Improving the accuracy of NO₂ and Ozone monitoring

J. Viallon, E. Flores, F. Idrees, P. Moussay, and R.I. Wielgosz

Standards and Measurements for Clean Air
14 October 2016, IPQ – Caparica, Portugal
Air Quality, NO$_2$ and O$_3$ measurements

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration</th>
<th>Averaging period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>60 nmol/mol</td>
<td>Maximum daily 8 hour mean</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO$_2$)</td>
<td>100 nmol/mol</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>20 nmol/mol</td>
<td>1 year</td>
</tr>
</tbody>
</table>

Typical ambient levels nmol mol$^{-1}$

http://alg.umbc.edu/usaq/
NO$_2$ and O$_3$ at BIPM

Dynamic gas standard generation
CCQM-K74.2010 (+2018)

NO analyzers under repeatability conditions

Ozone cross-section measurement by gas phase titration
Joele Viallon, Philippe Moussay, Edgar Flores, and Robert Ian Wielgosz
*Analytical Chemistry* Just Accepted Manuscript
DOI: [10.1021/acs.analchem.6b03299](http://dx.doi.org/10.1021/acs.analchem.6b03299)

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

Triad of reference ozone photometers
BIPM.QM-K1 (2007-....)
Ozone
Ozone SRP, from US to the world

2016: 55 SRPs acting as ozone standard for national, regional or global networks

NIST acting as Central Calibration Laboratory for WMO/GAW


International Bureau of Weights and Measures BIPM has published in the International database new calibration capabilities (CMC) in the field of chemistry (gas analysis)

July 14, 2016

International Bureau of Weights and Measures (BIPM) published in International database new calibration capabilities (CMC) in the field of chemistry (gas analysis) of the Directorate of Measures and Precious Metals (DMDM), Group for metrology in chemistry. Capabilities of calibration in the field of chemistry (gas analysis) for measurement of the concentration of ozone in the atmosphere by applying new national standard - the standard photometer for ozone SRP 54 can be found at:

Ozone, at ambient level... absorbs UV light at 253.64 nm

Flow of Ozone in air (0-1000 nmol/mol) or reference air

\[ x(O_3) = \frac{1}{\alpha(\lambda = 254\text{nm})L_{opt}} \frac{T}{T_{\text{std}}} \frac{P_{\text{std}}}{P} \ln\left(\frac{I}{I_0}\right) \]
BIPM-NIST program to maintain the comparability of the worldwide network of ozone reference standards

2003-2005: first international comparisons CCQM-P28

10 UV photometers agree with the reference value
12 UV photometers do not agree

2 systems based on Gas Phase Titration of ozone with NO already showed discrepancy between methods

NO + O₃ → NO₂ + O₂

UV photometry

gravimetry
Uncertainty budget revised in 2006

Measurement range [0-1000] nmol mol\(^{-1}\)

Typical standard uncertainty 1.12%

Dominated by ozone absorption cross-section

\[
x(\text{O}_3) = \frac{1}{\alpha(\lambda = 254\text{nm}) L_{\text{opt}}} \frac{T}{T_{\text{std}}} \frac{P_{\text{std}}}{P} \ln\left(\frac{I}{I_0}\right)
\]

Fundamental property of the molecule
Measured separately on known amount fractions
Measured by ~ 15 groups
Conventional value to be adopted
2007: launch of International Comparison BIPM.QM.K1

http://kcdb.bipm.org/appendixB/

On-going = series of bilateral comparisons between BIPM and participants, directly or using transfer standards

Degrees of equivalence at 420 nmol/mol of ozone in air:

www.bipm.org
Improved comparability and traceability

2002-2013: improved comparability between institutes taking part in BIPM comparisons

2013: BIPM.QM-K1 comparison recognised as the way to demonstrate metrological traceability in surface ozone measurements for WMO

Reference Instrument (BIPM-SRP27)

GAW Report No. 209

www.bipm.org
Measuring Ozone Cross-Sections at the BIPM

A laser ozone photometer measuring at 244 nm, 248 nm, 257 nm

Setup for (absolute) cross-section measurements on pure ozone at low pressure

Pure liquid ozone at $T = 73$ K

Values of the ozone absorption cross-section at 253.65 nm reported in the literature

Lead to actions for improved air quality* for the World’s Population


*20% increase in the number of sites that are out of compliance with current US, Canadian, and European ozone air quality health standards for the year 2012

BIPM O₃ X-Section measurements mean that O₃ values are 1.8% higher than historically reported

www.bipm.org
Nitrogen dioxide
Gas Standards for long term monitoring of nitrogen oxides

NPL is WMO/GAW Central Calibration Laboratory for NO

| Table 2 - Data Quality Objectives (DQOs) for NO and NO₂ under differing conditions |
|---------------------------------|----------------|----------------|----------------|
| Level                          | 1 (basic)     | 2 (enhanced)   | 3 (high)       |
| Site characteristics           | Continental basic | Continental background | Pristine, marine background, free troposphere |
| Mean mixing ratio NO₂          | > 1 ppb       | 0.1 – 1 ppb    | < 0.1 ppb      |
| Scope                          |                |                |                |
| (corresponding time resolution) |                |                |                |
| Detection Limit                |                |                |                |
| (1 hour, 3-σ)                  | NO: 50 ppt    | NO: 10 ppt     | NO: 1 ppt      |
|                                  | NO₂: 100 ppt  | NO₂: 20 ppt    | NO₂: 5 ppt     |
| uncertainty                     |                |                |                |
| (1 hour, 2-σ)¹                 | NO: 40 ppt or 3% | NO: 8 ppt or 3% | NO: 1 ppt or 3% |
|                                  | NO₂: 80 ppt or 5% | NO₂: 15 ppt or 5% | NO₂: 3 ppt or 5% |
| uncertainty                     |                |                |                |
| (1 month, 2-σ)²                | NO: 2.5%      | NO: 2.5%       | NO: 1 pp or 2.5% |
|                                  | NO₂: 3%       | NO₂: 3%        | NO₂: 3 ppt or 3% |
| data coverage                  |                | 66%            |                |
| suggested method                | CLD / PLC     | CLD / PLC      | CLD / PLC      |
| alternative method (backup or GC reasons) | CRDS, LIF; DOAS; TDLAS | CRDS, LIF; TDLAS | LIF |

