Atmospheric
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Discussions

Interactive comment on "A New Oxidation Flow Reactor for Measuring Secondary Aerosol Formation of Rapidly Changing Emission Sources" *by* Pauli Simonen et al.

Anonymous Referee #2

General comments:

The manuscript by Simonen et al., describes a new oxidation flow reactor designed to achieve shorter residence time relative to the potential aerosol mass (PAM) reactor. The aim of the new reactor is to provide a method of capturing SOA formation during studies of rapidly changing emission sources (e.g. combustion emissions). Although the subject of the manuscript is appropriate for publication in Atmospheric Measurement Techniques, the manuscript in its current state reads more like a technical report at certain parts and lacks sufficient discussion in many places. Most importantly, the manuscript does not contain sufficient emphasis on the atmospheric applicability or relevance in several places. In general, the use of such methodology for studying SOA

formation has some benefit if results are not over-interpreted, and used for comparative purposes or during screening experiments to quantify the "potential" SOA formation of a given source or precursor. This is because the methodology is fundamentally limited in terms of its ability to reproduce tropospheric conditions due to unrealistic partitioning behaviour at elevated supersaturation of oxidation products, high OH exposure over a very short period of time and complex OH vs non-OH chemistry resulting from high photon flux at non-tropospheric wavelengths, especially for mixtures of high OH reactivity. Consequently, results of such experiments must not be over-interpreted or used in absolute term. It is recommended that the authors address the general and specific comments adequately before the manuscript is considered for publication.

Specific comments:

1) In the abstract, the statement about long and short residence times of different reactors should be qualified by adding typical times to provide the reader with an idea about the main difference between existing techniques and the new TSAR reactor. The abstract should also contain more details about the main modification of the reactor design, which enables the operation at higher time resolution compared to the PAM reactor (e.g. volume, flow rate).

2) The introduction should include more critical evaluation of the limitations of existing reactors and chambers with regards to the ability to measure transients and provide typical examples of the residence times of the various reactors mentioned in order to make a case for the need of the new reactor being described in this manuscript.

3) Page 4, line 1-2: The O3 needed for this reaction chain is mixed with the sample prior to the residence time chamber. This has an implication on experiments where some of the VOCs react with ozone (e.g. alkenes and biogenic compounds). This should be stated and clarified with discussion of how it would or wouldn't be possible to separate such an effect from that of OH chemistry especially for mixtures of complex composition (i.e. real emissions). The authors touch on this effect later in the manuscript when

comparing the oxidation state of SOA produced by the TSAR and PAM reactors (page 12, line 26-27), which emphasise the importance of characterising this aspect of the reactor.

4) Page 6, line 19-20: Although the authors have shown that the assumption that sulfuric acid losses to the reactor wall are negligible, it is not clear whether this is meant to suggest that such assumption would also hold for oxidation products of organic compounds, which have a wider range of volatility distribution. This should be discussed in the manuscript as it represents a limitation on the ability to quantify SOA yield. On a related note, the sulfuric acid yield section (3.4) is too short to stand alone as it is. The discussion need to be expanded to address this comment.

5) Page 7, line 9: It is not clear why the authors did not use the PAM reactor in the OFR254 mode given intended purpose of comparing the results with TSAR which uses a 254nm light source. This should be explained and justified. In addition, the manuscript provides no discussion of the potential effect of the different light sources on the non-OH chemistry in the reactors. The authors should include such discussion in the manuscript in the context of the work published by Peng et al., (2016) quantifying the extent of OH vs. non-OH chemistry according to the conditions applied in the reactor. It is important to understand the role of water mixing ratio, photon flux and external OH reactivity in the experiments on non-OH chemistry (photolysis) in order to establish the atmospheric relevance of the experiments.

6) Page 11, line 21: What is the background mass of the TSAR? How variable is it depending on OH and humidity conditions? Is this characterised and corrected for on a regular basis? More discussion of this should be included.

7) Page 11, line 25-28: More discussion is needed for the apparent link between shorter residence time and the smaller size distribution produced in the TSAR experiment. The potential implication of such phenomena on the produced SOA particles and their properties needs to also be discussed.

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8) Page 12, line 1-2: How representative is the off-line OH exposure calibration of the actual reported OH exposure in a more complex VOC mixture such that found in the Toluene SOA experiment or other VOC mixtures with different OH reactivates? This is likely to be a source of significant uncertainty in the determination of OH exposure and it is not discussed adequately in the manuscript.

9) Page 12, line 9-15: The discussion of the different toluene SOA yields among the Kang et al., Ng et al., and Hilderbrandt et al., is very brief and over-simplified. There are so many factors affecting the different studies that could potentially contribute to the reported SOA yields and differences cannot be explained only be the presence or absence of seed particles.

10) Page 12, line 18: The Aiken et al., (2008) analysis method for HR-AMS data has been updated by Canagaratna et al., (2015), with the new method having a direct effect on the reported O:C values. The authors should either justify the reason why the opted to use the Aiken calibration or update the results using the Canagaratna method.

Editorial comments:

Page 4, line 11: section should be 2.2 not 2.1 (same correction should be applied to all subsequent subsections in this part of the manuscript). Page 10, line 14-16: the temperature and relative humidity should be reported as average with an associated standard deviation instead of the current mixing up of average with range.

References:

Peng et al., (2016), Non-OH chemistry in oxidation flow reactors for the study of atmospheric chemistry systematically examined by modeling. Atmos. Chem. Phys., 16(7), 4283-4305. doi:10.5194/acp-16-4283-2016