Application of capillary Atmospheric Pressure Electron Capture Ionization (cAPECI) for the ultra-sensitive detection of explosives, drugs and environmental toxins

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Introduction

Challenges:

- Search for an ionization method for analytes with high electron affinity (e.g. nitro-compounds) which is:
  - → sensitive
  - → selective
  - → fast
  - → cheap
  - → easy to handle
  - → soft, without fragmentation of the analyte
- GC coupling or direct sampling

Approach:

- → Use of the photoelectric effect at atmospheric pressure
- → Generation of thermal electrons by the interaction of UV-light with "metal" surfaces
- → Capture of thermal electrons by O_2 as reagent gas forming superoxide, O_2^-
- → Exclusive formation of negative ions through reaction with O_2^-
- → Avoidance of interactions with positive ions
- → Short reaction times through ionization inside the inlet capillary
- → Virtual elimination of ion-transformation processes
- → For GC coupling use of a heated ion source with matching transfer line

Methods

Experimental Setup

MS	Esquire 6000 QIT, Bruker Daltonik GmbH
Ion Sources	Custom capillary ion sources with anodized aluminum as photo emissive ma-terial
Radiation Source	PenRay Mercury low pressure UV lamp (λ = 185 nm and 254 nm)
GC	GC 7890 A, Agilent Technologies Inc.
Transfer Line	Custom temperature-controlled GC-transfer line

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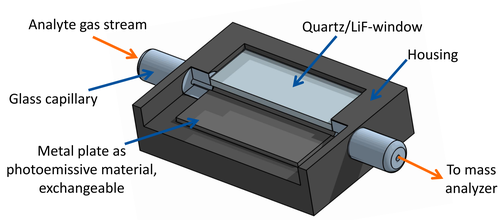
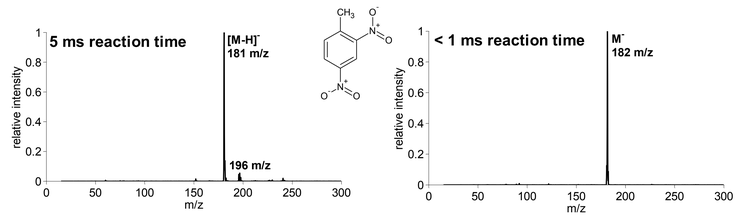
Ionization Method

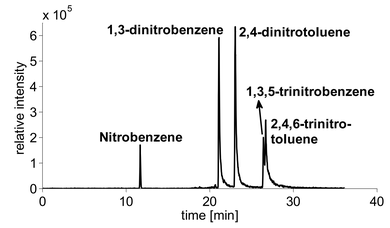
A UV-lamp mounted on top of the ion source provides the required radiation at λ=185 nm. The interaction of this radiation with metal surfaces produces thermalized electrons. A flute milled inside the metal and the window material leads to the same gas flow and ion transport characteristic as in standard capillaries. The photoemissive material is interchangeable.

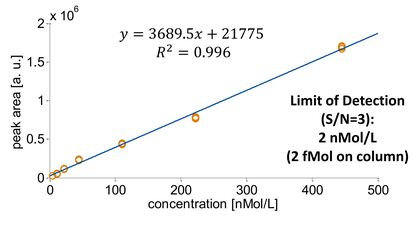


The reaction time is a crucial factor for the extent of ion transformation processes. Ionization inside the inlet capillary (< 1 ms reaction time) yields the M^- signal of 2,4-dinitrotoluene without additional signals.



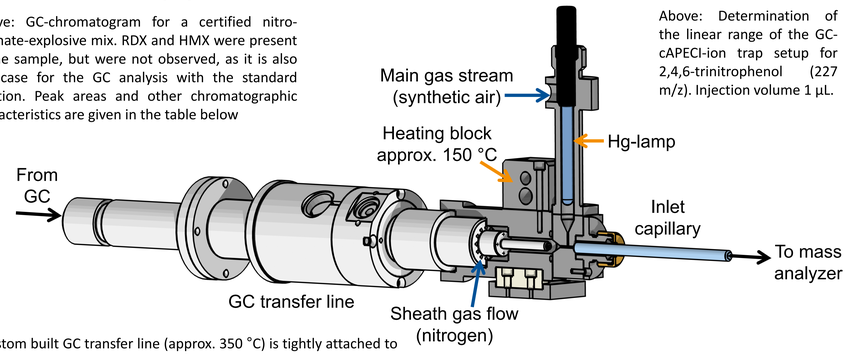
GC-cAPECI Measurements





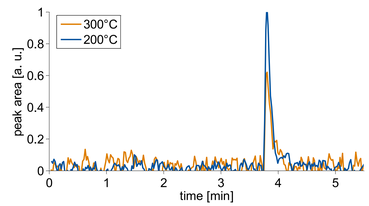
Above: GC-chromatogram for a certified nitro-aromate-explosive mix. RDX and HMX were present in the sample, but were not observed, as it is also the case for the GC analysis with the standard solution. Peak areas and other chromatographic characteristics are given in the table below

Above: Determination of the linear range of the GC-cAPECI-ion trap setup for 2,4,6-trinitrophenol (227 m/z). Injection volume 1 µL.



The custom built GC transfer line (approx. 350 °C) is tightly attached to the ion source held at 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 ion transfer time.

Ionization can also take place inside the capillary ion source as shown above. Then, the reaction times are shorter, leading to less background signals. However, the signal intensities are similar for both ion sources when coupled with GC.

