LEAK DETECTION AND ELIMINATION PROGRAM

ABERDEEN CHEMICAL PLANT

JUNE 30, 1987

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A. GENERAL

The emission standard for vinyl chloride requires the plant to have a formal leak detection program.

The Federal Register describes specific criteria which must be met within the program. This document describes the leak detection program. Each of the specific requirements will be met. Namely, this program describes:

The continuous VCM detection system which is used by the plant.

The portable hydrocarbon detectors which are used by the plant.

The calibration and maintenance procedures for the above equipment.

The Routine Leak Patrols and procedure when a leak is found by the portable hydrocarbon detector.

The location of the continuous monitoring points which are used for leak detection.

The criteria which will be used to identify the presence of an action level and a leak.

The action plan which will be used to eliminate a leak after it has been detected.

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B. VINYL CHLORIDE CONTINUOUS MONITORING SYSTEM

Introduction

The concentration of vinyl chloride in the atmosphere is continuously monitored by four flame ionization chromatographs, each of which is operated continuously. Each chromatograph is a Honeywell Model 1000 Process Gas Chromatograph manufactured by:

Honeywell Systems, Inc.
6625 McGrew Street
Houston, Texas

Each chromatograph sequentially measures, on a continuous basis, the vinyl chloride content in air samples taken from ten different locations. A total of forty (40) locations are monitored throughout the plant continuously and the concentrations at each point are recorded.

Description

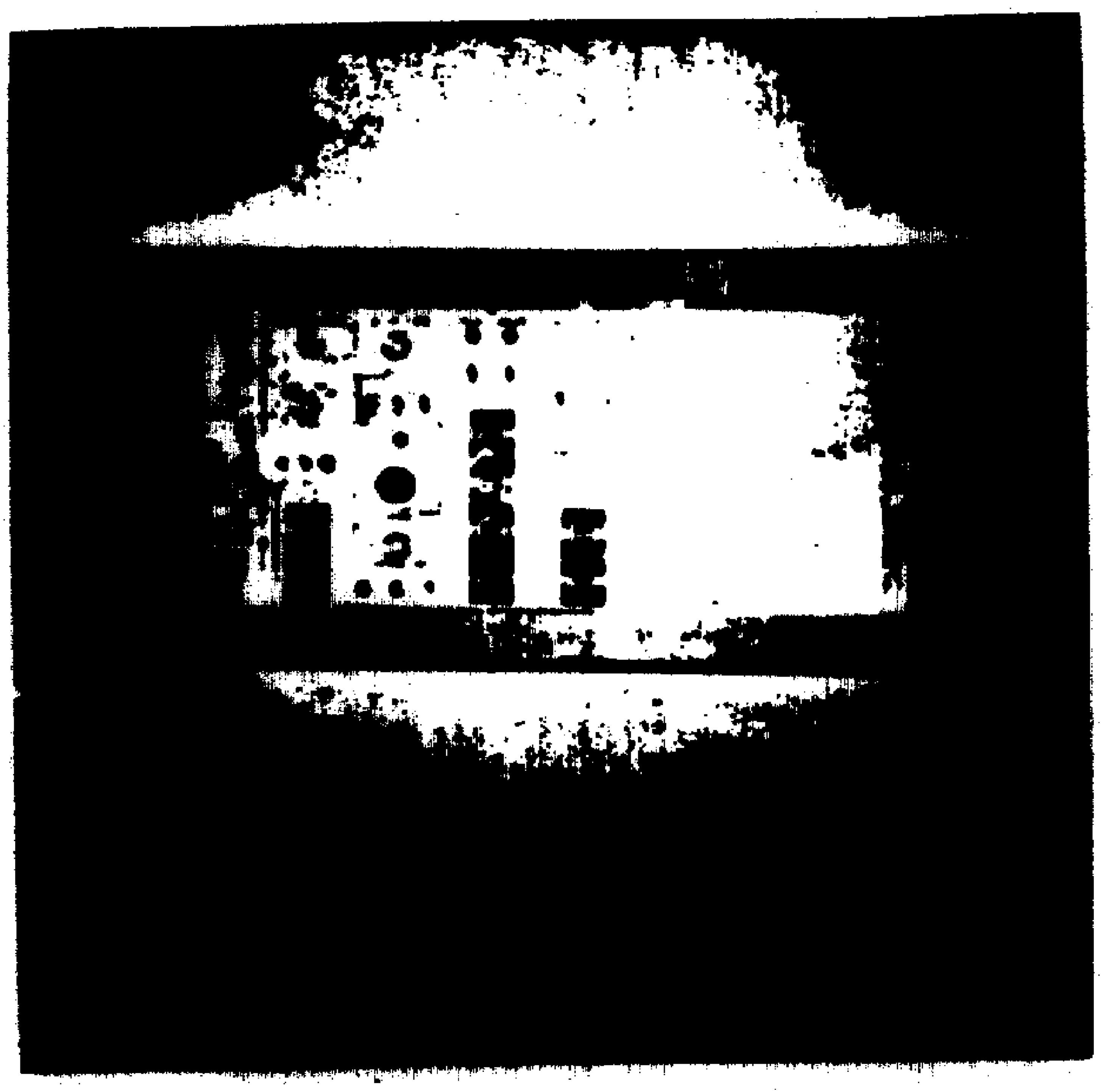
Analytical Technique

The Flame Ionization Detector used in the Honeywell 1000 Process Gas Chromatographs has a lower detection limit of 0.1 part per million.

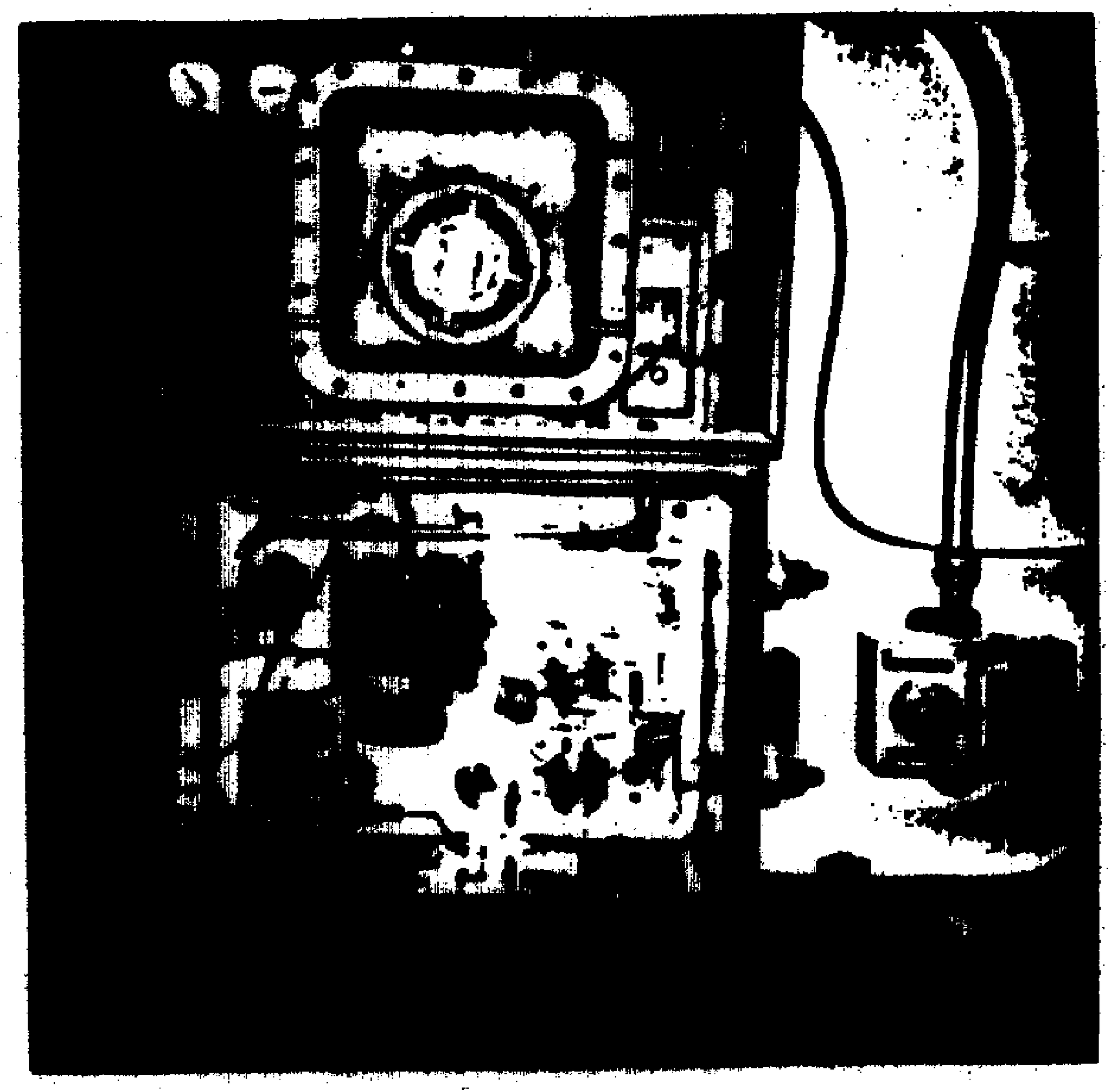
The special-purpose elements of the FID chromatograph are a flame cell, an FID Electrometer Assembly, a Temperature Control/Inverter Assembly, and a plug-in FID Amplifier Module which mounts in the Control Section.

The flame cell consists of an ignitor wire, a hydrogen-fed burner, and an electron collector. Within the cell, hydrogen combustion occurs in an electrical field created by the voltage from the ionization inverter. Because of the carbon-free property of hydrogen, ionization occurs only when a carbon-bearing sample is injected into the flame. Ionization causes current to flow from the collector in direct proportion to the amount of the hydrocarbon elements present in the sample. The output current from the flame cell is routed through the Electrometer (Preamp) in the Analyzer, and is applied to the input of the FID Amplifier in the Control Section. The gain is made available for external recording.

