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Federal Institute of Metrology METAS

New reference standards for fluorinated gases at pmol/mol (ppt, 10^{-12} mol/mol) concentrations



Myriam Guillevic
Céline Pascale
Bernhard Niederhauser



Empa

Materials Science and Technology

Simon A. Wyss
Martin K. Vollmer
Stefan Reimann



Dutch
Metrology
Institute

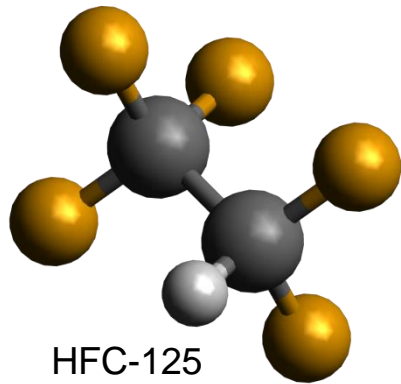
Gerard Nieuwenkamp



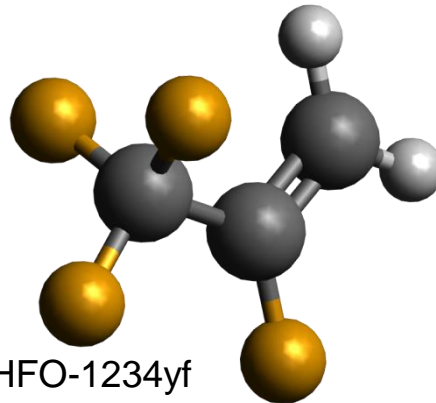
Martin Vicar

Objectives of the HIGHGAS project – F-gases

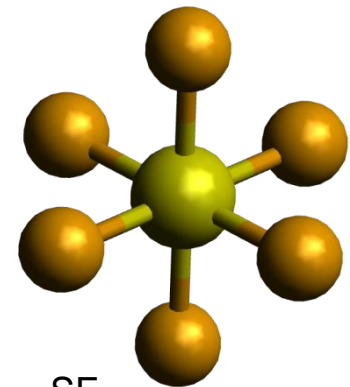
- To develop new dynamic generation methods for preparing traceable calibration gas mixtures
 - to better measure F-gases in the atmosphere (e.g. Empa)
 - to better estimate fluorinated gas emissions in Europe (AGAGE network, 4 stations in Europe)



HFC-125
1,1,1,2,2-Pentafluoroethane
 CF_3CHF_2



HFO-1234yf
2,3,3,3-tetrafluoropropene
 $\text{CH}_2=\text{CFCF}_3$



SF_6
Sulfure hexafluoride

Agenda

1. Dynamic dilution for pmol/mol (ppt) level SF₆ standard (Empa, METAS, CMI, VSL)

Gravimetric preparation + dynamic dilution

2. Reference gas mixture for F-gases (METAS, Empa)

Dynamic generation + dynamic dilution

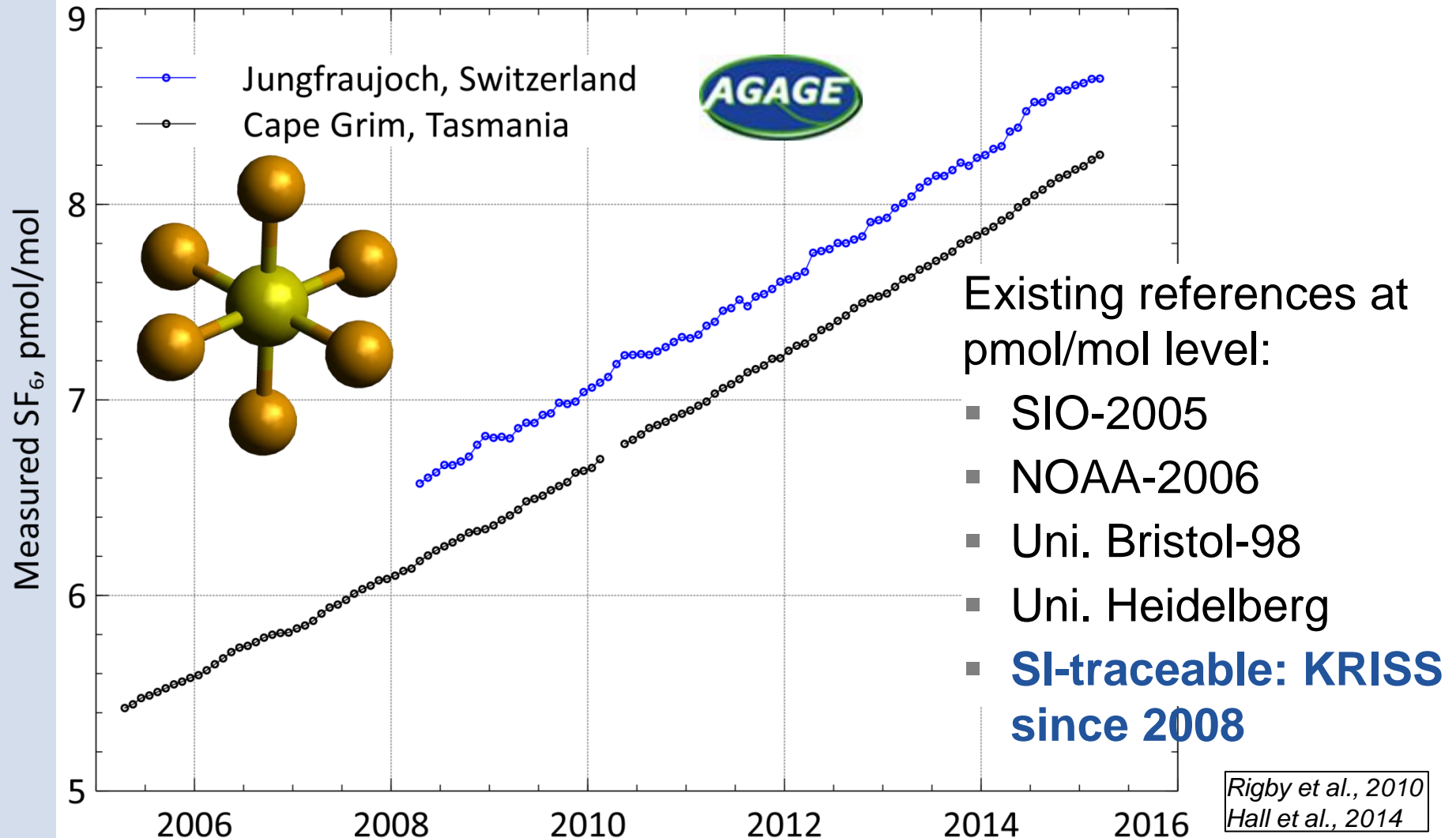
3. Novel portable device for field measurements (METAS, Empa)

Dynamic + all-in-one + portable

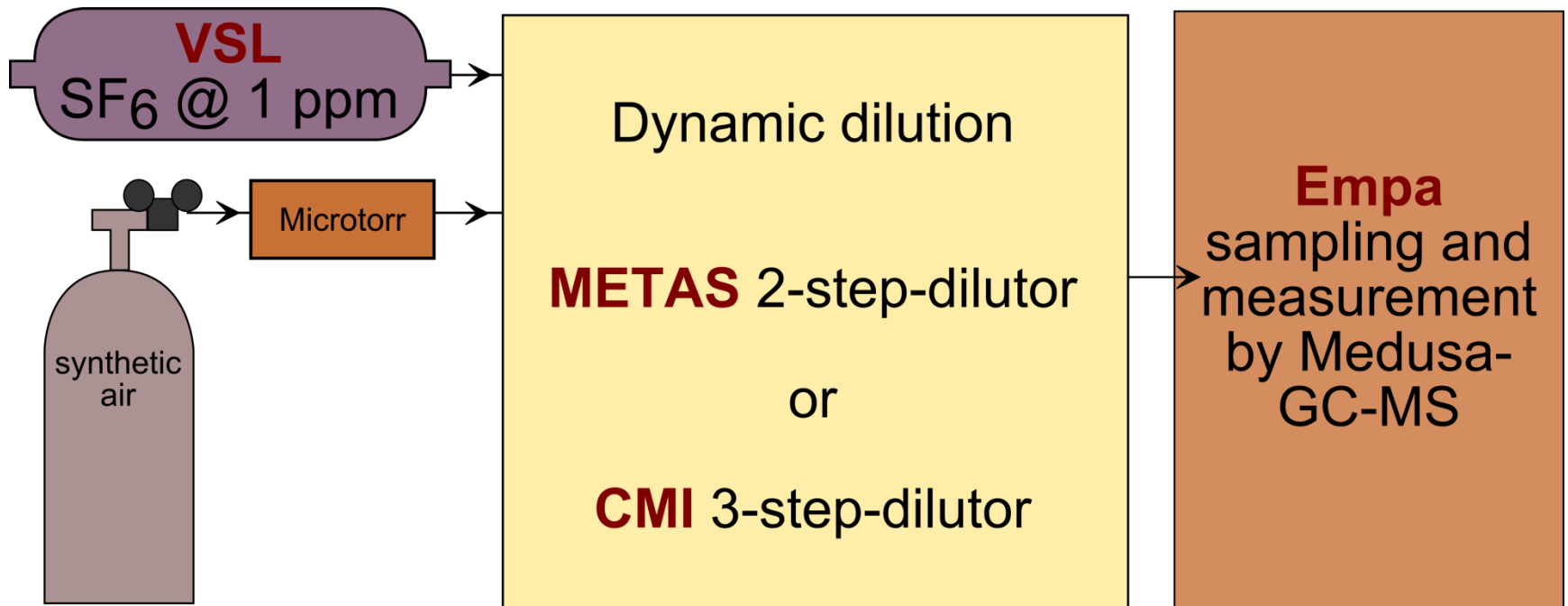
Note: all uncertainties presented hereafter are with $k=2$ (95% confidence interval)

