Characterization of Petrophase 2017 reference asphaltene using Magnetic Resonance Mass Spectrometry (MRMS)

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Introduction

The Petrophase 2017 asphaltene standard sample was analyzed by ultrahigh resolution mass spectrometry using a solarix 2XT 7T FTICR mass spectrometer (Bruker, Bremen, Germany). Laser desorption ionization (LDI) as well as atmospheric pressure photoionization (APPI) was used for ionization of the sample. Results were compared with results of elemental analysis.

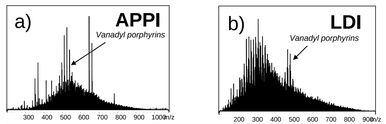


Fig. 1: a) APPI mass spectrum of the asphaltene sample; b) LDI mass spectrum of the asphaltene sample; c) Zoom–in of the APPI and LDI mass spectra at m/z 600 for better visualization of the high complexity of the sample

Methods

Mass spectrometry:

Data acquisition:
- solariX 2XR FTMS with 7 T superconducting magnet and new dynamically harmonized analyzer cell and 2ω detection
- mass range m/z 107 – 3000
- ionization: APPI and LDI positive ion mode
- resolving power of 1200,000 at m/z 400
- positive ion mode
- 200 single scans were averaged for the final mass spectrum
- APPI: 500 ppm in 90% toluene, 10% MeOH
- LDI: 150 laser shots using 21 % laser power with minimum laser focus

Mass calibration:
- external calibration with NaTFA clusters
- internal recalibration with a known homologous CH and S_1 series

Molecular formula assignment:
- PetroOrg 10.0 (Florida State University)
- Max. molecular formula: $C_cH_hN_3O_3S_4$
- H/C ratio: 0.2 ≤ H/C ≤ 2.3
- Electron configuration: odd and even
- Mass tolerance: 0.5 ppm

Asphaltene sample was kindly provided by PetroPhase 2017 organization committee.

Elemental Analysis:
- H, C and N: Thermo Scientific Flash 2000
- Sulfur: Leco SC632

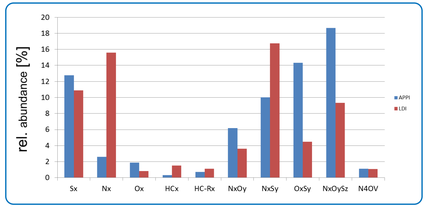


Fig. 3: Compound class distribution plot of the main classes of the asphaltene sample using APPI and LDI

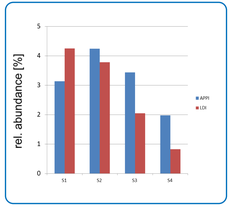


Fig. 4: Class distribution plot of the S_x classes using APPI and LDI.

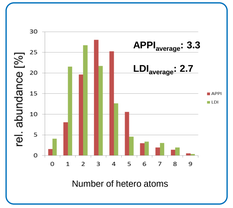


Fig. 5: Distribution of hetero atom content.

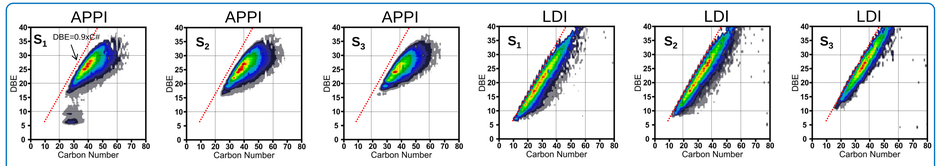
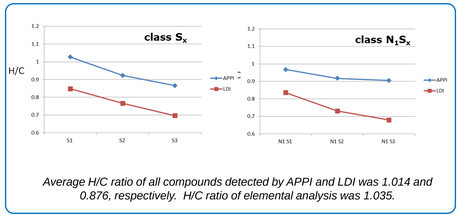


Fig. 6: DBE vs. C atom number plots of the S_1, S_2 and S_3 class detected by APPI and LDI.

Results

The observed APPI and LDI spectra of the sample were extremely complex (Fig 1). More than 52.000 different molecular formulae (incl. ^{13}C peaks) could be detected. Spetra could be acquired with very high mass accuracy with RMS error less than 250 ppb (Fig. 2). Main class distribution as well as S_x class distribution is shown in Fig. 3 and 4, respectively. High hetero atom content of up to nine hetero atoms of the detected compounds using APPI and LDI is shown in Fig. 5. Average hetero atom number of 2.7 using LDI was slightly lower than using APPI with 3.3. DBE vs. C plots of the S_1, S_2 and S_3 classes are shown in Fig. 6. A decrease in the H/C ratio was observed with number of sulfur atoms of main classes S_x and N_1S_x (Fig. 7). High aromaticity with an average H/C ratio were 1.014 and 0.876 using APPI and LDI, respectively. High sulfur content was consistent with results of elemental analysis with a sulfur content of 6.8 % and a H/C ratio of 1.035.



Average H/C ratio of all compounds detected by APPI and LDI was 1.014 and 0.876, respectively. H/C ratio of elemental analysis was 1.035.

Fig. 7: H/C *vs.* sulfur content plot of the a) S_x class and b) N_1S_x class detected by APPI and LDI. H/C ratio is decreasing with hetero atom content of both main classes S_x and N_1S_x.

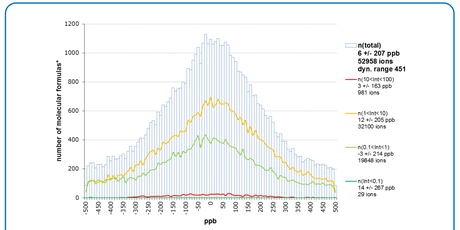


Fig. 2: Mass error distribution plot of the APPI measurement of the asphaltene sample. More than 52.000 different molecular formulae (incl. ^{13}C peaks) could be detected.

Table 1: Elemental analysis of the asphaltene sample.

Sample	C (wt. %)	H (wt. %)	N (wt. %)	S (wt. %)
Asphalt.	81.78	7.06	1.17	6.82

Conclusions

- High amount of vanadyl porphyrins (roughly 1%) were detected by LDI and APPI.
- High hetero atom content of the detected compounds were observed with average hetero atom content of 2.7 and 3.3 using LDI and APPI, respectively.
- High aromaticity of detected compounds is in good agreement with elemental analysis.

Petroleomics