Changing the Paradigm in Petroleomics with Comprehensive Two-Dimensional Gas Chromatography High Resolution Mass Spectrometry

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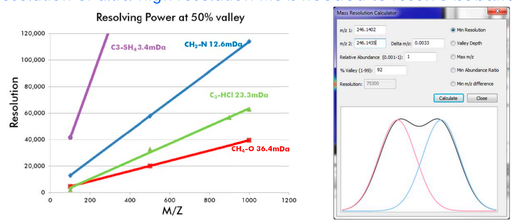
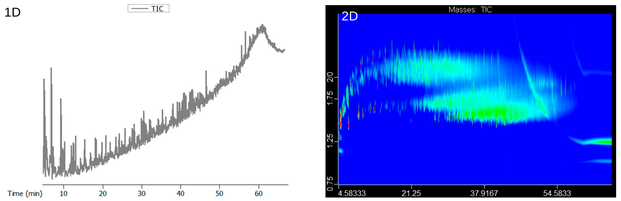
Introduction

Petroleomics is the characterization of the chemical constituents of naturally-occurring petroleum and crude oil using high resolution mass spectrometry.[1][2][3] In addition to mass determination, petroleomic analysis sorts the chemical compounds into heteroatom class (nitrogen, oxygen, and sulfur), type (degree of unsaturation), and carbon number.[4]

High resolution or ultra-high resolution MS is needed to resolve isobaric masses

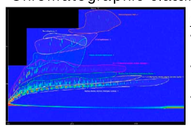


GC×GC provides superior chromatographic separation for complex matrices



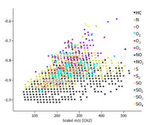
Is there any benefit in combining GC×GC and HRMS for Petroleomics?

Chromatographic classification



Compared to 1D
- Structured chromatogram
- Increased peak capacity
- Better deconvoluted mass spectra

Mass Classification



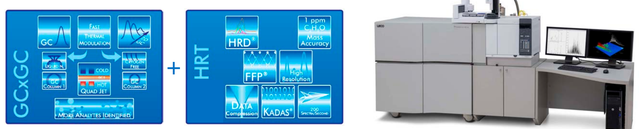
Compared to Low Resolution
- Increased mass resolution
- Chemical formula computation
- Unknown–unknown identification

Analytical Conditions

Primary Column: 60 m x 0.25 mm ID x 0.25 µm df (Rxi-17SilMS)
Sec. Column: 0.6 m x 0.25 mm ID x 0.25 µm df (Rxi-5MS)
Sample: 1 µL cold splitless **Column Flow**: 1.4 mL/min
Injection Temp: 40°C – (720°C/min) – 300°C
Oven Temp: 50°C (1.5 min) – (5°C/min) – 350°C (5.5 min); 67 min
Sec Oven: +5°C **Modulator**: +15°C **Modulation Period**: 1.5 s
MS Transfer Line Temp: 330°C
Mass Range (EI): m/z 15–535
Mass Range (CI): m/z 45–535 (CH_4); m/z 60–535 (NH_3)
Acquisition Rate: 150 spectra/s **Resolution**: 25,000
Source Temp: 250°C (EI); 230°C (CI)

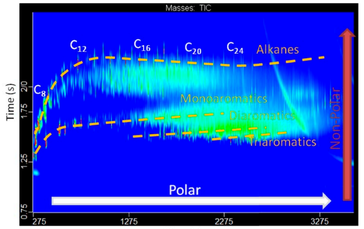
Benefits of GC-HRT 4D

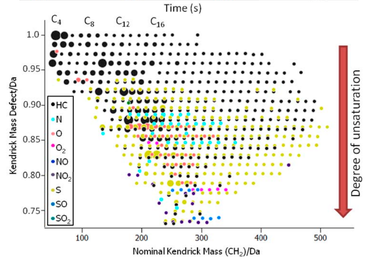
- Combination of GC×GC and accurate mass MS
- Highest acquisition rate, highest resolution, best mass accuracy of any GC×GC capable MS on the market
- Software for GC×GC-HRMS
- Fully integrated



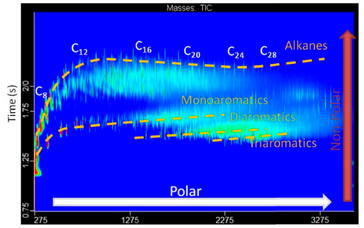
Results

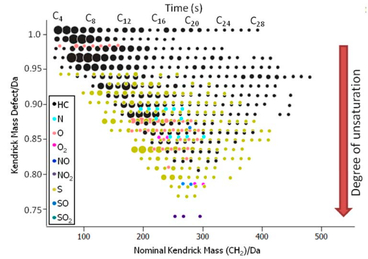
Electron Ionization: Dilbit 66 ug/mL



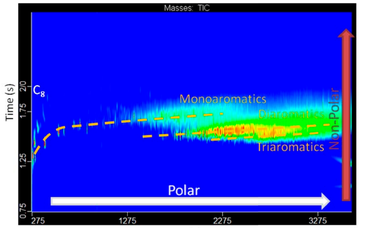


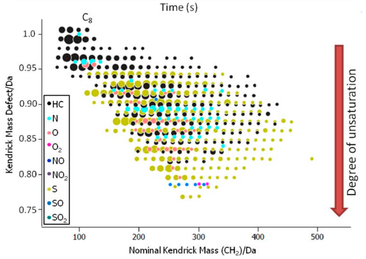
Chemical Ionization (CH_4): Dilbit 66 ug/mL





