Requirements from the speciality gas industry for greenhouse gas standards

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Content

Introduction

Long-lived greenhouse gases (Carbon dioxide, nitrous oxide, methane etc.) contribute to global warming

Very accurate measurements of these gases are required to underpin

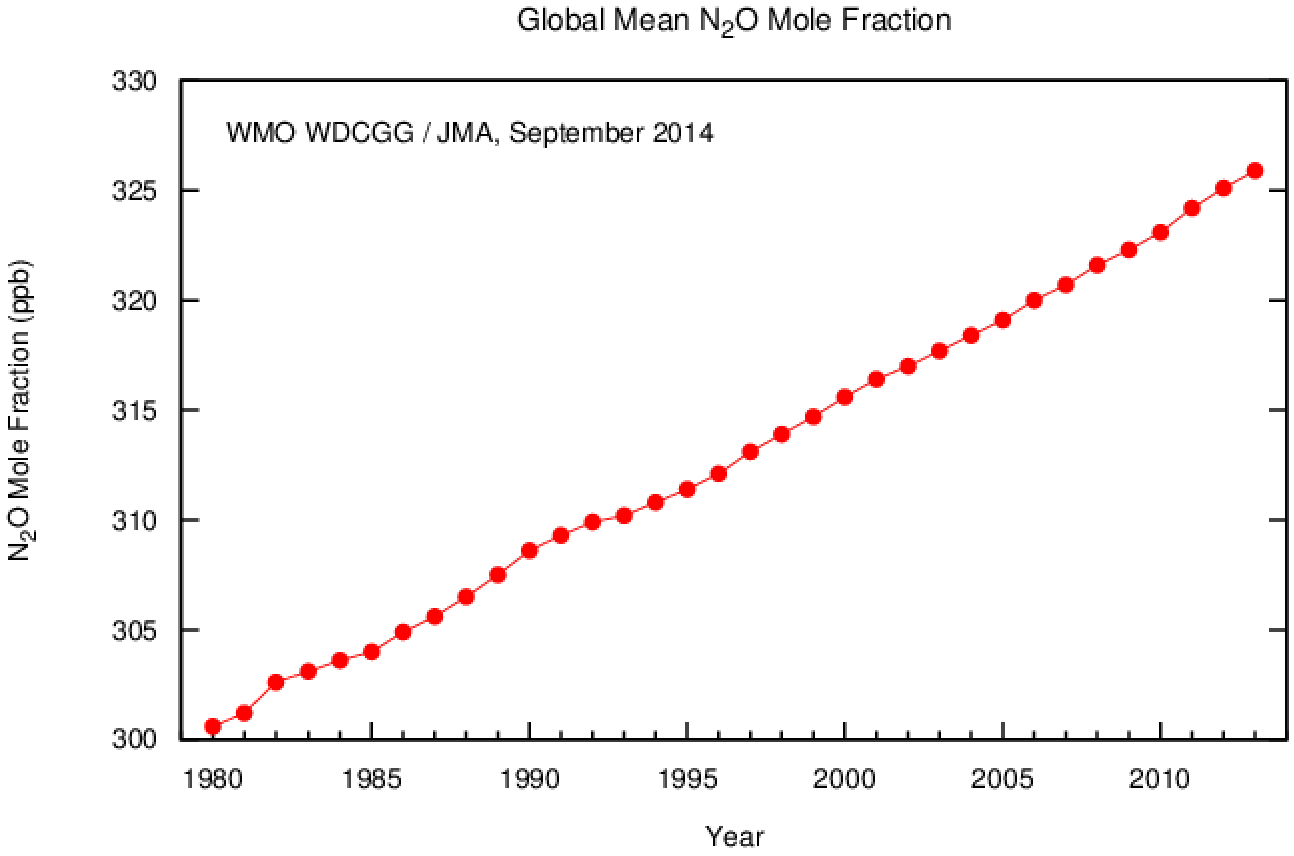
- Investments for mitigation and adaptation strategies
- Predictive modelling and trending

The provision of Reference Gas Standards that are stable, metrologically traceable and have low measurement uncertainties are required

- Initial production by National Measurement Institutes, e.g. NPL, VSL, NIST etc.
- Dissemination of ISO Guide 34 and ISO 17025 accredited gas calibration mixtures by commercial gases companies with low uncertainties

Allows robust data collection and analysis with traceability and measurement uncertainties calculated according to the ISO GUM

World Data Centre for Greenhouse Gases (WDCGG) Global annual mean mole fractions [1]



Reference [1]: "WMO Greenhouse Gas Bulletin, No.10, 2014."

