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Federal Institute of Metrology METAS

Traceable dynamic methods: why and how

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Agenda

1. Dynamic methods overview
2. Why ? Advantages and disadvantages
3. How ? Prerequisites and common pitfalls
4. Examples realised at METAS
5. Acknowledgments

Dynamic methods overview

- ISO standard 6145 with 10 parts
  Gas analysis — Preparation of calibration gas mixtures using dynamic ~~(volumetric)~~ methods
  - **Part 1:2003 Methods of calibration**
  - Part 2:2014 Piston pumps
  - Part 4:2004 Continuous syringe injection method
  - Part 5:2009 Capillary calibration devices
  - Part 6:2003 Critical orifices
  - **Part 7:2009 Thermal mass-flow controllers**
  - Part 8:2005 Diffusion method
  - Part 9:2009 Saturation method
  - **Part 10:2002 Permeation method**
  - Part 11:2005 Electrochemical generation

Why Dynamic Methods / Qualitative Estimation

Advantages:

- Abundance of gas volume
- Variable levels
- Vast range (pmol/mol … mmol/mol)
- Can be combined
- Low residence times:
  - Reduced reaction and surface interaction

Disadvantages:

- Laborious in calibration
- No certificate of mixture
- Higher MU for high level mixtures (>10 µmol/mol)
- Lack of convenience

Neutral:

- Costs ?
- Multicomponent

Why Dynamic Methods / Applications

- Stability or reaction problems of static mixtures
  K26, K46, K74, …
- Reactive analytes (SO_2, NO_2, NH_3, H_2O, H_2S, HCl, HCOH…)
- Problems with adsorption, desorption and condensation
- Very low concentration mixtures (< 1 µmol/mol)
- Instrument calibration / characterisation:
  - Linearity
  - Detection Limits
  - Cross interferences / specificity

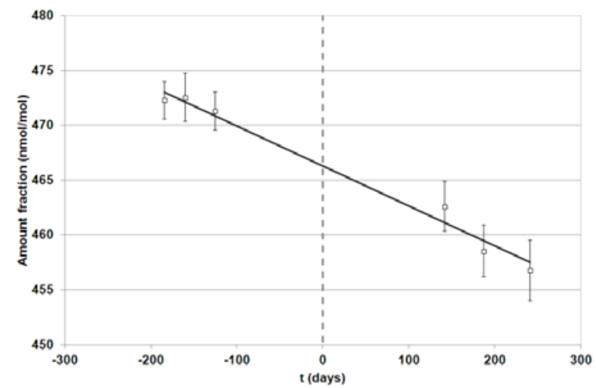
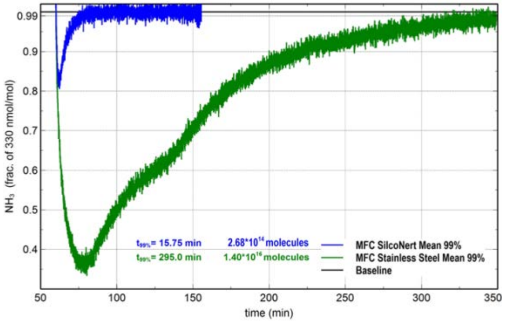


Figure 5 Example of the estimation of the drift in the amount fraction experienced in one of the travelling standards. The regression line has been fitted by ordinary least squares. The x-axis

P J Brewer et. al.: EURAMET QM-K26.a Final Report

The Adsorption Issue

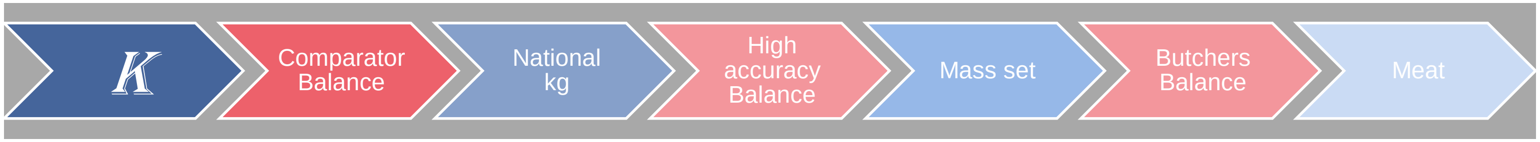
- Adsorption is a problem for most reactive analytes.
  - can be a dominant MU-component
- What can be done to reduce adsorption?



