

Answer to interactive comment by anonymous referee #2

General comments

In order to clarify the confusion made in the beginning of this paper, the part regarding the description of the WCC-SF₆ tasks, which are already published in WMO/GAW reports, will be thrown out or rephrased in the revised manuscript. In particular, an unintentional misapprehension about the traceability to the primary standard, for which one single CCL is responsible, will be clearly resolved through the manuscript. Some important aspects such as the compatibility goal of WMO recommendation and the traceable chain to establish quality assurance system will be distributed over the part regarding our scientific works. 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. In the experimental methods section, it will be discussed that the traceability will be connected by the calibrated analyzer (GC-ECD/Activated alumina-F1 column) using WMO scales. And the compatibility goal of WMO recommendation (± 0.02 ppt for the range 6-10 ppt) will be discussed in the parts where the instrumental and analytical improvements are described. Furthermore, various calibration methods will be briefly compared to deduct an efficient method for the determination of SF₆ mole fraction in terms of appropriate data quality and time cost.

Specific comments

P7900, L6: “...primary standards in the different laboratories around the world...”. For GAW this is not valid. According to the traceability concept of GAW, for the individual greenhouse gases there is only one primary standard, which is kept at the Central Calibration Laboratory (CCL). For the terminology see the GAW Glossary on the web.

⇒ *This sentence will be removed. And other sentences of similar context in the body text will corrected in compliance with the traceability concept of GAW.*

P7900, L10: The requirement of specific (not “several”) know-how is also relevant for the preparation of secondary standards, which generally cover the mole fraction range used for the working standards and transfer standards.

⇒ *Since this sentence is not necessary, it will be erased.*

P7900, L13 and several other lines: “DQO”: Have complete DQOs already been released by GAW? If so, please add a reference in the main text. In fact, there are recommendations for the network compatibility (see GAW Report No. 194). Please clarify.

⇒ *DQO will be corrected to the compatibility goal of WMO recommendation.*

P7900, L13: Write the full name of the institution, i.e. Korea Meteorological Administration, here since mentioned for the first time.

⇒ *Full name will be given.*

P7900, L15 and P7902, L5: One should rather say: “After the Central Calibration Laboratory(CCL) for SF₆ has been established by NOAA ESRL (USA), ...”

⇒ *P7900, L15 will be erased in the abstract. P7902, L5 will be corrected as pointed out.*

P7900, L19: As the WCCs range among the GAW Central Facilities, “facilities” should be replaced with “Central Facilities”.

⇒ *It will be corrected.*

P7900, L27 and in the main text: “a drift of 0.02 ppt”. During which time period?

⇒ *We performed a consecutive measurement by the order of reference-sample-reference for the production of single point of data. The ratio value of responses, $S_i \cdot 2 / (R_i + R_{i+1})$, then connotes the correction of the instrumental drift during this measurement. Any unclear statement like “a draft of 0.02 ppt” in the main text will be clarified.*

P7900, L27 and P7901, L2: “...a working standard...to be transferred to the GAW stations”. Confusing: Is it actually one standard? Each station will need its own working standard. Or do you think at a travelling standard?

⇒ *The part of “ready to be transferred to the GAW stations” will be erased since we don't mean a travelling standard.*

P7901, L5: “...nations...emissions...” This is a somewhat political statement and expresses a

rather optimistic view. Suggestion to rephrase and explain scientific aspects.

⇒ *It will be rephrased to “Most industrialized nations have devoted tremendous efforts to restricting and even reducing anthropogenic emissions of GHGs ~”.*

P7901, L9: “...not easy to quantify their mixing ratios owing to their globally and temporally insignificant variation.” Just the opposite is true. Global quantification is difficult for highly variable species, such as ozone.

⇒ *It is unnecessary comment and thus will be erased.*

P7903, L3: While the GAW strategic plan in general requires applying standard operating procedures, it should be pointed out here that these do not exist yet for SF₆. Moreover, there is consensus within GAW that high-quality measurements involving complex systems such as GCs, require Measurement Guidelines, which leave somewhat more flexibility than strict SOPs do.

⇒ *It will be clearly pointed out in the revised manuscript that SOPs for SF₆ doesn't exist. Accordingly, corresponding sentence will come out as follow*

“To establish high-quality measurement system, for instance GCs, to promote reliable compatibility between each site is therefore regarded as the highest priority to be taken, considering that standards operating procedure for SF₆ doesn't exist yet.”

P7903, L11: “...globally and spatially...”. “globally” refers to a spatial distribution. Is “spatially” intended to mean “regionally” ?

