Review of selected 2015 & 2014 publications using MS to analyze petroleum

Patrick Boyce
Marketing Team Manager, Waters Europe
Wilmslow, UK
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- Petroleum pitch & coal tar pitch using MALDI Tof MS
- Reactive and non-reactive sulphur species
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- RP UPLC IM-MS of naphthenic acids in OSPW
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- Rapid analysis of lubricants using ASAP IM-MS
- Characterization of bio-oil using ASAP QTof MS
Petroleum Pitch and Coal Tar Pitch & MALDI IM-MS
Klaus Muellen, MPI Polymer Research, Carbon 95 (2015) 672-680

- Pitch samples are high m.wt up to 2K Da, solids with poor solubility so difficult to analyze
- MALDI QTof MS used for petroleum pitch and coal tar pitch for large PAHs
  - Granulated or powdered pitch mixed with DCTB matrix 100:1
  - Synapt G2-Si HDMS, full scan MS with ion mobility enabled
- Describes differences between pitch samples at the molecular level
  - Elemental composition; C# vs DBE (iso-abundance) plots
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  - Synapt G2-Si HDMS, full scan MS with ion mobility enabled
- Describes differences between pitch samples at the molecular level
  - Petroleum: odd & even C# comparable
  - Coal tar pitch: even >> odd C#
Petroleum Pitch and Coal Tar Pitch & MALDI IM-MS
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- Describes differences between pitch samples at the molecular level
  - Elemental composition; C# vs DBE (iso-abundance) plots
  - Petroleum pitch: 30-130 carbon # and DBE 20-100 distribution
  - Coal tar pitch: 25-100 C# & DBE 25-75 distribution
Describes differences between pitch samples at the molecular level

- PAH = core (same DBE) + aliphatic chains (range of C#)
- Series of peaks spaced 14.016 Da = -CH2- (increasing aliphatic chain)
- Series of peaks spaced 24.000/26.016 = C2/C2H2 (24/26 rule)
  (expanding aromatic core)

![Petroleum pitch](image1)

![Coal tar pitch](image2)

*Fig. 2. Magnified mass spectra of the petroleum pitch (a) and the coal tar pitch (b). (A colour version of this figure can be viewed online).*
Petroleum Pitch and Coal Tar Pitch & MALDI IM-MS
Klaus Muellen, MPI Polymer Research, Carbon 95 (2015) 672-680

- Ion mobility spectrum aids in assignments
  - Expanded PAH core vs aliphatic side chain (drift time)?
  - Many aliphatic isomers or few (peak width)?

Petroleum pitch

Coal tar pitch
Reactive & Non-Reactive Sulphur in Petroleum
SPE on Ag loaded SCX
- 2/3 of total S is often thiophenic but can vary dramatically
- US limit for gasoline now 10 ppm
- Separates sulphur compounds based on class:
  - 90:10 DCM/ACE non-reactive thiophenes & diaryl sulphides
  - 50:50 DCM/ACN reactive (sulphides & disulphides)
  - 50:50 c.HCl/MeOH reactive (thiols)
- Compare analysis using
  - GC/MS
  - GCxGC SCD
  - FT-ICR MS (infusion)
10 samples: crude oil and distillates with known b.pt.range and total nitrogen (ppm) and sulfur (%) content
- GC/MS analysis, GCxGC SCD analysis, FT-ICR analysis
Reactive & Non-Reactive Sulphur in Petroleum
Ryan Rodgers, Florida State University
Energy & Fuels, 2015, 29, 6177-6186

- GC/MS EI analysis
  - Vacuum resid (9) + 15 Model compounds

- GCxGC – SCD analysis
  - GCxGC-SCD of ‘VGO (6) – Whole’
  - Non-reactive S: 70%
    - BNTs
    - DBTs
    - BTs
  - GCxGC-SCD of ‘VGO (6) – non-Reactive Fraction’
    - Thiophenes
  - GCxGC-SCD of ‘VGO (6) – Reactive Fraction’
    - Thiophenes

Model compounds & distillates
FT-ICR MS analysis

AgOTf added to the sample for sulphur cationization

Data processed in PetroOrg

HC class fractionated into aromatics (higher DBEs) and olefins (lower DBEs)

S class separated into non-reactive, reactive and thiols (note DBE S2 species in whole sample)

