SI-traceable reference gas mixtures for halogenated VOCs at atmospheric amount-of-substance fractions

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Halogenated VOCs and environment

Synthetic halogenated volatile organic compounds (VOCs) are emitted into the atmosphere and have a huge impact on the environment as:

- **contributors** to the **radiative forcing**
- **depletion** of the stratospheric **ozone layer**
- possibly **hazardous degradation products** of some halogenated VOCs (HFOs)

Therefore, the use of many halogenated VOCs is regulated by the Montreal and Kyoto Protocols and thus, it is important to monitor them in the atmosphere.

Measurements of halogenated VOCs are challenging

Comparable datasets based on long-term, accurate and traceable measurements of VOCs are essential to **identify trends** of regulated and unregulated species and to **verify emissions** resulting from inventories. For many halogenated VOCs, this cannot be achieved due to the **lack** of appropriate SI-traceable **reference gas mixtures (RGMs)** at **atmospheric levels** (pmol/mol).

MetClimVOC: aims for halogenated VOCs

The EMPIR project "Metrology for Climate Relevant Volatile Organic Compounds" (MetClimVOC, 2020 – 2023) aims at covering these gaps through the realization of accurate, stable and SI-traceable RGMs for halogenated VOCs relevant for climate change at atmospheric levels with an expanded uncertainty of < 3 %. These RGMs must fulfil the data quality objectives of the monitoring networks.

We generated RGMs for the following halogenated VOCs that are found in the atmosphere and were considered priority by stakeholders for two reasons:

(1) the existing, non-SI-traceable RGMs are not in agreement:

- HFC-32
- HFC-365mfc
- CH_2Cl_2
- CCl_4

(2) there is no RGM at atmospheric amount-of-substance fractions available:

- 1,2-dichloroethane
- HFO-1336mzzZ

Realization of SI-traceable RGMs for halogenated VOCs

A set of nine cylinders containing the selected halogenated VOCs at near-ambient and slightly varying amount-of-substance fractions was dynamically prepared based on the permeation method (ISO 6145-10) and dynamic dilution (ISO 6145). The steps (all SI-traceable) to generate RGMs are described below. All surfaces that are in contact with the RGM are SilcoNert®2000 coated to avoid losses due to adsorption.