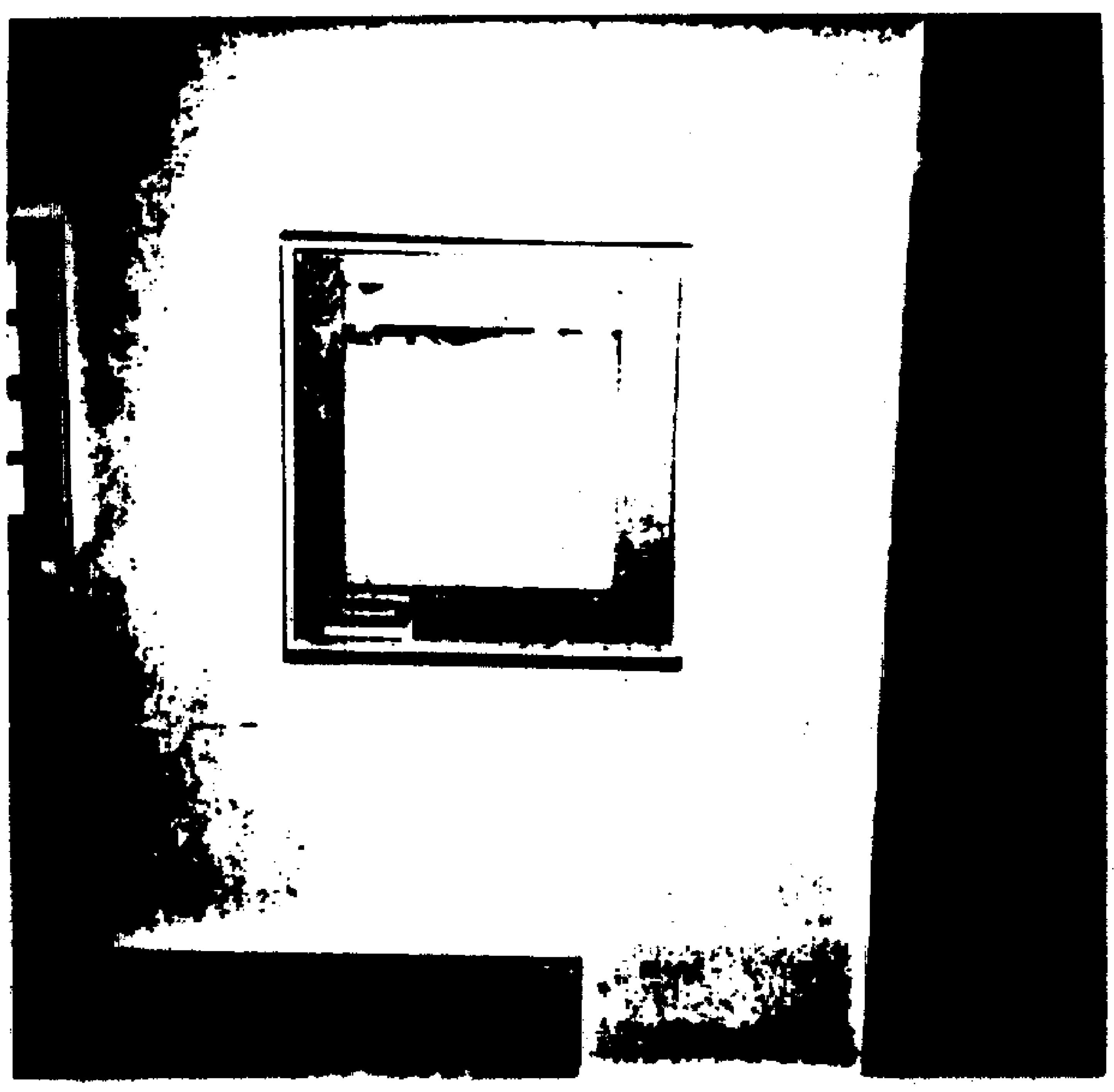
The FID Electrometer Assembly is physically divided into two major subassemblies: the Power Supply-Electrometer P.C. Card Assembly, and the Electrometer P.C. Card Assembly. The electrometer power supply accepts $\pm$ 20 volt inputs from the Control Section power supply, and produces regulated plus and minus 15 volt outputs for operation of the electrometer circuits and the inverter located on the Temperature Control/Inverter P.C. Card Assembly. The inverter output is a -100 volt ionization potential which is applied to the base (burner) of the flame cell.



SEQUENCE
AND ANALYZER CONTROL
MODULE



ANALYZER SECTION



RECORDER

SAMPLE POINT

Depressing the IGNITE pushbutton switch applies 115 vac to the primary of a transformer, which in turn produces approximately 2.2 vac across the ignitor coil inside the flame cell. Depressing the IGNITE pushbutton also produces a ground connection which enables the solenoid driver circuit to open the hydrogen shut-off valve. With 2.2 vac applied to the ignitor coil, and the hydrogen shut-off valve open, the flame will ignite within five to 10 seconds.

When the flame ignites, current flow from the flame cell collector is amplified by the electrometer circuit, the output of which is routed to both the Control Section FID Amplifier and to a level detect circuit on the Power Supply-Electrometer P.C. Card Assembly. When the level detect circuit senses an electrometer output of sufficient magnitude to indicate that the flame is lit, the circuit produces a logic level output which lights the FID Amplifier "FLAME ON" indicator. In addition, the circuit de-energizes a relay which extinguishes the analyzer "FLAME OUT" indicator, and provides a ground to the solenoid driver circuit so that the hydrogen shut-off valve will be maintained in the open position when the IGNITE pushbutton is released.

During sustained operation, the level detect circuit continuously monitors the output of the electrometer circuit, and any momentary output drop below a selectable threshold level will cause the FID Amplifier FLAME ON indicator to momentarily extinguish. If the reduced signal level continues beyond a selectable time delay, the level detect relay will energize, thus closing the hydrogen shut-off valve and illuminating the analyzer FLAME OUT indicator. If this condition occurs, the IGNITE pushbutton must again be pressed and held to re-light the flame.

Electrometer P.C. Card Assembly

The functional center of the electrometer circuit is a 3430J high gain integrated circuit amplifier. The flame cell collector current is brought into the circuit via resistor R1 and the divider network at the amplifier input. HIGH/LOW range selection is accomplished by a RANGE control input from the FID Amplifier. When LO range is selected, relay K1 is energized and R7 is placed in parallel with R8 to reduce the over-all sensitivity of the circuit.

The signal OUTPUT at pin 21 is routed to the FID Amplifier input in the Control Section, and to the level detect circuit on the Power Supply-Electrometer P.C. Card Assembly.

Power Supply - Electrometer P.C. Card Assembly

The Power Supply - Electrometer P.C. Card Assembly contains both the electrometer power supply and the level detect circuitry associated with monitoring the status of the hydrogen flame. The power supply (IC1, Q1, Q2, etc.) accepts plus 20 vdc and minus 20 vdc from the control section, and produces regulated plus and minus 15 vdc for the electrometer circuits and for the ionization inverter on the Temperature Control/Inverter P.C. Card Assembly.

The level detect circuit consists of the operational amplifiers in IC-2; the -LEVEL DET ADJUST control (R7); the associated decoding logic in IC's 3, 4, 5,; and the level detect relay, K1. The electrometer output is brought into the circuit at pin 21, and is routed through operational amplifiers IC 2-1 and IC 2-7 to the input of IC 2-10.

The level at IC 2-9 is set by R7, so that if the electrometer output drops below a selected threshold, the flame will be considered extinguished and a positive transition will occur out of IC 2-8. In practice, the threshold level is set just below the quiescent electrometer output when only air and hydrogen are passing through the detector.

If the output of IC 2-8 goes positive, signifying an inadequate signal level, the logic-0 at IC 4-6 illuminates DS2 on the electrometer front panel, and the logic-1 at IC 4-8 extinguishes the FID Amplifier FLAME ON indicator. In addition, any positive level out of 1C 2-8 will also trigger adjustable one-shot IC 3, which produces a selectable time delay before energizing relay K1 and illuminating DS1 on the electrometer front panel. This delay, which is adjustable from 2 to 20 seconds, and optionally from 2 to 200 seconds, ensures that the relay will not be energized by transient conditions in the flame cell or electrometer.

If the IC 2-8 output is still positive when the selected delay is completed, the resultant logic-1 levels at IC 5-1 and IC 5-2 produce a logic-0 at IC 5-6 which illuminates DS1 and energizes K1. In the energized condition, the closed contacts of K1 illuminate the analyzer "FLAME OUT" indicator and the open contacts remove the ground to the solenoid driver circuit, thus closing the hydrogen shut-off valve.

Temperature Control/Inverter Assembly

The temperature control circuit in the FID chromatograph is identical to that of the TC system.

The inverter circuit is of conventional design, and operates from the plus 15 vdc regulated input provided by the electrometer power supply. Transistors Q3 and Q4 and the associated elements form a free-running oscillator, the output of which is coupled through transformer T1 to produce plus and minus 100 vdc at the output. The -100 vdc is the ionization potential which is applied to the base of the flame cell.

Amplifier Module

The FID Amplifier is essentially the same as the TC Amplifier, except for the addition of a HI/LO gain range switch concentrically mounted around the MANUAL RANGE switch, and the addition of a FLAME ON indicator to the front panel. The HI/LO range switch controls relay K1 in the FID electrometer, to change the divider resistance values at the electrometer input, thus changing the electrometer sensitivity.

The FLAME ON indicator is controlled by a logic level input from the Power Supply - Electrometer P.C. Card Assembly in the electrometer. No time delay is provided between the level detect circuitry and the FLAME ON indicator, thus ensuring that any transient "flame off" conditions will be seen on the indicator.

Sample Analysis and Specific Chromatograph Parameters

Sample analysis is accomplished through a dual column with a backflush attachment. This column configuration insures that the analysis is specific for vinyl chloride. Separation and analysis is accomplished in the following manner:

The sample is injected with the dual column valve energized (light on), and with the backflush valve in the foreflush position. This allows the sample to be swept from the sample valve into column number one. Column number one separates inerts or other light components from the heavier components, but not from each other. The combined light components are allowed to pass into the second column where they are separated.

