Towards implementing an optical method for N_2O analysis at the CCL

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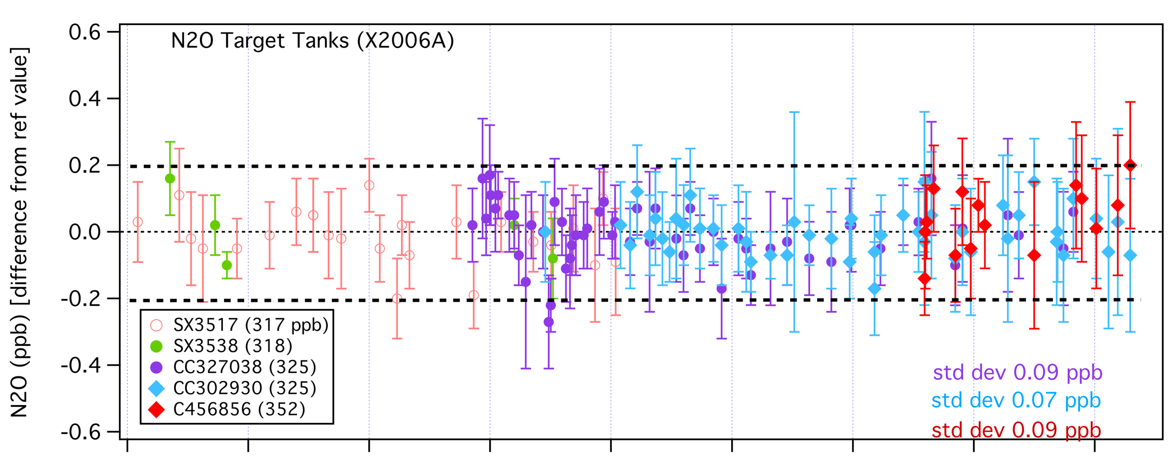
INTRODUCTION

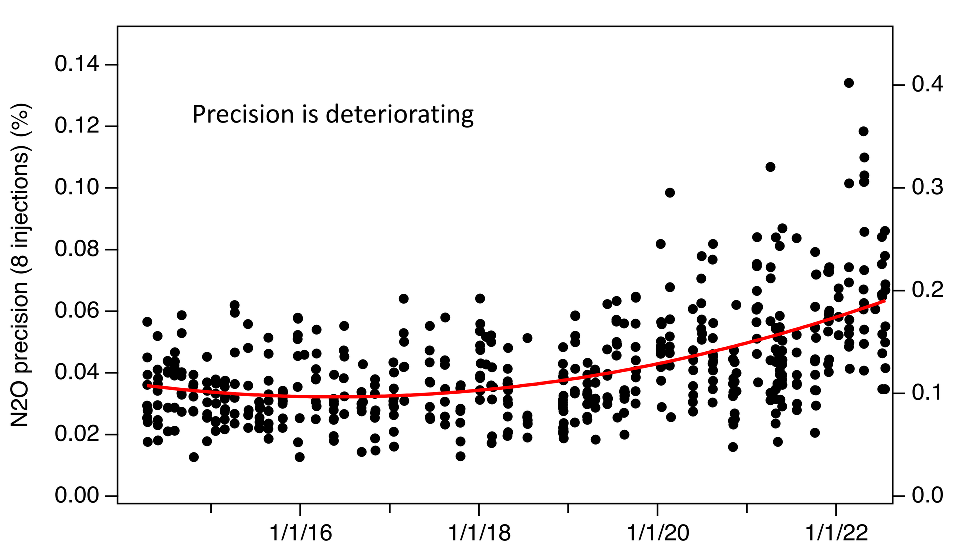
The NOAA Global Monitoring Laboratory serves as the WMO Central Calibration Laboratory for nitrous oxide (N_2O). We currently use gas chromatography with electron capture detection to value-assign standards. While this method has performed well, it is no longer state of the art. We are investigating laser-spectroscopic methods for N_2O analysis and with plans to implement in 2023.

Status of the GC-ECD system

The GC method in use continues to demonstrate consistency of value assignment on the WMO-X2006A scale, as demonstrated by routine analysis of "target tanks". However, daily precision is starting to deteriorate. Typical precision on eight injections has increased from ~0.03% (0.1 ppb) to 0.06% (0.2 ppb) in recent years.



Routine analysis of target tanks shows good consistency of value assignment on scale X2006A.

