

Chemical Characterization of Airplane Soot Particles and Surrogates Using Laser Desorption Ionization and Secondary Ion Mass Spectrometry

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Abstract

Collecting soot particles emitted by airplane engines in well-controlled conditions is a challenging task. This motivates laboratory studies aimed at finding a good surrogate (i.e. with similar physical and chemical properties) for such particles. We present here preliminary results of a comparative study on the chemical composition of soot particles emitted by three combustion sources: airplane SaM146 turbofan, Combustion Aerosol Standard (CAST), and laboratory kerosene diffusion jet flame. Two-step (desorption/ionization) laser mass spectrometry (L2MS) and Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS) were used as analysis techniques.

1 Introduction

Studies on soot particles formation mechanisms, physical and chemical properties, ageing, etc. are of high current interest due to their impact on climate and human health. For instance, these particles can carry (on their surface) a large variety of pollutants or harmful molecules which can be easily released in the environment or in the human body. Moreover, aircraft emissions could impact the Earth's global radiative forcing through creation of contrails and cirrus clouds [1, 2].

Despite a considerable number of experimental and theoretical studies performed during the last decades, a comprehensive view of the soot formation mechanism (especially the gas – particulate phase transition) is still missing [3]. A better understanding of the involved processes can have important implications in the optimization of internal combustion engines for various applications, from air to maritime and road traffic. For the particular case of aircraft emissions, collecting significant quantities of soot particles in well-controlled working regimes, representative of the actual field conditions, can be challenging and costly. This motivates the research for an appropriate laboratory-produced surrogate that should mimic the main properties of the aircraft soot (morphology, structure, chemical composition, optical properties, etc.).

We present here the preliminary results on the chemical composition of soot particles emitted by an airplane engine (SNECMA SaM 146 turbofan, sampling campaign realized in the frame of the MERMOSE

project – <http://mermose.onera.fr/en>), a mini-CAST soot generator, and a laboratory kerosene diffusion jet flame.

2 Experimental Section

2.1 Soot sources

The samples coming from the three sources mentioned above were collected on three types of substrate: very high efficiency quartz fiber filters (VHE), silicon wafers (Si), and borosilicate porous filters (BSi). In the case of airplane soot, four engine regimes were selected: take-off (100%), approach (30%) and climb (70% and 85 %). For the CAST generator, four samples were collected after burning propane (0.05 or 0.06 sLm) with various oxidation air flows (1.0, 1.15, 1.2 and 1.5 sLm).

Soot was also collected from a kerosene laboratory diffusion jet flame. A McKenna burner equipped with a central injector allows stabilization of different sooting diffusion jet flames surrounded by an ignition premixed flat flame of methane/air (Fig. 1). This apparatus allows ignition of different liquid hydrocarbons such as diesel and kerosene. The particles are collected on borosilicate filters using an extractive probe without perturbing the flame conditions. The ignition of the flat flame was maintained burning 1.14 sLm of methane with 10.9 sLm air, while for the diffusion flame we used 0.32 sLm N₂ for the nebulization of 180 g/h kerosene fuel. These settings resulted in a diffusion flame 30-32 cm high. The samples were collected at different heights above the burner (HAB): 6 cm, 12 cm, 18 cm and 24 cm.

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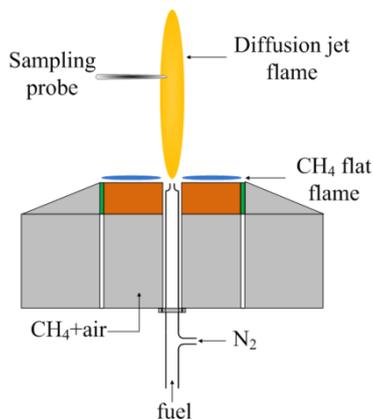


Figure 1. McKenna burner used to generate the kerosene flame.

