Measurement equivalence for stack emission monitoring

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Overview

- Introduction
- Production of PRGMs
- Available PRGMs
- International equivalence
- Proficiency testing schemes
- New developments
- Future work
- Conclusions
Introduction

Stack emission monitoring Measurements:

- Measurements performed at point sources
- Important for process control of air pollution and for implementing legislation

Gas analysis role:

- Disseminates the measurement traceability by the provision of accurate and precise gravimetrically prepared primary reference gas mixtures (PRGMs)
- International equivalence through key comparison
- Coordinates proficiency testing schemes to promote measurement equivalence to all industries in South Africa
Introduction

Primary reference gas mixtures

- Mixtures with the highest metrological quality
- Calibration of analysers used for measuring stack emissions
- To meet the requirements for the measurement traceability of monitoring and reporting emissions
Production of PRGMs

Weighing of the cylinder

Filing of the cylinder

Mixture homogenise

Short term stability of the PRGM

Certificate of analysis
## Available PRGMs

<table>
<thead>
<tr>
<th>Description</th>
<th>Concentration</th>
<th>Expanded uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO in air/nitrogen</td>
<td>1-10 % mol.mol⁻¹</td>
<td>0,5% relative</td>
</tr>
<tr>
<td>CO in air/nitrogen</td>
<td>1000 – 10 000 μmol.mol⁻¹</td>
<td>0,5% relative</td>
</tr>
<tr>
<td>CO in air/nitrogen</td>
<td>100 – 1000 μmol.mol⁻¹</td>
<td>0,5% relative</td>
</tr>
<tr>
<td>CO in air/nitrogen</td>
<td>10 – 100 μmol.mol⁻¹</td>
<td>1% relative</td>
</tr>
<tr>
<td>CO in air/nitrogen</td>
<td>1 – 10 μmol.mol⁻¹</td>
<td>1% relative</td>
</tr>
<tr>
<td>CO₂ in air/nitrogen</td>
<td>1-20 % mol.mol⁻¹</td>
<td>0,5 % relative</td>
</tr>
<tr>
<td>CO₂ in air/nitrogen</td>
<td>1000-10 000 μmol.mol⁻¹</td>
<td>0,5 % relative</td>
</tr>
<tr>
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<td>0,5 % relative</td>
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</table>
### Available PRGMs

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<tr>
<th>Description</th>
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</tr>
</thead>
<tbody>
<tr>
<td>SO(_2) in air/nitrogen</td>
<td>1000 – 10 000 (\mu\text{mol.mol}^{-1})</td>
<td>0.5% relative</td>
</tr>
<tr>
<td>SO(_2) in air/nitrogen</td>
<td>100 – 1000 (\mu\text{mol.mol}^{-1})</td>
<td>0.5% relative</td>
</tr>
<tr>
<td>SO(_2) in air/nitrogen</td>
<td>10 – 100 (\mu\text{mol.mol}^{-1})</td>
<td>1% relative</td>
</tr>
<tr>
<td>NO in nitrogen</td>
<td>1000 – 10 000 (\mu\text{mol.mol}^{-1})</td>
<td>0.5% relative</td>
</tr>
<tr>
<td>NO in nitrogen</td>
<td>100 – 1000 (\mu\text{mol.mol}^{-1})</td>
<td>0.5% relative</td>
</tr>
<tr>
<td>NO in nitrogen</td>
<td>10 – 100 (\mu\text{mol.mol}^{-1})</td>
<td>1% relative</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{OH}) in air/nitrogen</td>
<td>50 - 550 (\mu\text{mol.mol}^{-1})</td>
<td>0.5% relative</td>
</tr>
</tbody>
</table>
International equivalence

- CCQM K71 (2008)
  - Key multi-component comparison in the field of industrial emission measurements (stack gas)
Nominal amount-of substance fractions;
NO: 10-100 μmol/mol
SO₂: 20-200 μmol/mol
CO: 10-100 μmol/mol
CO₂: 100-160 mmol/mol
C₃H₈: 1-10 μmol/mol in nitrogen
International equivalence^2

- APMP QM S7
  - Methane in nitrogen 1000 µmol.mol\(^{-1}\) (2013/2014)
International equivalence

- CCQM K111
  - Propane in nitrogen 1000 µmol.mol$^{-1}$ (2014)
Development of propane reference mixtures

- Internal consistency study
- The four gas mixtures were analysed using A-B-A method
- One gas mixture was used as the reference
- Model equation:

\[ C_{sample} = \frac{A_{Sample}}{A_{Reference}} \times C_{reference} \]

<table>
<thead>
<tr>
<th>Cylinder number</th>
<th>Concentration (µmol/mol)</th>
<th>Means</th>
<th>%RSD</th>
<th>Sensitivity</th>
<th>Sensitivity ratio</th>
<th>%Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>M9 3862</td>
<td>1003.3</td>
<td>31851</td>
<td>0.194</td>
<td>31.73</td>
<td>1.0000</td>
<td></td>
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<td>M9 3831</td>
<td>1000.3</td>
<td>31715</td>
<td>0.260</td>
<td>31.71</td>
<td>0.9993</td>
<td>0.071</td>
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<tr>
<td>M9 3799</td>
<td>998.8</td>
<td>31730</td>
<td>0.186</td>
<td>31.77</td>
<td>1.0020</td>
<td>0.204</td>
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<tr>
<td>M9 3910</td>
<td>1000.1</td>
<td>31702</td>
<td>0.188</td>
<td>31.70</td>
<td>1.0003</td>
<td>0.032</td>
</tr>
</tbody>
</table>
Development of propane reference mixtures

- Internal consistency study
Proficiency testing schemes

- PT Scheme results for 800 to 850 µmol.mol\(^{-1}\) Sulphur Dioxide (SO\(_2\)) in nitrogen (2012)
Proficiency testing schemes

- PT Scheme results for 700 to 900 µmol.mol\(^{-1}\) Nitric Oxide (NO) in nitrogen (2014)
Future work

Development of new national measurement standards (NMS)

- Non-methane hydrocarbons and other VOCs
- Greenhouse gases
- Sulphur containing compounds reference materials
Conclusion

Gas analysis laboratory
- Provide PRGMs for traceable measurements
- Provides PT schemes
- Continuous improvement to meet the industry needs

International Comparison
- International equivalence

PT schemes
- Harmonise measurements
- Accurate and confidence in measurements
Acknowledgements

CONTACT DETAILS
Contact details for primary reference gas mixtures: gas@nmisa.org