2.3 Closed-path CO_2 gas analyzers

The eddy covariance method that uses a closed-path CO_2 gas analyzer (closed-path gas analyzer hereafter) was developed when no open-path CO_2 gas analyzers were yet available for long-term stable CO_2 measurements (e.g., Leuning and Moncrieff, 1990; Leuning and King, 1992; Suyker and Verma, 1993). The eddy covariance method that is based on the measurements from a closed-path gas analyzer evaluates CO_2 fluxes from the wind velocity fluctuations observed by an ultrasonic anemometer thermometer and fluctuations of the atmospheric CO_2 concentration observed by a closed-path gas analyzer. In the meantime, the LI-7500 (LI-COR, Inc., US), which was discussed in Section 2.2 "Open-path CO_2/H_2O gas analyzers", has become commercially available and has been used widely. As a result, the number of observational sites which newly adopt a closed-path gas analyzer for the eddy covariance method is probably decreasing. On the other hand, the use of a closed-path gas analyzer provides the following advantages (AsiaFlux Steering Committee, 2007): 1) long-term stable measurements can be made; 2) calibration can be automated; and 3) the magnitude of the density fluctuation correction is small. Advantage 1) can be achieved because the sensing element of a closed-path gas analyzer is protected from direct exposure to the atmosphere and rainfall. Automated calibration (advantage 2) is possible with a closed-path gas analyzer because of its automatic switch-over function which allows a standard gas to flow into the flow path of the analyzer. The disadvantages of a closed-path gas analyzer include: 1) its cumbersome and complex measurement system; and 2) attenuation of fluctuations of CO_2 concentration during the sampling procedure. Under some observational conditions, the use of a closed-path gas analyzer may be better-suited for the eddy covariance method than the use of an open-path gas analyzer (Ono *et al*., 2007). Thus, it may be to the investigator's advantage to acquire an understanding of the use of closed-path gas analyzers for the eddy covariance method, so that this technique becomes an option for measuring CO_2 fluxes.

The discussions in this section will mainly focus on CO_2 concentration measurements by closed-path gas analyzers although recently designed closed-path gas analyzers are capable of measuring both CO_2 and H_2O concentrations in the sampled air.

(1) Summary of the air sampling system that includes a closed-path gas analyzer

Fig. 2.3-1 shows a schematic of an air sampling system that includes a closed-path gas analyzer. A photo of the air sampling system in Fig. 2.3-1 is shown in Photo 2.3-1. In flux measurements with a closed-path gas analyzer, CO_2 concentration measurements are made on the sample air that is collected at the measurement point and sent to the analyzer through the tubing. The sample air is drawn into the analyzer with a pump. The length of tubing between the measurement point and the pump is determined based on the deployment location of the analyzer.

Flow path of sampled air

Regarding the flow path of sampled air (see Fig. 2.3-1), sampled air is first drawn in by a pump from the measurement point (negative pressure). The moisture in the pumped air is removed with a membrane dehumidifier made of resin. After the flow rate of the dried air has been regulated by a mass flow controller, the dried air is sent into the sample cell of the CO_2 analyzer (e.g., LI-6262 or LI-7000 manufactured by LI-COR). Inside the sample cell, CO_2 concentration of the dried air is measured, and the dried air is released out of the analyzer. In the system shown in Fig. 2.3-1, the moisture in the sampled air is removed. However, when H_2O concentration is simultaneously measured for evaluating the moisture flux, no moisture is removed from the sampled air. In this case, omit the dehumidifier shown in the schematic of the sampling system of the closed-path gas analyzer (Fig. 2.3-1) and directly bypass the dehumidifier with a tube. When no dehumidifier is used, caution is necessary as the likelihood of condensation within the sampling system increases according to the temperature and pressure changes within the pathway of the sampling system.

The suction flow rate for air sampling depends on the tubing length, tubing diameter, and the pump capacity. The air flow rate through the system after the pump is determined primarily by the maximum flow rate allowed by the CO_2 analyzer. For example, the maximum flow rate of the LI-6262 is 10 Lmin^{-1} (LI-6262 manual, LI-COR) while no such value is set for the LI-7000. (The LI-7000 manual states that its maximum flow rate is unlimited.) In Fig. 2.3-1, the rate of the sampled air flow through the system after the pump is set to 2.0 Lmin^{-1} in order to enhance the efficiency of the moisture removal by the membrane dehumidifier. Depending on the system configuration, the air discharge rate out of the pump can sometimes be increased to a value much larger than the maximum flow rate allowed by the CO_2 analyzer. One of the methods to achieve such air discharge rates out of the pump is called sub-sampling (Refer to Suyker and Verma, 1993, and Tips 2.3-13.) In this method, excess flow is vented out of the air sampling system between the pump and the CO_2 analyzer. When this method is utilized, a large suction flow rate can be achieved in the flow-path between the air inlet and the pump. As a result, the time lag between the air sampling and the output of the changing CO_2 concentration can be reduced.

The use of a mass flow controller is recommended for controlling the flow rate of the sampled air although a flow meter that is equipped with a flow rate control function can also be used for this purpose. A mass flow controller not only allows highly stable flow rate control, but can also suppress pressure fluctuations due to pump pulsation.