2.2 Analysis techniques: L2MS and SIMS

In the present work, two experimental techniques were used to analyze the surface chemical composition of the soot particles (with special focus on PAHs). The first technique relies on the coupling of three steps: laser desorption, laser ionization and time-of-flight mass spectrometry (L2MS – two-step laser mass spectrometry). This technique is detailed elsewhere [4]. Briefly, the samples are irradiated at normal incidence by a 10 ns laser pulse at 532 nm wavelength. The energy delivered to the sample promotes the desorption of neutral molecules from the sample surface, which form a plume expanding in the high-vacuum ($\sim 10^{-8}$ mbar) of the mass spectrometer. This plume is irradiated orthogonally by a second laser pulse which leads to the ionization of the neutral molecules, and the so-produced ions are detected by reflectron time-of-flight mass spectrometry. Two configurations, resonant two-photon ionization (R2PI) and single photon ionization (SPI), were used for the ionization step. The first configuration, which is suited for the high-sensitivity detection of PAHs, uses the 4th harmonic of a Nd:YAG laser (266 nm equivalent of 4.66 eV), by taking profit of a resonance exhibit by most of the PAHs around this wavelength (Fig. 2). However, this ionization technique is less sensitive to non-resonant species, e.g. aliphatics. Moreover, some of them can have ionization energies higher than 9.32 eV, thus they will require a three-photon ionization if 266 nm wavelength is used. To overcome this limitation, we developed a second ionization source by tripling the third harmonic of the Nd:YAG laser (355 nm) in a home-made Xe cell to generate coherent radiation at 118 nm (10.5 eV). This allows us to perform single-photon ionization on most of the compounds found on the soot particles (Fig. 2). By combining both ionization techniques with time of flight mass spectrometry, we are able to investigate complex sample compositions.

Analysis by ToF-SIMS was performed with an instrument at the Regional Platform of Surface Analysis in the University of Lille. Soot surface was probed by a Bi^{3+} pulsed ion beam at 25 keV in the static mode. The

primary ion source delivered a pulsed current of 0.29 pA, rastered over $500 \times 500 \mu\text{m}^2$ area.

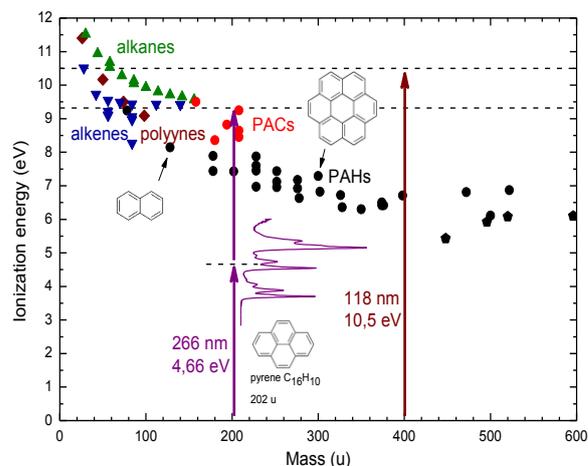


Figure 2. Ionization energies of various hydrocarbons. R2PI (266 nm) and SPI (118 nm) ionization schemes.

This technique provides complementary high-resolution information about classes of compounds identified onto the samples, as organosulfates or oxygenated hydrocarbons. A mass resolution of ~ 7500 can be reached for soot samples deposited on Si wafers (very flat surface). However, for VHE quartz filters which present higher surface roughness, the mass resolution is reduced to ~ 1500 (Fig. 3), which is comparable with the value reached by L2MS. In L2MS no differences were observed between the substrates.

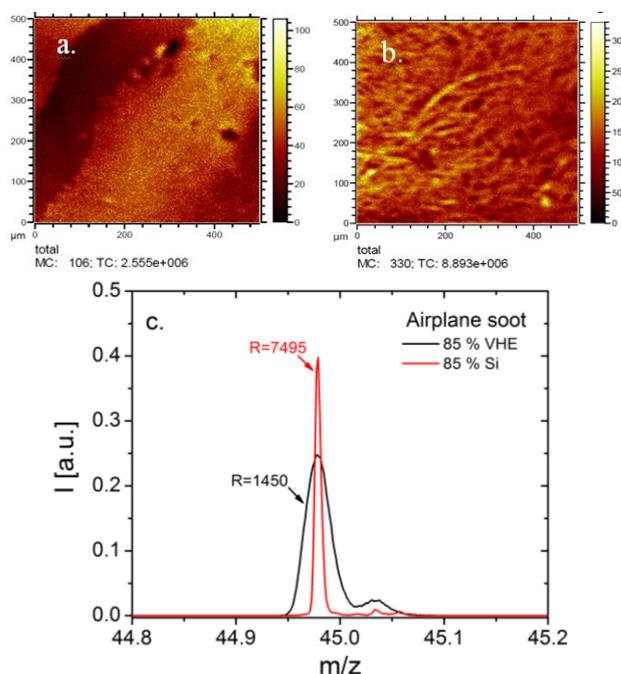


Figure 3. Effect of the substrate on ToF-SIMS mass resolution: a) total ion image of soot on Si wafer; b) total ion image of a quartz fiber filter; c) mass spectrum detail.