At a selected time during the analysis, column number two is switched out of the stream and the heavy components from column number one are routed to the detector via a restrictor. The light components, not yet eluted from column number two, remain in that column until the dual column valve is switched back to the dual column position. Then they are eluted through the detector. The resultant reverse flow through column number one causes those components still in the column to be eluted as a group.

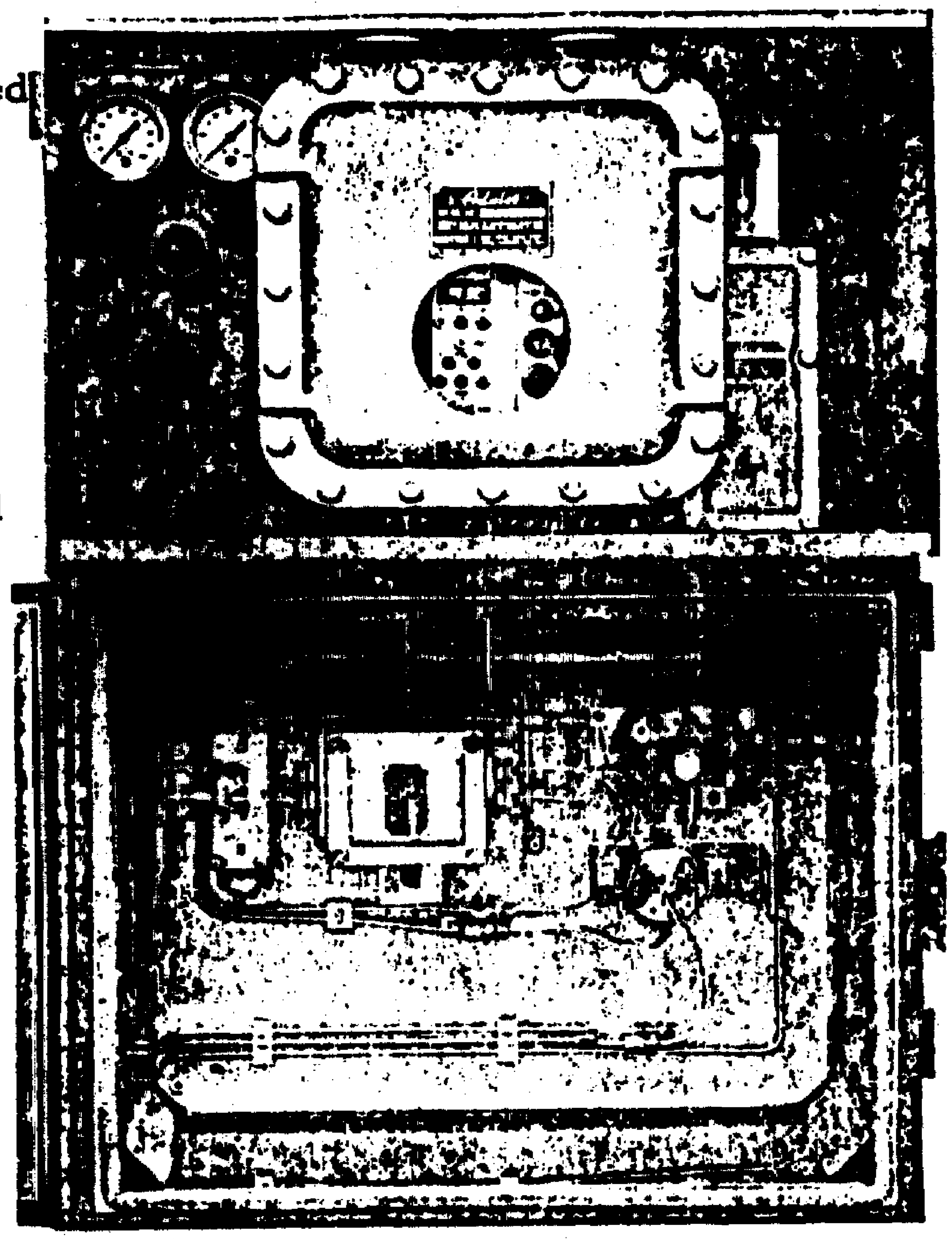
The specific parameters for the Honeywell chromatographic column are as follows:

analysis cycle time: 70 sec.
carrier gas: nitrogen
carrier pressure: 50 psig
column vent flow: 35 cc/min.
backflush vent flow: 45 cc/min.
heater air: 50 psig
oven temperature: 80°C
sample loop length: 48 in.
sample loop I.D.: 0.043 in.
column: 1/16"
column material: SS
packing: 15% bis(2-ethoxyethyl) adipate on chromosorb P

Parameters for the air and hydrogen are as follows:

hydrogen flow equals 40 cc/min. @ 50 psig
air flow equals 350 cc/min. @ 220 psig

The Analyzer Section of the Model 1000 has been designed to permit the high-speed analyses required by the technological advances of the past few years.



The basis of this high-speed analytical system is the Micro Packed Column-High-Speed Micro Detector combination.

The resolution of the Micro Packed Column is enhanced by the High-Speed Micro Detector designed and manufactured by Honeywell with the following features: the cell volume is approximately 0.05 microliter; a semi-diffusion type of detector cell is utilized rendering it relatively insensitive to flow rate; the detector response to the presence of a component is suitable for analysis times of less than 1 second.

The Micro Packed Column, Micro Detector and associated sample and column-switching valves have been packaged in an analyzer designed to yield the high thermal stability and accessibility.

The temperature of the analyzer oven is controlled by an all solid state, proportional temperature controller. Several modifications to the widely used heated air type of temperature control system have resulted in an analyzer design that permits the full sensitivity of the Micro Detector to be utilized.

The use of each control of the analyzer is given in Table 1.

TABLE 1

ANALYZER SECTION, OPERATING CONTROLS AND INDICATORS

Control or Device	Purpose or Use
AIR Control	Controls air pressure to the valve actuating solenoid(s) and to the low mass heater.
AIR Gauge	Indicates air pressure (0-100 lbs.) set by the AIR control.
CARRIER Control	Controls carrier pressure to the column(s) (ultimately controlling the flow) and to the needle valves for reference, etc.
CARRIER Gauge	Indicates the carrier pressure (0-160 lbs.) set by the CARRIER control.
REF and AUX 1,2,3 Needle Valves	Used to precisely adjust carrier flow rates through the reference side of the detector and through three auxiliary valves.
Heater Air Shut-off Valve	Allows the heater air to be shut off, while air pressure is maintained on the air-actuated valves.
Remote Valve Switches and Indicators	Used to remotely actuate the Analyzer valves. Light emitting diodes are illuminated to indicate the corresponding air-control solenoid is energized.
Preamplifier Meter and BAL ADJ Control	Used to balances the preamplifier output.
Preamplifier Test Jacks	Meter/scope test points for monitoring the indicated preamplifier parameters.
Temperature Set Point Control	Used to set the oven temperature. Clockwise rotation increases the temperature, and counterclockwise decreases the temperature.
Temperature Control Indicator	Indicates the status of the oven temperatur controller. Due to the proportional temperature control circuitry, and the overtemp switch on the heater barrel, the light will alternately glow and shut off, until the oven temperature begins to approach the ambient operating temperature. When the operating temperature has been reached, the indicator will remain on, but will be very dimly lighted.

TABLE 1 (Cont.)

ANALYZER SECTION, OPERATING CONTROLS AND INDICATORS

Control or Device	Purpose or Use
Heater Barrel Over-Temp Control	Located behind the brass plug in the front cover of the heater housing, this control permits adjustment of the temperature cut-off point of the overtemp switch. This temperature can be monitored by connecting a pyrometer to the I/C thermocouple wire coiled under the explosion-proof housing. This temperature is normally factory adjusted for about 300°C.

Sample Injection Procedure

In this multi-stream application, the sample system permits continuous purge from the stream switching system, to and through the analyzer. This insures that the sample being analyzed is from the proper stream.

Sample input is measured by a "gas" valve. The "gas" valve is an external-volume sample valve, in which the sample volume is a length of tubing external to the valve. This valve is used to inject gas samples, and is also the valve used for column switching.

The column configuration by which sample injection is accomplished is the dual column backflush configuration. Normally, a sample is injected with the dual column valve energized and with the backflush valve in the foreflush position. This allows the sample to be swept from the sample valve into column number one. Column number one separates inerts or other light components from the heavier components, but not from each other. The combined light components are allowed to pass into the second column where they are separated.

At a selected time during the analysis, column number two is switched out of the stream, and the heavy components from column number one are routed to the detector via the restrictor. The light components, not yet eluted from column number two, remain in that column until the dual column valve is switched back to the dual column position. The resultant reverse flow through column number one causes those components still in the column to be eluted as a group, and recorded as one peak. Note that the combined components bypass column number two via the column bypass restrictor.

The sample volume is 1346 µl. The injection valve specifications are as follows:

Sample valve:
- Material: SS
- Diaphgram: High-Temperature
- Part Number: 30740492-002

Backflush:
- Material: SS
- Diaphragm: High-Temperature
- Part Number: 30740492-002

Sample Handling Equipment

There are 40 sampling points at the Aberdeen Plant. At each sampling point, sample is drawn into a 1/8" I.D. nylon sampling line through a M.S.A. high efficiency small volume paper filter. The model number of these filters is DZ-78006. These end of line filters are manufactured by:

Mine Safety Appliance Company
408 Penn Center Blvd.
Pittsburgh, PA

Samples are drawn through each of the sampling locations served by a single Honeywell unit, by a single vacuum pump. The vacuum pump is model number 289-EXP, with trademark "Dia-Vac", manufactured by:

Combination Control, Inc.
Kulpsville, PA 19443

Sample is drawn into the sampling line at a maximum rate of 1.5 cfm at 0 in. Hg vacuum. Sample inflow is continuous.