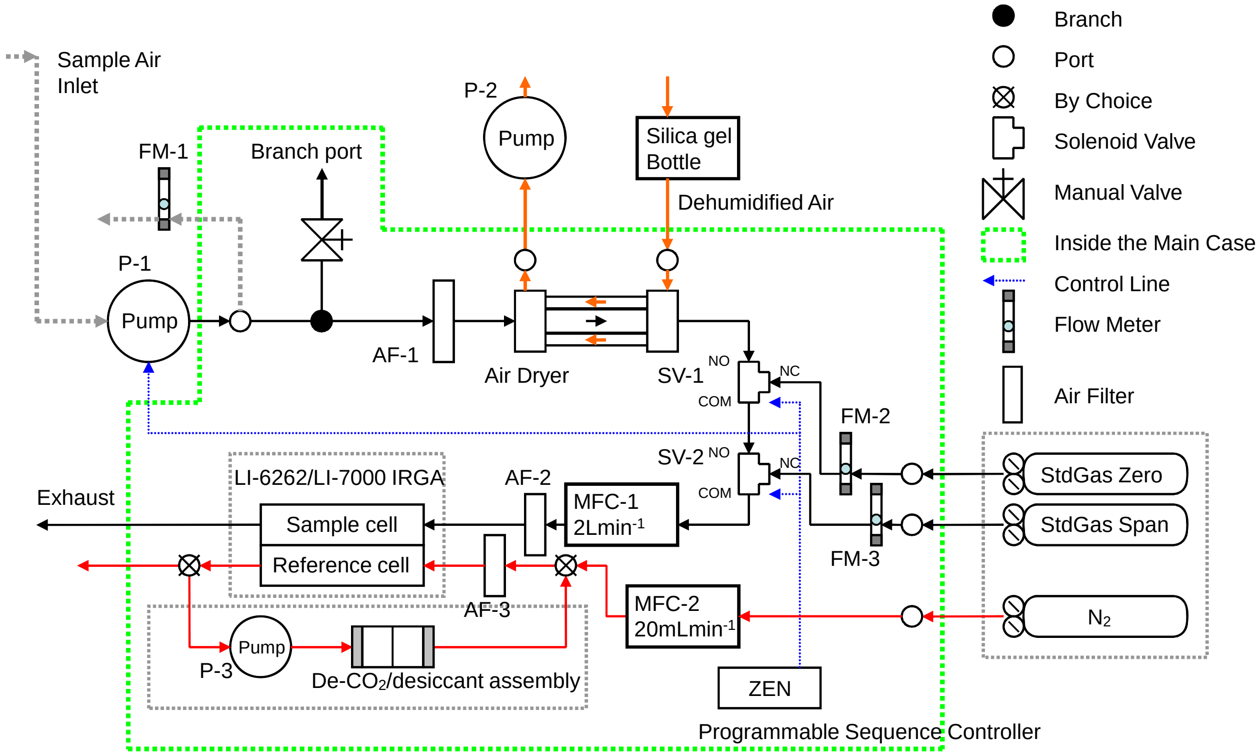

Fig. 2.3-1 An example of an air sampling system that includes a closed-path CO_2 gas analyzer.

(Figure: Ohtani *et al*., 2001, partially modified)

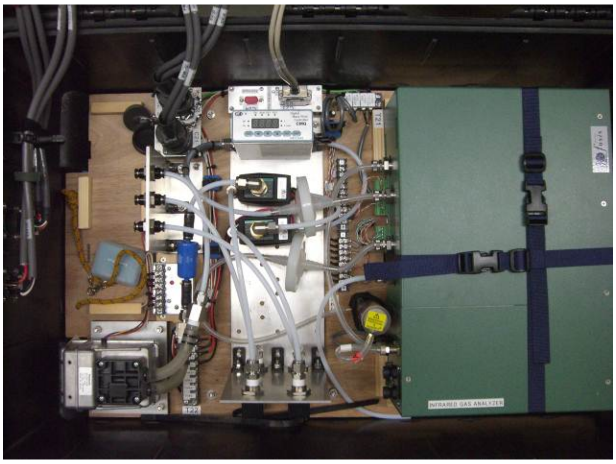

Photo 2.3-1 The air sampling system that includes a closed-path gas analyzer from Fig. 2.3-1.

Tips!

Dust generated from the pump within the air sampling system as well as insects and dust in the air can accumulate in the interior of the system piping and the cell of the CO_2 analyzer. To keep the system and cell interior free from dust and insects, the use of an air filter is recommended. For better results, the air filter should be placed at the inlet of the suction tube, immediately after the pump, and immediately before the CO_2 analyzer. The air filters that come with CO_2 analyzers manufactured by LI-COR are PTFE membrane filters with a pore diameter of 1 μm. Because similar filters are commercially available, the investigator can pick any alternatives to the LI-COR filters that can be easily handled (e.g., filters manufactured by Toyo Roshi Kaisha, Ltd, Japan.).

Tips 2.3-1

Tips!

When moisture is removed from the sampled air, H_2O concentration in the air cannot be monitored and moisture fluxes cannot be calculated with the closed-path gas analyzer. Advantages of moisture removal include the elimination of the need for the WPL correction and a reduction in the accumulation of dirt inside the sample cells. On the other hand, because the sample cells of the LI-7000 can be removed and cleaned, the analyzer can be used for long-term measurements without removing moisture from the sampled air.

