An Update on the WMO CO X2014A Scale

A.M. Crotwell[1,2], B. D. Hall[2], M. Madronich[1,2], G. Petron[1,2], P. Novelli[2] and T. Mefford[1]

Phone: 303-497-6494, E-mail: Andrew.Crotwell@noaa.gov

[1]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado 80309;

[2]NOAA Earth System Research Laboratory, Global Monitoring Division, 325 Broadway, Boulder, Colorado 80305

1. Introduction

NOAA/ESRL/GMD serves as the World Meteorological Organization Global Atmosphere Watch (WMO GAW) program Central Calibration Laboratory (CCL) for Carbon Monoxide (CO).

Maintaining a stable CO scale has proven to be difficult:

Growth of CO in aluminum cylinders is very common

Typically ~ 0 to 1.0 ppb/yr.

Currently the scale is defined by 14 primary standards, prepared gravimetrically in 2011, covering 30 to 1000 ppb CO. Most show significant growth of CO, which is tracked by on-going measurements using an internal tracer technique. Subsequent applications of this technique show that rates of drift applied in 2015 for the X2014A scale revision are too large.

2. Tracking Drift in Primary Standards (Internal Tracer Technique)

- **Need a stable reference point:**
  - Percent level gravimetric mixtures of CO and CH_4 in air
  - 0.1 – 0.9% CO, 3% CH_4
  - Growth of CO is insignificant
  - CO:CH_4 ratio is known and assumed stable at these mole fractions
- **Make static dilutions from 3 parent mixtures and zero air**
  - Suite of 16 dilution standards each episode
  - Target range: 25 – 1000 ppb CO
  - Uncertainty: 0.2 – 1.2 ppb CO
  - **Measure CH_4 against a well defined scale to calculate CO**
- **Calibrate primary standards against fresh dilution standards**
  - twice per year.
  - 10 measurement episodes since 2014

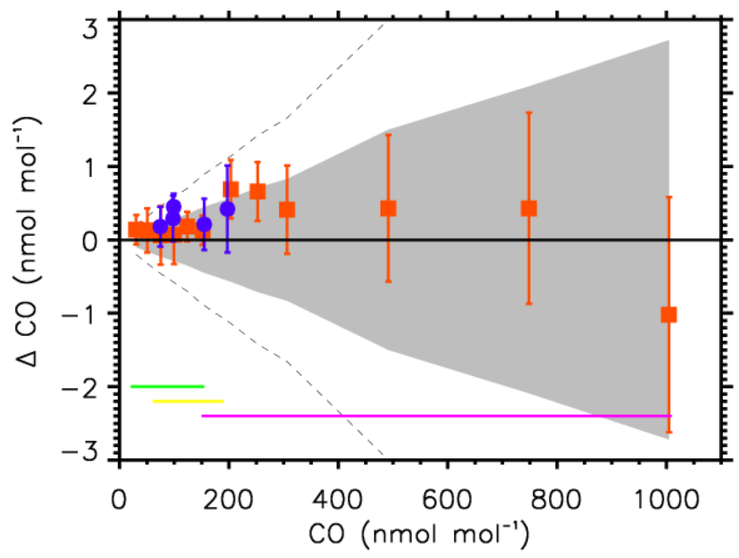
3. Analytical Techniques

Beginning May, 2017 - CO calibration system modified to run two instruments in parallel.

- Vacuum ultraviolet resonance fluorescence (VURF) spectroscopy
- Off-axis integrated cavity output (OA-ICOS) spectroscopy

Prior to this, each technique was used for calibrations at various points but never simultaneously.

4. Verification

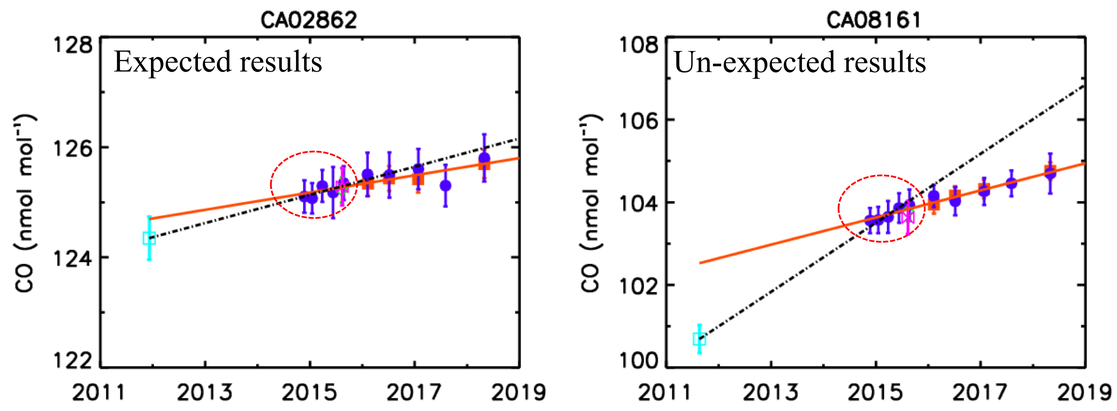


Measured value minus gravimetrically assigned values of additional sets of gravimetric standards made in 2015 and 2017. **No significant offset observed when measured immediately after production by VURF against dilution standards produced using the internal tracer technique**.

Shaded region and dashed lines are the 68 and 95% CI uncertainty envelopes for the gravimetric standards. Error bars on the data points are total uncertainty of the measurements using the internal tracer technique (68 % CI). Color bars show coverage range from the three parents.