Dynamic dilution for pmol/mol level SF₆ standard

- Present-day concentration: ~8.65 pmol/mol at JFJ, CH
- Annual increase: ~0.25 pmol/mol /yr (~3%)



Dynamic dilution for pmol/mol level SF₆ standard



Preparation of reference gas cylinder at VSL

- The 1 $\mu\text{mol/mol}$ (ppm) SF_6 mixture is prepared by **gravimetry** in accordance with ISO 6142: Gas analysis – Preparation of calibration gas mixtures – gravimetric method
- The balance gas is **synthetic air** : 20.9% O_2 in N_2 (argon is not present in the mixture)
- Analyses for validation are performed with an Agilent GC with a pulsed discharge helium ionization detector (PDHID)
- Calibration of the GC-PDHID is performed with VSL's Primary Standard Reference Materials, within the scope of an ISO 17025 accreditation. The **uncertainty is accepted in the CMC database of the BIPM: 1% at 1 $\mu\text{mol/mol}$**

Purification of matrix gas

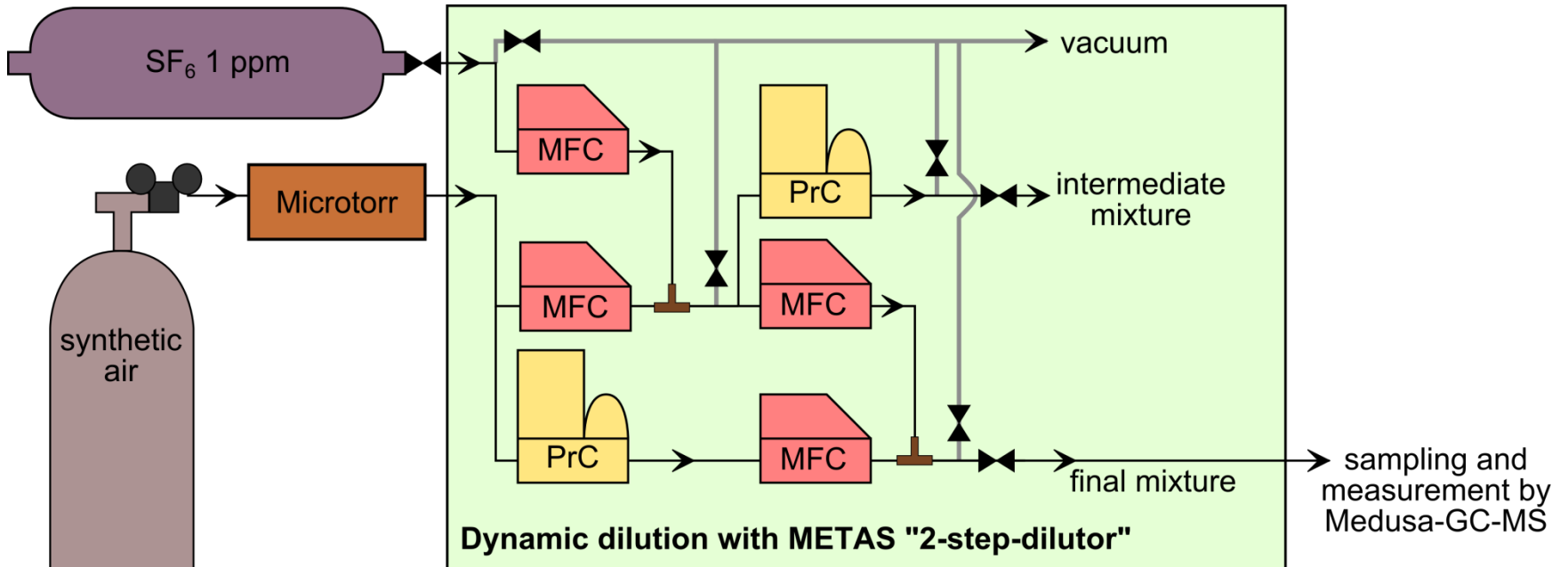
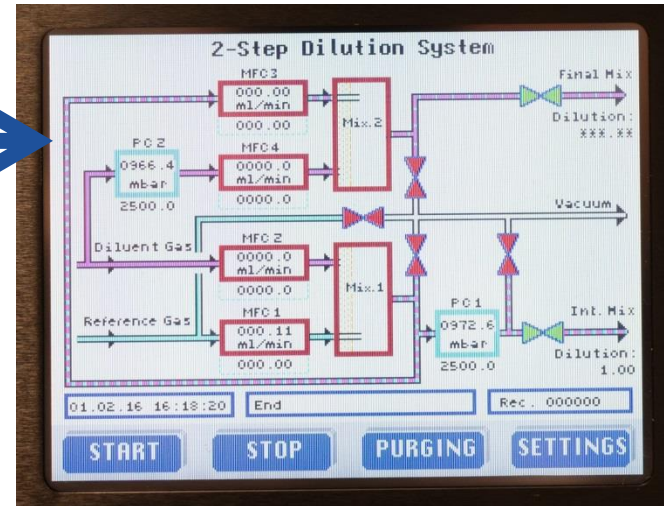
«Microtorr», SAES Getters, model MC 400-23V

- Commercially available purifier
- Works at ambient temperature
- Based on inorganic sorbent materials
- Acids, bases, organics and refractory compounds < 10 pmol/mol in purified air
- To our knowledge never tested for F-gases

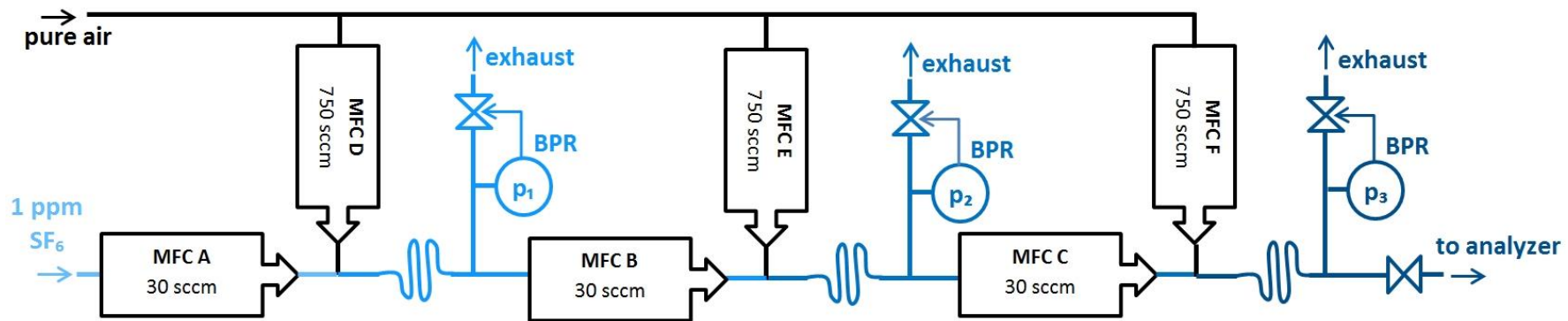
- Flow normally used: 1 L/min
- Purified SA was measured by Medusa-GCMS system to check for residual compounds



