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Rosenberg, N. J. and Verma, S. B., "A System and Program for Monitoring CO<sub>2</sub> Concentration Gradient, and Flux in an Agricultural Region" (1976). *Papers in Natural Resources*. 1187.  
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Reprinted from *Agronomy Journal*  
Vol. 68, March-April 1976, p. 414-418  
American Society of Agronomy, 677 S. Segoe Rd., Madison, WI 53711

**A System and Program for Monitoring CO<sub>2</sub> Concentration,  
Gradient, and Flux in an Agricultural Region**

**Norman J. Rosenberg and Shashi B. Verma**

# A System and Program for Monitoring CO<sub>2</sub> Concentration, Gradient, and Flux in an Agricultural Region<sup>1</sup>

Norman J. Rosenberg and Shashi B. Verma<sup>2</sup>

## ABSTRACT

Because of the changing global concentration of carbon dioxide and the possible effects of this change on photosynthetic activity worldwide, a program has been developed for monitoring atmospheric carbon dioxide concentration and gradients representative of a large agricultural region. The program is carried out at Mead, Neb. A meteorological tower is equipped with sampling intakes at various elevations up to 16 m, through which air is drawn to the laboratory for analysis with infra-red gas analyzers. An automatic calibration system has been developed to permit hourly checks of analyzer performance. Profiles of wind speed and air temperature are also measured. The equipment, the calibration techniques, and the errors associated with the measurements of CO<sub>2</sub> concentration and gradients are described. Some initial observations of CO<sub>2</sub> concentrations and fluxes are presented.

*Additional index words:* CO<sub>2</sub> profile, Infra-red gas analyzers, Automatic calibration, Field-photosynthesis, Turbulent transfer, Mass transfer, Micrometeorology.

THERE is need for detailed experimental data so as to better estimate the source and sink strengths for atmospheric CO<sub>2</sub> exerted by terrestrial vegetated surfaces and the buffering effect which these surfaces exert on the global concentration. In a report to the United Nations Conference on the Human Environment (Stockholm, 1972), the Commission on Monitoring, Scientific Committee on Problems of the Environment, International Council of Scientific Unions recommended that atmospheric carbon dioxide concentration and flux data be collected at reference stations world-wide for assessing secular changes of the global climate. In view (in fact, in anticipation) of this, an organized program to regularly observe and analyze patterns in CO<sub>2</sub> concentration and gradients at a well instrumented rural site has been initiated at one of the Univ. of Nebraska's Agricultural Meteorology laboratories (Mead, Neb.).

In this paper, we describe our measuring and calibration techniques as well as the errors involved in CO<sub>2</sub> analysis. Brown and Rosenberg (1968) proposed certain technical improvements in CO<sub>2</sub> sampling and analysis for field photosynthesis research. They also analyzed the errors in estimating photosynthetic fluxes caused by errors in measurement of CO<sub>2</sub> concentration and other factors. In this paper we describe further

technical refinements and improvements which make the routine observation of CO<sub>2</sub> concentration and gradients reliable. Our system functions in a general micrometeorological research facility where other, frequently unrelated, experiments are conducted concurrently. Some initial observations are presented.

## METHODS AND MATERIALS

*CO<sub>2</sub> Sampling and Analysis System.* A 19.2 m meteorological tower at Mead, Neb. (41° 09' N; 96° 30' W; altitude 351 m above m.s.l.) is equipped with sampling intakes through which air is drawn into a laboratory building about 60 m away for measurement of CO<sub>2</sub> concentration and gradients. The total analytical system is described in a schematic given as Appendix I. Component specifications are given in Appendix II. The system has capacity to sample air at eight locations or elevations. Individual diaphragm pumps, located near the tower (but external to the laboratory), are used for each sample line. These pumps draw air under vacuum and move it into and through the laboratory under positive pressure.

