

# **Real Time Analysis Of Polycyclic Aromatic Hydrocarbons From Atmospheric Pressure Combustion Sources**

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The present paper regards the comparison between on-line and off-line analyses of light hydrocarbons and polycyclic aromatic hydrocarbons (PAH) from atmospheric-pressure combustion sources for the validation of a recently developed apparatus for the real-time analysis of pollutants.

The experimental core of this apparatus is the time of flight mass spectrometry (TOF-MS), which has been implemented for obtaining in real time complete mass spectra up to hundred of thousands of Dalton (nanometric dimensions). The particulate source used for the standardization of the technique is a premixed laminar flame. The on-line transfer of combustion gases from atmospheric pressure to the high vacuum of a mass spectrometer has been performed by a combination of a steady sampling flow from the flame with a pulsed molecular beam up to the ionization chamber of TOF-MS.

The high sensitivity and fast response of the technique should allow the application also to practical complex sources such as exhausts from engines and from industrial plants for energy production and waste disposal beside to atmospheric aerosols. The validation of the technique has been performed in this work by comparing the composition profiles of light hydrocarbons and PAH measured by TOF-MS with those evaluated by means of sampling and conventional on-line and off-line analytical techniques.

Conventional techniques are based on gas chromatography (GC). GC was applied on-line with different detectors: flame ionization detector (FID) for the analysis of hydrocarbons from methane (C<sub>1</sub>) up to benzene (C<sub>6</sub>); thermoconductibility detector (TCD) for the analysis of CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. Off-line GC equipped with a quadrupole mass spectrometer (MS) was applied to the condensed phases sampled from the flame and dissolved in dichloromethane for the analysis of PAH.

## **1. Introduction**

Polycyclic aromatic hydrocarbons (PAH) are pollutants always present in the exhausts from combustion processes like engines and plants for energy production and waste disposal. Their ubiquity is largely a consequence of their high-temperature

thermodynamic stability due both to the delocalized orbitals that provide stable repositories for electrons and to the low H/C ratios that tie up little hydrogen, serving to increase system entropy. Some of the notable difficulties in the study of PAH are low solubility, low volatility, multisite reactivity, synthesis, and identification.

The analysis of PAH up to 300-400 u requires the application of conventional and time-consuming off-line analytical techniques as mass spectrometry, coupled or not to gaschromatography, to aromatic compounds sampled in combustion systems and dissolved in organic compounds (Bockhorn 1983; Ciajolo 1982; 1996; Tregrossi 1999). Moreover, this kind of techniques neglects the higher molecular weight aromatic species that are also present in the tarry carbonaceous particulates, generated from fuel-rich combustion (Apicella 2003).

Only recently off-line Laser Desorption Ionisation-Time of Flight-Mass Spectrometry (LDI-TOF-MS) of combustion formed samples have been found able to extending up to 1000 Da the MW range detected (Apicella 2006). Also in this case, the analysis is very time-consuming for the preparation of the samples and the choice of optimal configuration of the instrument. Moreover, this kind of analysis could not be quantitative but it gives only qualitative information.

The present paper regards the application of a real time technique for the on-line analysis of pollutants with masses up to PAH (400 u) from atmospheric pressure combustion systems. The technique is the time of flight mass spectrometry (TOF-MS), which have been implemented for obtaining in real time complete mass spectra up PAH and to molecules of hundred of thousands of Dalton (nanometric dimensions). The particulate source used for the standardization of the technique is a premixed laminar flame. The high sensibility of the technique will allow in the next future the application to real and therefore more complex sources such as engines, industrial plant exhausts and atmospheric aerosols.

Before the extension of the detection range of TOF-MS up to species never detected before, the validation of technique have been performed in this work by a comparison with composition profiles of PAH evaluated by means of conventional sampling and analytical techniques.

## **2. Experimental section**

A premixed laminar flame has been used as combustion source for this work, as it is the ideal system for the development and set up of innovative diagnostic methods for pollutant analysis. In fact, it is a system where the combustion conditions can be carefully controlled and reproducible. Premixed laminar flames have been produced on a commercial McKenna burner constituted of a sintered stainless-steel centre plug (60 mm diameter) and an outer sintered bronze section.