Requirements to accuracy of analytical results for trend assessment

Global abundances of long-lived greenhouse gases 2010 – 2103

	CO_2 [ppm]		CH_4 [ppb]		N_2O [ppb]	
	Mean	**Unc.**	**Mean**	**Unc.**	**Mean**	**Unc.**
2010	388.9	0.1	1808	2	323.1	0.1
2011	390.9	0.1	1813	2	324.2	0.1
2012	393.1	0.1	1818	2	325.1	0.1
2013	396.0	0.1	1824	2	325.9	0.1

$\Delta x = 0.8$ ppb N_2O

Reference [1]: "WMO Greenhouse Gas Bulletin, No.10, 2014."

Requirements for static reference standards in HIGHGAS

One “aim of HIGHGAS is to develop static reference standards:

		x_i	$u(x_i)$	rel. $u(x_i)$ %
CO_2	**µmol / mol**	400	0.1	0.025
CH_4	**µmol / mol**	1.8	0.002	0.111
N_2O	**nmol / mol**	325	0.1	0.031
CO	**nmol / mol**	300	2	0.667

To achieve these challenging requirements research will focus on improving passivation chemistry, stability, gravimetry, quantification of target impurities in the air matrix, and determining the isotopic composition using IRMS”. [2]

[2]: Publishable JRP Summary Report for JRP ENV52 HIGHGAS Metrology for High-Impact Greenhouse Gases

Requirements from the speciality gas industry for greenhouse gas standards

The key attributes required in a gas calibration cylinder include:

- Stability: the calibration standard shall remain at the certified value throughout the specified shelf life and as the contents are depleted in use. In order to achieve stability cylinders may require the passivation of the internal surfaces

- Accuracy: the standard is ‘fit for purpose’ and the measurement uncertainty is consistent with identified requirements for use and customer needs

- Traceability: metrological traceability depends upon a chain of standards linked back to an international primary standard through a series of calibrations, i.e. inter-comparisons between two standards in the chain. The value of each standard in the chain must have a defined measurement uncertainty

Therefore, to ensure measurement accuracy:

- stability, metrologically traceable calibration and defined measurement uncertainty are required.

Requirements from the specialty gas industry for greenhouse gas standards (cont’d)

In general accredited laboratories are involved in the supply of gas calibration standards to the ambient air measurement networks

ISO 17025 and ISO Guide 34 accredited laboratories:

- Are supplied with reference materials from NMIs to ensure metrological traceability
- The scope of accreditation normally defines:
    - mixture composition (components and concentration range)
    - the shelf life of the gas mixtures
    - the lowest uncertainty

From an industrial gas producer’s point of view the question is:

Is it necessary to change the scope of accreditation in the course of the HIGHGAS project?

Mixture composition	Range (mol / mol)	Rel. Uncert.
CO in N_2 or Air	5 ppm to 10%	0.5 to 1%
CO_2 in N_2 or Air	5 ppm to 30%	
CH_4 in N_2 or Air	5 ppm to 50%	

Typical scope of accreditation from gas manufacturers for greenhouse gas standards.

Example calculation for a 325 nmol / mol N_2O calibration standard from a specialty gas producer (ISO Guide 34 / ISO 17025) perspective

Is it possible to meet the accuracy and uncertainty requirements at a gas manufacturer's site?

Example calculations for a 325 nmol / mol N_2O in N_2 calibration standard in a accredited laboratory:

–Prepared using the high purity gases

–Prepared using the gravimetric method on a equal arm balance in a temperature controlled laboratory

–Determination of uncertainty follows the approach in ISO 6142 [3]

–10 l aluminium cylinder

–Filling pressure 150 bar

Three categories of uncertainty defined in ISO 6142 [3]

