THE NEW OZONE MONITOR

DE-FG43-92R340408

FINAL REPORT

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Ozone Monitor

Introduction:

This DOE funded project #DE-FG43-92R340 was first evaluated by NIST under their project #570. This instrument is the development of Dr. Eskil Karlson's invention of measuring the concentration of ozone by measuring the heat evolved when the ozone is catalyzed and converted back to oxygen. This invention has been patented.

This ozone monitor evolved through a number of prototype as described in the final report. The final instrument is accurate, reliable and can be installed as a part of a control system. This instrument can be built and calibrated for any necessary specific ozone concentration range. This instrument uses inexpensive parts and would be simple to maintain. The manufacturing cost is less than any equally reliable and accurate ozone monitor presently available.

The advantage this system has is that the ozone is directly measured as the temperature of the catalyst. It does not need UV lamps (which continually degrade in use and have a variable life) or use any chemistry where a material is continuously used up. This new ozone monitor directly measures the heat that is generated from the ozone as it converts back into oxygen as the gas mixture flows through the catalyst. The catalyst has theocratically an infinite life. It can clog if the system it is installed in, is dusty. But in systems that produce ozone, it is important that the gas is clean. Under normal clean gas conditions this instrument will give long term service free monitoring.

Background:

Dioxins have been classified as one of the most deadly of carcinogens. Because dioxins are formed, or can be formed from using chlorine in the bleaching of paper pulp and sterilization of drinking water, there is an increasing move away from chlorine to ozone. Chlorine can also react with trace amounts of hydrocarbons in water to form dangerous amounts of dioxins. Ozone is currently being used in Europe to sterilize drinking water instead of chlorine. In this country methods are currently being taken to replace the use of chlorine.

Ozone is typically produced on a commercial scale by causing oxygen to react with itself in a high voltage corona discharge. A new three-oxygen-atom molecule (ozone) is formed in the reaction. Ozone is a stronger oxidizing agent than any other chemical agent except fluorine. This makes ozone a stronger bleaching and sterilizing agent than chlorine. Ozone is easily produced in an ozone generator at the point of use. Because of the short half-life of ozone, it breaks back down into oxygen in a short period of time.

Ozone Detection:

The ozone gas detection is accomplished by measuring the voltage difference between the active and compensating thermocouples. The active thermocouple is connected to a heat sink that is in contact with the catalyst. The compensating thermocouple is connected to a heat sink that measures the ambient temperature of the gas mixture before it reaches the active thermocouple. The reaction of the ozone and the catalyst produce heat that is absorbed by the heat sink. The decomposition of ozone into oxygen releases heat according to the reaction:

$$2\,O_3 \;\text{--->}\; 3\,O_2 \qquad \Delta H^0{}_f = -\,142.7 \text{ kJ/mole}$$

The output voltage from the thermocouple is directly proportional to the heat released by by the decomposition of ozone into oxygen. The output voltage from the thermocouples is converted to the equivalent temperature.

Ozone Monitor Test Models:

The initial ozone monitor prototype was built and tested. The (Big Box Model) uses three separate chambers in a box. In each section of the box, there is a single heat sink. The single heat sink, made of aluminum, has a notch cut in the center. On the sides of the cut notch, an insulator was placed to separate the copper plate and copper plate cover with the catalyst from the aluminum heat sink. The thermocouples are attached to the copper plates.

The thermocouple used was Type E (Chromel - Constantan) because of its characteristic of having the highest output voltage per change in degree. The chromel was the positive wire and the constantan was the negative wire. The thermocouples were connected in series with the negative wires connected together. The thermocouples were connected in series with reverse polarities for the compensation thermocouples, so that the ambient temperature would be zeroed out. Thermocouple pairs had to be matched so that the ambient temperature of the gas mixture would be zeroed without having an offset. The active thermocouples were connected in series so that voltages would add and give a more accurate voltage reading.

