

# Atmospheric pressure laser ionization with a novel highly sensitive atmospheric pressure ionization interface for gas-chromatography-mass spectrometry

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## 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

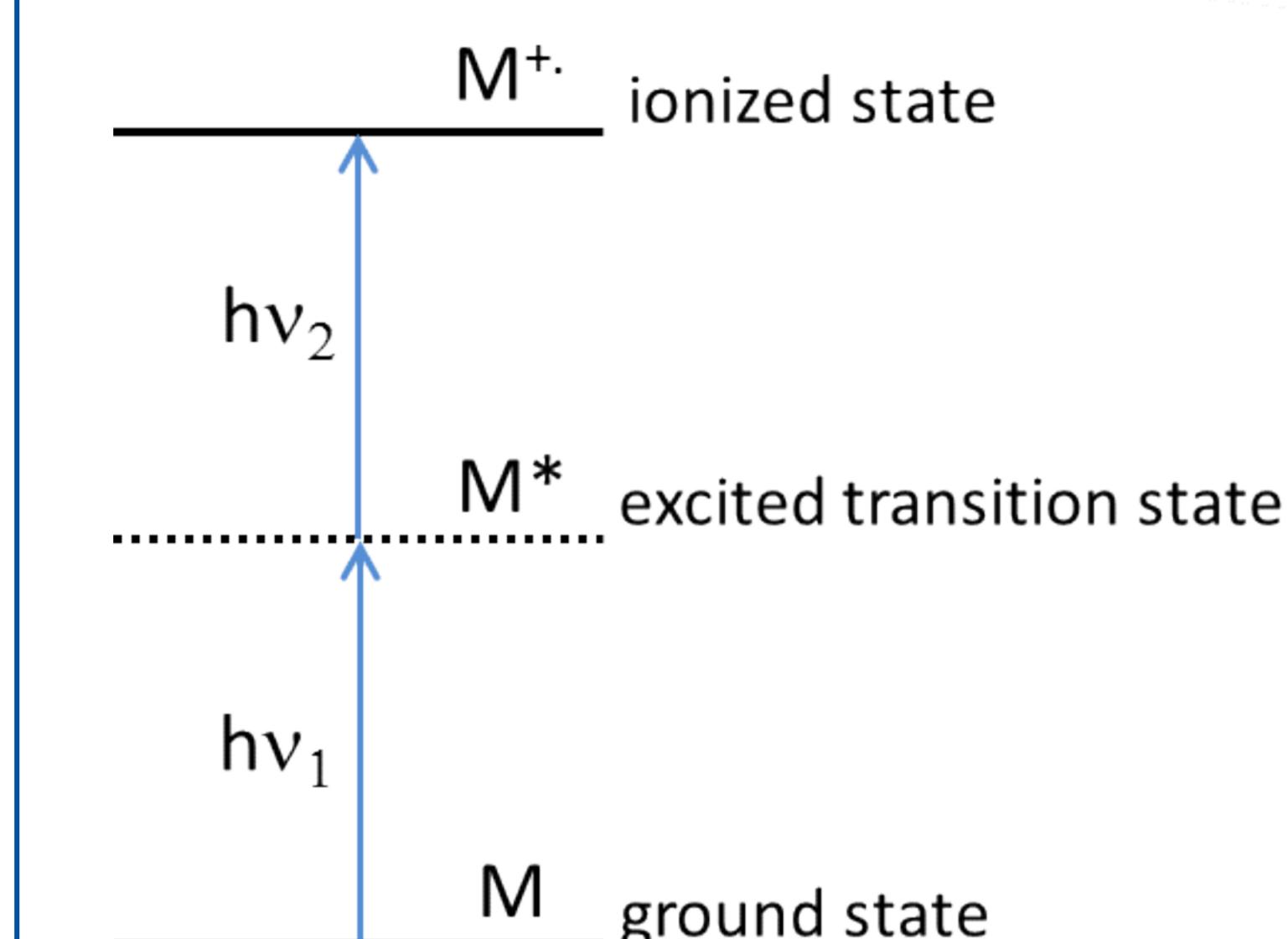
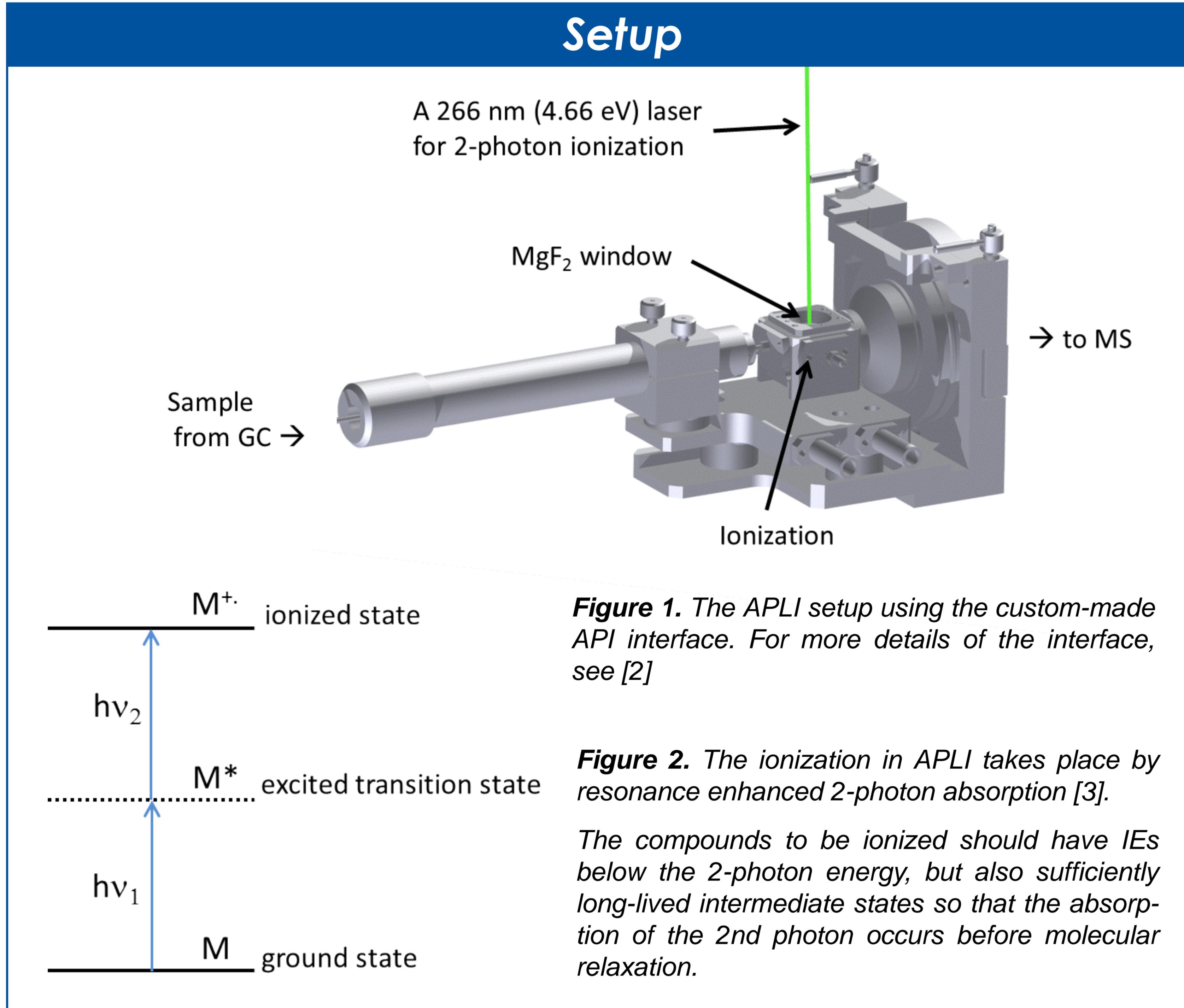
- EPA 8270 LCS Mix 1 from Supelco (Bellefonte, PA, USA): 77 compounds, conc. 100 pg/ $\mu$ L in  $\text{CHCl}_3$

