CAMPBELL SCIENTIFIC®

WHEN MEASUREMENTS MATTER

稳定同位素观测技术的最新进展

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May 22nd and 23rd, Beijing

Table of Contents

Other Laser Trace-Gas Spectroscopy Technologies

OA-ICOS, CRDS, WMS

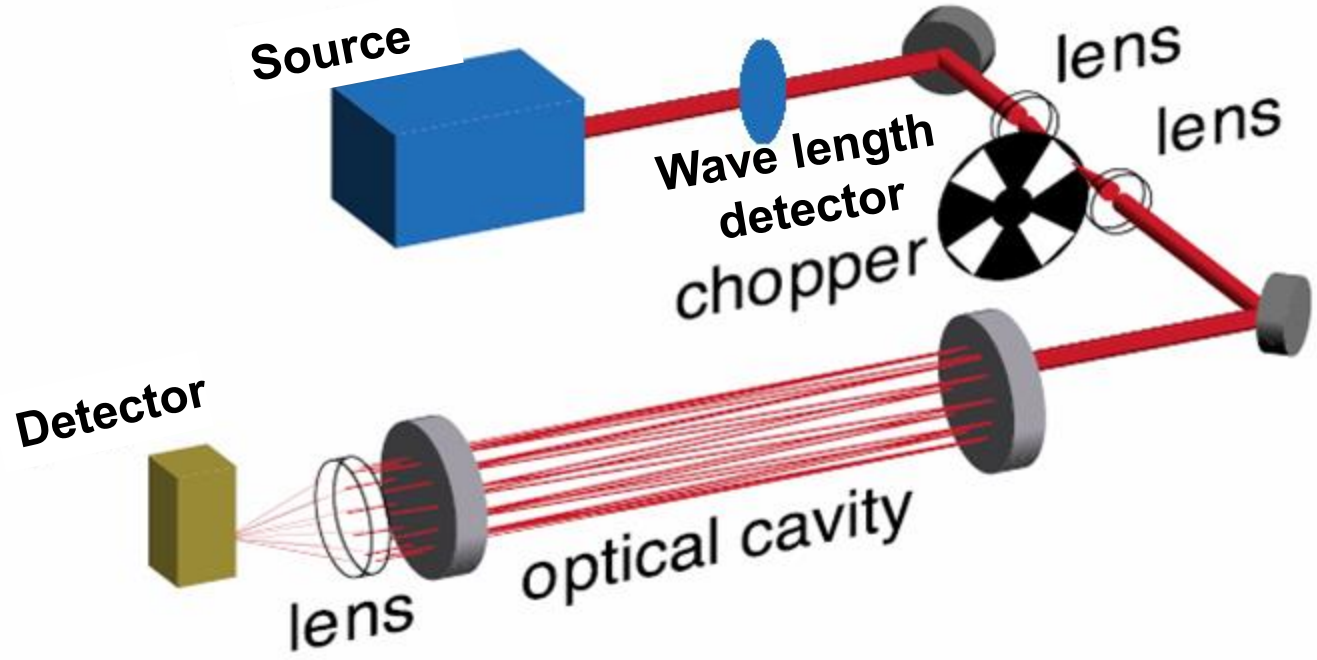
Off-Axis Integrated Cavity Output Spectroscopy (**OA-ICOS**)

- Los Gatos

Cavity Ring Down Spectroscopy (**CRDS**)

- Picarro

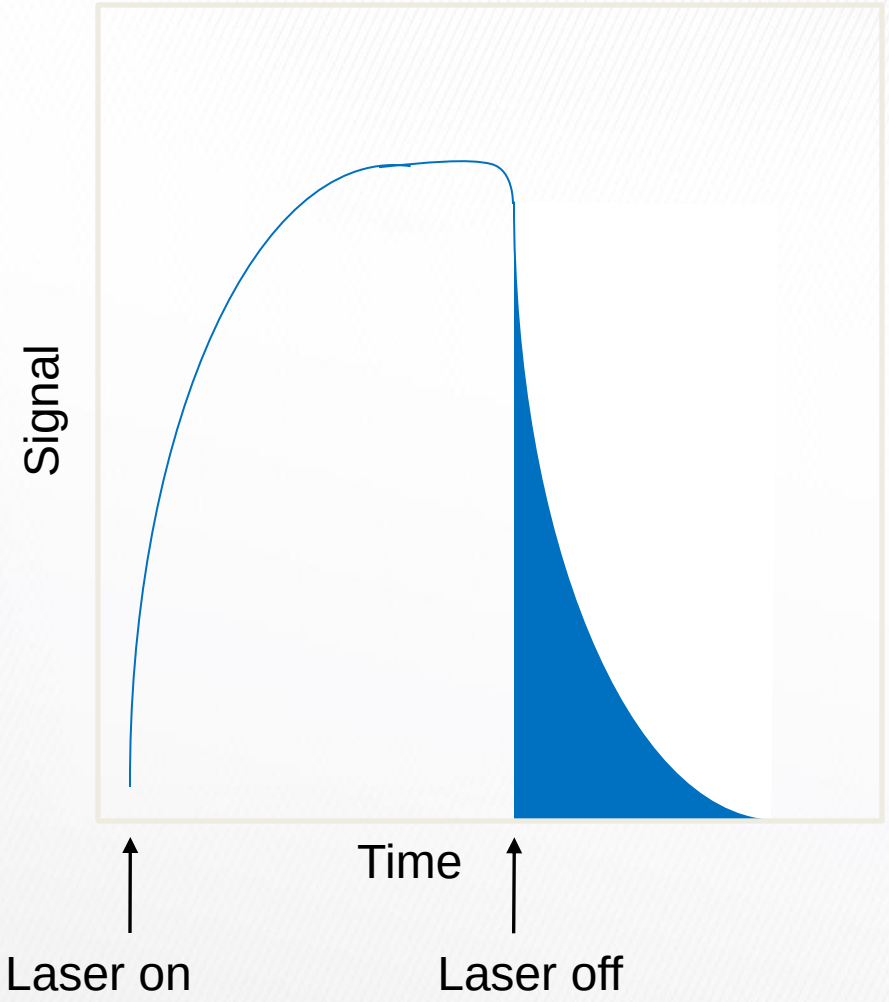
- Both manufactures developed a variety of trace-gas analyzers, for multi species w/ CO_2, H_2O, CH_4, …, NH_3, or Isotopes



An example CRDS or ICOS setup

- Multi kilometer optical path length

Cavity Ring Down

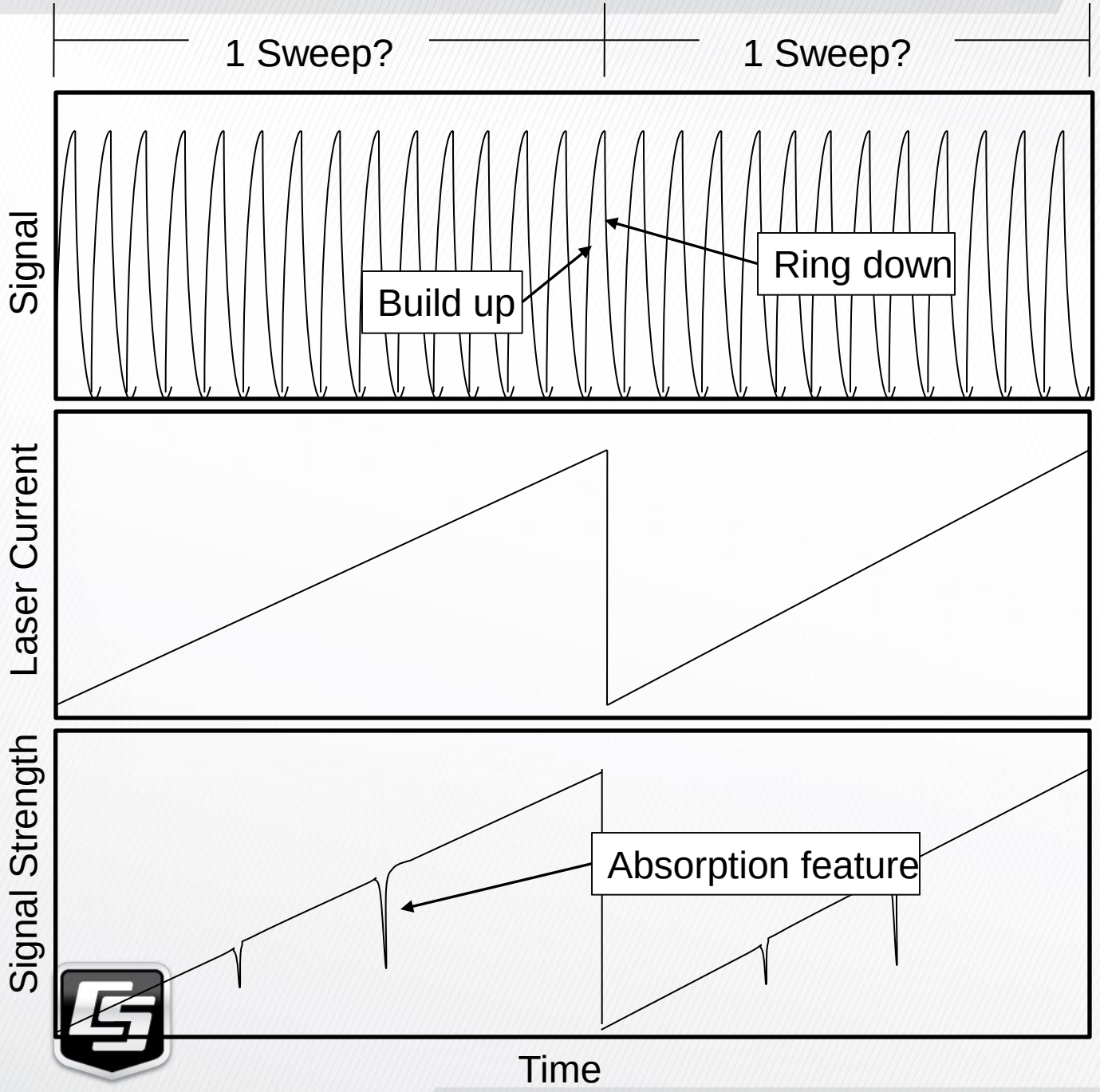


Build up - Beam injected into optical cavity

Ring down - Laser is pulsed off and signal decays (shaded in blue)

The ring down time is contingent on the concentration of the target species in the optical cavity and the mirror reflectivity.

