Rapid Compound Identification from Crude Oil enabled by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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The analysis of crude oil by means of different atmospheric pressure ionization (API) techniques is described. Crude oil is analyzed without any separation prior to API-Fourier transform mass spectrometry. The use of a quadrupole/hexapole device to selectively enhance a certain mass range is demonstrated. Automated generation of molecular formulae from accurate mass measurements enables rapid compound identification.

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].

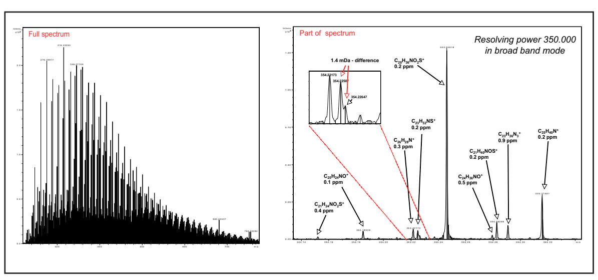

Figure 1: a) Electrospray spectrum in positive ion mode of crude oil, b) zoom of a)

The speciation of heteroatomic compounds, especially nitrogen and sulfur, is important due to their ultimate fate as NO_x and SO_x emissions upon combustion as well as their corrosive character for the production plant. The presence of such compounds in crude oil is also of interest for the understanding of asphaltenes and their deposition in e.g. pipelines [2]. Due to the tremendous complexity of the spectra (*Figure 1*) an automated processing of the data is mandatory.

Experimental

Analyses 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, Tustin) were carried out by changing to the appropriate spray chamber (change-over in less than a minute).

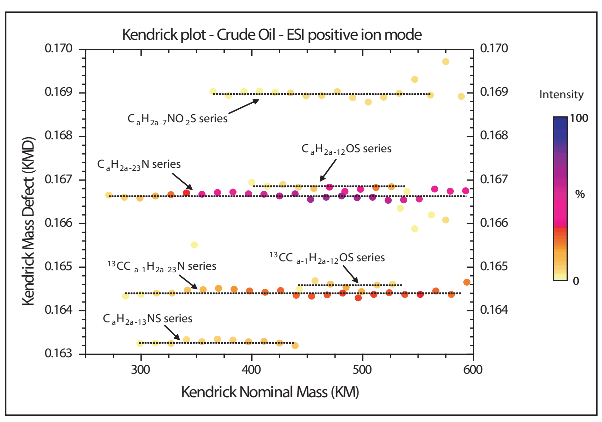

Figure 2: Zoom Kendrick plot of positive ESI mode.

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 @ 120 µL/h for ESI and @ 12 ml/h for APPI and APCI, respectively.

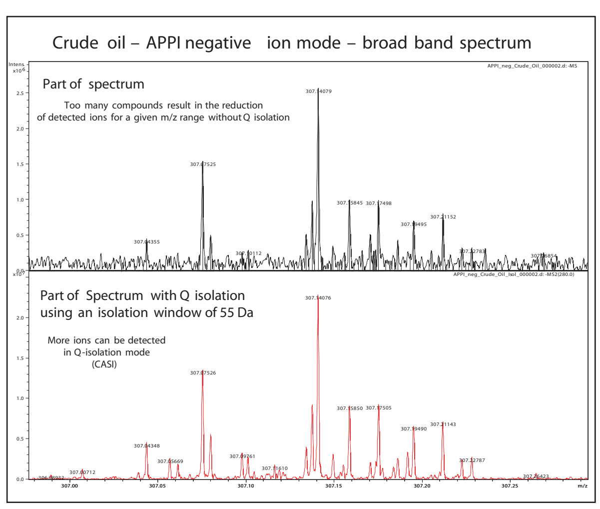

Figure 4: An example of CASI: Continuous accumulation of selected ions reveals low abundant species.

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: $C_aH_bN_3O_{30}S_3$, H/C ratio: 0.2 ≤ H/C ≤ 2.5, nitrogen rule: yes (APPI pos: 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.

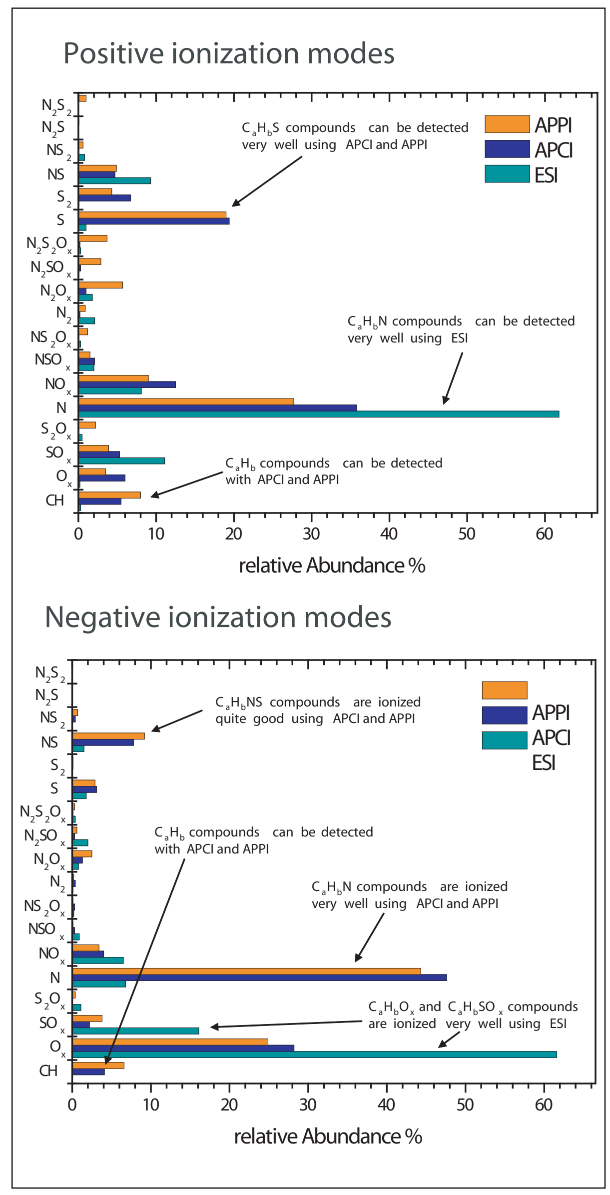

Figure 3: Detected compound classes in a) positive and b) negative ion mode of crude oil for different ionization methods (for clarity C_aH_b has been omitted for the individual compound classes)

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 homological 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 depending on the ionization technique and ionization mode is shown in *Figure 3*.

APPI (besides APCI) proved very useful technique for the analysis of non-polar compounds like hydrocarbons. Also, in positive mode APPI was the most effective method for compounds like $C_aH_bN_2S_2O_x$, $C_aH_bN_2SO_x$ and $C_aH_bN_2Ox$. However, using APPI in positive ion mode one has to take into account that [MH]+ as well as [M]+· ions are detected [3].

Ionization Method	Positive Ionization	Negative ionization
ESI	3820	3760
APCI	4540	3720
APPI	7450	3230
Total (non-redundant)	14700	

Table 1: Molecular formulae identified by different ionization methods

Setting a certain isolation mass range (e.g. Δ 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 ionisation 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

1. Marshall, A.G., Energy and Fuels, 15, 492, (2001); Rodgers, R. P. Et al. Anal. Chem., 77, 21A, (2005).
2. Marshall, A. G. et al., Acc. Chem. Res., 37, 53, (2004).
3. Purcell, J. P. et al., Anal. Chem., 78, 5906, (2006).

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