Research Notes, Apr-June 2011, Tests on Licor 7200 and Picarro G1301 CO2 analyzers.

6/29/2011, BWB

Motion Sensitivity Tests: May 5 2011

For different reasons, analytical signals of both analyzers likely exhibit a motion/vibration sensitivity. The rotational frequency of the LICOR chopper wheel can be modulated by motion . Vibration may affect the optical alignment. Pressure control in the Picarro ring-down cavity uses DC proportional solenoid valves, which have well know motion sensitivity.

Tests were performed using a platform with low frequency (0.1-0.3 Hz) motion about two axes. For this report, the pitch axis is defined as perpendicular to the Picarro analyzer cavity (fore-aft motion). The roll axis is perpendicular to the cavity (side to side motion). The axis of pressure control solenoids is perpendicular to the cavity, so we expect roll motion to exhibit the largest effect. The LICOR sensors were mounted vertically so it's not clear there should be any difference between pitch and roll. The two motion modes were at slightly different frequencies, and this may lead to some difference in the LICOR sensitivity.

Experimental conditions, LICOR results and a photo of the setup were discussed in the earlier **Motion_tests_05052011_boulder.pdf** document.

The figure **G1301MotionTestTimeSeries.png** shows a time series plot for G1301 CO2 and cavity pressure for pitch, roll, and no-motion conditions. A significant increase in variance is apparent, with roll motion showing the greatest effect, as expected.