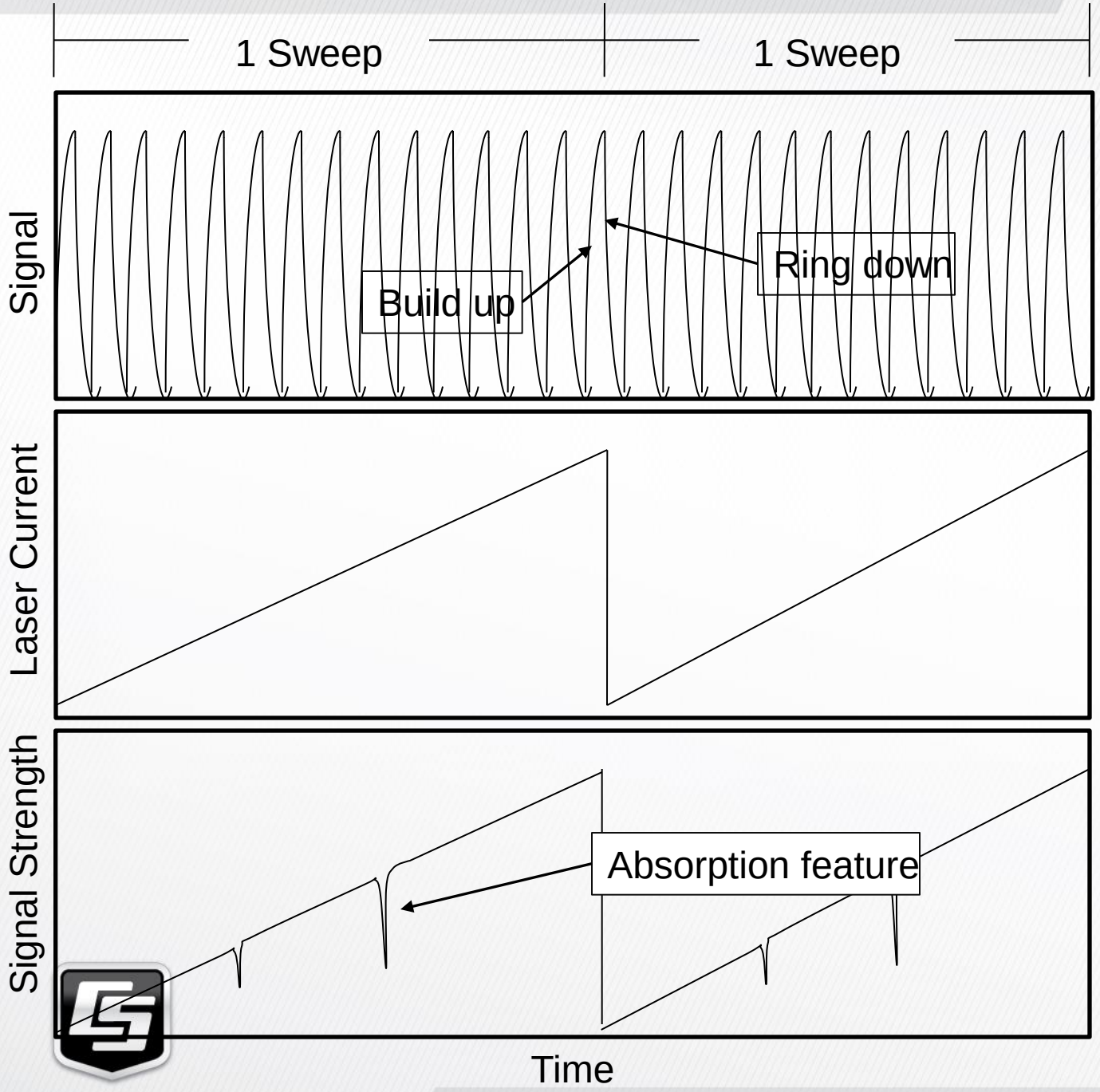
CRDS



Pulsed laser

May sweep laser or jump between features

Absorption determined from ring down events



ICOS

Determine mirror reflectivity from the ring down time

Sweep laser across several absorption features

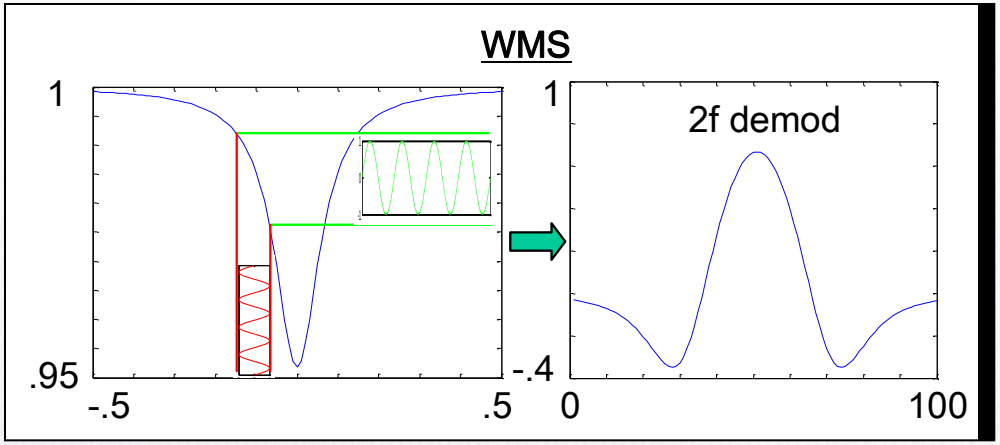
Make a direct absorption measurement, corrected for mirror reflectivity

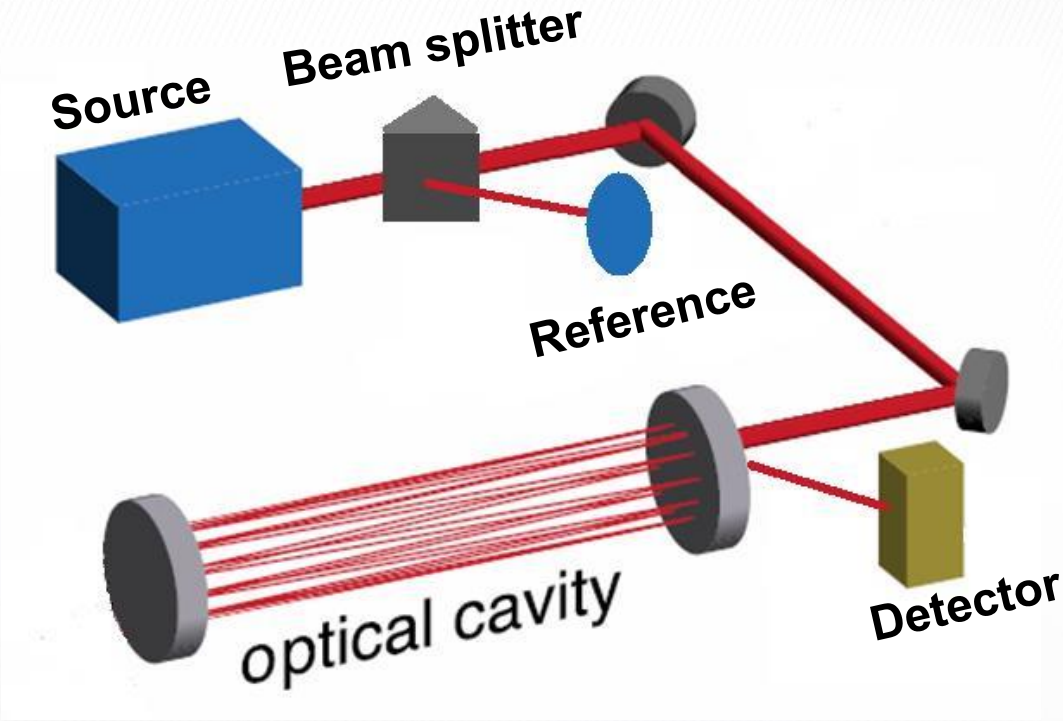
LGR 便携式温室气体分析仪

UGGA

WMS – Wavelength Modulation Spectroscopy, Li-7700

- Modulate scan at n
- If we demodulate at 2n we can get a signal that is proportional to the 2nd derivative
  - Demodulation is done optically

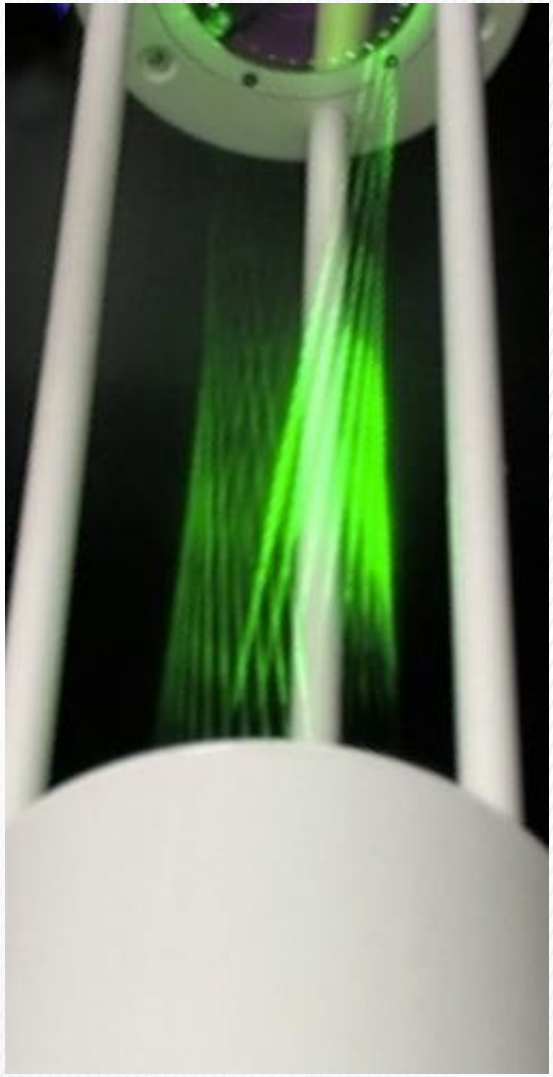




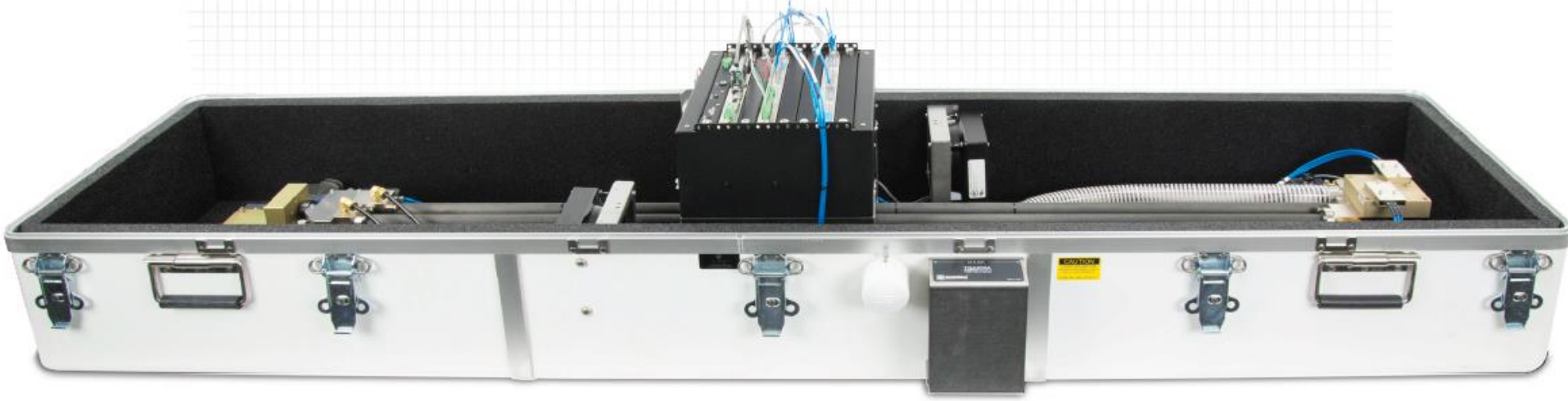
LI-7700 Setup

LI-7700

- Open Path
- Herriott Cell
  - Consists of 2 spherical mirrors
  - Light is introduced off-axis
  - 0.5 m x 60 passes = 30 m total path length
- CH4 analyzer only



TGA history and introduction



Introduction

- What is a TGA?
  - CSI has been manufacturing TGA's since 1993
  - TGA is a tunable diode laser absorption spectrometer (TDLAS), and new lasers are TE cooled
  - They are rugged, portable, and designed for use in the lab or out in the field
  - Uses a small sample cell volume for good frequency response no mater the application

