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Atmospheric Measurement Techniques Discussions

Interactive comment on "Improving measurements of SF_6 for the study of atmospheric transport and emissions" *by* B. D. Hall et al.

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Response to reviewer #1: AMTD doi:10.5194/amtd-4-4131-2011

We thank this reviewer for comments and suggestions. A revised manuscript has been prepared.

General Comments

The reviewer notes that the change in SF6 precision does not seem to be conclusively linked to the addition of the post-column, and could be the result of other factors.

We agree that this aspect of the paper was not adequately presented. We maintain

that addition of the post-column was a major factor, and have revised text and Figure 4 to support this argument.

1) We have modified Figure 4 to include all reference gases analyzed on the calibration instruments (color-coded by mole fraction) and added a second panel to expand the period 2004-2011. Here, we have noted changes to the instrument before and after the addition of the post-column.

2) We have revised the first paragraph in section 3.1 as follows:

3.1 Calibration instruments

With the three-column system, the SF6 precision was improved from 1-2% to better than 0.5%. SF6 precision determined from analysis of various gas standards is shown in Figure 4. The signal to noise (calculated as SF6 peak height of a 5.8 ppt sample relative to the standard deviation of the ECD baseline under stable conditions) improved from $\sim$115 to $\sim$160 following the addition of the post-column, The SF6 peak height increased by 37% while the baseline noise remained unchanged. The mean precision for 5-month periods before and after the addition of the post-column (40 ambient-level samples in each period) was 0.72 (0.24) % and 0.45 (0.13) %, respectively. Prior to the addition of the post-column precision was variable, and seemed to show some improvement in late 2005 resulting from a change in the crimp used to control CO2 dopant flow. The change from mass flow controllers to electronic pressure controllers (EPC) (early 2006) may have also helped, but the largest improvement corresponds with the addition of the MS-5A post-column in mid-2006. The change in flow controllers did not result in decreased variability of the SF6 retention time. In fact, a significant reduction in retention time variability occurred following the addition of the post column (σ=0.18 s with EPC and two columns, σ=0.10 s with EPC and three columns) rather than with the installation of the EPC. Further, a change in flow controllers (from custom-built MFC to commercial MFC (Pnucleus Tecnologies, Hollis, N.H.)) on two separate systems using only Porapak-Q columns (installed at South Pole and Summit, Greenland) made little

difference to the SF6 precision.

The reviewer notes that our statement about using N2O to estimate the improvement of SF6 precision at the NWR site is not clear (pg 4140, line 22).

We agree, and have removed this sentence.

The reviewer suggests that the performance of the calibration instrument was below average until 2005 and cites three recent AMT papers as examples (Popa et a.l (2010), Thompson et al. (2009) and Vermeulen et al. (2011).

We disagree. Thompson et al. (2009) list SF6 precision as 0.08 ppt, while Vermeulen et al. (2011) list 0.1 ppt. Vermeulen et al. (2011) show good repeatability of samples taken from a target tank (Figure 8c) from which a standard deviation is estimated to be $\sim$ 0.07 ppt. Popa et al. (2010) list 0.03 ppt precision, which is quite good. Overall, we do not feel that 1-2% precision (which corresponds to 0.04-0.06 ppt) prior to 2005 was "below average".

Specific Comments

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.

We agree, and have moved this sentence to paragraph 1.

âĂć 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.

We added a reference to Table 1.

âĂć 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 ?

Yes, different configurations might be possible. As mentioned, we used the current setup as a matter of convenience.

âĂć P 4135, L 26: By how much does the signal to noise ratio improve ?

We should have pointed this out. We have added a statement to this affect in section 3.1 (see revised paragraph above).

âĂć 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 ?

The GSV switch is the same for all chromatograms. We added a statement to this effect at pg. 4136, line 14.

âĂć P 4135, L 22: Is 2500ppm the finally chosen value? This information may be added to Table 1.

We have added this information to Table 1.

âĂć 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?

We have removed this statement. Based on data from other instruments, we believe that the change from older MFC to newer MFC did not affect the SF6 precision significantly.

