Highly Efficient Ionization of Nitro-aromatic Compounds using Photoelectron Induced Atmospheric Pressure Ionization (PAPI)

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Introduction

Nitro-aromatic compounds (NACs) are important to different research fields, e.g., the detection of explosives or in atmospheric chemistry. NACs are ubiquitous in the urban atmosphere, being well known for their phytotoxic and mutagenic properties. Widely used analytical approaches for NAC measurements are Ion Mobility Spectrometry (IMS) and Mass Spectrometry, equipped with various ionization methods, e.g., PTR (Proton Transfer Reaction) and DA-APPI (Dopant Assisted Atmospheric Pressure Photo Ionization). These methods are not selective towards NACs. Several approaches are known to increase the selectivity of these methods, but are not yet widely used. Most of them increase the complexity of the setup and/or the reaction chain necessary for detection.

In this work we present a comparison between three ionization methods for the detection of several NACs. These are PTR, a modified APPI design and a newly developed Photoelectron Induced Atmospheric Pressure Ionization (PAPI) stage.

PTR-TOF-MS

PTR-TOF-MS has gained importance in recent years (e.g., atmospheric chemistry, clinical studies). In PTR-MS ionization takes place inside a reaction drift tube by proton transfer. The reagent gas is protonated water, which is generated from water vapor flowing through a hollow cathode discharge. Only positively charged reagent ions are released to the drift tube.

DA-APPI

The VUV light for photoionization is provided by a home built spark discharge lamp mounted directly on the transfer capillary. This setup has some benefits over the usual setup, e.g., a reduced reaction time for ion transformation processes and the availability of VUV light with wavelengths below 105 nm (the LiF-cutoff) for ionization due to the windowless lamp design.

See also Session MP01; Poster #017

The VUV-light produces positive ions and electrons. The latter are rapidly captured to yield negative ions. Therefore, mass spectra are obtained in both the positive and negative modes. Frequently a dopant (e.g., toluene) is used to increase the concentration of charge carrying species (ions as well as electrons), but this approach renders the recorded mass spectra much more complex.

PAPI

The interaction of UV-light with metal surfaces (e.g., silver) produces photo-electrons. In air they are swiftly captured by oxygen in less than microseconds. O_2^- can then react with the analyte by charge or proton transfer, depending on the electron affinity and gas phase acidity, respectively. Ionization can take place directly inside the ion transfer capillary. Major advantages of this approach are:

- **exclusively negative ions** are generated
- **soft ionization** with very little fragmentation
- **high selectivity** leading to high S/N-ratios
- **short reaction times** (< 1ms)

See also Session MP01; Poster #004

Methods

PAPI

MS:	Bruker Daltonics esquire6000 quadrupole ion trap
Ion Source:	Quartz transfer capillary; internally partially coated with silver
Radiation Source:	PenRay low pressure Mercury UV lamp (254 nm)

PTR-MS

MS and Ion Source:	Ionicon PTR-HRTOF-MS

DA-APPI

MS:	Bruker Daltonics esquire6000 quadrupole ion trap
Ion Source:	Home built VUV spark discharge lamp operated with Ar. Mounted directly onto a transfer capillary
Dopant:	Toluene

Flow Tube System

Reaction Chamber:	1.2 l glass tube
Radiation Source:	6 lamps (280-550 nm); mounted around the reaction tube
Concentration measurement:	FT-IR (Nicolet NEXUS) with long path absorption White optics (32.8 m)

Experimental Setup

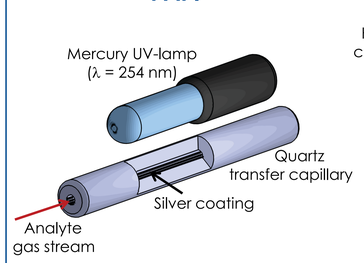


Figure 1) Schematic of the PAPI ion source; ionization occurs *inside* the transfer capillary