⇒ *Redundancy. “Spatially” will be erased*

P7903, L20: Since Fig. 1 is not mentioned in the text so far, this line might be an appropriate place to refer to Fig. 1 and explain the position of the CCL according to the GAW concept.

⇒ *Figure 1 will be tagged at corresponding sentence. Also the terms of reference for CCL [WMO/GAW report #172] will be briefly introduced as follow.*

“In GAW terminology, CCL as a central facility 1) hosts primary standard 2) serves the needs of the other quality assurance facilities and activities of GAW 3) prepare laboratory standards for calibration purpose 4) supply well-calibrated air to GAW analytic laboratories as needed for conducting inter-comparisons”

P7904, L4: "...a set of...". Should be replaced with: "...a set of gas mixtures calibrated in the WMO SF₆ mole fraction scale..."

⇒ *It will be replaced as suggested.*

P7904, L20 till end of paragraph: "...calibrated by the primary standards provided by the KRISS...". This statement needs more detailed explanations. Do you mean "calibrated in the scale based on the primary standards prepared by KRISS"? How has the transfer of the scale to the observing sites been made? Use of transfer standards. What about the role of working standards at the observing site? Any differences between the traceability concepts of a NMI (KRISS) and GAW should be pointed out clearly. This is of major importance for the entire paper. The terminology used in this context should be in agreement with GAW (see GAW Glossary on the web).

⇒ *This paragraph makes an unintentional misapprehension about the traceability to the primary standard, for which one single CCL is responsible. We intended to say that analytical ability of KRISS is good enough to contribute to the GAW networks, judging from that the resulting uncertainty of calibration curve falls within ~0.02 ppt. Definitely, we used WMO scale in order for the calibration of GC analyzer. Thus this paragraph will be erased in the revised manuscript in order to avoid any confusion. In addition, we will erase the part describing comprehensive WCC tasks that have been already published in WMO report in order to avoid the redundancy and focus more on showing what we learned in this study.*

P7906, L2: "A highly repeatable GC method" What does this mean? A method yielding highly repeatable results?

⇒ *Developed method shows good repeatability in measurement results. In order to achieve good repeatability, 1) the column were baked at 180 °C between measurement cycles to wash out potential contaminants 2) the sample loop was continuously rinsed 3) restrictor was installed at the ends of vent lines to keep the constant pressure (see the attached Fig. S1) 4) Dead volume along the sample feeding line was significantly reduced.*

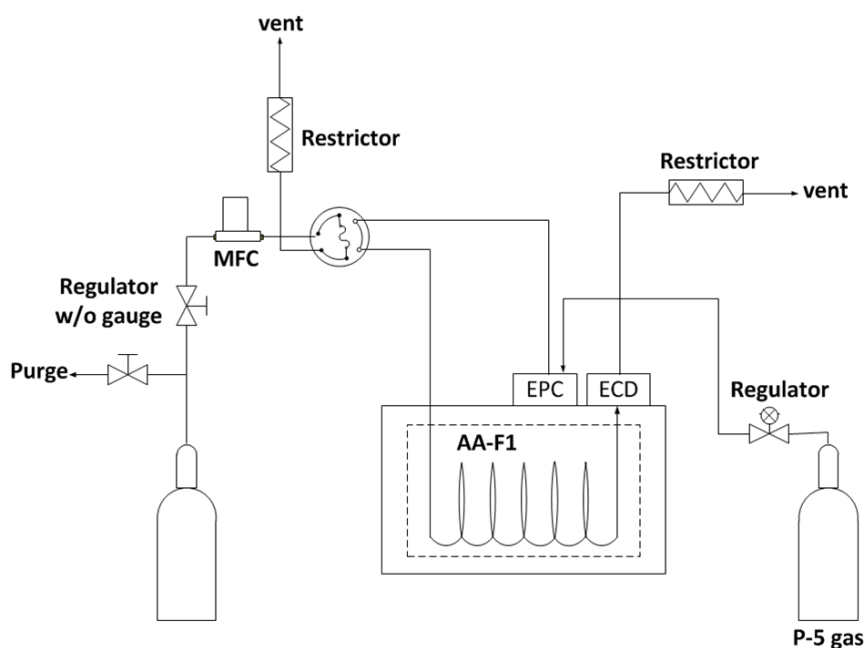


Fig. S1 Schematic diagram of the experimental setup

P7906, L10: “7 ml”. In Fig. 2, it is 1 and 2 ml, respectively.