Tips 2.3-2

Reference cell

Closed-path gas analyzers (LI-6262or LI-7000) evaluate the CO_2 concentration (or H_2O concentration) of the sampled air from the difference between the infrared radiation absorbed by the air in the sample cell and that absorbed by the air in the reference cell. Therefore, when the absolute magnitude of the CO_2 concentration is sought, the reference cell needs to be filled with CO_2-free gas (LI-6262 manual, LI-COR)

There are two major methods to keep the reference cell free from CO_2. (Refer to Fig. 2.3-1.) In the first method, gas free of CO_2 and H_2O (e.g., pure nitrogen) is flushed into the reference cell. In order to keep the cell constantly filled with nitrogen gas, the gas has to be supplied into the cell continuously. However, only a small flow rate is required for the gas supply. In Fig. 2.3-1, the flow rate is set to 20 $mLmin^{-1}$ as an example. The second method uses chemicals (LI-6262 manual, LI-COR). In the LI-6262, soda lime and magnesium perchlorate are used to produce air free of CO_2 and H_2O. This procedure is as simple as adding bottles containing the chemicals directly to the inlets and outlets of the reference cell. Though replacement of the chemicals may require some effort, the present method is a simple and convenient one for short-term measurements and for sites into which the transportation of cylinders of standard gas is not easily feasible. In the case of the LI-6262, if observations are made only for CO_2, the second method requires only the addition of the chemical bottles to the reference cells. However, if simultaneous observations of H_2O concentration are also required, a pump-induced forced circulation is necessary (LI-6262 manual, LI-COR). In the LI-7000, air free of CO_2 and H_2O is produced with similar chemicals, i.e., soda lime (or Ascarite) and magnesium perchlorate (or Drierite). The air within the reference cell can be circulated by the pump housed inside the LI-7000 (LI-7000 manual, LI-COR).

Tips!

While both the use of chemicals and a reference gas (CO_2 and H_2O free gas) come with advantages and disadvantages, these methods require replacement of either gas cylinders or chemicals. Gas cylinders need replacement when they run out, and chemicals need replacement when their effect wears out. (Make sure to replace the gas or chemicals *before* the gas runs out or the chemicals wear out.) The interval for the gas replacement can be extended with the use of a large gas cylinder. Although the appropriate interval for chemical replacement depends on the conditions under which the analyzer is used, manufacturers recommend a week for the interval. Our past experiences suggest that the chemicals actually last for 2 weeks to a month depending on the ambient conditions of the analyzer.

Tips 2.3-3

(2) Solenoid valves

One of the advantages of a closed-path analyzer is that the analyzer can be automatically calibrated. For the automatic calibration, the flow path of the sampled air needs to be branched to create flow paths for the calibration gas. (Refer to Fig. 2.3-1.) These flow paths are often created with the use of solenoid valves, which can be opened and closed by providing electric voltage (electric current). Furthermore, the use of three-way valves as in Fig. 2.3-1 is recommended. The three-way valves are equipped with three ports: COM, NO (normal open), and NC (normal close). When no voltage is supplied (no electric current), the COM and NO ports are connected. When voltage is supplied, the COM and NC ports are connected. When three-way valves are used, connect the COM port to the tubing that leads to the analyzer, the NO port to the tubing that originates from the sample air inlet, and the NC port to the tubing that leads to the calibration gas. When two kinds of calibration gas (i.e., zero gas and span gas) are used for calibration, connect two three-way valves in series with the COM port of the upstream valve connected to the NO port of the downstream valve. For steady sampling of atmospheric air, no electric current is sent to the valves. In this state, air that is taken in from the sample air inlet is drawn through the pump into the analyzer. In order to draw in calibration gas, supply electric current to the valve which is connected to the gas to be drawn in. Then, the NC port of the valve to which electric current has been supplied opens and calibration gas flows into the analyzer, and the NO port closes, which shuts off the air flow from the sample air inlet. If zero gas and span gas (two-point calibration gases with two different CO_2 concentrations) are drawn through the system with this procedure, the analyzer can be calibrated. In the case of automated calibration, the solenoid valves are controlled automatically with a PC or a data logger. Check the data from the time during which calibration gas was flowing and use the calibration data for data calculations.

Tips!

The prices of solenoid valves vary according to the material of their main bodies. Fluorine resin is chemically stable and weather resistant. Therefore, when the valves are used for measuring reactive gaseous constituents or for continuously flowing atmospheric air, fluorine resin material such as Teflon is frequently used for valve components. In terms of chemical reactivity, CO_2 is only weakly reactive to many materials. Therefore, when solenoid valves are used for measurements of CO_2, valves with gas contact parts made of metal can be used. When selecting solenoid valves for use, it is also desirable to select those of an appropriate size with respect to the flow rate. Refer to “orifice size” and/or “valve flow coefficient” in catalogs as a guide for selecting an appropriate size. The bigger the values of these variables, the larger the flow rate that the valves can accommodate. On the other hand, large valves require large operating power, and their inner volumes are large. Because of their large inner volumes, the displacement efficiency of large valves at the time of flow-path switchover is low, which needs to be taken into consideration for selecting the size of valves to be used for measurements. Furthermore, solenoid valves are available in AC and DC types and also in a number of voltage ratings, thus the investigator should select appropriate valves according to the power source of the measurement system.

