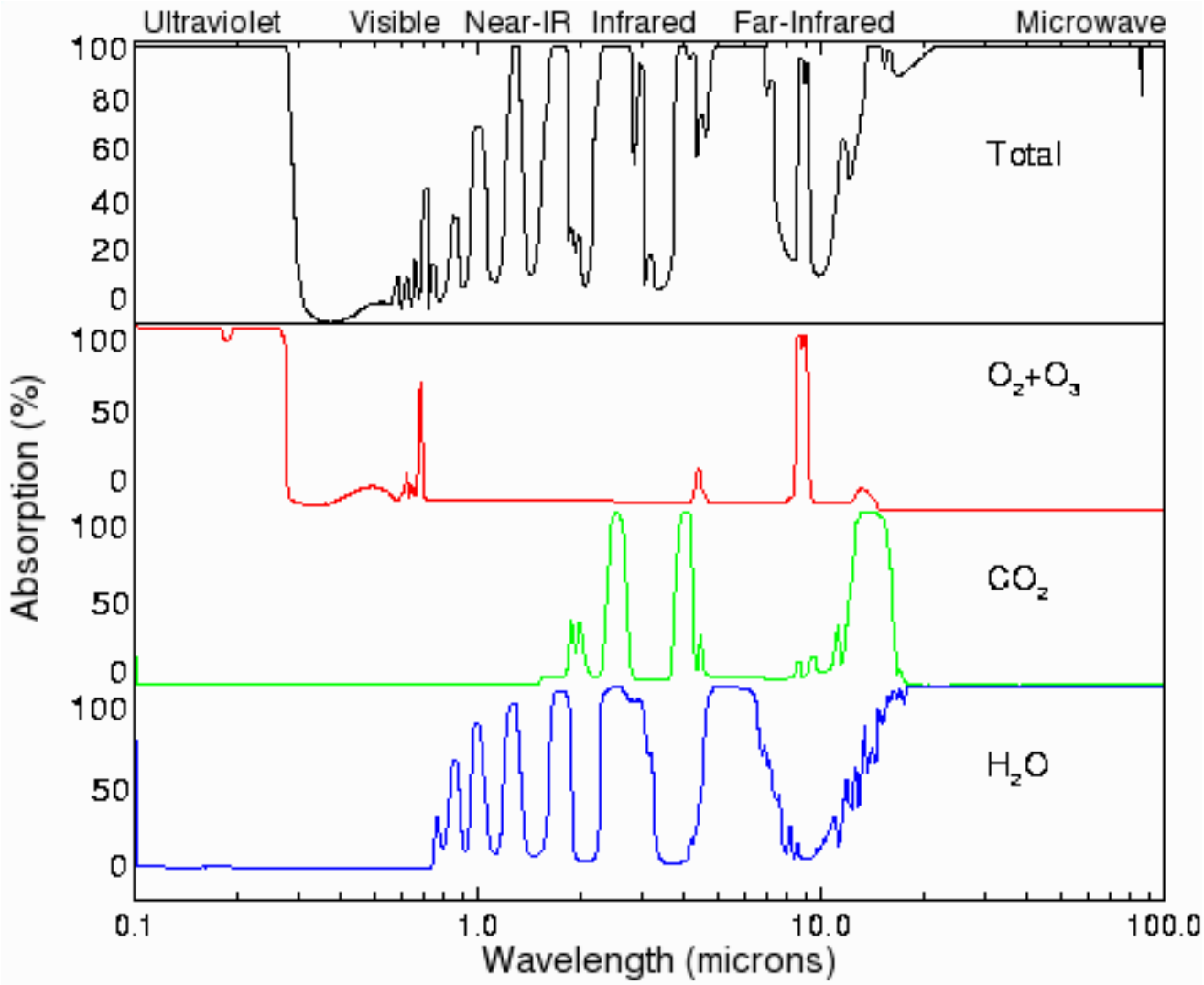
Determination of $p(CO_2)$ in air that is in equilibrium with a continuous stream of sea water