Two-step-dilutor from METAS

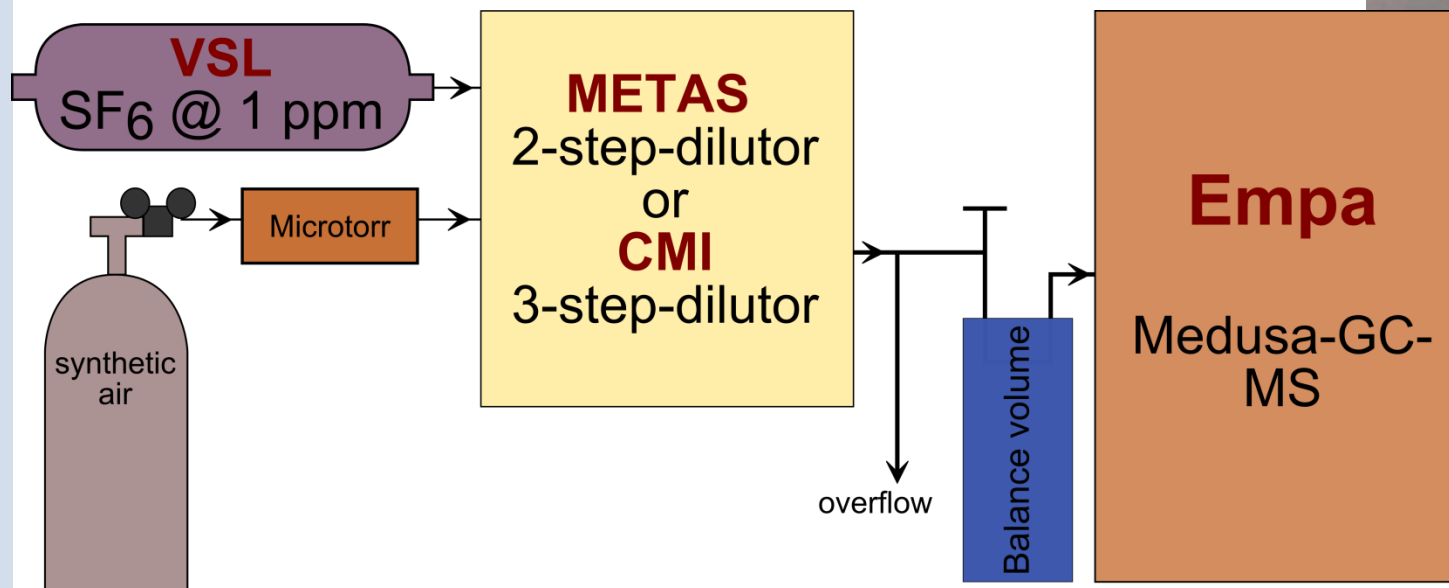
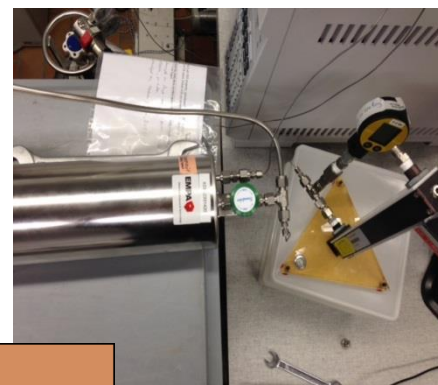


Three-step-dilutor from CMI



Measurement of diluted mixtures with the Medusa-GC/MS

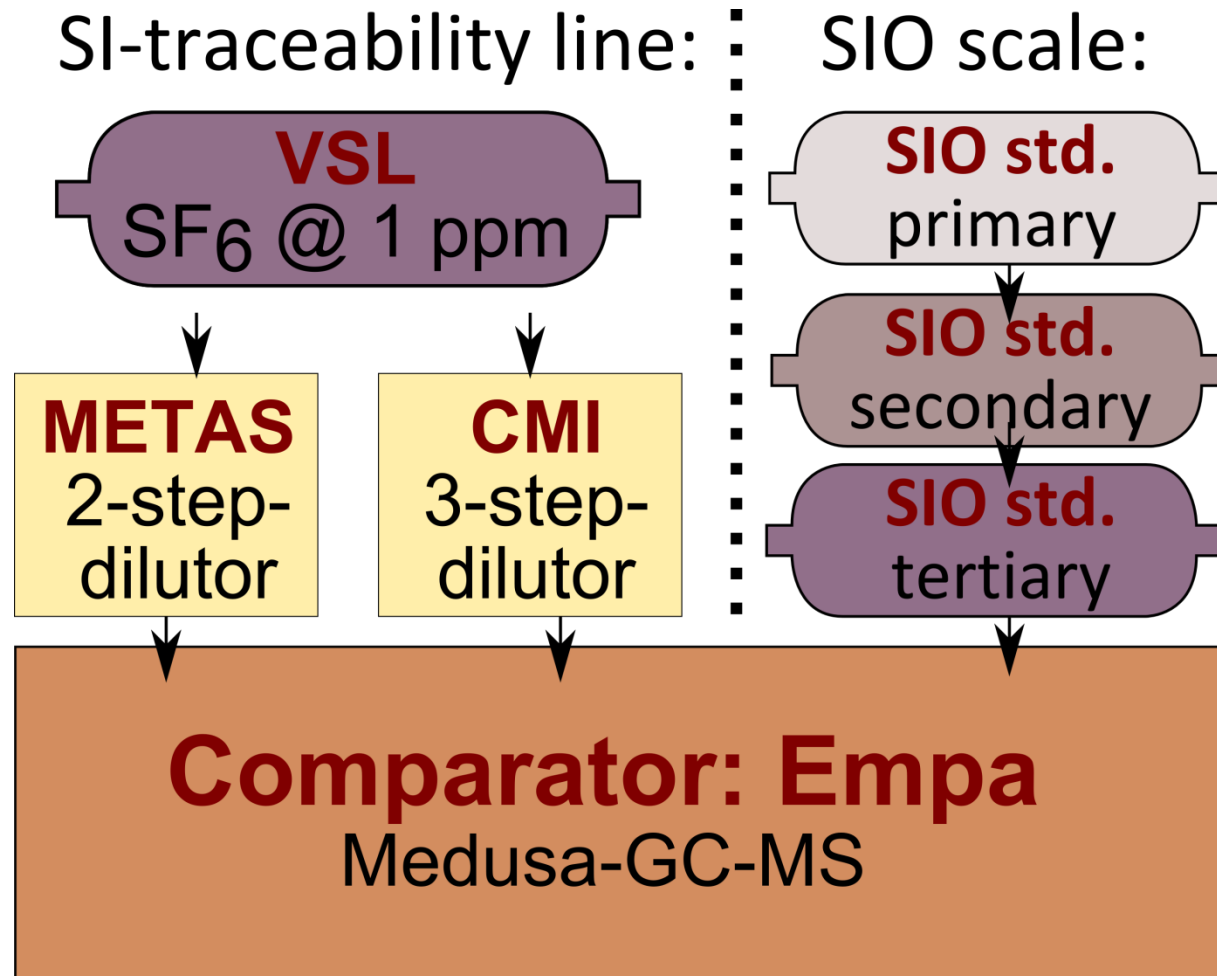
- Ensure a constant MFC downstream pressure by using an overflow and a ballast volume
- Sampling flow of the Medusa set to 70 mL/min
- Total outlet flow:
 - Of the 2-step dilutor: 4500 mL/min
 - 3-step-dilutor: 780 mL/min



