

Interactive comment on “Improving measurements of SF₆ for the study of atmospheric transport and emissions” by B. D. Hall et al.

Anonymous Referee #1

Received and published: 3 August 2011

The manuscript describes technical modifications of a widely used set-up for gas chromatography measurements of SF₆. It is a well written manuscript documenting an impressive improvement of measurement precision of the described chromatography systems.

While different modifications were made within a rather short period of time, the authors unfortunately do not investigate the impact of the individual measures taken, namely the improvement achieved by better control of gas flows by using EPCs rather than MFCs versus the modification of the general set-up by introducing the third chromatography column. Fig. 4 leaves me with the impression that the main improvement is owed to the replacement of MFCs in late 2005 rather than to the addition of the post-column

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in mid-2006. Figure 4 does not show a significant change from the late version 2 to version 3 of the set-up.

In my opinion the statement in the abstract "A method for improving measurement precision is described. We have modified a common GC-ECD method to achieve measurement precision of 0.5 % or better." (as well as corresponding statements in the main text and the conclusions section) is therefore too strong and should be put more careful. I am not convinced that the increased precision results predominantly from the method modification, and the improved version 2 of the system was certainly operated for too short a time period to reliably support this statement. In the case of future modifications of existing in situ instruments at measurement stations separate investigation of the different effects would be desirable to better understand the contribution of the flow control to the overall improvement. This is very briefly mentioned in the section about the in-situ instrument, but it remained unclear to me, how exactly N₂O is used as indicator.

I am a bit surprised by the large scatter in precision until early 2005, especially when considering that this is not an instrument in the field, but is operated under presumably well controlled pressure and temperature conditions in the lab. In comparison to similar GC systems with two columns and ArCH₄ as carrier gas (e.g. Popa et al. AMT 2010, Thompson et al. AMT 2009, Vermeulen et al. AMT 2011) the performance of the calibration instrument as illustrated by Fig. 4 and 5 seems to have been slightly below average until early 2005. Ideally, the revised version of the manuscript would contain a short section addressing the cause of the large variations in measurement precision prior to late 2005 and also an attempt to quantify the relevance of the different modifications made.

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In addition, these minor issues should be addressed prior to publication in AMT:

- P 4133, L 7/8: "Measurement precision ... methods". This states an important and crucial point that somewhat gets lost in between the literature review given here. This sentence might be moved to the next paragraph and be extended.
- P 4134, L 23: At which retention time does the GSV switch? Please mention this here or refer to Table 1 already at this point.
- P 4135, L 20ff: It remains a bit unclear what the advantage of a 3-column setup is. According to Table 1 the two Porapak columns are kept at the same temperature and have the same outer and inner diameters. Could an equivalent 2-column set-up with just one Porapak column plus the molecular sieve be used ?
- P 4135, L 26: By how much does the signal to noise ratio improve ?
- P 4135, L 10/11: Does the GSV switch occur at a fixed retention time or is it determined individually for each chromatogram by detection of the air peak ?
- P 4135, L 22: Is 2500 ppm the finally chosen value? This information may be added to Table 1.
- P 4140, L 22-25: Please give more details on this. How can N₂O be used to separate the effects of the various modifications? How did N₂O on the calibration instrument behave?
- P 4141, L 15: A 10 % difference to me seems a very small range to characterize a detector, and atmospheric SF₆ mixing ratios can differ by far more over short periods of time. It probably can be assumed that an ECD is approximately linear over the range covered by atmospheric mixing ratios, however, it remains unclear to me how the non-linearity of a detector can be accounted for by a calibration with only two standards. Please include the mixing ratios of the standards.

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Technical comments:

- P 4135, L 13: Moore et al. 2003 is listed as Moore et al. 2001 in the list of references.
- P 4137, L 8: Use the equivalent unit expression for N_2O and SF_6 .
- P 4137, L 23: Is the Plural "instruments" correct ? The text gives the impression of only one instrument being modified.
- P 4137, L 8: Should it not be "ECD" in this line (same for supplement, first phrase)?
- Figure 3: I suggest to have a legend box or label the curves.
- Figure 10: Include the red curve in both panels, (a) and (b).

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 4131, 2011.

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