



Introduction

- At ASMS 2013, a novel, highly sensitive atmospheric pressure ionization (API) ion source for gas chromatography-high resolution mass spectrometry (GC-HRMS) was presented [1].
- In this work, a more advanced version of the ion source [2] is used for atmospheric pressure photo-ionization (APPI), utilizing one-step photo-ionization of the analytes by VUV radiation, as well as for atmospheric pressure laser ionization (APLI) utilizing (1+1) resonance-enhanced multi-photon ionization (REMPI) [3].
- Results obtained from the GC-MS analysis of a mixture of 77 EPA priority pollutants are presented.
- The results are discussed in light of the ionization mechanisms in direct and dopant-assisted APLI.

Methods

Sample

- EPA 8270 LCS Mix 1 from Supelco (Bellefonte, PA, USA): 77 compounds, conc. 100 pg/ μ L in CHCl_2

Mass spectrometry

- Exactive Orbitrap (Thermo Scientific), equipped with a custom API interface
- APPI: VUV Kr discharge RF lamp emitting 10.0 and 10.6 eV photons and a power supply (Syagen)
- APLI: Small DPSS Nd:YAG laser (Crylas GmbH), $\lambda = 266$ nm (4.66 eV), pulse duration 0.9 ns, max repetition rate 60 Hz, beam diameter 0.5 mm, pulse energy 200 μ J, power density 10^8 W/ cm^2
- Ion source Temperature: 325°C
- Nebulizer gas: high purity N_2 (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 via a T-piece at 100 μ L/min.

GC 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: 325°C, Inj. V = 0.5 μ L (50 pg on column)

Setup

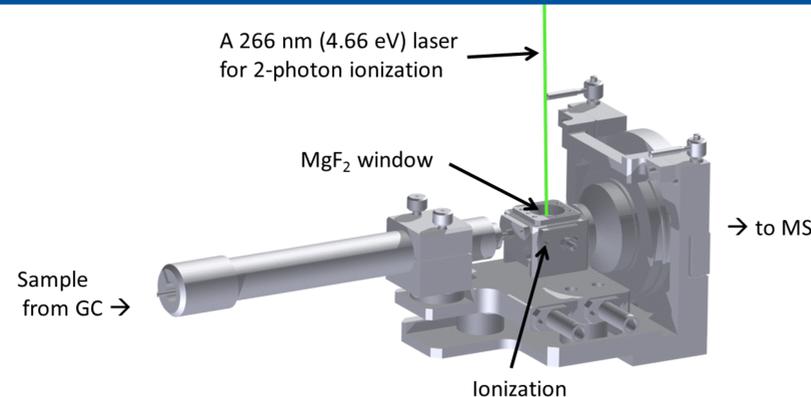


Figure 1. The APLI setup using the custom-made API interface. For more details of the interface, see [2]

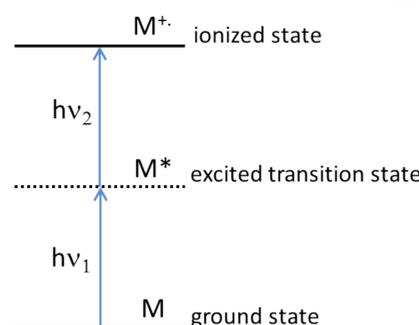


Figure 2. The ionization in APLI takes place by resonance enhanced 2-photon absorption [3].

The compounds to be ionized should have IEs below the 2-photon energy, but also sufficiently long-lived intermediate states so that the absorption of the 2nd photon occurs before molecular relaxation.

Comparison of (direct) APPI and APLI

Table 1. The compound groups present in the 8270 EPA mix and the proportions of compounds detected in (direct) APPI and APLI.

Compound group	Total nr. of compounds	APPI		APLI	
		Nr. of compounds detected (%)	Ions observed	Nr. of compounds detected (%)	Ions observed
PAH compounds	19	19 (100)	M^+	19 (100)	M^+
O-containing compounds (phenol, alcohol, carboxylic acid, ketone)	8	7 (88)	M^+ , MH^+ , fragment	7 (88)	M^+ , MH^+ , fragment
Nitro-compounds (all aromatic)	12	7 (58)	M^+	1 (8)	M^+
Halogenated (aromatic/aliphatic)	20	18 (90)	M^+	7 (35)	M^+
N-containing (N-heterocyclic, aromatic/aliphatic amine, azo)	8	8 (100)	M^+ , MH^+ , fragment	6 (75)	M^+ , MH^+ , fragment
Esters	7	7 (100)	Fragments	0 (0)	-
Ethers	3	0 (0)	-	0 (0)	-
All	77	66 (86)		40 (52)	

- Most of the compounds that were ionized by APPI but not by APLI were halogenated, nitro-compounds or phthalate esters. These compounds either have IEs above the 2-photon energy of the laser (9.32 eV) or their intermediate excited states are short-lived and therefore the absorption of the 2nd photon cannot take place at the available photon flux.

