

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

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Response to reviewer #2: AMTD doi:10.5194/amtd-4-4131-2011

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

General Comments This reviewer suggests that the advantages of this work over that described in Moore et al (2003) should be defined. The work of Moore et al was motivated by the need for rapid chromatography and temporal resolution. While conceptually similar, motivation and optimization of the two systems were different. We have added the following to section 2.

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The objective of Moore et al. (2003) was to improve the temporal resolution of N₂O and SF₆ by speeding up the chromatography. The work described here was done specifically to improve SF₆ precision without compromising N₂O. While conceptually similar, motivation and optimization of the two systems differed.

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 ~115 to ~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

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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 ($\sigma=0.18$ s with EPC and two columns, $\sigma=0.10$ 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 Technologies, 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.

Specific Comments - typo: page 4134 line 5: "Geller at al"

A correction has been made.

- page 4136 lines 17-23: does the SF6 signal to noise ration decrease with increasing CO2? If yes, could the SF6 measurement precision be even better at a lower level of CO2 doping?

The level of CO2 was chosen to optimize precision of N2O. A different level of CO2 might be more appropriate if detection of N2O is not desired. However, the SF6 signal to noise ratio changes only slightly with CO2. We do not have sufficient data to provide further comment.

- page 4141 lines 14-16: I think the calibration procedure should be explained in more detail. The non-linearity cannot be estimated with only two calibration gases, but that's how I understand the text now.

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 re-

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mote 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.

Fig. 4. What are the grey triangles and the black circles?

See revised Figure 4.

Fig. 10. I suggest moving the model-SF6 red line to the upper plot.

We have no objection.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/4/C1825/2011/amtd-4-C1825-2011-supplement.pdf>

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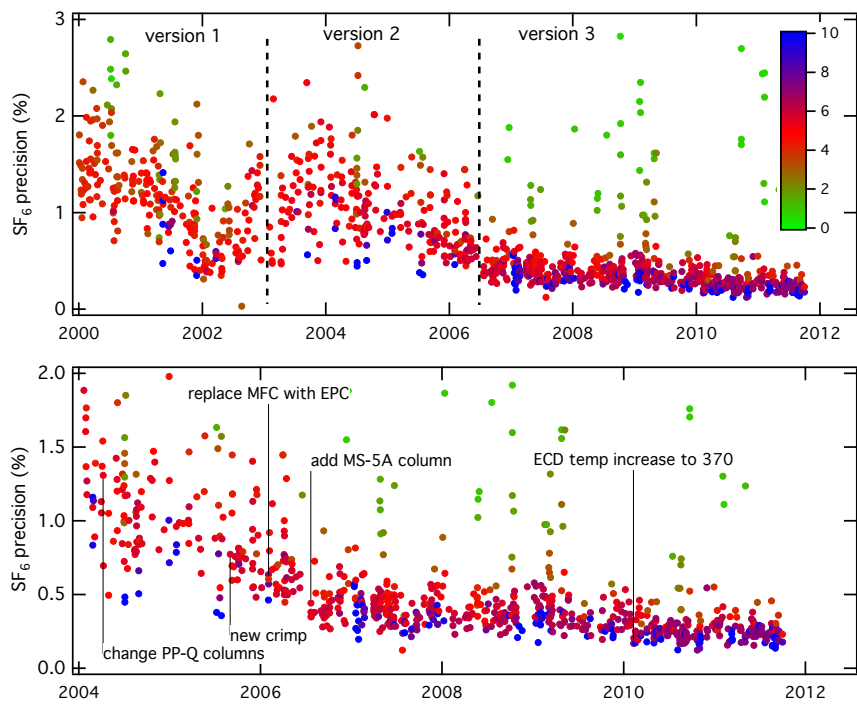


Fig. 1. Figure 4 (revised): History of SF₆ precision (%) from all samples analyzed on the GC-ECD systems used for calibrations (color-coded by SF₆ mole fraction (ppt)). Upper plot shows three GC versions.