A variety of solenoid valves are available not only in different materials but also with different numbers of valves (2-way and 3-way) and different combinations of NO and NC, thus it is suggested that the investigator order catalogs from the manufacturers. While a number of manufacturers produce solenoid valves, the author frequently uses those manufactured by CKD Corporation, Japan. In addition to CKD, solenoid valves are available from TAKASAGO ELECTRIC, INC., Japan; SMC Corporation, Japan; and KOGANEI CORPORATION, Japan.

Tips 2.3-4

(3) Pumps (characteristics and structure)

While a large number of pump structures and types are available, diaphragm pumps which are frequently used for flux observations will be discussed below. In a diaphragm pump such as those manufactured by Enomoto Micro Pump Mfg. Co., Ltd., Japan, fluid is extracted and delivered with the use of intake and exhaust valves that work in conjunction with a rubber diaphragm. Two pump drive systems for diaphragm pumps are motor-based and electromagnetic-based types. Because larger flow rates and higher pressures can be achieved by motor-based diaphragm pumps than by electromagnetic-based diaphragm pumps, the use of motor-based diaphragm pumps is recommended for measurements with a closed-path system. A motor-based diaphragm pump sharply reduces the volume of the pump chamber by flexing a diaphragm. At the pump inlet, a one-way valve is attached so that it allows air to flow only in the direction of the pump chamber. At the exhaust outlet, a valve is attached to allow the air to flow only out of the pump chamber. Thus, these valves ensure that the air flows only in a given direction in response to the flexing motion of the diaphragm. Because there exists no mechanical sliding component at the interface between the fluid (air in the present case) and the portion of the pump that meets the fluid, no fluid leaks out of the pump, which is considered an advantage of diaphragm pumps. Diaphragm pumps are available for a number of driving voltages (voltage ratings); therefore, select one for use according to the circumstances of the power source available at the field site of interest.

Brushes are used for electric contacts inside many of the DC motors that are used for generic mini-pumps. This type of pump frequently produces electronic noise and can fail as a result of brush abrasion when operated continuously over a long period. If a DC-driven pump is used, it is suggested that a brushless DC motor be used provided such an option is available.

A diaphragm pump due to its structure tends to induce flow rate pulsation. Pressure variations that result from the flow rate pulsation sometimes affect the measurement values of the gas analyzer. The following measures can be taken to mitigate the effect of the flow rate pulsation. First, when the pump is placed upstream of the analyzer, resistance such as a mass flow controller or a membrane dehumidifier made of resin can be placed between the pump and the analyzer. This measure can sometimes reduce the effect of the flow rate pulsation significantly. Second, when sample air is drawn by a pump located downstream of the analyzer, a buffer tank or similar device can be placed between the pump and the analyzer to mitigate flow rate pulsation.

When a diaphragm pump is placed upstream of the analyzer, dust which originates from the diaphragm inside the pump frequently contaminates the interior of the cell of the analyzer. To avoid such contamination, make sure to install a filter on the exhaust side of the pump.

Maintenance method

As diaphragms wear out, they need to be replaced regularly. When a diaphragm is damaged due to cracks or other causes, the flow rate may decline and air leakage may occur. Diaphragms and valves are sold separately as replacement parts, so it is advisable to purchase a few in advance as spares. When the flow rate declines, it is suggested to replace the diaphragm of the pump as a first measure. It is also recommended to replace the valves at the air inlet and outlet at the same time. If the flow rate does not recover despite the replacement of the diaphragm, the pump itself might have come to the end of its operational lifetime, and the whole pump should be replaced.

Tips!

The wear-and-tear of a diaphragm changes according to the use conditions. Even when the flow rate of a pump does not decline, it is advisable to replace the diaphragm regularly (e.g., schedule a replacement once a year). Although the operational lifetime of the pump is also expected to change according to the use condition, the investigator should refer to the operational lifetime of the pump suggested by the manufacturer. (Note: In most cases, it is likely that pumps can be used for a longer time period than the operational lifetime suggested by the manufacturer.)

There are numerous diaphragm pump manufacturers. The author has used pumps manufactured by Enomoto Micro Pump and ULVAC KIKO, Inc., Japan. These manufacturers distribute pumps as well as only the consumable parts. (The consumable parts of pumps manufactured by KNF Neuberger GmbH, Germany and Gast Manufacturing, Inc., US can also be purchased from the manufacturers.)

Tips 2.3-5

Tips!

Due to the degradation of the diaphragm or the pump structure itself, air leakage sometimes occurs inside a pump. As a result, air from the surroundings of the installation site of the pump sometimes gets drawn into the pump. In order to check for air leakage, the following simple method can be used. Seal the inlet of the pump with a cap such as that manufactured by Swagelok Company, US and attach a flow meter to the outlet of the pump. Operate the pump and check the flow meter reading. If the air leakage is large, the surrounding air is drawn into the pump through the leak and the flow meter reading becomes different from zero and indicates the degree of air leakage. Note that the proposed method is unable to detect small air leakages. Finally, when the pump operation required for the above-mentioned method is performed over a long time, the burden on the pump becomes large. Thus, caution is necessary while examining the pump for air leakage.