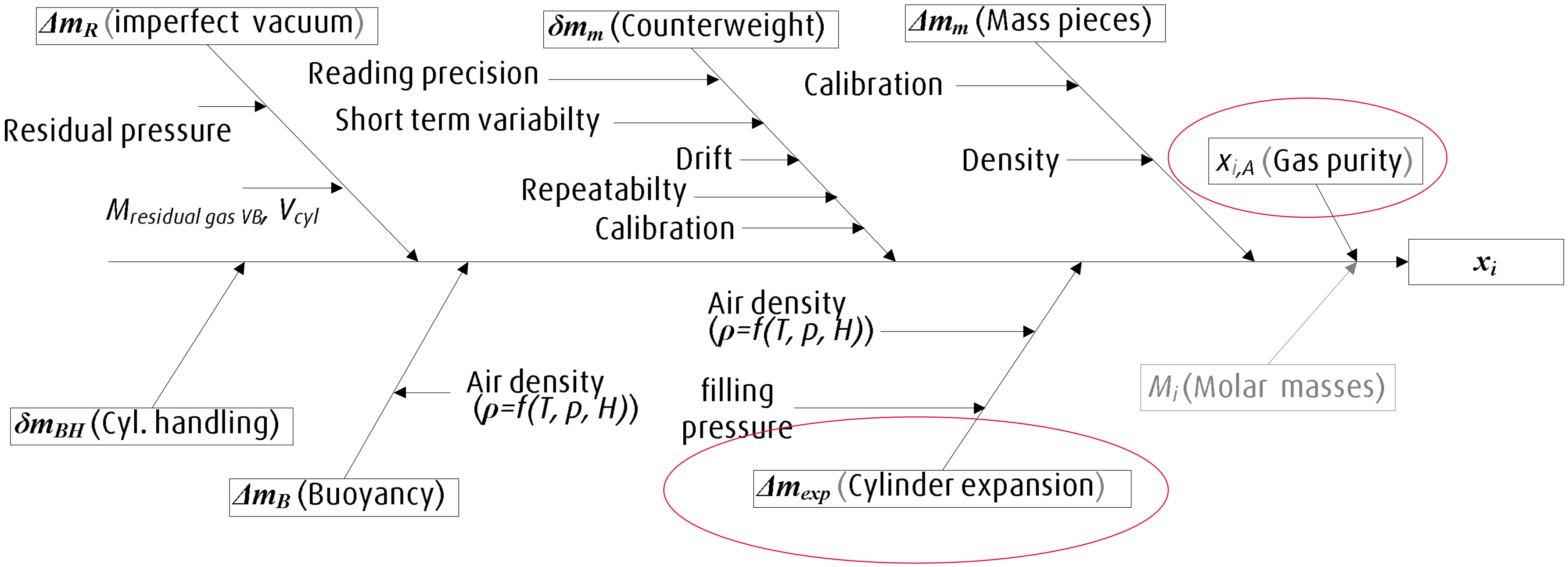
The gravimetric method described in ISO 6142 identifies three categories of uncertainty:

Uncertainty in the molar mass	Uncertainty in the weighing	Uncertainty in the purity analysis

$$u^2(x_i) = \sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial M_i}\right)^2 \cdot u^2(M_i) + \sum_{A=1}^{P}\left(\frac{\partial x_i}{\partial m_A}\right)^2 \cdot u^2(m_A) + \sum_{A=1}^{P}\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial x_{i,A}}\right)^2 \cdot u^2(x_{i,A})$$

Atomic weights of the elements 2009, International union of pure and applied chemistry (IUPAC)	$u(m_A)$ includes the uncertainty of balance, weights, buoyancy effects, residual gas …	Uncertainty contributions depend on the impurities of the parent gases and upon the accuracy of the analytical methods

Cause and effect diagram for main uncertainty sources



Δm_R (imperfect vacuum)

Residual pressure

$M_{residual\ gas\ VB}$, V_{cyl}

δm_m (Counterweight)

Reading precision

Short term variabilty

Drift

Repeatabilty

Calibration

Δm_m (Mass pieces)

Calibration

Density

$x_{i,A}$ (Gas purity)

x_i

δm_{BH} (Cyl. handling)

Δm_B (Buoyancy)

Air density ($\rho=f(T, p, H)$)

Air density ($\rho=f(T, p, H)$)

filling pressure

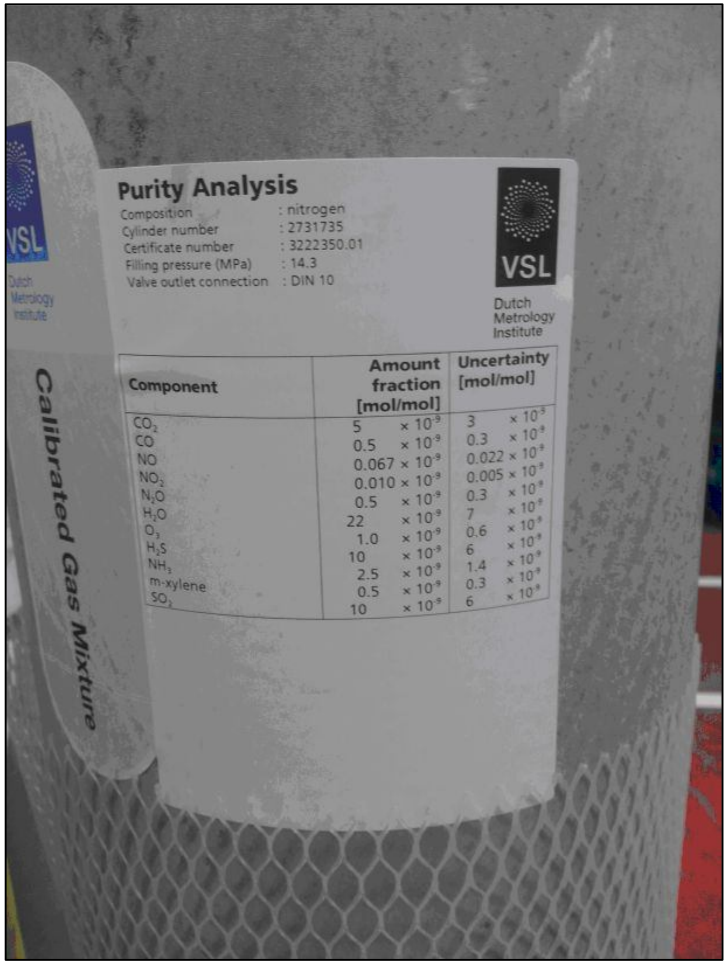
Δm_{exp} (Cylinder expansion)

