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Atmospheric
Measurement
Techniques
Discussions

Interactive comment on "A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO_2, CH_4, N_2O, SF_6 and CO" *by* S. van der Laan et al.

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First we would like to thank the referees for their valuable comments and suggestions with which we can improve this manuscript.

Comments on referee#1:

RC: "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? Was the efficiency of the methanizer determined over a range of CO? It is not clear why results using a two-point calibration are immune to this effect. The

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authors should explain this in more detail."

AC: CO was not affected by the disruption of the methanizer. This must be caused by the fact that the effect is concentration-dependent and CO has a much lower mixing ratio: there is still enough non-oxidized nickel powder left to convert all of the CO molecules to CH4. The concentration-dependency introduces a non-linearity in the response. With only one reference cylinder we would only be able to correct for this based on one mixing ratio since we then would use “0” as the second known point. With two cylinders within the ambient measurement range we can approximate the local slope of the calibration curve very well, though not to the accuracy of a properly working, non-concentration-dependent, methanizer. As the time between two reference cylinders is small compared to the time the methanizer regenerates (1h vs. 1 month), the effect is thus mostly canceled out by our calibration method (Eq. 6). ->this explanation is included in the text [sect. 4.1].

RC: "I would also like the authors to expand their comments on the non-linearity of the N2O and CO measurement. What was the percent deviation from linear? In the case of CO I assume this must derive from the methanization because the FID response should be linear.? 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?"

AC: The CO response is observed to be non-linear because of its large dynamical range. It will become more susceptible to error with measurements outside the range of the primary response curve. Because of the fact that the dynamical range of CO can be very large in a relative short time (i.e. daily variations have been observed of more than 200 ppb) and the CO measurements have a very limited relative precision, we find the results still acceptable. ->We have clarified this in the text accordingly [sect. 3 and 4.2]. -> Deviations from linear for the gases have been added [sect. 3]

RC: "To correct for the non-linear instrument response to N2O and CO, response

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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."

AC: The calibration response curves were determined at the site. -> This is clarified in the text [sect. 3]

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

AC: -> Text adapted accordingly.

RC: "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."

AC: -> Point taken.

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

AC: -> We do not feel the description of the system would benefit as the necessary details are already included in the description.

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

AC: -> Text adapted accordingly.

RC: "P. 1331, l. 23. The WMO reference scales are not 'absolute', 'internationally recognized' is a better descriptor."

AC: -> Text adapted accordingly.

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

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AC: -> Figures changed accordingly.

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

AC: -> Text adapted accordingly.

RC: "P. 1330, Additional Remarks l 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?"

AC: -> Text is extended with more details accordingly.

RC: "P. 1332, l. 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."

AC: -> Text adapted accordingly.

RC: "P. 1335, l. 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?"

AC: ->This is added to the text.

RC: "P. 1337, l. 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?"

AC: -> The text is extended with additional information accordingly.

Comments on referee#2:

RC: "The manuscript does not make as clear which parts of the method are constituting a progress and which parts are established chromatographic procedures that are already used by many labs. The described method is based on common gas chromatographic procedures for greenhouse gas analysis that have been described previously (e.g. Worthy, Measurement Procedures and Data Quality. In: Canadian Baseline Program; Summary of progress to 2002, Meteorological Service of Canada, Chapter 4, pages 97-120, 2003; Ramonet et al, The French Trace Gas Monitoring Program (RAMCES) Report of the eleventh WMO/IAEA meeting of experts on carbon dioxide concentration and related tracer measurement techniques, WMO- GAW No.148, 32-54, 2003; Jordan et al., Continuous GC measurements of trace gases at the Ochsenkopf monitoring station Report of the eleventh WMO/IAEA meeting of experts on carbon dioxide concentration and related tracer measurement techniques, WMO-GAW No.148, 32-54, 2003). There should be some reference to the literature for this."

AC: At stations indeed GC systems are used which measure two trace gases per detector based on chromatographic methods described in the above named literature. As both referees point out, the advancement made in our work is that all five gases are measured with only one device, preventing the need for a second instrument to measure CO2 or CO. -> references are added to the text. [sect. 2]

RC: "it should be raised that the carrier gas supply at far remote places is costly and that GC maintenance is not done by only providing the gases. Experience at other stations has proven that especially the many valves tend to have a limited life time of months to 1-2 years before needing maintenance and gas generators also may fail."

AC: Although the referee rises a good point in that there are potentially many extra costs related to measurements at remote sites, which some we also mention, this is not directly related to this setup. Some cost related improvements are already described: e.g. carrier gas saving valve V1_2. Station visits can of course be reduced by connecting multiple cylinders to a multivalve which switches to the next cylinder when it runs out. We do not have the same experiences (by far) as the referee regarding the short lifetime of the valves. Nevertheless, they should be checked regularly to make sure. -> Some additional remarks about the potential extra costs are added to the text [sect. 2.4]

RC: "Cavity Ringdown spectroscopy can do far better than 0.2ppm for CO2."

AC: Although these new instruments seem very promising there is however still little experience regarding long term performance (e.g. aging, mirror contamination, interference with other gases). -> Obtainable precisions depend mostly on the averaging time. We give the precision when averaging over 5 minutes in the text for better comparison [sect. 1].

RC: "The obtainable precision with the ECD is rather <0.2 ppb than <0.5 ppb for N2O and <0.05 ppt than 0.1 ppt for SF6. There are GC systems running with a higher precision then 0.4 ppb for N2O at monitoring stations (in contrast to "Our obtained precisions are as low as those of the best other measurement systems currently available.")"

AC: It has been suggested (i.e. during a CARBOEUROPE workshop in Levi, Finland 2005, and also Andy Crotwell and Doug Worthy personal communication) that GCs used to be equipped with a different type of ECD (non-micro) which performed somewhat better than the newer micro ECDs. These older type ECDs however are currently not available anymore. -> this is added to the text. [sect. 1 & 5]

RC: " "Therefore, we can assume that the shape of the response curve does not change significantly over time". It would be preferable if the authors would not need to "assume" but could document this by a record of target gas analysis with different mixing ratio levels ("target high" and "target low")."

AC: So far, we have (re)calibrated the response of Eq. (1) for N2O and CO three times at the site (December 2006, August 2007 and July 2008) , and observed that the change of shape of the response is indeed below significance. Furthermore the target serves as a permanent check of the measurement quality, and it would thus also reveal the eventual variation in the shape of the quadratic calibration curve. Indeed, a wider range of targets would potentially reveal changes in the shape of the response curve as well as other problems (i.e. drifting cylinders) more easily, but this would also be at the costs of ambient measurements. -> This is clarified in the text. [sect 3].

RC: "In the evaluation of the systems performance it is not appropriate to compare the limited periods of best possible performance with the WMO comparability goals or the total uncertainty of a calibration scale. A disagreement of different international SF6 calibration scales is rather irrelevant for the rating of the quality of the method described."

AC: ->Point taken. This is altered in the text. [sect. 5]

RC: "The calibrated ranges by the set of higher level calibration t is properly listed. It should be also mentioned which span the Ref high and Ref low cover."

AC: ->They are added in the text [sect 3]

RC: "p.5 should read: All sample loops are flushed for 0.55 (metric) minutes (not seconds) Two small language items to be corrected: p13.: "During this period the period" p14: For a subset of gigure 6, during optimal considtions we find the following “best case” august 2006."

AC: ->text is changed accordingly

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 1321, 2009.