The sample lines terminate in the laboratory building at individual rotameters where flow rate into the mixing chambers is controlled. Air from each separate level is continuously mixed in 7.6 liter (2 gal.) cylinders to smooth out the rapid fluctuation in CO<sub>2</sub> concentration. Periodically (usually every 15 min) air samples are drawn in sequence from the mixing cylinders through the infra-red gas analyzers (IRGA). Air from the highest elevation sampled (level 1) is passed through a Beckman model 315A to determine the absolute concentration of CO<sub>2</sub>. Then air from the same source (level 1) is passed through one side of a Beckman IRGA model 315B, used as a differential analyzer, for comparison with air originating at the next lowest level (level 2). The concentration difference between two samples is determined in this way. In the next step air from level 3 is drawn through the differential analyzer replacing the sample from level 1. Then the concentration difference between levels 2 and 3 is determined. This process is repeated until all necessary comparisons are made. The electrical output signal of the gas analyzers is recorded with an analogue to digital conversion meteorological data logging system housed in the laboratory.

*Calibration Procedures.* A system has been developed to permit automatic hourly calibration of both IRGAs. Analyzer output data during calibration runs is also recorded by the data logging system. The calibration system works in the following way. Once each hour an upscale standard gas of known CO<sub>2</sub> concentration is passed through the absolute IRGA and the analyzer response is recorded. Then a downscale gas is substituted. At the same time a single standard gas is passed through both sides of the differential IRGA. Zero concentration should be indicated by the IRGA when this is done. The response, whether zero or not, is recorded. Then two different standard gases of known concentrations (differing by a suitable working range) are passed through the two chambers of the differential IRGA to record an upscale response. With the IRGA responses measured and recorded during a calibration cycle, the drift of the analyzers can be monitored and the field observations can be adjusted for changing IRGA calibrations, if any.

A comparison of standard gases of the same nominal concentration, but supplied by different manufacturers, convinced us of the need for an independent calibration of our standard gases. Our primary standard gases are calibrated to an accuracy of  $\pm 0.3$  to  $0.5$  ppm by the Air Resources Laboratory of NOAA in Boulder, Colorado<sup>3</sup>. Our secondary standards are calibrated against these primary gases by differential gas analysis. The secondary standards are used in the automatic analyzer calibration procedure described above.

<sup>1</sup> Published as Paper No. 3829, Journal Series, the Neb. Agric. Exp. Stn. The work reported was conducted under Neb. Agric. Exp. Stn. Project No. 20-31 and Regional Research Project No. 11-33. Received 10 July 1975.

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<sup>3</sup> Based on 59 manometric standards (Dr. C. D. Keeling, Scripps Institution of Oceanography, Univ. of California, San Diego, personal communications, 1975).

**Errors in CO<sub>2</sub> Analysis.** It was found that even small pressure differences between the reference and sample sides of the differential IRGA resulted in measurable imbalances and that the error was increased with greater concentration of CO<sub>2</sub> in the sample gas. Concentration difference errors in the order of 1 ppm were possible. Such errors can produce serious bias in the calculation of CO<sub>2</sub> fluxes.

The problem of pressure imbalance has been eliminated by use of precise pressure regulation devices and flow meters. It is now possible to maintain the pressure differences between the analyzer tubes at  $0 \pm 1.0$  mb. These pressure differences are monitored periodically with a water manometer to detect any failures in pressure regulation.

Because the absorption bands of CO<sub>2</sub> and H<sub>2</sub>O overlap, the air stream should be dried before analysis in order to prevent interference from water vapor. In operation of the IRGA for absolute analysis we used to pass the air stream through a tube of indicating Drierite (CaSO<sub>4</sub>) before entry. Unfortunately use of a drying tube significantly increases the time constant in gas analysis. The drying tube has been replaced by a set of optical filters<sup>1</sup> incorporated into the path of the infrared radiation stream. These filters transmit only radiation in the 3800 to 5700 nm wavelength band. Thus the main water vapor absorption bands are removed. Use of drying tubes is no longer required and the time constant of the system is substantially reduced.

Air is moved into and through the laboratory under positive pressure. The entire system to the right of the pumps (P1-P8 in Fig. A.1) remains continuously under pressure. The analyzers themselves are under a slight positive pressure with CO<sub>2</sub>-free N<sub>2</sub> gas. Therefore the possibility of contamination by CO<sub>2</sub>-rich laboratory air has been effectively eliminated. After the automatic calibration procedure is completed the analyzer cells are purged with dry N<sub>2</sub>.

