

CO₂ Analyzers

OCN 633

Fall 2013

Basis of Operation

- Systems for both direct gas analysis and dissolved gases
- Systems for lab, shipboard and moorings
- Most analyze gas so dissolved gases are typically purged out of liquid phase into an absorption cell
- Primarily based on infrared (IR) absorption
- Alternative of open path optical sensors (still based on light absorption/fluorescence)

Manufacturers

- Contros Systems & Solutions GmbH (Germany)
- LI-COR Biosciences (USA)
- Pro Oceanus Systems Inc. (Canada)
- Sunburst Sensors (USA)
- YSI (USA) (mostly industrial)
- Picarro (USA) mostly lab/land field systems

Contros: HydroC CO₂ sensor

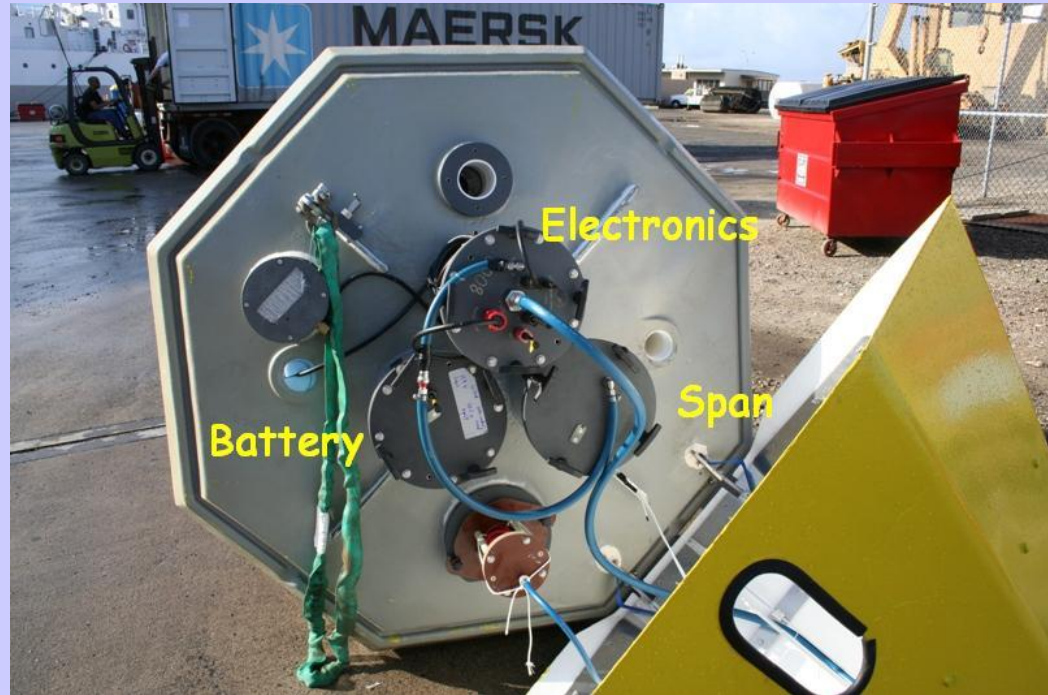
- Gas phase or aqueous determinations
- Long-term monitoring with internal optical sensor
- Optimized for high stability *or* low power
- Options for various pCO₂ ranges, housings
- Interface RS-232, RS-485 3000 m, FSK Modem 12km, ASCII NMEA-0183 data format
- Analog 0-5V, 0-10V, 0-20mA, 4-20mA
- Power supply input 10 – 32 V DC
- Titanium housings for 2000 m, 4000 m and 6000 m extended range
- Option internal ultra-low-power datalogger 2GB
- SmartDI™ sub-sea Datalogger with various options (additional sensor inputs; output formats in ASCII, etc; internal logging to CompactFlash disk)
- Available as flow-through version for mobile and lab applications, e.g. "underway" or "Ferrybox" systems



CRIMP-CO₂ System

- LI-COR 820 NDIR sensor with a 14 cm optical path
- Two point calibration: using CO₂ free air for the zero and with span gas of nominal 550 ppm CO₂ concentration (calibrated to ±0.01 ppm by the NOAA/CMDL in Boulder Co. using reference gases traceable to WMO)
- Seawater CO₂ concentrations determined by measuring CO₂ concentrations of air equilibrated with surface seawater using an *in situ* bubble-type equilibrator (Chavez et al., 1997)... bubble equilibrator does not necessitate pumping water to a “shower”
- Sample air passed through a Nafion® tube surrounded by silica gel to dry partially the sample gas before measurement
- Estimated accuracy of the air and seawater measurements based on laboratory and in situ comparisons is ~2 ppm.

