Traceable reference gas mixtures to calibrate analysers used to measure atmospheric VOCs

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VOCs and climate

Volatile organic compounds (VOCs) play an important role in the oxidative capacity of the atmosphere and climate change as:

- **ozone** and **aerosol precursors**
- **contributors** to the **radiative forcing**

Comparable datasets based on long-term, accurate and traceable measurements of VOCs are essential to identify **climate trends**. For many VOCs, this cannot be achieved due to the **lack** of **reference standards** (among others) that are:

- **stable**
- **traceable** to the international system of units (SI)
- at **low amount fractions** (atmospheric level; nmol/mol)

Current calibration strategies for VOCs at monitoring stations

Analysis of atmospheric VOCs is not straightforward because of their complex chemical speciation (thousand of species). The most common techniques used for measuring VOCs are:

- gas chromatography coupled to flame ionization (GC-FID)
- GC coupled to mass spectrometry (GC-MS)
- proton-transfer reaction MS (PTR-MS; in recent years)

Calibration strategy	Analysis technique	Compounds	SI-traceability
Direct use of SI-traceable reference standards in cylinders	GC-FID (only NMHCs) GC-MS	Non-methane hydrocarbons (NMHCs) Halogenated VOCs (SF_6, HFC-125, HFO-1234yf, HFCFC-132b, CFC-13)	**Yes** (to NPL (NMHCs), to NOAA, KRISS and METAS (SF6), and to METAS the rest of halogenated VOCs)
Dilution of higher amount fraction standards	GC-FID GC-MS	Oxygenated VOCs Biogenic VOCs (terpenes)	**Not fully assured** (some standards traceable to VSL, NIST and NPL, but not the dilution systems)
Permeation units	GC-FID GC-MS	Oxy-VOCs Terpenes	**Not yet** (SI-traceable portable generators developed but not routinely in use)
Dilution of terpenes in methanol + preconcentration on adsorption tubes	GC-FID GC-MS	Terpenes	**No**
Generation of 20-terpene mixtures in electropolished steel canisters	GC-FID GC-MS	Terpenes	**No**
Effective Carbon Number	GC-FID	NMHCs Oxy-VOCs Terpenes	**No**
Gravimetric dilution of pure substances following a hierarchy of standards	GC-MS	NMHCs Halogenated VOCs	**No**
Gas standards in cylinders	PTR-MS	NMHC Oxy-VOCs Terpenes	**No**
Liquid standards using a Liquid Calibration Unit	PTR-MS	NMHC Oxy-VOCs Terpenes	**No**
Ion transmission curve based on the kinetics of VOCs in the reaction chamber	PTR-MS	NMHC Oxy-VOCs Terpenes	**No**

Realization of SI-traceable reference gas mixtures (RGMs)

Despite progress done, **gaps for achieving SI-traceability** remain for most of the calibration strategies. The project "**Metrology for Climate Relevant Volatile Organic Compounds**" (**MetClimVOC**, 2020-2023) aims at covering these gaps through the realization of accurate, stable and traceable RGMs for VOCs relevant to climate change at atmospheric levels.

Dynamic generation of RGMs based on permeation (ISO 6145)

Permeation units contain the pure compound of interest (VOC) in liquid form. VOC in gaseous form is released through the polymeric membrane at specific permeation rates. The steps (all SI-traceable) to generate RGMs are described below.

