Final Report

AN INSTRUMENT FOR MEASURING TRACE QUANTITIES OF OXIDES OF NITROGEN IN AIR

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Contract No. CPA 70–70

For

Environmental Protection Agency
Methods Development Section
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North Carolina 27711

MONSANTO RESEARCH CORPORATION
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Monsanto

DAYTON LABORATORY

DAYTON, OHIO 45407

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FOREWORD

This Final Technical Report and Operating Manual, prepared by Monsanto Research Corporation under contract CPA 70-70, Project Number 6774, entitled "Oxides of Nitrogen Analyzer" covers work performed at the Dayton Laboratory of Monsanto Research Corporation and was sponsored by Environmental Protection Agency (formerly National Air Pollution Control Administration), Durham, North Carolina, Robert K. Stevens (Raleigh, N. C.) was the Project Officer.

ABSTRACT

An instrument for the measurement of NO_x was developed based on the chemiluminescent reaction of NO and NO_2 with atomic oxygen. The detectable limit is less than 20 ppb. Atomic oxygen was generated by an electrical discharge in an oxygen-argon atmosphere at one torr pressure. A pair of photomultiplier tubes connected in a bridge circuit configuration measures the chemiluminescent emission in the presence of appreciable background light from the discharge. Automatic background correction is periodically initiated by a digital programmer.

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ACKNOWLEDGEMENTS

The number of people who contributed significantly to this project is too great to allow naming all of them. However, special recognition goes to Rumult Iltis who was the initial Project Leader, G. W. Wooten on whose work the instrument was based, and Dr. A. D. Snyder whose advice and assistance was invaluable. Also, technicians Charles Elias, Patrick Rice and Larry DuFour contributed many ideas as well as their diligent efforts to the project.

1. INTRODUCTION

A large amount of research has gone into the development of techniques for measuring small amounts of pollutants in the atmosphere. The justification for that research is the need for sensitive instruments for monitoring air pollution in order to establish some degree of control over it when required. In order to obtain meaningful measurements of air pollution, it is usually necessary to move the instrument to the locality being monitored. In the case where continuous monitoring is required, portable field mounted instruments are essential.

The toxic character of the oxides of Nitrogen and their generation in commonly used equipment such as automobiles make them important pollutants in the atmosphere, especially in industrial and densely populated areas. The detection of these oxides, NO and NO_2, in quantities as low as few parts per billion in air is required for adequate monitoring in some localities. Trace quantities of NO and NO_2 have been detected in laboratory studies by measuring the chemiluminescence of their reaction with atomic oxygen.

This report describes an instrument based on the chemiluminescent reaction of NO and NO_2 with atomic oxygen. It is designed for field operation and is capable of continuously monitoring NO_x down to less than 20 ppb concentration. Its read-out system is compatible with most commonly used data acquisition systems.

2. SUMMARY

The NO_x instrument can be conveniently divided into four sections:

(1) The reactor/generator system.

(2) The flow system.

(3) The electronics system.

(4) The cabinet.

The reactor/generator assembly includes an oxygen generator, a reactor chamber, a dual photomultiplier detector and two high voltage power supplies. Atomic oxygen is generated by a high voltage discharge in an atmosphere of 85% argon and 15% oxygen at one torr pressure. The atomic oxygen enters a reaction chamber where it reacts with NO and/or NO_2 which enters via a sample inlet. One photomultiplier monitors the light emitted by the atomic oxygen stream before it mixes with the sample stream and another monitors the chemiluminescent reaction in the chamber.

The flow system consists of the vacuum system and of the plumbing and pressure controls required to maintain the correct flow rates into the reaction chamber. The flow rate of the sample is set by means of an orifice between the vacuum chamber and the inlet port which is at atmospheric pressure. The flow of clean diluent air which is used to zero the instrument is set to the sample flow rate by adjusting the upstream pressure of another orifice into the reaction chamber. Still another orifice provides a means for adding a small amount of a known concentration of NO or NO_2 to the diluent air at a predetermined rate. Stream switching is accomplished by means of solenoid valves.

The electronics system is composed of the programmer, the measuring and read-out circuits and the various power supplies which are required.

The digital programmer is comprised of a crystal controlled oscillator, counters, logic components and driven modules. The programmer performs all the stream and eletrical switching necessary for automatic zeroing and for span checking as well as for controlling the integration cycle of the measuring circuit. The switching functions are programmed by means of a peg board type matrix switch on the front panel.

A differential amplifier in the measuring circuit accepts the signals from the two photomultipliers and transmits the amplified difference signal through a filter to an integrator which repetitively integrates, holds, then resets to a predetermined value. The integrator output is transferred to a memory amplifier in a manner that the output of the memory amplifier is updated during each "Hold" period of the integration cycle. During the automatic zero cycle, the output of the integrator is switched to memory amplifier which supplies a signal to the "Initial Condition" input of the integrator such that the integral of any background signal is applied to the integrator as an initial condition. During the "Measure" cycle, the integrator output starts at the initial condition such that the final output is proportional to the chemiluminescence seen by the photomultipliers. The output is transferred to a read-out memory amplifier which is calibrated to read one volt full scale for any range.

The cabinet is a standard relay rack type enclosure with removable back and sides for easy access to the plumbing and assemblies inside. The programmer and measuring circuits are mounted on printed circuit cards to provide easily accessible modules. The electronics circuits are mounted on a slide assembly to facilitate check-out and maintenance procedures.

3. CONCLUSIONS AND RECOMMENDATIONS

The pulsed discharge method of generating atomic oxygen was abandoned because there was not sufficient time to develop the more sophisticated circuits necessary for that type of operation. Although the pulse technique requires further circuit development, it is superior to the D.C. discharge method in an instrument of this type which must operate for long periods virtually unattended. The low duty cycle of the discharge pulse can add several multiples to the effective lifetime of the discharge electrodes.

The rather elaborate digital programmer used in this instrument is the result of the original intent to provide a pulsed discharged oxygen generator. Adequate programming for the D.C. discharge instrument can be accomplished by electro-mechanical means or by a hybrid analog-digital programmer with a considerable reduction of costs.

Much of the measuring circuit for the NO_x instrument was designed under the restriction that integration of the signal was required for the purpose of filtering. That concept should be further investigated to determine if conventional filtering means are adequate. A considerable reduction in complexity and cost of the programmer and the auto-zero circuits as well as the measuring circuit can be accomplished if conventional filtering is adequate.

It is recommended that an electrodeless microwave discharge method for generating oxygen be substituted for the D.C. discharge system now used. The resulting stablization of the constantly changing background and sensitivity caused by the degradation of the electrodes with time should reduce the maintenance to an acceptable level.

The analog automatic zero circuit is limited to application where an auto-zero cycle can be tolerated relatively often. For instance, the best all-electronic analog memory circuit can be relied on no more than 15-20 minutes in a normal uncontrolled environment and even less if the relative humidity is high. By comparison, a servo or a digital memory can retain its value indefinitely. It is suggested that a servo type auto-zero circuit is adaptable to this type of instrument and should be considered in any new instrumentation where the auto-zero cycle can be limited to twice per hour or less and where no digital signal is available.

4. TECHNICAL DISCUSSION

4.1 REACTOR/GENERATOR

The research work done under contract No. CPA-22-69-8, "Feasibility Study for the Development of a Multifunctional Emission Detector," wherein a microwave discharge was used to produce atomic oxygen was reviewed. Because the microwave generators available did not appear adaptable to a portable instrument, alternate methods for the generation of atomic oxygen were studied (thermal, photolysis, radialysis, neutron bombardment, and electric discharge). The electric discharge appeared most appropriate for miniaturization.

A pulse technique with a low duty cycle was selected as a means for the electric discharge to minimize the problems due to heating and to extend the life of the discharge electrodes. A high voltage power supply capable of producing variable pulse rates and widths was designed to provide current regulation during the discharge.

Efforts to derive a stable signal from the pulsed discharge failed. Although the pulse appeared to be relatively stable, the signal appeared to be too unstable for sensitive measurements. As a result, the programmer was simplified to provide a D.C. discharge which resulted in a marked increase in the stability of the chemiluminescence signal.

It was found that the background light varied with the energy in the discharge. As a result, the discharge power supply was redesigned to provide a constant current to the discharge over a wide range of conditions.

The geometry of the reactor was optimized to improve sensitivity and signal-to-background ratio. Forty-nine experiments were run and tabulated as O_2 flow, Ar flow, diluent air flow, and pressure were varied. Optimum performance was calculated to occur when the following conditions were met.

O_2 flow - 15 cc/minute

Ar flow - 85 cc/minute

Diluent Air - 50 cc/minute

System pressure - one torr

These conditions resulted in a background of 70 n.a. and a signal level of 12-15 n.a. of PMT current for 500 parts per billion.

The initial development was done using a single photomultiplier to sense the light emitted from the reaction tube. As the work progressed, it became evident that the background light from the generator and other possible sources was much greater than the light emerging from the reaction of small concentrations of NO_x with the atomic oxygen. A special photomultiplier tube with an extended response curve and a band pass filter improved the signal-to-background ratio. However, the initial difficulty in obtaining those tubes resulted in the selection of a more common variety of photomultiplier tube.

In order to further improve the performance of the detector, the reactor tube was modified to accept two photomultiplier tubes. One PMT senses the light just upstream from the sample injection point and the other senses the light in the reaction tube which includes both background and signal. In that geometry, the difference between the two PMT currents, properly balanced, is proportional to the chemiluminescence in the reactor tube and is relatively independent of background light.

4.2 ELECTRONICS MEASURING CIRCUIT

The initial concept of the measuring circuit included provisions for a low level signal superimposed on a relatively large pulse. These concepts were partially retained when the system was converted to a D.C. discharge in that a large amount of gain (400) was provided in the differential amplifier. Provisions were made to balance the PMT outputs to compensate for differences in the PMT's and in the optical characteristics of the two areas in the reaction tube. System stability was improved markedly by increasing the input resistors by a decade to one megohm and decreasing the gain of the differential amplifier by a factor of 20. Further improvement was obtained by installing 0.01 microfarad capacitors across the input resistors.

A filter amplifier accepts the output of the differential amplifier and provides a somewhat cleaner signal to a variable gain amplifier. Switches on the front panel change the input and feedback resistors of the variable gain amplifier such that the gain changes by factors of two. Two switches provide four gains or ranges.

A commercial integrator with internal semi-conductor switching for on-off and reset functions and an inital condition input accepts the output of the variable gain amplifier. The integrator is programmed to continuously repeat the sequence, reset one second - integrate "on" ten seconds - "hold" one second. A programmed switch connects the output of the integrator to the input of another programmed switch during each "hold" period of the integrator. The second switch either connects the integrator to the read-out memory amplifier or the auto-zero integrator input depending on the mode of operation.

When in a "measure" mode, either "sample" or "standard", the output memory amplifier is updated during each "hold" period of the integrator. In the auto-zero mode, the second switch connects the integrator output to the input of the auto-zero which has a time constant of one. Thus, the auto-zero integrator output changes by the precise amount of the integrator output during the one second "hold" period. The integrator then resets to a new initial condition such that if the integrator input remains constant, the output of the integrator at the end of the next "integrate" period is zero. Thus, if only diluent "clean" air enters the instrument during auto-zero cycle, any offset in the system ahead of the integrator is automatically compensated for by adjusting the initial condition of the integrator. Since the auto-zero integrator holds its output, the compensation is retained from one auto-zero cycle until it is updated in the next.

The output of the read-out memory amplifier is calibrated to read 0-1 volt for full scale on any range. That output is brough to a connector for use with a data acquisition system. A recorder output is brought to a connector for continuous monitoring. A meter on the front panel provides continuous indication of the NO_x concentration.

4.3 PROGRAMMER

The digital programmer consists of four sections: clock, integrator programmer, sample programmer and standard gas programmer.

The clock is comprised of a 100 KH_z crystal controlled oscillator and a five decade counter which provides a pulse train at precisely one pulse per second.

The integrator programmer provides a fixed program which is continuously repeated except that it can be interrupted at any time by the reset switch on the front panel. The programmer is stopped as long as the reset switch is depressed, but it automatically starts a new cycle when the switch is released. The programmer provides three time intervals during which it transmits commands to the measuring circuit. During the first interval of one second, a signal is transmitted to the "reset" input of the integrator, thereby resetting the integrator to whatever voltage is present at its "initial condition" input. During the second interval of ten seconds, a signal is transmitted to the "integrate" input of the integrator causing it to integrate its voltage. In the third interval of one second, the integrator receives no signal cuasing it to hold the output it had at the end of the second interval. However, a signal is transmitted to logic circuit which updates either the output memory or the auto-zero memory depending on the state of the sample programmer.

The preceding sequence is repeated once each twelve seconds so that either the auto-zero memory on the read-out memory is updated five times per minute.

The sample programmer is advanced one count for each twelve second cycle of the integrator programmer. The normal state of the sample programmer is the sampling mode in which a signal is transmitted to the sample valve solenoid to open that valve and another signal switches "on" the discharge power supply. Two additional modes can be programmed by means of a "peg board" matrix switch on the control panel. "Standard light" and auto-zero" start and stop functions are programmed for any desired time which is measured in integrator cycle, or twelve second units.

In the "standard light" mode, the discharge power supply is turned off and a pair of light emitting diodes are turned on. The out put memory continues to be updated five times per minute.

In the "auto-zero" mode, the discharge voltage is turned on, the sample valve is closed, the diluent air valve is open and the integrator output is switched to the auto-zero circuit where it updates the auto-zero memory once each twelve seconds.

The sample cycle is terminated and another began at any time up to 999 integrator cycles, or 1998 minutes, by programming the recycle point on the matrix switch.

The standard gas programmer is advanced one count for each recycle of the sample programmer. Its function is to provide a calibration check for the instrument. At the end of thirty-two recycles of the sample cycle, the standard gas mode is initiated wherein the sample valve is closed and the diluent air valve and a "standard NO" valve are opened to provide a sample with a known concentration of pollutant. The number of sample cycles that occur before the "standard NO" cycle terminates is programmable on the matrix switch. The following "standard" cycle opens the standard NO_2 valve rather than the NO valve. Thus, the standard cycle alternates NO standard gas and NO_2 standard gas.

4.4 NO_x FLOW SYSTEM - GENERAL DESCRIPTION

The flow portion of the instrument consists essentially of the sample, diluent, argon-oxygen and NO-NO_2 gas flow sub systems. Appropriate system pressure in the discharge and reaction chambers is maintained with a vacuum pump. A simplified schematic illustration of the instrument flow system is shown in Figure 1. The instrument is packaged into a standard 22 inch wide by 28 inches high relay rack cabinet. The vacuum pump is attached to the system through a port on the back side of the cabinet.

