European Geosciences Union General Assembly, 17-22 April 2016, Vienna

On Development and Characterisation of a Mobile and Metrologically Traceable Reference Gas Generator for Ammonia and Other Reactive Species in Ambient Air Levels

Daiana Leuenberger Céline Pascale Myriam Guillevic Andreas Ackermann Bernhard Niederhauser – **Federal Institute of Metrology METAS, Switzerland**

JRP-Partners

MOTIVATION

Ammonia NH_3 in the atmosphere has harmful effects on ecosystems and human health by affecting the acidity of natural waters and soils, thus causing excess nitrogen input [1] and by facilitating secondary particle formation [2]. **NH_3 has thus been included in the air quality monitoring networks and emission reduction directives of European nations**.
Yet, NH_3 data quality, uncertainty estimations and traceability are insufficient [3].

The role of metrology

To enable analyses of trends and effects of reduction measures, **reliable and accurate atmospheric** measurements are required.

Measurement results have to be traceable **via certified NH_3 reference materials (CRM)** **to be reliable**. **Well-defined uncertainty contributions** [4] and their **uniform assessment ensure the comparability** of measurement results, e.g. of different air quality measuring stations.

The EMRP JRP ENV55 MetNH3 (Metrology for Ammonia in Ambient Air) aims at providing CRM in relevant Ammonia (NH_3) amount fractions (0.5-500 nmol/mol) with expanded (k=2) uncertainty **U_{NH3}<3% to the air monitoring community** by developing novel approaches for their production **[6]**.

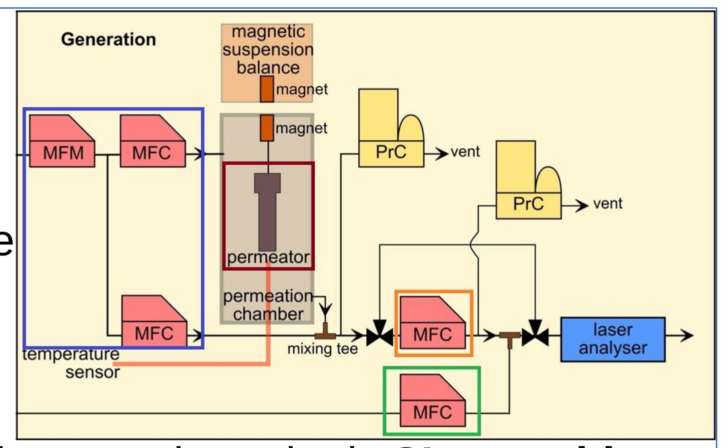
METHOD

Major difficulty: Adsorption of NH_3 on material surfaces causes losses in NH_3 amount fractions of gas mixtures in cylinders

Solution: Dynamic generation of NH_3 CRM

The Federal Institute of Metrology METAS has developed a mobile and metrologically traceable reference gas generator for reactive gases (ReGaS1).
This device is based on the **specific, temperature dependent permeation** of the **reference substance (NH_3)** through a membrane into **a flow of carrier gas** (N_2 or air) and subsequent **dynamic dilution** to desired amount fractions in **1 to 2 steps** according to $x_P = x_B \frac{\dot{V}_1}{\dot{V}_1+\dot{V}_2} + x_{DG}$ (where x_P (nmol/mol) is the resulting NH_3 concentration, x_B the primary NH_3 concentration, $\dot{V}_1$ the base gas flow, $\dot{V}_2$ the dilution gas flow, x_{DG} the background concentration of ammonia in the dilution gas).

