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Dynamic-gravimetric preparation of a suite of primary, metrologically traceable calibration standards for halogenated greenhouse gases

Myriam Guillevic (1), Martin K. Vollmer (2), Simon A. Wyss (2), Daiana Leuenberger (1), Andreas Ackermann (1), Céline Pascale (1), Bernhard Niederhauser (1), and Stefan Reimann (2)

(1) Federal Institute of Metrology METAS, Laboratory for Gas Analysis, Bern, Switzerland (myriam.guillevic@metas.ch), (2) Laboratory for Air Pollution and Environmental Technology, Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

For many years, comparability of measurements obtained with various instruments over the globe within a monitoring network has been ensured by anchoring all results to a unique suite of reference gas mixtures, or so called "primary calibration scale". Such suites of reference gas mixtures are usually prepared and then stored over decades in pressurised cylinders by a designated laboratory. For halogenated gases, this anchoring method is still highly relevant as measurement reproducibility is currently much better (<1 %) than the expanded uncertainty of a reference gas mixture (usually >2 %, k = 2 or 95 % confidence interval). However, newly emitted halogenated gases are already measured in the atmosphere at sub-pmol/mol levels [e.g. 1], while still lacking an established reference standard. For compounds prone to adsorption on material surfaces, it is difficult to evaluate mixture stability and thus variations in the molar fractions over time in cylinders at pmol/mol levels.

To support atmospheric monitoring of halogenated gases, we have developed a suite of reference gas mixtures for SF_6 (sulphur hexafluoride), HFC-125 (pentafluoroethane), HFO-1234yf (2,3,3,3-tetrafluoroprop-1-ene), HCFC-132b (1,2-dichloro-1,1-difluoroethane) and CFC-13 (chlorotrifluoromethane). The preparation method is dynamic and gravimetric, based on the permeation principle followed by dynamic dilution and cryo-filling of the mixture in cylinders. The obtained METAS-2017 scale is made of 11 cylinders containing these five substances at near ambient molar fractions, each cylinder having a slightly different molar fraction. Each prepared molar fraction is traceable to the realisation of SI units and is assigned an uncertainty estimate following international guidelines (JCGM 100:2008, [2]), ranging from 0.6 % for SF_6 to 1.3 % (k = 2) for all other substances. The smallest uncertainty obtained for SF_6 is mostly explained by the high substance purity level inside the permeator as well as low SF_6 contamination of the carrier gas.

Molar fractions in each cylinder were measured by Medusa-GC-MS [3]. The obtained internal consistency of the suite ranges from 0.23 % for SF_6 to 1.1 % for HFO-1234yf (k = 1). The expanded uncertainty after verification ranges from 1 % to 2 % (k = 2). Comparison of the METAS-2017 scale for SF_6 with the scale prepared by SIO (Scripps Institution of Oceanography, SIO-05) shows excellent agreement, the ratio METAS-2017/SIO-05 being 1.002. For HFC-125, the METAS-2017 scale is measured as 7 % lower than SIO-14, and 9 % lower than Empa-2013 for HFO-1234yf. Such an offset towards lower values for standards prepared using dynamic generation methods by contrast to methods using static gravimetry or static volumetry has been previously observed for other reactive compounds such as ammonia.

[1] M.K. Vollmer et al., First Observations of the Fourth Generation Synthetic Halocarbons, HFC-1234yf, HFC-1234ze(E), and HCFC-1233zd(E) in the Atmosphere, Environ. Sci. Technol., 49, 2703-2708, 2015.

[2] JCGM 100:2008, Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM).

[3] Miller et al., Medusa: A Sample Preconcentration and GC/MS Detector System for in Situ Measurements of Atmospheric Trace Halocarbons, Hydrocarbons, and Sulfur Compounds, Anal. Chem., 80, 1536-1545, 2008.