âĂć 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.

Two standards are used to determined detector response (assumed linear). All of

the data shown here except that from the Niwot Ridge in situ site are collected under background conditions, for which SF6 does not show large variations that would lead to non-linearity errors. We have added the following:

A 10% concentration difference is generally sufficient to establish the SF6 response curve (assumed linear over this range) because these instruments are located in remote places where SF6 concentrations seldom exceed that of the highest working standard by more than 20%. We have observed a slight non-linear behavior in the ECD in the calibration instrument, but errors are less than 0.03 ppt at concentrations within 30% of the working standard. Technical Comments Printer-friendly Version Interactive Discussion P 4135, L 13: Moore et al. 2003 is listed as Moore et al. 2001 in the list of references.

A correction has been made.

P 4137, L 8: Use the equivalent unit expression for N2O and SF6. âĂć

A correction has been made.

P 4137, L 23: Is the Plural "instruments" correct ? The text gives the impression of only one instrument being modified.

The plural is correct here, since two instruments, in three configurations, have been used since 1999.

P 4137, L 8: Should it not be "ECD" in this line (same for supplement, first phrase)?

We use the term μ-ECD to distinguish between the ECD currently available from Agilent, and that which is used in our calibration system (versions 2 and 3). Our ECD is an older style, and is sometimes called the Agilent “anode-purged ECD”. Agilent no longer offers this ECD and has replaced it with what is sometimes called the μ-ECD because of its smaller internal volume. We note in this section that we have performed limited testing with both types of the ECDs.

Figure 3: I suggest to have a legend box or label the curves. âĂć

The caption seems sufficient.

Figure 10: Include the red curve in both panels, (a) and (b)

We have added the red curve to both panels.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/4/C1818/2011/amtd-4-C1818-2011-supplement.pdf

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

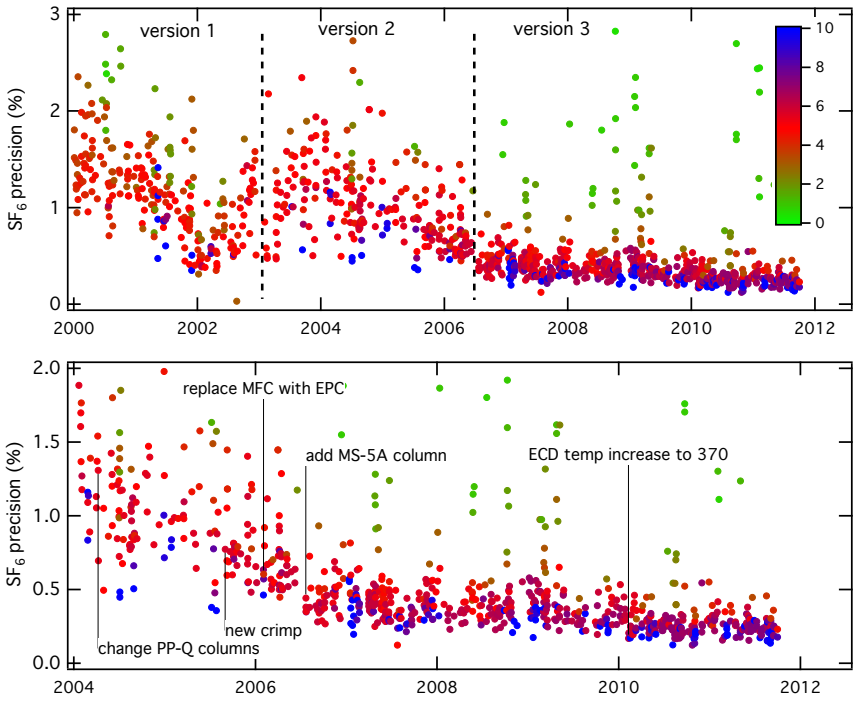

Fig. 1. Figure 4 (revised): History of SF6 precision (%) from all samples analyzed on the GC-ECD systems used for calibrations (color-coded by SF6 mole fraction (ppt)). Upper plot shows three GC versions.