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Gas chromatography hyphenated to (ultra-)high resolution mass spectrometry for the analysis of complex matrices

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Background and objectives

Complex matrices require highly selective analytical methods for a comprehensive analysis. In the case of gas chromatography – mass spectrometry (GC-MS), the selectivity of the system is mainly depended on the ability of the chromatography to separate compounds, and the resolution and acquisition rate of the mass spectrometer. While common instrumentation from different vendors combines GC or GCxGC with fast time-of-flight MS technology of unit resolution, nowadays state-of-the-art approaches are moving towards high or even ultra-high mass spectrometry. While previous TOF technology allows high mass resolution at acceptable acquisition rates, the hyphenation of Fourier Transform Ion Cyclotron Resonance (FTICR) technology has to overcome the lack of suitable interface technology and limited acquisition rates. Recently developed, and now available, is folded flight path (FFP) time-of-flight technology (LECO Inc., St. Joseph, USA) which provides high sensitivity, fast acquisition rates and ultra-high resolution. This opens up new possibilities for the analysis of complex matrices with GC-MS.

Setup 1: GCxGC-(EI)-fast high resolution oaTOFMS:

The ZOEX FastTOF™ GCxGC-TOFMS consists of an Agilent 7890 GC equipped with a ZOEX ZX2 thermal modulator hyphenated to a TOFWerk HTOF. A resolution of 4.000 – 5.000 with an accuracy of <20 ppm could be achieved with external tuning and an acquisition rate of 100 Hz. Electron ionization at 70 eV was used for ionization.

→ The resolving power of the system is high enough to distinguish between small isobaric fragments containing heteroatoms like oxygen.

→ The system is also fast enough for GCxGC-MS experiments.

→ The resolution of the orthogonal acceleration (oa)TOF is mainly limited by the ion flight path length of 1.2 m which is not enough to determine the elemental composition of heavier fragments or most molecular ions.

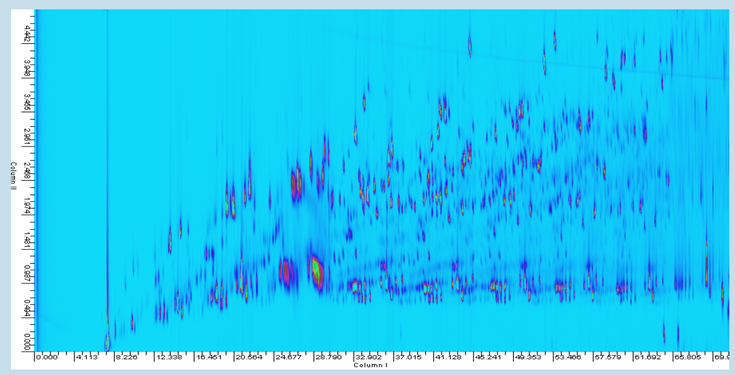

Fig. 1: GCxGC-HRTOFMS of a Fischer-Tropsch Oil. Oxygenated compounds could be located combining exact mass information from HRTOF and grouping of the compounds in GCxGC.

Setup 2: GC–(APCI)-ultra high resolution FTICR-MS:

A one dimensional gas chromatograph was hyphenated to a 7 Tesla Bruker Solarix FTICRMS system by Atmospheric Pressure Chemical Ionization (APCI). For the selected compounds (see Fig. 2) a resolution of 120.000 – 150.000 was achieved with an acquisition rate of about 0.7 Hz.

→ Ultra high mass resolution allows for the calculation of the elemental composition of the ions. For the creation of molecular formulas additional information from GCxGC-TOFMS (unit mass resolution, data not shown) and reaction pathway were used.

→ The assignment of the molecular ion is complicated due to fragmentation and the appearance of chemical reactions within the source.

→ Resolution and data acquisition rate are inversely related. Some of the compounds could not be separated due to very slow acquisition rates.

