

## ***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.***

### **Anonymous Referee #4**

Received and published: 22 July 2005

This contribution describes results obtained using time-of-flight mass spectrometry in combination with photoionisation by a focussed laser beam to analyse combustion generated molecules and small particles. The spectra reported for combustion in a low-pressure burner constitute more or less a repetition of previously reported results, except for the fact that the data are now presented on log-log scales rather than on the lin-lin scales used before (Grotheer et al., 2004). The aspect of coagulation specifically mentioned in the title appears to be discussed in much more detail in a separate paper

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submitted by the same group to the Proceedings of the 2005 European Combustion Meeting. The title of the paper under review also addresses the question whether combustion generated nanoparticles play a role as atmospheric pollutants. This question remained unanswered.

These few arguments would basically suffice to recommend rejection of the paper. To support future improvements, however, the most important shortcomings of this manuscript will be addressed below.

**Introduction.** The state of the art concerning the analysis of combustion generated precursor molecules and nanoparticles was already described in a very recent publication of the group (Grotheer et al., 2004). Hence, in the introduction to this study, it would have sufficed to refer to that paper, outlining the purpose of this work very briefly. Instead the authors have extended the length of the previous introduction by at least a factor of two, sometimes repeating the same statements already made before. Examples are the two sentences starting with “Exemplary number densities etc.”. Several literature results were listed “For the sake of brevity etc.”. However, many of these topics like the H fraction, the PAH-like structure or the 2- and 3-ring substructures are of no direct relevance to the present study. This kind of information would have been of importance only if the authors’ intention had been to demonstrate that what they see in their mass spectra has little or nothing to do with the original composition of the molecules contained in the exhaust gas (see below).

The introduction also reveals a disposition towards making statements that are either illogical or misleading. It is argued, for example, that “Although these emissions (of nanoparticles from vehicle engines) are small on a mass basis, their number densities exceed those of soot particles by orders of magnitude as a result of the small size involved. This then may lead to health effects which may be even enhanced through the water solubility of these particles (Sgro et al., 2003)”. The logical reasoning concerning the mass-to-number relationship should be just the other way round: the mass concentrations of nanoparticles are low because the particle are so small (assuming that the

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term “nanoparticles”, which is not defined in any detail by the authors, relates to those particles that feature masses beyond 50 ku, i.e. sizes of about 4-5 nm). The statement concerning health effects implies that Sgro et al. (2003) have provided relevant experimental or epidemiological evidence in this matter. Not at all. They have presented results on nanoparticle analysis together with some reasoning as to potential health effects, concluding “It remains a research question how the size of combustion generated particles affects their toxicity.” That sounds quite different.

Experimental. The experimental arrangement has already been described before (Grotheer et al., 2004). Reference to the previous work would have been sufficient, together with a very short summary of the instrumental concept. The lay-out of their low pressure burner was copied from the previous publication, but there is no mention in this manuscript that Fig. 1 is the same as the previous Fig. 1, except for two minor changes. (i) The unit “mb” in the top line was changed to “mbar”, but the required correction has not been performed in the line reading “1-10 mb” (note that mb is the abbreviation for millibarn, which is really not an appropriate unit for pressures). (ii) The last line specifying the laser power as “10 mJ/pulse” in the original was changed to “<3 mJ/pulse”; the latter specification, however, is incorrect because one spectrum in Fig. 3 depicts results obtained at 4 mJ/pulse. Copying material already published without reference constitutes an example of inappropriate scientific practice. The terminology and a discussion addressing such problems can be found in very recent publications (Giles, 2005; Wittmaack, 2005).

Almost every sentence of the experimental section exhibits deficiencies or inconsistencies. A few examples are given below:

(a) “The beam was focussed through a 150 mm cylindrical lens.” In the previous study the beam was “mildly focussed with a 500 mm lens” (Grotheer et al., 2004). One has to assume that the quoted lens parameters specify the focal lengths. But to understand what the authors really achieved by focussing, they should have measured the laser power densities in the volume from which the ion signals originate. Apparently, these

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very important experimental parameters were not explored.

(b) “Pressures in the sampling tube are between 4 and 15 mbar. Consequently, for atmospheric samples all concentrations were immediately reduced at the location of sampling by a factor of at least 60.” Which part of the tube do the quoted pressures relate to? How were they measured? What does “between” 4 and 15 mbar mean? Which parameter was varied to produce the difference? The authors are cheating the reader by stating that the concentrations were “immediately” reduced. This is simply impossible. There is no need to tell the reader that  $1000/15$  equals about 60. In fact, the second sentence is not a “consequence” of the first but merely a repetition of the quoted data in other words.