The ozone monitor (Big Box) has the dimensions of 3.5 inches wide, by 3.5 inches thick, by 9 inches long. The aluminum heat sinks have a dimension of 1 inch wide, by 1 inch thick, by 1 inch long. The copper and copper covered with catalyst plates have a dimension of 0.75 inch wide, by 1/64 inch thick, by 1 inch long. A small scale size of the big box ozone monitor was also built and tested. The small box was built at 1/3 the size of the big box ozone monitor. Photo A shows the big box ozone monitor and Photo B shows the small box ozone monitor.

When the big box ozone monitor was tested it had very poor sensitivity. It showed only a tenth of a degree change in temperature for a variation in ozone concentration. The very small change in temperature was from very little heat created on the plates. The open space in the box around the heat aluminum sink also allowed for some of the ozone not to make contact with the plates. The small box ozone monitor when tested showed better sensitivity. The small box ozone monitor showed a change of a few degrees for a variation in ozone concentration. The small box had better sensitivity over the big box because of less space inside the box around the aluminum heat sink. Both box ozone monitors did not provide the needed sensitivity for an accurate control of ozone production. The main problem

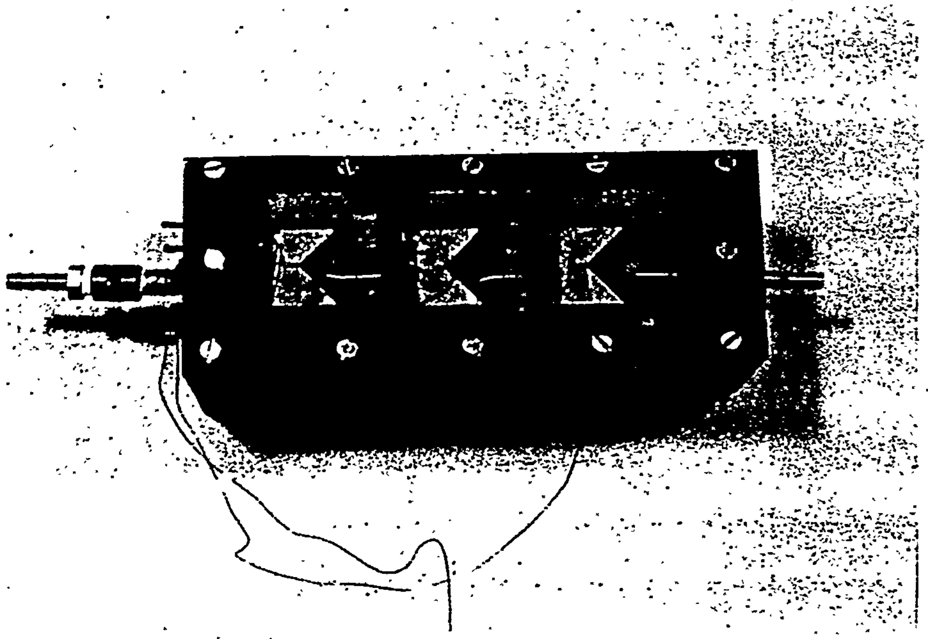


Photo A
Big Box Ozone Monitor

