Characterization of nanometric-size fractions of flame-formed particulate

Alfè, M., Stanzione, F., Ciajolo A.
Istituto di Ricerche sulla Combustione - C.N.R., Naples – ITALY

The adverse health effects of aerosol combustion-formed carbon pollutants, ranging from polycyclic aromatic hydrocarbons (PAH) to solid soot (Ciajolo et al., 2009), are due both to particle size (the health impact could becomes even more important going down to the nanometric size range, (Kennedy, 2007, Kumfer et al. 2009) and to the aromatic species (polymer-like species and PAH) often strongly adsorbed on soot particles (Mathieu et al., 2007, Alfè et al., 2008). The complex chemical nature of nanometric particles is currently under study representing a fundamental step to understand their role in health impact and in soot formation process. In this work a novel analytical approach was used to characterize in detail the species adsorbed fraction on combustion–formed particulate by means of extraction with diverse solvents and further mass spectrometric and FT-IR spectroscopy analysis of the chemical functionalities of both soot and soot extract.

1. Experimental

A sooting ethylene/O_2 flame (C/O=1, Φ=3.03) (Tmax=1650 K, cold-gas-flow velocity = 4cm/s) stabilized at atmospheric pressure on a commercial McKenna burner (Holthuis & Associates, Sebastopol, CA), was used as source of carbon particulate samples. A stainless steel water-cooled probe was used for combustion products sampling at 14 mm of height above the burner, where soot reaches the maximum concentration (Alfè et al., 2008).

Carbon particulate was recovered along the probe, the ice trap and the filter, constituting the sampling line, by using dichloromethane (DCM) washing. The total particulate was extracted with diverse solvents using an ultrasonic bath at room temperature.

The extraction with DCM, followed by a re-extraction of the particulate with carbon disulfide (CS_2) allowed to obtain a DCM-extract and a CS_2-extract. The DCM and CS_2 insoluble fraction (soot) were finally extracted with N-methylpyrrolidinone (NMP) in order to detach species strongly adsorbed on soot, obtaining a dry soot.

Soot extracts were analyzed by size exclusion chromatography (SEC) on a PL-gel styrene-divinylbenzene individual pore column (Polymer Laboratories, Ltd, UK, 5 μm of particle size diameter and pore dimension of 50 nm). The injection volume was 250 μl. The analyses were performed in NMP (temperature 80 °C, flow rate 0.5 mL/min) and, for DCM-extract, in DCM (room temperature, flow rate 1 mL/min). The on-line detection of species eluted from the SEC column was carried out using an HP1050 UV–visible diode array detector measuring the absorbance signal at $\lambda = 350$ nm.

FT-IR spectra of soot extracts and soot were measured on a Perkin-Elmer 1600 in the 400–4000 cm^{-1} wavelength range. Each spectrum was the result of a 20 scan accumulation, a value that provided a good signal/noise ratio.

Soot and KBr were heated at 120 °C for 3h and mixed together for preparing a 1% KBr pellet for the FT-IR analysis of soot powder.

Soot-extracts were dissolved in CCl_4 for the analysis in the 1000–4000 cm−1 wavelength region and in CS_2 for the analysis in the 400–1000 cm−1 wavelength region. Soot extracts were analyzed in a Perkin Elmer KBr sealed cell with 0.2 mm path-length.

The Atmospheric-Pressure Laser Desorption Ionization- Mass Spectrometer (AP–LDI-MS) system was used for the mass spectrometric analysis of soot extracts (Alfè 2008). Briefly, the samples were dissolved in DCM, dropped on the target plate and dried in air for the AP-LDI-MS analysis. AP–LDI-MS measurements were performed using an Agilent 1100 series LC/MSD ion trap SL (Agilent Technologies, Palo Alto, CA, USA) instrument operating in positive mode and equipped with a UV laser (nitrogen laser, 337 nm, mounted inside a laser and stage control box) producing a 10 Hz pulsed beam of UV light.. The ion trap scanned from m/z 50–2200. A typical analysis consists of 100–150 co-added mass spectra collected on the whole spot surface (1–2 mm diameter) in order to overcome the non-homogeneity of the sample on the target plate.

2. Results and discussion

The flame-formed carbon particulate analyzed in this work is representative of a mature soot sampled at the end of soot formation region where soot reaches the maximum concentration. DCM extraction of carbon particulate followed by CS_2 and NMP extraction has been performed for the following FT-IR analysis. The FT-IR analysis of the DCM-extract, CS_2 extract and soot after each extraction stage has been carried out. The NMP-extract could not be analyzed because the residuals of low volatile NMP solvent caused the interference of NMP on FT-IR spectra.

