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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Cavity ring-down spectroscopy sensor for detection of hydrogen chloride" *by* C. L. Hagen et al.

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This is a well written account concerning details and performance of a trace gas analyser developed for HCl, based on the high sensitivity laser absorption method known as CW-CRDS. The chosen spectral range is the near infrared HCl first vibrational overtone, close to the telecommunication region, where high performance lasers, optics, and detectors are easily available. This leads to a high sensitivity that compensates for the lower transition strength of this molecule relative to its fundamental band, situated in a less favourable spectral region, where only cryogenic or difference-frequency lasers are commercially available at present. The importance of the sensitive detection of this molecule in the atmosphere appears to be sufficiently well discussed. Also,

a fairly complete and equilibrated review of existing methods for HCl measurement is presented, at least this is my impression as a non-specialist. The argument justifying the development of an instrument is principally that the authors wanted to have full control of the sample handling which is an important issue when dealing with reactive and sticky molecules as HCl. In particular CW-CRDS allowed a small sample volume for fast exchange time with reduced pump size, and a special inlet for particle elimination by a virtual impactor was used, which avoids using a true filter which would irreversibly affect the measurement. Reference to existing commercial instruments appears to be sufficient, and I share the objection of the authors that these instruments are black boxes which cannot be easily adapted to all research applications. In addition, the lack of publications on their operation and internal details does not allow an easy direct comparison with research grade instruments as the one presented here.

The results reported appear to be novel and of interest to the community, in particular the instrument achieves a high performance with sub-ppb detection in a short time scale and will result really useful for field measurements. Thus this manuscript deserves publication in AMTD, best after some minor issues are addressed, which are listed below. In general, the manuscript is not uniform with respect to the level of technical details.

Detailed list of issues:

P.7222: please provide one or more references to original papers where the CW-CRDS technique is fully explained. This is especially needed as this paper is not supposed to, and does not, offer a detailed account of the technique.

Same page: the essence of the CW-CRDS technique is nicely outlined in a few sentences, but there is one missing detail which is important, in particular to understand fully some comments which occur later in the manuscript. This is about how one goes to produce those passages through resonance... and actually one can choose to modulate the cavity or the laser, with different advantages and drawbacks. It seems that here the cavity length is modulated by a piezo actuator, but that should be made explicit, in the text, and in the experimental scheme. That should allow explaining how a CRDS spectrum is actually obtained, which I think is not granted when reading the present manuscript.

P.7224, bottom: usually a fiber-pigtailed DFB laser includes an optical isolator. Please explain if this was the case of the used laser and comment on the fact that this isolator was not sufficient, and maybe how that became evident.

P.7225. "The bandwidth is approximately 5 times larger than needed in order to not distort the ring-down signals"... This does not seem to be right. The bandwidth associated with a ringdown of 170μs should be more like 1kHz ($2\pi f_c = 1/\tau$). Also, sampling at a digitization rate close to the detector response time, provides a ringdown signal whose fit procedure takes care of averaging the noise over the seemingly excessive number of data points, resulting in the same noise level on the ringdown value as when using a slower detection/digitization chain. Thus in general there is no penalty, and one advantage is a large dynamic range since the same detection chain allows to appropriately detect and process fast ringdown decays which may appear in correspondence of a strong absorption line. On the other hand, excess noise is certainly produced by aliasing when the digitization rate is slower than the detector response time (a low-pass analogue filter should then be used to match the two).

P.7226. Please explain what is limiting the ringdown acquisition rate to 25 per second.

Concerning the interesting strategy of fitting Voigt profiles using a pre-calculated table of values, does that mean that the laser scan is sufficiently stable in time that a fixed grid of frequencies can be used? Or is the situation more complex, as I suspect? It may be worth to give more details on this interesting point.

P.7227. The discussion about the integrated line intensity is a bit confusing... It may be clearer to make explicit reference to the Beer-Lambert law (of which the authors seem to be using the approximation for small absorptions $\Delta I/I = -kL$, which is completely

reasonable in this context...).

Same page: Please give references about the virtual impactor system and design.

P.7229: In order to get a more quantitative feeling about sensitivity improvement afforded by CW-CRDS over multipass or other techniques, authors could mention the (approximate) ratio of line strengths for the two HCl absorption bands being considered.

Same page. The ringdown statistics at a single frequency data point do not account for the presence of fringes on the acquired spectra. Thus, these only provide an upper limit on system performance which may be quite far from real system performance. Please provide the rms noise on the spectra baseline (or in the limit of zero sample absorption).

P.7230. "The scanning approach captures the baseline on either side of the absorption feature (useful for reliable ïňĄtting), but at the cost of lower detection sensitivity." Is this the only reason for a lower sensitivity, did the authors consider the presence of interference fringes in their CW-CRDS spectra?

Same page, the discussion about the calibration curve seems a bit optimistic. The agreement of many data points is within 2 sigma and the deviations appear systematically in excess for low concentrations. Could that depend on memory effects and on the sequence used to obtain these measurements? Also, the dynamic range of this calibration is a bit limited, just one decade starting from 1 ppb, while the instrument is then used to measure sub-ppb concentrations. I understand it is difficult to obtain lower or higher concentration for this molecule... but more discussion about this point would be welcome.

P.7233. The comparison of signals from the instrument and other devices is quite convincing and impressive, given the very low trace HCl level. However, this comparison appears to be of rather limited duration, and one is left with the doubt that the agreement may be episodic. If possible, the authors should discuss if such good agreement could be observed in practice over longer time scales, which would confirm that the instrument is calibration free at the level of required accuracy.

Same page: The argument leading to a possible improvement of a factor 5 is too simplistic. The limiting factor is typically the fringes in the acquired CRD spectra, which appear at a given averaging level. Faster ringdown acquisition will allow to reach this limit sooner, but not to improve the fringe level, thus the detection limit will stay constant.

In the conclusion section: It would be interesting to provide an outlook concerning the isotopic ratio measurement of HCl. . .

Fig.4: The units of the vertical scale are confusing. Is that the absorption per pass in the cell? It may be more general to give the absorption per cm, so one does not need to check out for the sample length. Also, it may be clearer to write $\times 10^{-7}$ on the scale labels.

To illustrate the quality of recorded spectra it would be interesting to add a figure displaying an absorption line with a high S/N, obtained at higher concentration, together with the Voigt fit and the corresponding residuals.

Fig.6: strange that the beginning of the Allan Variance is flat... any comments about that? Why the average concentration does not seem to be zero (upper plot)?

Fig.7: To allow easier comparison, the authors should use the same time units as in the previous AV figure. It looks line this AV shows quite a shorter system stability compared to the previous figure. . . any comment about this?

Fig.10: what are the units of time, days? What does MST mean?

A couple of general comments: I agree with the other referee that the memory effects and the good correspondence of measured and generated HCl levels may depend also on the water vapour partial pressure. Tests including a variation of this factor would be interesting. It would also be interesting to know if there is any dependence of the re-

sponse time (going from zero to a given concentration, and back), as a function of concentration. In particular, exposure to high HCl levels may produce a long exponential tail before the measurement is really back to zero within the instrument sensitivity of tens pptvs.

Technical corrections:

P.7222, line 12: “...the details of which...” => “. The details of this procedure...”

Fig.2: using a vertical log scale would allow to easily compare weak and strong absorption lines.

P.7224, line 25: “...positioned relative to the fiber beam-splitter output...”

Better define the flux unit (slpm) at its first occurrence.

P.7229, line 15: “...are somewhat better than those of past work...”

P.7233, line 10: “..., we note that the current...”

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 7217, 2013.