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Atmospheric Measurement Techniques Discussions

Interactive comment on "Technical Note: The single particle soot photometer fails to detect PALAS soot nanoparticles" *by* M. Gysel et al.

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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.

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.

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 !

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.

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

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