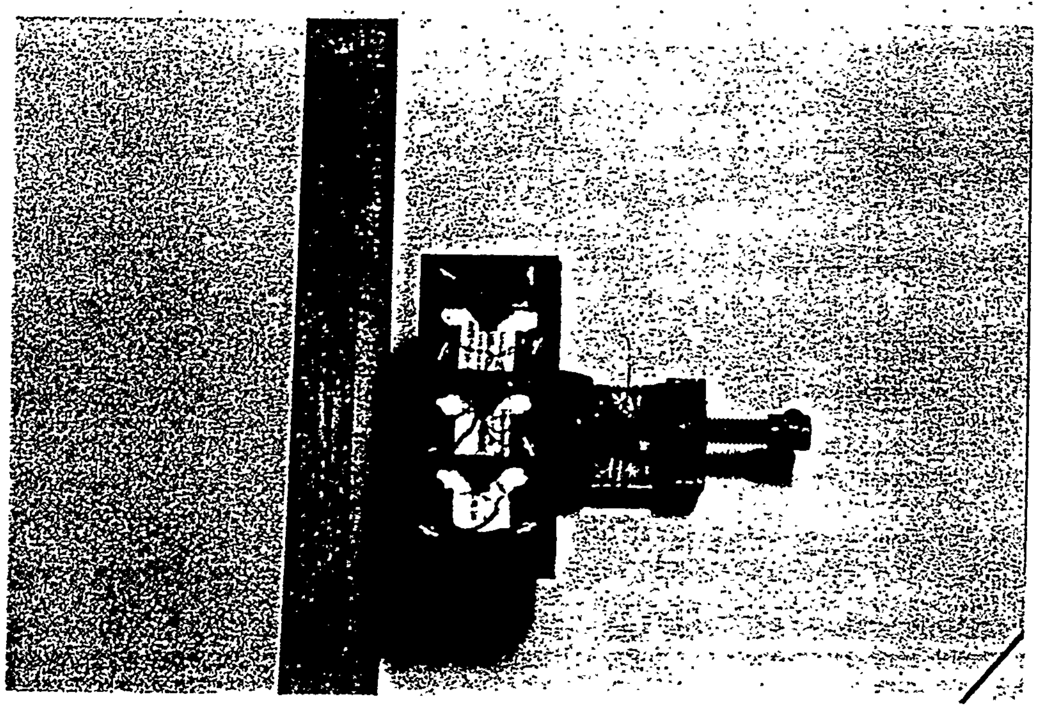


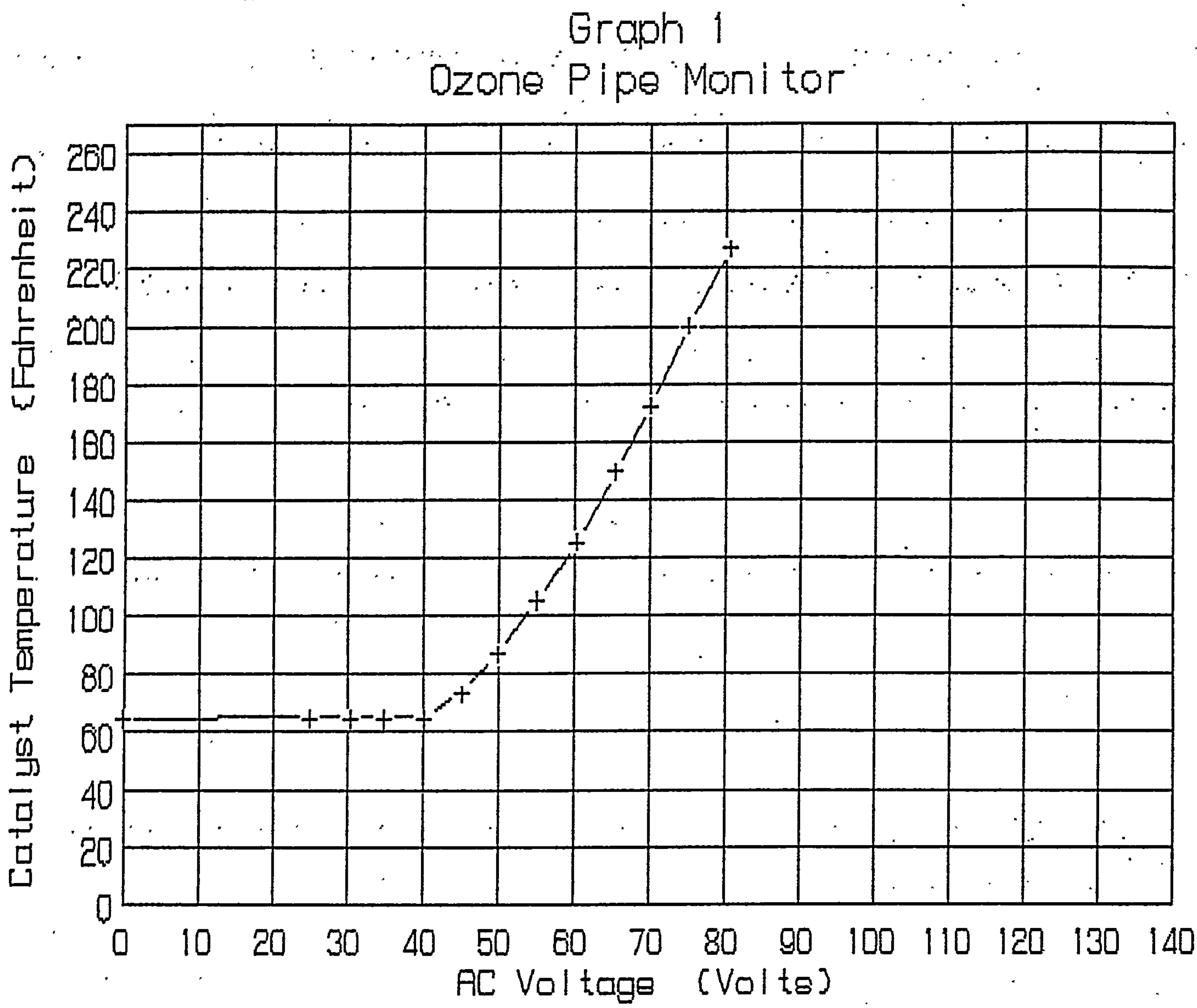
Photo B
Small Box Ozone Monitor

with the box ozone monitors was that there was not enough heat produced by the catalyst.

The solution to the problem with the box ozone monitors is to have more catalyst around the copper plate connected to the thermocouple. A change in the design of the ozone monitor was made from a box to a tube or pipe. In the new pipe design the copper plate connected to the thermocouple could be surrounded and packed with the catalyst. The first new pipe design tested used a piece of pipe. On the inside a tube of PVC was tightly fitted into the pipe. Inside the PVC a thin copper heat sink was connected to the active thermocouple. On both sides of the thin copper heat sink, the catalyst was packed in. To hold the catalyst inside the PVC tube, two plastic filters were placed inside the PVC tube in both ends. The plastic filters were glued in place by an epoxy. The PVC pipe was then glued into the pipe with epoxy. The PVC, plastic filters, and the pipe were all glued with epoxy to seal the ozone monitor so that all of the ozone would be forced into the plastic filters and then through the catalyst. In the first preliminary test of the new pipe ozone monitor it showed good sensitivity as the temperature changed as the ozone passed through. The temperature increased exponentially as the amount of ozone passing through the monitor increased to around 10%. Because of the absence of a cooling fan on the copper pipe and the insulating properties of the PVC pipe, the temperature inside the monitor exceeded 750 degrees Fahrenheit. The increasing heat from the reaction of the catalyst with the high concentration of ozone pushed the temperature inside the monitor very high. The plastic filters and PVC pipe were not designed for high temperatures.

To solve the problem of the plastic filters and PVC pipe not being able to handle the heat released from the reaction of the high concentration of ozone with the catalyst, the plastic filters were replaced by stone filters and the PVC pipe was replaced by a glass tube. The results from the test are shown in Graph 1 (Catalyst Temperature vs. AC Voltage). The glass insulator and stone filters were able to handle the heat from the reaction of the ozone with the catalyst with no problems. The catalyst used in the glass insulated pipe monitor were crushed into fine particles in order to give more catalyst surface area. The pressure created from the flow of the oxygen through the ozone generator is called the back pressure. This back pressure is also present on the ozone monitor. The back pressure caused problems with the stone filters inside the ozone monitor. The back pressure would force the fine catalyst powder through the stone filters. This problem, in