Tips 2.3-6

(4) Tubing

When a closed-path gas analyzer is used for eddy covariance measurements, air is sampled through tubing. For this purpose, a variety of tubing has been used, and the tubing length has varied between a few meters to 50 m or more according to the field site.

Typical tubing that is used with closed-path analyzers includes PTFE tubing, polyethylene tubing, stainless steel tubing, polyethylene-coated aluminum tubing (e.g., Decabon tubes, Hagitec inc., Japan), and plastic tubing (e.g., Bev-A-Line tubing, Thermoplastic Processes, Inc., US). For measurements of the atmospheric background CO_2, stainless steel tubing is often adopted as little CO_2 is adsorbed and penetrates into the tubing. However, stainless steel tubing is hard to work with when it is deployed on a tower, thus, stainless steel tubing is rarely used for tower-based CO_2 flux observations. Instead, pipework that is based on PTFE tubing is frequently used for tower-based CO_2 flux observations with closed-path analyzers. As for the inner diameter of the tubing, 4 ~ 8 mm is typically used. Properties of PTFE include excellent chemical resistance, heat resistance, and weather resistance. PTFE is also nonhygroscopic and non water-absorbing. For tower flux observations, it is necessary to place tubing in an outdoor environment in which the tubing is likely to be exposed for a long time to ultraviolet radiation and reactive gases such as atmospheric ozone. Therefore, the heat-resistant, weather-resistant, and nonhygroscopic properties of PTFE are highly beneficial for use in tubing for tower observations. Polyethylene tubing is more elastic, easier to handle, and less expensive than PTFE tubing. However, the weather-resistance of polyethylene tubing is inferior to that of PTFE tubing, and polyethylene tubing needs to be checked and replaced regularly.

Short tubing length is often used for observations at sites with short plant canopies such as farmland or grassland. In contrast, long tubing length is often used for observations at sites with tall plant canopies such as forests. Even for measurements above forests, if the measurement system as in Fig. 2.3-1 can be established in the middle of the observation tower, the tubing length can be made short. When an observation hut is situated at the bottom of a tower, the measurement system is sometimes installed inside the hut instead of in the middle of the tower. Although the maintenance of the measurement system in this case becomes easier, the tubing length becomes longer than it would be in the case with the measurement system installed in the middle of the tower.

Tips!

Make sure to use appropriate tubing connectors for connecting tubing sections. For connection points that need to be disconnected after the initial deployment, the use of one-touch connectors (e.g., products of NIHON PISCO CO., LTD., Japan) is convenient. For connection points that will not need to be disconnected after the initial deployment, a permanent connection should be selected with the use of fittings such as Swagelok tubing fittings. When tubing connectors are fixed with screws (e.g., connections between a connector and a pump or between a connector and a valve), it is recommended that thread seal tape be wrapped around the junctions to avoid leakage.

Tips 2.3-7

Tips!

Some tubing, e.g., PTFE tubing, is sometimes difficult to purchase in large lengths. For example, when the author intended to purchase PTFE tubing with a 6 mm inner diameter and an 8 mm outer diameter (for drawing sample air), 100m rolls were the next longest size available after 50 m rolls. As only 53 m of tubing was needed, 47 m had to be left unused. (Of course, the left-over tubing should not be discarded, but instead should be kept for other uses.) PFA tubing, a type of fluorine resin (fluoroplastic) tubing, is characterized by low permeability to the surrounding gases and is transparent in color, which allows the investigator to check for accumulations of dirt and dust inside the tubing.

Tips 2.3-8

Tips!

In relation to Tips 2.3-7, the standards of screws that are widely used for screw-in tube connectors include: 1) PT screws that conform to International Organization for Standardization, ISO standards (and also to Japan Industrial Standards, JIS); and 2) NPT screws that conform to American National Standards Institute, ANSI standards. While both of these kinds of screws are taper screws, the helix and pitch angles differ between the two kinds of screws, and mixed usage of these screws causes leakage. Therefore, make sure to check the standard of the screws to be used and also to match up the standards of the male and female parts. Furthermore, because tubing is sized in inches and millimeters, the investigator needs to be cautious when selecting tubing for use.

Tips 2.3-9

(5) Mass flow controller

A mass flow controller is a device to control the flow of sampled air for attaining a constant flow rate. It is highly recommended to install this device as a part of the measurement system. The detailed principles of the operation of a mass flow controller will not be discussed here. Temporary flow rate control can be performed manually with a flow meter with a needle valve (float type). However, a change in the flow rate with time cannot be avoided. In contrast, a mass flow controller is able to adjust the flow rate exactly to the pre-set flow rate. A mass flow controller also suppresses pump pulsation (pressure variation), thus serving a dual purpose.

Tips!

When a mass flow controller is used, the work required by the investigator to control the flow rate is substantially reduced. Some of the commercially available mass flow controllers are equipped with the capability of outputting the flow rate in analogue or digital format, which allows the investigator to monitor the flow rate. The author has used mass flow controllers manufactured by Horiba, Ltd., Japan and Yamatake Corporation, Japan. The author recalls that it was a thrilling experience to use a mass flow controller for the first time: the flow rate variation due to pump pulsation disappeared and the float of the flow meter stopped moving!