Effect of the dopants in APPI and APLI

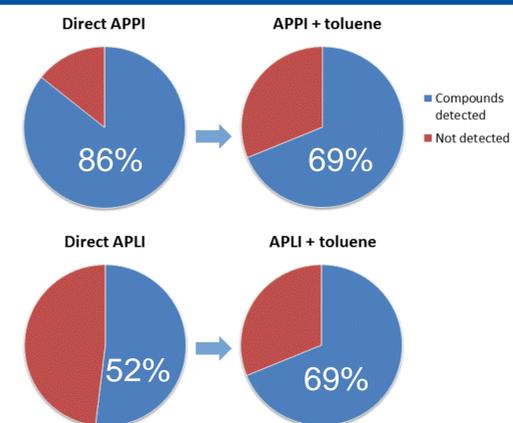


Figure 3. The proportion of all 77 EPA mix compounds detected in direct and toluene-assisted APPI and APLI.

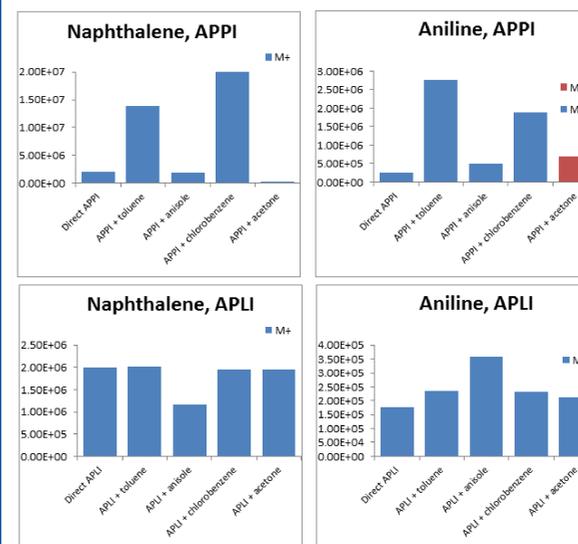


Figure 4. Effect of dopants on the signals of naphthalene and aniline in APPI and APLI.

Background in APPI and APLI

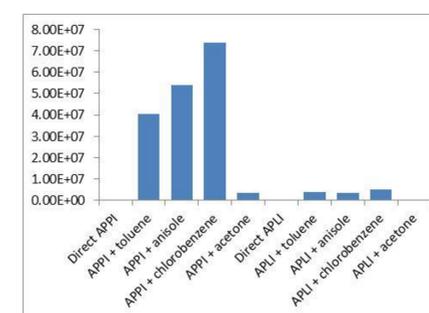


Figure 5. The TIC height in direct and dopant-assisted APPI and APLI (m/z 50-1000).

- In direct APPI and APLI the background was on the same level
- The introduction of dopants increased the amount of background ions in both APPI and APLI, but was much more pronounced in APPI (10 x)
- The highest background was observed in APPI with chlorobenzene, anisole and toluene dopants

Conclusions

- (Direct) APLI is highly selective towards compounds that have sufficiently high 2-photon absorption cross-sections and resonant intermediate excited states (around 5 eV \approx 250 nm), such as PAHs
- In APLI, addition of dopants widens the range of compounds that are ionized, but the overall ionization efficiency (for compounds that are also ionized by direct APLI) remains on the same level
- With the applied novel interface direct APPI is more universal than direct APLI, because virtually all compounds with IEs \leq 10.6 eV radiation are ionized
- In APPI, addition of dopants adds selectivity (via dopant chemistry) and ionization efficiency

Future experiments:

- Experiments in negative ion mode to facilitate the ionization of acidic, halogenated and nitro-compounds
- In APLI, the signal response is dependent on the laser intensity and irradiated area. Much higher signals for the analytes are expected with a high intensity laser (e.g. excimer laser)

Literature

- H. Kersten et al., 61st ASMS Conf., Minneapolis, MN, 2013.
- H. Kersten et al., 62nd ASMS Conf., Baltimore, MD, 2014, MP 684
- M. Constapel et al. Rapid Commun. Mass Spectrom. 19 (2005) 326.
- T.J. Kauppila, et al., 62nd ASMS Conf., Baltimore, MD, 2014, MP 299.

See also:

- A.C. Peterson et al. 62nd ASMS Conf., Baltimore, MD, 2014, MOD pm 4:10.

Acknowledgements

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