TABLE 1-1. Historical Summary of Campbell Scientific Trace Gas Analyzers				
	TGA100	**TGA100A**	**TGA200**	**TGA200A**
Ship dates	1993 – 2004	2005 – 2009	2008 – 2012	2014 –
CPU	Transputer (upgradeable)	New	New	New
Software	Transputer	DOS	TGA Windows	TGA TEC
Laser	Lead salt	Lead salt	Lead salt	Interband Cascade
Cooling options	LN_2	LN_2 or Cryocooler	LN_2	Thermoelectric
Dewar capacity (L)	1.5	10.4	14.5	None
Optical configuration	Beamsplitter at detector end.	Beamsplitter at detector end	Beamsplitter at laser end. Long sample and reference cells.	Beamsplitter at laser end
Absorption cells	Long sample cell/short reference cell	Long sample cell/short reference cell	Long sample and reference cells	Long sample and reference cells.
Temperature control	Fans only (TGAHEAT optional starting 2002)	TGAHEAT included	Software	Software

TGA100 and TGA100A

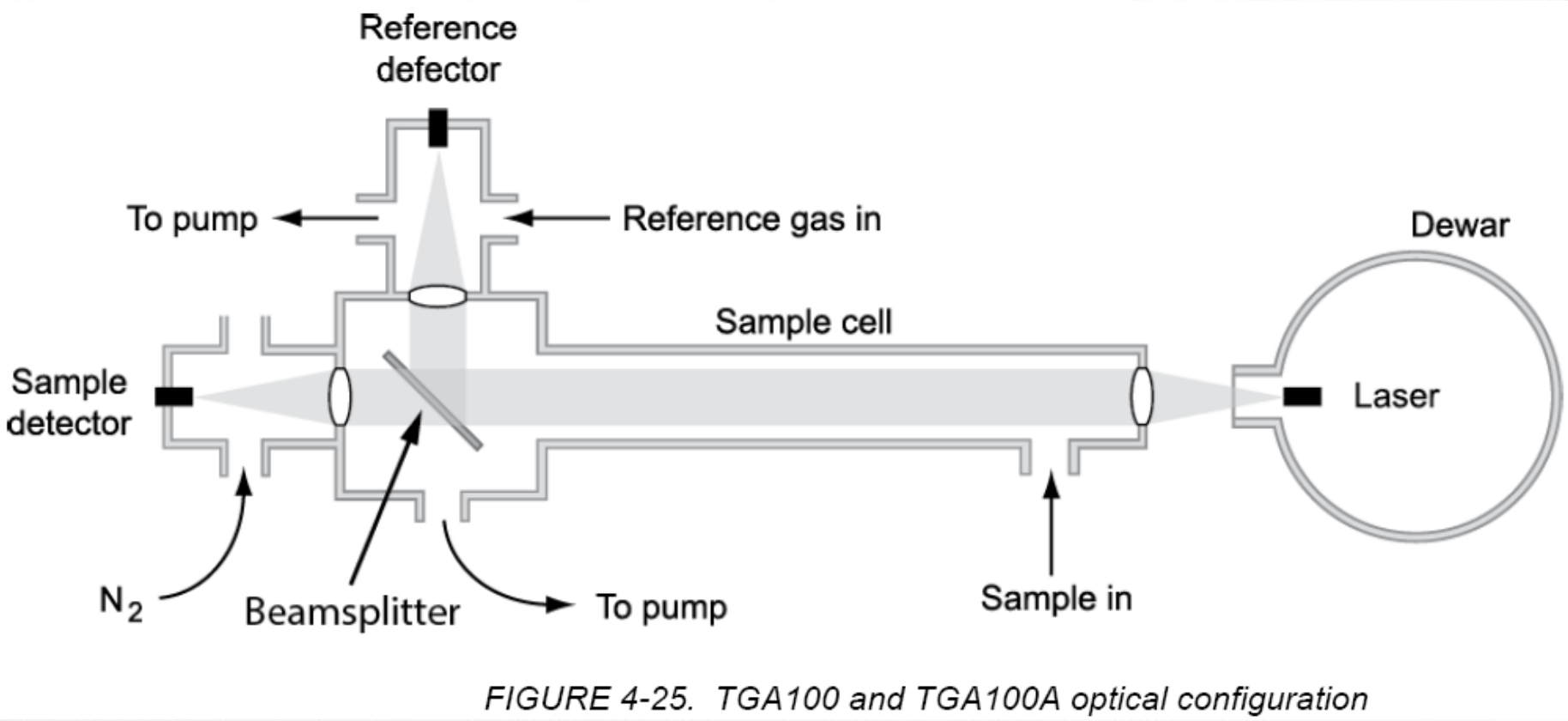


FIGURE 4-25. TGA100 and TGA100A optical configuration

TGA200 and TGA200A

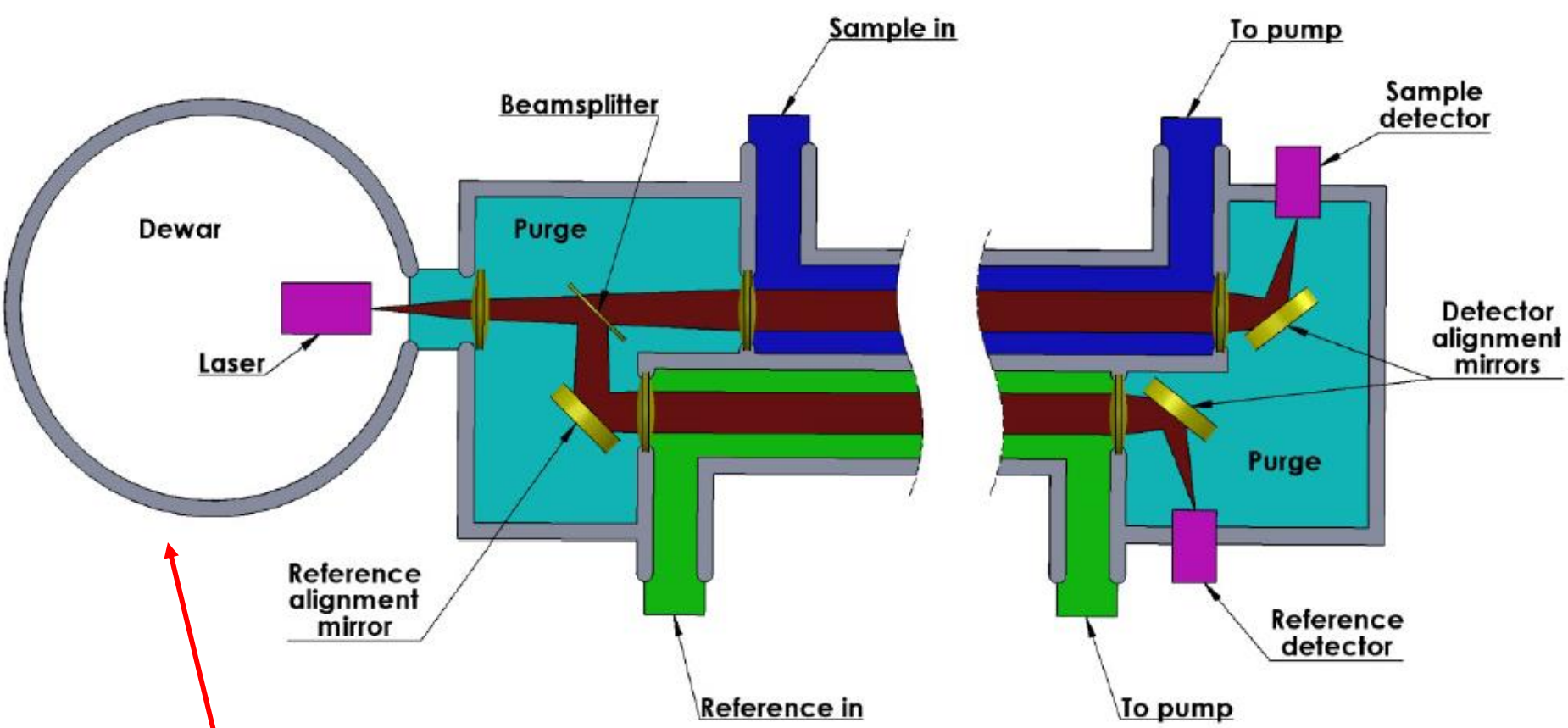


FIGURE 4-26. TGA200 and TGA200A optical configuration

Note: TGA200A is TE-cooled and be without Dewar.

Concentration Calculation

- Fundamental assumption: Temperature and pressure are the same for the sample and reference gases.
- The ref. and sample detector signals are:
  - Digitalized,
  - Corrected for detector offset and nonlinearity,
  - and Converted to absorbance.
- A linear regression of sample absorbance vs. reference absorbance gives the ratio of sample absorbance to ref. absorbance.

Concentration Calculation

$$C_s = \frac{(C_R)(L_R)(D)}{L_S + L_A(1-D)} \qquad (1)$$

where:

C_R = concentration of reference gas, ppm

L_R = length of the short reference cell, cm

L_S = length of the short sample cell, cm

L_A = length of the long sample cell, cm

D = ratio of sample to reference absorbance

- For TGA200 and TGA200A, L_A is zero, and L_S and L_R are both long (146.6 cm), so

$$C_s = (C_R)(D) \qquad (3)$$

Isotope Calculation

$$\delta^{13}C = \left(\frac{R_s}{R_{VPDB}} - 1 \right) \times 1000 \qquad (4)$$

where:

R_s = ratio of the isotopolog concentrations measured by the TGA ($^{13}CO_2/^{12}CO_2$)

R_{VPDB} = the standard isotope ratio ($^{13}C/12C$)

$\delta^{13}C$ is reported in parts per thousand (per mil or ‰)

