

Interactive
Comment

Interactive comment on “A flow-tube based laser-induced fluorescence instrument to measure OH reactivity in the troposphere” by T. Ingham et al.

Anonymous Referee #2

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The paper describes a new instrument for direct measurement of atmospheric OH reactivities, using a flow-tube with a movable OH injector and a laser-induced fluorescence detection system for monitoring the time dependent OH loss in samples of ambient air. Measured OH reactivity data are extremely useful as they provide a measure of the total loss rate of atmospheric OH and, as correctly pointed out in the introduction of the paper, establish an important additional constraint in field tests of atmospheric chemistry models. Here, the authors present a careful description and detailed characterization of their instrument which was already successfully deployed in several field campaigns. The paper is well written and I recommend its publication in AMT, after the authors have answered the following (minor) comments.

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Specific comments

I would welcome a table which summarizes the main characteristics of the instrument, e.g. sample flow rate, flow conditions in the tube, residence time, time resolution of measured OH reactivities, limit of detection, accuracy with/without NO present etc.

page 625, line 16-18: Yoshino et al (2006) report OH reactivities from Tokyo at different seasons. It should be noted that significant missing reactivity ($\sim 30\%$) was observed only in summer, spring and autumn. In winter season no significant difference (typ. 5%) was found within the measurement errors.

page 625, line 18-21: the reactivity measured by Ren et al. in New York City agreed to within 10% of the calculated values in the summer campaign (Ren et al. 2003). It should be noted that there was much larger missing reactivity ($\sim 30 - 40\%$) at rush hour in the morning and evening during the winter campaign (Ren et al. 2006).

page 625, line 25-26: 'and where there were simultaneous measurements of co-reactants, the measured OH reactivity was a factor of ca. 1.3 higher than calculated'. This sentence is misleading and requires either more explanation or should be deleted in this form. Shirley et al. refer to only two data points and conclude "However, with very little overlap between the measured OH reactivity and the measured VOC, it is not possible to examine the completeness of the measured VOC and other OH reactants".

page 627, line 10: 'An analysis of this method has also been given (Smith and Crosley, 1999)'. The sentence does not provide useful information and the quoted conference abstract is not easily available. I recommend to delete the sentence and the corresponding reference.

page 629, line 12: the sentence ' k'_{physical} is the non-reactive loss of OH mainly due to wall losses' is inconsistent, as wall losses are caused by reactive (!) collisions at the wall surface. Later (section 3.4) the authors explain that ' k'_{physical} also includes possible reactive (!) losses by impurities in zero air. I recommend to replace the index 'physical'

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by a different term, e.g. 'wall loss' or 'zero air'.

page 638: the title and first paragraph of section 3.3 imply that the anemometer is calibrated vs. the decay rate of a known reactant. In that case the anemometer calibration cannot be more accurate than the rate coefficient of, for example, OH+CO which has a stated 2σ uncertainty of about 10% (NASA/JPL 2006). The authors specify an accuracy of 5% for the anemometer calibration, which seems to be too optimistic. Or has the anemometer been calibrated independently (source of calibration? accuracy?) and the calibration was just tested against the decay rate of a known reactant? Please explain more clearly which calibration standard was used and how you derived the error (5%) of the flow velocity.

page 643: the initial ratio of $[\text{HO}_2]/[\text{OH}]$ is given as 1.75 ± 0.2 at $t=0$. How does the ratio change from the first to the last position of the decay curve?

page 643: how large is the additional systematic error of the corrected OH reactivity as a result of the correction algorithm, for example in Fig. 3. How much do uncertainties of S_x , C_x and $k_{\text{HO}_2+\text{NO}}$ propagate?

page 644, section 4.1: I am not sure what I can learn from this section. The only useful information are the measured OH reactivities given in line 10, but it is not clear whether the data are valid or what their error is. The text explains that the data were not corrected for the HO_2+NO recycling, because the $[\text{HO}_2]/[\text{OH}]$ ratio was not known. The uncertainty resulting from the missing correction is not quoted and a corresponding estimate should be given. If the estimate is not possible, I recommend to delete the entire section.

Technical comments

page 623, line 24: in chemical literature, 'carbonyl' refers to carbon monoxide as a ligand in a complex (e.g. nickel tetracarbonyl). Here, 'carbonyl compound' should be used for organic molecules that carry a carbonyl group as a functional group (e.g.,

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aldehydes).

page 624, line 28: k' denotes a loss rate coefficient, whereas $k'[\text{OH}]$ denotes a loss rate. Also, the labels at the y-axis of Figs. 4 and 5 should be named consistently, either loss rate coefficient or reactivity.

page 634, line 3: typing error: 'scalar' must be 'scaler'.

page 642, line 15: typing error: 'Eq.(9)' must be 'Eq.(7)'.

Fig. 5: the numbers at the y-axis must be positive.

References: typing error in Ren et al. (2006a): 'new York City'.

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