High Definition Mass Spectrometry (HDMS) application of ion mobility in oil and petroleum analysis

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WCTOW
Vancouver, May 13, 2013
Introduction

Overview of SYNAPT® HDMS™ Technology

Focus on Ion Mobility

DriftScope Software

Oil & Petroleum Example Data
UPLC/HDMS²

liquid phase separation

low energy

elevated energy

retention time aligned precursor and productions

Ion mobility

drift time aligned precursor and productions

ion mobility/gas phase separation
Separation by Drift Time
IMS Increases Peak Capacity: The Datacube

- Peak capacity = \( N_{\text{LC}} \times N_{\text{IM}} \times N_{\text{m/z}} \times F \)
  
  \[ F = \text{fraction of bins occupied} \]

- \( N_{\text{m/z}} > N_{\text{LC}} > N_{\text{IM}} \)

- However, LC, m/z and IM not completely orthogonal
Straight chain structure

Branched structure

C_{16}H_{26}

Drift Time

m/z

C_{7}H_{8}

C_{16}H_{26}

Straight chain structure
Single mass peak at $m/z$ 571 has five mobility resolved peaks under it.
DriftScope: Data Viewing & Interaction

Small cut asphaltene, m/z 335 – 335.5
CCS CALCULATIONS

Relating Drift Time to Size
DriftScope: CCS Calculation

The CCS Calibration Editor interface is shown, with various data plots and options for calibration:
- **File** menu options include 'Add new drift gas...' and 'Remove drift gas'.
- **Peaks** menu includes 'Select drift gas' and 'Save calibration'.
- **Calibrate** section displays a graph with 'max: 223657 Counts' and m/z values.
- **Measured Chart** shows peaks with 'max: 223657 Counts'.
- **Calibration Chart** with equation 'Qc = Ax + B', 'A = 258.6918', 'B = 0.2133', 'R² = 0.9992', and 'max: 1294 Qc'.
- **Delta Chart** with 'max: 10 ΔQc'.

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These data were collected using Waters ASAP – a thermal desorption technique, so no chromatographic separation.
DriftScope: Exporting Data
EXAMPLE DATA

IFPEN Collaboration

IFP Energies nouvelles is a public-sector research, innovation and training center active in the fields of energy, transport and the environment.
IFPEN uses FTICR-MS to analyse crude oils & their fractions

Collaboration: samples provided by IFPEN and comparative analyses made with FTICR-MS & SYNAPT HDMS

Samples: with thanks to Jérémie Ponthus, IFPEN

SAR fraction:
- Saturated 44.5%
- Aromatics 36.3%
- Resins 16.4%

Sample: from Nigerian Egina oil field
- Vacuum residue
- Resins fraction
- Most polar fraction
- Particularly nitrogen-rich oil
Typical data treatment: Kendrick plots using their in-house “KendrickInside” software

- exact Kendrick mass = IUPAC mass x (14/14.01565)
- Kendrick mass defect = (nominal Kendrick mass - exact Kendrick mass)

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ESI+ FTICR-MS analysis
- 1 mg/mL sample
- MeOH:Toluene (1:1) + 0.5% formic acid
- Resolving power 100,000 @ m/z 400

Results
- C_{18} to C_{60}
- DBE from 5 to 23
Total Mass Spectrum

1 dimethyl pyridine
2 isoquinoline
3 benzoquinoline
4 dibenzoacridine
5 crude oil

N containing compounds
Mass Spectrum

SYNAPT HDMS analysis
- 40K resolution
- Ion mobility enabled

ASAP+
- Direct deposit of solution, 6 mg/mL in toluene
- Thermal desorption and gas phase APCI
- Thermal ramp from 250 °C to 650 °C

ESI+
- 1 mg/mL
- MeOH:Toluene (1:1)

Calibrations
- External mass: leucine enkephalin, $m/z$ 556.2771, <2 ppm
- Mobility cell: Polyalanine, over range ~ approx. 85 Å² to 250 Å²
Waters Analysis: Egina Resins
- Oil fraction mobilogram: an organised area
Kendrick plot of the Synapt G2 HDMS data

Extraction of a nitrogen containing series (family 1) – with thanks to Jérémie Ponthus
Excel plot of the DriftScope family 1
Excel plot of the DriftScope family 1: series characterisation
Excel plot of the DriftScope family 1: C number characterisation

- $C_{22}$ (DBE 0)
  - 77.38 bins
  - 141 Å²

- $C_{14}$
  - 100 Å²

- $C_{22}$ (DBE 10)
  - 62.71 bins
  - 123 Å²

- $C_{36}$
  - 175 Å²
Summary

- Ion mobility separates species according to:
  - Size
  - Shape
  - Charge

- DriftScope helps to visualise mobility data
  - 3D: m/z, drift time, intensity
  - 4D: m/z, retention time, drift time, intensity

- Ion mobility offers:
  - Increased peak capacity due to additional separation
  - Comprehensive characterisation of samples
  - Ion size information from CCS calculations following the calibration of the mobility cell.
Ion Mobility mass spectrometry is applicable and offers benefits to the analysis of oil and petroleum samples.

The Synapt HDMS exact mass data can be used to generate Kendrick plots.

When mass and drift time are taken into consideration, it enables the identification of incorrect assignments of ions provided by high resolution data alone.

The calibration of the mobility cell with polyalanine allowed the calculation of the size of species within the sample.

The knowledge of size distribution in the sample could lead to novel catalyst design – of vital importance in the quality of the products generated from crude oil.
Acknowledgements

- Jeremy Phontus
  IFP Energies Nouvelles, Rond-point de l’échangeur de Solaize–BP 3, 69360 Solaize, France

- Eleanor Riches
  Waters Corporation, Atlas Park, Simonsway, Manchester M22 5PP, UK

Evaluating the multiple benefits offered by ion mobility-mass spectrometry in oil and petroleum analysis
Thank You For Your Attention