On-line detection of benzene and polycyclic aromatic hydrocarbons (PAH) has been performed by using a time of flight mass spectrometer (TOF-MS), which has been designed and implemented for obtaining in real time complete mass spectra from molecules of few mass units up to thousands of mass units (corresponding to nanometric dimensions).

The flames have been fed with different C/O ratios under and above the soot formation threshold (C/O=0.66) but in any case well above the stoichiometric limit (C/O=0.33). The combustion source used 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 expansion into the ionization chamber of TOF-MS (molecular beam).

The validation of the technique has been performed in this work by comparing the composition profiles of benzene and PAH measured by TOF-MS with those found in the literature evaluated by means of conventional analytical techniques based on gas chromatography (GC). The good agreement obtained with the literature suggests that the apparatus can be used for the on-line monitor of combustion systems. The high sensibility 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 mass spectrometric analysis moreover allows to detect and identify through the fragmentation paths more hydrocarbon species with respect to conventional techniques that can be useful for studying kinetic mechanism of pyrolitic reactions.

1. **Introduction**

In the present work, a novel apparatus based on Time of Flight Mass Spectrometry (TOF-MS), improved and optimized, have been used for benzene and PAH on-line detection and the profiles of these species have been evaluated along two different flames with C/O ratios of 0.6 and 0.65.
The profiles have been also compared, when available, with the same profiles measured in similar condition with conventional gas chromatographic techniques and reported in the literature (Ciajolo et al., 1994; Apicella et al., 2002). The comparison has been used for validating the TOF-MS apparatus as a technique for a real-time study of combustion processes, without the use of onerous and time-consuming off-line techniques.

2. Experimental

2.1 Set-up
An innovative set-up specifically designed for the on-line detection of combustion products of high masses has been used for the analysis of PAH in an atmospheric-pressure ethylene flame. The experimental set-up is deeper described in a previous work (Panariello et al., 2008).

Basically, it is composed of: (i) a combustion system, (ii) a sampling probe and transfer line, (iii) a supersonic molecular beam, and (iv) a reflectron TOF-MS instrument, designed and built by Kaesdorf s.r.l., where different types of ionization sources can be used.

The TOF-MS system can be operated with a mass filter, a disposal where a pulsed electric field is used to deflect the lowest mass ions. In these conditions, saturation of the MCP due to the very high signal intensities produced by the most abundant low-mass ions is avoided and the dynamic range of the detector is preserved.

The ionization has been performed by electron impact (EI), which consists of an electron beam produced by a hot tungsten loop filament. In the present experiment a pulse duration of 2 microseconds with a repetition rate of 20 Hz was used.

2.2 Hydrocarbon source
As combustion pollutant source, a fuel-rich ethylene/oxygen laminar premixed flame was used, produced by a McKenna burner. The burner can be translated allowing the sampling at different positions in the flame.

A water-cooled stainless-steel probe (2mm i.d.), connected to a suction pump, was used for the sampling of combustion gases. The probe is also equipped with a second jacket for the recirculation of inert gas in order to avoid condensation and/or aggregation inside the probe. Flow rates of gases and gas-phase fuel (C₂H₄, O₂) are controlled with mass flow controllers (Bronkhorst Inc.).

The sampled mixture was guided by a 3mm (i.d.) steel tube, heated at 200°C, from the probe up to the vacuum chambers of the TOF-MS system. The sampled gases enter the first chamber of the instrument through a solenoid actuated valve (General Valve Corp.) equipped with a 0.8mm aperture nozzle generating a pulsed supersonic jet. The valve has been modified in order to minimize the dead volume and to increase the suction efficiency. The valve is heated at 70°C. The central part of the supersonic jet is extracted by a skimmer to produce a pulsed molecular beam.
3. Results and discussion

The flame was operated at two different C/O ratios: 0.6 and 0.65 before and just above the soot formation limit (C/O = 0.62 (Bohom et al., 1988)), respectively. The two flames will be defined in the following no-sooting and slightly sooting flame, respectively.

The flame gas sampling is accomplished with a water-cooled stainless-steel probe connected to a suction pump. To avoid condensation inside the probe and the transfer line, the sampled gases are diluted within the probe by fluxing an inert gas (helium) in the inner jacket of the probe.