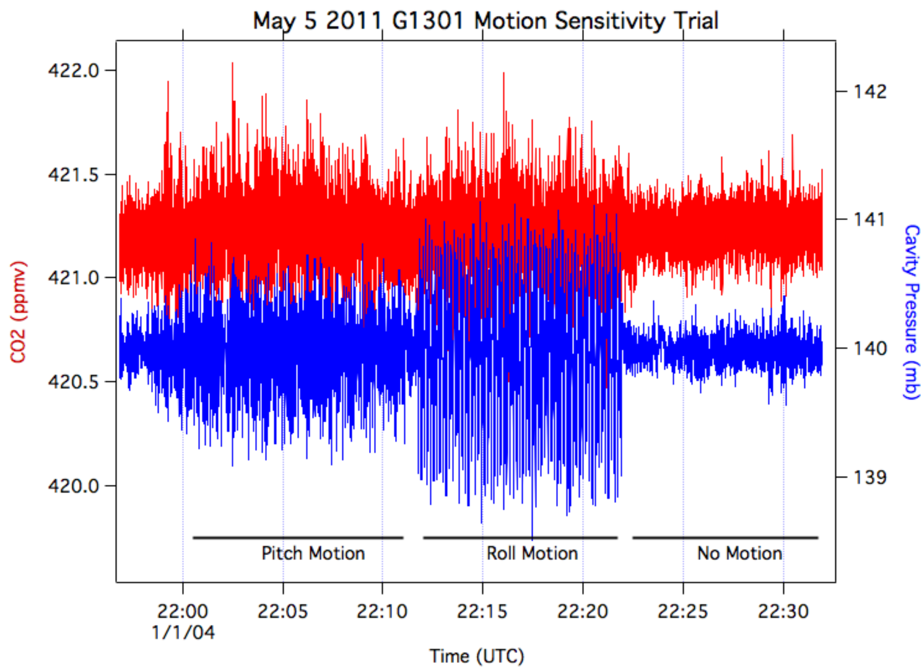
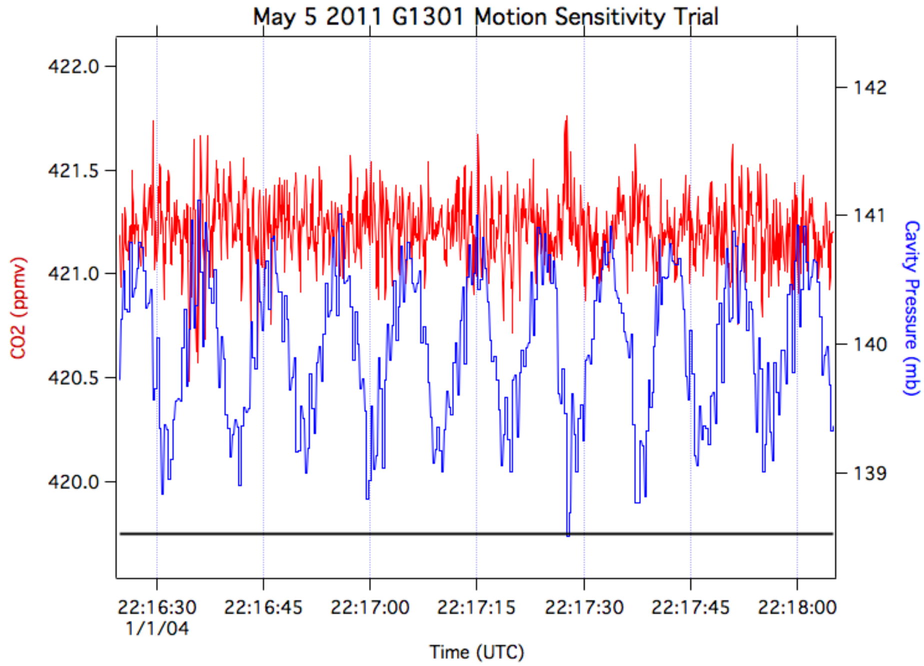
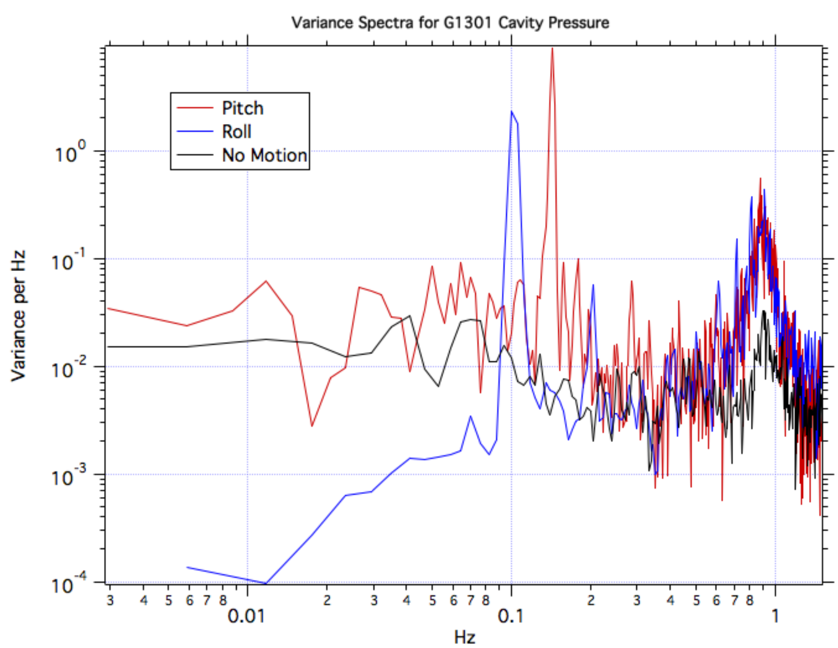
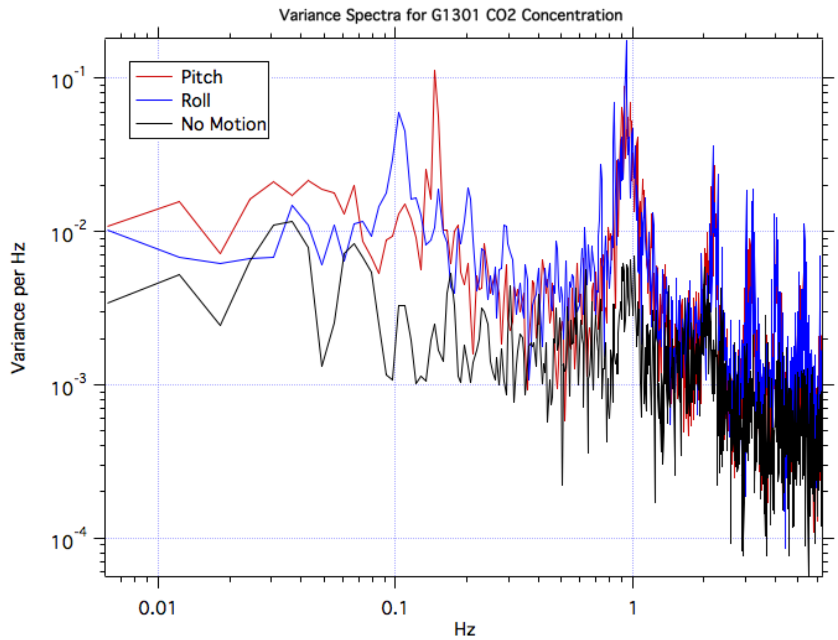


