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

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This manuscript describes a dynamic dilution with cryogenic filling to produce pmol/mol reference materials in high-pressure cylinders. The method is well-described and the paper is well-written. The technique described is different to static dilution, which is commonly used to prepare low mole fraction reference standards for atmospheric measurement of trace gases that influence stratospheric ozone and climate. The authors provide comparisons to previous calibration scales, some of which are not well developed. These data will improve our understanding of the atmospheric abundance of HCFC-132b, HFC-125, HFO-1234yf, and CFC-13. This work will help provide SI traceability to current measurements, and the method could be useful for gases that are reactive or adsorb readily to dry surfaces. I have relatively few comments and technical corrections.

The authors would like to express their gratitude to Reviewer 1 for his/her considerable effort to improve the quality of this manuscript with knowledgeable and concise comments and input. We hereafter provide point by point replies to them.

P5, L26: In equation (1), Vm is listed as the molar volume of the carrier gas (L/mol), which makes sense, but in Table 2, it is listed with units of g/mol. Is Vm correct in Table 2?

There is indeed a mistake in Table 2, the unit of \( V_m \) should be L/mol, as in Equation (1). Table 2 is now corrected.

P5, L26: Is Vm calculated by assuming it is an ideal gas?

We used NIST Tables of molar volumes (NIST Chemistry WebBook, <https://webbook.nist.gov>). The data are calculated for real gases, at 0°C and 1013.25 hPa. We added this information in the first occurrence of the quantity molar volume: ‘Values are from the NIST Chemistry WebBook, assuming real gas’.

P7, L30: I’m having a hard time with equation (5). The units don’t seem to work out. On page 8 you say that equation (5) can be simplified by removing \( qV_5 \), but this is not obvious. It seems that \( qV_5 \) remains in the term \( x_{residual} / (V_{total} + qV_5) \), unless an additional \( qV_5 \) is missing from (5). Because of this and the confusion over Vm, I am unable to verify the calculations for SF6 in cylinder MP-001 using data from Table 2.

There is indeed a mistake in Equation 5 as written in the manuscript, thank you for
pointing this out. It should be written:

\[ x_{\text{prep},i,j} = x_{\text{filled},i} \cdot qV_{5,j} \cdot \Delta t_{i,j} + x_{\text{residual},i} \cdot qV_{5,j} \cdot (\Delta t_{\text{total},j} - \Delta t_{i,j}) \]  

(1)

From the above correct equation, we can now simplify by removing the factor \( qV_{5,j} \), and re-arrange to:

\[ x_{\text{prep},i,j} = x_{\text{filled},i} \cdot \frac{\Delta t_{i,j}}{\Delta t_{\text{total},j}} + x_{\text{residual},i} \cdot (1 - \frac{\Delta t_{i,j}}{\Delta t_{\text{total},j}}) \]  

(2)

All calculations have been corrected and this does not change the results of the calculations, nor for the molar fractions neither for the ratios.

Table 2: The treatment of uncertainties seems reasonable, except for one minor component. You use the manufacturer’s data for purity (99%) and account for the uncertainty in the budget, which is acceptable. However, according to Vollmer at al. 2015 and references therein, HFC-125 is produced by hydrofluorination of perchloroethylene, with several intermediates, including HCFC-133a. Can you comment on the possibility that HFC-125 might contain HCFC-132b as an impurity? Does the purity uncertainty component for HCFC-132b need to be expanded to include this possibility?

Thank you for pointing this out. We fully agree that cross-contamination originating from impurities present in permeators can potentially be an important issue. We plan to investigate this in a more systematic way for the next generation of reference mixtures, by performing measurements of impurities present in each permeator. We have modified Section 4.2.2 of the main text to mention this:

'We plan for future reference gas mixture preparation to check the presence of substance impurities in permeators in a systematic way, to get a better estimate of the purity fraction as well as to quantify any potential cross-contamination, if any. For the METAS-2017 scale, we checked in particular the absence of HFC-132b as impurity in the HFC-125 permeator (see Section S5 in Supplement).'

