Discussion session 2: Supplementary and combined techniques

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Executive summary:

Combined techniques aim in achieving a **most complete characterization of soot** particles as possible. The aggregate / primary particle size distributions, number concentration, optical/radiative properties, bulk density, composition / chemical signature, crystallinity, fine morphology (overlapping, fractal dimension, pre-factor), rate of oxidation, surface growth and maturity are of interest. The discussion will (also) deal with coupling of optical and non-optical techniques enabling the determination of such information as well as the emerging diagnostic techniques that could be used for soot particles.

Introduction:

- Important parameters that are characterizing soot are introduced:
  - Radiative properties, size of primary particles and aggregates, nanostructure, composition, morphology (fractal dimension, fractal pre-factor).
- *Non exhaustive list of ex-situ* techniques and devices that are used for soot diagnostics are introduced:
  - TEOM 1105
  - CPMA (Cambustion)
  - DMS (Cambustion)
  - SMPS (TSI)
  - PPS (Pegasor)
  - Thermogravimetry (OC/TC)
  - Raman Spectroscopy
  - TOF-MS
  - NEXAFS & XPS
  - TEM
- *In-situ* techniques and devices that are used for soot diagnostics are introduced:
  - Elastic light scattering
  - Extinction
  - LIF
  - LIBS
  - Photo-acoustic sensor
- Recent papers based on coupling of different techniques are introduced:
  - Dastanpour, R., Momenimovahed, A., Thomson, K., Olfert, J., & Rogak, S. (2017). Variation of the optical properties of soot as a function of particle mass. *Carbon*, *124*, 201-211.

- Broda, K. N., Olfert, J. S., Irwin, M., Schill, G. P., McMeeking, G. R., Schnitzler, E. G., & Jäger, W. (2018). A novel inversion method to determine the mass distribution of non-refractory coatings on refractory black carbon using a centrifugal particle mass analyzer and single particle soot photometer. *Aerosol Science and Technology*, *52*(5), 567-578.
- Török, S., Malmborg, V. B., Simonsson, J., Eriksson, A., Martinsson, J., Mannazhi, M., & Bengtsson, P. E. (2018). Investigation of the absorption Ångström exponent and its relation to physicochemical properties for mini-CAST soot. *Aerosol Science and Technology*, 1-11.
- Kobayashi, Y., Tanaka, S., & Arai, M. (2018). PAHs Behavior and Graphitization Degree of Soot in a Hexane Diffusion Flame. *J Nanosci Nanotechnol*, *2*, 1-12.
- Pitz, M., Hellmann, A., Ripperger, S., & Antonyuk, S. (2018). Development of a 3D Light Scattering Sensor for Online Characterization of Aerosol Particles. *Particle & Particle Systems Characterization*, 1800045.
- Simonsson, J., Olofsson, N. E., Hosseinnia, A., & Bengtsson, P. E. (2018). Influence of potassium chloride and other metal salts on soot formation studied using imaging LII and ELS, and TEM techniques. *Combustion and Flame*, *190*, 188-200.
- Malmqvist, E., Brydegaard, M., Aldén, M., & Bood, J. (2018). CW Laser radar for combustion diagnostics. In *EPJ Web of Conferences* (Vol. 176, p. 01015). EDP Sciences.

This recent review shows the increasing use of combined methods for a better characterization of soot particles.

Following contributions from the participants are introduced:

Scott L. Anderson et al.: Application to the determination of heterogeneous sites on the surface of individual carbon particles

Single nanoparticle mass spectrometry: individual charged nanoparticles (NPs) are trapped in a quadrupole ion trap and detected optically, allowing their mass, charge, and optical properties to be monitored continuously.

The trapping of isolated nanoparticles is shown to be stable for more than 2 hours enabling the monitoring of their mass evolution when particles are exposed to various gases including oxidative environments or participating to their surface growth (as C_2H_2). This technique provides the ability to determine a number of active sites over the particle surface.

The contribution is mostly addressed to the LII community regarding the thermal emission of isolated carbon black nanoparticles. The group showed that emission spectra could be fitted by the Planck's law and a spectrally dependent emissivity ($\varepsilon \sim \lambda^{-z}$). They report that *z* exponent decreases with the particle temperature increase. This suggests the particle temperature affects the emissivity of the particles in the range 600-1600 nm. The authors report a predicted dependence of optical properties in the IR region (Lorentz Drude dispersion laws). Nevertheless the so obtained *z* parameter seems to be relatively high compared to classically admitted values (*z* is considered to be 1 for mature materials – constant $E(m)$).

Kim Cuong Le et al.: Representability of ex-situ Raman analysis

Demonstration of feasibility for determining *in-situ* Raman spectra and compare with “standard” analysis after deposition onto samples.

Raman spectra of soot produced by the same flame condition (C/O = 1.05, *P* = 40 mbar, HAB = 18 mm) were measured in the aerosol phase and on deposited substrate. Excitation powers were 5 W (aerosol phase) and 0.4 W (deposited soot).Nascent soot show sp-bondings, which seem to disappear during sampling.

This open the way to an *in-situ* determination of Raman spectra and also indicates that sampling may be intrusive regarding the *sp* hybridization.

Irfan Mulla, J. Yon: Comparison between LII-derived volume fractions and *ex-situ* approaches

This study reports a comparison between LII and *ex-situ* (PPS) determination of soot volume fraction in turbulent flames. It is shown that global trends are found to be similar all along the flame height of different turbulent butane and ethylene flames. Nevertheless, the ratio between both determined volume fractions has been shown to vary with flame composition indicating that, at least one or both techniques calibration seems to be dependent on the soot composition.

Hope Michelsen: Soot Maturity based on 2CLII + AMS + XPS and TPD

Over the last few years, multiple studies showed that analysis of LII derived fluence curves bring interesting information about absorption function behavior along the flame height. This effect is commonly attributed to the change of the soot maturity. The present study reports absorption property is related to the bulk material. It also reports a change of spectral dependence of $E(m)$ at the position where oxidation takes place. AMS reveals the presence of incipient particles at the bottom of the flame where $E(m)$ is also shown to evolve. An interesting additional information is brought by XPS that informs us on the ratio between *sp*2 and defects on the particle surface (XPS is sensitive on the surface chemistry). It appears that surface growth delays surface maturity while bulk matures. This study clearly highlights the interest of combining different independent techniques.