Methodology

- Non-dispersive infra-red (NDIR) analyzer
  e.g. LiCOR CO_2/H_2O analyzer
  CO_2 gas measurements

- Air-water CO_2 equilibration mechanism (flowing SW equilibrates with gas/air)
  Rain-type: showerhead + headspace air
  Bubbler type (bubble seawater with carrier gas)
  Thin film (CO_2 gas permeable membrane)

- Calibration against standard CO_2 gases
- Automation (engineering)



Need correction of H_2O or removal of H_2O before detection

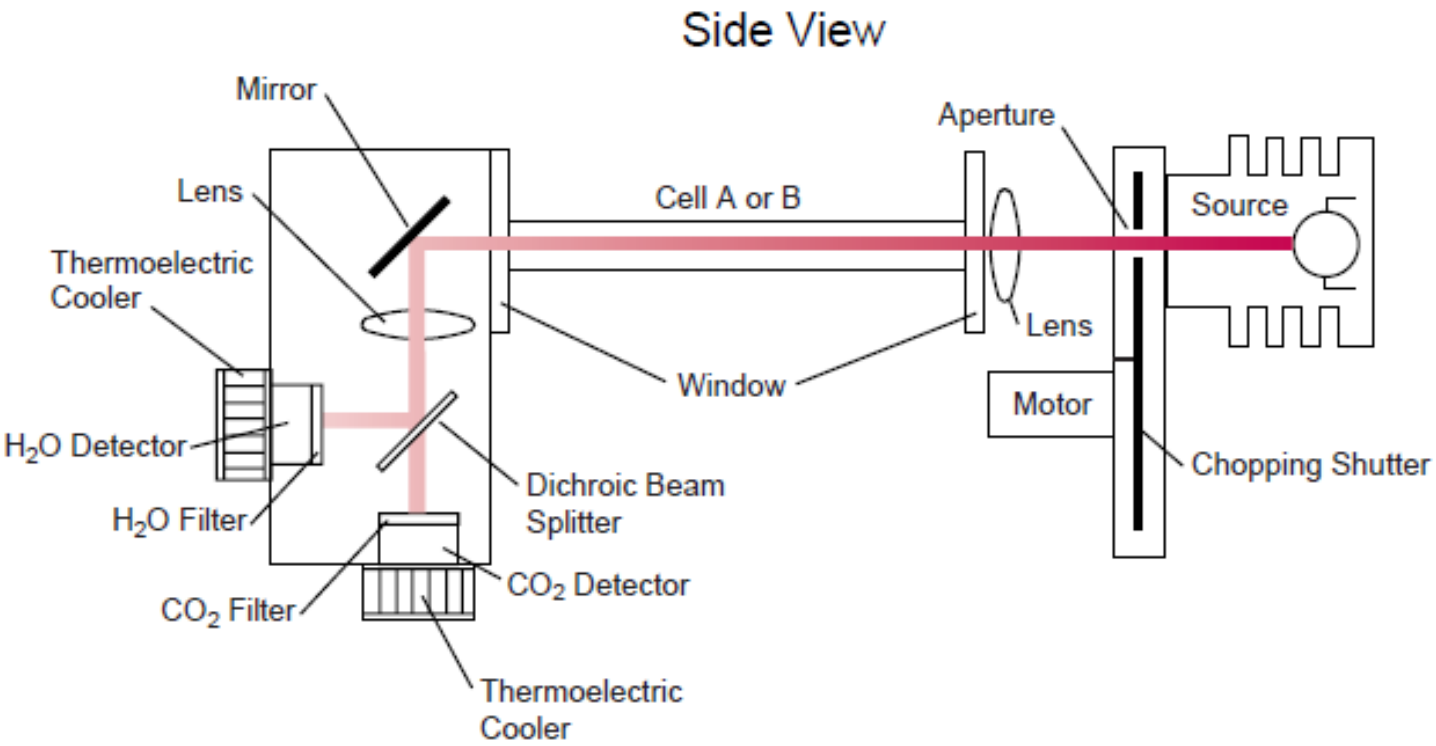


Figure 1-1. Schematic of LI-7000 optical path.

