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Atmospheric Measurement Techniques Discussions

Interactive comment on "World Calibration Center for SF_6 – supporting the quality system of the global atmosphere observation" *by* J. Lee et al.

J. Lee et al.

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General comments

As referee #1 suggested, we will focus less on the role of KMA/KRISS as WCC and more on the description of the work we attempted in this study. As such, we will rearrange the body text to emphasize the technical improvement accomplished in this study. The revised manuscript will be given by the order of 1) Title: "High precision analysis of SF6 at ambient level" 2) abstract 3) introduction 4) experimental methods 5) results 6) summary and conclusion. Briefly, in the experimental section, general aspects of SF6 analysis when using GC-ECD with an Activated Alumina-F1 column and the preparation of working standards will be addressed. As referee #1 pointed out, the baking procedure to suppress the degradation of the column will be stated in short. Also the performance of the Activated alumina-F1 column for the ambient level of N2O was simply tested to show the analytical uncertainty of ∼0.15%. In the result section, the analytical results using various calibration methods and comparison between the KRISS (SF6 in N2) and the WMO scales (SF6 in air) will be addressed. Finally, the work done will be summarized in the summary and conclusion section.

Specific comments

P7900, L10: replace "0.22" with "about 0.22" The growth rate of SF6 varies somewhat from year to year and was 0.28 ppt from state of the Climate in 2011, Supplement to the Bulletin of the American Meteorological Society, Vol. 93, No. 7, 2012. Hall et al (2011), Improving measurements of SF6 for the study of atmospheric transport and emissions, Atmos. Meas. Tech., 4, 2441-2451, doi:10.5194/amt-4-2441-2011.

=> We will refer the value of 0.28 ppt/yr given in the documents Referee #1 stated.

P7900, L10-12: The following sentence is not necessary. . . "Development of a working (or transfer) standard with very low concentration of SF6 requires expert technologies and several knowhow of gas metrology."

=> We will remove unnecessary sentences.

P7901, L1: I am not aware of Data Quality Objectives for SF6. I found DQOs for N2O and CH4 in GAW Report 185 (Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance), but I cannot find the same for SF6. Perhaps you are referring the comparability goals? If DQO for SF6 exist, please provide a reference.

=>A formal DQO for SF6 has not been published yet. Accordingly, we replaced the term of DQO with "compatibility goal of WMO recommendation" that is mentioned at the GAW report # 194.

P7901, L8: It would be better to say: "Accurate observations of GHG in the atmosphere are vital to determine sources and sinks."

=>We will modify this sentence, it will be written as "Accurate measurement of GHGs is crucial to the rationing of their sources and sinks∼" in the revised manuscript.

P7901, L14: There are potent greenhouse gases with concentration lower than that of SF6. NF3 is one example.

=>"one of the most potent GHG" will be substituted

P7902, L11-22: I don't see how any of this is relevant to the issue of SF6 and the function of the WCC. The WMO/GAW has adopted a particular SF6 calibration scale. Quality assurance efforts are needed to establish comparability (all measurement on the same scale, traceable to the same reference) and compatibility (level of agreement between measurements reported on the same scale). An independent SF6 scale would be useful, as there are only a few scales in existence. But this is external to the function of the WCC. The results of CCQM comparisons for other gases do not really have anything to do with SF6. You could say, instead, that "KRISS has experience organizing and participating in international comparisons, and that this experience will help KMA/KRISS fulfill their role as WCC."

=>We will erase all of the corresponding sentences in complience with the reviewer's comments.

P7902, L23: According to Fig. 1, it is not the explicit function of the WCC to distribute the WMO scale.