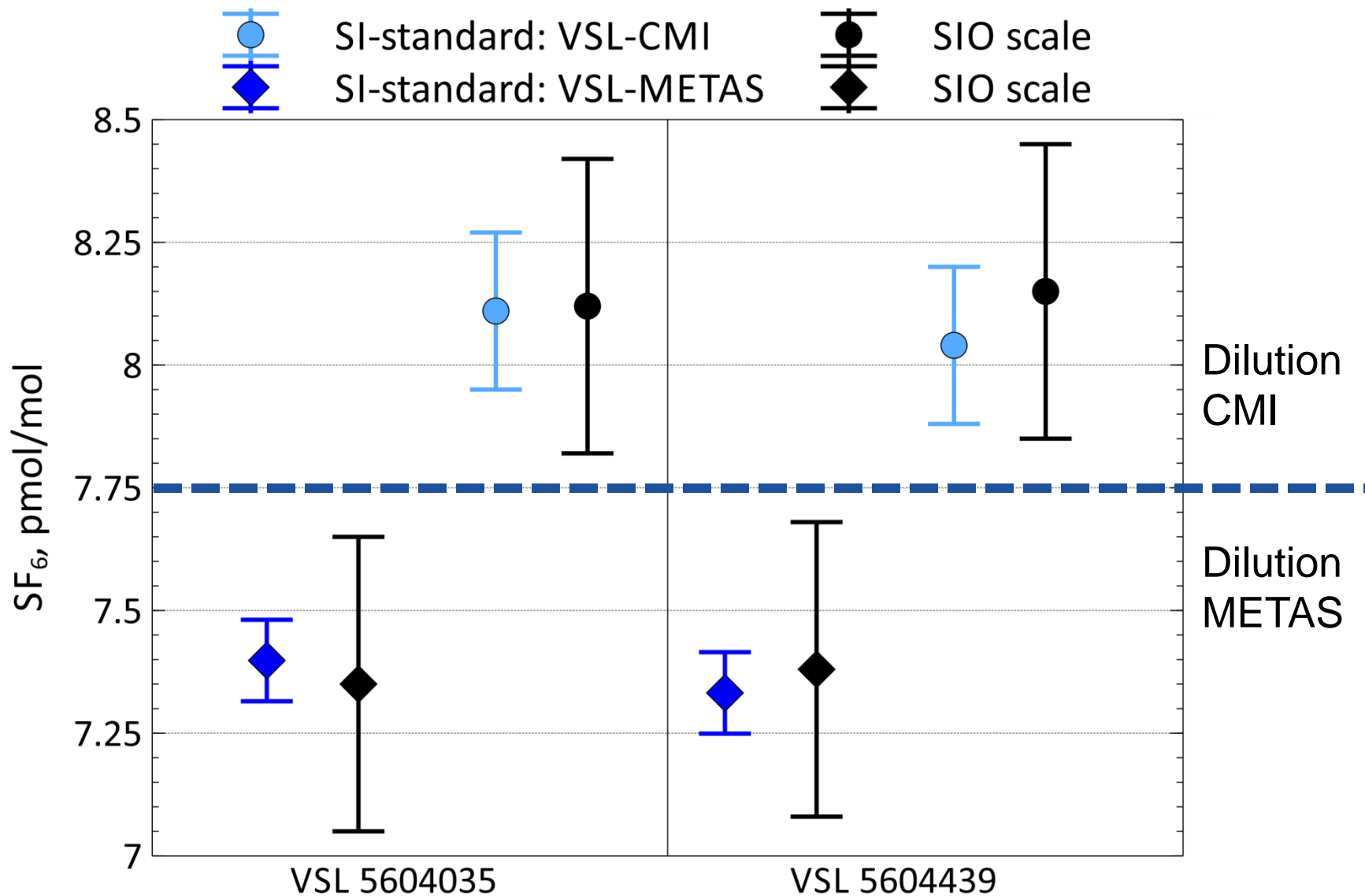
Measurement of diluted mixtures with the Medusa-GC-MS



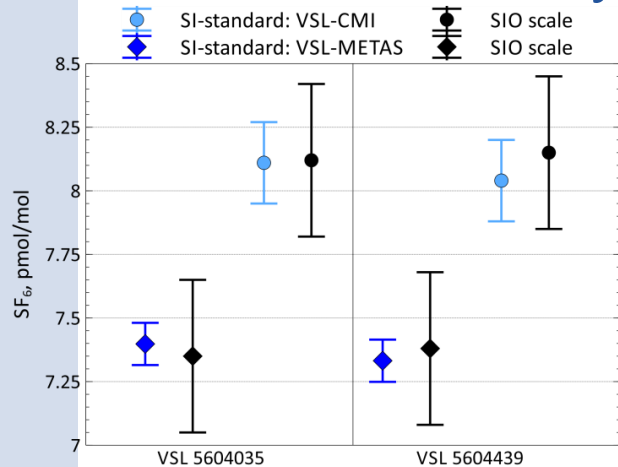
Comparison: SI-traceable standard and SIO scale



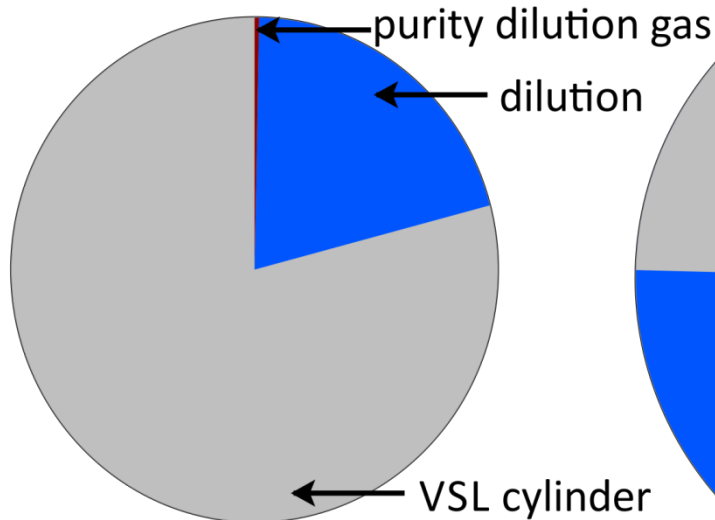
Comparison: SI-traceable standards and SIO scale



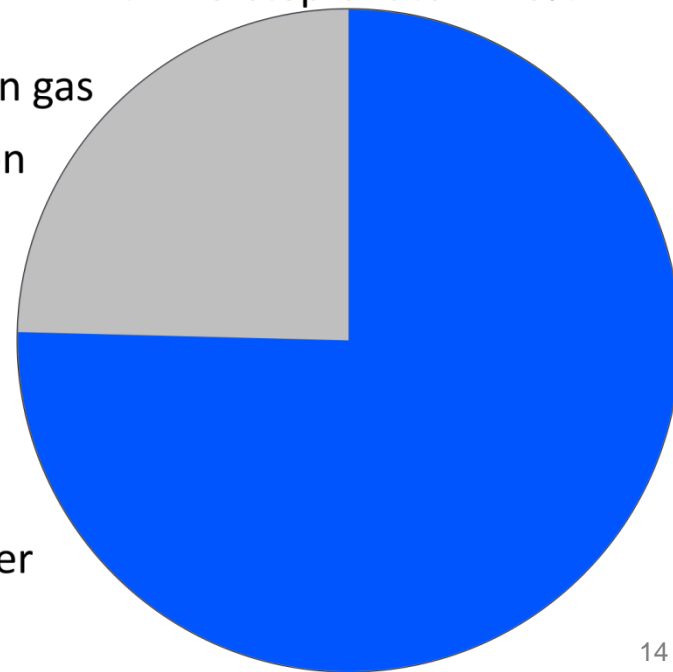
Comparison: SI-traceable standard and SIO scale Uncertainty budget



VSL diluted by:
METAS 2-step-dilutor: 1.1%

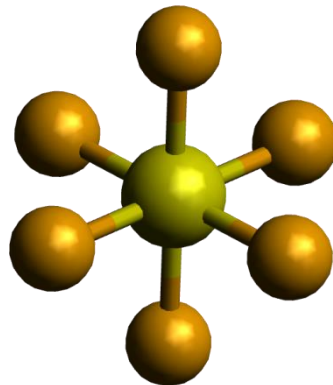


CMI 3-step-dilutor: 2.0%



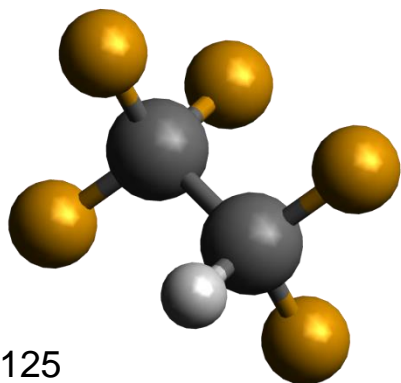
Dynamic dilution of SF₆ - conclusion

- Construction and validation of a 3-step-dilutor from CMI for SF₆
- Validation of a 2-step-dilutor from METAS for SF₆
- Comparison of a new SI-traceable SF₆ standard at pmol/mol level in agreement with existing SIO scale
- Expanded uncertainty for SI-standards less than our target of <3%