CRIMP-CO₂ and HIOOS Buoys



Pro Oceanus: CO₂-Pro

- Small lightweight sensor for measuring pCO₂ in water.
- For underway, in laboratory and on moorings (design tested to depths of 1000 m).
- IR detector
- PSI pump-driven fast interface provides an equilibrated gas sample to the detector.
- Source of water flow is required at 3 to 10 liters per minute
- Typically used with Sea-Bird Electronics 5-T pump

- Factory calibrated from 0-600 ppm CO₂ with calibration burned into EPROM (other ranges available)
- Maintains accuracy through automatic zero point calibration (AZPC) by routing gas stream through a CO₂ absorbent to provide a zero ppm CO₂ measurement that compensates for changes in optical cell performance
- AZPC is used in determinations of CO₂ until a new AZPC is performed.

Manufacturer Claims:

- High precision and accuracy
- RS-232 data interface
- Low power requirements
- Light weight and compact size
- Unique antifouling protection
- Raw data and ppm CO₂ included in data stream



CO2-Pro: Specifications

- Length:33 cm (43 cm with connectors), Diameter:17.3 cm
- Weight in air:19.8 lbs. (9 kg); in water:0.88 lbs. (0.4 kg)
- Hard anodized aluminum housing
- Depth rated to 1000 meters
- Input voltage: 12 ± 0.5 V DC through 4-pin impulse male connector (with power-saving option: 9.5-18 V DC)
- Power consumption (not including pump power): warm-up: 0.8 A at 12 V, operation: 0.4 A
- Data Logger: 2 mega-bytes EPROM
- Data output: RS-232 serial output
- Sample Rate: 0.6 Hz without controller; 0.3 Hz with controller
- Equilibration time constant: ~3 minutes (depends on pump flow rate)

Accuracy

pCO₂ \pm ~ 1 ppm

Gas stream humidity \pm 1 mb

Gas stream pressure \pm 2 mb

Calibration range 0-600 ppm (other ranges available by special order)

Temperature range 0-35°C

Precision

pCO₂ 0.01 ppm

Gas stream humidity 1 mb

Gas stream pressure 1 mb

Pro Oceanus: GTD Pro

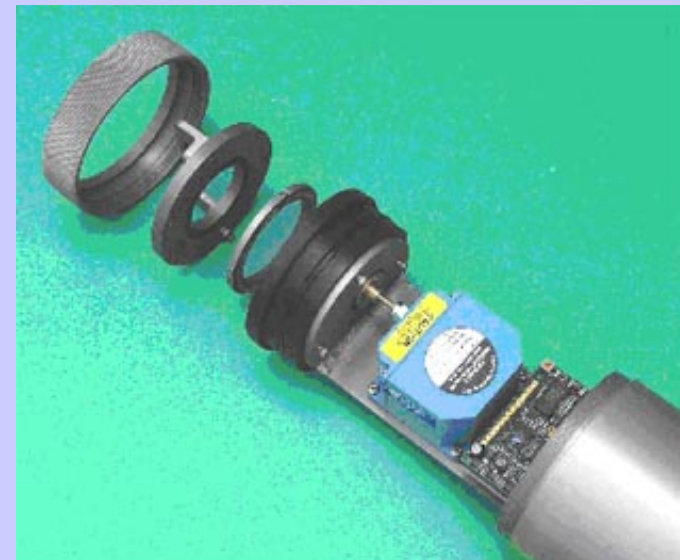
- First Pro-Oceanus Systems for use in laboratories, on moorings and aboard ships in underway mode

PSI Claims:

- High precision and accuracy
- User friendly set-up and operation
- RS-232/485 communications interface
- Compatible with Sea-Bird Electronics CTD's
- Low power requirements
- Light weight and compact size
- Hard anodized aluminum housing

Special Options

- Pumped Delrin plenum for flat interface to reduces the thickness of the water-side mass transfer boundary layer and reduces the time constant for equilibration. (Requires 3-10 l/min flow that can be provided by Sea-Bird Electronics 5-T pump at 3000 RPM available from Pro-Oceanus Systems Inc.
- Time constant = 10 min depending on flow rate.
- Alternate fast interface for PSI GTD-Pro.
- Time constant 3 min depending on flow rate.