The Control Section of the Model 1000 consists of solid state, plug-in modules. Each module is self-contained to permit easy replacement for troubleshooting or maintenance. The modules require front access only for replacement. The contacts are gold-plated over nickel for resistance to corrosive atmospheres.

The timing system is a 240 KHz clock which generates a digital pulse each second.

The anlaysis is programmed as follows:

A digital pulse is chosen just prior to setting the exact time the occurrence of the function is desired (Coarse). An adjustable delay, triggered by the digital pulse, is then set to provide the exact (Fine) time of the function. In the case of setting a component time-span (gate), the digital pulse triggers an adjustable time-window. Gate duration adjustments are direct-setting.

Auxiliary test equipment is not required to make any of the adjustments of the Model 1000 Control Section. Test points, with front panel access, are provided on each module for maintenance trouble-shooting.

The basic programmer (Control Section) is composed of the following sub-systems:

The MONITOR MODULE contains a multiple point selector switch and readout meter to permit checking auto zero range, power supply voltages, detector preamp output, signal amplifier output and digital clock status. The memory output can also be checked with this switch, if this option is included in the basic control section. The Power switch is located on this module, as well as a Status switch (Normal/Bypass) and a Standard Sample switch for remote introduction if a calibration standard is desired. A recorder jack is included on the front panel to permit the use of a service recorder, if a dedicated recorder is not required for bargraph readout. An auto zero function is also included in this module.

THE SEQUENCER MODULE is a solid state, digital timing system with direct setting time adjustments for the sequenced funtions. The adjustments for the sample valve "Inject Time" are located in this module. The basic sequencer is a 0-100 second clock with a digital pulse generated each second.

THE AMPLIFIER MODULE contains an auto zero status switch, manual range (Spectrum) switch, amplifier zero potentiometer, and a built-in calibration. The calibrator generates synthetic signals which may be used to set, or check, the full-scale range of the measured components. This module gives the basic 0-10 volt output signal.

THE VALVE MODULE is required for multi-column applications. Direct-setting switches are adjusted to provide the exact time for the signal required for the valve-switch to occur. An additional auto-zero circuit and its timing adjustment is provided in this module.

A COMPONENT MODULE is required for each component to be measured. The basic control section can be supplied with one to six component modules. Each module contains the necessary adjustments for setting the full-scale range of the measured component and for setting the time-span (gate). An auto zero is an integral part of the module.

The standard Control Section provides bargraph output signals for each measured component. A trend output of peak height or peak area (integration) for each component is also available. The necessary interface requirements for computer-input of data can be provided. Current or voltage output is available as a standard feature.

The signal from the detector bridge is amplified to a level of approximately 0.1 volt before leaving the analyzer section. Thus no low level signals are switched within the Model 1000 system. Since the electronic auto zero circuit performs the zeroing function in less than fifty (50) milliseconds, it is normally actuated by each component "on gate".

The specific functions of each control option are given in Tables 2 through 7.

TABLE 2

MONITOR MODULE, OPERATING CONTROLS AND INDICATORS

Control or Indicator	Purpose or Use
ON/OFF Switch	Controls AC input power to the Control Section.
PWR (Power) Indicator	Indicates the power on/off status of the Control Section.
DET/OFF Switch	Controls DC power to the bridge detector circuit in the Analyzer.
DET (Detector) Indicator	Indicates the power on/off status of the bridge detector.
STD SAMP/OFF Switch	Used to actuate a solenoid in the sample system (if provided) for automatic standard sample introduction. In the STD SAMP positi a contact closure is provided at the Control Section rear panel.
STD SAMP Indicator	Lamp is illuminated when sample is flowing, and is off for normal operation.
STATUS NORM/BYPASS Switch	Provides a contact closure which can be used as a maintenance "out of service" switch, etc. Terminal connections are provided on the Control Section rear panel for connection to remote indicators, alarms, or a computer.
STATUS Indicator	Lamp is illuminated to indicate "bypass", and is off for normal operation.
Meter Display	Provides a visual indication of the Control Section operating conditions, as selected by the Meter Function Switch.
Meter Function Selector Switch	Selects the Control Section parameters to be presented on the Meter Display.
+20 and -20 Positions	Display the respective output levels from tl Control Section DC power supply. Normal indication is approximately 50% of full-scale deflection, in the respective polarit direction.
SIG IN Position	Displays the signal amplifier input level received from the preamplifier in the Analyzer. ($\pm$0.1 volt range).

TABLE 2 (Cont.)

Control or Indicator	Purpose or Use
SIG OUT Position	Displays the output level of the signal amplifier. ($\pm$10 volt range).
AUTO ZERO Position	Displays the voltage required to bring the "baseline" back to zero. ($\pm$5 volt range).
CLOCK Position	Permits confirmation that the Control Sectic internal clock is functioning. Meter display will indicate 1/2-scale or better, and will drop to zero one second out of every 10 seconds.
C1 thru C6 Positions	Display the peak height voltages stored in the memory outputs for components 1 through 6. Can also be used for a rough setting of zero and span calibration of each memory.
RECORDER Connector	Provides AC power and chart advance levels to drive a portable "service" recorder for temporary spectra or gate readout. Back panel terminals are also available for permanent connections.
AUTO ZERO START Switches	A non-dedicated auto zero function which can be set to auto zero at any point during the analysis by dialing in the time (in seconds) on the thumbwheel switches. The fine adjustment allows delay of the start of Auto Zero from 0 to 2 seconds.

TABLE 3

SEQUENCER MODULE, OPERATING CONTROLS AND INDICATORS

Control or Indicator	Purpose or Use
SAMPLE VALVE Indicator	Lamp is illuminated when the valve is in the sample inject position.
MODE Selector Switch	Controls the operation of the Sequencer, and the readout to the recorder.
AUTO Position	Analysis events (sample inject, auto zero, component gating, etc.) occur automatically as programmed by Control Section front pane switches. The recorder is driven in the bargraph mode, and the amplifier output is enabled only during the selected "component gate" times.
GATE Position	Analysis events (sample inject, auto zero, component gating, etc.) occur automatically as programmed by Control Section front pane switches. The recorder chart is continuous driven, and the amplifier output is enabled only during the selected "component gate" times. This allows the programming gates to be visually checked.
SPEC (Spectrum) Position	Valve actuations occur automatically, as programmed by Control Section front panel switches. The recorder chart is driven continuously, and the amplifier output is continuously enabled. COMPONENT lights are gated to provide a visual indication of gate timing. NOTE The Amplifier module AUTO ZERO switch shou be in the OFF position. The AUTO/MAN swit must be set to MAN to select the desired signal range.
MAN (Manual) Position	All functions must be operated manually. (Valve switches left in AUTO will cause the corresponding valves to go to the "on" condition). The recorder chart is continuously driven, and the amplifier output is continuously enabled. NOTE The Amplifier module AUTO/MAN switch must b set to MAN to select the desired signal ran

TABLE 3 (Cont.)

Control or Indicator	Purpose or Use
Sample VALVE DURATION Thumbwheel Switches	Permits adjustment of the duration of the sample inject period. At the end of the set duration time (in seconds), the sample valve goes to the off (sampl purge) position.

TABLE 3 (Cont.)

Control or Indicator	Purpose or Use
CYCLE Selector Switch	Permits selection of analysis time (length).
Time (lower) Position	Analysis time (in seconds) is determined by the setting of the TIME thumbwheel switch (0-99 seconds).
"100" Position	Analysis cycle time is a fixed 100 seconds, regardless of the TIME switch setting. The analysis will run in the time programmed, and will wait for the remainder of the 100 seconds before starting another analysis.
"600" Position	Analysis cycle time is a fixed 600 seconds, regardless of the TIME switch setting. The analysis will run in the time programmed, and will wait for the remainder of the 600 seconds before starting another analysis.
Sample Valve AUTO/MAN Switch	Permits selection of automatic or manual sample valve control.
AUTO Position	Sample valve is automatically controlled by the Sequencer module with "sampling length" selected by the VALVE DURATION thumbwheel switches.
Middle (off) Position	Sample valve is in the "bypass" position, and the sample is flowing through the sampl volume ports.
MAN Position	Sample valve is in the "on" condition, and sample is being injected into the column.
SEQ. (sequence) RESET Pushbutton	Allows the Sequencer to be manually reset the start of an analysis. NOTE The SEQ. RESET pushbutton does not reset a auxiliary valves. Therefore, before pushi the SEQ. RESET button, wait for the VALVE lights to return to their initial "program start" conditions, or switch the sample val off until a complete cycle runs on the sequencer. If any VALVE light is on, then one complete cycle must be run before a satisfactory readout can be obtained. If the CYCLE switch is in the "600" positio SEQ. RESET advances the timer to 100 second and an additional 500 seconds is required b fore the timer is reset.

TABLE 4

AMPLIFIER MODULE, OPERATING CONTROLS AND INDICATORS

Control or Indicator	Purpose or Use
RANGE CALIBRATE Control	Permits adjustment of an internally-generate calibration voltage so that the full-scale range and peak memory output level for each measured component can be set.
AUTO/CAL Switch	In the AUTO position, which is the normal operational position of the switch, the inpu to the amplifier is the bridge preamp output from the analyzer. In the CAL position, the input to the amplifier is an internally-generated calibration voltage, the level of which is controlled by the RANGE CALIBRATE Potentiometer.
AUTO/ZERO/OFF Switch	Controls the operational mode of the Auto Zero circuitry, which automatically compensates for any drift in the bridge preamp "zero" (baseline) output level. Auto Zero is normally actuated for 50 milliseconds by each component "on-gate", and at other time as determined by the setting of the non-dedicated Auto Zero function(s). A moveabl jumper on each Component Module allows Auto Zero to be inhibited at the corresponding component gate opening, if so desired.
AUTO ZERO Position	Auto Zero level is automatically updated at each Auto Zero time to compensate for pream baseline drift.
Middle Position	Allows the last Auto Zero signal level to held in the Auto Zero circuitry. This lea the baseline at recorder zero when switchi to Manual or Spectrum operations.
Off Position	The Auto Zero function is inhibited with Auto Zero "off". The AMPLIFIER ZERO contro must be used to zero (balance) the output to the recorder.
AUTO/MAN Switch	In the AUTO position, the amplifier gain changes during each component gate, as determined by the setting of each component RANGE potentiometer. In the MAN position, the amplifier gain is controlled exclusivel by the setting of the MANUAL RANGE switch.

