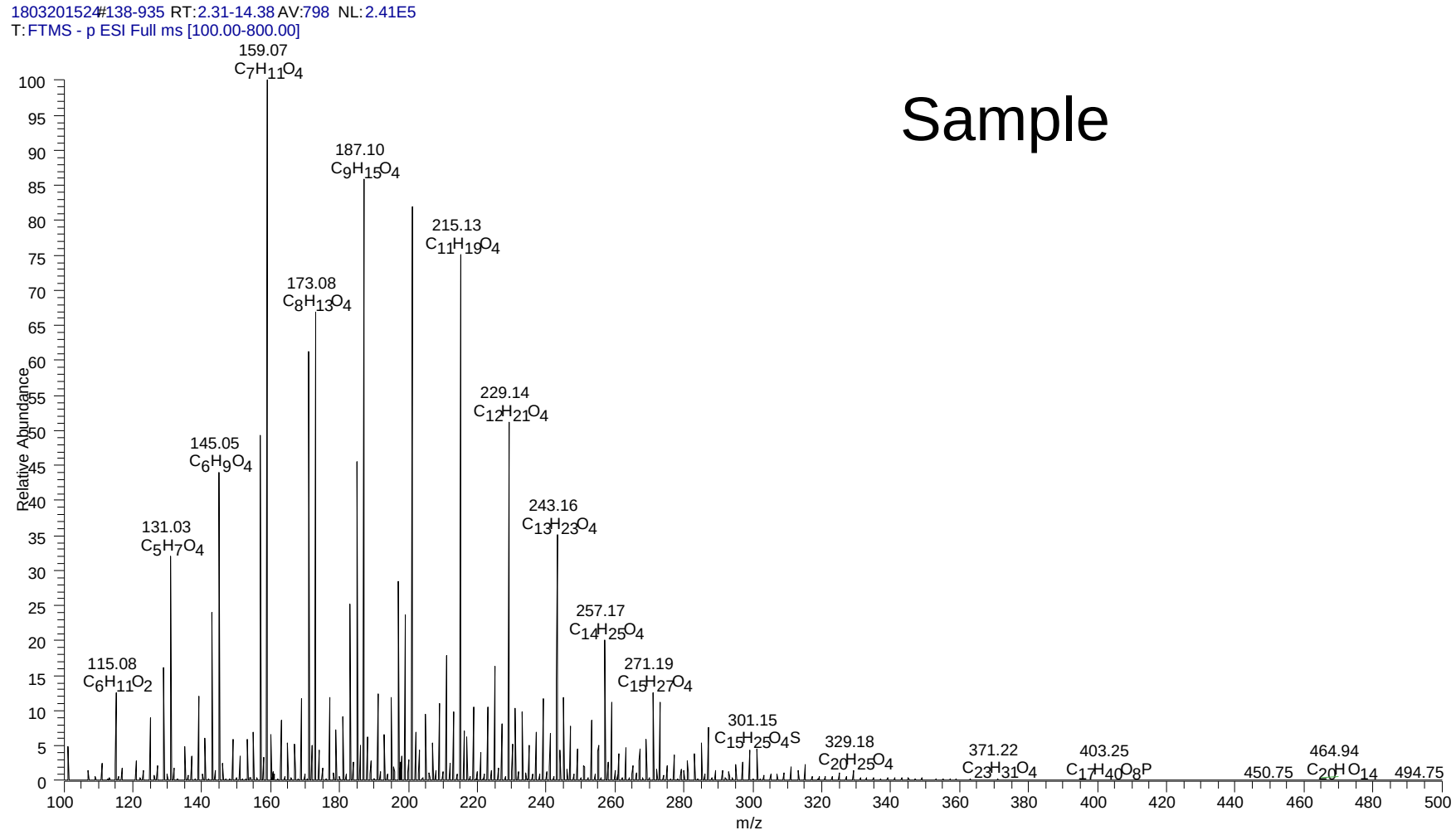
Concentrate to 1 mL

GC-MS Results: > 1000 mg/L

GC vs Orbitrap Results for Complex Samples

