Statistical analysis of crude oils by LDI-FTICR mass spectrometry

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Introduction
Crude oil is an extremely complex mixture of compounds. These compounds can be analyzed on the molecular level by Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry as a well established method known as petroleomics. Based on the detected compounds the relative abundance of compound classes can be calculated. These results can be compared with chemical properties of the oils. However, the abundance of the detected compound classes depends heavily on the ionization method used. In this study laser desorption/ionization (LDI) was coupled to a FT-ICR mass spectrometer for the analysis of crude oil. A thin film of crude oil on a stainless steel target was analyzed in a MALDI source using a UV laser at 355 nm without matrix addition.

Several different crude oils were analyzed and compared on the molecular level. The relative abundances of the compound classes with different number hetero atoms were compared. The relative abundances of the compounds classes were in some case quite small. Therefore, the reproducibility of the LDI measurements is a prerequisite to be able to distinguish the crude oils.

Each crude oil sample was measured several times to calculate the standard deviation of detected compound classes. Figure 1 shows as an example of mass spectrum at m/z 301 of different oil samples and three repetitive measurements.

Methods
Data acquisition:
- solariX FMS with 12 T superconducting magnet and new dynamically harmonized analyzer cell
- mass range m/z 150 – 2000
- resolving power of 450,000 at m/z 400
- positive ion mode
- 100 single scans were averaged for a final mass spectrum
- laser power was set to 12% to reduce fragmentation, laser focus was set to diameter of 30 μm, 4 laser shots were used for each scan
- 5 repetitive measurements were performed for each sample for better statistics.

Mass calibration:
- external calibration with arginine clusters
- internal recalibration with a known homologous series

Molecular formula assignment:
- Composers 1.0.6 (Sierra Analytics)
- Max. molecular formula: C_{n}H_{2}O_{m}N_{p}S_{q}
- H/C ratio: 0.2 ≤ H/C ≤ 2.3
- Electron configuration: odd and even
- Mass tolerance: 0.5 ppm

Statistics:
- Profile Analysis 2.1 (Bruker Daltonik) using averaging mass lists and bucketting as well as normal and logarithm scaling

Crude oil samples were kindly provided by SINTEF Materials and Chemistry, Trondheim, Norway.

Results
The distinction of the crude oils only based on different relative abundances of compound classes is crucial and can result to wrong results. Therefore, in our approach the distinction of crude oils has been performed on the molecular level using the mass list of the LDI-FTICR mass spectra. The mass spectra of the different oil samples were analyzed concerning relative abundance of compound classes (Fig. 2) for rough distinction of the crude oils. As shown in Figure 2 the oil differ in relative abundance of compound classes. However, the distinction of the oils only based on these results is critical and can results in wrong interpretation of data. Therefore, additionally the mass spectra were analyzed with the statistical method principal component analysis (PCA). The results of the PCA show that the oils could be easily separated in the PCA scoring plot with small variation of the repetitive measurements using average mass list for the PCA calculation (Figure 3). Better separation of the oils in the PCA scoring plot was observed with logarithm scaling than with normal scaling. However, the statistical analysis also indicated that extremely high resolution of the mass spectra is needed for the separation of the oils by PCA (Figure 4). Using bucketing with mass resolution of 2 mDa for PCA calculation instead of average mass lists resulted already in efficient separation of all crude oils.

Separation of the crude oils was impossible with a mass resolution of 20 mDa bucketing for PCA simulating mass spectrum with resolving power of only 20,000. Standard deviation was low for repetitive LDI-FTICR mass measurements.

Conclusions
- Crude oil samples can be distinguished on the molecular level by LDI ultra-high resolution mass spectrometry.
- LDI gives reproducible results with standard deviation less than 4% for abundant compound classes.
- Crude oils could be separated by principle component analysis (PCA).
- Average mass list and logarithm scaling is preferred for PCA to separate oils in scoring plot.

Table 2: Relative abundance of compound classes of oil 8 of five repetitive measurements as an example for reproducibility of LDI-FTICR mass spectra.

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