Installation

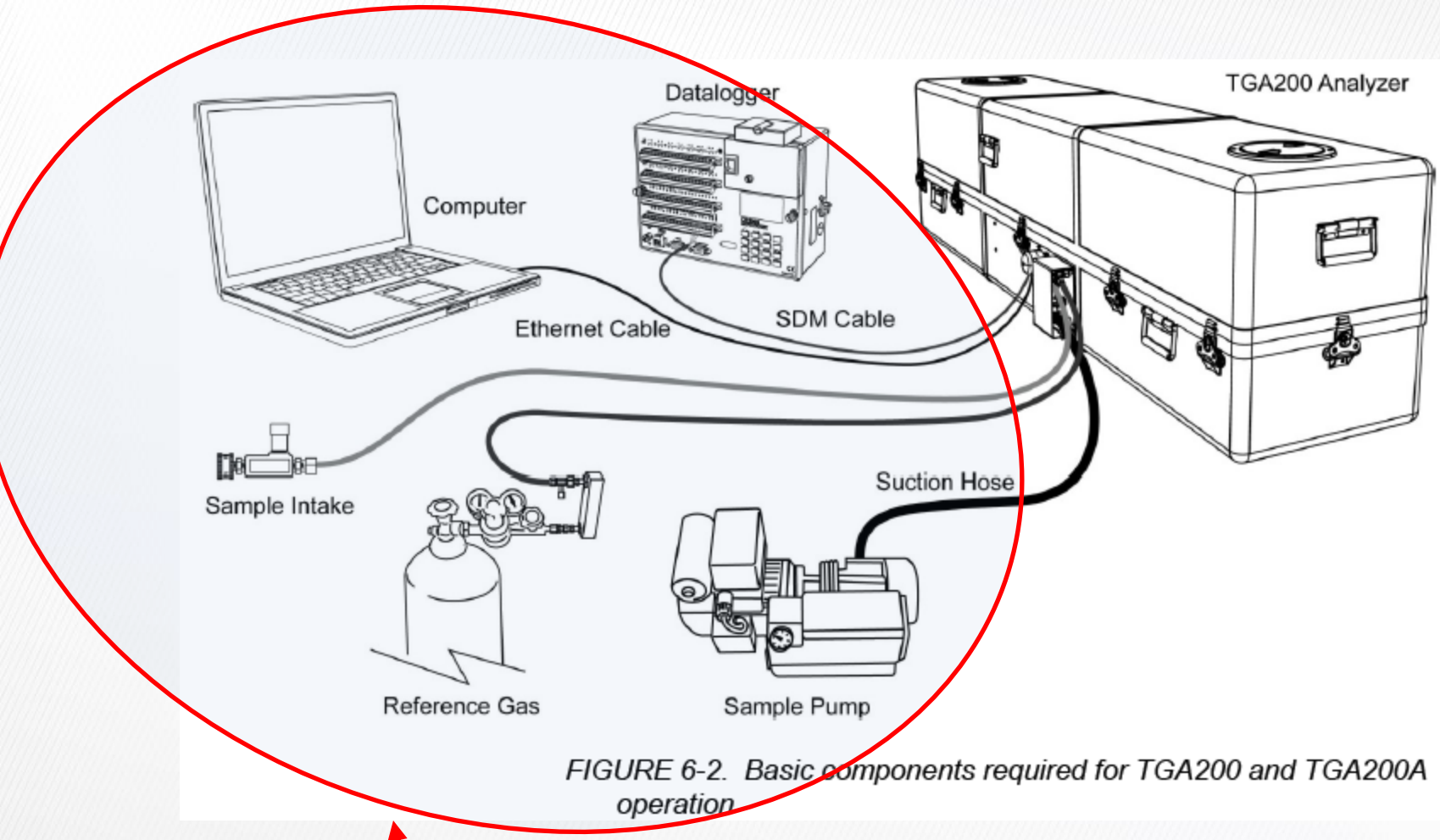


FIGURE 6-2. Basic components required for TGA200 and TGA200A operation

Note: These parts are not included in TGA200A.

TGA TEC software

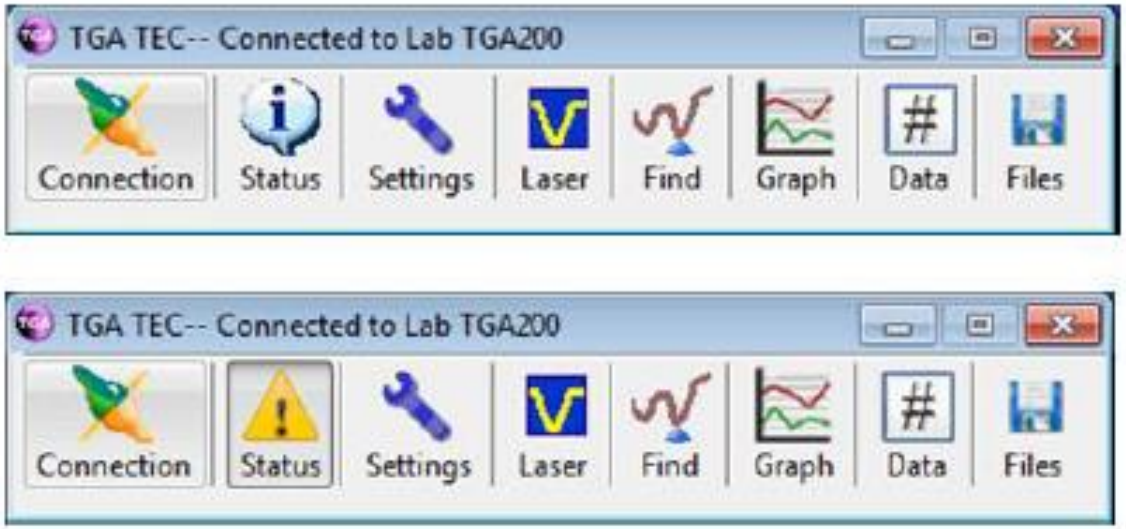


FIGURE 7-5. TGA Status with a detected error (bottom)

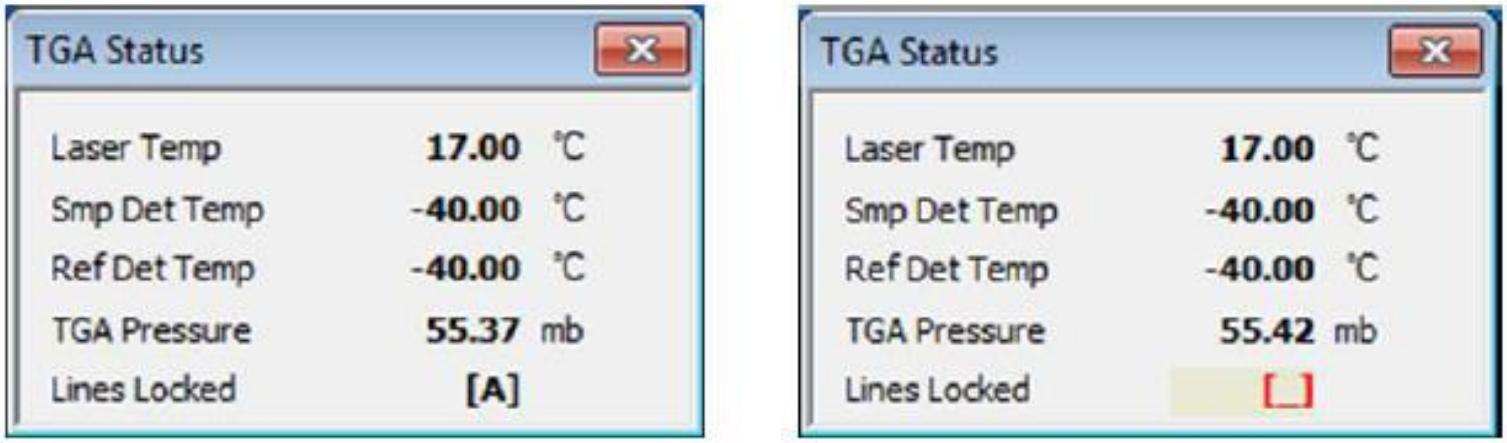


FIGURE 7-6. TGA Status window without error (left) and with error (right) and line lock manually disabled.

TGA TEC software – Laser Find

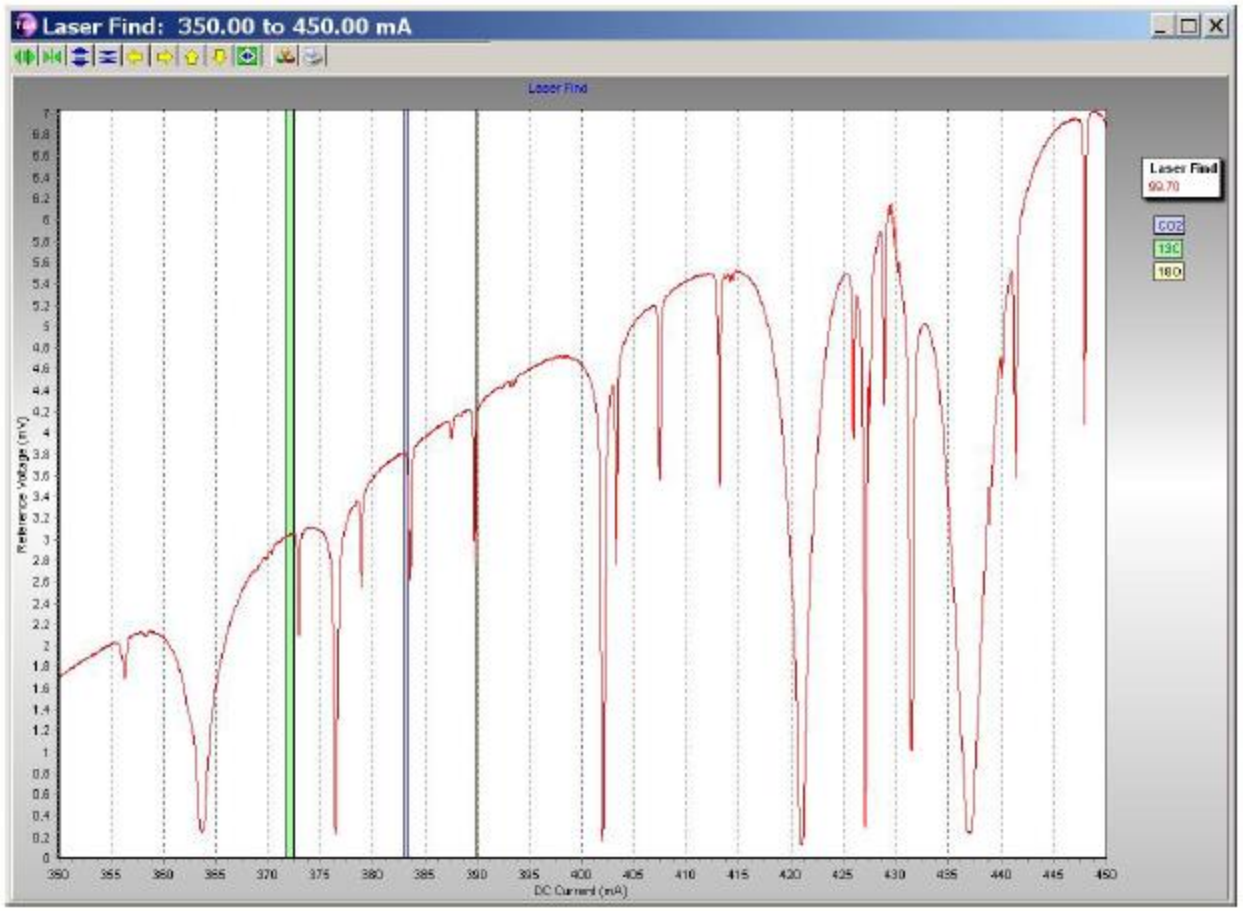


FIGURE 7-38. Interactive Laser Find window for a CO2 isotope laser.