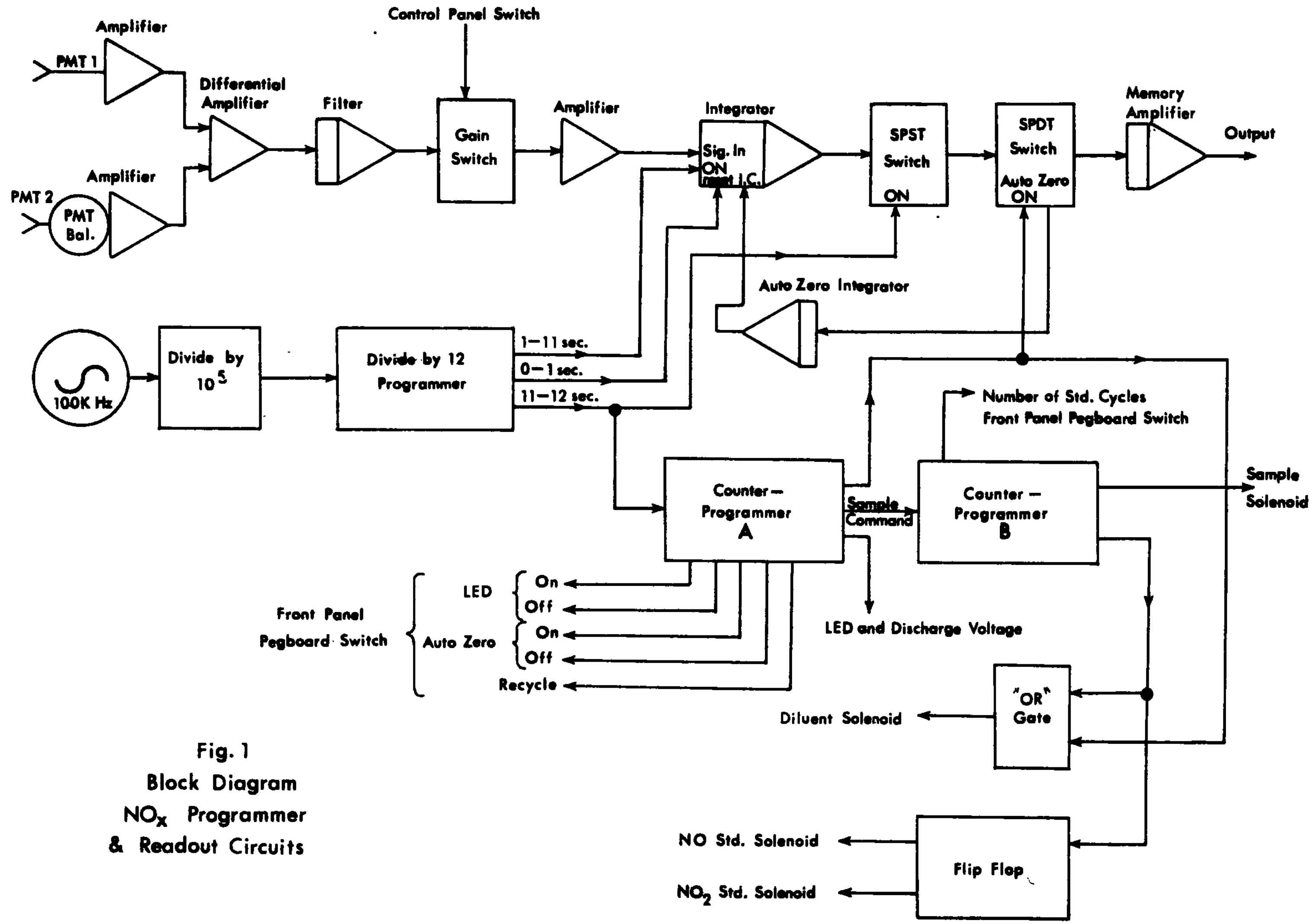


Fig. 1
Block Diagram
NO_x Programmer
& Readout Circuits

The outside air sample is drawn through the system at the sampling port (BH-2) and through the normally closed solenoid valves (SV-2 and SV-3) and filter (F-2). The volumetric flow rate of the air sample is controlled by the critical flow orifice (CFO-2). A flow calibration curve for this orifice is illustrated in Figure 2. Since the sample is drawn at the atmospheric pressure, the sample flow rate is essentially fixed at 54 cc/minute. The sample then enters the reactor chamber and is discharged through the vacuum pump (VP).

The ultra clean diluent air enters the system through the storage tank (TK-2) port (BH-1), normally closed solenoid valve (SV-1). The diluent air pressure is regulated by the pressure regulator on the storage tank as well as by diluent air regulator (PR-1). The diluent air flow rate is controlled by the critical flow orifice (CFO-1) using zero air is illustrated in Figure 3.

A 15% mixture of oxygen in Argon is utilized in this instrument for the discharge tube gas flow. The oxygen-argon gas mixture is released from a storage cylinder (TK-1). It flows through the port (BH-5), and the normally closed solenoid valve (SV-6). The gas pressure is regulated by the pressure regulator (PR-3) and the gas flow rate is controlled by the critical flow orifice (CFO-4). A flow rate calibration for this orifice with 15% oxygen, 85% argon mixture is illustrated in Figure 4. The oxygen-argon mixture enters the discharge tube and the reaction chamber. It is exhausted from the system with the other gases through the vacuum pump (VP).

Two ports are provided for admitting either NO or NO_2 calibration gases. One port is designed to utilize calibration gas from a pressurized cylinder. The calibration gas is released from the cylinder (TK-3) and admitted to the port (BH-3) pressure regulator (PR-2) filter (F-2) and critical flow orifice (CFO-3), and through the normally closed solenoid valve (SV-4). The flow rate of calibration gas is controlled by the pressure regulator (PR-2) and the quartz-tube critical flow orifice (CFO-3). A flow rate calibration for the critical flow orifice is illustrated in Figure 5. From the critical flow orifice the calibration gas enters the reaction chamber and is expelled by the vacuum pump (VP). Another port (BH-4) can be utilized for admitting calibration gases by a permeation tube. In this case, the permeation tube is connected to the permeation port (BH-4). Operation of the permeation port is controlled by the solenoid valve (SV-5).