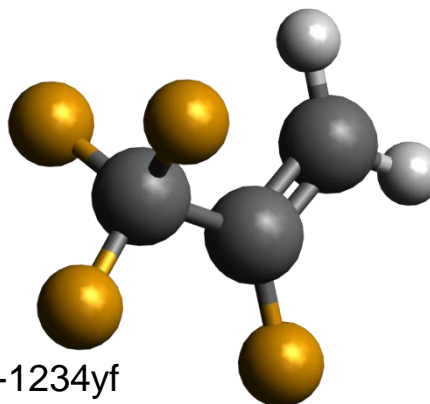




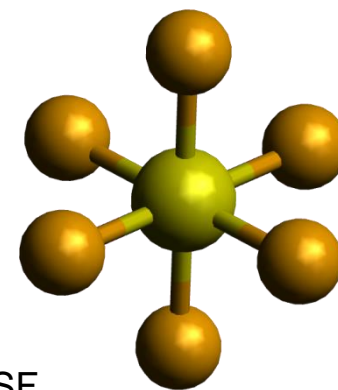
2. Single component reference gas mixture for F-gases



HFC-125
1,1,1,2,2-Pentafluoroethane
 CF_3CHF_2



HFO-1234yf
2,3,3,3-tetrafluoropropene
 $\text{CH}_2=\text{CFCF}_3$



SF_6
Sulfure hexafluoride



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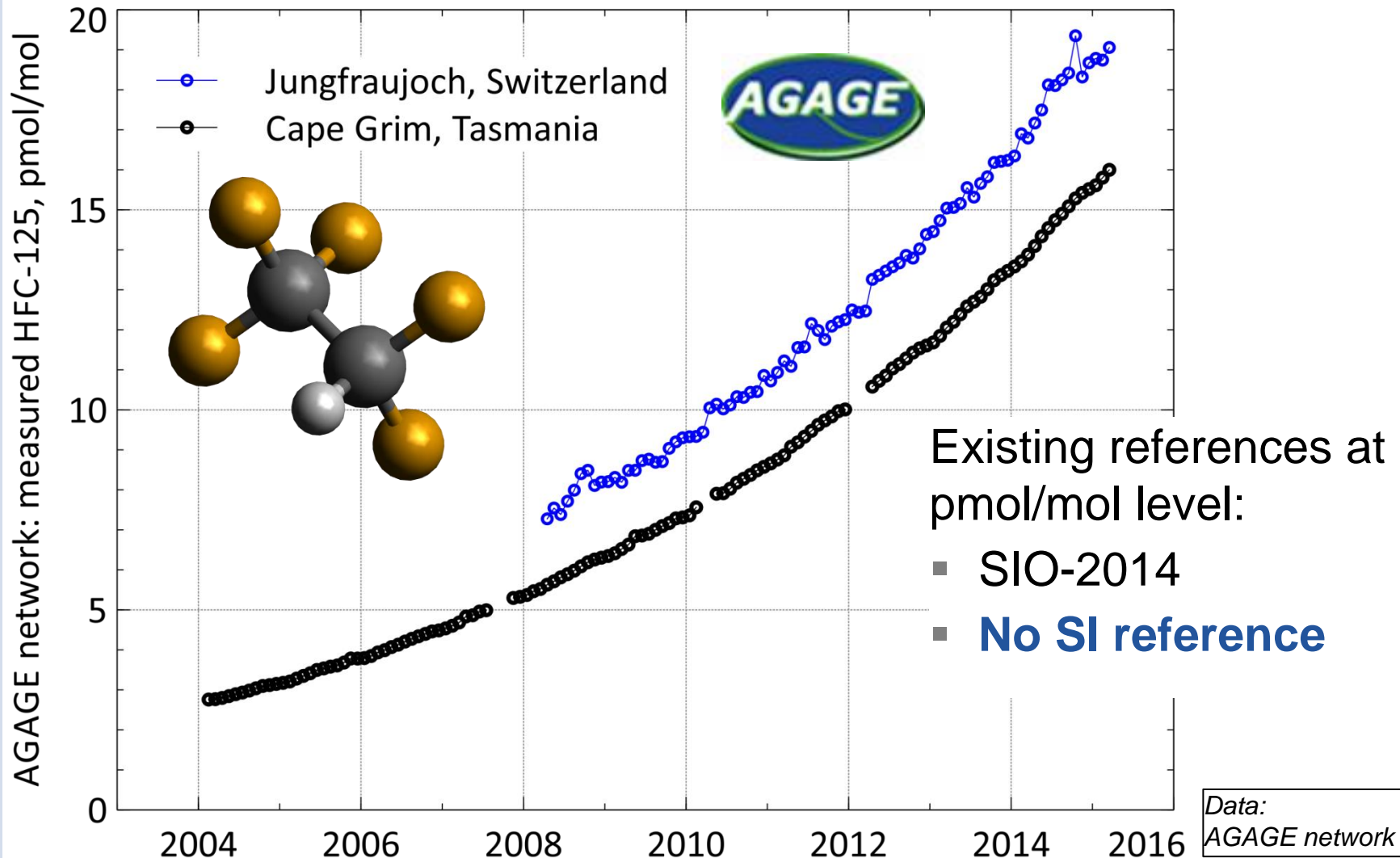
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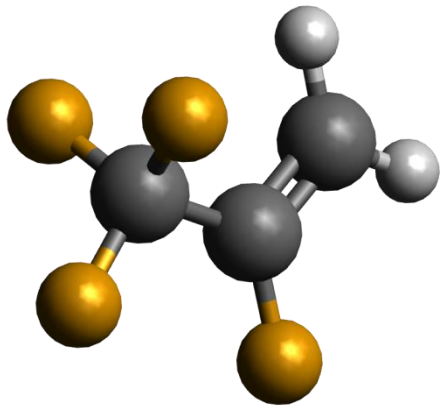
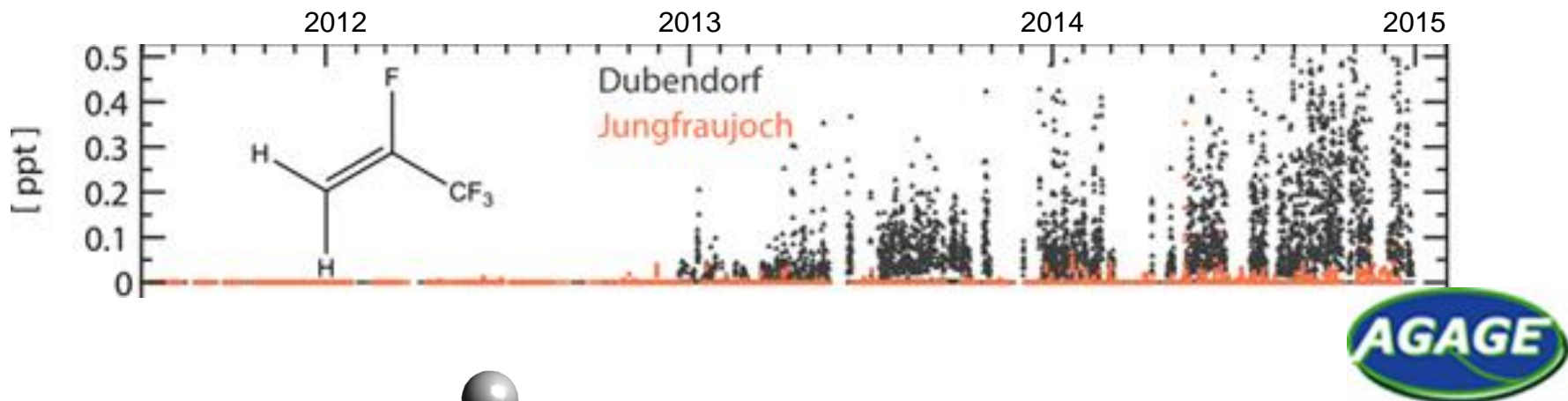
HFC-125: used as refrigerant

- Present-day concentration: ~ 19.05 pmol/mol at JFJ, CH
- Annual increase: ~ 2 pmol/mol /yr ($\sim 13\%$)



HFC-1234yf

- Last generation F-gases, progressively incorporated in car air conditioning systems
- Already detectable in the atmosphere



Existing references at pmol/mol level:

