

A Novel Corona Discharge Source with Liquid Point Electrodes

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Introduction

State of Knowledge:

Conventional APCI sources

- Generation of additional ion signals caused by interactions between analyte and highly reactive discharge species is often observed (e.g., leading to oxidation processes)
- Minimizing the direct interaction between the analyte gas flow and the chemically hot corona discharge region is essential for the reduction of unwanted analyte transformation processes
- Ambient conditions (e.g., background gas phase components, temperature, water mixing ratio, etc.) have pronounced influence on the reactant ion formation rate and thus on signal intensity and stability

Corona discharges operated in point to plane geometry:

- Point electrode is subject to bombardment with highly energetic electrons/ions
- Abundant neutral radical formation along with VUV light generation impose further oxidative stress to the surface
- Significant surface degradation
- Oxidation product deposition
- Other adverse effects such as abundant neutral radical generation

Challenge:

1. Reduction of unwanted analyte transformation processes
2. Reduction of ambient conditions on signal stability and ionization efficiency
3. Reduction of wall losses of reactant ions by e.g. diffusion processes
4. Controlled and more efficient generation of reactant ions
5. Prevention of point electrode degradation and thus ionization performance

Methods

Experimental Setup

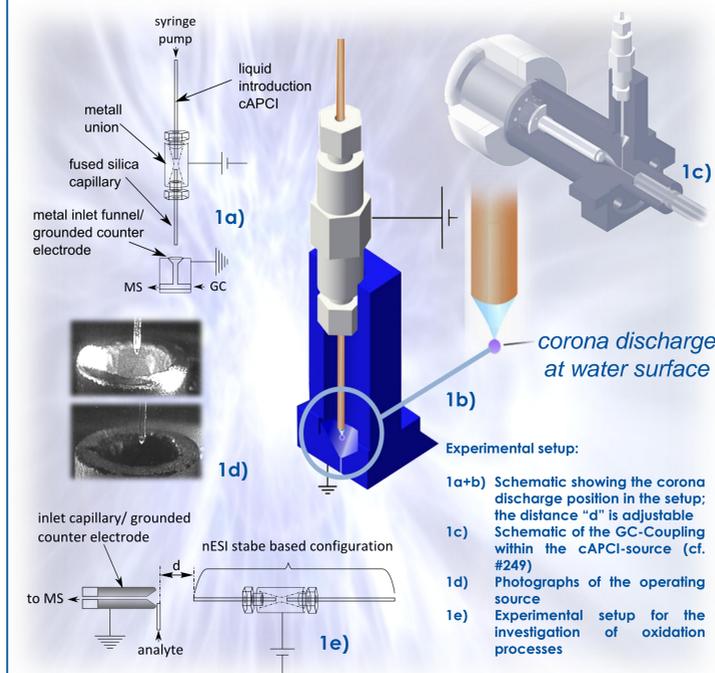
MS: Bruker HCT ion trap; Bruker micrOTOF
Ion Source: Custom built cAPCI source
Discharge Gases: Nitrogen (5.0), Synthetic Air (5.0)

cAPCI Source

Capillary Atmospheric Pressure Chemical Ionization Source:

- Previously presented APCI laminar flow ion source is refined to a capillary based ionization set-up (cf. #MP284)
- nESI stage based configuration using a liquid surface as the discharge point electrode
 - APCI discharge needle is replaced by a fused silica capillary connected to a syringe pump
 - ✓ Temperature dependent liquid flow : ~ 1 $\mu\text{L/h}$ (RT) - 500 $\mu\text{L/h}$ (RT - 450K)
 - ✓ Self-regulated gas flow (N_2 , synthetic air, etc.) within the discharge region
- 0,1% formic acid or 0,1% KOH in millipore water is used as electrode liquid in positive and negative mode, respectively
- Use of an aqueous surface as a continuously replenished corona discharge point electrode surface largely removes any dependence of the ion source performance on ambient operational parameters such as bulk gas humidity
- Highly stable and ultra clean environment for the reaction cascade leading to reactant ion generation in addition to high reactant ion concentrations
- Fully equilibrated reactant ion distribution
- Coupling to the capillary analyte flow by a heated metal funnel (0,5 mm exit ID) acting as plane counter electrode
- Reactive neutral species potentially generated in the hot plasma region recombine or react before they can interact with the analyte flow
- The complexity of the mass spectra is reduced to a minimum as the base signal is always the corresponding $[\text{M}+\text{H}]^+$