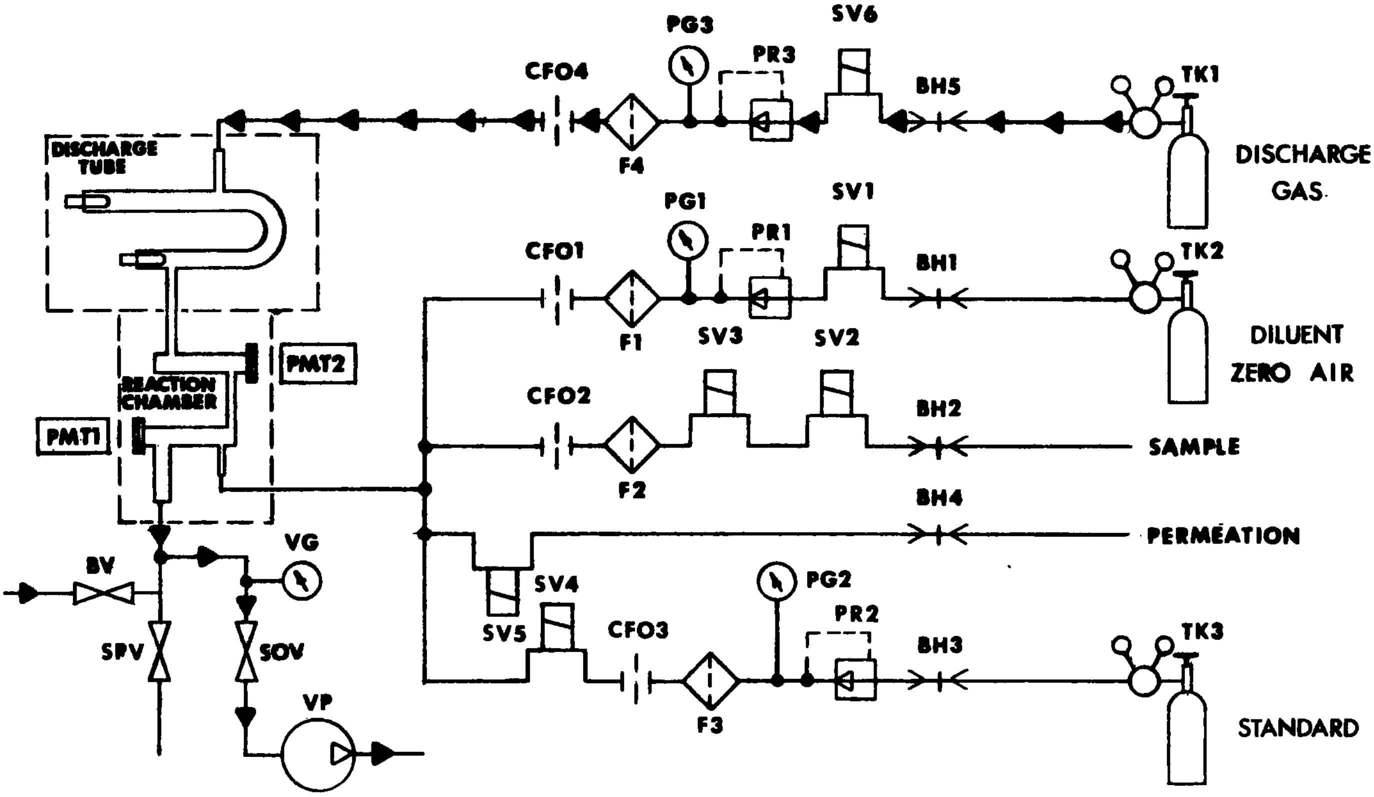


Fig. 2 Flow System Schematic Diagram

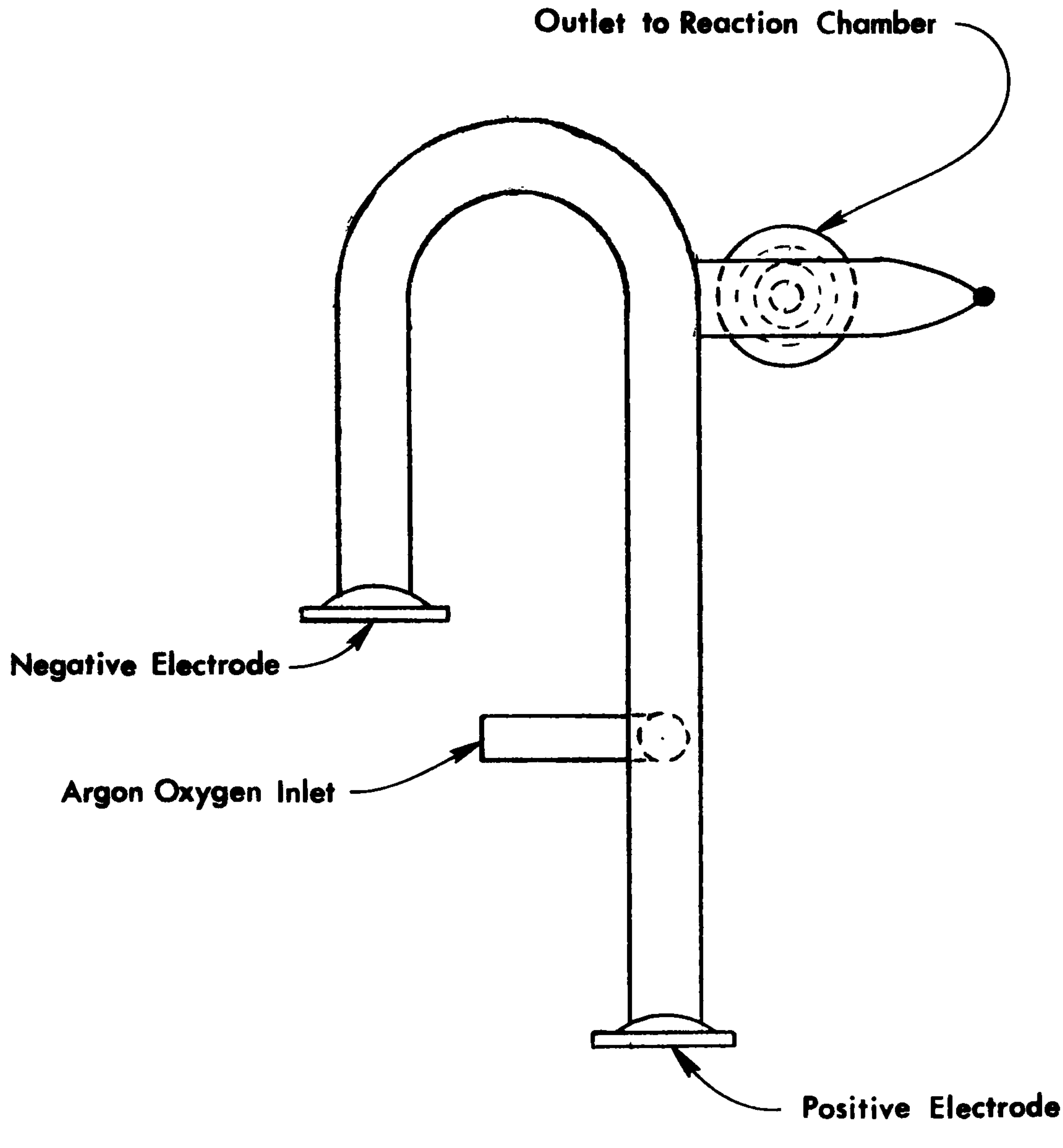


Fig. 3 Discharge Tube

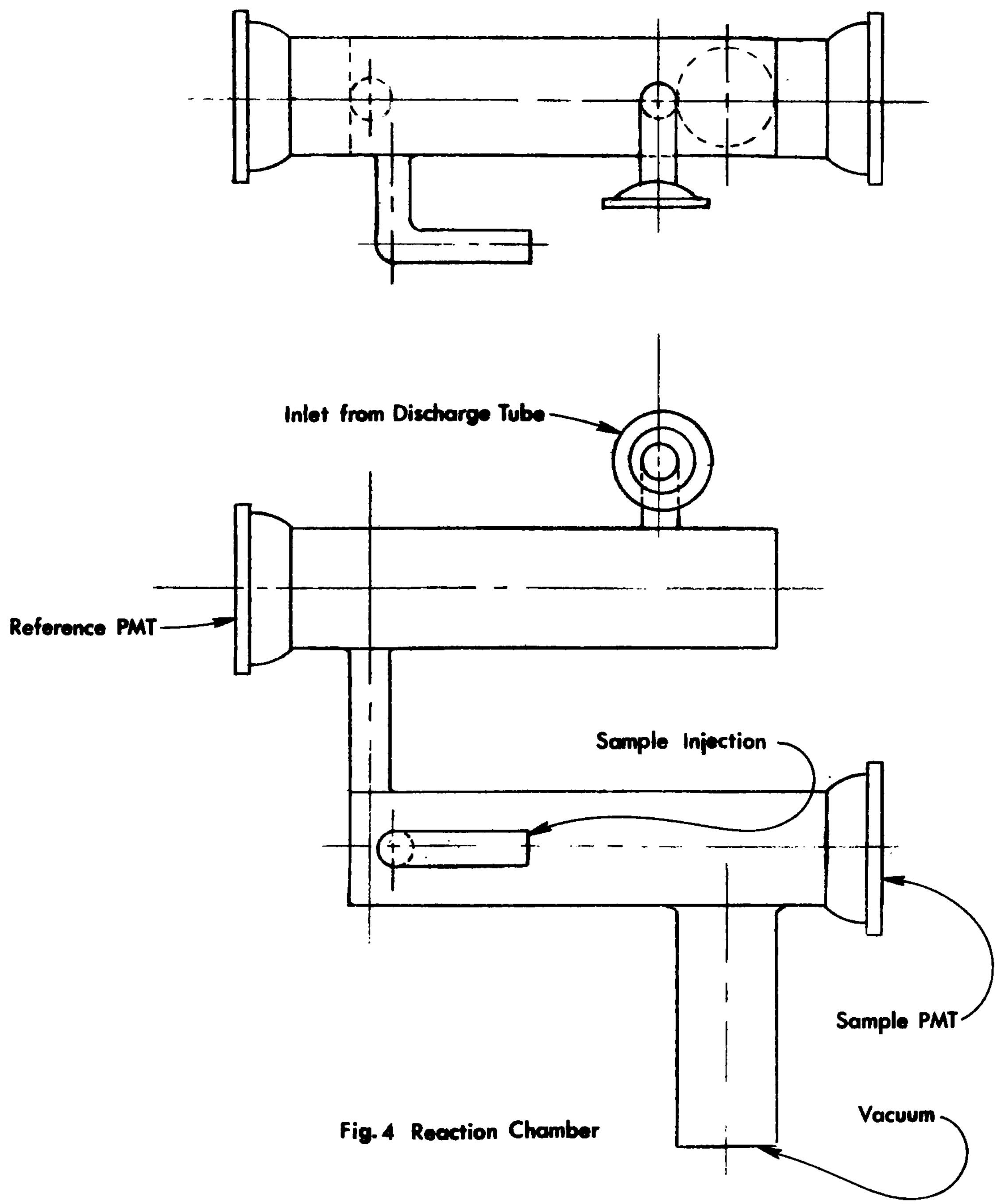


Fig. 4 Reaction Chamber

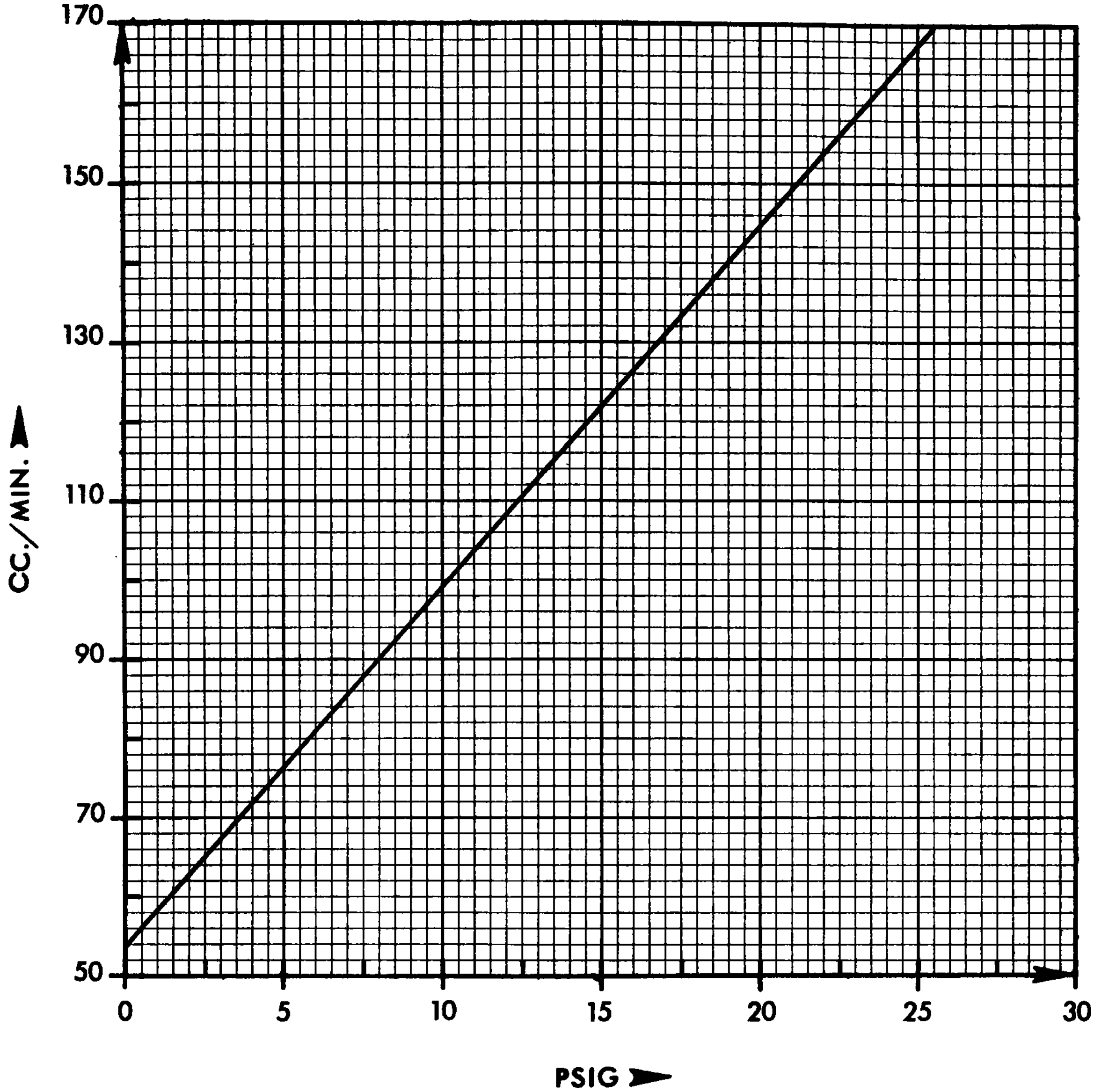


Fig. 5 Sample Flow (CF02) Calibration Curve

The vacuum range of 1 Torr in the discharge tube and reaction chambers is maintained with Welsh Model 1402 vacuum pump. Vacuum pressure is monitored with Leybold Hareaus Model TM201S vacuum gage. Pressure in the system can be controlled by either introducing outside air into the system through the bleed valve (BV) or by proper adjustment of the system shut-off valve (SOV). Toggle valve (SRV) is used to quickly expose the system to the atmospheric pressure.

The heat generated by the reactor assembly is dissipated with convective cooling provided by a blower. The blower provides a positive pressure inside the instrument cabinet and thus helps to keep dust from entering the instrument enclosure.

5. OPERATING PROCEDURE

5.1 PROGRAMMER

The control logic for the NO/NO_x instrument consists of four sections: Reset and Clocks logic, Integrator Programmer, Sample Programmer, and Standard Programmer. Of these, only the sample programmer and the standard programmer are programmed by the operator. However, some knowledge of the integrator programmer operation will aid the operator in programming the other two programmers.

The integrator programmer controls the operation of an electronic integrator whose output is a function of the NO/NO_x concentration in the gas being sampled by the instrument. The programmer first resets the integrator to an initial condition voltage, it then causes the integrator to integrate for ten seconds a signal proportional to NO/NO_x concentration. The programmer then stops integration, the integrator holds the result, and the integration result is used to update either the system's read-out memory or its auto-zero memory. One or the other of these memories is updated every twelve seconds. The sample programmer is advanced one count for easy cycle of the integrator programmer i.e., once every twelve seconds.

The standard programmer (which is actually a sub unit of the sample programmer) is advanced one count for each cycle of the sample programmer. The controls for the sample and standard programmers are; 1) Program reset pushbutton which when depressed resets all programmers to zero and when released allows the program to start. 2) A programming matrix board which allows the operator to select start and stop times for the progammable functions.

The upper five rows (horizontal) of the matrix are used to control the sample programmer. These rows represent functions and are labeled: STD light: Start - Stop, Auto-Zero: Start - Stop and Recyle. The columns (vertical) of the matrix represent time and are labeled: HUNDREDS (0 through 9), TENS (0 through 9) and UNITS (0 through 9). A unit of time represented by the columns is twelve seconds (for the sample programmer functions). The bottom row of the UNITS holes only is used to control the standard programmer. This row is labeled number of cycles of STD gas. These holes represent cycles of the sample programmer and thus have a time value dependent on the cycle length for which the sample programmer is set.

An example will illustrate the programming procedure. Suppose it is desired to "look at" standard light for two minutes, and then to have a five minute auto zero cycle followed by a five minute analysis of a sample gas. Programming in the NO/NO_x system is done on an "actual time minus one" basis. That is, to program for actual time "t", the programming pins are placed in holes corresponding to t-1 units. In this system 000 is programmed 999 (there are no negative numbers) time 002 is programmed 001, time 999 is programmed 998, and so on.

For the example program, standard light is to start at (t) 000 and stop at (t) 010, and elapsed time of (000-010) times 12 equals 120 seconds equals two minutes. Auto-zero is to start at (t) 010 and stop at (t) 035, and elapsed time for auto-zero of five minutes. Sample measurement is to start at (t) 035 and stop at (t) 060. Programming pins are placed as shown on the chart.

Function		Hundreds	Tens Pin	Units Pin
STD Light	Start	9	9	9
	Stop	0	0	9
Auto-Zero	Start	0	0	9
	Stop	0	3	4
Recycle		0	5	9

Note that the sample measurement time is programmed indirectly. During the program cycle, sample gas is automatically on when STD light and Auto-Zero are both off. Therefore, in the example program, when Auto-Zero goes of at (t) 035, sample gas is turned on and being analyzed from (t) 035 through the end of the cycle at (t) 060.

The example program would cause the NO/NO_x instrument to act as follows:

At the release of the Program Reset button the discharge high voltage is off, the sample gas valve is open, the diluent STD NO and STD NO_2 valves are closed and the integrator begins its one second reset period. After one second, the integrator begins its ten second integration period. The integrator is now integrating the "signal" caused by the Standard Light. At the end of the integration period, the integrator holds the integration result for one second while the read-out memory is updated with this result. The integrator is then reset and the reset-integrate-hold and update cycle begins again.

After ten such cycles the Standard Light is turned off, the sample gas valve is closed, the diluent valve is opened and the discharge high voltage is turned on. The integrator resets for one second and begins its ten second integration period. Now the signal integrated is due to NO/NO_x in the diluent and discharge gases. This time the integrated r result is used to update the Auto-Zero memory. The Auto-Zero memory voltage is used as the initial condition voltage which is set into the integrator during its reset period. This voltage is of a polarity such that at the next reset period the integrator is set to an initial condition voltage opposite in polarity and approximately equal in amplitude to the result obtained by the previous integration. Thus, the result of the next integration will be close to zero. Assuming the same integration input signal, after several reset-integrated-hold and update cycles the integrated result will be very near zero volts. In this manner the "background" signal produced by NO/NO_x present in the diluent and discharge gases is cancelled.

Note, however, that the read-out memory is not changed during the auto-zero process but retains the last result obtained prior to starting auto-zero. After twenty-five 12-second cycles of reset-integrate-hold and update auto-zero memory, the program begins the sample measurement at (t) 035 then the sample gas valve opens and the diluent gas valve closes. The integrator continues its cycle as before except that now it resets to an initial condition voltage equal to that held in the auto-zero memory (which will not be updated during this portion of the program). During the integrate periods the integrator will be integrating a signal proportional to the NO/NO_x concen-tration in the sample gas. During each hold-update period the read-out memory will be updated. Thus, every 12 seconds the system read-out will receive new information as to the NO/NO_x concentra-tion in the sample gas. At (t) 060 after twenty-five 12-second integrator programmer cycles the sample programmer will recycle and the Standard Light mode will be started again. As was mentioned before the Standard Programmer merely modifies the sample program at the proper time. The Standard Programmer logic counts cycles of the sample program and after thirty-two cycles causes the sample program to be modified to a standard program. When this happens, standard gas plus diluent is substituted whenever sample gas is called for by the program.

The operator may select the number of cycles (minimum one cycle, maximum ten cycles) that the sample gas/ diluent mixture is analyzed. This is done by placing a pin in the UNITS holes of the No. of cycles of STD gas row. The same t-1 rule used on the Sample Programmer applies here. Therefore, to program three sample programmer cycles of standard gas measurement one places a pin in Units two of No. of cycles of STD gas row.

The logic of the Standard Programmer causes the standard gas selected each time the standard program is entered to alternate between standard NO and standard NO_2.

If in our example program a pin is placed in Unit two of No. of cycles of STD gas row, then after 32 cycles of the sample program (6 hours and 24 minutes after starting program) a standard cycle will begin. The Standard Light and Auto-Zero portions of the program will be unchanged. When Auto-Zero ends, however, the sample gas valve will remain closed, th the diluent valve will remain open and the standard NO valve will open.

The standard cycle will repeat three times so that 36 minutes after entering the standard measurement mode the program will return to the sample mode. After another 32 cycles in the sample mode, the program will again enter the standard mode for three cycles. This time, however, the standard gas selected will be NO_2 and the NO valve will remain closed with the NO_2 valve opening instead.

5.2 START-UP PROCEDURE

After the instrument has been checked for obvious damage, the vacuum system should be connected and with all input valves closed, the vacuum chamber should be pumped down.

To insure proper out gasing, the initial pump down period should be several hours, preferrably overnight. During the pump down period, the oxygen-argon, diluent air, and standard NO bottles may be connected to their respective fitting at the rear of the instrument. After the vacuum chamber is evacuated to well below one Torr, the pressure is adjusted to one Torr by means of the bleed valve (BV-1). The power should be turned on and the instrument programmed for the auto-zero mode. (See programming instructions.) The argon-oxygen mixture valve can then be opened and the flow set by means of the inlet pressure (PR-3). After a two minute delay, the discharge voltage is automatically turned on and the electric discharge initiated.

The monitor meter should indicate low in the green band when the discharge is properly adjusted. The discharge power supply is current regulated and can be adjusted by means of the potentiometer, R4, in the discharge supply module. The diluent air can then be turned on and its flow adjusted. In all probability, the read-out circuit will be considerably unbalanced initially. At least one day is required for the entire system to stabilize sufficiently to provide significant readings. When in the auto-zero mode, the output of the integrator (point AA on the mother board) should approach zero at the end of each integration cycle, then reset to some level representing the unbalance of the background. As the system becomes stable, that unbalance becomes small. After sufficient time, the instrument can be programmed for a five minute read-out cycle followed by a five minute auto-zero cycle. It should be insured that the air entering the sample inlet is essentially free of NO_x. Therefore, any offset in the sample, after the initial switching transient decays, is the result of a difference in flow of the diluent and the sample. That difference can be adjusted out carefully adjusting the flow of the diluent pressure by means of SV-1.

After thirty-two cycles (auto-zero, read-out) a mixture of Standard gas and diluent air is substituted for the sample, by adjusting the flow of the standard gas (PR-2) and knowing its composition, the calibration can be checked. Some offset may result from the flow change and must be accounted for. Since the NO_x instrument contains an all electronic auto-zero circuit, the memory circuits can not be depended on for more than approximately 15 minutes, worst case, or one hour, typical. The frequency of the auto-zero cycle should be determined by the limitations of the memory devices. Differences in the photo multiplier outputs can be balanced out by means of the potentiometer, R4 on the differential amplifier board.

The instrument is calibrated to read out 500 ppb on 1000 ppb depending on the position of the range switch on the front panel. The ranges may be extended by a range multiplier switch on the front panel by factors of 2 or 4. Thus, the 500 ppb range can be extended to 1000 ppb or 2000 ppb and the 1000 ppb range can be extended to 2000 ppb or 4000 ppb. Each range is based on one volt full scale output. The recorder switch on the front panel matches the recorder full scale span to one volt. Thus, it is set at 10 m.v. for use with a 10 m.v. recorder. If the calibration should require adjusting, the three potentiometers on the "Gain" amplifier must be adjusted separately to provide the correct (one volt full scale) output when their respective positions on the range multiplier are selected.