The burner can move vertically by means of a micrometric screw in order to change the sampling position. A flame stabiliser is located at 30 mm of height above the burner in order to obtain a cylindrical flame. Combustion products are isokinetically sampled along the flame axis by means of a stainless-steel water-cooled probe with a conic orifice (i.d.=2 mm). However, in order to avoid condensation and agglomeration inside the probe and along the sampling line, the probe is equipped with another jacket with a recirculating inert gas for diluting the combustion gases. A commercial pulsed valve has

been modified to realize a molecular beam for the transfer of PAH and particulate to TOF-MS apparatus under minimal perturbation conditions.

The TOF-MS apparatus, not commercially available with the needed performances, has been projected with a joint venture among the Istituto di Ricerche sulla Combustione with the Departments of Physics and Chemical Engineering of Università di Napoli "Federico II" and the INFM-CNR. It was built up by a specialized German company (Kaesdorf s.r.l.). The TOF-MS. is composed by : a pumping system, two stainless chambers, ionizing chamber and detection chamber, respectively, a flight tube, two MCP detectors (linear and reflectron) and an acquisition system trough a PC.

The possibility of switching the ionizing sources allows using electron impact for ionizing low molecular species and laser radiation for ionizing high molecular weight species through the accurate selection of the suitable wavelength for PAH and particulate ionization without fragmentation.

More details on the experimental set-up have been reported in a previous paper (Panariello 2008).

A similar premixed flame is used for the conventional analysis of PAH. The flame is equipped with a steel water-cooled probe with a conic orifice (i.d.=2 mm). Downstream of the probe, an ice-cooled trap and a teflon filter allowed the sampling of condensable species and soot, respectively. Sampling for a long time was necessary to collect sufficient condensed material and soot for the analyses. Organic particulate collected on the probe wall, in the teflon filter and in the ice-cooled trap is extracted by dichloromethane (DCM) to separate the condensed species, that are soluble in DCM, from soot. The soot was washed with dichloromethane until there was no significant fluorescence signal in the washings, in order to extract the organic species adsorbed on it. PAH from two to seven rings will be analyzed in the DCM soluble fraction of particulate by means of a quadrupole mass spectrometer. GC-MS and particle beam mass spectrometry (PB-MS) with direct injection of samples in the source have been used for PAH analysis. More details are reported in a previous paper (Ciajolo 1994).

### 3. Results and discussion

The flame was operated at C/O= 0.8, i.e. well above the soot formation limit (C/O= 0.66), in order to increase the formation of pyrolytic products like PAH. The main characteristics of the flame is reported in Tab.1.

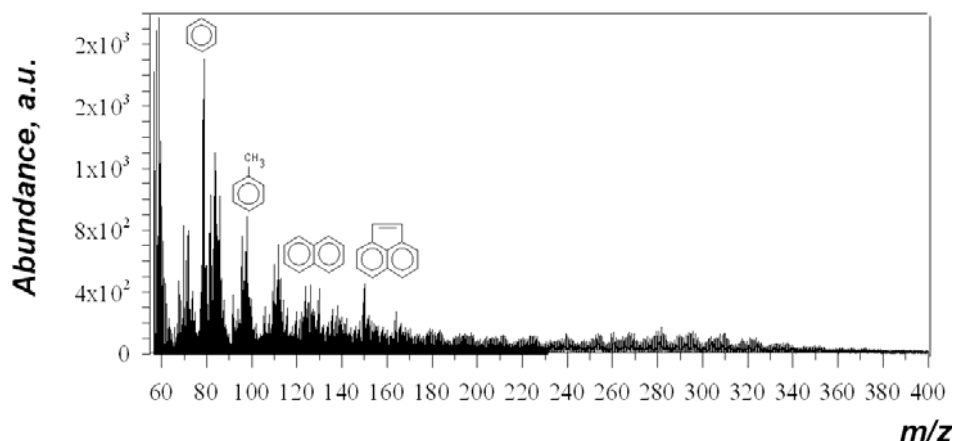
**Table 1.** *Characteristics of the ethylene flame with C/O=0.8 ( $\Phi=2.42$ )(Apicella et al. 2002).*

