Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2017-57-AC2, 2017

Atmospheric Measurement Techniques Discussions

Interactive comment on "System for δ^{13}C-CO_2 and $x CO_2$ analysis of discrete gas samples by cavity ring-down spectroscopy" *by* Dane Dickinson et al.

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Received and published: 31 August 2017

Authors' reply to Anonymous Referee #2 interactive comment (RC2):

NB: Original referee comments in black text. Author comments in red text.

We thank the reviewer for critiquing/commenting on our manuscript. We have included the complete text of RC2 below and made embedded replies so as to address directly the comments in context.

Dickinson et al. present a new and rather simple method that can easily analyze small discrete gas samples using a commercially available cavity ring-down spectroscopy gas analyzer. The major advancement in the performance of the system, compared to other methods, is a two-fold improvement in the throughput rate, which may be

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appreciated when such a system is regularly used for analysis of a large number of samples in the laboratory, as is the case described in the manuscript. Although it was developed for analysis of xCO2 and δ13C-CO2, the method can be extended to analyze other species with similar instrumentation. My general impression is that the real content of the manuscript is thin, and a significant part of the text focuses on apparent technical description/maintenance rather than technical advancement. For example, it is unclear whether there is any advantage in the precision/accuracy of the system compared to other methods, other than the precision improvement of the commercially available CRDS itself. The accuracy of the measurements is not included due to the separation of one story into two manuscripts that are simultaneously in review for two different journals, which I found it, at several places, inconvenient to be forced to read another manuscript of the same author to obtain necessary details. Considering the abovementioned points, I strongly recommend (even I know it is hard to convince) the authors combining the two manuscripts and publish one piece of nice work. One good paper is worth more than two OK papers.

We understand the impression of the reviewer - it might seem like a trivial adaptation to transform a continuous flow instrument into a discrete analyser. However, we strongly believe that there is considerable need for a detailed description of 'simple' discrete sample laser based isotope analyser. At present, there is no time and cost effective method for reliably measuring discrete gas samples by continuous sampling CRDS instruments such as the Picarro G2131-i and other models. Commercial peripheries (e.g. Picarro A0314 SSIM2) and previous published method (Berryman et al. 2011) are slow, complex, and cannot provide gas mole fraction data due to dilution processes inherent to the measurement process. There is clear need (in soil respiration headspace studies as just one example) for a practical simple way to make accurate measurements of small discrete samples with CRDS instruments (both for isotope ratio and mole fraction measurements).

The rationale given for the reviewer's concerns were was as follows:

1. That the work does not constitute a technical advancement.
2. That the paper does not properly compare the precision and accuracy of the presented method with previous/other methods.
3. That accuracy of our system is not addressed, which is instead referred to in a separate publication.

To point 1: To the best of our knowledge there is no published description of an equivalent method for conducting discrete gas sample measurements by CRDS instruments at a rate of 12 h^{-1} that gives both accurate isotope ratio and mole fraction data. Hence we stand by our work as an important advance to the state-of-the-art.

To point 2: This is not correct - we have compared our method against existing methods and equipment (Sect. 3.3). We do not make major claim that our method significantly improves precision compared to other methods, but we do report the precision we achieved, and we note that it is at least similar to other methods. As for accuracy, any measurement system or method that is "properly calibrated" is "accurate", by definition. In addition to performing an appropriate calibration, we have reported the uncertainty associated with applying our calibration to correct for memory effects inherent in syringe measures (p. 9: 0.02% of the sample peak height).

And to point 3: This is not correct - we have addressed the accuracy / bias of our method in Sections 2.3, 3.2, and Figure 4. It is true however that we have not addressed the accuracy of CRDS instrumentation in this work. We believe that such a question should be examined separately so as to not confuse or conflate the multiple phenomena that may cause errors in different CRDS measurements. There are numerous published papers that evaluate accuracy / calibration of CRDS instruments. Researchers that do not need to measure CO_2 compositions with high ^{13}C abundances will not find our other publication interesting, but they may nonetheless wish to perform measurements of small discrete syringe samples and find the present work extremely

useful. A vice-versa scenario is also probable.

Other comments:

1) Comparing the precision of the system and that of previous systems, how much of the improvement is due to the enhanced spectroscopic sensitivity of the CRDS?