Table 1
Summary of main features of the underway fCO_2 systems "A" through "G" which participated in the exercise

	"A"	"B"	"C"	"D"	"E"	"F"	"G"
Equilibrator							
Design	Shower head	Bubbler	Shower head	Thin film[a]	Showerhead	Bubbler	Showerhead
Total volume	1000 ml	1400 ml	13.1 l	119 ml	11.0 l	36 ml	1200 ml
Water volume	500 ml	1000 ml	2.3 l	21 ml	10.0 l	18 ml	~ 75 ml
Air volume	500 ml	400 ml	10.8 l	98 ml	1.0 l	18 ml	500 ml
Water flow rate	4–6 l min^{-1}	2.0 l min^{-1}	8.0 l min^{-1}	2.0 l min^{-1}	10–15 l min^{-1}	0 l min^{-1}[b]	1.2 l min^{-1}
Air flow rate	0.2 l min^{-1}	0.8 l min^{-1}	0.5 l min^{-1}	1.0 l min^{-1}	0.5 l min^{-1}	0.17 l min^{-1}	0.18 l min^{-1}
Vented?	Yes	Yes	Yes	No[c]	Yes	No	Yes
Time constant[d]	2–3 min	75 s	3–5 min	2–3 min	60–90 s	n/a	Unknown
Mean temperature difference[e]	0.30 ± 0.05	0.30 ± 0.04	0.24 ± 0.02	0.39 ± 0.12	0.17 ± 0.03	0.32 ± 0.03	0.56 ± 0.09
CO_2 measurement							
Method	NDIR	NDIR	NDIR	NDIR	NDIR	NDIR	NDIR
Wet/dry?	Wet	Wet	Dry	Dry	Dry	Dry	Wet
Analyzer calibration							
Number of standard gases	2	2	2	2	4	2[f]	2
Zero gas?	No	Yes	No	No	No	Yes	No
Measurement cycle							
Calibration frequency	6–8 h	6 h	6 h	4–6 h	1.5 h	15 min	2 h
Air measurement frequency	6–8 h	1 h	6 h	4–6 h	0.5 h	n/a	7 min
Interrogation interval	6 s	6 s	1 s	10 s	0.1 s	15 min	0.33 s
Averaging interval	(1[g]) 3 min	1 min	4 min	5 min	1 min	n/a	1 s
Reporting interval	(1[g]) 3 min	1 min	4 min	5 min	~ 13 min	20 min	~ 8 min
Data points per average	10; 30	10	240	33	600	1	3

[a] Film thickness approximately 0.75 mm.
[b] Semi-continuous technique.
[c] Vented only every 20 min.
[d] This is the overall time constant of the system (not the time constant of equilibration).
[e] Mean difference between equilibrator temperature and in situ temperature based on corrected temperature readings (Section 2.3.2).
[f] Standard gas generator was initially calibrated using all six calibration gases; linearity checks are carried out for every sample with only two calibration gases.
[g] Until June 9, 0230 UTC.

(Kortzinger et al., 2000)