Assignment of non-reactive structures only possible due to fractionation

Crude oil
Study investigating conditions during deposition

- 2, 3, 6-Trimethyl aryl isoprenoid (AIP) hydrocarbons
  - Biomarkers for green sulfur bacteria (GSB, family of Chlorobiaceae)
  - Chlorobactene, β-isorenieratene, and isorenieratene precursors

- 2, 3, 4-Trimethyl aryl isoprenoid (AIP) hydrocarbons
  - Biomarkers for purple sulfur bacteria (PSB, family of Chromatiaceae)
  - Okenone, renieratene, & renierapurpurin likely precursors

Presence presence of both PSB & GSB indicated in the water body during deposition

Samples

- Crude oils deasphalted by precipitation with hexane
- Deasphalted oils separated into fractions by chromatography on silica gel
  - saturated – hexane fraction
  - aromatic – benzene fraction
  - polar - ethanol fractions
- GC/MS on saturated and aromatic fractions
  - results shown on aromatic fractions
GC/MS (EI, single quad MS, full scan) analysis of fractions
- DB-5, 50mx0.32mmx0.25um
- 85-290 deg C, 3 deg C/min, He 1.2 mL/min
- XIC sum of m/z 133 & 134 for characteristic fragment ions of AIPs
- molecular ion peak (M+ •) at m/z 176 +14n, where n =0−13, consistent with the general formula of C\(_n\)H\(_{2n-6}\) as a trimethylbenzene series

AIP profiles
- Assignments seem literature based (no reference to standards or other structural elucidation work)

Distributions of AIPs in crudes from different oil fields
Aryl Isoprenoids in Paleocene Crude Oils
Chang Samuel Hsu, Florida State University
Energy & Fuels 2015, 29, 4690−4700

- GC/MS (EI, single quad MS) analysis of fractions
  - DB-5, 30mx0.32mmx0.25um
  - (60m for 65-290 deg C, 3 deg C/min. He 1.2

AIP skeletons of precursor molecules found

Co-elution isorenieratane & renieratane

Chlorobactane GSB marker

Okenane PSB marker

β-isorenieratane or β-renierapurpurane

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Biomarkers

Toxic

Involved in corrosion

Isomeric

Not amenable to GC without derivatization

Quan often by LC/MS (TQ or QTof)

SPE extraction of Athabasca bitumen samples with WAX cartridges

- MeOH:H2O 70:30 plus 5% formic
- MeOH:H2O 80:20 plus 5% formic
- MeOH:H2O 90:10 plus 5% formic
- MeOH 100% plus 5% formic
- DCM:MeOH 5:95 plus 5% formic
- DCM:MeOH 20:80 plus 5% formic
- DCM:MeOH 50:5 plus 5% formic

Fraction dried and reconstituted in toluene:methanol 1:1 at 10 ug/mL
Isomeric Separation and Structural Characterization of Acids in Petroleum by Ion Mobility Mass Spectrometry
Ryan Rodgers, Florida State University
Energy Fuels, 2015, 29 (6) 3626-3633

- Analysis by infusion into Synapt G2-Si HDMS (IM-MS mode), negative mode ESI
- Data processing in PetrOrg

Isomeric & linear aliphatic acids can be differentiated by ion mobility
Analysis by infusion into Synapt G2-Si HDMS (IM-MS mode) negative mode ESI

Data processing in DriftScope

Analysis by FT-ICR MS

Question: are the supposed DBE = 5 O2 species assigned in PetroOrg using Synapt IM-MS data really isomers or actually isobars?

FT-ICR MS data from same mass range shows no isobars in that region
Isomeric Separation and Structural Characterization of Acids in Petroleum by Ion Mobility Mass Spectrometry

Ryan Rodgers, Florida State University
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- Analysis by infusion into Synapt G2-Si HDMS (IM-MS mode) negative mode ESI

$O_2\text{ Class, DBE} = 1$

Isomeric & linear aliphatic acids can be differentiated by ion mobility
ASAP and APGC in petroleum characterization
ASAP & APGC - petroleum characterization

- Synapt G2-S HDMS
- ASAP and APGC
  - APGC applied to biomarkers, 40-350 deg C gradient
  - ASAP applied to saturate fraction of vacuum resid (1% in DCM); 50-650 deg C ramp
- Ionization pathways
  - Paraffins and isoparaffins standards are primarily ionized by nitrogen addition
  - Cyclic paraffins and aromatic compounds are primarily ionized by charge transfer
ASAP & APGC - petroleum characterization

