Accurate measurements of greenhouse gases – what we can learn from over 100 audits in 25 years

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Introduction

Empa operates the World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide since 1996. To date more than 100 audits were made to ensure traceability to a common reference [1].

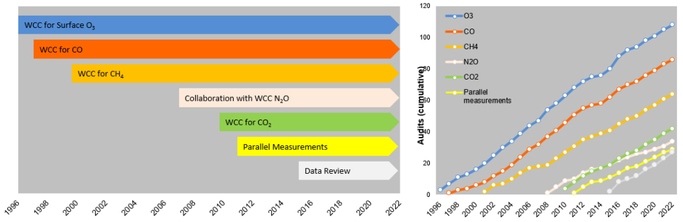

Figure 1: *Scope and history of WCC-Empa audits.*

Comparisons during the audits are made using gas cylinders for CO, CH_4, CO_2, and N_2O that cover a wide amount fraction range. This assessment of repeatability is complemented by parallel measurements for CO, CO_2 and CH_4 with a completely independent system for sampling, drying and analysis.

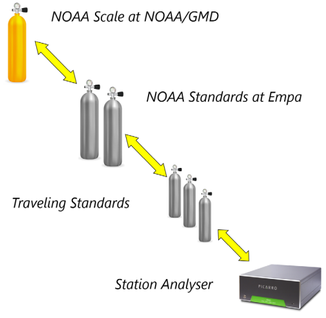

Figure 2: *Realisation of audits with travelling standards and traceability chain (schematic).*

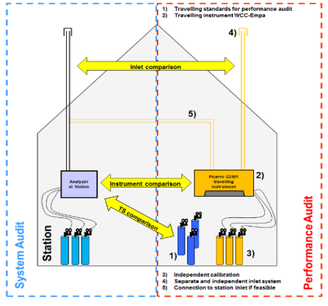

Figure 3: *Realisation of audits with a travelling analyser.*

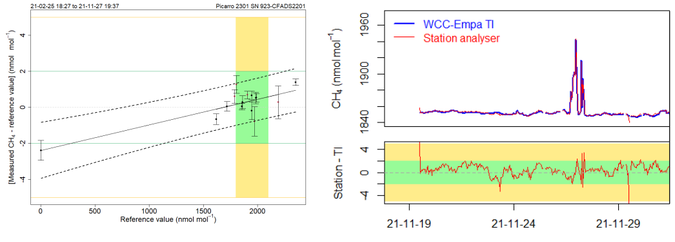

Figure 4: *Typical audit results obtained by travelling standard comparisons (left) and parallel measurements (right).*

CO_2 and CO measurements remain challenging

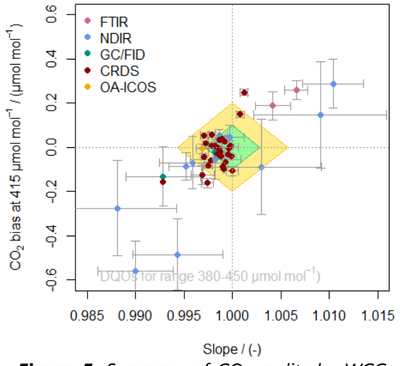

Figure 5: *Summary of CO_2 audits by WCC-Empa (Update from Zellweger et al. [2]).*

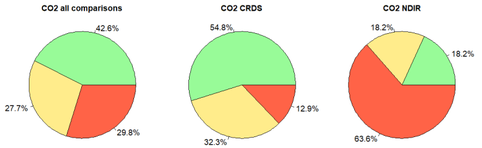

Figure 6: *Percentage of CO_2 comparisons within the compatibility (green) and extended compatibility goal (yellow).*

- 42 % of the CO_2 audits fulfilled the WMO/GAW compatibility goal of 0.1 µmol mol^{-1}.
- Additional 28 % were within the extended compatibility goals of 0.2 µmol mol^{-1}.
- Newer, laser spectroscopy based techniques showed better results compared to NDIR.