M_i (Molar masses)

Required gas purity to achieve u(N_2O) ≤ 0.1 nmol / mol

Results of traceable purity analysis from European NMI
Sample: Nitrogen cylinder (Grade N7.0, Linde Gas DE)

	x ppb	$u(x)$ ppb	**Method**
CO_2	5	3	CRDS
CO	0.5	0.3	CRDS
NO	0.067	0.022	CLD
NO_2	0.010	0.005	CLD
N_2O	0.5	0.3	CRDS
H_2O	22	7	CRDS
O_3	1	0.6	UV photometric
H_2S	10	6	Electrochemical
NH_3	2.5	1.4	laser photoacoustic
m-Xylene	0.5	0.3	GC FID
SO_2	10	6	UV fluorescence



Purity Analysis

Composition : nitrogen
Cylinder number : 2731735
Certificate number : 3222350.01
Filling pressure (MPa) : 14.3
Valve outlet connection : DIN 10

Component	Amount fraction [mol/mol]	Uncertainty [mol/mol]
CO_2	5×10^{-9}	3×10^{-9}
CO	0.5×10^{-9}	0.3×10^{-9}
NO	0.067×10^{-9}	0.022×10^{-9}
NO_2	0.010×10^{-9}	0.005×10^{-9}
N_2O	0.5×10^{-9}	0.3×10^{-9}
H_2O	22×10^{-9}	7×10^{-9}
O_3	1.0×10^{-9}	0.6×10^{-9}
H_2S	10×10^{-9}	6×10^{-9}
NH_3	2.5×10^{-9}	1.4×10^{-9}
m-xylene	0.5×10^{-9}	0.3×10^{-9}
SO_2	10×10^{-9}	6×10^{-9}

Required gas purity to achieve u(N_2O) ≤ 0.1 nmol / mol (cont'd)

N_2 and N_2O purity tables for calculation

	N_2 7.0 (Linde DE)		N_2O 6.0 (Linde HU)	
ppb	*x*	*u*(*x*)	*x*	*u*(*x*)
CO_2	5	3	150	90
CO	0.5	0.3	50	30
NO	0.067	0.022	50	30
NO_2	0.010	0.005	50	30
N_2O	0.05	0.03	99999500	141
H_2O	22	7		
O_2	0.5	0.3		
H_2S	10	6		
NH_3	2.5	1.4	50	30
SO_2	10	6		
N_2	99999949	12	150	90

—In order to achieve the required purity, data have been „adjusted“ for N_2O purity analysis in Nitrogen.

