

DEVELOPMENT OF A CARBON MONOXIDE DETECTOR DEPENDING  
ON POSITIVE ION EMISSION FROM HEATED PALLADIUM

by

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## PREFACE

Surface effects have had a profound influence in all engineering disciplines. The mechanical engineer deals with surface defects, the interaction of metals at interface points, and the problems associated with surface fatigue of a metal. The chemical engineer has had to deal with the surface effects of a catalytic metal in a chemical-industrial reaction. The solid state electrical engineer is concerned with defects of a solid state device caused by contamination of the surface during fabrication.

The surface effects of catalytic elements such as platinum, palladium and nickel have been a mystery for more than 75 years, with many theories being put forth for the explanation of the mechanisms of Pd and Pt surface phenomena. One area of interest is the emission of positive ions of sodium and potassium when palladium is heated. This ion emission was known to be dependent upon the presence of certain ambient gases and it was suggested that this effect would be exploited for construction of a detector for carbon monoxide.

This study had as its objective the development of a CO detector based on the change in positive ion emission from Pd in the presence of CO.

The author is deeply indebted to many people for their help in various stages of this work. In particular, the author would like to thank the other graduate students in the laboratory (Freedoon Tamjidi, Fred Moore, Ali Mir Tab) for their various suggestions during all phases of the experiments. The author would like to thank Mr. Michael Pomeroy for his assistance in developing the sophisticated electronics of the unit. Special thanks to Dr. S. A. Hoenig for his invaluable support and technical assistance in the development of the detection device.

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## TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS . . . . .	vii
ABSTRACT . . . . .	ix
1. INTRODUCTION . . . . .	1
2. DESCRIPTION OF SYSTEM . . . . .	2
Detector . . . . .	2
Gas Leak and Control System . . . . .	8
Electronics . . . . .	12
Detection Electronics . . . . .	12
Ultraviolet Penlight Power Supply . . . . .	12
Heater Filament Power Supply . . . . .	12
Detector Electronics Power Supply . . . . .	15
Processing of Signal Electronics . . . . .	15
3. OPERATIONAL SECTION . . . . .	16
Turn on Procedure . . . . .	16
Calibration Requirements and Procedure . . . . .	20
Procedure . . . . .	21
Operating Procedure . . . . .	22
Continuous Monitoring of the Atmosphere . . . . .	22
Carbon Monoxide Concentration of an Unknown Bottled Sample of Air . . . . .	23
4. MAINTENANCE PROCEDURES . . . . .	24
Pump Maintenance . . . . .	24
U.V. Source Maintenance . . . . .	24
Carbon Monoxide "Leak System" . . . . .	24
Detection Unit Maintenance . . . . .	25
Detection Electronics and Power Supply . . . . .	25
5. TROUBLESHOOTING MANUAL . . . . .	26
A. Control Panel . . . . .	26
B. Carbon Monoxide Controlled "Leak" System . . . . .	27
C. Detector Chamber . . . . .	27

TABLE OF CONTENTS--Continued

	Page
6. DETECTION CHAMBER DISMANTLING INSTRUCTIONS . . . . .	30
Parts List . . . . .	32
Maintenance for the Neptune Dyna Pumps	
Models 2, 3 and 4K . . . . .	33
Instructions for Repairing the Neptune Dyna	
Pumps Models 2, 3 and 4K with a Repair Kit . . . . .	33
Disassembly . . . . .	33
Assembly of Dyna Pump . . . . .	34
APPENDIX 1 - EXPERIMENTAL RESULTS . . . . .	35
APPENDIX 2 - NOISE AND DRIFT . . . . .	51
APPENDIX 3 - A REVIEW OF CARBON MONOXIDE MONITORING TECHNIQUES (as prepared by Beverly L. Martin and Stuart A. Hoenig) . . . . .	57
REFERENCES . . . . .	94

## LIST OF ILLUSTRATIONS

Figure	Page
1A. Diagram of Detection System . . . . .	3
1B. Air Smoothing Access Attachment . . . . .	4
2A. Detection Unit Assembly . . . . .	5
2B. Boron Nitride Insulator with Palladium Filament . . . . .	6
2C. Collector Screen with Ultraviolet Penlight Source . . . . .	7
2D. Access Flange Attachment . . . . .	9
2E. Layout of Detection Unit in Inner Case . . . . .	10
3. Schematic Layout of Detection Unit . . . . .	11
4. Ultraviolet Power Supply and Bulb . . . . .	13
5. Heater Power Supply for Nichrome Wire Filament . . . . .	14
6. Control Panel Layout . . . . .	17
7. Flow Meters and Control Valves . . . . .	18
8. Schematic Diagram of Control Panel . . . . .	19
9. Change in Temperature Versus Initial Palladium Filament Temperature . . . . .	39
10. Change in Emission Versus Temperature . . . . .	42
11. Change in Emission Versus Temperature for Various Carrier Gases . . . . .	44
12. Ion Current Versus CO/Air Ratio (Palladium Foil) . . . . .	47
13. Ion Current Versus CO/Air Ratio (Palladium Foil) . . . . .	48
14. Change in Emission Versus Concentration for Acetylene and Carbon Monoxide . . . . .	49

LIST OF ILLUSTRATIONS--Continued

Figure	Page
15. Drift Noise Versus Time . . . . .	52
16. Electron/Ion Noise Versus Temperature . . . . .	53

## ABSTRACT

An experimental system and procedure was developed to determine the concentration of carbon monoxide in air. The unit was designed to operate at the lowest possible temperature range, consistent with the optimum signal-to-noise ratio, to reduce the hazard of igniting explosive gas mixtures. Experiments indicated that the system provided a useful signal for carbon monoxide/air ratios as low as 25 parts per million.

The system operated by sensing the positive ion current emitted by hot palladium. In the presence of carbon monoxide the rate of emission from the palladium surface increases and is proportional to the concentration of carbon monoxide in the air stream. This ion current change is used as an indicator of the ambient CO level.

## CHAPTER 1

### INTRODUCTION

In recent years there has been a growing concern for the environment and its impact on human life. One of the main problems has been the increase in the levels of carbon monoxide in industrial atmospheres. With the advent of standards set by the Federal Government in recently passed legislation (Public Law 88-206, The Clean Air Act, 1971) the need for reliable gas detectors has greatly increased. The existing detector systems have been reviewed by Hoenig and Martin for the United States Public Health Service and their report will be included in the appendices. The concensus of the review indicates that many present detectors use either bulky and expensive equipment, or analyze gases by unreliable chemical methods.

The purpose of this research project was to develop a method for detecting small concentrations of carbon monoxide in an air sample. To this end a unique method for determining carbon monoxide concentration was evolved, and a portable detector designed around this concept.

The detection system is discussed below. For simplicity's sake the system will be divided into three distinct categories. These categories are: (1) Description of System, (2) Operation and Calibration Procedures, and (3) Maintenance and Troubleshooting Techniques.

## CHAPTER 2

### DESCRIPTION OF SYSTEM

#### Detector

The detector schematic diagram is shown in Figure 1A. The chamber is of brass tubing construction in three parts which are held together by connecting flanges.

Part one is termed the air smoothing chamber. Its purpose is to reduce the turbulence of the air stream before it enters the detecting chamber. The smoothing chamber has a number of screens to reduce turbulence of the incoming air (Figure 1B).

The second sub-component contains the actual detecting components (Figure 2A). Within this section of the chamber there is a 2" x 2" x .01" sheet of palladium in the shape of a cylinder. This cylinder is held in place by an insulating cylinder of boron nitride through which a heater coil is wound. The palladium is wrapped around the inside hole of the boron nitride sleeve (Figure 2B). A collector screen and an Ultraviolet Products Company UV source (Figure 2C) are also positioned through the center hole.<sup>1</sup>

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1. The ultraviolet source and all other commercially purchased parts are listed in the Parts List Section by manufacturer.

