Quantification of bitumen constituents by FT-ICR-MS – is it achievable?

Lisbet Sørensen[1a], Trond R. Størseth[1a], Anders Brunsvik[1b], Marianne Rønsberg[1a], Evangelia Tzoumani[2], Hilde Soenen[3], Stuart Forbes[4], Carol Banner[2]

1) SINTEF [a]Ocean and [b]Industry, Trondheim, Norway
2) Concawe, Brussels, Belgium
3) Nynas, Antwerp, Belgium
4) SF Analyticon, Cheshire, England

The challenge

- Bitumen, or asphalt is a highly viscous petroleum-derived substance. While it occurs naturally, it is commonly produced as a residue after distillation of crude oils. In essence, bitumen is a very complex mixture of (mostly) unresolved chemical constituents. A large fraction of bitumen is expected to be hydrocarbons (aliphatic and aromatic), but a fraction also contain nitrogen (N), sulfur (S) and oxygen (O) compounds.
- Due to the production method, it is expected that most chemical consitutents are 'heavy' (large, complex molecules with high boiling points).
- Most commonly used analytical techniques such as GC-MS and LC-MS are hardly applicable to bitumen due to either the high boling point (GC-MS) or the expected high content of apolar compounds (LC-MS).

Analytical strategy

- The primary aim of the presented work was to identify a suitable analytical strategy to unravel the chemical composition of bitumen. A secondary objective was to evaluate the potential for FT-ICRMS analysis to be used for *quantification* of relative compound or compound group concentrations within a sample.
- Two different approaches to SARA fractionation was applied:, 1) Methodology from ASTM D4124 and 2) *n*-hexane precipitation of asphaltenes followed by LC-separation of the maltene (SAR) fractions. The mass yield of each fraction was determined gravimatrically.
- Whole substance bitumen and all resulting fractions were analyzed by FT-ICRMS in both positive atmospheric pressure photoionization (APPI+) and negative electrospray (ESI-) modes. Accurate mass data was converted to molecular formulae and exported for further manipulation in R software.

Repeatability of fractionation and analysis

- Fractionation and analysis was performed in triplicate with acceptable repeitability.
- Relative standard deviations of gravimetric mass yield of fractions was in the ranges 1-5 and 15-40% for the LC- and ASTM-method, respectively.
- For the APPI FT-ICRMS data, the mean standard deviation in determination of total abundance per chemical class was 7%, and the same for number of masses detected within each sample was 15%.

SARA who?

- The mass yield of each fraction by each method was compared to the data obtained using the TLC-fractionation (IP469(.
- The three methods gave different results, with the largest discrepancy in distribution between the aromatics and resins fractions between the two methods applied in this work and the standard method.

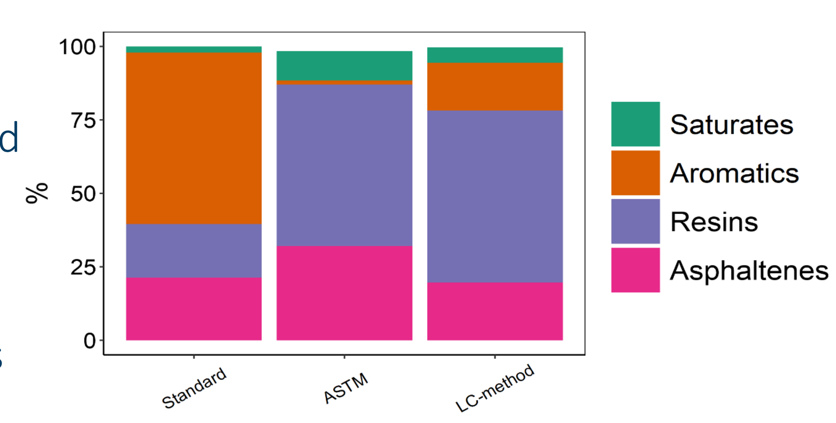

Figure 1 SARA composition of the bitumen sample from three different methods. The 'standard' here refers to IP469.