- Empa-2013
- **No SI reference**

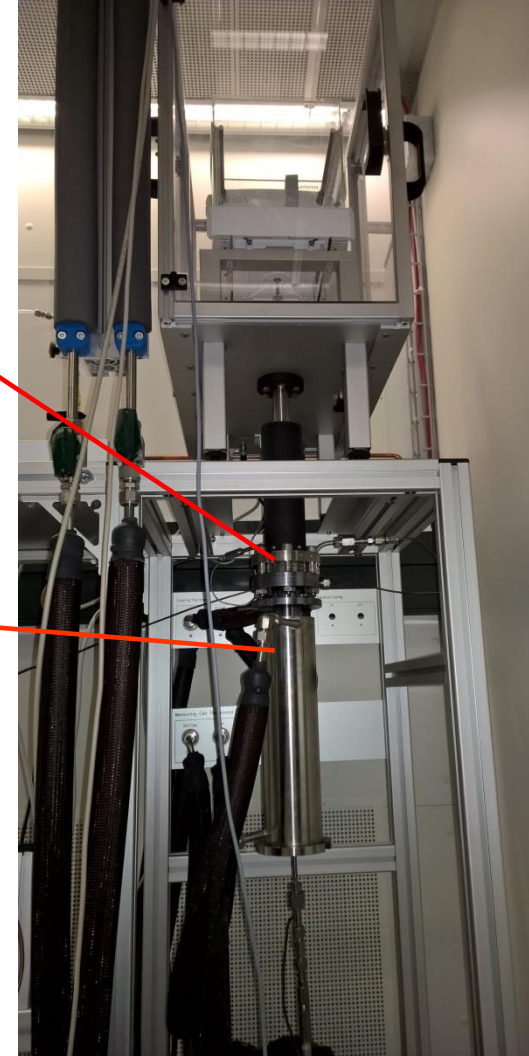
Vollmer et al., 2015

Dynamic generation by permeation at nmol/mol levels

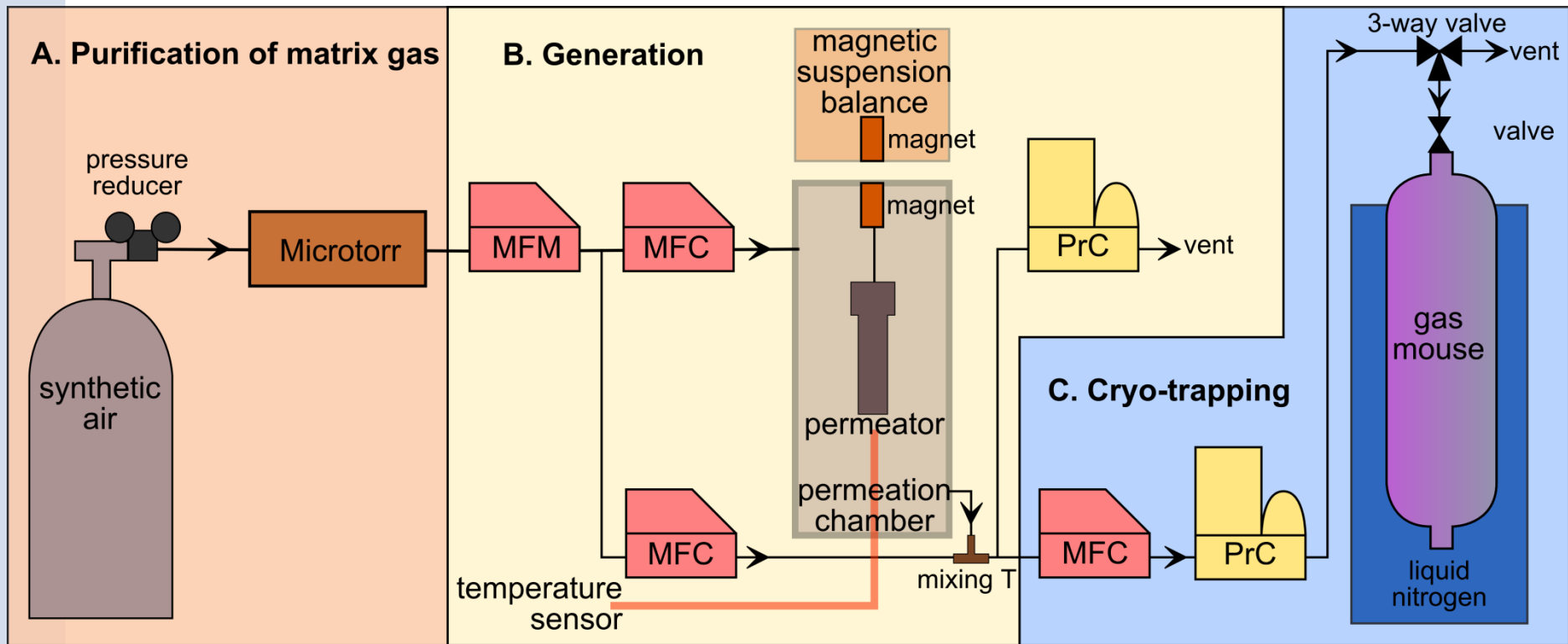
- New magnetic suspension balance tested at METAS:
 - stainless steel
 - silconert coating
 - Pressure up to 6 bara



