Field Testing And Error Analysis Of Cavity Ringdown Spectroscopy Instruments Measuring CO₂

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Assessment of Accuracy and Precision

In the table below are the various contributors to the analytical uncertainty for both the WS-CRDS system and the NOAA-ESRL NDIR system. Shown below and color coded are the uncertainty due to analyzer drift, temperature and pressure control, and also the error, unique to these early Ring2 systems, due to the atmospheric variability of the HDO/H2O isotopic ratio.

Comparison with NOAA-ESRL

A pre-deployment field trial (Crosson, 2008) at NOAA-ESRL in Boulder, CO compared the performance of a WS-CRDS system with a LICOR-7000. The total length of the test was 45 days, with 24 days in an “operational” mode, sampling the same sample air. For the LICOR-7000 system, four calibration gases were sampled every six hours, and the sample was dried. The WS-CRDS system was calibrated once over the duration of the field trial and the air sample was NOT dried. The largest difference between the mean of the measurements of each of the four calibration gases during the 24-day operational period and the known value of the tanks was 0.07 ppm. During a 60-hour test period, the root-mean-square difference between the WS-CRDS and LICOR-7000 systems was 0.064 ppm; over the entire 45-day trial the root-mean-square difference was less than 0.018 ppm. The majority of this difference is attributable to a slow drift (less than 0.8 ppm per day) of the WS-CRDS system, and can be easily corrected using reference gases sampled with a daily, or less, frequency.

Comparison of five WS-CRDS Systems

The deployment strategy was to locate the five WS-CRDS systems at existing communication towers which had climate controlled facilities and line power. In addition, and to enable real-time trouble shooting and daily data downloads, it was necessary to have Verizon Wireless cell phone coverage. Airlink Raven EVD0 were used to communicate with the WS-CRDS systems. Each tower had to be at least 100 m tall; the table below shows the location and sampling heights of each tower.

Figure 2 shows a block diagram of the WS-CRDS analyzer. The WS-CRDS analyzer utilizes a telecom-grade distributed feedback (DFB) laser measuring a single 12C16/16O2 spectral feature at a wavelength of 1603 nm and a single H2O spectral feature near 1603 nm (Crosson 2008). In WS-CRDS, light from a continuous-wave laser is injected into a precisely aligned optical cavity consisting of three very high reflectance mirrors (>99.995%). The light intensity inside the cavity then builds up over time and is monitored using a photo detector. The “ring-down” measurement is made by rapidly turning off the laser and measuring the light intensity in the cavity as it decays exponentially in time. This exponential decay is typically characterized using the characteristic decay time constant, (Crosson and Davis 2006). The typical empty-cavity decay constant is 30 µsec.

Conclusions

- 5 WS-CRDS systems deployed early 2007
- Remained in the field until November 2009
- Round-robin tests verified accuracy (0.1 - 0.15 ppm)
- Excellent long-term stability of systems
- Overall system error ~0.3 ppm mostly caused by HDO/H2O isotopic ratio effects
- Post calibrations should decrease error
- WS-CRDS error today ~0.1 ppm

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B51F-03. Atmospheric CO2 Inversions of the Mid-Continental Intensive (MCI) Region (Inverted). A. E. Schaefer; A. Deming; S. M. Ogle; K. Coddin, M. Diao; K. J. Davis; T. Lavoie; N. Miles; E. Andrews; D. Petron; D. H. Huntley.
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Continental atmospheric CO₂ observational network

Prevalent methods for making tower-based measurements of CO2 mixing ratio, notably non-dispersive infrared spectroscopy, require frequent system calibration and drying of the sample gas. Wavelength-scanned cavity ringdown spectroscopy (WS-CRDS) is an emerging laser-based technique for detecting trace quantities of gases, eliminating or significantly reducing the frequency of calibration and the need to dry the sample gas. We present results from ~24 months of field measurements from five WS-CRDS systems in MN, WI, IA, NE, and IL. These five systems, termed Ring2 (see Fig. 1 and Table 1), were deployed in support of the North American Carbon Program’s Mid Continent Intensive from April 2007 to November 2009. Analysis and results include an examination of long-term stability, discussion of overall uncertainty, and the effects of using the water vapor correction instead of drying the sample gas.

Table 1: Contributions to Analytical Uncertainty (ppm)

<table>
<thead>
<tr>
<th>Source</th>
<th>PSU WS-CRDS</th>
<th>NOAA-ESRL NDIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration scale uncertainty</td>
<td>0.04 ppm</td>
<td>0.07 ppm</td>
</tr>
<tr>
<td>Standard equilibration uncertainty</td>
<td>0.02 ppm</td>
<td>0.05 ppm</td>
</tr>
<tr>
<td>Cavity TEMP controlled error</td>
<td>0.01 ppm</td>
<td>0.05 ppm</td>
</tr>
<tr>
<td>Cavity PRESS controlled error</td>
<td>0.006 ppm</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Total analytical uncertainty without HDO</td>
<td>0.1 ppm</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Total analytical uncertainty with HDO</td>
<td>0.2 ppm</td>
<td>0.1 ppm</td>
</tr>
</tbody>
</table>

Figure 2 shows a block diagram of the WS-CRDS analyzer. The WS-CRDS analyzer utilizes a telecom-grade distributed feedback (DFB) laser measuring a single 12C16/16O2 spectral feature at a wavelength of 1603 nm and a single H2O spectral feature near 1603 nm (Crosson 2008). In WS-CRDS, light from a continuous-wave laser is injected into a precisely aligned optical cavity consisting of three very high reflectance mirrors (>99.995%). The light intensity inside the cavity then builds up over time and is monitored using a photo detector. The “ring-down” measurement is made by rapidly turning off the laser and measuring the light intensity in the cavity as it decays exponentially in time. This exponential decay is typically characterized using the characteristic decay time constant, (Crosson and Davis 2006). The typical empty-cavity decay constant is 30 µsec.