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Comparison of Xe/Kr atmospheric pressure photo ionisation (APPI) to atmospheric pressure chemical ionisation for the analysis of complex mixtures

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Introduction

Mass spectrometry is an ubiquitous analytical technique for analysis of complex samples from all research areas. The high resolving power and mass accuracy of FT-MS based techniques allow a comprehensive analysis. Nonetheless, non-targeted analysis often aims to cover a wide chemical space. Especially atmospheric pressure chemical and photo ionisation (APCI/APPI) [1] are widely used. The ionisation in API sources is most often based on a complex reaction cascade [2]. In this study, a light crude oil (CPC-Blend) was investigated for comparing gas phase ionisation mechanisms of complex mixtures. The study was carried out without using any solvents or dopants.

Method

In this study, APCI was compared to APPI utilizing a Xenon lamp with photon energies of 8.4/9.6 eV and a classical APPI utilizing a Krypton lamp with photon energies of 10/10.6 eV. For this purpose, a modified gas phase API source (based on Bruker GC APCI II) was used, which discard solvent effects. Sample was introduced as evolved gas from coupling of the gas phase API source to a thermo balance via a heated transfer line and interface (Figure 1). The mass spectrometric analysis was conducted on a Bruker apex II ultra FT-MS equipped with a 7 T superconducting magnet, which allows an in-depth analysis of the occurring effects. Besides standard mixtures consisting of fatty acid methyl esters and polycyclic aromatic hydrocarbons, various petrochemical samples and thermal decomposition products (pyrolysis) of different wood types as well as polymers were investigated.

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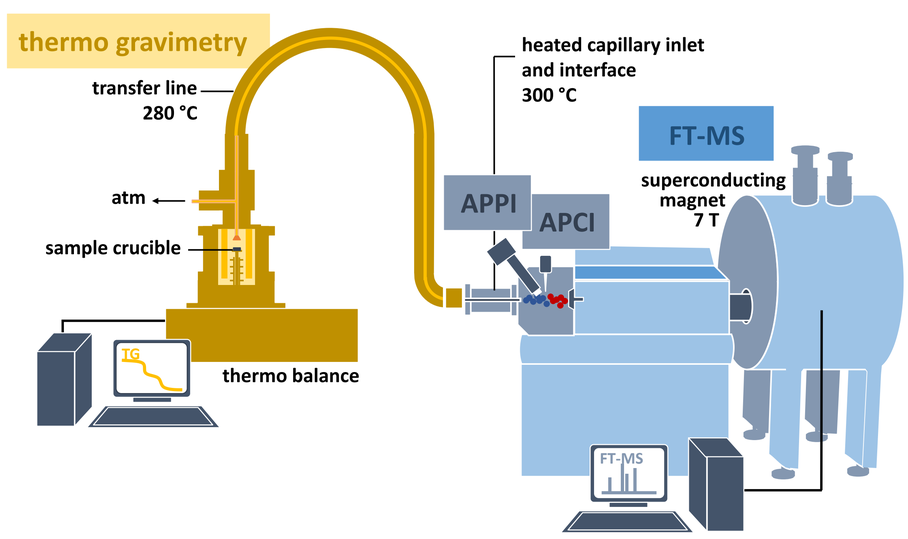

Fig. 1. TG FT-ICR MS set-up [3] utilized for studying (+)-Kr-APPI, (+)-Xe-APPI and (+)-APCI.