- ASAP applied to saturate fraction of vacuum resid (1% in DCM); 50-650 deg C ramp
  - saturate fraction of a petroleum resid

Comparable to online fractionation
Deeper Z# (equivalent to higher DBE #) and higher C# vaporized at higher temperatures
Fragmentation observed for NAs
Paraffins largely unfragmented
More features detected than with MALDI
ASAP & APGC - petroleum characterization

- APGC DB-5 30mx0.25mmx0.25um, 4-350 deg C at 25 deg C/min; 1.5 mL/min
  - Alkane standards

Paraffins ionize by N addition

C17 paraffin

C16 paraffin
ASAP & APGC - petroleum characterization

- APGC DB-5 30mx0.25mmx0.25um, 4-350 deg C at 25 deg C/min; 1.5 mL/min
  - saturate fraction of a crude oil

Complexity of sample: e.g.
monitoring parent ion of m/z 400 sterane biomarker not useful

Monitoring MRM transitions gives better specificity for biomarkers in petroleum

Simplified operation compared to EI
Oil Spill Source Identification Using UHRMS with MVA
Ryan Rodgers, Florida State Uni., Anal. Chem. 2013, 85, 9064–9069

- PCA of elemental composition, DBE & C# data from FT-ICR negative ion mode ESI
  - PCA in PetroOrg
- Identified persistent polar petroleum markers
  - Polar species resistant to biodegradation and ozonation remediation
- Heavy fuel oil spill – two suspect tanks ruptured
- Samples – neat Heavy Fuel Oil, & weathered samples from coastal deposits (55-817 days)
  - Dissolved in 1:1 toluene - methanol w/0.5% tetramethylammonium hydroxide in methanol
- GC analysis limited to compounds volatile below 400 deg C & limited for polars
- FT-ICR MS for comprehensive analysis
Oil Spill Source Identification Using UHRMS with MVA
Ryan Rodgers, Florida State Uni., Anal. Chem. 2013, 85, 9064–9069

HFOs can be differentiated using PCA
N & NS classes account for most of the differences
NS class is relatively stable
Oil Spill Source Identification Using UHRMS with MVA
Ryan Rodgers, Florida State Uni., Anal. Chem. 2013, 85, 9064−9069

- DBE 11 core structure – two aromatic rings plus thiophene plus pyrolic rings
- DBE 14, 17, 20 have 1, 2 and 3 extra aromatic rings
- Second distribution at DBE 17 indicates two HFOs have been mixed
Oil Spill Source Identification Using UHRMS with MVA
Ryan Rodgers, Florida State Uni., Anal. Chem. 2013, 85, 9064–9069

PCA analysis on weathered samples – no significant change in % abundance with duration of exposure

Analysis of source HFO validates statistical significance of NS class

PCA of different DBE values for NS class. PCA score varies linearly with weathering for Tank 4
Naphthenic acids in coastal sediments
Underivatized NAs and oxy-NAs analysed in sediments using UPLC Xevo G2 QTof, BEH C18 (10%-100% MeOH gradient), full scan MS, ESI negative mode

- Soxhlet extraction of 1 g sediments (3-5 years after spill) with further clean-up using Oasis MAX anion exchange SPE;
  - sediments spiked with 0.1 ug 1-pyrenebutyric acid & 12-oxochenodeoxycholic acid as surrogate standards
- LODs ranged from 0.1-1.0 ng g⁻¹ dw in sediment
- Semi-quan using Acros NAs mixtures as ISs
- PAHs have been assumed to be primary determinant for petroleum toxicity and used as proxies for oil pollution
- Toxicity of NAs increasingly a concern, up to 3% by weight of petroleum and quite soluble in neutral & alkaline waters compared to PAHs
- NAs and oxy-NAs found in sediment
Naphthenic Acids in Coastal Sediments
Jianying Hu, Peking University, Environmental Science & Technology 2014, 48, 4153-4162

Integration of XICs for semi-quan
Acros standards used as for quan
Higher NA levels found than PAHs
UPLC IM-MS Naphthenic Acids
Oil Sands Process-Affected Waters

- Persistent toxic pollutants
- UPLC BEH C18 Synapt G2 HDMS full scan MS with ion mobility enabled, ESI negative ion mode
- Samples – unprocessed and ozonated OSPW, & OSPW DCM LLE
- Complex range of NAs – O₂, O₃, N & S containing, aromatic and saturated cyclic structures, isomeric structures
UPLC IM-MS Naphthenic Acids Oil Sands Process-Affected Waters

