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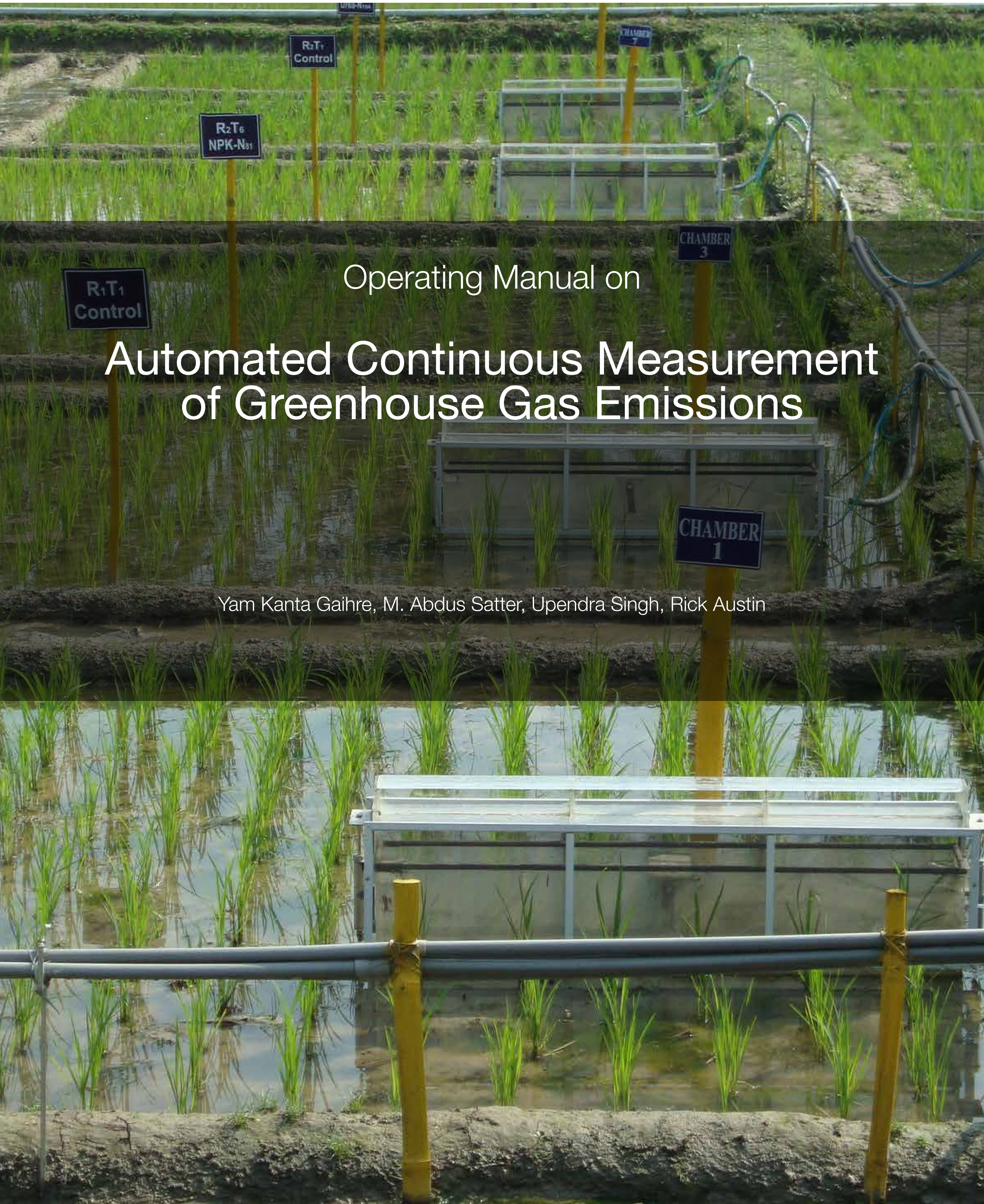

Operating Manual on

Automated Continuous Measurement of Greenhouse Gas Emissions

Yam Kanta Gaihre, M. Abdus Satter, Upendra Singh, Rick Austin

IFDC Technical Bulletin No. T-76

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Acknowledgments

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Citations

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Table of Contents

List of Tables

List of Figures

Summary

Agriculture is one of the major sources of greenhouse gases (GHG) which accounts for 10-12% of total anthropogenic GHG emissions. There is increasing interest in quantification of greenhouse gas (GHG) fluxes from agricultural soils. Fluxes of nitrous oxide (N_2O) and nitric oxide (NO) from agricultural soils show high spatial and temporal variations. The manual gas sampling technique, which is done on a weekly or biweekly interval, may not include those variations. The extrapolation of the emissions measured over wide interval of time over a season or a year that may either over- or under-estimate total emissions, is not desirable particularly for GHG emissions mitigation research. Therefore, automated continuous measurement, which includes all the temporal variations, gives a real estimate of GHG fluxes, particularly for N_2O and NO. This manual deals with automated continuous measurement system designed by International Fertilizer Development Center (IFDC) to measure N_2O and NO emissions. The manual briefly discusses the following:

- Background of GHG flux measurement.
- Construction of automated chambers and their installation in the field.
- Components of automated gas sampling and analysis system including their laboratory setup.
- Control and datalogging unit.
- Analysis of N_2O and NO.
- Calculation of GHG fluxes.
- Maintenance and monitoring of the system.

Operating Manual on

Automated Continuous Measurement of Greenhouse Gas Emissions

Introduction

Increasing concentration of greenhouse gases (GHG) such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) in the atmosphere is of the highest importance since these gases are responsible for global warming and climate change. Among different sources of GHG emissions, agriculture is one of the major sources, particularly for CH_4 and N_2O. Agriculture accounts for 10-12% of total anthropogenic GHG emissions. Of global anthropogenic emissions in 2005, agriculture contributed about 60% N_2O and about 50% of CH_4 (Smith et al. 2007). N_2O emissions occur mainly because of nitrogenous fertilizer use (Bronson et al. 1997) and change in water regimes. Similarly, nitric oxide (NO), an important atmospheric pollutant, is also emitted from agricultural soils. NO emissions from the soil are mainly affected by nitrogenous fertilizer application (Stehfest and Bouwman 2006). The global mean fertilizer-induced emissions for N_2O and NO are equivalent to 0.9% and 0.7% of applied N, respectively (Bouwman et al. 2002). On the other hand, flooded rice paddies are one of the major sources of CH_4 emissions. Since emissions from agricultural soils are anthropogenic, there is a greater scope for mitigation of those gases emissions following proper management practices.

Precise and reliable measurement of the fluxes is the first step to develop any mitigation strategies. Literature on soil GHG fluxes from agriculture show a pronounced temporal and spatial variability. Several techniques are currently used to measure the GHG fluxes at ecosystem scale. Two techniques commonly being used are micrometeorological (eddy covariance or gradient techniques) methods and chamber (enclosure) methods. The fluxes measured with eddy covariance are reliable but require expensive instrumentation and are applicable only for large land areas (at least 4 ha uniform plot). This method may not be suitable for inter-comparison of different treatments in experimental plots, which is necessary to develop mitigation strategies.

The literature on greenhouse gas (GHG) emissions show that static chamber methods are the most widely used methods to measure GHG fluxes from the soil. The chamber methods are relatively low cost, simple to deploy and applicable to small experimental plots. Chamber methods could be of different types such as open, dynamic and closed. The closed chamber, also called a static chamber, is in a common use. In this system, GHG fluxes are usually determined by directly measuring the short-term buildup or decrease in concentration of the gas of interest during chamber closure time. The gas samples from a closed chamber could be collected either by manual or automated sampling technique.

Manual closed chamber techniques can easily be applied to field trials with multiple small plots for measuring trace gas (CH_4, N_2O and NO) fluxes. Manual sampling is usually done only weekly or biweekly and rarely more frequently. On the other hand, automatic sampling techniques do allow flux measurements more frequently (near-continuous) without increased labor intensity. It provides more reliable results, as diurnal variations are captured better than with manual measurements. Manual sampling is a laborious task when repeated over a 24-hour period to account for the diurnal variations.

The continuous sampling generates large data sets that could be used for model calibration and validation. Automated sampling also allows flux measurement in remote locations where manual sampling might be uneconomical. However, automated chambers are considerably more expensive than manual chambers, and it is impossible to deploy a large number of auto-chambers. Issues are generally the same for automated and manual chambers except when frequent air samples are collected. The air flow/pumping rate in the automated system will determine how many samples are taken per enclosure period. The pumping rate should not affect chamber pressure and should be verified. The detection limits of the systems will determine sampling frequency and pumping rate, etc.

GHG emissions from agricultural soils show great temporal (over time) variations, particularly in N_2O. N_2O emissions are event-specific and generally appear only after irrigation (or rainfall, if upland crop), nitrogen fertilization and drying of flooded soil (Bronson et al. 1997). The manual sampling technique, which is done on a weekly or biweekly interval, may not include those variations. The main emission peaks may not be captured with manual sampling. Thus, extrapolation of the emissions (measured over a wide interval of time) over a season or a year may either over- or under-estimate total emissions. Since automated continuous measurement includes all the temporal variations, it gives a real estimate of GHG fluxes, particularly for N_2O and NO.

This operating manual deals only with an automated closed chamber technique that was designed by the International Fertilizer Development Center (IFDC) to measure N_2O and NO fluxes from rice fields. The automated chamber used here measures emissions from the soil without including rice plants. However, this automated chamber has the potential to measure other GHG fluxes, such as CH_4, with some adjustment of chamber design to include rice plants, which is described under section 'Chamber Design and Installation.' This automated chamber could be used for many upland crops, particularly when the chamber is placed between two rows of the crops.

The immediate scope of this manual is to serve as a guide to establish the GHG emissions measurement research in the USAID-funded project "Integrating Greenhouse Gas (GHG) Emissions Mitigation into the Feed the Future Bangladesh Fertilizer Deep Placement Rice Intensification Project." The project was implemented by IFDC in collaboration with Bangladesh Agricultural University (BAU) and Bangladesh Rice Research Institute (BRRI) to quantify the environmental impacts of urea deep placement (UDP) and alternate wetting and drying (AWD) on GHG fluxes, particularly N_2O and NO. However, the scope of this manual is not limited to this project and can be used as guide to establish the automated system in other crops and locations as well.

The automated gas sampling and analysis system includes four components: (i) automated gas chambers with compressed air-driven lids; (ii) the automated gas sampling unit; (iii) online gas analysis system; and (iv) a control and datalogging unit. The system runs continuously for 24 hours a day and 7 days a week throughout the crop-growing and fallow seasons. This manual describes each of the components in detail. The problems faced during running the system in the field are also included. The manual might be a useful document for new users of the automated gas sampling system.

Chamber Design and Installation

This section addresses the construction of automated gas chambers and their installation in the field. The gas chamber used in this measurement system is a closed chamber. The principle of closed chamber is that the chamber is installed in the soil and made airtight; thus, the gases emitted from the soil are accumulated in the chamber's headspace. During this closure time, the concentration of gases inside the chamber increases. The concentration increases if there are emissions from soil. On the other hand, concentration may decrease if the soil is consuming gases from the atmosphere. Several (two to six) air samples are collected during chamber closure time and analyzed to determine the gas concentration. Since this is the automated chamber, air samples are drawn to gas analyzers by a vacuum pump. The vacuum pump is installed either inside the gas analyzers or externally outside the analyzers.

Different designs of the chamber are in use to measure the GHG fluxes from the soils. Chamber dimensions depend on the objectives of the particular study (for example, measuring gas emissions with plant or without a plant inside the chamber). However, design should meet minimum requirements so that the calculated emission rate represents the actual emissions from the soil. The materials used in the chambers should be inert. They should not react with any gases from the soil system. Some of the commonly used materials are stainless steel, aluminum, polyvinyl chloride (PVC), polycarbonate, polyethylene or polymethyl methacrylate (Plexiglas, acrylic sheet) (Parkin and Venterea 2010). The chamber described in this manual is an automated closed chamber – closed during the sampling period and the rest of the time, also called a static closed chamber.

Chamber Construction

The automated chamber includes chamber base, chamber body (above ground part) that includes chamber lid, rubber gasket, two air cylinders, mixing fan, outer protective net, etc. The chamber body is made with Plexiglas (5 mm thick). The sheets are cut into required dimensions and joined using an organic solvent. The chamber is rectangular with inner dimensions of 120.5 cm x 15.4 cm x 31.2 cm length, breadth and height, respectively (Figure 1). When the chamber is installed over the aluminum base (inner dimension, 118.8 cm x 12.5 cm), it covers a surface area of 0.148 m^2 and volume of 0.0578 m^3 (57.8 L, headspace volume). Six crossbars are fixed inside the chamber along the length side (one at about 5 cm and another at 25 cm height) to support the chamber. The middle crossbar (upper) is used to hang the mixing fan. The sampling tube and air temperature sensor are also supported by crossbars. At the upper and lower ends of the chamber body, rubber gaskets are fixed to make the chamber airtight when closed.

A chamber has a removable compressed air-driven lid made with Plexiglas (10 mm thickness). Chamber lid is 122.6 cm long and 15.8 cm wide. Plexiglas used for the lid is thicker than that used for chamber body. Thicker Plexiglas is used to give extra weight so that it will be airtight when chamber is closed. An extra roof-like structure supported by four crossbars is also added on the lid to give sufficient weight (Figure 1). Moreover, sealing of the closed lid is achieved by a rubber gasket placed on the upper end of chamber.

Two air cylinders about 2.54 cm in diameter and 16.5 cm in length are fixed upright at both side walls (breadth side) of the chamber. Cylinders are equipped with a piston and operated by compressed air. The lower ends of both cylinders are connected with a nylon tube (1/4" outer diameter) that supplies compressed air. The piston in the air cylinder moves up when there is supply of compressed air, and chambers remain opened. When the compressed air is stopped, chambers remain closed. The chambers normally remain opened since compressed air is supplied continuously. Chambers are closed only during gas sampling time (40 minutes). The side wall (breadth side) of the chamber has three holes for the sampling tube, air temperature sensor and fan wire. All tubes and wires are fitted to be airtight. The detail of connection of tubes and sensors is described later in the section ‘Pneumatic Connections.’

The chamber lid and body is connected with an air cylinder, which opens and closes the lid. The upper end of the piston rods (8 cm long when extended) from both cylinders are connected to the chamber lid. The piston and chamber lid are joined by aluminum clamps (10 cm x 4.7 cm x 3.5 cm, length, breadth and height, respectively).

For protection of the chamber, particularly to keep rice plants from entering inside chamber, nets fitted with an aluminum frame (126.5 cm x 30 cm, length and height, respectively) are fixed at both length sides of the chamber.

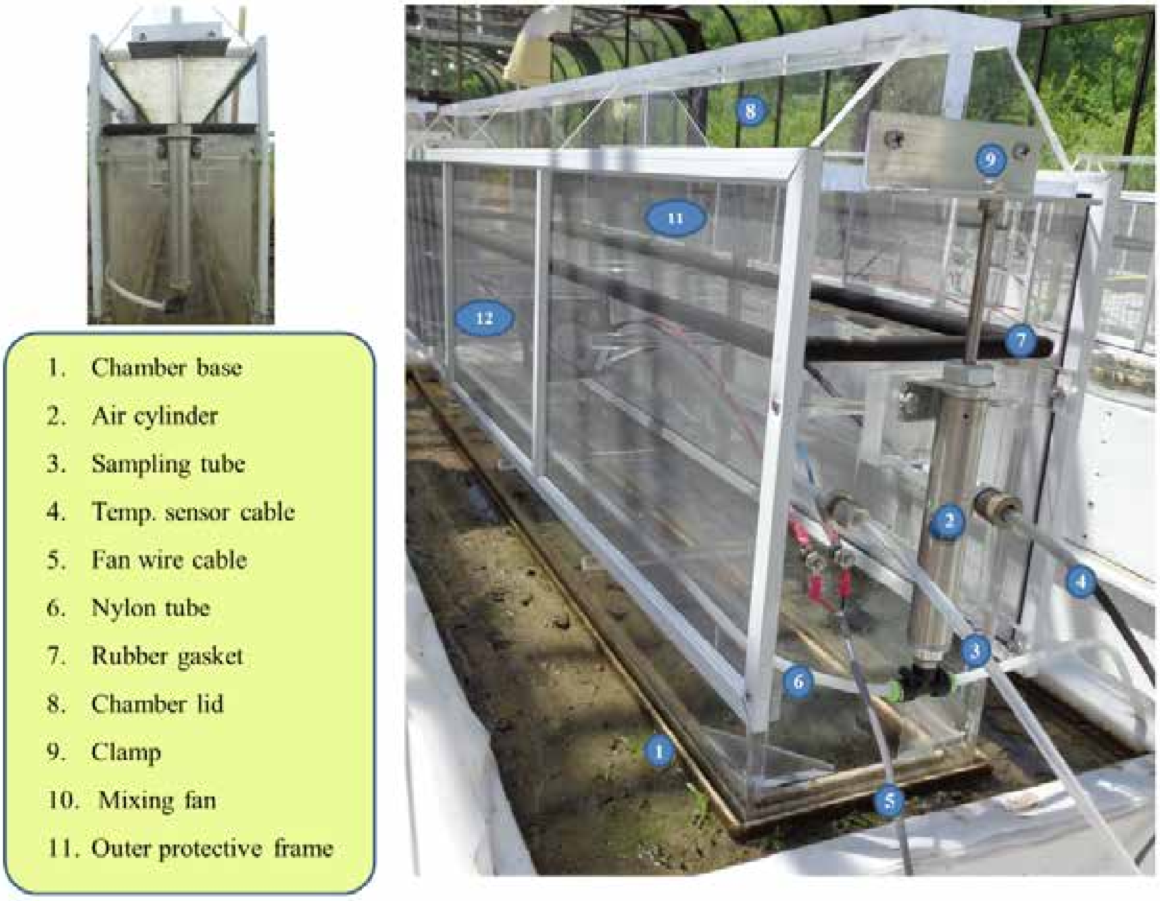

Figure 1. Gas Chamber (in an Open Position) Showing Different Parts; Inset Picture Shows the Breadth Side of the Chamber

Chamber Base

The chamber base frame is made of aluminum. The dimensions of the base must match the chamber to make it airtight. The base is 5 cm in height, including a 2 cm groove where water can be used as a sealing agent (Figure 2). The width of the groove should match the thickness of the Plexiglas sheet along with rubber gasket and should allow easy movement during placement and removal of chamber. The inner dimensions of the base are 118.5 cm x 12.5 cm x 5 cm, length, breadth and height, respectively. The chamber is placed on the groove of the base. Though the chamber is equipped with a rubber gasket, which may make it airtight even without water in the groove, the water in the groove provides extra assurance for its airtightness. However, the chamber is used in flooded rice fields except during the drying cycle of the field and during fallow season.

Figure 2. Chamber Base Frame (a) Before Installing in the Field and (b) After Installed in the Field

There are four spikes about 30 cm long fixed at the bottom side of the four corners of the base. The lower end of the peg is tapered for easy insertion into the soil. The pegs are used for holding the base along with chamber. This is prepared to protect the chamber during stormy weather in field conditions. Two loops are fixed at the middle of two breadth ends of the base where a bungee cord can be hooked to hold the chamber tightly with base.

Installation of Chamber in the Field

Connection of Wires and Tubes to the Chamber

Before installing the chamber in experimental plots, be sure all the accessories such as mixing fan, air temperature sensor, gas sampling tube and fan wire are fitted properly.

A DC fan (12 V, 1.3 W) is hung in a crossbar at the middle of a chamber. Two holes are made at the side wall of the chamber through which (breadth side) to pass the fan wires. Then the wires coming from the fan are connected with wires coming from the power source in the chamber wall using ring 'type 22-16 AWG connector' along with screw and lock nuts. The fan is used for uniform mixing of the gases inside the chamber.

A sampling tube (Teflon tube, 1/4" outer diameter) is passed inside the chamber from side wall. The endpoint of the sampling tube is hung in a cross bar in the chamber. After inserting sampling tube from chamber wall, the connection is made airtight. The sampling tube ends almost at the middle of the chamber at about 6-8 cm in front of the fan.

Similarly, an air temperature sensor is also passed into the chamber from the side wall (through another hole of the breadth wall). The connection is made airtight as with sampling tube. The temperature sensor is hung in the cross bar of the chamber as with sampling tube. Also, two air cylinders that are fixed in the breadth walls of the chamber are connected with nylon tubes (1/4" diameter). The length of tubes and wires depends on distance between chamber and laboratory.

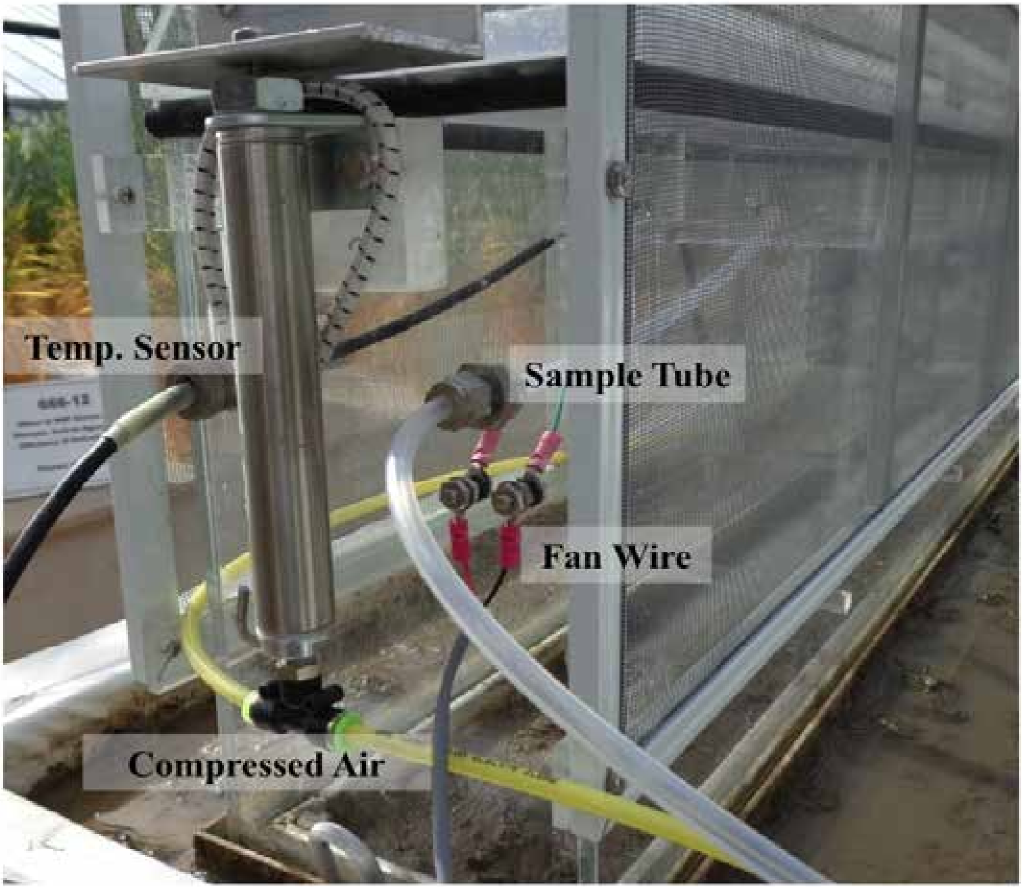

Figure 3. Connections of Wires and Tubes to the Chamber

Passing Wires/Tubes/Sensors Through PVC Pipes

Before installing the chambers in an experimental plot, the gas sampling tube (Teflon tube), compressed air tube (nylon tube), sensor wires (air temperature) and fan wires along with soil temperature and soil moisture sensor wires are tied together at certain intervals. To provide physical protection, all tubes and sensors are passed through 1/2" diameter PVC pipes. Ten foot long pieces of PVC pipe are used and joined via a straight or elbow connector up to the laboratory building. Care should be taken to avoid any leakage/breakage on the tubes, cables and wires when passing them through the pipes.

The PVC pipes coming from different chambers are supported by iron pegs of about 1' in height (above ground). A peg has a U-shaped open end to support the pipes and sharp tapering lower end for easy insertion into the soil. The number of pegs depends on the distance between chamber and laboratory. To avoid sagging of the PVC pipes, the distance between the two pegs should not be too long.

Piping of the tubes, cables and wires not only protects from physical damage, it also prevents moisture condensation in sampling tubes, particularly during rainy seasons and when there is high fluctuation of temperature in humid days. Though PVC pipes prevent moisture condensation, insulation of the sampling tube is more effective. The exposure of the sampling tube has caused moisture condensation during rain, which reduces the sample flow rate into the analyzers. The condensed water inside the sampling tube passes into the analyzers, affecting their performance. Moreover, insulation prevents the possible effects of light on the sampling tube and sensor wires.

Installation of Chamber Base

After selection of location for the chamber in experimental plots, a chamber base is inserted into the soil up to 5 cm in depth (or 30 cm spike). To avoid disturbance of the soil, the chamber base must be installed at least 24 hours before the first gas sampling. Based on the chamber dimensions, the base is installed between two rows of rice along the row. At each side of the base, there are six rice hills. While selecting the chamber location, at least two rows of rice should be used as a border. The spikes of the chamber base are inserted into the soil until the upper part of the base frame goes to soil surface to prevent the lateral diffusion of gases beneath the wall. The chamber base frame must be horizontally aligned, which could be checked with a leveler for accuracy. This is essential for proper alignment of the chamber.

Installation of Chamber

After connection of all sensors, tubes and wires and inserting them into PVC pipes, the chamber is installed in experimental plots. The chamber lower end, equipped with a rubber gasket, is placed on the previously installed base. The proper alignment of the chamber over base should be checked to make it airtight. In continuously flooded soil, the groove of the base remains underwater. However, care should be taken to ensure air seal between soil and chamber base when plots are dry.

After installation of the chamber, the soil temperature sensor is horizontally inserted into the soil at 5-7 cm depth inside the chamber. Similarly, the soil moisture sensor (gypsum block) to monitor soil moisture content is used in each chamber. Each gypsum block is inserted into the soil horizontally at 5-7 cm depth beside the soil temperature sensor. The nylon tube (compressed air) is connected to the air cylinders. The chamber lid is checked for smooth up and down movement.

The PVC pipes that contain all sensor wires and tubes are placed over U-shaped iron pegs up to the laboratory. All the tubes, wires and sensors are connected with gas analyzers and datalogger via manifold and multiplexer as described later.

Figure 4. Installation of Gas Chambers (a) Carrying a Chamber into the Field and (b) Installed Chambers in Field

Insulation of Sampling Tubes

Moisture condensation in gas sampling tubes is one of the major challenges during rainy seasons and hot humid days. Use of a moisture trap before samples pass to the analyzers is an effective way to prevent this problem. A membrane dryer is used to dry air samples. However, the limitation of the membrane dryer is that it dries up the humid air but cannot trap the water that has already entered into sampling tubes. Therefore, insulation of the sampling tubes, particularly in the field or use of a moisture trap before the sample passes to the gas dryer, is necessary. The portions of the sampling tubes which are exposed, i.e., near the gas chamber and inside the laboratory, where PVC pipes could not be used, are insulated with an elastic rubber foam pipe (or black rubber elastic pipe) 1/4"in inner diameter. For easy operation, the rubber pipes are cut along the length and placed around the sampling tube(s) and then wrapped with 1.5-2.0"-wide high-performance scotch adhesive tape.

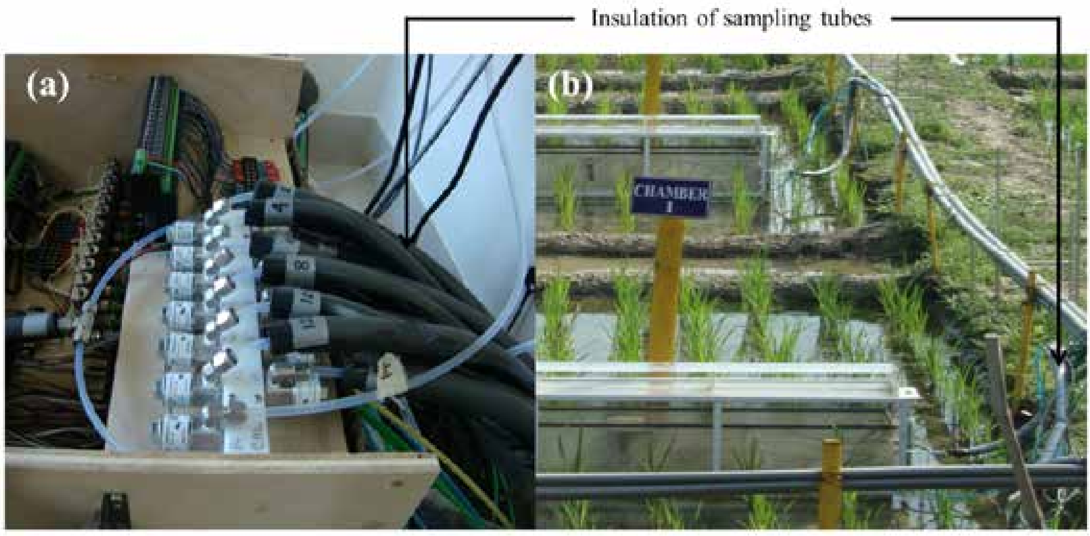

Figure 5. Insulation of Sampling Tubes (a) Inside Laboratory and (b) in the Field

Operating Principle/Gas Sampling

The basic principle of the system is the closed chamber technique of measuring GHG fluxes from the soils. The system presented here consists of 12 automated chambers linked to a sampling system and online gas analysis. Fluxes are derived by measuring the increase (or decrease) in gas concentration inside the chambers' headspace over the chamber closure time of 40 minutes. Detail of flux rate calculation is described under section 'Data Analysis.' Over the 40-minute closure time, five samples are collected at 8-minute intervals. In total, there are six samples including an ambient sample collected just before chamber closing. A schematic diagram of the sampling sequence is shown in Figure 6.

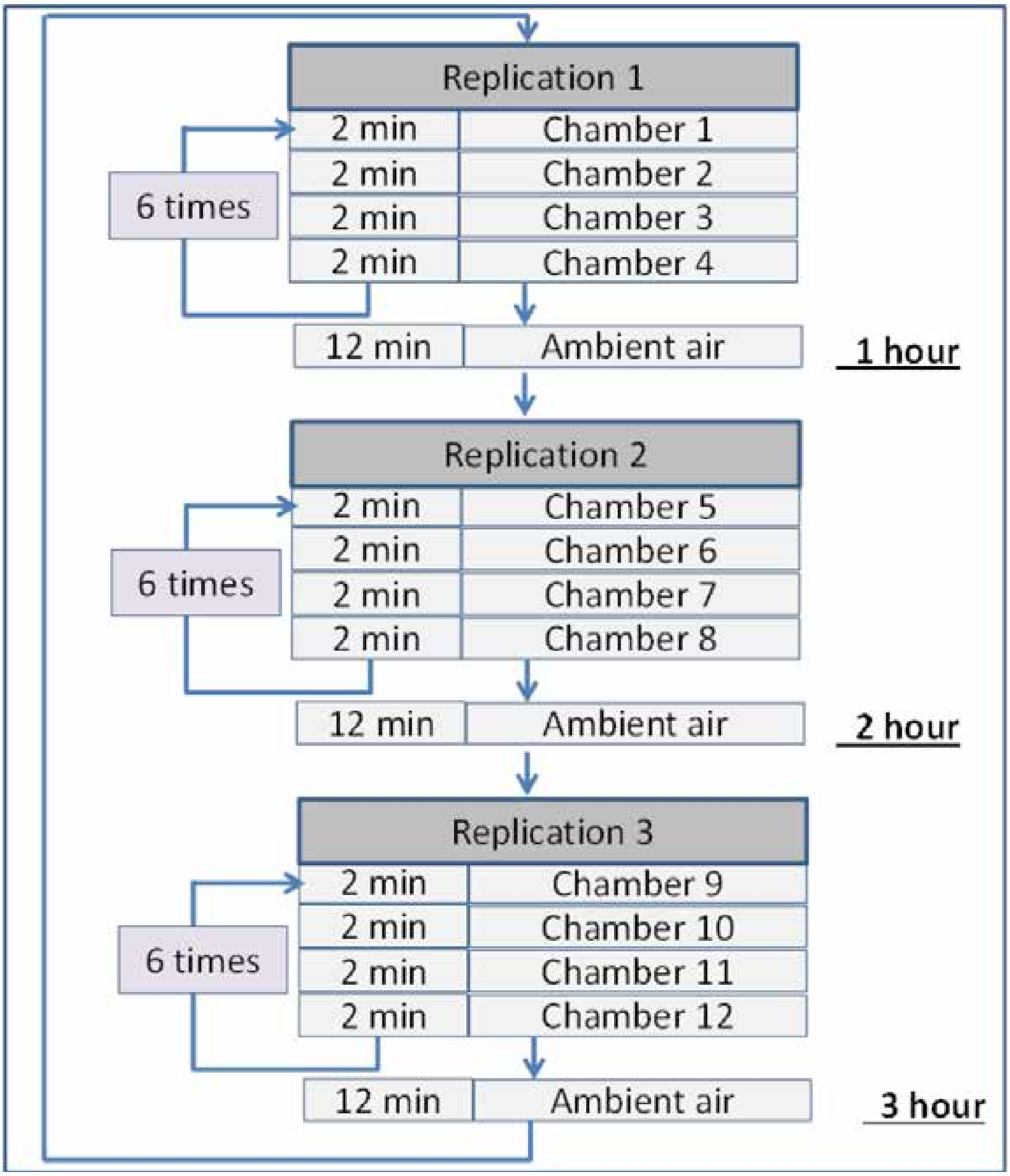

Figure 6. Schematic Diagram Showing Sampling Sequence with Four Chambers

The automated gas sampling system runs 24 hours a day, repeating a 3-hour sequence. There are three sets of four chambers, one set (one replication), i.e., four chambers are sampled in a 1-hour cycle. The 3-hour sequence consists of three one-hour sequences that are identical, except the first hour applies to chambers 1-4, the second hour applies to chambers 5-8 and the third hour applies to chambers 9-12. At the beginning of each hour, all chamber lids are open. Only four chambers remain closed for 40 minutes in the one-hour cycle as described below. During the first hour in a three-hour period (starting at 0, 3, 6, 9, 12, 15, 18 or 21 hours), the following occurs:

- Chamber 1 is sampled with the lid open for 2 minutes and then the lid is closed.
- Chamber 2 is sampled with the lid open for 2 minutes and then the lid is closed.
- Chamber 3 is sampled with the lid open for 2 minutes and then the lid is closed.
- Chamber 4 is sampled with the lid open for 2 minutes and then the lid is closed.

