Atmospheric
Measurement
Techniques

Open Access

EGU

Discussions

Interactive comment on "Implementation of a chemical background method for atmospheric OH measurements by laser-induced fluorescence: characterisation and observations from the UK and China" by Robert Woodward-Massey et al.

Anonymous Referee #2

Received and published: 13 March 2020

General

The paper describes the implementation of a chemical modulation technique for the FAGE-LIF OH instrument operated by the University of Leeds. The purpose of this technical upgrade is to quantify and correct for possible OH interferences, which cannot be detected by the traditionally used laser-excitation wavelength modulation technique. Both operational methods, chemical and wavelength modulation, allow to discriminate OH signals from background that is caused by scattered laser radiation, non-resonant

fluorescence, or solar radiation entering the instrument. However, only chemical modulation, in which ambient OH is scavenged by an added reagent in front of the instrument inlet, allows the detection and subtraction of signals from OH, which is artificially produced inside the instrument. Over the last eight years, some LIF groups have discovered, by use of chemical modulation, previously unknown significant interferences due to instrumental OH, when measurements were performed in biogenically influenced environments. Currently, it is not clear which precursors or formation mechanisms are responsible for the observed artefacts. It is also not clear how much these interferences depend on the specific instrumental design and its operating conditions. The comparison of measured and model simulated OH concentrations in the real atmosphere has always been considered as an important test of our understanding of atmospheric chemistry. It is obvious that progress in understanding can only be achieved if atmospheric OH measurements are reliable. The implementation of the chemical modulation technique in LIF-FAGE instruments as in the present case is therefore an important step in the further development of the research field. The current paper deals with this important topic and is worth to be published in AMT.

The paper provides a good overview of the topic and describes in detail the implementation in the Leeds LIF-FAGE instrument. The authors present interesting results of interference tests in the laboratory and of applications of chemical modulation with the Leeds instrument during field campaigns in the UK and China. The description of the technique and results is clear and well structured. In agreement with laboratory work from other groups, the authors find that OH interferences from ozone photolysis, nitrate radicals and ozonolysis of alkenes are generally negligible at natural atmospheric conditions, or can be sufficiently well corrected (ozone photolysis). In relative clean air in UK and in the polluted air in Beijing, China, the authors find no evidence of unknown OH artefacts larger than the detection limit. This means that either the instrumental design of Leeds is less sensitive to OH artefacts found in other instruments, or that different environmental conditions have not supported the formation of such artefacts. In any case, the application of the new method increases confidence in OH field data

obtained by the Leeds instrument. I recommend publication of the paper after the authors have adressed my comments below.

Major comments

Abstract

I am missing a quantitative statement about the possible extent of unknown interferences in the FAGE instrument of Leeds during the AIRPRO and ICOZA campaigns. Please specify upper limits as equivalent OH number densities and fractional contributions to the measured total OH signals (without scavenger) taking into account the measurement errors.

Internal OH removal efficiency

The authors present a clever idea to determine the internal removal efficiency of OH by propane. However, I think the evaluation of the data presented in Table 2 needs some revisions. The average value ($\pm 2\sigma$) for the internal removal is given in the text as (-0.5 ± 1.3)% at a propane mixing ratio of 110 ppmv and (-2.8 ± 2.3)% at 1100 ppmv. I believe that the stated errors are too small. The number of experiments mentioned for both cases (Table 2) is rather low (n=3). The calculated standard deviation from such small statistical sample underestimates the error of the mean value. I suggest to calculate weighted means with their standard errors (using error propagation). This would yield (0.0 ± 4.0)% at 110 ppmv propane and (2.9 ± 6.6)% at 1100 ppmv. While the mean values are not much different from the ones given in Table 2, the larger errors seem more plausible.