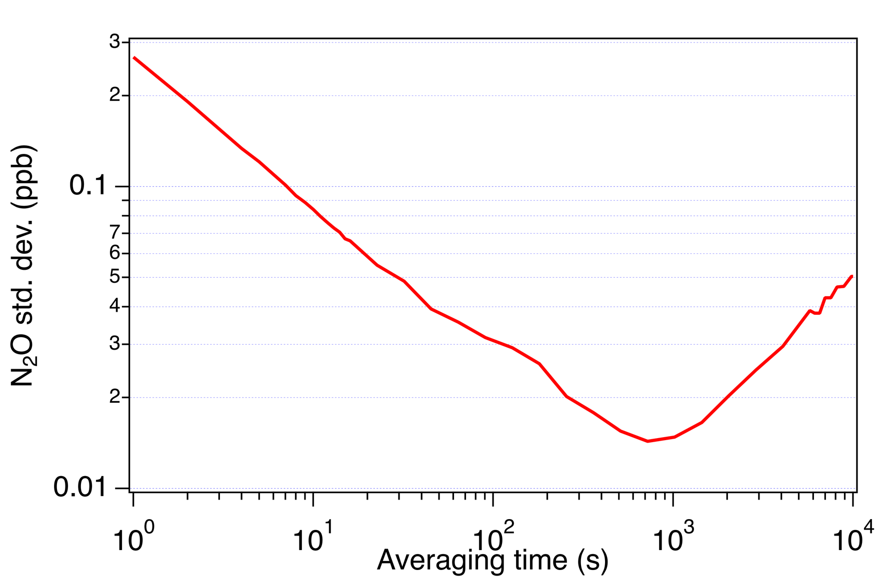


Daily repeatability since 2015 (based on 8 injections)

Note that value assignments are typically based on the average of three 8-sample episodes from separate analysis days.

Spectroscopic methods offer much better repeatability

Laser spectroscopy offers significant gains in repeatability, especially with the emergence of mid-IR laser systems.



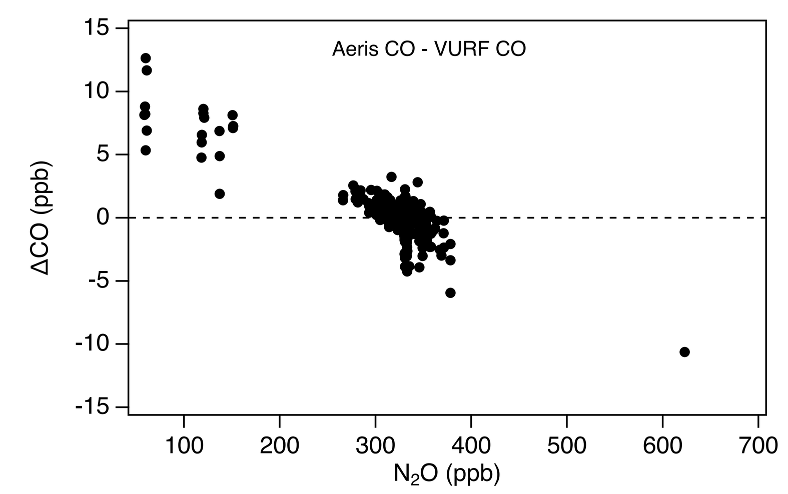
Laboratory testing of an Aeris Technologies "Ultra" N_2O/CO analyzer, sampling a continuous stream of dry of air from a gas cylinder.

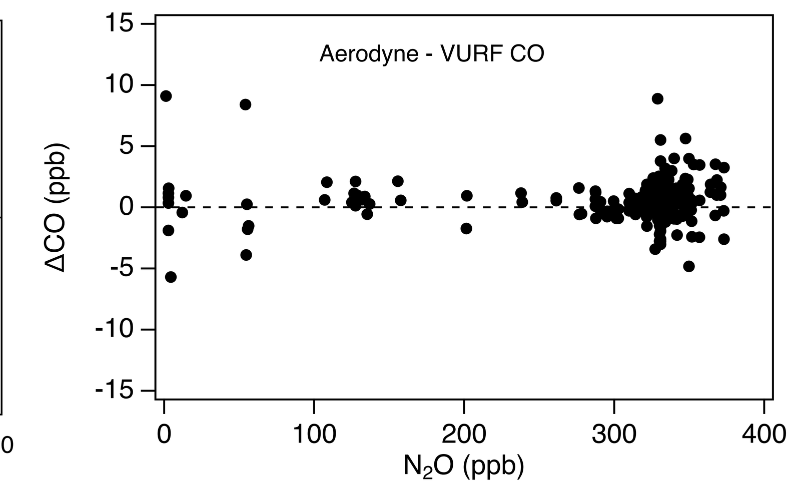
Initial testing of two laser-based systems

We analyzed samples on both the GC-ECD and laser-based systems for 2-3 months each.

