



# METAS

AtmoChem-ECV



## EMRP

European Metrology Research Programme  
■ Programme of EURAMET



The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

# SI-traceable reference gas mixtures for VOCs and water vapour at atmospheric concentration produced dynamically with a portable generator

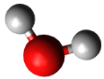
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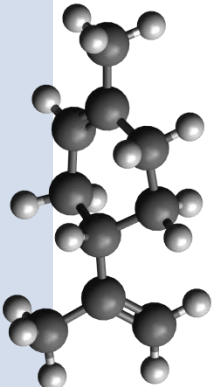
## Metrological traceability

- **Traceability**: measurement linked to the definition of SI-units through an unbroken chain of calibrations – m, kg, s, K, mol
- **Measurement uncertainty**: estimation of possible sources of uncertainties. Needed when comparing results obtained from different methods.
- **Method validation**: evaluation of all influencing parameters
- **Results independant of method, time and place**

# Target molecules



- Unstable in cylinders at atmospheric concentration
- Effects of adsorption/desorption on surfaces
- Any substance that can be filled as a liquid into a permeator



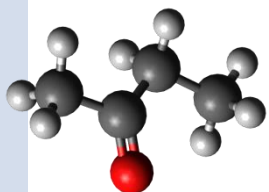
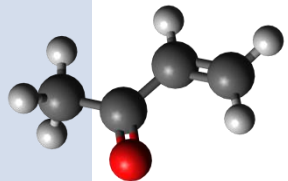
- Water vapour 1- 10  $\mu\text{mol/mol}$  (ppm)
- Ammonia  $\sim\text{nmol/mol}$  (ppb)
- Fluorinated gases : HFCs, HCFCs...  $\text{pmol/mol}$  (ppt)
- Volatile organic compounds (ppb):

- (R)-limonene

- $\alpha$ -pinene

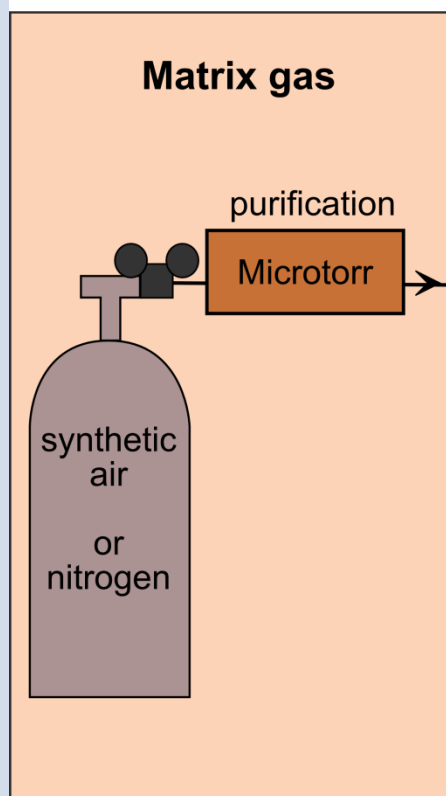
- MVK or butenone,  $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$

- MEK or butanone,  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$



## Method overview

Successfully applied to: NO<sub>2</sub>, water vapour, BTEX (benzene, toluene, ethylbenzene, xylene), NH<sub>3</sub>, HFC-125, HFC-1234yf, **at atmospheric concentration**