Temperatures of the gas samples entering the analyzer cells are monitored during both data and calibration cycles so that adjustments can be made for any significant difference in the temperature of field air samples and laboratory calibration gases.

Frequent calibrations are needed to avoid significant errors caused by gas analyzer zero and span drift. Normally we use a 15 min record cycle although more frequent observations are possible. Automatic calibration is programmed once every hour. In addition, to further refine our CO<sub>2</sub> gradient measurements, the 'zero-response' on the differential IRGA is obtained at the start of every record cycle by passing a sample of field air through both sides of the analyzer.

**Computation of CO<sub>2</sub> Flux.** Rates of CO<sub>2</sub> flux, F<sub>c</sub>, to and from the ground are computed from the measured profiles of CO<sub>2</sub> concentration ([CO<sub>2</sub>]), wind speed and air temperature (Verma and Rosenberg, 1975 and 1976):

$$F_c = f k^2 z^2 \left( \frac{\partial U}{\partial z} \right) \left( \frac{\partial c}{\partial z} \right) (\phi_m^{-2}) \left( \frac{K_c}{K_m} \right) \quad (1)$$

where  $\partial U/\partial z$  = wind speed gradient =  $u^*/kz \phi_m$ , with  $u^*$  = friction velocity;  $\phi_m$  = nondimensional wind shear (or diabatic correction factor for the log-law wind profile,  $\partial U/\partial z = u^*/kz$ ),  $K_m$  = exchange coefficient for momentum,  $K_c$  = exchange coefficient for CO<sub>2</sub> (assumed to be equal to the exchange coefficient for water vapor,  $K_w$ ),  $\partial c/\partial z$  = gradient of CO<sub>2</sub> concentration,  $k$  = von Karman's constant,  $f$  = conversion factor for CO<sub>2</sub> from ppm to specific weight, and  $z$  = distance measured in the vertical direction.

Both  $\phi_m$  and  $K_w/K_m$  have been found to vary with atmospheric thermal stability. Stability can be expressed in terms of the Richardson number (Ri) defined as  $Ri = g(\partial\theta/\partial z) \theta^{-1} (\partial U/\partial z)^{-2}$ , where  $\theta$  is the potential temperature;  $g$  is the acceleration due to gravity;  $\partial U/\partial z$  and  $\partial\theta/\partial z$  are the gradients of wind speed and potential temperature.

Stability correction formulae have been developed in recent micrometeorological investigations. Those of Pruitt et al. (1973) are used in our study of CO<sub>2</sub> fluxes:

Model of Pruitt et al., 1973  
(hereafter called the PML model)

$$\begin{aligned} \phi_m &= (1-16 Ri)^{-1/3} \text{ for unstable stratification,} \\ &= (1+16 Ri)^{1/3} \text{ for stable stratification;} \\ K_w/K_m &= 1.13 (1-60 Ri)^{0.071} \text{ for unstable stratification,} \\ &= 1.13 (1+95 Ri)^{-0.11} \text{ for stable stratification;} \\ k &= 0.42. \end{aligned} \quad (2)$$

This model has been tested over an oat field against two other independent methods (namely the lysimetric and energy balance methods) for measuring CO<sub>2</sub> flux. Results agreed within 10 to 12% on a short period basis and within 5 to 10% on a daily basis (for details, see Verma and Rosenberg, 1975). For some periods when daytime stability (advective inversions) were observed, the fluxes are computed assuming  $\phi_m = 1$  and  $K_w/K_m = 1$ .

Gradients (or derivatives with respect to height) of various profiles ( $c$ ,  $T$ , and  $U$ ) were evaluated using finite differences in the manner suggested by Panofsky (1965)<sup>2</sup>. If  $\psi$  is a profile variable, then the gradient is given by:

$$\frac{\partial \psi}{\partial z} = \frac{\psi_2 - \psi_1}{\sqrt{z_1 z_2} \ln \left( \frac{z_2}{z_1} \right)} \quad (3)$$

where  $z_1$  and  $z_2$  are the heights above the ground. This approximation is, of course, rigorous for logarithmic profiles. Using this approximation equation (1) becomes:

$$F_c = f k^2 \frac{(U_2 - U_1)(c_2 - c_1)}{\left( \ln \frac{z_2}{z_1} \right)^2} \left( \frac{K_w}{K_m} \right) (\phi_m^{-2}) \quad (4)$$

Measurements of [CO<sub>2</sub>], wind speed, and air temperature made at 5.6 and 16.0 m above the ground are used in equation (4). These elevations are selected so that, assuming fetch to height ratios of 100 to 200, the CO<sub>2</sub> flux computed should represent an integration of the region generally, rather than of the field in which the instrument mast stands.