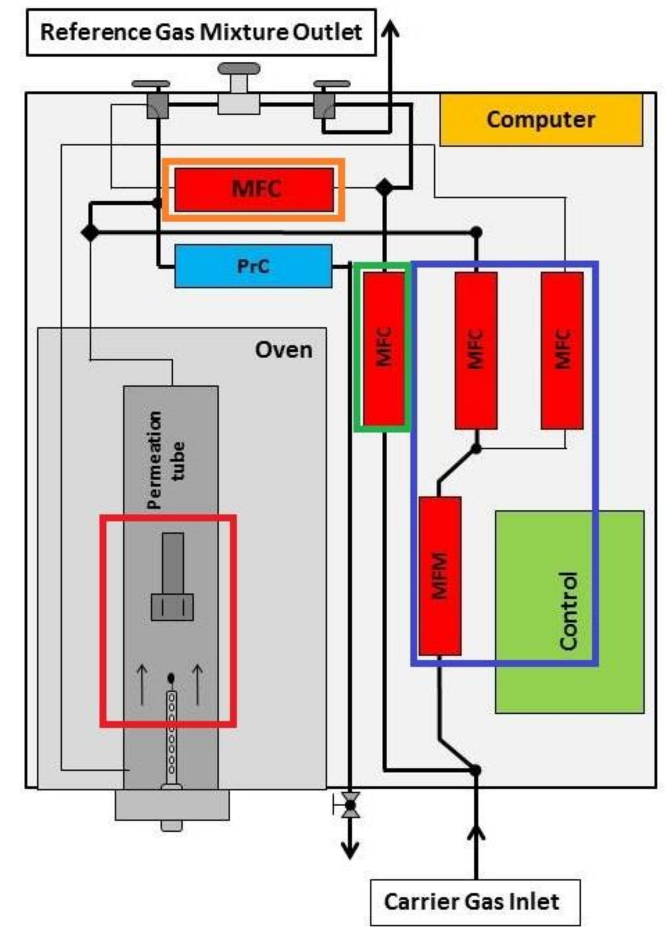
Permeation



Continuous, temperature and pressure dependent permeation of pure substance through polymer membrane into Purified matrix gas

Permeation rate $Pr = \frac{\Delta m}{\Delta t}$ of permeation tube is **SI-traceably** determined in temperature and pressure controlled chamber of **Magnetic Suspension Balance (MSB)** (resolution $= 10^{-6}$ g)

Alternatively, permeation tube with calibrated Pr is placed in the **permeation oven** of ReGaS1 flushed by continuous stream of matrix gas.