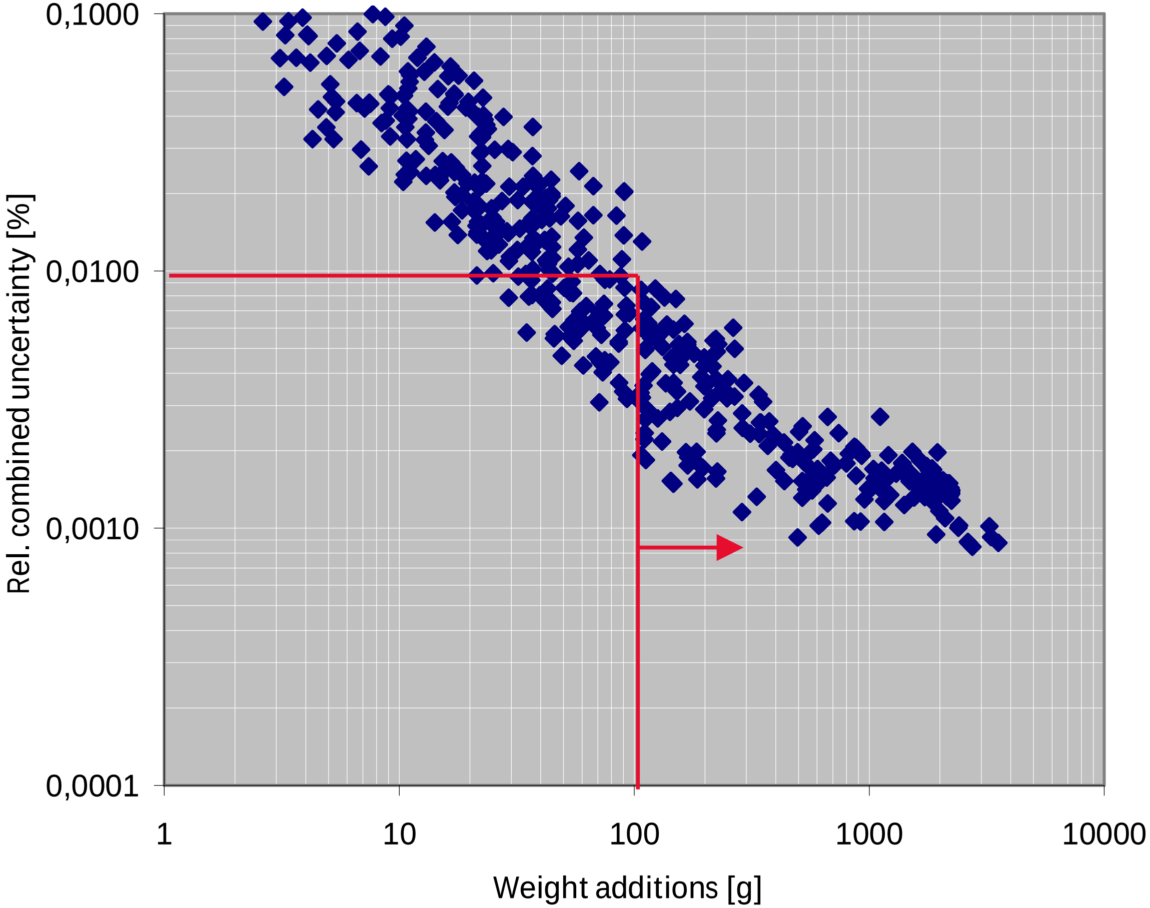
—The required N_2O detection limit of ~50 ppt cannot be currently achieved

—We are developing a method using TOF-APIMS[#] which might fulfil the required DL.

[#] Time of Flight – Air Pressure Ionisation Mass Spectrometer

Weighing scale for example calculations

Relative combined uncertainty of weighing results versus weight additions, Balance: Voland HCE 30 DOW



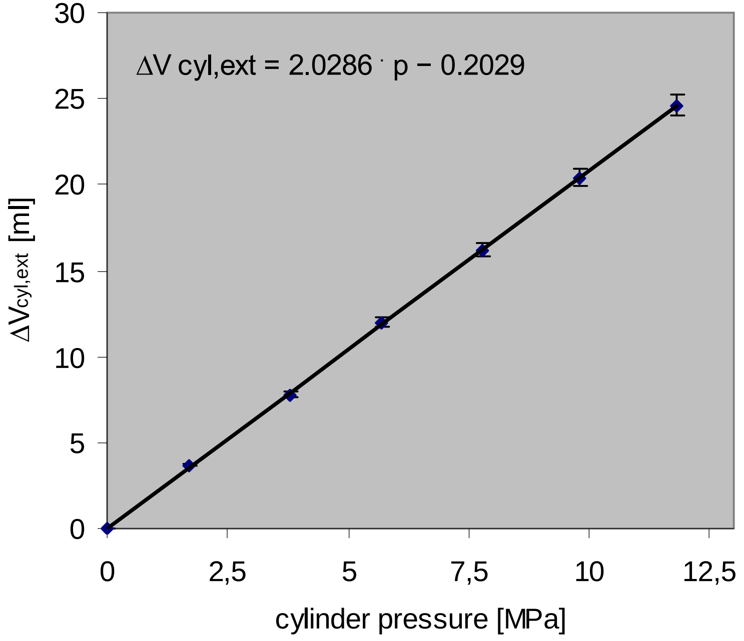
Required weighing uncertainty to achieve u(N_2O) ≤ 0.1 nmol/mol, results include u(M_i), u($x_{i,A}$) and u(m_A)

