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Separative and mass spectrometric techniques in the diagnostics of soot precursors

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Carbonaceous particulate matter formed in combustion systems can be operationally separated in two phases on the basis of its solubility in dichloromethane (DCM). The DCM soluble fraction, named soot extract, is a tarry phase composed of polycyclic aromatic hydrocarbons and a higher molecular weight fraction whose composition and structure is still unknown.
In this work separation techniques have been used in combination with mass spectrometry in order to clarify the structure of the larger soot extract fractions.

1. Introduction

The structure, the molecular weight (MW) distribution and chemical functionalities of carbonaceous particular matter formed in combustion systems are object of study since many years (Bockhorn, 2009) because of its adverse impact on human health and environment.
Hence, many demands are put on the development of analytical techniques for unveiling its chemical-physical nature and formation mechanism.
Laser Desorption Ionization-Mass Spectrometry (LDI-MS) of raw carbonaceous particulate matter of high MW polydispersity does not allow the analysis of the higher MW species less easily desorbed and detected in respect to the smaller molecules. In order to overcome this drawback, a new method was proposed (Morgan, 2008) in which the samples are pre-fractionated by thin layer chromatography (TLC), and LDI-MS analysis of the separated fractions is directly performed on the chromatographic plates. This method separates the more abundant small molecules from the less abundant large molecules to permit the generation of their mass spectra independently. Moreover, the concentration of sample by spreading over the TLC-plate is reduced limiting the multimer formation and improving the reproducibility of the spectra.
In the present work the TLC fractionation combined with LDI/MS analysis has been applied to the DCM-extract from particulate sampled in a premixed flame. Moreover, the narrow MW fractions separated by TLC have been further analyzed by Size exclusion chromatography (SEC), synchronous fluorescence and LDI-MS.

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2. Experimental

The experimental combustion system has been described in detail elsewhere (Ciajolo 1994, Apicella 2002). Briefly, carbonaceous particulate matter was collected from a premixed laminar ethylene flame. The fuel-rich flame was established on a commercial McKenna burner in very sooting conditions (C/O = 1, i.e. Φ = 3.03). The particulate collected was extracted with DCM until there was no detectable UV-fluorescence signal in the DCM washings. The extracted organic species were named DCM-extract.
DCM-extract, dried and weighed, was dissolved in chloroform for TLC analysis.

2.1 Thin Layer chromatography (TLC)

Polyester backed 20 x 20 cm TLC-plates with silica gel thickness of 250 µm (Whatman, UK) were used. The plates were cut into strips (5 cm x 10 cm) and washed with acetone and then chloroform before use. The DCM-extract sample was spotted onto the plates as a solution in chloroform; multiple spots were added to build up the amount of sample. The TLC plates were developed with different combinations of solvents. Typically, the plates were placed into a development tank containing the first solvent, and once the solvent front had reached a height of ~8 cm above the origin, the plate was removed and dried. The TLC-plate bearing the sample was then developed with a second solvent, until the solvent moved up the plate and away from the sample up to a height of approximately 5 cm.
The material at the furthest solvent front was labeled fraction 1, the intermediate material was named fraction 2 and the material immobile in both eluents was denoted as fraction 3. The different fractions on the TLC plates were then recovered for further analysis. For LDI-MS, the fractions of the TLC plates were cut into small sections and directly stuck on to the LDI-MS target using double-sided sticky tape. For SEC and UV-Fluorescence analysis, the samples were recovered by scraping the silica from the plates and extraction in N-methyl pirrolidone (NMP) followed by filtration at 1 µm to remove silica particles.

2.2 Laser Desorption / Ionisation Mass Spectrometry (LDI-MS)

A Bruker Daltonics Reflex IV MALDI-TOF mass spectrometer was used for LDI-MS analysis. Because the samples ranged in color from black to yellow and were able to absorb the UV-laser wavelength of 337 nm, no matrix was used, and only positively charged ions were analyzed.
A high-mass detector operating in the linear time of flight (TOF) mode was set to its highest value (10 kV) to investigate the higher molecular mass region and the digital gain (DG) was set to its lowest level (1x). In reflector-mode, where no high mass acceleration (HMA) is available it was necessary to increase the DG to 10x to obtain a satisfactory ion current. In general higher laser powers were needed to detect equivalent ion intensities compared to linear mode operation. In all cases shown, the summation of 10 spectra was taken using the pulsed ion extraction (PIE) method on the same sample spot. In both linear and reflector modes, the conditions used included no extraction delay and a mass range of m/z 0-10,000. The extraction voltage was set to 20 kV for all the analyses.

2.3 Size Exclusion Chromatography (SEC)
A 300 mm long, 7.5 mm i.d. polystyrene/polydivinylbenzene-packed Mixed D column with 5µm particles was used (Polymer Laboratories, Church Stretton, UK). The column was operated at 80 °C at a flow rate of 0.5 ml min^{-1}. NMP was used as the mobile phase. Detection was carried out using a Knauer Smartline diode array UV-absorbance detector. As NMP is opaque at 254 nm, detection of standard compounds and samples was performed at 270, 300, 350 and 370 nm, where NMP is partially transparent.