It is now 8 minutes into the hour; all the chamber lids are closed. Chambers 1-4 are sampled four times sequentially at 2-minutes intervals.

It is now 40 minutes into the hour.

- Chamber 1 is sampled for 2 minutes and then the lid is opened.
- Chamber 2 is sampled for 2 minutes and then the lid is opened.
- Chamber 3 is sampled for 2 minutes and then the lid is opened.
- Chamber 4 is sampled for 2 minutes and then the lid is opened.

It is now 48 minutes into the hour; all chamber lids are open.

For the next 12 minutes, there is no air sampling from the chamber. During these 12 minutes, all sample valves in the manifold are closed, and only the calibration valve remains open. Thus, for the next 12 minutes, ambient air (or calibration gases during calibration time) is sampled through the calibration valve.

During this 1-hour cycle, each of the four chambers are closed for 40 minutes, and there are six air samples for NO and N_2O analysis. The same sampling sequence is followed during the second and third hour cycles for chambers 5-8 and 9-12, respectively. The air samples are analyzed continuously using an online gas analysis system as described later.

Gas Sampling Unit

The sampling unit consists of tubing, sample valves (and calibration gas valve), suction pump (vacuum pump, internal and external), sample flow meter (inside gas analyzers), particulate filter, gas dryer, gas analyzers and a datalogger that controls sampling via relay controller and stores all the data.

Tubing and valves, suction pump and gas flow system, particulate filter and gas sample dryer are described in this section, while the gas analyzers and the datalogger, including relays, are described separately in other sections.

Tubing and Control Valves

Mechanism of Chamber Opening/Closing

Each chamber is connected to a 12-port compressed air manifold with 1/4” diameter nylon tube. The manifold is equipped with 12 Clippard valves that are used for opening and closing of the 12 chambers. The detail of connection of tubes and supply of compressed air is described under section 'Pneumatic Connection.' In general, Clippard valves remain open and supply compressed air continuously to the chamber; thus, the chamber lid remains open. When compressed air is supplied to air cylinders, the piston is pushed up, which opens the chamber lid. The sequence of opening and closing of the chambers is described earlier under section operating principle.

Opening and closing of the vales are controlled by the datalogger via relay controller. The relay controller receives a signal from the datalogger and relays it to the respective valve for opening and closing. Sequence of opening and closing of the chambers depends on the sampling sequence. Based on sampling sequences, only four chambers are closed in a 1-hour cycle, and the rest of the eight chambers remain open. Each chamber remains closed for 40 minutes.

For chamber closing, each particular valve receives a signal from the datalogger via relay controller. When the valve is closed, compressed air is released from the valve, which cuts the supply of compressed air to the chamber, causing the piston of the air cylinder to go down, thus closing the chamber lid. Four chambers close sequentially at 2-minute intervals, i.e., only one chamber is closed at a time as described in the section 'Gas Sampling.' After 40 minutes (after gas sampling is complete), the valve opens and supplies compressed air to cylinders, opening the chamber lid.

Mechanism of Sample Valve Opening/Closing

The chambers are connected to a 13-port sample manifold (equipped with solenoid valve, i.e., KIP valves) with ¼" diameter Teflon tube (for gas sampling). Out of 13 valves in a sample manifold, 12 are used for air samples that come from the respective 12 chambers. The other is used for the calibration of gases (i.e., connected to calibrator). The sequence of gas sampling is described earlier under the section "Operating Principle."

Each sample valve in the manifold is controlled by datalogger via relay controller. To control those valves, a 16-port (channel) relay is used. In the relay, 1 to 12 ports (or channels) are used to sample from gas chambers while port 14 is used for calibration gases. The other three ports are idle. Each port of the relay is connected to respective sampling valves. The relay receives a signal from the datalogger and relays to sampling valves. Only one valve is opened at a time, which allows gas samples from only one chamber to enter into the manifold at a time. Where there is no gas sampling from the chambers (last 12 minutes in every hour), the ambient air is sampled via the calibration valve. The calibration gas valve (Cal Valve, no. 14) in the sample manifold is connected to a T700 dynamic calibration gas diluter by 1/4" diameter Teflon tube. The calibration gases pass to the sample manifold through this tube and then pass to the N_2O and NO analyzers. The calibration gases pass to the analyzers only during calibration time (see section 'Calibration of Gas Analyzers').

Both KIP and Clippard valves in each manifold are controlled by a CR3000 datalogger via SDMCD16 AC/DC Relay Controllers. One relay controller is used for chamber opening/closing and another for gas sampling.

Chambers are also connected to air temperature and soil moisture sensors.

Suction Pump and Gas Flow System

A suction pump (or vacuum pump), either internal (fitted inside the gas analyzer, N_2O analyzer) or external (fitted in the exhaust of gas analyzer, NO analyzer), circulates air continuously from the chamber headspace into the analyzers via sample manifold. The sample flow rate is determined by the vacuum pump and flow controller of the respective gas analyzers. The total sample flow rate is ca. 1200 cc/min.

After drying of air samples (membrane dryer), the incoming air sample is divided to two analyzers, ca. 550±50 cc/min to NO analyzer and ca. 800±80 cc/min to N_2O analyzer. For accurate analysis, the flow rate should be stable throughout the sampling. If flow rate goes beyond acceptable range, analyzers show the sample flow warning. Based on gas sampling sequence (opening of sample valves), one sample valve (in a sample manifold) opens at a time. Then the air sample is extracted continuously from corresponding chamber for 2 minutes. After 2 minutes, the particular valve in the sample manifold closes and opens another one and continues accordingly following the sampling scheme.

Particulate Filter

The air sample from the sample manifold passes through a particulate filter, which filters any dust particles in the air sample.

Gas Sample Dryer

After filtration, the air sample passes to a gas dryer that dries the incoming air sample. The air sample is then divided into two tubes, each tube passes to NO and N_2O analyzers. The gas dryer works based on the principle described below.

Each air sample is passed to the gas sample dryer (MD™-Series gas sample dryer) after its filtration in particulate filter. The Perma Pure MD™-Series gas sample dryers use an exclusive Nafion® polymer tube surrounded by an outer tube. This is selectively permeable membrane tubing and continuously dries gas streams removing only water vapor (http://www.permapure.com/products/gas-sample-dryers/md-gas-dryers/). MD-Series gas dryers transfer moisture from one gas stream to a counter, following purge gas stream, much like a shell-and-tube heat exchanger transfers heat. The dry purge gas following over the exterior surface of the Nafion® tubing continuously extracts water vapor from the gas stream inside the tubing.

In this system, the portion of the dry air coming from the N_2O exhaust is used as dry purge gas instead of using a separate dry gas. Only the required amount (250 cc/min) to dry the air sample is used, and the rest of the dry air is exhausted. The exhausted dry air from the gas dryer is sucked out by the vacuum pump (Figure 7). The water concentration differential between the two gas streams drives the reaction, quickly drying the incoming air sample. However, it is observed that this dryer could not remove the condensed water from the sample air. Therefore, a moisture trap should be used before the gas dryer, particularly in humid areas where more water condensation is observed in sampling tubes. Nevertheless, both gas analyzers are equipped with a gas dryer.

The sampling unit also includes software to run the system and record data. Loggernet along with a CR3000 datalogger is used to control all the sampling and analysis system (chamber operation, sampling and data acquisition).

Pneumatic Connections

Pneumatic setup consists of connection of tubes for compressed air, gas sample and standard (or calibration) gases.

Compressed Air

As described earlier, opening and closing of the chamber lid is driven by compressed air produced with the air compressor. The air compressor is connected to a compressed air manifold using ¼”

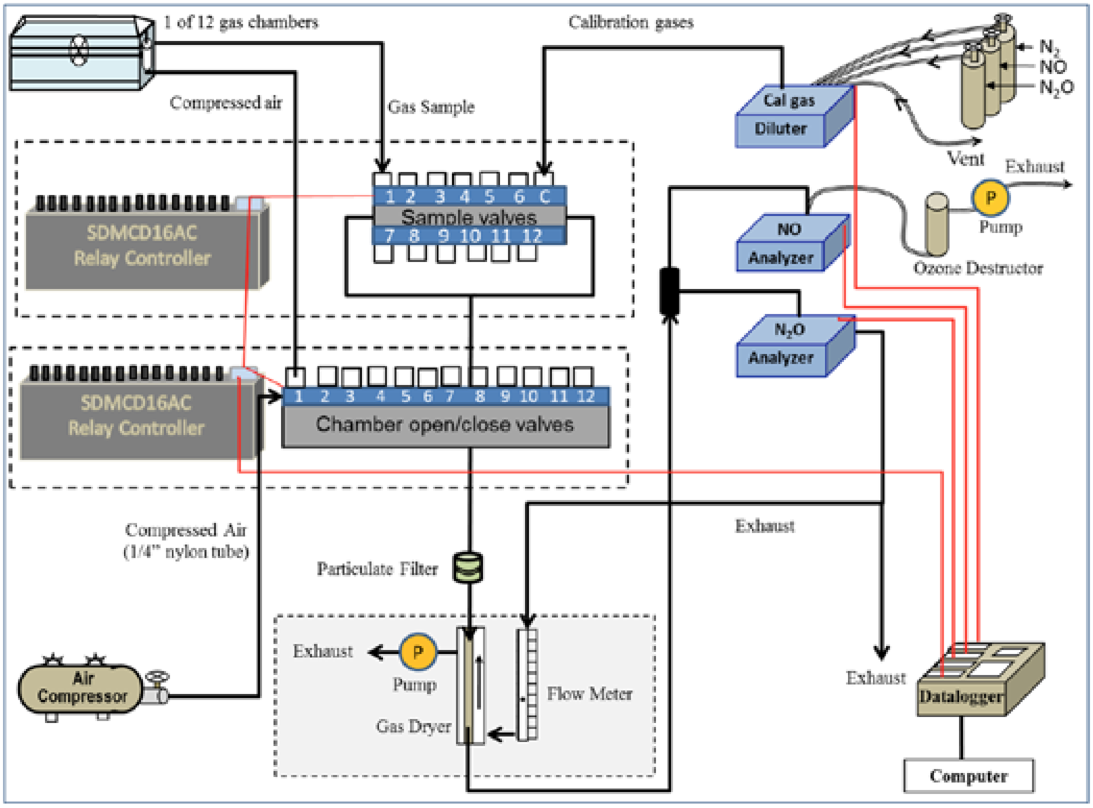

Figure 7. Schematic Diagram Showing Different Components of the Automated Continuous NO and N_2O Measurement System

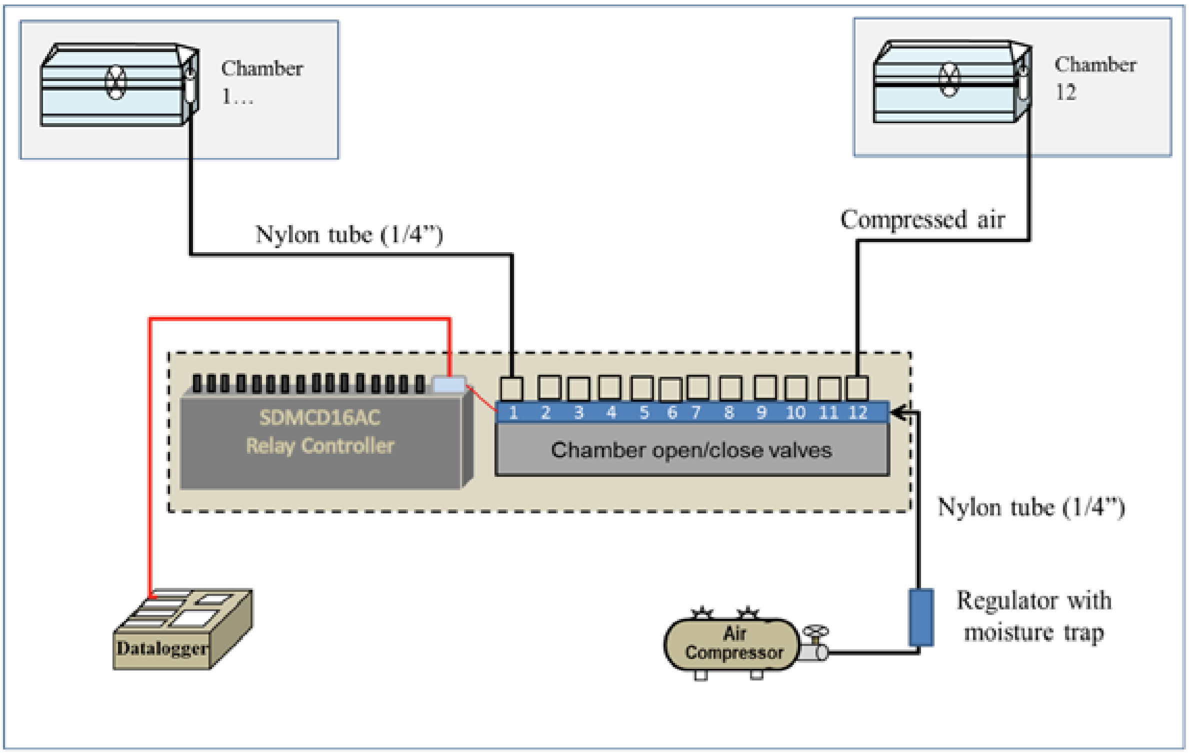

Figure 8. Pneumatic Connections for Compressed Air Showing Datalogger and Relay

diameter nylon tubes. The manifold is equipped with 12 Clippard valves (opening/closing valves) for opening and closing of the chamber lid. Each valve is connected with air cylinders of respective chamber by nylon tube (1/4" diameter) (Figure 8).

For proper opening of the chambers, the air pressure should be around 40-60 pounds per square inch (psi). If the air compressor's built-in pressure regulator is not controlling outgoing pressure properly, an external regular is used for the better control of outlet pressure. In this system, an external pressure regulator (ARO-Flo series) equipped with a water trap is fixed before the compressed air manifold. The outlet pressure is set to 60 psi. Pressure should not exceed 60 psi and should always be within the range of 40-60 psi. However, about 30 psi also found sufficient to make chamber open.

Though water is drained regularly from air compressor tank, it is better to use moisture trap that can absorb moisture from the compressed air (it is equipped with regulator here). Moist air may cause damage to the opening/closing valves and rusting of piston in air cylinder.

Air Compressor

A wide range of size/capacity of air compressors with variable power requirements is available. An air compressor with a 120-liter tank capacity (and maximum pressure of 120 psi) coupled with a 1.5 HP motor is used for this system. The compressor is switched to auto mode. The compressor tank pressure is set between 60 and 110 psi. When pressure goes down to 60 psi, the compressor starts automatically and runs until it reaches 110 psi. The lower value is adjusted based on the pressure requirement to open the chamber lid. Therefore, the tank pressure should not go below 60 psi. Water from the compressor tank should be drained regularly. The frequency of drain depends upon the humidity of air. However, it is advised to drain at least every 48 hours (see instruction manual of particular compressor).

Gas Sample

Gas samples collected from the chambers are passed to the analyzers using a Teflon tube with ¼" diameter. Teflon tube is inserted inside the chamber from the side wall (breadth side) up to the middle part of the chamber (near mixing fan). The tube is hung in a crossbar fixed inside the chamber. After inserting the tube, the fitting in the side wall is made airtight. Each Teflon tube coming from the chambers is connected with the respective sample valves in a sample manifold.

After gas samples enter the sample manifold, they pass to the analyzers. From both ends of the sample manifold, the tubes come out and are connected as a T-connection and then pass through a particulate filter for filtering of the air sample. Then the air sample is passed through the membrane dryer for drying the gas sample.

After drying, the air sample (Teflon tube) splits into two tubes using T-connection. One tube passes to NO analyzers and another to N_2O analyzers. After analysis, the exhaust gas from the NO analyzer passes through an external ozone destructor and then connected to a vacuum pump for exhaust. Similarly, after analysis of sample for N_2O, the exhausted air from N_2O analyzers splits into two tubes. One tube goes out of the laboratory building as exhaust while about 250 cc/min of the exhausted air is used as purge gas for drying the incoming air samples (see the section sampling unit). The dry air passes the membrane dryer via flow meter. After drying of incoming air sample, the exhaust air is finally connected to a vacuum pump for exhaust (Figure 9).

Standard Gases

For the calibration of gas analyzers, two standard gases, *viz.*, 25 ppm NO in nitrogen and 1000 ppm N_2O in nitrogen, are used. Ultra High Pure Nitrogen (99.99%) is used as zero gas, which is used for zero calibration and for dilution of NO and N_2O. Required concentration of the NO and N_2O gases are prepared by a T700 Dynamic Gas Diluter.

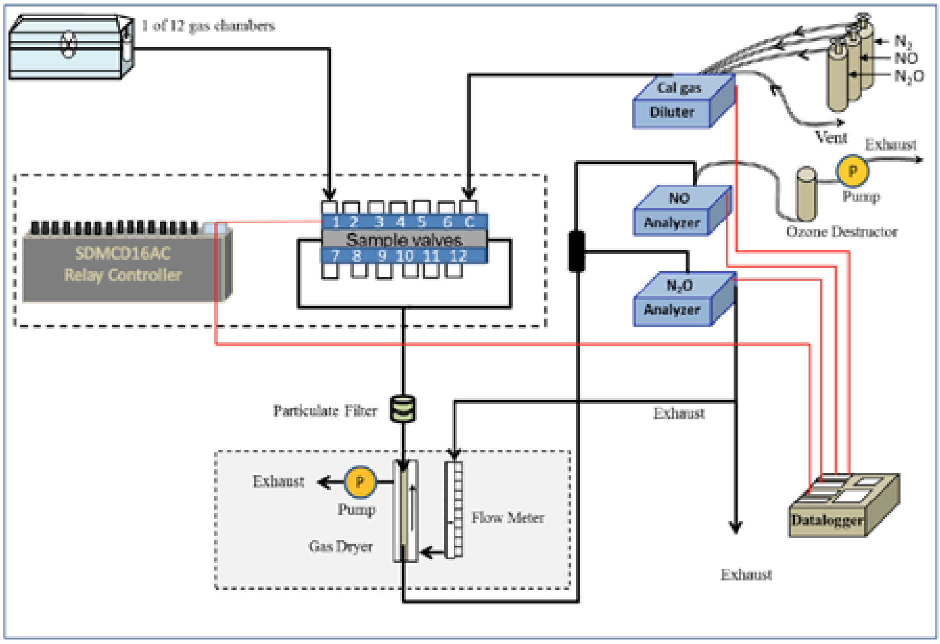

Figure 9. Pneumatic Connections for Air Sample and Standard Gases

The detail specifications of standard gases used in this system are as follows.

Nitric oxide (NO)

Concentration	25±3 ppm (V)
Cylinder	48 L ALUM
Content	7.172 m^3
Pressure	150 Bar (g)
Minimum usage pressure	5 BAR (g)
Shelf life	24 months
Recommended storage and usage temperature	10-40 ^oC

Nitrous oxide (N_2O)

Concentration	1000±20 ppm (V)
Cylinder	48 L ALUM
Content	7.170 m^3
Pressure	150 Bar (g)
Minimum usage pressure	5 BAR (g)
Shelf life	36 months
Recommended storage and usage temperature	10-40 ^oC

Ultra-pure nitrogen (N_2)

Concentration	99.99%
Cylinder	50 L STEEL
Content	9.6 m^3
Pressure	200 Bar (g)
Minimum usage pressure	5 BAR (g)
Shelf life	36 months
Recommended storage and usage temperature	10-40 ^oC

One bar is equal to 14.5 psi. Therefore, the cylinder pressure is about 3000 psi for N_2 and 2200-2500 for NO and N_2O. All cylinders are placed inside laboratory and fixed-in the wall with iron clamps.

All three gas cylinders are connected to the T700 with Teflon tubes. A Teflon tube with 1/4" outer diameter is used for connecting N_2 gas cylinders, while 1/8" diameter Teflon tubes are used for N_2O and NO gas cylinder (Figure 19). The vent of the T700 is also connected by 1/4" diameter Teflon tubes and bring outside the laboratory. The outgoing standard gas is connected to a calibration valve in the sample manifold; then the standard gas passes to the analyzers as described earlier in 'Gas sample.'

Gas Analysis

Air samples are supplied continuously to the analyzers. An air sample is drawn to the respective analyzer either by internal vacuum pump (N_2O analyzer) or external vacuum pump (NO analyzer). Analyzers analyze samples continuously and provide concentration values every 5 seconds. For the flux rate calculation, the average of the last three measurements (last 15 seconds) is used. The air sampling before that is used as purge gas that clears the sample tubes; thus, those values are not used.

NO Analysis

NO concentration of the air sample is measured by a Teledyne API (Advanced Pollution Instrumentation, USA) T200 Nitrogen Oxide analyzer. The T200 uses a chemiluminescent detection principle. It calculates the amount of NO present in an air sample by measuring the amount of chemiluminescence given off when a sample gas is exposed to ozone (O_3). The detail analysis principle is described separately under section 'Gas Analyzers.'

Since air sampling from each chamber continues for 2 minutes, each sample is analyzed for 2 minutes (every 5 seconds one measurement). However, only the last three measured values of the last 15 seconds of 2 minutes are taken in to account. Those three values are averaged, and the average value is stored in the datalogger (as 'rundata' file).

The analyzer is calibrated for two ranges of concentration, i.e., low range (40 ppb) and high range (400 ppb). Accordingly, for each analysis, the analyzer gives two concentrations of NO, one for low range (L) and another for high range (H). As described earlier, there are six samplings from one chamber in a 3-hour cycle. Those six samples are taken at 8-minute intervals for 40 minutes including one sample taken just before closing of the chamber. Both low range and high range values for six samplings are stored in a file (rundata.dat). Those six measured values are used to calculate the flux rates of NO (see section 'Data Analysis'). If the concentration is above 40 ppb, high range values are used, otherwise low range.

Note: If concentration is higher than 40 ppb only in one chamber, use high range values for only that chamber, not for all the chambers.

The NO analyzer is calibrated every week for both low range (40 ppb) and high range values (400 ppb) (see Calibration section for detail). Calibration gases are made with a Teledyne T700 Dynamic Dilution Calibrator.

Every hour, air sampling is completed by 48 minutes. The remaining 12 minutes are used for sampling ambient air. Concentration of NO in ambient air is stored in 'oneminutedata' file. Unlike the air sample from the chamber, concentration values of ambient air are stored every minute (average of last three measurements).

N_2O Analysis

N_2O concentration of the air sample is measured by a Teledyne API (Advanced Pollution Instrumentation, USA) T320U Gas Filter Correlation Analyzer. The T320U uses an infrared (IR) absorption principle. The detail analysis principle is described separately under section 'Gas Analyzers.'

As NO analysis, each sample is analyzed for 2 minutes, and the average of the last three measurements done in 15 seconds (one measurement every 5 seconds) is stored in the datalogger. The analyzer is calibrated for two ranges of concentration, i.e., low range (1600 ppb) and high range (8000 ppb). Accordingly, for each analysis, the analyzer gives two concentrations of N_2O, one for low range (L) and another for high range (H). As described earlier, there are six samplings from one chamber in a 3-hour cycle. Those six samples are taken at every 8-minute interval for 40 minutes. Both low range and high range values for six samplings are stored in a file 'rundata.dat.' Those six measured values are used to calculate the flux rates of N_2O (see section 'Data Analysis'). If the concentration is above 1600 ppb, high range values are used, otherwise low range.

Note: If concentration is higher than 1600 ppb only in one chamber, use high range values for only that chamber, not for all the chambers.

The N_2O analyzer is calibrated every week for both low range (1600 ppb) and high range (8000 ppb) values (see 'Calibration of Gas Analyzers' section for detail). Calibration gases are made with a Teledyne T700 Dynamic Dilution Calibrator.

As for NO, the ambient air is analyzed for the 12 minutes after gas sampling from the chamber, and data are stored every minute (average of last three measurements) in 'oneminutedata' file.

System Control Unit

There are four major components in the System Control unit:

1. Datalogger.
2. SDMCD16 AC/DC Relay Controller.
3. AM16/32B Multiplexure.
4. Control Valves.

Datalogger[1]

The automated gas sampling and analysis system is controlled by the datalogger via relays. Opening and closing of the chamber lid, air sampling sequence, recording of temperature and soil moisture content, calibration of gas analyzers and recording of measured NO and N_2O concentrations are programmed in the datalogger. LoggerNet is used as supporting software for datalogger. The datalogger used here is CR3000 from Campbell Scientific. Some general information of the CR3000 datalogger is presented here.

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[1] This section is adapted from 'Operator's Manual: CR3000 Micrologger available online at http://s.campbellsci.com/documents/us/product-brochures/b_cr3000.pdf

The CR3000 (also called Micrologger) is a compact, rugged, powerful datalogger. Housed in a portable, self-contained package, the datalogger consists of measurement and control electronics, communication ports, keyboard, display, power supply and carrying handle (Figure 10). The CR3000's low power requirements allow extended field use from a DC voltage source. CR3000s can measure almost any sensor with an electrical response. CR3000s measure electrical signals and convert the measurement to engineering units, perform calculations and reduce data to statistical values. The CR3000 will store data in memory awaiting transfer to the PC via external storage devices or telecommunications.

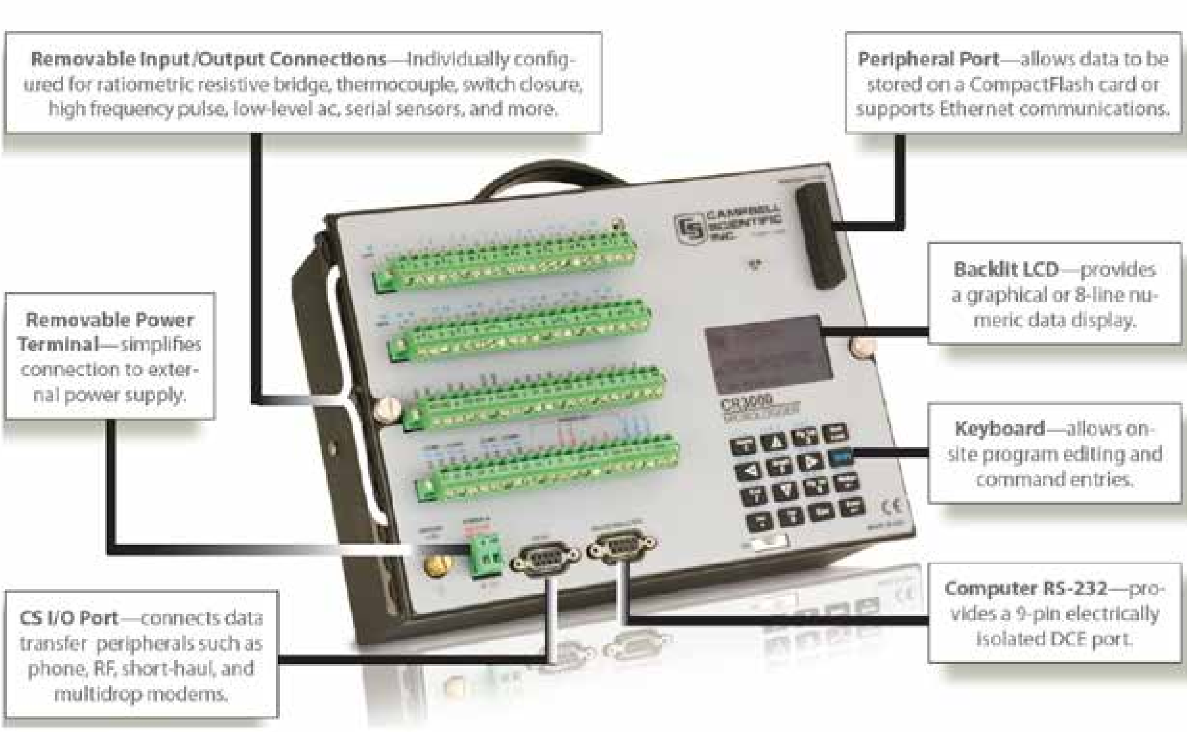


Figure 10. CR3000 Datalogger

The CR3000 has the following features:

- Program execution rate of up to 100 Hz.
- 16-bit analog to digital conversions.
- 16-bit microcontroller with 32-bit internal CPU architecture.
- Temperature compensated real-time clock.
- Background system calibration for accurate measurements over time and temperature changes.
- Gas Discharge Tube (GDT) protected inputs.
- Data values stored in tables with a time stamp and record number.
- 4 Mbytes data storage memory.
- Battery-backed SRAM and clock that ensure data, programs, and accurate time are maintained while the CR3000 is disconnected from its main power source.
- Measures SDI-12 or serial sensors with four independent COM ports.

CR3000 Data Acquisition

Data acquisition with the CR3000 is the result of a step wise procedure involving the use of electronic sensor technology, the CR3000 datalogger, a communication link (serial to USB cable) and datalogger support software (LoggerNet).

Data Retrieval

The products of interest from a data acquisition system are data in data files, usually stored on and accessible by a PC. Data are copied, not moved, from the CR3000 to the PC.

Data Collection

On-site serial communications are preferred if the datalogger is near the PC and the PC can dedicate a serial (COM) port for the datalogger. On-site methods such as direct serial connection or infrared link are also used when the user visits a remote site with a laptop or PDA.

Power Supply for CR3000

Reliable power is the foundation of a reliable data acquisition system. When designing a power supply, consideration should be made regarding worst-case power requirements and environmental extremes. Excessive switching noise or AC ripple present on a DC power supply can increase measurement noise. Noise sources include power transformers, regulators, and grid or mains power inclusively. Using high-quality power regulators reduces noise due to power regulation.

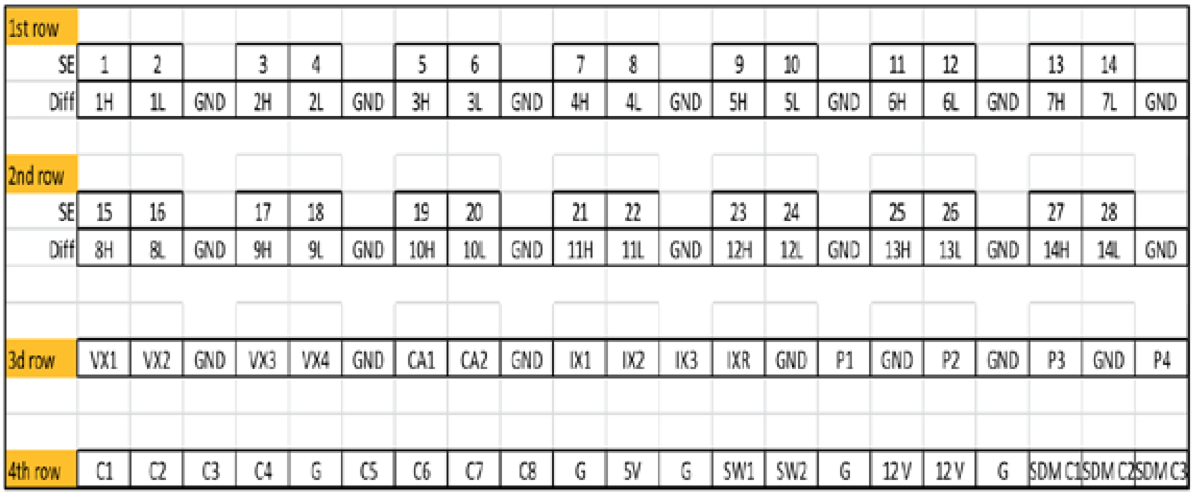
The CR3000 is powered by a nominal 12V DC source. Acceptable power source range is 10 to 16V DC. Many CR3000s are supplied with an integrated power supply base. Power to a power supply base is controlled by a manual switch on the right side of the case, below the keyboard display. External power connects through the green "POWER IN" on the face of the CR3000. The "POWER IN" connection is internally reverse polarity protected.

A lithium battery backs up the CR3000 clock, program and memory in case of power loss.

Single-Ended and Differential Input Channels

Single-ended channel: A sensor or measurement terminal wherein the analog voltage signal is carried on a single lead, which is measured with respect to ground.

Differential: A sensor or measurement terminal wherein the analog voltage signal is carried on two leads. The phenomenon measured is proportional to the difference in voltage between two leads.