Fig. 1 reports the FT-IR spectra of DCM- and CS_2-extract dissolved in CCl_4 (3500-1000 cm^{-1}) and in CS_2 (1000-600 cm^{-1}).

The DCM-extract spectrum presents the characteristic signals of C-H aromatic stretching (3030 cm^{-1}) and aromatic out-of-plane C-H bending due to solo (860-910cm^{-1}), duo (800-810, 810-860cm^{-1}), trio (750-770, 770-800, 800-810 cm^{-1}) and quatro (730-750, 750-770cm^{-1}) structures, (Zander et al., 1995, Centrone et al., 2005).

The aliphatic groups are responsible for the group of C-H stretch signals at 2975 cm^{-1}, 2925 cm^{-1} and 2850 cm^{-1} accompanied by asymmetric and symmetric C-H bending in the 1450-1380cm^{-1} region. The weak signal at 1720 cm^{-1} corresponds to the C=O stretching whereas a weak C=C stretching is detectable at 1595 cm^{-1}.

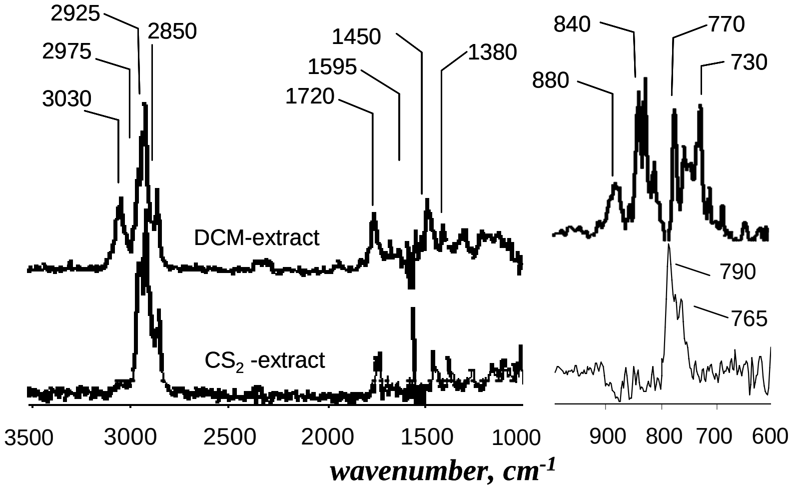

Fig. 1. Infrared spectra of DCM- and CS_2-extract of soot dissolved in CCl_4 (left part, 1000–3500 cm^{-1} wavelength region) and dissolved in CS_2 (right part, 600–1000 cm^{-1} wavelength region)

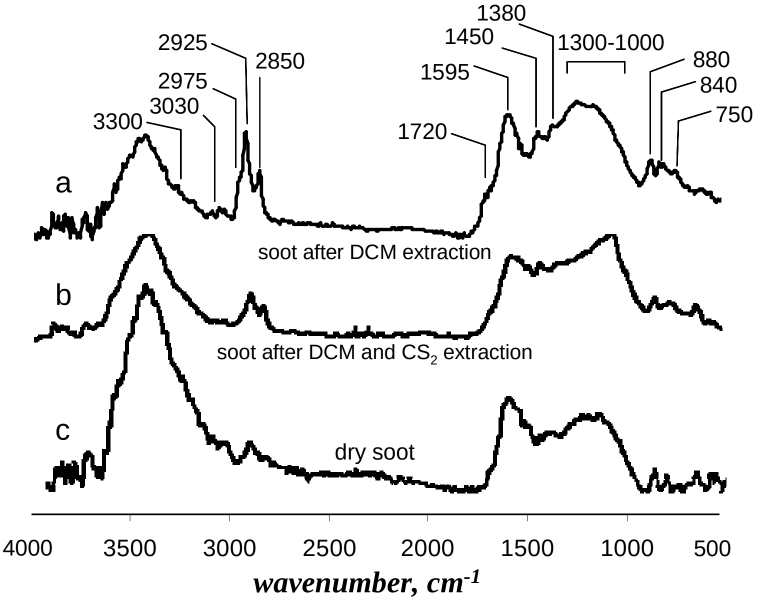

Fig. 2. Infrared spectra of soot after DCM (a) and CS_2 (b) extraction, and dry soot (c).