- Impact of ozonation seen
  - Z numbers -4 to -8
  - x number for Ox increased

- ESI-IM-TOFMS 2D separation technique was able to separate and characterize the NAs in OSPW using only filtration pre-treatment

- Extraction improves detection of low abundance NAs (399 peaks detected in extract)
UPC2 HRMS of naphthenic acids, SO2 & NO classes is OSPW
Approx. 1 billion m³ of OSPW is stored in tailings ponds in Northern Alberta, Canada

Many compounds in OSPW are also found in natural groundwater locally – better fingerprinting methods needed

RP LC leaves many isomers unresolved

OSPW samples acidified and DCM LLE; dried and recon. in acetone

UPC² with bare silica columns as inlet to Orbitrap MS
  – APCI positive and negative modes
**UPC² MS Oil Sands Process Water**


- UPC² with bare silica columns as inlet to Orbitrap MS
  - APCI positive and negative modes

Hydrophobic NAs much better resolved by UPC²

O₂ species well resolved

Oₓ species where x > 2 elute late by SFC and need optimized method

RT increases with DBE & C#

MS/MS spectra dominated by CO₂ neutral loss

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C₁₀H₁₈O₂ monounsaturated NA

**UHPLC C18**

[M-H]⁻

XIC m/z 169.1234
UPC² MS Oil Sands Process Water
J.W. Martin, Uni. Alberta,

- UPC² with bare silica columns as inlet to Orbitrap MS
  - APCI positive and negative modes
  - Same conditions optimized for NAs also work for SO₂ and NO classes

XIC m/z 114.09 (C₆H₁₁NO)

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Rapid Analysis of Lubricants using ASAP-IM-MS
Carlos Alfonso, Université de Rouen, J. Mass Spectrom. 2014, 49, 709–715

- Formulated lubricants – base oil, additives (detergents, corrosion inhibitors, antioxidants, viscosity modifiers)
- Analytical approaches used typically use techniques which focus on one class of compounds (HCs & volatiles by GC, polars by LC etc)
- ASAP-IM-MS (Synapt G2 HDMS) for direct characterization of lubricants
  - Full scan MS (50-2000 m/z), positive ion mode, ion mobility enabled, 2 mins, 650 deg C
  - Base oils, polymer and lubricants analysed without sample prep
- Exploratory work done on 5 additives, a polymer additive poly (alkyl methacrylate), two base oils and a formulated lubricant
  - Molecular ions for additives detected
  - Marker ions for PAM detected
Rapid Analysis of Lubricants using ASAP-IM-MS
Carlos Alfonso, Université de Rouen, J. Mass Spectrom. 2014, 49, 709–715

- Base oil 1 & 2
  - Base oil 2 is more complex
- Drift time decreases with increasing DBE
- Drift time increases with increasing C#
Rapid Analysis of Lubricants using ASAP-IM-MS
Carlos Alfonso, Université de Rouen, J. Mass Spectrom. 2014, 49, 709–715

- Lubricant analysis
  - Direct, 2 mins
- Many ions in lubricant common to base oils 1 & 2
  - Likely lubricant is a mix of these two
- Additives detected
- Polymer additives detected

- base oil 1 (blue circle)
- Base oil 2 (red cross)
- formulated
- lubricant (yellow circle)
Characterization of bio-oil using ASAP QTof MS
Rice Husk Bio-Oil (RHBO)
- Bio-oils are formed by pyrolysis of biomass in absence of oxygen
- Analysis with ASAP-QTof MS
  Extracted with 6 different solvents
  - Hexane, CCl₄, benzene, CH₂Cl₂, CHCl₃, ethyl acetate
  - Analysis by ASAP-QTof MS and GC/MS (Agilent 7890/5975 EI)

Quickly see DBE & C# profile for each fraction using ASAP QTof MS
Rice Husk Bio-Oil (RHBO)

- Bio-oils are formed by pyrolysis of biomass in absence of oxygen
- Analysis with ASAP-QToF MS
  Extracted with 6 different solvents
  - Hexane, CCl₄, benzene, CH₂Cl₂, CHCl₃, ethyl acetate
  - Analysis by ASAP-QToF MS and GC/MS (Agilent 7890/5975 EI)

ASAP QToF MS more comprehensive:
Many more compounds identified by ASAP QToF MS than GC/MS EI