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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.

Anonymous Referee #1

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Summary

This paper summarizes efforts by the Korean Meteorological Administration (KMA) and the Korean Research Institute of Standards and Science (KRISS) to establish the WMO/GAW World Calibration Center (WCC) for SF6. WCC responsibilities and KMA/KRISS qualifications are presented. The authors then describe analytical methods used to measure SF6 in air relative to the WMO SF6 reference scale, and present some interesting results from standards comparisons and precision tests.

General Comments

There are some interesting topics addressed in this paper, such as the precision ob-

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tained using activated alumina-F1 columns compared to Porapak Q columns, and comparison between the WMO/GAW SF6 scale (SF6 in air) and an independent KRISS scale (SF6 in nitrogen). However, the authors selected as the main topic (as the title indicates) to focus on the introduction of KMA/KRISS as the WMO/GAW WCC for SF6. This is a weak topic on which to base a publication. The roles of a WCC have been described in the WMO/GAW Strategic Plan and WMO/GAW reports.

The paper could be improved by focusing less on the role of KMA/KRISS as WCC and more on what the authors learned regarding precise SF6 measurement, preparing working or traveling standards, and preparing primary standards at ppt levels. It would be useful to know how the alumina-F1 column performs for N2O, because N2O is often analyzed along with SF6 on the same system. It would also be useful to know if this technique can be maintained over long time periods (eg. does anything build up on the columns over time and affect the precision?). Your precision for SF6 seems to be very good, and could represent an improvement over Porapak Q techniques. Even if N2O precision is not as good as common techniques, your method could be useful to those that can measure N2O using optical techniques but rely on GC/ECD for SF6. Further, an expanded comparison of standards prepared in nitrogen versus air would also be interesting, especially if the reason for the difference could be determined. The role of KMA/KRISS as WCC for SF6 could be included in any such discussion, but it should not be the focus of the paper.

In summary, with a little extra work, the information presented in this paper could be published if it were organized differently and with a different title.

A revision would benefit from editing by a native English speaker.

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

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2010-2011. See for example. . .

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.

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."

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 to compatibility goals? If DQO for SF6 exist, please provide a reference.

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

P7902, L14: There are potent greenhouse gases with concentrations lower than that of SF6. NF3 is one example.

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

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help KMA/KRISS fulfill their role as WCC".

P7902, L 23: According to Fig. 1, it is not the explicit function of the WCC to distribute the WMO scale.

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-linearity 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.

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

P7096 L22: delete sentence. "To have a good analytical precision, response of gas chromatogram was examined."

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 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?

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

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standards are internally consistent.

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.

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.

Technical Corrections

P7905, L11: Is "KWA" supposed to be "KMA"?

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

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

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