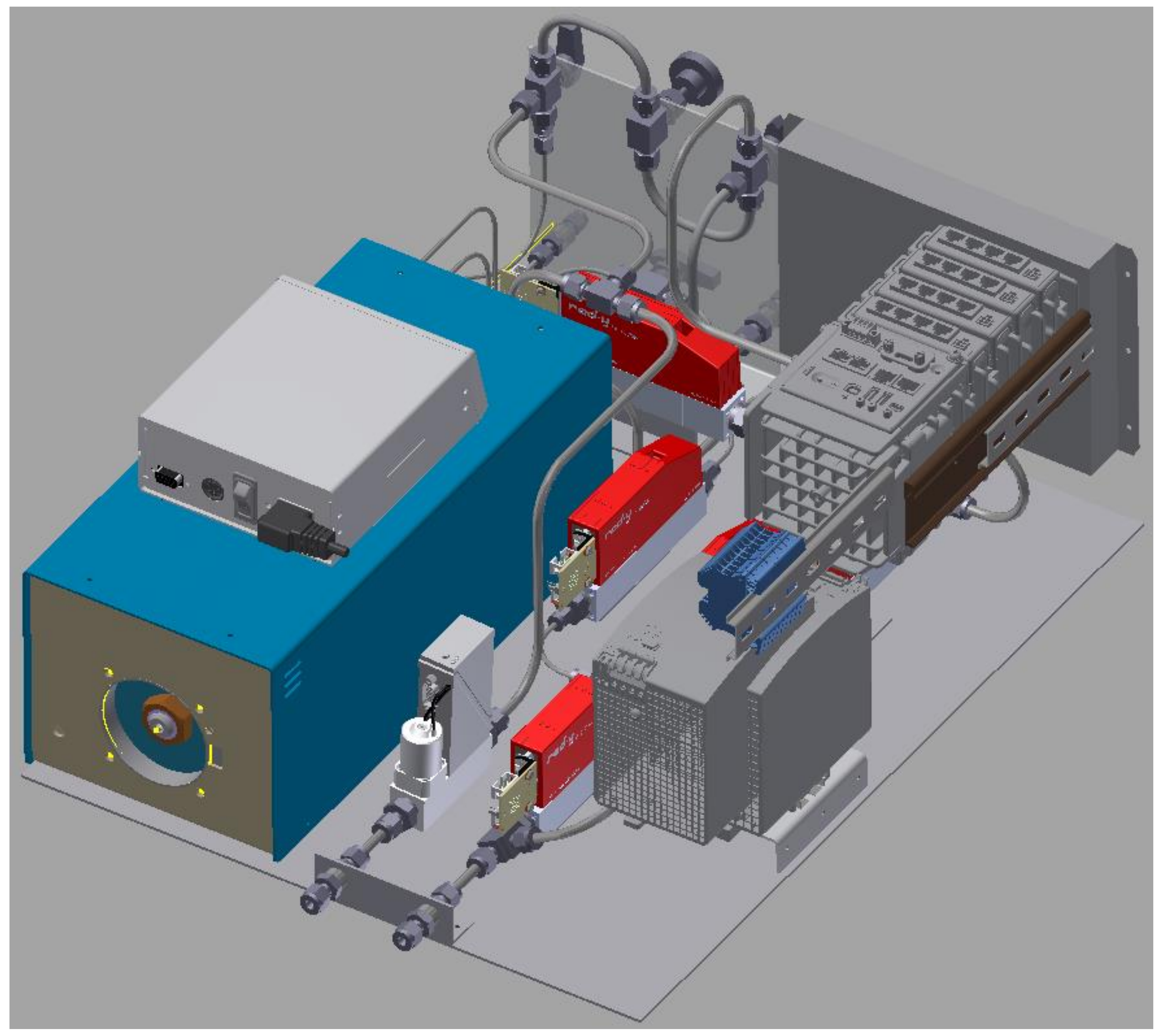
Dilution

The traceable NH_3 gas mixture from MSB or Permeation oven is diluted in 1 or 2 traceable steps to atmospheric amount fractions (0.5 - 500 nmol/mol)

First dilution step: Reduces NH_3 amount fractions generated in permeation oven to (> 50 nmol/mol)
Split flow: Subdivision
Second dilution step: Reduces NH_3 amount fractions generated in permeation oven to (> 0.5 nmol/mol)

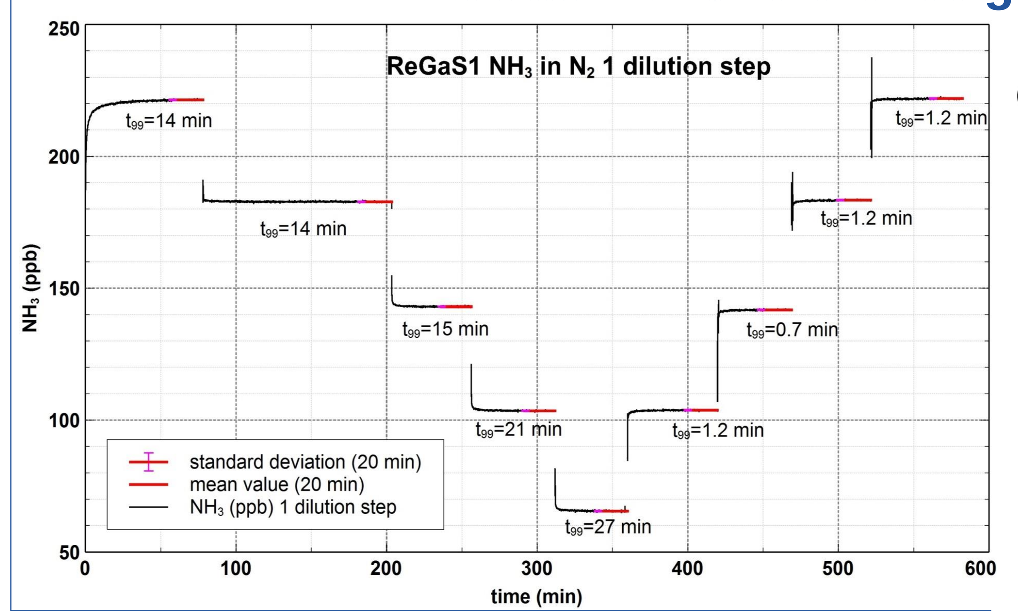
Equal components in MSB and ReGaS1, except for permeation chamber/balance in MSB and permeation oven in ReGaS1: two methods are comparable.

