

**Instrument:** Picarro Cavity Ringdown Spectrometer for CO<sub>2</sub>, CH<sub>4</sub>, and CO

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### **Principle of Operation:**

The Harvard Picarro instrument package consists of a G2401-*m* Picarro gas analyzer (Picarro Inc., Santa Clara, CA, USA) repackaged in a temperature-controlled pressure vessel, a separate calibration system with two CO<sub>2</sub>-CH<sub>4</sub>-CO gas standards, and an external pump and pressure control assembly designed to permit operation of the instrument at all ER-2 altitudes.

The Picarro analyzer uses Wavelength-Scanned Cavity Ringdown Spectroscopy (WS-CRDS). This time-based technique measures the decay rate of light intensity at different wavelengths in order to derive gas concentrations. The measurement starts by injecting single-frequency light into a 25-cm long and 33-cm<sup>3</sup> high-finesse optical cavity. This cavity uses a three high-reflectivity mirror (>99.995%) configuration. Once the light intensity reaches a threshold level, the light source is blocked and the time constant of the exponentially decaying light intensity is measured. In the absence of absorbers, ringdown times are on the order of tens of microseconds and the effective pathlength can reach up to 20 km. In the presence of absorbers, ringdown times are significantly shorter, with the shortest times corresponding to the wavelengths of strongest optical absorption (i.e., peak of an absorption line). High molecular selectivity as well as measurement accuracy and precision are achieved in part due to the patented wavelength monitor used. This monitor actively tunes the laser to absolute wavelengths with high precision. By targeting multiple wavelengths, an entire molecular absorption line is scanned. This approach increases measurement accuracy over relying on a single absorption wavelength. For CO<sub>2</sub>, CH<sub>4</sub>, CO, and H<sub>2</sub>O, absorption features in the 1.55 – 1.65 μm range are targeted using three different near-IR distributed feedback (DFB) diode lasers developed by the telecom industry. Once the absorption line is scanned, a multi-parameter fit is applied to the line shape in order to derive peak heights and subsequently gas concentrations. Measurement accuracy and precision also require temperature and pressure control of the gas sample. Using a combined scheme of active and passive control, the cavity is maintained at a temperature of 45 +/- 0.005 °C and a pressure of 140 +/- 0.02 Torr, providing a sample flow of approximately 500 sccm.

The environment around the Picarro analyzer is maintained at 35 °C and 760 Torr by a sealed, tubular pressure vessel. The internal structure that supports the analyzer is isolated from the walls of the vessel by grommets, providing vibration damping for the analyzer components and decoupling of the cavity assembly from deformations in the tube caused by external pressure changes.

Sample air enters the instrument through a rear-facing inlet to minimize ingestion of water droplets, is filtered by a 2 µm Zefluor membrane, and passes through a multi-tube Nafion drier to remove water vapor. A choked upstream Teflon-lined diaphragm pump provides sample air to the analyzer at 400 Torr, regardless of aircraft altitude, via a flow bypass. Prior to entering the analyzer, the sample air is further dried to a dewpoint of less than -70 °C using a dry ice cooled trap, and it is thermally conditioned to the pressure vessel temperature. A similar downstream pump, with an inlet pressure of 10 Torr facilitates flow through the analyzer at high altitude and ensures adequate purging of the Nafion drier.

To provide in-flight calibration of the instrument, two NOAA-traceable gas standards (low- and high-span) in 8.4 L carbon fiber wrapped aluminum cylinders are carried in a temperature-controlled enclosure. These standards replace the ambient air for one minute each, every 30 minutes, and serve to verify the accuracy and stability of the analyzer.

### **Specifications:**

Precision:	CO <sub>2</sub> ± 0.04 ppm; CH <sub>4</sub> ± 0.25 ppb; CO ± 7.25 ppb	
Weight:	170 lbs.	
Power:	115VAC / 400Hz, single phase:	500W max., 200W typical
	28VDC:	340W max., 100W typical
Response Time:	approx. 2.5 seconds	