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# *Interactive comment on* "Dynamic-gravimetric preparation of metrologically traceable primary calibration standards for halogenated greenhouse gases" *by* Myriam Guillevic et al.

**Myriam Guillevic et al.**

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The manuscript by Guillevic et al. titled "Dynamic-gravimetric preparation of metrologically traceable primary calibration standards for halogenated greenhouse gases" describes the preparation of novel traceable gas standards containing $SF_6$, HCFC-132b, HFC-125, HFO-1234yf, and CFC-13 in air by dynamic means using a permeation device. Many of these compounds are atmospherically important and no traceable reference standards are well established, therefore this is an important publication. The authors discuss the need and uses for these gravimetric standards and compare them to previous calibration scales.

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Discussion paper

**On the whole, the article is well written, with a few minor typos that can easily be amended. Please see below for my comments and feedback.**

We thank the reviewer for his/her time and constructive comments. Please find below a point-by-point answer to each comment.

**Minor changes: For coverage factors and confidence intervals k values should be in italics.**

The text was corrected accordingly.

**P1, line 1 remove 'g' from within.**

Text corrected.

**P3, line 3 add an 'and'.**

Text modified according to suggestion.

**P3, line 12 replace 'in' with 'of'.**

Text modified, also according to suggestion by R1: 'This QA/QC procedure includes regular intercomparisons [...]'.

**P3, line 13 remove end 's' from flasks.**

Text corrected accordingly.

**P6, line 20 transferred 'into'.**

Text corrected accordingly.

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**P7, line 2 'checking'.**

Text corrected accordingly.

**P10, line 1 why do you use _k_ = 1?**

We use _k_ = 1 for $u_{R_{prep,i,j}}$ because this standard uncertainty is then used in the bivariate weighted linear fit, together with $u_{R_{meas,i,j}}$ to find the parameters $a_i$ and $b_i$. The equations are detailed in the Supplement, Section S3.

**Comments: In the introduction there is discussion about calibration scales and static point source measurements. It may be worth briefly commenting on atmospheric measurement and sampling of these compounds to highlight the challenges and needs for reference standards.**

Thank you for this remark. Also in agreement with R1, we have now completed the third paragraph of the introduction, introducing atmospheric measurement and sampling:

'Atmospheric measurements of halogenated compounds are currently provided by several networks such as AGAGE (Advanced Global Atmospheric Gases Experiment), NOAA (National Oceanic and Atmospheric Administration), and GAW (Global Atmospheric Watch). Such measurements, used to precisely estimate atmospheric molar fraction of these halogenated substance together with associated trends, are crucial to understand and predict the evolution of stratospheric ozone and estimate their radiative forcing thereby refining future climatic projections. Furthermore based on these measurements and using atmospheric transport modeling, emissions can be quantified ('top-down' estimation, e.g., Prinn et al., 2000; Rigby et al., 2010; Brunner et al., 2017). The comparison of top-down reconstructions with bottom-up inventories shows agreement for some gases but also discrepancies that can be considerable for

others (Weiss and Prinn, 2011; Lunt et al., 2015; Hu et al., 2016; Simmonds et al., 2016; Sherry et al., 2017). The top-down approach thus is a complementing and independent way to review production/consumption/emission inventories and compliance with reduction targets, while assessments of climate forcing and stratospheric ozone rely on observations of atmospheric composition'.

**In the introduction you may want to refer to WMO data quality objectives.**

Thank you for this comment. We did not mention WMO data quality objectives in this article for several reasons. First, WMO is only one of the several networks/groups measuring halocarbons (e.g., AGAGE, University of California, Goethe Universität Frankfurt). To our knowledge, there are set DQO for $SF_6$ within WMO (Compatibility goal, 1 sigma: 0.02 pmol/mol and extended compatibility goal, 1 sigma: 0.05 pmol/mol), but not for the other halocarbons (see for example GAW Report No. 229, 18th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015), Table 1 p. 3). The WMO DQO for $SF_6$ applies to the data produce within the WMO network, not to other networks, which may have different DQOs or different methods to measure data quality. As our suite of standards is meant to be available to any group/network asking for it, we decided not to mention requirements of one specific network.

Second, the link between DQO as defined by WMO and expanded uncertainty of a produced reference gas mixture is not straightforward. It strongly depends on the method used to disseminate the primary standard to the end-users. Actually, within the scale system used by networks such as WMO for $SF_6$ or AGAGE for halocarbons, DQO becomes mostly relevant for the primary calibration scale propagation, not for its preparation. Within this framework, the best way to reach DQOs is to make the calibration chain between primary calibration scale and laboratory standard as short as possible as well as to improve measurement reproducibility. As the dissemination of the produced METAS-2017 primary calibration scales is beyond the scope of this

paper, we think it is not very relevant to mention WMO DQOs for $SF_6$. The dissemination of the METAS-2017 scale for CFC-13 to the AGAGE network is described in Vollmer et al. (2018). Note that AGAGE does not use DQO as a measure of network data quality.

**Emphasise the impact of HFCs etc. on climate forcing and why the dynamically prepared reference standards are so important. One interesting paper is Velders et al. 2009.**

The impact of HFCs on climate forcing is mentioned in the first paragraph of the introduction, p. 2 l. 11-15. We thank Reviewer 2 for the suggested reference and have now modified the paragraph to include it: 'HFCs (hydrofluorocarbons) were introduced as replacement for CFCs and HCFCs. Their emissions, though not harmful to the ozone layer, are still increasing and contributing to global warming due to their high radiative forcing (Harris and Wuebbles, 2014, Velders et al., 2009). For this reason the recent Kigali Amendement (Oct. 2016) added these HFCs to the Montreal Protocol'.