### 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),  $\lambda = 266 \text{ nm}$  (4.66 eV), pulse duration 0.9 ns, max repetition rate 60 Hz, beam diameter 0.5 mm, pulse energy 200  $\mu\text{J}$ , power density  $10^8 \text{ W/cm}^2$
- Ion source Temperature: 325°C
- Nebulizer gas: high purity N<sub>2</sub> (99.99999%), 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  $\mu\text{L}/\text{min}$ .

### GC chromatography

- A Thermo Scientific 450 Series GC oven, a TR-Dioxin 5MS column (30 m x 0.25 mm ID x 0.1  $\mu$ ) 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  $\mu\text{L}$  (50 pg on column)

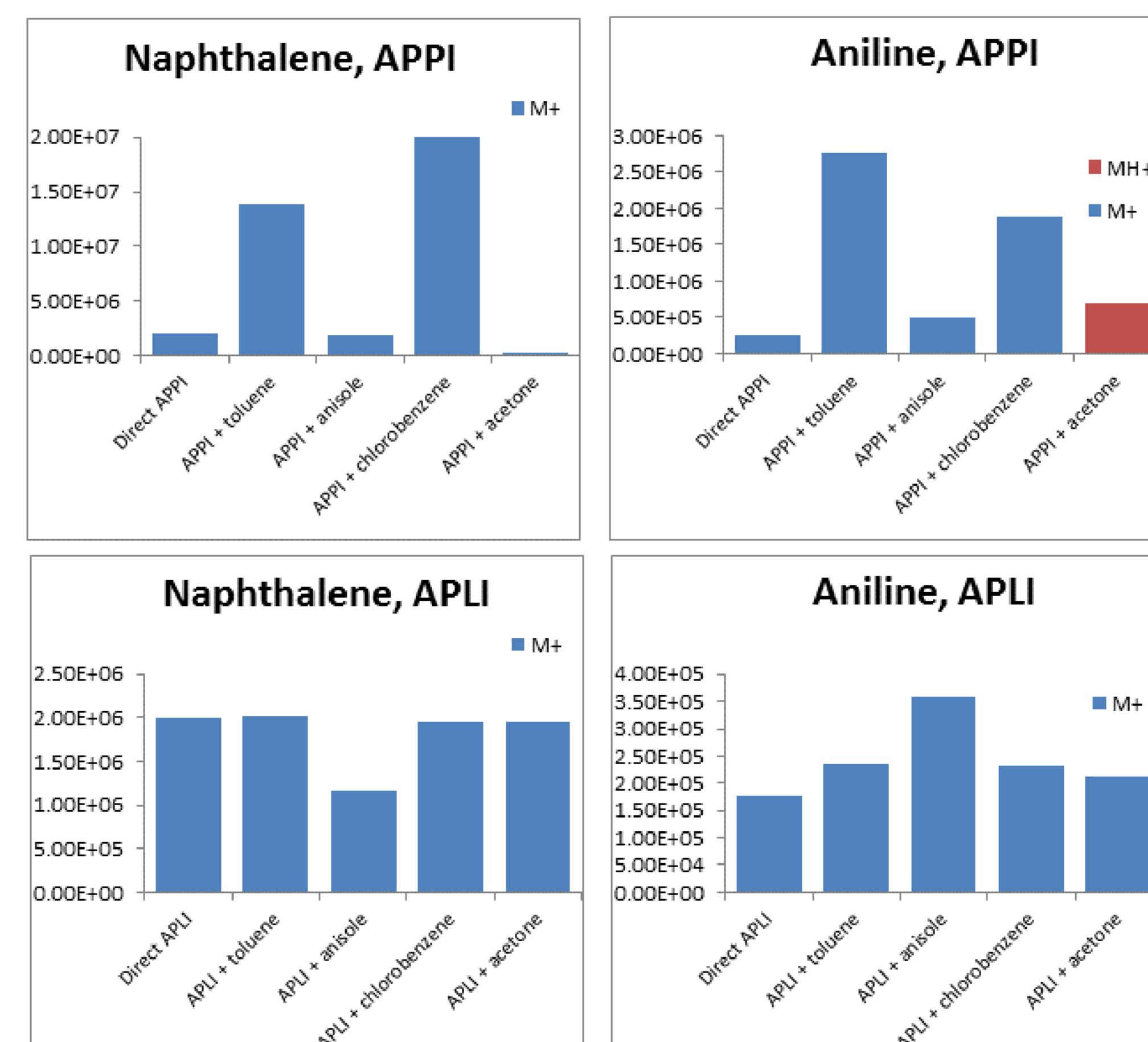
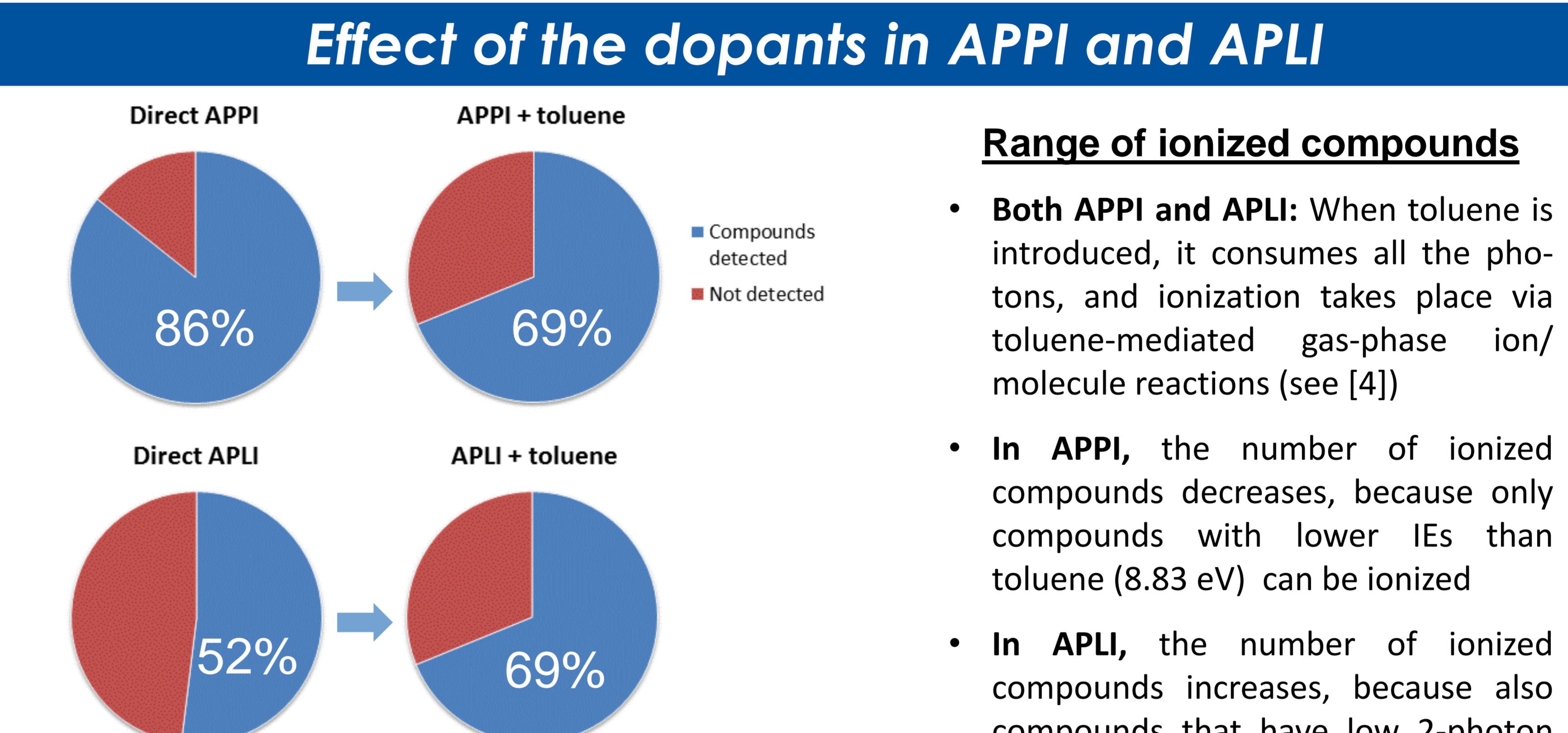


