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 PAH) *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 ion transport properties of unipolar 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. poster #MP284)

→ Anodized aluminum delivers a high and stable photo electron yield; surface aging/oxidation was not observed

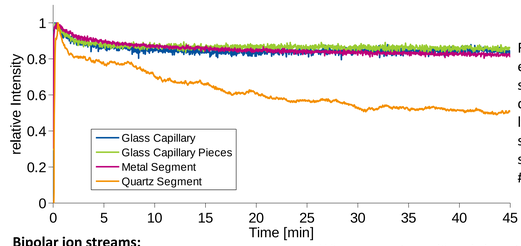
→ For GC coupling a heated ion source and a matching transferline is required

Methods

Experimental Setup

MS	Esquire 6000 QIT, Bruker Daltonic
Ion Sources	Custom capillary ion sources with anodized aluminum as photo emissive material
Radiation Source	PenRay Mercury low pressure UV lamp (λ = 185 nm and 254 nm)
GC	GC 7890 A, Agilent Technologies Inc.
Transferline	Custom temperature-controlled GC-transferline
Ion Current Measurements	617 Programmable Electrometer, Keithley (see #MP278 for setup details)

Ion Source Development



For the experimental setup and an in depth study of long term stability issues see poster #MP278.

Bipolar ion streams:

Ion currents are always constant with time

Unipolar ion streams (as in cAPECI):

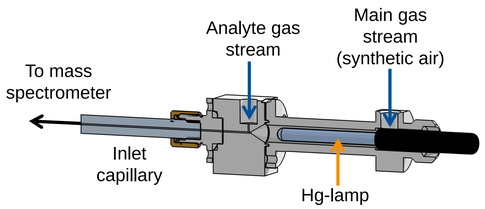
Within minutes stable ion currents for
- Borosilicate (BS) glass inlet capillary
- two connected BS glass capillaries
- metal capillary segment between two BS glass capillary sections

When a quartz capillary is inserted the ion current decreases with time (orange trace).

However:

For cAPECI a UV transparent material is necessary.

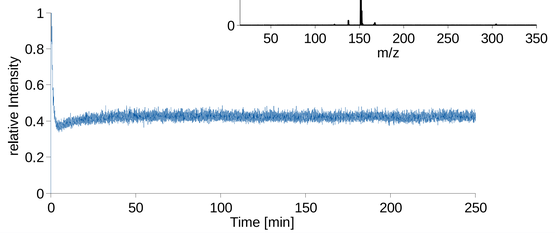
→ **Thus ionization upstream of the inlet capillary is required for stable ion currents**

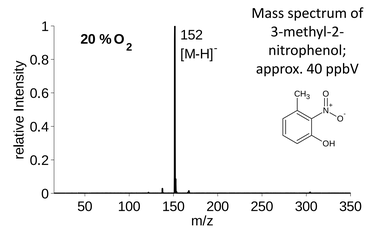


cAPECI: Principle of operation

A UV-lamp inside the ion source provides light at λ=185 nm. The interaction of UV light with the anodized aluminum generates nearly thermalized electrons, which are swiftly captured by oxygen. Thus the primary ions are mainly cluster ions of the type $[O_2(H_2O)_n]^-$.
The analyte gas stream is added where the inner diameter of the ion source exit funnel matches that of the capillary (0.6 mm), resulting in high gas velocities and short reaction times, comparable to that in capillary ion sources.

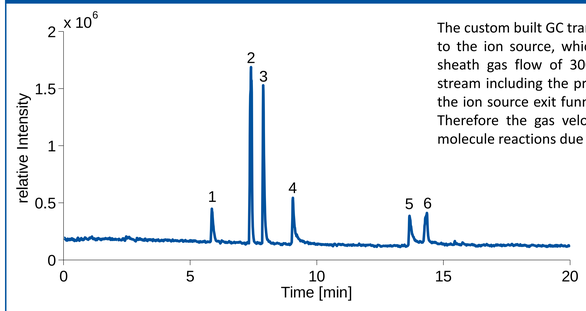
Variation of the signal intensity of cAPECI with time for constant analyte concentration and experimental conditions (see poster #MP278 for the signal decay with the previous ion source design).



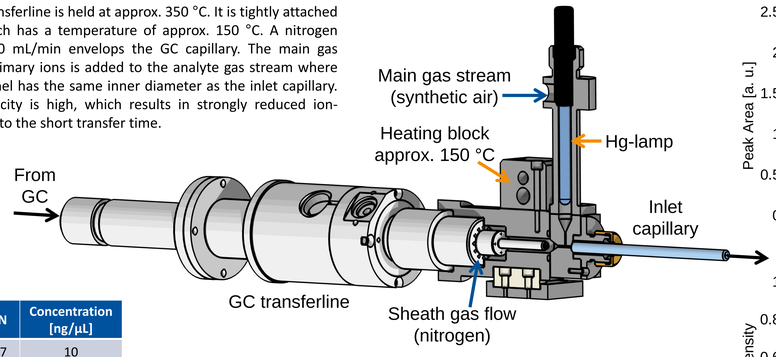


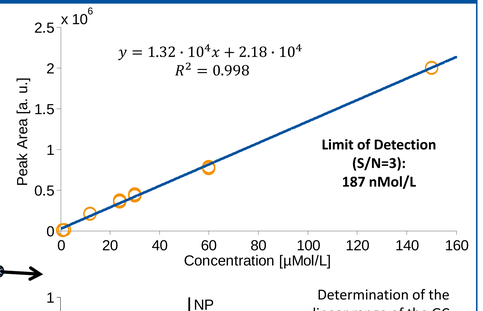
Mass spectrum of 3-methyl-2-nitrophenol; approx. 40 ppbV

