Introduction
Crude oil is known as a very complex mixture of organic compounds with various elemental compositions and chemical structures. An important analytical task in the oil industry is to quickly identify compounds from crude oils which could potentially harm the production plant. Therefore, detailed and quantitative information about the compound types in crude oil is of high interest for a molecular-based management of the refining process.

Isolation of single compounds is only partially possible with liquid chromatography, capillary electrophoresis or other separation methods due to the complexity of this mixture. Only ultrahigh-resolution Fourier transform ion cyclotron (FTICR) mass spectrometry with a resolving power of more than 300,000 can provide this separation in mass, thus giving insight into the distribution of compounds within a given complex mixture. The use of FTICR mass spectrometry for the assignment of compound classes as well as the elemental composition of single compounds of crude oil has been shown previously [1].

Experimental
Anaysis were accomplished using an apex™ Qe 9.4 T (Bruker Daltonics, Billerica) which was equipped with an external quadrupole/hexapole device and a DualSource™ (Bruker Daltonics, Billerica) which was operated in positive or negative ion mode. Infusion experiments in Electrospray (ESI), Atmospheric Pressure Chemical Ionisation (APCI) and Atmospheric Pressure Photo Ionisation (APPI) (Syagen, Tusint) were carried out by changing to the appropriate spray chamber (change-over in less than a minute).

To prepare the spray solution, 20 µL crude oil were dissolved in 1 ml toluene and further diluted 1:9 in 85% MeOH/15% toluene. This solution was sprayed at 120°C at a constant pressure of 5 bar. Results are shown as mass spectrum of the crude oil sample.

Data evaluation
Data evaluation was performed with Generate Molecular Formula (GMF)™ in TargetAnalysis™ (Bruker Daltonik GmbH, Bremen). The GMF module allows for setting various constraints for the molecular formula search. Here, the following constraints were used: max. molecular formula: C_{x}H_{y}N_{z}O_{w}S_{p}S_{q}, H/C ratio: 0.2 ≤ H/C ≤ 2.5, nitrogen rule: yes (APPI: no), mass tolerance: 0.5 ppm. The resulting molecular formulae were displayed using Kendrick plots.

The relative abundances of compound classes were calculated from the respective MS intensities. The fraction of spectra with MS intensities displayed in the top ten was 60%. For all measurements, molecular formulae were displayed using Kendrick plots (Figure 2). An automated generation of molecular formulae from accurate mass measurements enables rapid compound identification.

Results
For all measurements molecular formula were generated and displayed in Kendrick plots (Figure 2). Due to the very accurate mass detection using FT-ICR mass spectrometry the detailed analysis of Kendrick plots reveals series of homologous compounds.

The comparison of these distributions shows that polar compounds have been detected very efficiently using ESI, whereas non-polar compounds can be detected with APCI as well as APPI more effectively. The abundance of the detected compound classes depends on the ionisation technique and ionization mode is shown in Figure 3.

Figure 2: Zoom Kendrick plot of positive ESI mode.

Figure 3: Detected compound classes in a) positive and b) negative ion mode of crude oil for different ionization methods (for clarity C_{7}H_{14} has been omitted for the individual compound classes)
Setting a certain isolation mass range (e.g. \( \Delta m/z \) 50) in the external quadrupole allows for selectively enhancing low abundant species which are otherwise suppressed. The effect of this continuous accumulation of selected ions (CASI) is demonstrated in Figure 4.

In summary more than 14000 compounds have been identified (Table 1) using all ionization techniques, which clearly shows the need for different ionization techniques to gain a better understanding of the compositions of complex mixtures.

**Conclusion**

We demonstrate the use of ultrahigh accurate mass measurements in combination with automated elucidation of molecular formula. Only the combination of different ionization techniques and ultra high resolution mass spectrometry gives utmost insight into complex mixtures such as crude oil, which are not readily resolved by chromatographic strategies. In addition, selectively enhancing certain mass areas by means of CASI reveals low abundant species.

Therefore, ESI-, APCI- and APPI-FTICR mass spectrometry are very important and complementary tools for the rapid analysis of crude oil.

**References**


<table>
<thead>
<tr>
<th>Ionization Method</th>
<th>Positive Ionization</th>
<th>Negative ionization</th>
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<tbody>
<tr>
<td>ESI</td>
<td>3820</td>
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<tr>
<td>APCI</td>
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<td>APPI</td>
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<tr>
<td><strong>Total (non-redundant)</strong></td>
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Table 1: Molecular formulae identified by different ionization methods