

Classification and differentiation of crude oil by Fourier transform ion cyclotron resonance mass spectrometry using atmospheric pressure ionization

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Matthias Witt¹, Jens Fuchser¹ and Victor Furse²
¹Bruker Daltonik GmbH, Bremen, Germany
²Bruker Daltonics Inc., Billerica, MA, USA

Introduction

Crude oil is a very complex mixture. The composition of all organic compounds with various elemental compositions and chemical structures is not exactly known. However, the elemental composition depends on the origin of crude oil for instance Saudi Arabia, Brazil, Canada or Russia. It is only partially possible to isolate single compounds or reduce the complexity with liquid chromatography or other separation methods. Nevertheless, oil companies are highly interested in quantitative information of compound classes in crude oil. Furthermore, the classification of crude oil depending on their origin is of major interest. Speciation of hetero atomic compounds like sulfur or nitrogen compounds with specific double bond equivalents is necessary for crude oil classification on the molecular level. The elemental composition of single compounds of crude oil has been analyzed using ultra-high resolution Fourier Transform ion cyclotron resonance (FT-ICR) mass spectrometry.

Methods

Mass Spectrometer:

- APEX ultra 9.4 T (Bruker)

Ion mode:

- ESI in positive and negative ion mode

Compound:

- four different crude oils

Spray solution:

- 20 μ L crude oil in 1 ml dichloromethane.
- Dilution of 1:9 in 85% MeOH/15% toluene.

Solvent Flow:

- 120 μ L/h

Molecular formula search:

- Max. molecular formula: $C_{40}H_{70}N_3O_{30}S_3$
- H/C ratio: $0.2 \leq H/C \leq 2.5$
- Electron configuration: even
- Mass tolerance: 1 ppm

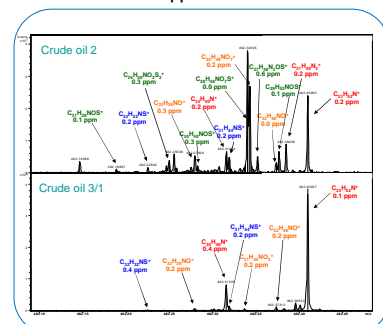


Fig. 1: Section of mass spectrum of crude oil 2 and 3/1 around m/z 462

Results

The molecular formula analysis of the masses at m/z 462 of crude oil 2 and 3/1 is shown in Figure 1 as an example for the variation in relative abundance of compounds in crude oil. Most peaks can be assigned in the spectrum with exactly one molecular formula with very small mass errors using specific criteria for the molecular formula search and consideration of homologous series. The crude oils can be classified on the basis of the relative abundance of compound classes by calculating all molecular formulas of all peaks in the mass spectra. The relative abundances of compound classes in all four samples is shown in Figure 2.

The crude oil can be easily classified due to significant differences in the relative abundance of different compound classes. However, crude oil 3/1 and 3/2 are nearly identical in the relative abundances in their major compound class C_nH_xN . Small differences in compound classes NS and NO_x have been found. However, these differences are not significant for a classification. A more detailed analysis has been done with double bond equivalents (DBE) vs. number of carbon atoms plots (Figure 3). In both plots the DBE of crude oil 3/1 is on average around one DBE higher than crude oil 3/2.

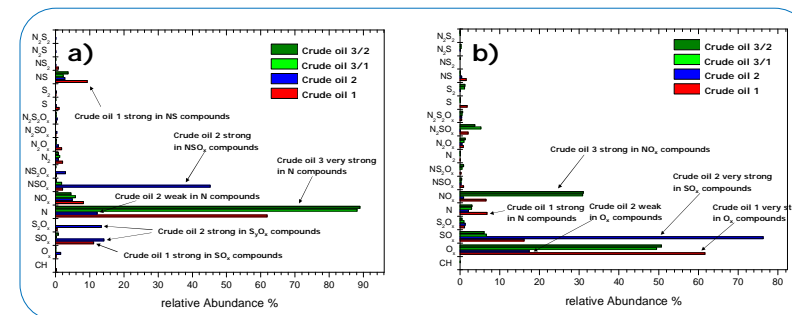


Fig. 2: Relative abundances of detected compound classes in a) positive and b) negative ion mode of crude oils

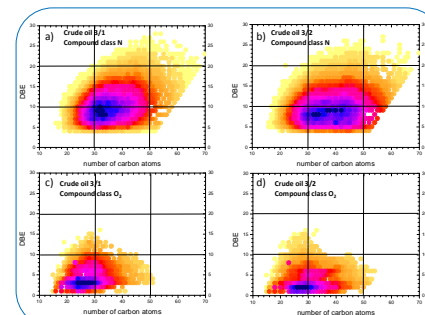


Fig. 3: DBE vs. carbon atoms of compound class N in positive ion mode of a) crude oil 3/1 and b) crude oil 3/2 and compound class O_2 in negative ion mode of c) crude oil 3/1 and d) crude oil 3/2.

Conclusions

- Crude oil samples can be characterized by their relative abundances of compound classes.
- Very similar crude oils can be distinguished with DBE vs. number of carbon atoms plots of specific compound classes.
- Fourier transform ion cyclotron resonance mass spectrometry can be used to classify crude oil from different locations.