1st row																					
SE	1	2		3	4		5	6		7	8		9	10		11	12		13	14	
Diff	1H	1L	GND	2H	2L	GND	3H	3L	GND	4H	4L	GND	5H	5L	GND	6H	6L	GND	7H	7L	GND
2nd row																					
SE	15	16		17	18		19	20		21	22		23	24		25	26		27	28	
Diff	8H	8L	GND	9H	9L	GND	10H	10L	GND	11H	11L	GND	12H	12L	GND	13H	13L	GND	14H	14L	GND
3d row	VX1	VX2	GND	VX3	VX4	GND	CA1	CA2	GND	IX1	IX2	IX3	IXR	GND	P1	GND	P2	GND	P3	GND	P4
4th row	C1	C2	C3	C4	G	C5	C6	C7	C8	G	5V	G	SW1	SW2	G	12 V	12 V	G	SDM C1	SDM C2	SDM C3

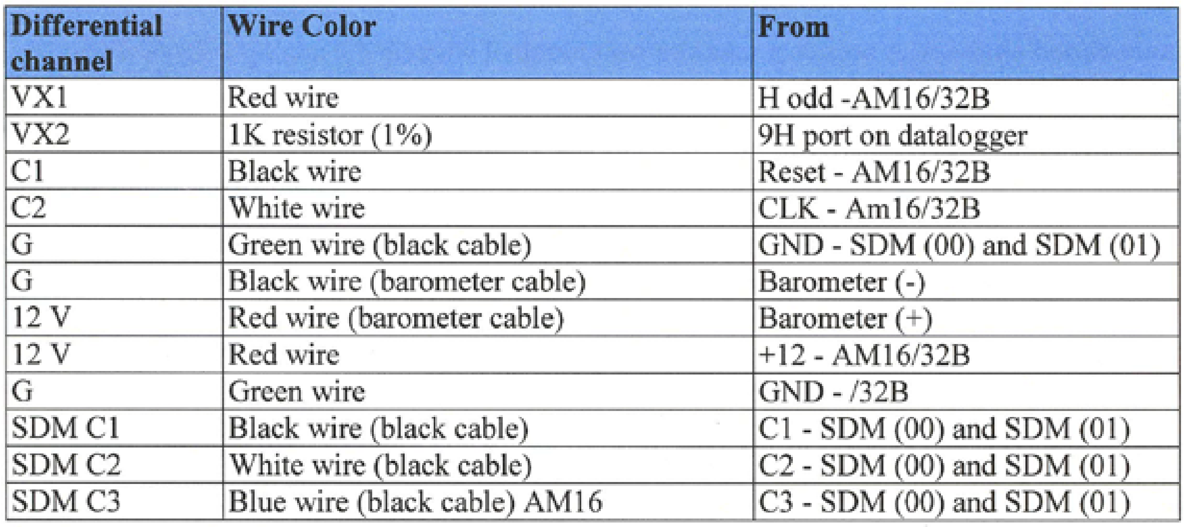
Figure 11. Schematic Diagram of CR3000 Datalogger Showing Single-Ended and Differential Channels

Datalogger Connections

Since the datalogger controls all of the operations for automated sampling and analysis system, all of the units such as SDM Relays, Multiplexer, T700 Dynamic Gas Dilutor, gas analyzers (T320U and T200) and barometers are connected with the datalogger.

Table 1 shows the third and fourth row channels of the datalogger and the connection of wires from multiplexer, SDM relays and barometer. Similarly, Table 2 shows single ended and differential channels and connection of relays and analyzers.

Table 1. Connections of Different Wires to Third and Fourth Rows of Datalogger



Differential channel	Wire Color	From
VX1	Red wire	H odd -AM16/32B
VX2	1K resistor (1%)	9H port on datalogger
C1	Black wire	Reset - AM16/32B
C2	White wire	CLK - Am16/32B
G	Green wire (black cable)	GND - SDM (00) and SDM (01)
G	Black wire (barometer cable)	Barometer (-)
12 V	Red wire (barometer cable)	Barometer (+)
12 V	Red wire	+12 - AM16/32B
G	Green wire	GND - /32B
SDM C1	Black wire (black cable)	C1 - SDM (00) and SDM (01)
SDM C2	White wire (black cable)	C2 - SDM (00) and SDM (01)
SDM C3	Blue wire (black cable) AM16	C3 - SDM (00) and SDM (01)

Table 2. Connections of Different Wires to Single Ended (SE) and Differential (Diff) Channels of Datalogger

Single ended channel	Differential Channels		Wire Color	From	Cable Description
1	1	H	Green wire	Barometer	Gray 4 conductor cable with shield
2		L			
		G	White & Shield wires		
3	2	H	Red wire	NO low range data, T200 A1	Gray 6 conductor cable with 3 shields
4		L	Black wire of red pair		
		G	Shield		
5	3	H	White wire	NO high range data, T200 A2	Gray 6 conductor cable with 3 shields
6		L	Black wire of white pair		
		G	Shield		
7	4	H	Green wire	NO sample flow rate, T200 A4	Gray 6 conductor cable with 3 shields
8		L	Black wire of green pair		
		G	Shield		
9	5	H	Red wire	N_2O low range data, T320U A1	Gray 6 conductor cable with 3 shields
10		L	Black wire of red pair		
		G	Shield		
11	6	H	White wire	N_2O high range data, T320U A2	Gray 6 conductor cable with 3 shields
12		L	Black wire of white pair		
		G	Shield		
13	7	H	Green wire	N_2O sample flow rate, T320U A4	Gray 6 conductor cable with 3 shields
14		L	Black wire of green pair		
		G	Shield		
15	8	H			
16		L	Black wire paired with red wire	L odd AM16/32B	Gray 6 conductor cable with 3 shields
		G	Shield wire	Shield AM16/32B	
17	9	H	White wire	H even AM16/32B	Gray 6 conductor cable with 3 shields
18		L			
		G	Black and shield wires paired with white wire	L even AM16/32B	Gray 6 conductor cable with 3 shields

System Timing

Measurement of time is an essential function of the CR3000. Time measurement with the on-board clock enables the CR3000 to attach time stamps to data, measure the interval between events and time the initiation of control functions.

Time Stamps

A measurement without an accurate time reference has little meaning. Data on the CR3000 are stored with time stamps. How closely a time stamp corresponds to the actual time a measurement is taken depends on several factors.

Storage of files and their retrieval is discussed under section 'Data Analysis.'

SDM Relays (SDMCD16AC/DC Relay Controller)[2]

The relays are used to relay the datalogger's command to sample valves (KIP valve) and chamber closing/opening values (Clippard valve). The relay, i.e., SDM-CD16AC, has 16 AC/DC relay control ports (Figure 12). Up to 16 units can be used on the same wiring with the datalogger (Table 3). Each relay port can be controlled by a datalogger or controlled manually with a manual override toggle switch. The toggle switch has three positions; "ON" and "OFF" for manual override, and "AUTO" for datalogger control. The relays can be powered by the datalogger; however, for most applications an external power supply is recommended.

SDM-CD16AC Power and Control Connections

The relay is connected with the datalogger (CR3000) as shown in Table 3 and Figure 13.

Figure 12. SDMCD16AC/DC Relay Controller

Caution: The order in which connections are made is critical. Always connect 12V first, followed by ground, then Control

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[2] This section is adapted from 'Instruction manual on SDM-CD16AC 16 channel AC/DC controller (Revision: 12/08),' available online at Campbell Scientific Website.

Table 3. Datalogger to SDM-CDD16AC Connections

Connection Order	SDM-CD16AC	Datalogger	Function
First	12 V	12 V on datalogger or external supply	Power
Second	GND	GND	Common ground
	C1	SDM-C1 (CR3000)	Data
	C2	SDM-C2 (CR3000)	Clock
	C3	SDM-C2 (CR3000)	Enable

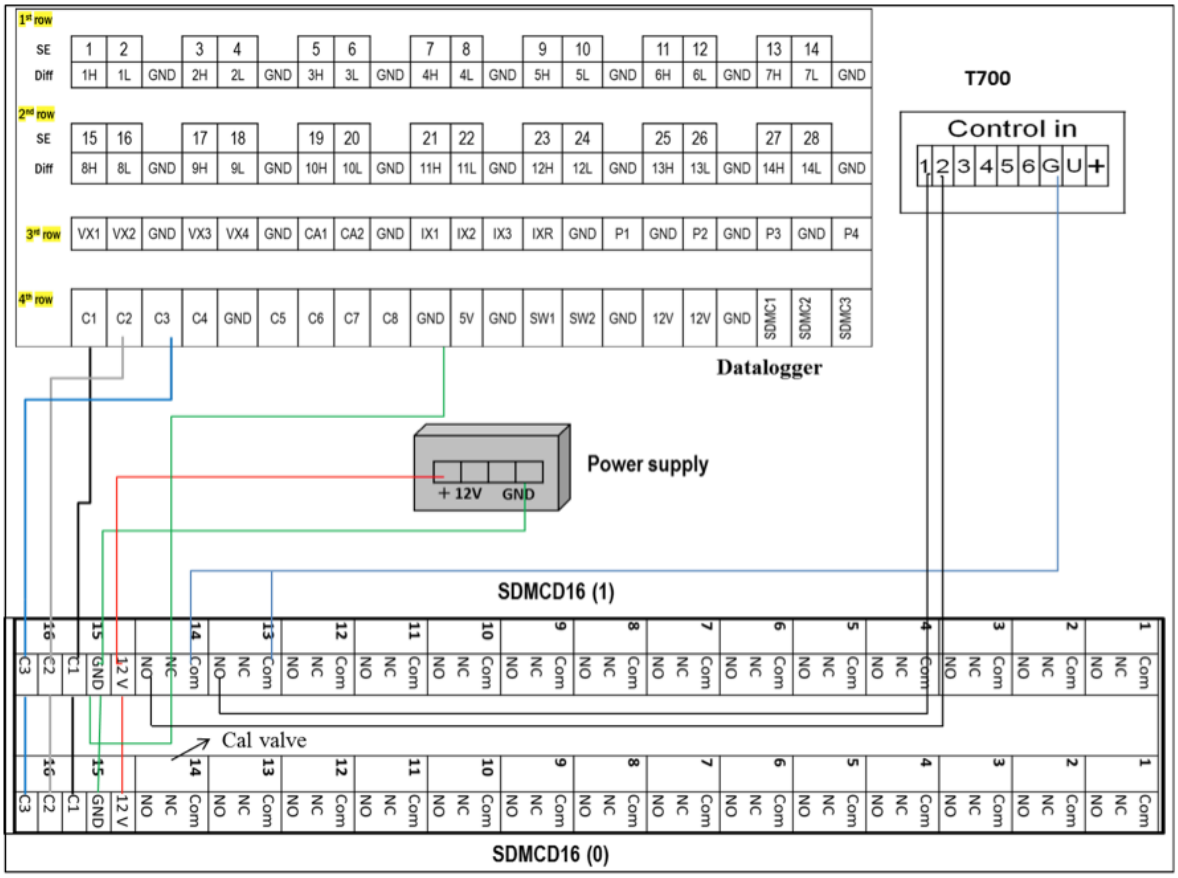


Figure 13. Schematic Diagram of the Wiring of SDM-CD16AC with Datalogger and T700 Showing External Power Supply

Special ports on CR3000

- Three special ports on the CR3000 are specifically used with the SDMCD16AC. They are SDM-C1, SDM-C2 and SDM-C3. They are located in the fourth row near the display. There is a ground next to them.

Internal Wiring of SDMCD16AC

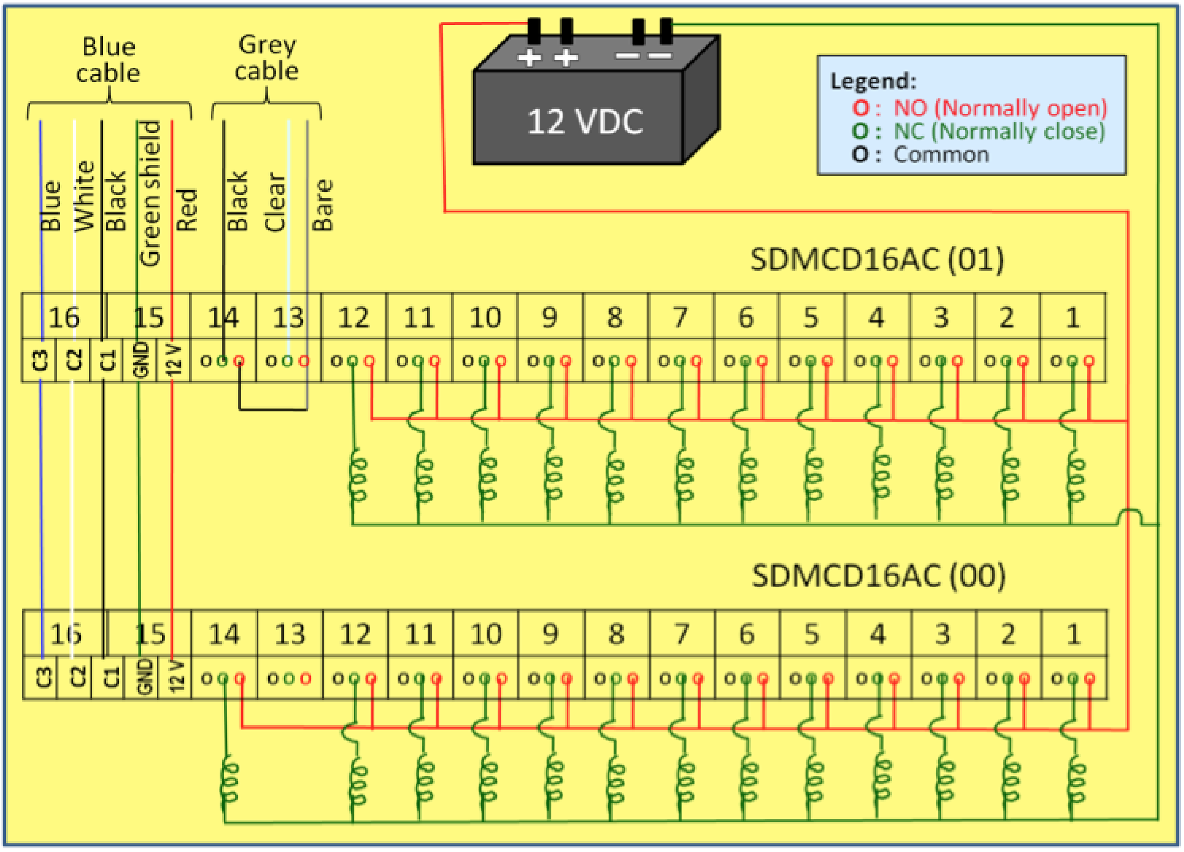


Figure 14. Internal Wiring of SDMCD16AC Relay Controller Showing Connection of Two Relays, One for Controlling Gas Sampling Valves and Another Controlling Chamber Opening/Closing Valves

Control Valves

There are two control valves in use:

i) Solenoid KIP valves (sampling valves).

ii) Clippard valves.

KIP values control gas sampling while Clippard valves control opening and closing of the chamber lid. Control mechanisms of the valves are described under section ‘Sampling Unit.’

As mentioned earlier, every hour at 48 minutes, samplings from chambers are completed. Thereafter, the 13th valve (or calibration valve) in the sample manifold remains open for next 12 minutes until another cycle of gas sampling starts. The calibration valve is controlled by the 14th channel in relay. When the calibration valve is open, either calibration gases (during auto calibration) or ambient air enter into the manifold. The calibration valve in the sample manifold is connected with the T700 Dynamic Gas Diluter with a 1/4” diameter Teflon tube. The calibration gases from the T700 pass through this tube into the N_2O and NO analyzers via sample manifold during calibration. When there is no calibration and gas sampling from chambers (every hour 12 minutes from 48 to 60 minutes), ambient air is sampled via vent of T700.

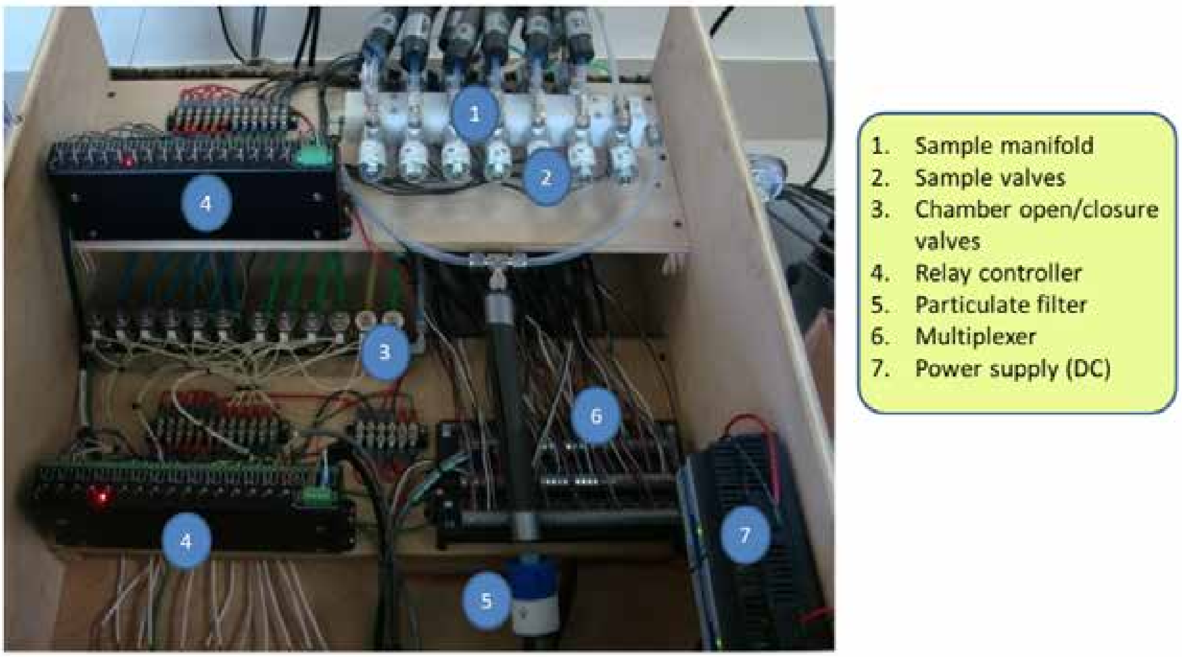


Figure 15. System Control Unit Showing Sample Manifold and Relay Controllers

Multiplexer (AM16/32B Multiplexer)

The primary function of the AM16/32B Multiplexer (Figure 16) is to increase the number of sensors that can be measured by a datalogger such as CR3000 (Campbell Scientific). The AM16/32B is positioned between the sensors and the datalogger. The AM16/32B is intended for use in applications where the number of required sensors exceeds the number of datalogger input channels. Most commonly, the AM16/32B is used to multiplex analog sensor signals, although it can also be used to multiplex switched excitations, continuous analog outputs or even certain pulse counting measurements. It is also possible to multiplex sensors of different, but compatible, types (e.g., thermocouples and soil moisture blocks). The AM16/32B is compatible with Campbell's CR3000 datalogger and with a wide variety of commercially available sensors. AM16/32B has 16 dual or 32 single sensor inputs. It can be powered by the datalogger.

Operation

There are two terminals in the AM16/32B Multiplexer that control operation of the multiplexer. They are control and measurement terminals.

Control Terminals

Control terminals control operation of the multiplexer. Figure 16 shows the control connections. The power (12 VDC), ground (GND), reset (RES), and clock (CLK) connections remain essentially the same regardless of datalogger used. AM16/32B 12 VDC connects to the datalogger 12V DC, ground ("GND") connects to the datalogger ground, reset ("RES") connects to the datalogger C1, and clock ("CLK") connects to the Datalogger C2 (see Table 3 and Figure 13).

Measurement Terminals

Most of the terminals on the AM16/32B are dedicated to the connection of sensors to the multiplexer. Depending on the panel switch selection ("4x16" or "2x32" mode), the sensor input terminals are organized into 16 groups (blue letters) of four sensor inputs or 32 groups (white letters) of two sensor inputs. The terminals accept solid or tinned stripped sensor leads. The four COM terminals marked

Figure 16. AM16/32B Multiplexure

ODD H, L and EVEN H, L located by the mode switch provide for attachment of the common signal leads that carry multiplexed sensor signals to the datalogger.

COM Terminals

The four terminals dedicated to the multiplexer-datalogger connection are located under the blue COM next to the mode switch. The terminals are labeled: ODD H, ODD L, EVEN H and EVEN L. In "4x16" mode the AM16/32B maintains the four COM terminals electrically isolated from one another. In "2x32" mode, the AM16/32B maintains an internal connection between ODD H and EVEN H and between ODD L and EVEN L.

Common "⏚" terminals are provided next to the COM ODD and COM EVEN terminals. They bus internally to the other thirty-two "⏚" terminals on the AM16/32B and are connected at all times (not switched). Their function is to provide a path to ground for sensor cable shields. A COM "⏚" terminal should be wired to the datalogger ground via the cable's shield according to Figures 13 and 17:

- Odd H to Datalogger VX1- Excitation
- Odd L to Datalogger CH 16 L (SE)
- Odd GND connects to datalogger GND
- Even H to Datalogger CH 17 H (SE)
- Datalogger CH 17 H connects to VX2 (AC Excitation) via 1 Kohm resistor
- Even L to Datalogger CH 17 GND
- Even GND Connects to Datalogger GND

Connection of Moisture and Temperature Sensors to Multiplexer

The terminals for sensor attachment are divided into 16 groups (panel switch set to "4x16") or into 32 groups (panel switch set to "2x32"). The groups consist of four or two Simultaneously Enabled Terminals (SETs). With panel switch set to "4x16" mode, the blue channel numbers apply. The SETs

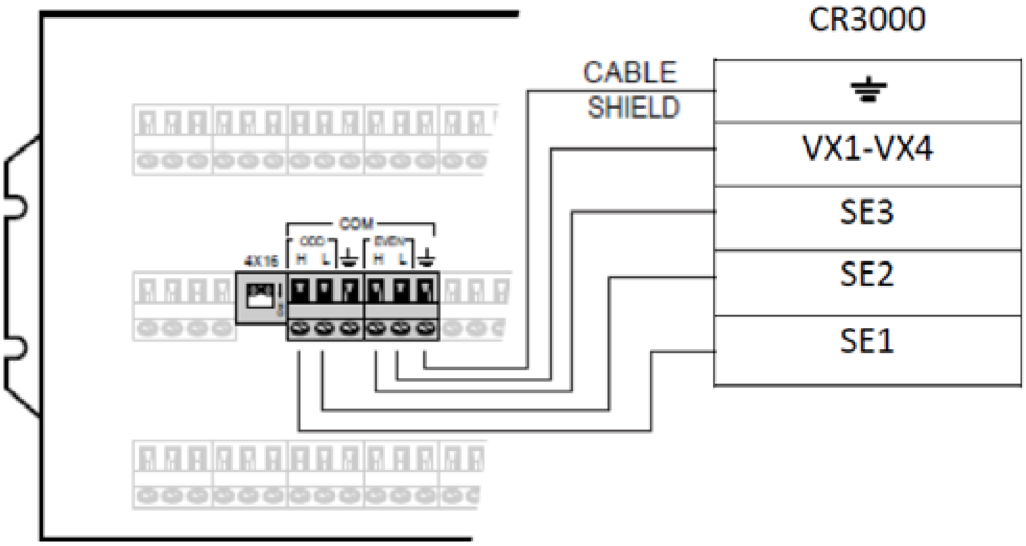
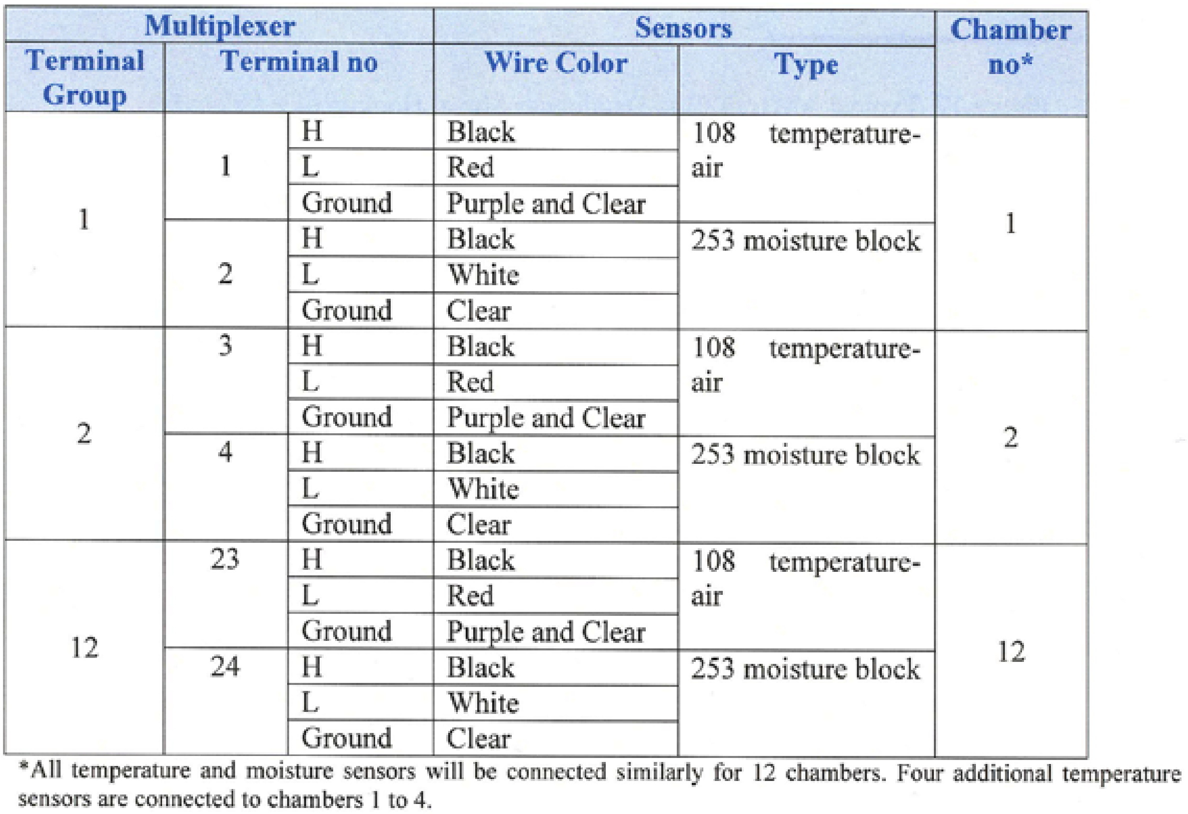


Figure 17. Typical AM16/32B to Datalogger Signal Hookup (4 x 16 mode)

are numbered starting at 1 (1H, 1L, 2H, 2L) and continuing until SET 16 (31H, 31L, 32H, 32L). In each SETs, the sensor input terminals of moisture and temperature are connected.

There are 16 temperature sensors (i.e., 12 sensors for air and 4 sensors for soil temperatures) and 12 moisture sensors. All 16 temperature sensors are connected to odd terminals (1H, 1L to 31H, 31L) while 12 moisture sensors are connected to even terminals (2H, 2L to 24H, 24L). The connection of each temperature and moisture sensors' input terminals to multiplexer (i.e., wiring) is presented in Table 3. Each temperature sensor has four terminal wires: colored black, red, purple and clear. The black and red terminal wires will be connected to 1H and 1L, respectively. The purple and clear wire together will be connected to a ground. All 16 temperature sensors (12 for air and four for soil) will be connected in the same way at every odd terminal of multiplexer – 1 to 23 for air temperature and 25 to 31 for soil temperature. Soil temperature sensors are placed only for chamber numbers 1 to 4.

Table 4. Connection of Temperature and Moisture Sensor Wire to Multiplexer

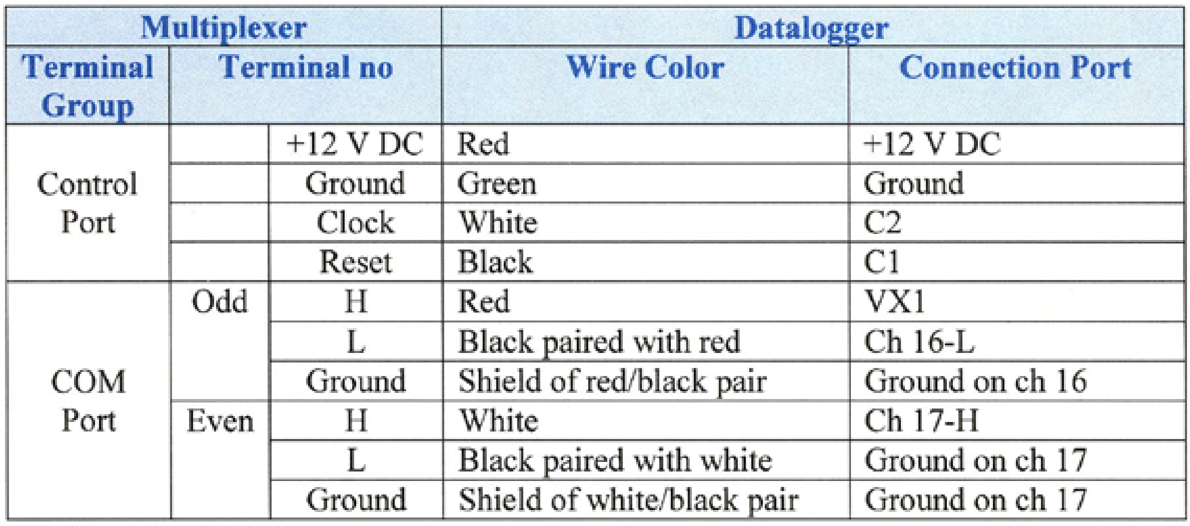


Multiplexer			Sensors		Chamber no*
Terminal Group	Terminal no		Wire Color	Type	
1	1	H	Black	108 temperature-air	1
		L	Red		
		Ground	Purple and Clear		
	2	H	Black	253 moisture block	
		L	White		
		Ground	Clear		
2	3	H	Black	108 temperature-air	2
		L	Red		
		Ground	Purple and Clear		
	4	H	Black	253 moisture block	
		L	White		
		Ground	Clear		
12	23	H	Black	108 temperature-air	12
		L	Red		
		Ground	Purple and Clear		
	24	H	Black	253 moisture block	
		L	White		
		Ground	Clear		

*All temperature and moisture sensors will be connected similarly for 12 chambers. Four additional temperature sensors are connected to chambers 1 to 4.

Connection of Multiplexer to Datalogger

Table 5. Connection of Temperature and Moisture Sensor Wire to Multiplexer



Multiplexer			Datalogger	
Terminal Group	Terminal no		Wire Color	Connection Port
Control Port		+12 V DC	Red	+12 V DC
		Ground	Green	Ground
		Clock	White	C2
		Reset	Black	C1
COM Port	Odd	H	Red	VX1
		L	Black paired with red	Ch 16-L
		Ground	Shield of red/black pair	Ground on ch 16
	Even	H	White	Ch 17-H
		L	Black paired with white	Ground on ch 17
		Ground	Shield of white/black pair	Ground on ch 17

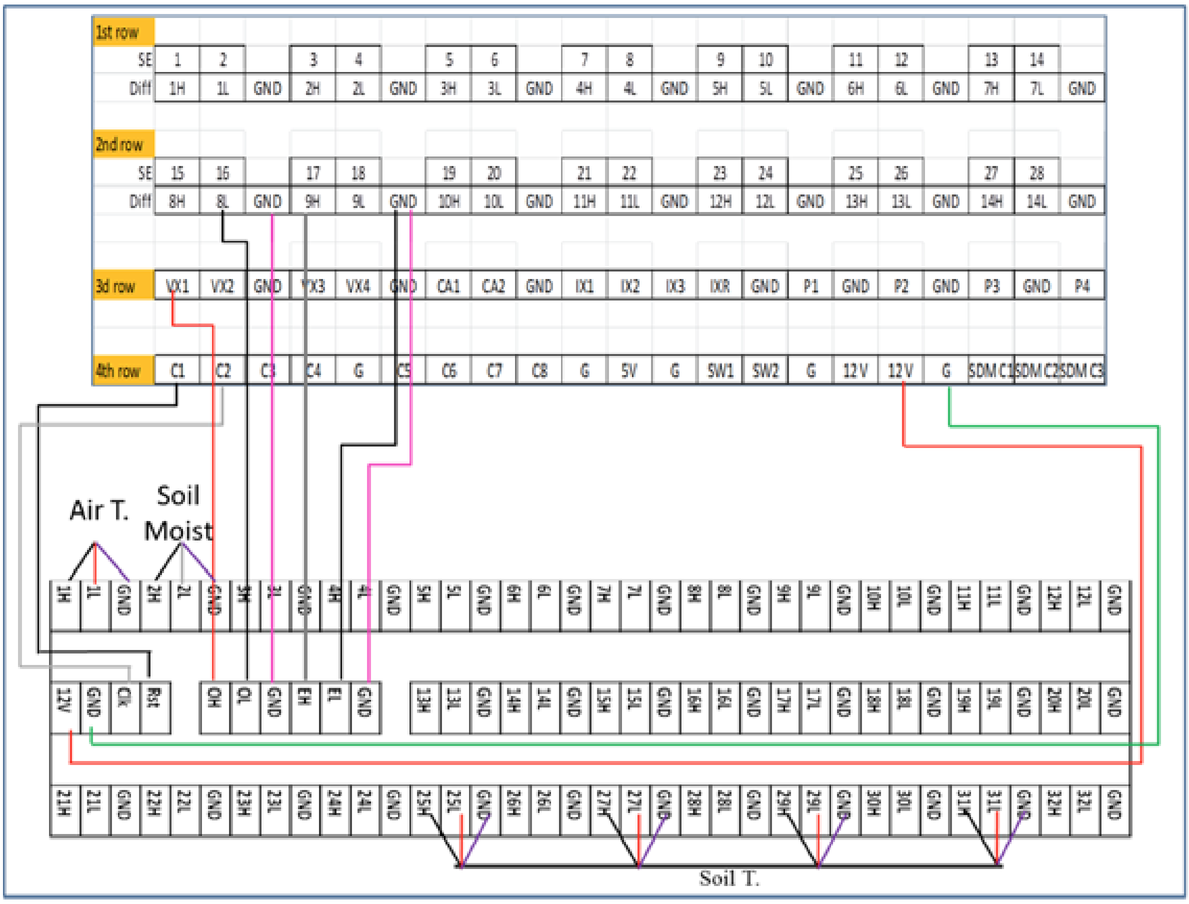


Figure 18. Schematic Diagram of Wiring Showing Connection of Sensors (Temperatures and Soil Moisture) to Multiplexer and Datalogger

Calibration of Gas Analyzers

To accurately measure gas concentration of an air sample, analyzers must be calibrated regularly. The concentration of standard gases used to calibrate the analyzers should be in a similar range with the concentration of samples. Several checks with ambient air are recommended after analysis of few samples. In this system, for both NO and N_2O, two ranges of calibration gases are used: low range and high range.