TABLE 4 (Cont.)

Control or Indicator	Purpose or Use
MANUAL RANGE Selector Switch	With the AUTO/MAN switch in the MAN positior this switch permits manual selection of the signal output range by attenuating or amplifying the bridge preamp output as follows:
	Position / Factor: 1 — 10 2 — 5 5 — 2 10 — 1 20 — X2 100 — X10 200 — X20 500 — X50 1000 — X100
AMPLIFIER ZERO Control	Permits manual adjustments of amplifier "zero" output, to balance the recorder.
GND. IN and OUT Test Jacks	Meter/scope test points for monitoring the amplifier input and output levels.

TABLE 5

COMPONENT MODULE, OPERATING CONTROLS AND INDICATORS

Control or Indicator	Purpose or Use
COMPONENT Indicator	Lighted during the time the associated component gate is open.
RANGE Control	Permits full-scale range (gain) adjustment for the associated component. The resultant gain setting is in effect onl when the associated component gate is open, and then only if the Amplifier Module AUTO/MAN switch is in the AUTO position.
MEMORY ZERO AND SPAN Controls	Used in conjunction with the Amplifier Module calibration voltage to calibrate the memory output signal (if used).
AUTO/OFF/CAL Switch	Controls the operational status of the respective Component Module.
AUTO Position	This position enables the normal operational mode of the module, in which tl gate circuitry, the bargraph output, ai the memory output are operational.
OFF Position	In this position, the bargraph output and all gate functions are inoperative and memory holds the last value and is allowed to update.
CAL Position	Used in conjunction with the AUTO/CAL switch on the Amplifier Module to calibrate the Component Module RANGE and MEMORY ZERO AND SPAN.
RESET Pushbutton	Used in conjunction with the memory calibration to reset the memory outpu to the baseline.
GATE Adjustments	Permit setting the starting time and duration of the associated component g
COARSE Thumbwheel Switches	Permit selection of gate "start" time one-second increments from 0 to 99 seconds following sample inject.

TABLE 5 (Cont.)

Control or Indicator	Purpose or Use
FINE Control	Permits the gate "start" time to be delayed from 0 to 2 seconds beyond the setting of the COARSE thumbwheel switches.
DURATION Control	Permits vernier selection of gate duration from 0 to 10 seconds.
GND and OUT Jacks	Meter/scope test points for externally monitoring the memory output.

TABLE 6

VALVE MODULE, OPERATING CONTROLS AND INDICATORS

Control or Indicator	Purpose or Use
ON Indicator	Indicates power is applied to the actuating sole
AUTO/OFF/MAN Switch	Controls the operational mode of the associated valve.
AUTO Position	In AUTO, the valve is actuated automatically at the times set on the ON-OFF/TIME thumbwheel switches.
OFF Position	The valve solenoid is de-energized.
MAN Position	The valve solenoid is energized.
AUTO ZERO Indicator	Indicates occurance of the respective Auto Zero function.
AUTO ZERO ON/TIME Thumbwheel Switches	Permits selection of an Auto Zero "start" time, in one-second increments, from 0-99 seconds following sample inject.
Valve ON/TIME Thumbwheel Switches	Permit selection of the ON (solenoid energized) starting time in one-second increments, from 0-99 seconds following sample inject.
VALVE Control	Permits the valve ON starting time to be delayed from 0 to 2 seconds beyond the setting of the valve ON/TIME thumbwheel switches.
Valve OFF/TIME Thumbwheel Switches	Permits selection of the OFF (solenoid de-energized) starting time, in one-second increments, from 0-99 seconds following sample injec
VALVE OFF Control	Permits the valve OFF starting time to be delay from 0 to 2 seconds beyond the setting of the valve OFF/TIME thumbwheel switches.

TABLE 7

DUAL PREAMP MODULE, OPERATING CONTROLS AND INDICATORS

Control or Indicator	Purpose or Use
Toggle Switch	The toggle switch selects one or the other of two detector bridge preamplifier circuits to be monitored on the balance meter.
Balance Meter	A 1-0-1 volt meter which is used in balancin the selected detector bridge/preamplifier circuit.
DET. BAL. Controls	Adjusts the balance of the respective detect bridge/preamplifier circuit.
Preamplifier Test Jacks	Meter/scope test points for monitoring the indicated preamplifier parameters.
Terminal Strips	Provide connections for respective detector leads.

LEAK DETECTION AND ELIMINATION PROGRAM

ABERDEEN CHEMICAL PLANT

C. HNU PORTABLE HYDROCARBON DETECTORS

1. Introduction

The Aberdeen Chemical Plant uses HNU portable hydrocarbon detectors for routine leak patrols, to precisely locate potential leak sources when suspected leaks are indicated by the continuous monitoring system and to monitor vessels prior to entry. This analyzer is the:

HNU Photoionization Analyzer Model PI-101

The HNU portable analyzer is manufactured by:

HNU Systems
383 Elliot Street
Newton Upper Falls, Mass. 02164

The plant has found the HNU portable hydrocarbon detector reliable and easy to maintain. If a potential leak source registers more than 2000 ppm (the maximum range of the HNU), the TLV portable analyzer is used to determine if it is a leak.

The model PI-101 has been designed to measure the concentration of trace gases in many industrial or plant atmospheres. The analyzer employs the principle of photoionization for detection. This process is termed photoionization since the absorption of ultraviolet light (a photon) by a molecule leads to ionization via:

$$RH + hv \rightarrow RH^+ + e^-$$

where RH = trace gas

hv = a photon with an $\geq$ Ionization Potential of RH

The sensor consists of a sealed ultraviolet light source that emits photons, which are energetic enough to ionize many trace species (particularly organics) but do not ionize the major components of air such as O_2, N_2, CO, CO_2, or H_2O. A chamber adjacent to the ultraviolet source contains a pair of electrodes. When a positive potential is applied to one electrode, the field created drives any ions, formed by absorption of UV light, to the collector electrode where the current (proportional to concentration) is measured.

To minimize adsorption of various sample gases, the ion chamber is made of an inert fluorocarbon material, is located at the sampling point, and a rapid flow of sample gas is maintained through the small ion chamber volume.

The analyzer will operate either from a rechargeable battery for more than 10 hours or continuously from the AC battery charger. A solid state amplifier board in the probe and a removable power supply board in the readout module enable rapid servicing of the unit in the field.

The useful range of the instrument is from a fraction of a ppm to about 2,000 ppm. For measurement at levels above 2,000 ppm, dilution of the sample stream with clean air is recommended. Some typical specifications for the model PI 101 Photoionization Analyzer are given in Table 8.

2. Operation

Turn the function switch to the battery check position. The needle on the meter should read within or above the green battery arc on the scaleplate. If the needle is in the lower portion of the battery arc, the instrument should be recharged prior to making any measurements. If red LED comes on, the battery should be recharged.

Next, turn the function switch to the on position. In this position the UV light source should be on. Look into the end of the probe to see the purple glow of the lamp.

A brief description of the instrument controls and functions is shown in Figure 1.

To zero the instrument, turn the function switch to the standby position and rotate the zero potentiometer until the meter reads zero. Clockwise rotation of the zero potentiometer produces an upscale deflection while counterclockwise rotation yields a downscale deflection. Note: no zero gas is needed, since this is an electronic zero adjustment (see below). If the span adjustment setting is changed after the zero is set, the zero should be rechecked and adjusted, if necessary. Wait 15 or 20 seconds to ensure that the zero reading is stable. If necessary, readjust the zero.

The instrument is now ready for calibration or measurement by switching the function switch to the proper measurement range. The instrument is supplied calibrated to read directly in ppm (v/v) 0-20, 0-200, 0-2000 of benzene with the span position set at 9.8. For additional sensitivity, the span potentiometer is turned counterclockwise (smaller numbers) to increase the gain. By changing the span setting from 10.0 to 1.0 the sensitivity is increased approximately ten fold. Then, the 0-20, 0-200, and 0-2000 ppm scales become 0-2, 0-20, and 0-200 ppm full scale, respectively. This span control is also utilized to make the instrument scale read directly in ppm of the compound being measure. E.g., it is adjusted to match the value of a calibration gas to that same reading on the instrument scale. The span control can be utilized to calibrate nearly any compound, measured by photoionization, to be direct reading on the 0-20 ppm range. For example, gain settings of 4.5 or 8.9, respectively, will provide direct reading capability (0-20, 0-200 ppm) for vinyl chloride and trichloroethylene, respectively. For a listing of approximate gain setting values see Table 11.

A small DC operated fan is used to pull air through the photoionization sensor at a flow rate of three to seven hundred cubic centimeters per minute (ca. 0.5 lpm). The fan provides nearly instantaneous response times (Figure 2) while consuming little power. The characteristics of a fan are such that it connot tolerate a significant pressure drop without affecting the flow rate and therefore either the instrument reading or response time. Since photoionization is essentially a nondestructive technique, changes in flow rate do not affect the signal but if a large pressure drop is imposed at the inlet the probe, the sample may not reach the sensor.

The instrument was designed to measure trace gases over a concentration range from less than 1 ppm to 2000 ppm. Higher levels of various gases (to percentage range) can be measured but the recommended procedure is to dilute the sample with clean air to a concentration of less than 500 ppm. This is generally within the linear range of the instrument and if the measured concentration is multiplied by the dilution ratio the correct concentration in the stream can be determined. A typical calibration curve is shown in Figure 3. Note that the calibration curve for benzene (the photoionization standard) is linear (over more than three decades) up to about 600 ppm (v/v).