RECONNECT TO WATER TRAP

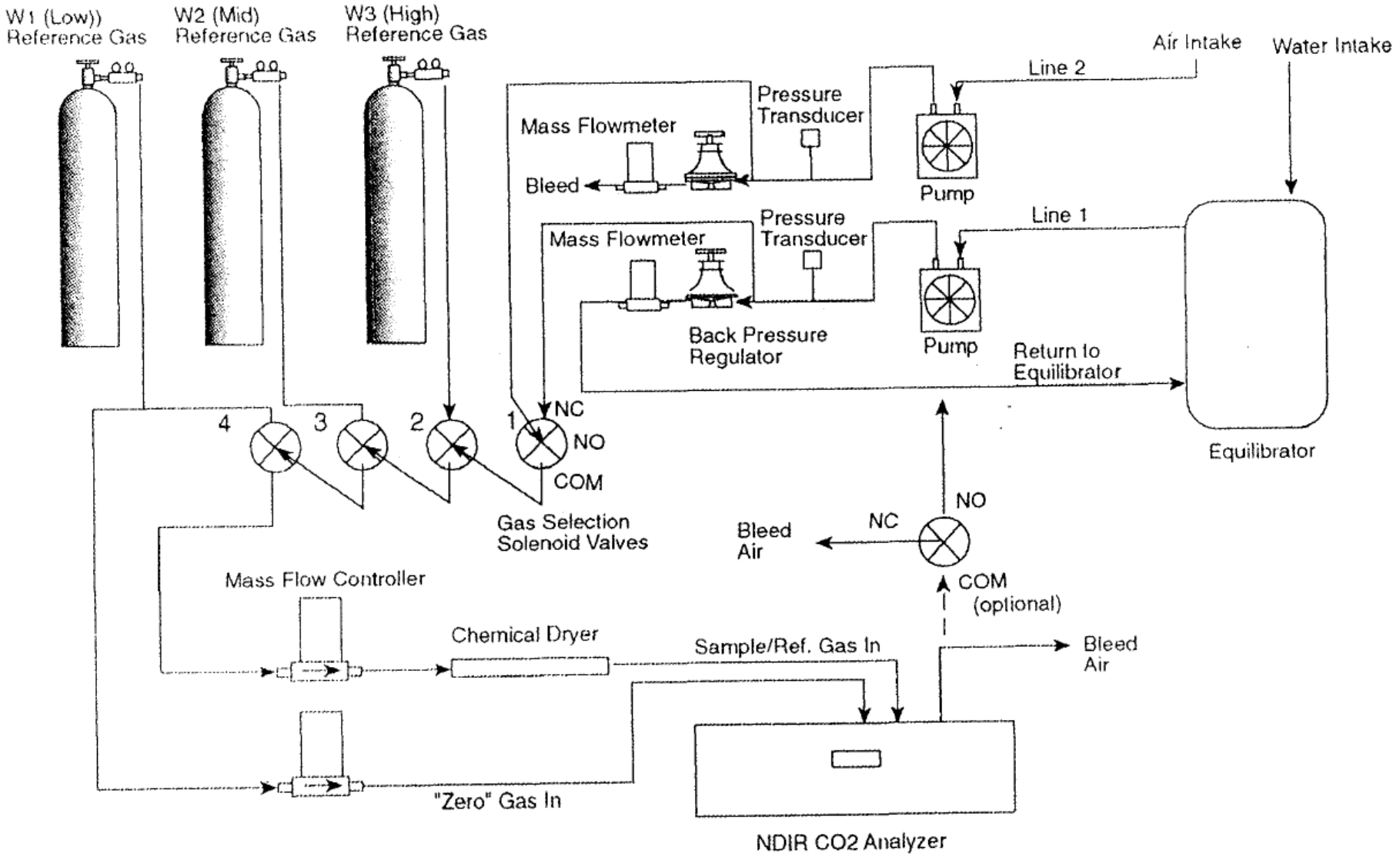