Gases	**m ± u(m) [g]**	**m ± u(m) [g]**	**↳ result**
Pures	N_2O 6.0 110.101 ± 0.008	N_2 7.0 1681.857 ± 0.020	4% N2O in N2 Premix 1 (0.007%)
Premix 1 / N_2 7.0	Premix 1 110.338 ± 0.008	N_2 7.0 1618.105 ± 0.020	2500 ppm N_2O in N_2 Premix 2 (0.010%)
Premix 2 / N_2 7.0	Premix 2 124.338 ± 0.008	N_2 7.0 1600.299 ± 0.020	180 ppm N_2O in N_2 Premix 3 (0.012%)
Premix 3 / N_2 7.0	Premix 3 287.424 ± 0.020	N_2 7.0 1436.967 ± 0.020	30 ppm N_2O in N_2 Premix 4 (0.014%)
Premix 4 / N_2 7.0	Premix 4 143,698 ± 0.008	N_2 7.0 1580.649 ± 0.020	2.5 ppm N_2O in N_2 Premix 5 (0.015%)
Premix 5 / N_2 7.0	Premix 5 224,160 ± 0.020	N_2 7.0 1500.183 ± 0.020	0.325 ppm N_2O in N_2 Final mixture
325.04 ± 0.063 nmol/mol N_2O in N_2			**$u_{rel}(N_2O)$= 0.020%**

Impact of buoyancy effect / changes in air density due to gas filling

- —Buoyancy effects due to cylinder expansion are a source of uncertainty for the preparation of gas standards
- —Changes in the external volume of a 9.5 litre aluminium cylinder at 12 MPa is 24.1 ± 1.5 ml [4]
- — These changes are linear and reversible
- —Average values for N2 and He are almost equal (changes in external cylinder volume do not depend on gas species)
- —The coefficient of expansion depends upon the cylinder material (different for steel and aluminium cylinders)

changes in cylinder volume due to N_2 gas filling



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[4]: S. H. Oh, B.M. Kim and N. Kang, ”Evaluation of changes in cylinder volume due to gas filling”, Metrologia 50 (2013)

Determination of air density from ambient pressure, relative humidity and laboratory temperature [5, 6]