1. Calibration of the permeation units

Permeation units are placed in a magnetic suspension balance (MSB; TA Instruments). Pressure, temperature and carrier gas flow are regulated within the MSB. After one week of membrane stabilisation, mass loss of the permeation unit with time (i.e. permeation rate) is estimated at different temperatures (min. 3 days per point) (Fig. 1).
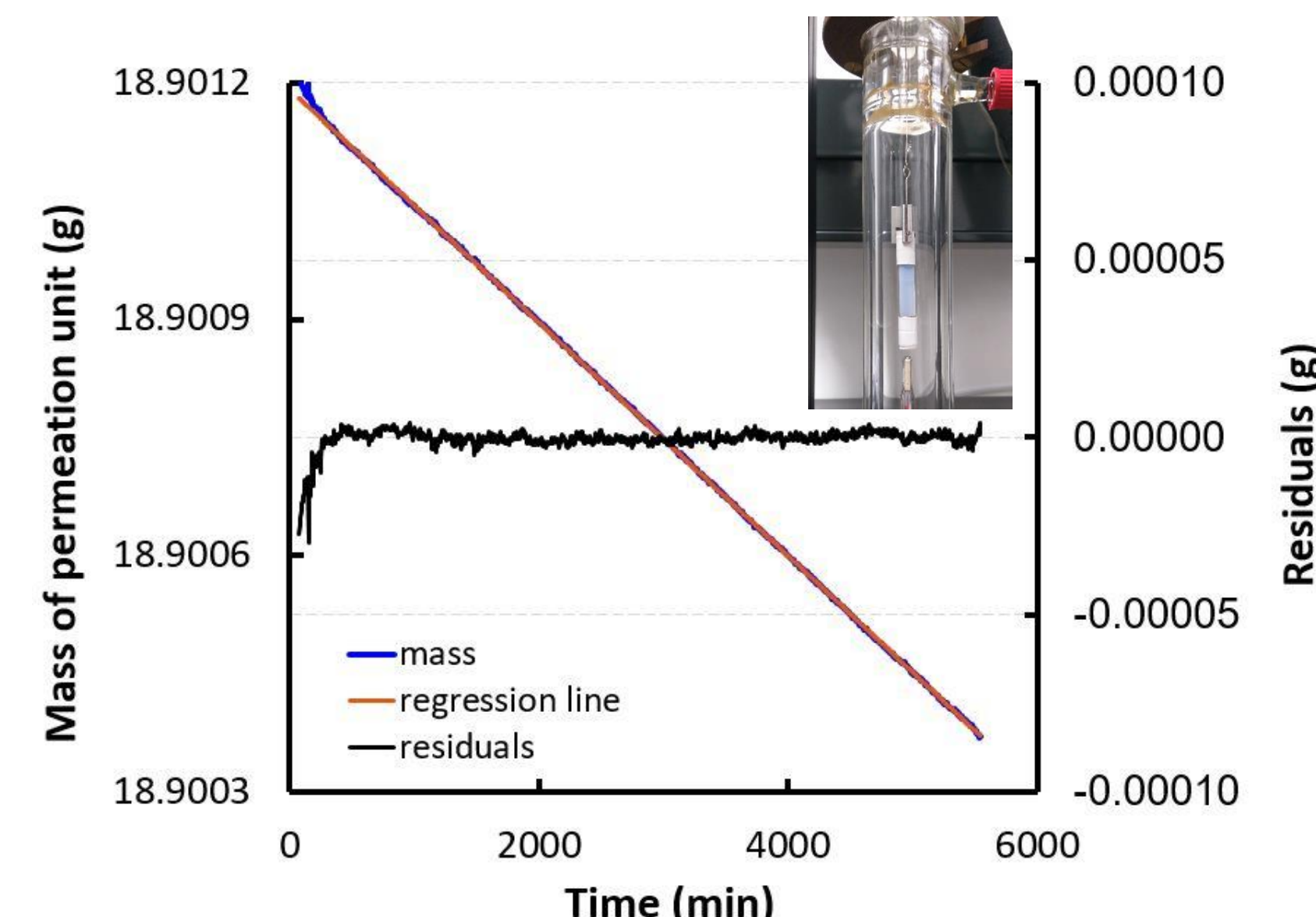