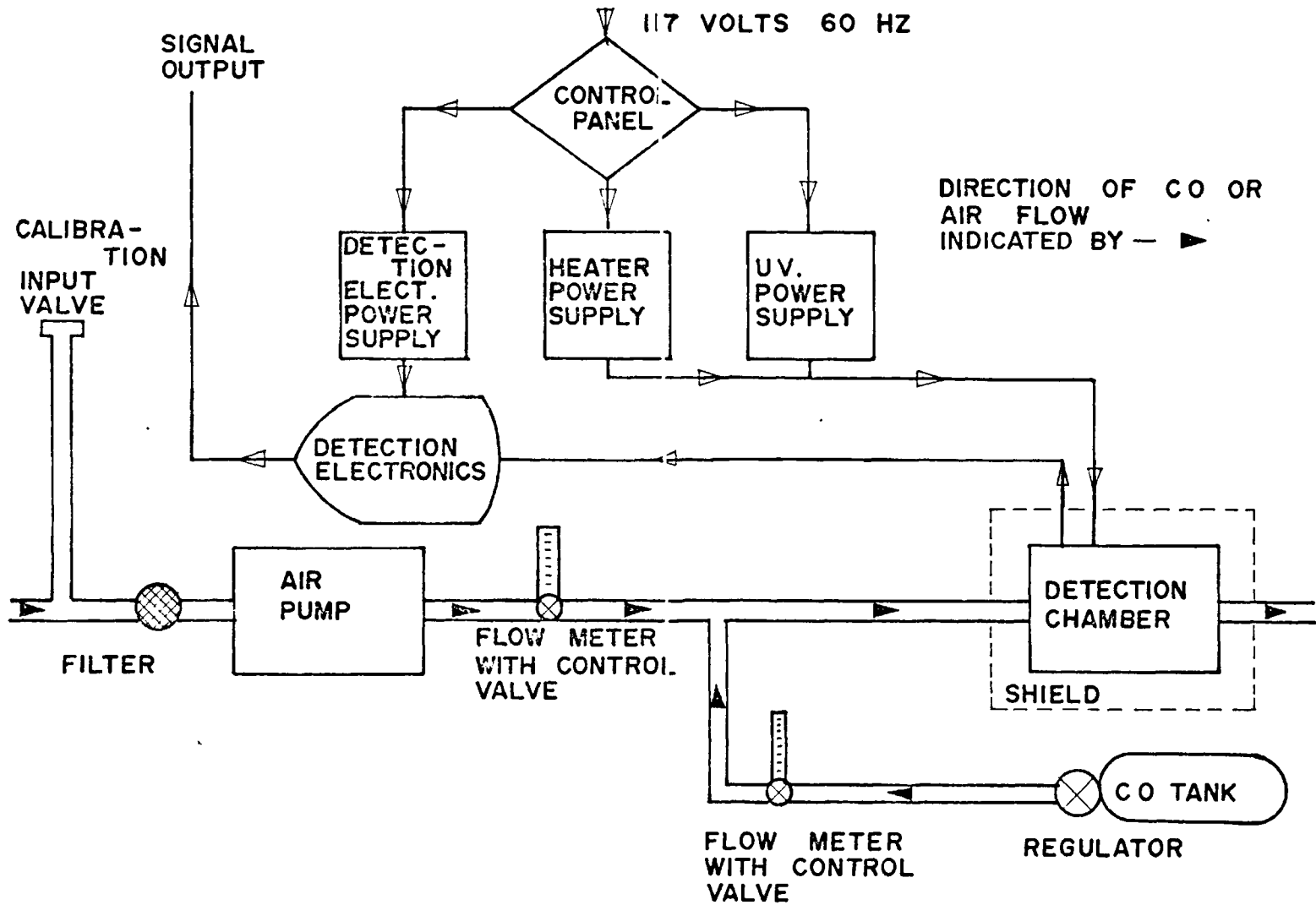


Figure 1A. Diagram of Detection System

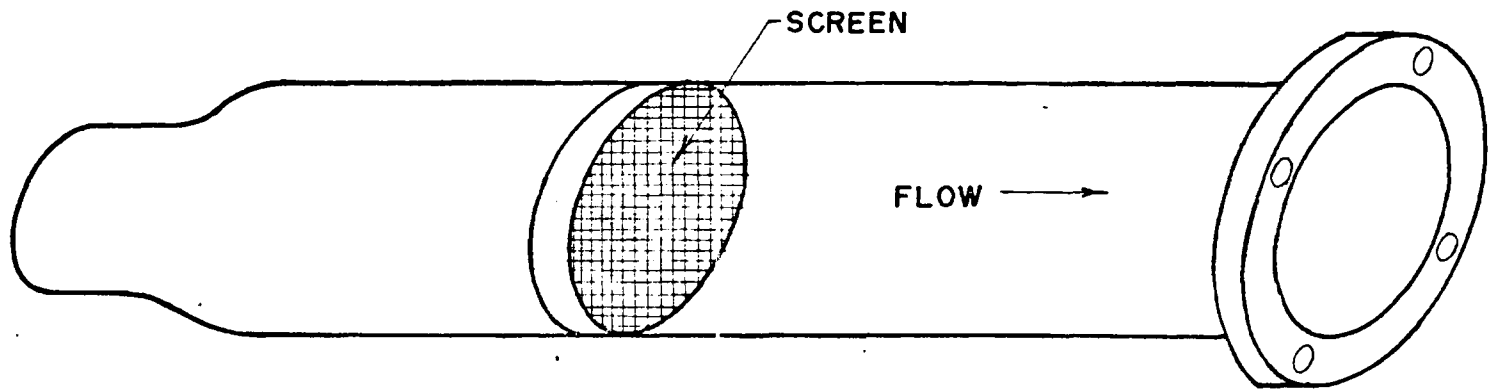


Figure 1B. Air Smoothing Access Attachment

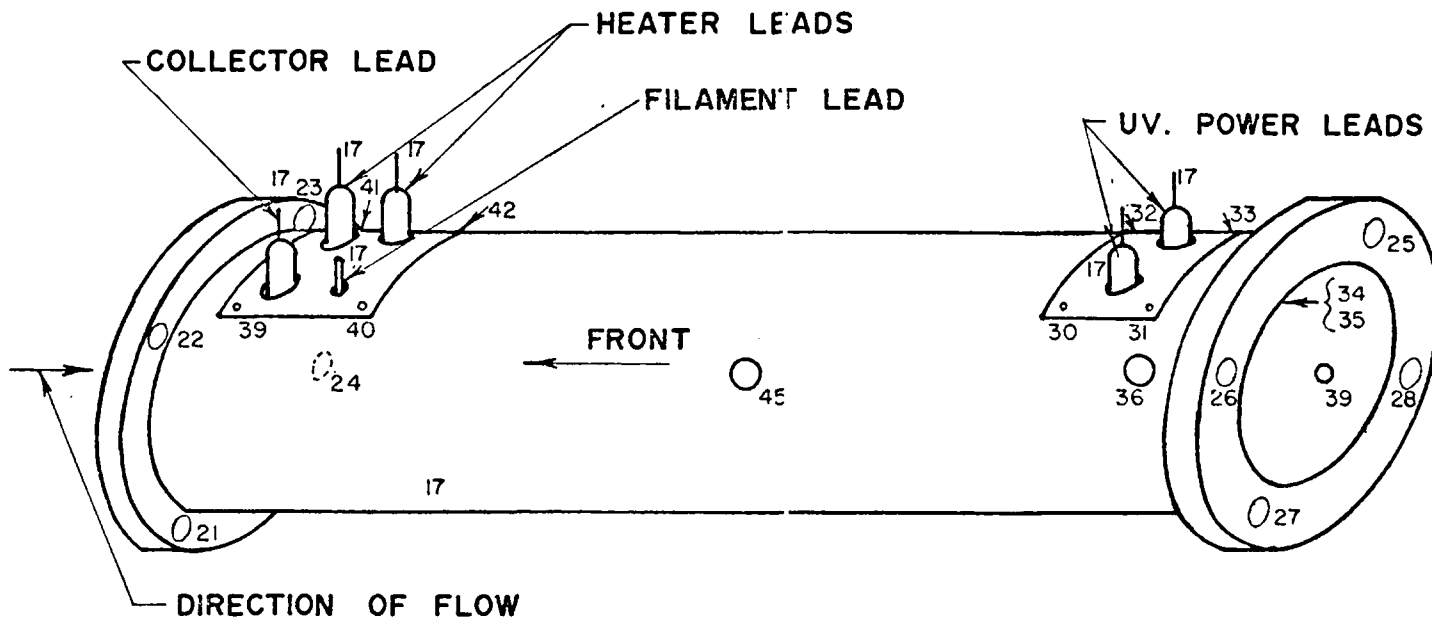


Figure 2A. Detection Unit Assembly

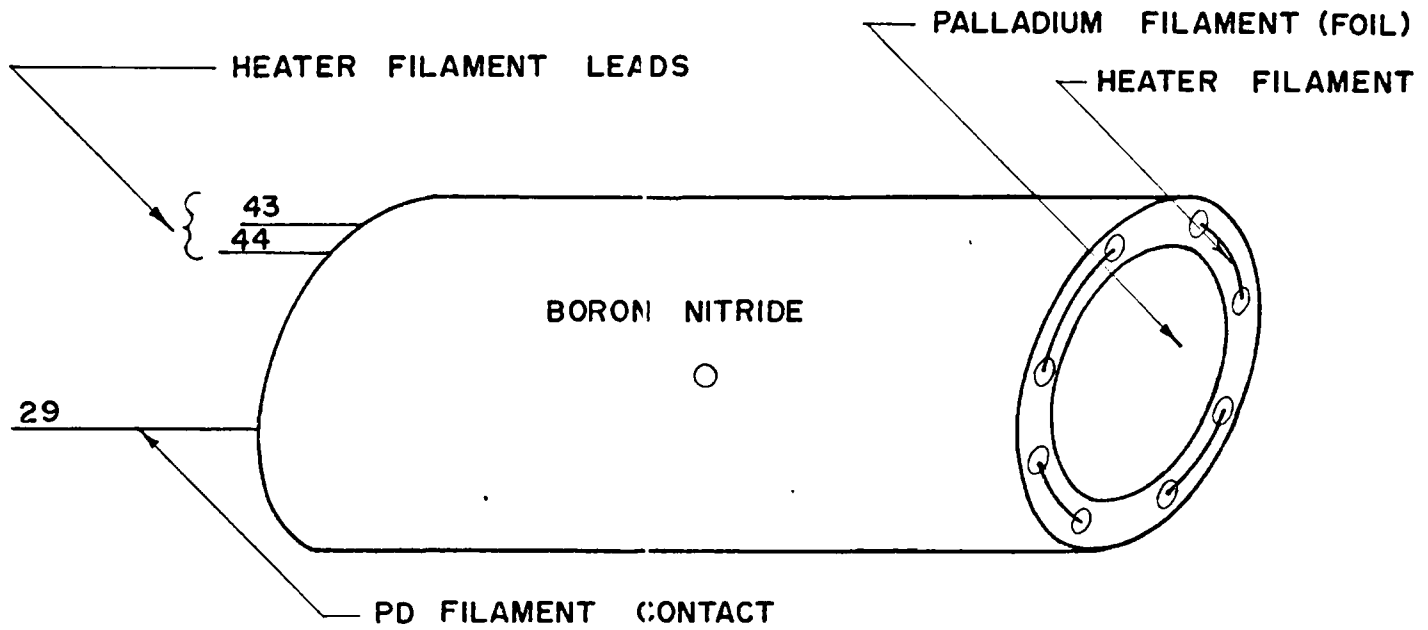


Figure 2B. Boron Nitride Insulator with Palladium Filament

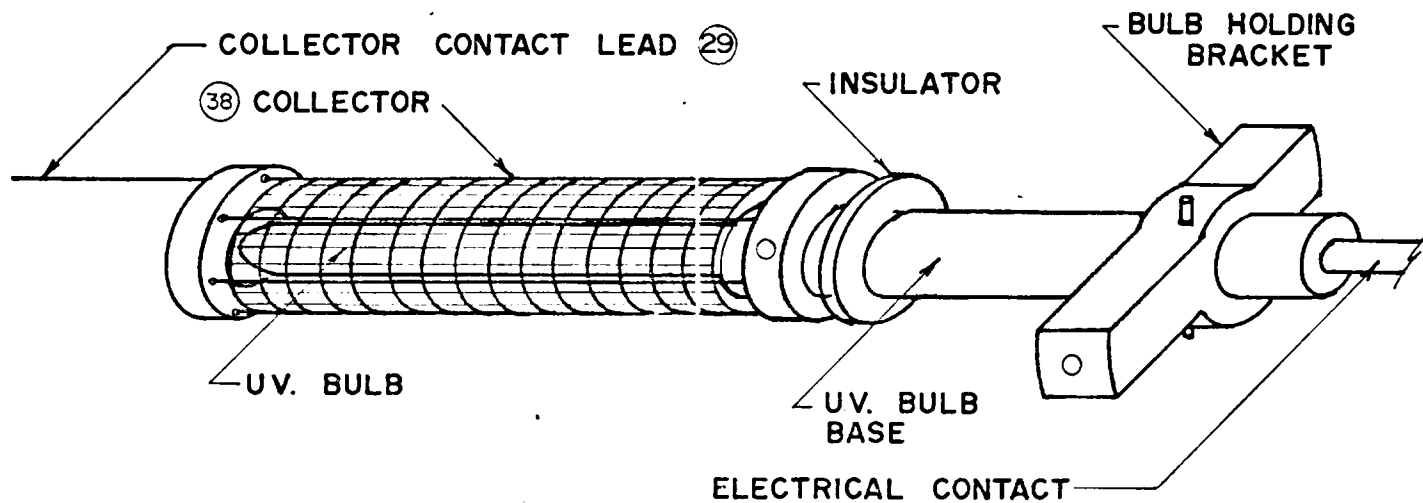


Figure 2C. Collector Screen with Ultraviolet Penlight Source

The third component is simply an extra support to allow easy removal of the collector screen and the ultraviolet penlight for maintenance (Figure 2D).

The entire detecting unit is wrapped with a sheet of fiber glass insulating material (Figure 2E). To reduce electrical pickup the unit is electrically insulated from ground by means of a double shield metal box (Figure 3).

Air is pumped through the detecting chamber at a constant flow rate by means of a Neptune Dyna-Pump. A flow meter with a control valve in the air line allows the rate of airflow to be monitored and set at the proper level.

#### Gas Leak and Control System

To maintain the palladium element at a constant level of efficiency during operation, a small flow of carbon monoxide is "leaked" into the detecting chamber. Without this flow of carbon monoxide, the efficiency of the palladium would decrease, within thirty six hours, to a level where much of the sensitivity would be lost. Shown as part of Figure 1A, the unit consists of a lecture bottle of C.P. quality carbon monoxide, a gas regulator, a precision flow control valve and a flow meter for controlling the flow rate.<sup>2</sup>

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2. The rate of flow of the carbon monoxide "leak" unit is 0.50 ml/min which mixes with the air drawn into the system to provide a CO/Air ratio of 220 parts per million. In view of the minute quantity of CO involved it is felt that no hazard to operating personnel will exist so long as the area has normal exhaust ventilation.

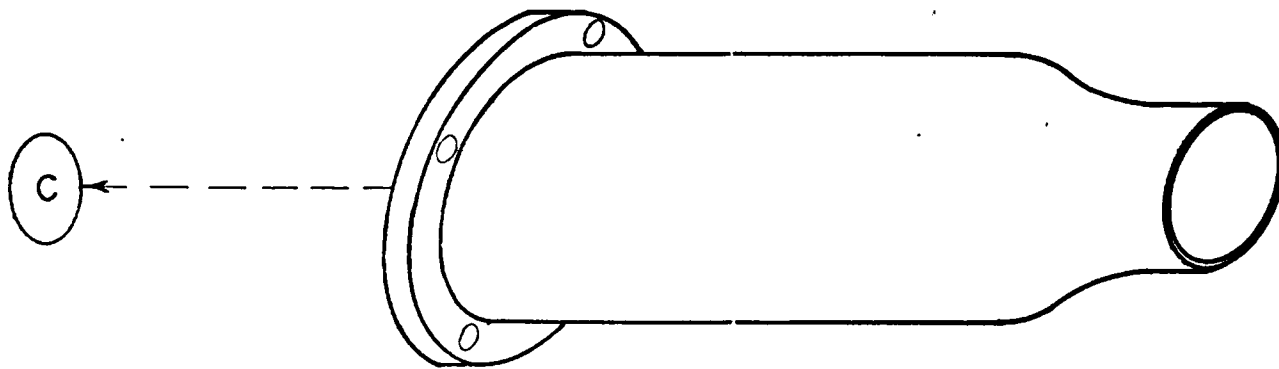


Figure 2D. Access Flange Attachment

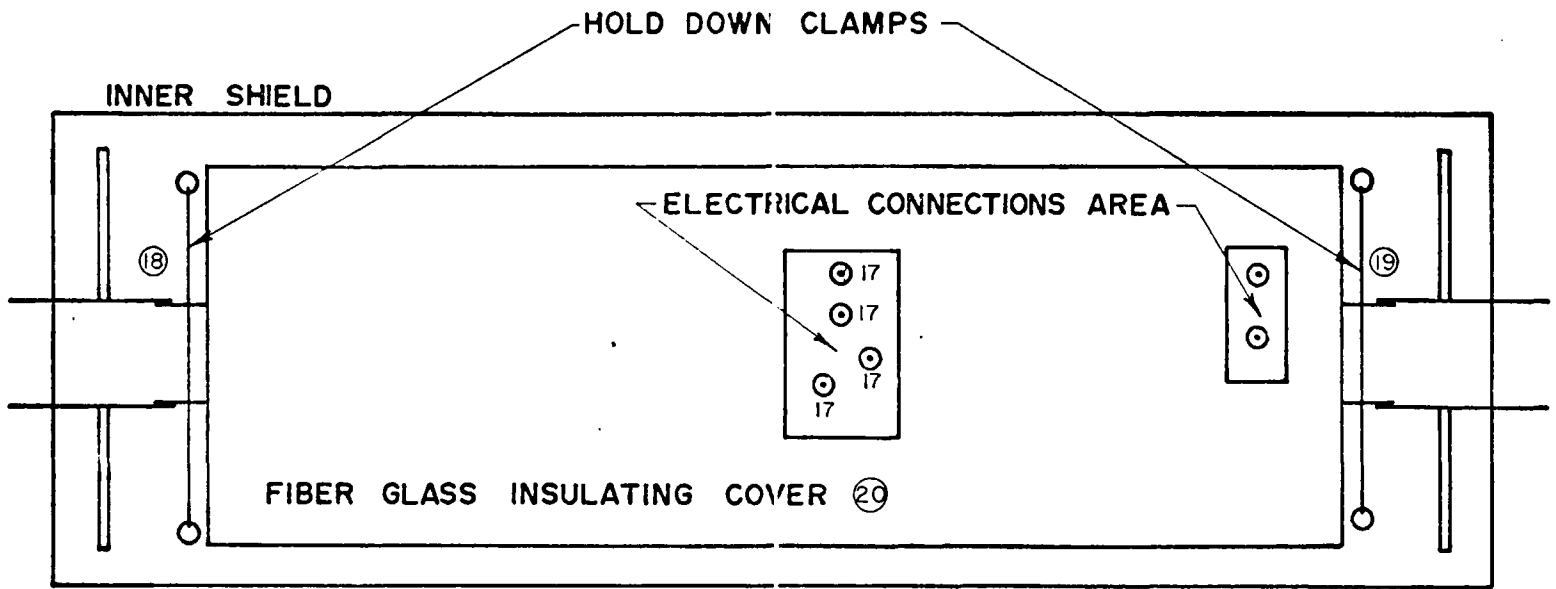


Figure 2E. Layout of Detection Unit in Inner Case

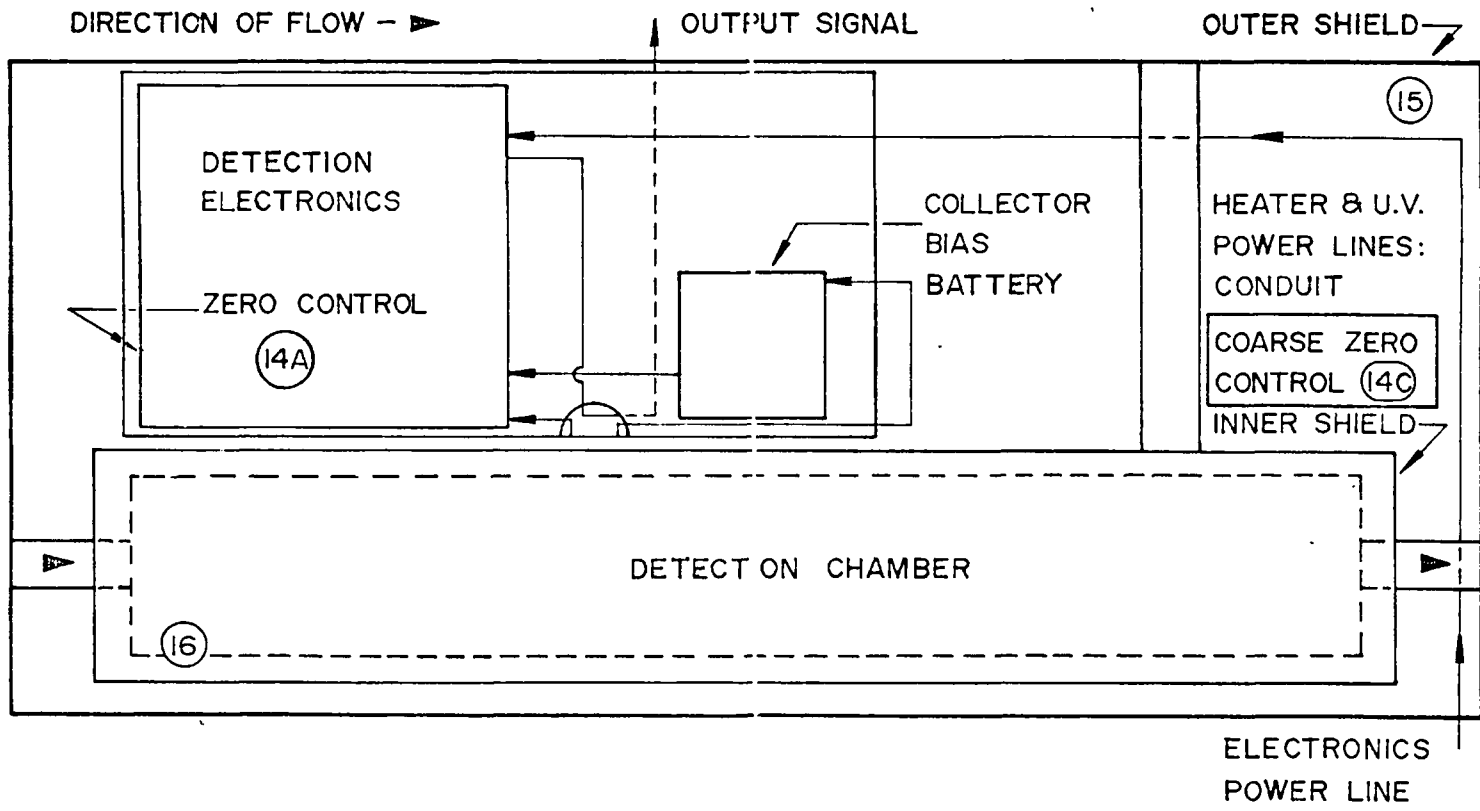


Figure 3. Schematic Layout of Detection Unit

## Electronics

The electronics package consists of five major components:

1. *Detection Electronics*
2. *Ultraviolet Penlight Power Supply*
3. *Heater Filament Power Supply*
4. *Detector Electronics Power Supply*
5. *Processing of Signal Electronics*

### Detection Electronics

A Keithly model 301 operational amplifier is used for the detection electronics.

### Ultraviolet Penlight Power Supply

The schematic diagram of the ultraviolet power supply is shown in Figure 4. Since it is necessary to operate the penlight bulb at a starting voltage of 800V AC, a transformer is used to raise the line voltage to this level.

### Heater Filament Power Supply

The schematic diagram of the heater filament power supply is shown in Figure 5. The heater element is a strip of nichrome wire wound through the boron nitride insulator. Its purpose is to heat the palladium to the proper operating temperature range. The power supply furnishes the power to heat this nichrome wire. The temperature of the palladium foil may be changed by increasing the current to the nichrome wire. This is accomplished by adjusting the rheostat (Item 7, Figure 6) on the control panel.

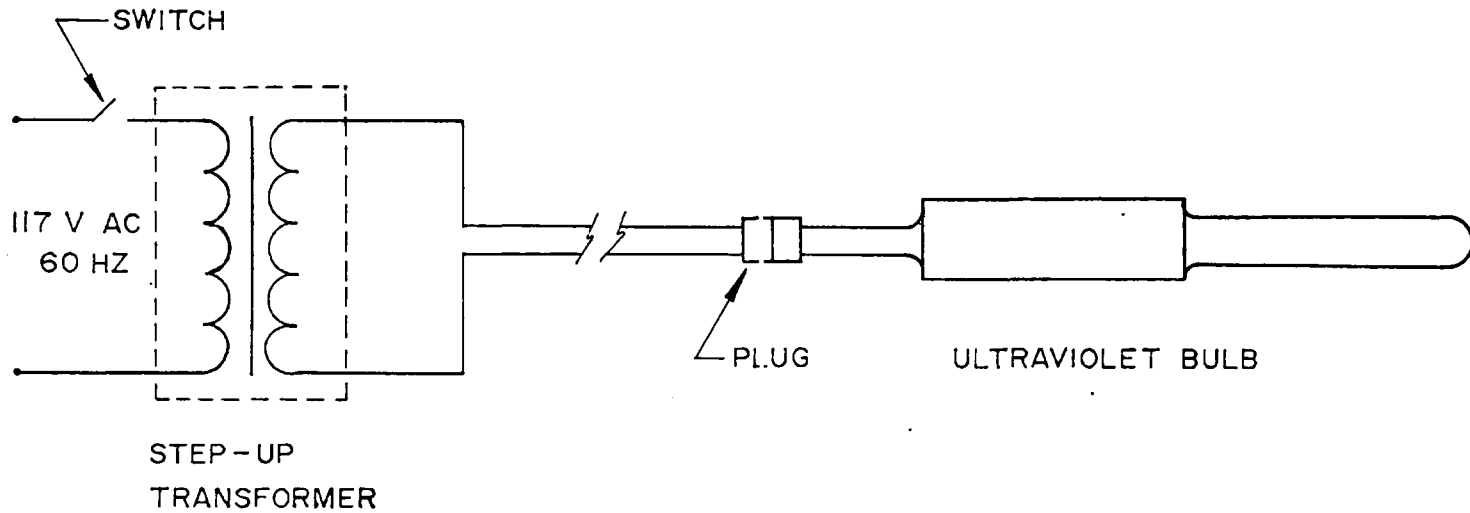


Figure 4. Ultraviolet Power Supply and Bulb

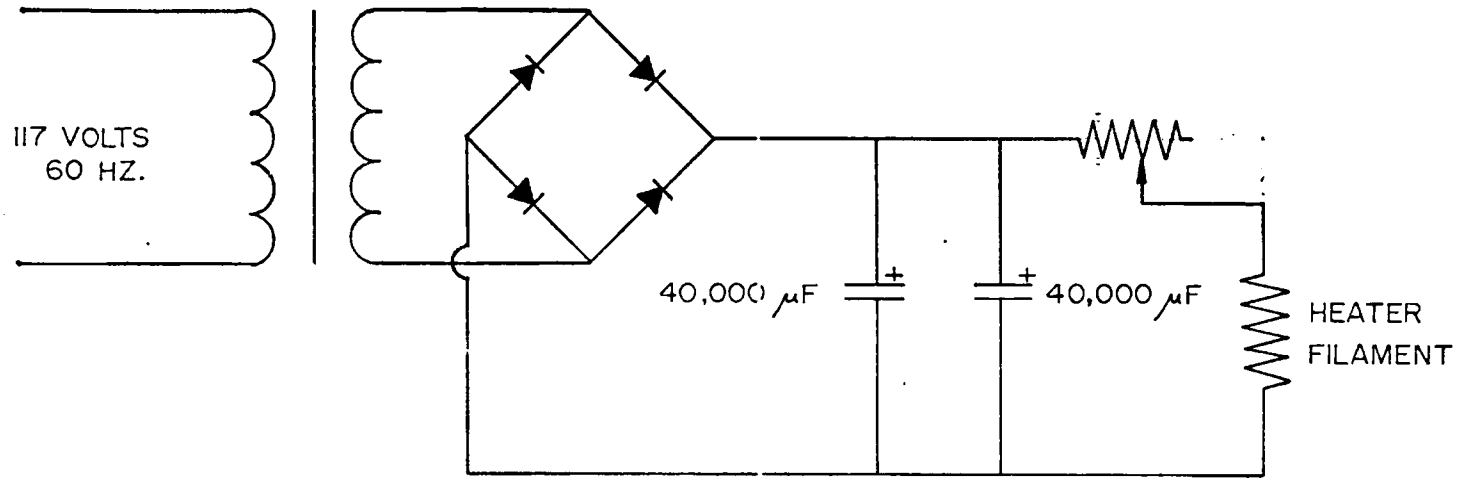


Figure 5. Heater Power Supply for Nichrome Wire Filament

## Detector Electronics Power Supply

The detector electronics are powered by a Burr-Brown Model 516 DC power supply.

## Processing of Signal Electronics

For continuous monitoring situations the output can be connected to a chart recorder. Instantaneous monitoring is normally accomplished by a meter built into the system. The use of a chart recorder is required for the calibration procedure, and this will be described under Calibration Procedure.