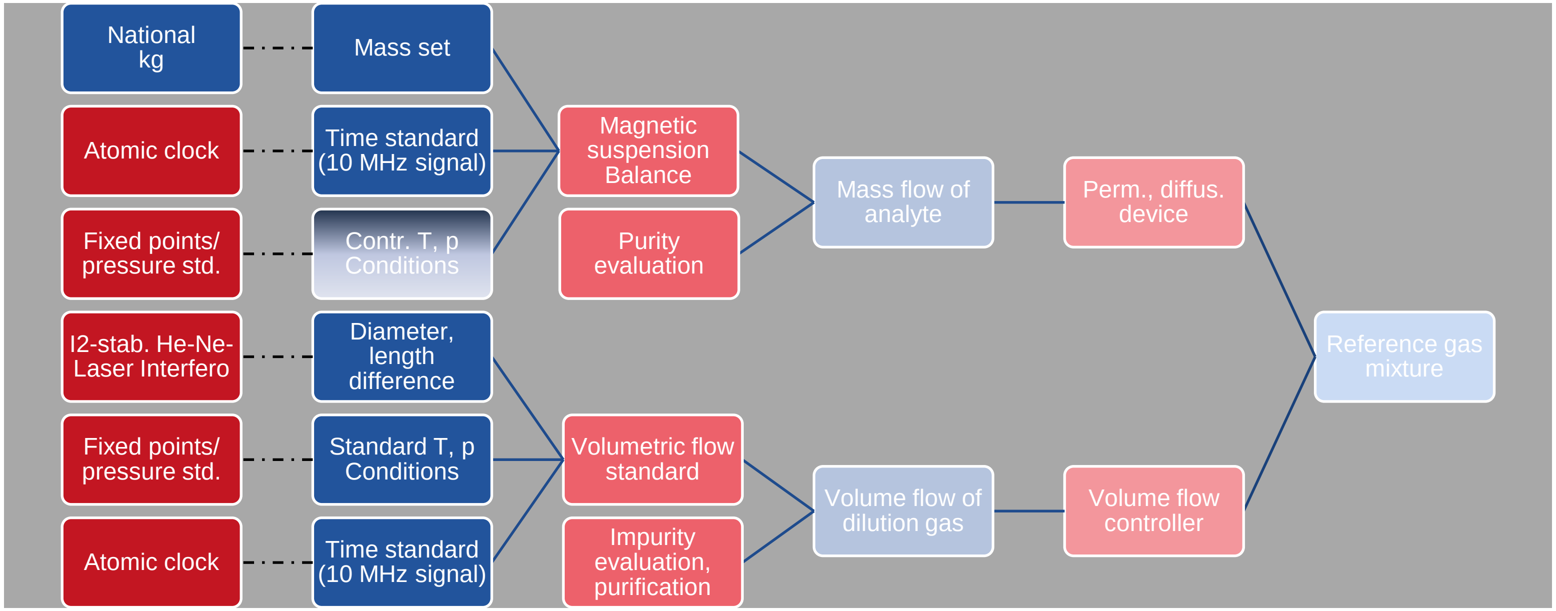
1. **Increase temperature**
   To increase the energy of molecules and boost desorption
2. **Decrease the surface** in contact with the mixture reduces the adsorption capacity
3. **Use** continuously **purged systems**
   in order to install a flow equilibrium
4. **Use of** materials with lowest bonding energy.
   Analyte-specific **coatings** decrease adsorption drastically

How: Prerequisites
Means of Calibration / the Traceability Issue

- Traceability chain for physical (base) quantities (example):