<b>Fuel</b>	44.5 % (3.02 NI min <sup>-1</sup> )
<b>Oxidant</b>	55.5% (3,76 NI min <sup>-1</sup> )
<b>Maximum temperature</b>	2 mm (1720 K)
<b>Maximum PAH concentration</b>	6 mm
<b>End of oxidation region</b>	4 mm

For TOF-MS analysis, the probe is equipped with a jacked with recirculation of an inert gas for diluting the sampled gases avoiding condensation inside the probe. A heated line connect the probe with the pulsed valve that is also heated. Electron impact at 70 eV is

used as ionization source in order to perform a more homogeneous comparison with the off-line mass spectrometer that uses the same ionization source.

In Fig.1 is reported the spectrum acquired with TOF-MS at 6 mm above the burner, where the PAH concentration is maximum (see Tab.1). The spectrum is reported in the range 60-400 Da, as before 60 Da the signals are quenched by using a mass filter deflecting electrostatically light masses in order to avoid the detector saturation and to increase the sensitivity for less abundant high molecular masses.



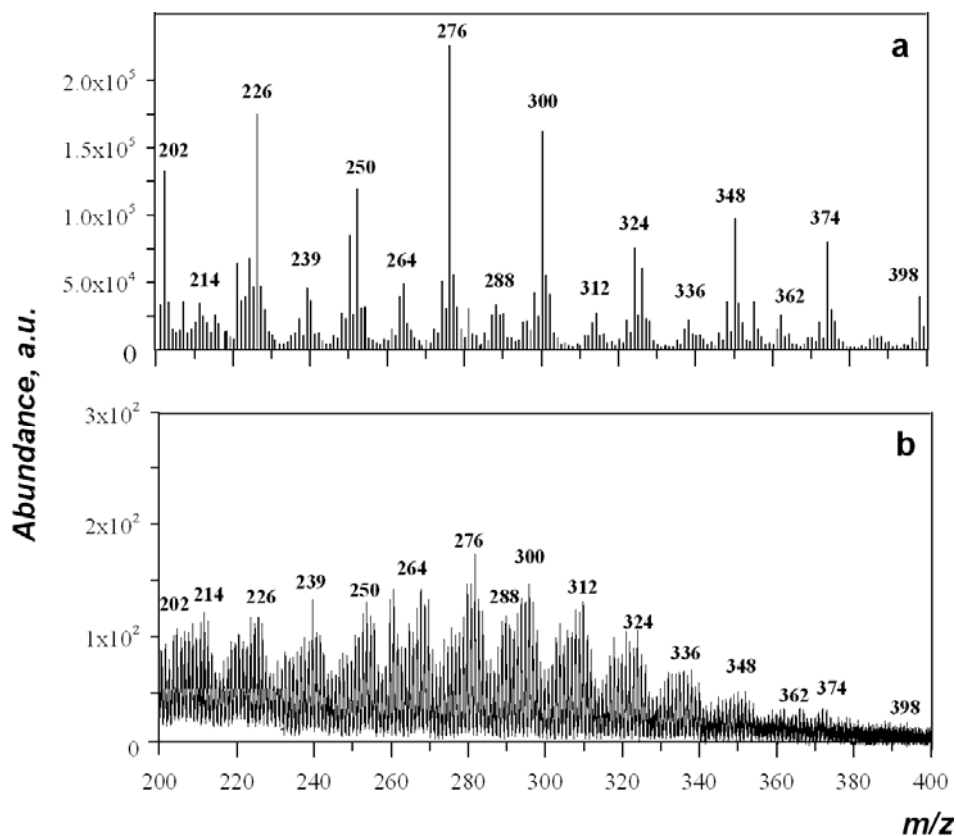
**Fig.1:** On-line TOF-MS spectrum of combustion gases sampled at  $z=6$  mm of height above the burner in the range  $m/z$  60-400 with the structures of the most abundant species: benzene, toluene, naphthalene and acenaphthylene.

It is possible to observe in the spectrum the typical pyrolytic products of a fuel rich flame as benzene, toluene, biphenyl, and the PAH, whose most abundant species are naphthalene and acenaphthylene.

