

# Potentiality of mass spectrometry in combustion product analysis

M. Passaro<sup>1,2</sup>, B. Apicella<sup>1</sup>, A. Tregrossi<sup>1</sup>, A. Ciajolo<sup>1</sup>

1. Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

2. Chemical Engineering, Materials and Industrial Production Department, University of Naples "Federico II", P.le Tecchio 80, 80125 Napoli, Italy

## General aspects

The analysis and characterization of flame-formed products (i.e. Polycyclic Aromatic Hydrocarbons (PAH) and soot) still represents a crucial point not only for a deepening of the knowledge on reaction pathways in flames, but also for the control and monitoring of air anthropogenic emissions due to their dangerous effect on human health and on the environment.

Gas Chromatography coupled to Mass Spectrometry (GC-MS) is the analytical technique usually applied to aromatic compounds relevant in the combustion field for the qualitative and quantitative analysis of PAH [1-2], according to the UNICHIM 825/1988 and EPA (US Environmental Protection Agency) methods 8270D and 610. However, GC-MS technique is limited to the detection of PAH up to coronene (7 rings, 300 Da) and lacks in the detection of high molecular weight aromatic species (>300 Da), commonly present in complex matrixes generated from fuel-rich combustion systems [3]. This strict limitation is mainly due to the low volatility of heavy aromatic species [4], which hinders the sample vaporization necessary for the gas chromatographic analysis. Moreover, the quadrupole analyzer generally coupled with GC, presents an upper mass range limit of  $m/z$  1000.

In the present work, different kinds of ionization systems and mass analyzers for mass spectrometric techniques have been explored in order to test their potentiality in extending the detection range of combustion products analysis with respect to GC-MS.

In particular, Atmospheric Pressure Photo-ionization–Mass Spectrometry (APPI-MS) and Laser Desorption Ionization–Time of Flight Mass Spectrometry (LDI-TOFMS) have been tested in the analysis of samples collected in a fuel-rich premixed flame of ethylene-oxygen. APPI-MS, especially in the configuration where the atmospheric pressure (AP) ionization source is coupled to an ion trap analyzer (IT), is a technique amenable to PAH investigations since it is able to detect non polar species in a mass range  $m/z$  0-2500 with ionization energies between 7-10 eV [5]. LDI-TOFMS has been already applied to soot extracts sampled from fuel-rich premixed ethylene flames extending the detection of flame-formed PAH up to the highest limit typical of the first soot particles (>2000 Da) [6] and some remarkable findings have been already reported in literature [6-7]. In fact, two sequences of PAH have been identified, each one characterized by a gap of  $m/z$  24 (attributed to a net sequential addition of  $C_2$  as an ethylene bridge). A gap of  $m/z$  12 between the two sequences can be attributed to the insertion of a methylene ( $-CH_2-$ ) into a bay region of angular PAH.

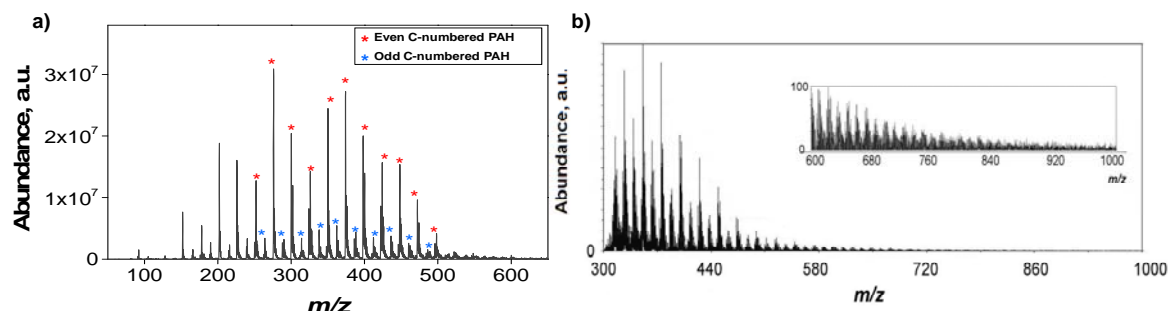
In the present work, an improved version of LDI-TOFMS apparatus has been employed, with a TOF/TOF orthogonal system, for a much higher sensitivity and resolution. Moreover, a recently developed mathematical approach for mass spectra analysis [8], based on Fast Fourier Transform (FFT) analysis, has been applied to mass spectra in order to determine periodicities which can indicate preferential growth paths.

First, samples obtained from premixed laminar Ethylene/Oxygen Flames at C/O= 0.8 and 1 and at different Heights Above Burner (HAB) have been collected in ice traps and on teflon filters. The DCM (Dichloromethane) soluble fraction has been then analyzed by GC-MS and has been deposited on a MALDI plate for LDI-MS analysis on a 4800 Plus MALDI TOF/TOF Analyzer (Applied Biosystems). The left part of the soot fraction soluble in DCM, after solvent removal, has been dissolved in toluene and analyzed by APPI-MS through an Agilent 1100 Series MSD Trap with a PhotoMate orthogonal APPI spray source.

A typical mass spectrum obtained with APPI-MS is reported in Figure 1.a) and it can be observed a double sequence of peaks, extending up to about  $m/z$  500, similar to those reported in previous works [6]. The FFT analysis revealed the presence of a sequence of major ion peaks with a spacing of 24 Da superimposed on a sequence of minor ion peaks which present the same spacing of 24 Da; the spacing between the major and the minor ion peaks is 12 Da.

The MS-MS tool of the APPI-IT instrument has been also employed in order to deepen the structure of the peaks, confirming their attribution to even and odd C-numbered PAH.

The same sequence of peaks can be observed by using LDI-TOFMS, as reported in Figure 1.b), but extending in a larger MW range, up to 1000 Da.



**Figure 1.** PAH sequences of an Ethylene/Oxygen flame at C/O=1 and HAB= 14 mm obtained by a) APPI-MS and b) LDI-MS.

By using LDI-TOFMS at higher laser power, another sequence starting at about  $m/z > 600$  and extending up to about  $m/z$  3000, has been observed with a regular and constant gap of  $m/z$  24, as confirmed by FFT analysis.

Hypotheses on the attribution of these peaks have been made and a tentative correlation with the aromatic moieties structures have been performed.

## References

- [1] Bockhorn, H., Fetting, F., Wenz, H.W. *Ber. Bunsenges*, 87, 1067 (1983).
- [2] Ciajolo, A., Barbella, R., Mattiello, M., D'Alessio, A. *Proc. Combust. Instit.*, 19, 1369 (1982).
- [3] Ciajolo, A., Barbella, R., Tregrossi, A., Bonfanti, L. *Proc. Combust. Instit.*, 27, 1481 (1998).
- [4] Fetzer, J.C. Winefordner, J.D. (Series Ed.), Wiley Interscience, Hoboken, NJ, Vol. 158 (2000).
- [5] Robb, D.B., Blades, M.W. *Anal. Chim. Acta*, 627, 34 (2008).
- [6] Apicella, B., Carpentieri, A., Alfè, M., Barbella, R., Tregrossi, A., Pucci, P., Ciajolo, A. *Proc. Combust. Instit.*, 31, 547 (2007).
- [7] Apicella, B., Alfè, M., Ciajolo, A. *Comb. Sci. Tech.*, 182, 640 (2010).
- [8] Apicella, B., Bruno, A., Wang, X., Spinelli, N. *Int. J. Mass Spectrom.*, 338, 30 (2013).