Author reply to review by Reinhard Niessner:

We would like to thank Reinhard Niessner for his useful comments, which helped clarifying and improving this paper. The review comments are repeated in black font and the author replies are highlighted in blue font (*"italic style is used for modifications to the manuscript"*).

Fortunately, now the aerosol community becomes notified more and more the possible difficulties faced, when solely using a soot characterization by heat treatment. Soot, as known by numerous papers, has many faces. Especially, when heat-treated (e.g. by LII techniques), not only evaporation starts, rather a combustion process is launched, depending on the nanocrystallinity of soot particles, and on the surrounding atmosphere as well.

The interaction of laser light with spark-discharged soot has been studied and modeled first by Robers, W.; Schroeder, H.; Kompa, K. L.; Niessner, R.; Photoionization and thermal ionization of aerosols by pulsed laser radiation. Zeitschrift fuer Physikalische Chemie (Muenchen, Germany) (1988), 159(2), 129-48. The consequence of irradiating PALAS soot by strong laser intensity is a shrinking of these particles, partly by evaporation.

The work by Robers et al. (1988) is now cited in the following new paragraph:
"PALAS soot can be brought to incandescence by using a pulsed laser (Robers et al., 1988) and it can be vaporised by the desorption/ionization laser of the aerosol time-of-flight mass spectrometer (ATOFMS; Su et al., 2005). These two methods apply laser pulses of much higher intensity than that of the continuous-wave laser applied in the SP2. This indicates that sufficient laser intensity plays an important role for reliable detection of PALAS soot by laser-induced incandescence, as further detailed in Sect 3.3."

There is an important difference between the measurement principle of the SP2 and the method applied by Robers et al. (1998). A pulsed laser is used in most LII applications for the detection of BC (and by Robers et al., 1998), and the thermal radiation is recorded for many particles at ones. This is a potential issue for the investigation of polydisperse samples, where the particles of different size reach the evaporation threshold at different times. The SP2 applies a continuous-wave laser and evaporation of the particles is intentionally forced. Non-refractory components of the particle evaporate first (at times <115 in Fig. AR1), leaving the most refractory component behind (black carbon in our case). The temperature of the bare BC core increases further, leading to a steep increase of the thermal radiation, until the vaporization temperature of BC is reached (at time ~130 in Fig. AR1). From that moment, the temperature of the BC core stabilises while gradual mass loss occurs due to evaporation (at times >~130 in Fig. AR1). Consequently, the thermal radiation also decreases. The SP2 records the thermal radiation of single particles with high time resolution. The presence of an incandescence signal is used to count the BC-containing particles and the peak amplitude of the incandescence signal, which occurs at a well-defined temperature and before evaporation of the BC core, is used to quantify the BC mass in single particles.

A short paragraph explaining the SP2 measurement principle has been added to the revised manuscript:
"Light absorbing particles are heated by the strong detection laser on the time scales of microseconds. Any non-refractory components of the particle evaporate first, leaving the most refractory component behind (BC in our case). The temperature of the bare BC core increases further, leading to a steep increase of the thermal radiation, until the vaporization temperature of BC is reached. From that moment, the temperature of the BC core stabilises while gradual mass loss occurs due to evaporation. Consequently, the thermal radiation also decreases. The SP2 records the thermal radiation of single particles with high time resolution. The presence of an incandescence signal is used to count the BC-containing particles and the peak amplitude of the incandescence signal, which occurs at a well-defined temperature and before evaporation of the BC core, is used to quantify the BC mass in single particles."