Concentration of NO for low range and high range calibration is set to 40 and 400 ppb, respectively. Since this is one point calibration (unlike using slope of different concentration such as 10, 50, 100 and 500 ppb), only one range of calibration is used. Selection of calibration range depends on the concentration of NO in air samples. It is assumed that the NO concentration from the soil will be within the range of 0-400 ppb. Therefore, calibration range is selected within 0-400 ppb. Both high range and low range values of samples are stored in datalogger (rundata file). However, for the calculation of emission rates, only either low range or high range values are used. If concentrations of air samples are lower than 40 ppb (0-40 ppb), the low range calibration is used. While concentration is higher than 40 ppb (40-400 ppb), the high range calibration is used.

Similarly, concentration of N_2O for low range and high range calibration is set to 1600 and 8000 ppb. Assumption of selecting calibration range is similar with NO. It is assumed that N_2O emissions from the soil will not exceed 8000 ppb during the chamber closure time of 40 minutes. If concentrations of N_2O in air samples are lower than 1600 ppb, the low range calibration is used for emission rate calculation. But when concentration of N_2O is higher than 1600 ppb, the high range calibration values are used.

The calibration gases are prepared by a Teledyne API T700 Dilutor. Ultra-pure nitrogen is used as diluent air or zero air. Calibration gases from pressurized gas cylinders pass to the T700 Dilutor. The dilutor prepares the required concentration of calibration gas adjusting the flow rate of diluent and calibration gases (see preparation of calibration gases). The calibration gas from the dilutor is passed to the analyzers in the same way as the air samples. The calibration gas is connected to the calibration valve in the sample manifold.

The system is set for weekly calibration. However, this can be adjusted if analyzers need frequent calibration. As described earlier, air sampling from the chamber is completed by 48 minutes. Thereafter, the calibration valve opens and all the other sample values remain closed. The calibration values open every hour at 48 minutes. The 12 minute time period, i.e., until another cycle of gas sampling starts, ambient air is sampled via calibration valve and analyzed by the analyzer in the same way as with air sample from the chamber. However, based on the current setup, there will be automatic calibration of analyzers every week. The calibration starts from 9:46 to 9:58 for zero air, 10:46 to 10:58 for NO and 11:46 to 11:58 for N_2O. During calibration, the first 2 minutes are used to mix the gases. Then, the first 5 minutes (48 to 53 minutes) are used for high range calibration, and the second 5 minutes (53 to 58) are used for low range calibration. For the remaining 2 minutes, there is sampling of ambient air.

Weekly calibration runs automatically, and the calibration values are stored in the 'Datalogger' as 'zerospan' file. Moreover, during calibration, the values can be seen on the LCD. Though calibration runs automatically, analyzers should be calibrated manually. Since each calibration (low range or high range) runs for 5 minutes, it takes about 3-4 minutes to stabilize the values. If the calibration values are beyond the acceptable range by 4 minutes, analyzers can be calibrated by pressing the ‘SPAN’ button on LCD. Multiple pressing of the SPAN button can be done during the last minute until getting stabilized target values. SPAN is done only for calibration gases, not for the zero air. For the zero air, it should be ZERO. The calibration procedure is described below.

Calibration Procedure

Open all the cylinders of diluent and calibration gases. Open outlet pressure of the tank, which should be within the range of 25-35 psi. Turn on the T700; this should be done at least 2 hours before calibration starts. Keep the T700 in STANDBY mode.

Calibration NO and N_2O Analyzers with Zero Air

Zero air (ultra-pure nitrogen) runs 0946 to 0958 for 12 minutes. From 46 to 48 minutes, mixing happens inside the dilutor. Gas will pass from the dilutor to the analyzers when the calibration valve is open by 48 minutes. The zero air is passed to the analyzer for 10 minutes. During this time, watch the LCD for the concentration values of NO and N_2O in corresponding analyzers. If the values are not acceptable (not near to zero), analyzers should be zeroed. For the NO analyzer 0±4 is acceptable while for N_2O the variation is wider and 0±20 ppb is acceptable. Follow the following step during zeroing the analyzers.

Total calibration time is 12 minutes (46 to 58 minutes).

After calibration starts, wait at least 5 to 6 minutes.

Zero for high range

On the LCD screen of both NO and N_2O analyzers:

1. Press CAL (either use touch screen or mouse).
2. Select HIGH and press ENTR.
3. Press ZERO (DO NOT PRESS SPAN) 3-4 times or more until getting stable values, and then press EXIT.

Zero for low range

Repeat same process as in high range except selection should be made for LOW instead of HIGH.

On the LCD screen of both NO and N_2O analyzers:

1. Press CAL (either use touch screen or mouse).
2. Select LOW and press ENTR.
3. Press ZERO (DO NOT PRESS SPAN) 3-4 times or more until getting stable values, and then press EXIT.

Both high and low range should be zeroed from 5 to 12 minutes.

Calibration of NO Analyzer

NO calibration gas runs from 1046 to 1058 for 12 minutes. For the first 2 minutes (from 46 to 48 minutes), mixing happens inside the dilutor. Gas will pass from the dilutor to the analyzers after 2 minutes when the calibration valve is open (by 48 minutes in an hour). NO with 400 ppb passes to the analyzers for 5 minutes (or until 7 minutes of 12 minute calibration time) and 40 ppb for the next 5 minutes (or from 7 to 12 minutes). During this time, watch the LCD screen of the NO analyzer for the concentration values of NO. If the values are not acceptable (not near to 400 ppb or 40 ppb), analyzers should be calibrated by pressing the SPAN button. The values 400±4 or 40±4 are acceptable. Follow the following step during calibration of NO analyzer.

Total calibration time is 12 minutes (46 to 58 minutes).

Calibration for high range (400 ppb)

After calibration starts, wait at least 5 minutes.

On LCD screen of NO analyzer:

1. Press CAL (either use touch screen or mouse).
2. Select HIGH and press ENTR.
3. Press SPAN (DO NOT PRESS ZERO) until getting stable values (3-4 times), and then press EXIT.
4. Make sure SPAN for high rage is finished before 7 minutes. After 7 minutes, gases switch from high to low range.

Calibration for low range (40ppb)

Wait until 10 minutes, and repeat the same process as in high range except selection should be made for LOW instead of HIGH

On LCD screen of NO analyzer:

1. Press CAL (either use touch screen or mouse).
2. Select LOW and press ENTR.
3. Press SPAN (DO NOT PRESS ZERO) until getting stable values (3-4 times), and then press EXIT.
4. Make sure SPAN for low range is finished before 12 minutes. After 12 minutes, sample gases switch from calibration gas to ambient air.

Calibration of N_2O Analyzer

N_2O calibration gas runs from 11:46 to 11:58 for 12 min. For the first 2 minutes (from 46 to 48 minutes), mixing happens inside the dilutor. Gas will pass from the dilutor to the analyzers after 2 minutes when the calibration valve is open (by 48 minutes in an hour). N_2O with 8000 ppb passes to the analyzers for 5 minutes (or until 7 minutes of 12 minute calibration time) and 1600 ppb for next 5 minutes (or from 7 to 12 minutes). During this time, watch the LCD screen of the N_2O analyzer for the concentration values of NO. If the values are not acceptable (not near to 8000 ppb or 1600 ppb), analyzers should be calibrated by pressing SPAN button. The values 8000±20 or 1600±20 are acceptable. Use the following steps during calibration of N_2O analyzer.

Total calibration time is 12 minutes (46 to 58 min).

Calibration for high range (8000 ppb)

After calibration starts, wait at least 5 minutes.

On LCD screen of N_2O analyzer:

1. Press CAL (either use touch screen or mouse).
2. Select HIGH and press ENTR.
3. Press SPAN (DO NOT PRESS ZERO) until getting stable values (3-4 times), and then press EXIT.
4. Make sure SPAN for high rage should be finished before 7 minutes. After 7 minutes, gases switch from high to low range.

Calibration for low range (1600 ppb)

Wait until 10 minutes, and repeat same process as in high range, except selection should be made for LOW instead of HIGH.

On LCD screen of N_2O analyzer:

1. Press CAL (either use touch screen or mouse).
2. Select LOW and press ENTR.
3. Press SPAN (DO NOT PRESS ZERO) until getting stable values (3-4 times), and then press EXIT.

Make sure SPAN for low range is finished before 12 minutes. After 12 minutes, sample gases switch from calibration gas to ambient air.

Note: Though in this system, calibration runs only once a week, users can choose their time and frequency of calibration.

Dynamic Dilution Calibrator (Model T700)[3]

The T700 Dynamic Dilution Calibrator is a microprocessor-controlled calibrator for precision gas calibrators. The T700 generates calibration gas mixtures by mixing bottled source gases of known concentrations with a diluent gas (zero air). Using several Mass Flow Controllers (MFCs), the T700 calibrator creates exact ratios of diluent and source gas by controlling the relative rates of flow of the various gases, under conditions where the temperature and pressure of the gases being mixed is known (and therefore the density of the gases).

The CPU calculates both the required source gas and diluent gas flow rates and controls the corresponding mass flow controllers by the following equation.

$$C_f = C_i \times \frac{GAS_{flow}}{Totalflow}$$

=Where,

Cf= final concentration of diluted gas

Ci= source gas concentration

GAS_{flow}= source gas flow rate

Totalflow= the total gas flow through the calibrator

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[3] This section is adapted from 'Operating Manual Model T700 Dynamic Dilution Calibrator', available online at http://www.teledyne-api.com/manuals/06873C_T700.pdf

Totalflow is determined as:

Totalflow= $\mathbf{GAS_{flow} + Diluent_{flow}}$

Where,

GAS_{flow}= source gas flow rate
$Diluent_{flow}$= zero air flow rate

This dilution process is dynamic. The T700's CPU not only keeps track of the temperature and pressure of the various gases, but also receives data on actual flow rates of the various MFCs in real time so the flow rate control can be constantly adjusted to maintain a stable output concentration.

The T700 calibrator's level of control is so precise that bottles of mixed gases can be used as source gas. Once the exact concentrations of all the gases in the bottle are programmed into the T700, it will create an exact output concentration of any of the gases in the bottle.

Pneumatic Connection

Up to four gas sources may be used in the T700. There are four ports labeled CYL1 through CYL4 on the back of the calibrator where calibration gases are connected. In this system, only two ports are configured and connected with nitric oxide (CYL1) and nitrous oxide (CYL2) (unused port should be capped). Teflon tube with 1/8" outer diameter is used to connect calibration source gas line. The

diluent gas (zero air) is used to dilute the calibration gases. There is a port labeled 'Diluent In' for connection of zero air source line. Ultra-pure nitrogen is used in this system and is connected using ¼" outer diameter Teflon tube. Both zero air and calibration gases should be supplied at a pressure of between 25 psi and 35 psi.

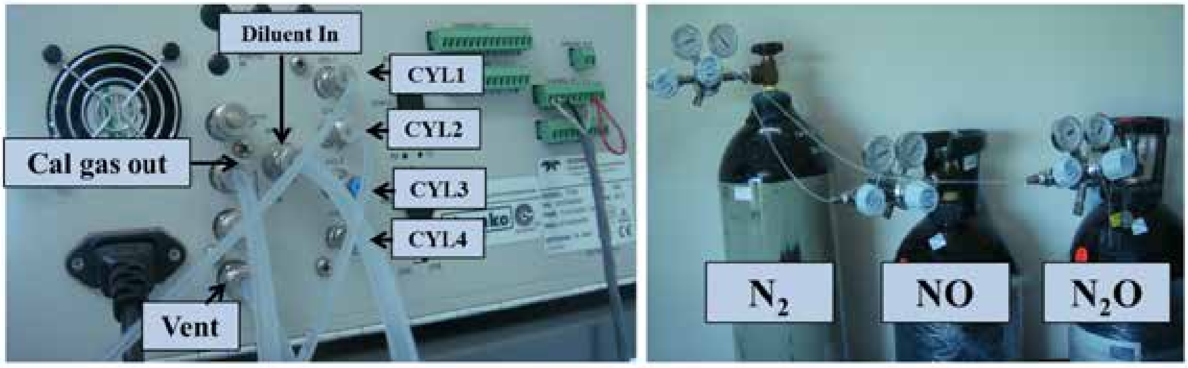
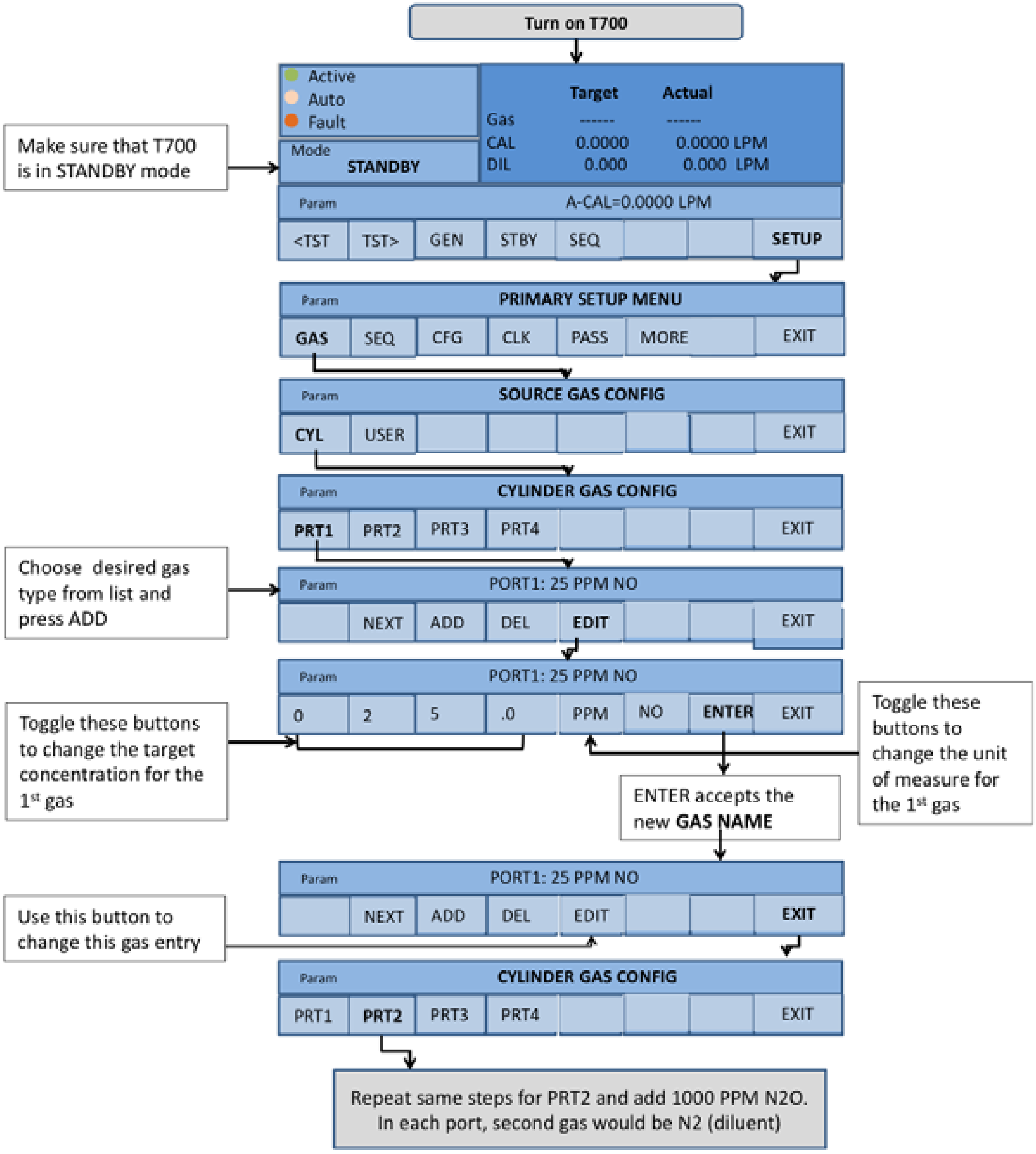


Figure 19. Pneumatic Connection of T700 Dynamic Dilutor

Connecting Diluent Gas to the Calibrator

- Attach the zero air source line to the port labeled 'Diluent In.'
- Use the fittings provided with the calibrator to connect the zero air source line.
    - First, finger tighten.
    - Then using the properly sized wrench, make an additional 1 and ¼ turn.



Make sure that T700 is in STANDBY mode

Choose desired gas type from list and press ADD

Toggle these buttons to change the target concentration for the 1st gas

Toggle these buttons to change the unit of measure for the 1st gas

ENTER accepts the new **GAS NAME**

Use this button to change this gas entry

Repeat same steps for PRT2 and add 1000 PPM N2O.
In each port, second gas would be N2 (diluent)

Figure 20. Setting Up the Ports for Multiple Gas Cylinders

Connecting Calibration Source Gas to the T700 Calibrator

- Connect the source gas line(s) to the port labeled CYL1 through CYL4 on the back of the calibrator (NOTE: Only two port are configured, CYL1 for NO, and CYL2 for N_2O).
- Source gas delivery pressure should be regulated between 25 psi to 30 psi.
- Use stainless steel tubing with a 1/8 inch outer diameter. In this setup, Teflon tube is used.

Exceeding 35 psi may cause leakage that could cause unwanted gases to be included in the calibration mixture. Each valve is rated for up to 40 psi zero air pressure and the source gas pressure should be between 25 to 30 psi and never more than 35 psi.
Figure 20 shows the steps for setting up the ports for gas cylinders.

System Purge

- By closing all of the four source gas input valves so that only zero air is allowed into the calibrator, the entire pneumatic system can be purges with zero air without having to manipulate the MFCs.

Span Gas/Zero Air Calibration Manifold Exhaust/Vent Lines

- The span and zero air manifolds' excess gas should be vented to a suitable vent outside of the room. This vent should be of large enough internal diameter to avoid any appreciable pressure drop, and it must be located sufficiently downstream of the output ports to assure that no ambient air enters the manifold due to eddy currents or back diffusion.

NOTE: The vent is used as 'EXHAUST' when calibration and diluent gases are passed to the 'Dilutor.' When calibration and diluent gases are not passing to the Dilutor but if 'calibration valve' in sample manifold is open, ambient air is sampled through the 'Vent.'

Startup and Functional Checks

After the electrical and pneumatic connections are made, an initial functional check is in order. Turn on the instrument. The front panel display will show a splash screen and other information during the initialization process while the CPU loads the operating system, the firmware and the configuration data.

The calibrator should automatically switch to STANDBY mode after completing the brief boot-up sequence. However, the T700 dynamic dilution calibrator requires a minimum of 30 minutes for all of its internal components to reach a stable operating temperature. During the warm-up period, the front panel display may show messages in the Parameters field.

Warning Messages

Because internal temperatures and other conditions may be outside be specified limits during the calibrator's warm-up period, the software will suppress most warning conditions for 30 minutes after power up.

- If warning messages persist after the 30-minute warm up period is over, investigate their cause using the troubleshooting guidelines (see Section 9 of the T700 manual).

Functional Checks

After the calibrator's components have warmed up for at least 30 minutes, verify that the software properly supports any hardware options that are installed. Check to ensure that the calibrator is functioning within allowable operating parameters (see list of text functions viewable from the calibrator's front panel as well as their expected values). These functions are also useful tools for diagnosing problems with the calibrator. The Final Test and Validation Data Sheet lists these values before the instrument left the factory.

To view the current values of these parameters, press the following buttons **<TST TST>** on the calibrator's front panel. Remember that until the unit has completed its warm-up, these parameters may not have stabilized.

Functional check should be done during every calibration and keep a record.

Operating Modes and Basic Operation

The T700 calibrator software has a variety of operating modes, which are controlled from the front panel touch screen. The most common mode that the calibrator will be operating in is the **STANDBY** mode. In this mode, the calibrator and all of its subsystems are inactive, although **TEST** functions and **WARNING** messages are still updated and can be examined via the front panel display. A variety of TEST functions are available for viewing at the front panel whenever the calibrator is in STANDBY Mode. These functions provide information about the present operating status of the calibrator and are useful during troubleshooting

The second most important operating mode is **SETUP** mode. This mode is used for performing certain configuration operations, such as programming the concentration of source gases, setting up automatic calibration sequences and configuring the analog/digital inputs and outputs. The **SETUP** mode is also used for accessing various diagnostic tests and functions during troubleshooting.

The mode field of the front panel display indicates to the user which operating mode the unit is currently running. Besides these two modes, another mode is the GENERATE mode.

Generate Mode

The Generate Mode allows the user to generate the desired calibration gas mixtures. Both Auto and Manual sequences can be generated.

<u>Auto: Basic Generation of Calibration Mixtures</u>

This is simplest procedure for generating calibration gas mixtures. In this mode, the user makes three choices:

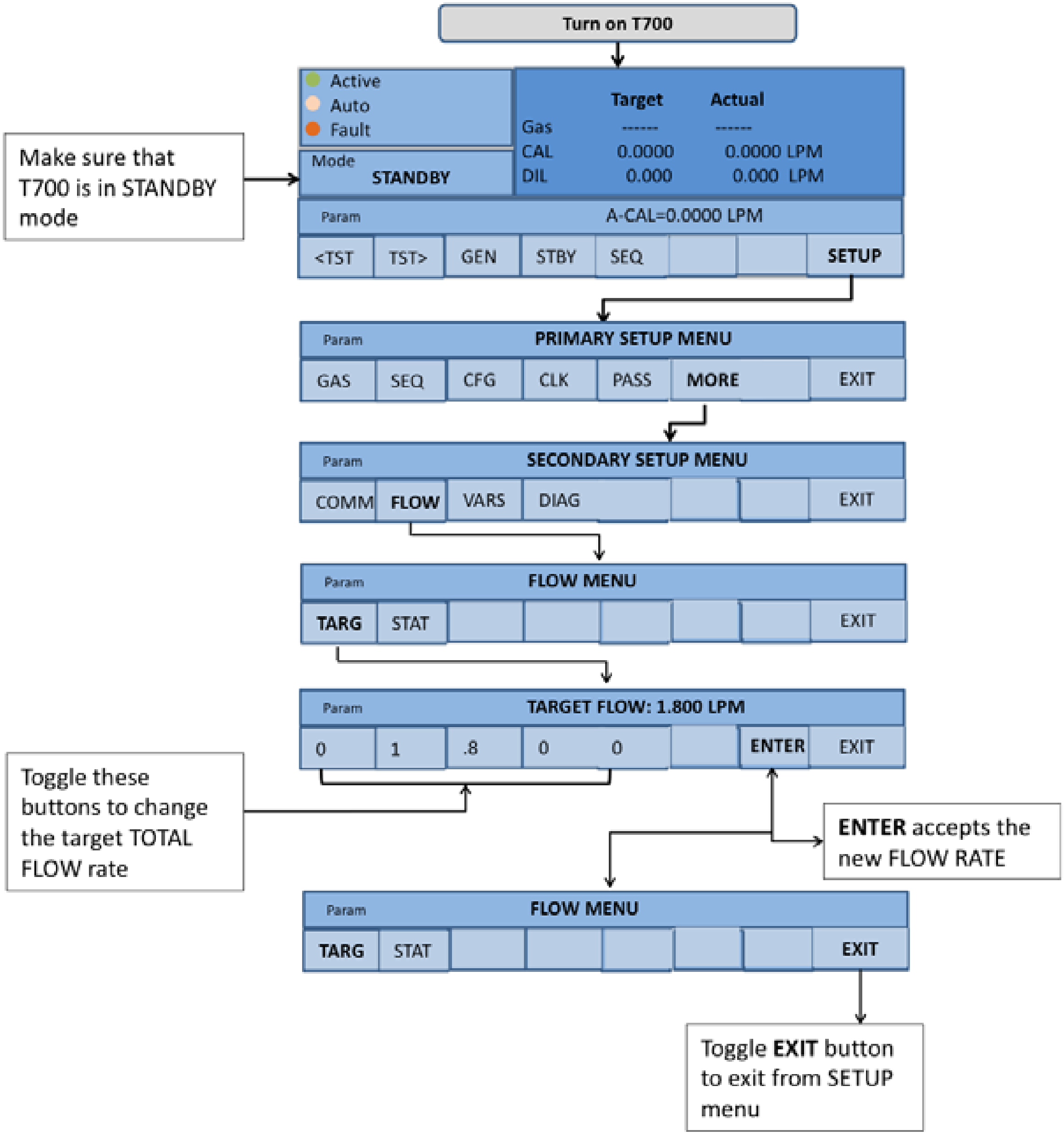
- The type of component gas to be used from the list of gases input during initial setup.
- The target concentration.
- The TOTAL FLOW to be output by the T700.

Using this information, T700 calibrator automatically calculates and sets the individual flow rates for the Diluents and chosen component gases to create the desired calibration mixture.

<u>Man: Generating Calibration Mixtures Manually</u>

This mode provides the user with more complete control of the gas mixture process. Unlike the AUTO mode, MAN mode requires the user set the both the component gas flow rate and diluent air flow rate. This allows the user control over the mixing ratio and total calibration gas flow rate.

The TOTAL FLOW is defined by the user depending on system requirements.



Make sure that T700 is in STANDBY mode

Toggle these buttons to change the target TOTAL FLOW rate

ENTER accepts the new FLOW RATE

Toggle **EXIT** button to exit from SETUP menu

Figure 21. Setting the T700's Total Gas Flow Rate

- The minimum total flow should equal to 150% of the flow requirements of all of the instruments to which the T700 will be supplying calibration gas.
- Example: If the T700 is expected to supply calibration gas mixtures simultaneously to a system in composed of two analyzers requiring 500 cc/min (0.5 LPM) and 700 cc/min (0.7LPM), the proper Total Flow output should be set at: (0.5+0.7) x 1.5 = 1.8 LPM

The steps to setup the total flow rate is shown in Figure 21.

Determining Source Gas Flow Rate

To determine the required flow rate of the component source gas, use the following formula:

$$C_f = C_i \times \frac{GAS_{flow}}{Totalflow}$$

Where:

C_f = final concentration of diluted gas

C_i = source gas concentration

GAS_{flow} = source gas flow rate

$Total_{flow}$ = the total gas flow through the calibrator

Example:

A target concentration on N_2O is 8 ppm (8000 ppb), and the concentration of the N_2O source is 100 ppm (100,000 ppb).

The total flow requirement of the system is 1.8 LPM.

The required source gas flow rate would be:

GAS_{flow} = (8000 ppb x 1.8 LPM)/100,000 ppb

GAS_{flow} = 14,400 ppb x LPM)/100,000 ppb

GAS_{flow} = 0.144 LPM

Determining Diluent Gas Flow Rate

To determine the required flow rate of the diluent gas use the following formula

$$\mathbf{DIL_{flow} = TOTAL_{flow} - GAS_{flow}}$$

Where,

GAS_{flow} = source gas flow rate

$\text{Total}_{\text{flow}}$ = total gas flow requirements of the system

DIL_{flow} = required diluent gas flow

Example:

If the requirement of the system is 1.8 LPM, and the source gas flow rate is set at 0.144 LPM,

The required diluent gas flow rate would be:

DIL_{flow} = 1.8 LPM – 0.144 LPM

DIL_{flow} = 1.656 LPM

Purge: Activating the T700's Purge Feature

The T700 calibrator's PURGE feature cleans residual source gases and calibration mixtures gases from the previous generated steps from the instrument's internal pneumatics as well as any external pneumatic lines downstream from the calibrator.

When activated, the PURGE feature:

- Opens the Diluent (zero air) inlet valve allowing zero air to flow into the calibrator from its external pressurized source;
- Adjusts the diluent air mass flow controller (MFC1) to maximum flow;
- Adjusts all of the component gas mass flow controllers installed in the calibrator to maximum flows, 10 SLPM and 100 SCCPM accordingly, to flush out the pneumatic system of the T700.

The PURGE air is vented through the VENT port of the rear panel of the instrument.

Automatic Calibration Sequences

The T700 calibrator can be set up to perform an automatic calibration sequencer of multiple steps. These sequences can perform all of the calibration mixture operations available for manual operation.

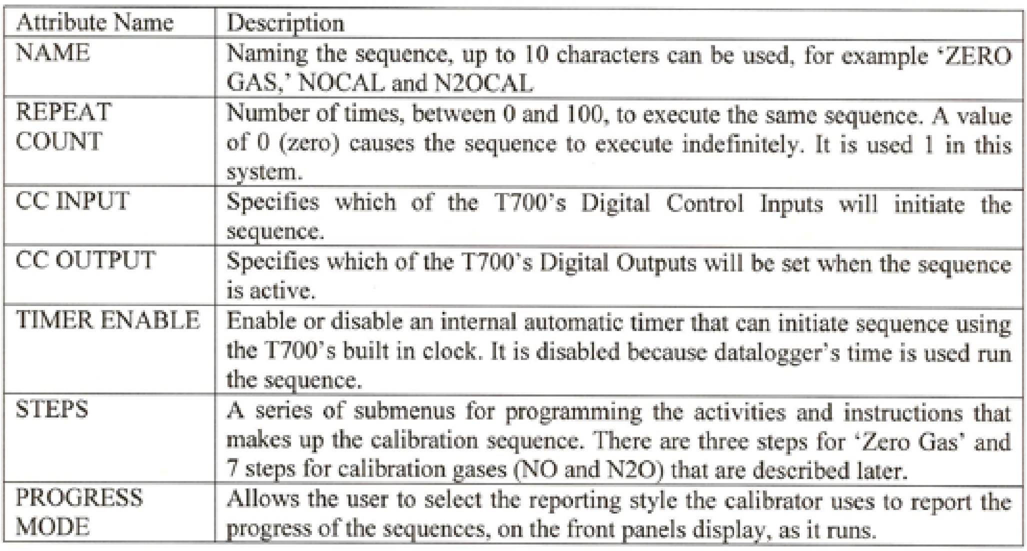
Programming Calibration Sequences

A sequence is a database of single or multiple steps where each single step is an instruction that causes the instrument to perform an operation. These steps are grouped under a user-defined SEQUENCE NAME. Procedures of programming automatic calibration sequence are briefly discussed herein. Please see 'T700 Operating Manual' for the detailed steps to generate an auto (and manual) calibration sequence.

There are three sequences used in this system.

Sequence 1: Zero gas (diluent gas, ultra-pure nitrogen).

Table 6. Automatic Calibration Sequence Setup Attributes



Attribute Name	Description
NAME	Naming the sequence, up to 10 characters can be used, for example 'ZERO GAS,' NOCAL and N2OCAL
REPEAT COUNT	Number of times, between 0 and 100, to execute the same sequence. A value of 0 (zero) causes the sequence to execute indefinitely. It is used 1 in this system.
CC INPUT	Specifies which of the T700's Digital Control Inputs will initiate the sequence.
CC OUTPUT	Specifies which of the T700's Digital Outputs will be set when the sequence is active.
TIMER ENABLE	Enable or disable an internal automatic timer that can initiate sequence using the T700's built in clock. It is disabled because datalogger's time is used run the sequence.
STEPS	A series of submenus for programming the activities and instructions that makes up the calibration sequence. There are three steps for 'Zero Gas' and 7 steps for calibration gases (NO and N2O) that are described later.
PROGRESS MODE	Allows the user to select the reporting style the calibrator uses to report the progress of the sequences, on the front panels display, as it runs.

Sequence 2: Nitric oxide (NO).

Sequence 3: Nitrous oxide (N_2O).

Each sequence is set up for a 12-minute period followed by 2 minutes of purge (with ambient air).

During setting up each automatic calibration sequence, the following seven attributes must be programmed.

In each sequence, the above seven attributes are programmed as follows.

