



SI-traceable standards for atmospheric monitoring of halogenated gases

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To support atmospheric monitoring of greenhouse gases and in particular halogenated gases, we have developed a method to produce reference gas mixtures at nmol/mol (ppb) to pmol/mol levels (ppt). This method is dynamic and SI-traceable. This work is conducted in the framework of the EMRP projects HIGHGAS and KEY-VOCs as well as METAS' AtmoChemECV project.

The method has been already applied to HFC-125 (pentafluoroethane, widely used in air conditioners), HFC-1234yf (2,3,3,3-tetrafluoropropene, a car air conditioner fluid of growing importance) and SF₆ (insulant in electric switch-gears). It is currently being extended to HCFC-132b and CFC-13. It is particularly suitable for gas species and/or concentration ranges that are not stable in cylinders and it can be applied to a large variety of molecules related to air pollution and climate change (e.g., NO₂, volatile organic compounds such as BTEX, NH₃, water vapour at ppm level, CFCs, HCFCs, HFCs). The expanded uncertainty is less than 3 % (95 % confidence interval or k=2).

The generation process is composed of four successive steps. In the first step the matrix gas, nitrogen or synthetic air is purified. Then this matrix gas is spiked with the pure substance, using a permeation device which contains a few grams of the pure substance (e.g., HFC-125) in the liquid form and loses it linearly over time by permeation through a membrane. This mass loss is precisely calibrated in our lab in Bern, using a magnetic suspension balance. In a third step the desired concentration 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 mass flow controllers. All parts in contact with the gas mixture – including the balance – are passivated using coated surfaces, to reduce adsorption/desorption processes as much as possible. In the last step the mixture can be i) directly used to calibrate an analyser, ii) sampled on sorbent tubes or iii) pressurized into Silconert2000-coated stainless steel cylinders by cryo-filling.

We focus here on standards made for the gases HFC-125 and HFC-1234yf. We present here the method, the uncertainty budget as well as first results of intercomparisons to other references.