An internal OH removal of 12% is theoretically calculated for the case that the sampled OH is exposed to the scavenger (1100 ppmv) for 2 ms on the way from pinhole to laser axis. The experimental value of 2.8% (Table 2) cannot be directly compared with this

C3

theoretical estimate, as is done in the paper. In the instrument, OH is built up gradually (in this case linearly) by HO_2 conversion along the line from pinhole to the laserbeam, followed by OH reaction with propane (and NO). In this sequential reaction system, the effective scavenging efficiency is about half the efficiency for OH radicals exposed to the reactant over the entire distance from the inlet to the laser beam. Thus, the experimental value has to be approximately doubled to be comparable with the theoretical estimate. A value of $2\times (2.9 \pm 6.6)$% = (5.8 ± 13)% would not be much different from the theoretical value of 12%. My conclusion is that 10% internal OH loss at 1100 ppmv of propane cannot be ruled out by these laboratory experiments.

Intercomparison OHwave and OHchem

In Figure 10, 12 and 14, OHwave is higher than OHchem by 16%, 5%, and 10%, respectively. The discrepancy is statistically significant (i.e., larger than the $\pm 2\sigma$ statistical errors of the fitted slopes). There must be reasons for the systematic deviations which should be discussed in more detail. I am not satisfied by the statement that the discrepancies can be explained by the instrumental uncertainties (26%, $\pm 2\sigma$). Two measurements are compared which actually use the same calibration. Thus, uncertainties of parameters used to quantify the OH production in the wand cannot be responsible for the differences between OHwave and OHchem. How much of the discrepancy between OHwave and OHchem can be explained by the uncertainty of the O_3-H_2O interference correction in OHwave? Are there other possible reasons? Finally, the differences could indicate an uncorrected bias due to an unknown interference in OHwave, which, I agree, would be smaller than the instrumental uncertainty of 26%.

Minor comments

Line 125. SI unit should be used for pressure (e.g., hPa) instead of Torr.

Line 149. initially to HO_2 and subsequently to OH ?

C4

Line 290-295. It should be explicitly stated that the determination of OHwave and OHchem uses the same calibration, which is carried out without IPI under the assumption of negligible transmission losses with IPI.

Line 290-295. For the given IPI conditions, I calculate a Reynolds number of 2290. This value is close to the critical point where laminar flow becomes turbulent. The state of the flow is expected to influence the mixing of the scavenger in the IPI flow and the loss rate of OH at the walls. Have the authors tested, how sensitive the scavenging efficiency and tube transmission depends on the IPI flow rate?

Line 345. I assume you mean (0.030 ± 0.091)% instead of 0.030 ± 0.091% ? Check also other instances in the paper.

Line 387. The number for the internal removal of -0.5 ± 1.3% is not consistent with the value in Table 2 showing -0.2 ± 1.1%.

Line 413. I assume, the water level is given as a volume mixing ratio and not as relative humidy. Please clarify.

Line 435. How long is the reaction time for isoprene and ozone before the gas is entering the pinhole of the FAGE cell?

Line 444. Which material was used for the additional 30cm flow tube?

Line 445. What is the meaning of 'τ = 0.15 s' ?

Table 1, footnotes. Labels are missing in the table body.

Table 3. Column width of 'Obs' needs reformatting.

Table 4. What is the meaning of the $\star$ symbol for the daytime contribution in the CalNex-LA study? Nighttime column: what is the conceptual difference between ~ 0 (e.g., PROPHET, AIRPRO summer) and 'Nighttime OH almost always $<$ LOD' (AIRPRO Winter)? The reported OH interferences in the PRIDE-PRD2014 campaign made con-

tributions up to 8% during daytime and up to 20% at sunset and nighttime.

Fig. 4, 6, 7c, and 9. Error bars are much larger than the scatter of the shown data. Therefore, the error bars do not seem to represent the precision of the shown data. If you show mean values of repeat experiments, you may want to display the statistical error of the mean rather than of single measurements.

Figure 1. Insert a scale to illustrate the size of the IPI.

Figure 4. Consider to include the diurnal profile of jO1D scaled to OH; as jO1D and OH often correlate extremely well, it could help to visualise the expected trend of OH while the IPI switches between modes.

Figure 6. For better understanding, you could add in the figure caption the information that OH is internally formed in the cell by the conversion of HO_2 with added NO.

Figure 8. The y-axis is labelled 'HOx' cell signal. Please clarify: was the sum of OH and HO_2 measured (i.e., with added NO), or only OH (without added NO) ?