The flow of the inert gas and the suction flow have been optimized experimentally, by using the maximum helium flow for minimizing aggregation and condensation inside the probe, but operating in isokinetic conditions in order to reduce perturbation effect on the reaction environment.

All the transfer line, from the probe up to the valve is heated at 200°C, in order to avoid condensation and aggregation. The valve is kept at 70°C.

A TOF-MS spectrum acquired at 5 mm height above the burner at C/O = 0.65 in the range m/z 70-220 along with its expanded region in the range m/z 200-500 is reported in Fig.1, as an example.

![Figure 1. A TOF-MS spectrum acquired at 5 mm height above the burner at C/O=0.65 along with its expanded region in the range m/z 200-500 (inset).](image-url)
As usually found in most combustion systems and reported in literature (Homann et al., 1985; Bockorn et al., 1983; Haynes et al., 1991; Ciajolo et al., 1994), polycyclic aromatic hydrocarbons are much less abundant than benzene and are mainly composed of two-ring compounds, such as naphthalene (128 u) and acenaphthylene (178 u) and to a lesser measure, of three- up to five-ring PAH as phenanthrene (178 u), fluoranthene (202 u), pyrene (202 u) and cyclopentapyrene (252 u). Other PAH heavier than 252 u, extending up to 398 u (ovalene) were detected (inset of fig.2) in still lower amounts and therefore their profiles are not reported here.

As mass peak of species heavier than 152 u can correspond to different isomers, whose number increases with molecular weight, (e.e. 202 u corresponds to fluoranthene, pyrene, acephenanthrylene and acenethylen) in the following PAH will be indicated with their MW.

In Fig.2 the axial profiles of the relative abundance of benzene for flame at C/O=0.65 measured by TOF-MS (a) and by conventional gas chromatographic techniques, adapted from literature (b, Ciajolo e al., 1994), are reported.

In all the graphs here presented the lines are only a guide for eyes and not mathematical interpolation of data.

![Figure 2. Axial profiles of the relative abundance of benzene at C/O=0.65 (a) and the same profile found in literature (Ciajolo et al., 1994) at the same C/O ratio (b).](image)

The agreement between TOF-MS profiles and those evaluated by conventional techniques (Ciajolo et al., 1994) is very good, both in terms of trend along the flame and in quantitative terms, as the absolute values reported on y- axis are comparable.

Indeed, TOF-MS concentration of benzene is reported as “normalised signal intensity”, which means that the area of each peak is evaluated, subtracting the contribution of other species, if necessary, dividing for the ionization efficiency at 70 eV found in literature (Nist) and, at least, dividing for the total area of the mass spectrum, including all the species up to benzene. It means that the absolute value reported for the concentration represents the percentage in volume reported in the literature graphs and therefore it is possible also to compare quantitatively the absolute values. Also the quantitative comparison is very comfortable.
In fig. 3, the axial profiles of the relative abundances (not normalized in this case) of the most abundant PAH (128u, 152u, 178u, 202u) are reported for C/O= 0.6 (fig.3a) and C/O=0.65 (fig.3b).

The profiles show that the PAH concentration rises reaching a peak value at 6 mm for no-sooting and 5mm for slightly sooting flame, and after this maximum, decreases reaching a plautau for both the flames.

As expected, PAH are more abundant in the higher C/O ratio conditions.

Figure 3. Axial profiles of the most abundant PAH (128u, 152u, 178u, 202u) at C/O=0.6 (a) and at C/O= 0.65 (b).

In fig. 4 the same profiles from the literature at C/O=0.64 have been shown.

Figure 4. Axial profiles of the most abundant PAH (128u, 178u, 202u) adapted from literature (Ciajolo et al., 1994) at C/O ratio 0.64(b).
The agreement between TOF-MS PAH profiles and those evaluated by conventional techniques is very good also for PAH for the slightly sooting flame. Literature data are not available for $C/O=0.6$ in a similar combustion system as the PAH concentration is so low that very long time of withdrawing should be necessary in order to have detectable PAH concentration. By contrast, TOF-MS system is able to real-time detect with sampling time of order of minutes (typically 5) and this is one of the most important advantages of the technique presented in this paper.

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References


