

3.3 An Autonomous Inexpensive Robust CO₂ Analyzer (AIRCOA)

B. Stephens, A. Watt and G. Maclean

National Centre for Atmospheric Research, Boulder, CO

3.3.1 Introduction

We present our design of a new autonomous, inexpensive, and robust CO₂ analyzer (AIRCOA), a description of our quality control procedures, and data examples from ongoing deployments. Our AIRCOA units require less than \$10K (US) in components, can be assembled and tested in 4 weeks or less, show intercomparability of 0.1 ppm or better during laboratory and field tests, and run autonomously for months at a time.

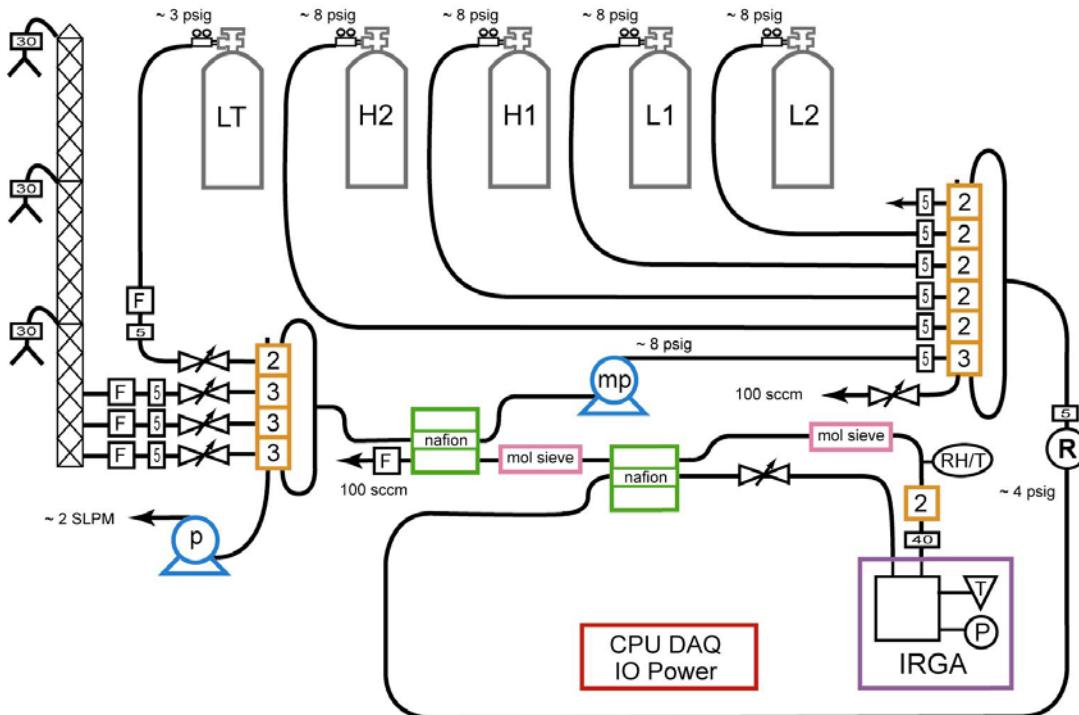


Figure 1: Schematic showing the AIRCOA design. Components include three sample air intakes with rain shields and 30 µm filters (30), mass-flow meters (F), 5 µm filters (5), manual needle valves, three-way (3) and two-way (2) solenoid valves and manifolds, Nafion driers, molecular sieve driers, a sample micropump (mp) and purge pump (p), four reference cylinders, one surveillance cylinder, two-stage pressure regulators, a single-stage pressure regulator (R), a humidity and temperature sensor (RH/T), a PC104 computer running Linux, PC104 relay and A/D boards, a power supply, and a LiCor 820 single-cell IRGA.

There is a strong motivation to improve atmospheric carbon flux constraints from continental scales (~10,000 km) to regional scales (~1000 km) so that they can be better related to the underlying ecosystem processes, land-use histories, and climate forcing. This requires a considerable increase in the temporal and spatial density of accurate atmospheric CO₂ observations, which would be significantly aided by lowered costs and improved reliability of continuous CO₂ analysis systems. As part of the Carbon in the Mountains Experiment (CME), we developed AIRCOA for the purpose of observing local scale CO₂ gradients across a network of towers at the Niwot Ridge carbon flux site, and have since begun deploying the same system in a regional CO₂ observing network.