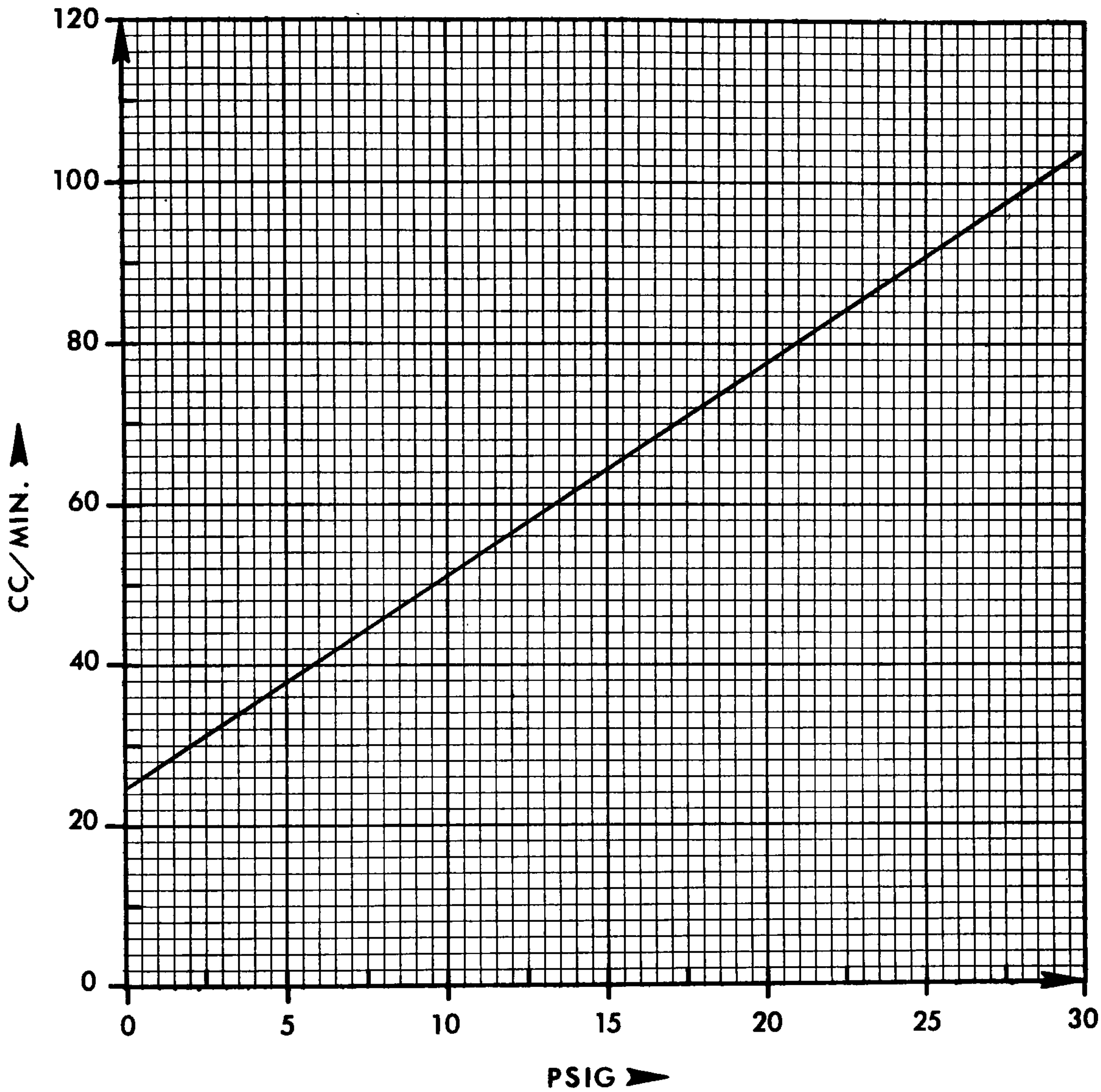


Fig. 6 Argon Oxygen Flow (CF04) Calibration Curve

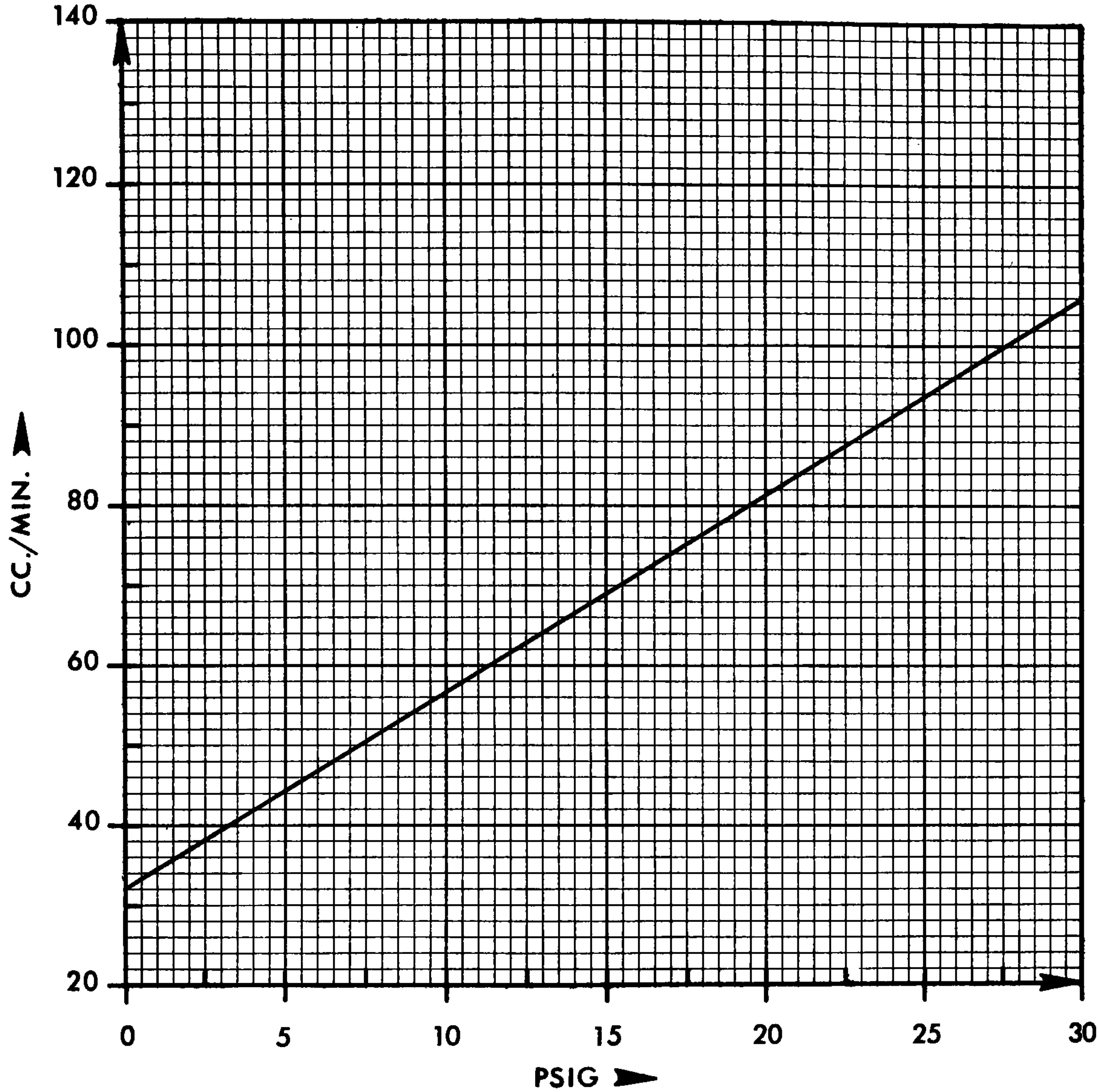


Fig. 7 Diluent Air Flow (CF01) Calibration Curve

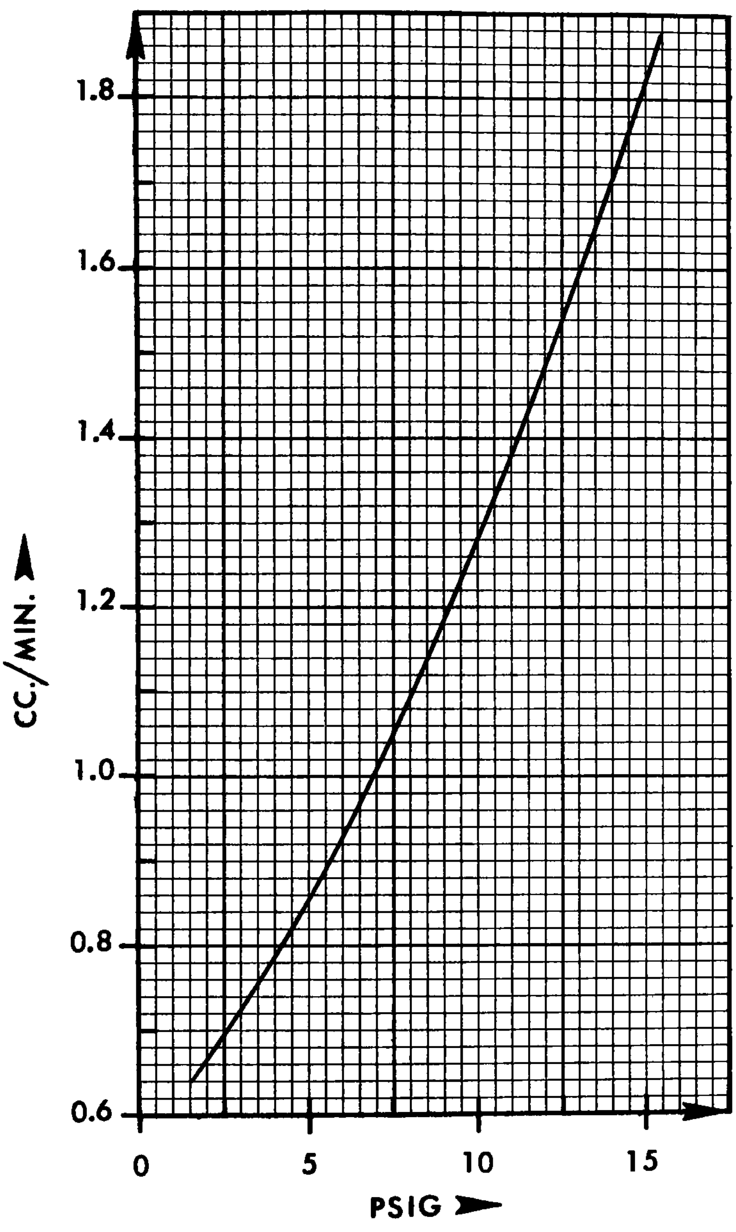


Fig. 8 Standard Gas Flow (CF03) Calibration Curve

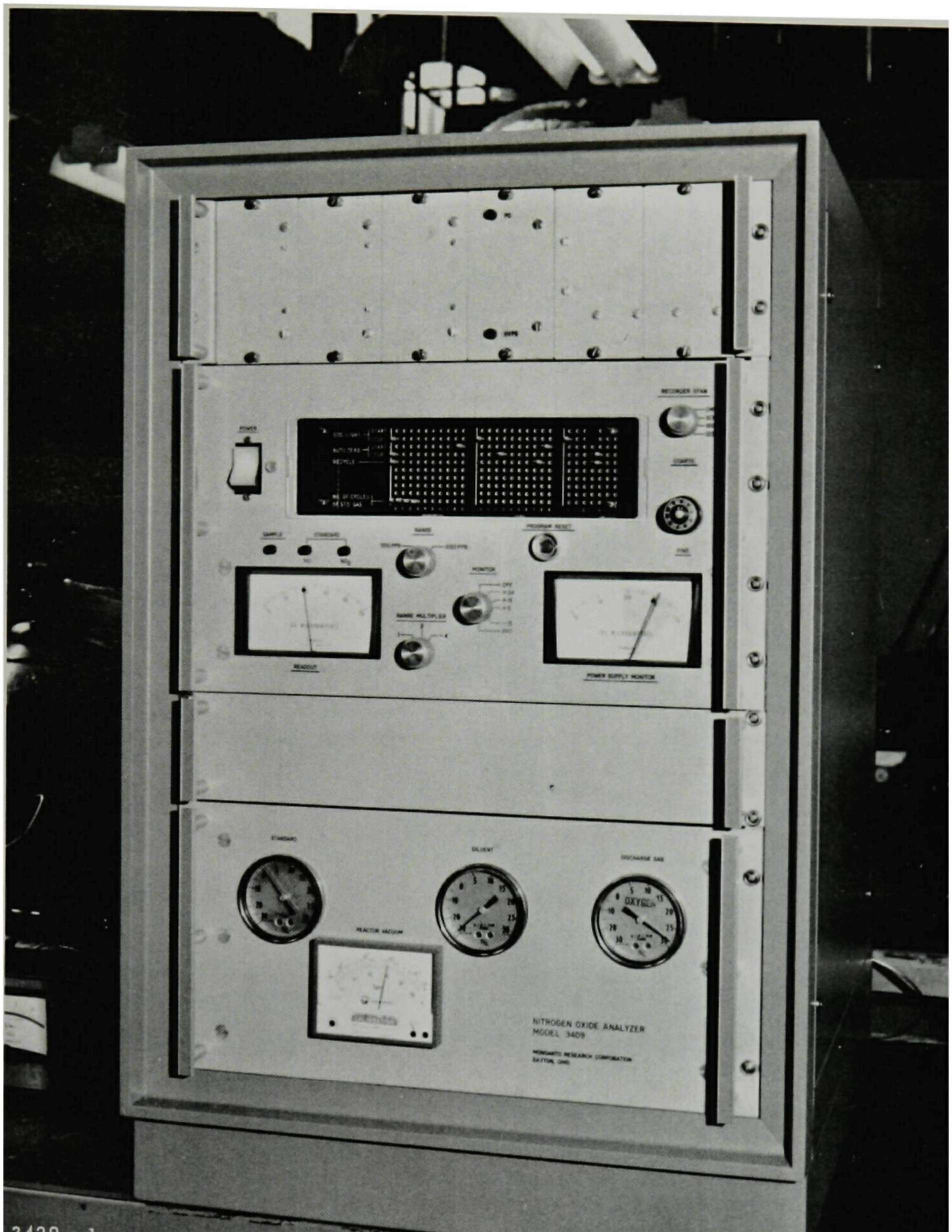


Figure 9. Photo of NO_x Instrument - Front

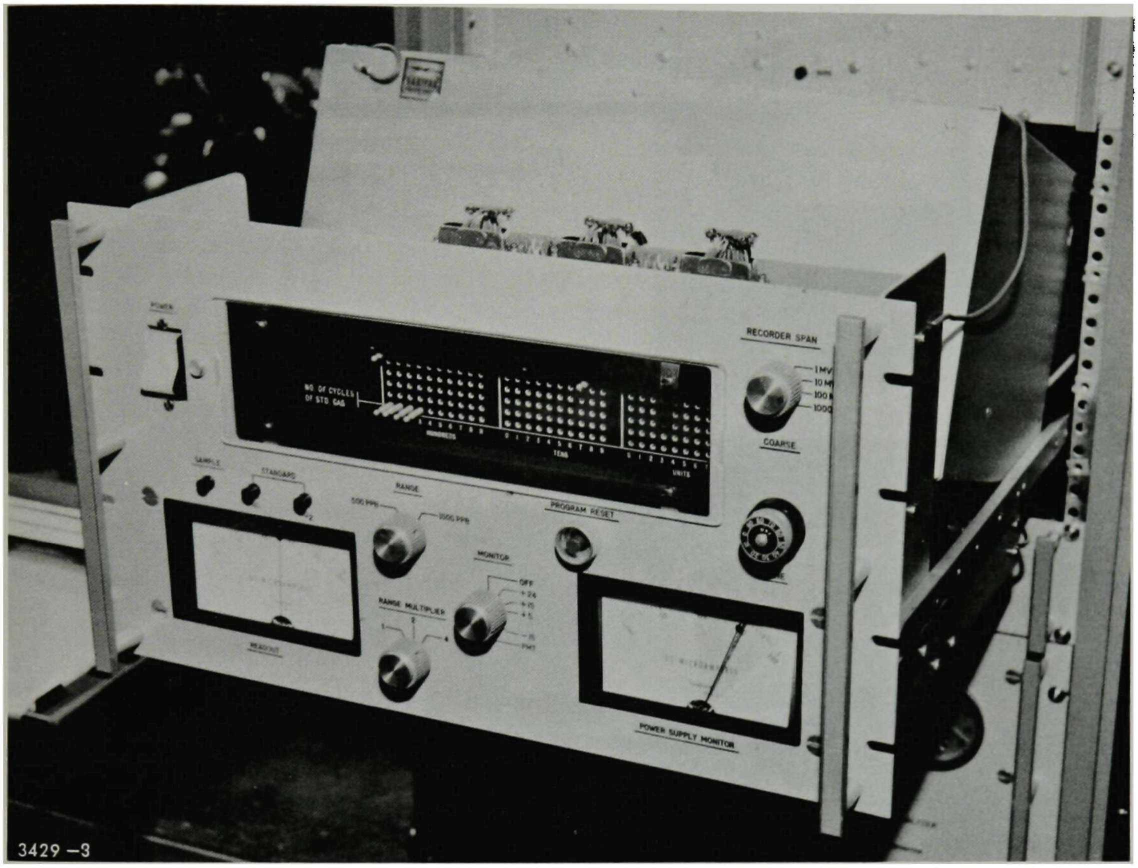


Figure 10. Photo of NO_x Instrument - Control Panel

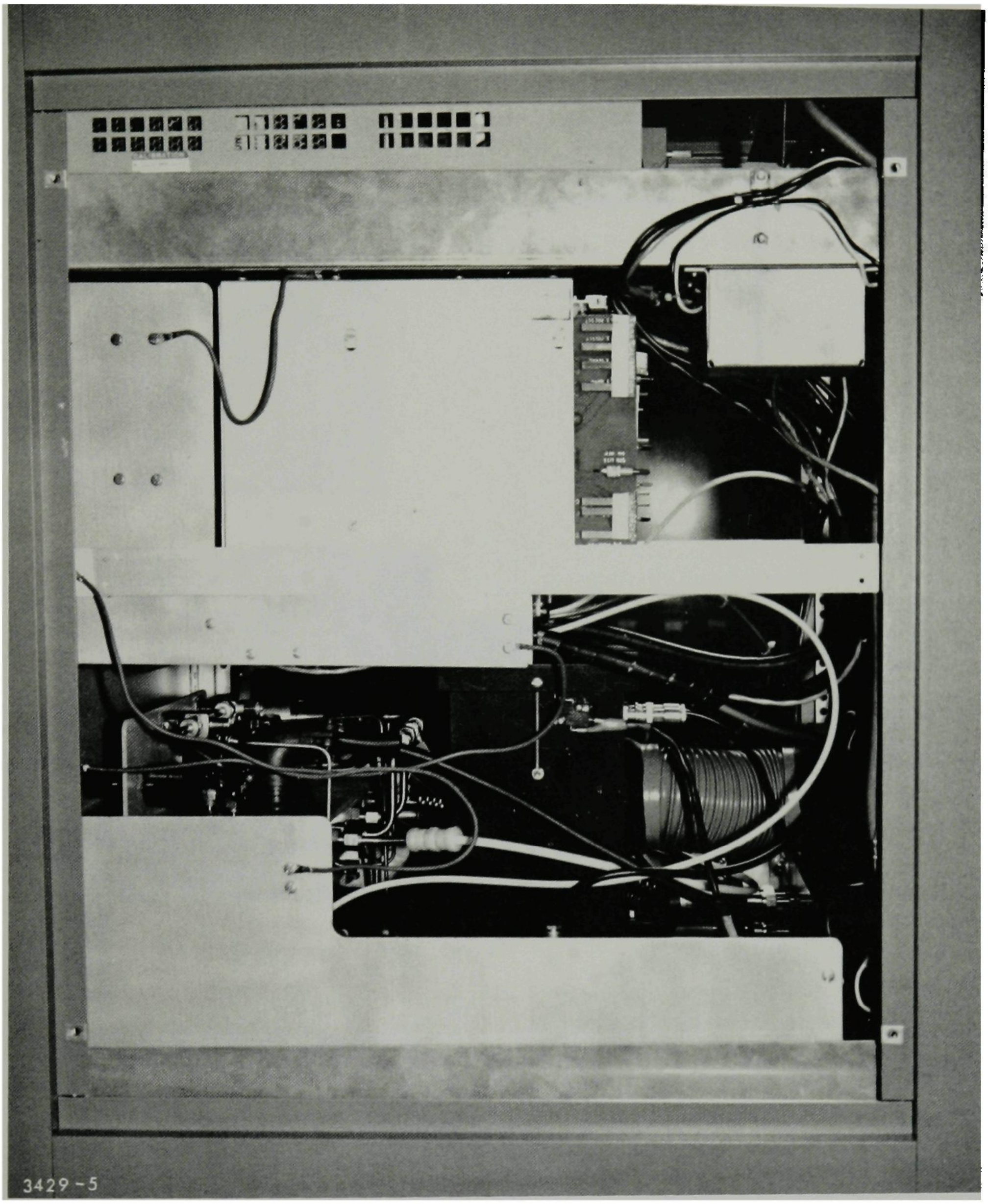


