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Airplane Soot Chemical Composition Analysis by Laser Desorption and Secondary Ions Mass Spectrometry

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Soot emissions from airplane engines affect both air quality and climate. Up to 10% increase of cirrus clouds formation has been observed in flight corridors during the last decade (Boucher 1999). So most likely soot particles emitted by air traffic allow the formation of ice at lower supersaturations compared to homogeneous ice formation. The potential of soot particles as cloud condensation nuclei is affected by their physico-chemical properties, for example the presence of Polycyclic Aromatic Hydrocarbons (PAHs) adsorbed on the soot surface plays a role in its reactivity and ice nucleation potential (Crawford *et al.* 2011).

The present work has been performed in the framework of the French national project MERMOSE, which aims to characterize the soot emissions from airplane engines and to determine their role in the formation of cirrus clouds. A first sampling campaign performed on the PowerJet SaM-146 turbofan (SNECMA/Saturn) provided soot particles collected on quartz fiber filters in four engine regimes (30%, 70%, 85% and 100%). Two-Step (Desorption/Ionization) Laser Mass Spectrometry (L2MS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) techniques were used to analyze the surface chemical composition of the soot particles, with special focus on PAHs. In L2MS, the adsorbed phase is probed by nanosecond laser desorption ($\lambda_d=532\text{nm}$), then the ejected molecules are ionized with a second ns laser ($\lambda_i=266\text{nm}$) and further mass-separated by ToF-MS.

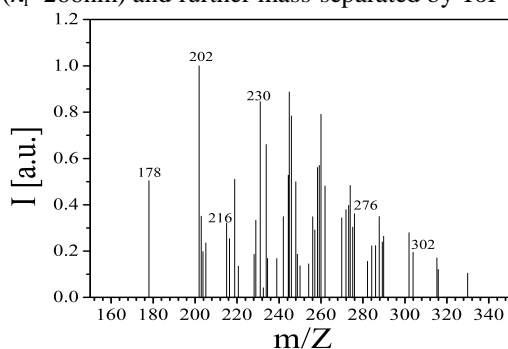


Figure 1. Positive polarity mass spectrum of a soot sample collected in the 100% engine regime.

Excellent sensitivity (limit of detection below 1 fmol per laser pulse) is reached by this technique especially for PAHs, thanks to their large REMPI (Resonance-Enhanced Multi-Photon Ionization) cross-sections at 266 nm. Figure 1 shows an example of a typical mass spectrum obtained during the L2MS experiments. In ToF-SIMS the sample is bombarded with a Bi_3^+ ion beam and the secondary ions generated are detected by ToF-MS. In both techniques the spectra were obtained using positive polarity, which is better suited for detection of PAHs. A good agreement was obtained between the two techniques for the total PAH content of the analyzed samples.

Moreover, the total PAH content followed the same trend as the OC/EC ratio measured with a thermo-optic analyzer (Improve protocol): the 30% engine regime soot presents a high concentration of PAHs and a high OC content, while the three other regimes give a relatively low content of PAHs and OC. Figure 2 summarizes these results.

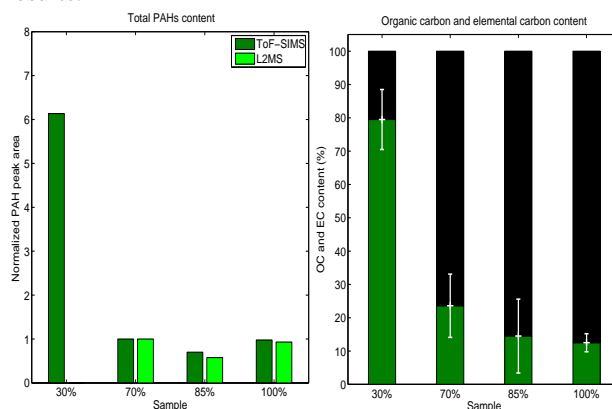


Figure 2. Left panel: total PAHs content of different samples analyzed by TOF-SIMS (dark green) and L2MS (light green) techniques; right panel: organic carbon (dark green) and elemental carbon (black) content of different samples analyzed.

This study is being extended to other compounds (e.g. organosulfates or oxygenated hydrocarbons) and to

surrogate lab generated soot. Furthermore, the ice nucleation properties of these samples will be measured using Raman spectroscopy.

Acknowledgments

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