Figure **G1301RollMotionDetail.png** details the time series during the roll test. The dominant frequency of the roll motion is quite apparent in the pressure data and less so in CO2. A higher frequency oscillation in the CO2 is more prominent. Note that pressure data are recorded at 3 Hz and CO2 at 12 Hz so a higher frequency pressure fluctuation might be missed here.



Figures **G1301MotionTestPressureSpectra.png** and **G1301MotionTestCO2Spectra.png** are spectra for the respective motion tests. Peaks for roll (0.1 Hz) and pitch (0.15 Hz) are prominent. Pressure variance is more than 10x greater than CO2 variance at these frequencies. In addition, a feature at ~0.9 Hz is present in all spectra. This feature shows ~10x motion enhancement in both plots. At this time the source of the 0.9 Hz signal (and the other higher frequency features in CO2) is unclear. Some of these issues might be solved by using alternate pressure control hardware, which was investigated in subsequent tests described below.





Water vapor cross-talk and dry-basis mixing ratio correction tests: May 19-25

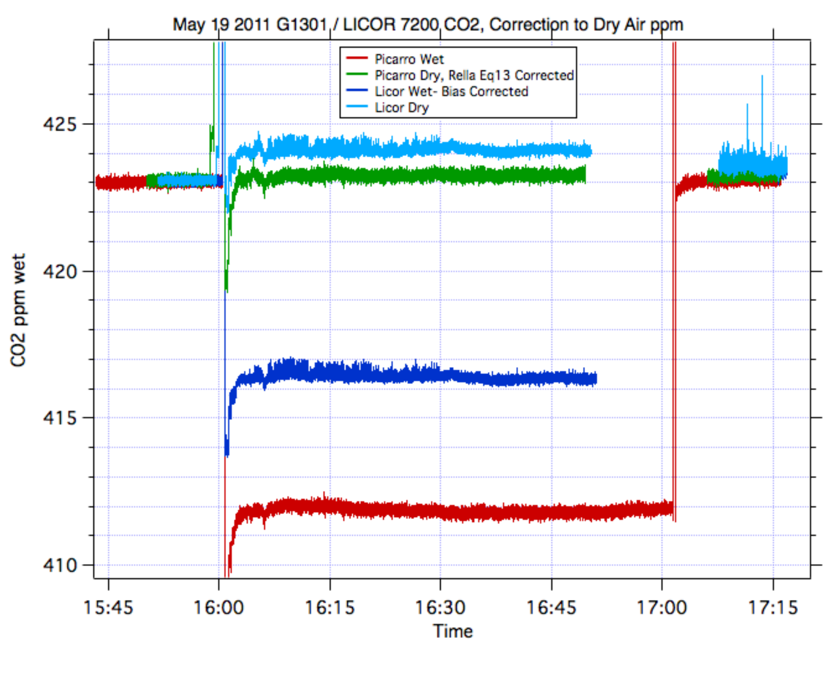
The presence of water vapor affects the analytical signals of both analyzers. Signal crosstalk occurs due to water vapor absorption within the CO2 bandpass of the LICOR and via line broadening in the Picarro. Theoretical corrections for both effects have been presented in the LICOR manual and by Rella 2010 (**Accurate Greenhouse Gas Measurements in Humid Gas Streams Using the Picarro G1301 Carbon Dioxide / Methane / Water Vapor Gas Analyzer, Chris Rella, White Paper, Picarro Inc., 2010**). In addition to crosstalk, a dilution correction is required to obtain the dry-basis mixing ratio. Water vapor concentration is required for the corrections. For these tests the H2O mixing ratio as measured by the LICOR 7200 was used for all calculations. A series of tests were conducted to evaluate the accuracy of the corrections and to investigate the feasibility of drying the air to alleviate the necessity of corrections altogether.