TGA200A’s Specification

Physical Specifications

TABLE 5-2. Physical Specifications of TGA Variants

	TGA100	TGA100A	TGA200	TGA200A
Length	211 cm (83 in)	211 cm (83 in)	211 cm (83 in)	211 cm (83 in)
Width	47 cm (18.5 in)	47 cm (18.5 in)	47 cm (18.5 in)	47 cm (18.5 in)
Height	55 cm (21.5 in)	55 cm (21.5 in)	55 cm (21.5 in)	55 cm (21.5 in)
Weight[a]	74.5 kg (164 lb)	88.9 kg (195.5 lb)	78.6 kg (173 lb)	62.8 kg (138.5 lb)[b]
Sample path length	153.08 cm (60.27 in)	153.08 cm (60.27 in)	146.6 cm (57.72 in)	146.4 cm (57.64 in)
Reference path length	4.52 cm (1.78 in)	4.52 cm (1.78 in)	146.6 cm (57.72 in)	146.4 cm (57.64 in)
Sample cell volume	480 ml	480 ml	420 ml	200 ml
Operating temperature	–20 to 45 °C	–20 to 45 °C	–20 to 45 °C	–20 to 45 °C

[a]Weight of the TGA100A and TGA200 is shown for most common configuration (LN_2 laser dewar and TE-cooled detectors)

[b]Does not include the weight of the power module (pn 30981) which is 5.4 kg (12.0 lb) with the accompanying power cable

Measurement Specifications

TABLE 5-1. Typical Measurement Noise[a]

Part Number	Description	Chemical Formula	Typical Noise[b]	Units
30478	Nitrous Oxide	N_2O	1.5	nmol mol^{-1}
30477	Methane	CH_4	7.0	nmol mol^{-1}
31121	Nitrous Oxide and Carbon Dioxide[c]	N_2O CO_2	1.8 0.3	nmol mol^{-1} µmol mol^{-1}
31119	Carbon Dioxide and $\delta^{13}C$	CO_2 $\delta^{13}C$	0.15 0.5	µmol mol^{-1} ‰
30877	Carbon Dioxide, $\delta^{13}C$, and $\delta^{18}O$	CO_2 $\delta^{13}C$ $\delta^{18}O$	0.5 2.0 2.0	µmol mol^{-1} ‰ ‰

[a]Preliminary: specifications are subject to change without notice
[b]Allan deviation with 100 ms averaging time
[c]Based on the $^{13}C^{16}O^{16}O$ isotopolog

Power Requirements

Analyzer (LN_2-cooled laser):	90 to 264 Vac, 47 to 63 Hz, 42 W (max) 24 W (typical)
Analyzer (TE-cooled laser):	90 to 264 Vac, 47 to 63 Hz, 34 W (max) 22 W (typical)
Heater:	90 to 264 Vac, 47 to 63 Hz, 150 W (max) 50 W (typical)

TGA200A’s Benefits and Features

TDLAS technology provides high sensitivity, speed, and selectivity

- Small sample cell volume that provides superior frequency response
- Thermoelectrically cooled laser; no cryogenic cooling required.
- Upgrades available to existing TGA customers (contact Campbell Scientific for more information)
- Choice of laser sources to measure N_2O, CH_4 or CO_2 isotopes
- 500 Hz measurement rate that supports excellent synchronization with our CSAT3 sonic anemometer, making TGA200A ideal for eddy covariance flux applications

Continued:

- Rugged environmental enclosure that allows the TGA200A to placed outside on the ground
- Simple Windows user interface for setup, configuration and real-time monitoring
- Complete greenhouse gas measurement flux solution provided by combining one or more TGA200As with Campbell Scientific's sonic anemometers, dataloggers, gas analyzers, or eddy covariance system
- Advanced sampling systems also available for low flow applications such as profile gradient or user-supplied chamber measurements

- **TEC Lasers**
  - 5 laser options depending on application
    - 3 lasers can measure more than just 1 gas species
    - All lasers are TE-cooled, so no LN2 required for cooling
    - No maintenance required

TABLE A-4. Suggested Reference Gas Concentrations

Gas Species		TGA100 or TGA100A	TGA200 or TGA200A	Balance of Tank
Methane (CH_4)		15,000 (1.5%)	500	N_2
Nitrous Oxide (N_2O)		2,000	60	Air or N_2
N_2O/CO_2	N_2O	2,000	90	Air or N_2
	CO_2	300,000 (30%)	15,000 (1.5%)	
N_2O/CH_4	N_2O	10,000	350*	N_2
	CH_4	20,000	850*	
Carbon Dioxide (CO_2) isotopic ratios, $\delta^{13}C$ only		100,000 (10%)	2500	Air
Carbon Dioxide (CO_2) isotopic ratios, $\delta^{18}O$ and $\delta^{13}C$		300,000 (30%)	10,000 (1%)	Air
Ammonia (NH_3)		5,000	160**	Air or N_2
Water or other		Contact Campbell Scientific		

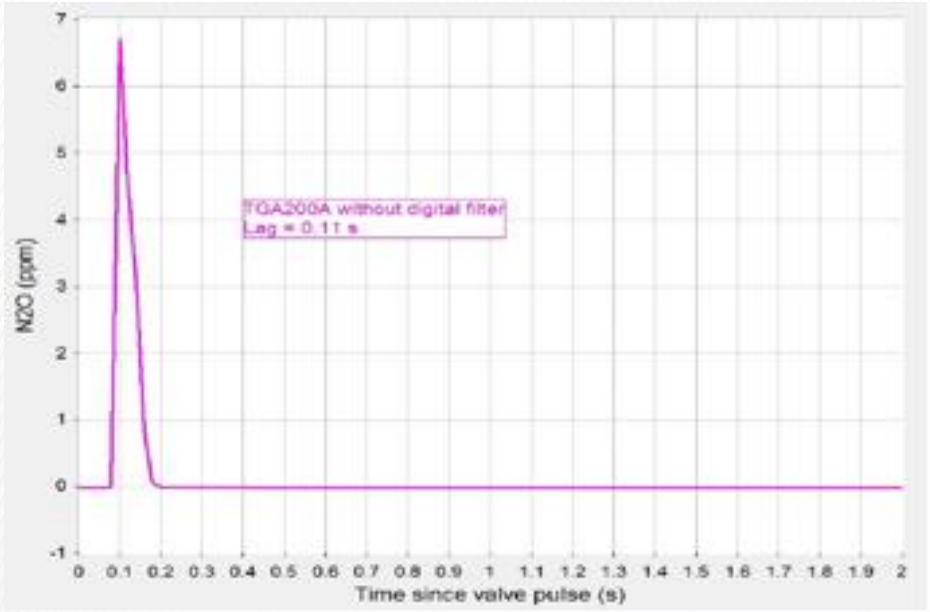
*the N2O/CH4 laser is not available for the TGA200A

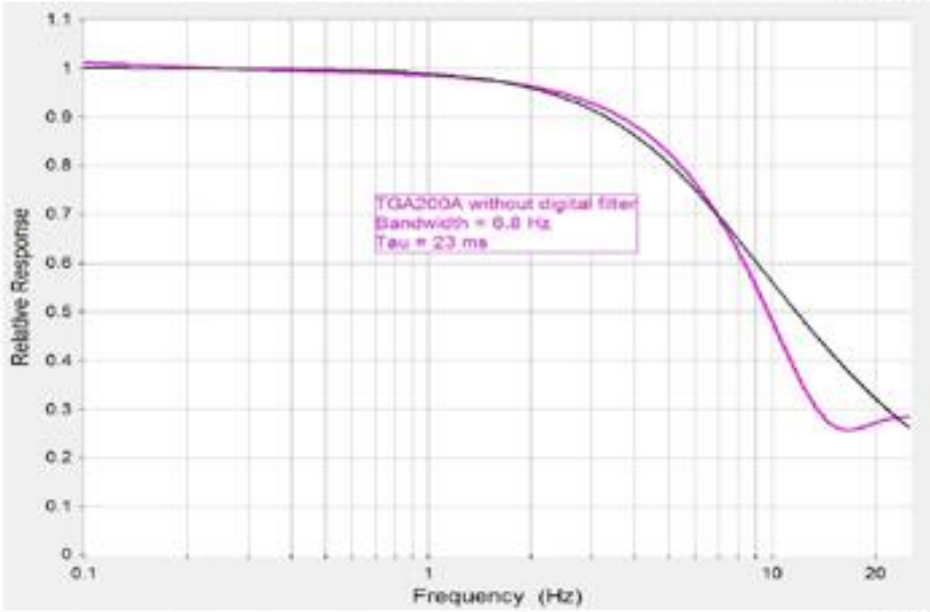
**the ammonia laser is not available for the TGA200A

Testing of TGA200A's frequency response - Method

- TEC LasersInject fast pulses of N2O into sample flow (ambient air) every 10 seconds
- Sample the TGA200A response at 50 Hz with CR3000 datalogger
- Impulse response
  - Remove trend (10 s moving average)
  - Overlay multiple pulses
  - Calculate lag time
- Frequency response
  - Fourier transform the impulse response
  - Normalize to 1 at low frequency
  - Calculate the characteristic time
- Inject pulses at the inlet of the TGA200A, with and without digital filtering, and at the inlet to the EC system

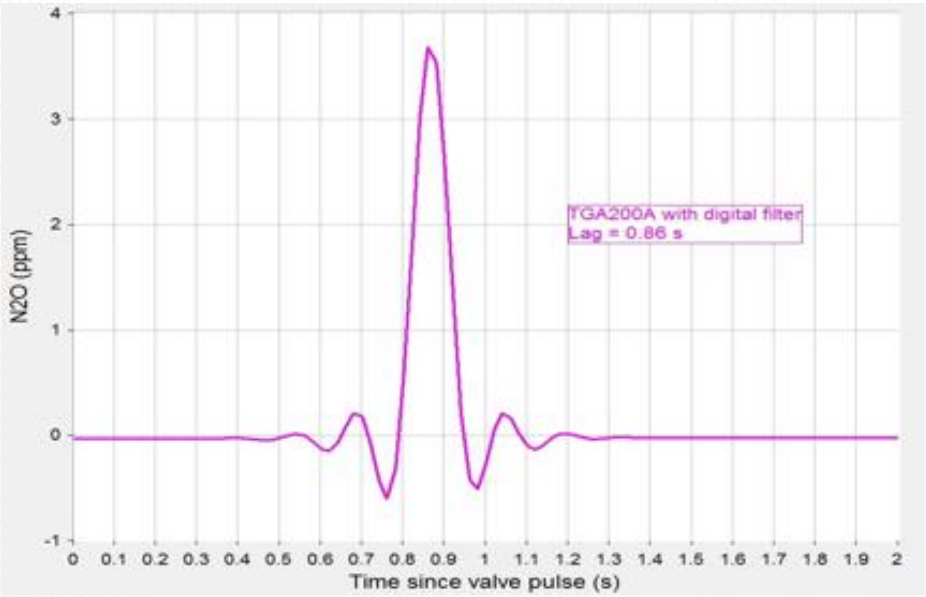
TGA200A with Digital Filter Disabled

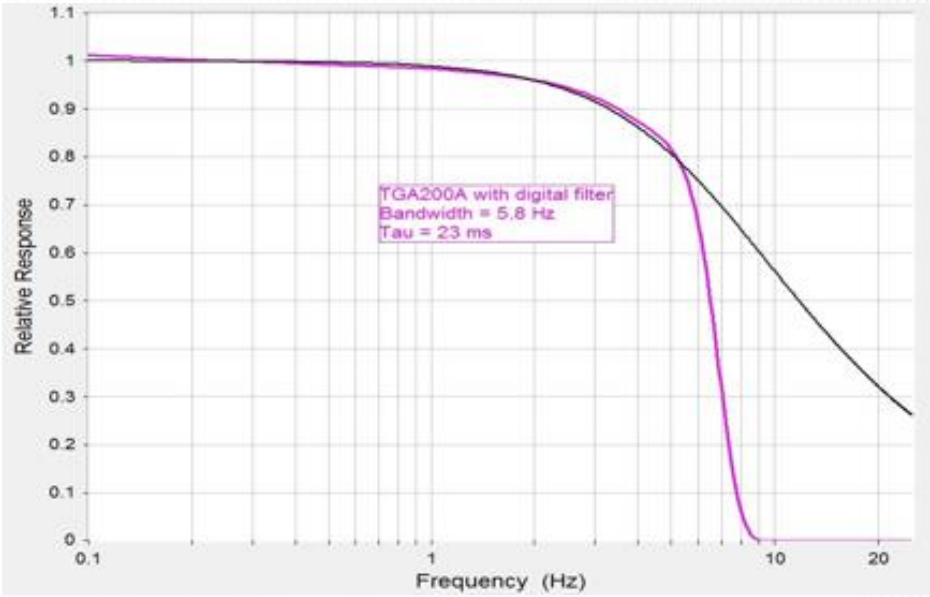




The first-order model corresponding to the characteristic time constant is overplotted in black.

