

***Interactive comment on* “The surface properties of SOA generated from limonene and toluene using specific molecular probes: exploration of a new experimental technique” by B. Demirdjian and M. J. Rossi**

**B. Demirdjian and M. J. Rossi**

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We thank both referees for their diligent and careful evaluation. In response to their comments we intend to submit a revised manuscript that will take into account most of their comments and suggestions.

On behalf of the authorship I would like to specifically respond to the questions as follows:

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Referee 1:

Q1-Surface areas from BET measurements. We go to great lengths in the present study in order to justify our approach to derive the effective surface area from the aerosol metrology. Essentially, the whole of Section 4.3.1 including Figure 5 deals with this question, namely, that the collection of the SOA aerosol on a filter preserves its metrological properties as long as the filter loading is not too large. The linearity of both tests, the number of aerosol probes ( $N_i$ ) as well as the relative uptake kinetics ( $k_{uni}/k_{esc}$ ) as a function of SOA mass displayed in Figure 5, confirm the assumption that there is no coagulation or accumulation effect that would change the aerosol metrology. Measurement of the BET surface of an aerosol collected on a filter has never been performed and would certainly be a research project in its own right. In addition, the cooling of the aerosols to 77K would certainly induce phase changes (freezing), and for sure would change their external surface as well, unless one proves this to the contrary. I do not think that the measurement of the BET surface area of a supported SOA has yet been performed because this would be much “trickier” than the approach we have chosen.

Q2-Uptake kinetics. Reaction in the bulk. The focus of the present work lies in the determination of the number (integral) of probe molecules, and not on the kinetics of uptake of the probe molecules. I agree with the referee that this could be done, but if this were our original intent, we would have chosen shorter residence times that afford results of higher precision. However, we will complete Table 1 by adding the values of  $k_{esc}$  for the four probes such that  $k_{uni}$  may be derived for the respective experiments. Regarding bulk reactivity we unmistakably state that limonene SOA presents a response to the  $NH_2OH$  probe that partially comes from the bulk. In discussing Figure 7 we will strengthen that statement as it clearly indicates a difference between toluene and limonene SOA: in the former, the uptake of the  $NH_2OH$  probe saturates whereas in the latter we observe steady-state uptake. This steady-state uptake is related to the renewal of functional groups diffusing towards the surface by bulk diffusion depending

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on the viscosity.

Q3-Polymerization and oxidizing species. In the experiments on soot aerosol where we obtain a response to O<sub>3</sub> (see Table 2) the functional groups are immobilized so that no polymerization can occur. Both SOA are only exposed to reducing species precluding oxidative polymerization. As a result we do not believe that polymerization occurs as a complicating factor in the present experiments. Moreover, it has been shown that polymerization is a relatively minor effect affecting 10-15% of the mass balance.

Q4-Acidic carbonyl groups and NH<sub>2</sub>OH. I apologize for the misunderstanding: the NH<sub>2</sub>OH probe eventually reacts with all carbonyls to form an oxime whereby the condensation reaction is general acid-catalyzed. This does not mean that the carbonyl group itself has to be acidic as the general acid may come from within the sample. Therefore, both the N(CH<sub>3</sub>)<sub>3</sub> and NH<sub>2</sub>OH probes are independent of each other and interrogate different functional groups. The manuscript will be modified accordingly to clarify this point.

Concerning the length of the manuscript we do not see any viable possibility to shorten it unless one wants to forego the communication of certain results. The manuscript has 52 references (4 autoreferences), and we decided not to address the soot literature as it would distinctly increase the length of the manuscript.

Referee 2:

Does this technique apply to liquids? See also response to Q2 above. The present technique may interrogate any condensed phase as long as its vapor pressure does not exceed 10-3 mbar which is imposed by the need to maintain molecular flow. At one extreme solid particles will not exchange their surface composition with the bulk, whereas highly fluid particles may, depending on the viscosity. "Surface" is not a static property: it depends on the diffusion time that both depends on the diffusion coefficient (and therefore of the viscosity) of the condensed phase as well as on the time scale of the experiment that is variable between approximately 0.1s to 20s. The present

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experiment addresses the interfacial composition of the condensed phase during the gas lifetime of the probe molecule. It is clear that highly fluid (but low vapor pressure) aerosols may exchange part of their interfacial surface with the inner bulk by diffusion. As the referee points out, the probe addresses in part the bulk in certain cases such as for limonene SOA, whereas for toluene SOA this does not seem to be the case. One may conclude therefore that SOA aerosol particles are much more fluid than toluene SOA allowing the exchange between the bulk and the interface. Under those conditions, the titration technique therefore does not exclusively describe the surface properties for limonene SOA, but does so for toluene SOA as displayed in Figure 7. We may lower the temperature of limonene SOA in the future, in which case we perhaps sufficiently slow down molecular diffusion such that the probes interrogate mostly the gas-condensed phase interface. We will strengthen this point in both the Abstract as well as at the end of the manuscript.

Evaporation of the condensed phase (aerosols). During the experiment MS analysis reveals some evaporation of light molecules such as H<sub>2</sub>O, alcohols and light aldehydes. However, the extent is barely measurable using gravimetric techniques. The referee poses the question as to the “real” surface of the SOA. This is worth being pursued in the manuscript and will be answered in the sense that “real” refers to functional groups that gas phase probe molecules “see”, regardless whether they exchange or turn over mass on the time scale of the experiment (limonene SOA) or not as in the case of toluene SOA.

O<sub>3</sub>-denuder (page 618): The moist KI denuder tube converts all effusing ozone into I<sub>2</sub> to unmeasurable levels. The final product is I<sub>2</sub> that is pumped off.

Page 623. Caloz et al. (1997) reveal pertinent details as to the measurement of k<sub>esc</sub>. We will amend the manuscript in order to give the definition of k<sub>uni</sub> that enables the derivation of equation (7).

Page 613. According to the manufacturers specification the used thickness of the

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PTFE membrane filters (175 micrometers) removes all particles down to 50 nm. The transmission increases to 10-20% below this value, but this is inconsequential because of the vanishing mass of the smallest particles and also because very small particles are easily filtered. For most filters the critical transmission “window” is 100 to 350 nm whose transmission is low for this type of filters (membranes).

Page 636: The optoacoustic technique favors the detection of surface species compared to bulk, depending on the penetration depth of the IR radiation across the spectral range 400 (large)-4000 (small penetration)  $\text{cm}^{-1}$ . The manuscript will be amended to strengthen this point.

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