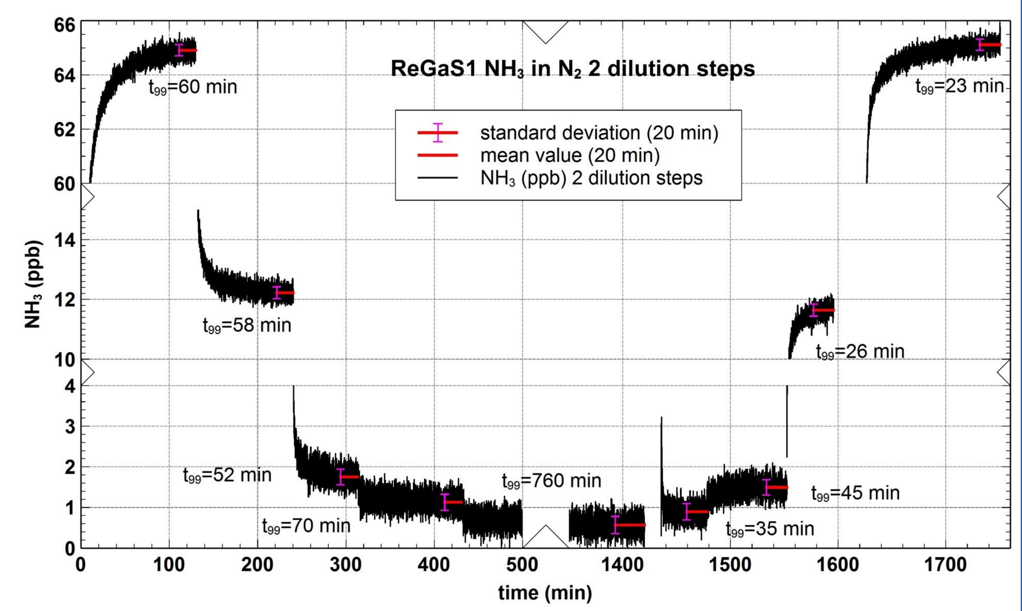
METAS ReGaS Reactive Gas Standard
Mobile, traceable reference gas generator for NH_3



ReGaS1 NH3 reference gas mixtures: First results

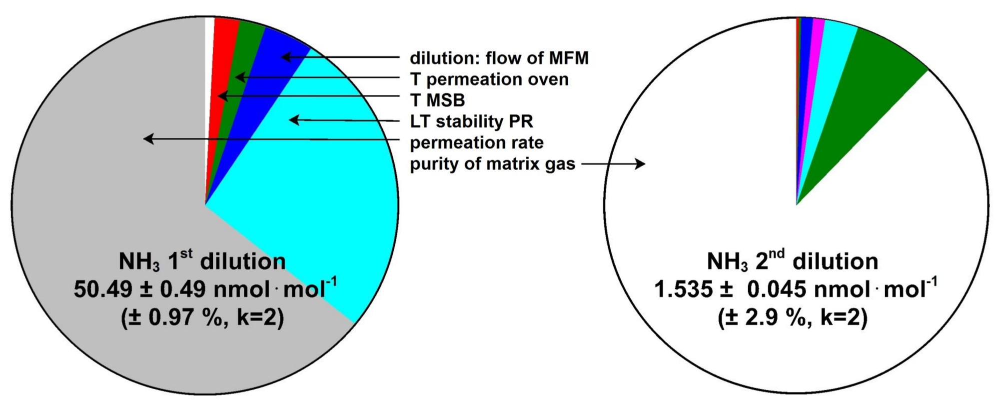
Very short response times
(1dilution step: < 30 min, 2 dilution steps: < 90 min)
Excellent stability
Low variability (<0.2 nmol/mol)
Good repeatability





As of autumn 2016, ReGaS1 can be hired for on-site or laboratory calibrations of NH_3 analysers or gas mixtures
Do get in touch!