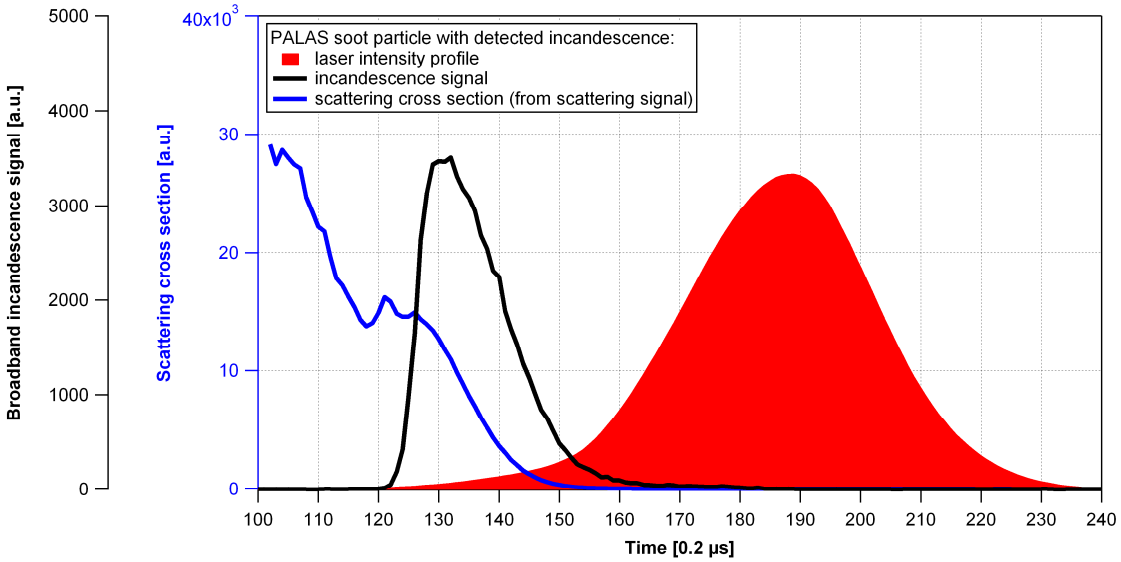

Figure AR1: Evolution of the scattering cross section and incandescence signal of a PALAS soot particle that reaches incandescence as it crosses the laser beam. This particle is a relatively large multiply charged particle selected at a nominal electrical mobility diameter of 500 nm (only the large multiply charged particles exhibited incandescence). Note, the absolute values of the time axis (bottom) are arbitrary.

But as we know from newer experiments, see

a)Schuster, Manfred E.; Haevecker, Michael; Arrigo, Rosa; Blume, Raoul; Knauer, Markus; Ivleva, Natalia P.; Su, Dang Sheng; Niessner, Reinhard; Schloegl, Robert; Surface Sensitive Study To Determine the Reactivity of Soot with the Focus on the European Emission Standards IV and VI. Journal of Physical Chemistry A (2011), 115(12), 2568-2580

b)Schmid, Johannes; Grob, Benedikt; Niessner, Reinhard; Ivleva, Natalia P.; Multiwavelength Raman Microspectroscopy for Rapid Prediction of Soot Oxidation Reactivity Analytical Chemistry (Washington, DC, United States) (2011), 83(4), 1173-1179.

c)Grob, Benedikt; Schmid, Johannes; Ivleva, Natalia P.; Niessner, Reinhard; Conductivity for Soot Sensing: Possibilities and Limitations. Analytical Chemistry (Washington, DC, United States) (2012), 84(8), 3586-3592.

a combustion process is initiated already at very low temperatures (ca. 450 K). This is the consequence of the extremely distorted nanocrystallinity of spark-discharged soot, and not of the different "density". Therefore we introduced a reactivity index for soot combustion, and the most reactive one is PALAS soot. The least reactive is highly oriented graphite. For details I would like to refer to the above citations and others published there. To make things even more complicated . if metal oxides (or earth alkaline salts) are part of such soot (also artificially generated from incomplete propane burning !) the reactivity becomes further increased, and an even lower combustion temperature for full oxidation is needed. A shift of 200 K towards lower temperatures is observed. A paper dealing with this is in press : H. Bladt, J. Schmid, E. Kireeva, O. Popovicheva, N. Persiantseva, M. Timofeev, K. Heister, J. Uihlein, N. Ivleva & R. Niessner; Impact of Fe Content in Laboratory-Produced Soot Aerosol on its Composition, Structure, and Thermo-Chemical Properties. Aerosol Science & Technology. The combustion process in above publications has been measured by FTIR analysis of evolving CO & CO2.
The consequence of these findings is : all methods based on heat treatment of soot, as the LII technique or thermo-optical combustion standard method will fail, if such reactive soot is present.