Compositional data of bitumen and fractions

- In the current study, only APPI(+) mode analysis provided reasonable compositional data. ESI(-) had a low number of detected masses for all samples. This indicates low presence of complex organic acids. In the following, only APPI data will be discussed.

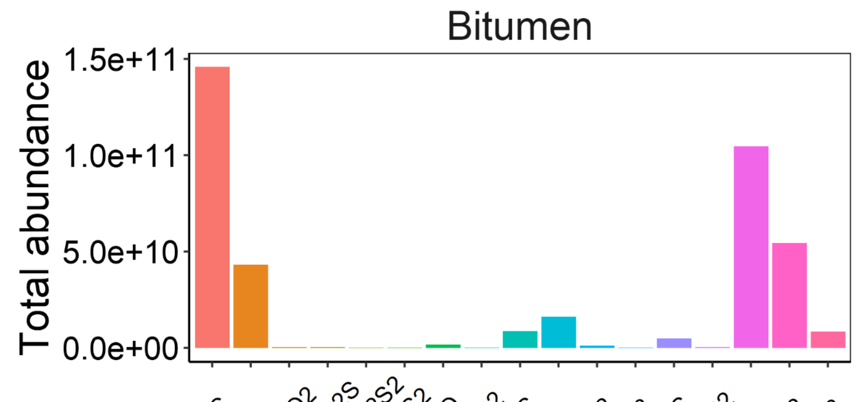

Figure 2 Total abundance of individual compound classes for the bitumen sample.

- As expected, the bitumen sample contained a range of hydrocarbons functionalized compounds ('NSO') over a large molecular size range.

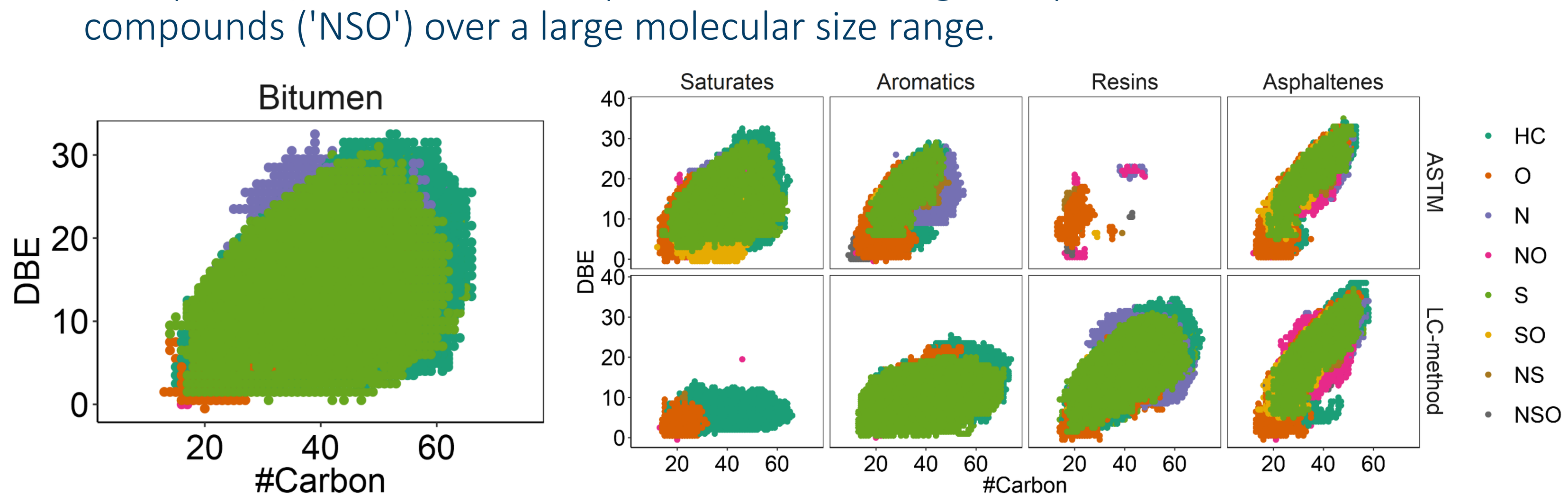

Figure 3 Double-bond equivalents (DBE) by carbon number for the bitumen whole substance and fractions analysed by APPI(+)-FT-ICRMS..