GTD Pro: Specifications

Physical Specifications

- Length: 12.5 in. (31.8 cm), Diameter: 4.5 in. (11.4 cm)
- Weight in air: 15.5 lbs. (7 kg), in water: 7.436 lbs. (3.38 kg)

Performance

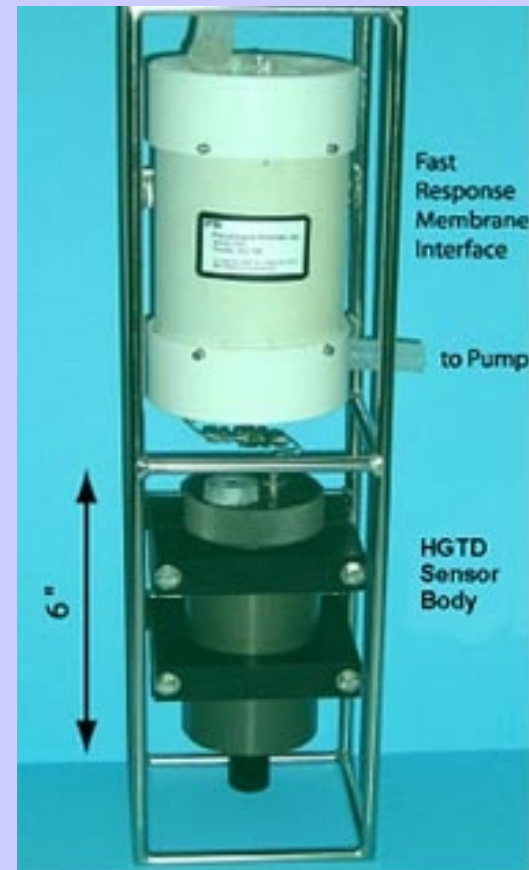
- Accuracy: <0.02 mb per year drift from calibration
- Precision: 0.002 mb
- Gas tension limits:
 - Min: 800 mb
 - Max: 2000 mb with standard pressure sensor

Electrical Characteristics

- Input voltage: 9-16 Volts DC
- Power Consumption:
 - While measuring: 0.8 W (67 mA at 12 V)
 - While sampling at 30 minute intervals: 27 mW overall

Pro Oceanus: Hurricane GTD

- Alternative to the Standard GTD-Pro
- Smaller and lighter than the Standard GTD-Pro
- Suited for deployment on profilers and gliders or in applications where a faster response, smaller and lighter weight instrument for measuring gas pressure is needed
- HGTD is equipped with fast response pumped tubular interface.
- Requires source of water flow at 3-10 l/min (optional SBE 5-T pump).



HGTD: Specifications

Physical Specifications

- Length: 9 in. (22.9 cm), Diameter: 3.25 in. (8.3 cm)
- Weight in air: 3.6 lbs. (1.6 kg), in water: 1.32 lbs. (0.6 kg)

Performance

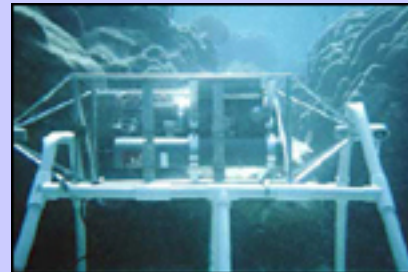
- Accuracy: <0.02 mb per year drift from calibration
- Precision: 0.002 mb
- Gas pressure limits:
 - Min: 800 mb
 - Max: 2000 mb (Other limits available by special order)

Electrical Characteristics

- Input voltage: 9-16 Volts DC
- Power Consumption:
 - While measuring: 0.8 W (67 mA at 12 V)
 - While sampling at 30 minute intervals: 27 mW overall

Sunburst SAMI Sensor

- Designed by Mike DeGrandpre (U. Montana)
- Built by Sunburst Sensors Inc.
- Systems now can be combined with pH and alkalinity sensors
- Reagent-based colorimetry
- Older systems were not user friendly and drifted... SAMI² has **allegedly** overcome problems



Sunburst Sensors General Specs.