And we added the following section in the Supplement:

'Based on the findings from Vollmer et al. (2015) who identified several potential impurities in HFC-125 inherited from its production pathway, we have measured the presence of impurities in the permeator for HFC-125. We have done this test using the reference gas mixture for HFC-125 prepared at 85 nmol/mol (cylinder MP15-4020, see Fig. S1) as part of the METAS-2015 suite for HFC-125. These measurements have been performed by injecting 1 L of this mixture directly in the Medusa-GC-MS at Empa. The detection of the HFC-125 peak was disabled to avoid saturation of the detector. For HFC-132b, there was no chromatographic baseline excursion suggesting that the mole fraction was well below the detection limit (defined here as three times the noise level). As the amount of gas used for a measurement was 1 L, i.e. half the normal gas quantity of 2 L, we roughly estimate the detection limit for HCFC-132b as twice the detection limit for a normal measurement of 2 L, i.e. 0.03 pmol/mol (instead of 0.015 pmol/mol).

In addition, the measurements showed the presence of:

- CFC-115: 31 pmol/mol (0.36 \cdot 10^{-3} mol per mol HFC-125)
- HFC-143a: 51 pmol/mol (0.6 \cdot 10^{-3} mol per mol HFC-125)
- HFC-134a: 31 pmol/mol (0.36 \cdot 10^{-3} mol per mol HFC-125)
- HCFC-124: 11 pmol/mol (0.13 \cdot 10^{-3} mol per mol HFC-125)
- SF6: 0.2 pmol/mol with LOD = 0.03 pmol/mol (2.5 \cdot 10^{-6} mol per mol HFC-125)
• HFO-1234yf: 0.06 pmol/mol with LOD = 0.02 pmol/mol, although we are not sure if this is a small impurity introduced potentially by contamination from a regulator.

• CFC-13: no baseline disruption (LOD = 0.14 pmol/mol).

In cylinder MP-001 containing 32.027 pmol/mol HFC-125, the SF₆ impurities originating from the HFC-125 permeator correspond to a contribution of $2.5 \times 32.027 = 0.00008$ pmol/mol SF₆. This can be neglected compared to the prepared 10.582 pmol/mol SF₆. The same conclusion applies to HFO-1234yf and to the other cylinders.

Figure 6: I don’t find this figure particularly helpful. It seems that the relevant information is in fig. 7 and Table S6. We agree and Figure 6 is now removed. Table S6 is therefore now included in the main text, as Table 7.

P1, L1: replace "withing" with "within" The text was corrected accordingly.

P1, L15: Perhaps be more specific, "... traceable to the SI-units, amount of substance, ..." The final unit we generate using the presented method contains indeed the mole, one of the SI-units, but to generate this unit we use as well for example flows, that are traceable to the SI-units second and meter. Also, the balance measures a mass, traceable to the unit kilogram, and the conversion to unit mole is realised using molar masses of molecules. Thus the final quantity, even being mole/mole, is traceable not only to the mole but to other SI units as well. We therefore prefer to keep the sentence as it is.

P1, L23: Consider rephrasing: "Such a combined system supports maximizing compatibility ..." Suggestion implemented.

P2, L9: (minor) Consider using mixing ratio or molar fraction instead of concentration Text modified accordingly, 'concentration' being substituted by 'molar fraction' for all occurrences.

P2, L13: Change "Kigali agreement" to "Kigali Amendment" Text modified accordingly.

P2, L16: Should probably spell out "Non-Article 5" Corrected.

P2, L16: "bottom-up" Corrected.

P2, L31: "detect gradients between" Corrected.

P2, L32: "attribute" rather than "attributing" Text modified accordingly.

P2, L29: Consider; "... while assessments of climate forcing and stratospheric ozone rely on observations of atmospheric composition". Text modified according to suggestion.

P3, L11: No mention of what "compatibility target" is. Consider simplifying as "The calibration scale approach enables a high degree of consistency, but still requires ...." Text modified according to suggestion.

