Analysis of crude oil mixtures by APPI-FTICR mass spectrometry

Matthias Witt
Bruker Daltonik GmbH, Bremen, Germany

Introduction
Due to the fact that crude oil deposits become heavier, analytical methods are needed to better utilize heavy crude oils. Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) is a very powerful technique to study oil on the molecular level. Therefore, FTICR mass spectrometry has been a well-established method in this analytical field (petrochemistry) since more than a decade. Routinely a resolving power of more than 800,000 can be achieved by FTICR MS with mass accuracies in the ppb range. Therefore, small mass differences between detected peaks below 1 mDa can be resolved which are common in spectra of very complex samples like heavy oils. Nevertheless, even with this technique not all compounds in oils can be detected due to ionization effects. Therefore, a complete understanding of the composition is still not available.

Not only the chemical composition of oil can be extracted from ultrahigh resolution mass spectra, the mass spectrum is also very specific for the analyzed oil. Therefore, the mass spectrum is also a fingerprint for the analyzed oil. Oils can not only be classified by statistical methods using FTICR MS, also mixtures of oils can be identified and also quantified based on the chemical composition and the relative abundance of compound classes. In our study two oils have been mixed in different ratios. This method was verified concerning accurate determination of the oil ratio and reproducibility.

Methods

Data acquisition:
- solanaX FTMS with 12 T superconducting magnet and new dynamically harmonized analyzer cell
- mass range m/z 150 – 2000
- ionization: APPI positive ion mode
- resolving power of 900,000 at m/z 400
- positive ion mode
- 128 single scans were averaged for the final mass spectrum
- 6 repetitive measurements were performed for each sample for better statistics
- flow injection measurements were performed with 100 μl sample solutions and a flow of 10 μl/min. An Agilent auto-sampler G1367A with 100 μl sample loop was used; sample concentration was 0.1 mg/mL in toluene/methanol 1:1

Mass calibration:
- external calibration with arginine clusters
- 6 repetitive measurements were performed
- Mass tolerance: 0.5 ppm

Flow injection measurements were performed for each sample for better statistics. The relative abundance of class N detected as a) radical cations and b) protonated species increased with increasing percentage of oil B in the mixture. The relative abundance of class O detected as a) radical cations and b) protonated species decreased with increasing percentage of oil B in the mixture. Also the DBE distribution is changing slightly with different ratio of oil A and B.

Fig. 2: DBE distribution plot of different ratios of crude oil A and B. The relative abundance of class N detected as a) radical cations and b) protonated species increased with increasing percentage of oil B in the mixture. The relative abundance of class O detected as a) radical cations and b) protonated species decreased with increasing percentage of oil B in the mixture. Also the DBE distribution is changing slightly with different ratio of oil A and B.

Fig. 3: Plot of relative abundance of compound classes N, O, and S detected as radical cations, protonated species and sum of both species versus percentage of oil B in mixture. Very good linear correlation was observed for compound classes N, and O with regression factors better than 0.99.

Table 1a: Calculation of percentage of oil B based on rel. abundance of compound classes of a 35% mixture of oil B

Table 1b: Calculation of percentage of oil B based on rel. abundance of compound classes of a 45% mixture of oil B

Conclusions

- Flow injection measurements of crude oil samples analyzed by APPI FTICR mass spectrometry are very reproducible with standard deviations less than 2% for abundant compound classes.
- Ratio of crude oil mixtures composed of two oils could be determined very accurately with a relative and absolute errors in average of only 2% and 1%, respectively.
- Measurements have shown very good reproducibility of APPI-FTICR measurement using flow injection.

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