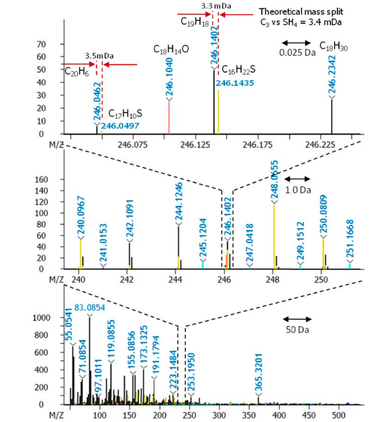
Chemical Ionization (NH_3): Dilbit 66 ug/mL





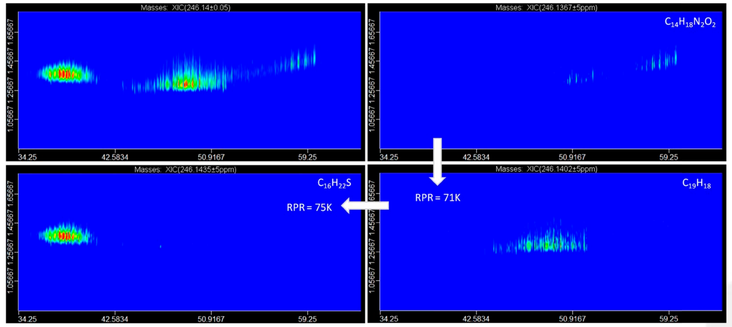
Top) Total ion chromatogram (TIC) of a dilute bitumen sample acquired using comprehensive two-dimensional gas chromatography high resolution time-of-flight mass spectrometry (GC×GC-HRTOFMS), operated in EI and CI modes. Bottom) Kendrick Mass Defect plot for all identified species shown. The EI Kendrick plot shows only whole integer RDBEs, and the CI Kendrick plots show only half integer RDBEs; the size of the dots indicate intensity. The combined plots illustrate a structured nature and the complementary information contained therein.

This technique can be used to distinguish the C_3/SH_4 Mass Split



The integrated mass spectrum, based on spectrally deconvoluted EI data, of a dilbit sample for all of the identified species in the Kendrick plot above.

Three isobaric compounds with resolution requirements > 70 000 FWHH were distinguished by GC×GC-HRTOFMS operated at RP = 25 000 FWHH

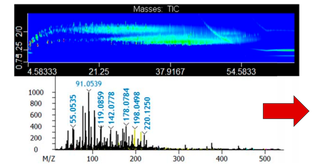


The XIC of m/z 246.14 shows three clusters of peaks. The accurate mass data for each of the peak clusters indicates there are three compound classes represented. The bottom two contour plots show an example of the $C_3\backslash SH_4$ mass split (0.0034 Da), an important feature in petroleomics. The figure also demonstrates isomer separations of each of the compound classes, a benefit not achievable with direct-infusion FT-MS.

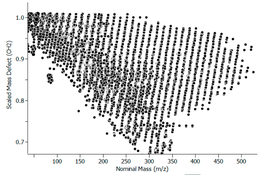
Delivering the Right Results

Experimental Workflow

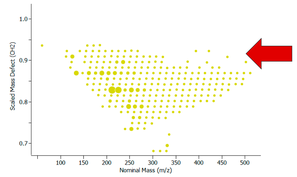
Integrate Spectrum



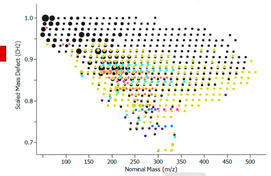
Kendrick Plot



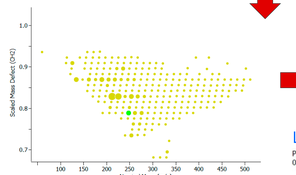
S-Class Compounds



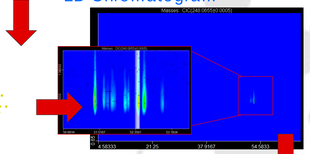
Filtered Kendrick Plot



Show Mass on Chromatogram

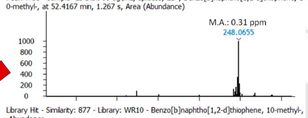


2D Chromatogram

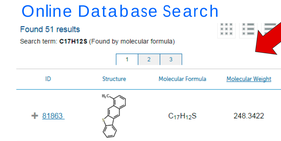


Library Similarity Search

Peak True - sample "EI Dibit 66 ug/mL, spitless, 2D", Benzo[b]naphtho[1,2-d]thiophene, 10-methyl-, at 52.4167 min, 1.267 s, Area (Abundance)



Online Database Search



Comprehensive two-dimensional GC coupled to HRTOFMS is a powerful tool for chemical characterization. This technique is ideal for petroleomics because it provides mass determination, heteroatom class, type, and carbon number information similar to direct high resolution mass spectrometry, and additionally gives well-defined chromatographic regions that facilitate structural elucidation and speciation.

References

[1] *Marshall, Alan G.; Rodgers, Ryan P. (2004). Accounts of Chemical Research* ***37*** *(1): 53–59.*

[2] *Marshall, A. G.; Rodgers, R. P. (2008). Proceedings of the National Academy of Sciences* ***105*** *(47): 18090–18095.*

[3] Ho, Yunju; Ahmed, Arif; Islam, Annana; Kim, Sunghwan (2014). Mass Spectrometry Reviews ***34****: 248 -263.*

[4] *Oliver C. Mullins; Eric Y. Sheu; Ahmed Hammami; Alan G. Marshall (8 November 2007). Asphaltenes, Heavy Oils, and Petroleomics. Springer. ISBN 978-0-387-68903-6.*