Using Molecular Sieve to Zero Infrared Gas Analyzers for Eddy Covariance or Atmospheric Profile Measurements

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Abstract

Infrared gas analyzers (IRGAs) used to measure carbon dioxide (CO_2) or water vapor for eddy covariance (EC) flux or atmospheric profile applications can drift over time. It is important to regularly monitor and set their zero (offset) and span (gain). The span of an IRGA is generally more stable than its zero, but even an error in the zero can lead to errors in EC flux and storage flux estimates.[1] Most commonly, the zero and CO_2 span are checked using cylinders of compressed gasses, and water vapor span is checked with a dewpoint generator.

Cylinders of compressed gases are difficult to transport to a field site because of their bulk, weight, and safety issues, and dewpoint generators are generally not designed for field use. Chemicals such as magnesium perchlorate and sodium hydroxide can be used to scrub water vapor and carbon dioxide from ambient air to zero an IRGA, but these chemicals are difficult to transport, use, and dispose of safely. Many IRGAs used in the field are not checked regularly because of these difficulties.

Molecular sieve can provide a safer, more convenient alternative for zeroing an IRGA in situ. Three example configurations are discussed: a field-rugged scrub module that includes a 2 l·min^{-1} pump for automated on-line zeroing of a closed-path EC system, a field-rugged scrub bottle with no pump for automated on-line zeroing of an atmospheric profile system, and a light-weight (1.2 kg), hand-held zero air generator with a battery-operated, 0.2 l·min^{-1} pump for manually zeroing an open-path IRGA. The molecular sieve provided air with CO_2 and H_2O concentrations equal to or lower than ultra-zero grade air, and required very little maintenance.

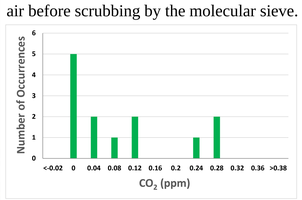
Molecular Sieve

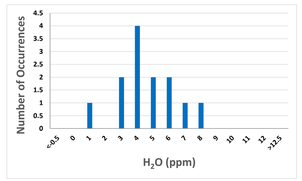
Type 13X molecular sieve is an effective desiccant and adsorber of CO_2. The CAS number for 13X molecular sieve is 6321-69-6. It is available through Campbell Scientific, Inc. as pn 27450.

Scrubbing Compressed Air

Molecular sieve is commonly used to scrub a tank of compressed zero air of CO_2 and H_2O. Given a high-pressure gas, safe operation is a necessary design feature. Agilent Technologies' BMT-4 contains 750 ml of 13X molecular sieve, and is made of heavy-walled aluminum, making it a good choice to scrub CO_2 and H_2O from tanks of compressed air.

Thirteen cylinders of Airgas Ultra Zero air were tested to verify specifications (CO_2 < 1 ppm, H_2O < 2 ppm) and to demonstrate the use of molecular sieve as a scrubber. A cylinder of zero air was connected to two inlets of a CPEC200 zero/span module. One inlet was connected directly, while the other inlet was connected through a BMT-4. The datalogger program was modified to alternate four times between these two inlets, such that the air stream spent 2 minutes on each. The CPEC200 measured the CO_2 and H_2O in the air streams. The difference was calculated to quantify the CO_2 and H_2O in the zero air before scrubbing by the molecular sieve.





All cylinders tested at CO_2 < 0.3 ppm; below specifications. Water vapor was between 0 and 8 ppm, but still well below practical requirements for an IRGA intended for ambient humidity. In all cases the zero air had equal or less CO_2 and H_2O after passing through the molecular sieve.

Atmospheric Profiles

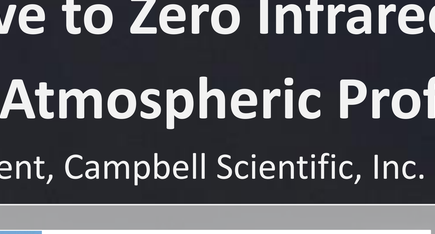
The AP200 CO_2 and H_2O atmospheric profile system (Campbell Scientific, Inc.) measures atmospheric CO_2 and H_2O at up to eight positions, usually spaced along a tower to measure a vertical profile. The AP200 is commonly used with an EC system to measure the storage term to give a more complete measurement of surface exchange.

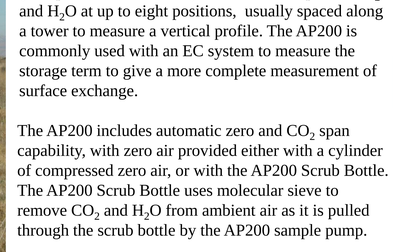
The AP200 includes automatic zero and CO_2 span capability, with zero air provided either with a cylinder of compressed zero air, or with the AP200 Scrub Bottle. The AP200 Scrub Bottle uses molecular sieve to remove CO_2 and H_2O from ambient air as it is pulled through the scrub bottle by the AP200 sample pump.