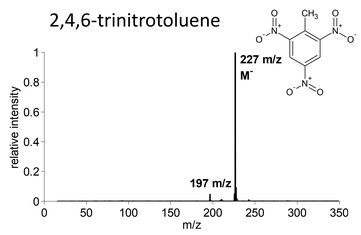


Above: Signal peaks of 2-nitrophenol for two different temperatures of the transfer line. Decreasing the temperature by 100 K yields a doubling of the peak intensity. Other compounds, e.g., RDX/HDX, are more prone to decomposition at higher temperatures than 2-nitrophenol, which should amplify this effect.

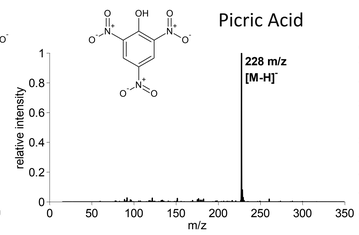
No.	Compound	Molar Mass [g/Mol]	Peak Width (FWHM) [s]	Peak Area	S/N	Concentration [ng/µL]
1	Nitrobenzene	123	3.2	0.23	607	10
2	1,3-Dinitrobenzene	168	4.5	0.86	502	10
3	2,4-Dinitrotoluene	182	8.3	1	535	10
4	1,3,5-Trinitrobenzene	213	10	0.25	166	50
5	2,4,6-Trinitrotoluene	227	10.5	0.50	228	10
	RDX/HMX	222/296				

Direct Sampling

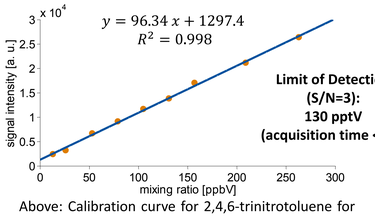
2,4,6-trinitrotoluene



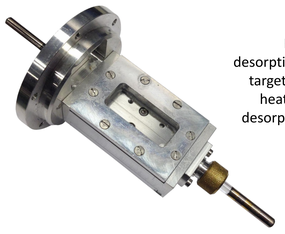
Picric Acid



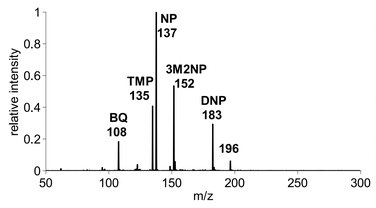
Left: The 2,4,6-TNT mass spectrum was obtained by desorption from a human tissue with a synthetic air gas stream.
Picric acid is measured sensitively by direct sampling. However, with GC-MS picric acid was barely observable even in comparably high concentrations (~ 50 µMol/L).



Above: Calibration curve for 2,4,6-trinitrotoluene for gas phase sampling.



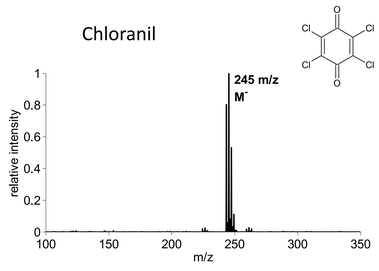
For direct sampling, desorption of analytes from targets may take place by heating the target or by desorption with an heated gas jet.



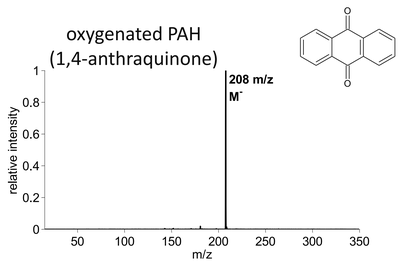
Left: Mass spectrum of a mixture of six compounds without GC-separation. Except for 2,4-dinitro-toluene all analytes yield only one signal, i.e. M^- or $[M-H]^-$. The signal at 196 m/z is possibly the oxygen adduct of 2,6-Dinitro-phenol.

Compound	Molar Mass [g/Mol]
2-Nitrophenol (NP)	138
2,4,6-Trimethylphenol (TMP)	136
3-Methyl-2-Nitrophenol (3M2NP)	153
2,4-Benzoquinone (BQ)	108
2,4-Dinitrophenol (DNP)	184
2,4-Dinitrotoluene (DNT)	182

Chloranil



oxygenated PAH
(1,4-anthraquinone)



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
- Benefits:
  - → sensitive: detection limit ≤ ppbV
  - → selective: outstanding signal-to-noise ratios
  - → easy: simple interpretation of the mass spectra
  - → fast: real time analysis, no sample preparation necessary
  - → cheap: only Pen-Ray-lamp and modified quartz capillary necessary
  - → easy to handle: no consumables (gases etc.) or adjustments necessary
  - → soft: hardly any fragmentation of the analyte; [M]- or [M-H]- is the dominant signal
- Reduced ion transformation processes by ionization within the inlet capillary
- GC-cAPECI measurements are performed with a similar ion source, upon attaching a custom GC transfer line
- Both ion sources show comparable signal intensities when coupled with GC, the ion source inside the capillary allows fast switching between GC and direct sampling
- GC analyses yield narrow peak widths and show good linearity (nMol/L to µMol/L)
- The temperature of the transfer line is a crucial factor for the signal intensity
- Direct sampling without sample preparation is possible
- With direct sampling more analytes are accessible
- Desorption from surfaces possible; spatial resolution down to the mm scale is envisioned

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