Fig. 1: Mass loss of an methyl vinyl ketone permeation unit with time

2. Generation of primary RGMs

Dilution systems (one and/or two dilution steps) are coupled to MSBs (Fig.2). These systems control pressure and mass flow rates of the carrier and dilution gas. RGMs at different amount fractions are generated by changing flow rates
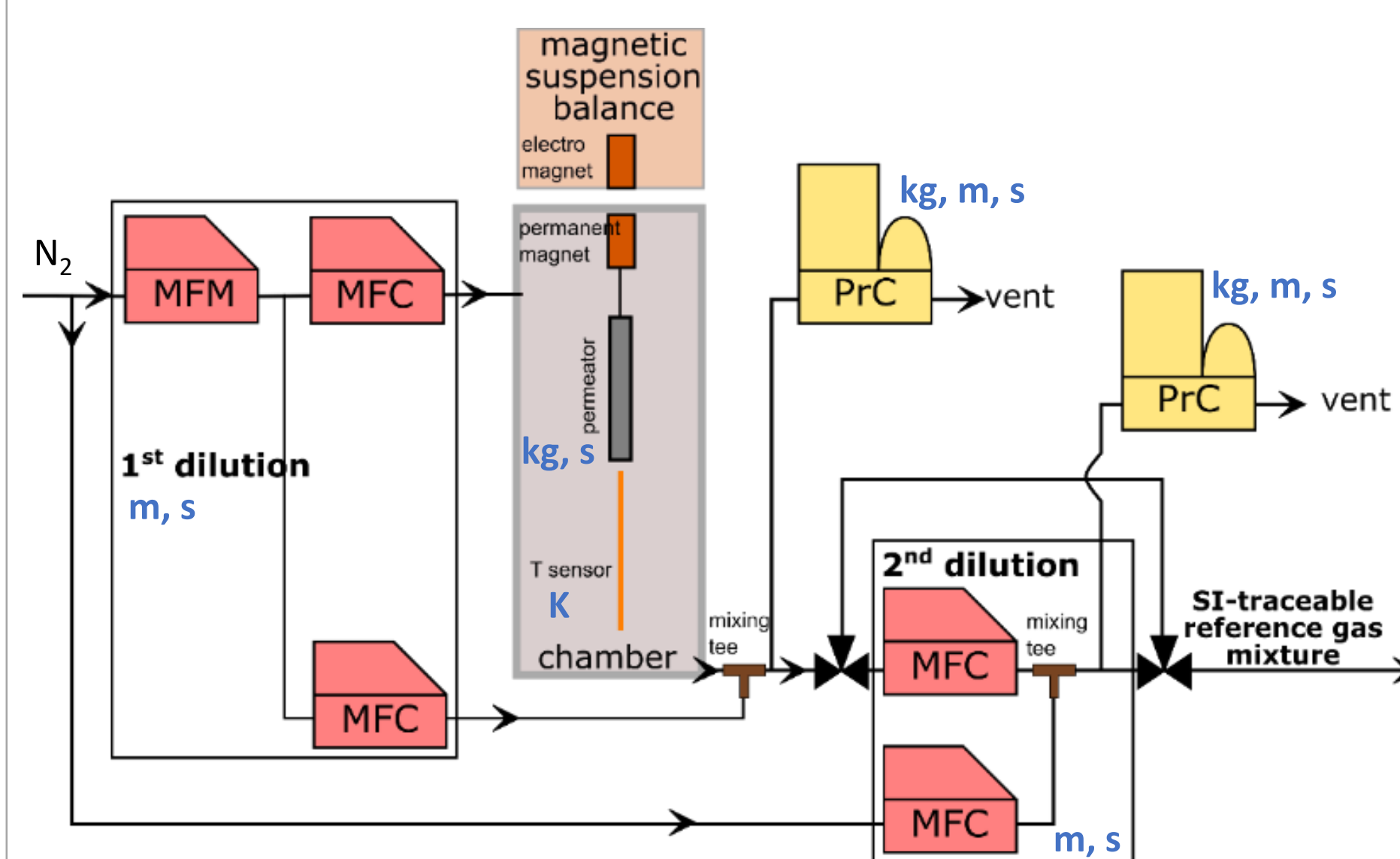

Fig. 2: Dilution system coupled to a magnetic suspension balance. SI-traceability indicated for the different elements of the system (in blue)

3. Stability, impurity and cross-contamination assessment

Periodic recalibration of the generation system elements, particularly permeation units, are needed to assess RGM stability. GC-FID and/or GC-MS are used to evaluate the purity of permeation units and sources of cross-contamination in the generation system.

