

Ionization of gaseous compounds in direct and dopant-assisted atmospheric pressure photoionization



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Introduction

A highly sensitive, custom-made APPI interface for GC-MS is utilized, where the photoionization takes place inside a closed piston [1]. With the interface, high ionization efficiency can be achieved without a dopant, unlike usually in APPI. Due to the highly purified matrix the interface provides an excellent possibility for comparing the ion formation in direct photoionization and dopant-assisted APPI.

Methods

Samples

- Ethylbenzene, bromobenzene, benzaldehyde and pyridine were injected as headspace (inj. V 0.05 μ L for pyridine, and 0.5 μ L for the other compounds, split ratio 10 000)
- Naphthalene, anthracene, quinoline and acridine were diluted in hexane and analyzed from a 1 μ M mixture, inj. V 0.5 μ L (0.5 pmol on column), splitless

Mass spectrometry

- Exactive Orbitrap (Thermo Scientific), equipped with a custom-made APPI interface
- Ion source T: 250°C
- Nebulizer gas: high purity N₂ (99.999999%), generated with an active gas purifier, flow rate 850 mL/min
- Measurements in positive ion mode with and without a dopant (toluene, acetone, anisole or chlorobenzene). Dopant headspace introduced through a T-piece at 100 μ L/min flow rate.

Gas chromatography

- A Thermo Scientific 450 Series GC oven, a TR-Dioxin 5MS column (30 m x 0.25 mm ID x 0.1 μ) and a GC transfer line
- GC temperature program: T (initial) = 50°C for 1 min, 30°C/min up to 150°C, 20°C/min up to 200°C, 30°C/min up to 300°C, 20°C/min up to 320°C, hold time 5 min.
- Column flow 1.50 ml/min (He), injector and transfer line T: 250°C

Setup

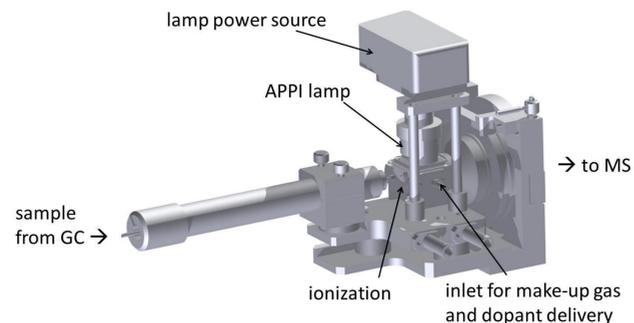


Figure 1. The custom-made APPI interface used in the study.

Studied compounds

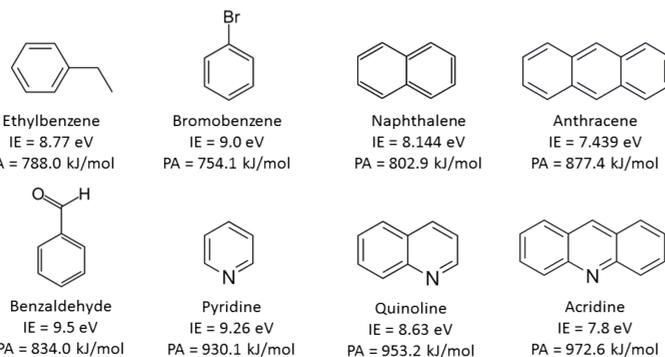


Figure 2. Structures, ionization energies (IE) and proton affinities (PA) of the studied compounds.

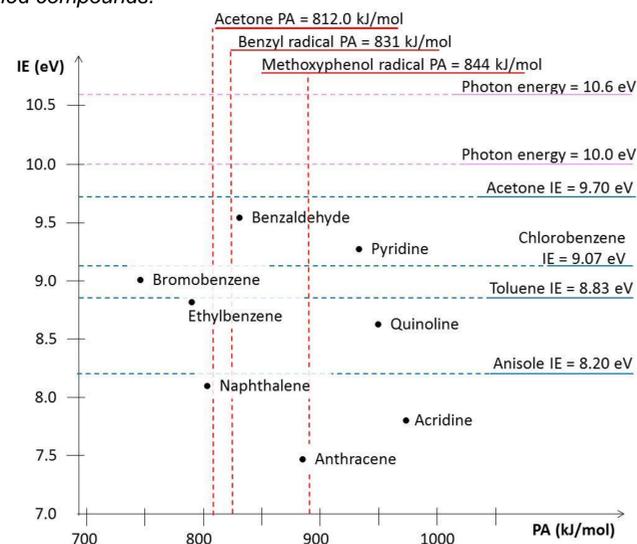


Figure 3. A diagram showing the ionization energies (IE) and proton affinities (PA) of the studied compounds and their relationship to the IEs and PAs of the dopants.