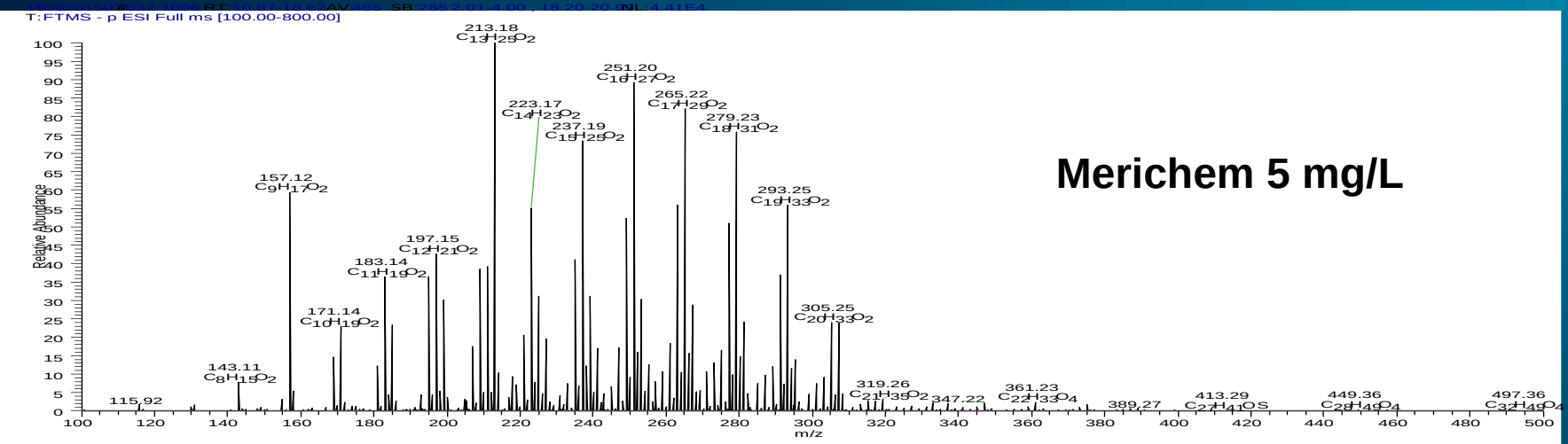


GC vs Orbitrap

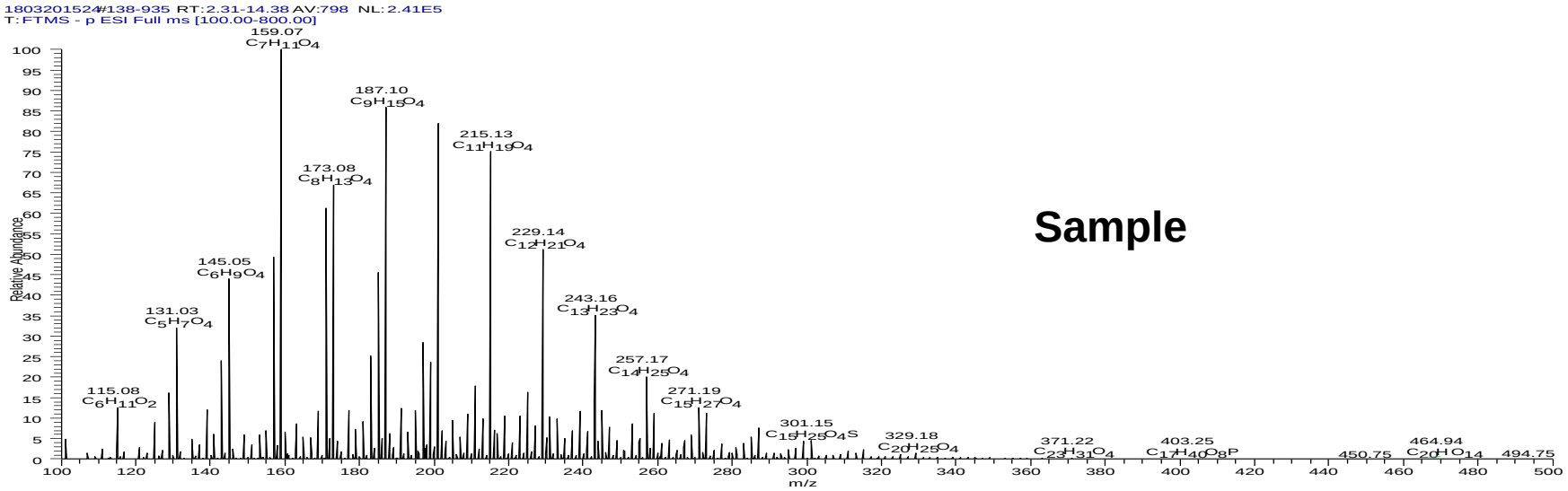


Sample