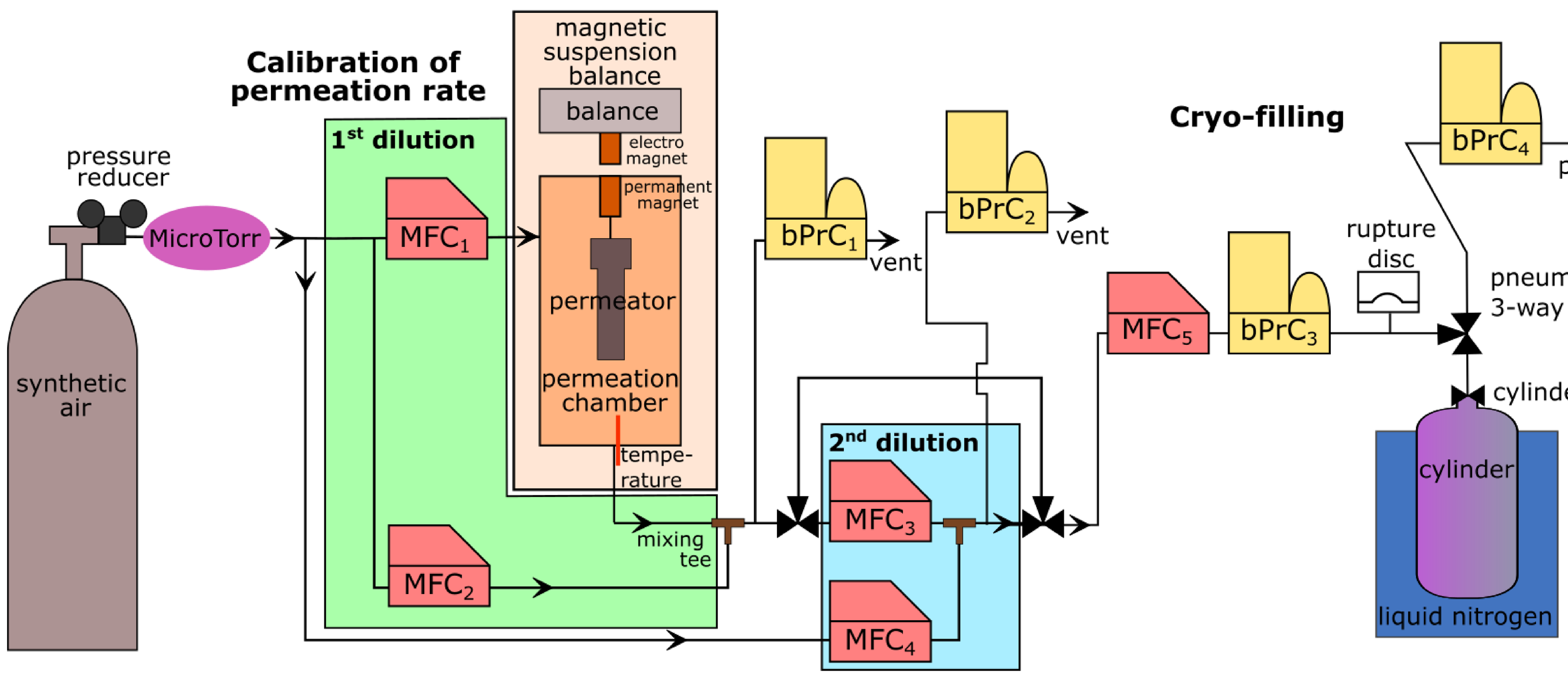

Fig. 1: schema of the magnetic suspension balance, dynamic two-step dilution system and the cryo-filling system. MFM: mass flow meter; MFC: mass flow controller; bPrC: back pressure controller.

1. Calibration of the permeation units

Permeation units are placed in a magnetic suspension balance (MSB; TA Instruments; Fig. 1). After several days of stabilisation, mass loss of the permeation unit with time (i.e. permeation rate) is continuously measured.

2. Generation of primary RGMs

A two step dilution system is coupled to the MSB (Fig. 1). This system controls pressure and mass flow rates of the carrier and dilution gas (i.e. synthetic air). RGMs at different amount-of-substance fractions are generated by changing flow rates.

3. Cross-contamination assessment

Before filling the RGM into cylinders, each RGM is measured on a preconcentration APRECON GC-MS system (Fig. 2) to detect potential cross-contamination. The carrier gas was measured as well on this system to check for impurities.

Fig. 2: APRECON GC-MS system.
Top right: preconcentration unit, below: GC and quadrupole MS

4. Cryo-filling

These primary RGMs were filled in series into nine SilcoNert®2000 coated cylinders (2 x 34 L & 7 x 2.25 L) using an improved cryo-filling system (Fig. 1). The cryo-filling system performs an automated leak test and rinsing procedure, and regulates the filling times, flow and pressure.

5. Uncertainty budget & internal consistency

Each of the previous steps has an uncertainty associated to it (Fig. 3), which contributes to the overall uncertainty budget (uncertainty propagation according to the *Guide to the expression of uncertainty in measurement* (GUM JCGM 101:2008, BIPM)).

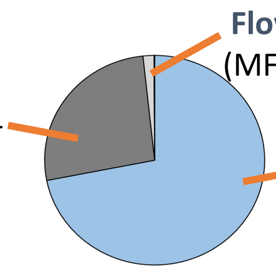

Fig. 3: Main contributors to the uncertainty of primary RGMs

To validate the production process, the internal consistency of the set of nine cylinders (Fig. 4) is determined.

Fig. 4: SilcoNert®2000 coated 34 L Essex tanks

6. Value assignment

We assigned two amount-of-substance fraction values per cylinder and substance: an SI-traceable value and a 'scale value' (= best-fit value) to meet the needs (smaller "uncertainty" by excluding the uncertainty of the production process) of the atmospheric measurement community. The reason behind this is that the analytical standard deviation of measurements of halogenated VOCs in the atmosphere is lower than the expanded measurement uncertainty of SI-traceable RGMs. The 'scale value' can be used to track long-term changes of amount-of-substance fractions in the atmosphere with as little measurement uncertainty as possible. However, for comparisons with results from stations using other RGMs or for the calculation of absolute amount-of-substance fractions, the SI-traceable value is needed.

Further information

To find more about **MetClimVOC**:

- visit the website: https://www.metclimvoc.eu
- contact us: **tobias.buehlmann@metas.ch**

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