## CHAPTER 3

### OPERATIONAL SECTION

#### Turn On Procedure

1. Connect power cord to 117V, 60 Hz outlet (see Item 1, Figure 6).
2. Connect outlet exhaust line to exhaust connection (see Item 2, Figure 6) on detecting system case.
3. Set control switch (Item 3) to "ON" position.
4. Adjust air flow on air flow meter (Item 4) to 5 standard cubic feet per hour.
5. Set control switch (Item 5) to "ON".
6. Allow unit to warm up for 2 hours then proceed.
7. Set control switch (Item 6) to "ON".
  - a. Adjust heater control (Item 7) for 2 amperes on heater filament meter (Item 8).
8. Allow a 1 hour warm up period.
  - a. Connect an oscilloscope to out jacks (Item 13).
  - b. Adjust oscilloscope controls to monitor a DC signal.
  - c. Adjust external zero control (Item 14B, Figure 6) to null out signal.

Note: If the operational amplifier is saturated and adjusting external control does not remedy the condition, adjustments of the two internal zero controls will be necessary. Set external zero control to midrange and adjust the zero control potentiometer on the Keithly operational amplifier (Item 14A) first. If this does not remedy saturation adjust the course zero control (Item 14C, Figure 3).

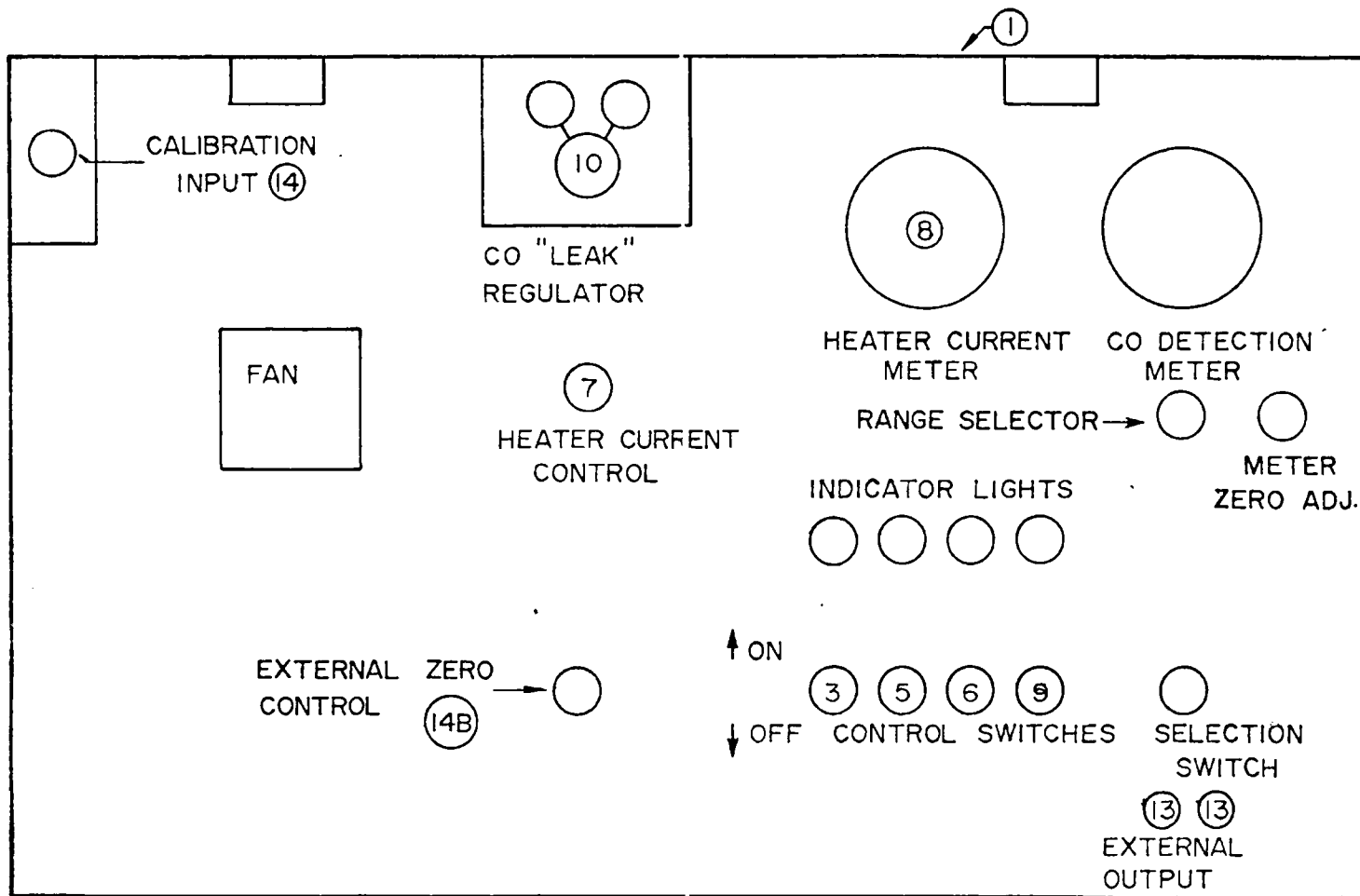


Figure 6. Control Panel Layout

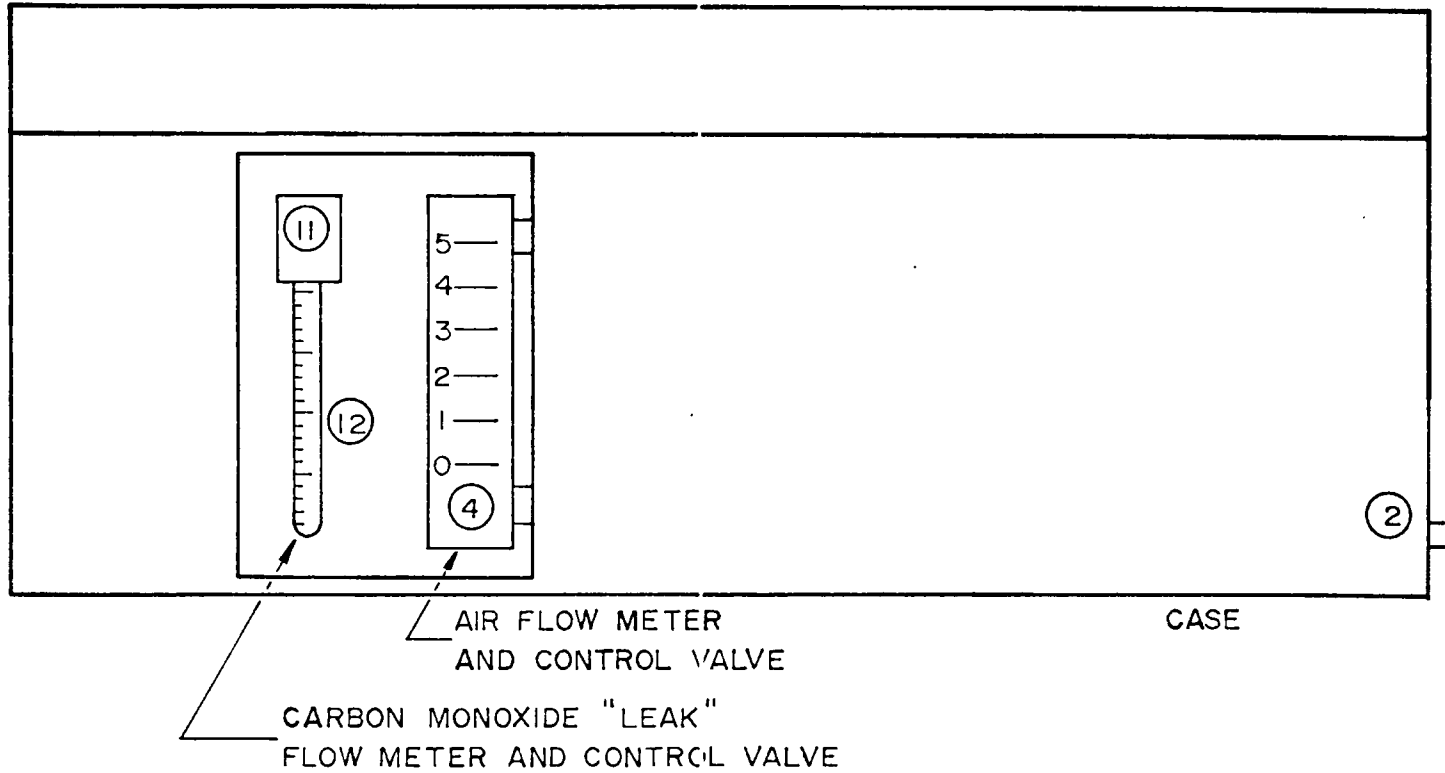


Figure 7. Flow Meters and Control Valves

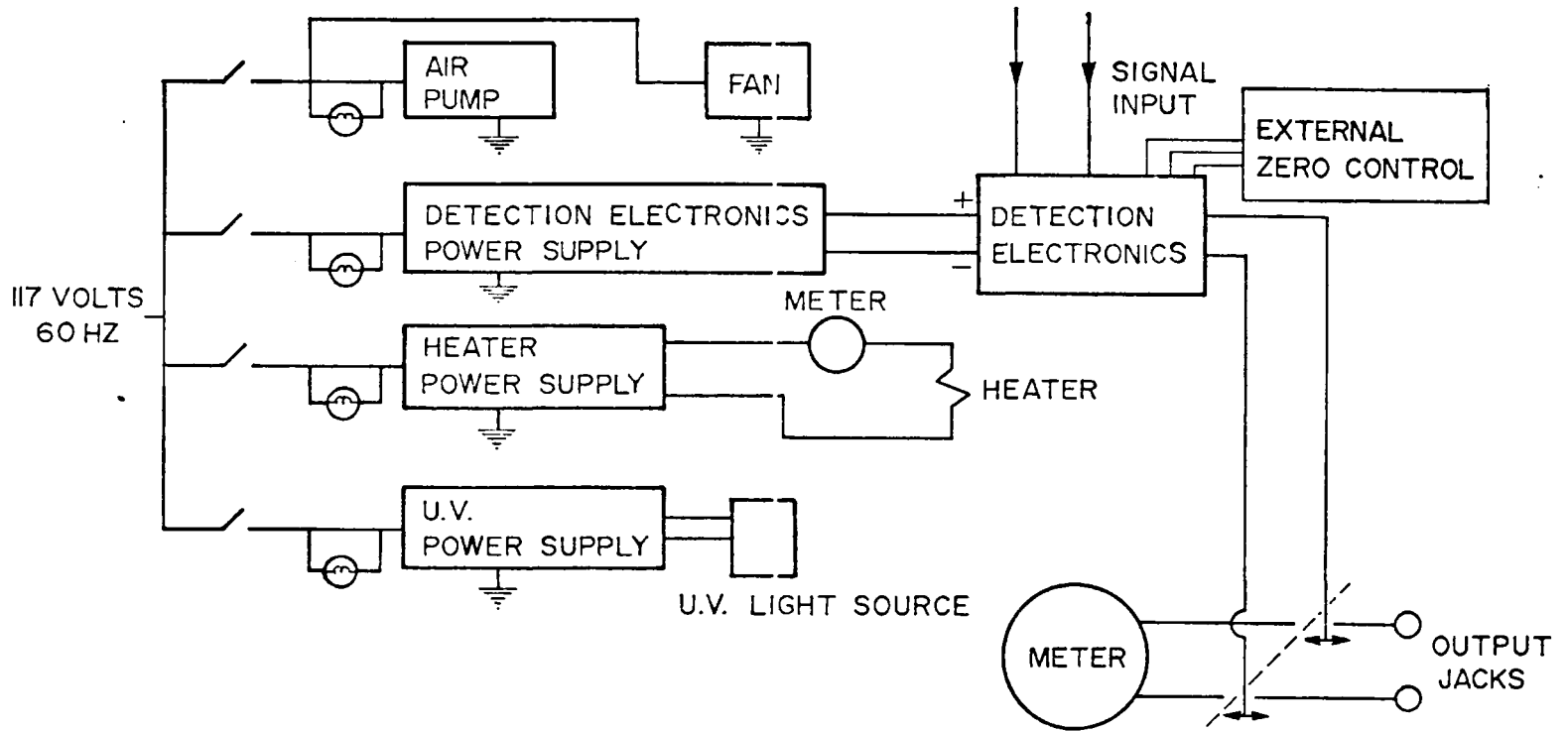


Figure 8. Schematic Diagram of Control Panel

Caution: Do not attempt to zero the operational amplifier using the meter zero control, damage may result. The range of the meter zero control and the CO detection meter will not accommodate a large DC offset. The zero meter control is used only when the null has been set by use of the external zero control.

d. Proceed to Step 9.

9. Set control switch (Item 9) to "ON".
10. Verify that the carbon monoxide adjustment regulator (Item 10) is fully counterclockwise.
11. Turn precision flow control valve (Item 11, Figure 7) to 3/4 open by turning counterclockwise.
12. Open internal CO tank valve and adjust regulator control (Item 10) until a reading of 2 ml/min is read on the carbon monoxide flowmeter (Item 12, Figure 7).
13. Adjust precision flow control valve (Item 11) until a reading of .50 ml/min (CO) is obtained on flowmeter (Item 12).

Note: Monitor these critical adjustments periodically to verify that the flows have not changed.

14. Allow a minimum of 36 hours for warm up before preceding to the calibration procedure.

### Calibration Requirements and Procedure

The calibration procedure should be performed each time the unit is turned on. It is anticipated that the unit will be left "ON" for long periods of time in which case recalibration runs may only be needed once every two weeks.

The purpose of this calibration procedure is to determine if:

- (a) the unit is operating properly, and
- (b) the magnitude of system drift and system noise.

### Procedure

1. Connect chart recorder to output jacks (Item 13).
  - a. Set recorder speed up to 1500 sec/in.
  - b. Set sensitivity to 250 mv/div.
  - c. Set damping to 3/4 of maximum.
  - d. Set zero control so that the indicator is centered in the middle of the chart paper.
2. Connect one side of an external tank of carbon monoxide through the enclosed flow meter-leak valve unit in the maintenance kit and connect the other side to the input air tee connection (Item 14, Figure 6). Do not turn on external CO flow at this time.<sup>3</sup>
3. Monitor output wave form on chart recorder.
  - a. If the system shows excessive drift, see Troubleshooting Manual.
  - b. If the system appears too noisy or is not working properly, see Troubleshooting Manual.
4. Turn on the external CO flow and introduce a known flow of carbon monoxide using the test set up.
5. Adjust the carbon monoxide input valve of test sample for a flow of .5 ml/min and maintain for a 5 minute ON TIME period. Turn off gas for 10 minutes. Repeat four times more.
6. Adjust carbon monoxide flow for 1 ml/min for a 5 minute "ON" period and a 10 minute "OFF" period. Repeat four more times.
7. Repeat Step 6 for a carbon monoxide flow of 1.5 ml/min.
8. Repeat Step 6 for a carbon monoxide flow of 2.0 ml/min.
9. Determine magnitude of increase of signal for the "ON" period and tabulate.
10. Take average value of the data and plot on graph paper. This is the emission vs. PPM carbon monoxide concentration.

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3. The internal carbon monoxide tank (tank in the unit) can be used for this operation if a tee connection with a precision flow valve is inserted into the carbon monoxide gas line.

11. Compare with the enclosed S/N vs. concentration graph (Figure 13 or 14) to determine the difference in magnitude of the curves.
12. If the magnitude of the difference is greater than 2 the unit is not working properly.
13. Steps 6 through 12 must be repeated every two to four weeks to insure the signal magnitude has not changed radically in the interim period.
  - a. Maintain a file of these calibration curves to determine lifetime and efficiency of the palladium catalyst.

### Operating Procedure

Following the calibration procedure on page 7 the unit is ready to monitor levels of carbon monoxide in the atmosphere. The procedure for both methods is listed below.

#### Continuous Monitoring of the Atmosphere

1. After calibration do not jar or bounce the unit as this will affect the accuracy and recalibration may be necessary.
2. Connect chart recorder to output jacks (Item 13, Figure 6).
3. Set recorder to desired sensitivity and chart speed.
4. Verify that the air flow is 5 SCFH and the CO leak flow is .5 ml/min.

Warning: Extreme variations in ambient air temperature will cause the unit to drift.

Note: This unit does respond to other gases and vapors, such as H<sub>2</sub>, acetylene, alcohol vapor, because they burn on the hot Pd and raise its temperature. If gases of this type are present they must be filtered out before the air sample enters the CO detection system.

5. Initiate recording of output signal to determine CO concentration.

## Carbon Monoxide Concentration of an Unknown Bottled Sample of Air

1. The temperature of the bottled air sample should be allowed to equilibrate with the room ambient air temperature to insure accurate results.
2. If the unknown sample is in an enclosed container, the sample should be fed into one side of the tee input nozzle (Item 14, Figure 6).

Warning: At all times the air flow through the unit should not exceed 5 SCFH, or faulty values of concentration and system drift will result.

## CHAPTER 4

### MAINTENANCE PROCEDURES

#### Pump Maintenance

1. Verify that the air flow is 5 SCFH. If its value is below 5 SCFH and adjusting the air flow control valve does not help, consult the Troubleshooting Manual.
2. The pump motor will require a drop of oil once every 3 months.

#### U.V. Source Maintenance

The ultraviolet source requires little periodical maintenance. The life expectancy of the bulb is approximately 3600 hours. After this time period the radiation falls below a datum level (datum level =  $20 \mu\text{a}/\text{cm}^2 \times 100$ ) causing the detection process to cease. The bulb should then be replaced. The power supply should require no periodic maintenance. A failure of this unit necessitates that the entire power supply be replaced.

#### Carbon Monoxide "Leak System"

1. Verify that the CO "leak" flow is  $0.50 \text{ ml}/\text{min} \pm 0.25 \text{ ml}/\text{min}$ .
2. If the flow is not of the proper magnitude check the pressure gauge of the lecture cylinder. If the tank is empty replace with a full one.
3. The regulator and flow meter will require no periodical maintenance.

### Detection Unit Maintenance

This unit requires only a reasonable amount of maintenance. However, it is most important to check the accuracy of the system by repeating the calibration procedure every two to four weeks.

### Detection Electronics and Power Supply

The detection electronics require no periodic maintenance. If trouble develops with this unit consult the operational manual on the Keithley Model 301 operational amplifier.

A failure of the Burr-Brown requires replacement of the entire unit. There is no periodic maintenance associated with this unit.

