A new method to produce SI-traceable, primary calibration standards for halogenated greenhouse gases

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

[1] Federal Institute of Metrology METAS, Laboratory Gas Analysis, Bern, Switzerland.

[2] Empa, Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

Corresponding author: Myriam Guillevic, <myriam.guillevic@metas.ch>

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 (such as HFC-1234yf) 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 level of uncertainty over time in cylinders at pmol/mol levels.

To support atmospheric monitoring of halogenated gases, we present here a method to produce an SI-traceable reference gas mixture at near atmospheric molar fraction, combining gravimetric and dynamic preparation. The generation process consists of four successive steps. In the first step the matrix gas, nitrogen or synthetic air is purified. In a second step, this matrix gas is spiked with the pure substance using a permeation device from which the pure substance (e.g., HFC-1234yf), liquefied in a reservoir, permeates through a polymer membrane. This process occurs in a temperature and pressure controlled chamber, with a constant matrix gas flow. The resulting linear mass loss rate is precisely calibrated using a magnetic suspension balance. In a third step the desired molar fraction is reached by dilution of the high concentration mixture exiting the permeation chamber with a chosen flow of the matrix gas in one or two subsequent dilution steps. All flows are piloted by thermal mass flow controllers. All surfaces in contact with the gas mixture are passivated with a silica-based, inert surface coating (SilcoNert2000®, SilcoTek Inc.) in order to reduce adsorption/desorption processes. In the last step the mixture is pressurized into Silconert2000®-coated stainless steel cylinders by cryo-filling. The final mixture has an expanded uncertainty of no more than 3% (k=2).

We present the realisation of a suite of multi-component reference gas mixtures for HFC-1234yf, HFC-125, SF_6, CFC-13 and HCFC-132b, composed of 11 cylinders each at a slightly different molar fraction, the associated uncertainty budget according to GUM [2] and first results of comparison to other existing primary calibration scales.

References

[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, DOI: 10.1021/es505123x, 2015.

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