The organic phase of black carbon nanoparticles

Master's (M2) internship proposal, 2018

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Scientific background: On Earth, black carbon (BC) nanoparticles, or "soot", are emitted directly into the atmosphere by combustion of fossil fuels and biomass. The sources are mainly anthropogenic: air, marine and land transports, residential heating and cooking, industry, and agricultural burning. In the atmosphere, BC strongly interacts with sunlight, and also acts as condensation nuclei, increasing the cloudiness, both effects influencing the Earth's radiative balance. Atmospheric BC is then washed by rainfalls and contaminates seas, rivers and soils ecosystems. BC is also a strong pollutant in urban area, where it constitutes about 40 % in mass of breathable atmospheric aerosol particulate matter (PM) worldwide [1,2]. BC is also associated with serious health problems, including respiratory, cardiovascular, cerebrovascular diseases, and cancer [3]. Along with the size, a growing body of evidences indicate that the chemical composition of BC are key factors in its toxicity [4]. In general, BC is a mixture of organic carbon (OC) and elemental carbon (EC) [5]. The EC fraction is made of refractive carbon, with structure varying from amorphous to graphitic. The OC fraction is made of (semi-)volatile organic compounds (VOC), including polycyclic aromatic hydrocarbon (PAH) and other organic compounds, with possible mutagenic and carcinogenic effects [3,4]. The OC fraction also plays a strong role in the BC's radiative impact [5], particularly through optical absorption between bonding and antibonding π orbitals of PAH species [6], mostly occurring at wavelengths of sunlight. Furthermore, soot particles are also found in abundance in the interstellar medium; they are produced by cool carbon stars and expelled in the stars' remnant before becoming a part of the interstellar dust [7]. They are observed through their spectral response (absorption, emission) to space radiations (UV, IR), which is the only information available to characterize their intimate physico-chemical structure, in particular their PAH content.

Scientific objectives of the internship: Widely used for BC characterization, monitoring and remote observations, spectroscopic methods are fairly indiscriminate for the structure of the OC phase, and must be complemented, when possible, by analytical chemistry measurements. Cross-checking spectroscopy and chemical analysis is an approach that we have recently undertaken in the particular case of soot emitted by a turbojet engine -whose particulate emissions are still poorly known, and largely unregulated- , with the purpose of assessing their radiative properties, their ice nucleation ability (which might depend on the hydrophilic nature of their surface, i.e. to the presence of organic species able to interact with water), and their eventual toxicity for the staff working around aircrafts at airports. Samples have been collected on a test bench of the SNECMA manufacturer, and submitted to a battery of microscopy and spectroscopy techniques for nanoscale characterizations (TEM, NEXAFS, XPS, FTIR) [8]. So far, only two analytical methods have been carried out: a thermo-optical analysis to obtain the gross OC/EC ratio, and laser induced desorption-time of flight spectrometry (L2MS) to specify the organic species adsorbed at the BC surface. L2MS, however, has a sensitivity to aromatic compounds far higher than to aliphatic ones, due to the wavelength of the desorbing laser [9], giving a fairly distorted picture of the chemical composition of the OC phase. To go further and complete this study, solvent-extracted gas chromatography-mass spectroscopy (SE-GC-MS) is a highly desirable method. It allows identifying and/or precisely quantifying many organic species, aromatic and aliphatic, even when present only in trace amounts. It has been already employed with success on aircraft soot during the NASA's APEX 1-3 campaigns [10]. Put together with our previous spectroscopic data, it will provide an unprecedented accuracy in the description of the physico-chemical structure of these aerosols. The topics of this internship are: (1) to develop the experimental procedure for the solvent extraction, first using commercial BCs, and then on laboratory BC produced by a Mini-CAST burner, analogues of aircraft soot [11]. The student will optimize this crucial step in order to handle small amounts of soot samples (typically, aircraft samples are <3mg). (2) to characterize the solvent-extracted samples with GC-MS, analyze and interpret the data, and compare them with the L2MS results and our previous spectroscopic data. (3) To characterize the BC's IR and

UV/visible absorption spectra before and after extraction to reveal the specific spectral features related to the OC phase.

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