- With the exception of the asphaltenes, the fractions resulting from the two different fractionation methods were very different in composition. It appears that the LC-method more 'evenly' distributed the masses between the fractions (supported by the gravimetric data above).

The toolkit

- Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (**FT-ICRMS**) with its to date not challenged mass resolution (>100,000), allows accurate mass determination and elemental composition identification. Depending on the selected ionization technique, the method is applicable to a wide array of analyte sizes and polarities. As such, it lends itself to the ***characterization*** of very complex samples – and to compare variation in composition of such samples. It does not rely on compounds being both amenable to and stabile throughout an online chemical separation, overcoming challenges observed in e.g., gas chromatography-based techniques.
- When targeting detection of the highest number of compounds in a very complex sample – fractionation of the sample *may* be useful to simplify the matrix of each fraction – thus revealing the identity of the maximum number of analytes.
- SARA (saturates, aromatics, resins, asphaltenes) fractionation is a relatively simple industry standard method that has been applied to petrogenic samples for decades, and in combination with FT-ICRMS for years. Currently, SARA fractionation remains a standard method to characterise the composition of bitumen samples.

Matrix suppression?

- The number of detected masses resulting from the bitumen was overall higher after fractionation than when analysing the whole substance. The LC-method provided the highest number of masses, and also a higher total abundance of measured masses.
- A possible explanation is that the LC-method fractionation most evenly distributed bitumen mass between four fractions, meaning each fraction was less complex than bitumen and several of the ASTM fractions.

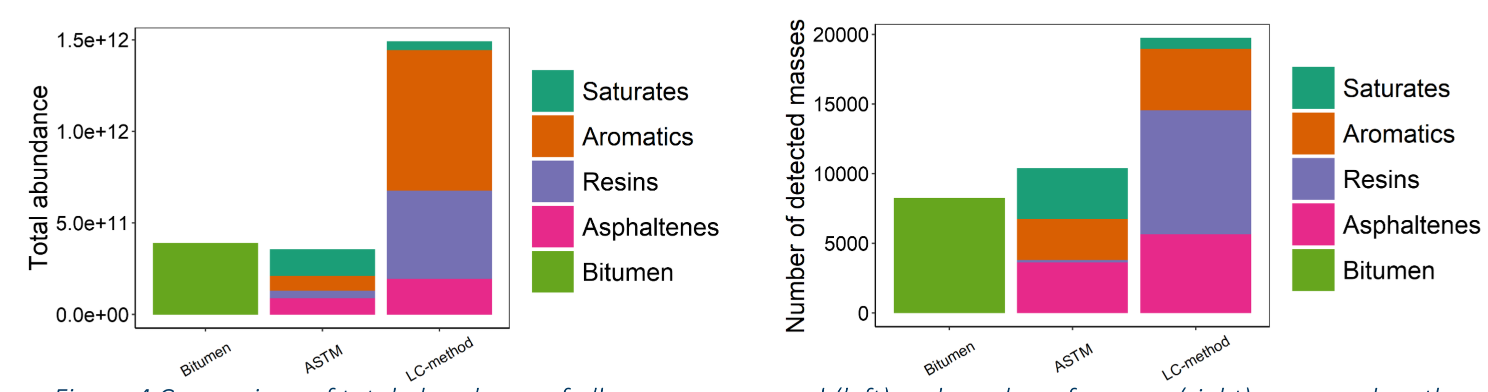

Figure 4 Comparison of total abundance of all masses measured (left) and number of masses (right) measured on the bitumen whole substance compared to the various fractions

Elemental composition

- The elemental composition of the bitumen sample was determined by standard methods including ASTM D5291 (Carbon, Hydrogen); ASTM D5768 (Nitrogen); MT/ELE/17 (Oxygen) and MT/ELE/05 (Sulfur). In addition, composition of each FT-ICR-MS identified constituents in combination with their relative abundance was used to calculate an approximated elemental composition of each fraction after analysis