Making accurate CO₂ measurements requires careful attention to gas handling, numerous automated quality control diagnostics, and a suite of reference cylinders closely linked to the WMO CO₂ calibration scale. Our approach builds on those of Zhao et al. (1997) and Trivett and Köhler (1999), but with considerable changes (see Figure 1). AIRCOA is based on a single-cell infrared gas analyzer (IRGA), which dramatically lowers the cost but increases the short-term noise and instrument drift rate. We overcome the short-term noise with signal averaging and instrument drift with frequent calibrations. Additional potential sources of CO₂ measurement bias that we address with automated diagnostics include: incomplete flushing of the sample cell and dead volumes, incomplete drying of the sample air, IRGA sensitivity to pressure broadening, IRGA sensitivity to temperature, leaks to ambient air, leaks of calibration gas through solenoid valves, and modification of CO₂ mixing ratio by the drying system or plastic components (see Table 1).

3.3.2 Instrument Design

As shown in Figure 1, we sample air from three heights on a tower, using inlets consisting of rain shields, and quartz wool and 30 µm polypropylene filters. The instrument box is generally indoors in an environment with moderate temperature variability, but in principle it could also be outdoors. Each inlet stream passes through a mass-flow meter (Honeywell, AWM3000V), and a 5 µm metal filter and needle valve (Beswick Engineering, CF and MLS series) before reaching a manifold of solenoid valves (Numatech, TM10 series). A brushless DC diaphragm pump (KNF Neuberger, N89) flushes the sample lines at 500 to 1000 sccm when they are not being analyzed. The one gas selected by these valves exits through both ends of the manifold and then passes through the first of two 2.44 m by 2.8 mm ID Nafion driers (Permapure, MD series). A smaller brushless DC diaphragm pump (KNF Neuberger, NMP015B) then compresses this gas to approximately 55 kPa above ambient at which point it passes through a second 5 µm metal filter and enters a second solenoid valve manifold.

Table 1: Potential sources of measurement error and AIRCOA solutions.

Measurement Concern	Solution
Short-term IRGA noise	Average for 100 seconds to get 0.1 ppm precision
Incomplete drying of air	Slow flow; two 2.44 m Nafion driers; downstream humidity sensor to verify
Incomplete flushing of cell	Sufficient flow; alternate calibration sequence low-to-high / high-to-low
Drift in IRGA sensitivity	4-hourly 4-point calibrations and 30-minute 1-point calibrations
Inadequate IRGA pressure calibration	Automated 4-hourly pressure sensitivity measurements
Leaks through fittings and valves	Automated 8-hourly positive pressure and 4-hourly ambient pressure checks
Temperature sensitivity of IRGA	Empirical temperature sensitivity correction from 30-minute 1-point calibrations
Drying system affecting CO ₂	Constant flows, pressures, and humidity in Nafions; CO ₂ in Nafion purge air
Other plastics affecting CO ₂	Minimize changes in pressure drop at inlet
Different sensitivity with and without Ar	Use calibration gases made with real air
Fossil CO ₂ in calibration gases	Comparisons to laboratory Siemens Ultramat 6F limit ¹³ C effect to 0.05 ppm
Regulator temperature effects	Laboratory tests show effect to be negligible; monitor for anomalous regulators
System diagnostics and verification	8-hourly analyses of surveillance gas run through entire inlet/drying system
Links to WMO scale	Laboratory calibration transfer facility; comparison to GMD flasks at NWR
Development of problems in the field	Near real-time data retrieval, processing, diagnostic checking, and display

This second manifold selects either a sample gas or a calibration gas to be analyzed. When the sample gas is not being analyzed it exits the valve manifold through a needle valve set to maintain constant pressure in the upstream Nafion drier. The four calibration gases typically span the range 340 to 480 ppm and are stored in high-pressure aluminium cylinders with Ceodeux valves (Scott Marrin Inc.) and two-stage brass regulators (Scott Specialty, model 14). These regulators are set to match the pressure in the sample line. We use 10 L high-pressure cylinders which last 12 months at our flow rates and calibration frequency. A fifth calibrated high-pressure cylinder stores a long-term surveillance gas which we run through the entire inlet system and treat as an unknown during analysis. The regulator on this cylinder is set to approximately 21 kPa above ambient and a needle valve is used to match sample pressures in the first Nafion drier.

