

# Improvements of the laser two-step mass spectrometry (L2MS) technique for the surface analysis of aerosol particles using VUV coherent sources

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Determination of the surface composition of soot particles is a key parameter for a better understanding of various issues such as their toxic effect on health, their inception and growth processes in flames, or their hygroscopic properties and potential role as water or ice condensation nuclei in the atmosphere.

At PhLAM laboratory, we improve the Laser Two-step Time-of-Flight Mass Spectrometry (L2MS) method in order to characterize the species adsorbed on soot particles at trace level. Particular advantages of the laser techniques are a low fragmentation and thus a high sensitivity for large molecular compounds compared to thermal desorption used in Aerosol Mass Spectrometer instruments for instance. The soot surface is probed either with the second (532 nm) or fourth (266 nm) harmonic of a nanosecond Nd:YAG laser. While mostly neutral species are produced at 532 nm, the production of ions or neutrals can be controlled by the laser fluence of the 266 nm beam.

Besides the dominating polycyclic aromatic hydrocarbon (PAH) component, we search for their derivatives (oxygenated, sulphur-containing ...) which are able to modify the physical and chemical properties of soot particles. To facilitate the identification of such species, we propose here to compare the mass spectra obtained with various ionization wavelengths. Resonant Two-Photon Ionization (R2PI) allows the specific detection of aromatic compounds thanks to resonant  $\pi^* \leftarrow \pi$  transitions. In contrast, Single Photon Ionization (SPI) at 118 nm (10.5 eV) provides a more accurate picture of the diversity of compounds adsorbed on the soot matrix including aliphatic species. Practically, desorbed neutral species are ionized either by the collimated 266 nm (4.6 eV) beam from a Nd:YAG laser or by the focused 118 nm beam generated in a home-made Xe-cell by tripling the third harmonic (355 nm) of the Nd:YAG laser (Butcher 1999). As an additional ionization source, F2 excimer laser at 157 nm is used for the exclusive ionization of PAHs with low selectivity. Differences between R2PI and SPI are evidenced in Fig. 1, especially in the 1-150 m/z range where aliphatic fragments are detected.

Depending on the laser fluence conditions, we can avoid fragmentation or use it for the identification of specific fragments.

Semi-quantitative analysis can be also achieved by comparing the results using synthetic soot with a well-known amount of the target species adsorbed on it. Sensitivities down to 0.1 femtomole per laser shot has been demonstrated (Faccinetto *et al.* 2015).

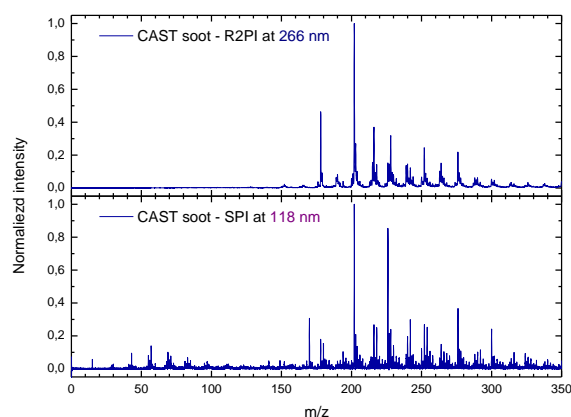


Figure 1. Comparison of the spectra obtained for the same CAST soot sample using R2PI at 266 nm and SPI at 118 nm.

Various samples have been analysed including pure PAH pellets, synthetic soot with a controlled-concentration coverage in PAHs or PAH derivative mixtures, and model laboratory flame soot. The identification potential of the method will be discussed in the light of complementary results obtained with other techniques especially Secondary Ion Mass Spectroscopy (SIMS) and Fourier Transform Infrared Spectroscopy (FTIR) which were used to strengthen the attribution in the case of complex mixtures.

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