GC vs Orbitrap

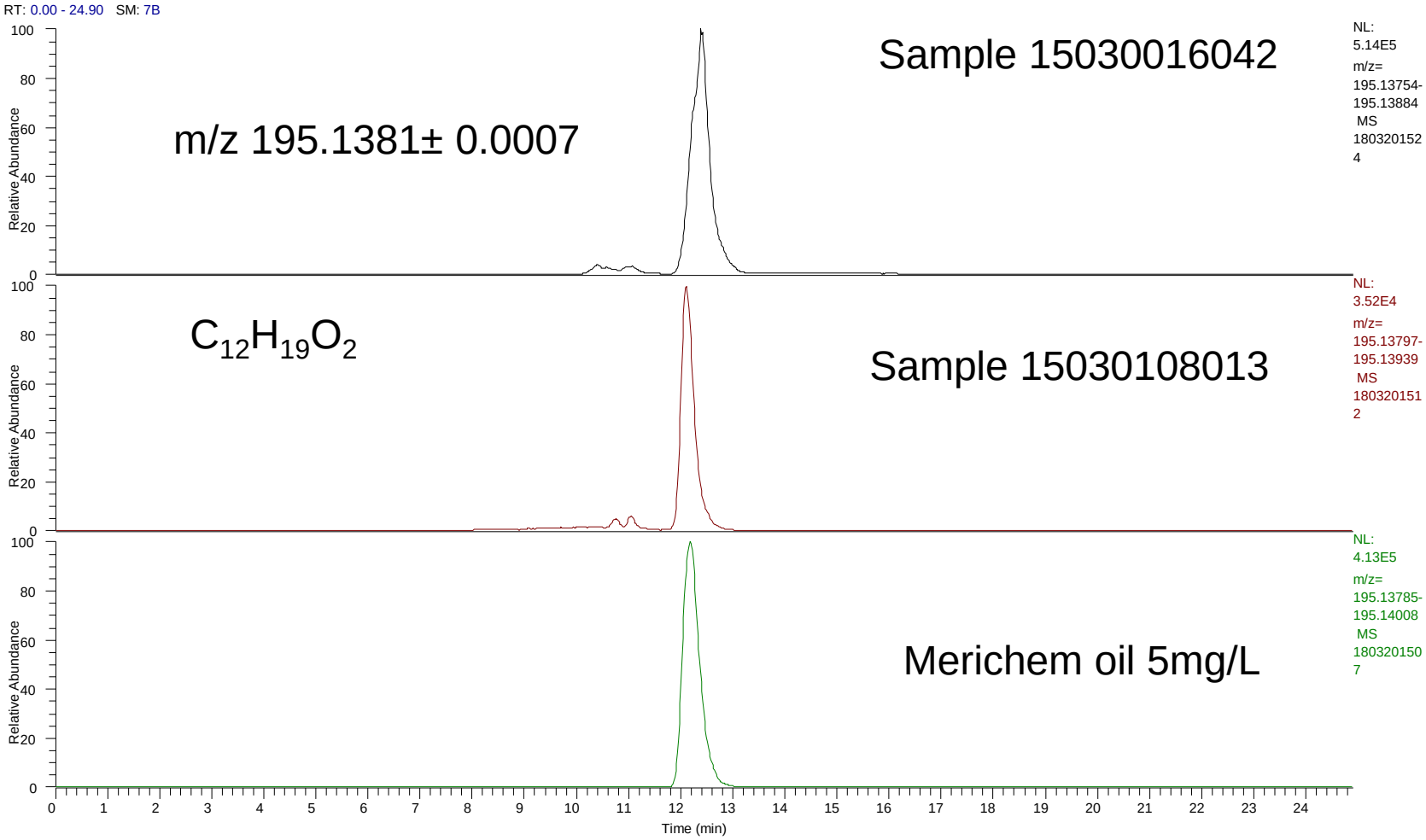


Merichem 5 mg/L

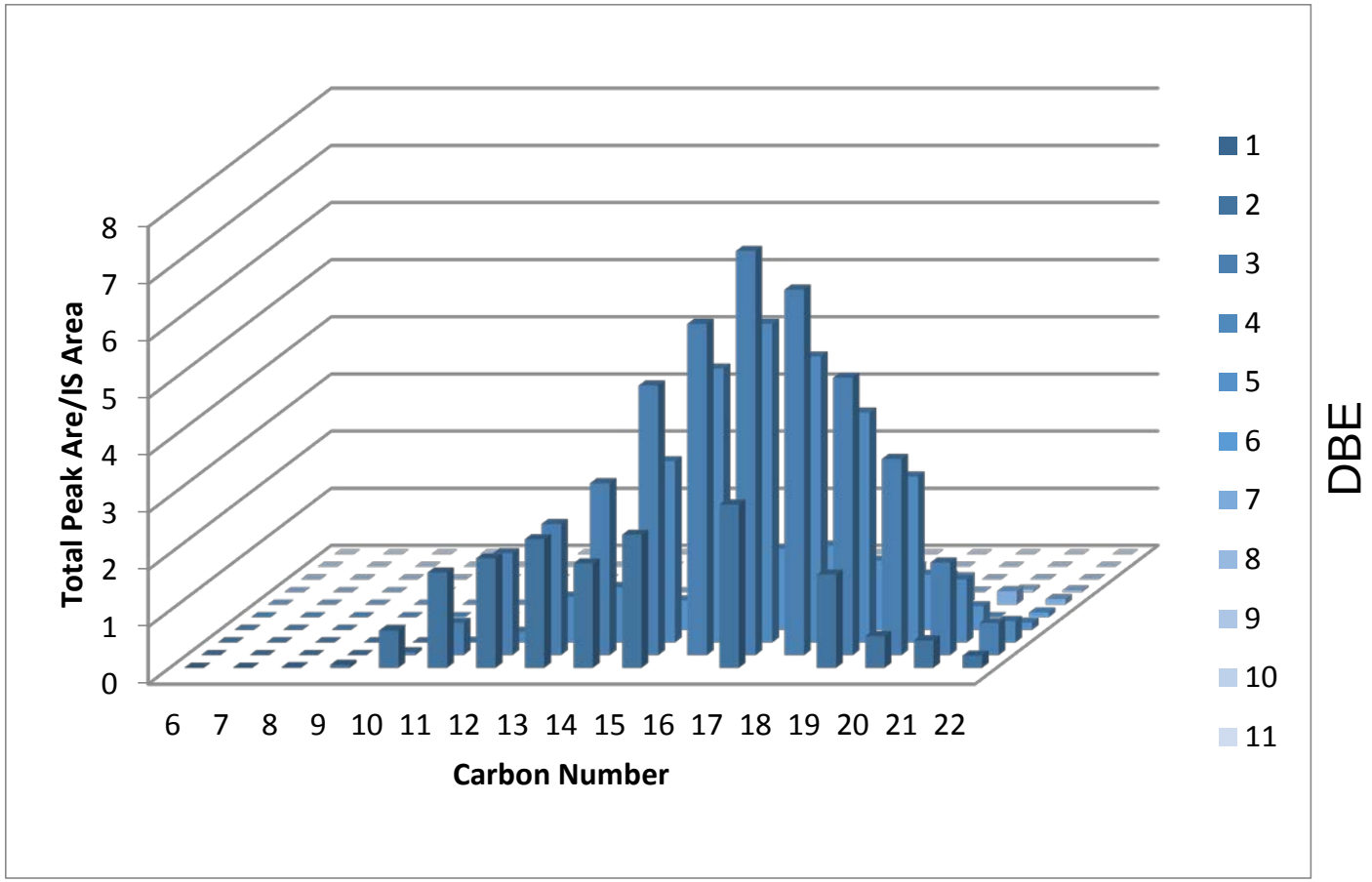


Sample