The sample or calibration gas selected for analysis next passes through another 5 μm filter and a miniature pressure regulator (Beswick Engineering, PRD series) with an output of approximately 28 kPa above ambient. The gas is then dried by a second Nafion drier and reduced in pressure by a needle-valve (Swagelok, S series) before reaching a single-cell IRGA (LiCor, Li820). We adjust this needle valve to set the sample flow to 100 sccm. After leaving the IRGA, the gas passes through a 40 μm metal filter, a normally-open needle valve used for leak checking purposes, and a humidity and temperature sensor (Vaisala, HUMITTER 50Y) used to verify drier performance. We then completely dry the gas once with molecular sieve 13X to use it as the purge gas on the second Nafion drier, and dry it a second time to use it as the purge gas on the first Nafion drier. Most of the moisture in the ambient air exits the first Nafion without ever reaching the molecular sieve driers. We use 200 ml molecular sieve driers which last 6 to 12 months depending on outside humidity. The gas passes through a final mass-flow meter before exhausting to the room. There is little flow impedance between the Li820 cell and this exhaust such that sample and calibration measurements are both closely matched to ambient pressure.

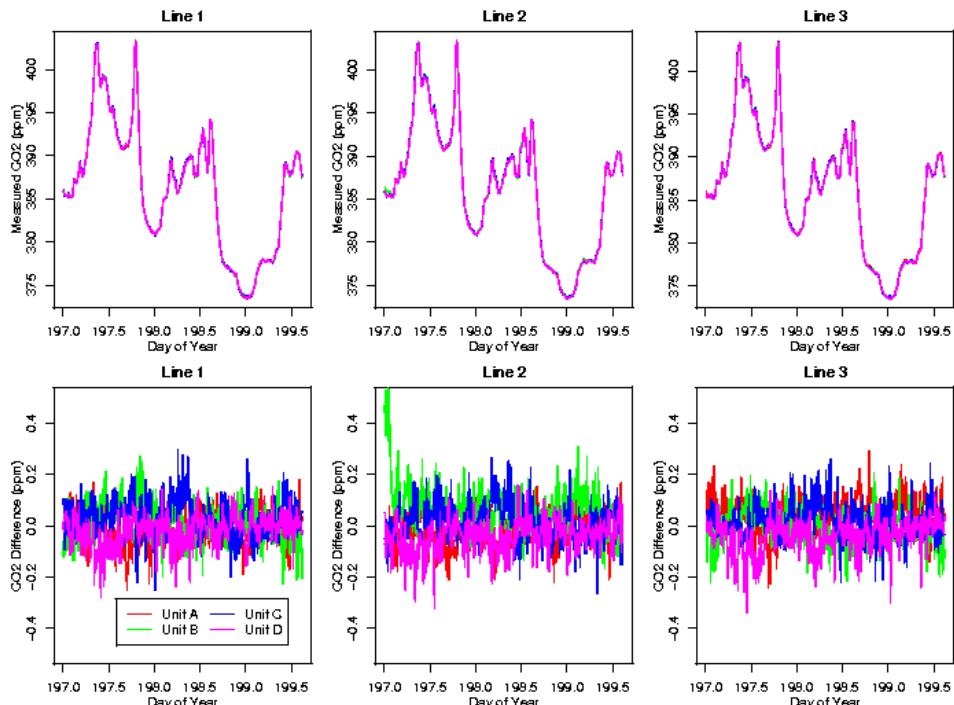


Figure 2: Measurements (top panels) made by 4 AIRCOA units on 3 days in Broomfield, CO during July 2005. These units were all in a laboratory with their inlet lines connected to a common manifold sampling outside air and common calibration cylinders. Comparison of measurements made by each unit during this period (bottom panels) shown as differences from the 4-unit median value at each sample time. The means (and 1-sigma standard deviations) for the 6 pair-wise differences were 0.05 (0.13) ppm or better.

The Li820 measures the pressure, temperature, and CO₂ mixing ratio of the gas. It actively and precisely controls the optical bench to 50 °C and has excellent stability with respect to ambient temperature of around 0.05 ppm/°C, which is a factor of 10 better than more expensive LiCor analyzers. We set the Li820 to use a 0.5 Hz digital filter and report values at 1 Hz. These filtered values have a 1-sigma rms noise of 0.6 ppm which averages to 0.1 ppm over 100 seconds. We switch the gas being analyzed every 150 seconds and ignore the first 50 seconds after each switch to allow for flushing of gases through the system. We then cycle between the three inlet lines on a 7.5 minute schedule. We make a calculation based on measured flows of how long the measured gas takes to get from the inlet to the sample cell and adjust the times of our reported measurements accordingly. Every 30 minutes we analyze one of the 4 calibration gases to estimate drift in the Li820 zero offset, while every 4 hours we measure all four calibration gases to estimate linear and 2nd-order calibration coefficients for the Li820. We alternate the sequence of

these 4 gases to look for problems associated with incomplete flushing of the sample cell and any dead volumes. Every 8 hours we analyze the long-term surveillance gas.