Experimental Setup



Liquid Point Electrodes

- By supplying high voltage to a small volume of electrical conductive liquid the surface starts to deform eventually forming a conical shape [1]
- In the case of high surface tension liquids, e.g., water at AP, corona discharges appear on a drop at charges lower than the Rayleigh limit, if the radius of the drop is within a specific region ($5.5 \mu\text{m} < r_{\text{waterdrop}} < 162 \mu\text{m}$) [2]
- Due to the bombardment of the water surface with highly energetic electrons water evaporates and thus the relative humidity of the atmosphere in the air gap spacing increases [3]. Direct ionization of water molecules occurs in addition to the chemical reaction cascade starting with N_2^+
 - Strongly increased, swift formation of primary reagent ions
 - Impact of ambient condition changes is significantly reduced
- Primary reagent ions (e.g., H_3O^+ , N_2^+) fully equilibrate within the background gas phase matrix, resulting in a thermal distribution of ion bound water clusters ($n = 4-9$ [3]), which represent the reagent ion population
- Due to evaporation of water molecules the surface of the point electrode is continuously replenished
 - The reactant ion generation does not suffer from surface degradation due to oxidative stress and bombardment with highly energetic electrons and ions

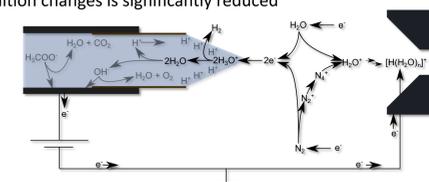


Fig. 1f: Simplified schematic of chemical reactions within the cAPCI source

Experimental Results

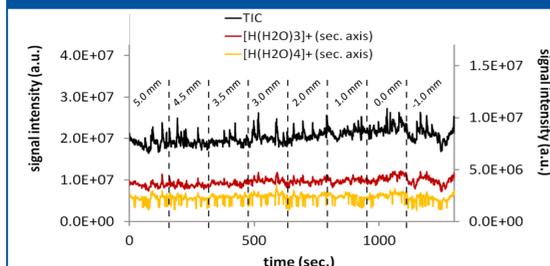


Fig 2a: Dependence of the TIC and the reactant ion population (illustrated by $[\text{H}(\text{H}_2\text{O})_3]^+$ and $[\text{H}(\text{H}_2\text{O})_4]^+$) on relative distance of the hot discharge zone to the analyte addition point.

Effects of the distance between the discharge zone and the neutral analyte addition point on reactant- and analyte ion populations:

The setup shown in figure 1e was used for the investigation of oxidation processes for the purpose of identifying the minimal distance between point and plane electrode in the cAPCI source

- Without analyte addition it is shown that neither the population nor the amount of detected reactant ions is changing by the relative discharge position (see fig. 2a, 2c and 2e)

BUT

- By decreasing the distance between the hot corona discharge region and the neutral analyte addition point the mass spectrum becomes increasingly complex.

- Cutting the distance too short prevents that reactive neutral species, potentially generated in the hot plasma region (e.g. OH, HO_2) have time to recombine or react before they can interact with the analyte. As consequence the $[\text{M}+\text{H}]^+$ signal decreases while additional signals (e.g. $[\text{M}]^+$, $[\text{M}+16]^+$ etc.) increase (cf. fig. 2d).
- At high enough distances only reactant ions in a well defined equilibrium distribution of $[\text{H}(\text{H}_2\text{O})_n]^+$ ($n = 4-9$) do reach the neutral analyte; highly reactive neutral species recombine or react away. Thus no oxidation products are detected and $[\text{M}+\text{H}]^+$ becomes the base signal in the mass spectra recorded.

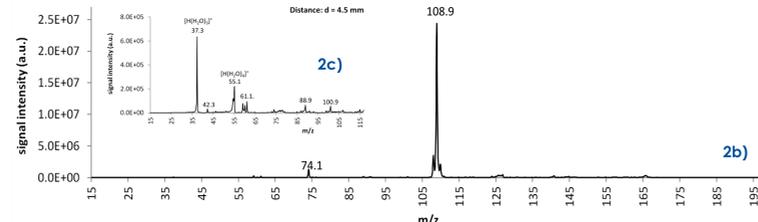


Fig 2b: Mass spectrum of anisole using the setup shown in fig. 1e, d = 5.0 mm
Fig 2c: Mass spectrum without analyte present using the setup shown in fig. 1e, d = 4.5 mm

