Progress in characterizing capillary Atmospheric Pressure Electron Capture Ionization (cAPECI)

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Introduction

Challenges:
- Development of an ion source with long term stability for analytes with high electron affinity (e.g. nitro compounds, oxygenated PAN) within the inlet capillary duct but without modifying the installed glass capillary (+ Bruker instruments)
- Coupling of GC with cAPECI-MS

Approach:
- Ionization upstream of the inlet capillary leads to ion dwell times > 10 ms and thus potentially to ion transformation reactions
- Modification of the inlet capillary of an API mass spectrometer is possible without affecting the capillary transport properties of unpolar ion currents as long as appropriate materials are used (see results, top right)
- Extending the capillary duct into the ion source retains the short reaction times typical for all capillary ionization methods (cf. postor #MP284)
- Anodized aluminium delivers a high and stable photo electron yield; surface aging/ionization was not observed
- For GC coupling a heated ion source and a matching transferline is required

Experimental Setup

MS: Enquire 6000 QTF, Bruker Daltonik
Ion Sources: Custom capillary ion sources with anodized aluminium as photo emissive material
Radiation: Perkin Elmer Mercury low pressure UV source (λ = 185 nm and 254 nm)
GC: GC 7890A, Agilent Technologies Inc.
Transfline: Custom temperature-controlled GC-transferline
Ion Current: 617 Programmable Electrometer, Measurements Keitley (see #MP278 for setup details)

Conclusions

- cAPECI is an emerging ionization method applicable for analytes with high electron affinity and/or gas phase basicity, such as:
  - Oxygenated PANs
  - Nitro group containing explosives
  - Phenols
- Ionization within a cAPECI inlet capillary strongly reduces ion transformation processes, but decreasing signal intensities with time result
- Constant signal intensities with time are observed for unpolar ion streams for fabically modified inlet capillaries, such as two joined glass capillaries or a metallic capillary segment between two glass capillaries
- Decreasing signal intensities are observed if quartz is part of the inlet capillary
- Using an ion source where the analyte is added to the reagent ions in a channel with the same inner diameter as the inlet capillary gives stable signal intensities and short reaction times
- Anodized aluminum as photo emissive material provides a non-aging surface and thus a stable electron yield with time
- GC-cAPECI measurements are performed with a similar ion source, where a custom built GC-transferline is attached
- GC measurements yield good linearity and narrow peak width (1min/s, to 1µM/L)
- With longer reaction time the oxygen concentration has a large impact on the occurrence of ion transformation products; at atmospheric conditions (20 % O2) many ion transformation products are observed in the mass spectra

Methods

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</table>

Influence of the Oxygen Concentration and the Reaction Time

Intensities of the observed ion signals for approx. 40 µg/mL 2-nitrophenol in dependence of the oxygen concentration; "Target" = sum of all signals except for the M+H+ 152 m/z.

The analysis is added to the main gas stream (synthetic air). The analysis is added to the main gas stream (synthetic air). The analysis is added to the main gas stream (synthetic air).

Analytic gas stream

Mass spectra of 3-methyl-2-nitrophenol with high (20 %) and low (0.2 %) background oxygen concentrations.

For higher oxygen concentrations more ion transformation products are observed. For short reaction times even with 20 % oxygen hardly any ion transformation products occur (cf. mass spectrum in section "ion source").

References

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