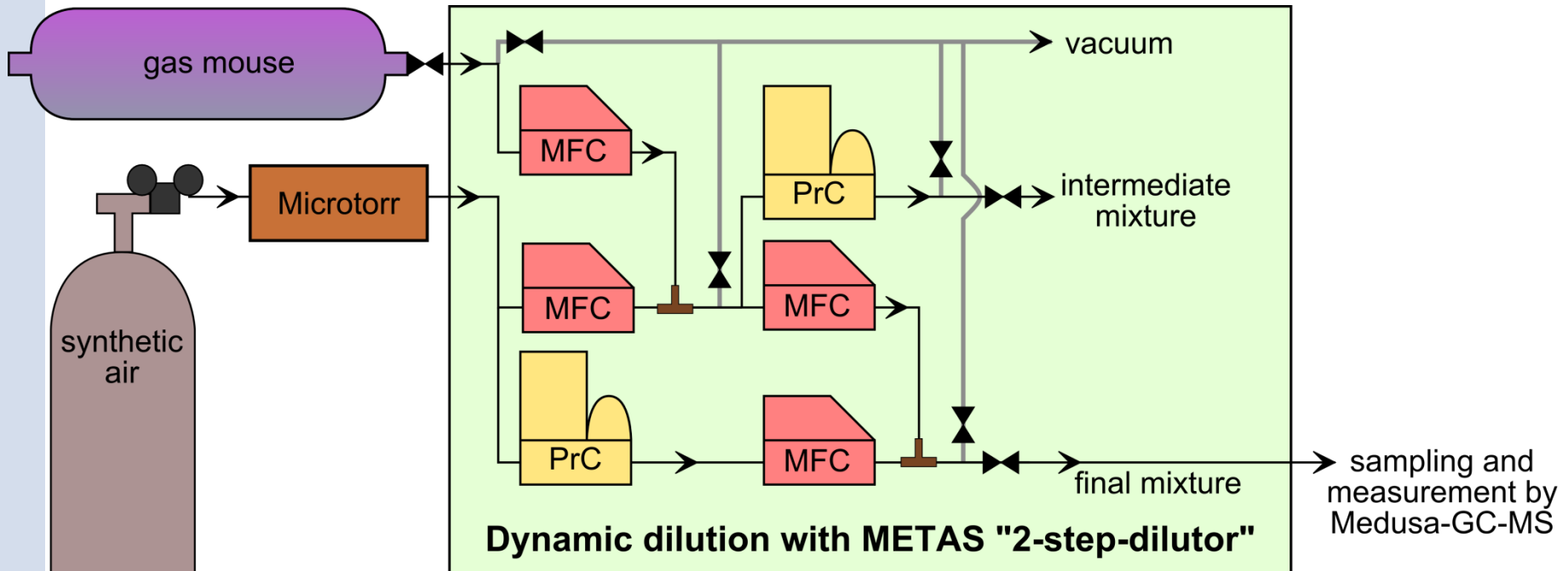
Permeator for HFC-125,
Fine Metrology



Dynamic generation at nmol/mol levels: overview



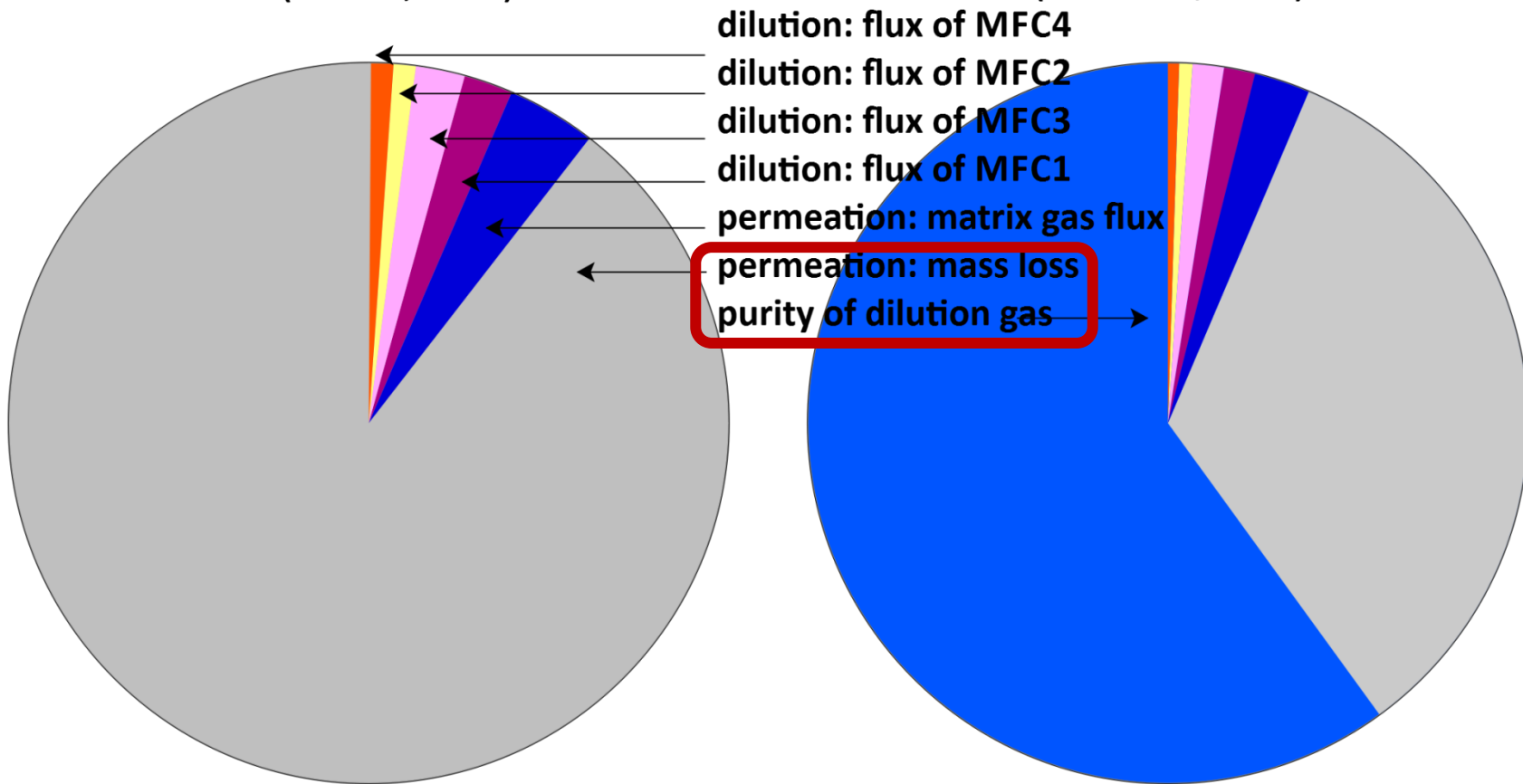
Method overview : dynamic dilution down to pmol/mol levels (close to ambient air)



Diluted mixtures: assigned values and uncertainty budget

HFC-125: $17.11 \pm 0.34 \text{ pmol} \cdot \text{mol}^{-1}$
($\pm 2 \%$, $k=2$)

HFO-1234yf: $2.14 \pm 0.06 \text{ pmol} \cdot \text{mol}^{-1}$
($\pm 2.5 \%$, $k=2$)

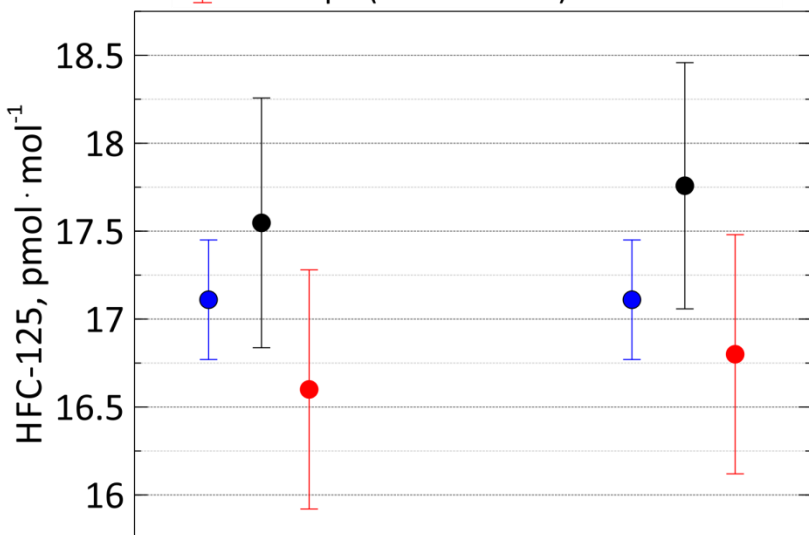


→ Will be improved in 2016-2017

Results: comparison to existing references

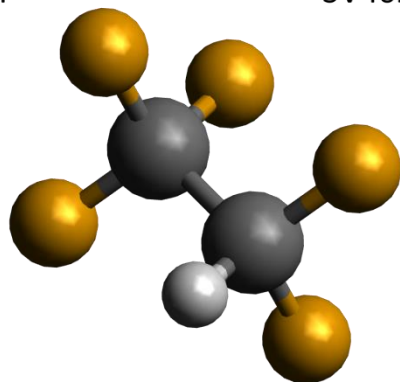
F-gases: amount of substance fraction in diluted mixtures, $\text{pmol} \cdot \text{mol}^{-1}$ (ppt)

- METAS (SI-standard: METAS-2015)
- Empa (scale: SIO-14)
- Empa (scale: NOAA)

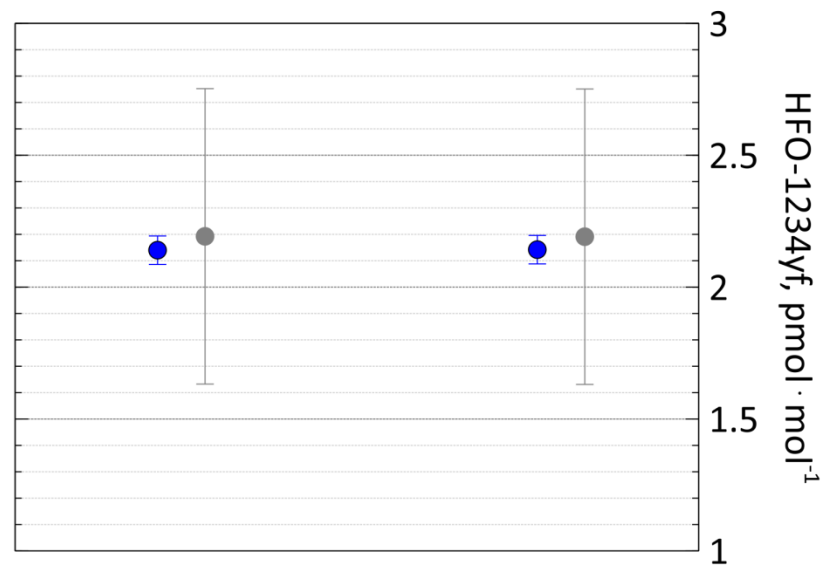


SV4034

SV4020

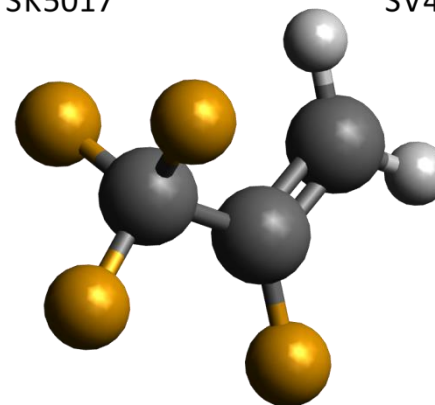


- METAS (SI-standard: METAS-2015)
- Empa (scale: Empa-2013)



