LEAK DETECTION AND ELIMINATION PROGRAM

ABERDEEN PVC PLANT

C. PORTABLE HYDROCARBON DETECTORS

1. Introduction

The Aberdeen PVC Plant uses portable hydrocarbon detectors for routine leak patrols, to precisely locate leak sources when leaks are indicated by the continuous monitoring system and to monitor vessels prior to entry. The leak detection program submitted in May, 1977 included Century Organic Vapor Analyzers. The plant has experienced problems with maintenance of these analyzers. Because of these problems, the plant has field tested another portable hydrocarbon analyzer. This analyzer is:

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 is more reliable, easier to maintain, and less subject to damage than the Century Organic Vapor Analyzer. The plant therefore wants to switch to using the HNU analyzer as a part of the leak detection and elimination program. The plant asks EPA to review the following information on the HNU Photoionization Analyzer and approve its use as part of the leak detection program.

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:

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

where RH = trace gas

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

The sensor consists of a sealed utlraviolet 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 ($\sim$10 eV) which are emitted from the lamp pass through a UV radiation by a

* 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 $<$ 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 $\pm$ 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 voltages. ON - In any other function position or measuring mode, the electronics are on. BATTERY CHECK - Indicates the condition of the battery. If needle position is in lower portion of green battery arc, the instrument should be recharged. STANDBY - UV lamp is off but electronics are on. This position will conserve power and extend the useful operating time between recharges of the battery. This position is also utilized to adjust the electronic zero. RANGES - 0-20, 0-200, 0-2000 direct reading ranges available at minimum gain for benzene. More sensitivity is available by adjusting the span potentiometer.
Zero Potentiometer	A ten turn potentiometer is employed to adjust the zero electronically when the instrument is placed in the standby position with the probe attached. This eliminates the need for a hydrocarbon free gas.
Span Potentiometer	A ten turn counting potentiometer is utilized for upscale setting of the meter on calibration gas. Counter-clockwise rotation increases the sensitivity (10 times). This pot can increase the sensitivity to make the instrument direct reading for nearly any gas which the instrument responds to.

* For position of layout controls see Figure 1.