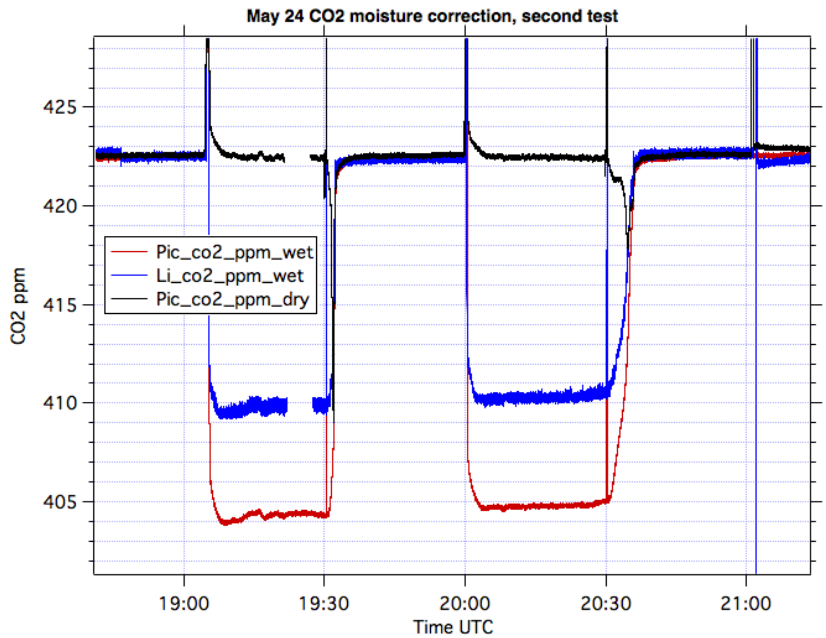
Moist air samples were produced with a Nafion humidifier (~24" MH-110-24P-4, Perma Pure Inc.). Reagent purity water was connected to the Nafion tube at a slow flow (~5 ccm). Compressed air with constant CO2 concentration passed through the outer jacket of the humidifier. The humidifier loop was immersed in a sink of warm water to increase water transfer and maintain constant temperature. The ultimate dew point of air from the humidifier ranged from 15 to 20 deg C, dependent on air flow rate and temperature. The Nafion membrane is mostly impermeable to CO2, according to the Perma Pure literature, and should not perturb the CO2 mixing ratio, other than through the addition of water vapor. In the May 24 and 25 tests, sample RH was recorded with a Vaisala HMP235

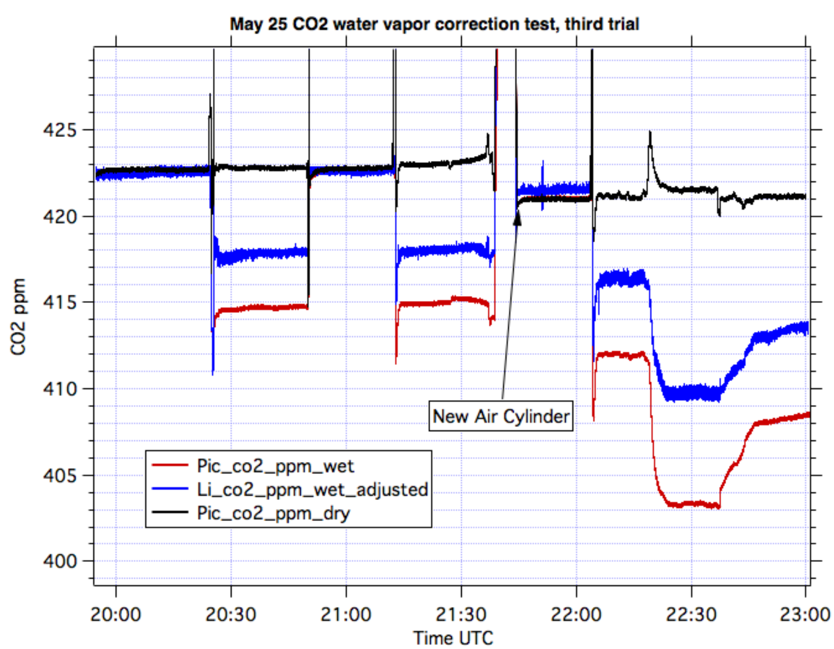
Details on the LICOR results were presented in the **Nafion_tests_05192011_boulder.pdf** document.

