

Interactive comment on “Coagulation of combustion generated nanoparticles and their measurement behind vehicle engines: can they play a role as atmospheric pollutants?” by H.-H. Grotheer et al.

H.-H. Grotheer et al.

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The "critical review" by Anonymous Referee #4 consists of two parts. (i) a brief first part containing three statements that "would basically suffice to recommend rejection of the paper" and (ii) a long second part containing suggestions how to prepare a manuscript and how to carry out experiments.

I will fully respond to (i). With regard to (ii) only the more important issues (according to my perception) will be addressed.

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(i) Three statements sufficient for rejection

1) Spectra reported for combustion are more or less only a repetition of previously (Grotheer et al., 2004) reported results, only scales have been changed. This is not true. The presented measurements are new and they have been carried out under conditions of much softer ionisation. As a result they show a different peak spacing relative to earlier measurements as correctly noticed by Anonymous Referee #4 at the end of his review.

2) The aspect of coagulation mentioned in the title is discussed in much more detail in a separate paper. True. Yet the message of the present paper is different. Surprisingly, we found these particles at the end of vehicle exhaust pipes. This is important and it happens despite of their high initial coagulation that we measured as well.

3) The role of nanoparticles as atmospheric pollutants has not been addressed. Correct. See my previous answer to Anonymous Referee #1. The title will be changed to "...can they survive an exhaust train and be released into the atmosphere?"

(ii) Suggestions concerning paper and experiment

Of course I will gratefully adopt suggestions such as consistent use of "mbar", use of the more appropriate W/cm^2 for the region of ionisation instead of mJ/pulse , use of the terminus "focal length", indicate the position of pressure reading in the probe, explain "slm", add "forepump" to Fig. 2, reduce the size of Fig. 5 and 6, name our MS manufacturer, etc.

The situation is less straightforward with regard to the Introduction. Anonymous Referee #1 suggests to describe the differences between nanoparticles and soot in more detail and this was done in the Introduction. Contrary to this, Anonymous Referee #4 suggests to abbreviate the Introduction. So we must leave this issue to the editor's discretion.

An obvious issue of disagreement is the one of molecules vs. particles around or above

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1000 u. First of all, there is no change of terminology on our side. Thus, the expression "soot precursors (nanoparticles)" is already contained in the title of our previous paper (Grotheer et al., 2004). Of course, a transition from molecules to particles has to occur. A way into 3-dimensionality could be stacking of PAHs and it was explored by several groups (eg Miller, 1990; Schuetz, Frenklach, 2002). Wang and Frenklach (1990) treat already PAH dimers as "solids". The product of stacking would be a molecular crystal which should exhibit Bragg reflections as indeed found by Dobbins (2000) in soot free flame regions. Consequently, we assume that nanoparticles are molecular crystallites. In support of this hypothesis, we could find flame conditions for which the nanoparticle mass spectra show a layered structure which shifts to more and larger layers when the reactor residence time is increased. Although this is beyond the scope of the present paper, it prevents me from using the expression "molecules" for this material. Insulin is certainly a different story.

Although these many suggestions are helpful they are difficult as well since they are mixed with personal accusations.

Example 1: Our "misleading statement" concerning Sgro et al, 2003. They write "It remains a research question how the size of combustion generated particles affects their toxicity. However, both the small size and the affinity for water of the $d = 2\text{-}4$ nm particles are characteristics which allow them to be easily uptaken and transported through the body." We summarize that in the present paper as "this (the high number) then may lead to health effects that may be even enhanced through the water-solubility of these particles". In my view this is an appropriate description. Anonymous Referee #4 finds it "misleading". In support of this he cites only the first one of the two phrases given above and adds his own statement: "That sounds quite different." In fact, in its truncated form that sounds really different.

Example 2: In order to help the reader we provide a figure of the apparatus that was used in our previous publication. In so doing this paper was of course cited. Nevertheless, for Anonymous Referee #4 this is "an example of inappropriate scientific

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practice." To underscore his view he even cites two papers dealing with plagiarism and self-plagiarism.

Example 3: Our sample passes through a nozzle (pressure ratio above 10) and becomes expanded. Admittedly, this passage needs a finite time, which, however, is small relative to other time-scales involved. May be that our description of an immediate expansion is an euphemism. By no means is it a "cheating of the reader" as stated by Anonymous Referee #4.

Example 4, the most important one: "The authors apparently disregard serious limitations of their methods and results." The problem is obviously the high power laser beam and "now, with or without knowing (?) the authors disclose the truth". This notion that we don't quite know what we do, continues: "Another surprise, not mentioned and possibly not yet identified by the authors can be identified in Fig. 4." The truth is that after a study of photo-ionisation effects we reported them clearly in the present paper (see end of 3.1): "We conclude that primary soot and especially coagulated nanoparticles are very prone to fragmentation when too high laser energies are used. We could show that fullerene signals appear when this process takes place and we assume that fullerenes are formed from excited fragments in the ion source." In the following phrase it is said very openly: "The exhaust gas measurements of this paper were mostly carried out under conditions of fragmentation as we were not aware of the described photo-ionisation effects." There is no aim of concealing anything. By contrast, deficits are openly addressed. This should be obvious to Anonymous Referee #4 as well.

How to proceed?

Anonymous Referee #4 recommends to take a close look aiming at an optimisation of our spectrometers. In fact, we have done so since some time and the result is as follows. For flames that can be burnt sufficiently rich we get a high number of particles so that the laser can be operated under safe conditions (ie small fragmentation, if any).

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In this case we get a fully developed nanoparticle mass spectrum which for masses < 1500 u shows a PAH pattern, for higher masses our resolution is insufficient for such a statement. Obviously, these spectra are in order. For vehicle engines, however, which are operated under near-stoichiometric conditions, the particle number is much smaller. Consequently, we still have to use high laser power densities with the result that we measure fragments. This is admittedly not the desired way, yet it is the best we can do at present. Perhaps we can do better in some future, perhaps there are other groups that do better even today. Since another research group at DLR found a high susceptibility of bacteriae and of human lung cells to these particles, the issue of exhaust gas and field-measurement is urgent.

In view of this and in accord with three other referees of the access peer-review my plea to the editor is: Accept.

L A Sgro, G Basile, A C Barone, A D'Anna, P Minutolo, A Borghese, A D'Alessio: Detection of combustion formed nanoparticles, Chemosphere 51, 1079-1090, 2003

J H Miller: The kinetics of polynuclear aromatic hydrocarbon agglomeration in flames. Proc. Combust. Inst. 23, 91-98, 1990

C A Schuetz and M Frenklach: Nucleation of soot: Molecular dynamics simulation of pyrene dimerization. Proc. Combust. Inst. 29, 2307-2314, 2002

M Frenklach and H Wang: Detailed modelling of soot particle nucleation and growth. Proc. Combust. Inst. 23, 1559-1566, 1990

H X Chen, R A Dobbins: Crystallogenesiis of particles formed in hydrocarbon combustion. Combust. Sci. Technol. 159, 109-128, 2000

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