Figure 1 Control Panel Functions of Photoionization Analyzer

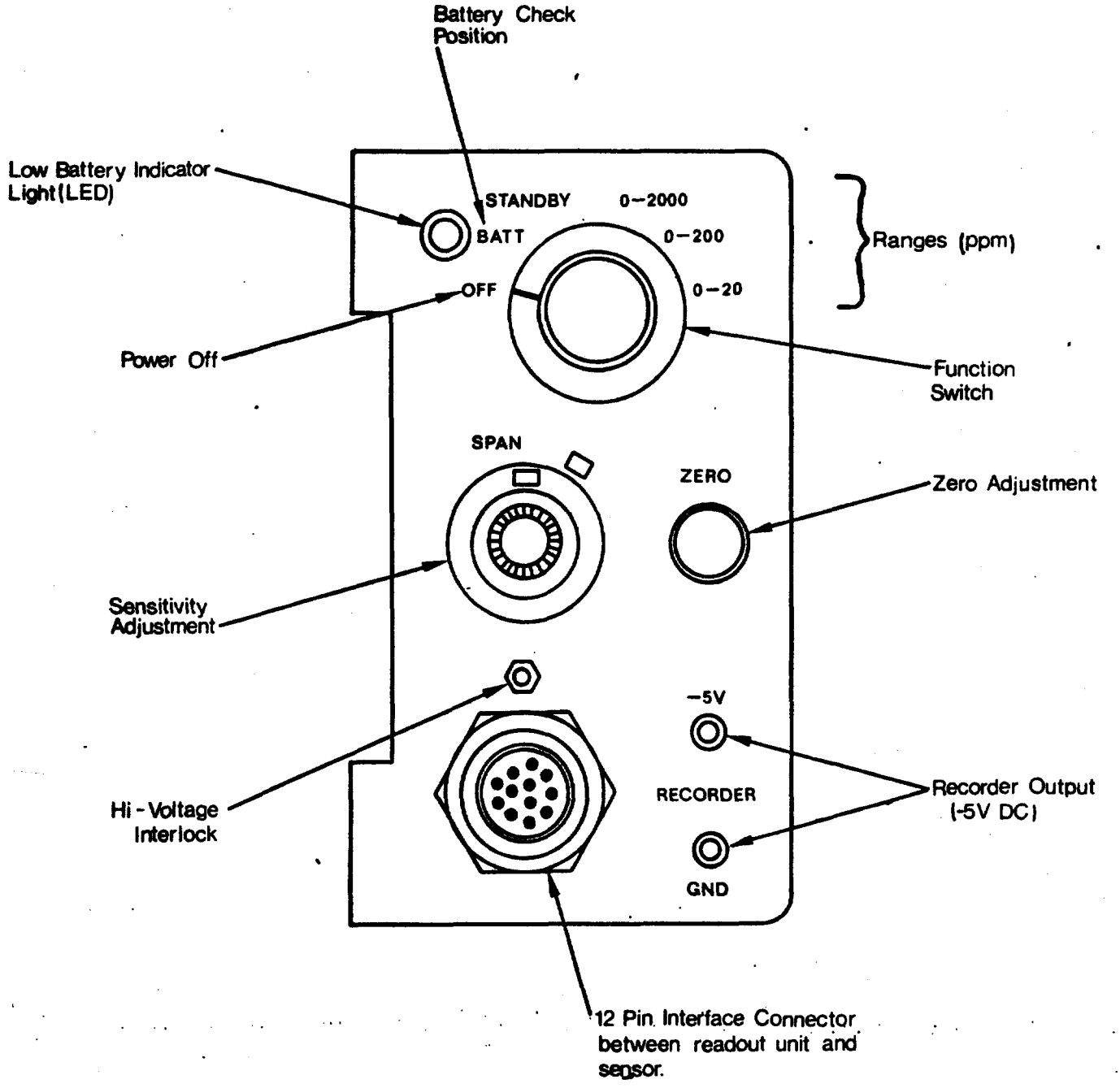

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TABLE 10

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, Cyclohexene
Unsaturated	3-5	Acrolein, Propylene, Cyclohexene, 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
$CF_3CCI=CCICF_3$	10.36
$n\text{-}C_5F_{11}CF=CF_2$	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 standard)
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.