## Comparison of (direct) APPI and APLI

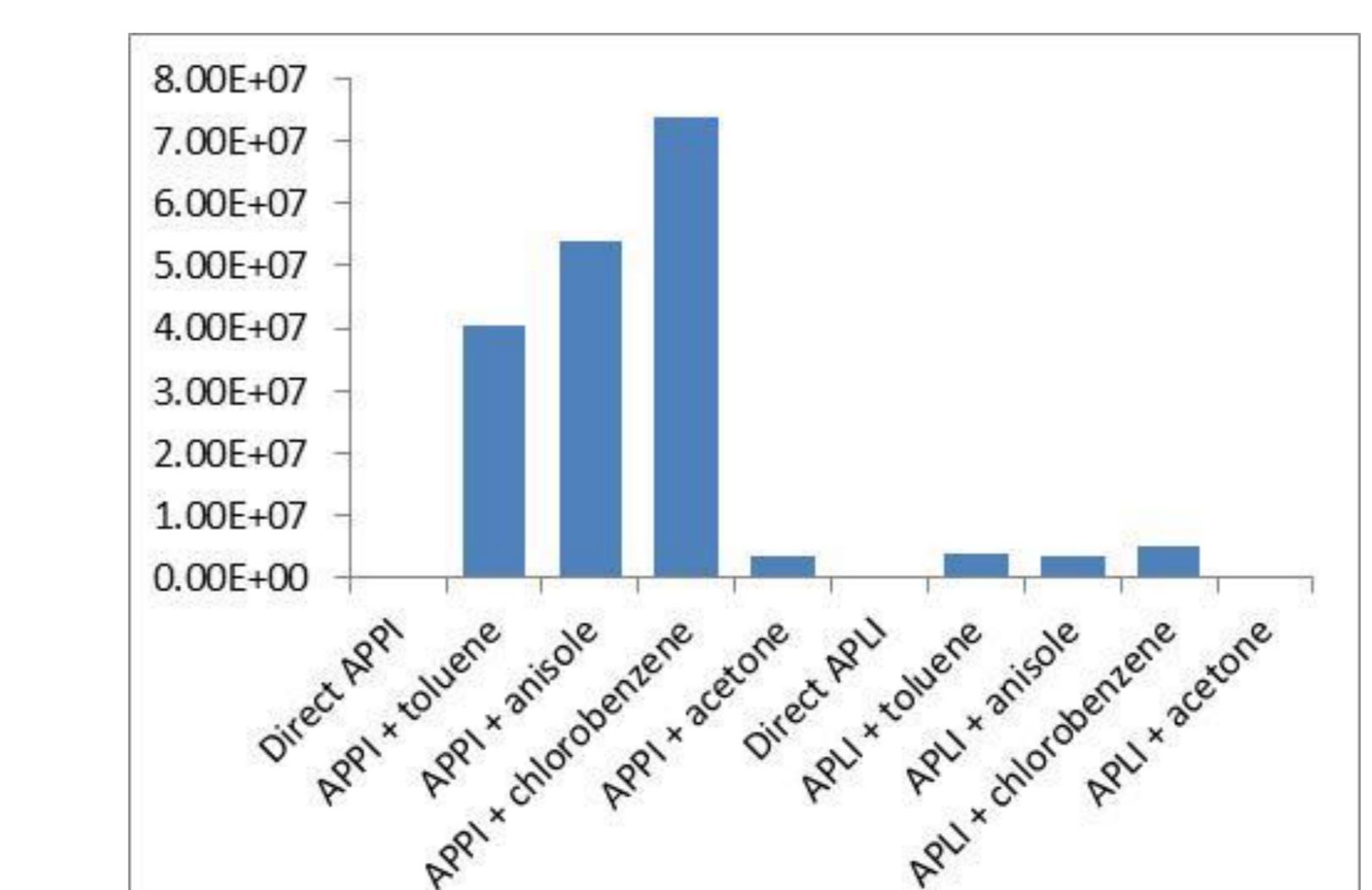
Table 1. The compound groups present in the 8270 EPA mix and the proportions of compounds detected in (direct) APPI and APLI.

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 <sup>+</sup>	19 (100)	M <sup>+</sup>
O-containing compounds (phenol, alcohol, carboxylic acid, ketone)	8	7 (88)	M <sup>+</sup> , MH <sup>+</sup> , fragment	7 (88)	M <sup>+</sup> , MH <sup>+</sup> , fragment
Nitro-compounds (all aromatic)	12	7 (58)	M <sup>+</sup>	1 (8)	M <sup>+</sup>
Halogenated (aromatic/aliphatic)	20	18 (90)	M <sup>+</sup>	7 (35)	M <sup>+</sup>
N-containing (N-heterocyclic, aromatic/aliphatic amine, azo)	8	8 (100)	M <sup>+</sup> , MH <sup>+</sup> , fragment	6 (75)	M <sup>+</sup> , MH <sup>+</sup> , 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 2<sup>nd</sup> photon cannot take place at the available photon flux.



## Background in APPI and APLI



## Effect of the dopants in APPI and APLI

### Range of ionized compounds

- Both APPI and APLI:** When toluene is introduced, it consumes all the photons, and ionization takes place via toluene-mediated gas-phase ion/molecule reactions (see [4]).
- In APPI,** the number of ionized compounds decreases, because only compounds with lower IEs than toluene (8.83 eV) can be ionized.
- In APLI,** the number of ionized compounds increases, because also compounds that have low 2-photon absorption cross-sections or short-lived intermediate excited states are ionized via toluene-mediated reactions (if their IE is sufficiently low).

### Ionization efficiency

- In APPI,** the introduction of dopants increased the signal of the analytes significantly, since dopant molecules are efficiently ionized by the photons and subsequently react with the analytes via charge exchange or proton transfer.
- In APLI,** the signal of the analytes was on the same level with and without dopant present. A number of factors may be responsible for this observation including unfavorable 2-photon cross sections of the dopants, dopant mixing ratios, generation of the dopant only along the comparably narrow laser beam path.

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

### See also:

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

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