Figures **May19_mmol_mol_DryCorrection.png**, **May24_mmol_mol_DryCorrection.png** and **May25_mmol_mol_DryCorrection.png** are time series plots. There was a slight bias of a few ppmv between the two analyzers in dry cylinder air, so these plots were adjusted such that the dry air concentrations agree. Following the introduction of water vapor to the air stream, the LICOR mixing ratio decreases by ~7 ppmv and the G1301 by ~13 ppmv. Application of the Rella 2010 correction to the Picarro data recovers the dry air concentration to within 0.2 ppm (423.018 ppm in dry air and 423.247 ppm in moist air after correction). The dry mixing ratio computed by the LICOR seems to be an over correction by more than 1 ppm. <Ludovic investigated adjustments to the LICOR correction algorithm which reduce the correction error.>

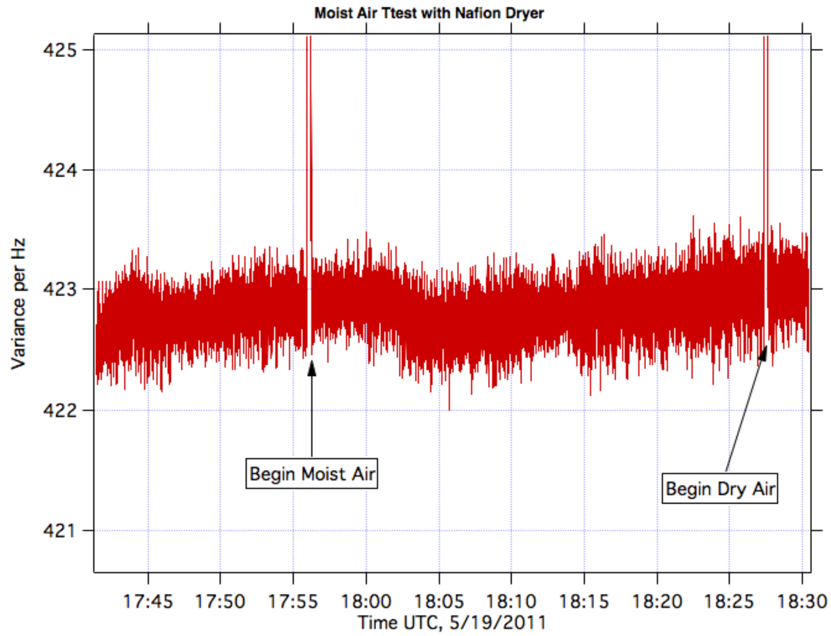
The corrected Picarro data show spikes and other features during periods when humidity is changing due to a time lag between the Picarro CO2 and LICOR water vapor responses.







A test with the Nafion dryer was performed on May 19 (**G1301DryerTest.png**). After an initial period of dry cylinder air (dew pt ~ -50°C) the sample switched to humid at 17:56 (dew pt ~15 °C?). There is a general drift in the CO_2 mixing ratio of +/- 0.3 ppm during this test but no indication of a bias in the humid air relative to the dry. Based on water vapor measurements from the LICOR, the Nafion dryer achieves a dew point reduction of more than 50°C at a flow rate of 4 SLPM (15°C to -40°C).