### 1. Matrix gas purification

# 1. Purification of matrix gas in 2 steps

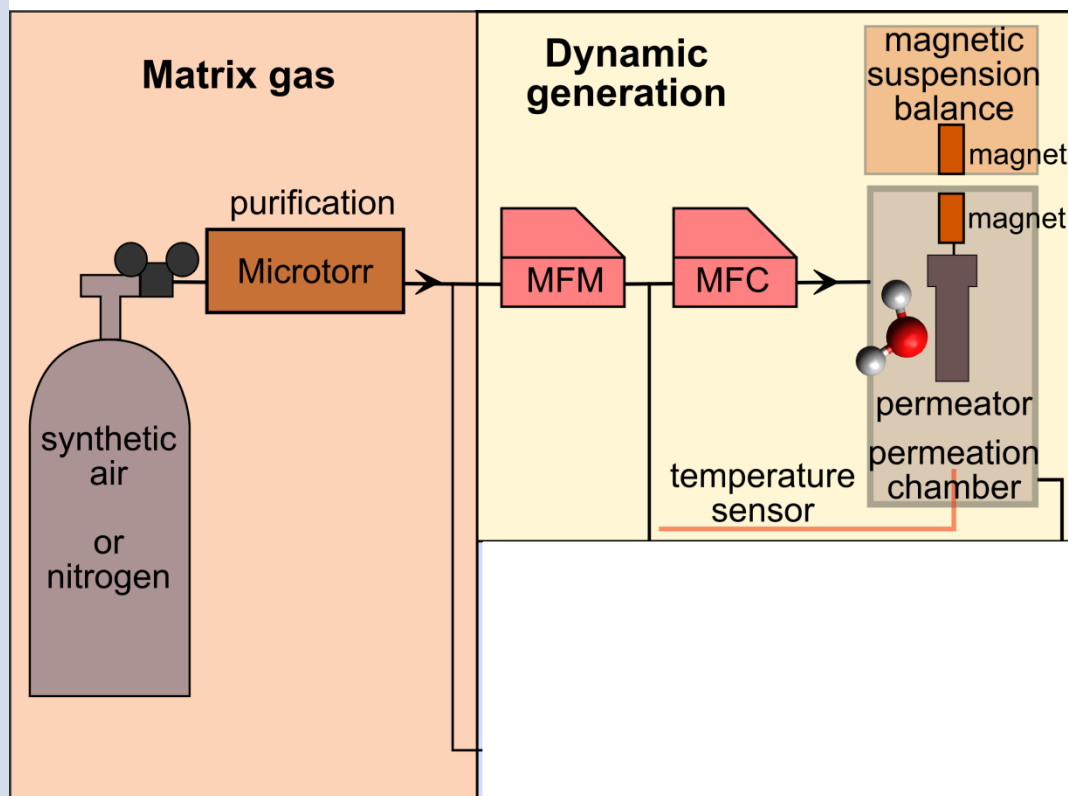
- 1) clean dry air /nitrogen in cylinder
- 2) further purification with commercially available cartridge « MicroTorr », SAES Getters

- Flow normally used: 1 L/min
- Purified nitrogen measured by CRDS “LaserTrace” from TigerOptics
- Minimum reached : 7 ppb water in nitrogen
- Currently testing efficiency to purify from VOCs

See talk by R. Pearce this session 16:00



# Method overview



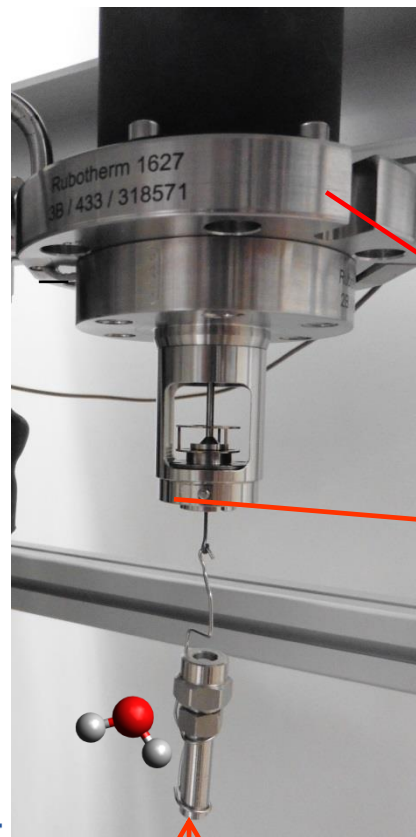
2. Adding pure substance to matrix gas

## 2. Adding pure substance to matrix gas

- Dynamic : continuously produced over time
- New magnetic suspension balance tested at METAS:

- stainless steel
- SilcoNert2000 coating
- Temperature control 30-70°C
- Pressure control up to 6 bar-a

$$\text{Molar fraction} \propto \frac{\text{mass loss rate}}{\text{total carrier gas flow}}$$

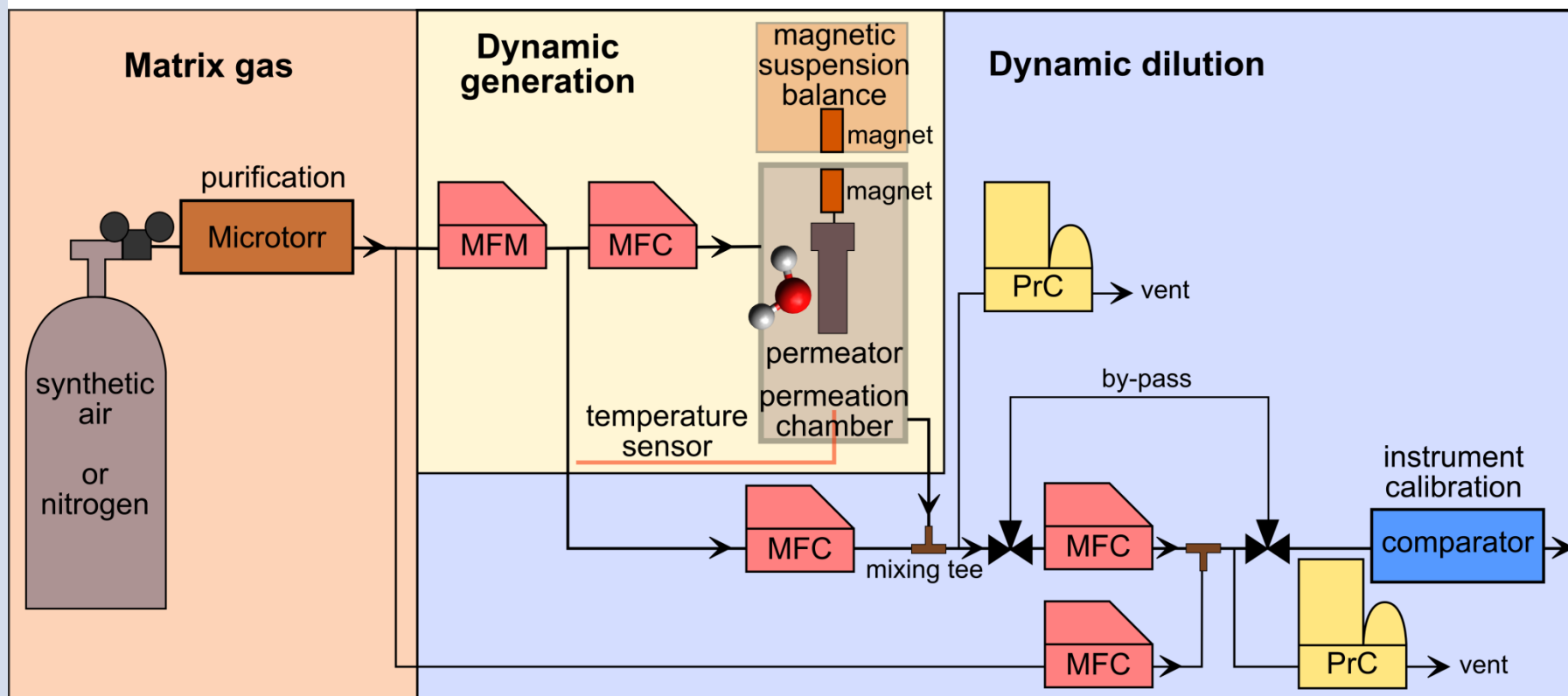


Permeator,  
Fine Metrology



# Method overview

## 3. Dynamic dilution





### 3. Dynamic dilution

- 2 successive dilution steps
- Using mass flow controllers (MFC) from Vögtlin
- Pressure controlled
- SilcoNert2000 on all metal surfaces