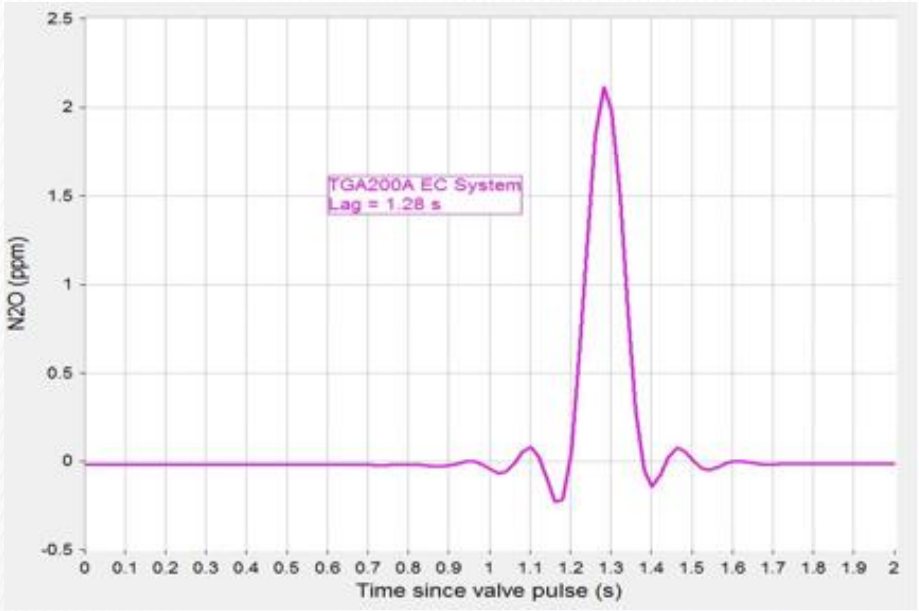
TGA200A with Digital Filter Enabled

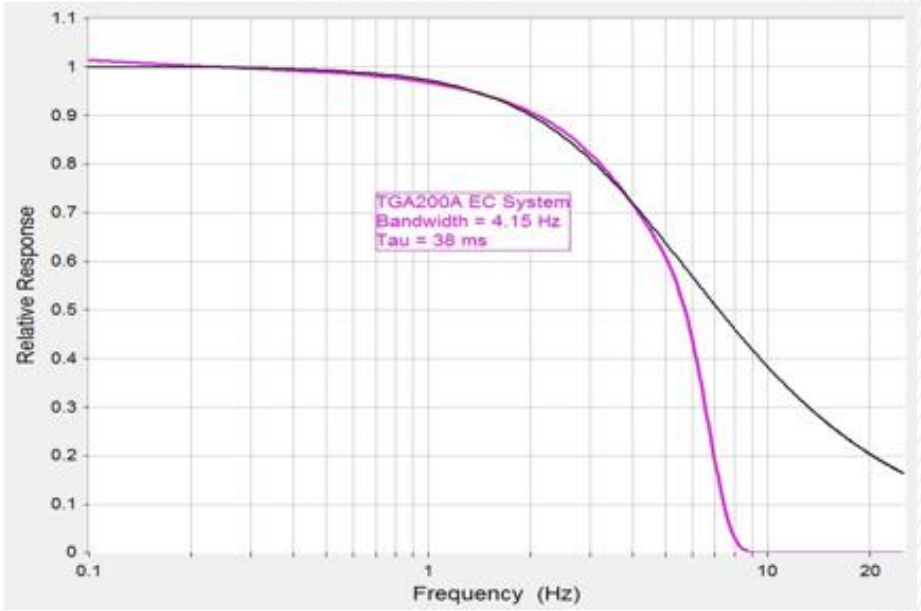




The first-order model corresponding to the characteristic time constant is overplotted in black.

TGA200A with Complete EC System





EC system flux loss is very low, even at low measurement height and strong winds: 88% of flux measured at 2m height, 10 m/s wind speed.

Case Study

Profiling/Gradient Plumbing Scheme

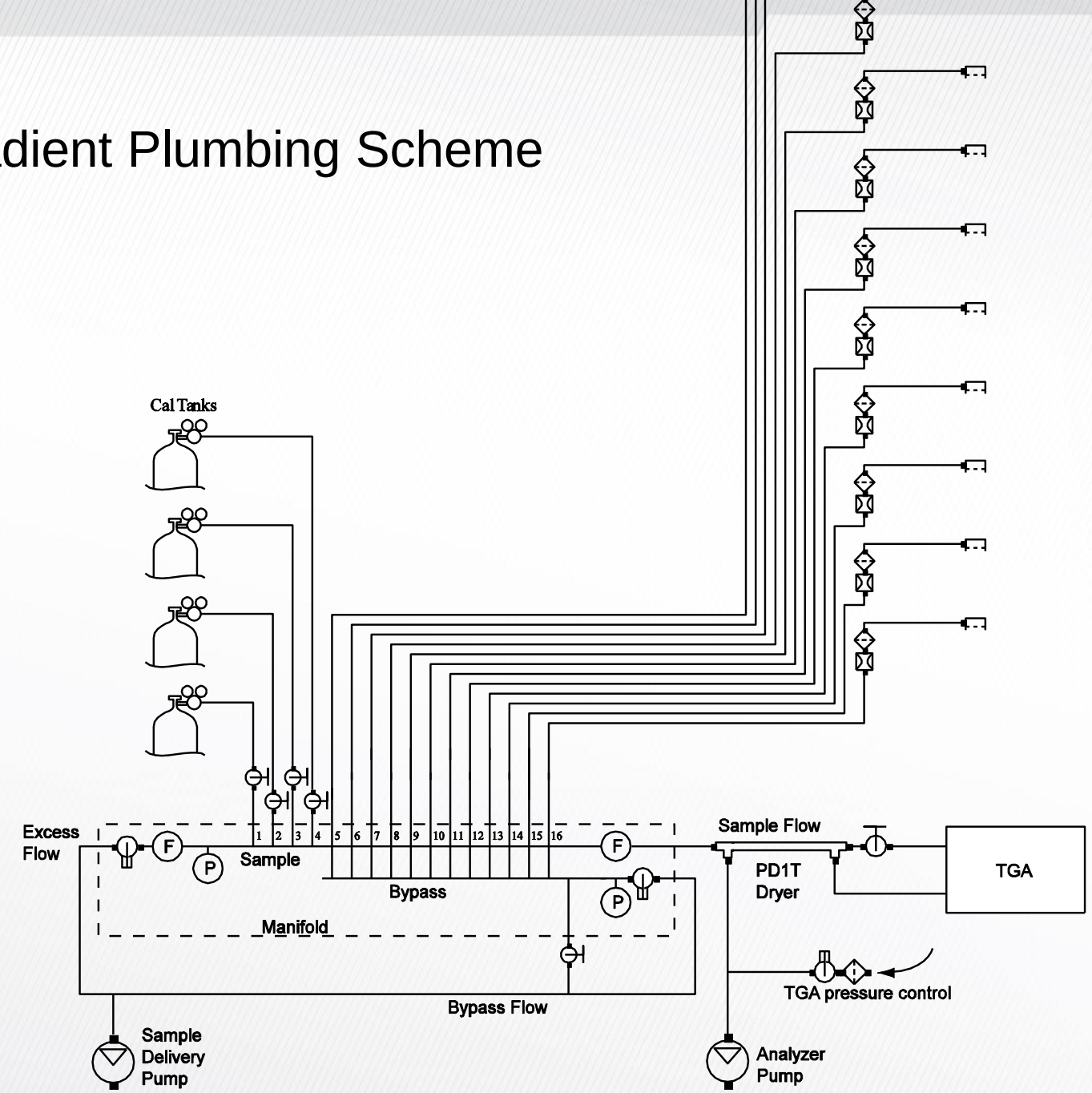


FIGURE 4-19. PD200T air sample dryer

PD200T

The PD200T consists of a 200-tube, 48 in Nafion® dryer element manufactured by Perma Pure, Inc., that is housed in a rugged dryer shell designed and manufactured by Campbell Scientific. The PD200T includes a filter holder, a flow meter to measure purge flow, needle valves to adjust the sample and purge flow rates, and mounting hardware. Common accessories are spare filter membranes (pn 9838) and a 4 – 40 lpm flow meter (pn19541) to measure the sample flow. The PD200T is shown in FIGURE 4-19.

Overview

- Does not ship with
  - Sample Vacuum Pump

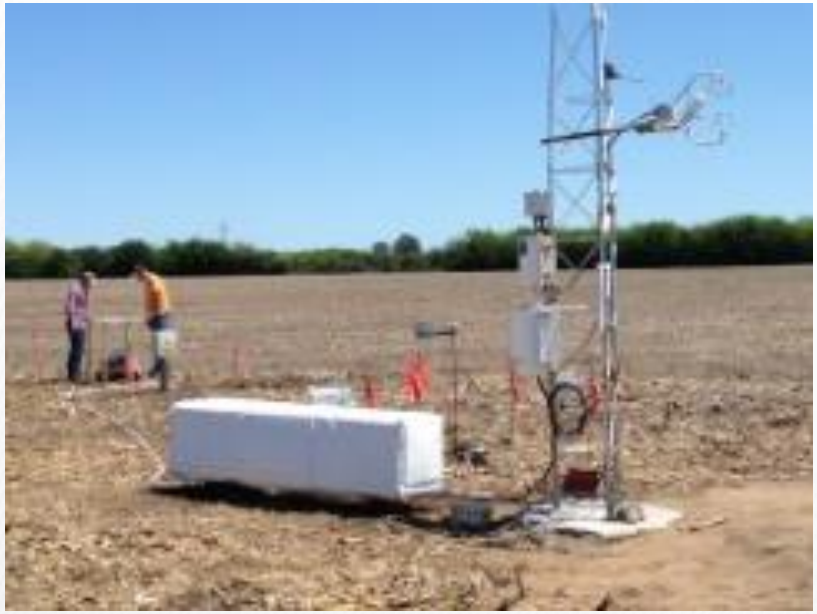
The TGA requires a sample pump to pull the sample and reference gases through the TGA at low pressure. The actual flow rate and pressure required will depend on the application. Two sample pump options are available from Campbell Scientific. The XDD1 has a capacity of 1 slpm at 50 mb (0.8 slpm with 50 Hz power), and is adequate for low flow applications. The RB0021-L has a capacity of 18 slpm at 50 mb (15 slpm with 50 Hz power), and is used for high-flow applications. The pumps are supplied with the tubing and fittings needed to connect to the TGA. A brief overview of each of the pumps is given in the following descriptions.