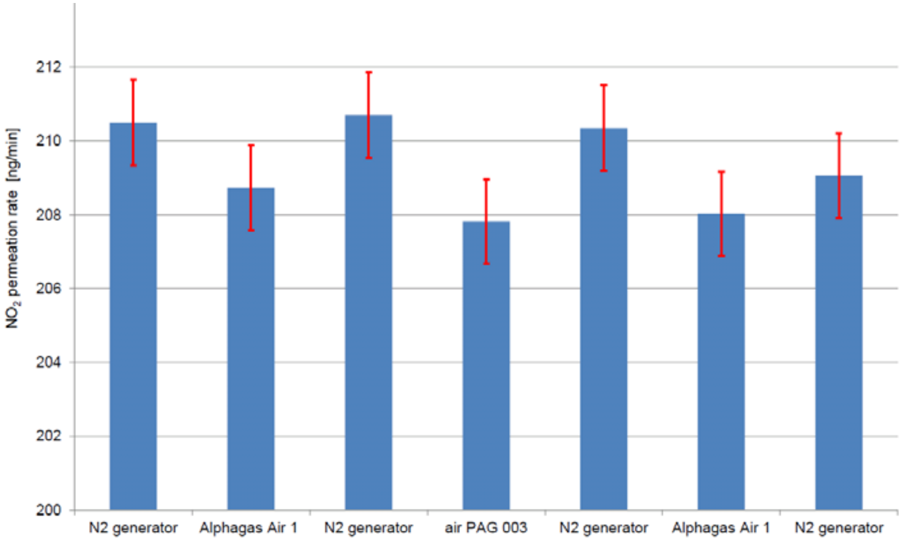


- For dynamic RM (mixtures) realisations of derived quantities:



How: Prerequisites
Means of Calibration / The Traceability Issue

- All mass and volume flows have to be calibrated by traceable – **preferably continuous** – standards
- Scrupulous control of conditions, fluid type and matrix
- **Commutability/Portability** of calibrations is not simply given
  - Example1: fluid dependence of permeation mass flow*.



* H.-P. Haerri et. al.: Dilution and permeation standards for the generation of NO, NO2 and SO2 calibration gas mixtures, submitted Meas. Sci. Technol. 27 (2016)

How: Avoid Calibration Pitfalls

Most high accuracy flow controlling instruments are gas type dependent.

- N_2-purity-specs from producers of PSA generators lead to erroneous portability of calibration data

Technical Specifications	NG 2000(A)	NG 3000(A)	NG 4000(
Max Flow Rate	2000 cc/min (0.07cfm)	3000 cc/min (0.10cfm)	4000 cc/min (0.
Max Pressure	80 psi / 5.5 bar		
Max Relative Humidity	70% Non-Condensing		
Max Altitude	2000 Metres		
Nitrogen Purity		99.9995%	
Particles	<0.01µm		
Gas Outlets	1 x 1/4" BSPP		
Phthalates	None		
Suspended Liquids	None		
Operating Temperature	5°C - 25°C / 41°F - 75°F		

Operating and Physical Specifications

Nitrogen Flow Rate (max):	
BORA 500	500 ccm
BORA 750	750 ccm
BORA 1250	1250 ccm
SIR 3	3 Lpm
SIR 3A	3 Lpm (nitrogen) & 3 Lpm (instrument air)
SIR 5	5 Lpm
Nitrogen Purity:	
BORA 500 & 750	99.999%
BORA 1250	99.995%
SIR 3, 3A & 5	99.999%
O_2 Concentration (N_2 Outlet):	< 10 ppm
Nitrogen Outlet Pressure (max):	75 psig
Nitrogen Outlet Connection:	1/8" (compression fitting)
Operating Noise Level:	
BORA 500, 750 & 1250	< 48 db
SIR 3, 3A & 5	< 60 db
Power Source:	115 VAC / 60 Hz; 230 VAC / 50 Hz
Castor Wheels:	SIROCCO Models
Dimensions:	
BORA 500, 750 & 1250	9"W x 14"H x 17"D
SIR 3, 3A & 5	19"W x 26"H x 33"D

molar fraction Ar in N_2	density g/L @ 0°C, 1atm (simple additive model)	rel. error
0	1.25053	0.000%
0.002%	1.25054	0.001%
0.933%	1.25551	0.398%
1.180%	1.25683	0.503%

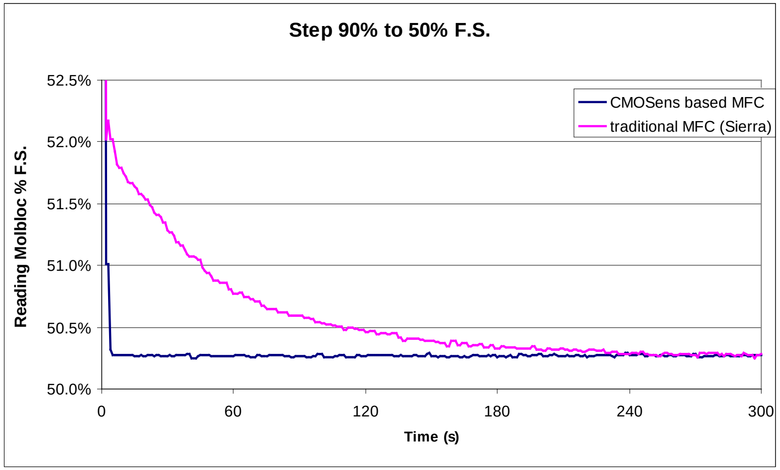
How: Avoid Calibration Pitfalls (continued)