Results and Discussion

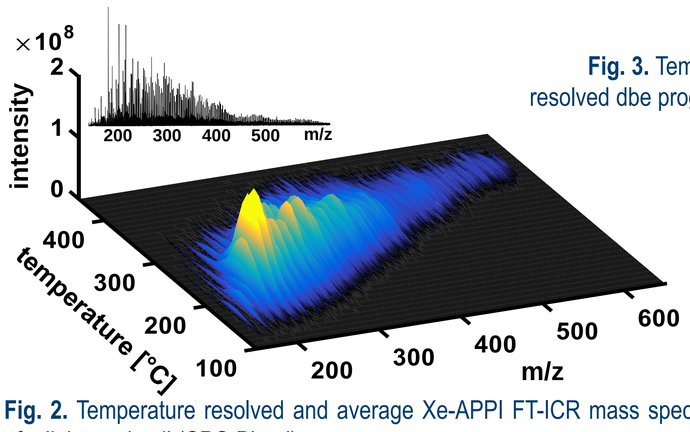

Fig. 2. Temperature resolved and average Xe-APPI FT-ICR mass spectrum of a light crude oil (CPC-Blend).

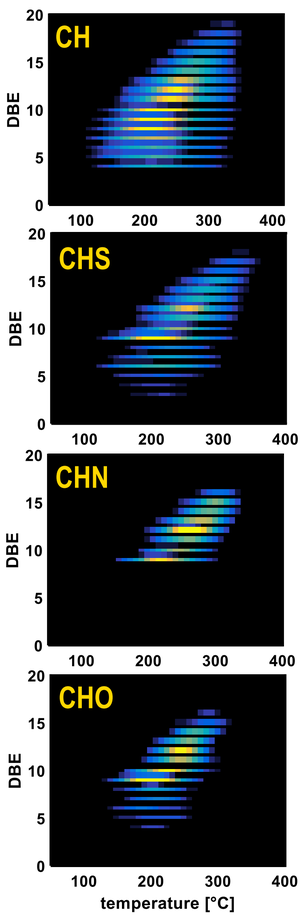

Fig. 3. Temperature resolved dbe progression.

Based on the pyrolysis of polystyrene (not shown here), it turned out that also with Xe-APPI a broad oligomeric pattern up to the pentamere (*m/z* 518) can be observed. Interestingly, the pattern changes drastically from APCI to APPI. Despite the fact that all decomposition products are pure hydrocarbons, other species are ionized more efficiently in Kr- and Xe-APPI. This effect was also observed for distillation cuts of a crude oil. Analysis of the elemental composition assignments reveal a clear shift of the distribution between protonated (even) and radical cations (odd). APCI revealed mostly protonated ions for all investigated samples, whereas APPI give mostly radical ions. The proportion of odd-species was even higher for Xe-APPI.

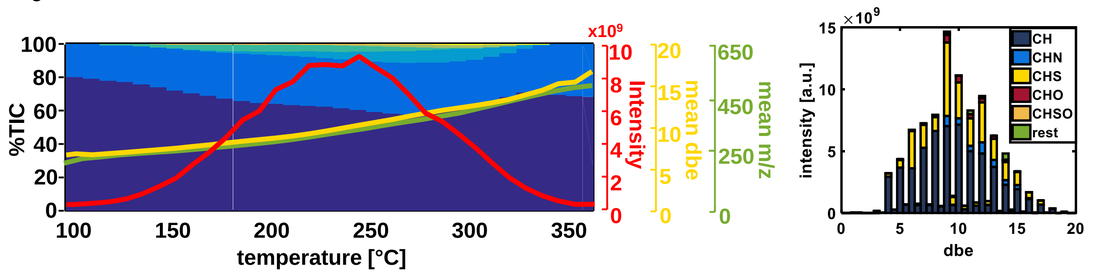

Fig. 4. left. Temperature resolved Compound classes (CH, CHS, CHN, CHO, CHSO, rest) total ion count (TIC), mean dbe and mean *m/z* progression. **right**. DBE distribution for an average mass spectrum.