We do not know. We have explicitly acknowledged that the improved precision we report may be due to improved CRDS instrumentation rather than advantage in our method. We do not mean to claim that our method gives significant advancement in precision (but it is important that our method is not worse in precision). Our primary claims are: high throughput rate, accurate simultaneous mole fraction and isotope ratio data, practicality, low cost, time-efficiency. In revision we will adjust some of the text to make our reports of achieved precision more modest.

2) The method uses 30 sample data for the analysis. Have the authors considered making a curve fit to the data set and using the steady value of the fit instead? In this way, the measurement will not be sensitive to the baseline signal any more.

We understand this suggestion to mean that a steady baseline reading might not be necessary if we used a curve-fitting algorithm on the syringe sample data. We did think about this, but we foresaw two major problems:

- First, gas replacement / mixing in the optical cavity entails that the composition in the cavity prior to introduction of a syringe sample affects the CRDS measurement (memory effect), and consequently, for such an algorithm to work, the CRDS data prior to the syringe sample introduction would need to be an input variable. This is practically the same as recording the baseline.
- Secondly, designing a software script to perform such a task in real-time is not trivial. Aside from such curve-fitting probably requiring computationally expensive non-linear optimisation, Picarro instrumentation and software is not user-friendly

for real-time data flagging and analysis. Yet in order to realise the suggestion, the fitting algorithm would need to "know" the exact time when the syringe sample was introduced into the analyser so as to provide a start-point. Building a computerised device to signal the position of the manual syringe input valve is not a simple solution in comparison to our baseline recording and peak detection process.

Detailed comments:

P3/L29: what does "stable operation" imply here? As the cavity temperature is strictly controlled, is any difference expected if the whole system is located in an unconditional room?

It is true that the optical cavity is well controlled, however other researchers have nevertheless noted environmentally induced variations in measurements, which are thought to arise out of residual uncompensated fluctuations to the cavity (Kwok et al. 2015). Ambient temperature fluctuation is also mentioned as a potential source of instrument drift in pamphlets published by the instrument manufacturer. An environmentally controlled lab simply mitigates all risk for error in this regard.

P5/L26: Can the authors explain why zero air (0.05 ppm CO2) is included and why is the range claimed to include the zero air? I do not see the value of adding zero air, and the isotopic signature of the zero seems strange.

The greater the range of data used in the WLS optimisation of Eqs. 2-5, the lower the resulting uncertainty for correcting syringe bias / memory effects. By measuring zero air, we acquired excellent "negative peak" data, which thus improved the statistical estimates of the correction constants K_{C12} and K_{C13} (see Fig. 4). In terms of isotope ratio signature for zero air, well there is no sensible/measurable ratio that can be made: isotopic ratio "measurements" of zero air must be recognised as spurious given the CRDS instrument develops too much noise at ppb levels of $^{13}CO_2$ for meaningful ratio

assessments. (Isotope ratio data for ZERO were excluded from WLS optimisation.)

P5: I wonder whether there is systematic but significant bias between the "true" value of the syringe sample and the bottle sample, which could be introduced during the sampling process.

We compared the syringe sample values against CRDS measurements of bottle standards (not against gravimetric values of the standards). The calibration/post-correction therefore transforms "syringe measurements" into "bottle measurements" eliminating the systematic bias between those two gas delivery methods. Any constant bias introduced by the syringe sampling process (e.g. ambient air contamination) would be seen as a liner offset (constant term) within the dataset shown in Figure 4, however no such offset was observed. Any other error or "inconsistent bias" from sampling would simply add to the random errors of the syringe measurements (and give worse inter-sample precision).

P10/L10: Were the 9-month period measurements calibrated? It is difficult to judge when the accuracy of the system is not mentioned in the manuscript.

Each individual sample measurement from the 9-month dataset was calibrated for syringe bias, but was not individually calibrated for random instrument drift. The reviewer is correct in noting that these data are therefore a simultaneous test of method accuracy and instrument accuracy. However, the purpose of these data is to examine consistency of the syringe method under typical laboratory practices over a long period of time. We have explicitly explained that the observed increase in variance seen in these data is likely due to instrument drift but could equally be due to transient inconsistencies in the syringe method. We will further clarify this point in revision.

P10/L31: The traditional continuous-flow IRMS can do much better than 0.1‰ The reference should not be limited to an old paper Prosser et al., 1991.

The reference was simply mentioned as a guideline value: From our experience and

with current information of CF-IRMS producers, 0.1‰ is a typical value and not entirely obsolete. However, to avoid any misrepresentation, we will remove this out-dated reference and avoid making a direct performance comparison to state-of-the-art CF-IRMS.

References:

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