The AP200 Scrub Bottle has two outlet connections: one for normal operations; and one that allows the user to assess the state of the molecular sieve. This test port samples the scrubbed air from part way through the column of molecular sieve to indicate when to replace the sieve.

An AP200 Scrub Bottle was tested in an accelerated lifetime test (February – October 2014) at the Campbell Scientific test site in Logan, Utah. The bottle was connected to an AP200 atmospheric profile system, configured as follows:

- A step was added to the zero/span cycle to measure the AP200 Scrub Bottle test port
- The zero/span cycle was configured to run hourly, rather than daily
- The CO_2 span setting was suppressed; a tank of CO_2 span gas was measured but not set



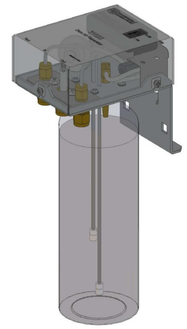


The AP200 Scrub Bottle will easily last a year in normal operation. The test port gives an indication it is time to replace the molecular sieve with a large safety margin.

Reference

[1] Fratini, G., McDermitt, D. K., and Papale, D. (2014) "Eddy-covariance flux errrors due to biases in gas concentration measurements: origins, quantification and correction." *Biogeosciences*, **11**, pp 1037 – 1051.

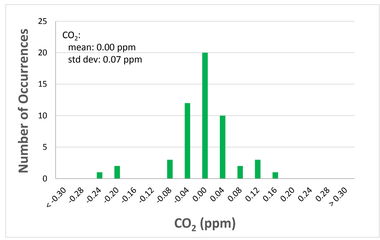
Portable Zero Air Generator

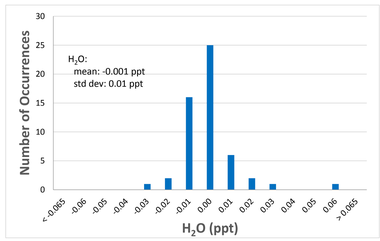


The Zero Air Generator (Campbell Scientific, Inc. pn 31022) is a convenient tool for zeroing an IRGA. The Zero Air Generator is very similar to the AP200 Scrub Bottle but includes a small diaphragm pump to circulate air through the IRGA. The flow rate (0.2 l·min^{-1}) flushes the calibration shroud or sample cell of the IRGA effectively without excess pressurization. Power consumption is very low and requires just one pair of AA batteries for approximately 40 hours of use. The Zero Air Generator weighs only 1.2 kg making it extremely useful in zeroing IRGAs in remote field sites.

An accelerated usage test was performed at Campbell Scientific, Inc., from January to May, 2016. Open-path IRGAs (EC150 and IRGASON) were zero and spanned using traditional compressed gases and dewpoint generator, and then air from the Zero Air Generator was measured. The run time for the pump was recorded for each test.

A total 54 IRGAs were tested, for a total run time of 15.5 hours. At the end of the test there was no indication of CO_2 or H_2O in the scrubbed air stream, and no indication of battery exhaustion. Other tests (data not shown) showed the batteries generally run for approximately 40 hours before the flow begins to decrease.





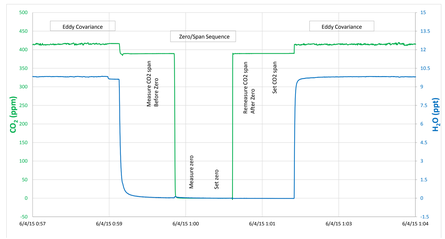
Closed-Path Eddy Covariance

The CPEC200 (Campbell Scientific, Inc.) is a closed-path EC flux system used for long-term monitoring of atmosphere–biosphere exchanges of CO_2, H_2O, heat, and momentum. It includes an EC155 CO_2/H_2O analyzer, CSAT3A sonic anemometer, pump module, and system enclosure that houses a CR3000 datalogger, and an optional valve module for on-line automated zero/span.

The CPEC200 Scrub Module is an accessory to the CPEC200. It is used to provide a source of zero air for zeroing the EC155 CO_2/H_2O analyzer. It uses a small, low-power (2W) diaphragm pump that is mounted in a temperature-controlled and weathertight fiberglass enclosure. Ambient air is drawn through molecular sieve to remove CO_2 and water vapor, and push zero air to the EC155 at approximately 2 l·min^{-1} flow.

The pump and its heater are powered only when in use, to avoid any significant effect on system power consumption.

Only an annual maintenance is required to replace molecular sieve in one of the three stages.



Conclusions

Molecular sieve can safely, easily, and effectively remove CO_2 and H_2O from air for zeroing an IRGA. It is available in a variety of scrubber devices optimized for various applications:

- Remove traces of CO_2 and H_2O from cylinders of compressed gas
- On-line automated field zero; with or without pump
- Hand-held zero air generator with battery-powered pump

Molecular sieve scrubbers make checking and setting the zero of a CO_2/H_2O analyzer easy and convenient, improving data quality and confidence.

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