Figure 11. Photo of NO_x Instrument - Side View with Side Panel Removed (Left)

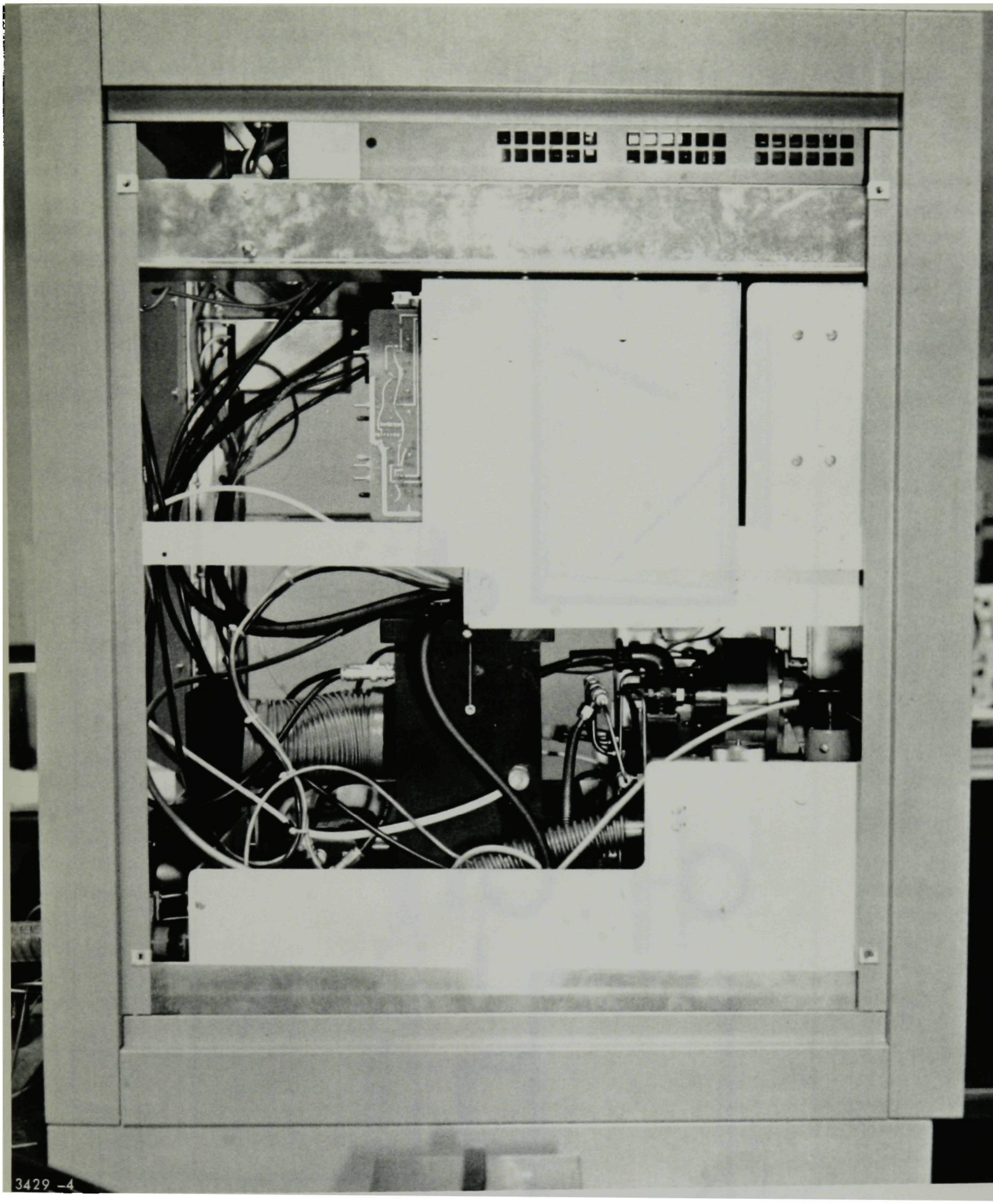


Figure 12. Photo of NO_x Instrument - Side View with Side Panel Removed (Right)

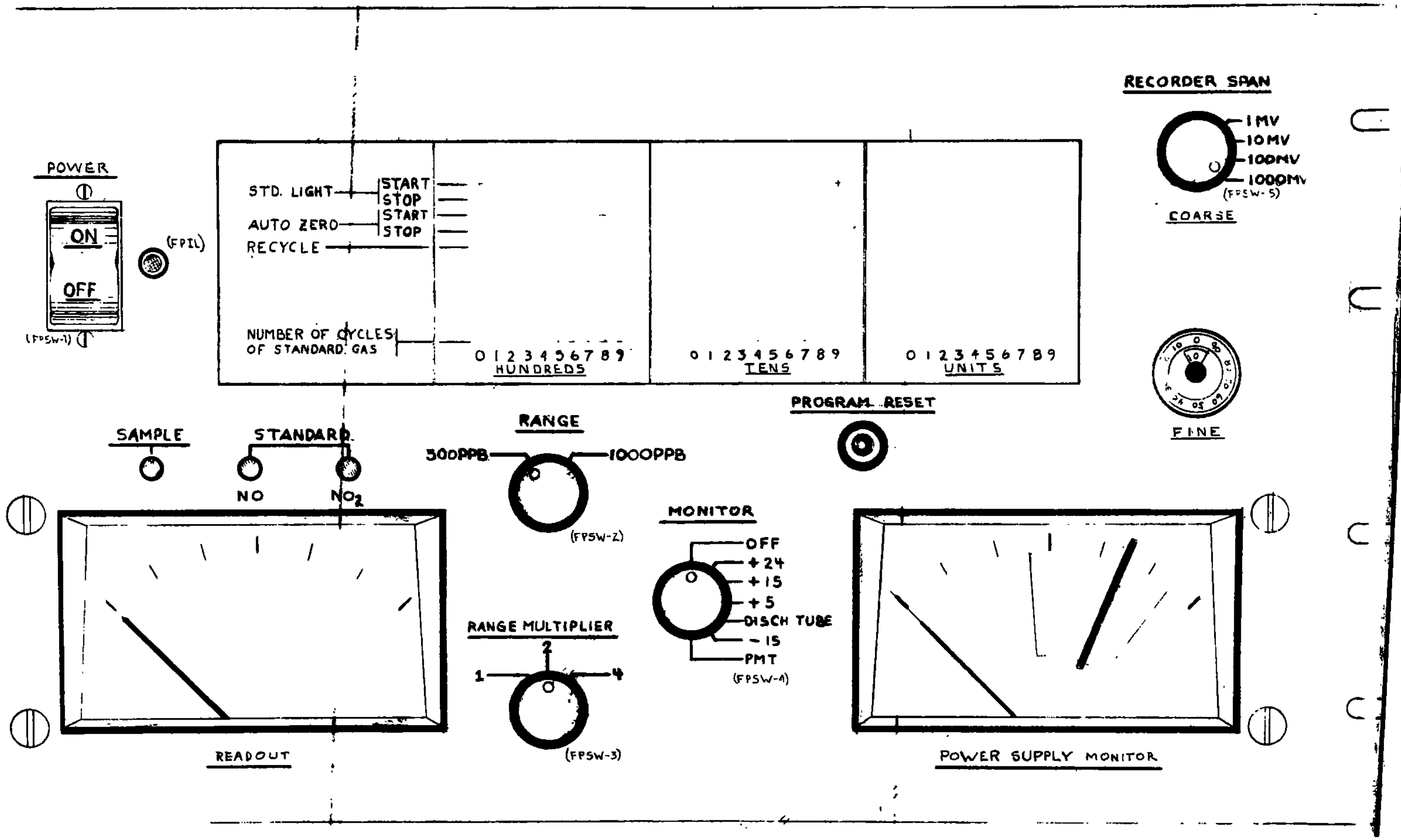


Figure 13. Sketch of Control Panel

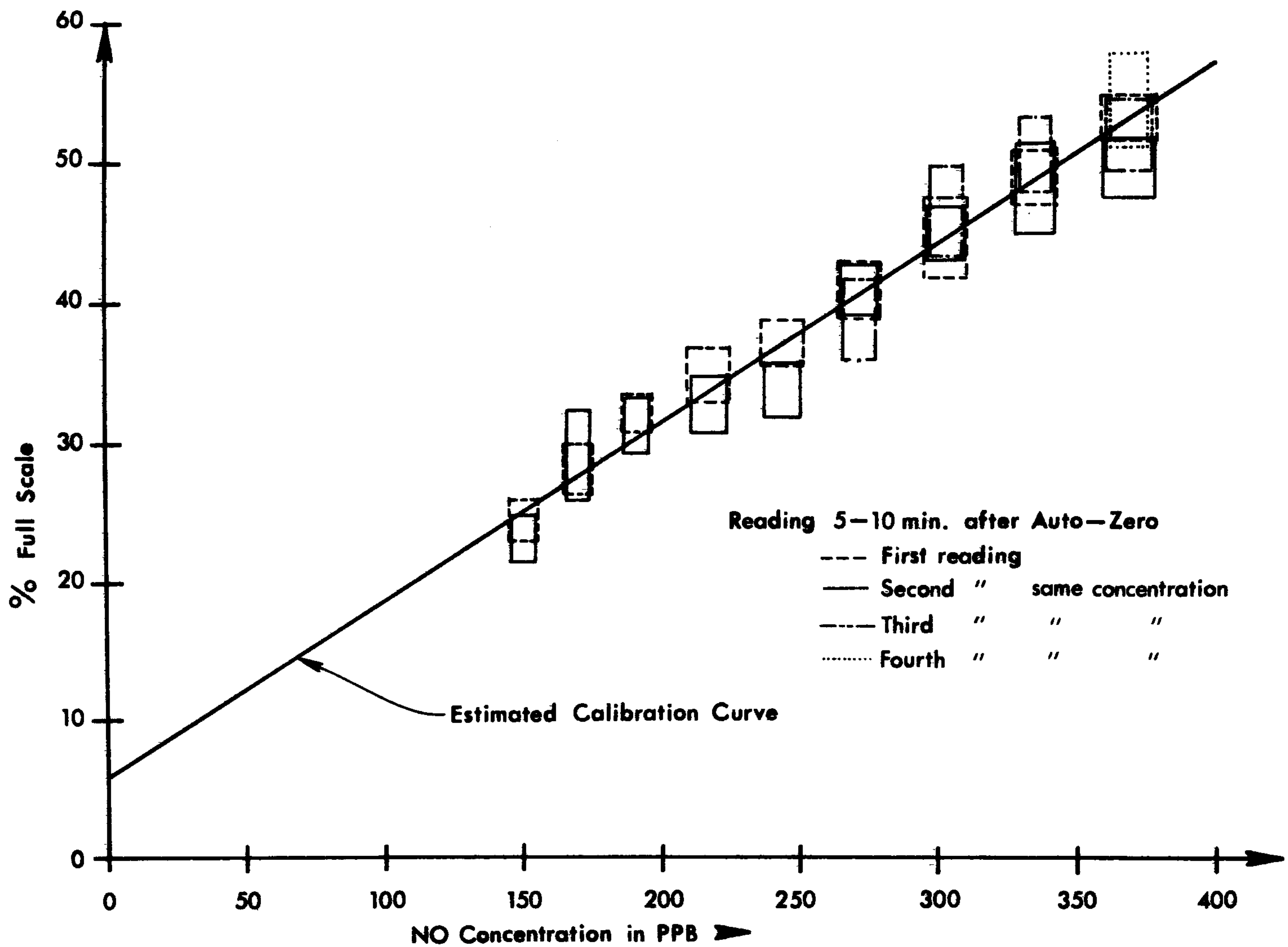

60
50
40
30
20
10
0
% Full Scale
0
50
100
150
200
250
300
350
400
NO Concentration in PPB
Reading 5—10 min. after Auto—Zero
First reading
Second " same concentration
Third " " "
Fourth " " "
Estimated Calibration Curve