If the probe is held close to AC power lines or power transformers, an error may be observed. For measurements made in close proximity to such items, their effect on measurements can be determined by the following procedure. Zero the instrument in an electrically quite area, in the standby position, then move the instrument to the questionable area involved. If AC pickup is going to be a problem, the meter (in the standby position) will indicate the magnitude of the error.

The instrument is equipped with an automatic solid state battery protection circuit. When the battery voltage drops below ~11 volts, this circuit will automatically turn off the power to the instrument. This prevents deep discharging of the battery and considerably extends the battery life. If the instrument is unintentionally left on overnight, the battery will be unharmed because of the battery protection circuit. If the instrument battery check reads low and the lamp doesn't fire, plug the charger into the instrument. The power to the analyzer should then be returned.

To charge the battery, place the mini phone plug into the jacket on left side of the bezel prior to plugging charger into 120 VAC. When disconnecting charger, remove from 120 VAC before removing mini phone plug. The battery is completely recharged overnight (ca. 14 hours). To ensure that the charger is functioning, turn the function switch to the battery check position, place phone plug into jack and plug charger into AC outlet. The meter should go upscale if charger is working and is correctly inserted into the jack.

The instrument can be operated during the recharge cycle. This will lengthen the time required to completely recharge the instrument battery.

3. Detection Principle and Theory

The detection principle of this portable instrument is photoionization. A wide variety of organic compounds and some inorganic compounds can be measured with this technique. Photoionization (with 10 eV photons) applied to the analysis of trace gases in air can eliminate fragment ion formation (signals) from the major components of air yet still allow the ionization of many impurities of interest in industrial atmospheres. This is demonstrated by the listing of ionization potentials* in Table 12. Note the high (12 eV) ionization potentials for the major components of air. In addition, the choice of a suffi ciently low ionization energy often permits the selective ionization of one or two components in a complex gas mixture.

While the ionization potential serves as a rough guide to whether or not a response is obtained, it does not predict what the quantitive response actually is. In some cases, a species with an ionization potential 10.3 or 10.4 eV will give a response. In these cases, however, the response is usually low because of its low ionization effeciency at 10 eV. A partial list of actual relative sensitivities obtained with a photoionization analyzer is given in Table 13. The use of the tables should allow a determination of the specificity of the instrument in a given application on many industrial processes; this instrument may not respond to the starting materials or by-products but will respond to a product. An example of this is seen in the vinyl chloride monomer plants where neither ethylene or dichloroethane is detected but vinyl chloride is detected.

A block diagram of the major components of the photoionization analyzer is shown in Figure 4. The instrument is separated into two units interconnected by multiconductor electrical cable. The probe contains a fan for moving the air into the sensor, the ultraviolet lamp which is ignited by applying a DC voltage between the anode and cathode, the ionization chamber which contains a pair of electrodes and is adjacent to the lamp, and a signal amplifier. The photons (~10 eV) which are emitted from the lamp pass through a UV radiation by a

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* Ionization potential is defined as the energy required to move an electron an infinite distance from the nucleus or more simply, the energy required to produce a positive ion and an electron.

molecule which has an ionization potential of 10 eV or less will lead to ion formation via:

$$RH + h\nu \rightarrow RH^{+} + e^{-}$$

A positively biased high voltage electrode is used to push any ions formed by absorption of UV to the collector electrode where the current (proportional to concentration) is measured. This current is then converted to a proportional voltage by the amplifier in the probe. An electrical diagram of the instrument is depicted in Figure 5. The amplifier is gain stabilized by negative feedback and provides a voltage source output to drive the analog meter readout as well as the gain control network. The sensitivity of the instrument is controlled by changing the loop gain of the amplifier. A 12 volt battery provides the primary power for a high efficiency DC-DC converter which supplies the various potentials required for instrument operation.

TABLE 8

SPECIFICATIONS FOR MODEL PI 101

PHOTOIONIZATION ANALYZER

performance (benzene referred)

range 0.1 to 2000 ppm
detection limit 0.1 ppm
sensitivity (max) 0-2 ppm FSD over 100 division meter scale
repeatability + 1% of FSD
linear range 0.1 to 600 ppm
useful range 0.1 to 2000 ppm
response time $\leq$ 3 sec to 90% of full scale
ambient humidity to 95% RH
operating temperature ambient to 40°C*

physical

size:	probe 6.3 DIA x 28.5L (cm)	(2-1/2 x 11-1/4")
	readout 21W x 13D x 16.5H (cm)	(8-1/4 x 5-3/16 x 6-1/2")
	stowed 21W x 13D x 24H (cm)	(8-1/4 x 5-3/16 x 9-1/2")
	cable 80 cm long (32")	

weight: probe .55 kg (20 ounces)
readout 3.2 kg (7 pounds)
total (shipping) 5.4 kg (12 pounds)

controls and functions

mode switch Off, Battery Check, Standby (zero), 0-2000, 0-200, 0-20 ppm
low battery indicator light
zero (10 turn ± 300% FDS max)
span (10 turn counting dial 1.0 to 10 times nominal sensitivity)
readout 4-1/2" (11.3 cm) meter Taut Band movement graduated 0-5-10-15-20, divisions
signal output for recorder 0-(-5V) FSD
power output for recorder 12 VDC - jack on side of instrument

power requirements of operating times

continuous use, battery > 10 hours
continuous use with HNU recorder reduces instrument battery operating time to 1/2 normal time
recharge time, max < 14 hours, 3 hours to 90% of full charge
recharge current, max .4 Amps @ 15 VDC

TABLE 8 - (Cont.)

construction

Designed to withstand the shock and abuse to which portable instruments are often subjected. The readout is housed in a two piece aluminum case, and finished with a solvent resistant baked acrylic textured paint.

The probe is fabricated from extruded aluminum sections and machined plastic.

serviceability

The probe and readout are of a modular design allowing rapid servicing and/or replacement of mechanical and electrical components. All module interwiring includes quick disconnects.

maintenance

The instrument contains only one moving part, and consumes no gases or reagents. The only routine maintenance procedure is cleaning the light source window every several weeks.

calibration check

Check instrument calibration at least once per week with HNU calibration standard to ensure that the high sensitivity of the instrument is maintained.

* Instrument is temperature compensated so that a 20°C change in temperature corresponds to a change in reading of $< \pm 2\%$ full scale at maximum sensitivity.

TABLE 9

BRIEF DESCRIPTION OF INSTRUMENT CONTROLS AND FUNCTIONS*

Control	Function
Six Position Switch	OFF - Shuts off all power and removes DC volta
	ON - In any other function position or measur mode, the electronics are on.
	BATTERY CHECK - Indicates the condition of th battery. If needle position is in lower portion of green battery arc, the instru ment should be recharged.
	STANDBY - UV lamp is off but electronics are o This position will conserve power and ex the useful operating time between rechar of the battery. This position is also u lized to adjust the electronic zero.
	RANGES - 0-20, 0-200, 0-2000 direct reading ra available at minimum gain for benzene. sensitivity is available by adjusting th span potentiometer.
Zero Potentiometer	A ten turn potentiometer is employed to adjus the zero electronically when the instrument is placed in the standby position with the probe attached. This eliminates the need for a hydr carbon free gas.
Span Potentiometer	A ten turn counting potentiometer is utilized upscale setting of the meter on calibration Counter-clockwise rotation increases the sens vity (10 times). This pot can increase the sensitivity to make the instrument direct rea for nearly any gas which the instrument respon to.

* For position of layout controls see Figure 1.