## SOME INITIAL OBSERVATIONS

**CO<sub>2</sub> Concentrations.** Fig. 1 shows a set of typical daily CO<sub>2</sub> concentration waves measured at 0.5, 1.0, 4.0, and 16 m above ground. During the fall of 1972 the 2 ha experimental field in which the tower stands was planted to oats which reached a height of about 40 cm. The surrounding area was planted to soybeans, alfalfa, and pasture grasses in commercial sized fields ranging from 5 to 50 ha. Some small areas of trees are also within the "fetch" of the tower.

With the onset of photosynthesis, immediately after sunrise on each day, a sharp drawdown in CO<sub>2</sub> concentration occurred. Concentration at each elevation leveled off at about 10 hours (solar time) with only slight change until 16 hours. The morning transition from lapse profiles of CO<sub>2</sub> ( $\partial C/\partial z < 0$ , or respiration conditions) to inversion profiles of CO<sub>2</sub> ( $\partial C/\partial z > 0$ , or photosynthesis conditions) occurred first at the lower elevations. The change from lapse to inversion was usually sharp and abrupt. The return to a respiration-type lapse profile in the afternoon is, typically, much less sharply defined. The shape of the diurnal CO<sub>2</sub> concentration waves and the day to day variations depend primarily upon ambient light intensity and windspeed conditions.

There is considerably less diurnal variation in CO<sub>2</sub> concentration at an elevation far removed from the crop canopy (e.g. 16 m) as compared to an elevation just above the canopy (e.g. 0.5 m). Typically the amplitude of these CO<sub>2</sub> concentration waves at 0.5 m was about 2 to 4 times that at 16 m.

**CO<sub>2</sub> Flux.** Figure 2 shows some typical daily patterns of CO<sub>2</sub> flux measured during the period June to October 1973. The sign convention adopted here

<sup>1</sup> Manufactured by Grubb Parsons and Co. Ltd., Newcastle upon Tyne, England. Spectral transmittance of these filters is given in Janac (1971).

<sup>2</sup> Panofsky, H. A. 1965. Reanalysis of Swinbank's K<sub>z</sub> observations. Unpub. report, Penn. State Univ., Dep. of Meteorology, p. 66-76.

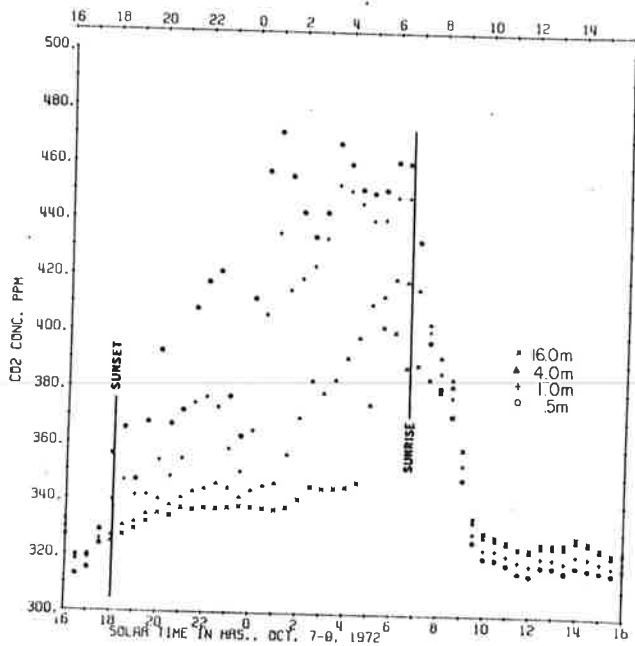


Fig. 1. Typical daily CO<sub>2</sub> concentration waves at different elevations, Mead, Neb.