2.4 UV-Fluorescence (UV-F) Spectroscopy
A quartz cell with 1 cm path length was used in a Perkin-Elmer LS50 luminescence spectrometer set to scan at 240 nm min^{-1} with a slit width of 5 nm. Synchronous spectra were obtained at a constant wavelength difference of 20 nm using NMP as solvent.

3. Results and Discussion

In the search for a proper fractionation of the DCM-extract, several TLC plates were developed with different combination of solvents. Different trials have been made, with the following sequence of solvents: 1) methanol/acetone; 2) acetone/methanol/pentane; 3) acetone/chloroform; 4) chloroform/acetone.
The best results (separation of fraction with intermediate MW) were obtained with the solvent sequence 4) able to separate the material at the furthest solvent front (fraction 1), the intermediate material (immobile in chloroform and mobile in acetone) (fraction 2) and the material immobile in both eluents (fraction 3).
Fig 1a shows the SEC chromatograms of the TLC fractions of the DCM-extract as a function of the MW, obtained by polystyrene calibration. An early eluting peak was observed, which corresponds to material of molecular size unable to penetrate the porosity of the column packing, and referred to as “excluded” from the column porosity.

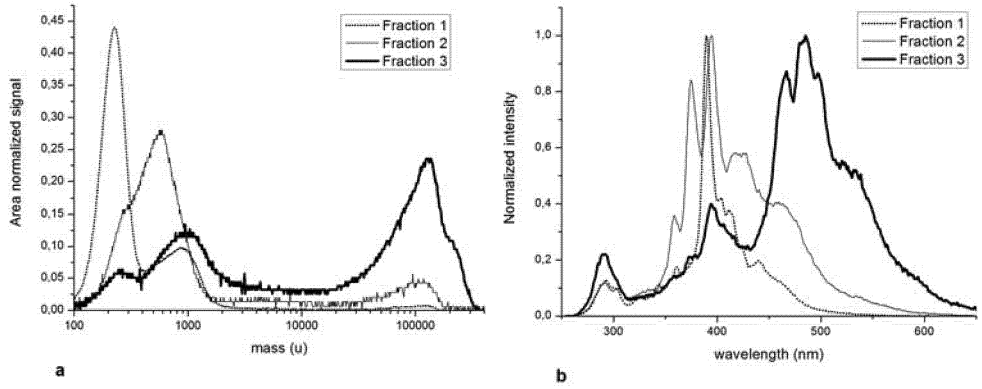

Figure 1. SEC chromatograms of TLC fractions of the DCM-extract (a);synchronous fluorescence spectrum with $\Delta\lambda$=20 nm (b).

The exclusion limit of the column, defined according to the standards of polystyrene behaviour, is about 200,000 u. However, molecular conformation is considered to be the

factor that causes molecules to become excluded from the column porosity rather than the molecular weight. It is important to notice that the intensity of the excluded peak increases from fraction 1 to 3 (the most intense signal corresponding to the less mobile fraction). Fraction 1 (Fig 1a) is mainly composed by low MW species, up to around 300 u, probably the PAH typically detected by gas chromatography-mass spectrometry (GC-MS). This is confirmed also by synchronous spectroscopy, reported in Fig.1b, where typical signals of small PAH are present. Fraction 3 is shifted to higher MW with respect to Fraction 2 and Fraction 1 (Fig.1a) and longer emission wavelength (Fig.1b) confirming the presence of larger aromatic species. More in detail, the SEC chromatogram of fraction 2 exhibits a small shoulder overlapped to the higher tail of fraction 1, corresponding to masses between 200u and 300u, and a main peak with the maximum around 500 u. Fraction 3 is constituted by a MW regions partially overlapped to the higher tail of fraction 2, but extending in a large MW range, with a maximum around 1000 u and a shift-off around 2500 u.

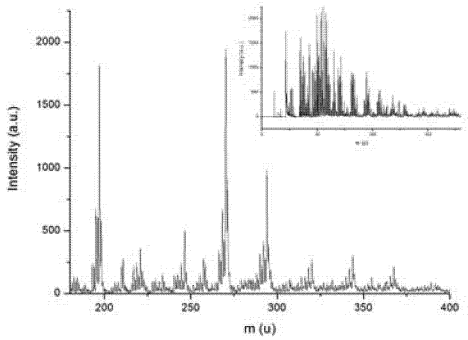

Figure 2. Reflectron LDI-MS spectrum of fraction 1 at 90% of laser power. In the inset zoom in the low MW region.

TLC fractionation presents a series of advantages with respect to collecting the eluent fraction directly from a SEC column: a smaller amount of sample is necessary and long time-consuming operations are avoided. Furthermore, the recovery of the fractions from extremely dilute NMP (used as eluent in SEC) solutions is complex, because NMP can oxidize and polymerize under the usual conditions used for evaporating NMP from solution (Berrueco, 2009). Therefore, by using directly a small section of TLC plate on the LD target, it is possible to avoid problems of eventual presence of residual NMP or contamination on the target.

