

# Comparison of Xe/Kr atmospheric pressure photo ionisation (APPI) to atmospheric pressure chemical ionisation for the analysis of complex petrochemical 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 often based on a complex reaction cascade [2]. In this study, standard substances and a light crude oil were investigated for comparing gas phase ionisation mechanisms of complex mixtures. The study was carried out without using any dopants.

## Results and Discussion

Fig. 1. Maximum intensity for radical cations and protonated ion species for each of the tested standard components. Settings were adapted for comparable spectra due to different ionisation efficiency of the techniques.

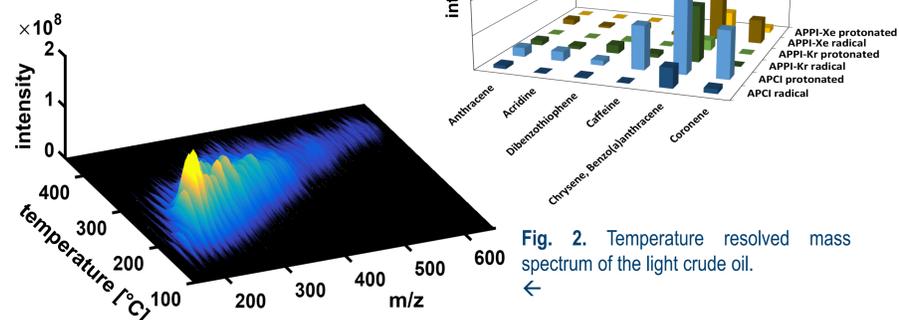


Fig. 2. Temperature resolved mass spectrum of the light crude oil.

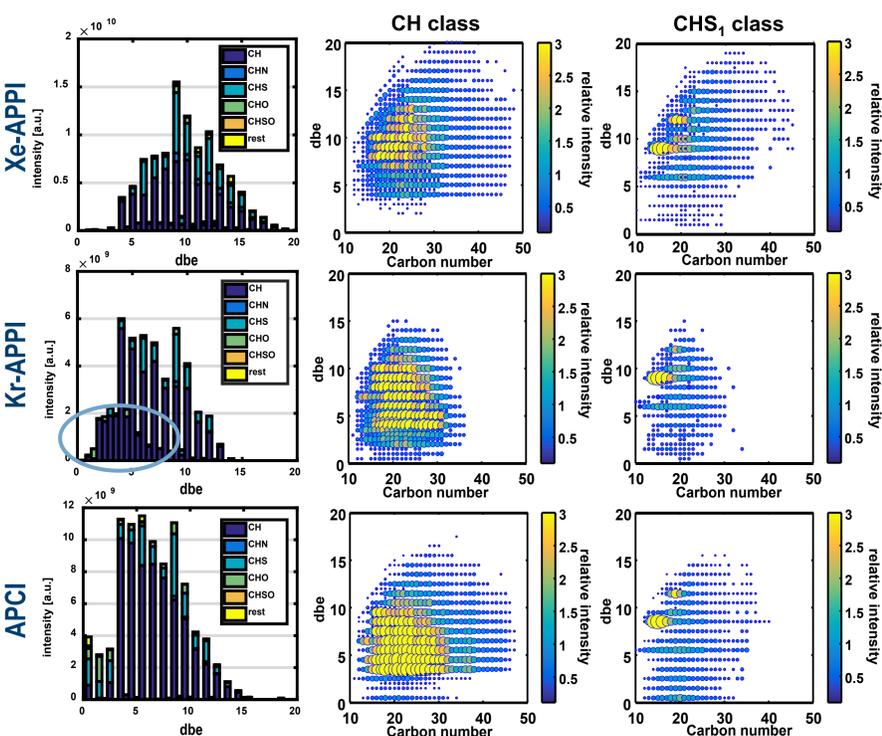


Fig. 3. Stacked bar plots for different compound classes showing the radical cation and protonated ion distribution (left) as well as dbE versus carbon number diagrams (middle, right) for a light crude oil measured with APCI and APPI-Kr/Xe FT-ICR MS.

## 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 a important aspect, Xe-APPI can be applied. The absence of protonated compounds leads to a further simplification of the spectra, in particular, concerning the problematic 1.1 mDa split ( $^{13}\text{C}$  vs. M+H). This aspect is of high interest for ultra complex samples, such as in Petroleomics.