Tips 2.3-10

Tips!

A minimum pressure difference is required between the inlet and the outlet of a mass flow controller. The value of the required minimum pressure difference depends on the model. In order to fulfill the requirement of the minimum pressure difference, appropriate decisions need to be made about the pump settings and the opening and closing of a relief valve. (Note: If the pressure difference is too large, the burden on the pump becomes large and water condenses inside the piping. Thus, it is suggested that the pressure be set to a value slightly larger than the value of the required minimum pressure difference.)

Tips 2.3-11

(6) Dehumidifier

The process of moisture removal from the sample air for gas analyzer needs to be carried out without disrupting the gas composition or the air flow. For this process, the use of a dehumidifier that employs a semipermeable membrane, such as Perma Pure dryer (Perma Pure LLC, US) equipped with Nafion tube (DuPont, US) is recommended. This dehumidifier consists of a dual-tube structure; the inner tube is made of a membrane material that is selectively permeable to water vapor. Furthermore, semipermeable membrane dryers are classified into two types. The first type is made of a single semipermeable- membrane tube, and the second type is made of a bundle of semipermeable-membrane tubes. The former is well-suited for drying small volumes of gas while the latter is well-suited for drying large volumes of gas. Use the former type, i.e., single tube type, such as the MD-Series manufactured by Perma Pure, for an observational system in which a closed-path analyzer is used for the eddy covariance method. In single tube-type dryers, sampled air (air containing water vapor) flows through the inner tube, and dry air (purge gas) flows through the outer tube. According to the difference in water vapor pressure across the semipermeable membrane, moisture in the sampled air passes through the membrane and is extracted from the sampled air stream. When sampled air flows inside the tubing of the dryer, moisture removal takes place at high speed; thus, the air flow is not disrupted. Note that the moisture removal efficiency decreases when the flow rate is high. Furthermore, the recommended flow rate of the purge gas is twice to five times the flow rate of the sampled air. For purge gas, gas in a cylinder or air that has been filtered through a desiccant (e.g., silica gel) can be utilized. Finally, the use of a heatless dryer such as the HD-0.5 manufactured by CKD Corporation enables the production of dry air without maintenance for several years.

The closed-path gas analyzers of the present day are able to simultaneously measure CO_2 and H_2O. Therefore, when these analyzers are used, moisture removal from the sampled air does not need to be performed in some cases. However, when moisture flux can be measured with the use of a separate instrument, it is recommended that a closed-path gas analyzer is used for only CO_2 measurements to eliminate the influence of water vapor concentration fluctuations on the CO_2 concentration fluctuations. In this case, remove moisture from the sampled air with a semipermeable-membrane dryer.

Tips!

Even when a dehumidifier that uses semipermeable-membrane tubing is employed, all of the moisture in the sampled air cannot be removed completely. In order to enhance the efficiency of moisture removal, the flow rates of the sampled air and purge gas may be adjusted or multiple dehumidifiers can be connected to the air sampling system. Although the adoption of either method does not result in zero water vapor concentration, these methods can reduce the water vapor concentration in the sampled air and eliminate almost all of the fluctuations of the water vapor concentration. (That is, the influence of water vapor concentration fluctuations on CO_2 concentration fluctuations can be eliminated.)

Tips 2.3-12

(7) System control methodology

Changing the flow path with solenoid valves to introduce calibration gas is the minimum system control required for a closed-path measurement system for the eddy covariance method. In the course of switching to the calibration gas, the pump may need to be powered off depending on whether the sub-sampling method is used. When the sub-sampling method is adopted, the exhaust vent is available for sampled air upon injection of calibration gas. Thus, the pump does not need to be powered off. On the other hand, when the sub-sampling method is not adopted, the pump needs to be powered off upon the solenoid valve switchover (or an exhaust vent is required). During the injection of the calibration gas, continue recording the output signals from the CO_2 analyzer with a data logger in the same way as during the time of the measurements of the sampled air.

Make sure to set up the measurement system in such a way that the opening and closing of the solenoid valves (or the turning off and on of the pump) takes place at a fixed time. Time control can be achieved using a relay control with a PC. Alternatively, relays containing microcomputers, such as programmable relays (OMRON Corporation, Japan), can now be used for time control. In recent years, these relays have become available at low cost, and programs created by the investigator allow easy time control of the relays without a PC.

Solenoid valve control by a PC or a programmable relay takes place independently from the data logger, thus cannot be synchronized perfectly with the data recording. The issue of synchronization can be resolved with the use of a data logger manufactured by Campbell Scientific, Inc., US, e.g., the CR1000 and CR3000 which allow digital outputs with programmable control. When the control port of one of the above-mentioned data loggers is on, five volts are output. This voltage output can be used to control the relay, which in turn opens and closes the solenoid valves. Therefore, the use of one of these loggers enables synchronized data recording and solenoid valve control without the need for additional equipment. Finally, the above-mentioned control is possible with any data loggers with functions similar to those of the data loggers manufactured by Campbell.

Tips!

The sub-sampling method is used to set the flow rate between the inlet for air sampling and the pump to the maximum value. By including an exhaust outlet after the pump in the sampling system, excess gas can be removed and a large flow rate can be achieved. This method helps suppress the attenuation of CO_2 concentration fluctuations and the time delay caused by the transport of sampled air within the tubing (Suyker and Verma, 1993).

