

Interactive comment on "System for δ^{13} C-CO₂ and xCO₂ analysis of discrete gas samples by cavity ring-down spectroscopy" by Dane Dickinson et al.

Anonymous Referee #1

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Summary

Excellent paper that improves upon a previous method to determine ${}^{13}CO_2/{}^{12}CO_2$ ratios and CO_2 concentration in discrete gas samples using a CRDS instrument (Picarro G2131-i). Methods are described in enough detail to replicate study and to apply to own research. Major advantages of this method over previous methods are: 1) high throughput time (though clarification needed for throughput time of previous method) and 2) increased precision of syringe samples (though clarification needed for high/variable ppm CO₂ applications). Disadvantages are larger sample sizes than past syringe methods (50 mL vs. 30 mL), higher time costs due to manual involvement of operator and determination of a specific system's K constants for correcting memory effects. However, I think the advantages will outweigh the disadvantages in many applications and this method should prove very helpful to future carbon cycle research.

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This work is timely, important and novel, and I think only a few changes are needed for final publication.

Highlights

- Thorough consideration and measurement of memory effects, precision and consistency.
- Inclusion in supplementary info of worksheet for syringe bias correction.
- Nearly perfect writing that is easily understood and to-the-point.

Areas for improvement

- It isn't clear how samples of unknown different concentrations (such as those collected from headspace in a soil incubation experiment with different amounts of labile C, for example) can be accurately measured in the same run, because the authors state that the precision is best when the reference gas CO₂ mole fraction is similar to that of the sample gas and only differ in terms of ¹³C content. It would have been helpful to have some discussion of this application in the paper, especially since the Introduction places this research into the context of headspace samples.
- Related to the first point, the reader would benefit from clarification regarding the reported δ^{13} C-CO₂ precision. The precision seemed to be lowest with atmospheric samples (0.15‰), yet headspace samples are always higher in concentration than atmospheric. It would help if the authors were more clear about how the precision would increase with typical headspace concentration rates. On P10, L9-21, the authors report precisions of 0.33 to 0.35‰ for higher concentrations; I wonder if those would be more typical of what to expect with headspace samples.

Line by line edits

P2, L19: It would help place this in context if you could report the previous' systems sample turnover rates.

P3, L17: No capitalization needed for "Hermetic".

P3, L29: "insturment" should be corrected to "instrument".

P4, L15-L20: It might help to reader to explicitly state whether this data processing was done in real-time or after the run was completed. Specifically, I am wondering if the detrigger was detected in real-time, which would make manual operation of the instrument easier than if the user had to guess when the detrigger happened to know when to inject the next sample.

Figures 5 and 6: In the figure captions, I think that using the terms "intra-sample" and "inter-sample" would be better here and more obviously connect to the text in the results and discussion.

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