# Fourier transform ion cyclotron resonance mass spectrometry

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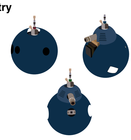
## Analytical challenges

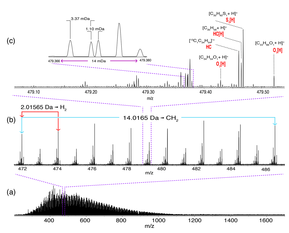
- **Sample collection**
  - Method, time frame
- **Sample preparation**
  - Extraction, fractionation, solubility, pH
- **Ionization**
  - Polarity, fragmentation, ion types
- **Mass spectrometry**
  - Resolving power, mass accuracy
- **Structure/isomers**
  - Chromatography, ion mobility, MS/MS
- **Data**
  - Processing, quantity, analysis, visualization

## FTICR MS

- **Fourier transform ion cyclotron resonance mass spectrometry**
- **Variety of ionization methods to suit range of sample types**
  - ESI, nanospray, MALDI, LDI, APPI, APCI, and more
- **Variety of dissociation methods for structural information**
  - CID, ETD, ECD, EID, EDD, IRMPD, UVPD, and more
- **Can couple with orthogonal separation methods**
  - LC, GC, ion mobility, and more
- **Performance and suitability for complex samples**
  - Highest resolving power and mass accuracy of any mass spectrometer
- **Research at Warwick - 12 T and 15 T FTICR instruments**
  - Petroleum and fractions (e.g. asphaltenes), fuels, biofuels/bio-oils, environmental, archaeology, development of data processing algorithms



## FTICR MS data



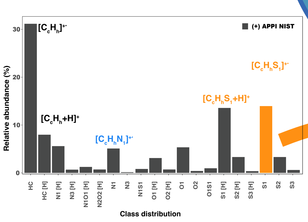

## Data analysis

**The use of patterns within petroleum-related data sets can be used to aid assignment of molecular formulae. Once molecular formulae have been assigned, they are categorized accordingly:**

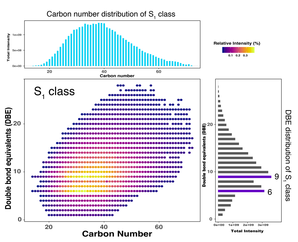
- **Compound class or heteroatom class**
  - Number of each heteroatom (e.g. $N_1$, $S_1$, $O_2$, etc.)
  - "[H]" tag included in name for even-electron ions; lack of "[H]" tag indicates odd-electron ions
- **Carbon number**
  - Indicative of size of ion, amount of alkylation
- **Double bond equivalents (DBE)**
  - Rings and double bonds involving carbon frame
  - Even-electron ions have half-integer values, odd-electron ions have integer values
  - For a molecular formula of $C_cH_hN_nO_oS_s$ :

$$DBE = 1 + c - h/2 + n/2$$

## Compound class plots

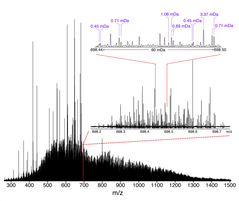


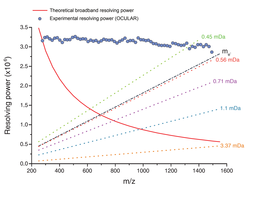

## DBE vs. carbon number

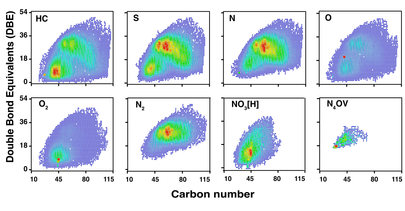



## OCULAR

**New design of experiment, developed at Warwick for constant ultrahigh resolving power across full m/z range (note carbon number of >100)**
**244,779 unique molecular formula assignments (current world record)**
**Resolving power ~3 million across full m/z range; ~300 peaks per Da**

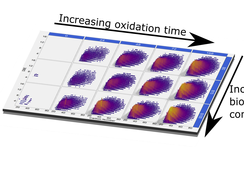


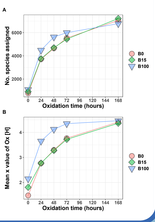




## Engine oil oxidation

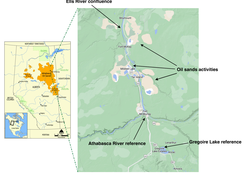
**Influence of biodiesel content on oxidation of base oils for use in engines**
**Three samples: B0 (100% diesel), B15 (85% diesel, 15% biodiesel), and B100 (100% biodiesel)**
**Benchtop oxidation testing up to 168 hours**



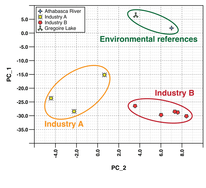




## Oil sands and the environment

**Maps showing oil sands activity within the Athabasca River basin area of Alberta, Canada**

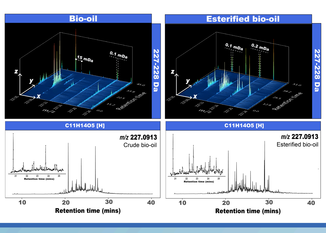


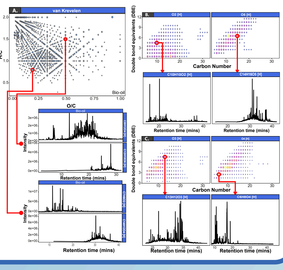

**Principal component analysis (PCA) based on FTICR MS analysis, demonstrating ability to differentiate sample origins**




## Coupling with chromatography

**Examples of GC coupled with FTICR at Warwick, using KairosMS software for data analysis (note many isomers per molecular formula)**
**DBE vs. carbon number plots: single data points are unique molecular formulae**
**van Krevelen diagrams: multiple molecular formulae per data point**




## Acknowledgements and References

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