Fig. 14

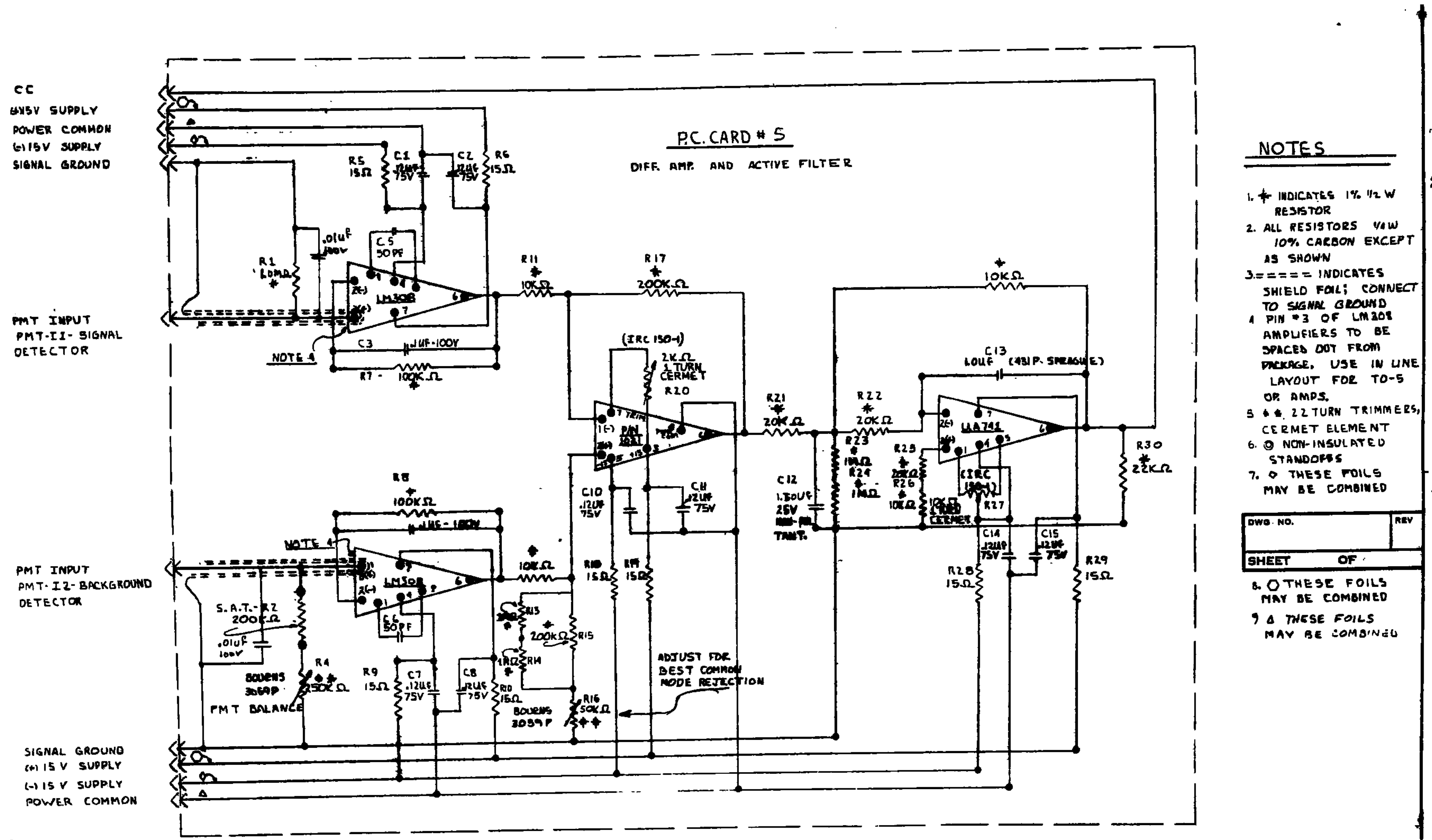


Figure 15. Schematic Diagram, Differential Amplifier

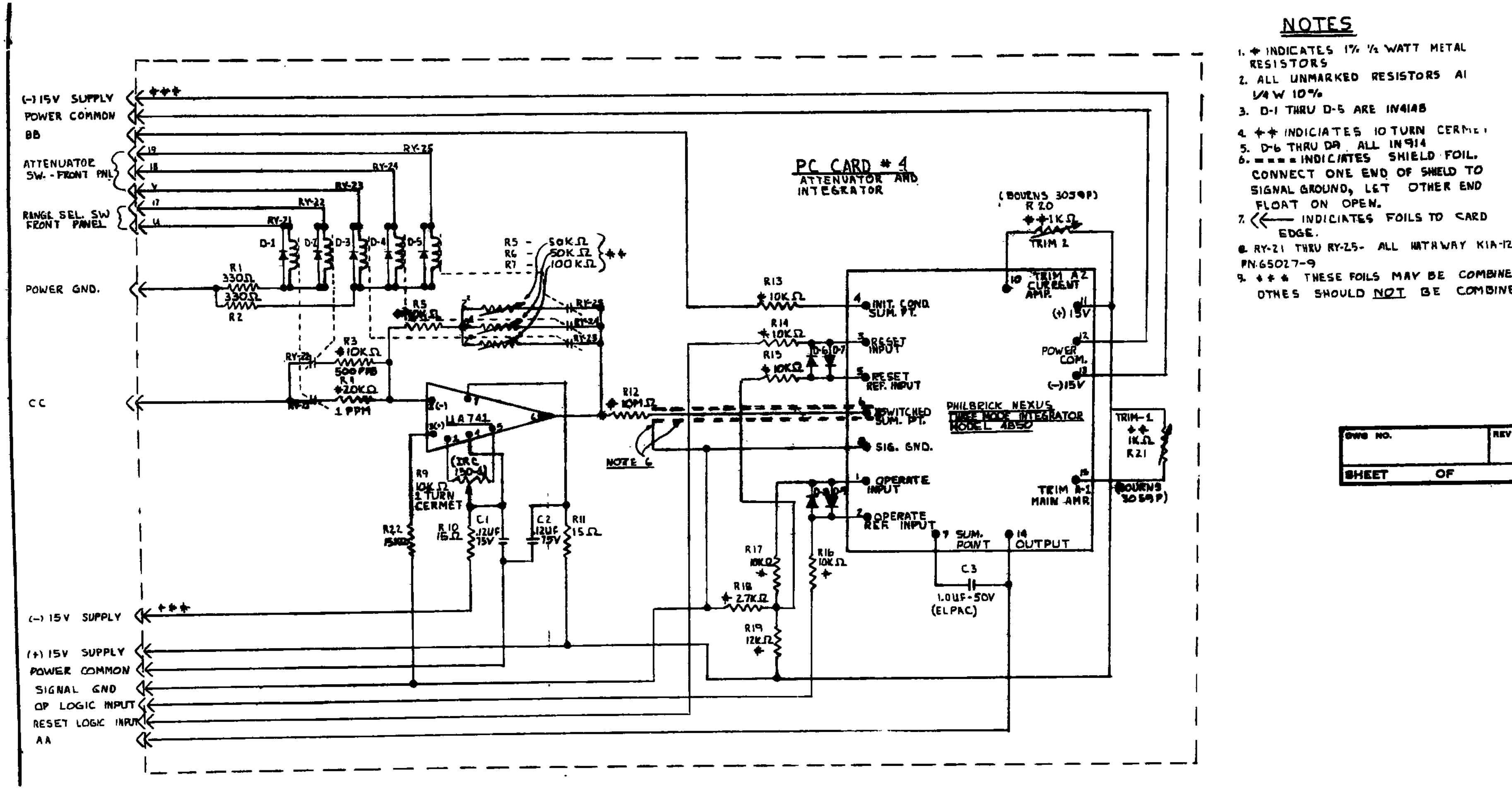


Figure 16. Schematic Diagram, Integrator

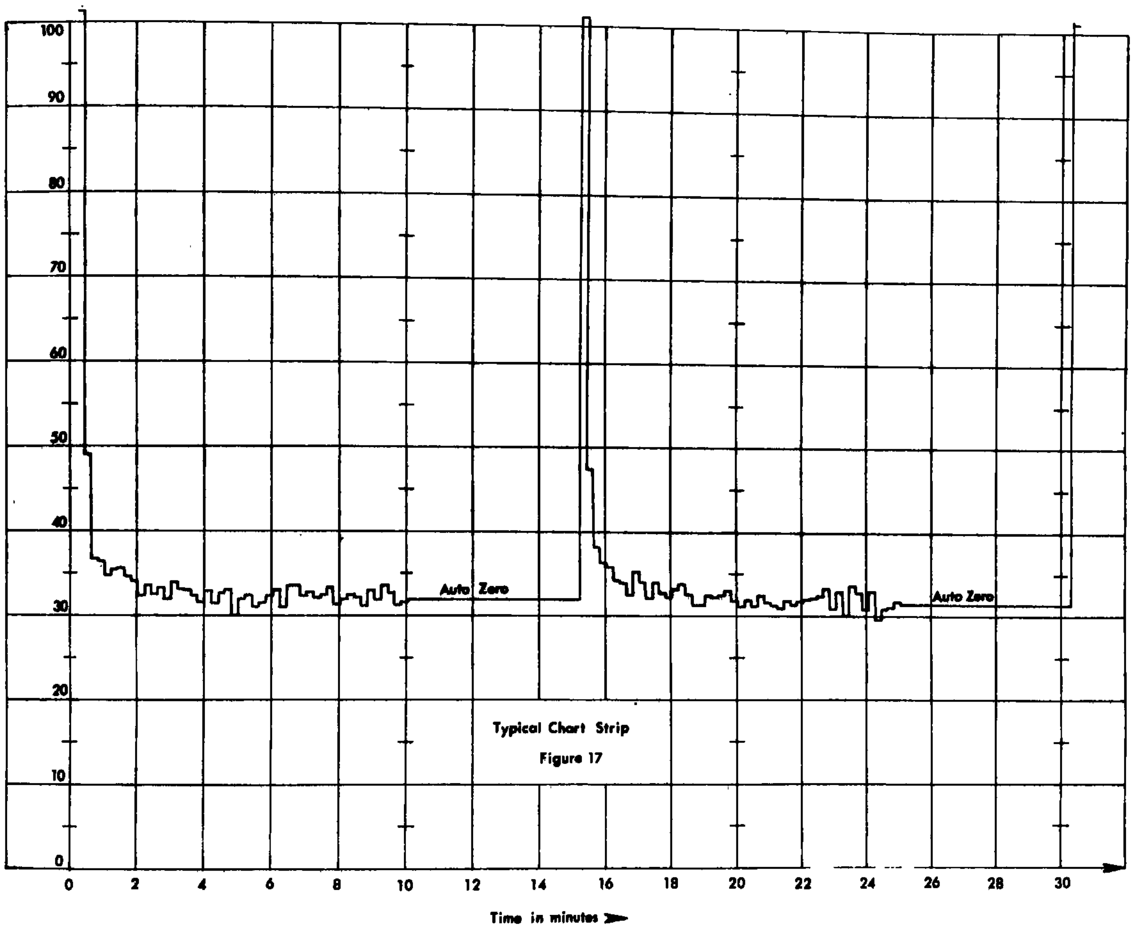
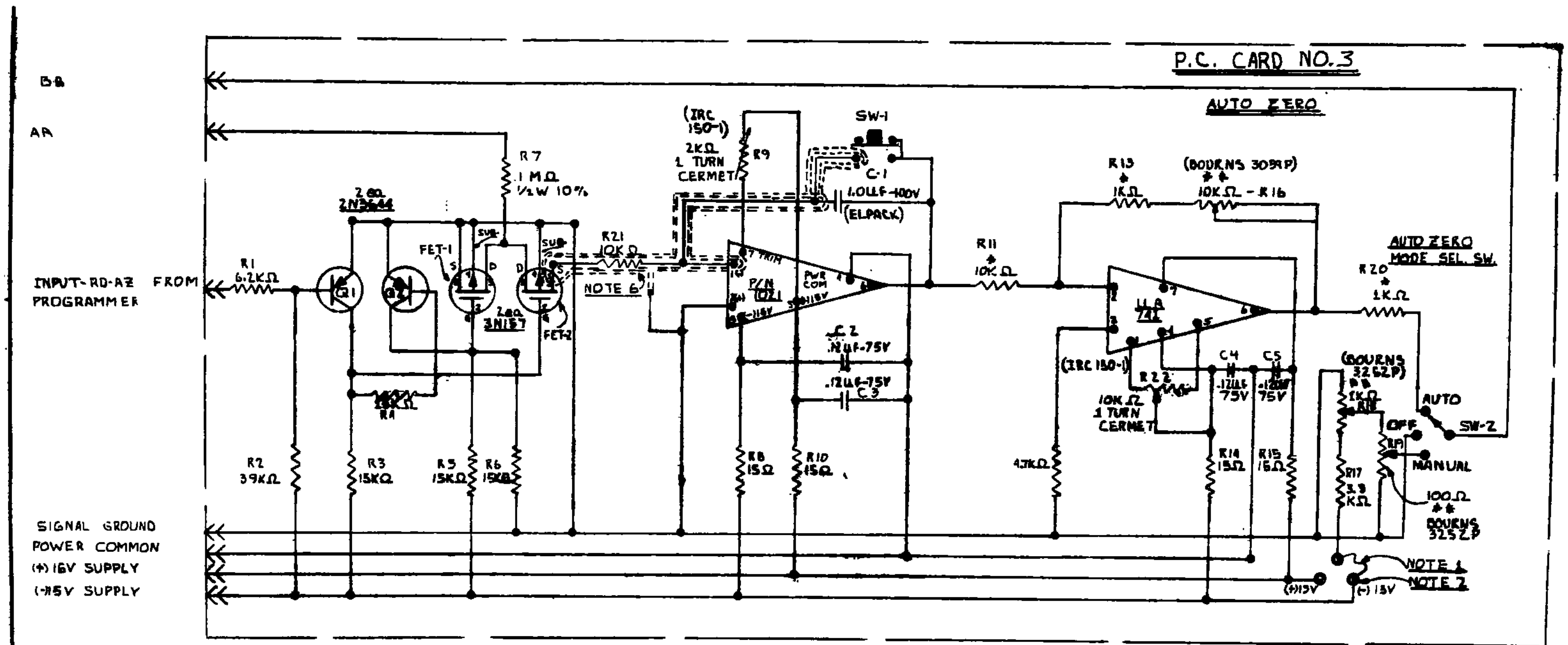