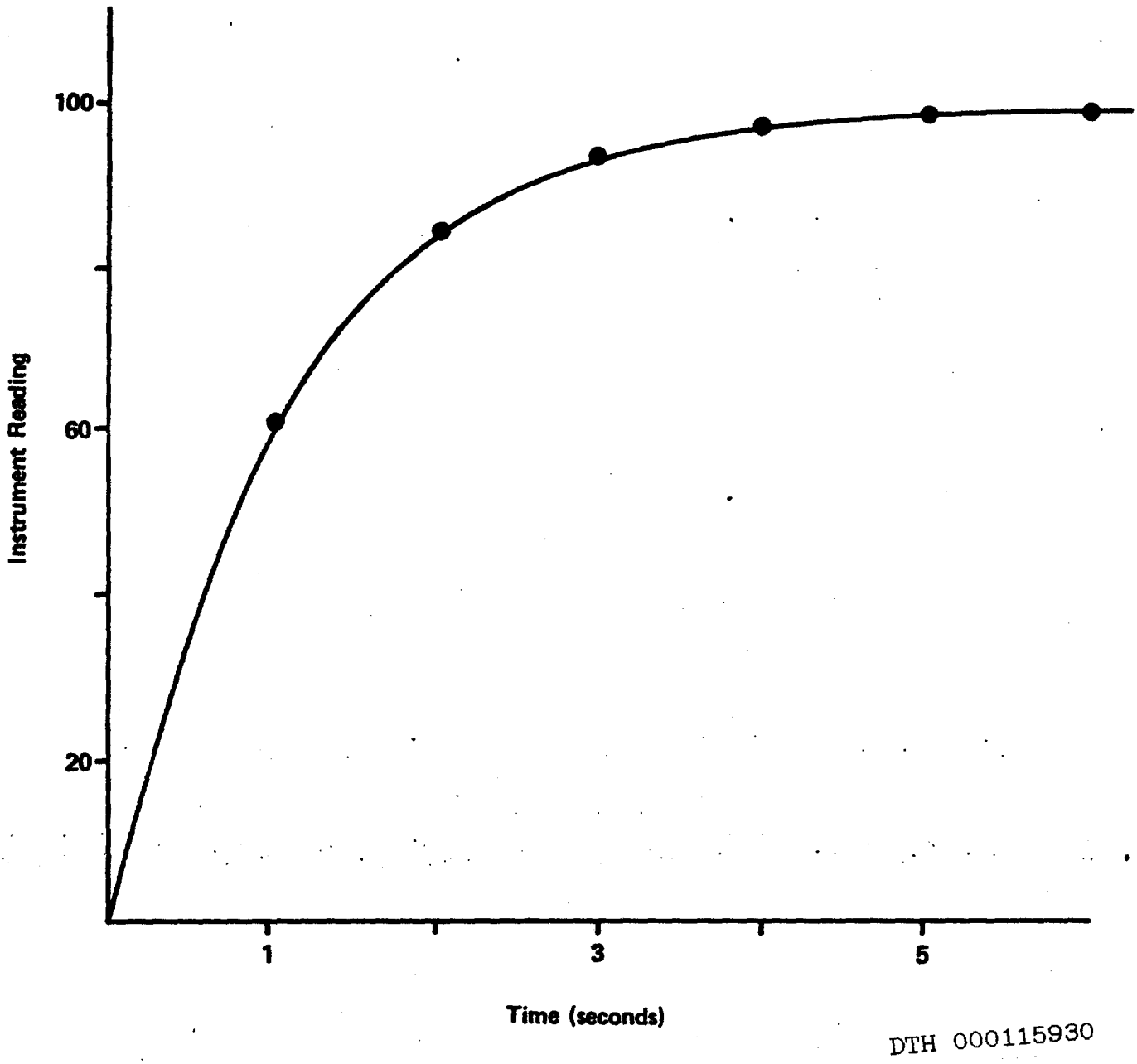

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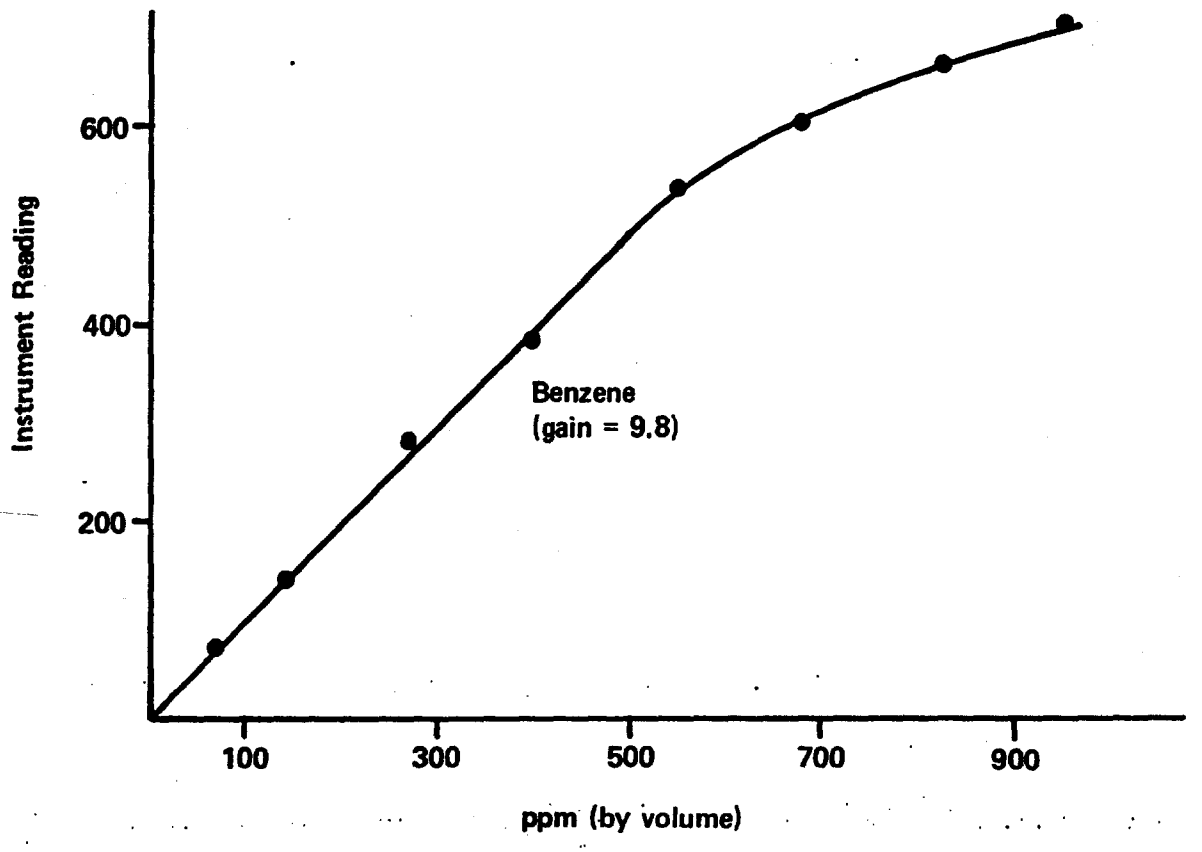
Figure 3 Typical Calibration Curve for Photoionization Analyzer.