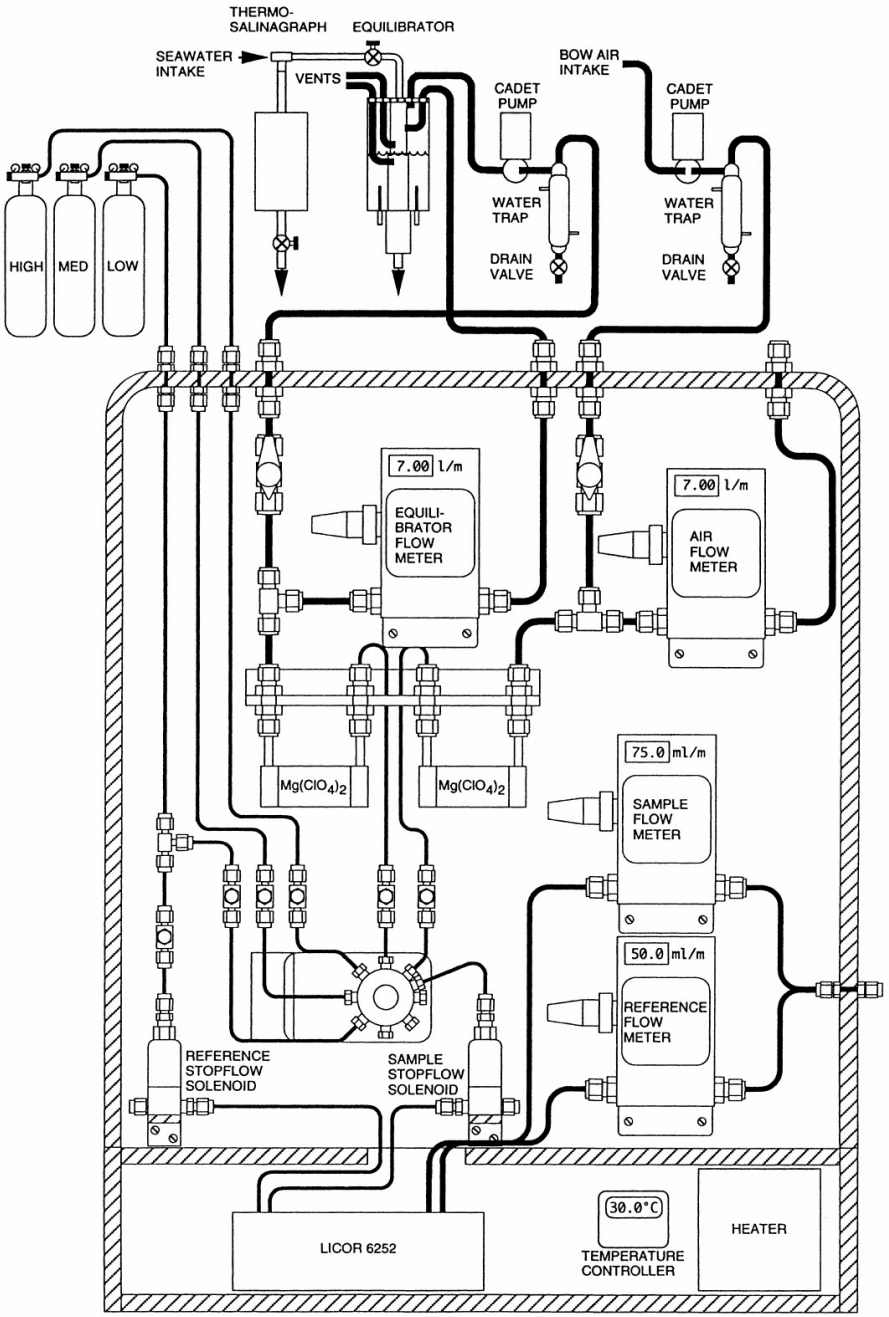