4. Generation of secondary RGMs

Portable generators based on permeation (e.g. ReGaS2 (METAS)) can be used to generate secondary RGMs. In the case of ReGaS2, the calibration of its elements against METAS primary standards of flow, pressure and temperature ensures SI-traceability.
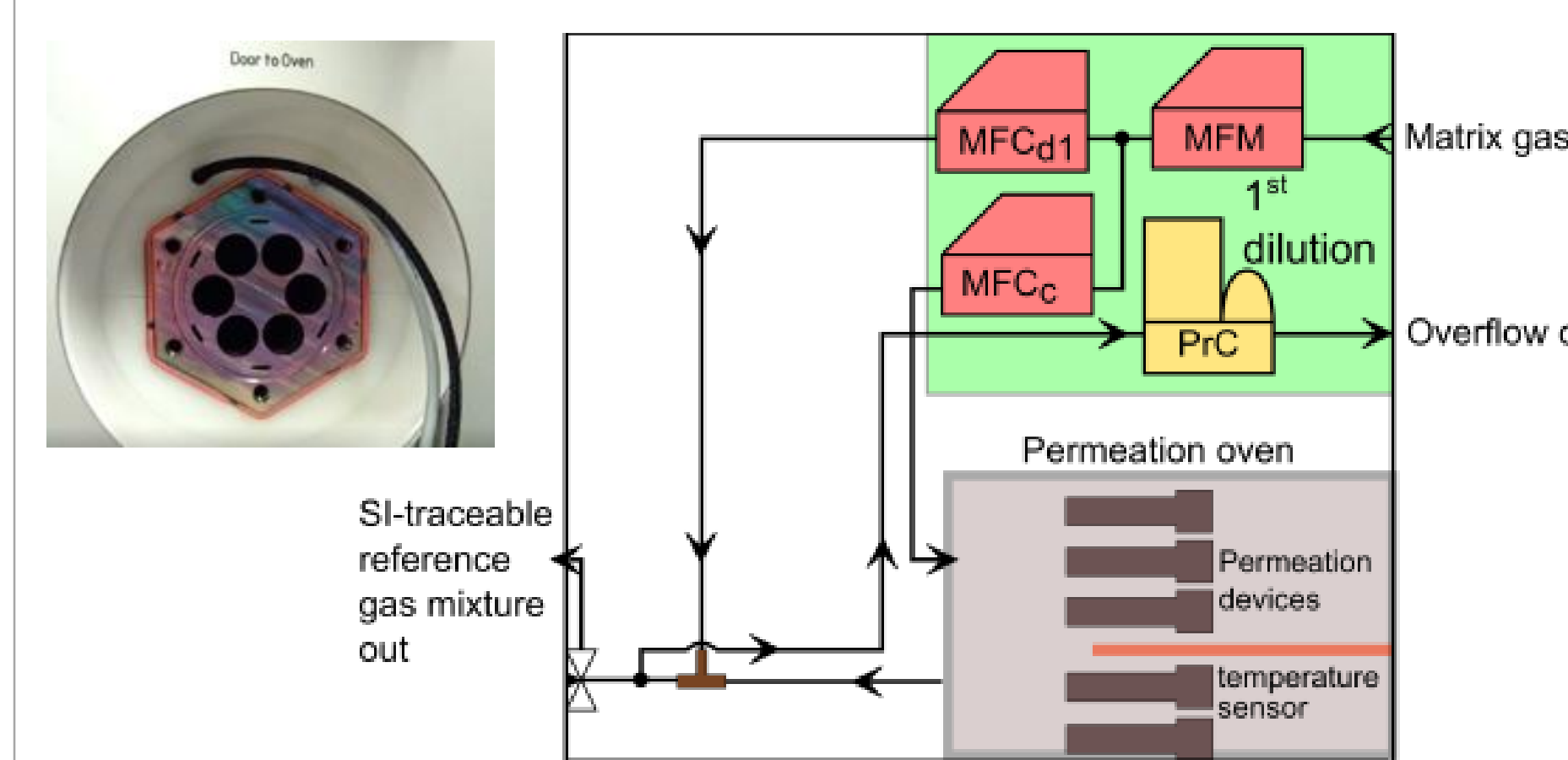

Fig. 3: Permeation oven and dilution system of METAS portable generator ReGaS2.

