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Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #1

Received and published: 14 March 2018

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.

Comments:

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?

P5, L26: Is Vm calculated by assuming it is an ideal 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 q_V5, but this is not obvious. It seems that q_V5 remains in the term x_residual/(t_total*q_V5), unless an additional q_V5 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.

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?

Figure 6: I don't find this figure particularly helpful. It seems that the relevant information is in fig. 7 and Table S6.

Technical Corrections.

P1, L1: replace "withing" with "within"

P1, L15: Perhaps be more specific, "... traceable to the SI unit, amout of substance, ..."

P1, L23: Consider rephrasing: "Such a combined system supports maximizing com-

patibility ..."

P2, L9: (minor) Consider using mixing ratio or molar fraction instead of concentration

P2, L13: Change "Kigali agreement" to "Kigali Amendment"

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

P2, L16: "bottom-up"

P2, L31: "detect gradients between"

P2, L32: "attribute" rather than "attributing"

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

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 ...."

P3, L12; Consider replacing "consists in" with "includes"

P5, L3: Consider re-phrasing. "The permeation rate depends exponentially on temperature; ..."

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?

P15, L14: change "apply for" to "applies to"

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).

Fig. 1: It would help if a box was drawn around the permeation chamber, similar to the box around MFM,MFC1, and MFC2.

Table 2: Is the entry for Permeation supposed to be ng/s instead of ng/min?

Vollmer, M. K., et al. (2015), Abrupt reversal in emissions and atmospheric abundanceâĂĺof HCFC-133a (CF3CH2Cl), Geo- p

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