Stabilisation times:

Traditional thermal MFC specify:

$t_{98} \approx 300$ ms … 700 ms

Calibration errors compared to continuous fixed mode may easily occur and increase MU



Pressure conditions:

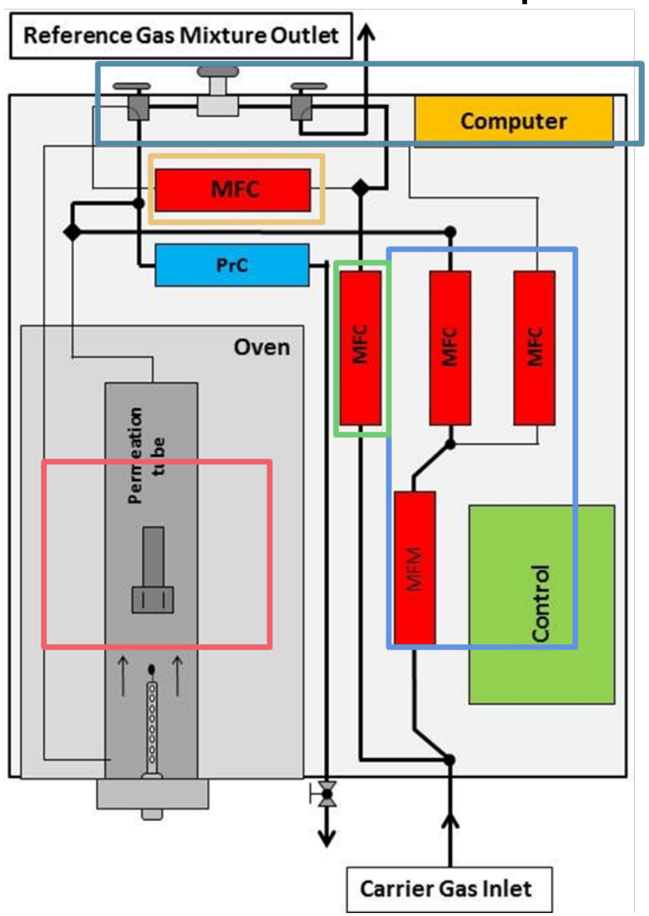
Upstream and downstream pressures different from calibration conditions may cause important differences and increased MU

Reference conditions:

s for standard and n for normal is not uniformly used (huge variety)

Example 1
ReGaS1 for NH3 – Generation

- Transportable, traceable combination of permeation and 2nd dilution step.



Temperature dependent permeation of pure substance (NH_3) through polymer wafer in carrier gas stream (**permeation method** ISO 6145-10)

Dynamic dilution of NH_3 in carrier gas stream **1st dilution step** NH_3 mixtures **>50 ppb (U_{NH3}= <1% rel.)**

Splitting off part of 1st dilution NH_3 mixture >50 ppb

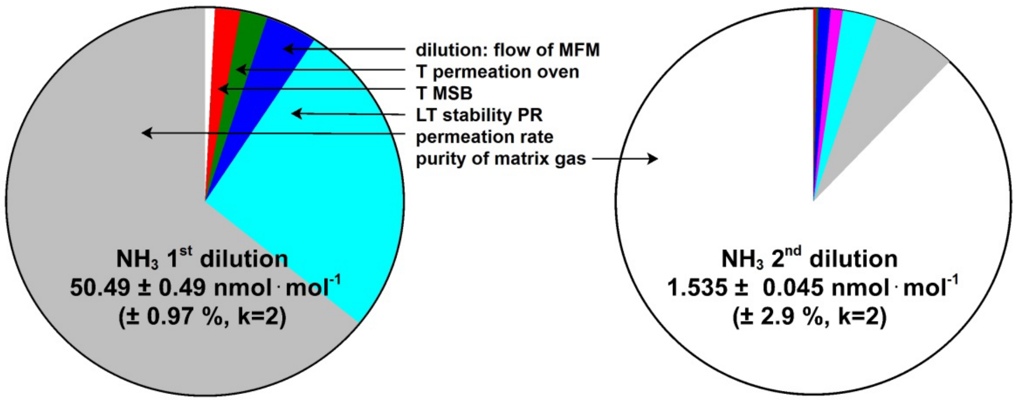
2nd dynamic dilution of NH_3 in 1st dilution mixtures >50 ppb **NH_3 → mixture 0.5-50 ppb → ambient air range (U_{NH3}= 1-3 % rel.)**