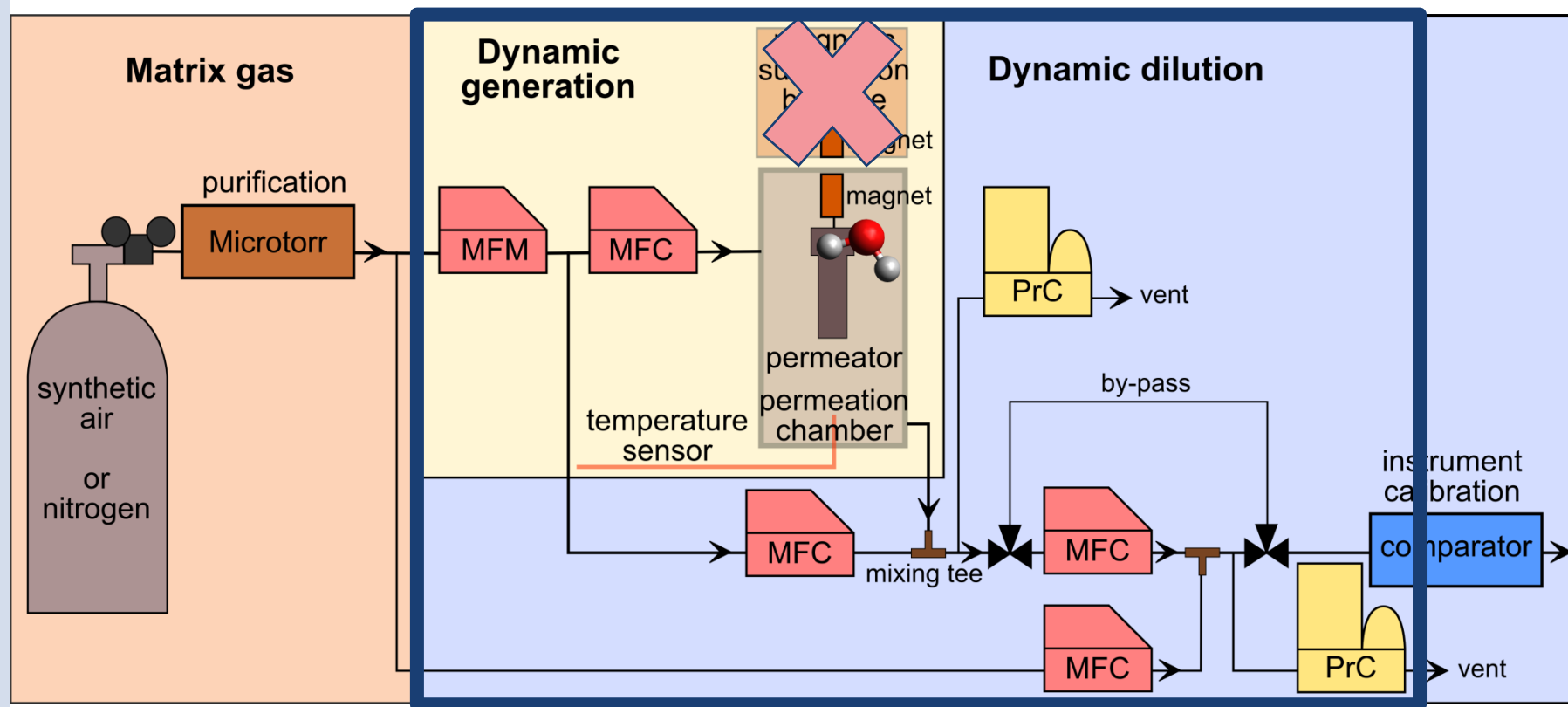


## Results: water generation at $\sim 10 \mu\text{mol/mol}$ (ppm)

- Carrier gas: nitrogen purified with Microtorr cartridge
- Entire system dried down to 100 ppb water
- Generated concentration measured with laser Intrument from TigerOptics
- Expanded uncertainty at  $10 \mu\text{mol/mol}$  (95% confidence interval): 1%, 100 nmol/mol
  - 65% residual water
  - 26% mass loss permeator
  - 9 % flow