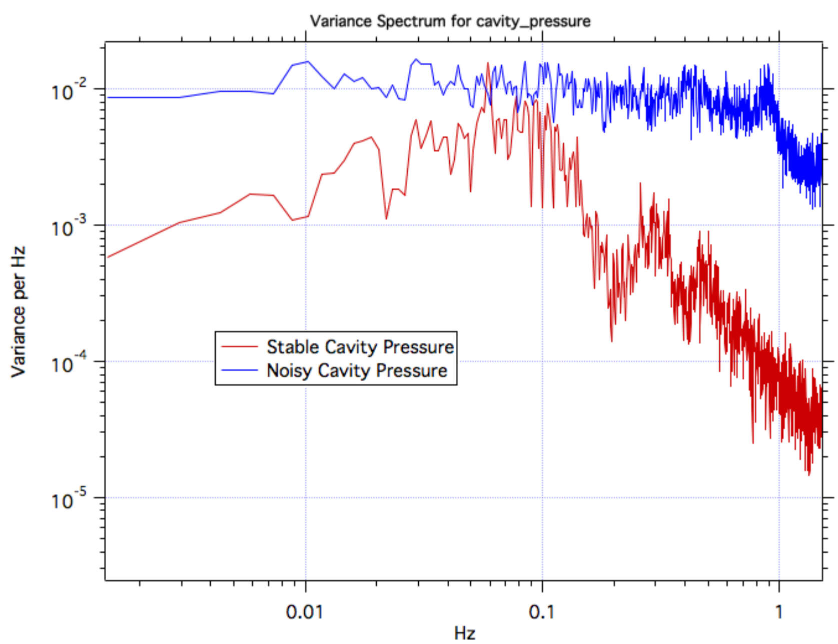


Frequency Response Tests: May31 & June 2

<Ludo should have most of the plots for these tests…>

Pressure Control Tests with the G1301: June 21,22

As noted earlier, cavity pressure in the G1301 is sensitive to motion. In addition, the pressure noise level seems high even at rest. In earlier tests it was observed that pressure noise was greater in high flow mode (**May19_G1301_PressureSpectra.png**). In general, it may be reasonable to assume pressure noise is proportional to flow rate, but other features of the plumbing and control system may enhance this effect. For this reason we investigated alternate pressure control hardware.



In high flow mode, the Picarro uses the inlet proportional valve to regulate sample flow and cavity pressure in downstream mode. Outlet solenoid valves are fully open. For this test, sample flow was controlled with a 750 micron critical orifice (Lenox Laser) installed at the sample inlet and the inlet solenoid was commanded fully open with a 15 volt DC power supply. An MKS Baratron pressure gauge was installed at the vacuum port (outlet) and an MKS 253B butterfly throttling valve was added downstream of the gauge to control pressure in upstream mode. An MKS 651C pressure controller, connected to the gauge and valve, controls pressure in the vacuum line and cavity. The photo **PControlTest 2.JPG** shows the set up.

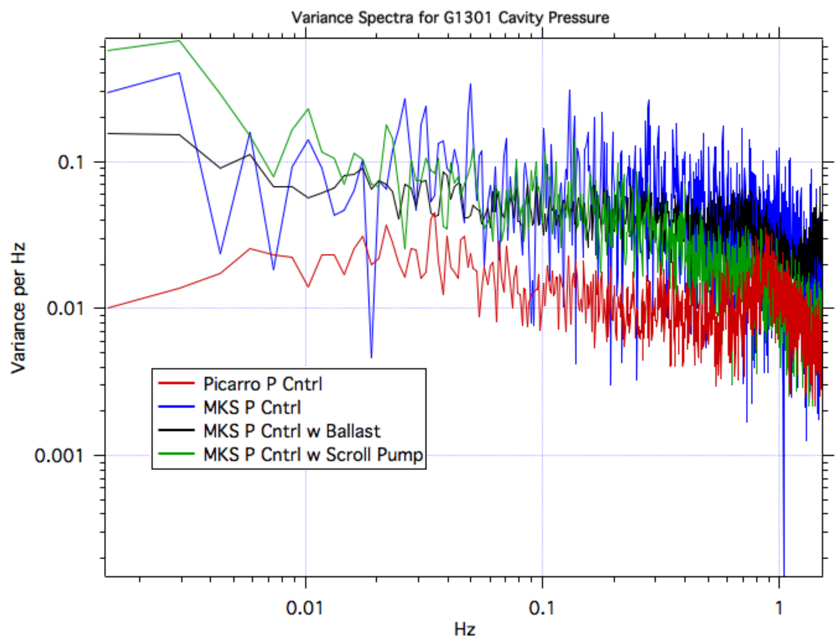
The controller was set to achieve 140 torr cavity pressure, as measured by the Picarro pressure sensor. The actual pressure at the outlet port was ~70 torr, indicating significant pressure drop between the cavity and outlet port, presumably due to check valves, valve bodies and other plumbing restrictions.