⇒ *It is typo. It will be corrected to 1 and 2 ml.*

P7906, starting at L1: The KRISS scale is an issue by itself and has not directly to do with the WCC-SF₆. Please clarify.

⇒ *The KRISS standard is not related with the attempted calibration and WCC-SF₆.*

P7909, section 4: Since a great part of this section is more a summary than conclusions, the title should be changed to “Summary and Conclusions”.

⇒ *The title of this section will be changed as pointed out.*

P7910, L5 and earlier parts of the text: The authors talk about “a working standard”. May one assume that more standards of this kind will be prepared to supply all GAW stations measuring SF₆? Moreover, it should be described if the stations will get one working standard or a suite of these in order to establish the response curve of the detector?

⇒ *This part will be removed to avoid the misapprehension. We don't supply calibrated working standards to the other GAW stations till now. In this study, the working standard was tried to test the validity of attempted calibration methods.*

⇒ *To establish the response curve of detector, the NOAA cylinders are used for direct*

calibration of GC-ECD. Thus the prepared working standards must be consistent with the WMO scale. The other parts causing somewhat confusion or misapprehension about the working standard will be corrected and rearranged for the context to be clarified.

3) Technical corrections

P7899, title and entire text: Since WMO is on British English, replace “Center” with “Centre”, as used within WMO/Global Atmosphere Watch.

⇒ *All “center” will be replaced to “centre”.*

P7901, L11: Style: “composed” should be replaced with “supported”.

⇒ *“composed” will be replaced to “supported”.*

P7901, L17: “the amount of SF₆ mole fraction is reported ...” might be replaced with a shorter expression such as “the abundance of SF₆ is reported ...”.

⇒ *This suggestion will be reflected in the modified manuscript.*

P7901, L23: Insert “to” (and contributed to the GAW programme).

⇒ *“to” will be inserted.*

P7901, L26: Mixture of singular and plural. Replace “This data are” with “These data are”.

⇒ *This point will be reflected.*

P7903, L22: Confusing citation, should be replaced with: “...are described in Box 7 of the GAW Report No. 172 and ...”

⇒ *This section will be removed*

P7902, L14: Style: “...comparison programs since the last 10 yr.” should be replaced with: “comparison programmes during the last 10 yr.” With reference to line 23 please note that the spelling in the paper should not be a mixture of British and American English.

⇒ *“program” will be replaced to “programme”.*

P7903, L2: “QA” should be spelled out when mentioned for the first time: “Quality

Assurance (QA)...”

⇒ *All acronyms mentioned for the first time will be spelled out.*

P7903, L9: “...for their implementation ...”. It is not clear to what “their” is related to.

⇒ *Section 2 will be skipped in the revised manuscript for the reason that this section much overlaps the published WMO reports and we’d like to focus more on what we learned regarding precise SF₆ measurement as suggested.*

P7904, L4 till end of paragraph: Issues are described in a rather confusing way. Suggestion to rephrase, for example: “Accordingly, the KMA shall possess a set of gas cylinders directly calibrated in the GAW SF₆ mole fraction scale by the CCL, which ensures the shortest link possible, to distribute the scale to GAW stations by way of transfer standards, and to perform site audits. For the purpose of the linkage, in November 2010 the KMA obtained from NOAA gas cylinders in the range of 4 – 15 pmol mol⁻¹ of SF₆.”

⇒ *Section 2 will be skipped in the revised manuscript. Nevertheless, kind suggestion is very much appreciated.*

P7904, L9: Replace “scientific...(SAGs)” with “WMO/GAW Scientific Advisory Groups (SAGs)”

⇒ *Section 2 will be skipped.*

P7905, L7: “...are maintained by calibration against the WMO...” Might be shortened by saying: “...are calibrated against the...”

⇒ *Section 2 will be skipped.*

P7905, L9: Replace “Meantime” with “In the meantime”

⇒ *Section 2 will be skipped.*

P7905, L11: Typo: Replace “KWA” with “KMA”.

⇒ *Section 2 will be skipped.*

P7906, L4: Replace “an Agilent” with “Agilent”. Same line: What does “2 ea” mean?

⇒ *“an” will be erased. 2m x 2ea = 4m.*

P7906, L7: Typo: It is plural. “Samples pass...”

⇒ *It will be corrected.*

P7906, L11 and L16: Typo. It should read “Porapak”

⇒ *All “Propak” will be replaced to “Porapak”*

P7906, L20: Don’t confuse the scale and gas in a cylinder (serving as standard).

⇒ *“NOAA cylinder” will be used, instead.*

P7907, L15: Better say: “...the analytical ability of KRISS satisfies the level recommended by WMO/GAW, 0.02 ppt.”

