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Atmospheric Measurement Techniques Discussions

Interactive comment on "Deployment of a sequential two-photon laser induced fluorescence sensor for the detection of gaseous elemental mercury at ambient levels: fast, specific, ultrasensitive detection with parts-per-quadrillion sensitivity" *by* D. Bauer et al.

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We have placed the comments from the referees in italics. Our replies are in normal type. New text is in normal type unless it is an addition to a sentence and here the additions are in bold type. The reply to both reviews is appended as a pdf.

Referee Two "Given that the first goal of this paper is the description of the experimental

set-up, I am missing details such as laser energy, beam sizes (for example you say one beam has been expanded for better overlap with the second beam: is the second dye laser producing a larger beam?) and PM voltage (do you change the voltage applied to the PM regularly and why? This is not clear, especially not how this is taken into account in the calibration). A schema of the set-up would be helpful."

A schematic is now included, and more detail is provided on the experimental setup including names of instruments, laser power and beam size.

The manuscript already contains the following text: The voltage and hence the gain of the PMTs was adjusted to optimize the sensitivity and dynamic range of the 2P-LIF signal however tube B had higher gain and required more frequent adjustment. All data was processed to account for the varying amplification of the PMTs, then background subtracted.

This simply means that we established gain curves, i.e. PMT sensitivity as a function of voltage for each PMT and then normalized the signals to account for any change in PMT voltage to put all signals on the same scale.

“Being not an Hg-expert, I had trouble following the different excitation schemes (page 5655 and 5656): maybe a figure showing the different transitions would help to make it easier?”

A figure has been included.

“At this point I would appreciate an explanation about why you use two different excitation schemes? I was guessing that generating the 2nd generation laser wavelengths is easier (and you say so at the end, page 5672), but it would be good to have an explanation here. Maybe there are other reasons?”

We are simply trying to improve the sensitivity to get better sensitivity so that with the 50 Hz system we can average 10 shots and attain the precision required for eddy-correlation measurements. We have added:

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The first generation system was deployed at RAMIX. In an effort to investigate the possibility of increasing sensitivity for high frequency measurements we have made preliminary measurements using a “second generation” system.

“Throughout the manuscript I was wondering why you use two PM, and little by little I understood that this is for better signal. Please explain this when you mention the 2 PM for the first time (Page 5658). You mention that the set-up could be improved by using even more PM: do you have plans to do so? How about using a lens to collect more photons?”

We have added the following text: “The use of two PMTs allowed the dynamic range of the detection system to be increased, increased the number of photons detected and, as discussed below, allowed us to distinguish between real fluctuations in Hg(0) concentration and random fluctuations associated with photon statistics.”

We are currently seeking funding to do additional deployments of the instrument. The PMTs are rather expensive but we hope to be able to purchase more. Even with a fluorescence cell the PMTs are close to the excitation beam because there are no filters. We have tried lenses but get no improvement perhaps because an increase in collection efficiency is offset by transmission losses. Even S1-UV fused silica has losses at 185 nm.

"Same page, you use a cold trap (what temperature): is this just for condensing water? Are you sure no Hg can be trapped? "

We have added: “If the ambient temperature is significantly above the trailer temperature and the humidity is high the sample air is passed through a cold trap, set in an ice-bath, to prevent condensation on the sampling lines inside the trailer.”

Mercury is almost insoluble in water (this is the reason that elemental mercury is not scavenged by precipitation and has a very low deposition rate). The vapor pressure of mercury at 200 K is higher than its atmospheric partial pressure so no mercury will be

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trapped at 273 K.

"Same page, you use 254nm instead of 253.7 and 408 instead of 407.8: please use same wavelength everywhere. "

This has been done.

"Page 5659: you introduce the RAMIX manifold: the short explanation on this manifold that you give page 5666, would be better placed here."

We have added: “The manifold is described in detail by Finley et al. [2013].”

"Page 5663/4: you discuss the signal in air compared to helium. The paragraph is not very clear to me. You say before that the quenching rate for the higher states is not known, so what values did you use to calculate the expected fluorescence efficiency of 0.5%?"

We have added text: As noted above in the low laser power linear fluorescence regime we would expect a fluorescence efficiency of less than 0.5% based on quenching of the 63P1 state, additional quenching of the 71S0 and 61P1 states would reduce the fluorescence efficiency even more.

In “Section 2.0” we note: The 63P1 state has a radiative lifetime of 119 nsec and the quenching rate coefficient with O2 is 3.6 x 10-10 cm3 moecule-1 s-1 [Michael and Suess, 1974]; Breckenridge and Umemoto, 2007]. The fluorescence efficiency in air at atmospheric pressure can be calculated using the Stern-Volmer relationship and gives a fluorescence efficiency of 4.7x10-3 and an effective radiative lifetime of 0.56 nsec.

"Abbreviations are sometimes not well defined: Please define RGM the first time you use it (line 10 in the abstract). Line 21 of the abstract you could already introduce the abbreviation TGM. "

This has been done.

"What is a KCl denuder (page 5654, line 9)?"

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The text has been changed to:

The current approach to measurement of RGM relies almost exclusively on sampling on KCl-coated annular denuders followed by pyrolysis and CVAFS analysis of the Hg(0) produced by RGM decomposition [Landis et al., 2002].

The Landis et al. paper describes the technique in great detail and includes detailed schematics of the types of annular denuder that are used.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/7/C2718/2014/amtd-7-C2718-2014-supplement.pdf

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Interactive comment on Atmos. Meas. Tech. Discuss., 7, 5651, 2014.