Traceability of Measurement Results in Gas Composition Analysis

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Importance of Gas Analysis

- **Economic Value**
  - Natural Gas (calorific value)
  - Ethylene (chemical process industry – purity)
  - Reactive gases (electronic industry – H₂O)

- **Environmental regulations**
  - Industrial stack emissions (NOₓ, SO₂)
  - Automotive gases (CO, CO₂, C₃H₈, NO)
  - Occupational hygiene (VOC, particles)
  - Ambient air quality (Benzene, O₃, CH₄, N₂O)

- **Legislation**
  - Breath Analysis (ethanol)
  - Odor Control (n-butanol)
Measurement Process

SI

Validation, Measurement Uncertainty

Pure Compounds

Calibration Standards

Comparison Method

Sample

Calibration Function

Measurement Result

Traceability
The Result of Traceability

Accurate Measurements

\[ y - U \leq \tau \leq y + U \]

Accreditation

Validated Analytical Methods

Certified Calibration Reference Materials

External Quality Assessment Schemes
For static gas mixtures, the traceability chain starts with a primary realisation of the definition of the mole fraction or amount of substance fraction for a specified chemical entity.

\[
y_B \left[ \frac{n_B}{\sum_i n_i} \right] \frac{m_B}{\sum_i \frac{m_i}{M_i}}
\]

\(n_B = \text{amount of substance of entity } B\)
Dynamic gas generation
A primary realisation (PSM) of the amount fraction in a static gas mixture involves (ISO 6142:2001):

- accurate weighing (incl. buoyancy correction) of pure parent gases (or liquids) in a clean high pressure cylinder \( (u_c \approx 0.01-0.1\%) \)
- Impurity analysis of the parent gases/liquids
- Analytical verification of the composition against a coherent set of primary standards \( (u_c \approx 0.05-1\%) \)
- Stability testing

Problems: low amount fractions (nmol/mol) for reactive gases, sorption on cylinder wall, isotopic variation, phase separation
A primary realisation of the mole fraction of such a gas mixture is called a Primary gas Standard Material (PSM).
Stability of PSMs

Stability 600 Qmol/mol NO in N2

\[ \Delta_{av} = +0.004 \quad \text{s.d.} = 0.105 \]
Experimental Set-up KCs (I)

Coordinating NMI
Pure gases
gravimetry
PRM

Participating NMI
Pure gases*
gravimetry
PSM*
comparison
secondary methods (NDIR, GC, FTIR, ....)
For *dynamically* generated gas mixtures, the traceability chain starts with a primary realisation for amount concentration (mol/m$^3$) for a specified chemical entity.

\[
C_B = \frac{n_B}{V} \frac{m_B}{VM_B}
\]

*N.B. Pressure and temperature need to be defined as well!*

Usually, permeation, diffusion or injection of a pure gas in a flowing gas stream produces the primary realisation.
CCQM.K1c

CCQM.K1c  NO in Nitrogen  100 µmol/mol

deviation from gravimetric reference values (%)
CCQM-K3

Results for Carbon Monoxide

Relative difference (%)
CCQM-K3

Results for Carbon Dioxide

Relative difference (%)
CCQM-K3

Results for Propane

Relative difference (%) vs. Laboratory
Comparison of 120 ppm ethanol/air standards

CCQM-K4
CCQM-K7

CCQM K7: Benzene at 50-60 nmol/mol

Absolute Deviation from Reference Value (nmol/mol)
CCQM GAWG Key Comparisons

- CCQM-K1abcd NMI CO, CO₂, NO, SO₂ in nitrogen
- CCQM-K1fgh NMI Natural gas (C₁-C₄)
- CCQM-K3 NMI CO, CO₂, C₃H₈ in nitrogen
- CCQM-K4 NPL Ethanol in air
- CCQM-K7 NIST Benzene, toluene, xylenes in air
- CCQM-K10 NIST BTX in air, ambient concentrations
- CCQM-K15 KRISS CF₄ and SF₆ at emission levels
- CCQM-K16 NMI Natural gas (C₁-C₆)
- CCQM-K22 NMIJ VOC in nitrogen
- CCQM-K26ab NPL NO and SO₂ at ambient level
- CCQM-P41 NMI Greenhouse gases (CO₂, CH₄)
CCQM GAWG Pilot Studies

- CCQM-P20b  NIST  Purity o-xylene
- CCQM-P23  NMi  Gravimetry
- CCQM-P24  LNE  Dynamic blending
- CCQM-P28  BIPM  Ozone
- CCQM-P41  NMi  Greenhouse gases
- CCQM-P42  NIST  H$_2$S in nitrogen
Regional key comparisons

- Euromet.QM-K1c  NMi  NO in nitrogen
- Euromet.QM-K3  NMi  Automotives
- Euromet.QM-K4  NPL  Ethanol in air

- APMP.QM-K3  KRISS  Automotives
- APMP.QM-K4  NMIJ  Ethanol in air
New Experimental Set-up

Coordinating NMI

Participating NMI

Pure gases

Gravimetry

Analytical comparison under repeatability conditions

Series of PRMs
Murphy’s Laws

- Nothing is as easy as it looks.
- Everything takes longer than you think.
- Anything that can go wrong will go wrong.
- If there is a possibility of several things going wrong, the one that will cause the most damage will be the one to go wrong.
- If anything simply cannot go wrong, it will anyway.
- If you perceive that there are four possible ways in which a procedure can go wrong, and circumvent these, then a fifth way, unprepared for, will promptly develop.
- Left to themselves, things tend to go from bad to worse.
- If everything seems to be going well, you have obviously overlooked something.
- Nature always sides with the hidden flaw.
P23 Pilot Study - NDIR