3 Results and discussion

3.1 Airplane soot

Airplane soot samples collected in four engine regimes (as described above) have been analyzed by L2MS and ToF-SIMS. The complex mass spectra recorded were processed with home-made routines to extract information on some main families of compounds: PAHs and derivatives (oxygenated, nitrogenated, organosulfates, aliphatics etc.). Our main focus for these preliminary studies was on PAHs in the m/z range 128 - 300. Fig. 4 displays ToF-SIMS mass spectra on samples collected in the four engine regimes. In the high-mass range of the mass spectra recorded by both L2MS and ToF-SIMS, main mass peaks are distributed every 12 or 14 u and accompanied by satellite peaks. This distribution is commonly attributed to PAH molecules [5]. Some differences occur however in the mass spectra recorded by L2MS and ToF-SIMS, mainly an important fragmentation degree is observed in SIMS, while the L2MS mass spectra display less (or no) fragmentation. Moreover, PAHs with an odd number of carbons are detected as radical ions $(M-1)^+$ in ToF-SIMS, in contrast with L2MS where the molecular ion $(M)^+$ was detected. The distribution maximum by SIMS is slightly shifted to higher masses compared to L2MS spectrum.

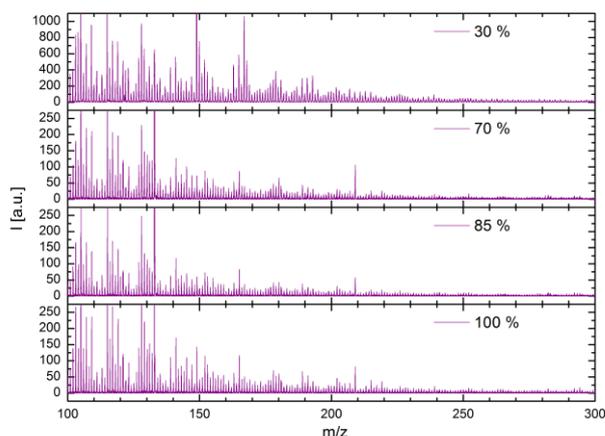


Figure 4. ToF-SIMS mass spectra of the four engine regimes airplane soot samples (quartz fiber filter).

Despite these differences, a good agreement is found between the total PAH contents measured by the two techniques. Briefly, the 30% engine regime soot mass spectrum shows a much higher PAH content compared to the other regimes. Furthermore, the total PAH content measured by mass spectrometry is in very good agreement with the organic to total carbon (OC/TC) ratio measured according to the IMPROVE A protocol using the Sunset Lab Thermo-optical method [6]. It is thus concluded that the total PAH content represents a good indicator of the amount of organic carbon contained in the soot particles. The detailed analysis of these data will be presented in a forthcoming paper.

3.2 CAST soot

Among the four CAST samples analyzed in this work (see section 2) we will focus our attention on the one generated using a fuel flow of 0.05 sLm and an oxidation air flow of 1.2 sLm, as it seems to give the closest PAH distribution and total content to the airplane soot samples collected at high engine regimes (70, 85 and 100 %). As a general feature among all CAST samples, we observed a decrease of the PAH content (supposed to be representative of the OC content) with the oxidation air flow, in good agreement with recent results reported by Moore et al. [7] on the use of a mini-CAST soot generator.

Two L2MS spectra (recorded with R2PI and SPI ionization) of the CAST sample are presented in Fig. 5. As discussed above, the 266 nm R2PI mass spectrum show mainly peaks associated with the most stable PAHs [5], while the SPI ionization scheme gives also access to aliphatic compounds. The main masses of aromatic species are 202, 226, 276 and 300 u for the two ionization schemes.

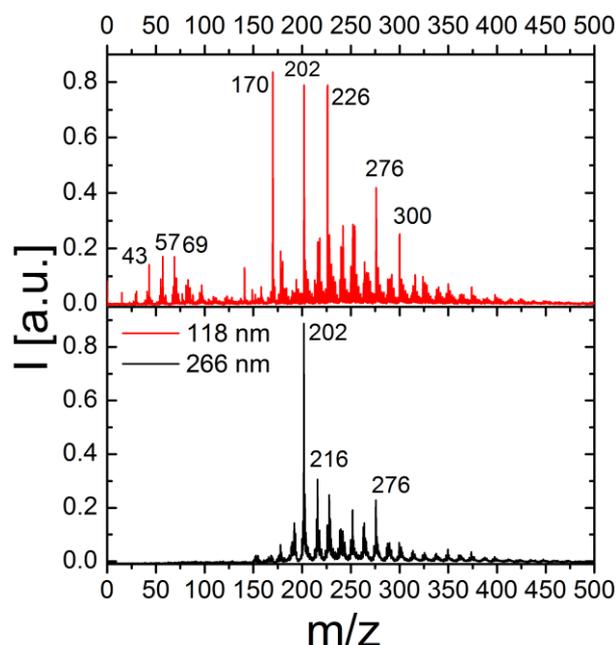


Figure 5. CAST soot L2MS mass spectrum: comparison between 266 nm and 118 nm ionization schemes.