Differences in the reactivity of different soot types are a highly relevant complication for thermal(-optical) methods. However, this manuscript is about LII and a clear distinction has to be made between the thermal(-optical) methods and LII techniques. The heating time scale of the thermal(-optical) methods is in the order of minutes to hours (5K/min in the above-mentioned studies) and the maximal temperatures are typically <1000 K. In contrast, the time scale in the SP2 is in the order of µs and the incandescent particles are heated to >4000 K (Moteki and Kondo, 2010). For this reason evaporation dominates over chemical reaction in the SP2. Figure AR2 shows the scattering cross section of a PALAS soot particle that does not reach incandescence as it crosses the laser beam. Some decrease of the scattering cross section is observed in the leading edge of the laser beam (at times <120 in Fig. AR2), which can be attributed to evaporation of non-refractory components of the PALAS soot particle. The scattering cross section then remains stable (times >120 in Fig. AR2), indicating that the BC mass remains constant, i.e. the BC does neither evaporate nor react away. This is clear evidence that insufficient laser power is responsible for missing incandescence of most PALAS soot particles in the SP2, corroborating our conclusion that PALAS soot requires higher laser power due to its peculiar morphology.

The following paragraph has been added to the revised manuscript:
"The nanocrystalline structure differs between different BC types and with that also their chemical reactivity. PALAS soot has been shown to be the most reactive BC material among several BC types, and this results in a lower combustion temperature during thermal(-optical) analysis (e.g. Schmid et al., 2011; Schuster et al., 2011). The question to be answered here is whether the PALAS soot particles lose a substantial fraction of their mass through combustion before they reach their vaporisation temperature in the SP2. The heating rate of BC particles in the SP2 is around nine orders of magnitude faster than that applied in thermal(-optical) analysis, which leaves very little time for combustion. Analysis of the time-resolved scattering signal of the non-incandescent PALAS soot particles revealed that the BC in these particles does neither evaporate nor react away in substantial amounts, while the particles cross the laser beam. Consequently, the high chemical reactivity of PALAS soot can be excluded as a reason for its missing incandescence signal."

Further evidence that unreliable detection of PALAS soot is not a consequence of the high chemical reactivity was achieved by variation of the laser intensity. An additional data point has been added to Figs. 2a and 3 including the following discussion:
"Varying the laser power provided further evidence that unreliable detection of small PALAS soot is caused by the influence of particle morphology on the threshold laser intensity rather than chemical reactivity effects. An increase of the counting efficiency from ~12% to ~20% (dark green diamond in Figs. 2a and 3) was achieved for PALAS soot particles with a mobility diameter of D_{mob} = 305nm, by increasing the laser power as much as possible (~45% higher intensity)."