Full flexibility over generation range as either dilution step can be used

Example 1
ReGaS1 for NH3 – Generation

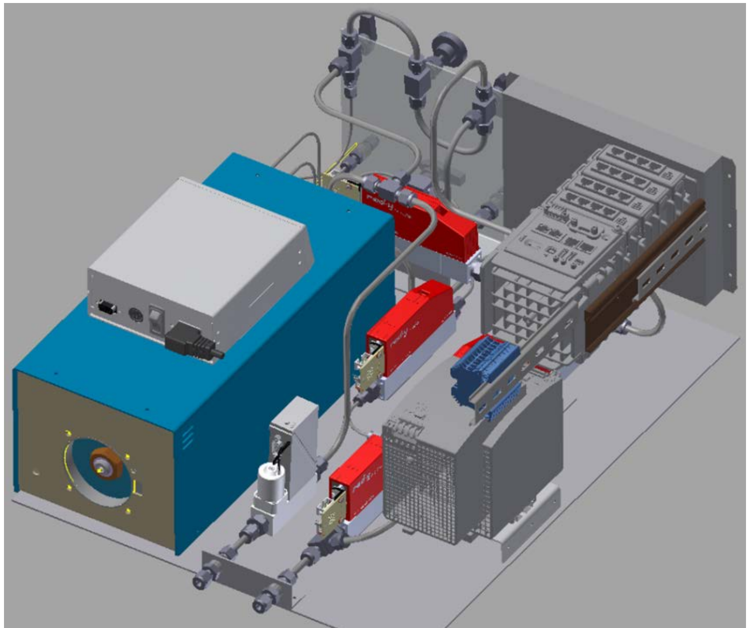
- Modifications of VICI Dynacalibrator® 150 oven:
  - SilcoNert® 2000-coated stainless steel interior
  - Exchange of original lid by METAS-made, leak tight lid holding temperature probe
- First use of coated MFC for 2nd dilution and fully coated lines and fittings

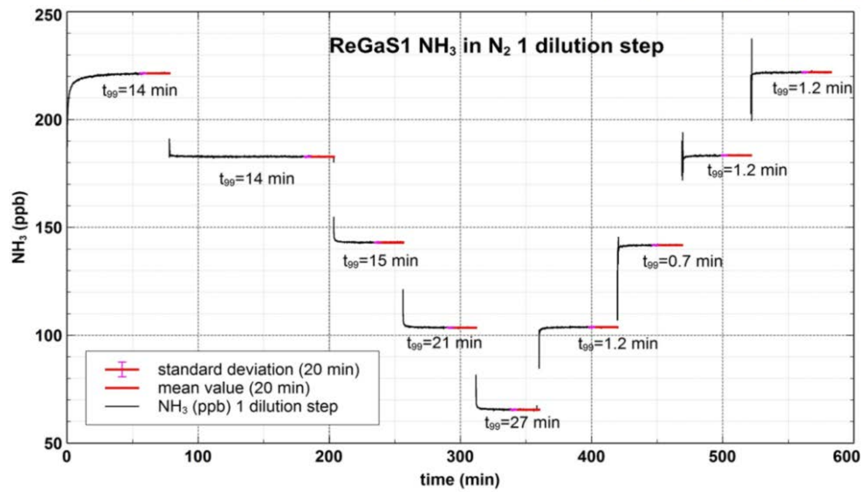
ReGaS1 NH_3 reference gas mixtures: preliminary uncertainty budget

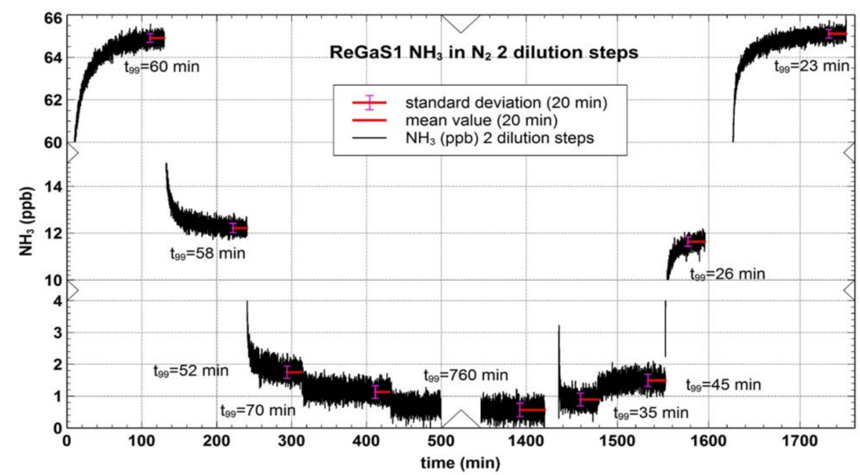


Uncertainty of NH_3 reference gas mixtures in low amount fractions **primarily depending on purity of matrix gas**

