Direct coupling of normal-phase HPLC to atmospheric pressure laser ionization FT-ICR MS for the characterization of crude oil samples

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Experimental Section

Sample and chemicals

A nitrogen-rich crude oil sample obtained from Shell was deasphalted by diluting 20 µL of the crude with 100 µL dichloromethane, followed by subsequent addition of 6 ml of n-hexane. The content was sonicated for 30 min, left standing overnight at room temperature, and filtered to give the maltenes fraction. Chemicals used for sample preparation and solvents for the chromatographic separations are of HPLC grade and supplied by Sigma-Aldrich (Taufkirchen, Germany).

Liquid Chromatography

The chromatographic separations were performed on a stationary phase of polar aminocyano-bonded silica column (5 µm, 250 X 2.0 mm) (Göhler Analysentechnik, Chemnitz, Germany). A gradient of n-hexane (HEX) with isopropyl alcohol (IPA) was used as the mobile phase. An increase of the isopropyl alcohol concentration was achieved according to the following stepwise gradient: 100% HEX (0-5 min), 99.5% HEX+0.5% IPA (5-10 min), 99% HEX + 1% IPA (10-15 min), 98% HEX + 2% IPA (15-20 min), and 95% HEX + 5% IPA (20-25 min) and then returned to 100 % n-hexane until 30 min.

All experiments were performed on an Agilent 1100 HPLC system (Agilent technologies, Waldbronn, Germany). Eluents were degassed before and during the experiments and were pumped at a flow rate of 1 mL/min. All tubing and fittings were of stainless steel. 1 µL of the deasphalted crude oil was injected by an autosampler onto the

chromatographic column, which was kept at room temperature and was connected to a diode array UV detector set at wavelength λ = 254 nm. For offline measurements, fractions were collected from the outlet of the detector in 20 seconds segments from 0.6 – 3.0 minutes of retention time. From 3.0 minutes on, one-minute fractions were collected. The fractions that were collected every minute were concentrated to ca. 0.5 mL by removing the volatile n-hexane with a stream of argon. For online measurements, the outlet of the UV detector was connected to the mass spectrometer by using PEEK capillaries equipped with a micro-splitter to control the flow rate of the eluent, which was adjusted to 100 µL/min.

High-resolution mass spectrometry

Mass spectra for online and offline measurements were obtained using a 12 T LTQ FT-ICR MS (Thermo Fisher, Bremen, Germany) equipped with a home-built APLI source.[1] Pulsed laser radiation (50 Hz, 10mJ) was obtained from a KrF* excimer laser (ATL Lasertechnik GmbH, Wermelskirchen, Germany), radiating at the wavelength of 248 nm. A commercial APCI sprayer (Thermo Fisher, Bremen, Germany) was used to introduce the sample to the mass spectrometer without the use of a corona needle. The sample was vaporized in the heated nebulizer at 300 °C with a stream of nitrogen as sheath gas. The generated cloud was ionized with the laser beam, positioned between the MS orifice and the exit of the ion source. The resolving power for online measurements was around 200000 at m/z 400.

Additional offline measurements were performed on a research type LTQ-Orbitrap capable of operating with 3 s transients. All obtained offline spectra exhibit an average mass resolving power of 750k (at m/z 400). The ionization conditions were kept the same as for the online mode. The sample was injected through the APCI nebulizer at a flow rate of 25 µL/min and was measured in the positive mode. The different fractions were diluted in toluene to a final concentration of 100 ppm. The measurements were carried out with a transfer capillary temperature of 275 °C, a skimmer voltage of 33 V, and a tube lens voltage of 125 V. The spectra were acquired with a mass range of m/z 150-1000 and processed with the LTQ FT Ultra 2.5.5 (Thermo Fisher) data acquisition system. For online measurements between 3 and 5 microscans were set resulting in a scan rate of one spectrum every 3 s.

Data analysis

Mass spectra were externally calibrated which resulted in a mass accuracy better than 1 ppm (0.77 and 0.65 ppm on average for offline and online measurements, respectively). The peak lists were converted to molecular formulae by Composer software package (Sierra Analytics, USA), and controlled using Xcalibur software (Thermo Fisher, Bremen, Germany). The following chemical constraints were applied:

Number of H unlimited, 0<C<200, 0<O<2, 0<N<2, 0<S<2, 0<DBE<40. The calculated molecular formulae were controlled by sorting them into compound classes based on Kendrick mass defects and their DBE distribution.[2] The obtained mass lists were transferred into Excel and Origin for data evaluation and presentation of the figures shown. For selected ion monitoring (SIM) measurements, the peak list was exported directly from Xcalibur into Excel sheets, where multiple sorting based on the Kendrick scale was applied in order to group different classes of compounds according on the hetero-element present.[3]
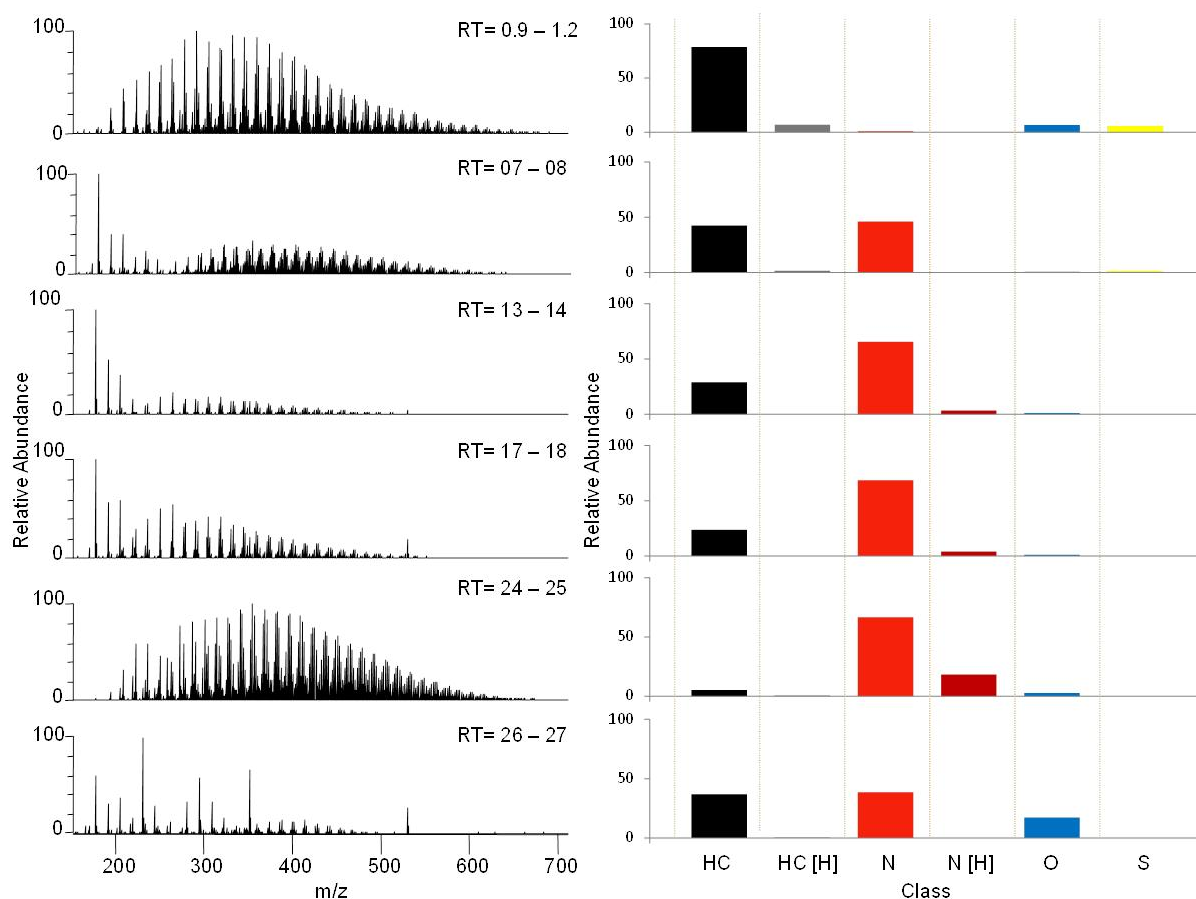

Figure S1. High resolution mass spectra of offline HPLC fractions of deasphalted crude oil obtained in positive APLI ionization mode at different retention times (left column) and the corresponding compound class distribution illustrated as relative abundance (right column). (Protonated molecules are denoted using [H], while the cation radicals are shown without [H]).
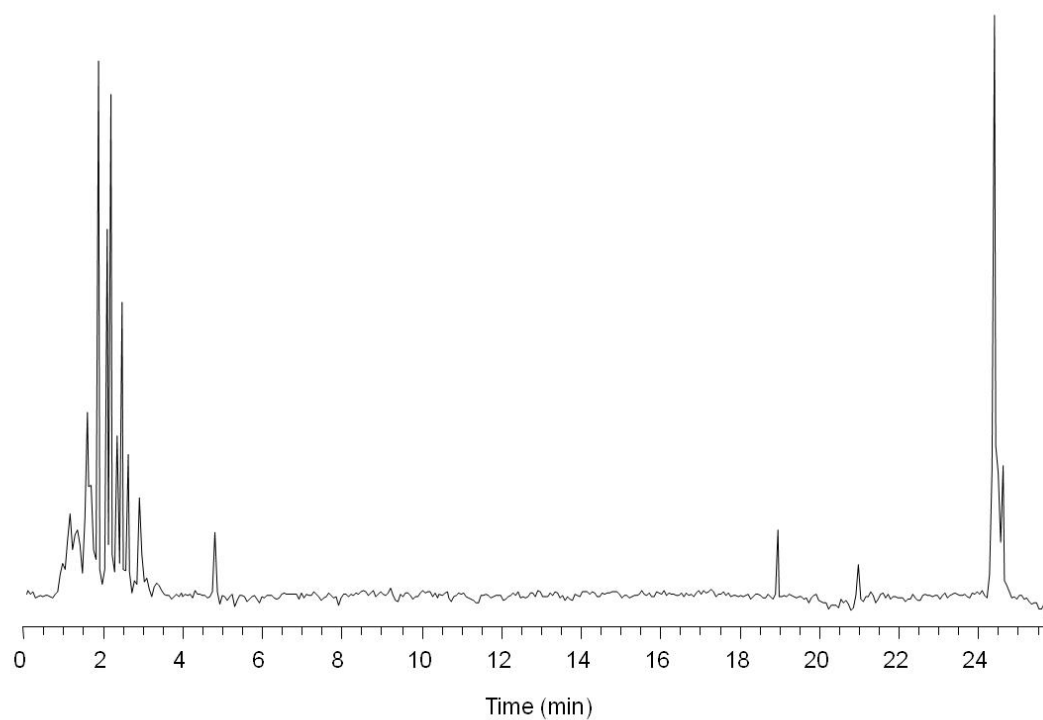
Figure S2. Total ion chromatogram of the online HPLC/APLI-FT-ICR MS measurement.

References

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