Advantage of the Ultra High Resolution



Naphthenic acid Speciation



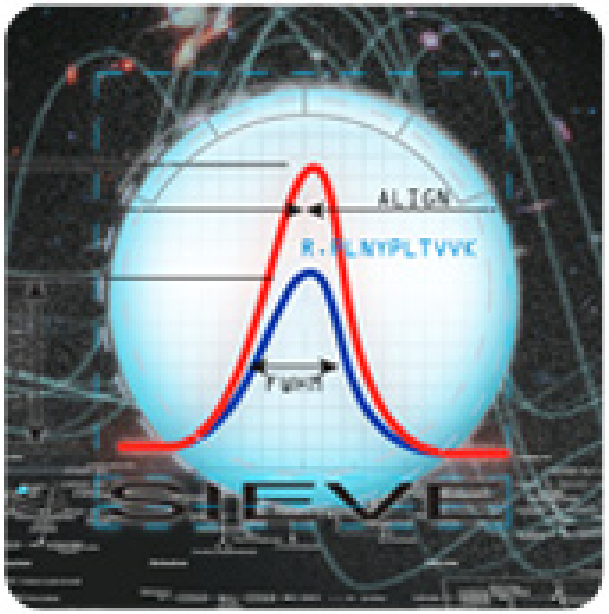
The other “Stuff”?