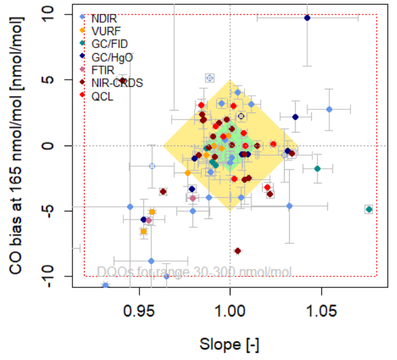

Figure 7: *Summary of CO audits by WCC-Empa (Update from Zellweger et al. [3]).*

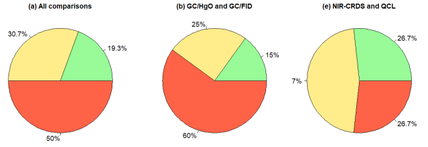

Figure 8: *Percentage of CO comparisons within the compatibility (green) and extended compatibility goal (yellow).*

- Only 50 % of the CO audits fulfilled the extended WMO/GAW compatibility goal of 5 nmol mol^{-1}.
- Newer, laser spectroscopy based techniques showed better results compared to GC techniques.
- CO measurements remain challenging.

Why are accurate CO measurements difficult?

- CO in air standards are often unstable and show an amount fraction independent upward drift over time.
- Drift depends on other factors (cylinder size / material).
- Non-linear calibration functions for many instruments/techniques.
- Instrumental drift (zero and/or span).

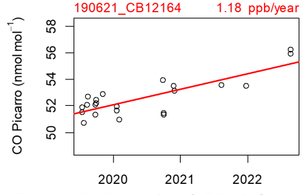

Figure 9: *Example of CO drift in high pressure cylinders.*

Use standards with higher CO amount fractions to minimize the influence of drift.
Take advantage of the linearity of spectroscopic measurement techniques.
Result: Improved reproducibility, higher accuracy.

Internal consistency of calibration standards

- Linear instruments can be used to assess internal consistency of a calibration scale.
- CRDS instrument was calibrated with one standard (CB09915) and CO_2 free air.
- Overall, a very good internal consistency of the WMO-X2019 CO_2 calibration scale was found for the amount fraction range up to 500 µmol mol^{-1}.
- Potentially still a small amount fraction dependent bias, especially at the upper end of the calibration scale.
- Similar results were found for the WMO-X2004A CH_4 calibration scale.

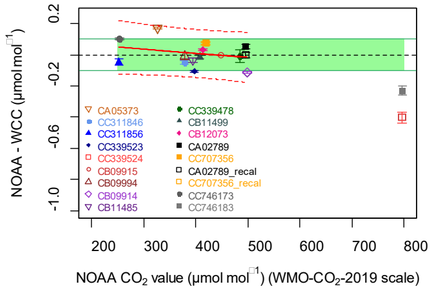

Figure 10: *Internal consistency of NOAA WMO-X2019 CO_2 standards at WCC-Empa.*

Calibration approach including zero air

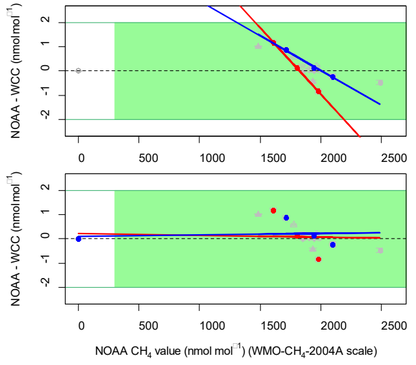

Figure 11: *Examples of linear calibration functions for CH_4, with and without inclusion of zero air.*

- Current approach by many laboratories: set of standards covering ambient range, linear regression.
- Step changes are possible when exchanging the set of standards.
- Alternative: Inclusion of zero air in case of an internally consistent calibration scale, linear instruments, and reliable zero air.
- Reduces step changes.
- Depends less on the uncertainty of individual standard.
- Gives reliable results beyond the range covered by the set of standards.
- Applicable also for CO and CO_2.

Conclusions and recommendations

- NOAA hosts the WMO GAW reference scales and provides reference gases for CO_2, CH_4, CO and N_2O.
- The reproducibility and internal consistency of these standards is enabling measurements of high quality, and the data WMO/GAW quality objectives for CO_2 and CH_4 can be met.
- Take advantage of the linearity of spectroscopic techniques to further improve measurements, and include zero air in the calibration strategy.
- This holds true especially for CO, where standard stability/drift remains a limiting factor for accurate CO measurements at ambient levels. Issue of drifting standards needs to be resolved.
- CO calibrations: focus on higher standard, in combination with CO free air for analytical techniques with good linearity.

[1] Buchmann, B., et al. (2009), Chimia, 63(10), 657-660.
[2] Zellweger, C., et al. (2016), Atmos. Meas. Tech., 9, 4737-4757.
[3] Zellweger, C., et al. (2019), Atmos. Meas. Tech., 12, 5863–5878.