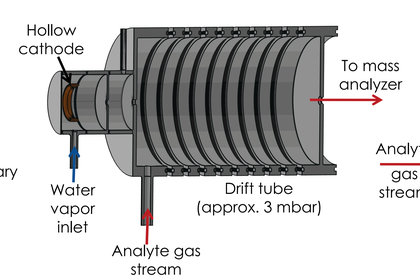


Figure 2) Schematic of the PTR-MS ion source

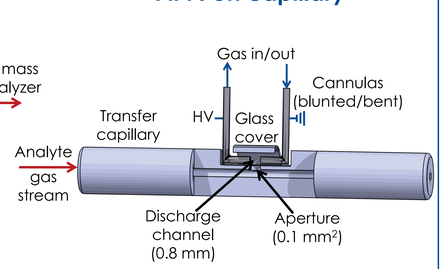
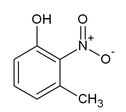


Figure 3) Schematic of the VUV spark discharge lamp mounted onto the transfer capillary

Linearity of PAPI and PTR

Analyte:
3-Methyl-2-Nitrophenol

For mass spectra see section "Photolysis Study"



Limits of Detection (3σ):
PTR-MS: **< 250 ppt** (30 s)
PAPI: **< 1 ppb** (<1s)

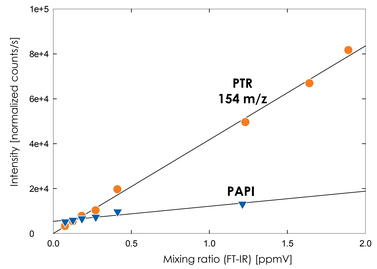
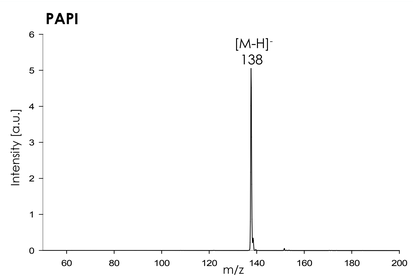
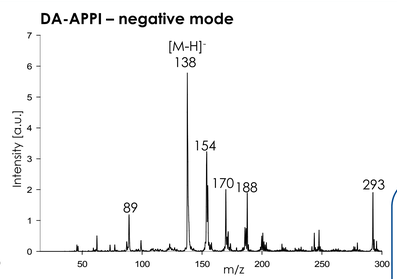


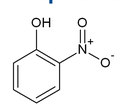
Figure 4) Concentration dependency of the signal intensity for PAPI-MS and PTR-MS

Comparison of PAPI, PTR and DA-APPI Mass Spectra





2-Nitrophenol



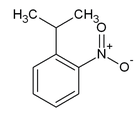
Molar Mass: 139 g/mol

Several nitro-aromatic compounds were analyzed.

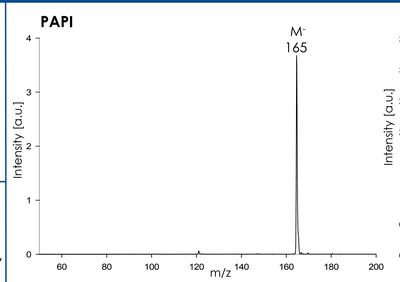
Two examples are shown, representing:

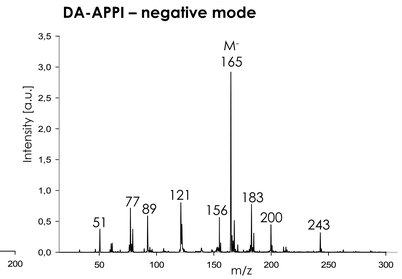
- OH-containing species
- Alkylated nitro-compounds