Tips 2.3-13

Tips!

Photo 2.3-2 shows the control board of a CR1000 and a solenoid valve control which is based on a mechanical relay. Fig. 2.3-2 is an example program prepared with the CRBasic software. In experiments by the author, solenoid valve control has been successfully achieved. However, this success does not necessarily guarantee the success of all future solenoid valve controls by other investigators, thus the example shown in the figure should be used only as a reference. The program example is for switching on control port 1, i.e., port C1, (turning on the solenoid valve) for 10 minutes between 11:50 and 12:00 and between 23:50 and 24:00. Incidentally, in some cases, the use of Photo MOS relays which have recently become available allows direct control of the relay with a control port.

Tips 2.3-14

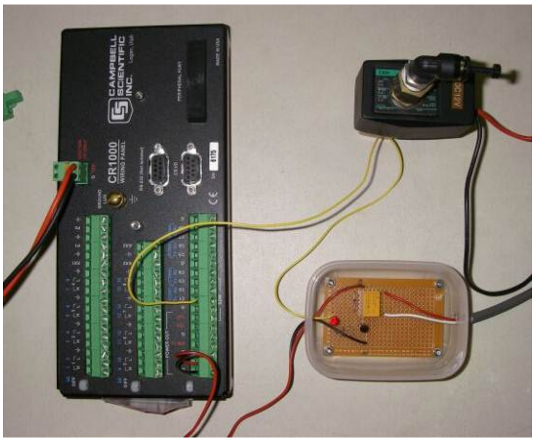

Photo 2.3-2 CR1000 control board and an example of a circuit which controls a solenoid valve with the use of a mechanical relay.

```
'CR-Basic for CR1000
'Main Program
…
BeginProg
…
If IfTime (710,1440,Min) Then PortSet (1,1 )
If IfTime (720,1440,Min) Then PortSet (1,0 )
If IfTime (1430,1440,Min) Then PortSet (1,1 )
If IfTime (1440,1440,Min) Then PortSet (1,0 )
…
EndProg
```

Fig. 2.3-2 An example of a program written with the CRBasic software.

(8) Calibration

A CO_2 analyzer is calibrated by drawing CO_2 gas (standard gas) of different known concentrations into the sample cell. In the calibration procedure, gases of two different concentrations are usually used: a gas with no CO_2 (zero gas) and a gas with a CO_2 concentration slightly higher than that of the air to be measured (span gas). These two gases are used to calibrate the zero point (offset) and span. The value of the zero offset can be detected from the data obtained from the time of the zero gas supply. As for the span drift, it can be calculated from the difference between the output value from the time of the zero gas supply and that from the time of the span gas supply. The zero point offset and span drift can be checked at the time of flux calculations after the data collection. For a more refined calibration of the analyzer, span gases of two different concentrations can be used. In this case, use 1) a standard gas with a CO_2 concentration that is slightly lower than that at the observational site of interest and 2) a standard gas with a CO_2 concentration that is slightly higher than that at the observational site of interest. The calibration method is the same as that in which a zero gas is used. However, with the use of two span gases, the range of CO_2 concentrations to be calibrated can be set according to the CO_2 concentration to be observed, and a more accurate calibration is possible than in the case in which a zero gas and a span gas are used for calibration.

Tips!

Even if a CO_2 analyzer is calibrated frequently, the calibrations are meaningless if a standard gas with low accuracy is used. Thus, it is desirable to use standard gas, the accuracy of which is higher than that of the CO_2 analyzer. In addition, stability of the standard gas over time is also important. Generally, the concentration of the gas in the cylinder increases with a decrease in the residual pressure, thus the gas cylinder needs to be replaced before the residual pressure becomes too low (if possible, before the residual pressure becomes less than 3 MPa.)

Air (air balance) is recommended as the balance gas for the CO_2 gas. (Here, balance gas means the same as base gas or carrier gas.) Although nitrogen is also used as the balance gas for the CO_2 gas, standard gas with air balance is recommended for measuring CO_2 concentration in the air. For details, refer to Pearman (1977), Pearman and Garratt (1975), Griffith (1982), Griffith *et al.* (1982), Nakazawa (1982), and Murayama (2001).

Tips 2.3-15

Tips!

When H_2O concentration is measured simultaneously with CO_2 concentration, the analyzer needs to be calibrated for its H_2O concentration output. There is little water vapor in the standard gas or pure air that is used for CO_2 calibration, thus either gas can be used as the zero gas for H_2O calibration. As for the span adjustment, a dew-point generator (e.g., LI-610, LI-COR) can be used. A dew-point generator produces air with a desired dew-point. The use of an LI-610 allows on-site calibration. (However, make sure to set the dew-point temperature lower than the air temperature of the site.)

Tips 2.3-16

(9) Data output from the analyzer

The value of the concentration measured by the analyzer is output as a digital or analog signal. The LI-6262 is capable of RS-232C output (digital) or voltage output (analog). There are two options for the analog output: raw voltage output and DAC output. The raw voltage output is the output in which no corrections or calculations have been applied, thus, calibration coefficients are required to convert the raw voltage output to concentration values. On the other hand, DAC output is the output in which the value of the concentration has been converted to voltage signals ranging from 0 to 5 V. The LI-6262 is equipped with a data smoothing function, which enables smoothing of the output signal. However, because this function is not necessary for eddy covariance measurements, the smoothing function needs to be turned off by setting the relevant value to 0 seconds.