The CS_2-extract exhibits a very weak aromatic C-H stretch (3030 cm^{-1}) and the predominance of aliphatic functionalities signals at 2975 cm^{-1}, 2925 cm^{-1} and 2850 cm-1. The aromatic C-H out-of-plane bending peaks in the region 800-900 cm^{-1} are not observed and only a peak around 800 cm^{-1} is noticeable. In spite of the aromaticity character of the CS_2 extract, demonstrated in the following mass spectrometric and UV-visible analysis , the absence of aromatic hydrogen in the FT-IR spectra is noteworthy. It could be interpreted as a larger condensation degree of the aromatic structures, i.e. a negligible content of aromatic hydrogen, contained in the CS_2 extract.

Fig. 2 reports the FT-IR spectra of soot after sequential extraction with DCM, CS_2 and NMP. Soot after the whole extraction sequence is labeled dry soot. The FT-IR spectra are generally broader in the shape and characterized by a progressive reduction of the aliphatic bands (2975-2850 cm^{-1} and 1450-1380 cm^{-1}) for effect of the sequential extraction. This indicates that the aliphatic signals are mainly due to species adsorbed on soot surface and progressively removed by the solvent extraction. A small presence of aromatic hydrogen is noticeable just in soot extracted with DCM. The increase of the C=C stretching features (1595cm^{-1}) and the broadening of the region from 1000 to 1300 cm^{-1}, can be a consequence of the overlapping of the C–C and C–H plane deformation signals consistently with the presence of a complex carbon network (Santamaria et al., 2010).

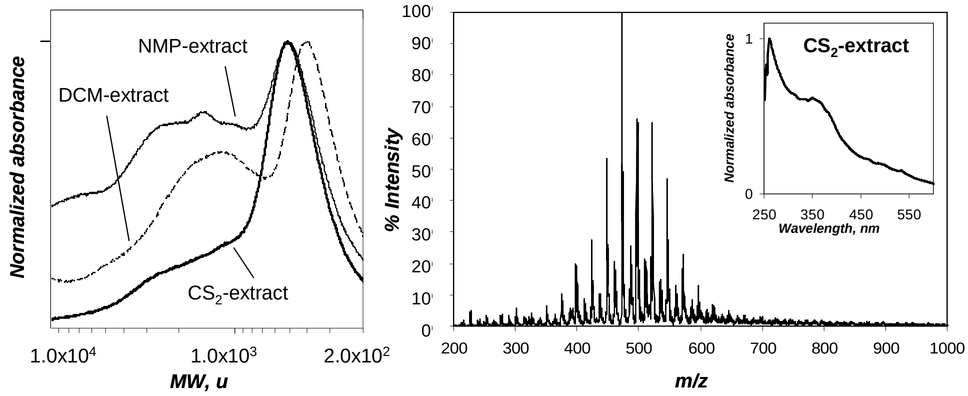

Fig. 3. SEC chromatograms (λ = 350 nm) of DCM-extract, CS_2-extract and NMP-extract (left), AP–LDI–MS and UV-Visible spectrum (inset) of CS_2-extract (right).

The DCM-extract, CS_2-extract and NMP-extract were dried, dissolved in NMP and analyzed by SEC. Fig. 3 reports the SEC chromatograms of the DCM-extract, CS_2-extract and NMP-extract of ethylene flame soot as a function of MW by transforming the elution time into MW on the basis of MW calibration with polystyrene standards.

Overall, a MW distribution of soot extracts develops in the 100-1E^4 u range. As previously found (Alfè et al., 2008), DCM-extract components are mainly distributed into two main peaks: a large peak at 200 u (mainly composed of PAH) and a second one peaked at 900 u (consisting of aromatic units arranged in a polymer-like network). The NMP-extract exhibits a broader distribution in the whole MW range (Ciajolo, 2009, Alfè et al., 2008).

Interestingly enough, the CS_2 extract mainly exhibits one peak at ~600 u attributed to large-PAH (L-PAH, C>24) demonstrating the selectivity of CS_2 in extracting mainly the residual L-PAH (i.e. the tail of the PAH peak present in the DCM-extract). AP-LDI-MS spectrum of CS_2 extract (right part of Fig. 3) confirms that CS_2-extract is mainly constituted of L-PAH in the 400-600 u range. Also the UV–visible spectrum, reported in Fig. 3, is typical of L-PAH exhibiting a broad peak around 400 nm (Fetzer, 2000).

DCM-extract was further fractionated by using SEC elution with DCM. The chromatogram is reported in Fig. 4. Four fractions were obtained and characterized by UV-Visible and AP-LDI-MS.