ReGaS1 NH3 reference gas mixtures: preliminary uncertainty budget [4]



		Rel. expanded measurement uncertainty (f=2)	Rel. contribution to total measurement uncertainty	remarks
Permeation rate		$Pr = < 1.7\ \%$	$Pr = 20\% - 80\ \%$	Long-term
Dilution steps (qv_{tot})			$qv_{tot} = < 30\ \%$	
	1 (qv_1)	$qv_1 = 0.2\ \%$		
	Split (qv_3)	$qv_3 = 0.3\ \%$		
	2 (qv_4)	$qv_4 = 0.2\ \%$		
Additional significant contributions				
Purity of matrix gas		increasing with decreasing NH_3 amount fractions ($0.05 \pm 0.05 \frac{nmol}{mol}$), significantly increases total measurement uncertainty by up to $100\ \%$		
Temperature regulation in perm. oven		Instability increasing with increasing temperatures, corresponding to an increase in the uncertainty of $2\ \%$ for a difference in $T = 0.1\ K$.		

Conclusions

- **Quality, uncertainty estimations and traceability of NH_3 data from atmospheric measurement networks are insufficient**
- **METAS in the framework of EMRP JRP ENV55 MetNH3 (Metrology for Ammonia in Ambient Air) aims at providing CRM in relevant Ammonia (NH_3) amount fractions (0.5-500 nmol/mol)** with expanded (k=2) uncertainty **U_{NH3}<3% to the air monitoring community**
- **New development: METAS ReGaS1 mobile reference gas generator as secondary reference traceable and comparable with the primary reference (MSB).**
- **Second dilution step and traceability of all components are novelties compared to commercially available gas generators.**
- **Generation of NH_3 CRM requires high purity matrix gas:**
  - **Ambient air humidity rates (>1% RH) cause dissolution of NH_3 in H_2O multilayers**
  - **Matrix gas with x_{NH3} >0.05 nmol/mol cause U_{NH3} >3% in NH_3 CRM at amount fractions <1.5 nmol/mol**
- **Reduction of adsorption losses and stabilisation time by surface coating with SilcoNert 2000**

EMRP
European Metrology Research Programme
Programme of EURAMET

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

Acknowledgments
The authors gratefully acknowledge the support and valuable input of the colleagues at METAS' departments workshop, electronics development and LabView development.
Many thanks to industrial partners VICI International and FinePermeation as well as to JRP partner of MetNH3.
For more information on EMRP JRP ENV55 MetNH3 "Metrology for Ammonia in Ambient air, visit www.metnh3.eu

Related contributions at EGU 2016

- BG2.12 EGU2016-16414; Mo, 18/04/16 15:30-17:00, Foyer M Poster M.25
- AS4.15 EGU2016-8355; Thu, 21/04/16 13:45-14:00, Room -2.47
- AS4.15 EGU2016-11907; Thu, 21/04/16 17:30-19:00, Hall A Poster A.438

References:
[1] Stevens C J et al.: Nitrogen deposition threatens species richness of grasslands across Europe. Environ. Pollut. 158 2940-5, 2010.
[2] Sutton M.A. *et al.* (2009): Atmospheric Ammonia: Detecting Emission Changes and Environmental Impacts. Springer.
[3] EMEP-EEA air pollutant emission inventory guidebook – 2013, Part A, Chapter 5, Table 3-3
[4] ISO-Guide 98-3 "Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement" (GUM).
[5] Vaittinen et al.: Adsorption of Ammonia on stainless steel and treated polymer surfaces. Appl. Phys. B, 2013.
[6] Pogány A. *et al*. :Metrology for ammonia in ambient air – concept and first results of the EMRP project MetNH3, Proc. 17th Intern. Congress of Metrology DO I: 10.1051/metrology/20150 00, 2015

Dr. Daiana Leuenberger
daiana.leuenberger@metas.ch
Federal Institute of Metrology
Laboratory Gas Analysis
www.metas.ch