

## Reviewer 1

We thank the Reviewer for their constructive comments on our manuscript. Please find our responses below highlighted in **yellow**, and changes to the manuscript in **bold**.

“The manuscript entitled “Validation of a new cavity ring-down spectrometer for measuring tropospheric gaseous hydrogen chloride” by Furlani et al. discusses the implementation of a commercial spectroscopic HCl instrument for ambient air measurements. The study indicates that the Picarro HCl CRDS instrument can be implemented with low detection limits, high precision, high time resolution, and similar/better accuracy compared to a cadre of other trace HCl measurement techniques. Discussion of sampling and analytical issues is thorough and thoughtful. Statistical treatment and reporting is adequate. Studies of inlet effects is detailed and provides important information for potential users in the future.”

This paper is high quality and should be published in *Atmospheric Measurement Techniques* pending consideration of a small number of comments provided below.

Line 229 and Figure 1: Please provide a reference (within the associated text) to the approach of using the Allan-Werle deviation.

Response: Added reference to Hagen et. al. “Instrument LODs were calculated as three times the Allan-Werle deviation (Figure 1, **Hagen et al., 2014**) when overflowing a 15 cm inlet (3.17 mm i.d.) with zero air directed into the CRDS for ~10 hours.” (P11, L239)

Lines 246-248: “spectroscopic techniques offer a distinct advantage as they are absolute measurements and accuracy determinations rely on propagating uncertainty in measured parameters” This statement is then met with the reality of the present study [in subsequent lines of this paragraph] in which concurrent denuder measurements are used to determine accuracy. Why not stand upon the ‘distinct advantage’ that spectroscopic measurements provide? [See also: next comment.]

Response: We take the Reviewer’s point. We have clarified our text to explain our reasoning that while the spectroscopic detector is itself absolute, it does not represent the full method. Our validations test the full method, including sample collection. The following text has been added:

**“We assess the total method uncertainty using intercomparisons with the gold standard for atmospheric acid detection (EPA Compendium method IO-4.2, United States Environmental Protection Agency (United States Environmental Protection Agency, 1999)) due to the greater uncertainty when considering the potential total system error from sorption/desorption to all sampling surfaces (i.e. instrument and inlet).”** (P12-13, L261-265)

Lines 248-251: “In the absence of determining accuracy of the CRDS system from its operating parameters...” Is this due to lacking knowledge of these parameters due to the commercial nature of the instrument or are the intercomparison differences seen to be greater in importance, greater in magnitude, or both? Overall -- please clarify the motivation for the accuracy determination approach that was undertaken.

Response: The Reviewer is correct. We are unable to determine these parameters due to the commercial nature of the instrument. As described above, we use intercomparisons to validate the complete method, including any physical surface effects of the total method. We suspect very little of the total method error is related to the detector parameters.

Calibration questions: What is the impact of uncertainty in the permeation tube HCl concentration on the mixing ratio determination by the CRDS instrument? For instance, why aren't the error bars in the horizontal direction in Figure 2 comparable to those in the vertical direction? How can a measurement have lower uncertainty than the standard from which it was calibrated? Please clarify this issue. Perhaps I am confused about details of the study, but so too may be a future reader.

Response: The Reviewer raises a good point. The errors in the horizontal represent systematic errors propagated throughout the analysis of the collected samples and the vertical error bars represented the standard deviation of the CRDS signal once stabilized. One reason the error in the horizontal is much greater is the need for a calibration in the offline analysis of the IC samples. We use our validation experiments to determine an uncertainty in the CRDS, so we choose not to represent that error here.

To clarify, we have removed any instance in the text where we refer to the intercomparison experiments as calibrations due to the higher associated error in the offline extraction techniques used.

“We configured a commercial HCl cavity ring-down spectrometer (CRDS) for sampling HCl in the ambient atmosphere and developed ~~calibration and~~ validation techniques to characterize the measurement uncertainties.” (P1, L14-L16)

“The accuracy was determined to reside between 5–10%, calculated from laboratory ~~calibrations~~ and ~~an~~ ambient air intercomparisons with annular denuders.” (P1, L18-L19)

“The 140 ng min<sup>-1</sup> of HCl in dry N<sub>2</sub> from the PD was mixed into a zero air dilution flow of 2.1 to 8.0 L min<sup>-1</sup>, to provide standard addition HCl **mixing ratios** that ranged from 12 to 45 ppbv.” (P8, L169-L171)

“When the HCl gas entrained in flows of higher RH ( $\geq 50\%$ ) a negative bias was observed, although the measurements generally remained within the quantified error in the PD output.” (P15, L292-L294)

“Data was background corrected to levels measured prior to the standard addition ~~calibration~~ and the signal was normalized to the HCl enhancement during the final 10 seconds of each HCl pulse.” (P20-P21, L83-L385)

The suitability of a CRDS analyzer for measuring ambient atmospheric HCl **was** explored through **laboratory and ambient air intercomparisons, assessing their inlet and analyzer sampling challenges to established atmospheric sampling techniques for strong acids.** (P23-25, L462-464)

Figures 2 and onward: Numbering of figures in textual references is often (always?) incorrect.

Response: The numbering in references has been corrected throughout.

Line 362: Please clarify whether the effect of sampling line flowrate on  $\tau_1$  was investigated experimentally or if this point is a supposition.

Response: This is a supposition from conclusions drawn in the literature for similar methods. The sampling flowrate for this instrument is fixed and therefore we could not directly test this. We have added the following to clarify.

“The sampling flow rate and cavity temperatures are constant for the commercial software and not adjustable, **therefore changing the value of  $\tau_1$  was not explored in this study.**” (P20, L372-L373).

Line 363: Change to “An additional set of experiments was...”

Response: Corrected.

## References

Hagen, C. L., Lee, B. C., Franka, I. S., Rath, J. L., Vandenboer, T. C., Roberts, J. M., Brown, S. S. and Yalin, A. P.: Cavity ring-down spectroscopy sensor for detection of hydrogen chloride, *Atmos Meas Tech*, 7(2), 345–357, doi:10.5194/amt-7-345-2014, 2014.

United States Environmental Protection Agency: Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air: Determination of reactive acidic and basic gases and strong acidity of atmospheric fine particles (<2.5  $\mu\text{m}$ ) (Compendium Method IO-4.2), 1999.