SEQUENCE 1: ZERO GAS

NAME : ZERO GAS
REPEAT COUNT : 1
CC INPUT : 100000000000
CC OUTPUT : DISABLED
TIMER ENABLE : DISABLED
STEPS : 5

(1) ZERO GAS, 1.8 LPM
(2) DURATION: 12 MIN
(3) PURGE
(4) DURATION: 0.2 MIN
(5) STANDBY

PROGRESS MODE : STEPS

SEQUENCE 2: NOCAL

NAME : NOCAL
REPEAT COUNT : 1
CC INPUT : 010000000000
CC OUTPUT : DISABLED
TIMER ENABLE : DISABLED
STEPS : 7

(1) 400 PPB NO, 1.8 LPM
(2) DURATION: 7 MIN
(3) 40 PPB NO, 1.8 LPM
(4) DURATION: 5 MIN
(5) PURGE
(6) DURATION: 0.2 MIN
(7) STANDBY

PROGRESS MODE : STEPS

SEQUENCE 3: N2OCAL

NAME : N2OCAL
REPEAT COUNT : 1
CC INPUT : 110000000000
CC OUTPUT : DISABLED
TIMER ENABLE : DISABLED
STEPS : 7

(1) 8000 PPB N2O, 1.8 LPM
(2) DURATION: 7 MIN
(3) 1600 PPB N2O
(4) DURATION: 5 MIN
(5) PURGE
(6) DURATION: 0.2 MIN
(7) STANDBY

PROGRESS MODE : STEPS

NOTE: There are five steps for zero gas and seven steps for calibration gas while creating a sequence. First step is to select name, followed by its duration of run, purge and duration of purge and at last T700 should be in STANDBY mode.

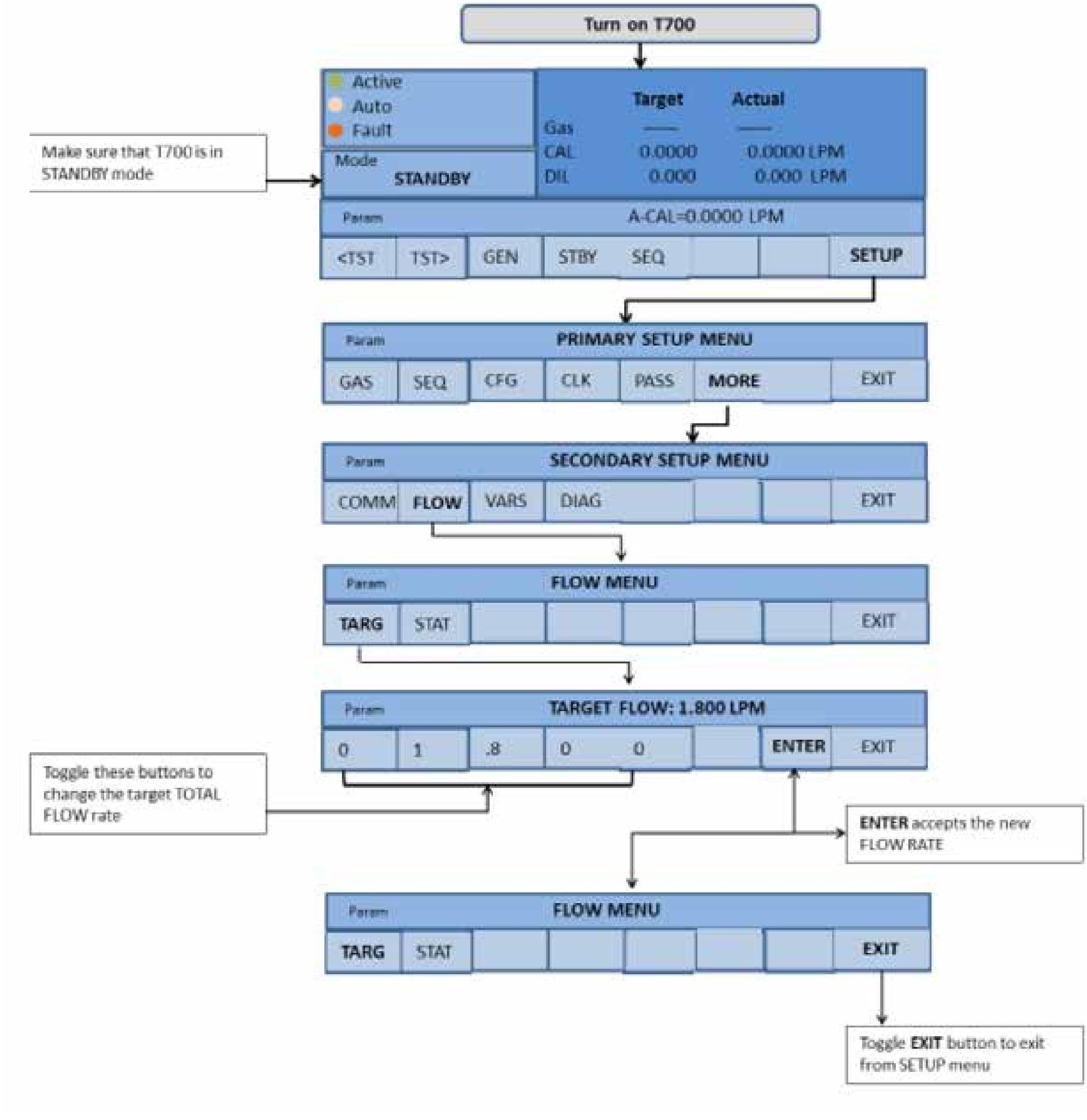
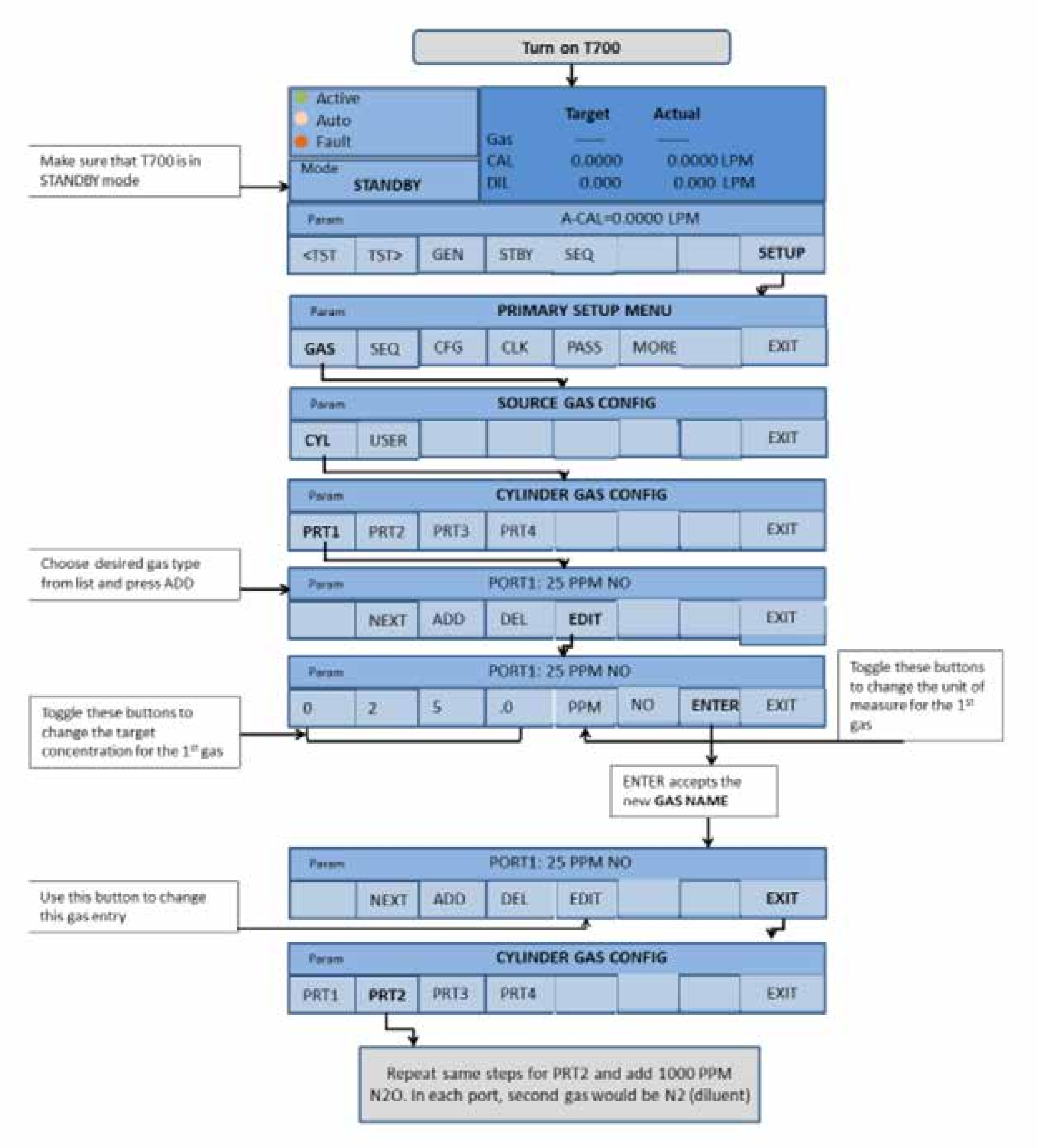


Figure 22. Activating an Automated Calibration Sequence from T700 Front Panel for Zero Gas



Make sure that T700 is in STANDBY mode

Choose desired gas type from list and press ADD

Toggle these buttons to change the target concentration for the 1st gas

Toggle these buttons to change the unit of measure for the 1st gas

ENTER accepts the new **GAS NAME**

Use this button to change this gas entry

Repeat same steps for PRT2 and add 1000 PPM N2O. In each port, second gas would be N2 (diluent)

Figure 23. Activating an Automated Calibration Sequence from T700 Front Panel for NO

It is generally a good idea to end each calibration sequence with a **PURGE** instruction followed by an instruction to return the instrument to **STANDBY** mode.

Even if a **PURGE** is not included, the last instruction in a sequence should always be to place the **T700** in **STANDBY** mode.

In this system, after completion of each sequence, ambient air is sampled for 2 minutes the start of sampling from chambers. This will allow system purging and stabilize the analyzers as well.

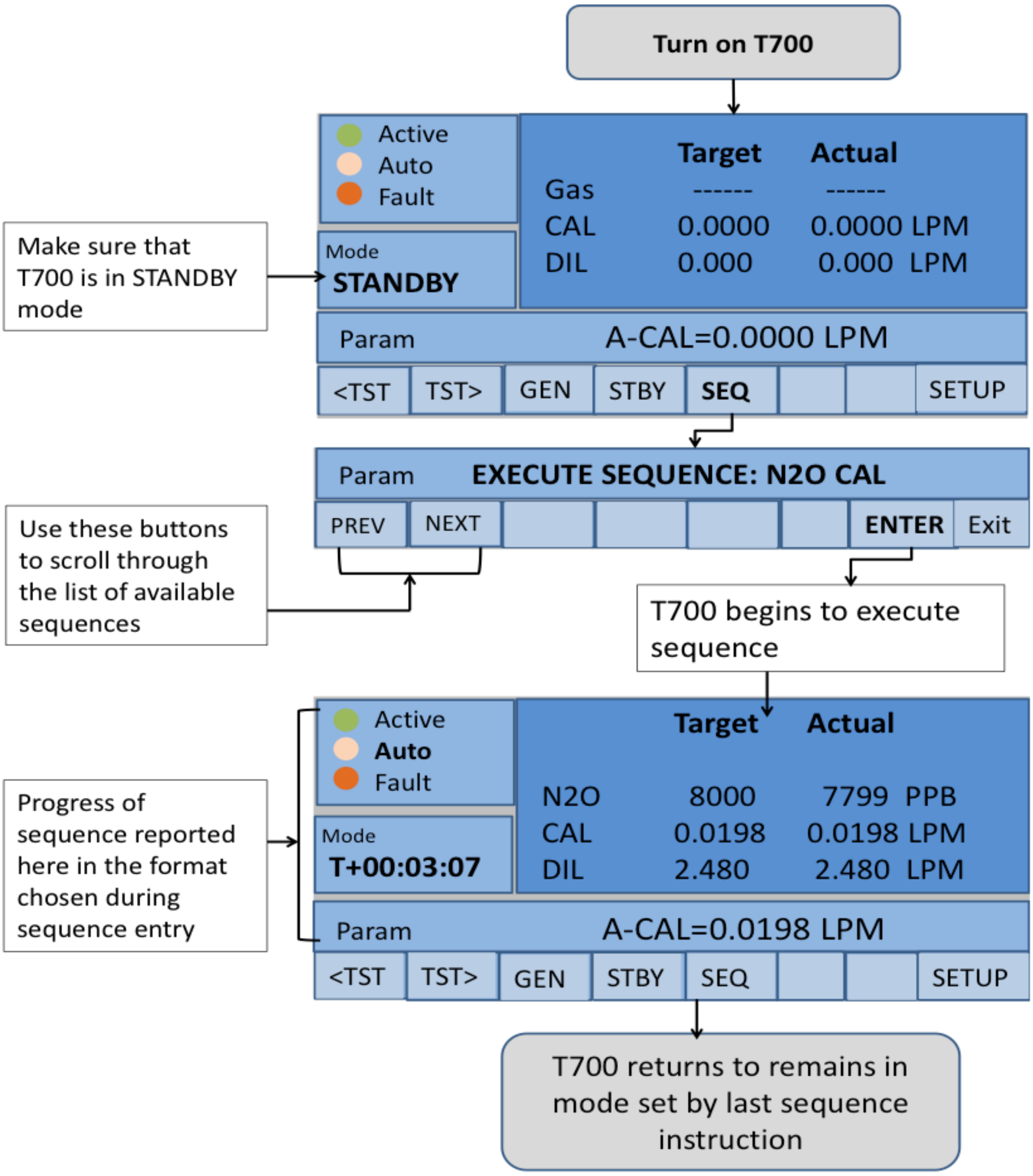


Figure 24. Activating an Automated Calibration Sequence from T700 Front Panel for N_2O

Activating a Sequence from the T700 Front Panel

To activate an already programmed sequence from the front panel, following steps shown in flow chart should be followed.

Make sure that the T700 is in STANDBY mode, then press SEQ and choose the sequence that needs to be run. For this system, there are three sequences, i.e., zero air (N_2), calibration gases NO and N_2O. Scroll the PREV or NEXT buttons to choose the sequence, then press ENTER. Thereafter, the T700 begins to execute the sequence. Each sequence runs for 12 minutes; 2 minutes for mixing gases, 5 minutes for high range calibration and 5 minutes for low range calibration.

Calibration Gases and Their Preparation

Standard and Diluent Gases

Ultra-pure nitrogen is used as zero air or diluent air. Standard gases used are 25 ppm NO in nitrogen and 1000 ppm N_2O in nitrogen. Those gases are supplied by Linde Bangladesh. The required concentrations of NO and N_2O were prepared using ultra-pure nitrogen as diluent gas. Dilution was made using the T700 Dynamic Dilution Calibrator as described below.

Preparation of Calibration Gases

The T700 Dynamic Dilution Calibrator generates calibration gas mixtures by mixing bottled source gases of known concentrations with a diluent gas (zero air).

The total flow rate is required to determine the flow rates of calibration and diluent gases. Typical sample flow rate for the analyzers are:

T200: 400-500 cc/min

T320U: 700-800 cc/min

The total flow rate = 1100 to 1300 cc/min = 1200 cc/min (average)

Total flow rate is multiplied by 1.5, i.e., 1200 x 1.5 = 1800 cc/min or 1.8 L/min.

Note: The minimum total flow should equal 150% of the flow requirements of all of the instruments to which the T700 will be supplying calibration gas.

Therefore, 1.8 L/min is considered as minimum required flow rate to calculate the flow rates of calibration and diluent gases.

The ranges of standard used for calibration
For T200 NO Analyzer,
Low NO: 50 ppb
High NO: 500 ppb

For T320U N2O Analyzer,
Low N_2O: 200 ppb
High N_2O: 10,000 ppb

It is decided to calibrate at 80% of range. Therefore, the low and high range for NO and N_2O analyzers are as follows.

T200 NO Analyzer: 40 and 400 ppb

T320U N2O Analyzer: 1600 and 8000 ppb

Gas Analyzers

This section briefly discusses N_2O and NO analyzers and their analysis principle.

N_2O Analyzer[4]

The T320U (Teledyne Advanced Pollution Control Instrumentation) Gas Filter Correlation Nitrous Oxide Analyzer is a microprocessor-controlled analyzer that determines the concentration of nitrous oxide (N_2O) in a sample gas drawn through the instrument. It uses a method based on the Beer-Lambert law, an empirical relationship that relates the absorption of light to the properties of the material through which the light is traveling over a defined distance. In this case, the light is infrared radiation (IR) traveling through a sample chamber filled with gas bearing a varying concentration of N_2O. It can analyze up to 200 ppm N_2O.

It requires that the sample and calibration gases be supplied at ambient atmospheric pressure in order to establish a stable gas flow through the sample chamber where the gases ability to absorb infrared radiation is measured.

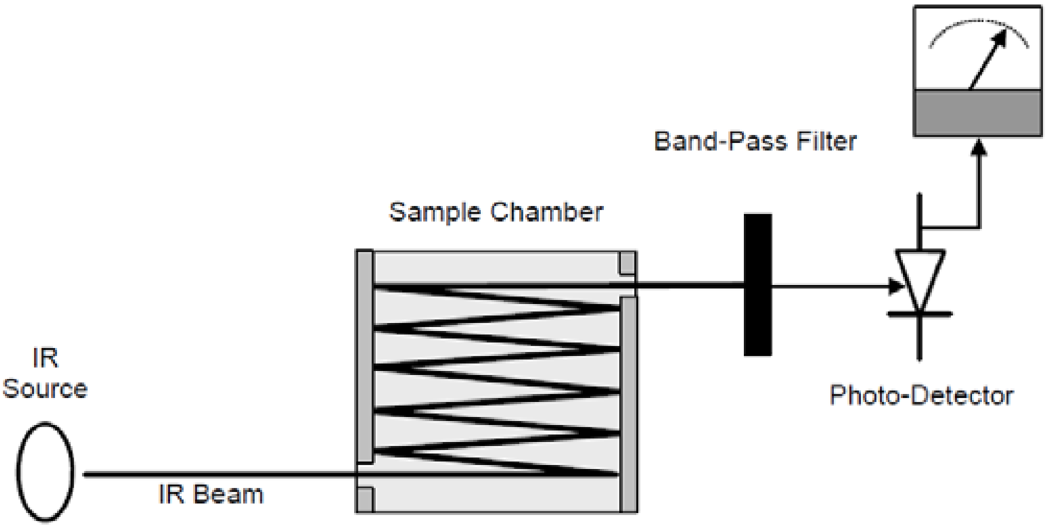


Figure 25. Measurement Fundamentals of T320U (N_2O Analyzer)

Measurement Method

Beer's Law

The basic principle by which the analyzer works is called the Beer-Lambert law or Beer's law. It defines how light of a specific wavelength is absorbed by a particular gas molecule over a certain distance. The mathematical relationship of these three parameters is shown in following equation.

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[4] This section is adapted from the 'Operating Manual: Model T300/T300M Carbon Monoxide Analyzer' available online at http://www.teledyne-api.com/manuals/06864B_T300_M.pdf, and Manual Addendum: Models T320 and T320U N_2O Analyzers (Addendum to T300/T300M Manual, PN 06864) available online at http://www.teledyne-api.com/manuals/06867B_T300U_Addendum.pdf.

$I = I_o e^{-\alpha Lc}$

Where,

I_o is the intensity of the light if there was no absorption.

I is the intensity with absorption.

L is absorption path; or the distance the light travels as it is being absorbed.

C is the concentration of the absorbing gas.

α is absorption coefficient that tells how well N2O absorbs light at the specific wavelength of interest.

Measurement Fundamentals

In the most basic terms, the T320U uses a high-energy heated element to generate a beam of broadband IR light with a known intensity (measured during instrument calibration). This beam is directed through multi-pass cell filled with sample gas. The sample cell uses a mirror at each end to reflect the IR beam back and forth through the sample gas a number of times (Figure 25).

The total length that the reflected light travels is directly related to the intended sensitivity of the instrument. The lower the concentrations the instrument is designed to detect the longer the light path must be in order to create detectable levels of attenuation.

Upon exiting the sample cell, the beam shines through a band-pass filter that allows only light at a wavelength of 4.7 µm to pass. Finally, the beam strikes a solid-state photo-detector that converts the light signal into a modulated voltage signal representing the attenuated intensity of the beam.

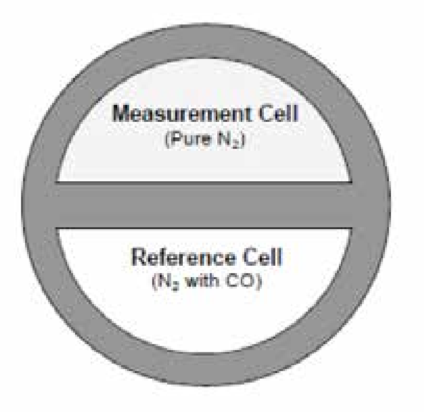


Figure 26. Gas Filter Correlation (GFC) Wheel Used to Absorb Water Vapor in IR path of T320U

Gas Filter Correlation

It is to be mentioned that water vapor also absorbs light at 4.7 µm. To overcome the interfering effects of water vapor, the T320U adds another component to the IR light path called a Gas Filter Correlation (GFC) Wheel.

A GFC Wheel is a metallic wheel into which two chambers are carved. The chambers are sealed on both sides with material transparent to 4.7 µm IR radiation creating two airtight cavities. Each cavity is mainly filled with composed gases. One cell is filled with pure N_2 (the measurement cell). The other is filled with a combination of N_2 and a high concentration of N_2O (the reference cell).

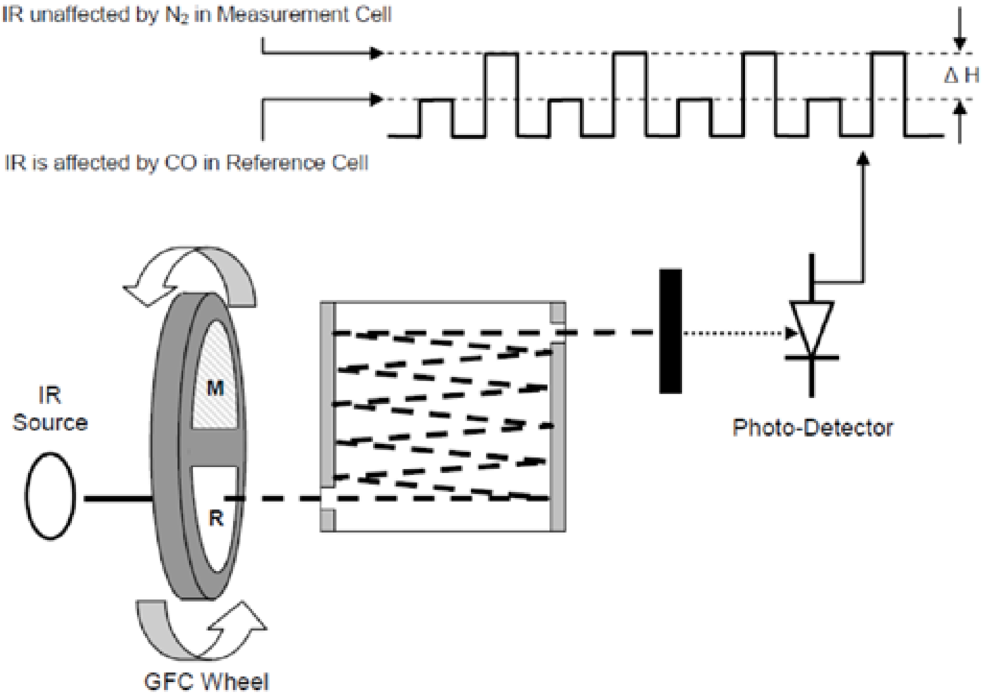


Figure 27. Measurement Fundamentals of N_2O Analyzer with GFC Wheel (CO should be replaced with N_2O)

As the GFC Wheel spins, the IR light alternately passes through the two cavities. When the beam is exposed to the reference cell, the N_2O in the gas filter wheel strips the beam of most of the IR at 4.58 µm. When the light beam is exposed to the measurement cell, the N_2 in the filter wheel does not absorb IR light. This causes a fluctuation in the intensity of the IR light striking the photo-detector, which results in the output of the detector resembling a square wave.

The Measure Reference Ratio

The T320U determines the amount of N_2O in the sample chamber by computing the ratio between the peak of the measurement pulse (N_2O MEAS) and the peak of the reference pulse (N_2O REF).

If no gases exist in the sample chamber that absorb light at 4.58 µm, the high concentration of N_2O in the gas mixture of the reference cell will attenuate the intensity of the IR beam by 60% giving a M/R ratio of approximately 2.4:1.

Adding N_2O to the sample chamber causes the peaks corresponding to both cells to be attenuated by a further percentage. Since the intensity of the light passing through the measurement cell is greater, the effect of this additional attenuation is greater. This causes N_2O MEAS to be more sensitive to the presence of N_2O in the sample chamber than N_2O REF and the ratio between them (M/R) to move closer to 1:1 as the concentration of N_2O in the sample chamber increases.

Once the T320U has computed this ratio, a look-up table is used, with interpolation, to linearize the response of the instrument. This linearized concentration value is combined with calibration SLOPE and OFFSET values to produce the N_2O concentration which is then normalized for changes in sample pressure.

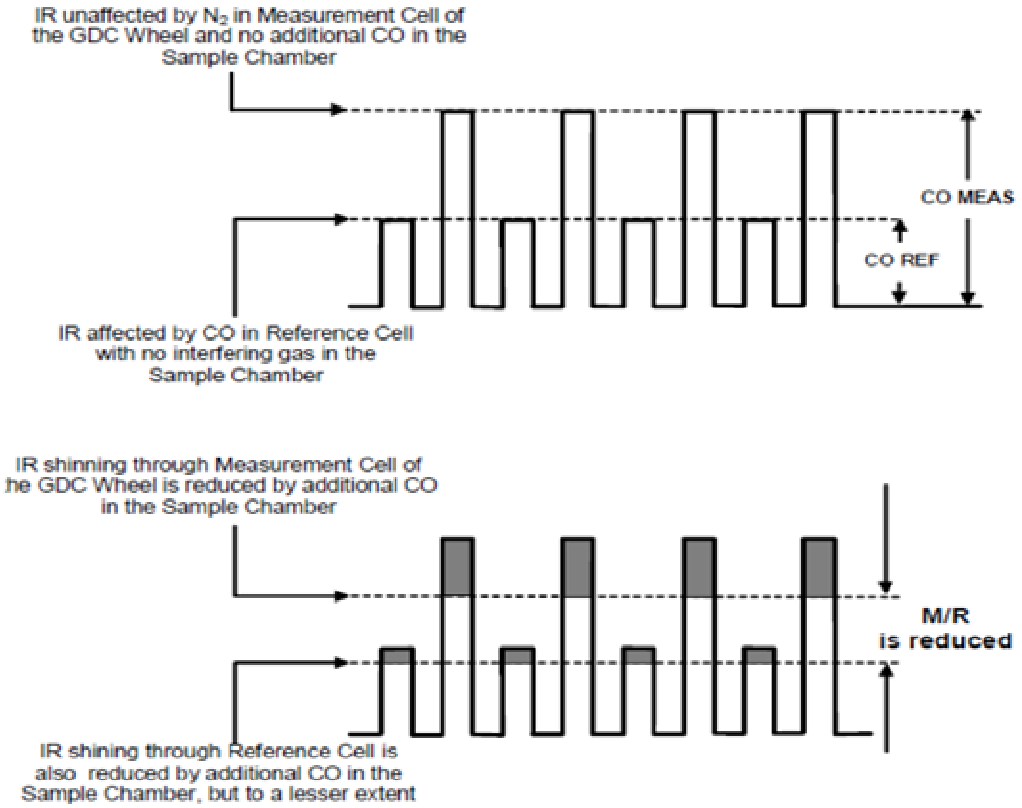


Figure 28. Effect of N_2O in the Sample on N_2O MEAS and N_2O REF (CO should be replaced with N_2O)

Interference and Signal to Noise Reaction

If an interfering gas, such as H_2O vapor, is introduced into the sample chamber, flue spectrum of the IR beam is changed in a way that is identical for both the reference and the measurement cells; but without changing the ratio between the peak heights of N_2O MEAS and N_2O REF. In effect, the difference between the peak heights remains the same.

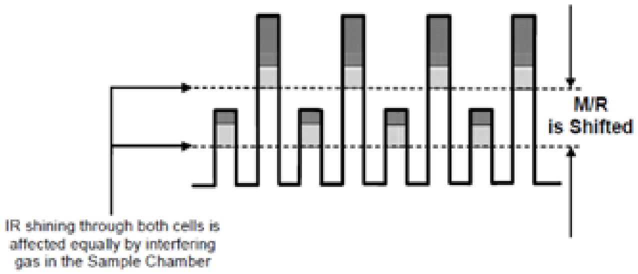
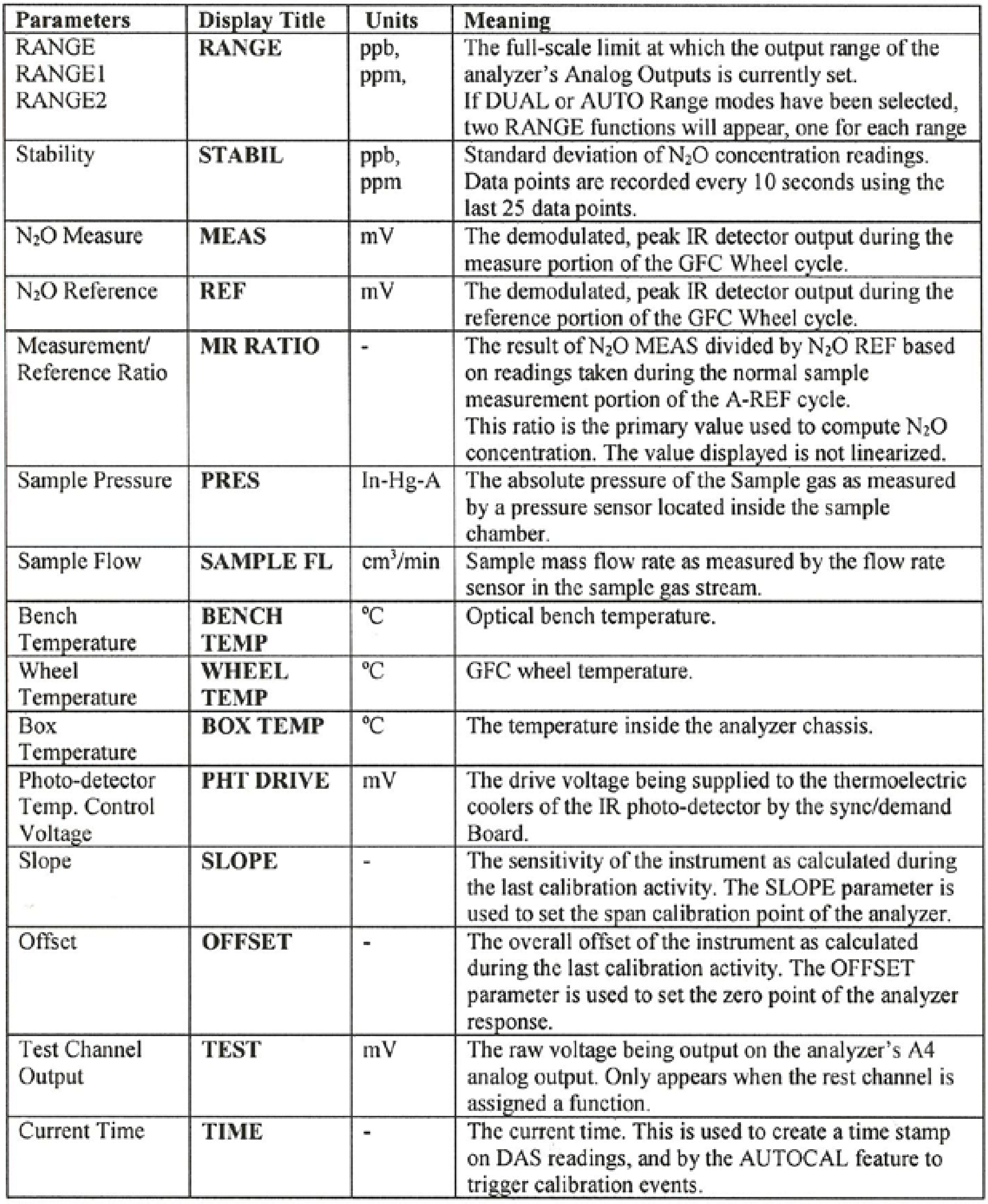


Figure 29. Effects of Interfering Gas on N_2O MEAS and N_2O REF

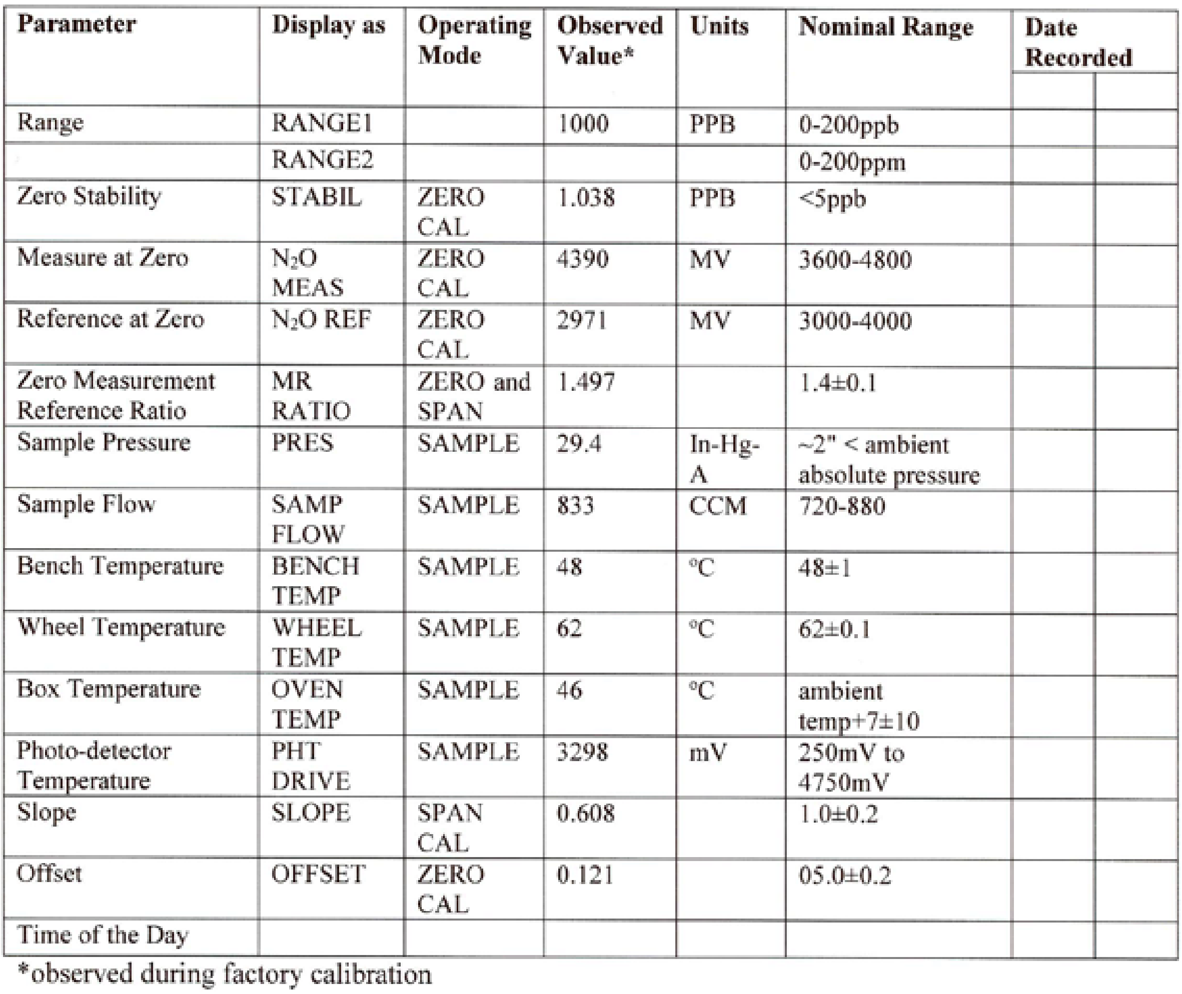
Table 7. List of Test Functions and Their Definition for T320 N_2O Analyzer



Parameters	Display Title	Units	Meaning
RANGE RANGE1 RANGE2	**RANGE**	ppb, ppm,	The full-scale limit at which the output range of the analyzer's Analog Outputs is currently set. If DUAL or AUTO Range modes have been selected, two RANGE functions will appear, one for each range
Stability	**STABIL**	ppb, ppm	Standard deviation of N_2O concentration readings. Data points are recorded every 10 seconds using the last 25 data points.
N_2O Measure	**MEAS**	mV	The demodulated, peak IR detector output during the measure portion of the GFC Wheel cycle.
N_2O Reference	**REF**	mV	The demodulated, peak IR detector output during the reference portion of the GFC Wheel cycle.
Measurement/ Reference Ratio	**MR RATIO**	-	The result of N_2O MEAS divided by N_2O REF based on readings taken during the normal sample measurement portion of the A-REF cycle. This ratio is the primary value used to compute N_2O concentration. The value displayed is not linearized.
Sample Pressure	**PRES**	In-Hg-A	The absolute pressure of the Sample gas as measured by a pressure sensor located inside the sample chamber.
Sample Flow	**SAMPLE FL**	cm^3/min	Sample mass flow rate as measured by the flow rate sensor in the sample gas stream.
Bench Temperature	**BENCH TEMP**	°C	Optical bench temperature.
Wheel Temperature	**WHEEL TEMP**	°C	GFC wheel temperature.
Box Temperature	**BOX TEMP**	°C	The temperature inside the analyzer chassis.
Photo-detector Temp. Control Voltage	**PHT DRIVE**	mV	The drive voltage being supplied to the thermoelectric coolers of the IR photo-detector by the sync/demand Board.
Slope	**SLOPE**	-	The sensitivity of the instrument as calculated during the last calibration activity. The SLOPE parameter is used to set the span calibration point of the analyzer.
Offset	**OFFSET**	-	The overall offset of the instrument as calculated during the last calibration activity. The OFFSET parameter is used to set the zero point of the analyzer response.
Test Channel Output	**TEST**	mV	The raw voltage being output on the analyzer's A4 analog output. Only appears when the rest channel is assigned a function.
Current Time	**TIME**	-	The current time. This is used to create a time stamp on DAS readings, and by the AUTOCAL feature to trigger calibration events.

