Development of a Fast, High-Precision Analyzer for N_2O and CO Measurements in Field Applications

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Instrument Modes / Options

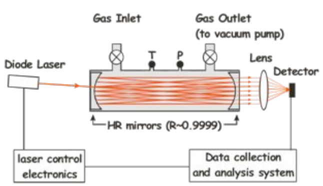
Mode 2: High Flow (external pump)
1 to 50 L/min flow rate
1 to 20 Hz data rate

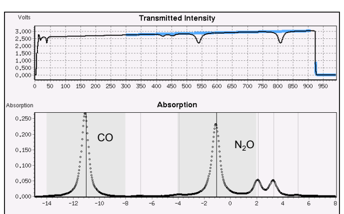
Mode 1: Low Flow (internal pump)
0.15 to 0.5 L/min flow rate
0.01 to 1 Hz data rate

(optional) Multiport Inlet Unit: Autosample 16 inlets

Cavity Enhanced Laser Absorption

Baer, D. S.; Paul, J. B.; Gupta, M.; O'Keefe, A. Sensitive absorption measurements in the near-infrared region using off-axis integrated cavity output spectroscopy. *Appl. Phys. B: Lasers and Optics* ***2002, 75 (2), 261 – 265.***





- Path-length enhancement
  $L_{eff} = L / (1-R) \sim 0.3\text{-}25$ km
- Robust - alignment insensitive
- Cryogen-free components
- Fast (up to 600 Hz) scan-rate
- Measurements at up to 20 Hz

Performance

Precision

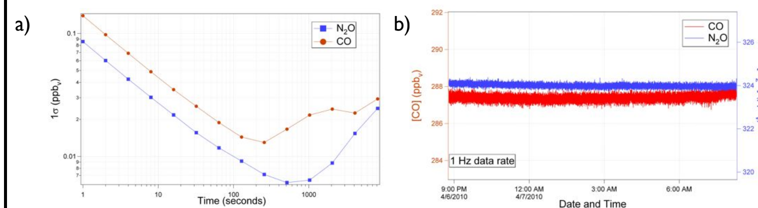


Figure 1. Long Term Performance of N_2O/CO analyzer. (a) Allen Deviation plot of measured dry air. A 1-second precision of 0.09 ppbv for N_2O and 0.14 ppbv for CO was obtained. Long Term precision of better than 0.070 ppbv is obtained for both analytes without any calibration. b) Time trace of the data used to obtain the Allen plots in a).

Linearity

Measurements at NOAA ESRL: courtesy of A. Crotwell, P. Novelli, E. Dlugokencky, and B. Hall

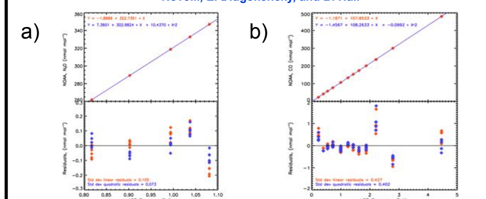


Figure 2. N_2O (a) and CO (b) secondary standards run against reference cylinders to create a response curve to test the linearity. Each secondary standard was run 5 times (180 sec flush cycle, 60 sec averaging period) and each run was bracketed by an analysis of the reference cylinder. The normalized responses (standard / reference) are plotted verses the assigned value including (top) linear and a quadratic fits and (bottom) residuals. The small difference between the residuals from the linear and quadratic fits indicates instrument response is linear to within our ability to assign values to the secondary cylinders.

Time response

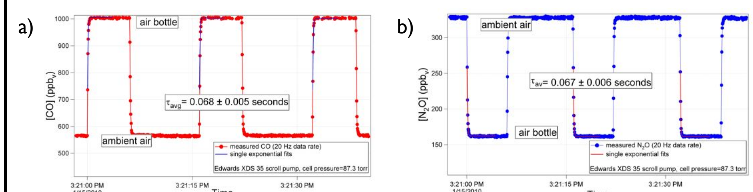


Figure 3. Time response of the analyzer operating in high flow mode. A fast solenoid valve is used to rapidly switch between ambient air and dry bottled air. Figure a shows the measured CO while Figure b shows the measured N_2O. Two different air bottles were used to acquire the data in a) and b). Exponential fits of the instrument response shows a 1/e time of 0.068 seconds for CO and 0.067 for N_2O. All data was acquired at 20 Hz.

Reproducibility

Measurements at NOAA ESRL: courtesy of A. Crotwell, P. Novelli, E. Dlugokencky, and B. Hall

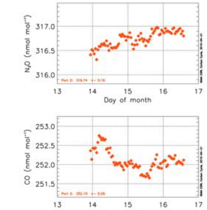


Figure 4. 60-second averages taken every 45 min over 2.5 days (Nov 13 – 16, 2009) Instrument exhibits very low drift over this period. Running a reference or calibration gas every few hours would remove the small drift exhibited.

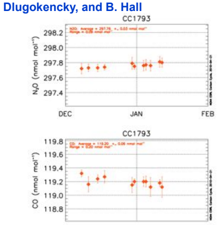


Figure 5. Cylinder CC1793 calibrated against reference cylinder used to produce N_2O and CO response curves. The results are plotted verses analysis date. The full range of measured values over one month is only 0.09 ppbv for N_2O and 0.2 ppbv for CO.

Field Deployments

Caldecott Tunnel, Walnut Creek, CA, USA

Figure 6. The N_2O/CO Analyzer was deployed using the LGR Mobile Laboratory, a fully functional vehicle capable of autonomous operation on battery power. Measurements of N_2O and CO were performed on vehicle emissions in real time.

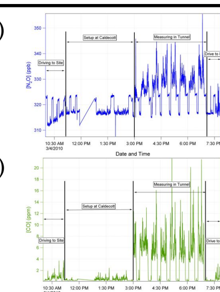


Figure 6. Real time N_2O (a) and CO (b) data of vehicle emissions taken at Caldecott tunnel. The N_2O/CO analyzer was configured with LGR's Multi-Inlet Unit (MIU) to automatically sample the tunnel emissions, ambient background, and a reference cylinder.

Conclusions

- **N_2O/CO Analyzer provides measurements of [N_2O] and [CO] at 20 Hz data rate**
- **Short-term precision: better than 0.2 ppb$_v$ in 1 second for both N_2O and CO**
- **Long-term precision: better than 0.1 ppb$_v$ for both N_2O and CO**
- **Linear response over large ranges: 50-1000 ppb$_v$ CO, 260-360 ppb$_v$ N_2O**
- **Fast flow response: >10 Hz, sufficient for eddy flux measurements**
- **Low drift: better than 0.2 ppb$_v$ for both N_2O and CO**
- **Low-power: 150 watts**
- **Independent verification of performance specification by NOAA ESRL**