GC-MS Performance of a Novel Capillary Atmospheric Pressure Chemical Ionization (cAPCI) Source

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Introduction

State of the Art:

- Atmospheric Pressure Chemical Ionization (APCI):
  - Charge exchange reactions produce proton-bound water clusters [H₂O]⁺⁺ (generally proton bound sodium clusters [NaH₂O]⁺⁺) as reactant ions [1].
  - Reactant clusters either directly interact with the analyte by ligand switching or association reactions, respectively, or further dissociate in the intermediate pressure regions within the ion transfer stages of the mass spectrometer via electrical driven collisional desorption reactions [1].
- In common APCI source generation of additional ion signals in the observed mass spectra due to oxidation or other ion transformation processes is often observed.

Capillary Atmospheric Pressure Ionization (cAPCI) Sources:

- Fluid dynamic conditions in common APCI sources are often complex and difficult to control [2].
- As a consequence the operation points of classical APCI sources tend to be unstable.
- Ionization within such sources potentially leads to memory effects, poor reproducibility, and signal fluctuations due to extended ion transformation processes resulting from the large reaction times within the source.
- cAPCI sources spatially separate the primary ion generation region from the analyte gas flow, thus the direct contact of the analyte and e.g. the hot corona discharge region is avoided.
- Due to the turbulent flow in the inlet capillary vigorous analysis/reagent ion mixing leading to efficient chemical ionization.
- APCI sources are designed with the aim of well controlled operational conditions (see WMP268) such as:
  - gas flows, gas temperature, primary ionization region, ion-molecule reaction region.
- Challenge:
  - Development of a highly stable ion source within the inlet capillary using protonated water clusters [(H₂O)⁺⁺] in reagent ions, thus minimizing corona ion signal.
  - Determination of the analytical performance of a cAPCI source coupled to a gas chromatographic (GC) stage.

Methods

Experimental Setup

- Capillary Atmospheric Pressure Chemical Ionization (APCI) Source:
  - Reactive ion generation by corona discharge source using liquid point electrode (see WMP 274)
  - Well established reactant ion equilibrium distribution [(H₂O)⁺⁺] (4 eV) [3].
  - Reactive neutral species potentially generated in the hot plasma region recombine or react before they can interact with the analyte.
- Temperature controlled metal extension of the MS inlet capillary.
  - Adjustable APCI source temperature (RT – 150 °C).
  - Due to the small inner diameter of the source the gas velocities are kept high.
- Mixing of two different gas flows inside the capillary extension
  - Shaped gas embedded GC flow carrying the reactive analyte (GC tranferline temperature approx. 250 °C).
  - Regulated nitrogen flow (N₂) including fully thermalized and equilibrated reactant ions.
- Inlet capillary is used as reaction chamber for chemical ionization.
- [M+H]⁺ is the dominant ion signal in the mass spectron.

GC Coupling:

- Re-design of the commercially available transferline (TT1) for the Bruker Multi purpose Atmospheric Pressure Ion Source (MPS) [4].
- Extension of the heated GC column enclosure with a metal channel matching the inlet capillary diameters at the exit.
- Neutral analyte embedded in the adjustable sheath gas flow is thus injected into the capillary gas flow at high velocity.
- Analyte loss at the walls and peak broadening is minimized.
- Depending on the individual settings the analyte dwell time in the gas transfer region is in the order of milliseconds.

Results

- Table 1: List of analyte present in the GC-ESI source (Fig. 2).

Conclusions

- Novel corona discharge source was successfully implemented (cAPCI source).
- GC-MS performance of the cAPCI source was investigated:
  - Signal dependency on sheath gas flow needs further investigations.
  - Ion source temperature appears to be of minor importance for the performance of GC-APCI.
  - High gas velocities and envelope of gas within the source reduce ion interaction with the walls to a minimum.
- Hardly any fragmentation or other common ion transformation processes encountered with classical APCI occurs; [M+H]⁺ is the dominant ion signal.
  - Reactive species (e.g. OH radicals) do not reach the analyte mixing region.
  - Exclusively soft ionization by proton bound clusters.

Future research:

- Gas flow of GC-FID and GC-APCI-MS measurements.
- Reduction of chromatographic tailing.
- Application of different matrices for the reactant ion generation.
- GC coupling of the APCI source.
- Investigations with the APCI source in the negative ion mode.

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References


Figure 1: Schematic of the experimental setup of the GC-cAPCI stage.

Figure 2: Gas chromatogram of the GC-ESI source containing 11 analytes (see Table 1). (a) GC-APCI source coupled to TOF MS in sheath gas flow and a source temperature of 180 °C. (b) GC-APCI source coupled to TOF MS in sheath gas flow and a source temperature of 100 °C.

Figure 3: The ionization efficiency on the signal intensity of the analyte as a function of four different sheath gas flows (source temperature 60 °C).

Figure 4: Bar diagram of sheath gas variation on the signal intensity. The ionization efficiency for three different sheath gas flows (source temperature 60 °C).

Figure 5: Bar diagram of sheath gas variation on the signal intensity. The ionization efficiency for three different sheath gas flows (source temperature 60 °C).