Atmos. Chem. Phys. Discuss., 9, C8657–C8660, 2009
www.atmos-chem-phys-discuss.net/9/C8657/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Toward a real-time measurement of atmospheric mercury concentrations using cavity ring-down spectroscopy" *by* X. Faïn et al.

X. Faïn et al.

xavier.fain@dri.edu

Received and published: 17 December 2009

We thank the anonymous referee for his/her attention and thoughtful comments that we addressed in our revised manuscript and which certainly improved our paper. The reviewer comments are answered in details below.

General Comments:

A few issues were encountered and these were clearly presented as ongoing work. A notable one is the disagree in the empirical versus theoretical determination of the Hg(0) concentration. This definitely needs to be resolved in future work.

Authors' Reply (AR): Our 2537B Tekran analyzer has been calibrated daily using its internal permeation source, and our laboratory has performed manual Tekran injections using an external calibration unit (Tekran model 2505), which has resulted in good agreement. In addition, we have performed simultaneous measurements of Hg0 levels using the Tekran 2537B with a second unit which has resulted in agreement of measurements within 4%. We hence have great confidence in the internal consistency of our measurements with the Tekran 2537B analyzer. The reasons for the 21% observed difference between theoretical and Tekran-based Hg0 absorption cross sections are presently unclear for us, but they may be based on problems with our modeling approach. Consequently, we decided to apply a calibration factor, which is based on comparing direct CRDS absorption measurements with Tekran 2537B analyzer (i.e., 6.03 , see Table 2). Based on this, we calculate an absorption cross section for Hg0 of 1.9 10-14 cm2/atom. Future work will attempt to reconcile theoretical and experimental approaches for calibration of our CRDS measurements. It is worth to note that little work has been conducted on determination of the Hg0 absorption cross section. Edner et al. (1989) report an experimental estimate, and more recently Spuler et al. (2000) published a theoretical value, similar to the Edner et al. estimation, but without detailing their calculations. We modified our manuscript, specifically section 5.1, addressing the reviewer's comment by extending the discussion about the observed difference between theoretical and Tekran-based Hg0 absorption cross sections.

I would increase the font size a bit.

AR: We provided new figures with increased font sizes.

I was hoping to see a first attempt to measure Hg(0) in ambient air, but it was not included in this manuscript. To me, this would be a nice addition.

AR: We are actually working on improving our CRD setup (improvements discussed in section 6 of our manuscript), and we will run measurements of Hg0 in natural atmospheres soon. For ambient field measurements, the laboratory prototype needs to be

stabilized in a specifically temperature-enclosed unit and this hence requires further development.

Specific Comments:

Section 3.4, p. 22154 – the perm tube was held at 50C. You sure it was not 30C? This seems like a more reasonable temperature for such a volatile species.

AR: Our mercury permeation tube (HE-SR 1.7 CM, Vici Metronics, Inc.) could be use at temperatures ranging from 20 to 80 deg C. However, we chose to use our permeation tube (P/N: 137-017-0030-S56-C50) at the temperature where its rate was certified by Vici Metronics (i.e., 50 deg C for a rate of 31.24 ng/min +/- 2 ng/min).

p. 22158, line 13 – reword "allowed supplying"

AR: This sentence was reworded: "The vapor generation system could supply Hg0 concentrations ranging from 0.2 to 573 ng/m3."

p. 22158, line 26 – I would remove the wording in () as it's already provided in this manuscript.

AR: We agree with the reviewer that both CRDS and atomic fluorescence detections (i.e., Tekran 2537B in our manuscript) are discussed in details before section 4.2. However, we would prefer to keep the wording in () on line 22158 as it helps highlighting the difference between these detection approaches.

p. 22160, line 22 – what is meant by the phrase "below-background atmospheric Hg(0) studies"?

AR: Here, "background atmospheric Hg(0)" refers to 1.7 ng/m3, as stated in the first paragraph of the introduction. "below-background atmospheric Hg0 studies" relates to any environmental study requiring detection of Hg0 at levels below 1.7 ng/m3, i.e., any study were people could observe Hg0 oxidation. That would include, among others, investigations of atmospheric mercury in polar areas or at the upper troposphere lower

stratosphere transition zone. To make the sentence clearer, we rephrased it.

p. 22162 – I would not rule out variations in the real Hg(0) mixing ratios. It is nearly impossible to hold it constant over half to full hour time frames.

AR: We agree with the reviewer that generating a perfectly constant Hg0 mixing ratio is extremely challenging, and we consequently repeated the 5-min CRDS measurement with a cavity that was sealed air-tight for several hours. However, we observed similar variability in CRDS by measuring both the flushed cavity and the closed cavity. Thus, we are comfortable to state that this variability originated from our CRDS setup. We report here CRDS measurement over a 5-min period. Although our vapor generation system would likely not provide perfectly constant Hg0 concentration over half to full hour time frames, it probably did it over the 5-min sampling described in section 5.2.

Figure 1 – I would add to the caption that these data were obtained with a Tekran instrument to avoid misinterpretation that it was with the CARDS.

AR: We corrected this caption.

Additional references:

Edner, H., Faris, G. W., Sunesson, A. and Svanberg, S.: Atmospheric atomic mercury monitoring using differential absorption lidar techniques, Applied Optics, 28(5), 921, 1989.

Spuler, S., Linne, M., Sappey, A. and Snyder, S.: Development of a cavity ringdown laser absorption spectrometer for detection of trace levels of mercury, Appl. Opt., 39, 2480-2486, 2000.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22143, 2009.