gives CO<sub>2</sub> flux toward the ground as positive and away from the ground as negative. Positive fluxes of CO<sub>2</sub> from the air above to the photosynthesizing vegetation occur for 11 to 12 hours daily. The magnitudes of these fluxes depend, primarily, upon solar radiation, wind speed, and air temperature. Average radiation, wind speed, and air temperature for the days depicted in the figure are given in Table 1. The peak daytime fluxes ranged from about 0.5 in early June to 1.5 or 2.0 ( $\text{g} \times 10^{-7} \text{cm}^{-2} \text{sec}^{-1}$ ) in early August and 0.5 ( $\text{g} \times 10^{-7} \text{cm}^{-2} \text{sec}^{-1}$ ) in late September. Negative fluxes measured over the crop at night represent the sum of the soil and crop respiration which depends primarily on the soil and air temperature. Detailed results on CO<sub>2</sub> fluxes are reported in Verma and Rosenberg (1976).

#### ACKNOWLEDGMENTS

This study was conducted with support of the Environmental Data Service, National Oceanic and Atmospheric Administration, U.S. Dep. of Commerce, under Contract 2-35385. Mr. Dale E. Sandin, Research Technician, contributed to the design and was responsible for construction of the system. Thanks are extended to Mr. Thomas Harris of the Air Resources Laboratory, NOAA, Boulder, Colo. for calibrating our primary standard gases.

#### SUMMARY

A program and the instrumentation regularly used to observe atmospheric carbon dioxide concentrations, gradients, and fluxes representative of a large agricultural region are described. Calibration procedures and errors encountered in CO<sub>2</sub> analysis are discussed. The accuracy of gradient measurements is generally close to  $\pm 0.2$  ppm, whereas the absolute concentrations are measured with an accuracy of  $\pm 1$  to 2 ppm.

The system for measurement of CO<sub>2</sub> concentration and gradients is programmed for automatic calibration. IRGA output is recorded automatically during every record and calibration cycle. Profiles of wind speed and air temperature are also measured simultaneously for use in computing CO<sub>2</sub> fluxes. In order to study the modifying influences of season and changing weather conditions, these measurements are continued throughout the year.

Table 1. Solar energy receipts and mean daily temperature and windspeed on selected days during 1973 at Mead, Neb.

Date	Solar radiation	Mean windspeed	Mean air temperature
	ly day <sup>-1</sup>	at 5.6 m m sec <sup>-1</sup>	at 5.6 m C
10 June 1973	718	6.68	25.9
12 July 1973	712	4.33	27.3
5 Aug. 1973	631	4.95	23.2
18 Aug. 1973	585	4.06	25.3
23 Sept. 1973	247	3.73	16.6