FIGURE 4-14. XDD1 sample pump

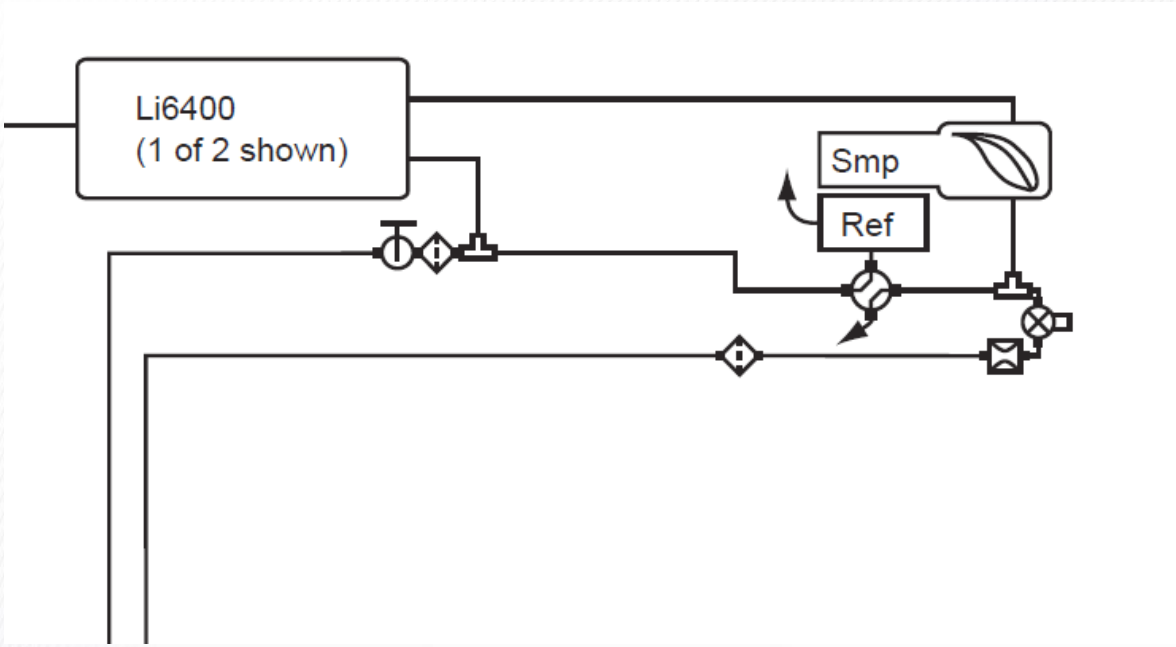
FIGURE 4-13. RB0021 sample pump

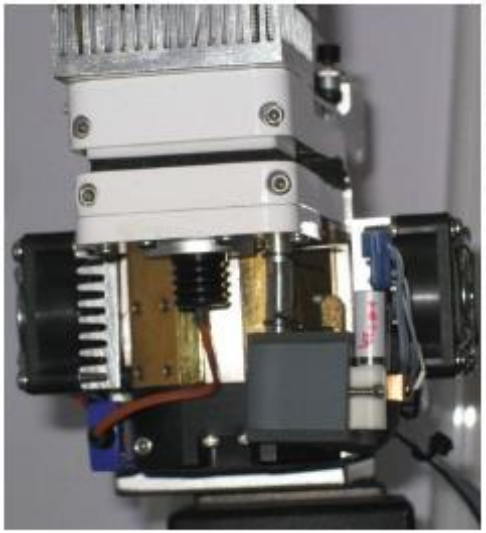
- **Pumps (See TGA Manual PG. 15-18)**
  - Example Pump Shelters

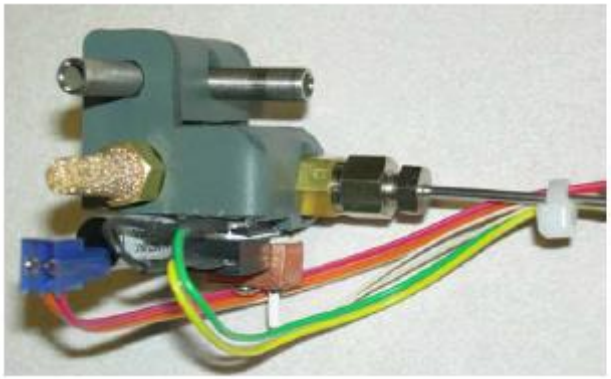
- **Configurations & Applications**
  - Argentina (N2O, Eddy Covariance)

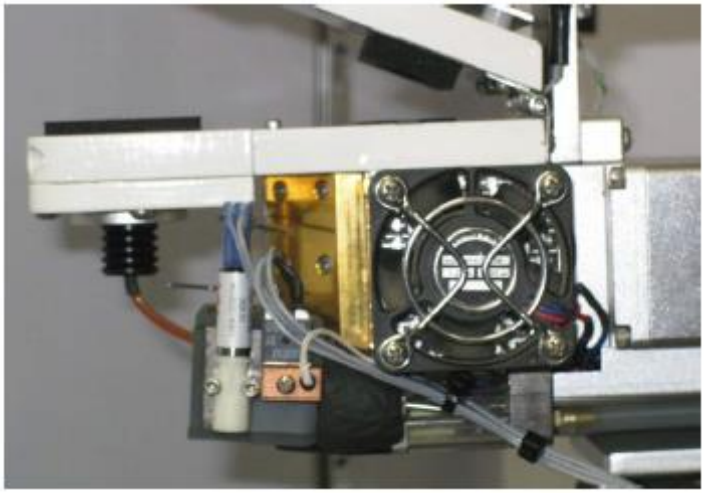


- **Example Configurations & Applications**
  - CO2 Isotopes (CO2, δ13C, δ18O), Leaf Chamber


Li6400
(1 of 2 shown)
Smp
Ref







- **Example Configurations & Applications**
  - CO2 Isotopes (CO2, δ13C, δ18O), Leaf Chamber

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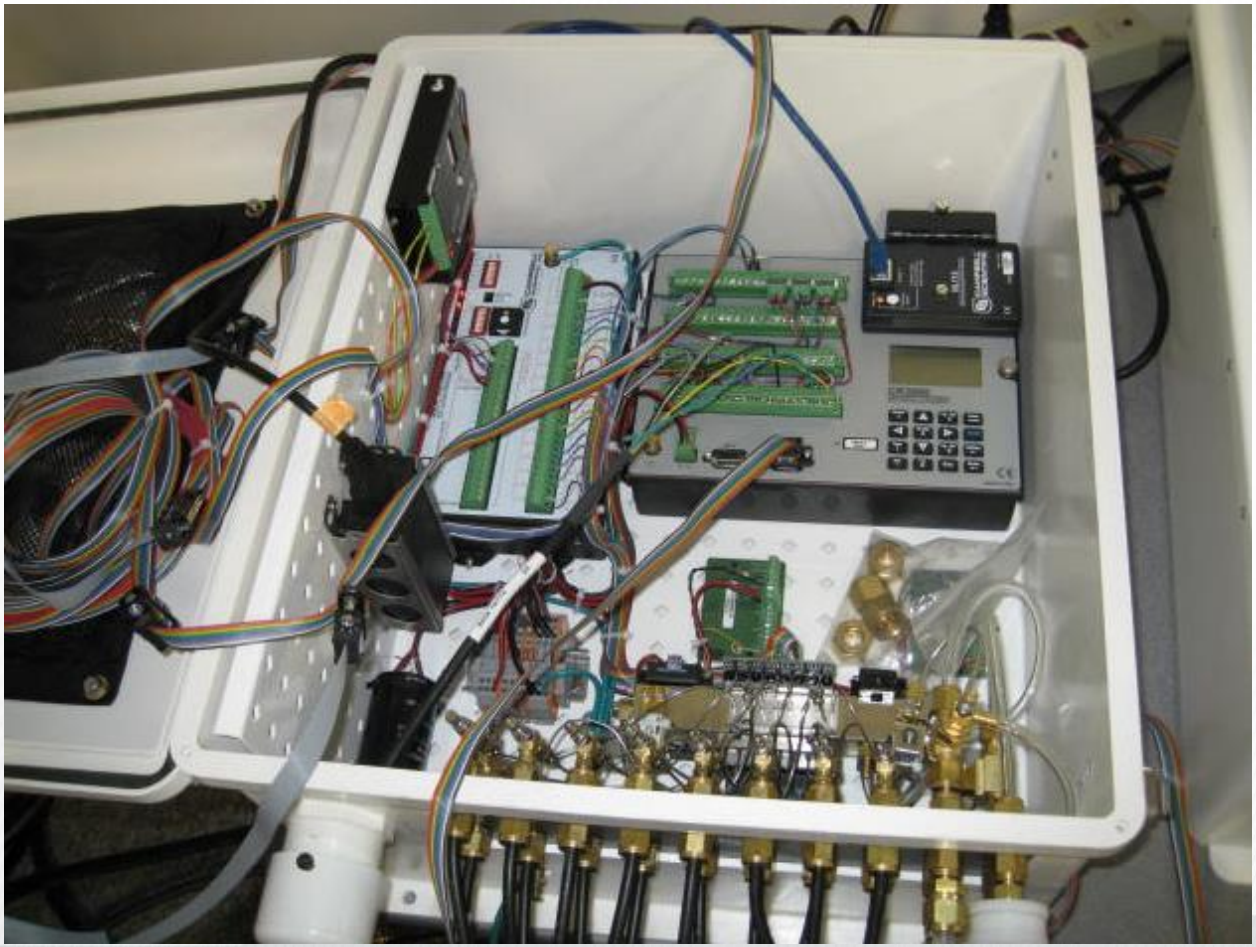
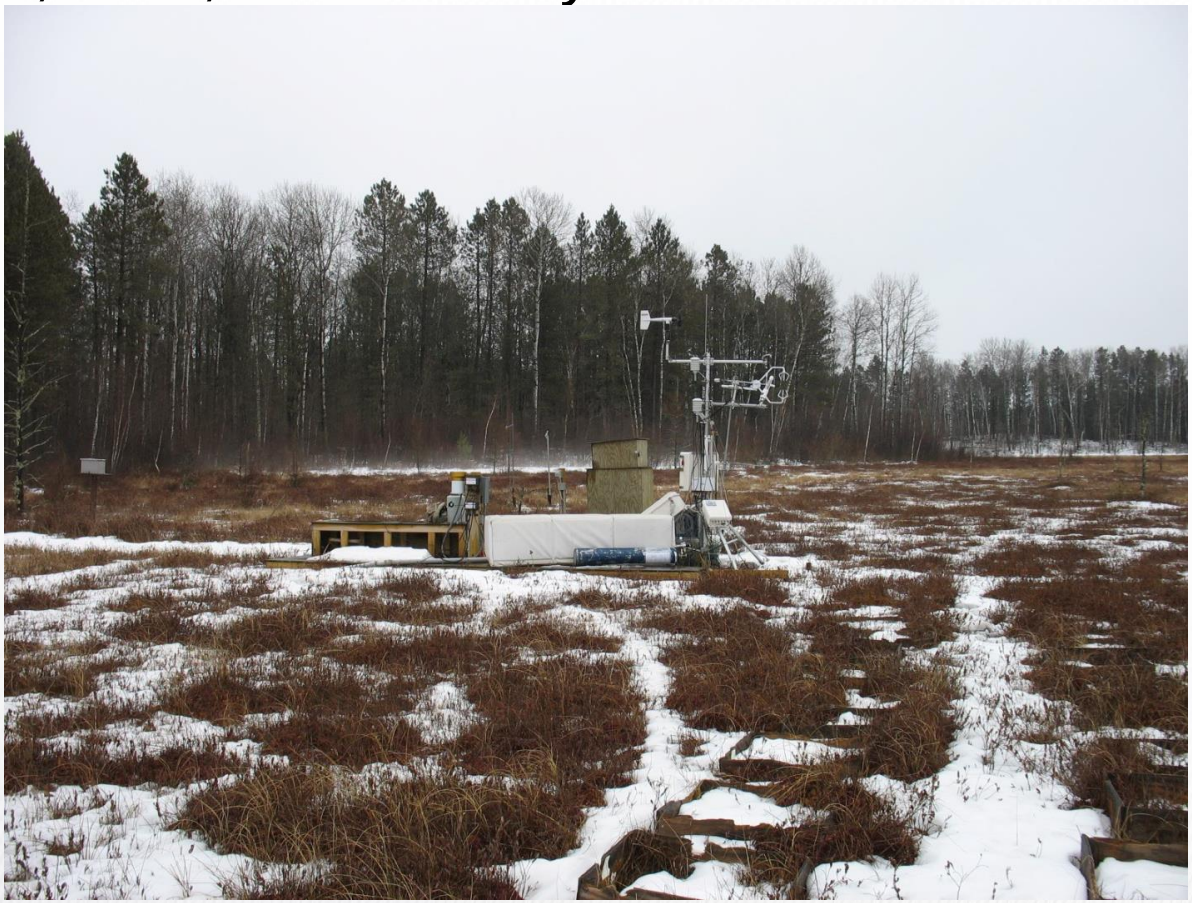
  - CO2 Isotopes (CO2, δ13C, δ18O), Leaf Chamber