What we looked for:

- CO/N_2O spectral overlap
- agreement with the GC-ECD
  (all systems calibrated against the same secondary standards)
- long-term reproducibility
- effect of argon in primary standards





Using CO from a VURF instrument as a reference, we tested the influence of N_2O on CO. The Aeris Ultra showed a CO-N_2O dependence. This was not surprising given that the CO absorption feature is an N_2O/CO doublet. ***For calibration work, we prefer minimal N_2O/CO dependence.***

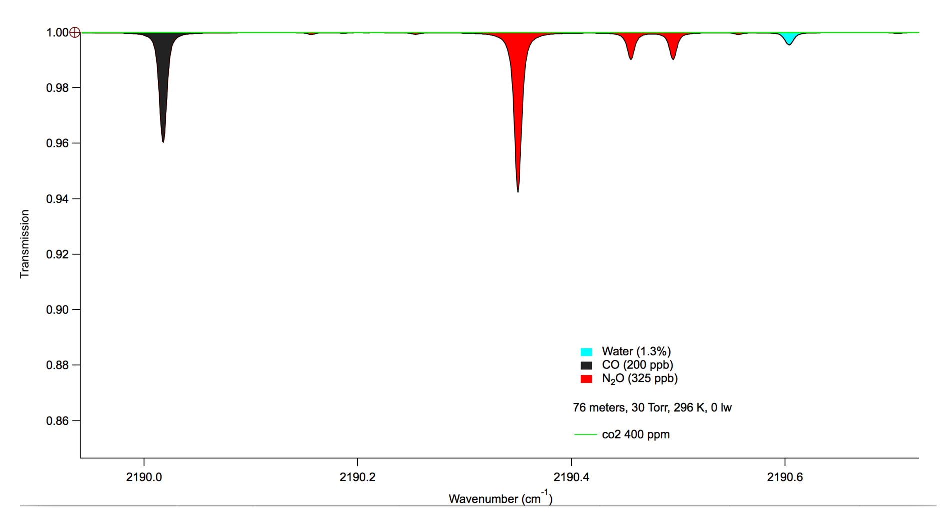
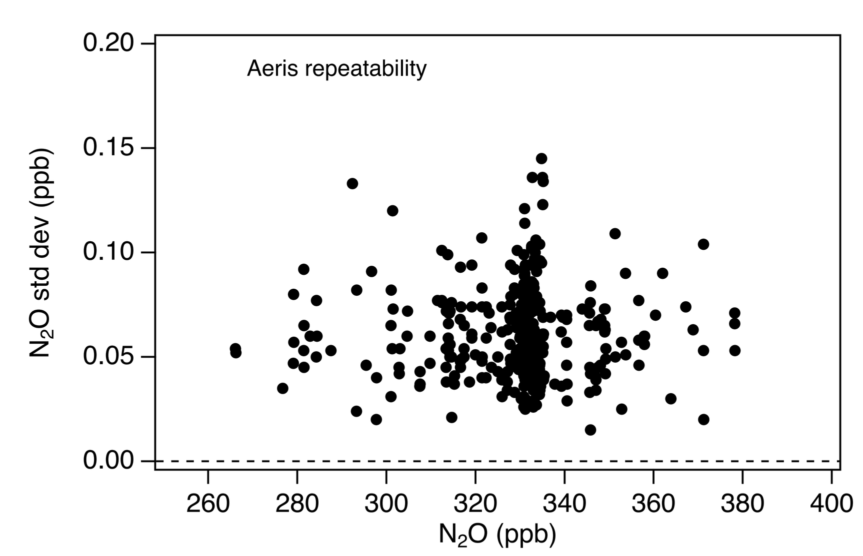
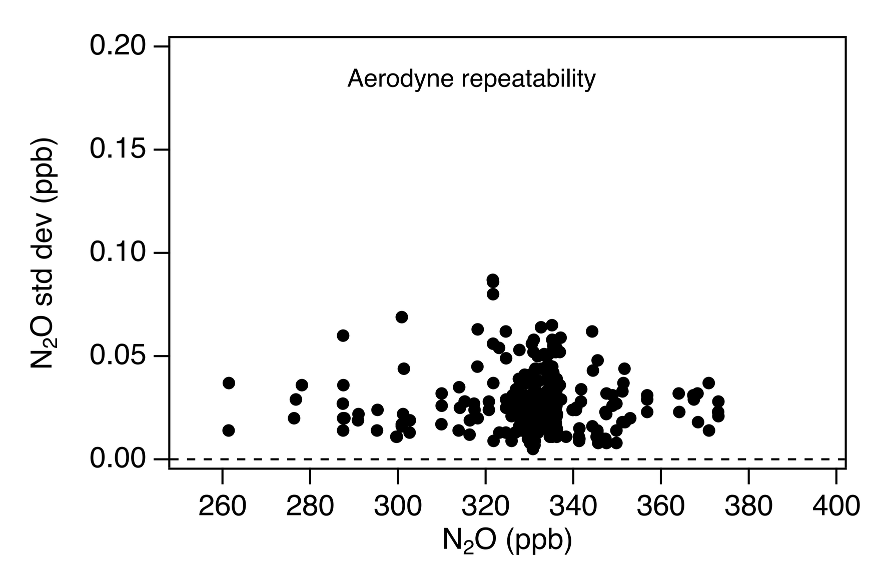