Similarly, the LI-7000 is also capable of outputting digital signals using an RS-232C connection (the latest versions of the LI-7000 also allow a USB connection) and outputting analog voltage signals (only in DAC output). Analog (DAC) output can be allocated to DAC1 to DAC4 (equivalent of Channel 1 to Channel 4) by assigning appropriate measurement values to appropriate channels. The investigator can set the range of the measurement values of DAC1 and DAC2 to either 0 ~ 5 V or –5 ~ +5 V as the full scale (e.g., set the range of 0 ~ 5 V for the CO_2 concentration range of 300 ~ 500 ppm). Furthermore, a smaller voltage range such as 0 ~ 2.5 V or +0.625 ~ –0.625 V can be selected as the full scale for DAC3 and DAC4. As with the LI-6262, both the digital and DAC outputs from the LI-7000 can be smoothed using the smoothing (filtering) function; however, this function in principle is not needed for eddy covariance measurements.

(10) Location of pump deployment

In the system illustrated in Fig. 2.3-1, the pump is placed upstream of the analyzer, and the interior of the sample cell is pressurized. (The entire portion of the system after the pump is pressurized.) With this pump arrangement, sampled air must pass through the pump before reaching the analyzer. Therefore, with this arrangement, it is impossible to avoid disturbing the sampled air during its passage through the pump. To avoid this circumstance, the pump can be placed downstream of the analyzer. With this method, the entire system is under negative pressure. Because concentration measurements are made prior to the passage of the sampled air through the pump, there is no influence of the disturbance of the sampled air by the pump on the concentration measurement.

If the tubing for drawing in the sampled air is long (e.g., as in a forest), suction resistance becomes large and the pressure inside the tubing becomes low. (The value of the negative pressure becomes large.) When the negative pressure becomes large, it becomes more likely that the air surrounding the tubing leaks into the tubing through the tubing junctions. Therefore, if the tubing length of the system is long, it is recommended to set the pump upstream of all the branching points.

If the observational site is agricultural land or grassland and a short length of tubing can be used for observation, the pump can be placed downstream of the analyzer. However, make sure to minimize the number of branches and connections due to solenoid valves and tubing connectors.

Tips!

For the measurement of CO_2 concentration, small leakages of sampled air under positive pressure reduce the flow rate of the sampled air by only a small amount, and thus the influence of the leakages on the measurement is not large. In contrast, leakage of sampled air under negative pressure causes the surrounding air to enter the system, which significantly influences the concentration measurement. Since the force exerted by negative pressure due to the suction of the pump is larger than one might imagine, extreme care is necessary for the tubing joints. If the piping for the system becomes complex, it is recommended to apply positive pressure (pressurization) rather than negative pressure to the system for easier maintenance and long-term continuous operation.

In order to check the location of leaks in a pressurized system, the use of liquid leak detectors such as Snoop (Swagelok) is effective. Prior to the system operation, check for leaks with liquid leak detectors by applying positive pressure to the system including the portions to which negative pressure will be applied during the time of measurement.

Tips 2.3-17

(11) Attenuation of fluctuations of CO_2 concentration of the sampled air

When a closed-path gas analyzer is used, fluctuations of CO_2 concentration in the measured air (sampled air) are attenuated. The magnitude of attenuation increases with increasing frequency. This issue is considered the biggest weakness of the eddy covariance method that uses a closed-path gas analyzer. The attenuation of fluctuations of CO_2 concentration is caused by the transport of air in the tubing and/or the response speed of the analyzer. The degree of attenuation of the fluctuations varies among measurement systems, and the investigator needs to be aware of the frequency response characteristics of the particular measurement system from the power spectra and other data obtained from the system. If the contribution of the attenuated fluctuations to the fluxes is significant, corrections need to be made to the CO_2 concentration data (high frequency fluctuation correction). A number of correction methods have been proposed, however, the influence of the choice of the correction method is small for observational sites such as forest sites where the periods of fluctuations that contribute to fluxes are relatively long.

A number of publications are available on high frequency fluctuation correction. Refer to Appendix 2.3-1 for some of these publications.

Tips!

When measurements are made with a closed-path gas analyzer, air temperature fluctuations of the sampled air become attenuated in the course of transportation through the tubing. Therefore, the influence of the correction for air density fluctuations (the WPL correction) becomes small. (The correction amount is small.) If 1) the tubing is long, 2) air temperature fluctuations are negligibly small, and 3) moisture has been removed from the sampled air, then the WPL correction will not be necessary (Suyker and Verma, 1993). Furthermore, if water vapor concentration is simultaneously measured with CO_2 concentration, the mixing ratio of CO_2 in the sampled air can be determined. In this case, the WPL correction also becomes unnecessary (Grelle and Lindroth, 1996).

Tips 2.3-18

Appendix 2.3-1: References on corrections for high frequency signals

Aubinet M. *et al*. (2000) Estimates of the annual net carbon and water exchange of forests: the EUROFLUX methodology. Advances in Ecological Research, 30, 113-175.

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