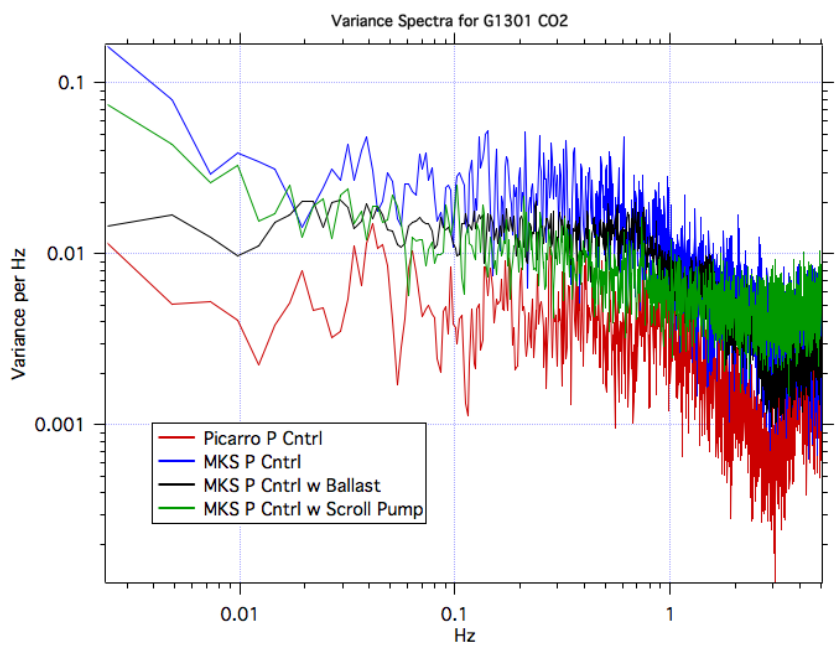
Figures **G1301PControlPressureSpectra.png** and **G1301PControlCO2Spectra.png** show spectra for the tests. The red trace is for pressure control using the Picarro solenoid valves. Other traces are with the MKS system and a variety of pump configurations. The pressure noise level with the Picarro controller is similar to before (see previous plot). Pressure and CO_2 noise levels with MKS pressure control are a bit higher overall which may be due to a higher sample flow rate. Note the absence of a peak at 0.9 Hz in MKS pressure spectra.

Pressure fluctuations from the diaphragm vacuum pump may propagate back into the cavity pressure. A test with a ballast volume (~3-4 L) between the pump and control valve (black trace) yielded slightly less noise (sigma = 0.27 torr without ballast and 0.23 torr with ballast) but the reduction is not evident in the spectrum. Using a scroll pump without ballast yields a somewhat more significant improvement (sigma = 0.19 torr). It is probably wise to use a large ballast volume in the future as extra insurance against pump pulsations.

The plumbing configuration for the MKS tests was not ideal. Plumbing restrictions between the cavity and Baratron gauge may lead to imprecise control. But these tests demonstrate that external pressure control is feasible. A proper implementation would require a reconfiguration of the analyzer internal plumbing, bypassing the solenoid valves. There may also be a check valve installed after the cavity which can contribute to flow and pressure variance.

For now the analyzer has been returned to Picarro for modifications aimed at improving pressure control and correcting the CO_2 computation for pressure variance. I asked them to replace the outlet check valve with a filter if possible. An upgrade to the software is available which uses high rate pressure data for a real time correction to the CO_2 line-fitting routine. We will try the motion tests again following modifications.


Variance Spectra for G1301 Cavity Pressure
Variance per Hz
0.1
0.01
0.001
0.01
0.1
1
Hz
Picarro P Cntrl
MKS P Cntrl
MKS P Cntrl w Ballast
MKS P Cntrl w Scroll Pump


Variance Spectra for G1301 CO2
Variance per Hz
0.1
0.01
0.001
0.01
0.1
1
Hz
Picarro P Cntrl
MKS P Cntrl
MKS P Cntrl w Ballast
MKS P Cntrl w Scroll Pump