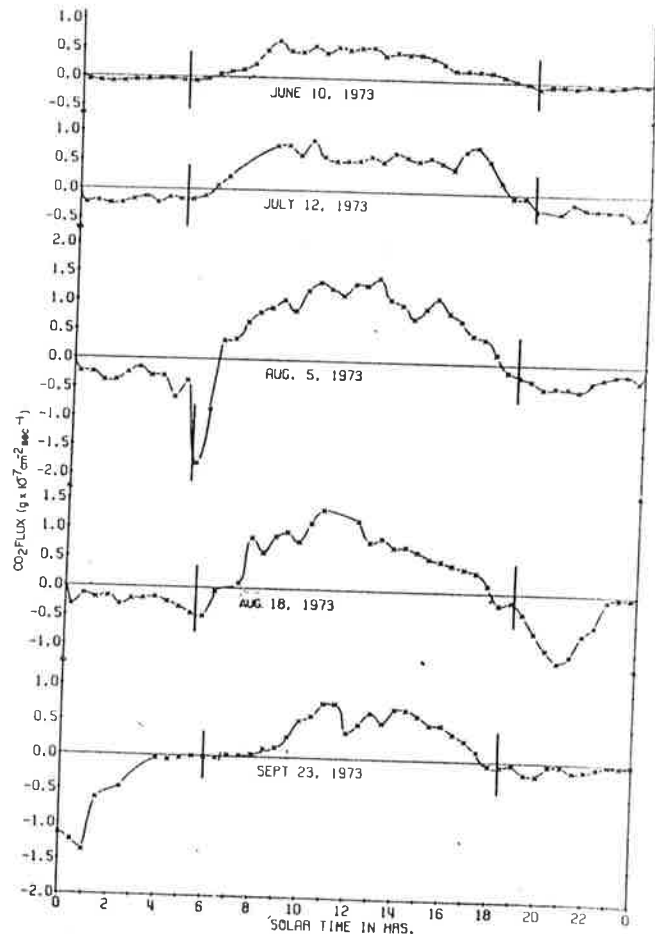


Fig. 2. Typical patterns of the diurnal flux of CO<sub>2</sub> between 5.6 and 16.0 m during June to October 1973 at Mead, Neb. Sunrise and sunset times are indicated by the vertical lines.

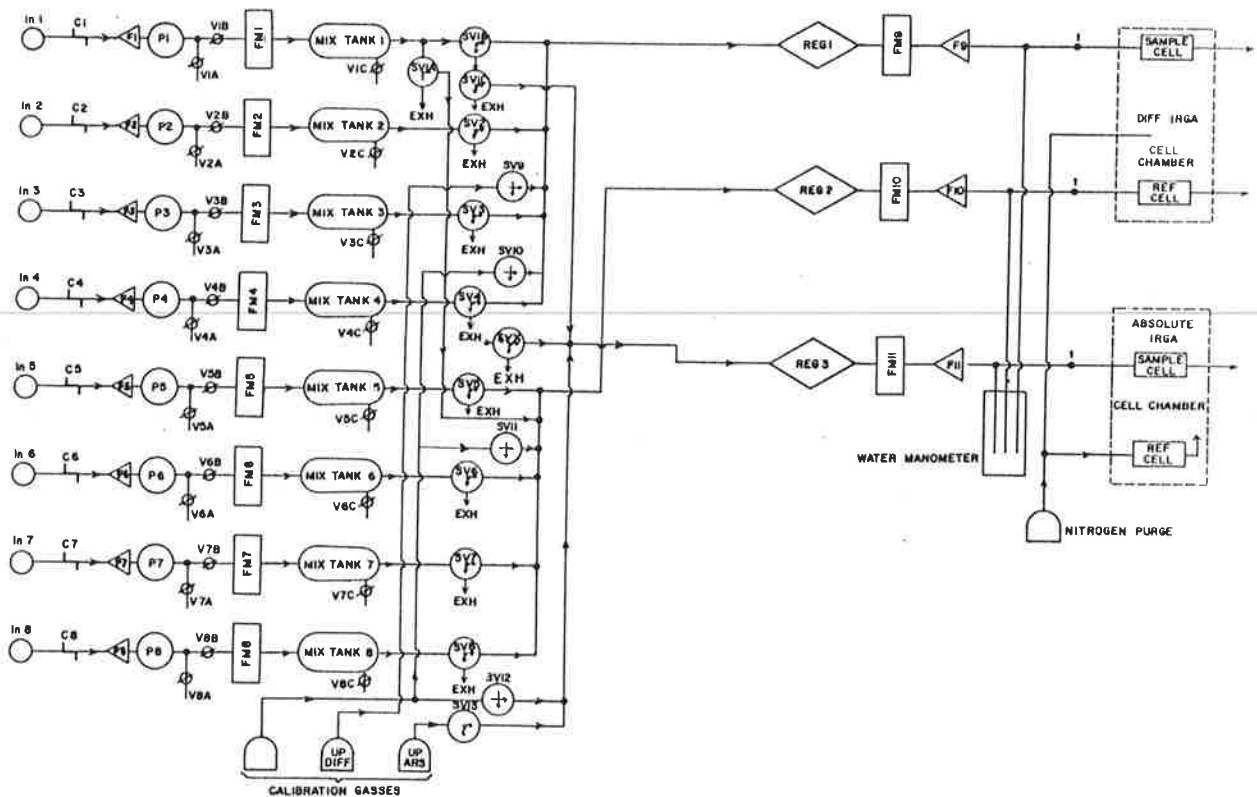


Fig. A.1. Appendix I. Detailed schematic of the CO<sub>2</sub> sampling and analysis system used at the Univ. of Nebraska Micrometeorology Laboratory.