- Sensor type: reagent based colorimetry
- Thermistor: accuracy 0.1°C, precision $\pm 0.01^\circ$
- Weight in air / seawater: 7.3 kg / 1 kg
- Operating range: -2°– 30° C, 0-500 m depth
- Dimensions: 58 cm x 15 cm diameter

Sunburst SAMI² CO₂

- <http://www.sunburstsensors.com/products.html>
- **SAMI² - CO₂**
 - measures $p\text{CO}_2$ in water
 - range: 150 – 700 ppm (other ranges avail.)
 - duration: ~17,000 measurements
 - response time: ~5 minutes
 - precision: < 1 ppm
 - accuracy: ± 3 ppm based on lab calibration*
 - Long-term drift: < 1 ppm over 6 months

*Based on NIST-traceable calibrated NDIR



Sunburst SAMI² pH

- Seawater pH_T (pH - total hydrogen ion scale)
- pH range: 7-9
- Salinity range: 30 – 36
- Duration: ~10,000 measurements
- Response time: ~3 minutes
- Precision: < 0.001 pH units ; Accuracy: ± 0.003 pH units (based on CRM* intercomparison)
- Long-term drift: < 0.001pH units over 6 months
*pH CRM from Andy Dickson (UCSD)

YSI 8500 CO₂ Monitor

- Opto-chemical based measurement (reaction with fluorescent dye; hydroxypyrene trisulfonic acid)
- System designed mainly for bioreactors, (e.g. monitoring fermentation and cell culture processes).
- Not particularly useful for oceanographers because concentration range is 1-25%
- Claim ability to measure every 15 seconds (response time is 7 seconds)

YSI-Sontek Inc.

- Sorry.... No published info on them.
- The instrument is a prototype that was just tested at CRIMP-CO₂ buoy as part of the ACT CO₂ sensor evaluation
- Results currently being compiled and will be available in a few weeks...

Picarro GHG

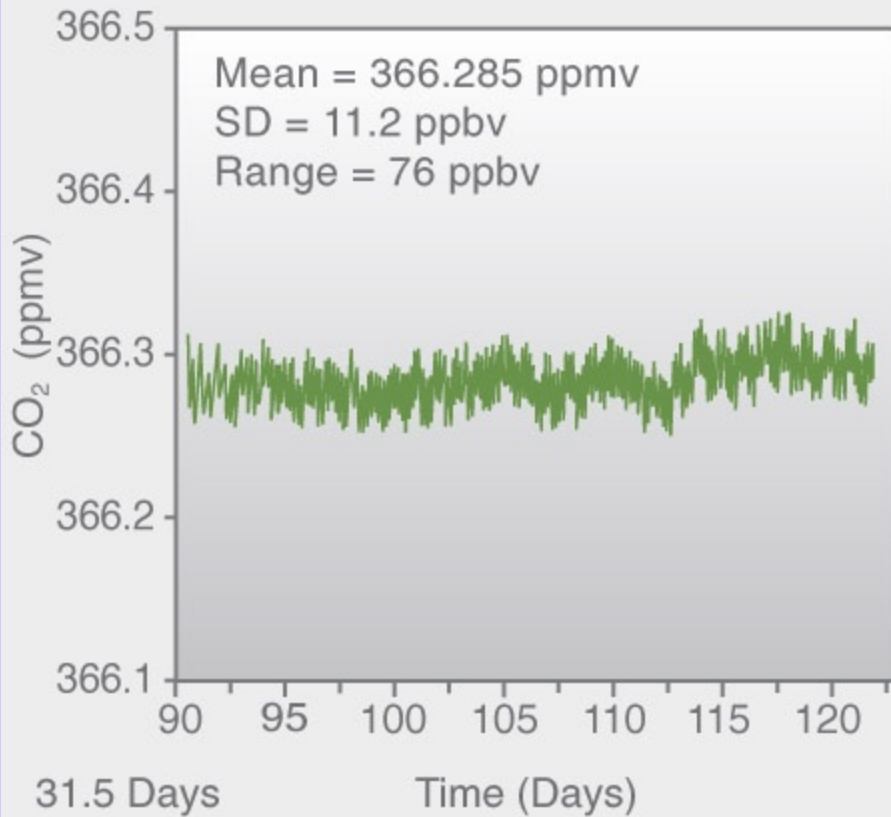
- Make gas analyzers (CO_2 , CH_4 , H_2O , NH_3)
- Also especially interesting because make eddy correlation analyzer systems for direct flux determinations