## CHAPTER 5

### TROUBLESHOOTING MANUAL

#### A. Control Panel

<u>SYMPTOM</u>	<u>CAUSE</u>	<u>ACTION</u>
1. Power On - Lights do not indicate.	(a) Burned out bulb. (b) Faulty switch. (c) Power not being supplied to unit.	(a) Replace bulbs. (b) Replace switch. (c) Verify power is connected to unit.
2. Heater filament current meter does not register.	(a) Meter burned out or out of adjustment. (b) Failure of heater unit power supply. (c) Broken wire or connection. (d) Heater filament broken.	(a) Replace or adjust meter. (b) Troubleshoot power supply to find source of failure. (c) Fix broken connection. (d) See special instructions on detection chamber overhaul.
3. Pump not operating.	(a) Burned out pump motor.	(a) Replace pump.
4. Pump operating but air flow is less than 5 SCFH.	(a) Air pump diaphragm is bad. (b) Clogged air lines.	(a) Remove air pump and replace diaphragm (see enclosed pump instructions). (b) Remove obstructions.

- |  |                                |                             |
|--|--------------------------------|-----------------------------|
|  | (c) Clogged air filter.        | (c) Replace air filter.     |
|  | (d) Leak in air lines.         | (d) Replace broken tubing.  |
| 5. U.V. indicator light does not indicate. | (a) Burned out indicator bulb. | (a) Replace indicator bulb. |
|  | (b) Broken connection.         | (b) Repair wiring.          |

### B. Carbon Monoxide Controlled "Leak" System

<u>SYMPTOM</u>	<u>CAUSE</u>	<u>ACTION</u>
1. Low reading on CO flow meter.	(a) CO tank empty.	(a) Replace with full tank.
	(b) Break in tubing.	(b) Replace broken tubing.
	(c) Faulty flow meter.	(c) Remove and clean flow meter.
	(d) Faulty leak control valve.	(d) Remove and clean control valve.

### C. Detector Chamber

<u>SYMPTOM</u>	<u>CAUSE</u>	<u>ACTION</u>
1. No output.	(a) Heater filament burned out.	(a) Disconnect heater leads and measure heater resistance with a VOM meter to determine whether an opening exists. If it exists see special Chamber Dismantling instructions for replacement of heater element.

- (b) Operational amplifier has driven into saturation by system drift.
- (b) Re-zero the amplifier using zero control (Item 14B, Figure 6).
- (c) U.V. penlight output has fallen below acceptable datum level as measured with U.V. meter. (This is done only when bulb is not lit or the bulb output is suspected of being low. Datum level is  $20 \mu\text{u}/\text{cm}^3 \times 100$ .)
- (c) Replace U.V. source (this will require dismantling of detection chamber). (See special instructions.)
- (d) U.V. power supply is burned out.
- (d) Replace power supply.
- (e) Catalytic surface has been "poisoned."
- (el) Allow unit to heat up for an additional 24-48 hour period and try again.
- (e2) Expose surface to  $\text{H}_2$  gas after first passing He gas through chamber to vent air from the system. Try detecting CO again.
- (e3) Remove Pd catalyst and sandblast to provide fresh surface.
- (e4) Prepare a solution of 0.9 M Aqua Regia. Dip Pd cylinder in solution for 10 seconds. Remove and rinse in distilled  $\text{H}_2\text{O}$ . Allow Pd cylinder to dry before installing into chamber.

(f) Detector electronic inoperative.

(f) Consult operational amplifier manual on Keithly operational amplifier.

2. There is a detectable output but the system is drifting.

(a) Unit has not warmed up.

(a) Extend warm up period an additional 24-48 hours.

(b) System has experienced air temperature gradients.

(b) Allow system to temperature stabilize.

(c) Air contains combustible gases, other than CO, to which the unit is sensitive.

(c) Unless filters are used to clean air of unwanted gases nothing can be done to the unit to correct this condition.

## CHAPTER 6

### DETECTION CHAMBER DISMANTLING INSTRUCTIONS

1. Remove two outer shields which cover the detector cylinder (Items 15 and 16).
2. Unsolder all electrical leads from the detector cylinder (Item 17).
3. Unbolt the hold down brackets which secure the chamber in place (Items 18 and 19).
4. Remove chamber and unwrap fiber glass insulation (save this insulation as it will be used again (Item 20)).
5. Remove the eight allen screws from the center flange assembly and from the end flange (Items 21 through 29). This exposes the inter-mechanism of the unit.
6. Unsolder the collector lead in the chamber (Item 29). To remove the U.V. source perform the following steps:
  - a. Unscrew four screws, which secure the power connection pass-through lugs, from the chamber (Items 30-33).
  - b. Pull the cap out a slight distance so that the internal wires can be unsoldered. Unsolder these two internal wires (Items 34 and 35).
  - c. Unscrew the two screws which secure the U.V. source to the chamber (Items 36 and 37).
  - d. The penlight source can now be removed from the detector chamber.
  - e. Once the source is removed the collector screen (Item 38) can be removed and a new U.V. source installed.
  - f. Installation is the reverse procedure of dismantling.
7. To remove heater filament and catalyst follow these steps:
  - a. Unscrew screws which secure the pass through lugs to the detector cylinder (Items 39-42).

- b. Pull out cap a slight distance and unsolder the two heater power leads and the Pd foil ground lead (Items 43 and 44). (Caution should be taken in this step to prevent the Pd foil ground lead from breaking off the Pd element.)
- c. Unscrew the screw which secures the boron nitride (B.N.) cylinder in the chamber (Item 49).
- d. Remove cylinder by pushing toward the end indicated as "Front" on Figure 2A. Use caution to prevent damage to the B.N. insulator.
- e. Once the B.N. cylinder is removed the Pd catalyst can be removed and work to be done to it, or the heater filament can be changed.

Parts List

<u>ITEM</u>	<u>MANUFACTURER</u>	<u>MODEL</u>
Air Pump	Neptune Dyna Pump Neptune Products, Inc. Box 542 Dover, New Jersey 07801	3
Lecture Bottle of C.P. Grade Carbon Monoxide	Matheson Scientific Jersey Blvd. & Utica Street Cucamonga (L.A.), California	None
Ultraviolet Penlight Source and Power Supply	Ultra Violet Products, Inc. 5114 Walnut Grove Avenue San Gabriel, California 91778	Bulb-Pen Ray P.S. Model Set-1
Heater Power Supply	Components available at most electronics supply houses.	None
Air Flow Meter	Dwyer Instruments, Inc. Box 373 Michigan City, Indiana 46360	Series 500
Carbon Monoxide Flow Meter	Dohrmann Instrument Company 1062 Linda Vista Avenue Mountain View, California	0-200
Gas Regulator (for CO Bottle)	Victor Equipment Company San Francisco, California	S0
Detection Electronics	Keithley Instruments, Inc. 28775 Aurora Road Cleveland, Ohio 44139	Model 301
Detection Electronics Power Supply	Burr-Brown Research Corp. 6730 South Tucson Blvd. Tucson, Arizona	516
Switches, Indi- cator Lights, Meters, Rheostat	Available at most electronics supply houses.	None
CO Calibration Flowmeter	Gilmont Flowmeter (Cole-Parmer Instrument Co.) 7330 North Clark Street Chicago, Illinois	Size 10

Maintenance for the Neptune Dyna Pumps  
Models 2, 3 and 4K

Models 2 and 3 have a brushless motor and require a few drops of 20 weight motor oil every three months. No further maintenance is necessary. Model 4K is a ball bearing motor and does not require any oiling.

Instructions for Repairing the Neptune Dyna Pumps  
Models 2, 3 and 4K with a Repair Kit

### Disassembly

Remove the two screws on the top of the pump. Remove the cap. Look down in the pump and loosen the visible screw. Invert the pump and remove the three bottom screws. This will allow you to remove the motor and cap assembly from the base assembly. The diaphragm now will be exposed. It may be removed with a screwdriver by prying off the snap-on ring or a teflon ring, whichever the case may be. This will expose the top valve seat. Remove the perforated brass retaining screen and rubber valve with a sharp nail or pick. Invert the pump and unscrew the two plugs. Remove the perforated screen and rubber valve from the bottom valve seat and fine mesh screen from the other hole. After all the above operations are completed, clean out both valve seats with cotton and solvent. Let this dry for not less than five minutes.

## Assembly of Dyna Pump

Using parts from the repair kit, with pump in normal position, insert rubber valve and perforated brass retaining screen in valve seat keeping convex side up. The perforated brass screen should be pressed into original position. Invert pump to check if it is secure. Repeat same operation to bottom valve seat. (The valve seat on the bottom is not the hole directly opposite the top valve seat.) Put the fine mesh screen securely in remaining hole. Turn the pump around to check if it is secure. Replace the two plugs into original position. Turn pump to normal position and replace the diaphragm. Secure with the snap-ring or teflon ring depending on which one was used. (If snap-on ring is used be careful not to damage the diaphragm.) Re-assemble motor and cap to base, making sure all screws are tight. Test the pump for performance.

If there are other questions on this subsystem the manufacturer suggests that they be referred to the factory. (NEPTUNE PRODUCTS, INCORPORATED, P. O. Box 542, Dover, New Jersey 07801.)

## APPENDIX 1

### EXPERIMENTAL RESULTS

The emission of positive ions from heated solids has been of scientific interest for many years. Typical references are those of: Richardson 1903, Bangham 1929, Brady and Zemany 1952, and Chupakin, Bibikova and Polyakov 1967). The ions are known to be those of sodium and potassium which exist as impurities in the metal lattice. When the metal is heated, these atoms diffuse to the surface and are ionized. The ions then escape from the metal and exist as free ions.

The rate of ionization is a function of the impurity content and the rate of diffusion. However, these are not the only factors involved. The fraction  $\alpha$  of the arriving impurity atoms that escape as ions is given by the Saha equation as:

$$\alpha = \frac{g_+}{g_0} \exp\left[\frac{e(\phi - I)}{kT}\right]$$

Where:  $g_+/g_0$  = statistical weights of the ionic atomic states

$e$  = electron charge

$\phi$  = work function of the host metal

$k$  = Bohzman's constant

$T$  = temperature

$I$  = ionization potential of the impurity atom

Notice that in this equation the metallic work function  $\phi$  and the ionization potential  $I$  of the impurity atom appear in the exponential part of the Saha equation. It is apparent that a high work function and a low ionization potential are necessary if significant ion emission is to occur. This is a major reason for our choice of palladium as the positive ion source.

Palladium has other advantages, i.e., it is only slightly oxidized in air at temperatures up to 750°C. This suggests that its surface condition will not change during long term ion emission studies. Even more significant for our purpose is the well known capacity of palladium for adsorption of hydrogen and carbon monoxide (Taylor and McKinney 1931, Pope 1971, Hoenig, Carlson and Abramowitz 1967).

It was hoped that the expansion of the Pd lattice which occurs during adsorption of  $H_2$  (Lewis 1967) would also occur with CO and thereby produce a substantial increase in the rate of diffusion of impurity atoms to the Pd surface. This would in turn result in an increased positive ion current which would serve as a method for detection of  $H_2$  or CO. This detection technique was demonstrated by Hoenig (Hoenig, Carlson and Abramowitz 1967) for hydrogen. During these experiments it was noted that some indication of sensitivity to CO was present. The present research program was directed to the development of an improved version of a CO detector using the Pd ion emission system.

The work involved performing a number of experiments to determine if it was feasible to build a practical detection instrument. The

final production version of the detection system used a foil sheet of palladium which had been sandblasted to pit the surface. An ultra-violet penlight source was also used to expose the Pd surface to UV radiation. This pretreatment of the Pd surface and the addition of the UV light were made to increase the system sensitivity to CO. The details of the studies leading to these additions will be discussed below.

### Experimental Studies

1. *Change in filament temperature versus initial filament temperature.*
2. *Effects of various collector to filament bias voltages on the heat release when CO was absorbed by palladium.*
3. *Change in emission (electron and ion) versus temperature at fixed CO/air ratios.*
4. *Investigation of techniques for restoration of ion emission after poisoning has occurred.*
5. *Change in emission versus CO concentration.*
6. *Effects of gases other than carbon monoxide.*

All of these experiments had one question in common: "Could a practical detector be developed?"

#### 1. Temperature Increase of Pd Upon Absorption of CO

The heat release observed when H<sub>2</sub> is absorbed by Pd is well known (Aston 1966, Taylor and McKinney 1931). We felt that a similar effect would be observed with CO. A possibility existed that this heat release could be used to develop a detector for CO. For these early experiments, the carrier gas was nitrogen from compressed gas tanks.

This method was used to obtain constant flow rates and minimize contamination. It was also felt that since nitrogen is relatively inert, it would not confuse the heat release due to absorption with any thermal effects resulting from combustion of CO.

In this study a palladium wire filament was used since it could be directly heated and therefore its temperature could be controlled more exactly. Measurements of filament temperature were monitored by a .010 inch diameter chromel-alumel thermocouple spot welded to the wire filament. The instrument used to measure the thermocouple potential was a Leeds-Northrup thermocouple potentiometer. The procedure was to allow the unit to temperature stabilize in a continuous nitrogen flow, and note the initial temperature. A known concentration of carbon monoxide in the nitrogen carrier gas was then allowed to enter the detection chamber and the resulting change in filament temperature was again noted. The carbon monoxide was then turned off and the change in temperature recorded once more. The observed increase in temperature was taken as being due to absorption rather than combustion because of the absence of oxygen in the detection chamber. The conclusion is that this change in temperature is due to the heat of solution as the CO penetrates the atomic lattice of the Pd.

The filament was then raised in temperature by applying more current and the procedure repeated. Figure 9 is a plot of the change in palladium temperature versus initial filament temperature for constant carbon monoxide concentration. It is important to note that the temperature peak occurs at a relatively low temperature. This was

CHANGE IN TEMPERATURE °C

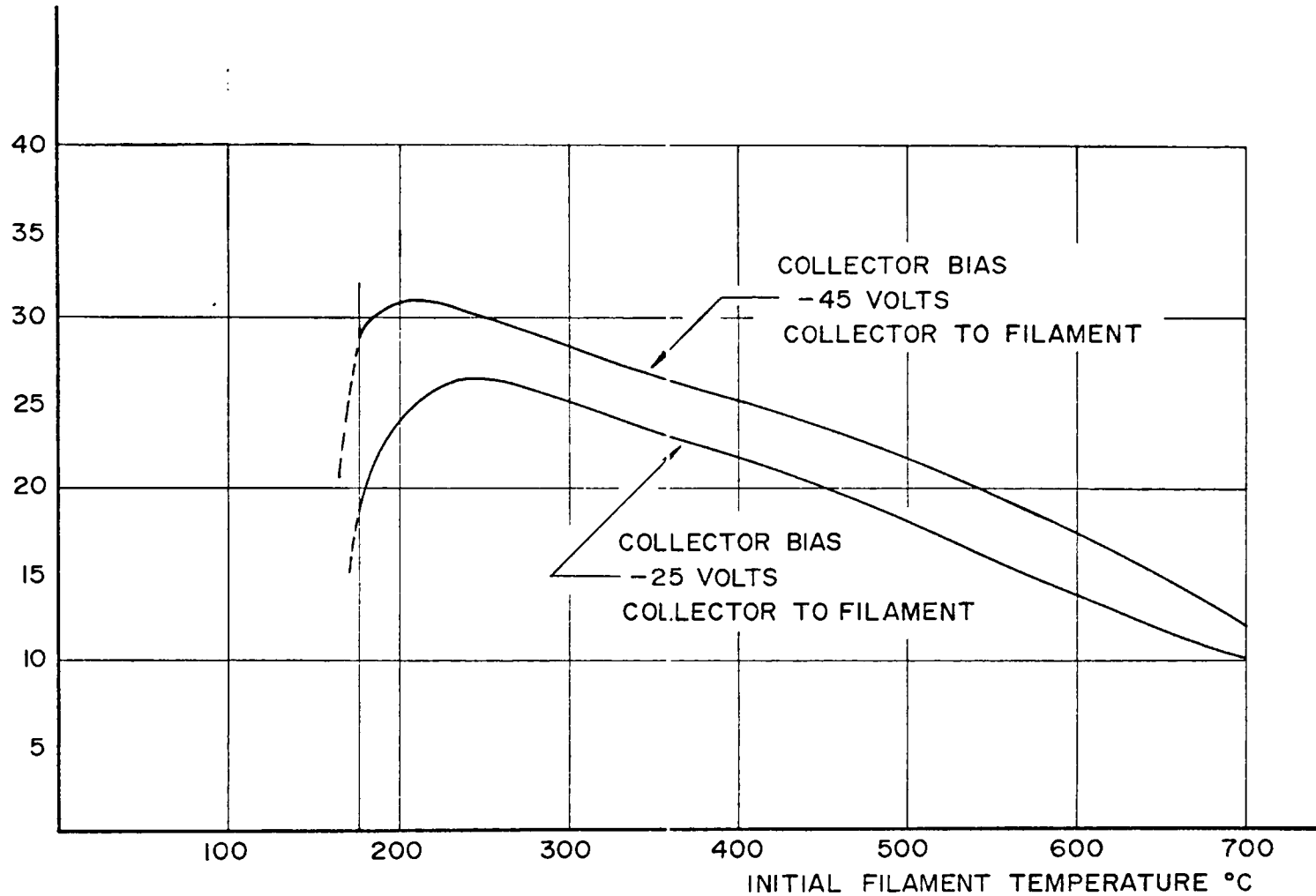


Figure 9. Change in Temperature Versus Initial Palladium Filament Temperature

an unexpected result but may be important in that it may relate to low temperature ion emission, which is the principle behind the detector.

As the initial temperature of the filament goes up the magnitude of the change in temperature decreases in a linear way. At the low end the peak falls off very rapidly to a point where it is no longer detectable. This is in agreement with the work of Taylor and McKinney where it was found that as the temperature of the palladium increased above 280°C the quantity of CO absorbed decreased. This would explain why our observed change-in-temperature decreased as the filament was raised to higher initial operating temperatures, as shown in Figure 9. The rapid decline in the change-in-temperature at the low filament temperatures suggests that there is an activation temperature at which the absorption process begins.

## 2. Effects of Various Collector to Filament Bias Voltages on the Heat Release when CO is Absorbed by Palladium

In an effort to determine if the heat release was a function of a collector to filament bias voltage, it was decided to introduce such a bias between the Pd filament and a collector screen. The results of this action for two cases is shown in Figure 9. Only two voltages were used in this study because of time limitations. For the top curve the collector to filament bias was - 45 VDC. The lower curve represents a collector to filament bias of - 25 VDC. Although the larger bias voltage produced a greater temperature change, it also contributed a large amount of A.C. signal noise. The lower bias voltage produced a smaller temperature change, but there was a significant reduction in A.C. noise.

It was, therefore, decided to operate with a collector to filament bias of - 22 VDC.

This empirical effect of an electric field on the heat released in an absorption process is quite surprising and merits further investigation. It certainly would not have been dictated by conventional theories of absorption.