Too much data: > 2000 signals by sample

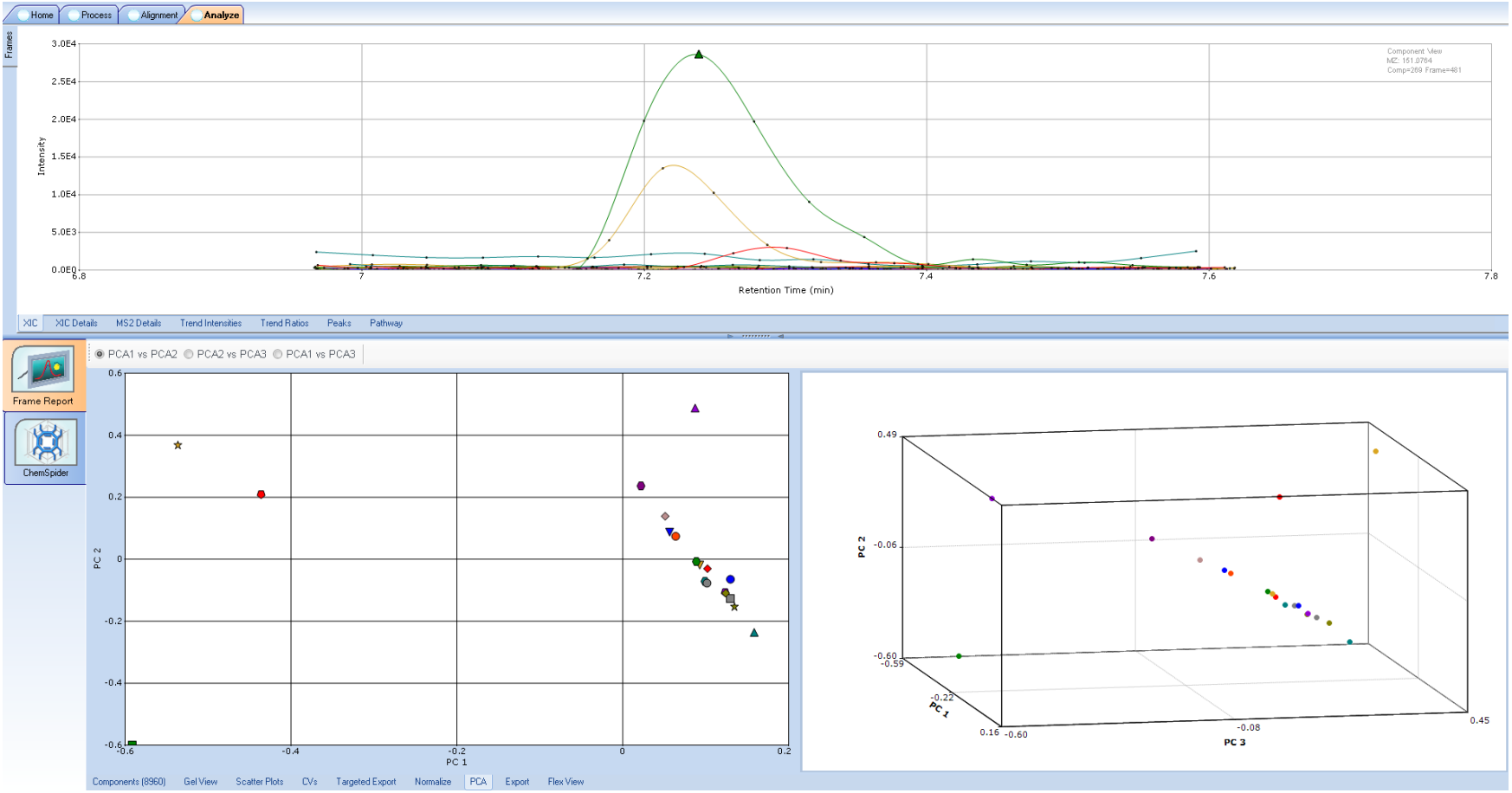
Proposed solution for processing the other “stuff”

