

Interactive comment on “A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO₂, CH₄, N₂O, SF₆ and CO” by S. van der Laan et al.

Anonymous Referee #1

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The manuscript entitled 'A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO₂, CH₄, N₂O, SF₆ and CO' provides a well prepared documentation of an analytical system designed to simultaneously measure four important greenhouse gases plus carbon monoxide. The approach relies on standard gas chromatographic methods for the analyses. This work is noteworthy because it configures a two channel GC to perform several rapid, multiple-specie measurements. The manuscript is technical in nature, and contains the necessary details that it could be reproduced in other laboratories. The topic is well suited to ATM and I recommend its publication. I have a few comments the authors should consider in the revision.

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General comments:

The efficiency of the CO₂ and CO conversion to methane is key to the precision and reproducibility of the measurements. In Figure 5 the manuscript presents an example where a disruption of the methanizer affects the CO₂ results. Did CO show the same recovery? It is not clear why results using a two-point calibration are immune to this effect. The authors should explain this in more detail.

I would also like the authors to expand their comments on the non-linearity of the N₂O and CO measurement. What was the per cent deviation from linear? In the case of CO I assume this must derive from the methanization because the FID response should be linear. Was the efficiency of the methanizer determined over a range of CO? On page 1337, the authors suggest a single point calibration for CO is acceptable because of its large concentration range. Wouldn't CO be more susceptible to error as the measured range is far beyond the reference?

To correct for the non-linear instrument response to N₂O and CO, response curves were calibrated in the lab and applied to field measurements. This approach is applicable only if all components of the system are stable. It appears to have worked very well for the instrument presented here. However I feel a more conservative approach for long term calibration, for example: annual, on-site calibration using transfer standards, should be mentioned.

Other Minor Comments:

P. 1326, l. 16. 'Well known' is vague, the standards were likely certified to WMO reference scales?

P. 1325. l 1. Note that the Los Gatos CO and N₂O instruments still require LN₂ for operation and so are not yet viable field instruments.

P. 1327. The description of the system would benefit if a table listing the GC operating parameters was included in Table 1.

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P. 1330, Chromatograms. The authors should mention here which CH₄ peak they choose to quantify.

P. 1330, Additional Remarks I 21. What is used as the cooling agent for the glass flask water traps? How often does it need to be replenished? Could this be a problem for very remote sites?

P. 1331, I. 23. The WMO reference scales are not 'absolute', 'internationally recognized' is a better descriptor.

P. 1332, I. 16-17. The authors state that the instrument response to CO₂, CH₄ and SF₆ were linear to 'a very good approximation linear'. This should be more specific.

P. 1335, I. 8-9. The authors state they have calibrated the instrument response to CO and N₂O three times and found no significant difference. Over what period of time were these tests conducted?

P. 1336, Figure 6. This figure (and Figure 7) is too small for detailed viewing.

P. 1337, I. 18-20. The manuscript states that the typical diurnal cycles are indicated by the maximum mixing ratios in Figure 7. The meaning of this is unclear. While the time series is not the focus of the paper, some discussion of the field measurements is needed. What is the source of the very high mixing ratios? Do they typically occur during certain times of the day? Is wind direction driving the high/low mixing ratios? Do the high mixing ratios represent emissions from a specific location? A map of the location might help here. 1. 21-24. How do the seasonal cycles and amplitudes of the Radon selected measurements compare to other background locations at similar latitude such as Mace Head or Iceland?

P. 1338, Conclusions. The authors should note that the two different precisions derive from 1) the whole record and 2) for optimal operating conditions.

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