- **Example Configurations & Applications**
  - CO2 Isotopes (CO2, δ13C, δ18O), Leaf Chamber

- **Example Configurations & Applications**
  - CH4, CO2, & H2O Eddy Covariance



- **Example Configurations & Applications**
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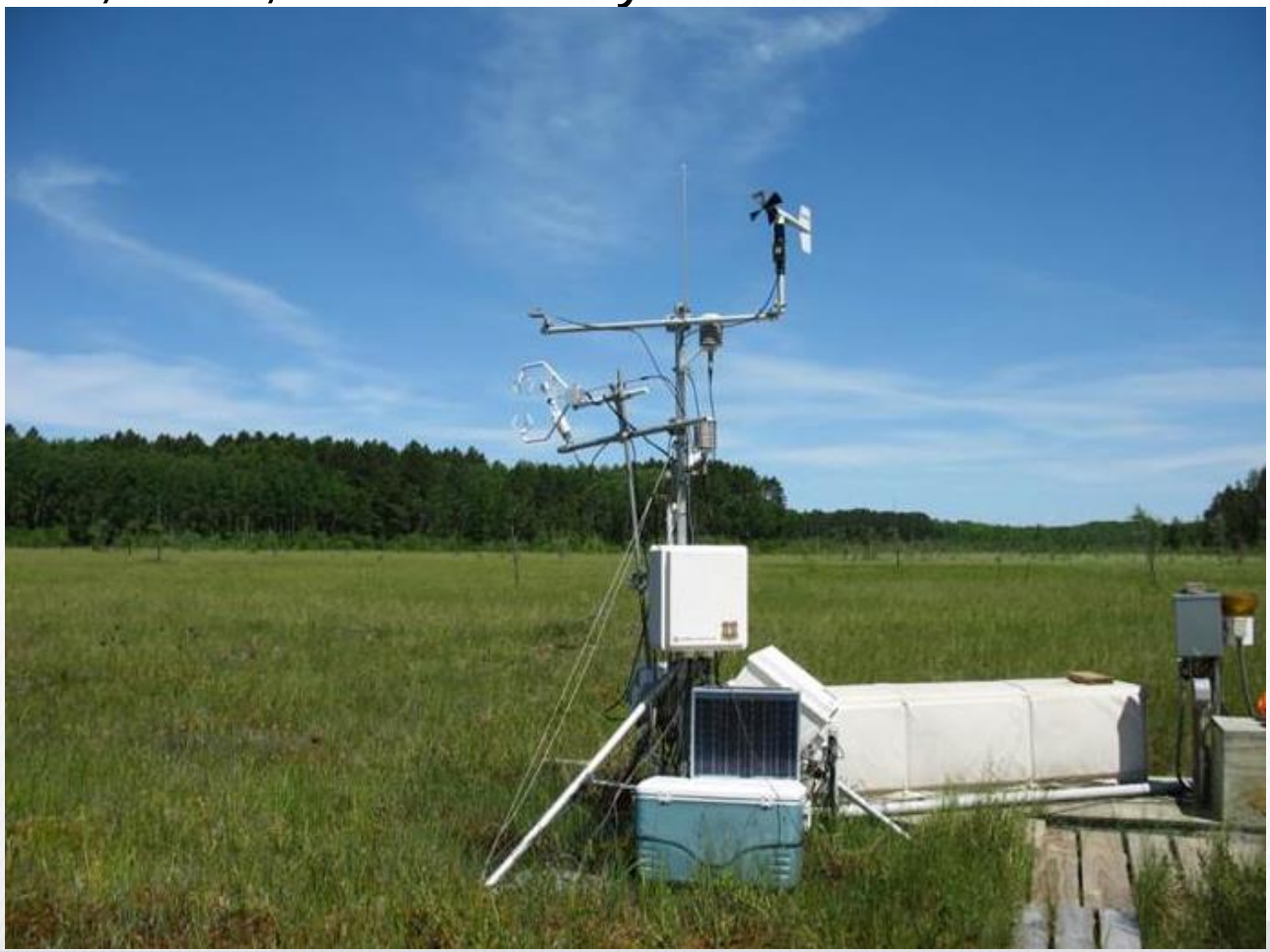

- **Example Configurations & Applications**
  - N2O Fluxes For Multi-Site Gradient

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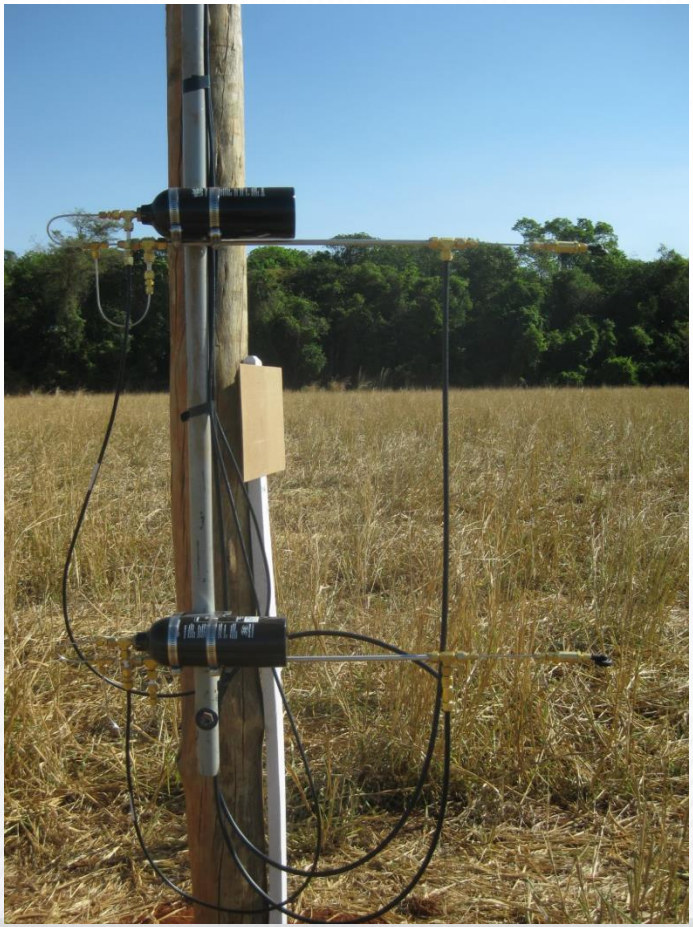

- **Example Configurations & Applications**
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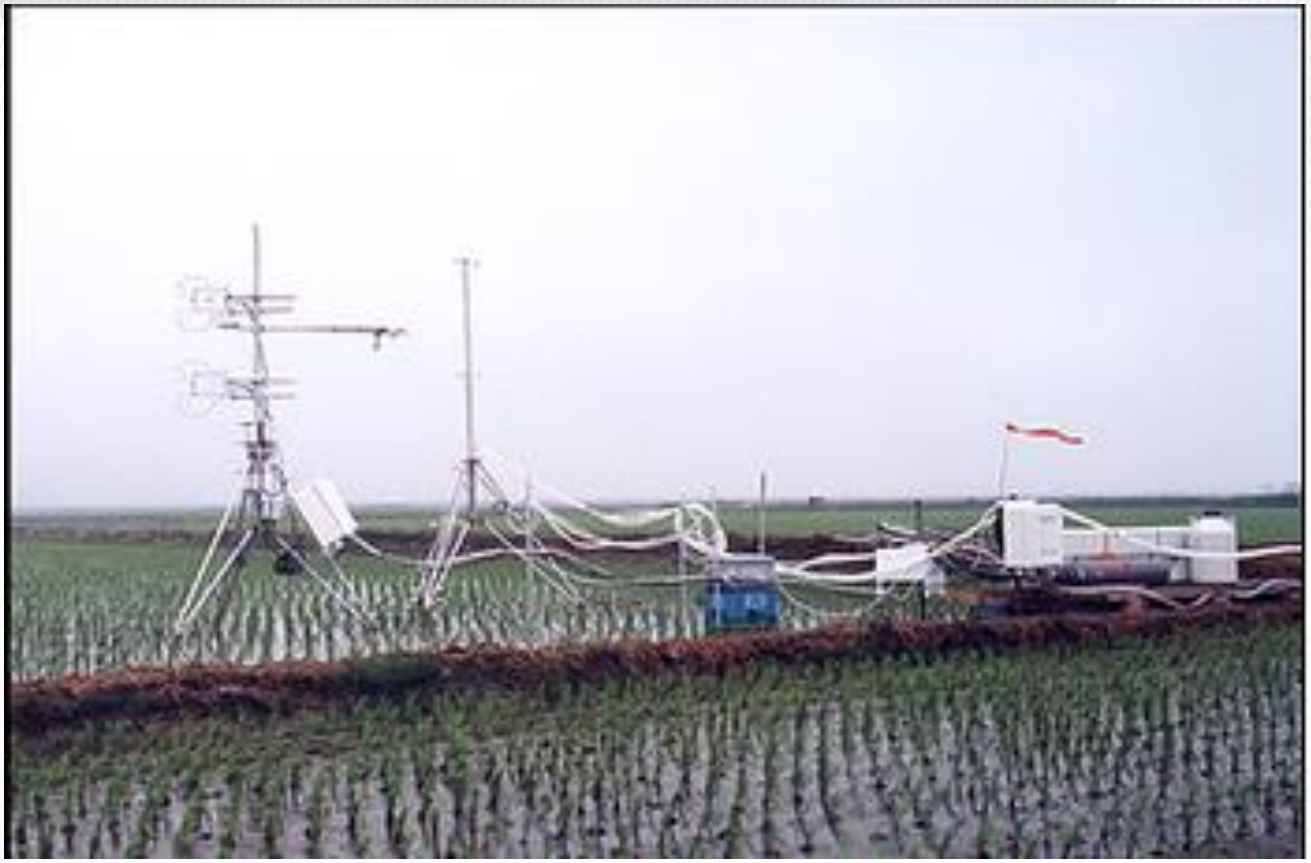

Location： Seoul, Korea

Application: Eddy covariance fluxes and vertical profiles of methane, carbon dioxide, and water vapor

Products : TGA100 CR23X CSAT3 KH20 CR9000

References

TGA Series Trace-Gas Analyzers instruction manual, Revision: 10/14, Campbell Scientific

TGA Training 2015, Campbell Scientific

James Somers and Steve Sargent, [2015], Frequency Response of a New Close-Path, Trace-Gas Analyzer for Eddy-Covariance Flux Measurements

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WHEN MEASUREMENTS MATTER

Thank You !

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