Figure courtesy of Dave Nelson (Aerodyne)

The Aerodyne instrument we are currently testing is configured to measure at wavelengths with no N_2O/CO overlap.



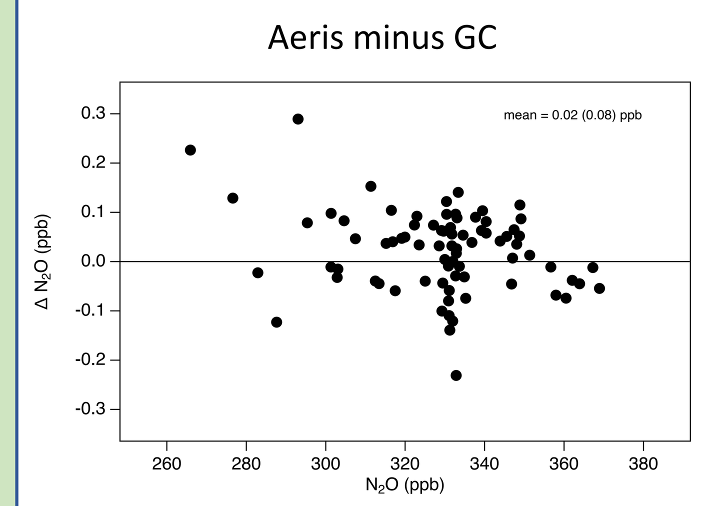


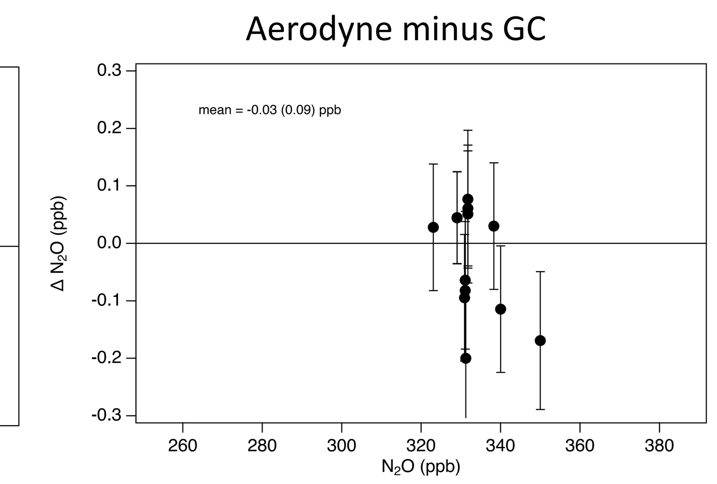
Repeatability of two laser-based systems averaging over 60 seconds (7-8 aliquots).
- the Aeris system was operated in flow-through mode
- the Aerodyne is operated in evacuate/fill mode.

While the Aeris system performed well for both N_2O and CO, for the CCL, we should strive for repeatability that is consistently less than 0.05 ppb.

While the Aerodyne shows excellent repeatability (~0.03 ppb), the unit tested is not as reproducible as we had hoped. Successive measurements of the same tank over several days can sometimes result in reproducibilities (1 sigma) around 0.07 ppb. We are hope to improve this in the near future.