Thus, the difference in the peak heights and the resulting MR ratio is only due to N_2O and not to interfering gases. In this ease, GFC rejects the effects of interfering gases and so that the analyzer responds only to the presence of N_2O.

Table 8. List of Test Functions Including Observed Value During Final Calibration in the Factory



Parameter	Display as	Operating Mode	Observed Value*	Units	Nominal Range	Date Recorded	
Range	RANGE1		1000	PPB	0-200ppb		
	RANGE2				0-200ppm		
Zero Stability	STABIL	ZERO CAL	1.038	PPB	<5ppb		
Measure at Zero	N_2O MEAS	ZERO CAL	4390	MV	3600-4800		
Reference at Zero	N_2O REF	ZERO CAL	2971	MV	3000-4000		
Zero Measurement Reference Ratio	MR RATIO	ZERO and SPAN	1.497		1.4±0.1		
Sample Pressure	PRES	SAMPLE	29.4	In-Hg-A	~2" < ambient absolute pressure		
Sample Flow	SAMP FLOW	SAMPLE	833	CCM	720-880		
Bench Temperature	BENCH TEMP	SAMPLE	48	°C	48±1		
Wheel Temperature	WHEEL TEMP	SAMPLE	62	°C	62±0.1		
Box Temperature	OVEN TEMP	SAMPLE	46	°C	ambient temp+7±10		
Photo-detector Temperature	PHT DRIVE	SAMPLE	3298	mV	250mV to 4750mV		
Slope	SLOPE	SPAN CAL	0.608		1.0±0.2		
Offset	OFFSET	ZERO CAL	0.121		05.0±0.2		
Time of the Day							

*observed during factory calibration

Functional Checks

After the analyzer's components have warmed up for at least 60 minutes, verify that the software properly supports any hardware options that were installed. Then check to make sure that the analyzer is functioning within allowable operating parameters. A series of TEST functions is available for

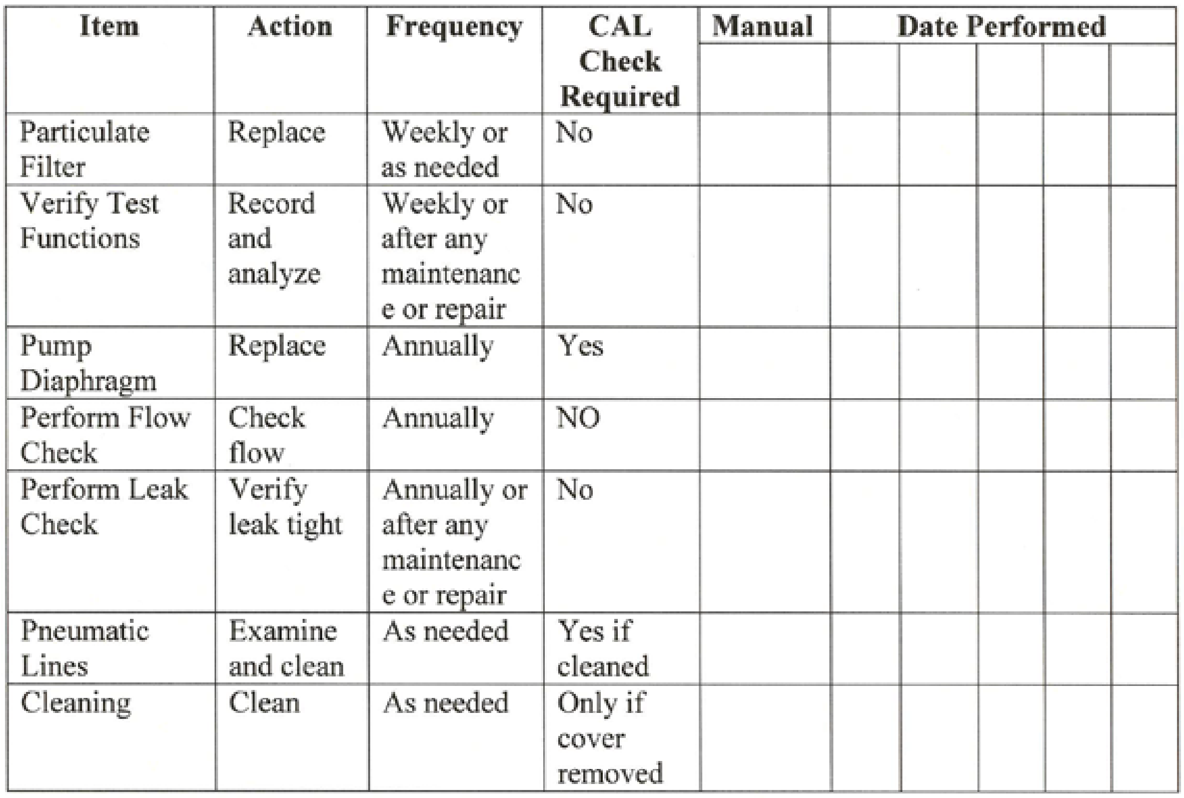
viewing at the front panel whenever the analyzer is at the SAMPLE mode. To view the test functions, press on of the <TST TST> buttons repeatedly in either direction. The enclosed 'Final Test and Validation Data Sheet' list these values as they were before the instrument left the factory.

Remember that until the unit has completed its warm-up these parameters may not have stabilized.

These parameters provide information about the present operating status of the instrument, diagnosing performance problems with the analyzer, and are useful during troubleshooting.
Table 7 shows the available test functions and their definition. Values of test functions observed during final calibration in the factory and their nominal ranges are shown in Table 8. Test functions should be recorded after each calibration.

Maintenance Schedule

Table 9. Maintenance Schedule for T320U N_2O Analyzer



Item	Action	Frequency	CAL Check Required	Manual	Date Performed				
Particulate Filter	Replace	Weekly or as needed	No						
Verify Test Functions	Record and analyze	Weekly or after any maintenance or repair	No						
Pump Diaphragm	Replace	Annually	Yes						
Perform Flow Check	Check flow	Annually	NO						
Perform Leak Check	Verify leak tight	Annually or after any maintenance or repair	No						
Pneumatic Lines	Examine and clean	As needed	Yes if cleaned						
Cleaning	Clean	As needed	Only if cover removed						

Predicting Failures using the Test Functions

The test functions can be used to predict failures by looking at how their values change over time (Table 10). Initially it may be useful to compare the state of these Test Functions during final calibration performed in the factory (Table 8). The following table provides some predictive information based on Test Functions. Based on the test Function, required troubleshooting and repair can be done. See the T320 Operating Manual for detail troubleshooting and Repair.

NO Analyzer[5]

The T200 Nitrogen Oxides Analyzer is a microprocessor-controlled instrument that determines the concentration of nitric oxide (NO), total nitrogen oxides (NOx, the sum of NO and NO_2) and nitrogen dioxide (NO_2) in a sample gas drawn through the instrument.

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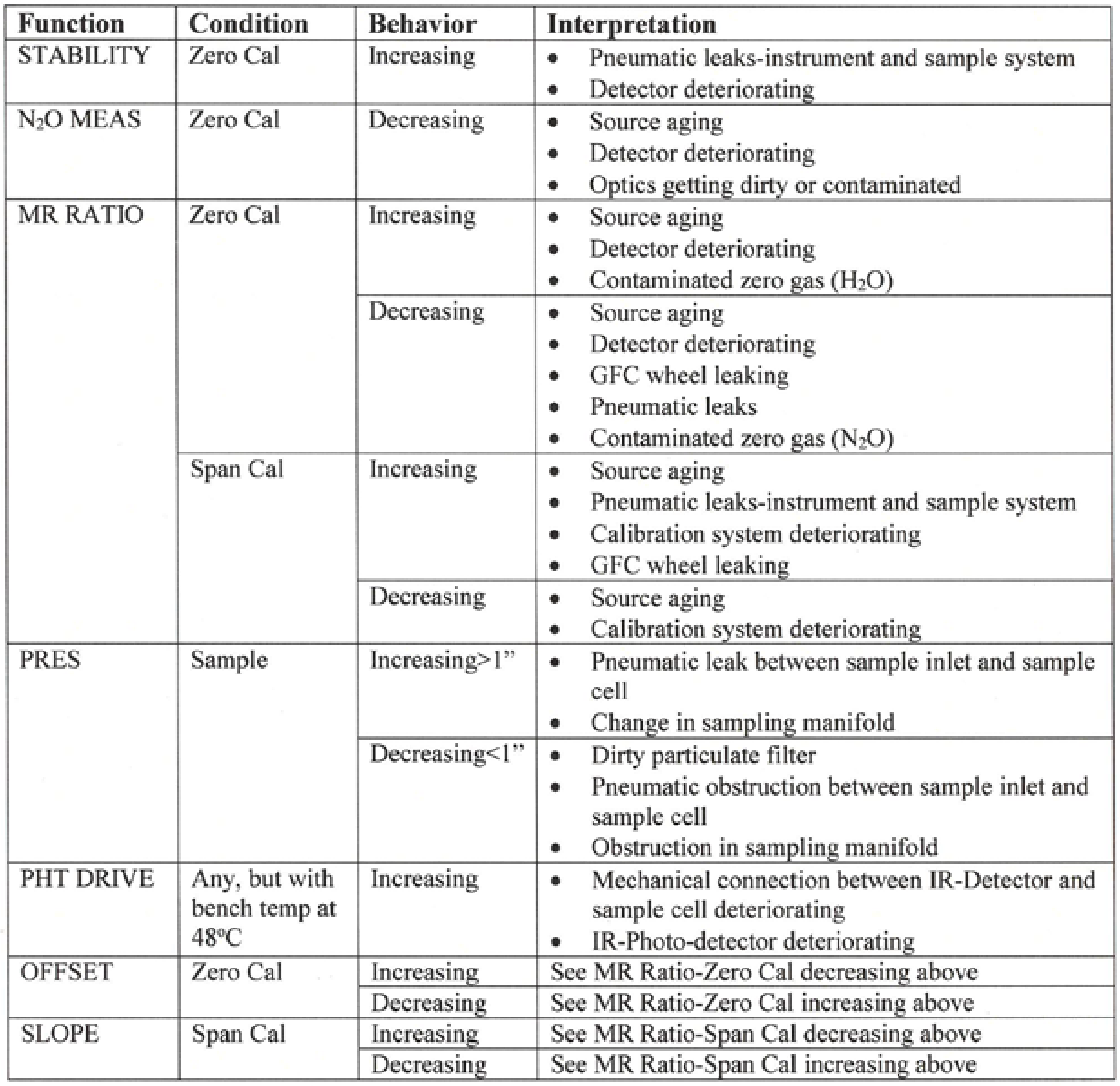
[5] This section is adapted from the 'Operating Manual: Model T200 Nitrogen Oxide Analyzer' available online at http://www.teledyne-api.com/manuals/06858C_T200.pdf

Table 10. Predictive Use of Test Functions (T320U N_2O Analyzer)



Function	Condition	Behavior	Interpretation
STABILITY	Zero Cal	Increasing	• Pneumatic leaks-instrument and sample system • Detector deteriorating
N_2O MEAS	Zero Cal	Decreasing	• Source aging • Detector deteriorating • Optics getting dirty or contaminated
MR RATIO	Zero Cal	Increasing	• Source aging • Detector deteriorating • Contaminated zero gas (H_2O)
		Decreasing	• Source aging • Detector deteriorating • GFC wheel leaking • Pneumatic leaks • Contaminated zero gas (N_2O)
	Span Cal	Increasing	• Source aging • Pneumatic leaks-instrument and sample system • Calibration system deteriorating • GFC wheel leaking
		Decreasing	• Source aging • Calibration system deteriorating
PRES	Sample	Increasing>1”	• Pneumatic leak between sample inlet and sample cell • Change in sampling manifold
		Decreasing<1”	• Dirty particulate filter • Pneumatic obstruction between sample inlet and sample cell • Obstruction in sampling manifold
PHT DRIVE	Any, but with bench temp at 48°C	Increasing	• Mechanical connection between IR-Detector and sample cell deteriorating • IR-Photo-detector deteriorating
OFFSET	Zero Cal	Increasing	See MR Ratio-Zero Cal decreasing above
		Decreasing	See MR Ratio-Zero Cal increasing above
SLOPE	Span Cal	Increasing	See MR Ratio-Span Cal decreasing above
		Decreasing	See MR Ratio-Span Cal increasing above

- It requires that sample and calibration gases be supplied at ambient atmospheric pressure in order to establish a constant gas flow through the reaction cell where the sample gas is exposed to ozone (O_3), initiating a chemical reaction that gives off light (hv).
- The instrument measures the amount of chemiluminescence to determine the amount of NO in the sample gas.

Measurement Principle

1.Chemiluminescence creation in the T200 Reaction Cell

The T200 measures the amount of NO present in a gas by detecting the chemiluminescence that occurs when nitrogen oxide (NO) is exposed to ozone (O_3). This reaction is a two-step process:
In the first step, one molecule of NO and one molecule of O_3 collide and chemically react to produce one molecule of oxygen (O_2) and one molecule of nitrogen dioxide (NO_2). Some of the NO_2 molecules created by this reaction retain excess energy from the collision and exist in an excited state, where one of

the electrons of the NO_2 molecule resides in a higher energy state than normal (denoted by an asterisk in the following equation).

$NO + O_3 \rightarrow NO_2{}^* + O_2$

The second step occurs because the laws of thermodynamics require that systems seek the lowest stable energy state available, therefore the excited NO_2 molecule quickly returns to its ground state, releasing the excess energy. This release takes the form of a quantum of light (hv). The distribution of wavelengths for these quanta range between 600 and 3000 nm with a peak at about 1200 nm.

$NO_2{}^* \rightarrow NO_2 + hv_{1200\ nm}$

All things being constant (temperature, pressure, amount of ozone present, etc.), the relationship between the amount of NO present in the reaction cell and the amount of light emitted from the reaction is very linear. If more NO is present, more IR light is produced. By measuring the amount of IR light produced with a sensor sensitive in the near-infrared spectrum the amount of NO present can be determined.

In addition, sometimes the excited NO_2 collides with other gaseous molecules in the reaction cell chamber or even the molecules of the reaction cell walls and transfers its excess energy to this collision partner (represented by M in the equation below) without emitting any light at all. In fact, by far the largest portion of the excited NO_2 returns to the ground state this way, leaving only a few percent yield of usable chemiluminescence.

$NO_2{}^* + \mathbf{M} \rightarrow \mathbf{NO_2} + \mathbf{M}$

The probability of a collision between the $NO_2{}^*$ molecule and a collision partner M increases proportionally with the reaction cell pressure. This non-radiating collision with the $NO_2{}^*$ molecules is usually referred to as *third body quenching*, an unwanted process.

Even under the best conditions only about 20% of the NO_2 that is formed by the reaction (described in the 1^{st} equation) is in the excited state. In order to maximize chemiluminescence, the reaction cell is maintained at reduced pressure (thereby reducing the amount of available collision partners) and is supplied with a large, constant excess of ozone (about 3000-5000 ppm) from the internal ozone generator.

2.Chemiluminescence detection in the T200 Reaction Cell

The Photo Multiplier Tube

The T200 uses a special kind of vacuum tube called a photo-multiplier tube (PMT), to detect the amount of light created by the NO and O_3 reaction in the reaction cell.

Photons enter the PMT and strike a negatively charged photo cathode causing it to emit elections. These electrons are accelerated by an applied high voltage and multiplied through a sequence of similar acceleration steps (dynodes) until a useable current signal is generated. The more light present (in this case photons given off by the chemiluminescent reaction described above), the more current is produced. Therefore the more NO present in the reaction cell the more current is produced by the PMT.

The current produced by the PMT is converted to a voltage and amplified by the preamplifier board and then communicated to the T200's CPU via the A → D converter circuitry on the analyzer.

Optical Filter

A high pass optical filter, only transparent to wavelengths of light above 645 nm, placed between the reaction cell and the PMT (Figure 30) in conjunction with the response characteristics of the PMT creates a very narrow window of wavelengths of light to which the T200 will respond.

The narrowness of this band of sensitivity allows the T200 to ignore extraneous light and radiation that might interfere with the T200's measurement. For instance, some oxides of sulfur can also be chemiluminescent emitters when in contact with O_3 but give off light at much shorter wavelengths (usually around 260 nm to 480 nm)

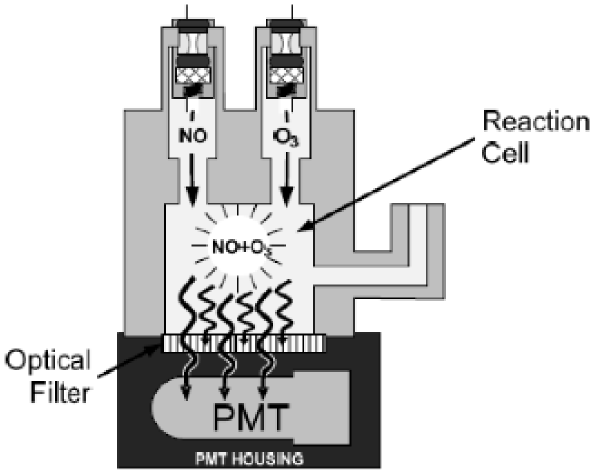


Figure 30. Reaction Cell with PMT Tube and Optical Filter of T200

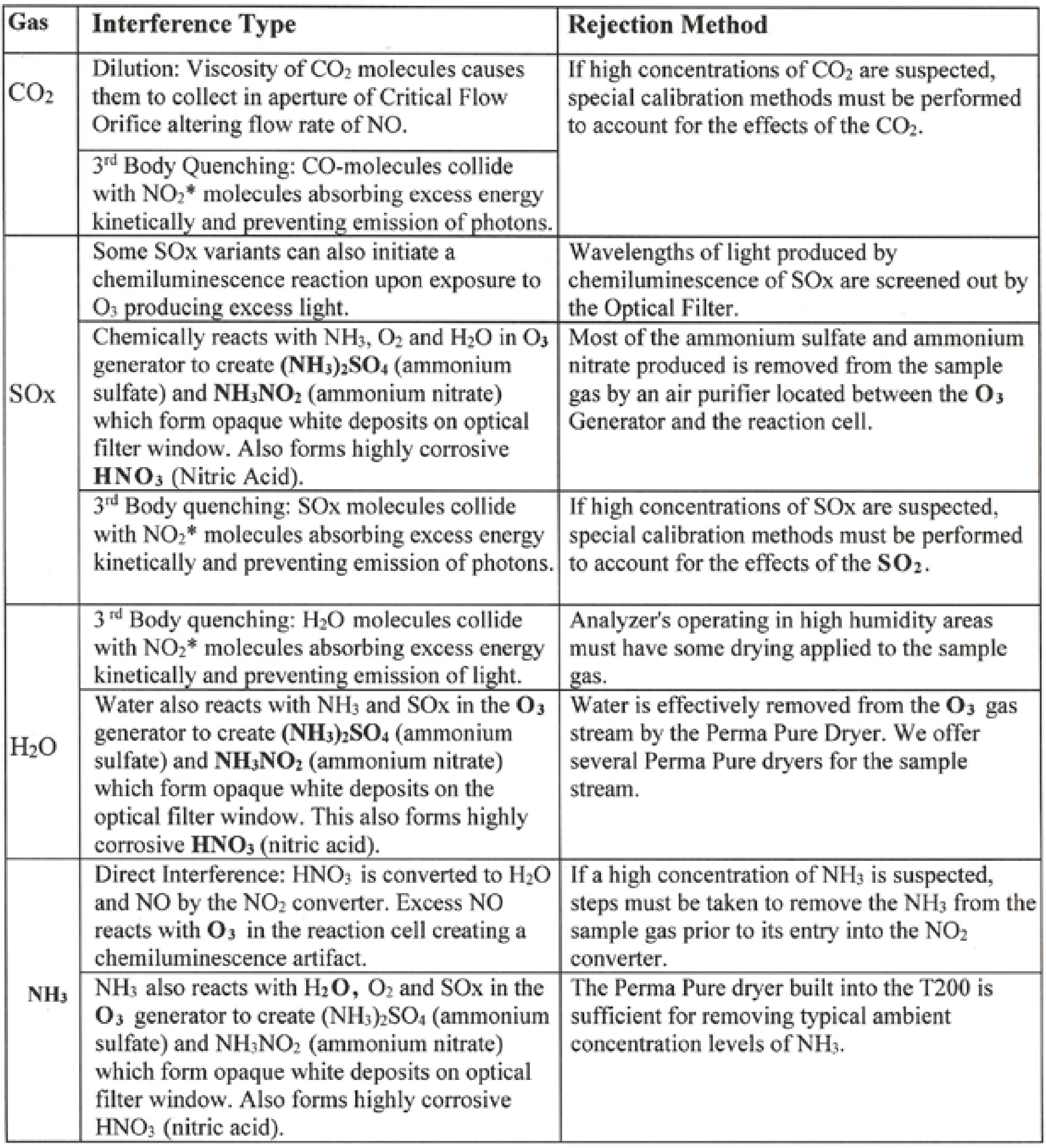
3. *Auto Zero*

Inherent in the operation of any PMT is a certain amount of noise. This is due to a variety of factors such as black body infrared radiation given off by the metal components of the reaction cell, unit to unit variations in the PMT units and even the constant universal background radiation that surrounds us at all times. In order to reduce this amount of noise and offset, the PMT is kept at a constant 7°C (45°F) by a Thermo-Electric Cooler (TEC).

4. *Measurement Interferences*

It should be noted that the chemiluminescence method is subject to interferences from a number of sources. The T200 has been successfully tested for its ability to reject interference from most of these sources. Table 11 lists the most common types of interferents that could affect the performance of T200.

Table 11. List of Interferents in T200 Nitrogen Oxide Analyzer



Gas	Interference Type	Rejection Method
CO_2	Dilution: Viscosity of CO_2 molecules causes them to collect in aperture of Critical Flow Orifice altering flow rate of NO.	If high concentrations of CO_2 are suspected, special calibration methods must be performed to account for the effects of the CO_2.
	3rd Body Quenching: CO-molecules collide with NO_2* molecules absorbing excess energy kinetically and preventing emission of photons.	
SOx	Some SOx variants can also initiate a chemiluminescence reaction upon exposure to O_3 producing excess light.	Wavelengths of light produced by chemiluminescence of SOx are screened out by the Optical Filter.
	Chemically reacts with NH_3, O_2 and H_2O in O_3 generator to create **$(NH_3)_2SO_4$** (ammonium sulfate) and **NH_3NO_2** (ammonium nitrate) which form opaque white deposits on optical filter window. Also forms highly corrosive **HNO_3** (Nitric Acid).	Most of the ammonium sulfate and ammonium nitrate produced is removed from the sample gas by an air purifier located between the **O_3** Generator and the reaction cell.
	3rd Body quenching: SOx molecules collide with NO_2* molecules absorbing excess energy kinetically and preventing emission of photons.	If high concentrations of SOx are suspected, special calibration methods must be performed to account for the effects of the **SO_2**.
H_2O	3rd Body quenching: H_2O molecules collide with NO_2* molecules absorbing excess energy kinetically and preventing emission of light.	Analyzer's operating in high humidity areas must have some drying applied to the sample gas.
	Water also reacts with NH_3 and SOx in the **O_3** generator to create **$(NH_3)_2SO_4$** (ammonium sulfate) and **NH_3NO_2** (ammonium nitrate) which form opaque white deposits on the optical filter window. This also forms highly corrosive **HNO_3** (nitric acid).	Water is effectively removed from the **O_3** gas stream by the Perma Pure Dryer. We offer several Perma Pure dryers for the sample stream.
NH_3	Direct Interference: HNO_3 is converted to H_2O and NO by the NO_2 converter. Excess NO reacts with **O_3** in the reaction cell creating a chemiluminescence artifact.	If a high concentration of NH_3 is suspected, steps must be taken to remove the NH_3 from the sample gas prior to its entry into the NO_2 converter.
	NH_3 also reacts with H_2**O**, O_2 and SOx in the **O_3** generator to create $(NH_3)_2SO_4$ (ammonium sulfate) and NH_3NO_2 (ammonium nitrate) which form opaque white deposits on optical filter window. Also forms highly corrosive HNO_3 (nitric acid).	The Perma Pure dryer built into the T200 is sufficient for removing typical ambient concentration levels of NH_3.

i) **Direct Interference**

Some gases can directly alter the amount of light detected by the PMT due to chemiluminescence the reaction cell. This can either be a gas that undergoes chemiluminescence by reacting with O_3 in the reaction cell or a gas that reacts with other compounds and produces excess NO upstream of the reaction cell.

ii) **Third Body Quenching**

As described by the equation above ($NO_2^* + \mathbf{M} \rightarrow \mathbf{NO_2} + \mathbf{M}$), other molecules in the reaction cell can collide with the excited NO_2^*, causing the excited NO_2^* to return to its ground state without releasing a photon of light. This is known as third party quenching.

Quenching is an unwanted phenomenon and the extent to which it occurs depends on the properties of the collision partner.

- Larger, more polarized molecules such as H_2O and CO_2 are the most significant quenching interferents of NO chemiluminescence.
    - ▶ The influence of water vapor on the T200 measurement can be eliminated with an optional, internal sample gas dryer.
    - ▶ The interference of varying CO_2 amounts at low concentrations (less that 0.5%) is negligible.
    - ▶ In case with excessively high CO_2 concentrations (larger than 0.5%), the effect can be calibrated out by using calibration gases with a CO_2 content equal to the measured air.
    - ▶ Only very high and highly variable CO_2 concentrations will then cause a measurable interference. For those applications, it is recommended to use other analyzer models.
- Smaller less polar and electronically "harder" molecules such as N_2 and O_2 can cause interference of this type as well; however, the concentrations of N_2 and O_2 are virtually constant in ambient air measurements, hence provide a constant amount of quenching that is accounted for in the calibration of the instrument.

iii) Light Leaks

The T200 sensitivity curve includes a small portion of the visible light spectrum; therefore, it is important to ensure that the reaction cell is completely sealed with respect to light. To ensure this:

- All pneumatic tubing leading into the reaction cell is opaque in order to prevent light from entering the cell.
- Light penetration is prevented by stainless steel filters and orifices.

iv) **Reaction Cell Temperature Control**

The stability of the chemiluminescence reaction between NO and O_3 can be affected by changes in the temperature and pressure of the O_3 and sample gases in the reaction cell. In order to reduce temperature effects, the reaction cell is maintained at a constant 50°C, just above the high end of the instrument's operation temperature range.

Pneumatic Operation

Regular leak checks should be performed on the analyzer (see maintenance schedule in T200 Operating Manual).

Note: The sample gas is the most critical flow path in the analyzer. At any point before and in the reaction cell, the integrity of the sample gas cannot be compromised. Therefore, it is important that the sample air flow system is both leak tight and not pressurized over ambient pressure.

1. ***Sample Gas Flow***

The gas flow for the T200 is created by a pump that is pneumatically downstream from the rest of the instrument's components. An external pump is pneumatically connected to the analyzers exhaust port located on the rear panel.

In this setup, the pump is connected with external ozone destruct.

The pump creates a vacuum of approximately 5 in-Hg-A at one standard liter/minute, which is provided to various pneumatic components by a vacuum manifold located just in front of the rear panel (Figure 31).

2. *Flow Rate Control: Critical Flow Orifice*

The sample gas flow in the T200 is created via the use of several flow control assemblies including 'a critical flow orifice,' 'two o-rings,' 'a sintered filter' and 'a spring.'

The most important component of each flow control assembly is the critical flow orifice. Critical flow orifices are a simple means to regulate stable gas flow rates. They operate without moving parts by taking advantage of the laws of fluid dynamics. By restricting the flow of gas through the orifice, a pressure differential is created. This pressure differential created by the analyzer's external pump draws the gas through the orifice.

The actual flow rate of gas through the orifice (volume of gas per unit of time), depends on the size and shape of the aperture in the orifice. The larger the hole, the more gas molecules (moving at the speed of sound) that pass through the orifice.