For off-line analysis of PAH two techniques are generally used: the gas chromatography connected with a quadrupole mass spectrometer (GC-MS) or a particle beam mass spectrometer, with a direct injection in the ionization chamber of the spectrometer (PB-MS). In the case of GC-MS, the organic particulate dissolved in DCM is separated through a GC and each PAH is analyzed by a mass spectrometer. The same quadrupole mass spectrometer can be used for obtaining a complete mass spectrum of PAH, without separation, with the direct injection into the ionization source through the use of a particle beam (PB). By using GC-MS the PAH detection up to 300 Da is obtained whereas the use of PB-MS extends the detection up to 400 Da. For comparison with TOF-MS analysis, the PB-MS spectrum is used as it presents the simultaneous detection of all masses. The detected masses start from 200 Da as the devolatilization of the solvent before ionization drags also the light masses hindering their detection.

In Fig. 2 a PB-MS spectrum of organic particulate is reported along with the TOF-MS spectrum both acquired at 6 mm above the burner. The spectra appear very similar in terms of peaks detected and both present a progressive increase followed by a signal decrease, with a maximum around 276 Da. Both the mass spectra consist of a sequence of major ion peaks with a spacing of 24 u superimposed on a sequence of minor ion

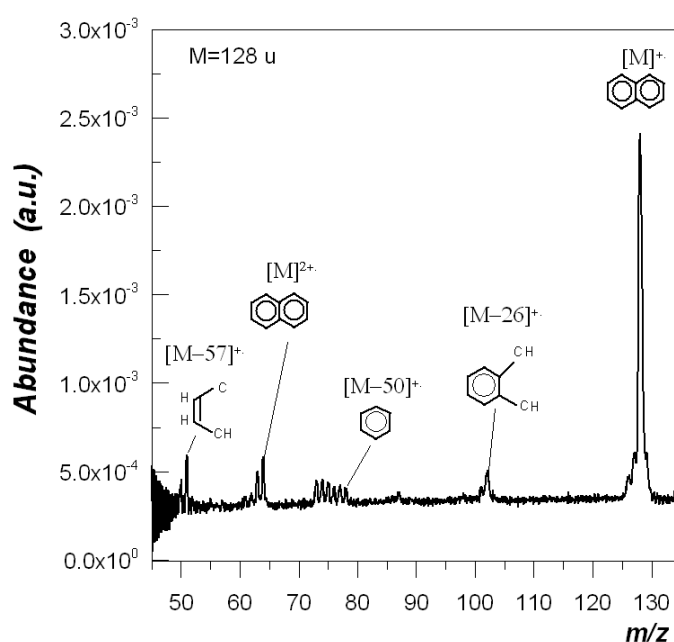
peaks which present the same spacing of 24 u; the spacing between the major and the minor ion peaks is 12 u. In the mass range  $m/z$  200-300 the GC-MS analysis has allowed the attribution of the sequence of major ion peaks, spaced by 24 u, mainly due to PAH with an even number of carbon atoms (even-C-numbered PAH) where the molecular weight difference corresponds to net sequential addition of C<sub>2</sub> as an ethylene bridge. (Tregrossi, 1999).



**Fig.2:** PB-MS spectrum of soot extract (top) and on-line TOF-MS spectrum of combustion gases (bottom) both sampled at  $z=6\text{mm}$  of height above the burner in the range  $m/z$  200-400.

By contrast, the sequence of minor peaks, spaced at 12 u relative to the major peaks, were ascribed to odd-C-numbered PAH containing cyclopenta-fused rings coming from the insertion of a methylene (-CH<sub>2</sub>-) into a bay region of angular PAH. The attribution of the minor odd-C-numbered peaks to cyclopenta-fused ring PAH is corroborated by the similar intensity of  $(M-1)^+$  and  $M^+$  mass peaks, due to the easy loss of hydrogen linked on methylene bridge, observed in the PB-MS spectra. However, the difference between even-C-numbered PAH and odd-C-numbered PAH in TOF-MS spectrum (Fig. 2b) is not so evident like in PB-MS spectrum (Fig. 2a). Moreover, in Fig. 2b, but also in Fig. 1, it is possible to observe a high number of peaks for every mass number, more than the main peaks interpreted as parent peaks. This feature is not due to background