P3, L12: Consider replacing "consists in" with "includes" Text modified according to suggestion.
P5, L3: Consider re-phrasing. "The permeation rate depends exponentially on temperature; ..." Text modified according to suggestion.

P12: I’m glad you included some possible reasons for some cylinders failing verification tests. Do you consider the possibility that some fraction of a component could be lost to the surface of the cylinder before the water is added? Maybe future experiments could be done in which the H2O is added earlier in the sequence?

Indeed, there is always the possibility that some compounds are partially lost to the surface of the cylinder, and adding water earlier in the sequence of fillings would be a judicious approach. In this study, the strategy we applied to evidence potential losses on cylinder surfaces was to use cylinders of different volumes, filled at different pressures, with different coating materials. In the literature, tests of adding water after filling cylinders with gas mixtures for CCl$_4$ showed a desorption of CCl$_4$, suggesting that adding water afterwards may be acceptable in certain cases (Yokohata et al., 1985).

Besides, for cylinders which failed the verification test and which showed anomalously low levels of e.g. HFO-1234yf, we still don’t know if the loss occurred due to adsorption in the cylinder or previously, on other stainless steel surfaced of the preparation system. This is a point we plan to investigate in the future by comparing molar fraction measured in the gas coming out of cylinders to molar fraction measured in the gas stream coming directly from the second dilution step of the magnetic suspension balance (MSB). This system being physically only a few meters apart from a new APRECON-GC-MS installed at METAS, it will be possible to have the MSB system connect to one inlet port of the APRECON-GC-MS, a cylinder filled with this same mixture to another port, and compare if the two molar fractions are identical, within measurement uncertainty. This was not done in this paper as the APRECON-GC-MS system was not validated yet. We hope to include this in a future study.

P15, L14: change "apply for" to "applies to" Text corrected.

P15, L27: I think you have the NOAA/SIO ratio backwards. Rigby et al 2010 adjusted NOAA data by the factor 0.998, so that means that SIO/NOAA = 0.998, consequently NOAA/SIO would be 1.002. While the Rigby et al 2010 comparison is out of date (NOAA updated their SF6 scale from NOAA-2006 to NOAA-X2014), the ratio 1.002 is consistent, within uncertainties, with those calculated by P. Krummel (http://www.wmo.int/pages/prog/arep/gaw/documents/GGMT2017_T03_Krummel.pdf). Thank you for this precise observation. We now use the ratio of 1.002 obtained by calculating the weighted mean of comparison ratios as presented by P. Krummel et al. (GGMT, 2017). Figure 7 was updated accordingly.

We also realised that on Figure 7, we show the known factor UB98/SIO for HFC-125 but it is not mentioned in the main text. We now added a small section:

**UB-98:** Before using the SIO-14 scale for HFC-125 within AGAGE, a primary calibra-
tion scale prepared by University of Bristol was in use (UB-98 O’Doherty et al., 2004, 2009). The known conversion factor UB-98/SIO-14 is 0.9237 (C. Harth and R. Weiss, pers. com., 2018).

Fig. 1: It would help if a box was drawn around the permeation chamber, similar to the box around MFM, MFC1, and MFC2. Figure 1 is now modified according to suggestion. The permeation chamber is now drawn by an orange box. Additionally another box is drawn around the ensemble ‘magnetic suspension balance’, made of the balance plate and its associated electromagnet, the permeator hooked to the permanent magnet, both in the permeation chamber.

Table 2: Is the entry for Permeation supposed to be ng/s instead of ng/min? The given value of 1654.77 for the permeation rate is correctly assigned a unit of ng/min. However there is indeed a mistake in Table 2, because the time values $t_{1SF_6}$ and $t_{2SF_6}$ should be in minutes, not in seconds. Table 2 is now corrected accordingly. Table S1 contained the same unit mistake and is now corrected as well. Note that all calculations are still valid, and the units in Figure 2 are correct. This mistake likely comes from the fact that $\Delta t_{ij}$ are reported in seconds.

References