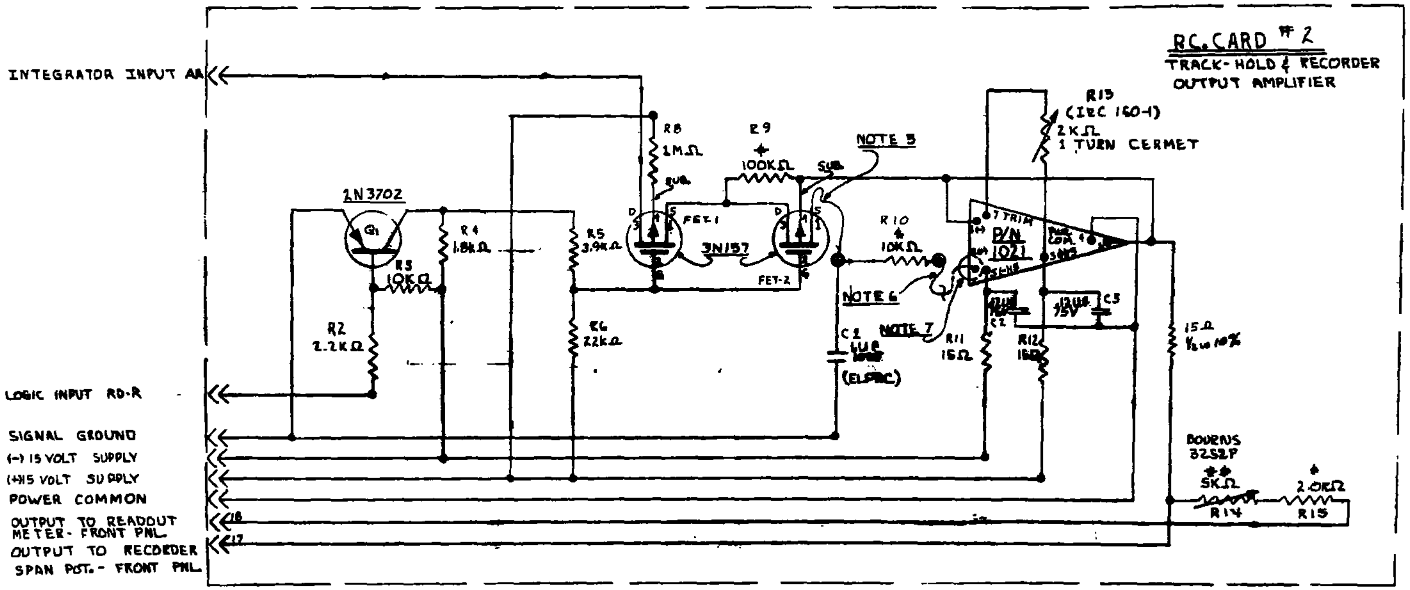
Figure 17. Typical Recorder Trace



NOTES

1 TEFLON JUMPER- INITALLY CONNECT TO (-)15V
2 NON-INSULATED STANDOFF
3 ALL RESISTORS 1/4 W 10% EXCEPT AS NOTED
4. ✦ INDICATES 1/2 W 1% METAL FILM RESISTOR
5. ✦✦ INDICATES 22 TURN CERMET TRIMMER
6 INDICATES SHIELD FOIL-CONNECTED TO SIGNAL GROUND

Figure 18. Schematic Diagram, Auto Zero



NOTES

1. ALL RESISTORS 1/4W 10% EXCEPT AS NOTED
2. ✦ INDICATES 1/2W 1% METAL FILM RESISTORS
3. ✦✦ INDICATES 22 TURN CERMET TRIMMER
4. ⊕ INDICATES TEFLON INSULATED STANDOFF
5. PIN 1 CONNECTS DIRECTLY TO INSULATED STANDOFF AND DOES *NOT* TOUCH P.C. BOARD.
6. ALL JUMPERS ARE TEFLON INSULATED
7. PASS HOLE IN PC. BOARD UNDER PIN #2 OF AMP.; JUMPER CONNECTS DIRECTLY FROM PIN 2 TO INSULATED STANDOFF AND DOES NOT TOUCH BOARD.

Figure 19. Schematic Diagram, Read-Out Amplifier

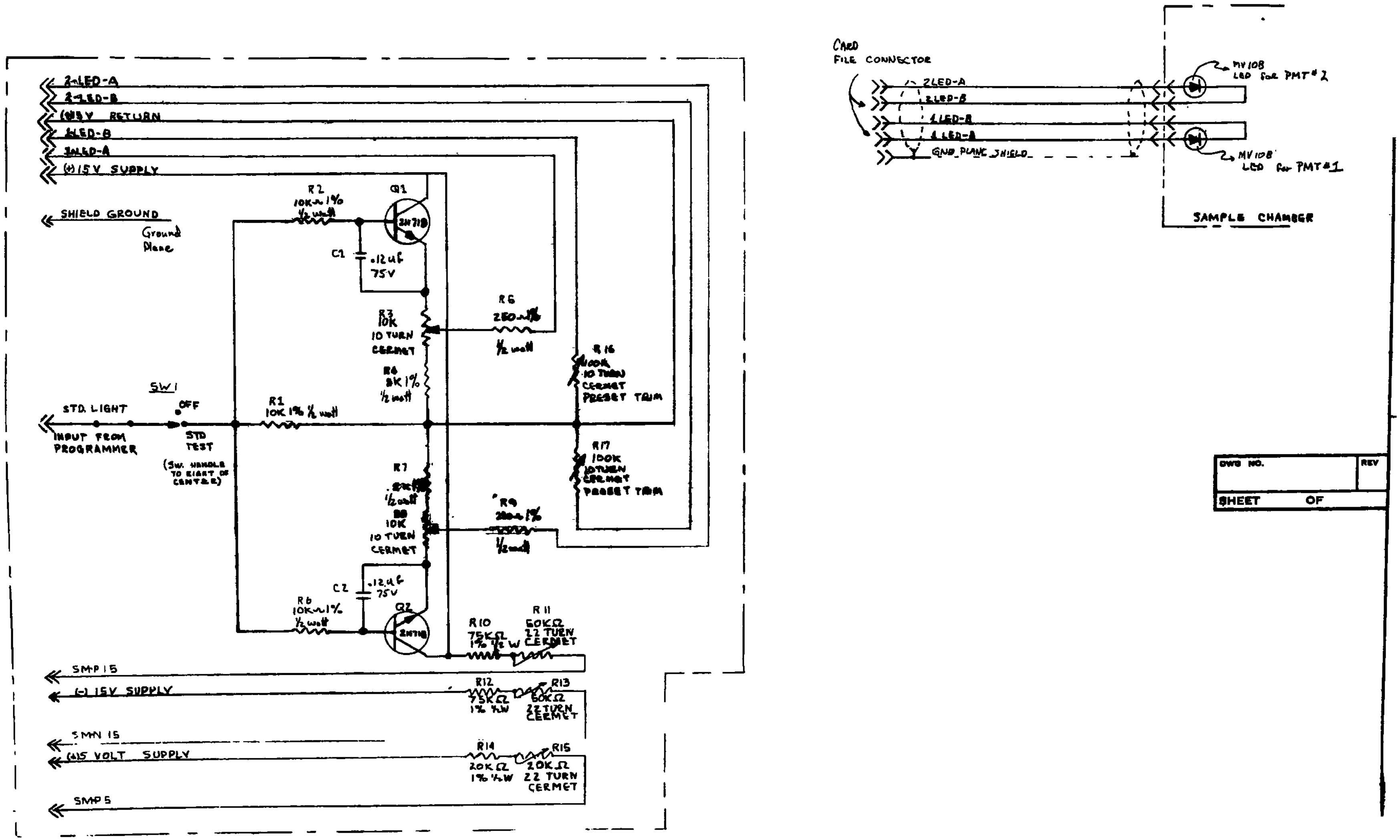
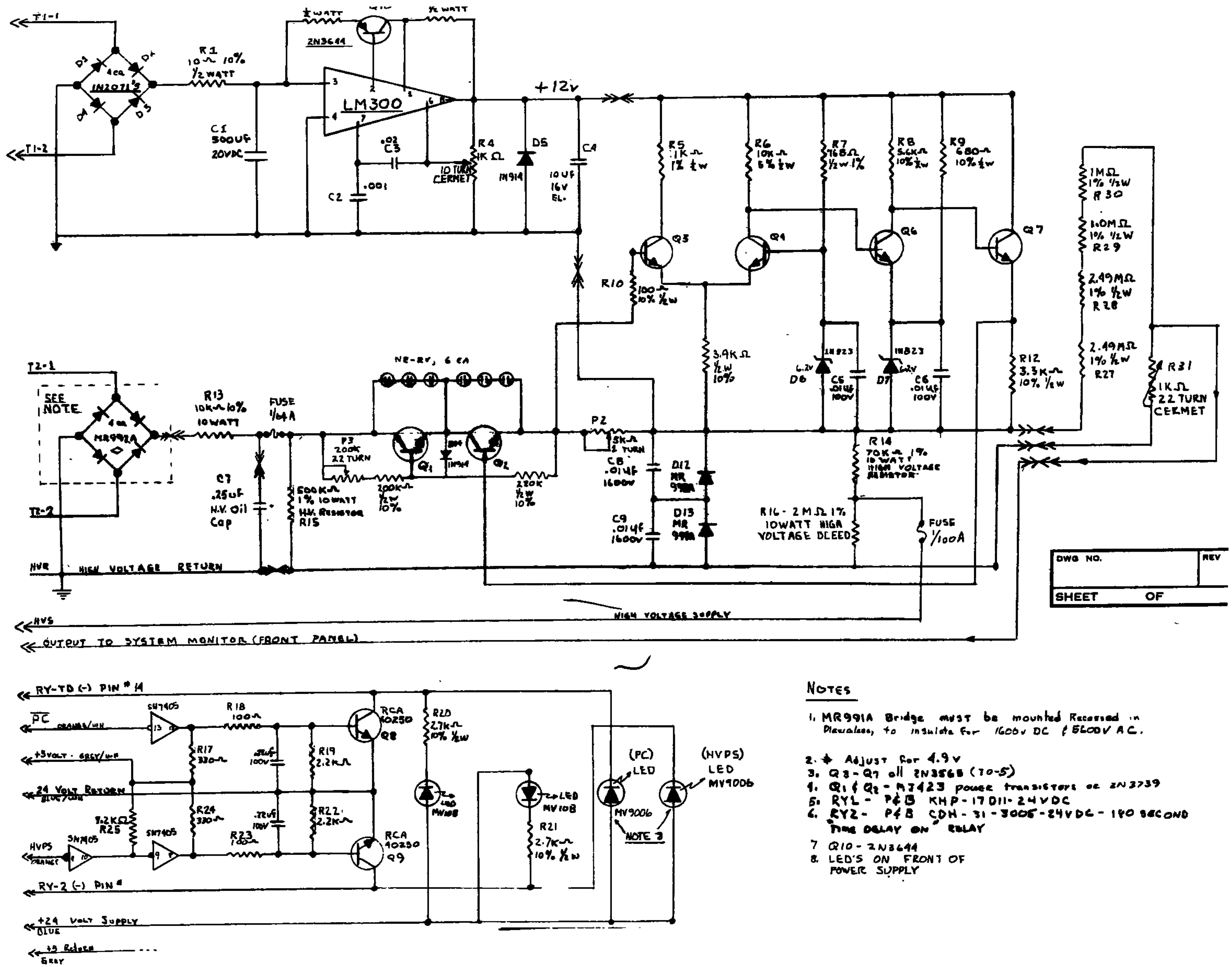


Figure 20. Schematic Diagram, Standard Light



1600 to 900V
6 ma max

Figure 21. Schematic Diagram, Discharge High Voltage Supply

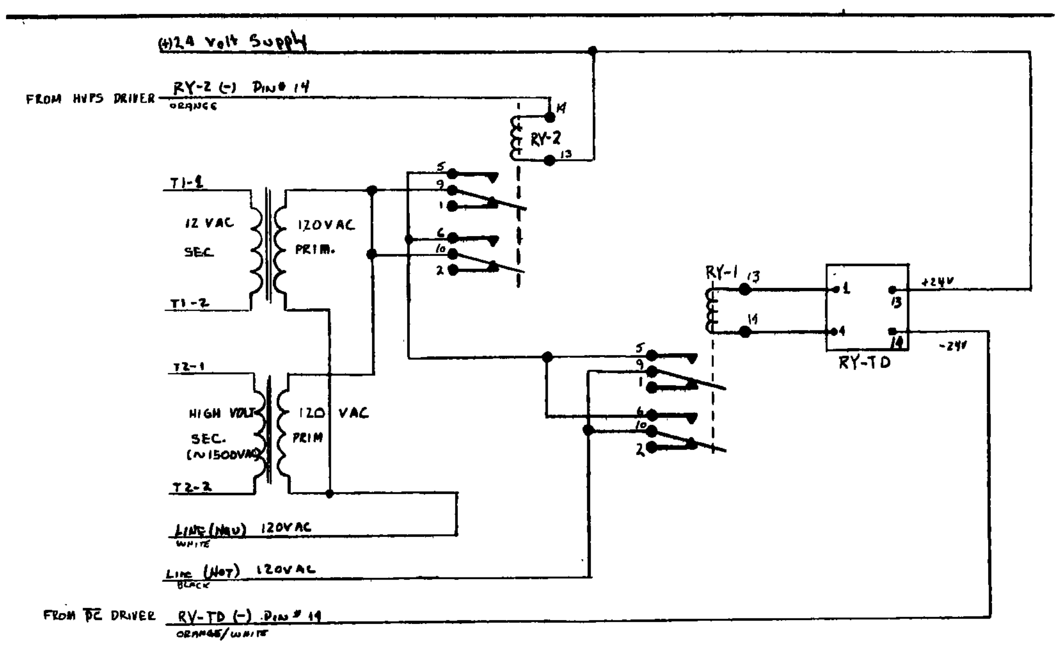
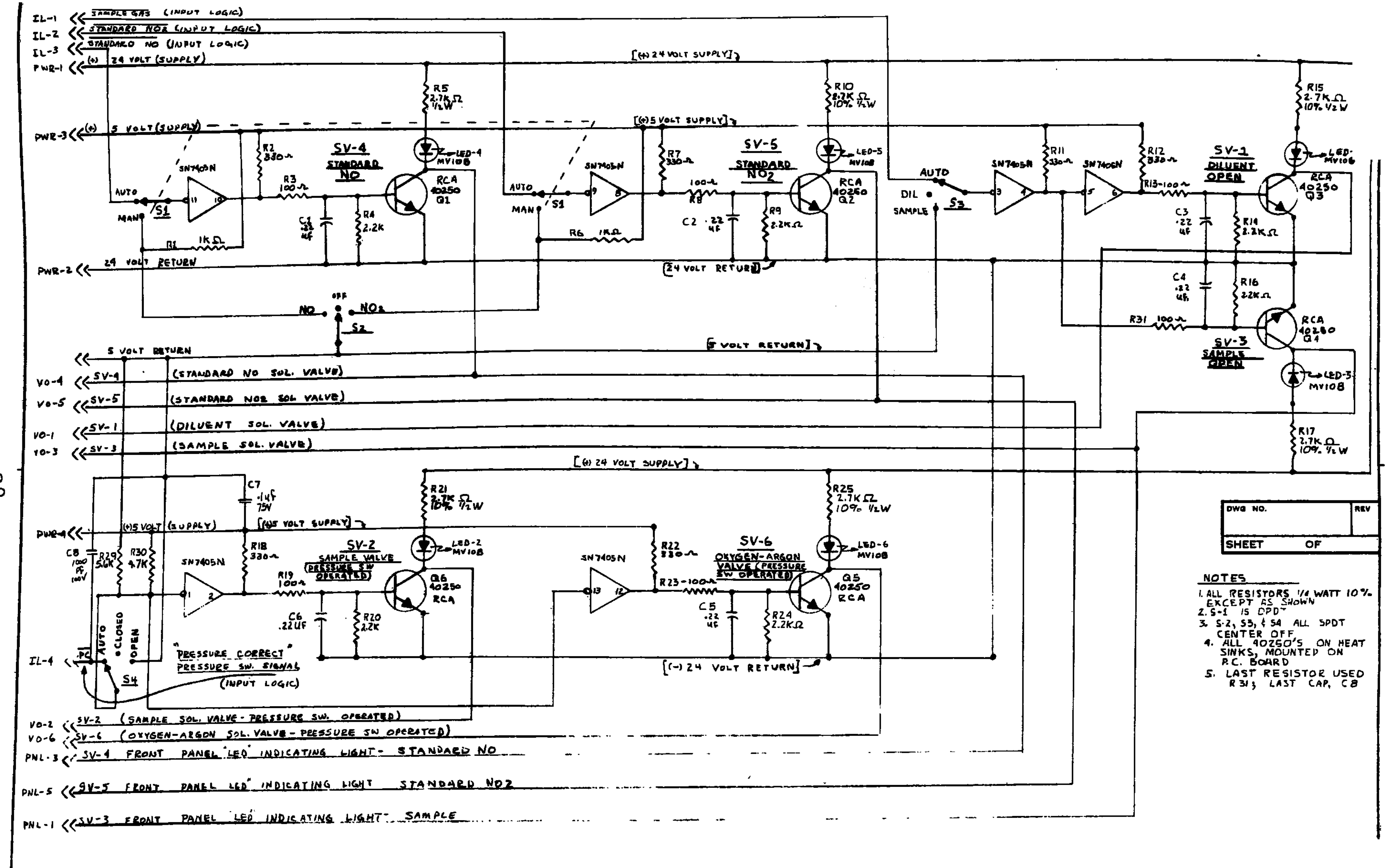