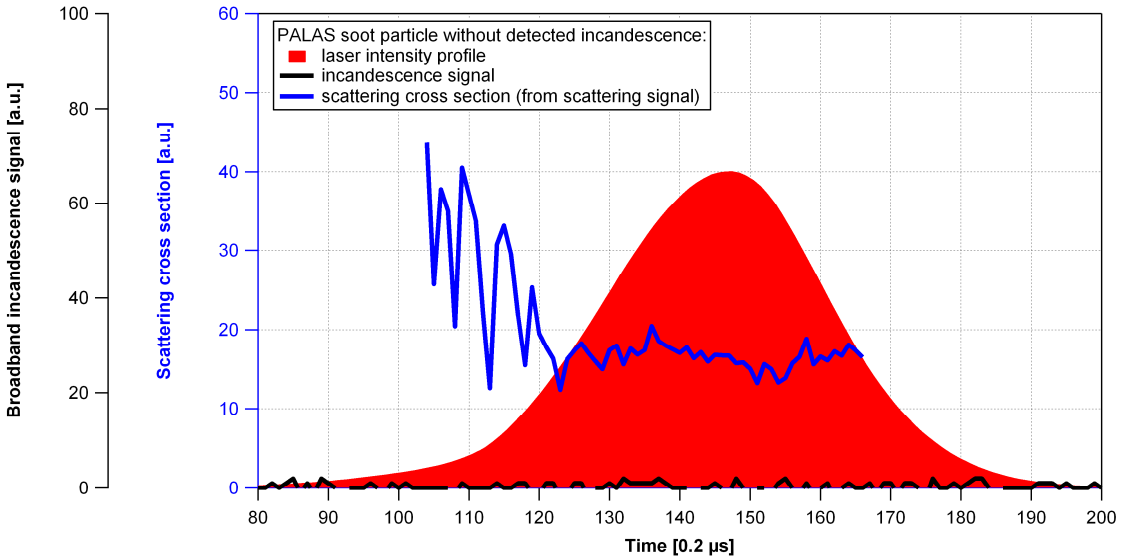

Figure AR2: Evolution of the scattering cross section and incandescence signal of a PALAS soot particle that does not reach incandescence as it crosses the laser beam. This particle is a singly charged particle selected at a nominal electrical mobility diameter of 500 nm (almost all singly charged particles did not reach incandescence). Note, the absolute values of the time axis (bottom) are arbitrary.

The authors speculate about SP2's ability to detect diesel soot in an inadequate way. The latest diesel engine technologies produce already soot like the PALAS soot ! In Fig. 3 of above mentioned article 2011 in Anal. Chem. we showed the behavior of diesel soot sample 11, which is representative for the now released engine line of the world's largest diesel truck producer. It's nearly identical with the PALAS soot, and the nanocristallinity expressed by the Raman multi-wavelength data explains this. Currently, biofuel is mixed in to diesel fuel. First experiments show a larger reactivity due to the formation of surface-oxidized patches on the carbon particle core, leading to lower combustion temperatures when heated up. Only diesel engines qualified below EURO 4 standard emit inert soot!

In the manuscript and the reply to the previous comment we made the point that PALAS soot particles require a higher laser power for reliable detection by the SP2 due to their peculiar morphology. Chemical reactivity was excluded as a cause for missing incandescence. Consequently, the high chemical reactivity of diesel soot from EURO 5 engines will not prevent those particles from reaching incandescence in the SP2. Indeed, diesel soot from a EURO 5 diesel engine was reliably detected by six SP2s during a recent intercomparison study (Laborde et al., in press). The chemical structure of the BC does have an influence on the incandescence signal and must be considered when choosing the appropriate calibration material for the SP2. However, this is out of the scope of this manuscript.

A final comment to the aerosol community from an analyst's view: a single, unique method for soot characterization does not exist, nor can be expected, and is consequently only as good as its calibration. For SP2 it is so far a fullerene-equivalent soot, but only valid above a certain size range. Therefore, a combination of techniques, depending on the purpose of the respective study must be applied. Calibration has to follows this. Hence, an unique calibrator aerosol can't be expected to become exist.
Selection of the appropriate calibration material for the SP2 is out of the scope of this manuscript and has been addressed in previous literature (Moteki and Kondo, 2010; Laborde et al., 2012, Baumgardner et al., 2012).

In conclusion, the technical note should become published, but only after taking into consideration what has been said above.

References:

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Laborde, M., Schnaiter, M., Linke, C., Saathoff, H., Naumann, K.-H., Möhler, O., Berlenz, S., Wagner, U., Taylor, J. W., Liu, D., Flynn, M., Allan, J. D., Coe, H., Heimerl, K., Dahlkötter, F., Weinzierl, B., Wollny, A. G., Zanatta, M., Cozic, J., Laj, P., Hitzenberger, R., Schwarz, J. P., and Gysel, M.: Single Particle Soot Photometer intercomparison at the AIDA chamber. *Atmos. Meas. Tech.*, in press, 2012.

Moteki, N. and Kondo, Y.: Dependence of laser-induced incandescence on physical properties of black carbon aerosols: measurements and theoretical interpretation. Aerosol Sci. Technol., 44, 663-675, 2010.