⇒ *It will be corrected.*

P7907, L23: Typo: Remove “a” before “laboratories”.

⇒ *“a” will be erased.*

P7908, L2: Typo? : “co.” in “RIX co.”

⇒ *It will be replaced to “RIX Industries”.*

L7908, L9: Unspecific sentence: “...air sample cylinder... overlaid with the WMO SF₆ mole fraction scale”. Should be replaced with a sentence like: “...overlaid with the chromatogram of a WCC-calibrated gas”.

⇒ *It will be replaced as suggested.*

P7909: There are a particularly large number of problems with the style of English.

⇒ *We found no use of a subject, unclear sentence structures, redundancies and mixture of singular and plural. Thus whole section will be totally revised.*

P7910, L3: “working cylinder” should be replaced with “working standard”, the term used elsewhere in the text.

⇒ *All of “working cylinder” will be replaced.*

P7910, L23 and L26: Non-uniform use of space around a hyphen.

⇒ *It will be corrected.*

P7911, L25: Remove the comma between “Report” and “No.”

⇒ Comma will be removed.

P7912, Table 1: Suggestion to rephrase the title line, for example: “Comparison data from the GC analyzer; each area data point results from 3 successive analyses”. R and S should be explained.

⇒ *It will be rephrased to “Repeat measurements of reference and sample in order to compensate for instrumental drift between measurement cycles; each area data point results from 3 successive analyses.”*

P7913, Table 2: “CRMs” should be explained (spelled out).

⇒ *The title line will be replaced with “Analytical result for SF₆ standard gases from NOAA”. CRM is Certified Reference Material, by the way.*

P7915, Table 4: The title should be more precise by saying, for example: Measurement results of comparisons between two SF₆ scales.

⇒ *The title line will be rephrased to “Measurement results of comparisons between NOAA and KRISS scales”.*

P7916, Fig. 1: This figure is not mentioned in the text (as already noted above). Design/colour: The text in the blue box (top left) is hard to read. Mind the contrast of colours. Replace “Roundrobin” with Round-robin”. Caption: Replace “CCI” with “CCL”.

⇒ *This figure will be mentioned in the text and redrawn as suggested. (Fig. S2)*

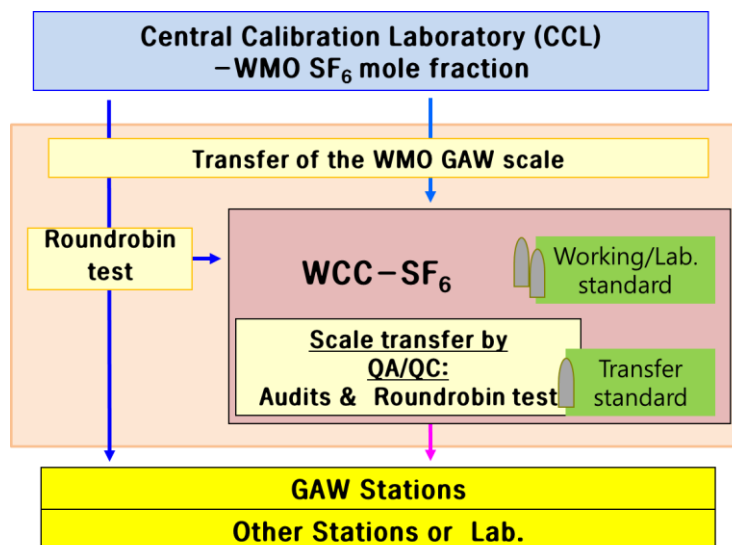


Fig. S2 Traceability chain of SF₆ through the CCL and GAW stations

P7917, Fig. 2: Font size on axes: Suggestion to enlarge as shown in Fig. 4. “Heater” obviously means “ECD”. Replace “PP-Q” with “Porapak-Q”. Give length of the Activated alumina-F1 column. The number for the flow is different from the one given in the main text. Use uniform unit for volume (ml or cc). Caption: Replace “...column selection installed at...” with “type of column installed in the GC”. Caption: Typo, replace “minites” with “minutes”

⇒ *Figure will be enlarged as much as possible. And caption will be corrected as suggested.*

P7919, Fig. 4: Caption: Typo, it should read “minutes”.

⇒ *It will be corrected.*

P7920, Fig. 5: Replace “Calibration” with “calibration”.

⇒ *It will be corrected.*

P7921, Fig. 6: Caption: Typo: Replace “minites” with “minutes”.

⇒ *It will be replaced.*