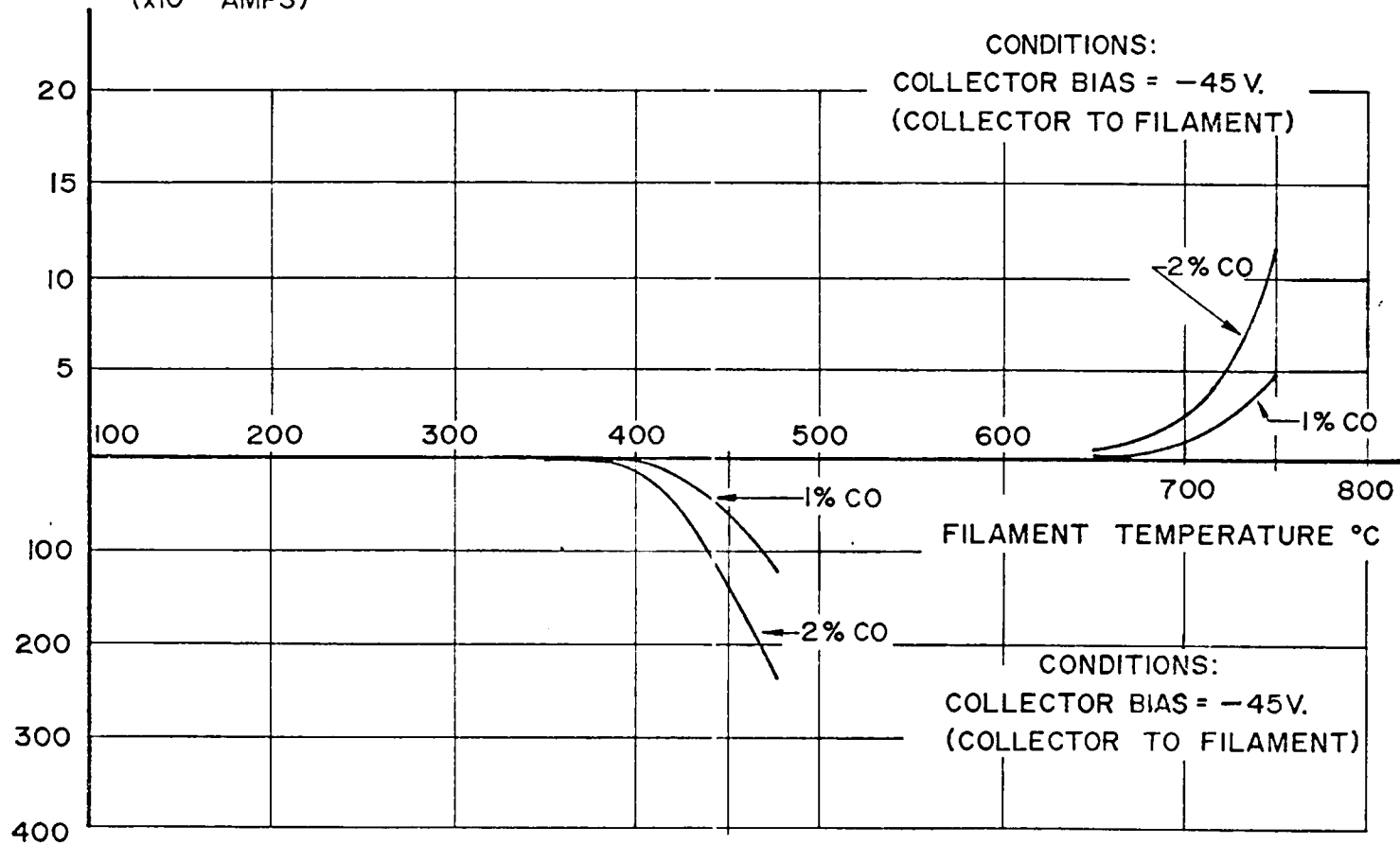
### Positive Ion and Exo-Electron Emission from Pd Due to Adsorption of CO

The expansion of the Pd lattice that occurs upon absorption of CO might be expected to induce emission of exo-electrons from the Fermi sea in the Pd lattice. For this reason it was considered important to determine first, if this electron emission did indeed occur and second, if the electron emission was more sensitive than ion emission for the detection of carbon monoxide.

These experiments also used a palladium wire filament. The operational method was to allow a known constant concentration of carbon monoxide to enter the carrier gas stream and pass through the detection chamber. The resulting change in ion and electron emission was measured at various filament temperatures. During this experiment, carrier gases other than nitrogen were used to see what effect they would have on the magnitude of emission. The collector to filament bias was - 22 VDC for reasons discussed earlier.

The results are shown in Figure 10 which illustrates the change in emission current as a function of temperature of the palladium filament for two carbon monoxide/air ratios. Data was taken for both

CHANGE IN ELECTRON EMISSION  
( $\times 10^{12}$  AMPS)



CHANGE IN ION  
EMISSION ( $\times 10^{12}$  AMPS)

Figure 10. Change in Emission Versus Temperature

electron and ion emission. It was expected that at low temperatures (200 to 500°C) positive ion emission would be the dominant contribution to the emission signal, while at high temperatures (500 to 800°C) electron emission would dominate. The experimental data verified this hypothesis. Figure 11 shows a plot of the change in electron and ion emission versus temperature for nitrogen as well as other carrier gases, namely, oxygen and air from compressed gas tanks. The top half of the plot is the change in electron emission as a function of temperature. The bottom half is the change in ion emission. As the curves indicate, there are slight differences in ion current using various carrier gases. The important point to note is that the ion emission starts at a much lower temperature than the electron emission, and its magnitude is much greater. This suggests that ion emission is the more sensitive method for detection of CO. The ability to operate at the lowest possible temperature is important as a safety factor because a hot filament could ignite an explosive CO/air mixture.

#### Investigation of Techniques for Restoration of Ion Emission after Poisoning has Occurred

Occasionally during the experiments the ion emitting properties of the palladium foil or filament were lost. Some sort of surface layer formation was suspected, but the concept was not verified. However, several empirical techniques for restoration of surface properties were investigated.

One of these methods involved techniques to reduce or activate the surface of the palladium by passing hydrogen gas through the

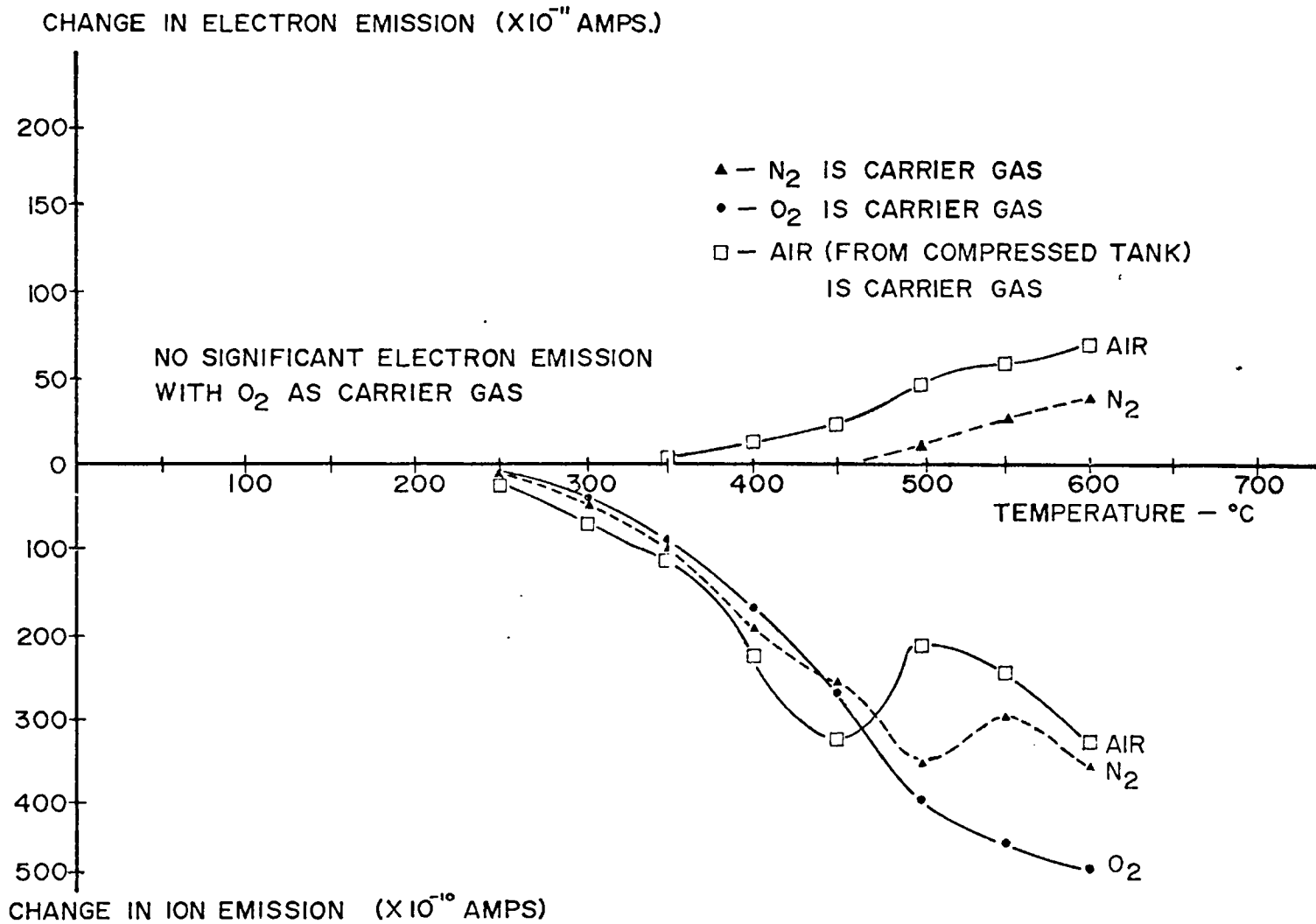


Figure 11. Change in Emission Versus Temperature for Various Carrier Gases

detection unit for 15 minutes while holding the system at its normal operating temperature (200°C). The success of this method was limited and this technique was abandoned.

Another technique involved sandblasting the surface of the palladium element. The element was then washed in distilled water, dried and exposed at 200°C to hydrogen for 15 minutes. This method proved to be more successful. The rate of ion emission increased by 100 fold over the rate of emission under the "poisoned" condition; and the sensitivity of the Pd element to CO remained high. It is believed the sandblasting pitted the surface of the palladium providing more surface area for absorption of CO. The subsequent increase in impurity ion emission agreed with this hypothesis. Other supporting evidence for this concept was reported by Rekova and his associates (Rekova, Fogel and Nesterov 1970). They showed that positive ion emission increased when the Pt emitter used in their experiment was plastically deformed.

#### Changes in Positive Ion Emission Versus CO Concentration at Constant Temperature

Having chosen the approximate operating temperature on the basis of experiments discussed above, the system was changed from a palladium wire to a sheet of palladium foil shaped in the form of a cylinder. This configuration and certain chamber improvements were incorporated in the final model to improve the rate of ion emission from the surface of the palladium element. A new series of ion emission experiments were run to determine the system signal-to-noise level. The results are shown

in Figures 12 and 13. These figures are the most important curves in the text. They relate the amount of emission versus the concentration of carbon monoxide present in the air stream. These two curves are the calibration comparison curves used for the calibration procedure described previously in the manual. It should be noted that there is scatter in the data, particularly at low CO/air ratios. Part of this scatter is due to difficulties involved in metering a precise flow of carbon monoxide into the air stream, but there are also other factors involved and these will be elaborated on in the conclusion section. As the curves indicate, the amount of emission is a fairly linear function of the CO/air ratio when the data is averaged to suppress the scatter.

#### Experiments with Gases other than CO

These studies were necessary to determine if other contaminant gases in an air ambient system would affect the CO detection system. This proved to be the case and this is a serious defect in the present system. Typical results are shown in Figure 14 for acetylene with air as the carrier gas.

As the figure shows, the emission increases with acetylene just as it does with carbon monoxide. In fact, the response is somewhat larger. What is occurring is combustion of the acetylene catalyzed by the Pd foil. When gases like acetylene, methane, propane, etc., burn on the surface of the palladium, they raise its temperature. The resultant increase in ion emission is due to the rise in temperature of the Pd element. Gases of this type might be removed by filtering

SIGNAL TO NOISE RATIO

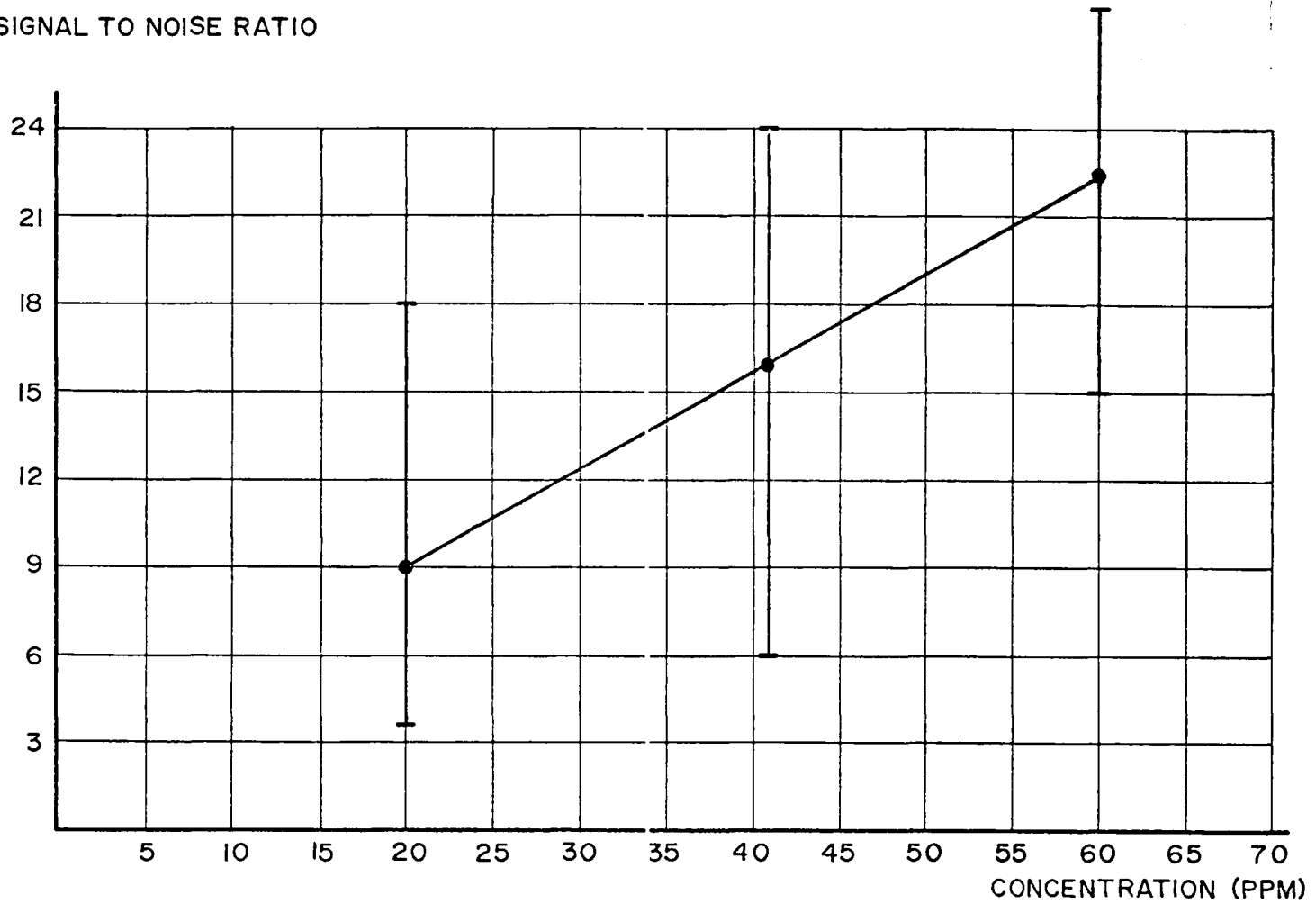


Figure 12. Ion Current Versus CO/Air Ratio (Palladium Foil)

# SIGNAL TO NOISE RATIO

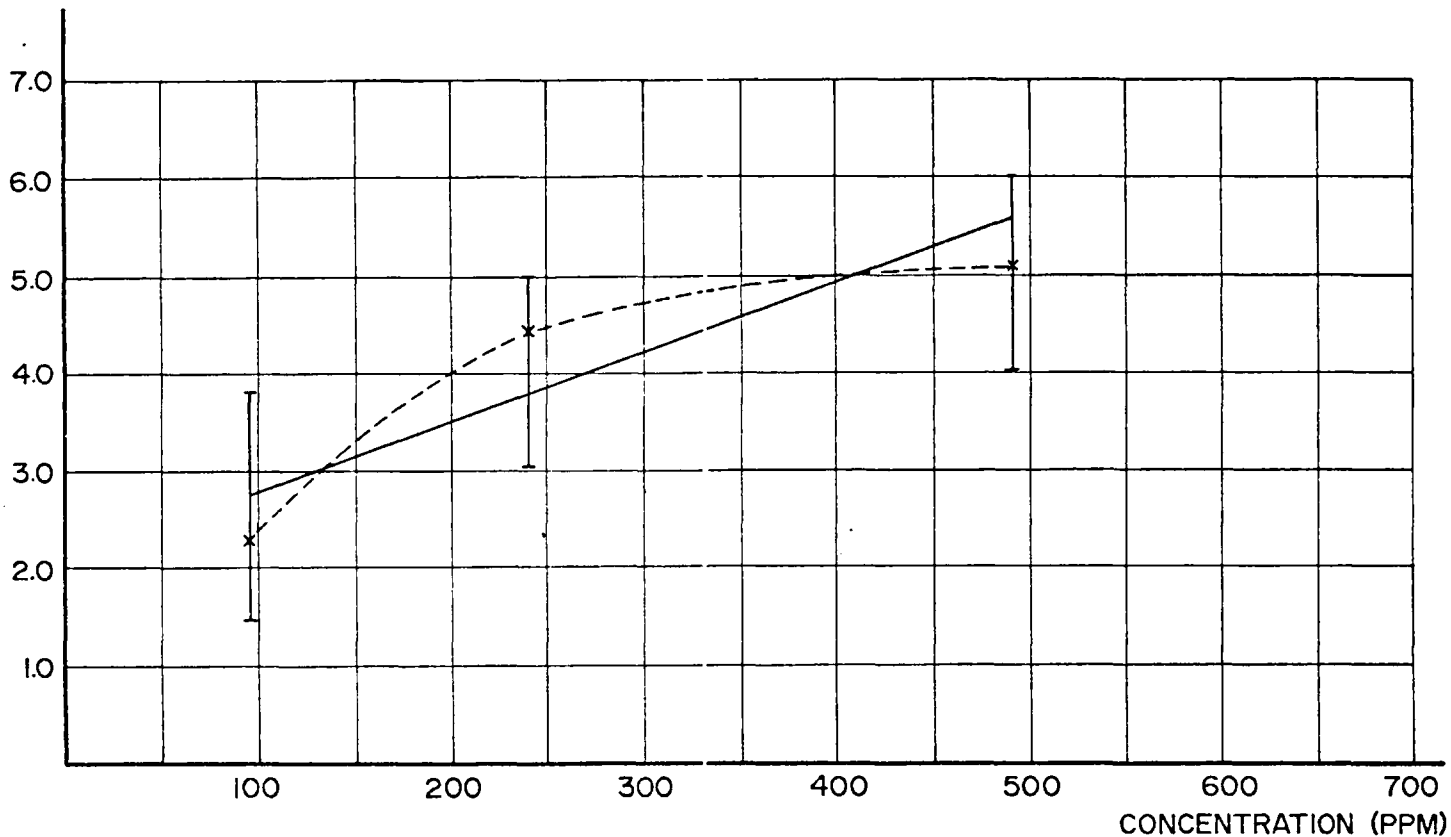


Figure 13. Ion Current Versus CO/Air Ratio (Palladium Foil)