5. Primary Standards: X2014A Assignments and Additional Measurements

- X2014A drift corrections (dot-dashed lines) for each standard based on initial gravimetric value and the mean of the first 5 measurements vs the dilution standards (red circles in figures below).
- Subsequent measurements show:
  - **X2014A drift corrections are too high.**
  - Non-linear drift prior to measurement OR initial gravimetric values are wrong



Initial Gravimetric Value

Measured vs dilution standards by VURF

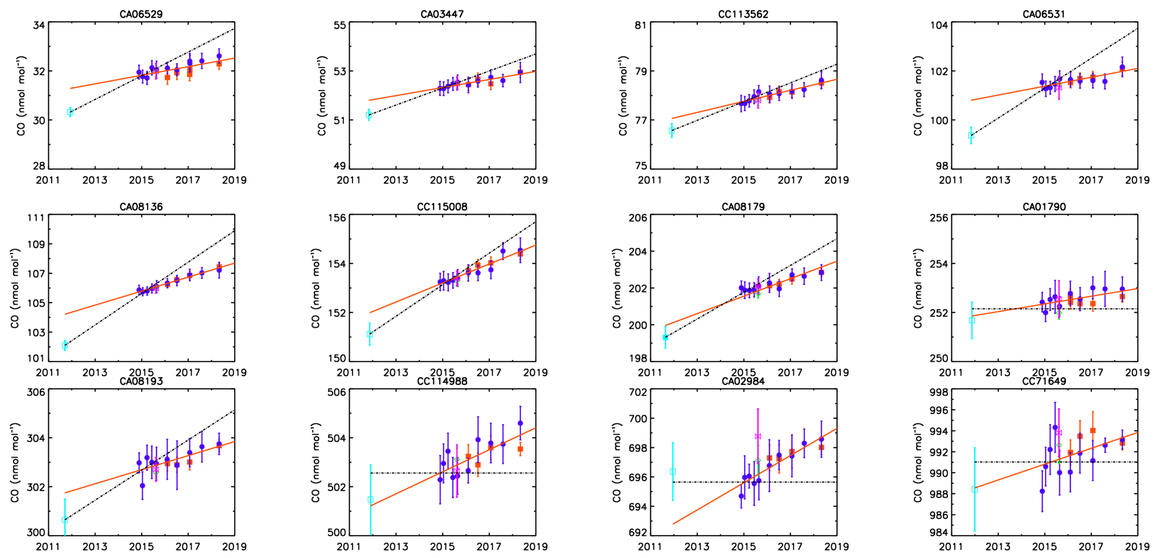
Dot-dashed line = X2014A assignment

Measured vs 2015 gravimetric standards

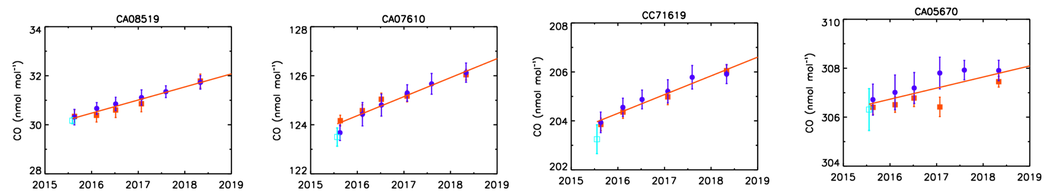
Measured vs dilution standards by OA-ICOS

Red line = fit to OA-ICOS and VURF measurements

Error bars are uncertainty of initial gravimetric value and of measurements vs. dilution standards, both at 68% CI

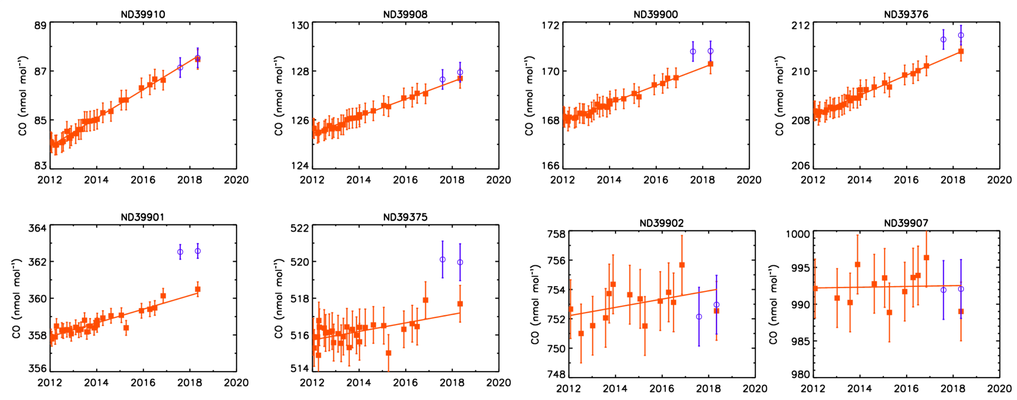


6. Results for 2015 Gravimetric Standards (4 of 12)



Measurements of the 2015 gravimetric standards began immediately after they were made and show excellent agreement with initial gravimetric values for all 12 standards. Same color scheme as in section 5. Error bars are uncertainty of initial gravimetric value and of measurements vs. dilution standards, both at 68% CI

7. Analytical Bias



A bias between the two instruments (OA-ICOS and VURF) occurs when measuring secondary standards vs primary standards (8 of 11 shown). Data on a provisional scale which corrects the bias in X2014A. Error bars are estimated reproducibility of the system (68% CI).

8. Conclusion

- **The internal tracer technique is accurately tracking growth of CO in the primary standards.**
- X2014A scale is biased but will be corrected with a scale revision (in 2019).
- There appears to be a measurement bias between the OA_ICOS and VURF instruments when measuring secondary standards. This bias is not present when calibrating primary standards. The cause is under investigation and we now run both instruments in parallel.