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 imitate intermediates and pollutants in the urban atmosphere, being well known for their production, and mutagenic properties. Many are listed as hazardous air pollutants (HAPs), and are used in the manufacture of various products (e.g., in the production of explosives, dyes). Their detection in the atmosphere is therefore of great importance. For this purpose, different analytical approaches for NAC measurements are Ion Mobility Spectrometry (IMS) and Mass Spectrometry, including various ionization methods, e.g., PAPI (Photoelectron Induced Atmospheric Pressure Ionization), PTR-MS (Proton Transfer Reaction Mass Spectrometry), 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 the measurement. One example is the use of the VUV light for photoionization. In this work we present a comparison between three ionization methods for the detection of several NACs. 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 formation.

**Experimental Setup**

**PAPI**
- Mercury UV lamp: \(\lambda = 254 \text{nm}\)
- Hollow cathode
- Photoelectron Induced Atmospheric Pressure Ionization (PAPI)

**PTR-MS**
- 6 lamps (280-550 nm); mounted on the gas stream
- Quartz transfer capillary; internally blunted/bent
- High Efficiency of Ionization of Nitro-aromatic Compounds using DA-APPI – negative mode

**APPI on capillary**
- Corrugated (blunted/bent)
- Transfer capillary
- Gas inlet
- To mass analyzer

**Comparison of PAPI, PTR and DA-APPI Mass Spectra**

**Linearity of PAPI and PTR**

**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.
  - PTR: For compounds with acidic proton, otherwise \([M+H]^+\) or \([M]^+\) for adduct/dimer formation in rare cases.
- DA-APPI: Generally only one signal for each compound is observed.

**Photo-oxidation Study**

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