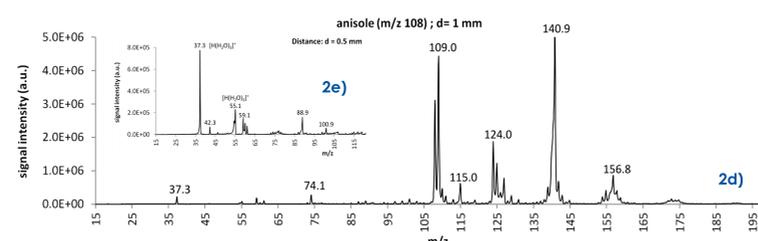


Fig 2d: Mass spectrum of anisole using the setup shown in fig. 1e, d = 1 mm
Fig 2e: Mass spectrum without analyte present using the setup shown in fig. 1e, d = 0.5 mm

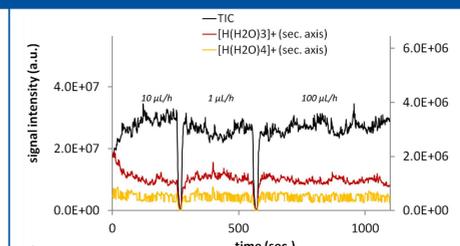


Fig 3a: Dependence of the TIC and the reactant ion population (illustrated by $[\text{H}(\text{H}_2\text{O})_3]^+$ and $[\text{H}(\text{H}_2\text{O})_4]^+$) on the concentration of formic acid in the liquid flow

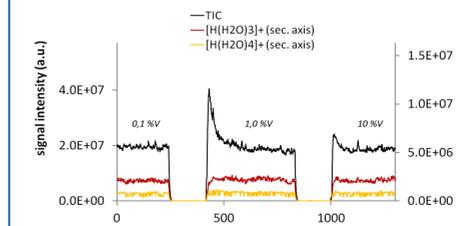


Fig 3b: Dependence of the TIC and the reactant ion population (illustrated by $[\text{H}(\text{H}_2\text{O})_3]^+$ and $[\text{H}(\text{H}_2\text{O})_4]^+$) on the concentration of formic acid in the liquid flow

Effects of the cAPCI Solution Conditions on the Reactant Ion Generation

Neither the liquid flow rate nor the acid concentration noticeably affects the reactant ion generation efficiency (see fig. 3a and 3b). This independency, the observed currents in the low μA range [6], and the cluster ion generation clearly demonstrate that the corona discharge is the main primary ion source [2].

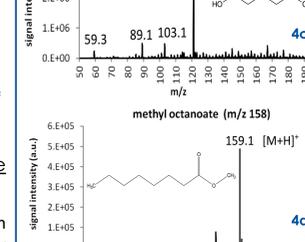
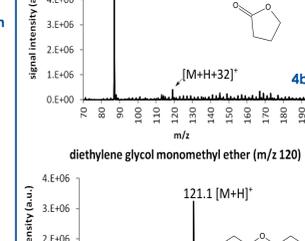
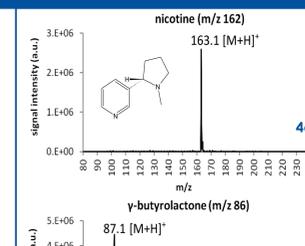


Fig 4: CAPCI mass spectra of nicotine (a), diethylene glycol monomethyl ether (b), diethylene glycol monomethyl ether (c) and methyl octanoate (d)

Conclusions

- Reagent ions added to the analyte flow are fully equilibrated with the background gas phase matrix; reactive neutral species from the hot corona discharge area react or recombine before reaching the analyte flow
 - Unwanted analyte transformation processes are reduced
- Due to the clean and stable matrix within the reactant ion generation region the reactant ion population is easily controlled
 - Due to the locally elevated water concentration within the corona discharge region direct electron ionization of water becomes feasible
 - Controlled and increased generation of reactant ions
- Due to continuously evaporating water molecules the water mixing ratio in the primary corona discharge zone is essentially constant for given operational conditions (p, T, flow rate)
 - Impact of changes of ambient conditions on signal stability are minimized
- Surface degradation due to electron/ion bombardment and oxidative stress of the electrode become negligible due to the continuous replenishment of the point electrode surface
 - Erosion of the point electrode and thus signal dependencies on the surface condition of the electrode are minimized
- Direct coupling of the equilibrated reactant ion population into the analyte gas flow of the transfer capillary of the AP MS
 - Reduction of wall losses of reactant ions by diffusion processes due to long residence times within the ion source
- Extremely user friendly handling of the source

References

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Acknowledgement

Financial support is gratefully acknowledged:
• Bruker Daltonics GmbH (Bremen, Germany)
• iGenTraX UG (Haan, Germany)
• DAAD (Bonn, Germany)