Introduction

The relationship of crude oils based on their chemical composition is of major interest in the oil industry. Similarities of crude oils can be analyzed by different analytical methods. In this study, atmospheric pressure photoionization (APPI) coupled to Fourier transform ion cyclotron resonance (FTICR) mass spectrometry was used to analyze ten crude oil samples from the North Sea.

In comparison to other methods, this technique is based on detailed chemical composition of these complex mixtures. Therefore, similarities of crude oils can be directly related to relative abundance of compound classes and molecular composition of each compound class based on carbon number and double bond equivalent distribution. Multiple measurements of oils were performed to demonstrate the reproducibility of this technique.

The statistical method Principal Component Analysis (PCA) was used in this study. Our results agree with a study by Hur et al. that the detailed molecular composition is responsible for the distinction of crude oils. [1]

Keywords

- Instrumentation and Software
- Flow Injection Analysis solarix XR
- Statistics CASI
- Reproducibility FTMS
- PCA ProfileAnalysis
- Crude Oil Composer

Authors

- Anders Brunsvik, Kolbjørn Zahlsen
  SINTEF Materials and Chemistry, Trondheim, Norway
- Matthias Witt
  Bruker Daltonik GmbH, Bremen, Germany

Statistical Analysis of Crude Oils from the North Sea by Atmospheric Pressure Photoionization FT-ICR Mass Spectrometry
Flow injection measurements were performed with 100 μL sample solutions and a flow rate of 10 μL/min. An Agilent autosampler G1367A with 100 μL sample loop was used; sample concentration was 0.1 mg/mL in toluene/methanol 1:1 for positive ion mode and 0.5 mg/mL in toluene/methanol 1:1 for negative ion mode.

Mass calibration
- External calibration with arginine clusters
- Internal recalibration with a known homologous hydrocarbon series

Molecular formula assignment
- Composer 1.0.6 (Sierra Analytics)
- Max. molecular formula: C_cH_hN_3O_3S_3
- H/C ratio: 0.2 ≤ H/C ≤ 2.3
- Electron configuration: odd and even
- Mass tolerance: 0.5 ppm

Statistics
- ProfileAnalysis 2.1 (Bruker Daltonik) using average mass list and logarithm scaling for bucket generation

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

Results
Identical mass peaks have been detected for the crude oils but with different intensities indicating different relative abundances of the compound classes as shown Fig 1. The relative abundances of the detected compound classes by APPI-FTICR mass spectrometry using positive and negative ion mode are shown in Figure 2. The most abundant classes CH, N_1, O_1 and S_1 in positive ion mode (Fig. 2a) are identical for all oils which correlates with the similarity of the oils from the North sea.

The relative intensities of the most abundant compound classes detected in negative ion mode were different especially the N_1 and the O_1 classes. Distinction of the oils only based on the relative intensities of the detected compound classes can be inaccurate and can result in wrong conclusions. Therefore, principle component analysis (PCA) based on mass list of the mass spectra and therefore using molecular level results were used to distinguish the oils. The PCA scoring plots of the measurements in positive and negative ion mode are shown in Figure 3 and 4, respectively.

The oils could be well separated using the full mass spectrum (Fig. 3a) as well as results of 50 Da quadrupole isolated mass window (Fig. 3b) with high reproducibility shown in the perfect clustering of the repetitive measurements.

Methods

Data acquisition
- solariX XR FTMS with 12 T superconducting magnet and new dynamically harmonized analyzer cell
- Mass range m/z 150 – 2000
- Ionization: APPI positive and negative ion mode
- Resolving power of 900,000 at m/z 400
- 128 single scans were averaged for the final mass spectrum
- 5 repetitive measurements were performed for all samples, 25 repetitive measurements were performed for oil 4 for reproducibility study
Also, good separation of oils in the PCA scoring plot was observed for the measurements in negative ion mode using average mass lists. However, distinction of the oils was degraded using only 2 mDa buckets instead of peak lists, indicating that ultra high resolution is required for statistics. Good reproducibility of APPI measurements based on relative abundance of compound classes is shown in Table 1.