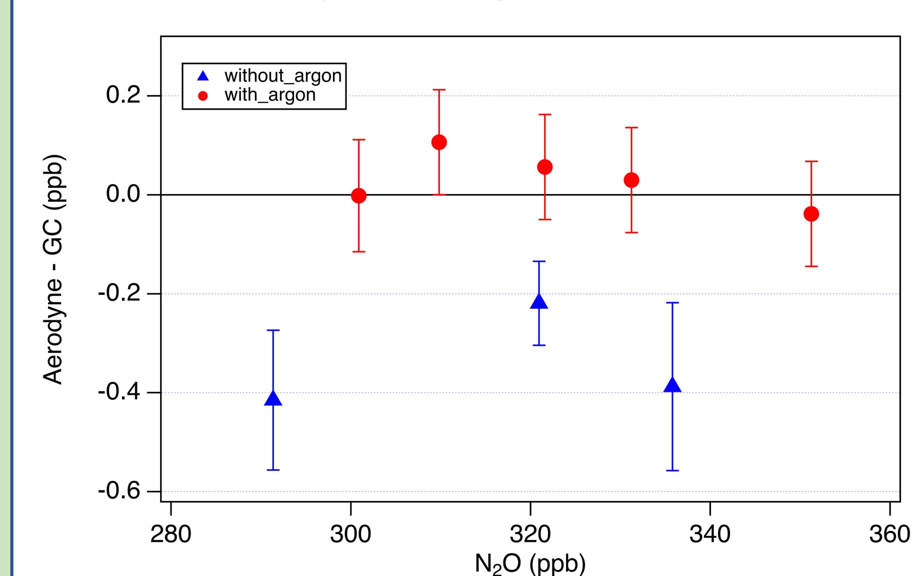
Traceability considerations





Both spectroscopic systems showed good agreement, on average, with the GC when we calibrate to the same set of secondary standards. Most of the scatter is due to uncertainty in the GC data. Error bars shown are 1-sigma from the GC measurement, and are similar in magnitude in both cases (not shown in the left plot for clarity).

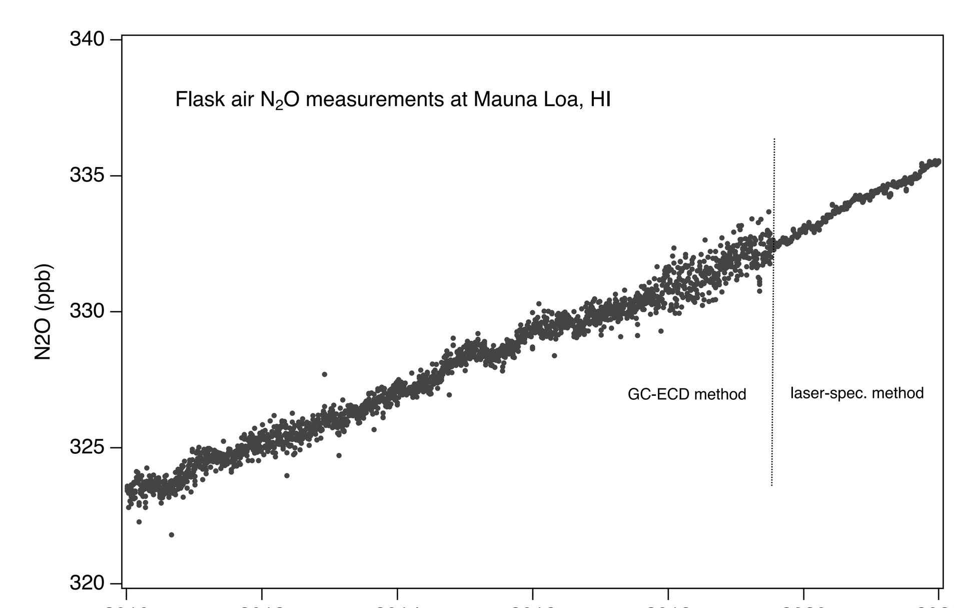
Impact of argon in standards



Standards that do not contain argon show a ~0.1% negative bias on the Aerodyne system, slightly less than the 0.2 % bias reported by Kelley et al. 2014.

For scale development, primary standards will need to contain argon.

What we hope to achieve



The figure above shows what is possible with modern laser-based systems. N_2O data from flasks collected at Mauna Loa, HI was much improved after the implementation of a laser-based analytical system in the Boulder laboratory. To support measurements like these across WMO/GAW, the CCL needs to implement a better method for calibration (value assignment).

Both laser-based systems tested to date offer at least a factor of two improvement over the current GC system. We are hoping to improve on that and make the transition to a laser-based method in the coming months.

Kelley et al. (2014), dx.doi.org/10.1021/ac500581b | Anal. Chem. 2014, 86, 4544–4549