SK5017

SV4042



Conclusion

- Used **dynamic** generation methods to make reference gas mixtures for F-gases
- Developed a method for pressurisation by **cryo-trapping**
- Made **SI-traceable** reference gas mixtures at ambient concentration (pmol/mol levels) with an expanded uncertainty (k=2) of:
 - 2% for HFC-125 @ 17.11 pmol/mol
 - 2.5% for HFC-1234yf @ 2.14 pmol/mol
- METAS-2015 reference uncertainty \leq existing references (SIO, Empa) and results in agreement



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3. Design for a novel portable device to generate F-gases reference gas mixtures for field measurement



METAS



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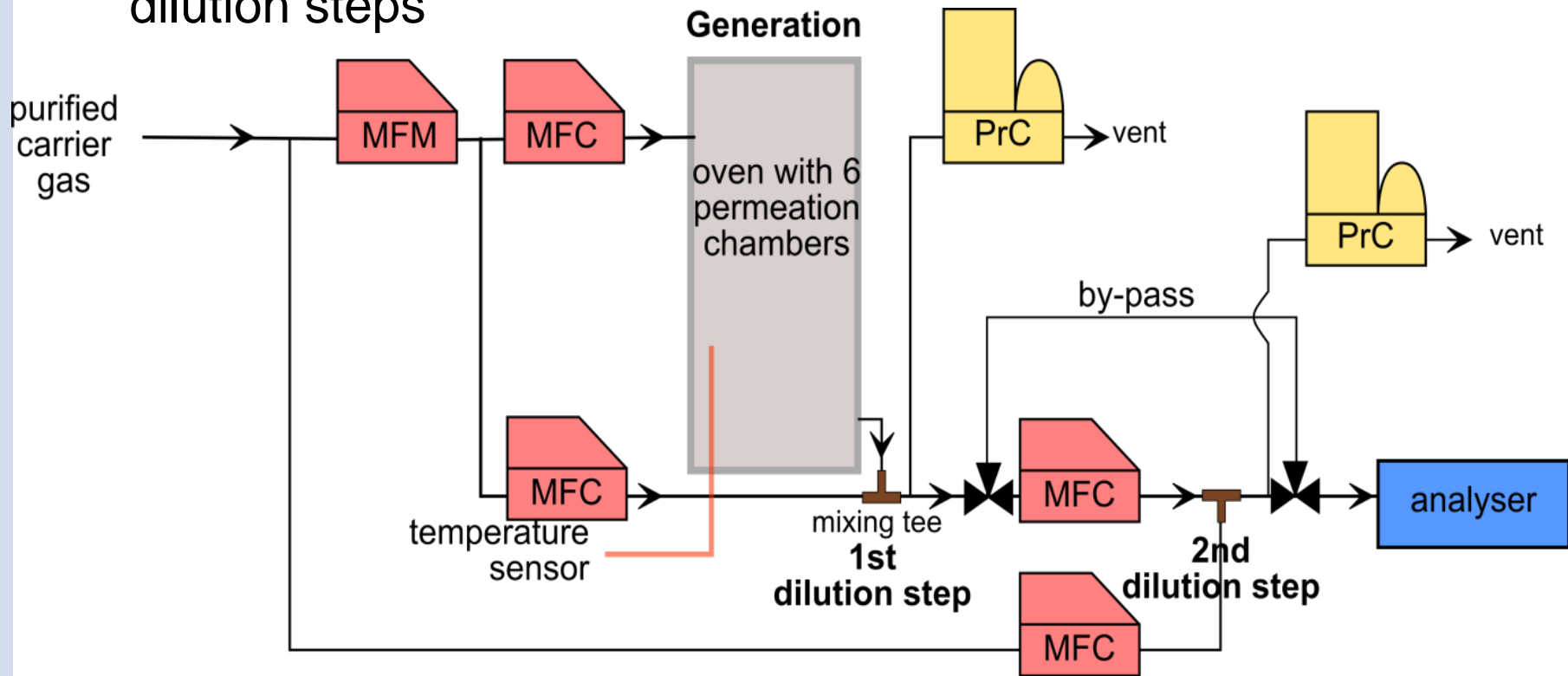
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Design – portable generator

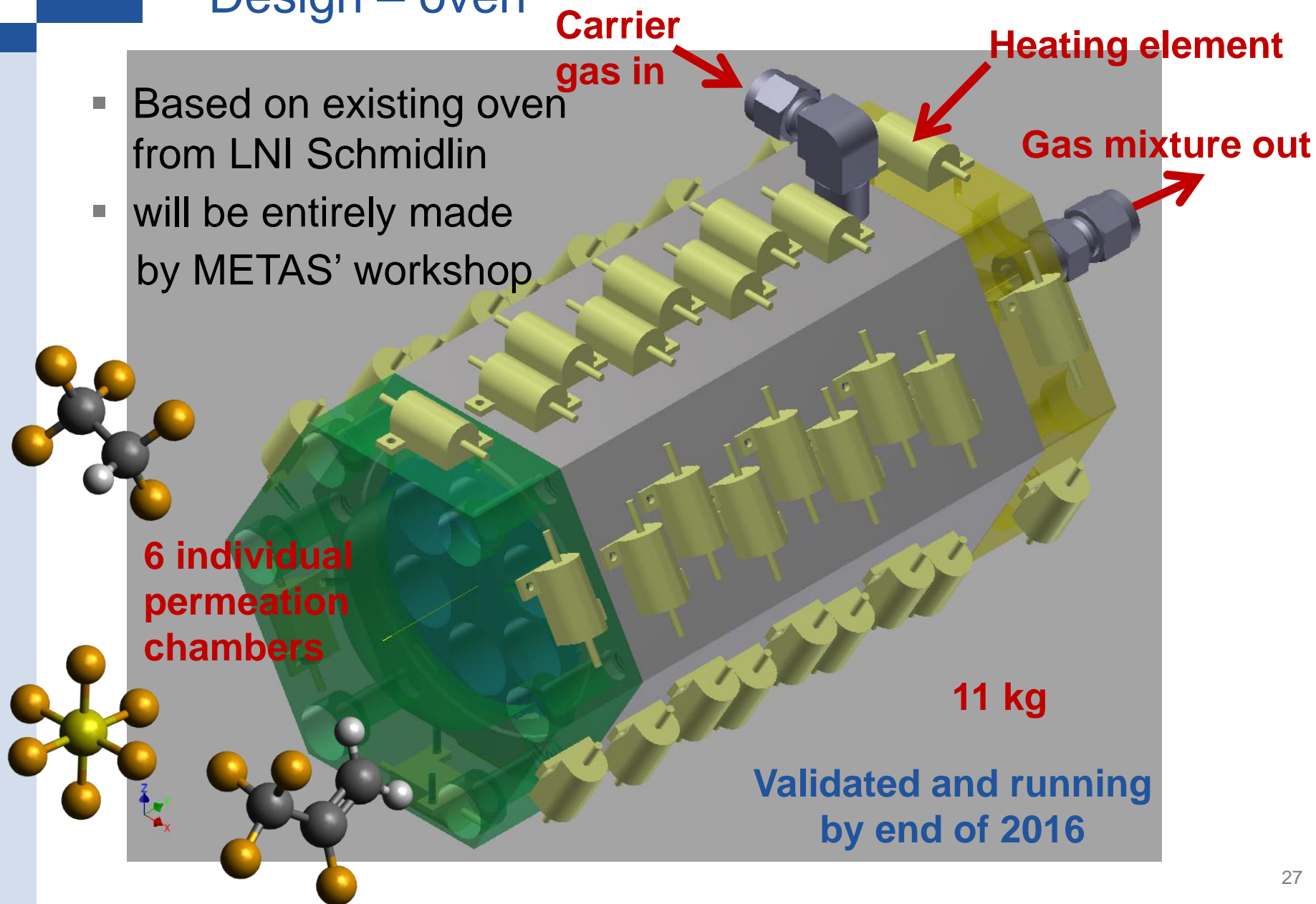
- **All-in-one, portable setup:** Generation of multi-component reference gas mixture by combining permeation and dynamic dilution steps



- Inspired by METAS' 2-step-dilutor and «Traceable mobile permeation generator» validated for NO₂ in the EMRP ENV01 «MACPoll» project

Design – oven

- Based on existing oven from LNI Schmidlin
- will be entirely made by METAS' workshop



Thank you for your attention

Questions?