50,000 ppm Carbon Monoxide

Results from NMi VSL analysis
P23 Pilot Study - NDIR

1,000 ppm Carbon Monoxide

Results from NMi VSL analysis
P23 Pilot Study - NDIR

10 ppm Carbon Monoxide

Corrected NDIR Response vs Concentration (ppm)

Results from NMi VSL analysis
Preliminary Findings

• Agreement poor, two laboratories consistently high response
  – KRISS suggested $^{13}\text{C}/^{12}\text{C}$ ratio problem
  – Pure CO used may have non-natural abundance?

• Plan: Reanalyze using method immune to isotopic interference
  – Most 50,000 ppm cylinders sent to NIST for analysis by GC-TCD
  – Most 1,000 ppm cylinders sent to Metas for GC-FID with methanisation
P23 Pilot Study - TCD

Results from NIST analysis
P23 Pilot Study – Methanised FID

Results from Metas analysis
$^{13}$C Depletion

Bias from P23 NDIR Regression

50,000 ppm

Results from NIST analysis using GC/MSD
Conclusions P23

- NDIR is sensitive to $^{13}\text{C}/^{12}\text{C}$ ratio
  - Only those with gas-filled cells (most are)
  - $^{13}\text{C}$ depleted in some regions of the world
  - $^{13}\text{C}$ removed for delivery into $^{13}\text{C}$ labeled chemical market
  - Bias can be as high as 1.5% relative

- NDIR users must insist that their supplier use naturally abundant Carbon Monoxide
  - A “correction factor” is not possible for this bias
Function of Standards from NMIs

Primary Realisations of Standard gas Mixtures (PSMs)

Transfer Reference gas Standards (PRM, PRGM, SRM, ...)

Certified gas Reference Material (CRM, CRGM, NTRM, ...)

NMI

Gas Manufacturer
Valid Traceability Chain - PRM

NIST → NMI → NPL → BAM

INMetros

PRM

International Acceptance under CIPM MRA

Accreditation by AB
ISO/IEC 17025 Calibration Laboratory

Accreditation by AB
ISO/IEC 17025 Test Laboratory

End Users

Gas Manufacturing Industry
- Scott Specialty Gases
- Air Products
- Air Liquide
- Messer
- White Martins
- Linde
- BOC
- etc.

Scott Specialty Gases
Air Products
Air Liquide
Messer
White Martins
Linde
BOC
etc.
Standardisation

- ISO/TC 146 Air Quality
- ISO/TC 158 Gas Analysis
- ISO/TC 193 Natural Gas
- ISO/TAG 4 Metrological Issues
Standardisation in ISO TC 158

- Standardisation in the field of gas analysis
- Co-operation between Metrology Institutes, Gas Manufacturing Industry, Instrument Manufacturers, End Users
- National mirror committees
- Fully validated measurement and production procedures including uncertainty evaluation
- Major products ISO 6142:2001 (Gravimetry) and ISO 6143:2001 (Comparison methods)
- Gas Analysis Symposium (6–8 October 2004 – Amsterdam)
Determination of the composition of calibration gas mixtures – Comparison methods

Multi point calibration with appropriate gas mixtures

Calculation of the uncertainty of the composition using uncertainties in both the calibration standards and the detector responses (GLS).

\[
u^2(x_c) = \left[ \frac{\partial G}{\partial y_c} \right]^2 u^2(y_c) + \sum_{k=0}^{M} \left[ \frac{\partial G}{\partial b_k} \right]^2 \text{var}(b_k) + 2 \sum_{k=0}^{M-1} \sum_{l=k+1}^{M} \left[ \frac{\partial G}{\partial b_k} \right] \left[ \frac{\partial G}{\partial b_l} \right] \text{cov}(b_k, b_l)\]
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<td>s(r)</td>
<td>0.6996 0.88%</td>
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<tr>
<td>s(L)</td>
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<td>MAD</td>
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<td>0.24 0.30%</td>
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| Reference values              |                               |
| value                         | 79.4700                       |
| u                             | 0.7947 1.00%                  |

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**Results of Methane**

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**Z-scores of Methane**

![Z-scores of Methane graph]
### Consensus values (raw)

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### Median, MAD, AAD

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### Consensus values (corrected)

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### Results of Ethane

#### Z-scores of Ethane

![Z-scores of Ethane graph]

### Laboratory Values

![Laboratory Values graph]
Accreditation in Europe

Present Situation

Accredited as Calibration Laboratory

Belgium (1)                France (2, incl BNM-LNE)
Italy (1)                  Netherlands (4, incl NMi)
Spain (3)                  Sweden (1)
Switzerland (3)            United Kingdom (7, incl NPL)

Accredited as Test Laboratory

Germany (2)
Conclusions

- All conditions for achieving traceability of measurement results in gas analysis can be fulfilled. Close co-operation between NMIs, Standardisation Bodies, Accreditation Bodies, EQAS organisers and the Gas Manufacturers Industry are essential.

- Primary Gas Calibration Standards have been realised for many applications and tested in key comparisons

- Accreditation of most producers of gas calibration standards as a calibration laboratory has been realised now in most countries in Europe and in Japan.