SIEVE differential expression software

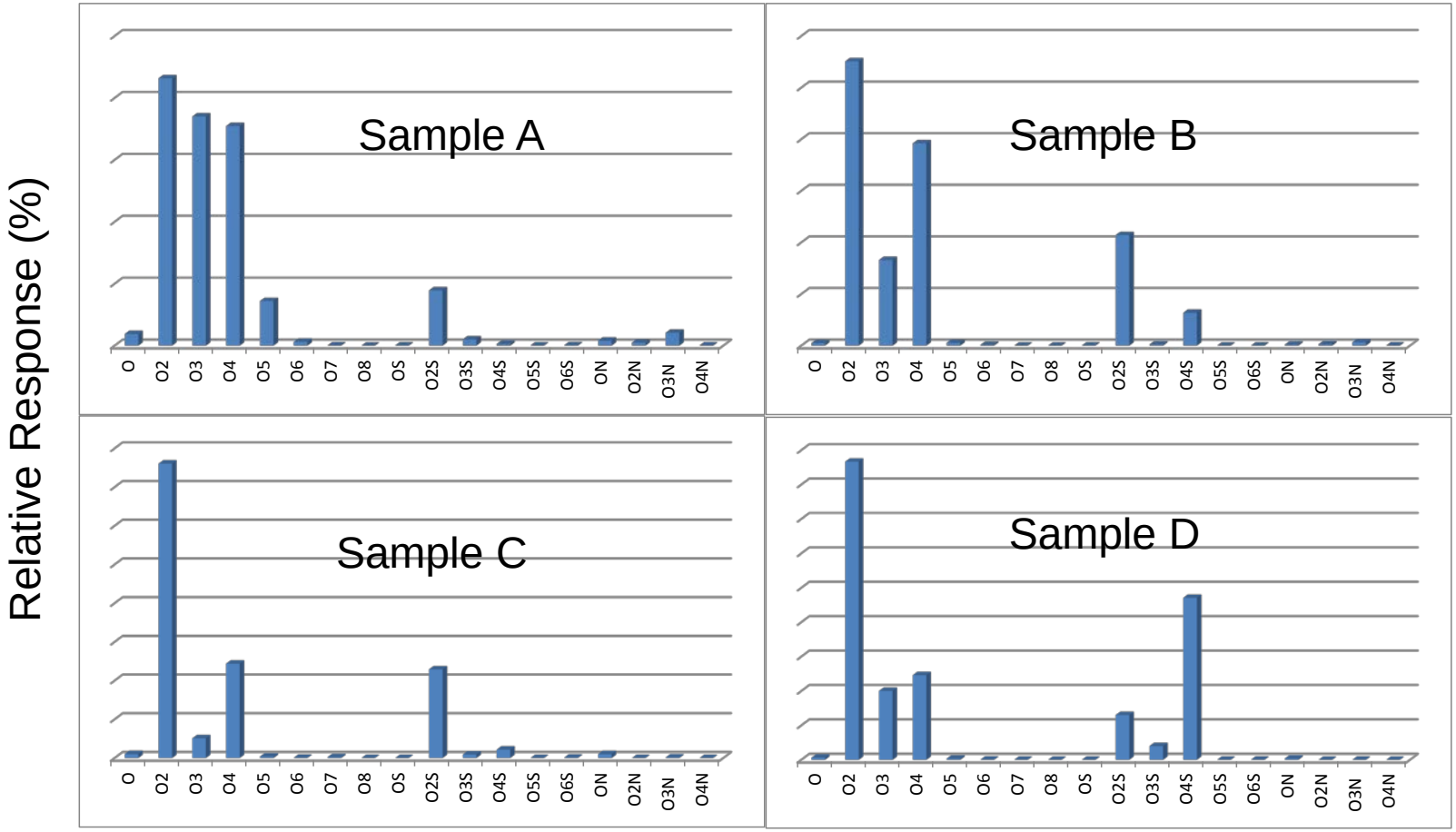
makes it easy to define and automate experiments for both control-versus-treatment and trend analyses.



Principal Component Analysis



Automatic deconvolution of the data



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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