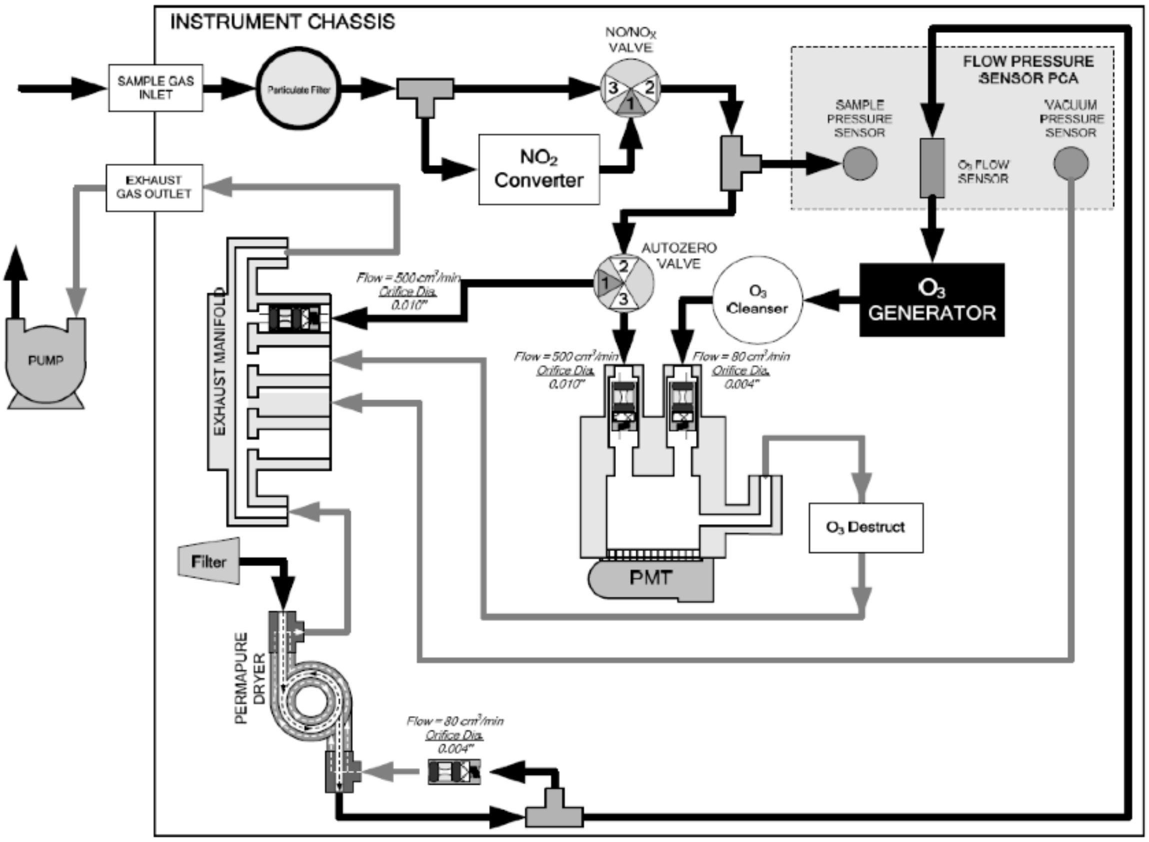


Figure 31. Internal Pneumatic Layout for T200 with External Pump

3. *Ozone Gas Generation and Air Flow*

The excess ozone needed for reaction with NO in the reaction cell is generated inside the analyzer because of the instability and toxicity of ozone. Besides the ozone generator itself, this requires a dry air supply and filtering of the gas before it is introduced into the reaction cell.

Due to its toxicity and aggressive chemical behavior, ozone must also be removed from the gas stream before it can be vented through exhaust outlet.

The O_3 Generator

The T200 uses a dual-dielectric, Corona Discharge (CD) tube for creating its O_3, which is capable of producing high concentrations of ozone efficiently and with low excess heat (Figure 32). The primary component of the generator is a glass tube with hollow walls of which the outermost and innermost surfaces are coated with electrically conductive material.

Air flows through the glass tube, between the two conductive coatings, in effect creating a capacitor with the air and glass acting as the dielectric. The layers of glass also separate the conductive surfaces from the air stream to prevent reaction with the O_3. As the capacitor charges and discharges, electrons are created and accelerated across the air gap and collide with the O_2 molecules in the air stream splitting them into elemental oxygen.

Some of these oxygen atoms recombine with O_2 to O_3. The quantity of ozone produced is dependent on factors such as the voltage and frequency of the alternating current applied to the CD cells. When enough high-energy electrons are produced to ionize the O_2 molecules, a light emitting, gaseous plasma is formed which is commonly referred to as a corona, hence the name corona discharge generator.

Ozone Generator Dry Air Supply

Ambient air usually contains enough water vapor to greatly diminish the yield of ozone produced by the ozone generator. Water also reacts with chemicals inside the O_3 Generator to produce caustic substances such as ammonium sulfate or highly corrosive nitric acid that will damage the optical filter located between the reaction cell and the PMT.

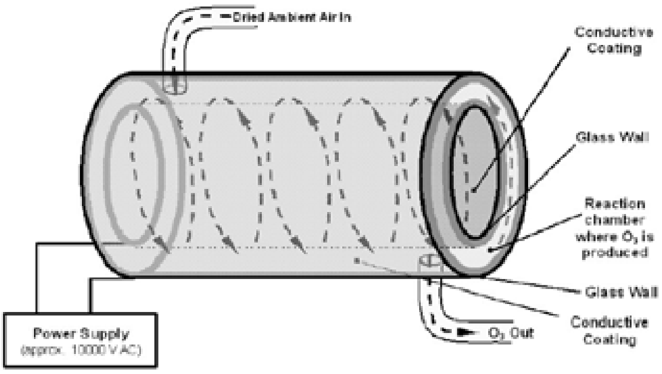


Figure 32. Ozone Generator Principle in T200 NO Analyzer

To prevent this, the air supply for the O_3 generator is dried using a special Perma Pure® single tube permeation dryer. The dryer consists of a single tube of Nafion® that is mounted within an outer, flexible plastic tube. Nafion® is a co-polymer that absorbs water very well but not most other chemicals. As gas flows though the inner Nafion® tube, water vapor is absorbed into the membrane walls. The absorbed water is transported through the membrane wall and evaporated into the dry purge gas flowing through the outer tube, countercurrent to the gas in the inner tube.

The process by which the water vapor molecules are collected and transported through Nafion® material is called per-evaporation and is driven by the humidity gradient between the inner and outer tubes as well as the flow rates and pressure difference between inner and outer tubing. Unlike micro-porous membrane permeation, which transfers water through a relatively slow diffusion process, per-evaporation is a simple kinetic reaction. Therefore, the drying process occurs quickly, typically within milliseconds.

Because this chemical reaction is based on hydrogen tends between the water molecule and the Nafion® material, most other chemical components of the gas to be dried are usually unaffected. Specifically, the gases of interest for the T200, NO and NO_2 do not get absorbed and pass the dryer unaltered.

On the other hand, other small polar gases that are capable of hydrogen bonds such as ammonia (NH_3) can be absorbed this way, too. This is an advantage since gases such as NH_3 can cause interference for the measurement of NOx, NO and NO_2.

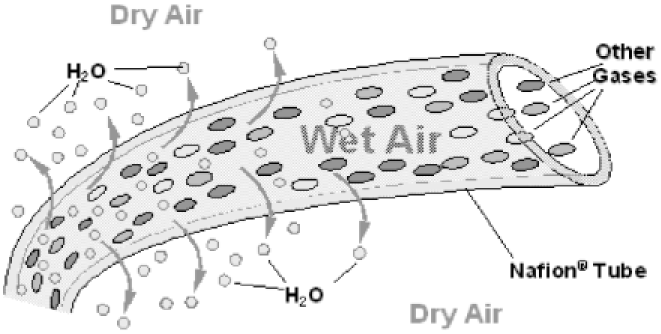


Figure 33. Semi-Permeable Membrane Drying Process in T200 NO Analyzer

To provide a dry purge gas for the outer side of the Nation tube, the T200 returns some of the dried air from the inner tube to the outer tube. This means that any time the analyzer is turned on after having been OFF for 30 minutes or more, the humidity gradient between the inner and outer tubes is not very large, making the dryer's efficiency low. Since it takes a certain amount of time for the humidity gradient to become large enough for the Perma Pure® Dryer operate efficiently, in such cold start cases the O3 generator is not turned on until 30 minutes has passed in order to ensure that it is not operating until its air supply is properly dry. During this 30-minute duration, the O_3 GEN OVERRIDE menu displays "TMR" on the front panel screen.

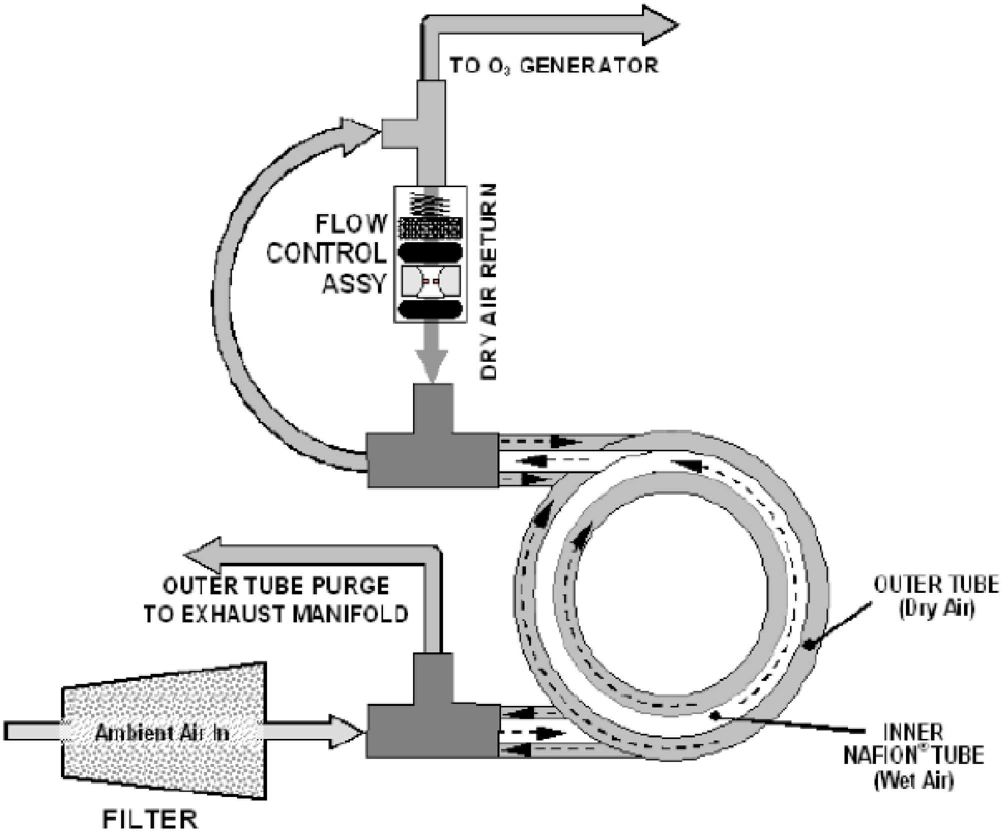


Figure 34. T200 Perma Pure® Dryer for T200 NO Analyzer

Note: One additional external (before gas sample passing to the analyzer) Perma Pure® Dryer is also installed.

The Perma Pure® Dryer used in the T200 is capable of adequately drying ambient air to a dewpoint of ≤ -5°C (~4000 ppm residual H_2O) at a flow rate of 1 standard liter per minute (slpm) or down to ≤ -15°C (~1600 ppm residual H_2O) at 0.5 slpm. The Perma Pure® Dryer is also capable of removing ammonia from the sample gas up to concentrations of approximately 1 ppm.

Ozone Supply Air Filter

The T200 uses ambient air as the supply gas for the O_3 generator and may produce a variety of byproducts. Small amounts of water, ammonia and various sulfur oxides can combine to create ammonium sulfate, ammonium nitrate, nitric acid and other compounds. Whereas sulfates and nitrates can create powdery residues inside the reaction cell, causing sensitivity drift, nitric acid is a very aggressive compound, which can deteriorate the analyzer’s components. In order to remove these chemical byproducts from the O_3 gas stream, the output of the O_3 generator flows through a special filter between the generator and the reaction cell.

Ozone Destruct

Even though ozone is unstable and typically reacts to form O_2 the break-down is not quite fast enough to ensure that it is completely removed from the exhaust gas stream of the T200 by the time the gas exits the analyzer. Due to the high toxicity and reactivity of O_3, a highly efficient catalytic converter scrubs or converts all of the O_3 from the gas exiting the reaction cell. The conversion process is very safe. It only converts ozone to oxygen and does not produce any toxic or hazardous gases.

The O_3 destruct is located just inside the NO_2 converter. As this is a true catalytic converter, there are no maintenance requirements as would be required for charcoal-based ozone destructs.

Note: One additional external ozone destruct is also installed.

1. *Pneumatic Sensors*

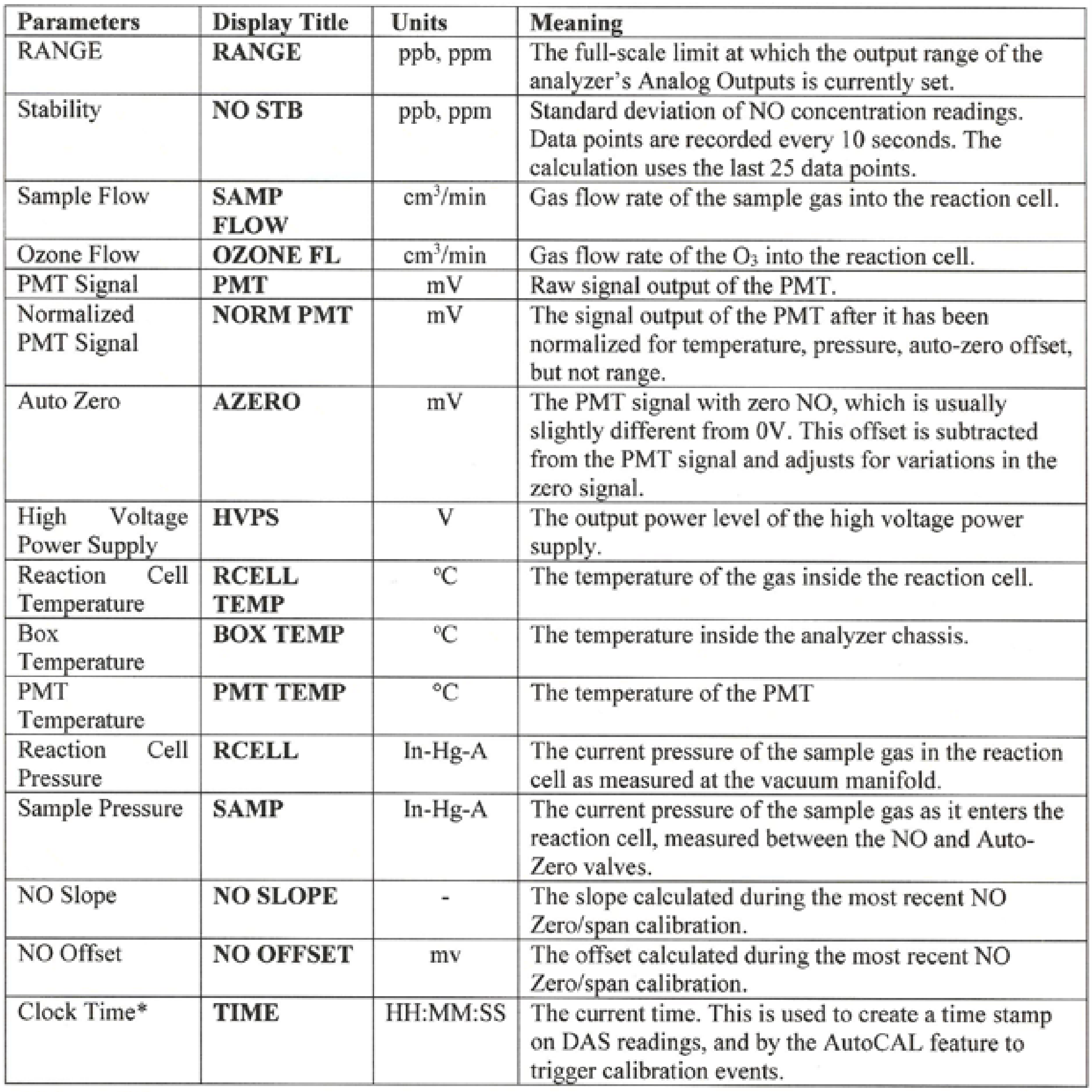
The T200 uses three pneumatic sensors to verify the flow and pressure levels of its gas streams. They are located on the pneumatic pressure/flow sensor board. The measurements made by these sensors are used for a variety of important calculations and diagnostics.

Functional Checks

As in the T320U N_2O analyzer, a functional check is done after warming of the analyzer for at least 60 minutes. A series of TEST functions is available for viewing at the front panel whenever the analyzer is at the SAMPLE mode. To view the test functions, press on of the <TST TST> buttons repeatedly in either direction. The enclosed 'Final Test and Validation Data Sheet' list these values as they were before the instrument left the factory.

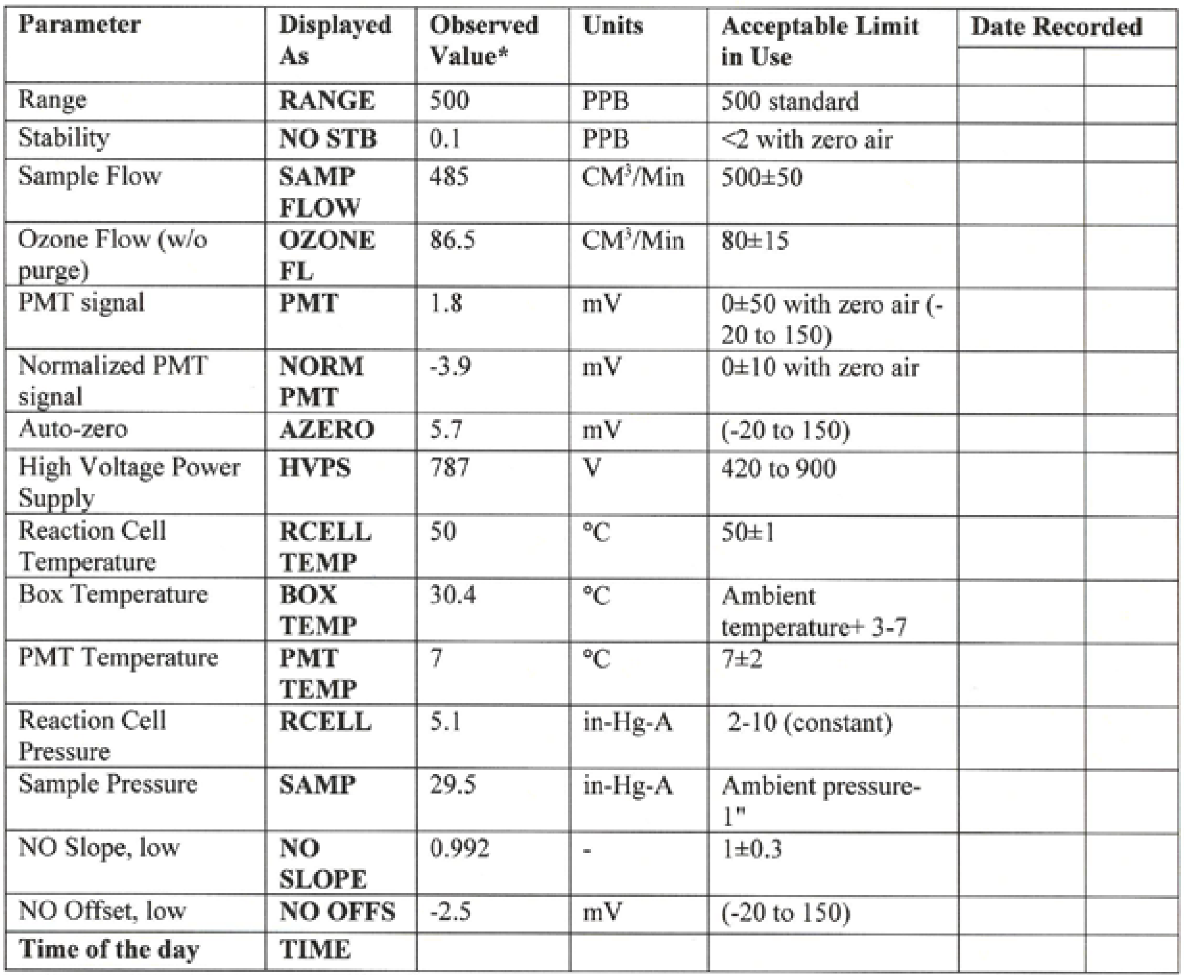
Remember that until the unit has completed its warm-up these parameters may not have stabilized. These parameters provide information about the present operating status of the instrument, diagnosing performance problems with the analyzer, and are useful during troubleshooting.
Table 12 shows the available test functions and their definition. Values of test functions observed during final calibration in the factory and their nominal ranges are shown in Table 13. Test functions should be recorded after each calibration.

Table 12. List of Test Functions and Their Definition for T200 NO Analyzer



Parameters	Display Title	Units	Meaning
RANGE	**RANGE**	ppb, ppm	The full-scale limit at which the output range of the analyzer's Analog Outputs is currently set.
Stability	**NO STB**	ppb, ppm	Standard deviation of NO concentration readings. Data points are recorded every 10 seconds. The calculation uses the last 25 data points.
Sample Flow	**SAMP FLOW**	cm^3/min	Gas flow rate of the sample gas into the reaction cell.
Ozone Flow	**OZONE FL**	cm^3/min	Gas flow rate of the O_3 into the reaction cell.
PMT Signal	**PMT**	mV	Raw signal output of the PMT.
Normalized PMT Signal	**NORM PMT**	mV	The signal output of the PMT after it has been normalized for temperature, pressure, auto-zero offset, but not range.
Auto Zero	**AZERO**	mV	The PMT signal with zero NO, which is usually slightly different from 0V. This offset is subtracted from the PMT signal and adjusts for variations in the zero signal.
High Voltage Power Supply	**HVPS**	V	The output power level of the high voltage power supply.
Reaction Cell Temperature	**RCELL TEMP**	°C	The temperature of the gas inside the reaction cell.
Box Temperature	**BOX TEMP**	°C	The temperature inside the analyzer chassis.
PMT Temperature	**PMT TEMP**	°C	The temperature of the PMT
Reaction Cell Pressure	**RCELL**	In-Hg-A	The current pressure of the sample gas in the reaction cell as measured at the vacuum manifold.
Sample Pressure	**SAMP**	In-Hg-A	The current pressure of the sample gas as it enters the reaction cell, measured between the NO and Auto-Zero valves.
NO Slope	**NO SLOPE**	-	The slope calculated during the most recent NO Zero/span calibration.
NO Offset	**NO OFFSET**	mv	The offset calculated during the most recent NO Zero/span calibration.
Clock Time*	**TIME**	HH:MM:SS	The current time. This is used to create a time stamp on DAS readings, and by the AutoCAL feature to trigger calibration events.

Table 13. List of Test Functions Including Observed Value During Final Calibration in the Factory (T200 NO Analyzer)



Parameter	Displayed As	Observed Value*	Units	Acceptable Limit in Use	Date Recorded	
Range	**RANGE**	500	PPB	500 standard		
Stability	**NO STB**	0.1	PPB	<2 with zero air		
Sample Flow	**SAMP FLOW**	485	CM^3/Min	500±50		
Ozone Flow (w/o purge)	**OZONE FL**	86.5	CM^3/Min	80±15		
PMT signal	**PMT**	1.8	mV	0±50 with zero air (-20 to 150)		
Normalized PMT signal	**NORM PMT**	-3.9	mV	0±10 with zero air		
Auto-zero	**AZERO**	5.7	mV	(-20 to 150)		
High Voltage Power Supply	**HVPS**	787	V	420 to 900		
Reaction Cell Temperature	**RCELL TEMP**	50	°C	50±1		
Box Temperature	**BOX TEMP**	30.4	°C	Ambient temperature+ 3-7		
PMT Temperature	**PMT TEMP**	7	°C	7±2		
Reaction Cell Pressure	**RCELL**	5.1	in-Hg-A	2-10 (constant)		
Sample Pressure	**SAMP**	29.5	in-Hg-A	Ambient pressure-1"		
NO Slope, low	**NO SLOPE**	0.992	-	1±0.3		
NO Offset, low	**NO OFFS**	-2.5	mV	(-20 to 150)		
Time of the day	**TIME**					

*observed during factory calibration

Note: While recording the test functions, care should be given for operating mode of the analyzer.

Maintenance Schedule

Table 13 shows a typical maintenance schedule for the T200. Please note that in certain environments (i.e., dusty, very high ambient pollutant levels), some maintenance procedures may need to be performed more often than shown.

Note: During calibration check, DO NOT press the ENTER button at the end of each operation. Pressing the ENTER button resets the stored values for OFFSET and SLOPE and alters the instrument's calibration.

Predicting Failures Using the Test Functions

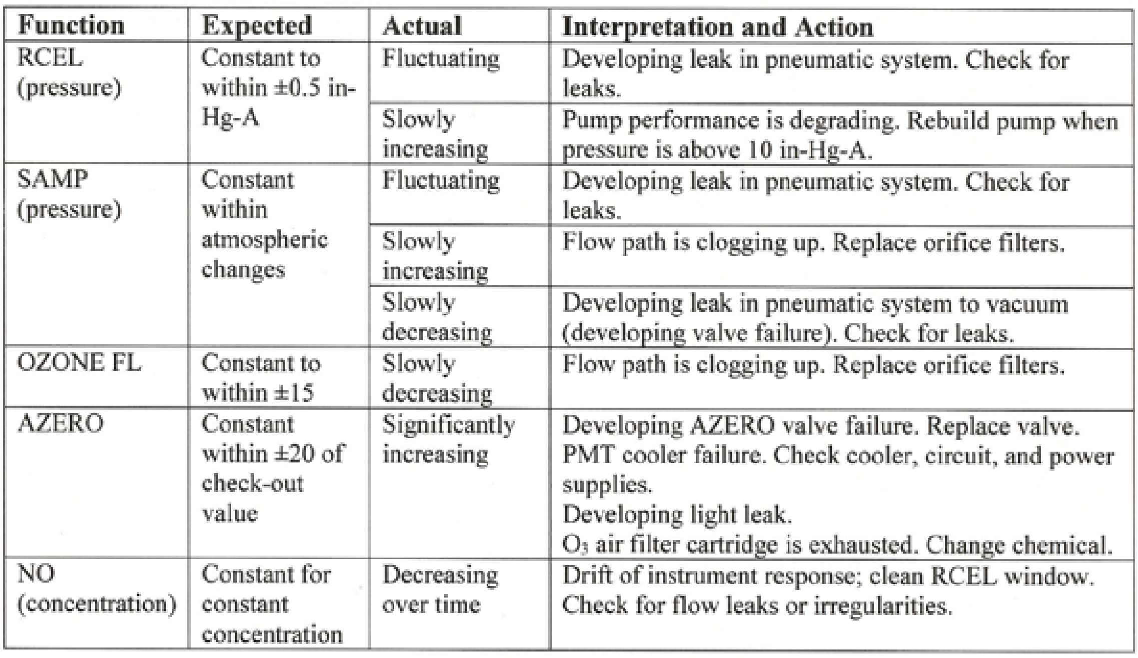
Predictive diagnostic functions including failure warnings and alarms built into the analyzer's firmware allow the user to determine when repairs are necessary.

Table 14. Maintenance Schedule for T200U NO Analyzer

Item	**Action**	**Frequency**	**CAL Check Required**	**Date Performed**				
Test Functions	Review and evaluate	Weekly	No					
Particulate Filter	Replace	Weekly or as needed	No					
Zero/span check	Evaluate offset and slope	Weekly	No					
Zero/span calibration	Zero and span calibration	Every 3 months	Yes					
Ozone cleanser	Change chemical	Annually	Yes					
Reaction cell window	clean	Annually or as necessary	Yes					
DFU filters	Change particle filter	Annually	No					
Pneumatic sub-system	Check for leaks in gas flow paths	Annually or after repairs involving pneumatics	Yes if a leak is repaired					
Reaction O-rings and sintered filters	Replace	Annually	Yes					
PMT sensor hardware calibration	Low-level hardware calibration	On PMT/preamp changes or if slope is outside of 1±0.3	Yes					
Pump	Rebuild head	When RCELL pressure exceed 10 in-Hg-A (at sea level)						
Inline Exhaust scrubber	Replace	Annually	NO					
NO_2 Converter	Replace converter	Every 3 years or if conversion efficiency drops below 96%	Yes					
Desiccant bags	Replace	Anytime PMT housing is opened for maintenance	n/a					

The test functions can be used to predict failures by looking at how their values change over time. Initially it may be useful to compare the state of these Test Functions during final calibration performed in the factory (see the table provided with analyzer). The following table provides some predictive information based on Test Functions. Based on the Test Function, required troubleshooting and repair can be done. See the T200 Operating Manual for detailed troubleshooting and repair.

Table 15. Predictive Use of Test Functions (T200 NO Analyzer)



Function	Expected	Actual	Interpretation and Action
RCEL (pressure)	Constant to within ±0.5 in-Hg-A	Fluctuating	Developing leak in pneumatic system. Check for leaks.
		Slowly increasing	Pump performance is degrading. Rebuild pump when pressure is above 10 in-Hg-A.
SAMP (pressure)	Constant within atmospheric changes	Fluctuating	Developing leak in pneumatic system. Check for leaks.
		Slowly increasing	Flow path is clogging up. Replace orifice filters.
		Slowly decreasing	Developing leak in pneumatic system to vacuum (developing valve failure). Check for leaks.
OZONE FL	Constant to within ±15	Slowly decreasing	Flow path is clogging up. Replace orifice filters.
AZERO	Constant within ±20 of check-out value	Significantly increasing	Developing AZERO valve failure. Replace valve. PMT cooler failure. Check cooler, circuit, and power supplies. Developing light leak. O_3 air filter cartridge is exhausted. Change chemical.
NO (concentration)	Constant for constant concentration	Decreasing over time	Drift of instrument response; clean RCEL window. Check for flow leaks or irregularities.

Ancillary Measurements

Various soil, crop and climatic factors determine the GHG fluxes from soils. To explain the GHG fluxes and their proper interpretation and to develop functional relationships, all these related factors should be taken into account. Some of the important factors that need to be measured and their frequency of measurement are provided here. However, the parameters to be measured depend on the objective of the study.

The following parameters should be measured at least once a season.

- Soil texture.
- Bulk density.
- Soil pH.
- Total organic C.
- Total N content.

The dynamics of labile C such as dissolved organic carbon (DOC) and nitrogen (ammonium-N and nitrate- N), moisture content and soil redox properties are important to interpret the peak emissions of N_2O and NO. It is desirable to determine those parameters as frequent as possible, particularly at every dry-wet cycle where there is peak emissions event occurs.

Climatic factors such as air temperature, relative humidity (RH), precipitation (rainfall), wind speed and solar radiation are also needed to interpret the GHG emissions. It is better if there is a weather station nearby an experimental site. Collect hourly averages of each parameter.

Air temperature, soil temperature and soil water content is required to measure at the time of every flux measurement. Therefore, install sensors for continuous logging for surface soil and air temperatures and soil moisture content in experimental plots.

Procedures for the installation of the sensors for temperature and moisture are described below.

Air and Soil Temperatures

Soil and air temperatures can be measured using a temperature probe (Model 108). This temperature probe is designed for measuring air/soil/water temperatures. The 108 temperature probe uses a thermistor to measure temperature in air, soil and water. It accurately measures air, soil or water temperature in a variety of applications. The sensor consists of a thermistor encapsulated in epoxy-filled aluminum housing. This design allows the probe to be buried or submerged in water to 15 m (50 ft) or 21 psi.

When measuring air temperature, a 41303-5A radiation shield is normally used to mount the 108 and limit solar radiation loading. To measure air temperature, the probes (or sensors) should be located over an open level area (at least 9 m in diameter) at the height of 1.5 m (±1.0m). This diameter and height is applicable to get representative air temperature of the particular area. However, the height could be adjusted based on the objectives of the study and could be used in a confined area also.

However, for calculating GHG fluxes, air temperature is measured from inside the GHG chamber. The objective of air temperature measurement is to correct the gas volume inside chamber at every gas sampling time that is used for measuring GHG fluxes. The temperature probe is hung inside the gas chamber about 10 cm from the soil surface and is supported by the crossbar used in chamber.

For the soil temperature measurement, the 108 probe is placed horizontally at 5 cm depth. The 108 tends to measure the average temperature over its length, so it should generally be buried such that the measurement tip is horizontal to the soil surface at the desired depth. The placement depth could be adjusted based on the objective of the study. Both air and soil temperature data are logged every minute continuously using the Campbell scientific datalogger (CR 3000) as described earlier. Moreover, average air temperature is logged at every 2 minutes from each particular chamber along with gas sampling.

The connection of the temperature probe to the datalogger is made via AM16/32B Relay Multiplexer (see under section 'Multiplexer'). Every probe has four sensor wires: black for voltage excitation, red for temperature signal, and purple and shield for ground connection. Sixteen temperature probes are used:

12 for air temperature (one probe per chamber) and four probes for soil temperature (for chambers 1-4). All temperature probes are connected to odd terminals in the multiplexer (such as 1, 3 to 31).

Connection of each probe to the multiplexer and datalogger is shown under sub-section 'Multiplexer.' Detail of temperature probe connection and datalogger programs can be found in the manual on Model 108 Temperature Probe.

Maintenance and troubleshooting[6]

The 108 Probe requires minimal maintenance. For air temperature measurement, check monthly to make sure the radiation shield is clean and free of debris. Periodically check cabling for signs of damage and proper moisture intrusion.

There may be some temperature logging problems when the connection of the probe to the multiplexer and datalogger is not stable. The following are some of the problems and their troubleshooting.