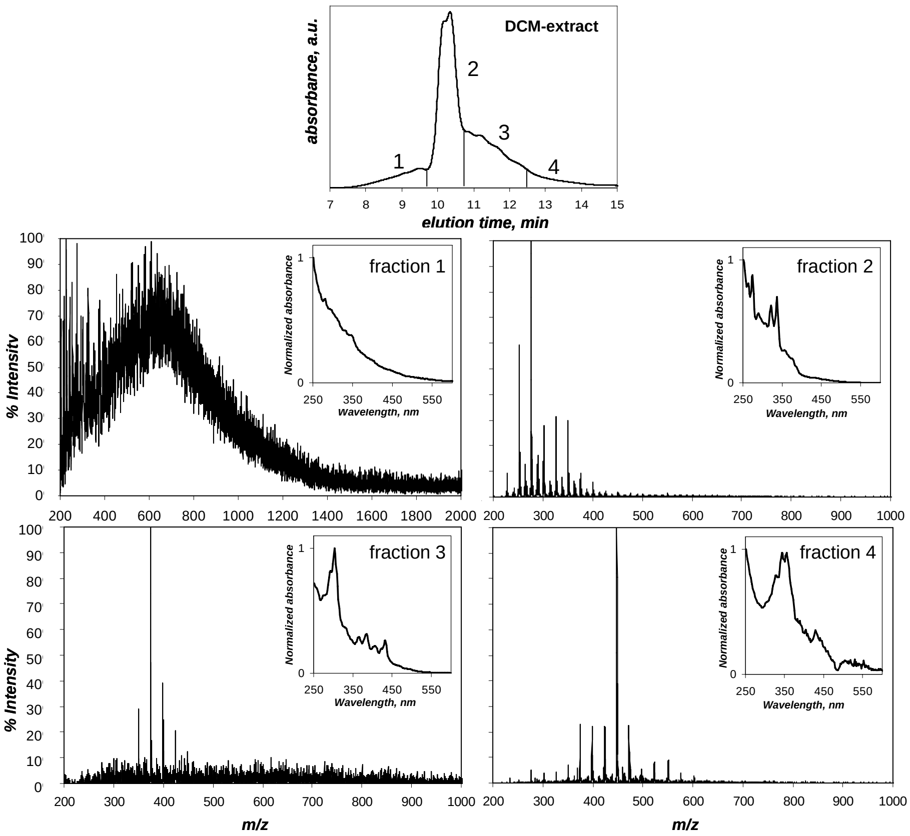

Fig. 5. SEC (DCM elution) chromatogram of DCM-extract (upper figure), AP–LDI–MS spectra and UV-Visible spectra (inset) of DCM-extract subfractions.

The fraction 1 of the DCM-extract shows a broad shape of UV-Visible absorption typical of polymeric/graphitic materials, as also confirmed by the continuous sequence of masses in the m/z 300–1200 peaked at m/z 600 that is quite similar to that evaluated by SEC in NMP (Fig. 3). Fraction 1 was dried, dissolved in NMP and re-injected in the SEC column eluted with NMP, to confirm the MW attribution.

The fractions 2-4 exhibit UV–visible spectra with a fine structure typical of PAH with an increasing degree of condensation at higher elution times indicating that the higher MW PAH eluted later on from the column. The AP-LDI-MS analysis of the fraction 2 extends up to 400 u whereas it extends up to about 600 u for the last eluted fraction 4 confirming the elution of PAH in order of increasing MW. The mass spectra consist of a sequence of major ions with a spacing of 24–26 u superimposed on a sequence of minor ions that present the same spacing of 24–26 u but displaced at 12 u relatively to the sequence of the major ions.

Overall, it appears that the SEC separation performed with DCM is able to separate the polymeric-like material from PAH and, at the same time, it allows the separation of PAH as a function of MW.

Conclusions

The extractive treatment of combustion-formed carbon particulate with solvents with increasingly solubilization power, namely DCM, CS_2 and NMP, has shown to be effective in separating fractions having different molecular weight and characteristics. In particular CS_2 showed to be particularly selective in extracting large PAH from the other polymeric aromatic material.

The solubility separation coupled with SEC chromatographic separation allowed to perform a more detailed characterization of the whole complex matrix of aromatic products, associated to the carbon particulate.

FT-IR analysis of soot extracts and soot after extraction has shown that most of hydrogen detected on particulate is due to soluble aromatic material. SEC separation was able to select fractions having composition typical of polymeric aromatic structures and large PAH as demonstrated by mass spectrometric identification.

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