Fig. 6 shows a zoom of the mass spectrum recorded through SPI for the region below m/z 100. The most intense peaks (m/z 15, 29, 43, 57, 71 and 85) correspond to C_nH_{2n+1} formula. They are accompanied by peaks corresponding to C_nH_{2n} and C_nH_{2n-1} series. The unsymmetrical shapes of the associated peaks points to a fragmentation process after the ionization step. The fragmentation pattern is characterized by the presence of fully saturated hydrocarbons, namely alkanes (C_nH_{2n+2}). The presence of alkanes is supported by the detection of m/z 170 and 184 associated to aliphatic species as they are only seen by SPI at 118 nm. Furthermore this fact is confirmed by the ToF-SIMS

mass spectra where the molecular fragments of this series were identified. The possible molecules linked to these peaks are: dodecane ($C_{12}H_{26}$) and tridecane ($C_{13}H_{28}$) isomers. Nitrogenated or oxygenated fragments could be possibly involved, since additional peaks at $m/z +16$ or $m/z +18$ were detected in the high mass peak region. This affirmation is supported by the ToF-SIMS mass spectra which present higher mass resolution ($0.005 m/z$). In this sample, the C_nH_{2n-1} peaks (base peak m/z 69 in the low-mass distribution) are an indication of the presence of alkenes (C_nH_{2n}).

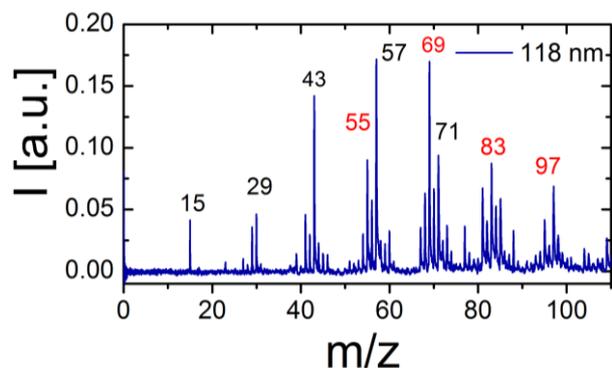


Figure 6. Detail of the CAST SPA spectrum recorded by L2MS with 118 nm (SPI) ionization.

3.3 Kerosene soot

Commercial Jet-A1 kerosene was used for soot generation. The L2MS mass spectra recorded with R2PI ionization scheme for the four soot samples collected at different HABs in the kerosene flame are displayed in Fig. 7. Compared with the airplane samples, the kerosene soot spectra present a mass spectrum richer in heavy PAHs, expanding to m/z 470, characterized by a single mass distribution dominated by the m/z 202 peak ($C_{16}H_{10}$). Note that the spectra in Fig. 7 are normalized for sake of visibility, however the overall signal is clearly stronger in the 12-18 cm HAB region, as it will be confirmed by ToF-SIMS measurements (see below). The mass distribution maximum seems to be shifted to higher mass in the oxidation zone (HAB 24 cm), while the heaviest PAH mass is detected in the mature soot zone (HAB 18 cm). This evolution can provide clues about the transition between young and mature soot and, therefore, bring valuable insights in understanding the nucleation process in turbulent laboratory flames [4].

In contrast with the high-mass region, the $m/z < 100$ section of the mass spectrum is totally signal free, in both ionization schemes. Note however that the presence of aliphatics in different flames (especially in the inception zone) was previously detected with 118 nm ionization [8]. To check this, we recorded the ToF-SIMS spectra displayed in Fig. 8. They display two different peak distributions: the first one at low masses and the second one covering m/z 180 – 700 region (for 12 and 18 cm HAB) with strongest features in the m/z 200 – 500 range respectively. Careful analysis of the former (low mass) distribution led to the conclusion that the observed masses cannot be attributed to aliphatics,

but to fragments of higher mass molecules (fragmentation is known to play a prominent role in ToF-SIMS measurements). Moreover, the high-mass distribution is related to PAHs and other compounds. Finally, the higher overall signal observed in the HAB 12-18 cm zone confirms the results obtained by L2MS. This points out to a better resemblance of soot collected in this region of the kerosene flame with the airplane soot in low engine regime (30%), while the oxidation zone soot (HAB 24 cm) would better mimic the airplane soot produced at high engine regimes (70-100 %).