Class distribution plot

![Class distribution plot](image)

Figure 2: Class distribution plot of different crude oils by APPI-FTICR mass spectrometry in a) positive and b) negative ion mode; oil 8 and oil 8a are identical oils from different batches.

PCA scoring plots using positive ion mode

![PCA scoring plots using positive ion mode](image)

Positive ion mode, broad band spectrum

Positive ion mode, CASI spectrum m/z 425-475

Figure 3: PCA scoring plots of APPI-FTICR mass spectra in positive ion mode of all oil samples using average mass lists with logarithm scaling with a) full mass spectrum and b) CASI spectrum m/z 425-475 - oil 8 and oil 8a are identical oils from different batches.

PCS scoring plots using negative ion mode

![PCS scoring plots using negative ion mode](image)

Negative ion mode, average peak list

Negative ion mode, 2 mDa bucketing

Figure 4: PCA scoring plots of APPI-FTICR mass spectra in negative ion mode for all oil samples using a) average mass lists with logarithmic scaling and b) 2 mDa bucketing with logarithmic scaling - oil 8 and oil 8a are identical oils from different batches.
Conclusion

- APPI-FTICR mass spectra are very reproducible.
- Crude oils could be perfectly separated by PCA in positive as well as in negative ion mode.
- Average peak lists for bucketing calculation gives best results for the PCA scoring plots.
- Separation of the oils in the PCA scoring plot is even possible with reduced mass range using CASI.

Table 1: Relative abundance of compound classes of oil 4 and standard deviation of 25 repetitive measurements.

<table>
<thead>
<tr>
<th>Class</th>
<th>Oil 4 1st</th>
<th>Oil 4 2nd</th>
<th>Oil 4 24th</th>
<th>Oil 4 25th</th>
<th>Std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>47.596</td>
<td>47.629</td>
<td>48.179</td>
<td>48.272</td>
<td>0.47</td>
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<tr>
<td>HC [H]</td>
<td>13.290</td>
<td>13.303</td>
<td>13.448</td>
<td>13.344</td>
<td>0.50</td>
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<tr>
<td>N</td>
<td>7.476</td>
<td>7.544</td>
<td>7.450</td>
<td>7.430</td>
<td>0.70</td>
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<tr>
<td>N [H]</td>
<td>2.170</td>
<td>2.189</td>
<td>2.158</td>
<td>2.189</td>
<td>1.03</td>
</tr>
<tr>
<td>NO</td>
<td>1.059</td>
<td>1.079</td>
<td>1.141</td>
<td>1.141</td>
<td>2.29</td>
</tr>
<tr>
<td>NO [H]</td>
<td>1.713</td>
<td>1.764</td>
<td>1.733</td>
<td>1.754</td>
<td>1.52</td>
</tr>
<tr>
<td>O</td>
<td>6.085</td>
<td>6.060</td>
<td>5.925</td>
<td>5.884</td>
<td>1.11</td>
</tr>
<tr>
<td>O [H]</td>
<td>1.983</td>
<td>1.992</td>
<td>1.940</td>
<td>1.992</td>
<td>1.60</td>
</tr>
<tr>
<td>O2</td>
<td>0.332</td>
<td>0.332</td>
<td>0.311</td>
<td>0.322</td>
<td>5.59</td>
</tr>
<tr>
<td>O2 [H]</td>
<td>0.488</td>
<td>0.591</td>
<td>0.394</td>
<td>0.363</td>
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<tr>
<td>OS</td>
<td>0.498</td>
<td>0.467</td>
<td>0.477</td>
<td>0.425</td>
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<tr>
<td>OS [H]</td>
<td>1.101</td>
<td>1.090</td>
<td>1.090</td>
<td>1.069</td>
<td>1.55</td>
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<tr>
<td>S</td>
<td>12.688</td>
<td>12.525</td>
<td>12.359</td>
<td>12.390</td>
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<tr>
<td>S [H]</td>
<td>2.876</td>
<td>2.833</td>
<td>2.812</td>
<td>2.791</td>
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<tr>
<td>S2</td>
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<td>0.311</td>
<td>0.270</td>
<td>0.301</td>
<td>5.21</td>
</tr>
</tbody>
</table>

References


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