Catalyst Temperature vs. AC Voltage



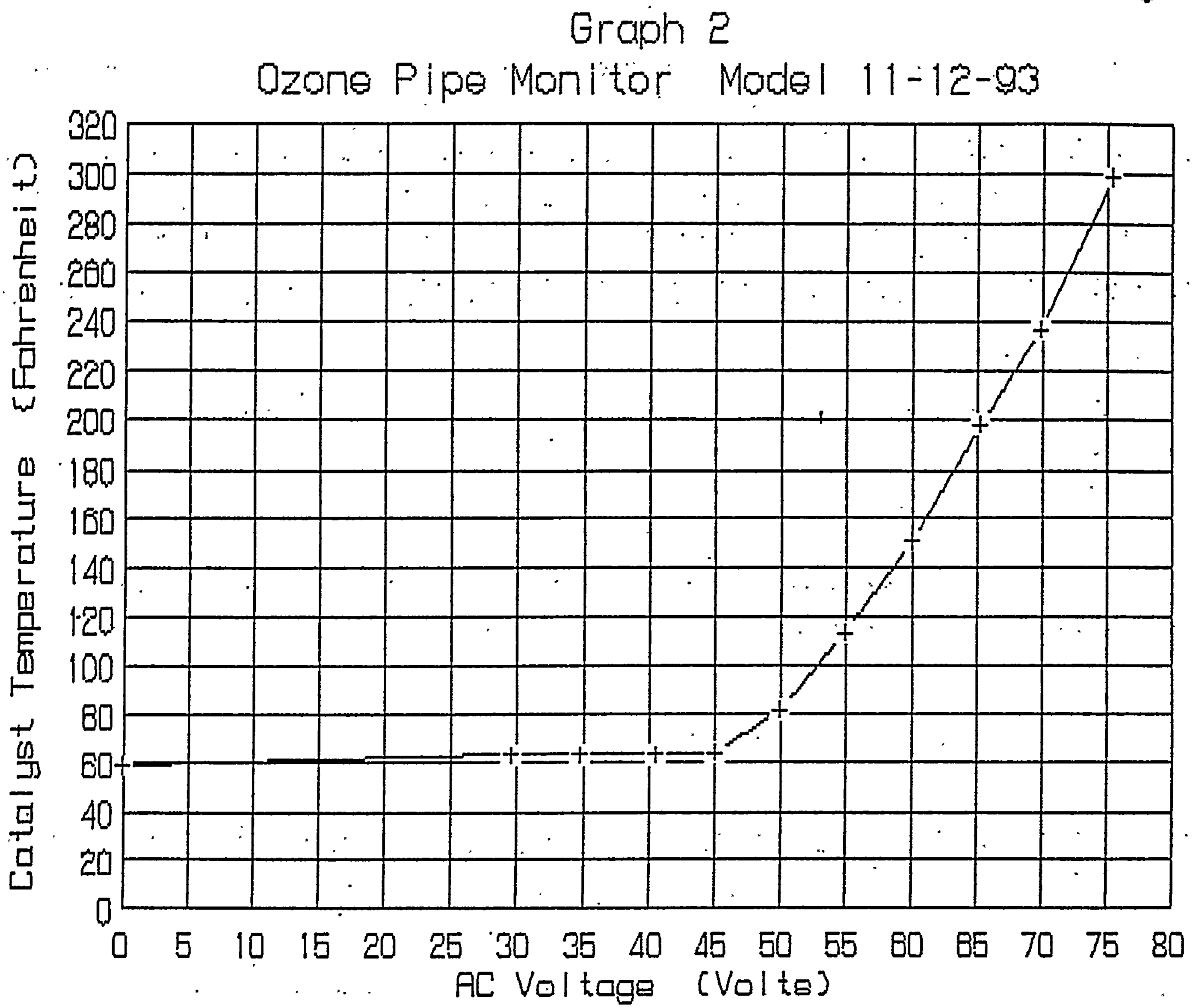
Ozone Generator Pressure		1 psi
Oxygen Flow		10 scfh
Water Flow		50 GPH
Transformer	T182850	
Chopper Card	3013	

time, would ruin the ozone monitor by depleting the amount of catalyst in the monitor.