**APPENDIX II**  
**Component List**  
**CO<sub>2</sub> IRGA Flow and Control System**  
 (See Figure A.1)

- "In 1" through "In 8"  
 Filter (Gas flow), part no. 129712W, Model DZ-78006  
 MFR: Mine Safety Appliances, Pittsburgh, Penn.  
 Paper Filter Removed, replaced with 40 mesh stainless steel screen
- Line between C1 through C8 and F1 through F8  
 Tubing bundle, Ten Tube, Polyethylene, 3/8" O.D. x .062"  
 Wall. Part no. 1202-610  
 MFR: Samuel Moore & Co.  
 9119 West Monroe  
 Houston, TX 77017
- All other lines  
 1/8" I.D. Copper Tubing
- F1 through F8  
 Air filter, Part no. S-103  
 MFR: Neptune Products, Inc.  
 353 East Blackwell St.  
 Dover, N.J. 07801
- P1 through P8  
 Model 4K Neptune Dyna-Pump (Standard)  
 115 Vac. 60 Cycle  
 MFR: Neptune Products, Inc.  
 353 East Blackwell St.  
 Dover, N.J. 07801
- FM1 through FM8  
 Flowmeters, 0-5 LPM, Cat. no. 520-23  
 MFR: Dwyer Instr. Inc.  
 P.O. Box 373  
 Michigan City, IN 46360

- Mix Tanks 1 through 8  
 Surplus Air Force oxygen tanks, 280 cu. inches
- SV1A through SV8 and SVX  
 Solenoid valves, 3 way, stainless steel, Cat. no. V53 DA 2050  
 MFR: Skinner Electric Valve Co.  
 New Britain, Conn.
- SV9 through SV13  
 Solenoid valves, 2 way, stainless steel  
 Cat. no. V52 DA 1052  
 MFR: Skinner Electric Valve Co.  
 New Britain, Conn.
- All other valves (V1B, V2A, V3C, etc.)  
 Common needle valves, 1/8" I.D.
- Reg 1 through Reg 3  
 Differential regulator, Model H-21AT, 0-5 PSI range  
 MFR: ITT-Hammel-Dahl  
 175 Post Road  
 Warwick, R.I. 02888
- FM9 through FM11  
 Flowmeter, 0.2-4.0 LPM Air, 4" scale  
 Cat. no. VFB-SSV-65-PF  
 MFR: Dwyer Instruments, Inc.  
 P.O. Box 373  
 Michigan City, IN 46360
- F9 through F11  
 Guard filter, porous stainless steel element, 5-9 micron  
 Nominal Pore Size, Part no. B541  
 MFR: Hoke, Inc., Cresskill, N.J.
- Water Manometer  
 Outer Tube: 2" I.D., Inner Tubes: 1/4" O.D., 1/8" I.D.  
 0-24 CM with IMM Divisions  
 MFR: Univ. of Nebraska shop



## COMMENTS

The purpose of V1A, B&C through V8A, B&C is to enable nitrogen purging of the system, should moisture collect in the sample lines or mixing tanks. All tanks are mounted at an angle with the "C" valves attached at the lowest point. Purge can be accomplished by disconnecting lines at the pump, opening the "A" and "C" valves and applying nitrogen gas below valve "A".

Solenoid valves SV9 through SV11 are used for calibration of the analyzers and are controlled by an external timing system. Calibration is performed between normal recording cycles.

Absolute analysis is normally obtained by samples from line No. 1 through solenoid valves SV1B and SV1C. However absolute analysis of other lines may be obtained by connecting the input of solenoid valve SVX to the exhaust of other solenoid valves.

The sequence of sampling, both field samples and calibration gases, is controlled by patching pulses generated by the data logger. For example, line 1 can be compared with lines 5, 6, or 7. Almost any combination can be obtained except that lines 1 through 4 cannot be compared against each other and the same holds true for lines 5 through 8. However these lines may be re-routed to any input at any elevation or location, thereby permitting further flexibility in differential analysis.

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