GC-cAPECI Measurements



The custom built GC transferline is held at approx. 350 °C. It is tightly attached to the ion source, which has a temperature of approx. 150 °C. A nitrogen sheath gas flow of 300 mL/min envelops the GC capillary. The main gas stream including the primary ions is added to the analyte gas stream where the ion source exit funnel has the same inner diameter as the inlet capillary. Therefore the gas velocity is high, which results in strongly reduced ion-molecule reactions due to the short transfer time.





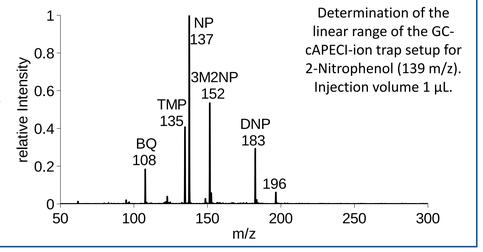
No.	Compound	Abbr.	Molar Mass [g/Mol]	Peak Width (FWHM) [s]	Peak Area	S/N	Concentration [ng/µL]
1	2-Nitrophenol	NP	138	4.8	1045348	427	10
2	2,4,6-Trimethylphenol	TMP	136	2.2	8121439	306	10
3	3-Methyl-2-Nitrophenol	3M2NP	153	2.9	5446208	709	10
4	2,4-Benzoquinone	BQ	108	4.1	2342989	124	50
5	2,4-Dinitrophenol	DNP	184	5.7	1743635	114	10
6	2,4-Dinitrotoluene	DNT	182	7.4	2002459	104	50

Left

GC chromatogram of the six compounds listed in the table. Each compound showed only one signal - either M^- or $[M\text{-}H]^-$, therefore, only the TIC is shown in the chromatogram.

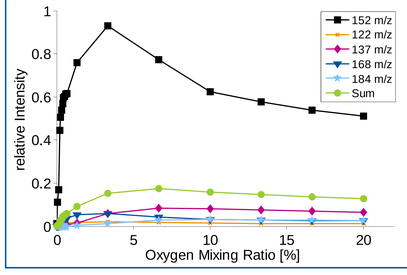
Right

Mass spectrum of the same mixture as in the chromatogram, but without chromatographic separation. Except for 2,4-Dinitrotoluene all analytes are observable with one signal (M^- or the $[M\text{-}H]^-$). The signal at 196 m/z is possibly the oxygen adduct of 2,6-Dinitrophenol.

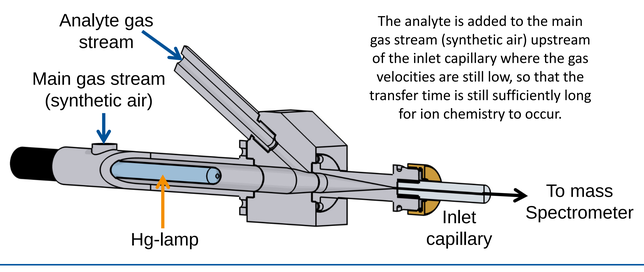


Determination of the linear range of the GC-cAPECI-ion trap setup for 2-Nitrophenol (139 m/z). Injection volume 1 µL.

Influence of the Oxygen Concentration and the Reaction Time

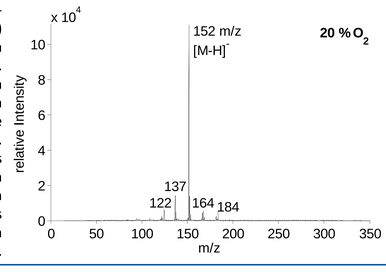


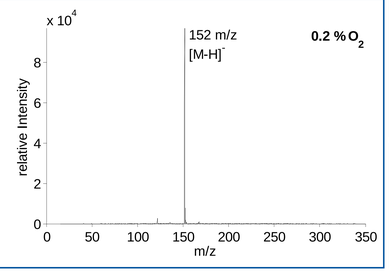
Intensities of the observed ion signals for approx. 40 ppbV 3-methyl-2-nitrophenol in dependence of the oxygen concentration; "Sum" stands for the sum of all signals except from the $[M\text{-}H]^-$, 152 m/z.



The analyte is added to the main gas stream (synthetic air) upstream of the inlet capillary where the gas velocities are still low, so that the transfer time is still sufficiently long for ion chemistry to occur.

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





Conclusions

- cAPECI is an emerging ionization method applicable for analytes with high electron affinity and/or gas phase basicity, such as
  - Oxygenated PAHs
  - Nitrogroup 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 unipolar ion streams for 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 (nMol/L to µMol/L)
- With longer reaction time the oxygen concentration has a large impact on the occurrence of ion transformation products; at atmospheric conditions (20 % O_2) many ion transformation products are observed in the mass spectra

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