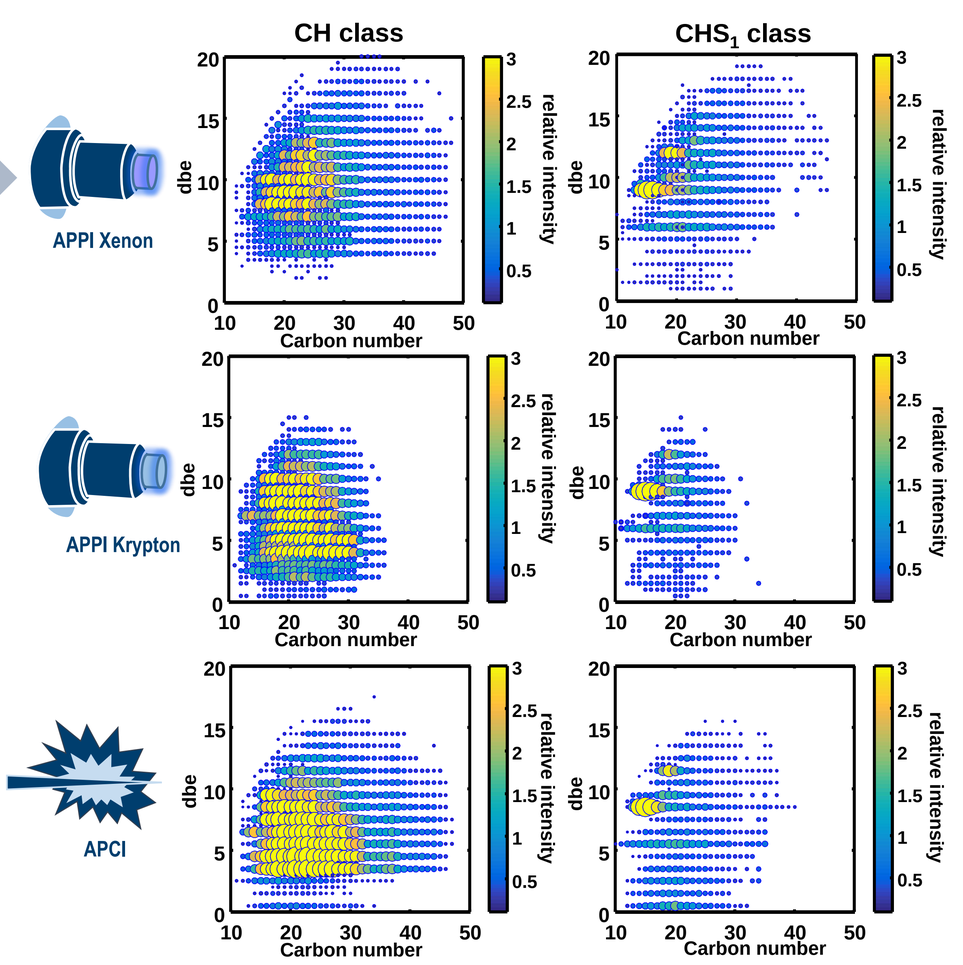

Fig. 5. Dbe versus carbon number diagrams for a light crude oil measured with APCI and APPI-Kr/Xe FT-ICR MS.

Distinct differences are exhibited utilising the time resolved dbe distribution of several compound classes. Nitrogen-containing species generally reveal a higher dbe with dbe 9 and 12, most probably carbazol-derivatives, the most abundant series, whereas the CH- and CHS-class cover a broader range from dbe 4 up to 19. The double bond equivalent versus carbon number diagrams reveal a shift of the distribution towards higher dbe values for Xe-APPI compared to Kr-APPI and APCI.

Conclusion

In summary, the lower energy flux of Xe-APPI will result in a lower ionisation efficiency and higher limit-of-detection. Nonetheless, for investigations where sensitivity is not the most important aspect Xe-APPI can be deployed and the absence of protonated compounds leads to a further simplification of the spectra, in particular, concerning the trouble-some 1.1 mDa split (^{13}C vs. M+H). This aspect is of high interest for ultra complex samples, such as in Petroleomics.

Literature

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[2] Huba, Huba et al., Science of the Total Environment, DOI: /10.1016/j.scitotenv.2016.06.044
[3] Rüger, C. P.; Miersch, T.; Schwemer, T.; Sklorz, M.; Zimmermann, R. Analytical chemistry 2015, DOI: 10.1021/acs.analchem.5b00785

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