Figure 1 Control Panel Functions of Photoionization Analyzer

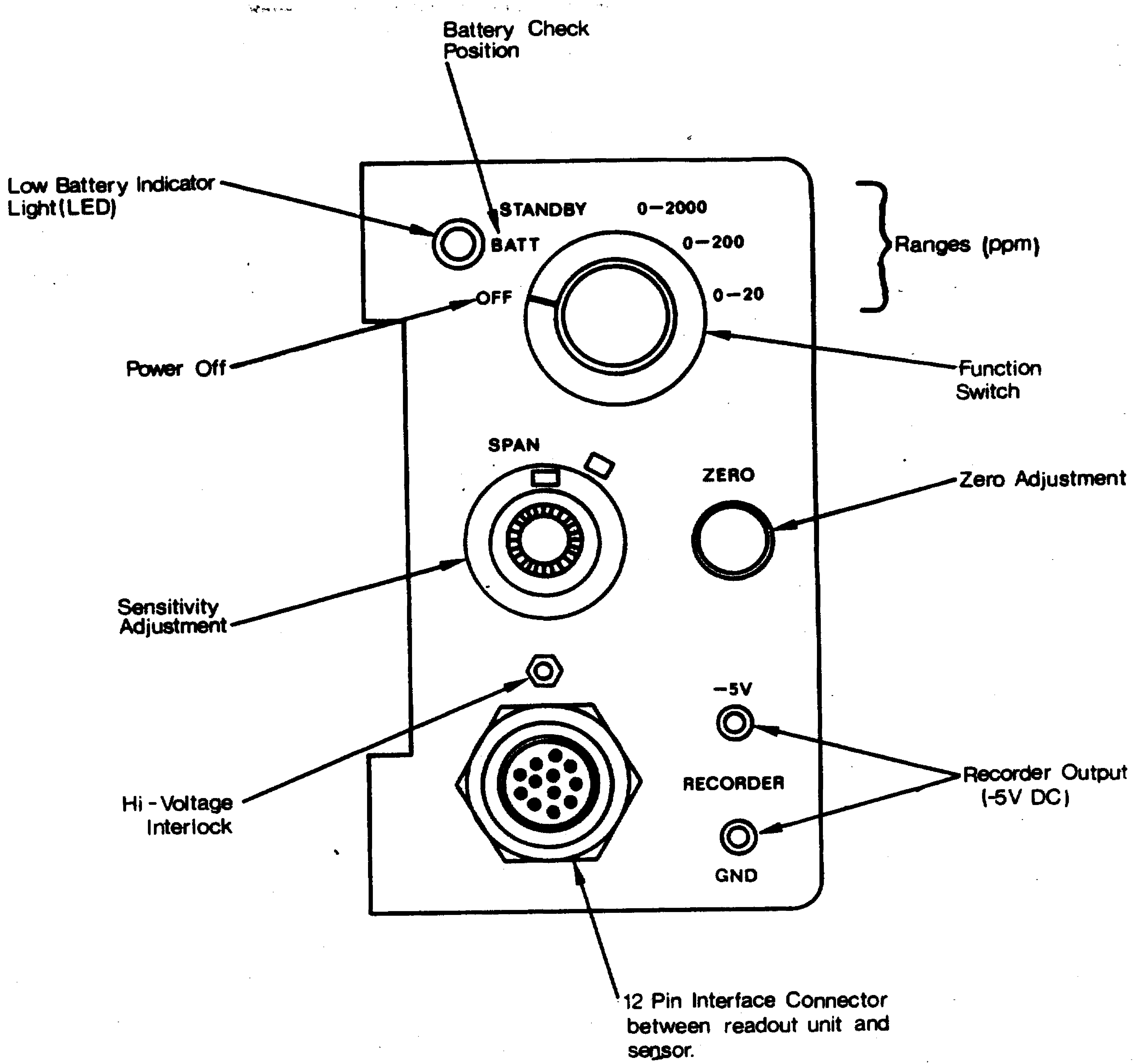

TABLE 10

VERIFICATION OF ELECTRONIC ZERO FOR

PHOTOIONIZATION ANALYZER*

Sample	Instrument Reading (ppm)	% of F.S.
Room Air	0.7	35
Room Air Passed Through 6" x 3/4" OD Charcoal Scrubber	0.1	5
Zero Air	0.25	12.5
Zero Air Passed Through 6" x 3/4" OD Charcoal Scrubber	0.04	2

* Maximum Gain = 2 ppm full scale.

TABLE 11

RELATIVE PHOTOIONIZATION SENSITIVITIES*

FOR VARIOUS GASES

Chemical Grouping	Relative Sensitivity	Examples
Aromatic	10.0	Benzene, Toluene, Styrene
Aliphatic Amine	10.0	Diethylamine
Chlorinated Unsaturated	5-9	Vinyl Chloride, Vinylidene Chloride, Trichloroethylene
Carbonyl	5-7	MEK, MIBK, Acetone, Cyclohexe
Unsaturated	3-5	Acrolein, Propylene, Cyclohex Allyl Alcohol
Sulfide	3-5	Hydrogen Sulfide, Methyl Mercaptan
Paraffin (C_5-C_7)	1-3	Pentane, Hexane, Heptane
Ammonia	0.3	-
Paraffin (C_1-C_4)	0	Methane, Ethane...

* Sensitivities in ppm (v/v).

TABLE 12

SOME DERIVATIVES OF OLEFINS

Molecule	IP (eV)
vinyl chloride	9.995
cis-dichloroethylene	9.65
trans-dichloroethylene	9.66
trichloroethylene	9.45
tetrachloroethylene	9.32
vinyl bromide	9.80
1,2-dibromoethylene	9.45
tribromoethylene	9.27
3-chloropropene	10.04
2,3-dichloropropene	9.82
1-bromopropene	9.30
3-bromopropene	9.7
$CF_3CCl{=}CClCF_3$	10.36
n-$C_5F_{11}CF{=}CF_2$	10.48
acrolein	10.10
crotonaldehyde	9.73
mesityl oxide	9.08
vinyl methyl ether	8.93
allyl alcohol	9.67
vinyl acetate	9.19

TABLE 13

RELATIVE SENSITIVITIES FOR VARIOUS GASES

(10.2 eV LAMP)

Species	Photoionization Sensitivity*
p-xylene	11.4
m-xylene	11.2
benzene	10.0 (reference standa
toluene	10.0
diethyl sulfide	10.0
diethyl amine	9.9
styrene	9.7
trichloroethylene	8.9
carbon disulfide	7.1
isobutylene	7.0
acetone	6.3
tetrahydrofuran	6.0
methyl ethyl ketone	5.7
methyl isobutyl ketone	5.7
cyclohexanone	5.1
naptha (86% aromatics)	5.0
vinyl chloride	5.0
methyl isocyanate	4.5
iodine	4.5
methyl mercaptan	4.3
dimethyl sulfide	4.3
allyl alcohol	4.2

Figure 2 Time Response for the Photoionization Analyzer.

