Markers of immature soot in the refractory mass spectrum obtained by the soot-particle aerosol mass spectrometer

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The maturity, for example degree of graphitization has in premixed flames been related to combustion conditions and residence times of the soot in the flame. Soot maturity affects key soot properties such as absorptivity, nanostructure and reactivity. The miniature Combustion Aerosol Standard (mini-CAST) based on a quenched diffusion flame can be used to produce highly repeatable soot properties. With the mini-CAST, nascent soot with immature soot properties can be obtained by reducing the oxygen-fuel ratio and increasing N_2 in the premixed gas (e.g. Maricq, 2014). Recently, a technique to study the chemical composition of refractory black carbon (rBC), the soot-particle aerosol mass spectrometer (SP-AMS; Onasch et al., 2012), was developed. In the SP-AMS, refractory species are vaporized by focusing an Nd-YAG laser (1064nm) on a beam of particles. The laser effectively vaporizes refractory components by heating the particles to ~4000K. The vapors are ionized by electron impaction (70eV) and ions are detected in a high-resolution time-of-flight mass spectrometer. Notably the SP-AMS is able to distinguish between different soot properties, separating mature and immature soot. The relationship between immature soot properties and mass spectra in the SP-AMS has previously attracted attention and proposed markers have been the fullerene-carbon signal and the C_1^+/C_3^+ ratio (Corbin et al., 2014; Onasch et al., 2015). Even so, well defined markers of immature soot without interference from organic components remain to be reported.

An SP-AMS and a mini-CAST was used to study soot properties with varying degree of maturity. Four out of the seven recommended mini-CAST operation points (OP) were selected, where 1 represents the most mature soot and 7 represents the least mature soot. The soot was thermodenuded at 250°C in order to remove volatile compounds. Refractory species, of which rBC is the sum of all ion signal from elemental carbon clusters, were determined by laser vaporization. Non-refractory species (e.g. organic compounds) were determined by vaporization on a heated (~900K) porous-tungsten vaporizer with the laser turned off.

Figure 1 shows trends in the rBC mass spectra as the maturity of the soot decreases with increasing OP. The trends in the refractory mass spectra illustrated in Figure 1 represents the fraction of the total rBC signal originating from mid-carbons (C_6-C_{29}) and fullerene-carbons (C_{30}-C_{59}). In addition, the PAH fraction of the total non-refractive organic signal (OA) is shown for the same OP but with the particles bypassing the thermodenuder. The observed trends in Figure 1 show increasing contributions from mid- and fullerene-carbons as the maturity of the soot decreases. While mid- and fullerene carbons show a distinct increase from OP3 to OP5, the PAH fraction of OA increases continuously with OP.

The ratio of organic compounds (which were measured without the Nd-Yag laser) to rBC was approximately 10% after passing the thermodenuder. Thus, it is highly unlikely that mid-carbons, which for immature soot (OP5 and OP7) account for more than 25% of the rBC signal, are formed artificially from low volatile organic components during laser vaporization. Similarly, fullerene-carbons contribute to approximately 10% of the rBC signal for nascent soot. For mature soot (OP1 and OP3), mid-carbons and fullerene-carbons contribute to less than 3% of the total rBC signal.

From our preliminary results, we suggest that the SP-AMS can distinguish between immature and mature soot properties. Pronounced markers of immature soot properties are increasing signals from mid- and fullerene-carbons in refractory mass spectra of the SP-AMS.

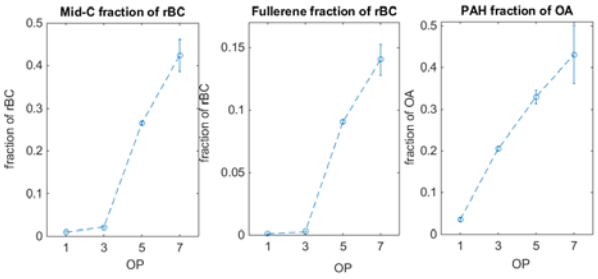

Figure 1: SP-AMS markers of immature soot. The soot maturity decreases with increasing OP. Thermodenuded soot refractive Mid-carbon ion fraction of rBC (left) and fullerene-carbon ion fraction of rBC (middle). Bypass soot PAH fraction of OA (right).

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