The importance of dynamically prepared reference gas mixture for the mentioned gases was actually not well known before this study, therefore it is not mentioned in the introduction. However this finding is emphasised in Section 4.2, and especially when discussing the results for HFC-125 (Section 4.2.2) and HFO-1234yf (Section 4.2.3). It is mentioned again as the last sentence of the conclusion: 'Dynamic generation methods and/or minimisation of contact on surfaces should therefore be favoured when preparing primary reference gas mixtures for such reactive substances'.

**Section 2.1 Please give the numeric calibration range.**

We added to the first paragraph of Section 2.1 the following sentence: 'The resulting prepared molar fraction range covered by this suite goes from 0.9 pmol/mol up to 42 pmol/mol (see details for each substance in Table 3)'.

**Section 2.4 Describe how equivalent cylinders (e.g. 3 & 4 or 2 & 9) were prepared in parallel.**

All cylinders were prepared in series, i.e. we use the same mixture exiting the MSB-dilution system to fill all cylinders, one after the other, as described in Section 2.4 p. 7: '[...] The cylinder valve is then manually closed, the cylinder disconnected and left standing vertically outside the building to warm up. A new cylinder is placed in the liquid nitrogen bath, connected to the filling system, and the filling procedure starts again'.

Equivalent cylinders are not filled in parallel but one after the other. For one given substance, equivalent cylinders are therefore not more correlated than any other couple of cylinders.

**Section 3.1 State detection limits (LODs).**

We have completed Section 3.1 as follow: 'Detection limits, defined here as three times the noise level, are 0.015 pmol/mol for $SF_6$, 0.02 pmol/mol for HFC-125, 0.01 pmol/mol for HFO-1234yf, 0.015 pmol/mol for HCFC-132b and 0.07 pmol/mol for CFC-13'.

**Regarding the stability of the permeation temperature, how critical is this? How can you tell if a sufficiently long stabilisation time has been reached to achieve equilibrium for the permeation device?**

The sensitivity of the permeation rate to temperature is discussed in Section 2.5.1, p. 8, paragraph 'Permeation chamber temperature stability': 'Once carrier gas flow and pressure are kept constant, the permeation rate varies only with temperature. The stability of the permeation chamber temperature is 0.02 °C over 20 min ($k = 2$). Based on our experience measuring temperature sensitivity of permeation rate, this corresponds

to approx. 0.1 % change in permeation rate'.

The estimation of the needed stabilisation time is explained in Section 2.2, p. 5, l. 22-24 : 'After inserting a permeation device, a stabilisation period is required mainly depending on chamber temperature, pressure and permeator membrane properties, before the mass loss becomes linear over time. This linear mass loss vs time is then determined for at least 8000 min to minimise the standard deviation of the measured mass loss due to balance noise.' We completed this information as follow: 'The time window $t_{2,i} - t_{1,i}$ during which the mass data are used is determined so that the residuals of the fit to the mass loss over time are centered around zero and randomly distributed (see example for CFC-13 on Fig. 2 and Section S1 in the Supplement).'. We also modified the legend of Fig. 2 accordingly.

**Does the pressure of the cylinder have an influence? The authors suggest not, however the lower pressure cylinders seem to be more problematic, could this be attributed to wall effects? Surface reactions are mentioned for HFO-1234yf – was performance better in the treated cylinders? Why use stainless steel if dynamically produced standards often show lower values than statically prepared standards for reactive substances?**

We discussed potential wall effects in Section 3.2.2, p. 12 l. 28-32: 'We however observe that most outliers are cases of substance loss (Fig. 5) and affect cylinders having the smallest total amount of gas filled and the highest surface/volume ratio (i.e. Essex cylinder 4.5 L, 24 bars). We would therefore in the future favour filling in cylinders of larger volume and pressure, as well as a further automatising the cryo-filling process to limit human intervention as much as possible as well as to increase the safety of the procedure.'.

Following as well suggestion from R1, we added the following information: 'Furthermore, we plan to investigate if the observed substance losses occurred by adsorption

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on cylinders walls or beforehand in the preparation system. To do so, a comparison of the molar fraction in the mixture exiting the magnetic suspension balance/dynamic dilution system with the same mixture filled in cylinders will be performed. The recent installation of a measurement system for halogenated gases at METAS in the same laboratory makes this possible. If the adsorption indeed occurs in the cylinders, it will be tested if adding water vapour earlier in the sequence of fillings may help to limit this adsorption.'.

Yes, it seems performance was better in the cylinders passivated with SilcoNert2000 coating, as cylinders MP-003 to MP-006 show no outliers presenting a substance loss. All other cylinders are made of stainless steel passivated by electropolishing of extremely high quality (Essex Industries), with two different volumes and associated maximum pressures (see main text, Table 1). The larger type of cylinder has been used for decades by the AGAGE network and is moreover the container of choice for the Cape Grim Air Archive, showing excellent stability over time for most halogenated compounds (e.g., Prinn et al., 2000).

**Is your system not Silco treated?**

Thank you for this remark, indeed the preparation system is almost entirely SilcoNert2000-treated but this was not mentioned. The text is now modified in Section 2.3 according to this suggestion: 'Note that most metal surfaces in contact with the carrier gas and the produced gas mixture are passivated by applying SilcoNert2000 coating. This includes all metal tubing, all metal surfaces of the MFCs and MFM in contact with the gas, and most of the permeation chamber'.

**Figure 6 is unclear and I recommend removal or overhauling it.** We agree and Figure 6 is now removed.

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