noise, as found by a comparison with a background spectrum, and it is probably originated from the fragmentation of high molecular weight species, molecules or particles. In this case, the absence of fragmentation pathways in PB-MS spectrum (Fig.2b) could be explained with the absence of particles in the DCM-soluble fraction of organic particulate. For testing the hypothesis of particles fragmentation a standard PAH (pure naphthalene, Aldrich) was fed into the valve of the TOF-MS and its TOF-MS spectrum was acquired and reported Fig. 3a. The naphthalene spectrum, obtained by using the same ionization source (electron impact at 70 eV) used for measurements in flame, present a parent peak with very low fragmentation, in good agreement with the published NIST spectrum (Fig.3b) therefore confirming that the experimental condition used do not induce PAH fragmentation.

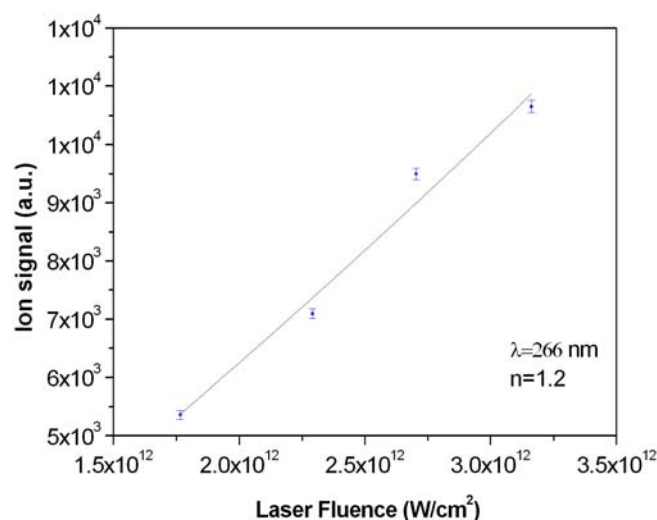


**Fig.3:** On-line TOF-MS spectrum of naphthalene in the range  $m/z$  40-140.

The hypothesis of particles fragmentation contribution to flame spectrum is also corroborated by the laser fluence dependence of the TOF-MS spectrum acquired in flame by using laser ionization (Panariello, 2008). Indeed, a means to better characterize the observed ions is to study their ionization behaviour by varying the photon fluence through a variation of the laser power density. In this way, it is possible to determine the ionisation order  $n$ , defined by:

$$I_m^+ = \text{const}(P_L)^n$$

where  $I_m^+$  denotes the intensity of the ion signal of mass  $m$  (which ideally should contain only one constituent), and  $P_L$  denotes the power density of the laser pulse. The value of  $n$  was determined based on the slope of the  $\lg(I_m^+)$  vs.  $\lg(P_L)$  plot reported in Fig.4.



**Fig.4:** Total number of ions vs. laser power density..

In the absence of saturation effects the slope represents the number of photons required for the ionization process. For PAH peaks, obtained ionizing with a wavelength of  $\lambda=266$  nm, a straight line is obtained with a slope  $n=1.2$ . Other authors using similar laser wavelength (248 nm) (Arhens 1998; Grotheer,2007) reported a slope  $n= 2$  for PAH, indicating photonionization with 2 photons, whereas they found (Grotheer 2007) a single photon process (slope  $n=1$ ) for particles. Therefore, the slope  $n=1.2$  could indicate the contribution of different processes like PAH ionization ( $n=2$ ) and particles fragment ionization ( $n=1$ ).

Further work was planned for verifying this hypothesis and in particular the acquisition of spectra in the same experimental conditions but with ionization by a shorter wavelength or by a picoseconds pulses, in order to limit the occurrence of fragmentation processes.

#### 4. Conclusions

A molecular beam TOF-MS apparatus purposely designed for combustion pollutant real-time analysis from atmospheric pressure sources was tested for the analysis of PAH from a premixed flame. The good agreement in terms of peaks detected and general trends of signals between on-line TOF-MS spectrum and off-line PB-MS spectrum acquired from the same combustion system was a good test for the reliability of TOF-MS apparatus.

Therefore, in the next future the detection will be extended to molecules of hundred of thousands of Dalton (nanometric dimensions) whose characterization is still an open problem.

## 5. References

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