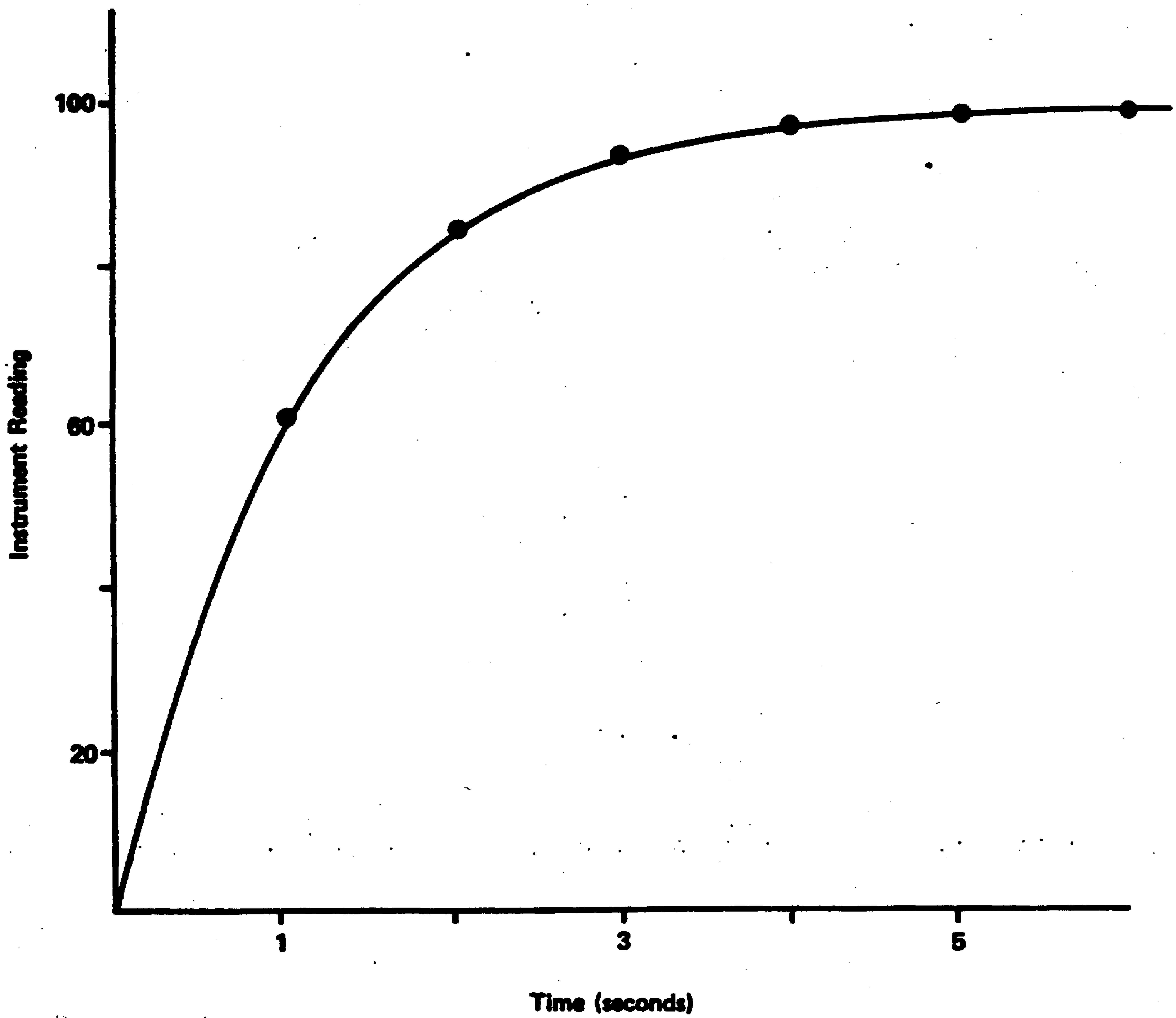

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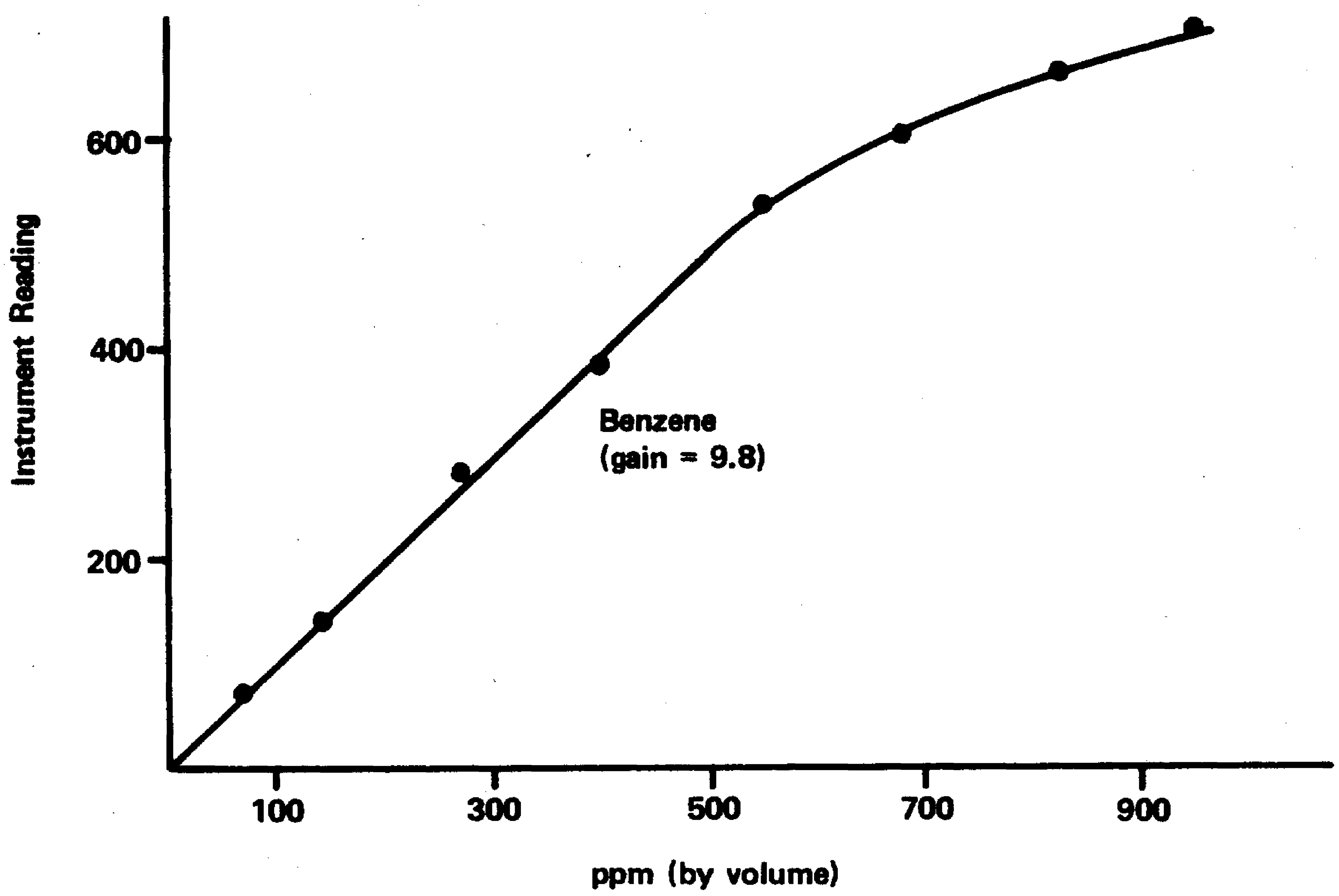
Figure 3 Typical Calibration Curve for Photoionization Analyzer.



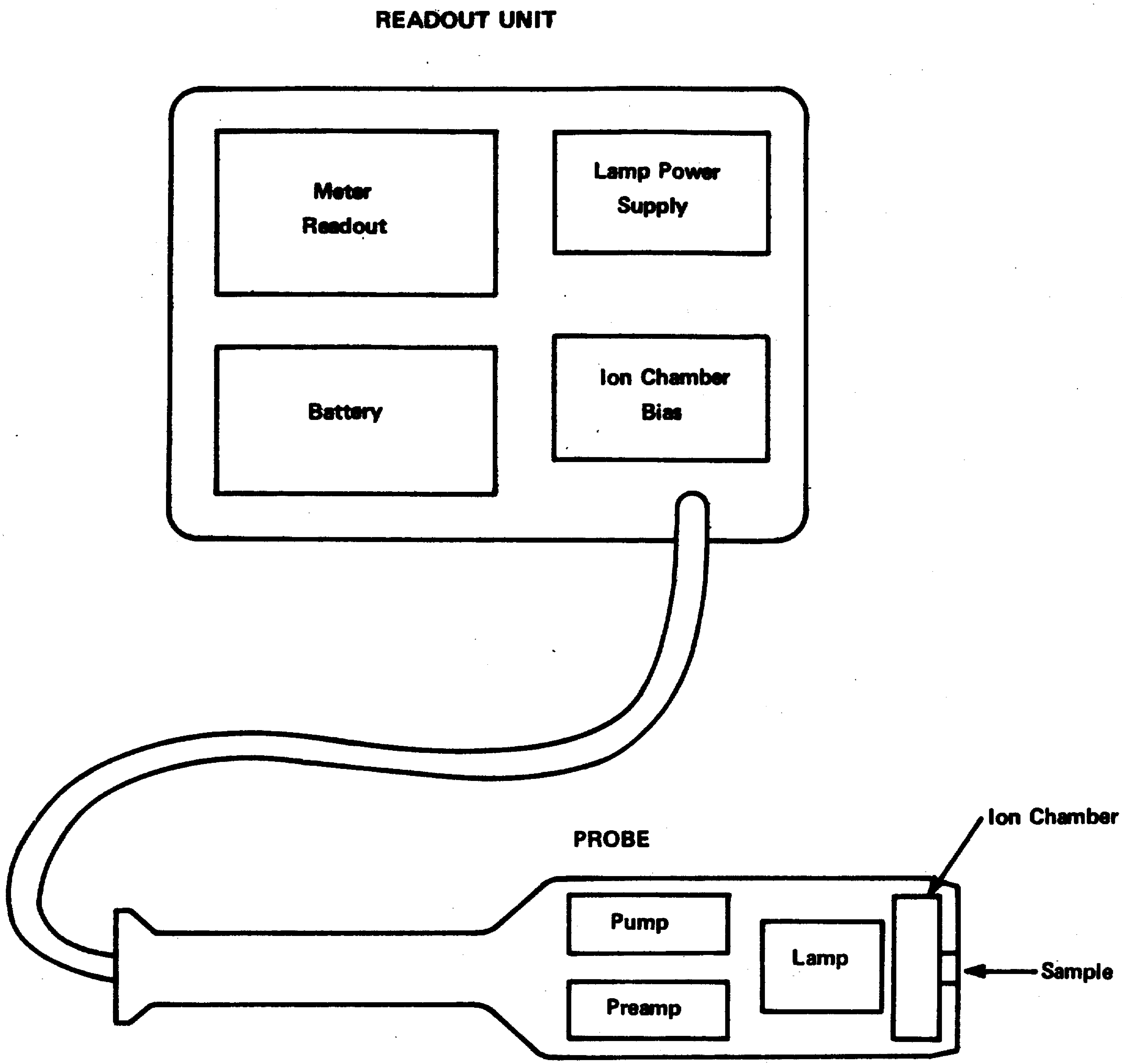
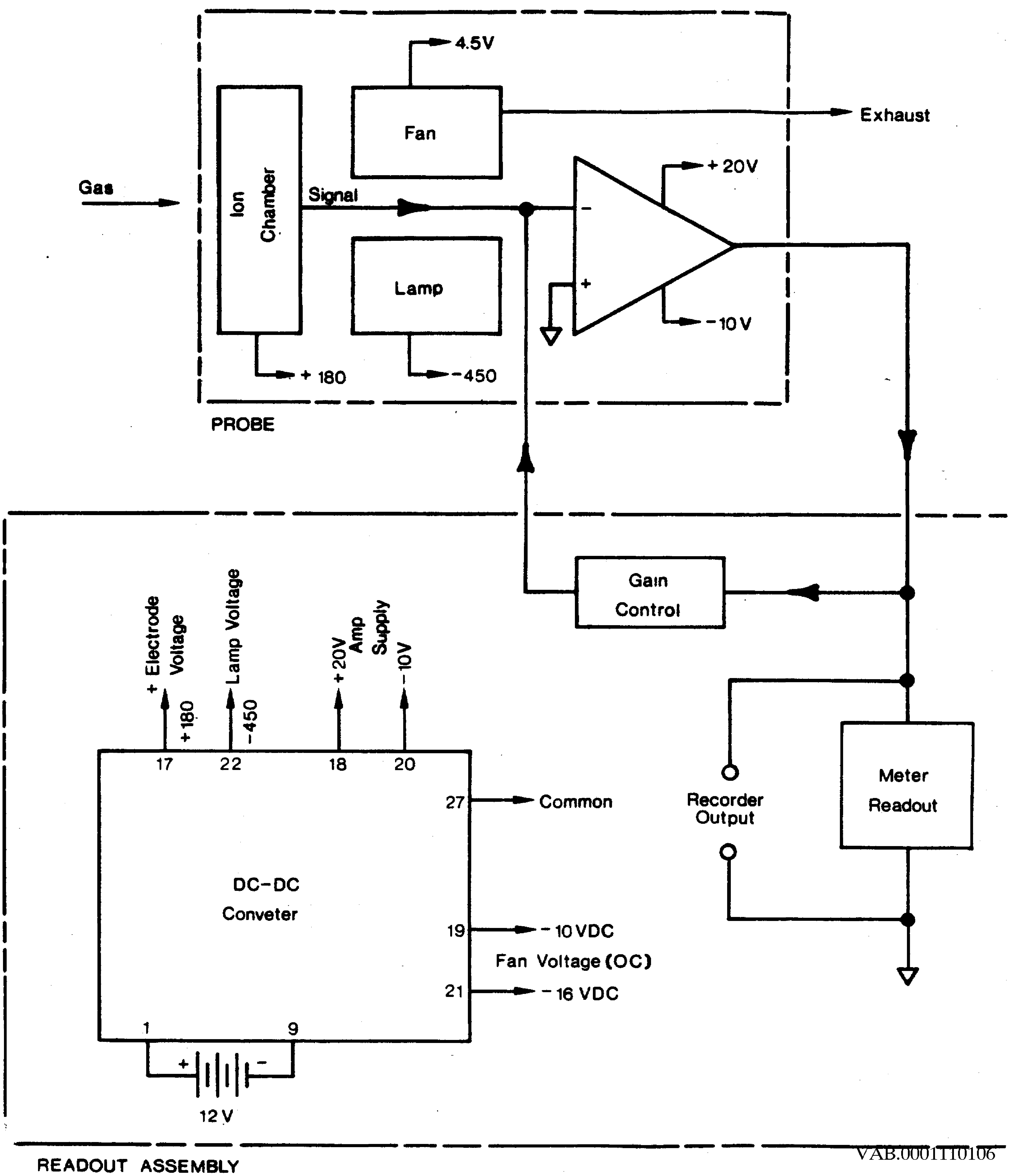


Figure 4 Block Diagram of Portable Photoionization Analyzer.

Figure 5 Electrical Block Diagram of Photoionization Analyzer



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