CHANGE IN EMISSION (ION)  
SIGNAL TO NOISE ( $10^{-10}$ )

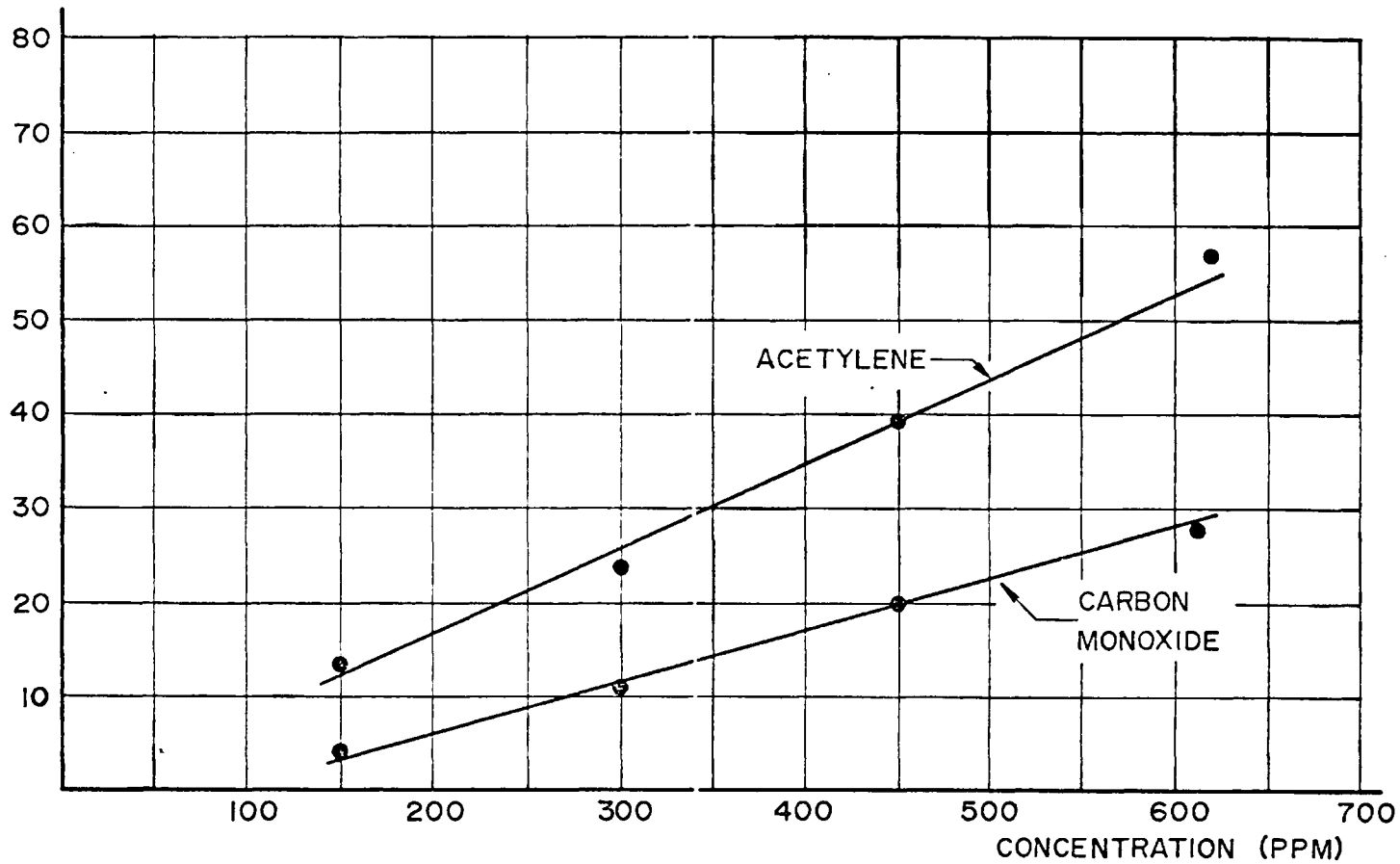


Figure 14. Change in Emission Versus Concentration for Acetylene and Carbon Monoxide

techniques, but filters of this type were not installed on the CO system at this time.

## APPENDIX 2

### NOISE AND DRIFT

In these experiments we observed two types of "noise." The first type is noise which fluctuates about the output signal level. We choose to call this noise "electronic/ionic noise." The electronic/ionic noise level for the high temperature (500 to 800°C) electron emission data runs was much greater than that for the low temperature (200 to 500°C) ion emission data runs. Figure 15 is a plot of the magnitude of the electronic/ionic noise as a function of temperature for both ion and electron emission. As the graph indicates, the high temperature region has a far greater amount of this noise than the low temperature region. This again led to the conclusion to use the low temperature operating region. The noise present at high temperatures was of such magnitude as to destroy the ability of the detector to measure small concentrations of carbon monoxide.

Another variable of operation (noise) that had to be investigated was the amount of "signal drift" noise. A plot of this type of noise as a function of time is shown in Figure 16. The drift could be interpreted as being a change in concentration of carbon monoxide and therefore would obscure the true carbon monoxide level. This drift was found to be completely random in nature, and trying to process it out electronically proved to be impossible. We decided to operate at a

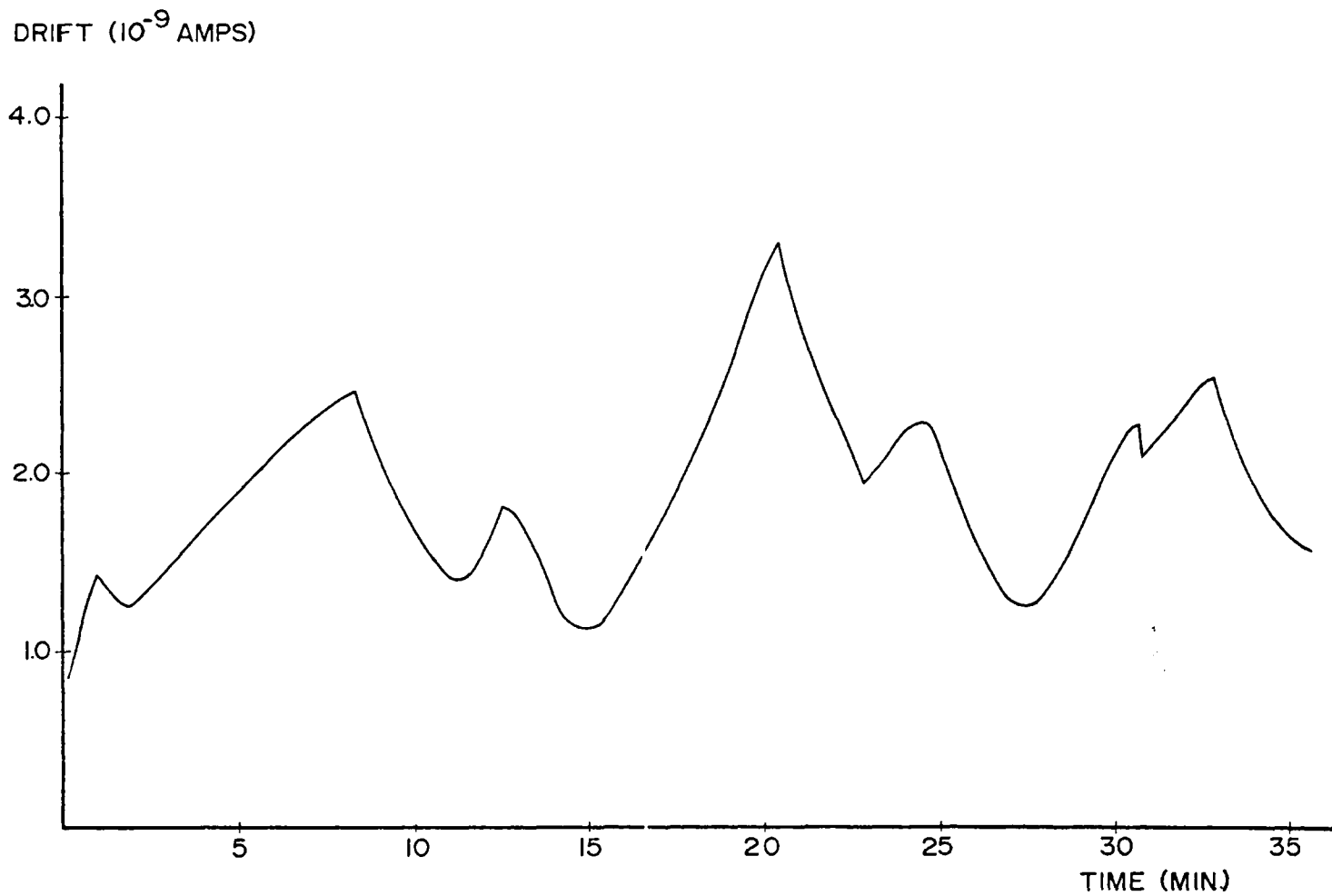


Figure 15. Drift Noise Versus Time

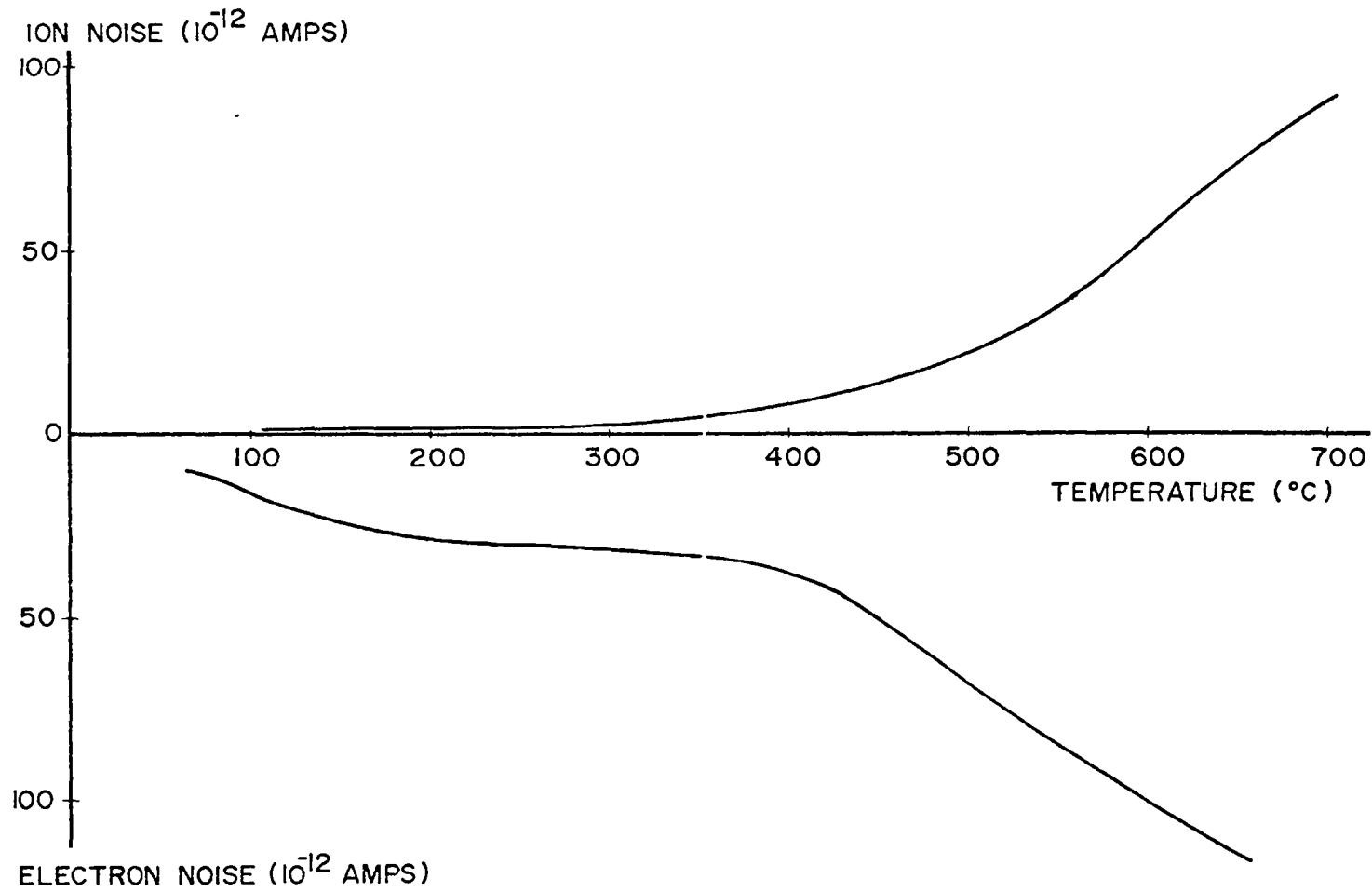


Figure 16. Electron/Ion Noise Versus Temperature

temperature and carrier gas flow rate, where this type of noise was at a minimum. Results of earlier experiments suggested that at low temperatures (200 to 300°C), this drift was an order of magnitude less than that at high temperatures (400 to 600°C).

### Conclusions

As stated earlier, the purpose of this research was to take a known physical principle and develop a useful detection instrument. As the data indicated, this objective has been attained.

A number of following characteristics, however, should be stated. The problem is that it will also react to other gases, i.e., hydrogen, methane, ethyl alcohol vapor, acetylene, etc. If any of these gases are present in the air, the emission will increase and mask the true concentration of carbon monoxide. The effect of these gases is simply combustion changing the surface temperature of the palladium filament. If necessary, a filter could be used to remove these gases from the airstream.

The research clearly shows one important fact. Although the system will detect carbon monoxide, its total reliability is still somewhat questionable. The reason for this statement is the difficulty in explaining the need for occasional reactivation of the palladium foil. For example, throughout these experiments the unit has for no apparent reason just stopped detecting even large concentrations of carbon monoxide. This necessitated the development of techniques of filament surface activation. These techniques were outlined in the troubleshooting manual, but at times even these methods failed. On these

occasions the unit was usually allowed to remain in the "warmup" mode in hopes that the catalyst would once again become active. This would be only partially successful and if it did not work, the activation techniques were repeated until the proper level of activity was attained.

Another reliability anomaly that would occur was that the system noise would change in magnitude from one day to the next. While it is believed that most system drift was due to change in air temperature, certain changes in noise level could not be explained in terms of temperature changes. There were occasions when the ambient air would be at a constant temperature, but the noise level would still undergo a large level shift. Analysis of output data seemed to indicate that a sudden random increase in emission was causing this random noise. It may well be that as the carbon monoxide diffuses into the surface of the palladium, it causes the palladium lattice structure to expand. As a result of this effect, impurity atoms such as sodium and potassium are "released" from the palladium. Sudden increases in ion emission are attributed to the palladium releasing clusters of positive ions. On the output signal, this would appear as a drift noise component. No techniques were developed to eliminate this noise level shift since it was not a predictable occurrence.

The items listed above are some of the major difficulties associated with this product development. We believe with more investigation, the reliability of the unit could be greatly improved. With increased reliability, the need for periodical calibration would no

longer be necessary. The unit would then become an important tool in the battle to improve our environment.

## APPENDIX 3

A REVIEW OF CARBON MONOXIDE MONITORING TECHNIQUES  
(as prepared by Beverly L. Martin and Stuart A. Hoenig)

A REVIEW OF CARBON MONOXIDE MONITORING TECHNIQUES

by

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*Contract IR01 EC-00467-01*

ABSTRACT

Carbon monoxide detectors are described in terms of their mode of operation, *i.e.*, catalytic, thermal conductivity, *etc.* For each device the range, sensitivity, and operational characteristics are given.

## INTRODUCTION

Carbon monoxide is a flammable, colorless, odorless gas, quite toxic to the human body. This toxicity is due to the affinity of CO for hemoglobin (more than 200 times that of oxygen [1]). As a result, the body suffers from an oxygen deficiency even when only small concentrations (100 ppm) of CO are present in the atmosphere.

Carbon monoxide, a product of incomplete combustion, can readily enter the atmosphere from a great many sources; these include faulty flues, auto exhaust, malfunctioning heating appliances, and almost any combustion equipment. Workrooms can become CO traps as a result of improper venting, negative building pressures, faulty draft controls, or recirculation of already contaminated air. The result of these CO leaks is a danger to human life. Prevention involves first monitoring and then controlling the level of CO in the human environment.

A monitoring device for this purpose must meet the following requirements: It must indicate the *Threshold Limit Value* (top level at which exposure is permissible during a forty-hour work week) as two thirds of its range [2]. This *Threshold Limit Value* is presently set by the American Conference of Governmental

Industrial Hygienists. In 1964 this value was 50 ppm of the total air volume,\* which compares unfavorably with most device capabilities today. The monitor should be capable of continuous operation and require little or no maintenance; it should be usable in either a portable or fixed application; fast in response; accurate; and simple to operate.

This report will review the detectors for carbon monoxide which have been reported in the literature or offered for sale. In each category the mode of operation, advantages, disadvantages, and sensitivity are reported.

The sensitivity data were taken directly from the manufacturers' catalogs without change, except where obvious misstatements were made. To the best of our knowledge no central facility exists for test and comparison of CO detector systems. We suggest that the claims of most manufacturers be viewed with distinct suspicion.

In view of the rapid development of detectors for noxious gases and the entrance of many new organizations into the detection field, it is suggested that a permanent facility be developed to test gas detectors and report on their feasibility. As an example, oceanographic equipment is tested at sea by the National

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\* A conversion table to change ppm to  $\text{mg/m}^3$  is given in this report (Table 2).

Oceanographic Instrumentation Center, Washington, D. C. 20390.

The results are available to the scientific community and are most useful when equipment must be purchased or specified.

### COLORIMETRIC METHODS

One of the most popular and basic methods of gas detection has always been the colorimetric method. This technique may be subdivided into wet and dry methods for detection of CO.

#### Dry Methods

Hoolamite is a mixture of iodine pentoxide and fuming sulfuric acid, deposited on granular pumice stone in the proportions listed below.