Fig. 1. Schematic of the plumbing of the underway system. For the three-way gas solenoid valves *NC* stands for normally closed, *NO* for normally open, and *COM* for common.

Wanninkhof and Thoning, 1993



(Feely et al., 1998)

Fig. 1. Schematic diagram of the automated underway pCO_2 system. Seawater-equilibrated air first passes through a cold trap and then through a magnesium perchlorate drying tube to remove water vapor prior to analysis by the Li-Cor™ (model 6252) infrared analyzer.

Annexe

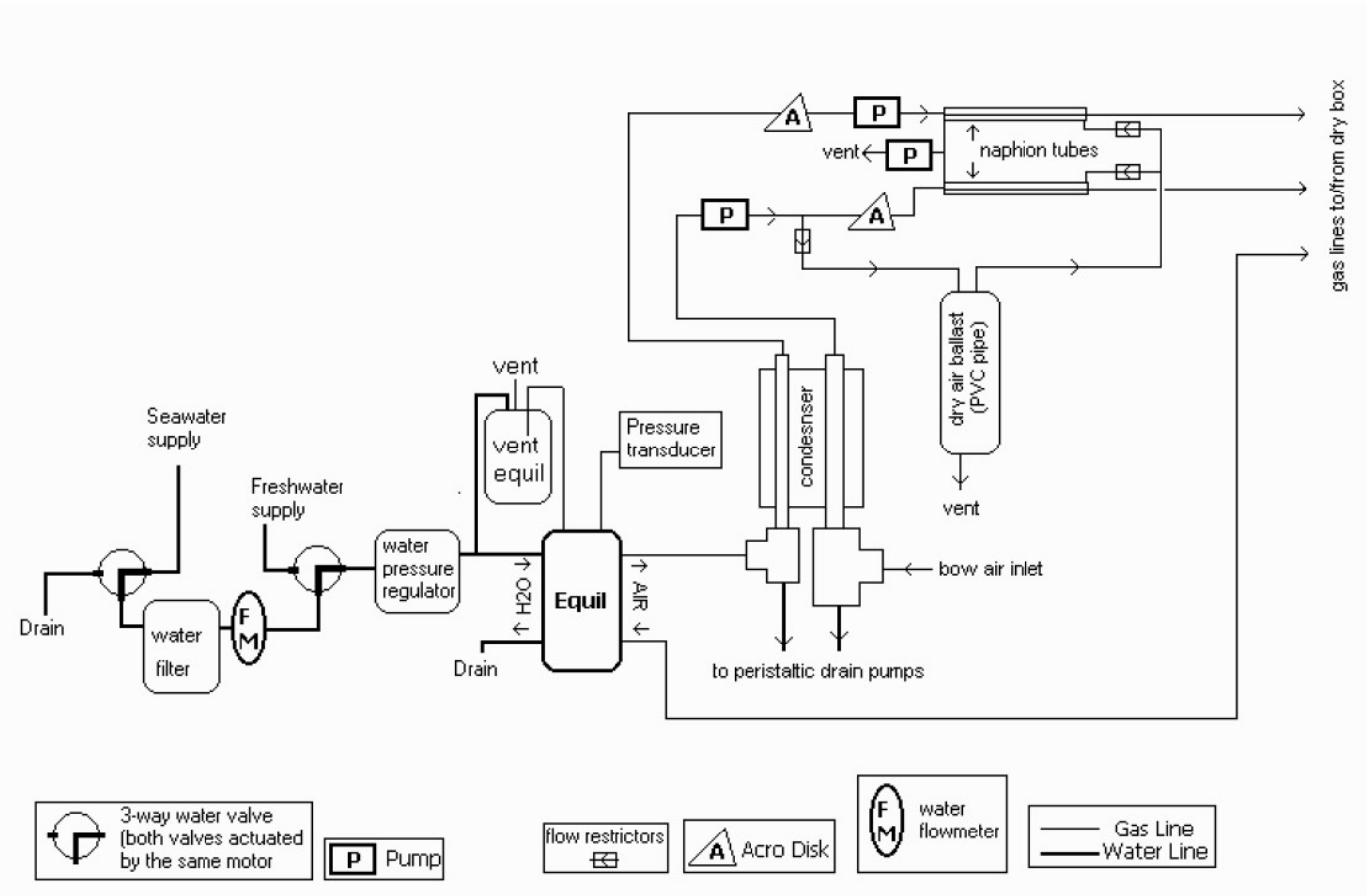
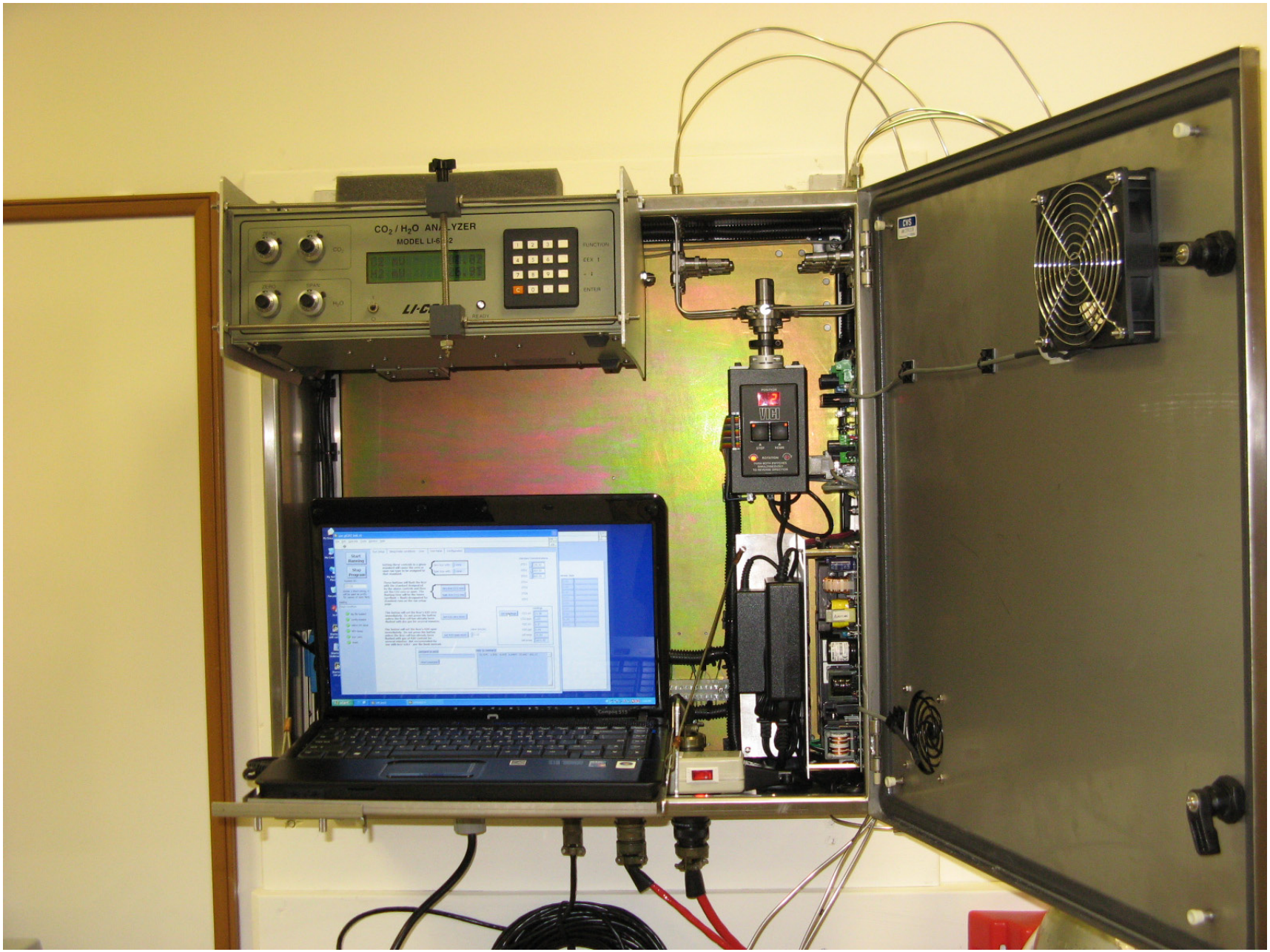


Fig. 1 Schematic showing the layout of the analytical system described here (based on system designed by Craig Neill, Bjerknes Center for Climate Research, Norway).

(2007 CO_2 Handbook)


EVSCO
FLUKE
RECONNECT TO PRESSURE TRANSDUCER


CO_2 / H_2O ANALYZER
MODEL LI-6262
FUNCTION
ENTER
READY
VICI