Nitrogen dioxide measurements

Chemiluminescence detectors (CLD)

Most used, recommended method
indirect method

Interferences (HNO₃, O₃, etc.)

Non-dispersive ultraviolet analyzers (NUA)

Cavity Attenuated Phase Shift (CAPS)

Differencial Optical Absorption Spectroscopy (DOAS)

Fourier Transform Infrared Spectroscopy (FTIR)

Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS)

Database of spectroscopic parameters
(HITRAN or PNNL or NIST library)

Synthetic calibration

Open path instrument

Sampling instrument

Calibration with Reference Materials

www.bipm.org
Dynamic gas standards to underpin international comparisons

Reference = NO₂ mole fraction as generated + measured by BIPM dynamic system

Permeation/diffusion tubes as sources
• Regular/constant weighing
• Matrix gas flow control
• Purity analysis
Magnetic Suspension Balance

- Mass load 20 g
- Resolution 2 μg
- Stability over 3 days ~ 0.5 μg

Measurement of the mass of the permeation tube emitting the analyte

Deduction of the permeation rate \( q_m / (\text{ng min}^{-1}) \)

\[ q_m = \frac{dm}{dt} \]

And the amount of substance fraction

\[ x_A = \frac{q_m V_m}{q_v M_A} \]
CCQM-K74 International comparison of nitrogen dioxide in nitrogen standards (2010)

- \(\text{NO}_2/\text{N}_2\), nominal amount fraction 10 \(\mu\text{mol mol}^{-1}\)
- Set of 17 transfer standards prepared by VSL
- Analysis using FTIR & UV absorption

Highly Accurate Nitrogen Dioxide (NO\(_2\)) in Nitrogen Standards Based on Permeation,
### CCQM-K74 BIPM typical uncertainties

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>unit</th>
<th>Standard relative uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_m$</td>
<td>8357.30</td>
<td>ng min$^{-1}$</td>
<td>5.00×10$^{-4}$</td>
</tr>
<tr>
<td>$V_m$</td>
<td>22.40037</td>
<td>L mol$^{-1}$</td>
<td>1.52×10$^{-5}$</td>
</tr>
<tr>
<td>$q_v$</td>
<td>0.452</td>
<td>L min$^{-1}$</td>
<td>1.00×10$^{-3}$</td>
</tr>
<tr>
<td>$M_{NO_2}$</td>
<td>46.0055</td>
<td>g mol$^{-1}$</td>
<td>3.04×10$^{-5}$</td>
</tr>
<tr>
<td>$x_{HNO_3}$</td>
<td>104.00</td>
<td>nmol mol$^{-1}$</td>
<td>2.02×10$^{-1}$</td>
</tr>
<tr>
<td>$M_{HNO_3}$</td>
<td>63.013</td>
<td>g mol$^{-1}$</td>
<td>1.86×10$^{-5}$</td>
</tr>
<tr>
<td>$x_{N_2O_4}$</td>
<td>0</td>
<td>µmol mol$^{-1}$</td>
<td>0.866 nmol/mol</td>
</tr>
</tbody>
</table>

**HNO$_3$ quantification by FTIR referenced to molecular parameters (HITRAN)***

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Standard Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x(NO_2)$</td>
<td>8.86 µmol mol$^{-1}$</td>
<td>0.03 µmol mol$^{-1}$</td>
</tr>
</tbody>
</table>
Preparing for a repeat comparison CCQM-K74.2018

Generation of dynamic mixtures of HNO₃ in nitrogen by permeation

\[
x_{\text{HNO}_3} = \frac{q_m V_m}{q_v M_{\text{HNO}_3}} - \frac{M_{\text{NO}_2} x_{\text{NO}_2}}{M_{\text{HNO}_3}} - \frac{M_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}}}{M_{\text{HNO}_3}}
\]

HNO₃ permeation [200-500] nmol mol⁻¹
Permeation rate ~ 30 % H₂O
H₂O accurate quantification is crucial
BIPM and VSL agreed to work together again to coordinate CCQM-K74.2018

Levels of HNO₃ in recent standards much lower than in 2010

K74.2010 key results
- $u$(KCRV)=0.4 %
- Consistency between participants $\pm$ 3 %
Conclusions

- Standards for air quality are challenging due to the reactivity of target compounds
- Maintenance of dynamic standards is a valuable solution, either based on spectroscopy or continuous weighing of a source material
- The BIPM has been maintaining dynamic generation facilities to underpin international comparisons to demonstrate NMIs comparability
- Within the last 15 years, important progress have been made in global comparability of standards at the national level
Acknowledgements

**NIST**
James Norris, Frank Guenther, Joseph Hodges

**BIPM**
Philippe Moussay, Faraz Idrees, Edgar Flores, Robert Wielgosz

**Secondees from NMIs**
- M. Sega (INRIM, Italy), A. Rakowska (GUM, Poland), C. Pascale (METAS)
- S. Lee (KRISS, Korea), K. Tworek (GUM, Poland)