The LDI-MS spectra of the three fractions are reported in Figs 2-4. The spectra are obtained in reflectron configuration, as the resolution is remarkably improved (as compared to linear mode operation), without any significant loss of sensitivity at the MW range of interest. For all the fractions, spectra at different laser powers have been measured and selected spectra at 90% of laser power have been reported. The mass spectra of fraction 1, reported in Fig.2, show that it is constituted of small PAH in the range 200-400 u, as demonstrated by the presence of peaks with the typical sequence

with gaps at 12 and 24 mass units. In the inset of Fig. 2 a zoom of the low MW region allows to observe that, although at this high laser power the best signal/noise ratio in the range of interest is achieved with respect to the other lower laser power employed (not shown here), a massive peak fragmentation occurs.
The spectrum of fraction 2, reported in Fig.3, presents a mass distribution at higher MW, centered around 700 u, in good agreement with the SEC results (Fig.1b). As shown in the inset, also in this case a large fragmentation occurs, with a similar sequence of peaks with respect to fraction 1 (main peaks with spacing at 12 u with a lot of satellite peaks around).

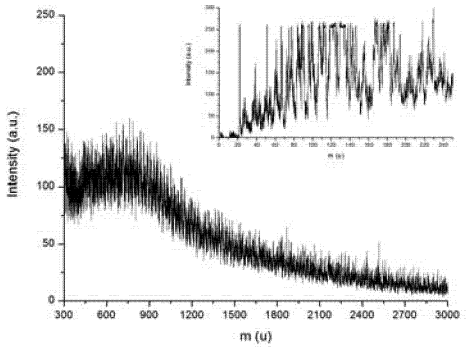

Figure 3. Reflectron LDI-MS spectrum of fraction 2 at 90% of the laser power. In the inset zoom in the low MW region.

Fraction 3, whose LDI-MS spectrum is reported in Fig.4, presents a MW distribution further shifted towards larger values, with a maximum around 1000u, in agreement with SEC (Fig.1a). By contrast, the fragmentation paths appear to be different with respect to the other fractions. At 60% of laser power, fraction 3 starts to fragment giving masses mainly around 500 u. Only at higher laser power (90%), peaks at lower MW, less than 200u, appear, probably due to a successive fragmentation of the daughter peaks at 500u. As it is well known, fragmentation pathways can give useful insights on mass structure of the molecules investigated.
The features observed in the spectra, along with the information from SEC and UV-F, demonstrate a structure of fraction 2 similar to PAH of fraction 1, but with bigger condensed aromatic units. For fraction 3, it is possible to hypothesize a mixed aliphatic/aromatic structure, which can justify the two-step fragmentation: at lower laser power, aliphatic chains can start to fragment, giving condensed aromatic units of around 500u, similar to the molecules present in fraction 1 and 2, which can after definitely fragment at very high laser power, able to share also aromatic structure.
These interesting features can be interpreted, in agreement with previous study on flame –formed carbon particulate (Apicella, 2007, Apicella, 2009, Alfè, 2008), considering two main classes of species present in soot extract and probably constituting soot precursors. The former class has mainly aromatic moieties, with structure progressively becoming bigger and, probably, tridimensional for the insertion of pentagons. The

second class has a polymeric structure with small aromatic moieties linked by aliphatic bridges and probably extends up to higher MW, as shown by the presence of another peak in SEC chromatogram of fraction 3 (Fig.1a), near to the exclusion limit of the column, not detected here by LDI-MS because of the occurrence of fragmentation and/or as the MW is above the range detectable by LD-MS (around 20,000 u in reflectron mode). These conclusions, however, need more study in function of LDI-MS parameters that have been planned for the future.

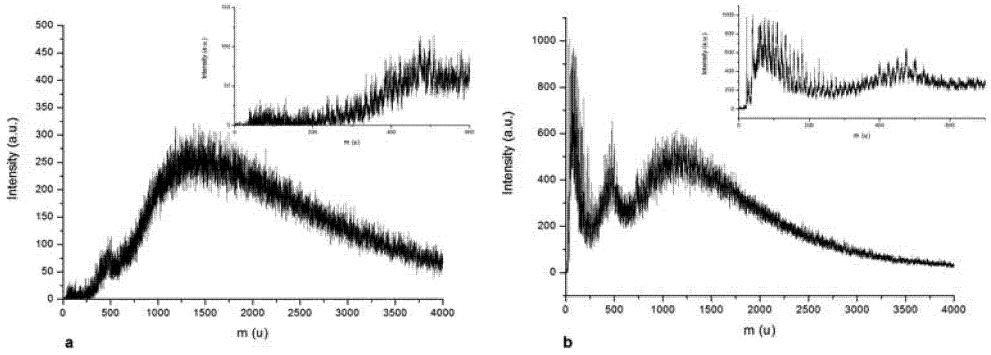

Figure 4. Reflectron LDI-MS spectrum of fraction 3 at 60% (a) and 90% (b) of the laser power. In the insets zoom in the low MW region.

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