=>We will make a correction for the figure 1 given as follow;

Figure 1. Traceability chain of SF6 through the CCL and GAW stations (see the attached figure 1)

P7904, L22: A comparison of linear versus non-linear SF6 calculations might help here. How non-linear is the SF6 response? What affect would this have on atmospheric measurements if one assumes linearity? This is discussed briefly on page 7908, but it could be moved to section 3.3 where the non-linear is mentioned. The reason this is important is that you say on P7904 that 5 standards are needed to determine non-linear response, but then you get the same result when only two standards are used. Perhaps this topic could be expanded. For example: over what range is the linear method useful? At some concentration limit, the linear approximation will lead to a difference between linear and non-linear methods, and this difference could be significant with respect to compatibility goals.

=>Non-linear response of ECD is shown well in the second order polynomial fitting of the regression curve. An error regarding the assumption of linear response is then clearly denoted in that one-point calibration deviates significantly from the multi-point calibration methods, which are given in the below table. It is also shown that the reference point (FB03444), of which concentration is only ~0.4 ppt higher than the analyte concentration of interest, makes considerable error in the determination of SF6 mole fraction, suggesting that the linearity of ECD response cannot be guaranteed out of the concentration difference of at least 0.4 ppt.

Table 1. Calulated result of SF6 depending on the calibtation points using the WMO scales (unit: pmol/mol). (see the attached figure 2)

P7905, L5: delete "which are to be prepared by sampling naturally (or filling artificially) SF6 sparser or denser air"

=>It will be deleted.

P7906, L22: delete sentence. "To have a good analytical precision, response of gas chromatogram was examined"

=>It will be deleted.

P7907, L13: I don't understand what you mean by "measured mole fractions" of the WMO standards. The WMO standards have assigned values. Did you assign new values to the WMO standards on a different scale? Or do you mean to say that the SF6 response curve you determined is consistent with WMO assigned values? The

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only true test of WCC capability to maintain the WMO scale would be to analyze a separate unknown sample using the WMO standards to define the reference scale, and compare your result with CCL analysis of the same sample. Has this been done?

=>The word “measured value” was misused. We didn’t intend to assign new value to the WMO scales. Thus “measured value” will be removed in the revised manuscript and the corresponding paragraph (from L10 to L20) will be rephrased as follow. “For the calibration of the GC-ECD, the responses of the WMO scales (from NOAA) were taken at 5 individual cylinders prepared at mole fractions of 3.946, 5.920, 7.972, 9.595, and 11.887 ppt. The response curve fits well into the secondary polynomial function within a least squares of R2 $\sim$ 0.999981, showing the validity of the regression curve, as well as the internal consistency of the WMO scales. Furthermore, response values obtained from the calibrated analyzer should be traceable to the NOAA’s values, so that all the differences between the WMO scales and the calibrated values will fall within the certified standard deviation of $\sim$ 0.02 ppt.”

Table 2: Is the C_calibrated result determined from the best-fit polynomial function determined from the response and WMO values? If so, this only shows that the WMO standards are internally consistent.

=>C_calibrated was the value calculated from the polynomial regression curve obtained by the analysis results of the 5 WMO standards. Thus it will be replaced with C_calculated. We intended to show perfect internal consistency of NOAA’s cylinders and sufficiently good analytical capability of KRISS. If the analytical capability of KRISS were not good enough, the difference between the preassigned values and corresponding calculated values could be larger than 0.02 ppt.

P7910, L5: I don’t understand this statement. Was the value of the working standard determined on an independent scale? In section 3.4 you present values of the working standard on the WMO scale, calculated two different ways. By definition, the working standard MUST be consistent with the WMO scale.

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=>This statement will be erased. We intended to describe major uncertainty budget: the first is the preassigned standard deviation of the WMO scale and the second is the standard deviation of analytical repeatability.

Fig. 2: Section 3.2 states that the sample flow rate was 200 ml/min and the sample volume was 7 ml, but the figure shows 100 ml/min and 2 ml volume.

=>Sorry for the typo. The numbers in the body text will be corrected.

Technical Corrections

P7905, L11: is “KWA” supposed to be “KMA”?

=>It will be corrected.

Fig 2.: Add dimensions of alumina-F1 column(s). Use consistent units (cc or ml).