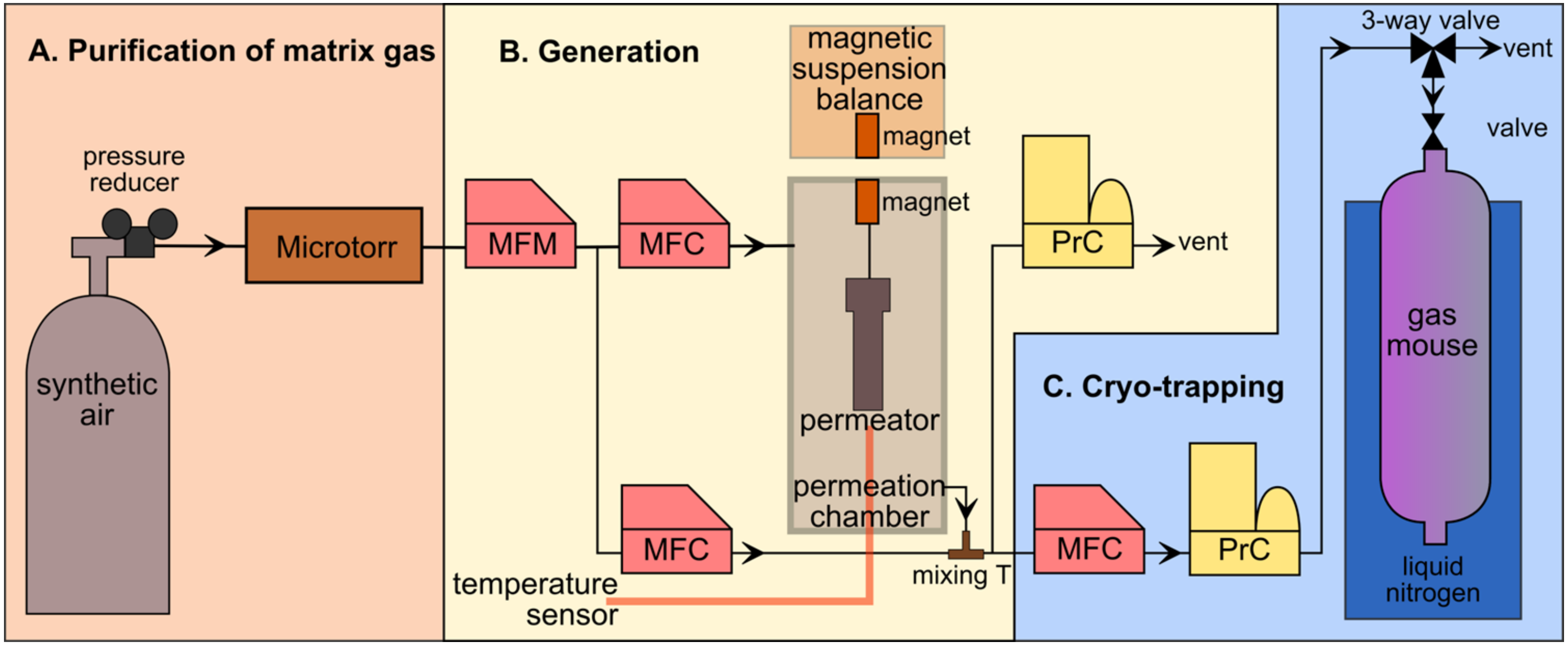
Example 1
ReGaS1 for NH_3 – Generation







Example 2
Cryotrap of permeation mixtures of F-Gases and…



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