Every 4 hours we also perform automated system checks to determine the Li820 pressure sensitivity and to measure system leak rates to ambient at positive pressure and from the solenoid valves at ambient pressure. We make considerable efforts to minimize and monitor system leaks. Because of silicone seals in the Li820, plastic fittings on the Nafion driers, viton seals in the solenoid valves and manifolds, and plastic and viton seals in the micropump it is not practical to completely eliminate them. A leak of calibration gas with a 100 ppm difference from sample air through the solenoid valves at a rate of 0.1 sccm would result in a 0.1 ppm bias in our measurements. We set an operational target of 0.015 sccm for the total of all solenoid valve leaks and an absolute data-rejection cutoff of 0.03 sccm. It is more difficult to estimate the effect of positive-pressure leaks to ambient, but because of the potential for diffusion against flow they are not negligible. We test at 5 kPa overpressure and use the same target and cutoff rates as for the ambient leak-up test.

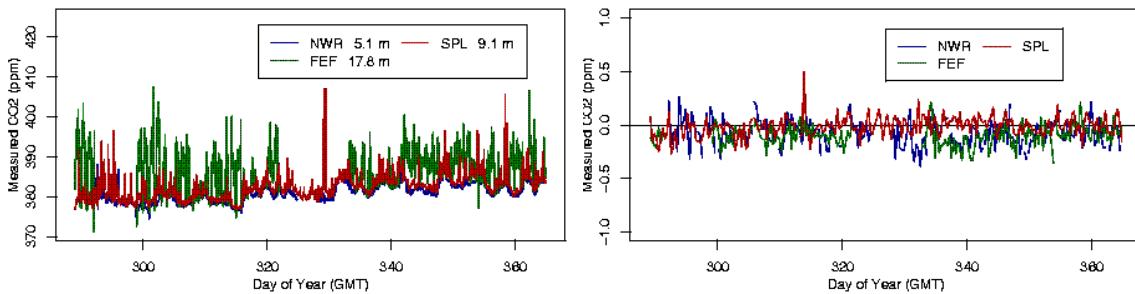


Figure 3: Measurements (left) made by 3 AIRCOA units from October 16 through December 30, 2005 in the field in Colorado: at Niwot Ridge (NWR), at Fraser Experimental Forest (FEF), and at Storm Peak Laboratory (SPL). Only values from the highest intake lines at these sites are shown. Comparison of surveillance cylinder measurements (right) made by each unit during this period, shown as differences from their laboratory assigned values. The means (and 1-sigma standard deviations) of these differences were -0.08 (0.13), 0.10 (0.10), and -0.01 (0.10) ppm respectively.

A PC104-based computer running Linux performs automated data acquisition and valve control. We access this system through a dedicated internet connection and retrieve, process, and display data and system diagnostics in near real time. If any of the automated diagnostics suggest a problem, we are then able to perform more detailed troubleshooting interactively. We cannot overstress the value of this direct connectivity and rapid processing for maintaining the systems and producing high-quality CO₂ measurements.

3.3.3 Results

In a week-long laboratory inter-comparison between 4 AIRCOA units all sampling outside air from a common mixing volume and using common reference cylinders, unit-to-unit differences on coincident measurements showed 1-sigma variability of 0.13 ppm and systematic biases of 0.05 ppm or less (see Figure 2). During isolated field operation comparability is more difficult to assess, but we use 8-hourly analyses of surveillance tanks to estimate performance. We installed three AIRCOA systems in the field at the start of September 2005. Despite the added complexity of different sets of calibration gases and larger temperature variations in comparison to the laboratory tests, the units still perform very well. While periods of systematic bias of up to 0.2 ppm are evident, averaged over a period of 2.5 months the 1-sigma variability for these three units ranged from 0.10 to 0.13 ppm and the systematic bias ranged from 0.01 to 0.10 ppm (see Figure 3). This figure also illustrates that the systems have been operating with relatively few data gaps during their initial deployments. We are working closely with other investigators developing and deploying similar single-cell IRGA based systems, as well as investigators deploying longer-established but

more expensive technologies, in an effort to improve the inter-comparability between independent observing networks.

References

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