=>Dimensions will be added. (2 m 2 ea, ID 2.0 mm, OD 1/8”, 80-100 mesh)

Fig. Captions 2,4,6: replace “minites” with “minutes”

=>These will be corrected.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/5/C3612/2013/amtd-5-C3612-2013-supplement.pdf

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Interactive comment on Atmos. Meas. Tech. Discuss., 5, 7899, 2012.

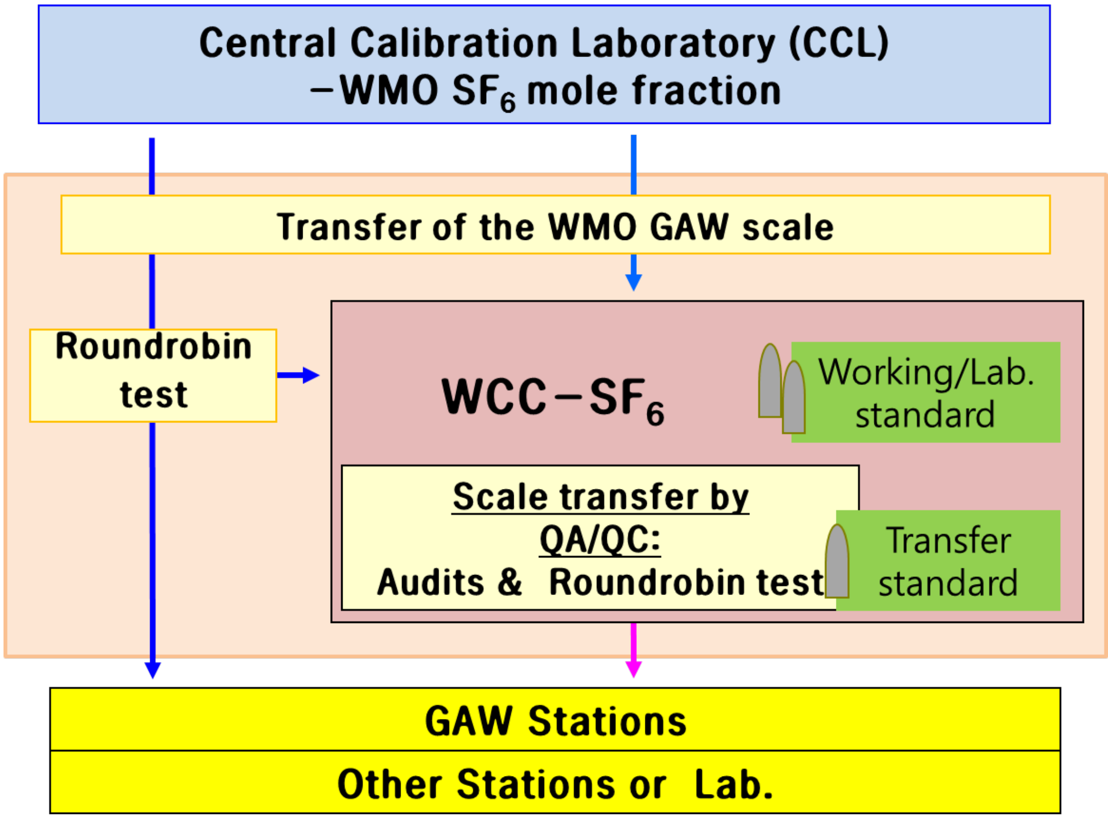

Fig. 1.

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Calibration method	Multi-point	Three-point		Two-point	One-point	
the WMO scales used for calibration	FB03441 FB03443 FB03444 FB03447 FB03450	FB03441 FB03443 FB03444	FB03443 FB03444 FB03447	FB03443 FB03444	FB03443	FB03444
Calculated value	7.520	7.516	7.524	7.524	7.446	7.541
Difference from multi-point calibration method	/	-0.004	+0.004	+0.004	-0.074	+0.021

Fig. 2.