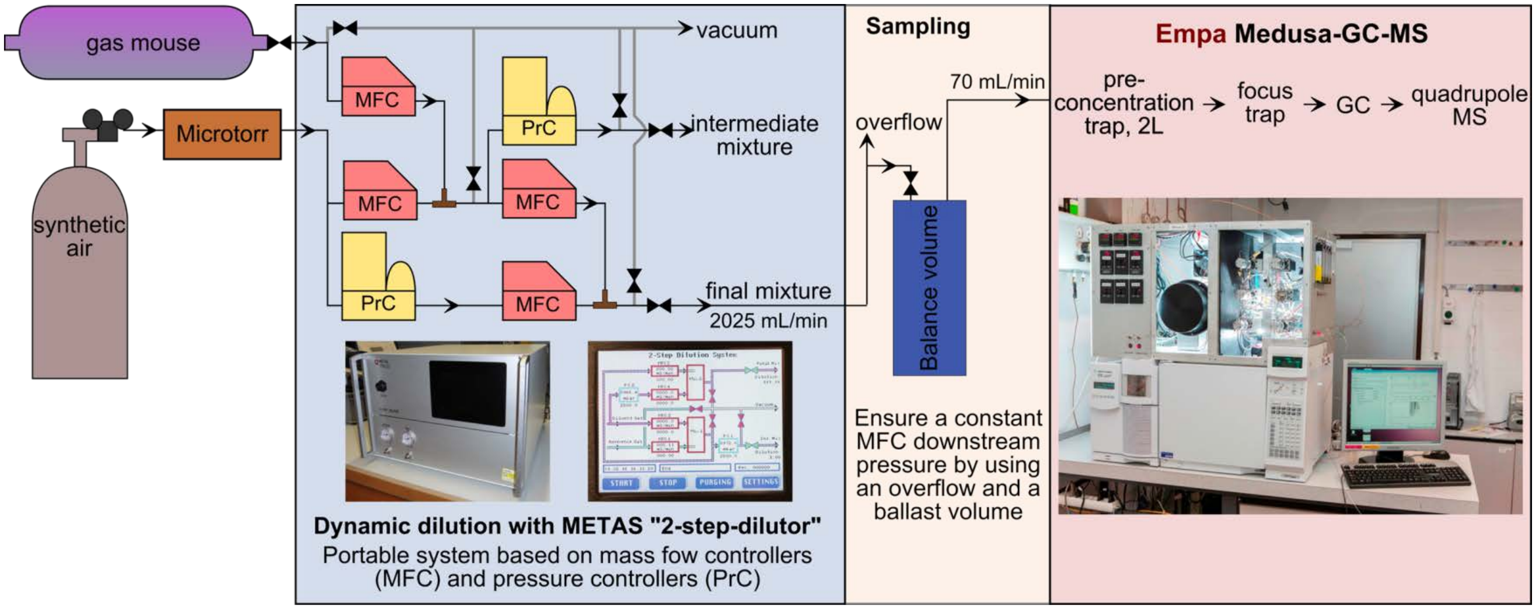
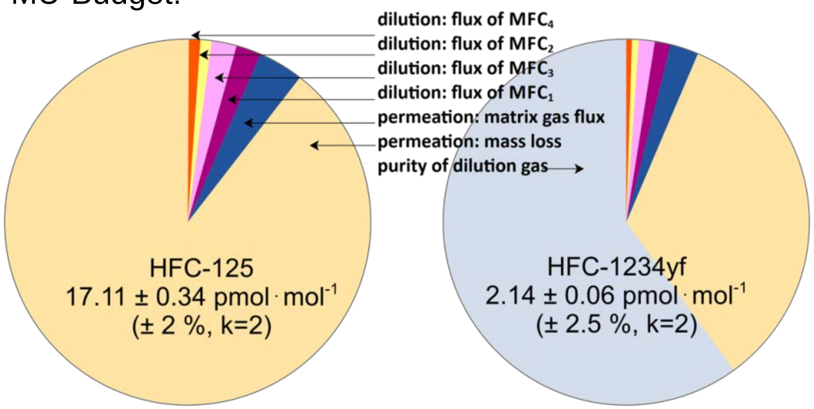
Example 2
… 2 step dilution and analysis on GC-MS



MU-Budget:



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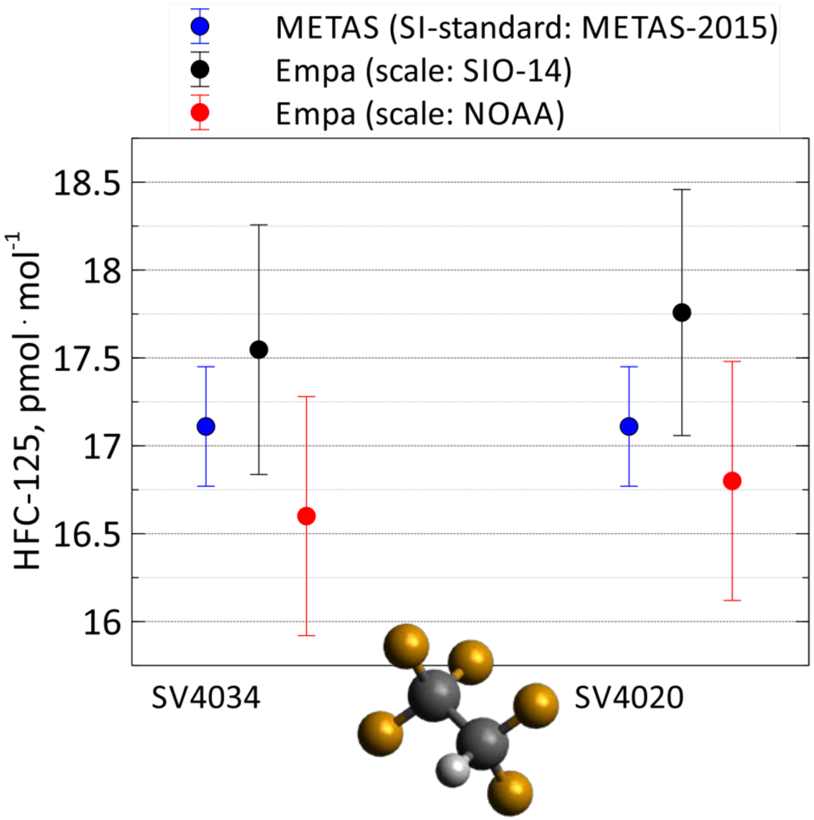
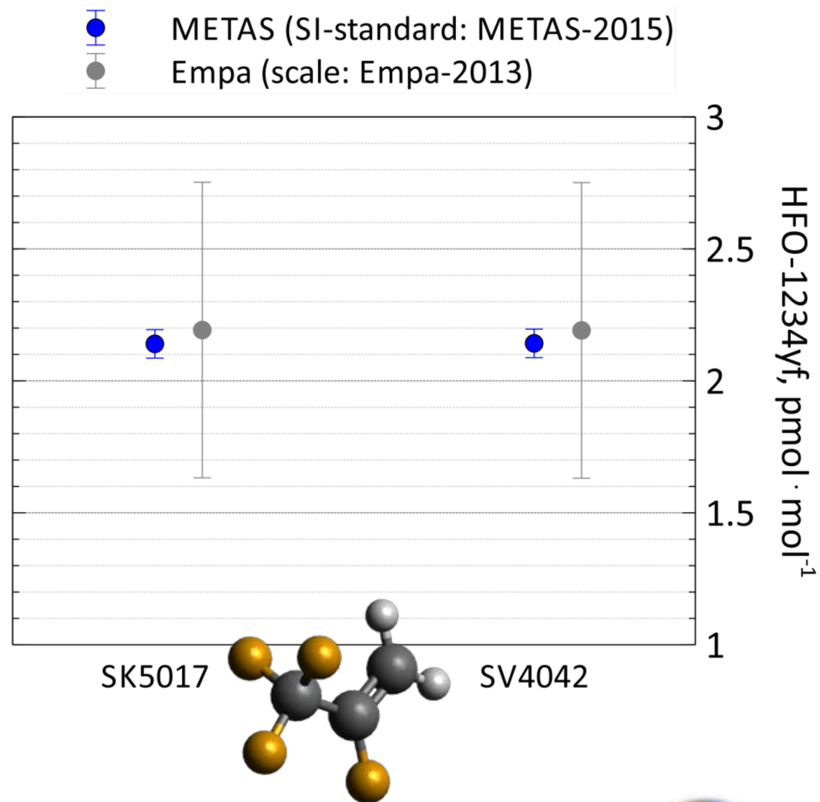
Example 2
Results of comparison vs. existing references

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





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Conclusions

- Dynamic generation methods can be made traceable
- They show clear advantages for adsorptive/reactive substances at very low concentrations
- Representative calibrations are most essential
  - Continuous mass flow for minor component
  - No surrogate fluid calibration for dilution gas
- Recommendation to use CMOSens- or MEMS- based Flow controlling
- Recommendation to use coated material for the realisation of instrumentation for adsorptive/reactive substances: net decrease of stabilisation times

METAS

Thanks

- To members of the gas analytical lab at METAS for most fruitful collaboration **
- To mechanical and electronics workshop people at METAS for construction of ReGaS and 2-step dilution device
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