Picarro Gas Analyzers

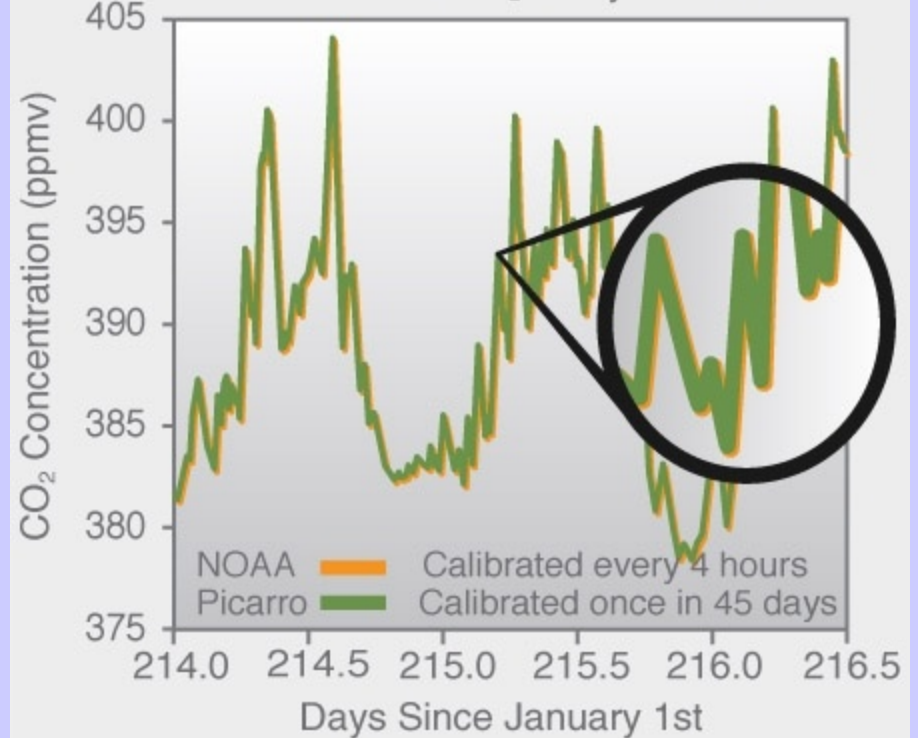
- WS-CRDS Analyzer for CO₂ and H₂O - Model G1200
- Simultaneous, precise measurement of CO₂ and H₂O
- ppb sensitivity, precision & accuracy with virtually no drift
- Fast, continuous, real time interference-free measurements
- Large dynamic range with high linearity
- Field and laboratory deployable with no consumables
- Rugged and insensitive to changes in ambient temperature

Picarro Performance

CO₂ 5 Minute Average



Comparison of
NDIR and Picarro CO₂ Analyzers at NOAA



Picarro Flux Measurements

Picarro G1301-f 10-Hz Analyzer for Eddy Covariance Flux

- Picarro G1301-f analyzer is a trace gas monitor capable of measuring gases in real time with ppb sensitivity at 10Hz.
- Instrument is well suited for Eddy Covariance Flux measurements.
- Based on Wavelength-Scanned Cavity Ring Down Spectroscopy (WSCRDS), a time-based measurement utilizing a near-infrared laser to measure a spectral signature of the molecule.
- Gas is circulated in an optical measurement cavity with an effective path length of up to 20 km
- A high-precision wavelength monitor makes certain that only the spectral feature of interest is being monitored, reducing sensitivity to interfering gas species, and enabling ultra-trace gas concentration measurements even if other gases are present
- Analyzer maintains linearity, precision, and accuracy over changing environmental conditions with minimal calibration
- Precise temperature and pressure control systems ensure accurate measurements over long periods of time with minimal calibration

ACT pCO₂ Evaluation

<http://www.act-us.info/evaluations.php#pco2>

ACT Code	Document Name	File Size
pCO₂	Detailed Testing Protocols used for evaluating the performance of pCO ₂ analyzers are available for download	193k
ACT DS10-01	Performance Demonstration Statement for Contros HydroCTM/CO ₂	1.7mb
ACT DS10-02	Performance Demonstration Statement for PMEL MAPCO ₂ /Battelle Seaology pCO ₂ Monitoring System	2.1mb
ACT TD10-03	Performance Demonstration Statement for Pro-Oceanus Systems Inc. PSI CO ₂ -Pro	2.1mb
ACT DS10-04	Performance Demonstration Statement for Sunburst Sensors SAMI-CO ₂	2.6mb
ACT VS09-04	Advancing moored pCO ₂ instrumentation in coastal waters. 2011, Marine Technology Society Journal 45(2): 43-51.	2.6mb

pCO₂ Analyzers Technical Advisory Committee

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