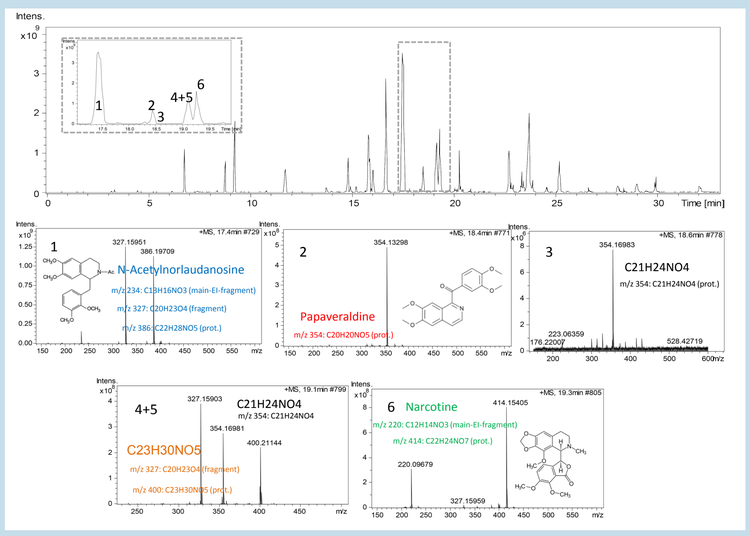

Fig. 2: GC-(APCI)-FTICR-MS of a forensic extract to identify possible impurities.

Setup 3: GC-(EI)-ultra high resolution oaTOFMS:

Different forensic, metabolomic and petrochemical matrices were analyzed with LECO- Pegasus HRT-TOFMS in high resolution (25.000) and ultra high resolution (50.000) mode with an optimized acquisition rate of 12 Hz.

→ Acquisition rate is optimized by the system automatically. A maximum acquisition rate of 200 Hz is achievable. Fast acquisition rates allow for proper deconvolution of most compound spectra.

→ Elemental composition could be calculated for all ions.

→ Fragmentation patterns (70 eV electron ionization) provide information about isomeric compounds.

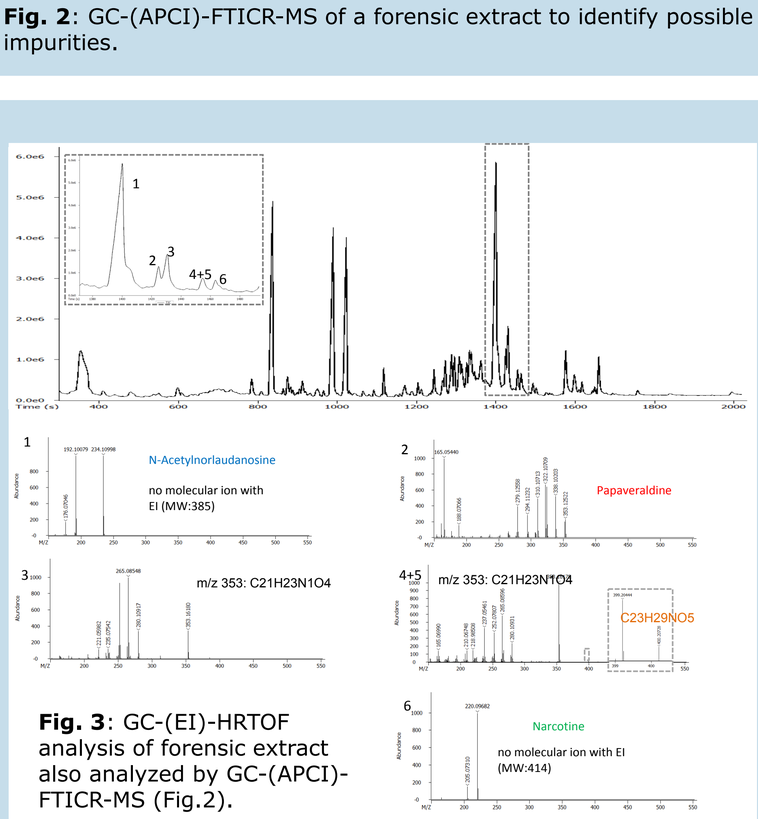

Fig. 3: GC-(EI)-HRTOF analysis of forensic extract also analyzed by GC-(APCI)-FTICR-MS (Fig.2).

Conclusions

Very fast high resolution oaTOF as well as ultra high resolution FTICR-MS technology could be hyphenated with GC(xGC) for a more advanced comprehensive analysis of complex matrices. Furthermore the recently introduced LECO FFP technologies combines the advantages of both technologies namely fast acquisition rates and ultra high mass resolution.

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