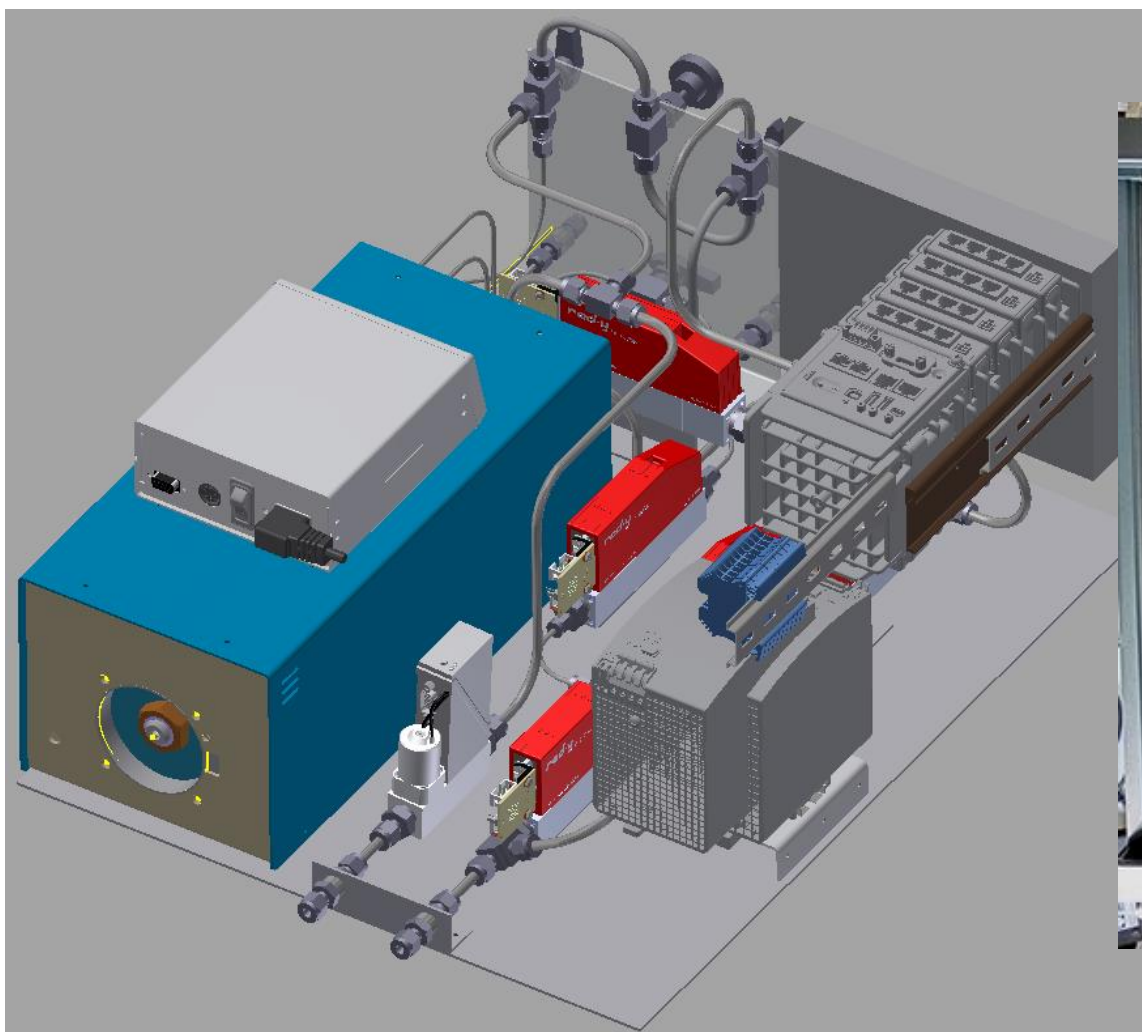
## Design – portable generator

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

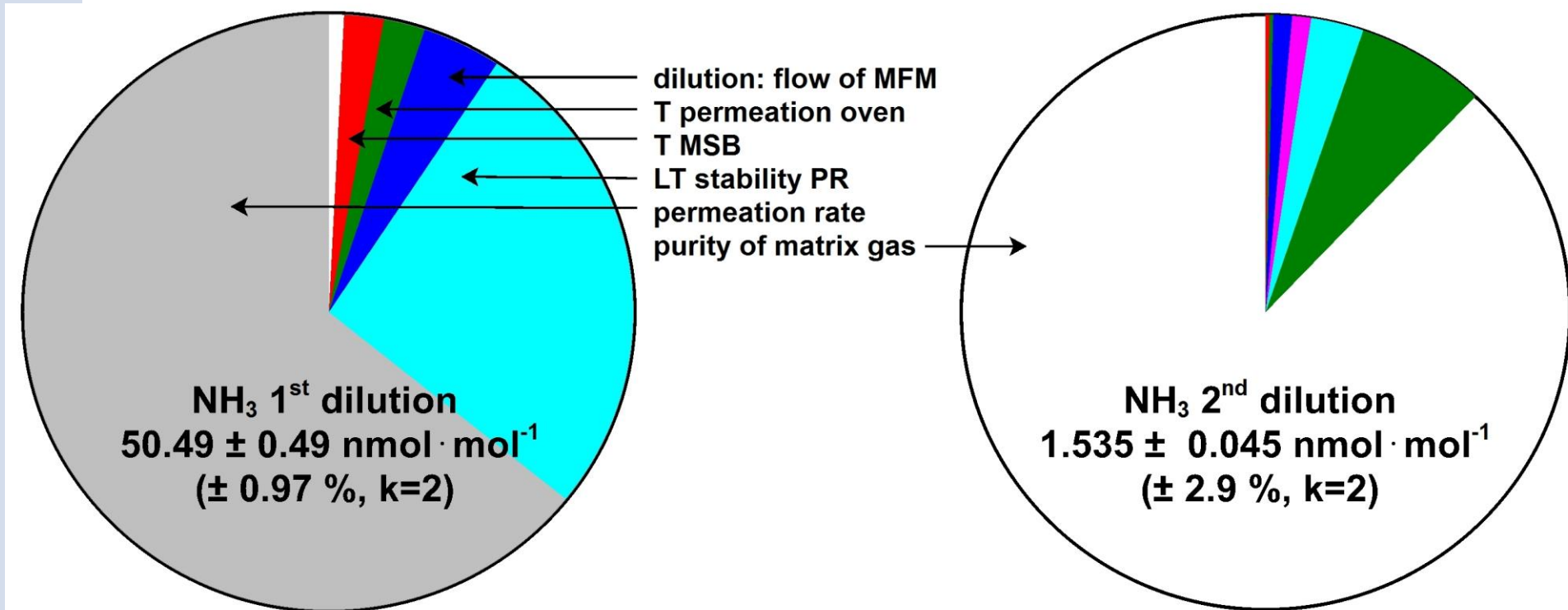


# Design – generator for ammonia $\text{NH}_3$

Project MetNH<sub>3</sub>



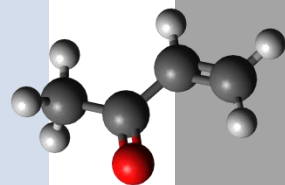
# Results: ammonia generation at ~nmol/mol (ppb)



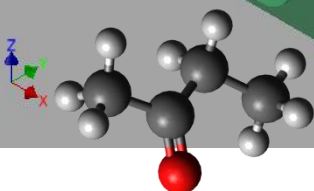
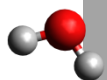


# Design for VOCs – with multiple permeators

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



**6 individual permeation chambers**



**Carrier gas in**

**Heating element**

**Gas mixture out**

**11 kg**

**Validated and running  
by end of 2016**

*Reference gases for fluorinated gases:  
poster A.438 in this session  
17:30 – 19:00 today, Hall A*

*More on making zero air standard: talk by R.Pearce 16:00 –  
16:15*

*Thank you for your attention  
Questions?*

*Many thanks to METAS Gasanalytik team, workshop and  
electronics workshop*