<u>Component</u>	<u>Parts</u>	<u>Percent</u>
<i>Iodine Pentoxide</i>	10	11
<i>Fuming Sulfuric Acid</i>	50	55
<i>Pumice Stone</i>	30	33
<i>Iodine</i>		.25 - 2.0

When this mixture comes in contact with CO, it liberates iodine. The pumice changes from the original white to increasing depths of blue-green, violet-brown, and finally black. The depth of color indicates the concentration of CO present.

The detection range of this method extends from .07% to 1% volumetric (700 ppm to 10,000 ppm). Below 700 ppm hoolamite shows no change of color [3].

Other gases that react with hoolamite in the same manner as CO causing interference with the detection method include acetylene, alcohol, ammonia, benzene, ether, ethelene, gasoline, hydrogen sulfide, hydrogen chloride, and natural gas [4]. These chemicals must be removed by a filter before the air sample passes into the hoolamite to avoid erroneous measurements.

In commercial systems the hoolamite is contained in small sealed glass tubes since moisture causes the substance to deteriorate. On either side of the hoolamite is a layer of activated charcoal and cotton wool which acts as a filter against interfering gases. To test an air sample, the ends of the glass tube are broken off, and the tube is inserted in a pumping device. The pump sends a steady flow of air through the tube. After a pre-determined time, the hoolamite sample is compared to a color chart and the CO concentration can be determined.

Presently, Mine Safety Appliances [5] and Unico [6] are both manufacturing a carbon monoxide detector approved by the National Bureau of Standards for use in industry. The device uses a pump similar to the one used for the hoolamite detection method. It draws a fixed quantity of the sample atmosphere through a small

tube of chemically treated material sensitive to CO. These detector tubes are filled with a complex silico-molybdate catalyzed by palladium sulfate. When in contact with CO, the silica gel changes from its original yellow to increasingly darker shades of green. The concentration of CO is determined by a comparison of the tube with a color chart. Error often occurs at very low concentrations because of the difficulty of this color matching procedure. The range of this method is from .001% to .1% volumetric (10 ppm to 1,000 ppm). Interference is caused by nitrogen dioxide, which also reacts with the gel.

A similar detector by Mine Safety Appliances, using the length-of-stain to indicate the concentration, has a range of from 10 to 2,000 ppm. The sampling operation takes approximately three minutes, but involves much guesswork when detecting concentrations of CO below the *Threshold Limit Value* of fifty parts per million. A number of gases or vapors interfere with this test material. A table listing certain gases and the level at which they effect the CO test is given in Table 1 [7].

Column 1 of Table 1 shows the actual gas or gases metered into the test system. Column 2 shows the outputs actually observed for three different cases. The first NO filter ahead of the indicating tube, the second an ascarite filter only, and third an ascarite-KMnO<sub>4</sub> together. It is clear that the two component filters *must* be used if NO or NO<sub>2</sub> are present.

It is apparent from Table 1 that as little as three parts per million of nitrogen dioxide can cause a fifty percent detection error below the *Threshold Limit Value*. Fortunately, most of these interferences can be eliminated by using a filter composed of ascarite and  $\text{KMnO}_4$ . For continuous monitoring this filter must be changed on a regular basis to insure its proper activity.

Another colorimetric detector, by Dansk Impulsfysik of Denmark, uses a square plastic plate with a round spot of palladium chloride on the front. The spot turns darker with a higher CO concentration. It is matched to a color chart for indications of "SAFE", "MARGINAL", or "DANGEROUS" CO levels. When exposed to fresh air and sunlight, the spot fades back to its original color and can be reused until it is overexposed and fails to return to its original color. The spot is said to be sensitive to .01% volumetric (100 ppm) of CO. Humidity slows the reaction, however, and cigarette smoke causes a discoloration because of its NO and  $\text{NO}_2$  content.

Unico has a CO alarm that trips when a toxic level is reached. A detecting sensor of high impact polystyrene changes color from yellow to brownish-black in presence of CO. The change of color is detected by a photoelectric system. Reaction time for this device varies as shown below. The lowest concentration readily detectable is 50 ppm. The required maintenance involves replacing the detection sensor after each exposure.

<u>Concentration</u>	<u>Response Time</u>
50 ppm	1 hr.
100 ppm	20 min.
600 ppm	6 min.
1,000 ppm	3 min.
3,000 ppm	80 sec.

Response time of Unico CO alarm [8].

### Wet Methods

There are two colorimetric wet detection methods involving palladium. Both utilize the fact that CO will reduce palladium in solution. In the first method, CO is allowed to diffuse into a palladium chloride solution, reducing it to metallic palladium. An excess of potassium iodide converts the unreacted palladium chloride to colored palladium iodide, which can be measured colorimetrically [9].

The second method involves the same reaction, but instead of potassium iodide, ammonium molybdate is added. This reaction produces molybdenum blue which is measured optically [10].

A wet chemical method utilizing the oxidation of CO by hopcalite measures the resulting carbon dioxide (CO<sub>2</sub>) by absorbing it in an excess of barium hydroxide in solution [11]. The excess alkali is measured by titration with oxalic acid to the first endpoint stable for over fifteen seconds. From this point, the concentration of CO is determined by the equation

$$.1 \times \frac{B-A}{V-100} \times \frac{273-t}{273} \times \frac{760}{P} \times 100 = C_{CO}$$

where

*B* = volume of standard acid used for blank test (without carbon monoxide)

*A* = volume of standard acid in actual test

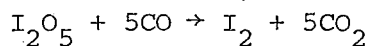
*V* = volume of sampling flask (-100 is volume of alkali added)

*t* = temperature

*P* = pressure (mm of Hg)

The main disadvantage of this method is the time involved to make the measurement.

The iodine pentoxide method is another example of a wet chemical method of CO detection. It is based on the chemical reaction



A sample of the gas to be tested is first passed through a reagent to remove interfering gases. It then goes through a tube of iodine pentoxide heated to about 150°C. This liberates iodine in proportion to the CO concentration. The air sample then passes through an absorption bulb of potassium iodide solution. The bulb retains the iodine liberated in the reaction. The system is purged to be sure all the iodine has been retained. The concentration of CO is found when the potassium iodide is analyzed for the iodine content. There are several methods of analyzing the potassium iodide-iodine solution including titration, electrical reduction and spectrophotometry.

The iodine pentoxide method is extremely accurate, even to such small concentrations as one part per million. The disadvantage of the system is the large amount of maintenance required daily, including replenishing chemicals and checking the recorder. Interferences with the  $I_2O_5$  method of detecting CO include mercaptans, hydrogen sulfide, hydrogen, olefins, acetylenes, and water vapor [12].

### Thermal Methods

Two techniques exist here: the first involves a catalyst which induces the oxidation of CO to  $CO_2$  and senses the heat released by the reaction. The other system depends upon the difference in thermal conductivity between CO and air.

A typical catalytic system is that manufactured by Thermo-netics [13], the Codet IV, which measures the heat released using a thermopile (thermocouples in series to boost emf). The thermopile has a linear millivolt output which is amplified and used to drive a pen recorder. This detector is highly portable, but not meant for continuous monitoring. Maintenance includes zeroing the recorder, selecting a range, and replacing the dehydrator (after four hours continuous monitoring or forty hours intermittent use). Possible ranges include

0- 500 ppm	(0-.05%)
0-1,000 ppm	(0- .1%)
0-5,000 ppm	(0- .5%)

The time for a reaction is 25 seconds, however the sensitivity is only  $\pm 50$  ppm.

Devco Engineering's Carbon Monoxide Monitoring System [14] uses the same temperature sensing method as that of Thermonetics. This device can be used for constant monitoring, and gives an audible warning if a pre-set CO level is reached. Reaction time is 30 seconds, with a sensitivity of  $\pm 2\%$  of full scale. The ranges possible for this device are 0-100 ppm, 0-200 ppm, and 0-500 ppm. The manufacturer suggests that maintenance is minimal for the purpose of operational ease. However the span of detection has to be checked and the particulate filter replaced every sixty days.

The Mine Safety Appliances detector, Model 701, measures the heat given off in oxidation with two thermistors. These are part of a wheatstone bridge circuit buried in the hopcalite bed. The thermistors react to heat by unbalancing the bridge circuit and causing an up-scale detector reading. This method has a range of 0-500 ppm, and a reaction time of 50 seconds. It is limited by high humidity and tobacco smoke, both of which impair the accuracy. The device is continuous and has an accuracy of 1% of the full scale. It also has an alarm set to go off at 50 ppm.

A somewhat different application of this technique determines CO concentration by passing the gas-air mixture over a heated wire.

The combustion of the gas on the surface of the wire causes a change in its temperature and thus in its resistance.

All of these catalytic methods suffer from the same problems. First, the catalyst will induce a reaction of almost any combustible gas, *i.e.*, methane. These interfering gases must be removed before the gas enters the test system. Second, the catalyst loses its effectiveness with time. This decay is especially rapid if  $H_2S$  or  $SO_2$  is present.

An interesting catalytic technique still under investigation is based on the reactions of the Mond nickel process. A sample of air is taken into the reaction chamber and passes through a nickel gauze set up as an electrically heated filament at  $60^\circ C$ . Any CO present is converted to nickel carbonyl. The gas then travels through a glass fibre fabric filter and is heated indirectly to  $150^\circ C$ . The nickel carbonyl decomposes and deposits pure nickel on the fabric. The nickel changes the electrical resistance of the fibre at a rate dependent on the CO concentration. Since the method depends on the rate of nickel deposit instead of on the absolute value, the inventor suggests that this should eliminate frequent zero setting and fabric replacement [15].

This cannot really be correct because the electrical resistance of a metal film depends upon length ( $l$ ), thickness ( $t$ ), and width ( $w$ ) of the film as

$$R = \rho \frac{\ell}{tw}$$

where  $\rho$  is a constant for any given material. As ( $t_0$ ) initial thickness changes by some increment ( $\Delta t$ ) then ( $R$ ) changes from its initial value ( $R_0$ ) by an increment  $\Delta R$  as

$$\frac{\Delta R}{R_0} = - \frac{\Delta t}{t_0}$$

It is clear that as the thickness of the film ( $t$ ) increases due to CO exposure the sensitivity of the system decreases

$$\frac{\Delta R}{\Delta t} = -A \frac{1}{t^2}$$

where  $A$  is a constant.

Turning now to thermal conductivity techniques we note that the system uses two cells traversed by high resistance wire such as platinum. One cell is filled with a reference gas and sealed; the other contains the gas being analyzed. The platinum wires are heated by a constant current and cooled by convection with the gases in the cells. If the gases differ in thermal conductivity the wires reach different equilibrium temperatures. The wire temperature is monitored by measuring the wire resistance and using the relation,

$$R_T = R_0 [1 - \alpha(T - T_0)] \quad \alpha = 0.003 \text{ per } ^\circ\text{C for } P_t.$$

This system is quite effective in detecting any difference in thermal conductivity between the reference gas (air or  $N_2$ ) and the gas being measured. This allows its application as a CO detector, however the apparatus must first be calibrated with a known CO/air mixture. There are innumerable variations and reinventions of this system. However all thermal conductivity systems are subject to error since any gas having a thermal conductivity different than the reference gas will trip the alarm.

A unique version of the thermal detector system depends upon the suggestion that CO and  $CO_2$  *always* exist in a 2:1 ratio [16]. The device detects the  $CO_2$  by thermal conductivity techniques and relates it to the "presumed" CO level. There is no reason to suspect that the  $CO_2$  to CO is always 2 to 1.

### INFRA-RED SPECTROSCOPY

Several companies manufacture carbon monoxide detectors that work on principles of infra-red spectroscopy. The method is accurate, in most cases, down to 15 ppm, but there is interference from  $CO_2$  since its absorption spectrum is so similar to that of CO. This problem can be solved by using a dispersive infra-red system. A dispersive detector uses only the particular absorption frequencies of the material to be measured. This eliminates most of the

interference and results in a more accurate reading. Because of the interferences in the non-dispersive system the sample gas must be filtered to remove interfering elements including  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This in turn requires regular maintenance to insure that the filter is 100% effective.

### NON-DISPERSIVE DETECTORS

Non-dispersive infra-red analyzers are accepted as being the most accurate gas analyzer in use today, and are often used for the calibration of other analyzers.

Robert Bosch Corporation of Germany [17] has an exhaust gas detector with ranges of 0-5%, (0-50,000 ppm), and 0-2.5% (0-25,000 ppm) volumetric. The operation has a single disk radiating non-dispersive infra-red energy at  $700^\circ\text{C}$ . The light is split to form two beams, one active and the other a comparator beam. The comparator beam goes through an inert calibration gas (nitrogen) which absorbs light only at wavelengths where CO does *not* absorb light. The other, active beam, passes through the test gas where any CO that is present absorbs energy at its own specific wavelengths. Both beams then pass through a chopper, which mechanically pulses them. From there they alternately enter adjoining detector cells filled with pure CO. It is in this pair of cells that CO detection occurs. The active beam has lost energy at certain

wavelengths where CO has a peak in its adsorption spectrum. The reference beam has not lost this energy and the CO filled reference cell which receives the comparator beam is heated more than that which receives the active beam. The differential heating causes a pressure difference and therefore a gas flow between the two interconnecting detection cells. This gas flow is then converted into an electrical signal proportionate to the CO content of the test gas. Reaction time for this process is from five to ten seconds with an accuracy of from 0.5 to 1%. Maintenance includes a daily calibration of the zero point, changing the filter paper disc when it is uniformly blackened, and keeping the water trap clean. Obviously this is a non-dispersive detector that achieves increased sensitivity by taking advantage of the difference in the absorption spectrum of  $N_2$  and CO.

A more conventional non-dispersive system is manufactured by Beckman Instrument Corporation [18]. Mine Safety Appliances has a Lira Model 300 non-dispersive continuous detector with possible ranges of 0-.2% (0-2,000 ppm), 0-1% (0-10,000 ppm), and 0-10% (0-100,000 ppm) volumetric. The principle of operation is somewhat similar to that of the Bosch CO detector except for having two infra-red sources, and a membrane placed between two detection cells. Reaction time for this detector is five seconds for a ninety percent reading with an accuracy of two percent of the full scale. Maintenance consists mainly of checking the sensitivity and zero drift periodically.

Intertech Corporation [19] has two non-dispersive CO detection systems that work on the same method as the two previously mentioned detectors. The first is a continuous CO tester, suggested for exhaust gas sampling. It has possible ranges of 0-5% (0-50,000 ppm) or 0-10% (0-100,000 ppm) volumetric with an accuracy of two percent of full scale, and a reaction time of two seconds. The device is small (9" x 9" x 15") and portable (22 lbs.), with an internal power supply. The second system, called the Uras-2, is much larger but has the same operating principle. It has three possible ranges of 0-100 ppm, 0-50 ppm and 0-25 ppm, and a reaction time of .5 seconds. The Uras-2 is continuous monitoring, and calibrates itself periodically by means of a contained cylinder of calibration gas. Maintenance includes filtering out gases with absorption bands overlapping that of CO, making drift checks so the system does not drift out of the automatic calibration range, checking the air flow, replacing calibration gases, and checking the humidity control. All this must be done once a day to keep the system running well. It also needs a stable temperature and poses problems because it is very large, expensive, electronically complex, and therefore subject to malfunction.

#### DISPERSIVE INFRA-RED SYSTEMS

Systems of this type make use of a prism or grating to disperse light into its component wavelengths. A particular wavelength is

selected which is strongly absorbed by CO and weakly absorbed by CO<sub>2</sub>, O<sub>2</sub> or water vapor. This wavelength is then used in a typical calibrated CO absorption cell. The dispersive system is much less sensitive to interference by CO<sub>2</sub> or H<sub>2</sub>O but the optical system is much more complex and delicate.

A dispersive IR system for CO is manufactured by NDRC. The wavelength used for CO absorption is split into a detector and a reference beam. The beams pass through a test and a reference cell and then to a balanced thermopile. Possible ranges include 0-2% (0-2,000 ppm), 0-1% (0-10,000 ppm), and 0-3% (0-30,000 ppm) volumetric. The reaction time is ten seconds. Maintenance includes adjusting the amplifier gain, heater current, and bucking potential [20].

Dispersive IR systems have been somewhat unsatisfactory in portable systems where the analysis of a number of contaminants was to be done by a single unit. The problem is primarily due to poor design and manufacturing quality control rather than the physics of the IR technique [21].

### GAS CHROMATOGRAPHY

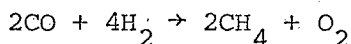
With this technique, all the components of a sample of air can be analyzed if the column, oven and detector are properly adjusted. For operation a carrier (inert) gas carries the air sample through an absorption column which is in a temperature

controlled oven. The separation of gases occurs here, since each component of the gas is held in the adsorption column for a different length of time, called the retention time. As the components leave the column their appearance is recorded as a function of time. The components are distinguished by their time of appearance. The concentration of each component is proportional to the area under its recorded peak.

Most gas chromatographs use a simple thermal conductivity detector that responds to all common gases (CO, CO<sub>2</sub>, N<sub>2</sub>, etc.) with the same sensitivity. Electron capture or flame ionization systems are available for trace detection of organics like CCl<sub>4</sub> or DDT.

The gas chromatographic systems used for CO detection are accurate to about 0.01% volumetric (100 ppm), although Unico claims to have one that can detect concentration as low as 22 ppm accurately, and Monsanto [22] has a table-top device with ranges as low as 0-5 ppm, 0-10 ppm, and 0-20 ppm.

One gas chromatograph being developed measures CO by a CH<sub>4</sub> technique. A precolumn filter eliminates anything other than these two gases. Any CO in the air sample is catalyzed to CH<sub>4</sub> according to the reaction,



The methane is then measured by a flame ionization detector [12].

The gas chromatograph is semi-continuous and takes five minutes for a single analysis. Gas chromatographic systems are rather bulky, the smallest one fills a single suitcase. A source of carrier gas is needed. A power supply for the oven (if any) and the detector is required. If close oven control is maintained the power supply can be quite large. The gas chromatograph is ideally suited for laboratory analyses of CO/air mixtures from 0.1 to 10,000 ppm but it should be operated by trained personnel.

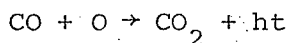
### MASS SPECTROSCOPY

Mass spectroscopy may be used to determine CO concentration. The technique is simple in theory but complex in practice. A sample of the gas to be analyzed is pumped to a vacuum of  $10^{-5}$  torr and traversed by a beam of electrons. A fraction of the gas is ionized and the ions are drawn through a combination of electric and magnetic fields. This disperses the ions as a function of their mass to charge ratio and the ion current at mass 28 is a measure of the fraction of CO in the initial sample.

The major problem with mass spectrometry, aside from complexity, is the fact that the mass 28 CO peak is the same as that of  $N_2$ .

