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Interactive comment on “A cavity ring-down spectroscopy sensor for measurements of gaseous elemental mercury – Part 1: Development for high time resolution measurements in ambient air” by A. Pierce et al.

Anonymous Referee #1

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The authors present a further development of a laser based system for fast measurement of elemental mercury in air described initially by Fain et al. (2010). A system for automatic wavelength locking and stabilization of the laser wavelength has been developed. Measurement of the differential absorption using an on/off-line tuning of the wavelength has been implemented. Ozone interference has been solved by thermal decomposition of ozone in the air sample. Instrumental challenges due to the temperature fluctuations, ozone interference, and frequency conversion efficiency are

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discussed. The paper is well organized and written.

From the perspective of a physicist the presented work might be impressive. From the perspective of an atmospheric scientist who would welcome any improvement in the measuring techniques, the work is disappointing since the resulting detection limit of 0.35 ng m⁻³ with an integration time of 5 min is comparable with the performance of the portable commercial instrument based on atomic absorption spectroscopy with Zeeman background correction (Lumex, mentioned by Fain et al. (2010) but not here) and is worse than that of the Tekran instrument which with 5 min sampling time has a detection limit of ~0.1 ng m⁻³. The objectives of the work as stated by Fain et al. (2010) were to develop a technique suitable for micrometeorological flux measurements, i.e. capable of fast (~10 Hz and more) measurements at ambient levels (~2 ng m⁻³). The presented performance falls far behind this objective and after another two years of development even behind the detection limit of 0.1 ng m⁻³ with 10 s resolution reported by Fain et al. (2010) for an instrument whose improvement is the subject of this work. This being according to the Table 1 of Fain et al. (2010) the 7th attempt on GEM detection by CRDS, I would expect a short discussion of the fundamental limits of the CRDS technique for this application. The authors could then compare their results with this benchmark and discuss the ways to get near it. Without such discussion the conclusion of “more of the same”, i.e. better temperature control, better laser, ozone scrubber, appears to be rather clueless. I also wonder what the content of the announced Part 2 might be which cannot be presented in this paper.

Several other questions and suggestions appear during the reading of the manuscript:

1. In section 3.2 the different methods of background correction are discussed without mentioning the Zeeman background correction as realized successfully in the commercial Lumex instrument for measurement of ambient mercury. Neither is Lumex instrument mentioned in Section 3.5 in which the preliminary field performance is compared with other instruments. At least the latter should be added to put the presented results into perspective.

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2. The on/off-line tuning does not remove completely the ozone interference. The authors rightly explain that this might be partly because of the very high absorption by ozone leaving too few photons left for measurement. But it could also be due to differential absorption of ozone for the on/off wavelengths which could be measured directly with mercury free air containing defined mixing ratios of ozone. Such measurement combined with ozone measurement would perhaps enable an exact correction for ozone interference. Because of the problems with ozone pyrolysis mentioned below in point 5 this might be a preferable solution to the ozone interference.

3. Fig. 6 shows that $\sim 10^\circ\text{C}$ change in instrument temperature causes 30% change in differential extinction. The text in Chapter 4.3 reads as if this problem were solved by a foam enclosure which reduced the temperature fluctuations to $< 10^\circ\text{C}$. As Fig. 6 shows apparently the state with the foam enclosure it can illustrate an improvement but hardly a solution of this problem.

4. The authors suspect the temperature dependence to be due to the temperature-sensitive elements of the cavity but discuss it in Chapter 4.3 in terms of absolute and differential extinctions, i.e. spectroscopical properties. This might be misunderstood by the readers.

5. The removal of ozone interference by pyrolysis poses two problems which are not addressed. First, particulate mercury will be released at high temperature (see Rutter and Schauer, Atmos. Environ. 41, 8647-8657, 2007) and the resulting and already present reactive gaseous mercury will be at least partly pyrolysed to GEM (Lyman and Jaffe, Nature Geoscience 5, 114-117, 2012). Consequently, it will not be GEM which will be measured with ozone pyrolysers and this should be mentioned in the text. Secondly, upstream pyrolyser will make the measurements with high temporal resolution difficult because of its residence time.

6. The authors present absolute and differential extinctions. For people not familiar with the technique it would be helpful to know what Hg absorption coefficient they use for

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calculating the mercury concentrations. As the locking wavelength does not coincide exactly with the maximum of the atmospheric absorption other absorption coefficient than its literature value has to be used. Or did they calibrate the instrument? If so, how?

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 8995, 2012.

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