(c) “The concentration drop together with our short residence times of only some ms leads to a reduced influence of fast subsequent reactions. This is obviously at the expense of sensitivity as most of the sample is lost into the forepump.” The term “our” residence times is laboratory slang. Where is the forepump in Fig. 2? Arguments in terms of reduced reaction rates are at variance with the fact that the authors present detailed data on coagulation. Wouldn't they refer to coagulation as one kind of a reaction? The statement concerning sensitivity is not understandable. If one wants to study the composition of an exhaust gas while minimising reactions on the way from the source to the volume in which ionisation takes place, one has to optimise the inlet system. That is one part of the story. To achieve optimum sensitivity in ion detection is then a question of the field of view and the transmission of the mass spectrometer. The latter parameters are not even mentioned by the authors. Neither do they name the manufacturer of their instruments. Instead they provide the rather useless information that the two instruments were made by the same manufacturer.

(d) The gas flow is quantified by the mysterious unit “slm”. What is that? Was the intention to quote the flow as standard litres per minute? May be, but the reader has to make a guess.

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Results. Just as a starter for this part of the review it is worth pointing out that the authors apparently tried to change established terminology in the field. Or did they merely use laboratory slang in preparing the manuscript? In the description of Fig. 3 they state “Around 1000 u is the distribution of primary nanoparticles, etc”. These “particles” are molecules which are commonly referred to as “precursors”. Accordingly, this notation was used previously by the group (Grotheer et al., 2004), but now they seem to have changed their mind without providing an explanation. A change in terminology is not acceptable. Or should we, in the future, refer to a porcine insulin molecule (mass 5777.6 u) as a “particle”, only because its mass exceeds 1000 u?

With regard to the lay-out of figures, the authors do not seem to have thought about the question how a certain set of data can be presented in graphical form with the aim of minimising the required space and at the same time making the information easily readable. Consider, for example, Fig. 5. The message contained in the data can easily be presented in a one-column wide graph. The inset is not required because the occurrence of equally spaced peaks in the mass region  $m/z < 1000$  is not specific to this experiment, but a common feature discussed below. The spectra in the main part of the figure overlap in the low-mass as well as in the high-mass region. Hence it would be sufficient to present the full spectra only for shortest and the longest residence times and to cut-off the other spectra where overlap occurs. The size of the tick labels, the labels in the figure and the titles of the axes is too small by about a factor of two. Or do the authors claim that the information presented is so important that the figure must be two columns wide?

The real problem, not only of the present but also of the previous work (Grotheer et al., 2004) is that the authors apparently disregard serious limitations of their methods and results. The disclosed spectra provide clear evidence that the signals originated from matter that was heavily degraded by impact of the high-power laser beam. Instead of soft photoionization of intact molecules and small nanoparticles, the experimental conditions favoured severe loss of hydrogen as well as disintegration and fragmentation of

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the analysed molecules. The need for applying high laser power densities is related to the low signals observed in the mass region above  $m/z$  100000 (see Fig. 3) which is of prime interest to the authors. Upon increasing the laser power, the signals in the mass region  $m/z > 2000$  increased strongly, but remained constant or even decreased in the low-mass region. This observation implies a severe loss of molecules with  $m/z < 2000$ . In their previous study (Grotheer et al., 2004) the group reported expanded mass spectra in the region between  $m/z$  400 and 2000. The spectra are dominated by a series of equally spaced peaks separated by  $m/z$  24, equivalent to a difference in composition by one carbon dimer per peak spacing. The peaks were referred to as “fullerene-like”, as if the original molecules were mostly fullerenes. Now, with or without knowing (?), the authors disclose the truth: the observed peak structure is laser-beam induced. The most direct evidence comes from Fig. 7 which shows convincingly that the characteristic peaks with a spacing of  $m/z$  24 are observed only when photoionization is produced by a focussed laser beam (using a 154 mm instead of a 150 mm lens). The noisy reference spectrum obtained with an unfocussed laser beam reveals no characteristic pattern of equally spaced peaks. The immediate conclusion is that the peaks are only observed above a certain threshold in laser power density.

Another surprise, not mentioned and possibly not yet identified by the authors can be identified in Fig. 4. The results were obtained with the same burner as in the previous study (Grotheer et al., 2004), in which case the measured peak spacing was  $m/z$  24. However, in Fig. 4 the peak spacing is  $m/z$  12, corresponding to a difference in composition of the (degraded) molecules by one carbon atom per peak spacing. The differences in peak spacing indicate that the observed spectral features are erratic, probably reflecting significant, yet unspecified differences in laser power density in the different experiments.

In summary, this paper reports a set of mass spectra observed when directing a laser beam at the exhaust gas of combustion sources. Owing to the routine application of high laser power densities, the observed spectra are severely affected by artefacts, i.e.

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they do not reflect the original composition of the molecules and the particulate matter carried along with the gas. The authors would be well advised to take a very close look at the performance of their spectrometers with the aim of really optimising and quantifying the experimental parameters.

Recommendation to the editor: Reject.

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