

# Comparison of atmospheric pressure chemical ionisation and electron ionisation for the analysis of persistent organic pollutants

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## Introduction

There is an increasing level of interest in the use of atmospheric pressure chemical ionisation (APCI) mass spectrometry for the analysis of persistent organic pollutants in environmental samples [1,2,3]. This technique has shown the potential to be highly sensitive when compared to the traditional use of an electron ionisation (EI) as a source of ions. One of the principal reasons for the increase in sensitivity is due to the relatively soft nature of APCI, resulting in significantly less in-source fragmentation of the molecular ion. This study aims to quantify these differences for a range of persistent organic pollutants, and investigate the impact of various changes to source conditions on the spectra of the compounds.

## Methods and Materials

Comparisons were made using an APCI source (APGC) on a tandem quadrupole instrument (Xevo TQ-XS) and an electron ionisation source tandem quadrupole mass spectrometer (modified Quattro Micro GC). Additional spectral data was gathered on an APGC Q-IMS-ToF (Synapt G2-S), as well as an experimental EI source fitted to a Q-IMS-ToF (Synapt G2). Samples analysed include polybrominated diphenyl ethers (PBDE), polychlorinated biphenyls (PCB) and polychlorinated dibenzo-p-dioxins and furans (PCDD, PCDF), in addition to various pesticides and novel brominated flame retardants. The influence of source conditions including electron energy, source temperature and corona current were evaluated to determine the effect on the spectra of these species.

## Results and Discussion

Data acquired on the EI Q-IMS-ToF showed that dioxins exhibit around 45% intact molecular ion and furans around 55%, with little variation with chlorination level. The equivalent APCI spectra demonstrated more than 95% relative abundance of the molecular ion of tetrachlorinated dioxins and furans, and greater than 90% for the octachlorinated species.

For polychlorinated biphenyls, the EI Q-IMS-ToF data showed increasing fragmentation with chlorination level, with tetrachlorinated biphenyls showing 60% intact molecular ion and heptachlorinated biphenyls showing only 44%. The APCI source gave a molecular ion relative abundance of greater than 95% for all chlorination levels, with some congener specific variability.

With the EI tandem quadrupole, a significant reduction in the relative abundance of the molecular ion, (when compared to the in-source fragment species) was observed for increasing bromination levels of PBDEs, with the decabrominated spectrum showing less than 5% molecular ion. For the APCI source tandem quadrupole, the molecular ion comprises of over 80% of the total signal observed regardless of bromination level.

The increased relative abundance of the APCI source provides a significant improvement in the limit of detection for targeted MS/MS analysis on the tandem quadrupole, when compared to using an EI source. The APCI source also demonstrates protonation for certain species, if the source conditions are adequately controlled. This provides three possible modes of operation: charge transfer, protonation and mixed mode, all of which can be used for quantitative analysis dependant on the analyte requirements.

## References:

1. ten Dam G et al (2016) *Journal of Chromatography A*.
2. Portolés T et al (2015) *Analytical Chemistry*, **87**, 9892-9899
3. van Bavel B et al (2015) *Analytical Chemistry*, **87**, 9047-9053