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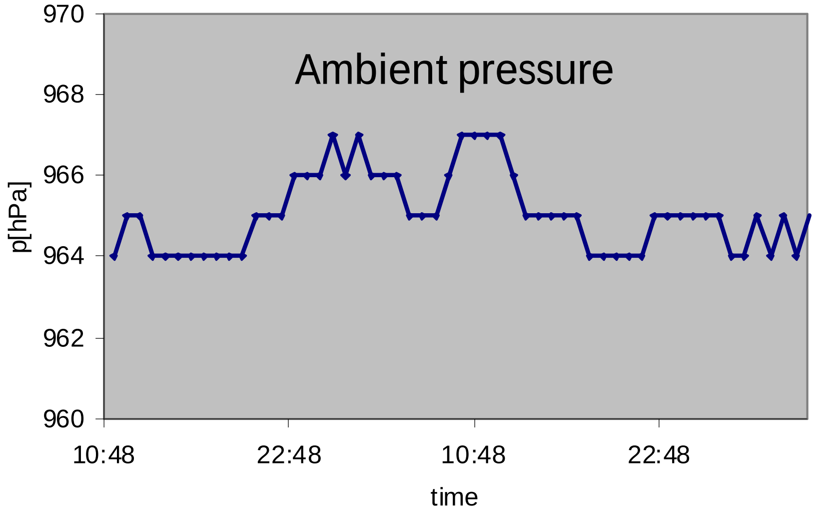
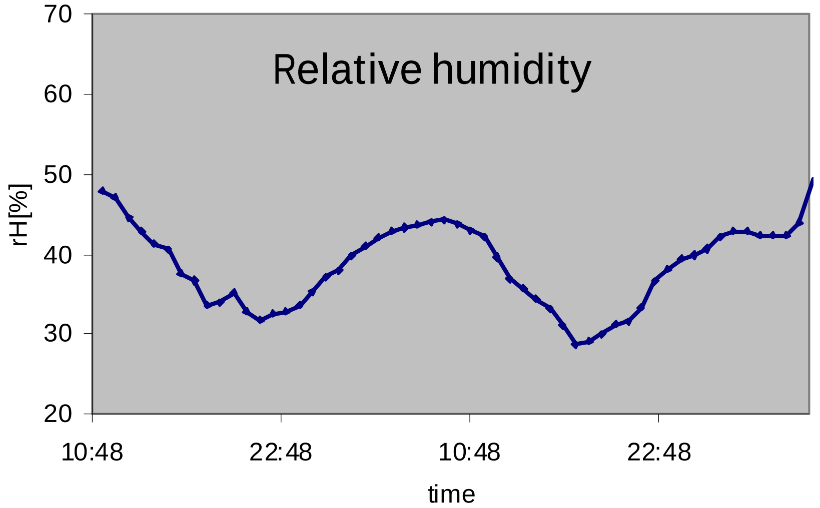
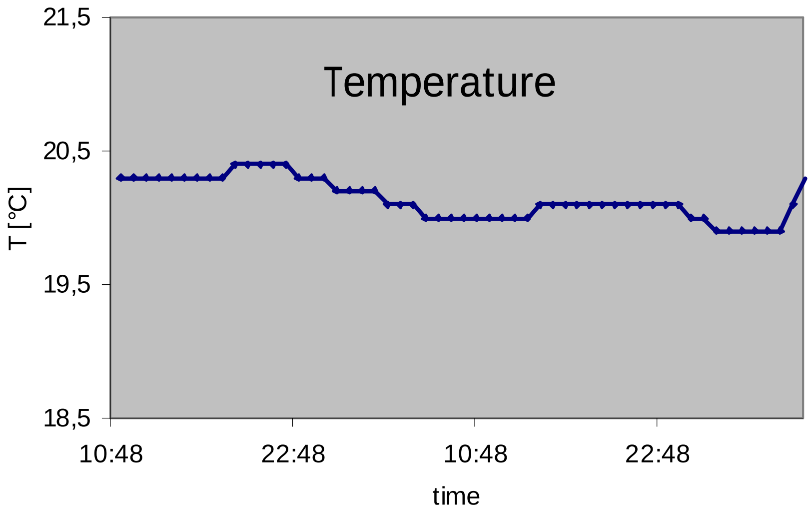
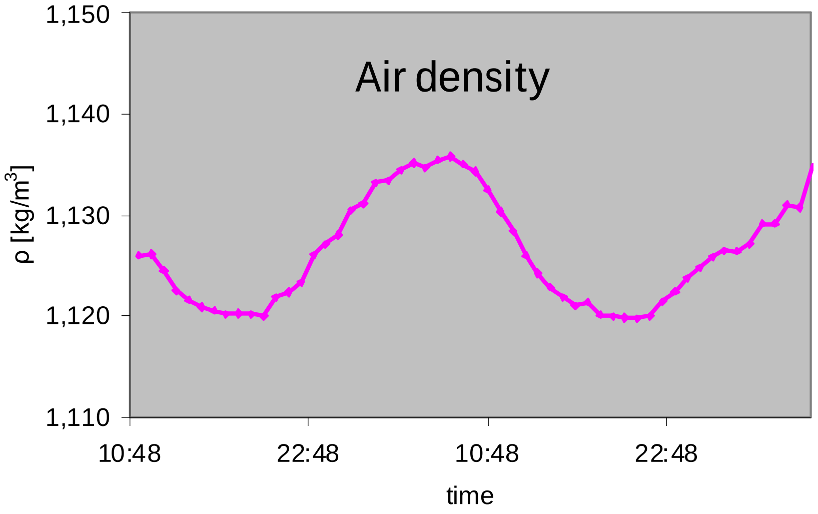








Impact of buoyancy effect / changes in air density due to gas filling (cont'd)

- The weighing result is influenced by buoyancy the effect

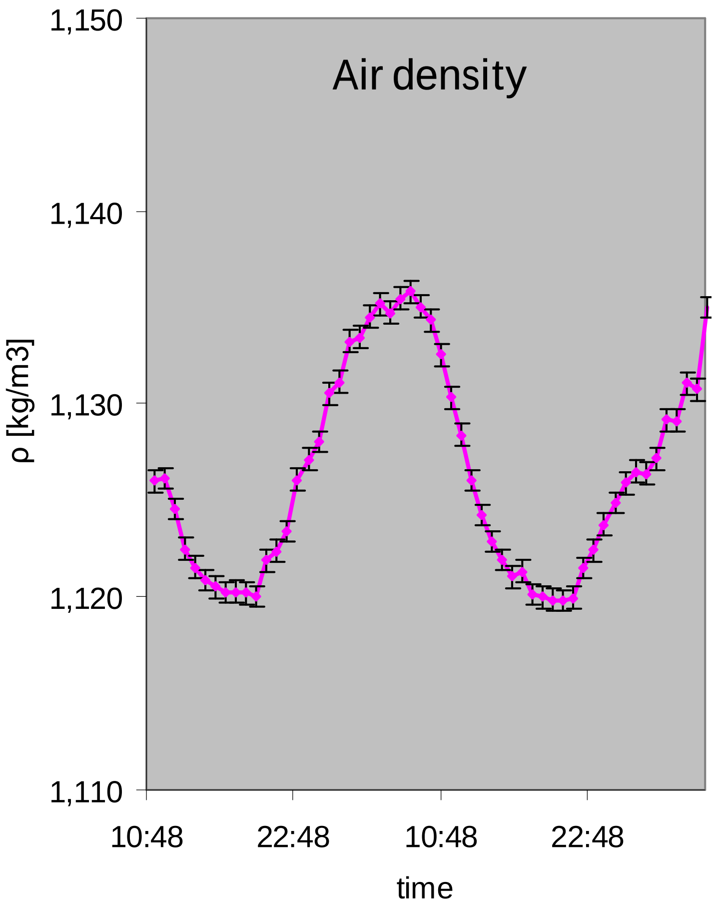
- If V is the cylinder volume and ρ_{air} the air density before filling and $V+\Delta V$ and $\rho_{air} + \Delta\rho_{air}$ the values after filling, then the difference is [7]:

$$\Delta m_{\exp} = (V+\Delta V)\cdot(\rho_{air} + \Delta\rho_{air}) - V\cdot\rho_{air}$$

$$\approx V\cdot\Delta\rho_{air} + \Delta V\cdot\rho_{air}$$

$$\approx V\cdot\Delta\rho_{air} + K_{cyl}\cdot p_{fill}\cdot\rho_{air}$$

- For a target uncertainty of $u(\Delta m_{exp})$ of 5mg the uncertainty for the changes in air density must be less than 0.0005 kg / m^3!



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[7]: W. Hässelbarth, "Teilbericht 2 zum Projekt grav. Unsicherheit unter Berücksichtigung von Korrelationen", Linde AG (2014)

Correlations between weighing results

Common practice for the determination of weighing uncertainty is the “basic version” of uncertainty propagation which is limited to the calculation of the standard uncertainty of the amount fraction by the addition of squares of the input quantities.

—This model does not account for correlations between the input quantities

—Strong correlations do exist between the weighing results of direct “neighbours” in a filling sequence

—Negligence of correlations can cause an over- or underestimation of uncertainty

—Consideration of correlations is done by addition of covariances $u(m_i,m_k)$ $(i \neq k)$ between different weighing steps [7]:

$$\sum_i \left(\frac{\partial x_a}{\partial m_i}\right)^2 \cdot u^2(m_i) \rightarrow \sum_i \left(\frac{\partial x_a}{\partial m_i}\right)^2 \cdot u^2(m_i) + \sum_i \sum_{k \neq i} \left(\frac{\partial x_a}{\partial m_i}\right) \cdot \left(\frac{\partial x_a}{\partial m_k}\right) \cdot u(m_i, m_k)$$

Summary

Research is necessary to achieve the target uncertainties in static gas calibration mixtures as a part of the HIGHGAS project, specifically:

- Detection limits for traceable purity analysis needs to be improved in order to meet tight specifications (e.g. $DL(N_2O) < 0.1$ ppb)
- Gravimetric filling process must further developed to meet the challenging uncertainty limits
- High accuracy measurement methods to quantify changes in air density needs to be developed
- Measurement uncertainties are derived using the ISO GUM and covariances are correctly accounted for

Requirements from the specialty gas industry for greenhouse gas standards

- The availability of Reference Standards from MNI's to allow traceable purity analysis
- Provision of Reference Gas Standards that are stable, metrologically traceable and have low measurement uncertainties to:
  - Allow the dissemination of ISO Guide 34 and ISO 17025 accredited gas calibration mixtures with the necessary low uncertainties

Contributors and References

Thanks to:

- Dr. Werner Hässelbarth, Berlin
- Erich Herbst, Linde Gases Div. (DE), Central Analytics

References:

- [1]: WMO Greenhouse Gas Bulletin, No.10, 2014
- [2]: Publishable JRP Summary Report for JRP ENV52 HIGHGAS Metrology for High-Impact Greenhouse Gases
- [3]: ISO 6142, Gas analysis - Preparation of calibration gas mixtures - Gravimetric method
- [4]: S. H. Oh, B.M. Kim and N. Kang, Evaluation of changes in cylinder volume due to gas filling, Metrologia 50 (2013)
- [5] P. Giacomo, Equation for the determination of the density of moist air (1981). Metrologia, 18, 1982,
- [6] R.S. Davis, Equation for the determination of the density of moist air (1981,91). Metrologia, 29, 1992,
- [7] W. Hässelbarth, "Teilbericht 2 zum Projekt gravimetrischen Unsicherheit unter Berücksichtigung von Korrelationen", Linde AG (2014)

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Thanks for your attention.