

Photoelectron Induced Atmospheric Pressure Ionization (PAPI) - a Selective Ionization Method for Molecules with High Electron Affinities



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Introduction

Challenge:

Development of 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

⇒ **State of the art ionization methods are not able to fulfill all of the requirements stated above simultaneously**

New Approach:

- Use of the photoelectric effect at atmospheric pressure
- UV-light interaction with metal surfaces yields low energy electrons
- Electron capture forms exclusively negative ions
- No interaction of oppositely charged species
- Chemical ionization of photo labile analytes by the use of a reactant gas (e.g. O₂)
- Ionization inside the transfer capillary: only little reaction time for ion transformation processes
- A similar approach is known for IMS, but leads to poor detection limits and high reaction times

Application

- Atmospheric chemistry
 - Detection of explosives
- see also Session MP01; Poster #006

Experimental Setup

Direct Photoelectron Induced Ionization

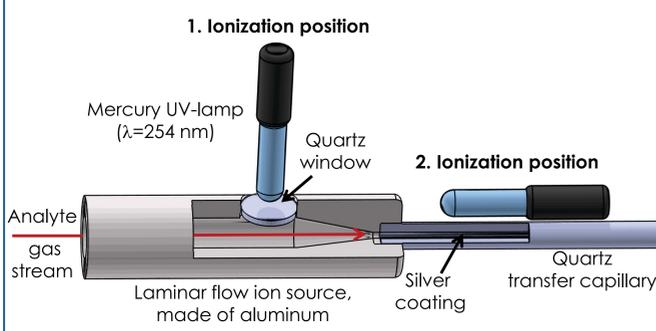


Figure 1) Schematic of the direct PAPI ion source, with two possible ionization positions: 1. inside laminar flow ion source 2. inside transfer capillary

Indirect Photoelectron Induced Ionization

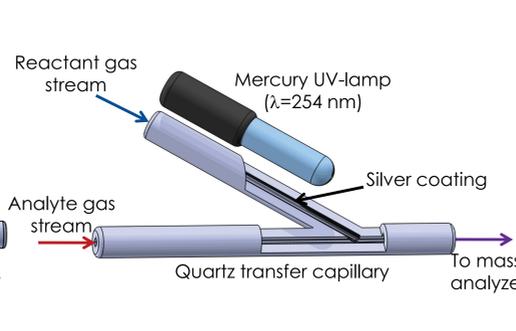


Figure 2) Schematic of the indirect PAPI ion source; see section "Indirect Ionization"

Indirect Ionization

→ For photolabile analytes
Operation sequence:

- Use of reactant gas (e.g. O₂)
- The transfer capillary features a quartz capillary branch (same i.d.) partially coated internally with silver
- UV light (lamp/laser) interaction with metal surface yields slow electrons
- Direct ionization of reactant gas by electron capture
- Ionized reactant gas is added to analyte gas stream
- Efficient charge transfer from O₂⁻ to analyte or deprotonation
- Reaction time: less than 300 μs; after ionization hardly any ion transformation reactions occur

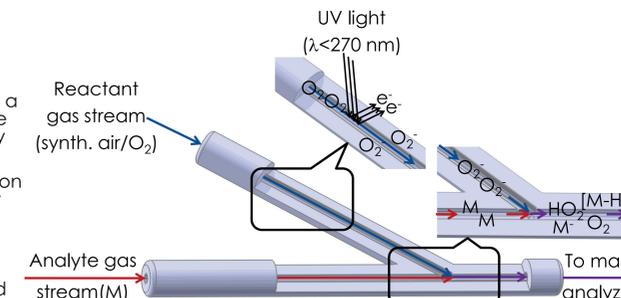


Figure 3) Indirect photoelectron induced ionization inside modified transfer capillary

For most nitro-compounds indirect ionization is not necessary.
Example:
For 10 ppb 3-methyl-2-nitrophenol only **0.001 %** of the molecules are photolyzed at **254 nm** ($J = 0.0259 \text{ s}^{-1}$; $t = \sim 400 \text{ μs}$)

Conclusions

• A new ionization method for analytes with high electron affinity/gas phase acidity based on the photoelectric effect is introduced

Benefits:

- **sensitive:** detection limit ≤ ppbv
- **selective:** outstanding signal-to-noise ratios
- **fast:** real time analysis, no sample preparation necessary
- **cheap:** only PenRay-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
- Ionization inside the transfer capillary reduces ion transformation processes
- Ionization of the analyte without exposure to UV light is possible
- Work functions in ambient air are comparable to those at high vacuum
- For some metals, the electron yield is highly surface dependent, oxide layers decrease the electron yield by several orders of magnitude
- Silver surfaces give relatively constant high electron yields at 254 nm

Ionization Mechanism

Signal Dependence on Electron Affinity/Acidity

Kinetic energy of generated electrons:

$$\sim 0.12 \text{ eV}$$

Kinetic energy after collisions with buffer gas:

$$\sim 0.025 \text{ eV}$$

In air almost all slow electrons are captured by oxygen after approximately 20 ns ($k = 2 \cdot 10^{30} \text{ cm}^6 \cdot \text{s}^{-1}$):



→ reaction with analytes with high electron affinity:

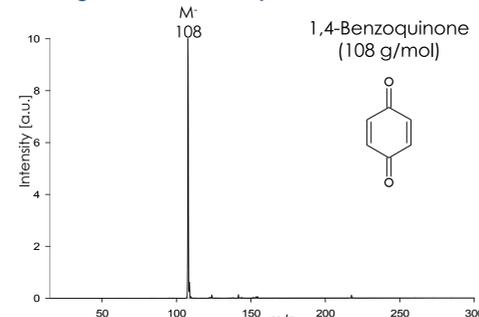


→ reactions with analytes with acidic proton:

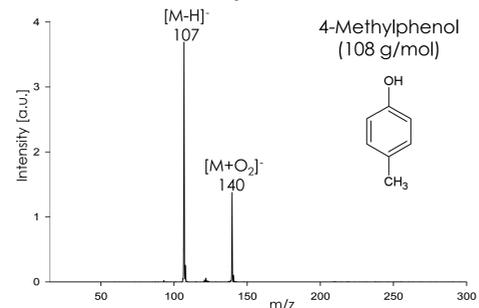


and partially $\text{O}_2^- + \text{M} \rightarrow [\text{M} + \text{O}_2]^-$

High Electron Affinity



Gas Phase Acidity



Signal Dependence on Reaction Time

Ionization of dinitrotoluene isomers with several ionization methods leads to distinct signal patterns. Some isomers (mostly 2,4-DNT) show a dominant [M-H]⁻ signal while the others exhibit a M⁻ signal. Photoelectrically induced ionization of 2,4-DNT in air inside the laminar flow ion source leads to deprotonation. Reducing the reaction time of the generated ions from 5 ms to less than 1 ms (ionization inside transfer capillary) leads to M⁻.

In pure nitrogen only the M⁻ signal is observed in both cases. By adding oxygen the [M-H]⁻ signal increases at the 5 ms reaction time ionization position (Fig. 4).

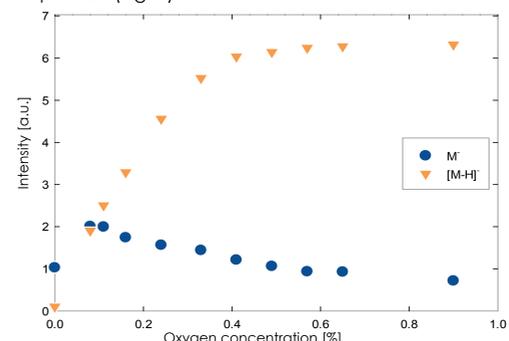
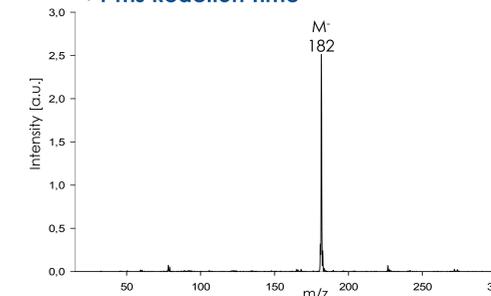
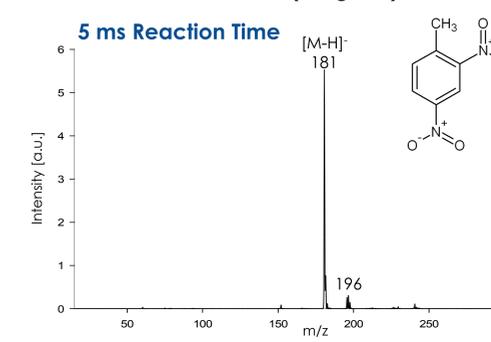


Figure 4) Dependence of the M/[M-H] signal intensities on the O₂ concentration for the 5 ms ionization position

< 1 ms Reaction Time



5 ms Reaction Time

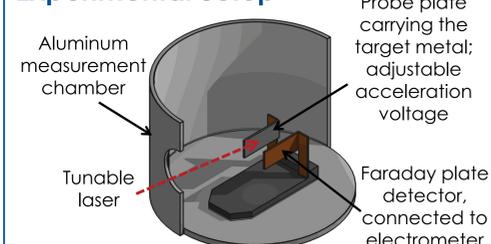


Analyte	Electron Affinity [eV]	Gas Phase Acidity [eV]	Observed Signal
Oxygen	0.61	14.89	-
1,4-Benzoquinone	2.22	15.89	M ⁻
4-Methylphenol	-0.45	14.77	[M-H] ⁻ / [M+O ₂] ⁻
2-Nitrophenol	1.12	13.77	[M-H] ⁻
1-Nitro-2-Isopropylbenzene	1.29	15.07	M ⁻
Sulfur hexafluoride	1.15	-	M ⁻

Table 1) Calculated electron affinities and gas phase acidities

Determination of Work Functions and Surface Dependency of the Photoelectric Yield

Experimental Setup



Work Functions

Work functions are normally measured in high vacuum with "clean" target metal surfaces. The work functions listed in Table 2 are determined in laboratory air and are thus potentially affected by surface layers. Surprisingly, the measured values are with the range of reported literature values. The disagreement of the measured value for gold is still under investigation.

Metal	Experimental Work function [eV]	Literature values ⁹⁾ [eV]
Silver	4.62	4.25 - 4.74
Gold	4.37	4.74 - 5.31
Aluminum	4.17	4.06 - 4.28
Tantalum	4.35	4.00 - 4.80
Lead	4.23	4.25 - 4.14

Table 2) Work functions determined in ambient air

Photoelectric Yields

The efficiency of the photoelectric effect for a metal at a fixed wavelength is strongly surface dependent. Oxide layers may decrease the photoelectric current by several orders of magnitude. In table 3 the photoelectric yield for aluminum is compared for different surface conditions with that of a noble metal (silver). Both exhibit work functions below 4.88 eV (254 nm; Hg-low pressure lamp)

	Relative Photoelectric Current	
	Aluminum	Silver
"Clean"	1	1
After some days	0.01	0.75
Water vapor	0.40	0.38

Table 3) Relative photoelectric currents of aluminum and silver at 254 nm

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