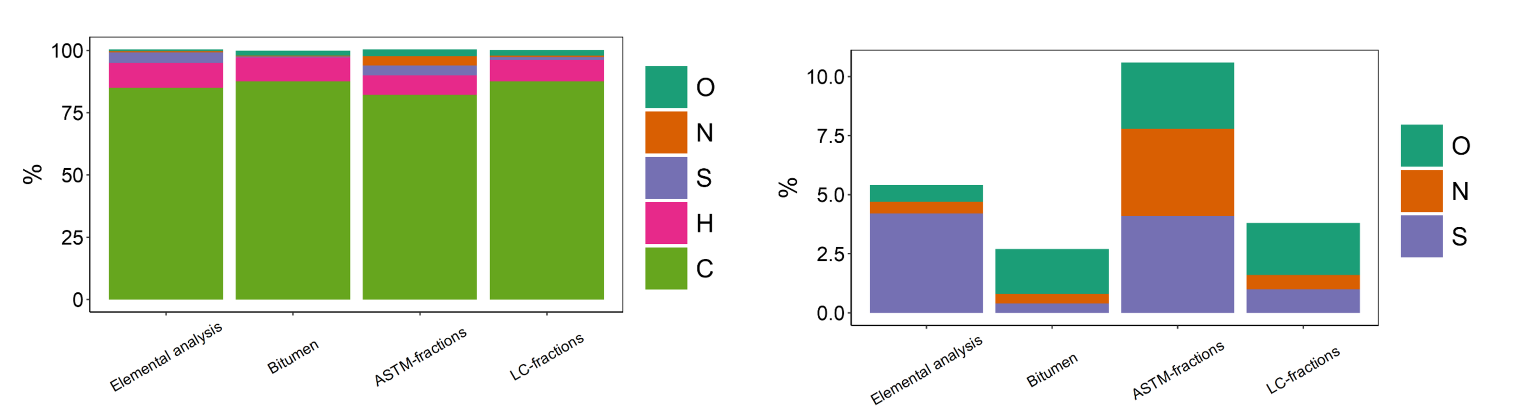

Figure 5 Comparison of elemental composition as determined by the standard methods, and as determined by FT-ICRMS analysis of bitumen full substance or after summing relative contributions of four SARA fractions by the two methods

Observations:

- N-compounds suppressed in full substance analysis, more 'visible' in fractions
- ASTM method "exaggerates" presence of nitrogen compared to other methods
- Sulfur least comparable between FT-ICRMS data and elemental analysis
- More oxygenated compounds in all APPI analysis than elemental analysis

Preliminary conclusions

- The methodology demonstrated good repeatability for both fractionation and analysis.
- Fractionation leads to higher total abundances and a different compositional picture compared to analysing the bitumen sample directly.
- Different fractionation techniques gives different results.
- So far this work has focused on proof-of-concept to one sample, and there is a lack of statistical power to draw conclusions.

Further work to tackle the challenge of quantification

- In an ideal (unrealistic) scenario there would standards and response factors for 'all' compounds or at least all 'representative' structures, but this is not achievable in the foreseeable term due to the number of potential chemicals and chemical groups in bitumen. To overcome this, whether or not a defendable semi-quantitative approach is possible to achieve needs to be investigated.
- Further challenges that will to be addressed are 1) the extent of ion suppression and matrix effects by analysis of further bitumen samples, 2) dealing with ionization and response discrimination based on chemical structure with a selected subset of representative compounds spiked into varying matrix complexity.

IP 469, Determination of saturated, aromatic and polar compounds in petroleum products by thin layer chromatography and flame ionization detection. 2006
ASTM D4124-09 Standard Test Method for Separation of Asphalt into Four Fractions
Aske, N.; Kallevik, H.; Sjöblom, J. Determination of Saturate, Aromatic, Resin, and Asphaltenic (SARA) Components in Crude Oils by Means of Infrared and Near-Infrared Spectroscopy. Energy Fuels 2001, 15 (5), 1304–1312.
Fan, T.; Buckley, J. S. Rapid and Accurate SARA Analysis of Medium Gravity Crude Oils. Energy Fuels 2002, 16 (6), 1571–1575.

Technology for a better society