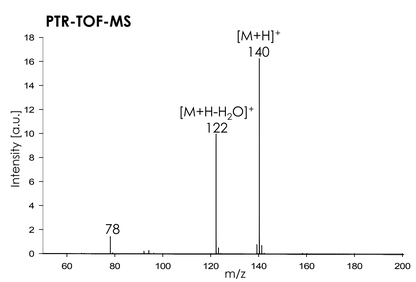
2-Nitro-Isopropyl-Benzene

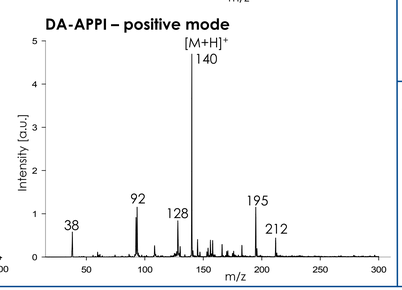


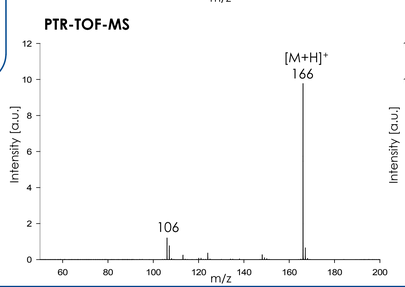
Molar Mass: 165 g/mol











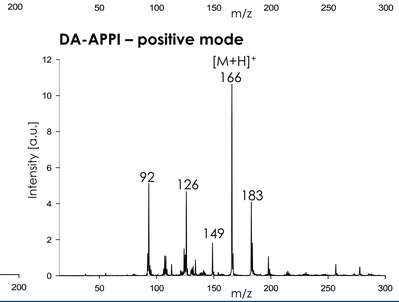
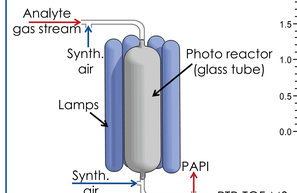


Photo-oxidation Study

Product study of the photo-oxidation of
3-methyl-2-nitrophenol
Mixing ratio: ~260 ppbV
Reaction time: ~ 22 min



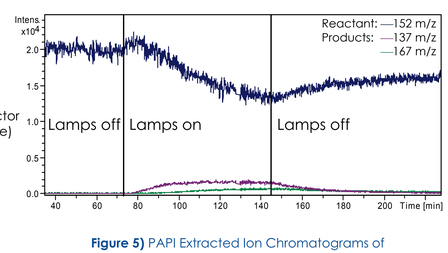


Figure 5) PAPI Extracted Ion Chromatograms of reactant and product mass signals

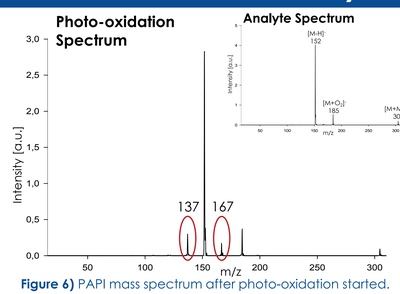


Figure 6) PAPI mass spectrum after photo-oxidation started. Insert: Spectrum before photo-oxidation started.

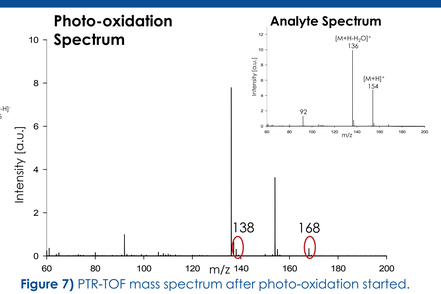
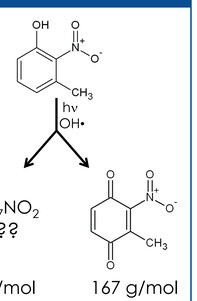


Figure 7) PTR-TOF mass spectrum after photo-oxidation started. Insert: Spectrum before photo-oxidation started.



Conclusions

- All three ionization methods were capable of detecting nitro-aromatic compounds efficiently
- Signal pattern (amount of fragmentation/ion transformation processes) is different:

PAPI

→ Generally only one signal for each compound is observed
→ $[M-H]^-$ for compounds with acidic proton, otherwise $[M]^-$
→ O_2^- adduct/dimer formation in rare cases

PTR

→ $[M+H]^+$ formation
→ Fragmentation observed, particularly for hydroxy-nitro-species

DA-APPI

→ Main signals are $M^+/[M+H]^+$ in positive mode; $M^-/[M-H]^-$ in negative mode
→ Very complex mass spectra due to the use of a dopant

- PTR-TOF-MS shows a very good linearity over a wide concentration range. Linearity ranges of FT-IR (high conc.), PTR-TOF-MS (large conc. range), and PAPI (low conc. range) is of benefit for atmospheric chemistry studies
- The estimated detection limits of PAPI are in the pptV-range
- The low background noise level of PAPI mass spectra allows for detection of minor product signals
- Optimum performance is obtained through parallel PTR *and* PAPI MS measurements, resulting in virtually orthogonal structural product information (proton affinity/gas phase basicity vs. electron affinity/gas phase acidity

Literature

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