Results

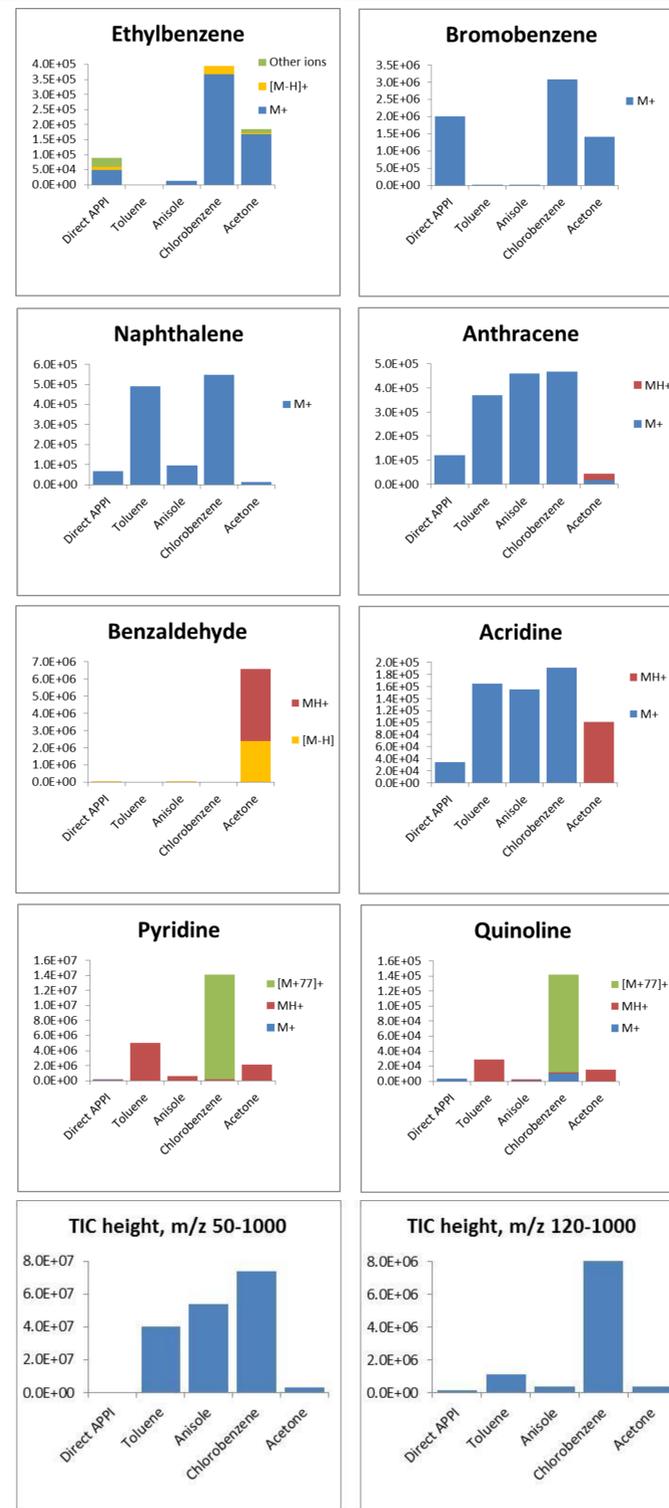


Figure 4. The intensity of analyte ions/TIC in direct and dopant-assisted APPI.

Direct APPI:

- All compounds were ionized
- Benzaldehyde formed [M-H]⁺ ions
- Pyridine formed M⁺ and MH⁺ ions
- The rest of the compounds formed M⁺ ions

Dopant-assisted APPI:

- Introduction of dopants enhanced the ionization of the analytes with IEs below the IE of the dopant, and suppressed it for analytes with IEs above that of the dopant
- Acetone as the dopant promoted formation of MH⁺
- Pyridine and quinoline formed MH⁺ with all other dopants, but [M+77]⁺ with chlorobenzene
- Acridine formed MH⁺ ions with acetone, but M⁺ with all other dopants, despite its high PA → behaviour cannot be explained thermodynamically → possibly kinetic control

Deuterated toluene as the dopant:

- Pyridine and quinoline formed [M+D]⁺ ions → the proton originates from toluene M⁺

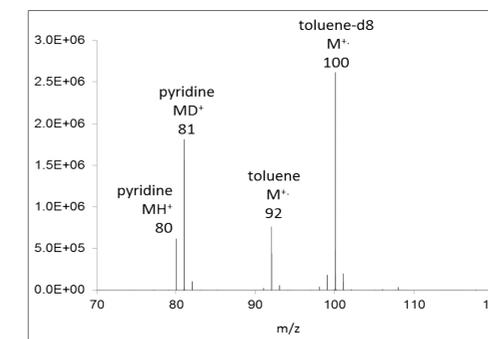


Figure 5. Ionization of pyridine in the presence of toluene-d8 and a trace of toluene.

Effect of the dopants on the background:

- The background increased after introduction of all the dopants (over 30 x with chlorobenzene)
- The main ion in the background was the dopant M⁺ or MH⁺ (in case of acetone), but also other ions were observed, most with chlorobenzene
- High amount of background ions can prevent the entrance of analyte ions to the trap and thus suppress the analyte signals.

Conclusions

Direct APPI:

- Direct photoionization and formation of M⁺ is the main reaction
- Self-protonation may take place in case of pyridine

Dopant-assisted APPI:

- Direct photoionization is hindered, since the dopants consume the photons completely
- The ionization takes place through dopant-mediated gas-phase ion/molecule reactions
- Water clusters are not present in this ion source and therefore protonated molecules can be formed through self-protonation or proton transfer with the dopant
- Not all the observed ionization reactions could be explained thermodynamically → kinetic control may be involved

Future experiments:

- Analysis of the same compounds and dopants with atmospheric pressure laser ionization (APLI)
- Halogenated benzene dopants will be tested for a group of compounds with similar functionalities as in pyridine and quinoline, in order to investigate the formation of [M+77]⁺ ion

Literature

- H. Kersten *et al.*, 62nd ASMS Conf., Baltimore, MD, 2014, MP 684.
- See also:
- A.C. Peterson *et al.* 62nd ASMS Conf., Baltimore, MD, 2014, MOD pm 4:10.
 - T. Benter *et al.*, 62nd ASMS Conf., Baltimore, MD, 2014, MP 315.

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