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Atmospheric Measurement Techniques Discussions

Interactive comment on "A novel semi-direct method to measure OH reactivity by chemical ionisation mass spectrometry (CIMS)" *by* Jennifer B. A. Muller et al.

Anonymous Referee #3

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This manuscript reports a methodology to measure total OH reactivity using Chemical Ionization Mass Spectrometry (CIMS) instruments initially designed to monitor ambient OH radicals. This methodology was implemented on the Hohenpeissenberg CIMS instrument, which can now sequentially measure OH, sulfuric acid, and total OH reactivity. The ability of performing long-term measurements of total OH reactivity, together with the OH radical, is of particular interest for the scientific community to assess long-term trends in the ambient load of OH co-reactants and in the atmospheric oxidation capacity.

The methodology is well described, the performances of the CIMS setup well presented, and the authors have carefully documented its current limitations. 0-D modeling results are very useful to investigate and quantify these limitations. It is shown that this technique is suitable for the Hohenpeissenberg area, and other areas exhibiting low NO mixing ratios.

This manuscript is clear and concise, and I therefore recommend publication in AMT after the authors address the following comments:

1/ Limitations and uncertainties associated to this measurement technique are thoroughly investigated in section 3. This is a relatively long section and it would be beneficial for the reader to insert an additional table at the end this section to summarize all the sources of uncertainties.

2/ Was the photolysis of ambient OVOCs by the mercury lamp radiation investigated? The amount of radicals produced from OVOC photolysis will not likely be significant compared to the HOx production from water photolysis but could this lead to a significant change in kOH?

Minor comments:

P3 L11: “The CIMS system is frequently calibrated…”. Please indicate how often calibrations are performed.

P3 L14: How is the generated OH concentration determined during calibration experiments?

P4 L17-18: “…leading to the quantification of the contribution from recycling and other artifacts…”. The term “recycling” may not be the most appropriate here since it does not include OH radicals produced from HO2+NO in the CIMS inlet in the presence of SO2 and propane. I would not use this term.

P5 L16: How was the reaction time inferred? Please clarify whether this is calculated or measured?

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P5 L24: Please report values for the generated air flow rate and the CIMS sampling flow rate. The CIMS sampling flow rate of 2280 mL/min is reported P11 but this is too late.

P8 L20: The authors should explain (or remind the reader) why the OH reactivity value is integrated over 10 min but the time resolution is twice longer (20 min). We would expect a time resolution of 10 min.

P10 L12-13: How did the authors come up with NO contamination levels of 140 ppt and 20 ppt in the SO2 and zero air mixtures, respectively? Was it measured? Or are these conservative upper limits? Something else?

P11 L5: Please double-check the uncertainty values stated for the scaling rate. How were they calculated? The 1σ determination using the IUPAC rate constant for OH+propane seems very small. The IUPAC compilation indicates that Δlogk for OH+propane is $\pm$0.08 at 298K, which I think translates into a 1σ uncertainty of approximately 10%. How can the uncertainty on the scaling rate be lower than the uncertainty on the rate constant?

P11 section 3.3: This section compares scaling rate values derived from flow tube calibrations to values inferred from atmospheric chamber experiments. This provides a nice validation of the flow tube calibration method. The authors should also discuss the comparison of kw values derived from these different experiments? Were the kw values consistent within uncertainty?

P12 L14-15: How is the upper limit for OH reactivity measurements quantified? Is the calculation based on a 3σ detection limit of OH in zone 2?

P12 L26: Sup. mat. S1 is cited for more details about the tagged mechanism. However there is no information about the tagging feature in S1.

P14 Eqs. 7-10: How was this complex empirical function determined? Can physical meanings be associated to some of the terms?

P16 L22: A scatter of 10-20% is reported. Under which conditions was it observed (nature of trace gases, OH reactivity level, etc.). How many σ is it?

P17 L7-9: Please be quantitative. How accurate is “high accuracy” and “lower accuracy”? Table 1: How many σ did the authors used to calculate the limits of detection? What are the precisions on Δt and kw values?

Fig. 14: It would be useful to add a time series for NO since it can disturb the measurements. Could the measurement underestimation due to the presence of NO also be quantified and shown as another time series?

Technical corrections

P1 L27: “. . .termed also total OH loss rate. . .” should read “. . .also termed total OH loss rate. . .”

P4 L20-23: This sentence should be rephrased. It’s not clear what is meant by “. . . is the final OH concentration without UV light subtracted from the final OH concentration with the UV lamp on.”

P4 Eq. 1: Missing negative sign in the exponential factor. kw should also be added in this equation for consistency with Eqs. 2-4

P4 L32: Delete the word “lawful”

P6 L7: “. . . within the flow tube from point of the inlet to . . .” should read “. . . within the flow tube from the inlet tip to . . .”

P6 L18-19: “The scaling rate, i.e. the times of SO2/propane injection. . .”. Shouldn’t it read “The scaling rate, the inverse of the reaction time between T1 and T2. . .”

P7 L3-6: “volume flow” should read “volumetric flow rate”. Several instances.

P7 L12: “Additionally” should read “Additional”

P9 L26: “synthetic air has been measured for a range of VOC and OH reactivity calculated" should read "synthetic air has been screened for a range of VOC and OH reactivity calculated from a quantification of these contaminants"

P13 L18: Replace "annulled" by "cancelled"

P19 L24: "Calculations and propagation of uncertainties was performed..." should read "Calculations and propagation of uncertainties were performed..."

P19 L27: Double-check the 5% value reported for LN([OH]T1/[OH]T2). It's 7.1% in section 3.2.1.

P19 L31-32. Some units are missing.

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