Symptom: Temperature is NAN, -INF, -9999, -273

Verify the red wire is connected to the correct Single-Ended analog input channel as specified by the measurement instruction, and the purple wire is connected to datalogger ground.

Symptom: Temperature is NAN, -26

Verify the black wire is connected to the switched excitation channel as specified by the measurement instruction.

Symptom: Incorrect Temperature

Verify the multiplier and offset parameters are correct for the desired units (see section 7 of Manual on Model 108 Temperature Probe). Check the cable for signs of damage and possible moisture intrusion.

Symptom: Unstable Temperature

Try using the 60 or 50 Hz integration options, or increasing the settling time (see section 8 of Manual on Model 108 Temperature Probe). Make sure the clear shield wire is connected to the datalogger ground and that the datalogger is properly grounded.

Soil Moisture[7]

Soil moisture content is measured using a Soil Matric Potential Sensor (Model 253-L, Watermark 200) (Figure 35). Alternately, it could be measured using Model 257-L. The 253 soil matric potential sensor is a solid-state, electrical-resistance device with a granular matrix that estimates soil water potential between 0 and -2 bars (0 and -200 kPa). This range is typical for wetter or irrigated soils.

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[6] This section is adapted from 'Instruction manual on Model 108 Temperature Probe (Revision: 3/14),' available online at Campbell Scientific Website.

[7] This section is adapted from Instruction Manual on 253-L and 257-L Soil Matric Potential Sensors (Revision 9/13), available at Campbell Scientific Website.

The 253 is the 'Watermark 200 Soil Matric Potential Block' modified for use with Campbell Scientific Multiplexers. The –L option on the Model 253-L indicates that the cable length is user-specified. For 253 applications, most of the cable length used is between the datalogger and the multiplexer, which reduces overall cable costs and allows each cable attached to the 253 to be shorter. The cable length of each 253 only needs to cover the distance from the multiplexer to the point of measurement. The typical length for the 253 is 25 to 50 ft. The 253 sensor needs to be connected to an AM16/32-series multiplexer, and is intended for applications where a larger number of sensors will be monitored. If 257 sensors are used, it connects directly to the datalogger.

The 253 (and 257) consists of two concentric electrodes embedded in a reference granular matrix material. The granular matrix material is surrounded by a synthetic membrane for protection against deterioration. An internal gypsum tablet buffers against the salinity levels found in irrigated soils. The sensor is 8.26 cm (3.25") long with a 1.91 cm (0.75") diameter and has weight of 363 g (0.8 lbs). If cultivation practices allow and proper protection could be made, the sensor can be left in the soil all year, eliminating the need to remove the sensor after harvesting of each crop. This allows regular monitoring of moisture content during both cropping and fallow seasons.

Installation and Removal

Placement of the sensor is important to get representative moisture content. If moisture content is monitored to determine the irrigation requirement, it should be located in the root system of the crop.

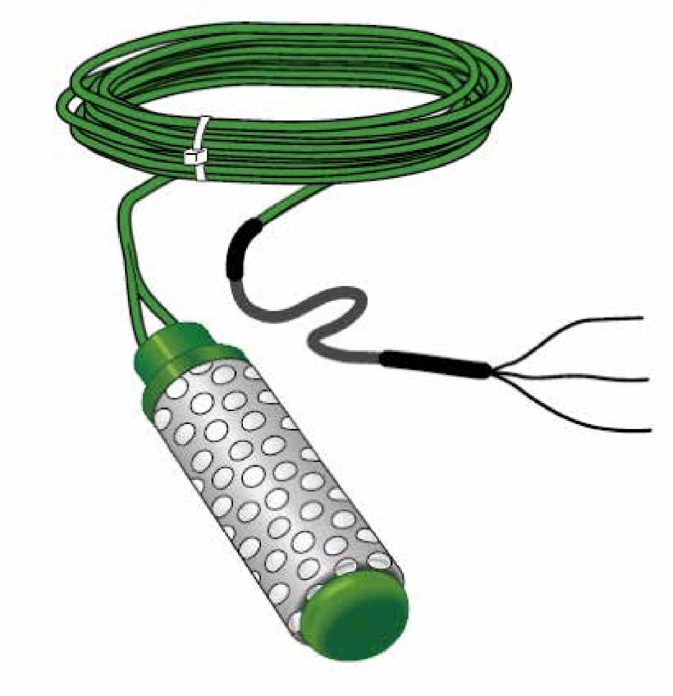


Figure 35. 253-L Soil Matric Potential Sensor

However, in GHG emissions studies, the objective of studying the dynamics of moisture content is to interpret the emissions results. Following are the normal steps for the installation of moisture sensor.

1. Soak sensors in water for one hour then allow them to dry, ideally for 1 to 2 days.
2. Repeat step 1 twice if time permits.
3. Make the sensor access holes (in soil) to the required depth. Often, a 22 mm (7/8 in) diameter

rod can be used to make the hole. However, if the soil is very coarse or gravelly, an oversized hole (25-32 mm) may be required to prevent abrasion damage to the sensor membrane. The ideal method of making an oversized access hole is to have a stepped tool that makes an oversized hole for the upper portion and an exact size hole for the lower portion.

4. If the hole is oversized (25 to 32 mm), mix a slurry of soil and water to a creamy consistency and place in into the sensor access hole.
5. Insert the sensors in the sensor access hole. A length of ½ inch class 315 PVC pipe fits snugly over the sensor collar and can be used to push in the sensor. The PVC can be left in place with the wires threaded through the pipe and the open end taped shut (duct tape is adequate). This practice also simplifies the removal of the sensors. When using PVC piping, solvent weld the PVC pipe to the sensor collar. Use PVC/ABS cement on the stainless steel sensors with the green top. Use clear PVC cement only on the PVC sensors with the gray top.
6. Force the soil or slurry to envelope the sensors. This will ensure uniform soil contact (Note: Snug fit in the soil is extremely important. Lack of a snug fit is the premier problem with sensor effectiveness).
7. Carefully fill the hole and tamp down to prevent air pockets, which could allow water to channel down to the sensor.
8. When removing sensors prior to harvest in annual crops, do so just after the last irrigation when the soil is moist (Caution: do not pull the sensor out by the wires. Careful removal prevents sensor and membrane damage)
9. When sensors are removed for winter storage, clean, dry and place them in a plastic bag.

Wiring of Moisture Potential Sensors (253-L)

The following schematic diagram (Figure 36) shows the wiring of the 253 sensor to the multiplexer and datalogger. Each moisture sensor is connected to even terminals of a multiplexer (such as 1, 2, 4 to 24) (for this particular setup). The 253 is for use with analog multiplexers including models AM32, AM416, and AM16/32 series. Sensor leads are connected to channels on the multiplexer and the common channels of the multiplexer are connected to the datalogger wiring panel. The sensor has two green leads. One of the green leads has a ridged strip while the other is smooth. Campbell Scientific connects a white lead to the ridged green lead, a black lead to the smooth green lead, and adds a clear shield wire that is not connected to the sensor. The white lead connects to the high end of a multiplexer channel, the black lead to the low end of the multiplexer channel and the clear lead to a multiplexer ground channel. A 1000 ohm resistor at the datalogger wiring panel is used to complete the half bridge circuitry. Please see Instruction Manual (Models 253-L and 257-l Soil Matric Potential sensors) for detail of wiring (connection with multiplexer and datalogger) and datalogger program.

Calculation of Soil Water Potential

The datalogger can calculate soil water potential (kPa) from the sensor resistance (R_s) and soil temperature (T_s). Soil temperature needs to be measured precisely since soil temperatures vary widely where placement is shallow and solar radiation impinges on soil surface. However, this may not be applicable in continuously flooded fields where there are diurnal changes in soil temperature but where moisture content may remain constant.

For applications where soil water potential is in the range of 0 to -200 kPa, water potential and temperature responses of the sensor can be assumed to be linear. The following equation normalizes the resistance measurement to 21°C.

$$R_{21} = \frac{R_s}{1-(0.018 * dT)}$$

Where, R_{21} = resistance at 21°C

R_s = the measured resistance

$dT = T_s - 21$

T_s = soil temperature

Water potential is then calculated from R21 with the relationship,

$$\mathbf{SWP = 7.407 \times R_{21} - 3.704}$$

Where, SWP is soil water potential in kPa

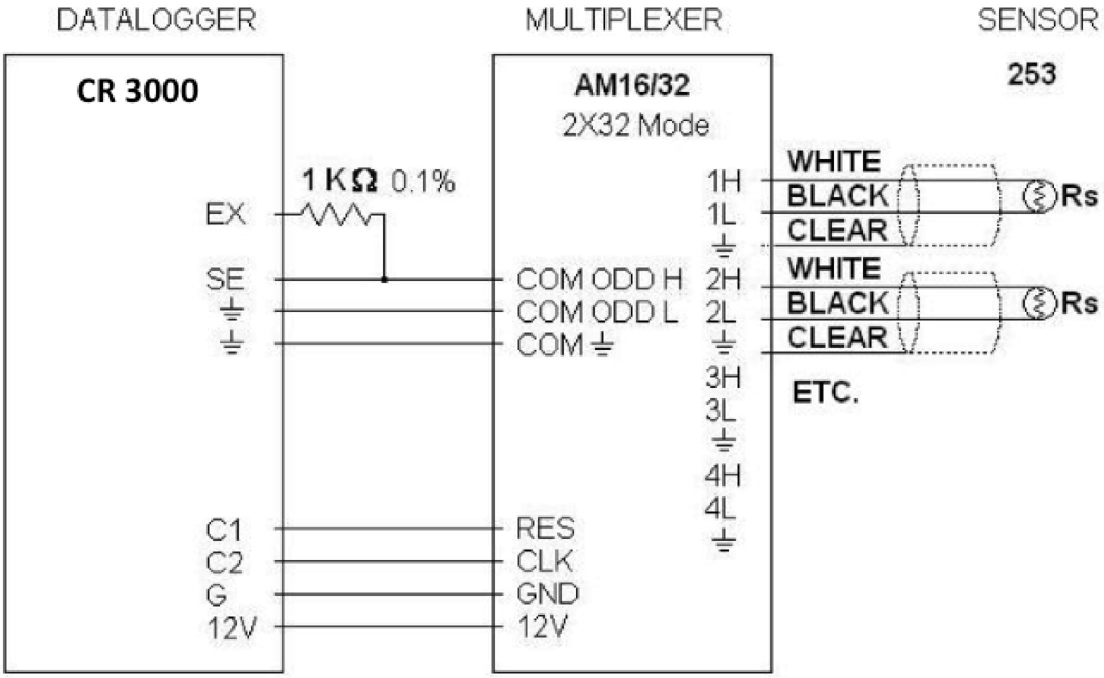


Figure 36. Schematic Diagram of 253 Sensors Wiring

Soil water potential (SWP) could also be expressed as MPa (kPa x 0.001) and bar (kPa x 0.01).

Interpreting Results

As a general guide, measurements indicate soil matric potential as follows:

0 to – 10 kPa = Saturated soil
-10 to -20 kPa = Soil is adequately wet (except coarse sands, which are beginning to lose water)
-20 to -60 kPa = Usual range for irrigation (except heavy clay)
-60 to -100 kPa = Usual range for irrigation for heavy clay soils
-100 to -200 kPa = Soil is becoming dangerously dry for maximum production

Troubleshooting

To test the sensor, submerge it in water. Measurements should be from -3 to +3 kPa. Let the sensor dry for 30 to 48 hours. You should see the reading increase from 0 to 15,000+ kPa. If the reading does not increase to 15,000 kPA, replace the sensor. If the reading increases as expected, put the sensor back in the water. The reading should show zero in 1 to 2 minutes. If the sensor passes these tests but it is still not functioning properly, consider the following:

1. The sensor may not have a snug fit in the soil. This usually happens when an oversized access hole has been used and the backfilling of the area around the sensor is not complete.
2. The sensor is not in an active portion of the root system, or the irrigation is not reaching the sensor area. This can happen if the sensor is sitting on top of a rock or below a hard pan, which may impede water movement. Reinstalling the sensor usually solves this problem.
3. When the soil dries out to the point where you are seeing readings higher than 80 kPa, the contact between soil and sensor can be lost because the soil may start to shrink away from the sensor. An irrigation that only results in a partial rewetting of the soil will not fully rewet the sensor. Full rewetting of the soil and sensor usually restores soil to sensor contact. This is most often seen in the heavier soils and during peak crop water demand when irrigation may not be fully adequate. The plotting of readings on a chart is most useful in getting a good picture of this sort of behavior.

Data Analysis

The automated gas sampling and analysis system generate a huge data set on N_2O and NO concentration, soil and air temperatures, soil moisture content, atmospheric pressure and data on calibration of gas analyzers. Storage of the data and calculation of N_2O and NO flux rates are discussed in this section.

Data Storage

All the data are stored in the datalogger and can be downloaded regularly by computer using the LoggerNet software. Since the datalogger has a limited storage capacity, data should be downloaded frequently. However, during downloading data using the LoggerNet software, the new data are appended with previous data. All those files are stored in the Campbellsci and LoggerNet directories. The data are stored in three separate files. They are 'CR3000_OneMinuteData.dat,' 'Rundata.dat' and 'ZeroSpan.dat'. After each download, it is better to make a backup file in another directory. However, original files should not be deleted from the LoggerNet directory; thus, data should only be copied, not moved or cut.

All files are in .dat file format. Those files can be opened with Microsoft Excel. To open .dat file: open blank Excel file, choose file that need to be opened, text import wizard will appear, then select delimited, next-choose comma then date-Finish; the .dat file now open in excel.

OneMinuteData

This file stores following data every minute:

- Air temperature from 12 chambers and soil temperature from four chambers
- Soil moisture from 12 chambers
- Sample flow rate of both N_2O and NO analyzers
- N_2O and NO concentration (low range values)
- Atmospheric pressure

All data stored in this file are average values measured over a minute. Temperatures are measured in degrees C. Soil moisture is stored in two units, one as resistance in kilo Ohms (kOhms) and another as potential in kilo Pascal (kPa). The resistance is converted to potential values based on soil temperature. The average soil temperature from 4 chambers is used to covert resistance values to potential. Sample flow rate (cc/min) of both N_2O and NO analyzers are also stored every minute. Similarly. Mixing ratio (concentration) of N_2O and NO low stable values are also stored in this file. If concentration of those gases exceeds the low range limit, they are not included and show only the upper limit value of low range data. Atmospheric pressure (millibar) measured by barometer is also stored in this file.

The soil temperature and soil moisture content are used to interpret the GHG fluxes. Since GHG fluxes in general are presented on an hourly basis, soil moisture and temperature could also be presented on an hourly basis. Nevertheless, every minute of data is useful to check the performance of sensors and if there is problem with datalogging. The sample flow rate is used to check whether gas sampling is running smoothly or not. A low sample flow rate below the normal range could indicate a problem with gas sampling. Check whether the particulate membrane filter needs to be replaced, if the external pump is running smoothly and if there is any possible blockage in the sampling line.

For every hour until 48 minutes, concentration of N_2O and NO (low range values) is measured from gas chambers. The concentration measured from the chambers is stored in a rundata file (described later). For the remaining 12 minutes (i.e., 49-60 minutes), or when a 1-hour cycle of gas sampling is complete, i.e., at 48 minutes in each hour, N_2O and NO concentration is measured from ambient air for 12 minutes until the next cycle of sampling starts. Therefore, every 12 minutes in an hour, both N_2O and NO analyzers measure ambient concentration of N_2O and NO except calibration time (0948 to 1000, 1048 to 1100 and 1148 to 1200). Since within 12 minutes there is no significant change in gas concentration in ambient air, this 12 minute data gives the analyzers variability; thus, it is used to determine the minimum detection limit of the analyzers. However, care should be taken to exclude the data, particularly if manual calibration is done during that 12-minute period.

Air pressure and air temperature are used to calculate the flux rate. However, those data are also stored in a rundata file along with N_2O and NO concentration.

Zerospan Data

This file stores the following data every 30 seconds for 13 minutes (46 to 59 minutes) during automated calibration time (see 'Calibration' section also):

- Concentration of NO and N_2O, both low and high stable values.
- Standard deviation of NO and N_2O measurement for both low and high values.
- Atmospheric pressure.
- Air temperature.

The aforementioned data are only recorded when calibration is following automated sequence. As described under 'Calibration,' auto calibration runs every week for 3 hours, from 0948 to 0958 for zero air, 1048 to 1058 for NO and 1148 to 1158 for N_2O. However, the data in this files stores from 46 to 59 minutes for each hour because gas mixing start 2 minutes earlier and records data 1 minute after analysis completion. NO and N_2O concentration data is used to see whether the analyzer's performance (or sensitivity) is decreasing. Moreover, variation of NO and N_2O measurement can also be seen looking their standard deviation. If the concentrations are exceeding the targeted low or high range values, analyzers must be calibrated using span button as described earlier.

Rundata

This file stores the following data every 2 minutes during each gas sampling from a particular chamber.

- N_2O low stable and high stable values.
- NO low stable and high stable values.
- Air temperature.
- Atmospheric pressure.
- N_2O and NO emission rates.

Concentration of N_2O and NO and their corresponding air temperature is recorded every 2 minutes from a particular chamber. As described earlier under gas analysis section, both NO and N_2O analyzers analyze a sample every 5 seconds. However, the average of only the last three measurements is stored in a datalogger. During a 1-hour cycle, four chambers are sampled, and each chamber sampled six times, one before closing of gas chamber and another five after closing of the chamber at each 8-minute interval. Thus, there are six measurements from a chamber with six corresponding air temperatures. The N_2O and NO concentrations are used to calculate the emissions rates. Based on the concentration, either low range or high range values are used. Air temperature is used to correct the headspace air volume. Flux rate calculation is described under sub-section 'Calculation of GHG Flux Rates.'

Calculation of GHG Flux Rates

The concentration of NO and N_2O increases (or decreases) during chamber closure time. It is assumed that the concentration of NO and N_2O increase linearly. Therefore, the fluxes are calculated from the slope of the liner increase or decrease in concentration of respective gases against the chamber closure time (Figure 37). The slope is then corrected for air temperature, atmospheric pressure and the ratio of chamber volume to surface area.

Table 16. Change in Concentrations of N_2O and NO and Corresponding Air Temperature During Chamber Closure Time of 40 Minutes, Concentration are Measured at Every 8-Minute Interval

Time	N_2O (ppb)	NO (ppb)	Temperature (°C)
0	317.5	-1.0	29.41
8	384.5	0.355	33.36
16	428.5	2.243	34.72
24	466.2	3.333	35.71
32	493.4	4.613	36.5
40	518.4	6.241	37.21

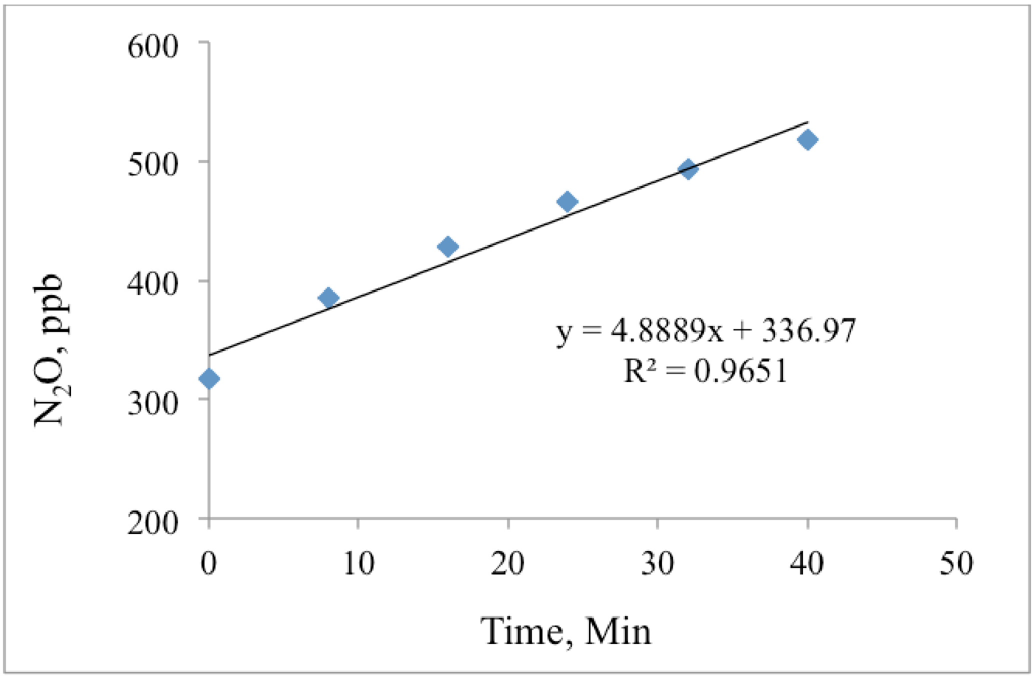


Figure 37. Linear Regression Curve of the N_2O Concentration and Chamber Closure Time

Note: For the flux calculation, only increment is considered, i.e., change in concentration over change in time. Intercept is not considered.

Emission rate in ppb/min is converted to μg/m^2/h using following formula.

Emission rate (μg NO or $N_2O/m^2/h$) =

$$\frac{\text{ppb min}^{-1} \text{ x V x MW x 60}}{[0.08206 \text{ x } (273+T)\ ^0K] \text{ x A x 1000}}$$

Where,

V is the volume of the gas chamber in L (57.8)

MW is the molecular weight of the respective gas in ng/nmol (NO: 28, N_2O: 44)

60 is conversion factor for time (min h^{-1})

0.08206 is the gas law constant (L atm $mol^{-1}\,^0K^{-1}$)

T is the temperature inside the chamber (°C)

A is the area covered by chamber (m^2, 0.146) and

1000 is conversion factor for mass (ng μg^{-1})

N_2O flux (μg/m^2/h)

$$= \frac{\text{ppb min}^{-1} \text{ x V x MW x 60}}{[0.08206 \text{ x } (273+T)\ ^0K] \text{ x A x 1000}}$$

$$= \frac{4.89 \text{ x } 57.8 \text{ x } 44 \text{x } 60}{[0.08206 \text{ x } (273+34.85)] \text{ x } 0.146 \text{ x } 1000}$$

$$= \mathbf{202.41}$$

If it is expressed as N_2O-N, then the emission rate is 128.87 /m^2/h.

NO emission rate can also be calculated using same formula replacing molecular weight of N_2O with NO.

A wide fluctuation could be observed for both N_2O and NO fluxes. Emissions from agricultural soils are mostly event specific and significant emissions occur with irrigation/rainfall and with application of nitrogenous fertilizer. Pearson's correlation coefficient (r^2) for the linear regression is calculated and used as a quality check for the measurement. Flux rates are considered significant only if r^2 is >0.8, fluxes are considered and could be discarded if r^2 is <0.8. Moreover, the minimum detection limit (MDL) is calculated to determine to estimate caused by gas sampling and analysis as described below.

The flux rates are used for a variety of purposes based on the objectives of the study. Hourly flux rates can be used to calculate daily, weekly or seasonal total emissions. Total emissions can be calculated for rice-growing and fallow seasons. Graphical presentation of fluxes helps to interpret the emissions event with crop management practices such as irrigation or rainfall, fertilization, etc.

A single automatic chamber produces up to 3000 flux estimates per year, which ensures significantly increased temporal accuracy compared to manual approaches.

Visual assessment of graphical output of hourly flux rates from the chamber help to check the quality of emission data.

Minimum Detection Limit

It is important to consider the sampling and analytical error (precision of gas analyzer) while measuring gas fluxes. When a chamber is placed on the soil surface and made airtight, headspace gas concentration increases over time because of emissions from soil or decreases if soil consumes the gas. If there is no gas emission from the soil, then theoretically the headspace gas concentration should remain the same, thereby the flux rate should also be zero. However, sampling/analytical error may result in a data pattern that shows an apparent flux even though there is no significant emission from the soil (Parkin et al. 2012). This flux is observed due to sampling and analysis errors. This error should be estimated to determine the real gas flux. The minium flux which is observed due to sampling and analysis error can be estimated as minimum detactable flux, or minimum detection limit (MDL).

MDL can be estimated by sampling ambient air or running the zero air for at least 10 minutes. This automated system samples ambient air every hour for 12 minutes. This measurement can be used to estimate the MDL. The concentration of NO and N_2O measured from ambient air over a 10 minute period is selected and calculated the standard deviation (Table 17). It is assumed that those samples are collected from a chamber over a 40-minute deployment (closure) time. Thus, two times the standard deviation is considered as slope (ppb/min) and is calculated in the same way for samples from the chambers.

Then this slope is converted to flux rate using chamber area and volume. Theoretically, the flux rate calculated from the concentration of ambient air samples should be zero. Any difference from zero would essentially be due to sampling and analytical error. Therefore the variability of the flux estimated from the ambient air samples is considered as MDL for the fluxes. Once MDL is determined, the flux rates within the range of MDL could be considered as negligible. This means the fluxes below MDL (or ±MDL) are merely due to sampling and analysis error. The following are some of the options to report the flux data that fall below MDL (Parkin et al. 2012 and references therein):

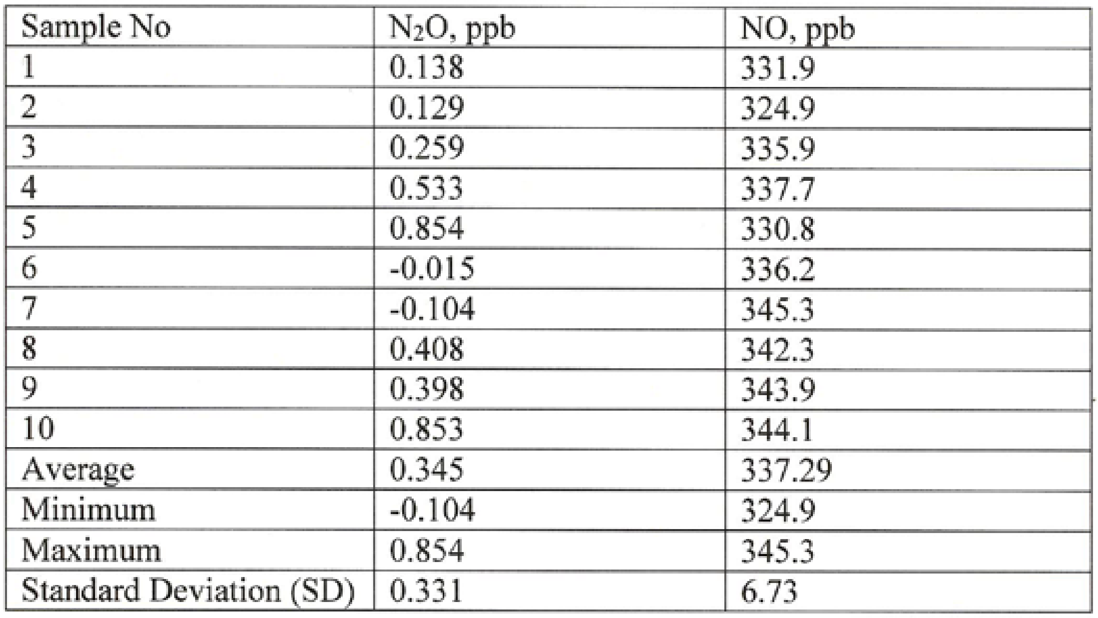
i) Report the value as “below detection limit”

ii) Report the value as zero

iii) Report some values between zero and the MDL (such as one half of the MDL), or

iv) Report the actual measured value even if it falls below the MDL

Table 17. Concentration of N_2O and NO in Ambient Measured Over 10 Minutes



Sample No	N_2O, ppb	NO, ppb
1	0.138	331.9
2	0.129	324.9
3	0.259	335.9
4	0.533	337.7
5	0.854	330.8
6	-0.015	336.2
7	-0.104	345.3
8	0.408	342.3
9	0.398	343.9
10	0.853	344.1
Average	0.345	337.29
Minimum	-0.104	324.9
Maximum	0.854	345.3
Standard Deviation (SD)	0.331	6.73

Calculation of MDL

N_2O and NO concentrations are used from Table 17.

MDL for NO (ppb/min) = 2xSD/CDT = 2 x 0.331/40 = 0.016

The slope (emission rate) is converted to mass per unit area per hour (µg NO-N/m^2/h) with following information.

Chamber deployment (closure) time (CDT): 40 min

Area covered by chamber: 0.146 m^2

Headspace volume of the chamber: 57.8 L

Temperature: 30°C

MDL for NO flux is 0.44 µg NO-N/m^2/h

MDL for N_2O (ppb/min) = 2xSD/CDT = 2 x 6.73/40 = 0.336

MDL for N2O flux is 8.79 µg N_2O-N/m^2/h

Monitoring and Maintenance

For the smooth running of the automated gas sampling and analysis system, it should always be closely monitored and needs some regular maintenance.

Automated Chambers

Mixing Fan

The fan in the chamber should run continuously, particularly during chamber closing time for the uniform mixing of gases. Disturbance in the fan not only affects the uniform mixing of gases but also increases air temperature when the chamber is closed. Therefore, the chamber needs regular inspection. The fan may not work either due to problem in the fan itself or due to a problem in its wires. The fan wires may be disconnected during field operations, but they should be connected immediately following. The fan may need to be replaced if there is problem.

Air Cylinders

Regular monitoring is required to see whether compressed air is leaking from the connection of the Nylon tube and air cylinder. If leakage is significant, the chamber lid may not stay open. Moreover, due to a greater supply of compressed air, the air compressor may start frequently, affecting its efficiency. Monitoring is also required to see whether the air cylinder is rusted. The movement of the piston may also be hampered due to its misalignment.

Air Sealing Between Chamber Base and Soil

The chamber base should always be airtight with the soil. This may not be a problem where chamber plots are continuously flooded, but care should be taken when plots are dry. There might be deep cracking during drying time, causing a leakage of air when the chamber is closed. Moreover, during the dry cycle, it may allow lateral diffusion of gases from the chamber area.

Tubes (Teflon and Nylon)

Both the sampling and compressed air tubes should be checked for possible physical damage (such as rodent damage). Moreover, monitoring is required for a possible chance of blockage of those tubes.

Particulate Membrane Filter

Since the membrane filter (placed before dryer) filters incoming gas samples, it needs to be replaced regularly. It is advised to change it every 2-4 weeks depending on the rice-growing season. It may need to be changed frequently during the dry season (every 15 days) compared with the wet season (every month). During the rainy season when there is less dust in the air, the time interval becomes longer. But during the dry period, with more dust in the air, the filter becomes frequently dirty. If it is not changed, the sample flow is reduced, and analyzers show sample flow warming. It is also noticed that, if the filter gets dirty within 10 days, it needs to be replaced.

Air Compressor

Smooth running of the air compressor is essential for the regular supply of compressed air, which controls opening (and closing) of the chambers. Care should be given for regular servicing such as checking the air filter and draining water from the tank. Since compressed air passes through the Clippard valves, air should be dust-free. Therefore, the compressed air room should be clean and dust free. Water accumulates in the compressor tank, so it should be drained every 24-48 hours. Draining should be frequent during the rainy season due to humid air.

The outlet pressure of compressed air is controlled to 60 psi using an external regulator. The regulator is equipped with a moisture trap. The regulator should always be maintained at 60 psi, and the moisture trap should be regularly drained. Leakage of compressed air may occur from Clippard valves (open/closure valves) in the manifold, which also affects opening of the chamber.

Standard Gases

The cylinders of standard gases should be monitored regularly for possible leakage. The cylinder pressure should be recorded regularly after every calibration. Outlet pressure (to dilutor) should be checked regularly and needs to maintain about 35 psi for ultra-pure nitrogen and 25-30 psi for NO and N_2O. To minimize disruptions to continuous sampling and analysis, there should be spare zero and calibration gases.

Analyzers

The Analyzers' performance and sensitivity should be monitored regularly. Every week after calibration, test parameters should be recorded such as sample flow rate, stability, etc. Sensitivity of the analyzers could be checked calculating minimum detection limit from ambient air analysis (12 minutes every hour after sampling from chambers) and observing calibration values after every calibration.

Calibration of the Analyzers

Analyzers should be calibrated properly. Regular checking of calibration data (zerospan.dat file) gives an idea where analyzers need calibration. If the recorded concentrations of respective calibration gases are beyond the acceptable range, the analyzer should be calibrated.

The Reaction Cell Cleaning

Cleaning of the reaction cell (NO analyzer) is required every year. Proper care is needed during its cleaning and assembly. The analyzer should be turned off following the guidelines provided in the operating manual.

Data Quality

To ensure quality data, regular visual assessment of graphical and numerical output is required. Similarly, processing data as much as possible (such as flux rate calculations, averaging temperature and moisture data) is better. Regular backups should be done for the data. The regular download and visual assessment helps to find any problems with datalogging such as temperature data labeled with 'NAN,' which is due to a loose connection of sensor wires, particularly the ground connection.

Power Supply

To ensure continuous power supply, alternate power sources such as Generators and UPS (uninterrupted power supply) are needed as backup power. A high power automatic generator (10 kilovolt amperes [KVA]) is used. An online UPS (2 KVA) can be used as backup supply until generator starts.

Regular servicing of generator and UPS (Uninterruptible Power Supply) is needed to ensure the continuous supply of power.

Recordkeeping

A log book should be maintained to record all the monitoring and maintenance activities such as change of particulate filter, observation of calibration gases (amount and pressure), disturbance in gas sampling, record of functional test parameters of analyzers, calibration date, power outage, etc.

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