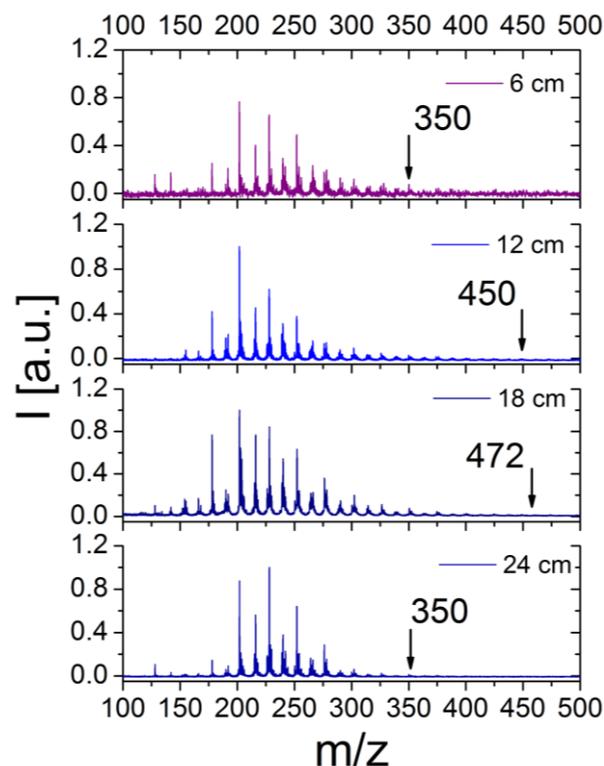


Figure 7. L2MS mass spectra (266 nm ionization) of soot collected (on BSi filters) in the kerosene flame at various HABs.

4 Conclusions and future work

Chemical composition of soot samples from three different sources (airplane, CAST, laboratory flame) was analyzed using two mass spectrometry techniques (L2MS and ToF-SIMS). The results given by the two techniques are in overall good agreement. In the case of airplane soot sample, we evidenced an evolution in PAH mass distribution and total content with the engine regime. The PAH total content is shown to follow the same trend as the OC/TC ratio (measured elsewhere).

When analyzing the CAST soot, we could identify combustion conditions which can generate good surrogates (taking into account the PAH distribution) for airplane soot in various engine regimes. With kerosene flame soot, this match can be optimized by selecting the sampling zone HAB. Among all samples, the kerosene flame soot seems to present the richest composition. For a better insight, these measurements

will be linked with laser diagnosis into the flame: laser induced incandescence (LII) and fluorescence (LIF in the UV-Visible range), which allow the mapping of soot particles and their gaseous precursors.

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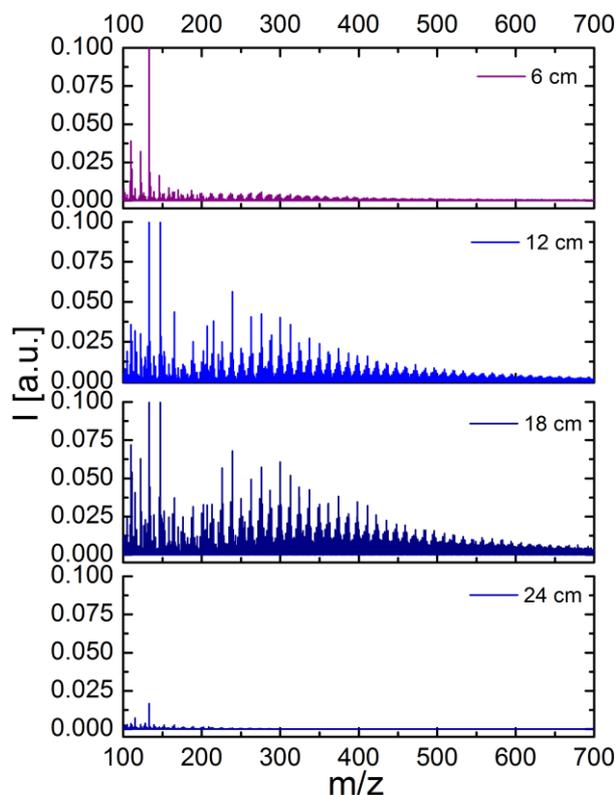


Figure 8. ToF-SIMS mass spectra of soot sampled in the kerosene flame at various HABs.

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