## SPECTROPHOTOMETRIC ANALYSIS

Test data has been reported on a spectrophotometric analysis technique that detects radiation emitted from chemiluminescent reactions of CO, NO, and SO<sub>2</sub> with atomic oxygen according to the reaction

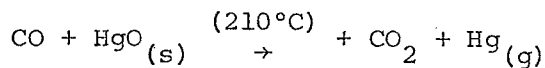


The reaction produces a characteristic glow, the intensity of which increases monotonically with the concentration. The reaction with CO, however, is too insensitive to be useful at low concentrations [23].

## MERCURY VAPOR METHOD

Bacharach, a Division of AMBAC Industries [24], is manufacturing a CO detector, model US 400 which analyzes the ambient air by the mercury vapor method.

A sample atmosphere is passed through an air dryer, a charcoal filter to remove unwanted gases, and a heat exchanger which preconditions the sample and heats it to a constant temperature. The sample is then brought into contact with a heated, solid-state mercury oxide pellet. The amount of CO is determined by a measurement of mercury vapor reduced from the metal oxide by oxidation of the CO in the sample.



This mercury vapor is measured by an ultraviolet filter photometer. The Hg vapor is then removed from the air before it is discharged.

This device claims to have ranges extending as low as 0-5 ppm, 0-25 ppm, and 0-50 ppm, with a sensitivity of  $\pm 1$  ppm. It is continuous and has a response time of 10 seconds. Maintenance includes replacing inlet dryer, inlet filter and exhaust filter (monthly), replacing mercury oxide pellet, cleaning the system, and checking the calibration (half-yearly), replacing photocell lamp, inspecting valves for wear, checking calibration (yearly), and replacing indicator lamps as necessary.

The major interferences with this system occur with oxygenated hydrocarbons, olefins, free hydrogen and ozone [12].

### BLOOD SATURATION

It is difficult to determine the CO level in blood because of its low concentration unless the donor has been exposed to severe CO poisoning.

In blood, the spectrum of carboxyhemoglobin is distinct from that of oxygemoglobin and hemoglobin, therefore spectrophotometric methods may be used to determine the blood CO content. The only problem is that the concentration must be high for good accuracy. Another difficulty that must be included is obtaining the blood sample, since permission must be given to take it.

The pyrotannic acid method has ranges of 0-.05% (0-500 ppm), 105-.1% (500-1,000 ppm), and .1-.2% (1,000-2,000 ppm) volumetric with corresponding accuracy of .01, .02, and .03. A collected sample of from 100-250 ml of air is mixed for 15-20 minutes with a blood solution of .1 ml of blood with 1.9 ml of water. The blood is then transferred to a test tube and .04 grams of a mixture of pyrogallic and tannic acids is added, mixed, and allowed to settle. After 15-20 minutes, it can be compared to a color chart to show the percent blood saturation. The percent CO in the air can be calculated from a graph. Interference with this method is caused by acidic gases such as sulfur dioxide and hydrogen sulfide [4]. These must be filtered out before testing.

This last method of finding the blood saturation utilizes the National Bureau of Standards approved detecting tubes put out by Mine Safety Appliances and Unico. The CO is liberated from the caroxyhemoglobin by potassium ferricyanide. It is then drawn through an indicating tube, causing a color change dependent on the CO concentration. Difficulty appears in high saturations when there is a lack of uniformity in the color tubes in the total length of the sensitized area. With this method it is possible to measure from 0-10% volumetric (0-100,000 ppm) with a 1% error [25].

## POSITIVE ION EMISSION

In 1967 a new system for CO detection was reported [26]. This device uses a heated palladium wire which generates a current of positive ions ( $k^+$ ,  $Na^+$ ) as Na and k impurities diffuse to the surface. When CO or  $H_2$  is present the Pd lattice expands and the rate of diffusion increases. The system is being developed as a practical CO detector system under the sponsorship of the Bureau of Occupational Safety and Health of the Environmental Control Administration.

The system is effective at CO concentrations as low as 50 ppm. It is anticipated that a packaged version of this system will be available during 1971.

### SUMMARY

We list below all the various types of CO detectors discussed above. For each system some 11 items are listed, when no information is given this indicates that the data was not available.

#### I. Colorimetric

##### A. Dry

##### 1. Hoolamite

- a. range .07-1%
- b. monitoring (intermittant)
- c. maintenance
  1. making test
  2. check pump
- d. interferences
  1. acetylene
  2. alcohol
  3. ammonia

- 4. benzene
  - 5. ether
  - 6. ethelene
  - 7. gasoline
  - 8. hydrogen sulfide
  - 9. hydrogen chloride
  - 10. natural gas
  - 11. color solution
  - e. time - 3 min.
  - f. portable
2. Color Change (MSA, Unico)
- a. range .001-.1%
  - b. monitoring (intermittant)
  - c. maintenance
    - 1. making test
    - 2. check pump
  - d. interference
    - 1. guesswork
    - 2. NO<sub>2</sub>
  - e. time - 3 min.
  - f. portable
3. Length-of-stain (MSA)
- a. range 10-2,000 ppm
  - b. monitoring (intermittant)
  - c. maintenance
    - 1. making test
    - 2. check pump
  - d. interference
    - 1. color resolution
    - 2. NO
    - 3. NO<sub>2</sub>
  - e. time - 3 min.
  - f. portable
4. "Detector" (Dansk)
- a. range to .01%
  - b. monitoring (continuous)
  - c. maintenance
    - 1. renewing
    - 2. check for overexposure
  - d. interference
    - 1. humidity
    - 2. cigarette smoke
    - 3. color resolution
    - 4. NO
    - 5. NO<sub>2</sub>
  - e. time - variable with concentration, 15 min.-26 min.
  - f. portable

5. Alarm (Unico)
  - a. range to 50 ppm
  - b. monitoring (continuous)
  - c. maintenance-replace sensor when overexposed
  - d. time-variable
  - e. portable, needs power source.

B. Wet

1. Iodine Pentoxide
  - a. range to 1 ppm
  - b. monitoring (continuous)
  - c. maintenance (daily)
    1. replenish chemicals
    2. check recorder
  - d. not portable

II. Thermal

A. Oxidation (Thermonetics)

1. range
  - a. 0-500 ppm
  - b. 0-1,000 ppm
  - c. 0-5,000 ppm
2. monitoring (intermittant)
3. maintenance
  - a. zero recorder
  - b. select range
  - c. replace kehydrator
  - d. replace chemicals
4. time - 25 sec.
5. portable
6. accurate to 50 ppm

B. Oxidation (Devco)

1. range
  - a. 0-100 ppm
  - b. 0-200 ppm
  - c. 0-500 ppm
2. monitoring (continuous)
3. maintenance
  - a. check detection span
  - b. replace particulate filter
  - c. replace catalyst
  - d. zero recorder
4. time - 30 sec.
5. wall mounted
6. sensitive to 2%

C. Oxidation (Mine Safety Appliances)

1. range, 0-500 ppm
2. monitoring (continuous)
3. maintenance
  - a. replace catalyst
  - b. zero recorder
  - c. check battery
4. interference
  - a. high humidity
  - b. cigarette smoke
5. time - 50 sec.
6. portable
7. sensitive to 1% of full scale

III. Infra-red Spectroscopy

A. Non-dispersive

1. Bosch of Germany
  - a. range
    1. 0-5%
    2. 0-2.5%
  - b. monitoring (continuous)
  - c. maintenance
    1. Daily calibration of zero point
    2. change filter
    3. clean water trap
  - d. interferences
    1. CO<sub>2</sub>
    2. H<sub>2</sub>O
  - e. time, 5-10 sec.
2. Mine Safety Appliances
  - a. range
    1. 0-.2%
    2. 0-1%
    3. 0-10%
  - b. monitoring (continuous)
  - c. maintenance
    1. check sensitivity
    2. check zero drift
  - d. interference
    1. CO
    2. H<sub>2</sub>O
  - e. time - 5 sec.
  - f. not portable
  - g. accuracy to 2% of full scale

3. Intertech
    - a. portable model
      1. range
        - a. 0-5%
        - b. 0-10%
      2. monitoring (continuous)
      3. maintenance
        - a. calibrating
        - b. filter check
      4. interferences
        - a. CO<sub>2</sub>
        - b. H<sub>2</sub>O
      5. time - 2 sec.
      6. portable
      7. accurate to 2% of full scale
    - b. fixed model
      1. range
        - a. 0-100 ppm
        - b. 0-50 ppm
        - c. 0-25 ppm
      2. monitoring (continuous)
      3. maintenance
        - a. filter check
        - b. drift checks
        - c. air flow check
        - d. replace calibration gas (when needed)
        - e. humidity control check
      4. interference
        - a. H<sub>2</sub>O
        - b. CO<sub>2</sub>
      5. time - .5 sec.
      6. self-calibrating
  4. Beckman
    - a. range, 0-100%
    - b. monitoring (continuous)
    - c. maintenance
      1. check zero drift
      2. filter checks
    - d. interference
      1. CO<sub>2</sub>
      2. H<sub>2</sub>O
    - e. time - .5 sec.
    - f. fixed
    - g. accurate to 1% of full scale
- B. Dispersive-NDRC
1. range
    - a. 0-.2%
    - b. 0-1%
    - c. 0-3%

2. monitoring (continuous)
3. maintenance
  - a. adjust amplifier gain
  - b. adjust heater current
  - c. adjust bucking potential

#### IV. Gas Chromatographs

- A. range - about .01%
- B. Monitoring (intermittant)
- C. Maintenance
  1. zero checks
- D. Time - 1 min., 1 hr.

#### V. Mercury Vapor

- A. Ranges
  1. 0-5 ppm
  2. 0-25 ppm
  3. 0-50 ppm
- B. Monitoring (continuous)
- C. Maintenance
  1. monthly
    - a. replace inlet dryer
    - b. replace inlet filter
    - c. replace exhaust filter
  2. half yearly
    - a. replace mercury oxide pellet
    - b. clean system
    - c. check calibration
  3. yearly
    - a. replace photocell lamp
    - b. inspect valves for wear
  4. as required - replace indicator lamps
- D. Interference
  1. oxygenated hydrocarbons
  2. olefins
  3. free hydrogens
  4. ozone
- E. Response time - 10 seconds
- F. Fixed or portable applications
- G. Sensitivity to  $\pm 1$  ppm

TABLE 1

Interferences by Oxides of Nitrogen  
in Carbon Monoxide Determination

METERED PPM			PPM CO BY NBS TUBE		
CO	NO <sub>2</sub>	NO	Direct	Preceeded by Ascarite	Preceeded by KMNO <sub>4</sub> and Ascarite
400	0	0	400		
400	7	0	200		
400	50	0	150		
400	95	0	100	400	
20	0	0	20		
20	3	0	10		
100	0	0	100		
100	0	7	100	100	
100	0	15	50	50	100
100	0	65	10	10	25
20	0	0	20		20
20	0	15	5		10

TABLE 2

## Conversion Tables for Gas and Vapor Concentrations\*

*Milligrams per cubic meter to parts per million and vice versa*

Molec- ular Weight	Col. 1 mg./m <sup>3</sup> ppm.	Col. 2 1 ppm. mg./m <sup>3</sup>	Molec- ular Weight	Col. 1 mg./m <sup>3</sup> ppm.	Col. 2 1 ppm. mg./m <sup>3</sup>	Molec- ular Weight	Col. 1 mg./m <sup>3</sup> ppm.	Col. 2 1 ppm. mg./m <sup>3</sup>
1	24.450	.0409	45	.543	1.840	89	.275	3.64
2	12.230	.0818	46	.532	1.881	90	.272	3.68
3	8.150	.1227	47	.520	1.922	91	.269	3.72
4	6.113	.1636	48	.509	1.963	92	.266	3.76
5	4.890	.2045	49	.499	2.004	93	.263	3.80
6	4.075	.2454	50	.489	2.045	94	.260	3.84
7	3.493	.2863	51	.479	2.086	95	.257	3.89
8	3.056	.327	52	.470	2.127	96	.255	3.93
9	2.717	.368	53	.461	2.168	97	.252	3.97
10	2.445	.409	54	.453	2.209	98	.2495	4.01
11	2.223	.450	55	.445	2.250	99	.2470	4.05
12	2.038	.491	56	.437	2.290	100	.2445	4.09
13	1.881	.532	57	.429	2.331	101	.2421	4.13
14	1.746	.573	58	.422	2.372	102	.2397	4.17
15	1.630	.614	59	.414	2.413	103	.2374	4.21
16	1.528	.654	60	.408	2.554	104	.2351	4.25
17	1.438	.695	61	.401	2.495	105	.2329	4.29
18	1.358	.736	62	.394	2.54	106	.2307	4.34
19	1.287	.777	63	.388	2.58	107	.2285	4.38
20	1.223	.818	64	.382	2.62	108	.2264	4.42
21	1.164	.859	65	.376	2.66	109	.2243	4.46
22	1.111	.900	66	.370	2.70	110	.2223	4.50
23	1.063	.941	67	.365	2.74	111	.2203	4.54
24	1.019	.982	68	.360	2.78	112	.2183	4.58
25	.978	1.022	69	.354	2.82	113	.2164	4.62
26	.940	1.063	70	.349	2.86	114	.2145	4.66
27	.906	1.104	71	.344	2.90	115	.2126	4.70
28	.873	1.145	72	.340	2.94	116	.2108	4.74
29	.843	1.186	73	.335	2.99	117	.2090	4.79
30	.815	1.227	74	.330	3.03	118	.2072	4.83
31	.789	1.268	75	.326	3.07	119	.2055	4.87
32	.764	1.309	76	.322	3.11	120	.2038	4.91
33	.741	1.350	77	.318	3.15	121	.2021	4.95
34	.719	1.391	78	.313	3.19	122	.2004	4.99
35	.699	1.432	79	.309	3.23	123	.1988	5.03
36	.679	1.472	80	.306	3.27	124	.1972	5.07
37	.661	1.513	81	.302	3.31	125	.1956	5.11
38	.643	1.554	82	.298	3.35	126	.1940	5.15
39	.627	1.595	83	.295	3.39	127	.1925	5.19
40	.611	1.636	84	.291	3.44	128	.1910	5.24
41	.596	1.677	85	.288	3.48	129	.1895	5.28
42	.582	1.718	86	.284	3.52	130	.1881	5.32
43	.569	1.759	87	.281	3.56	131	.1866	5.36
44	.556	1.800	88	.278	3.60	132	.1852	5.40

\* Courtesy of the GELMAN INSTRUMENT COMPANY, P. O. Box 1448, Ann Arbor, Michigan 48106.

TABLE 2 (Continued)

Molec- ular Weight	Col. 1 mg./m <sup>3</sup> ppm.	Col. 2 1 ppm. mg./m <sup>3</sup>	Molec- ular Weight	Col. 1 mg./m <sup>3</sup> ppm.	Col. 2 1 ppm. mg./m <sup>3</sup>	Molec- ular Weight	Col. 1 mg./m <sup>3</sup> ppm.	Col. 2 1 ppm. mg./m <sup>3</sup>
133	.1838	5.44	189	.1294	7.73	245	.0998	10.02
134	.1825	5.48	190	.1287	7.77	246	.0994	10.06
135	.1811	5.52	191	.1280	7.81	247	.0990	10.10
136	.1798	5.56	192	.1273	7.85	248	.0986	10.14
137	.1785	5.60	193	.1267	7.89	249	.0982	10.18
138	.1772	5.64	194	.1260	7.93	250	.0978	10.22
139	.1759	5.69	195	.1254	7.98	251	.0974	10.27
140	.1746	5.73	196	.1247	8.02	252	.0970	10.31
141	.1734	5.77	197	.1241	8.06	253	.0966	10.35
142	.1722	5.81	198	.1235	8.10	254	.0963	10.39
143	.1710	5.85	199	.1229	8.14	255	.0959	10.43
144	.1698	5.89	200	.1223	8.18	256	.0955	10.47
145	.1686	5.93	201	.1216	8.22	257	.0951	10.51
146	.1675	5.97	202	.1210	8.26	258	.0948	10.55
147	.1663	6.01	203	.1204	8.30	259	.0944	10.59
148	.1652	6.05	204	.1199	8.34	260	.0940	10.63
149	.1641	6.09	205	.1193	8.38	261	.0937	10.67
150	.1630	6.13	206	.1187	8.43	262	.0933	10.72
151	.1619	6.18	207	.1181	8.47	263	.0930	10.76
152	.1609	6.22	208	.1175	8.51	264	.0926	10.80
153	.1598	6.26	209	.1170	8.55	265	.0923	10.84
154	.1588	6.30	210	.1164	8.59	266	.0919	10.88
155	.1577	6.34	211	.1159	8.63	267	.0916	10.92
156	.1567	6.38	212	.1153	8.67	268	.0912	10.96
157	.1557	6.42	213	.1148	8.71	269	.0909	11.00
158	.1547	6.46	214	.1143	8.75	270	.0906	11.04
159	.1537	6.50	215	.1137	8.79	271	.0902	11.08
160	.1528	6.54	216	.1132	8.83	272	.0899	11.12
161	.1519	6.58	217	.1127	8.88	273	.0896	11.17
162	.1509	6.63	218	.1122	8.92	274	.0892	11.21
163	.1500	6.67	219	.1116	8.96	275	.0889	11.25
164	.1491	6.71	220	.1111	9.00	276	.0886	11.29
165	.1482	6.75	221	.1106	9.04	277	.0883	11.33
166	.1473	6.79	222	.1101	9.08	278	.0879	11.37
167	.1464	6.83	223	.1096	9.12	279	.0876	11.41
168	.1455	6.87	224	.1092	9.16	280	.0873	11.45
169	.1447	6.91	225	.1087	9.20	281	.0870	11.49
170	.1438	6.95	226	.1082	9.24	282	.0867	11.53
171	.1430	6.99	227	.1077	9.28	283	.0864	11.57
172	.1422	7.03	228	.1072	9.33	284	.0861	11.62
173	.1413	7.08	229	.1068	9.37	285	.0858	11.66
174	.1405	7.12	230	.1063	9.41	286	.0855	11.70
175	.1397	7.16	231	.1058	9.45	287	.0852	11.74
176	.1389	7.20	232	.1054	9.49	288	.0849	11.78
177	.1381	7.24	233	.1049	9.53	289	.0846	11.82
178	.1374	7.28	234	.1045	9.57	290	.0843	11.86
179	.1366	7.32	235	.1040	9.61	291	.0840	11.90
180	.1358	7.36	236	.1036	9.65	292	.0837	11.94
181	.1351	7.40	237	.1032	9.69	293	.0834	11.98
182	.1343	7.44	238	.1027	9.73	294	.0832	12.02
183	.1336	7.48	239	.1023	9.78	295	.0829	12.07
184	.1329	7.53	240	.1019	9.82	296	.0826	12.11
185	.1322	7.57	241	.1015	9.86	297	.0823	12.15
186	.1315	7.61	242	.1010	9.90	298	.0820	12.19
187	.1307	7.65	243	.1006	9.94	299	.0818	12.23
188	.1301	7.69	244	.1002	9.98	300	.0815	12.27

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52

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