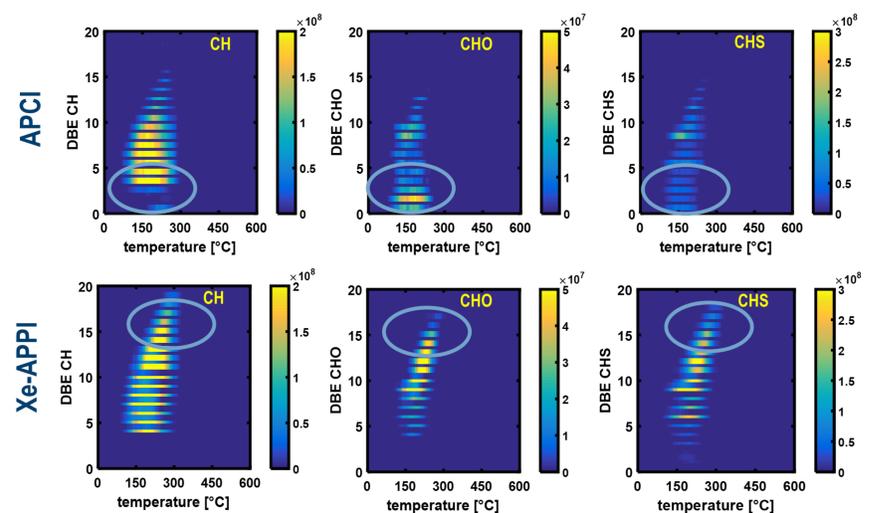
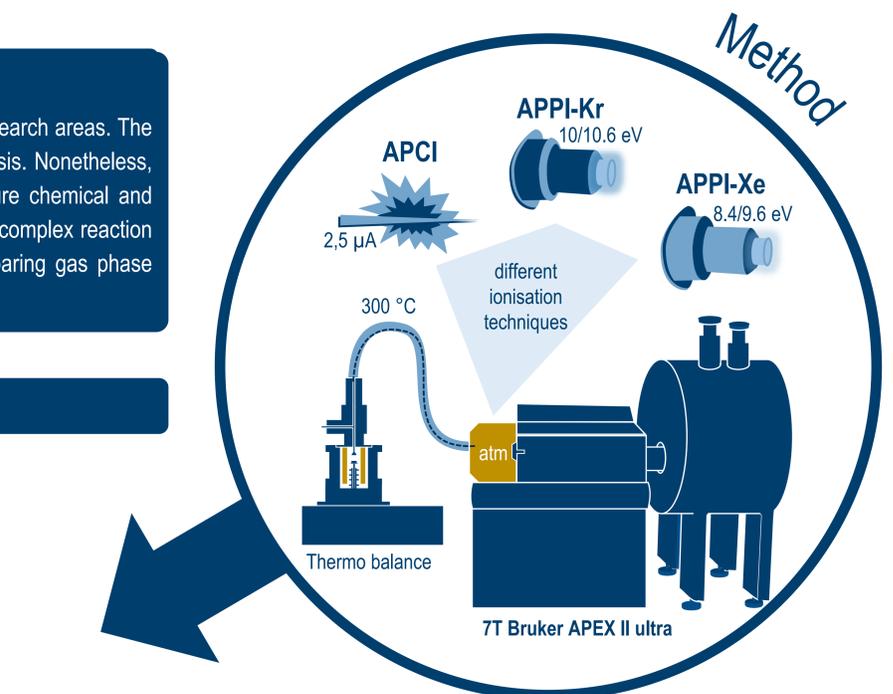


Fig. 4. Temperature resolved dbE plots for different compound classes for APCI- and Xe-APPI-FT-ICR MS.

The high resolving power of FT-ICR MS enables differentiating between radical cations and protonated ions in complex mixtures. The investigated techniques showed distinct differences in the ion type formation:

### APCI:

- mostly protonated species for all compound classes
- low dbE compounds can be ionised better

### APPI-Kr:

- protonated species as well as radical cations, especially for low dbE CH-compounds

### APPI-Xe:

- mostly radical cations for all compound classes
- cut off at dbE 4, better ionisation of high dbE species

In general: For higher molecular species, more radical cations than protonated species were found.

## Literature

- [1] Li et al., Analytica Chimica Acta, DOI: 10.1016/j.aca.2015.08.002
- [2] Huba, Huba et al., Science of the Total Environment, DOI: /10.1016/j.scitotenv.2016.06.044
- [3] Rüter, C. P.; Miersch, T.; Schwemer, T.; Sklorz, M.; Zimmermann, R. Analytical chemistry 2015, DOI: 10.1021/acs.analchem.5b00785