Figure 22. Schematic Diagram, Discharge Voltage Control



LEGEND

PNL - FRONT PANEL CONNECTION
PWR - POWER SUPPLY
IL - INPUT LOGIC
VO - VALVE OUTPUT

Figure 23. Schematic Diagram, Solenoid Drivers

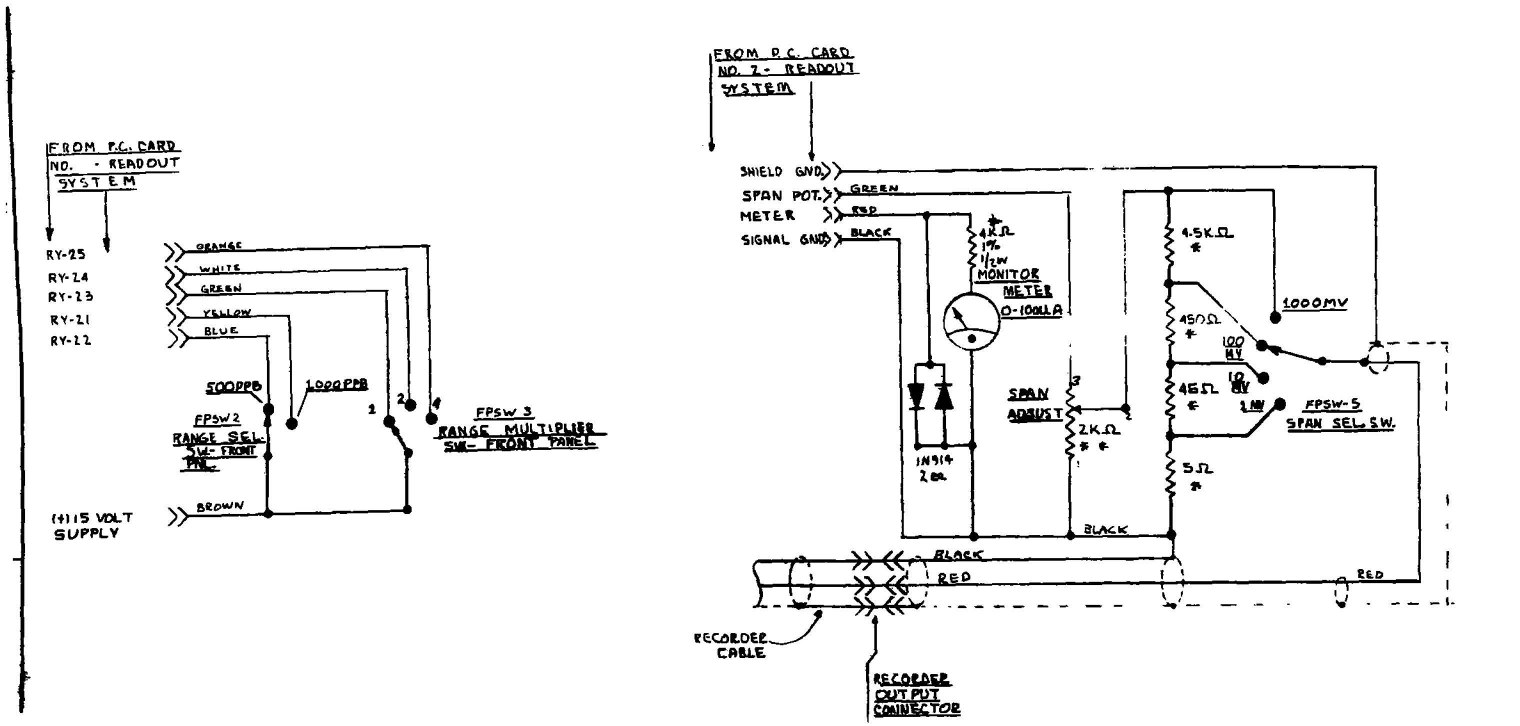


Figure 24. Schematic Diagram, Front Panel Circuits

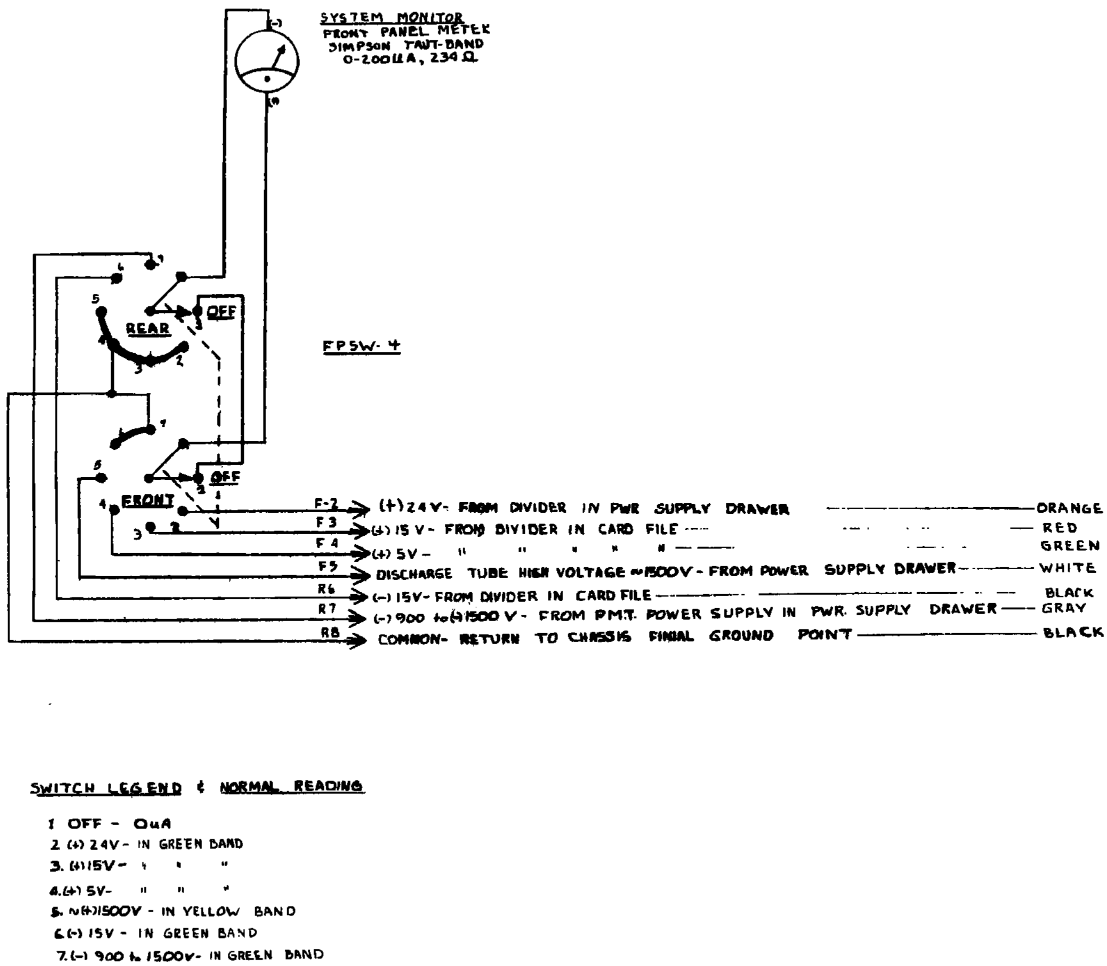
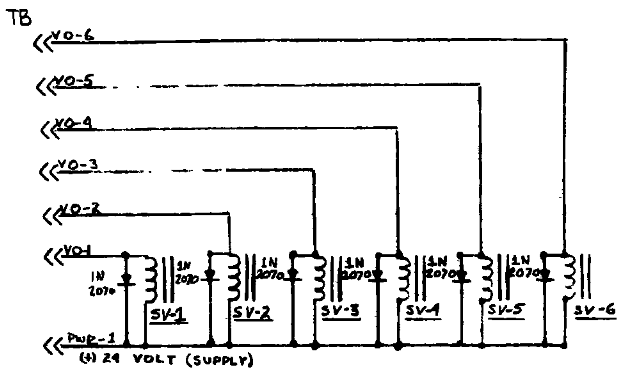
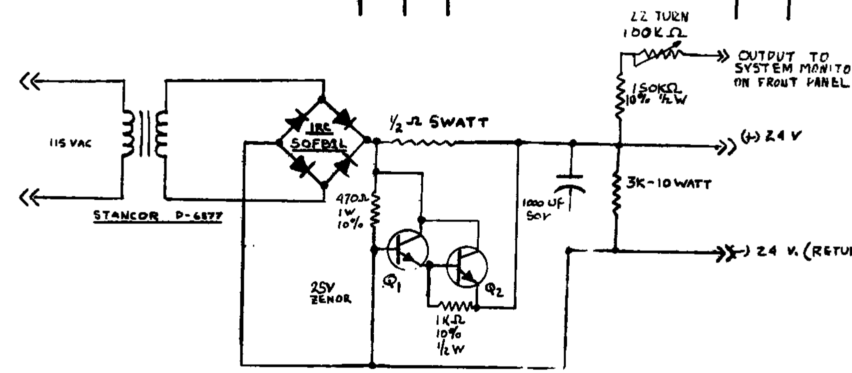


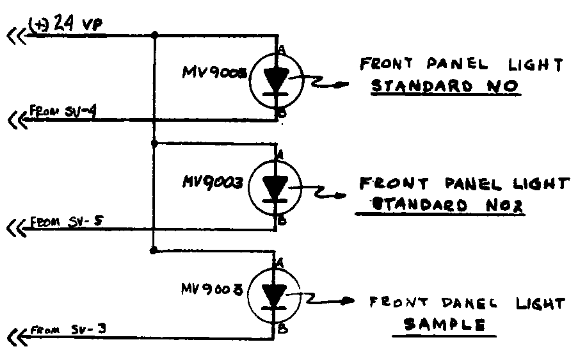
Figure 25. Schematic Diagram, Monitor Meter Circuit

REVISIONS				
ZONE	SYM	DESCRIPTION	DATE	APPROVAL



NOTES
DIODES CONNECTED ACROSS SOL. COIL AT TERM STRIP





SUBCHASSIS CONNECTOR FOR PMT & 24 VOLT SUPPLY
(LOCATED IN POWER SUPPLY DRAWER)
ELCO CONNECTOR- SERIES 8016

FROM	PLUG PIN NO.	WIRE COLOR	SOCKET PIN NO	TO	FUNCTION
PSTB1-2	A } JMPR	WHITE	A } JMPR	PMT-TB-2	LINE NEUTRAL
PSTB1-2	B	"	B	24V XFMR	" "
PSTB1-1	C	BLACK	C } JMPR	" "	LINE HOT
PSTB1-11	D	GREY	D	PMT INTER-LOCK SW.	LINE HOT
PSTB1-3	E	GREEN	E	PMT SUPPLY CASE	LINE GROUND
NONE	F	NONE	F	NONE	NONE
"	H	"	H		
PSTB1-10	J	BLACK	J	PMT-TB-1	PMT INTERLOCK RETURN-LINE HOT
NONE	K	NONE	K	NONE	NONE
"	L	"	L	"	"
"	M	"	M	"	"
PSTB1-9	N	YELLOW	N	24V SUPPLY	SYS. MONITOR
NONE	P	NONE	P	NONE	NONE
PSTB1-5,6,&7	R	RED	R	24V SUPPLY	(+) 24 V OUT
NONE	S	NONE	S	NONE	NONE
PSTB1-4	T	BLUE	T	PMT SUPPLY	SYS MONITOR
NONE	U	NONE	U	NONE	NONE
PSTB1-8	V	RED/GRN	V	24V SUPPLY	24 V. RETURN
NONE	W	NONE	W	NONE	NONE
"	X		X	"	"

DWG NO.	REV
SHEET OF	

Figure 26. Schematic Diagram, Solenoid and Lamp Circuits

Table 1

Tabulation of NO Concentration

Dil. Flow PSIG ±0.3	PSIA	11 PPM NO Flow cc/min. ±.01	PPB NO $\frac{11(NO)(1000)}{53+NO}$
3	17.7 ±.3	0.73 ±.03	150 ±6
4.5	19.2 ±.3	0.83 ±.03	170 ±6
6.0	20.7 ±.3	0.93 ±.03	190 ±6
7.5	22.2 ±.3	1.06 ±.04	216 ±8
9.0	23.7 ±.3	1.19 ±.04	242 ±8
10.5	25.2 ±.3	1.33 ±.04	270 ±8
12.0	26.7 ±.3	1.48 ±.04	299 ±8
13.5	28.2 ±.3	1.65 ±.04	332 ±8
15.0	29.7 ±.3	1.82 ±.05	365 ±10