5. Uncertainty budget of the calibration

Each of the previous steps has an uncertainty associated to it (Fig. 4), which will contribute to the uncertainty budget of the calibration and, in turn, to the overall uncertainty of the measurement (uncertainty propagation according to the *Guide to the expression of uncertainty in measurement* (GUM JCGM 101:2008, BIPM)).
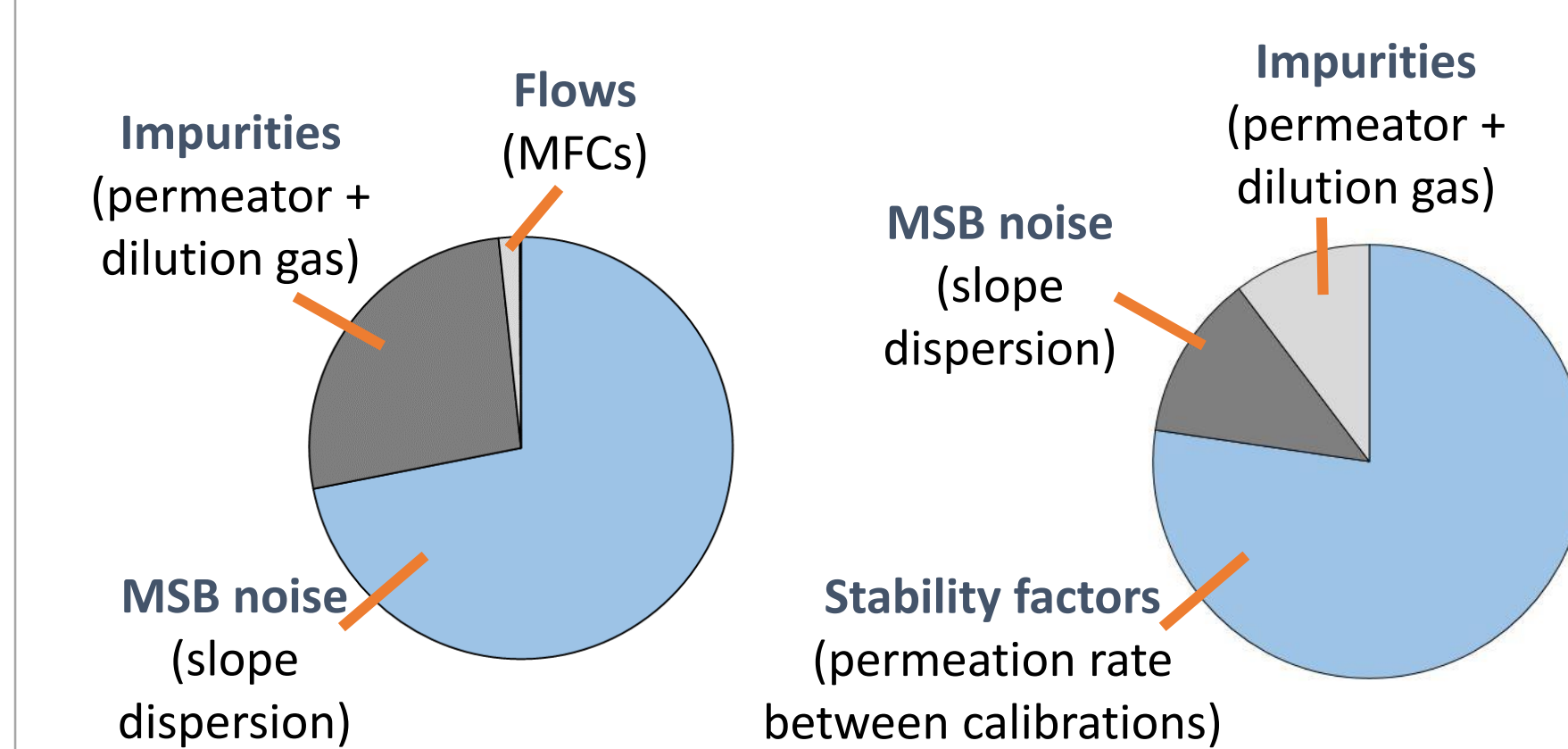

Fig. 4: Main contributors to the uncertainty of primary (left) and secondary (right) RGMs generated using the permeation method

Other contributors to be considered (site specific):

- potential **reactions** and **losses** in sampling and analytical system (e.g. lines, filters…)
- **analytical system** (e.g. stability, linearity…)
- **environmental conditions** (e.g. pressure, humidity, ozone and temperature range)

Further information

To find more about **MetClimVOC**:

- visit the website: https://www.metclimvoc.eu
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