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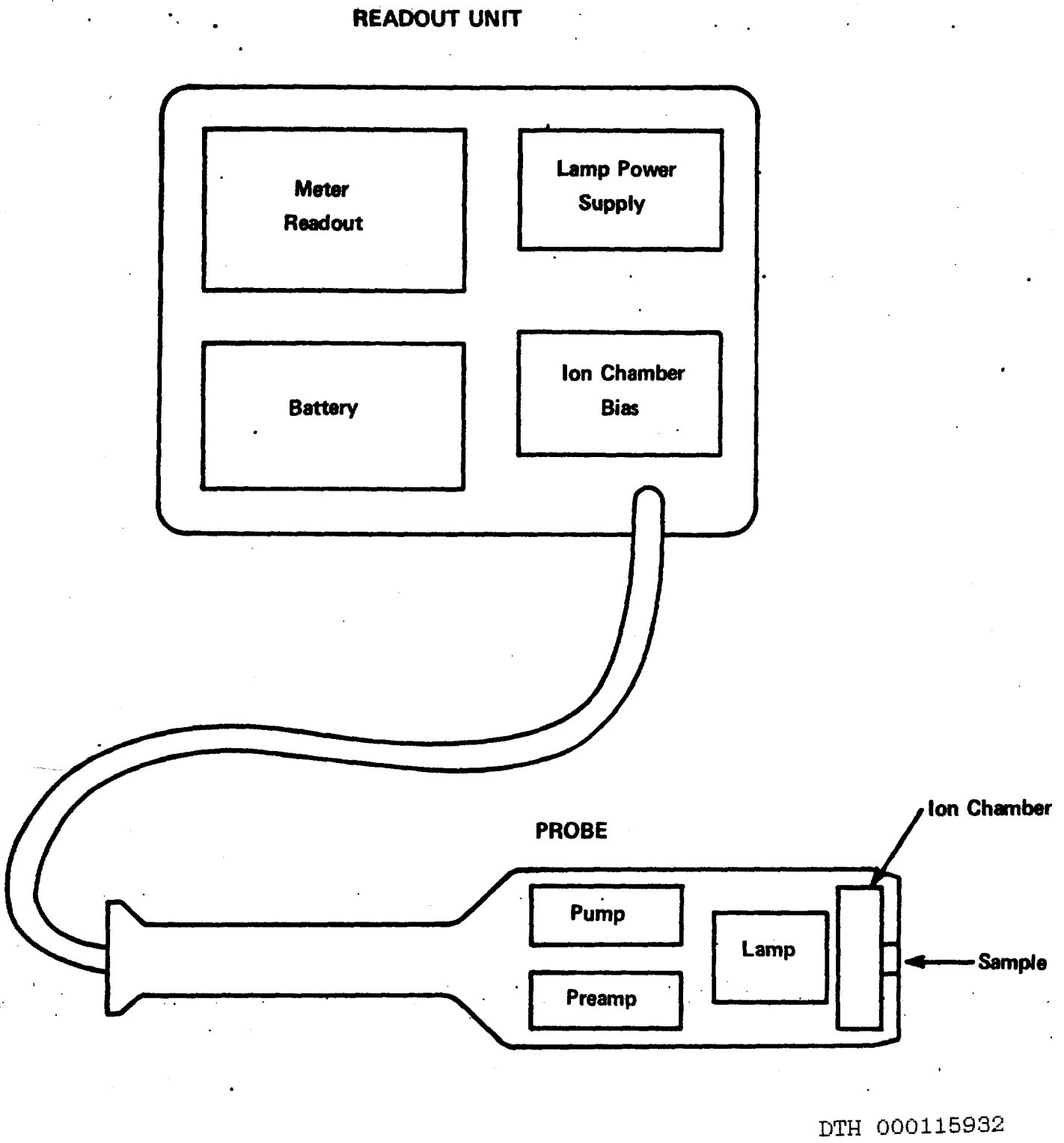

Figure 4 Block Diagram of Portable Photoionization Analyzer.

Figure 5 Electrical Block Diagram of Photoionization Analyzer