To solve the new problem of the catalyst being forced through the stone filters by the ozone generator back pressure, the ozone pipe monitor Model 11-12-93 was built. For the ozone pipe Model 11-12-93, insulation (fiber glass) was placed between the catalyst and the stone filters. The insulation was used because of its ability to withstand heat and be able to hold the fine catalyst powder in place. The ozone pipe monitor Model 11-12-93 was tested using a cooling fan to pull the excess heat from the monitor. The results are shown in Graph 2 (Catalyst Temperature vs. AC Voltage).

To improve the time constant of the ozone pipe monitor Model 11-12-93, the glass insulator needed to be improved. An insulator that could handle the heat and also transfer the heat to the copper pipe was needed. By increasing the the heat transfer out of the system the time constant (time needed for the monitor to reach a steady state temperature) could be decreased. The glass tube was replaced by a thin piece of Teflon only 0.004 inch thick and ozone monitor Model 11-14-93 was created. Photo C shows the ozone pipe monitor Model 11-12-93 and Photo D shows the ozone pipe model 11-14-93. Figure 1 shows the internal composition of the Model 11-14-93 Ozone Pipe Monitor.

Catalyst Temperature vs. AC Voltage



Ozone Generator Pressure	3.5 psi
Oxygen Flow	4.5 scfh
Water Flow	50 GPH
Transformer T182850	
Chopper Card 3013	

Cooling Fan on Ozone Monitor

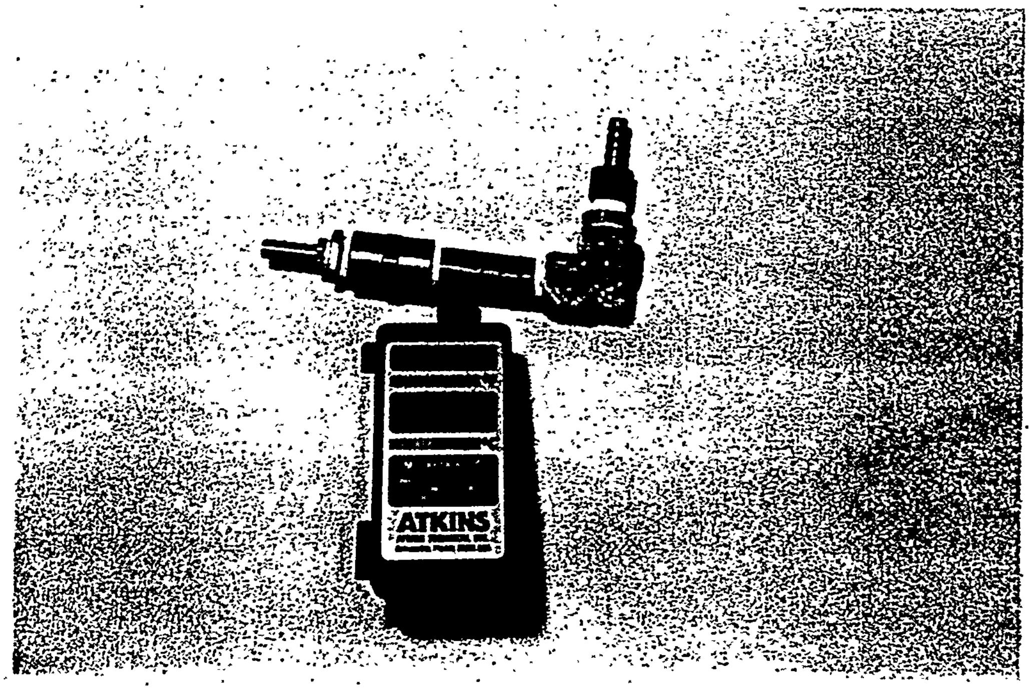


Photo C
Ozone Pipe Monitor Model 11-12-93

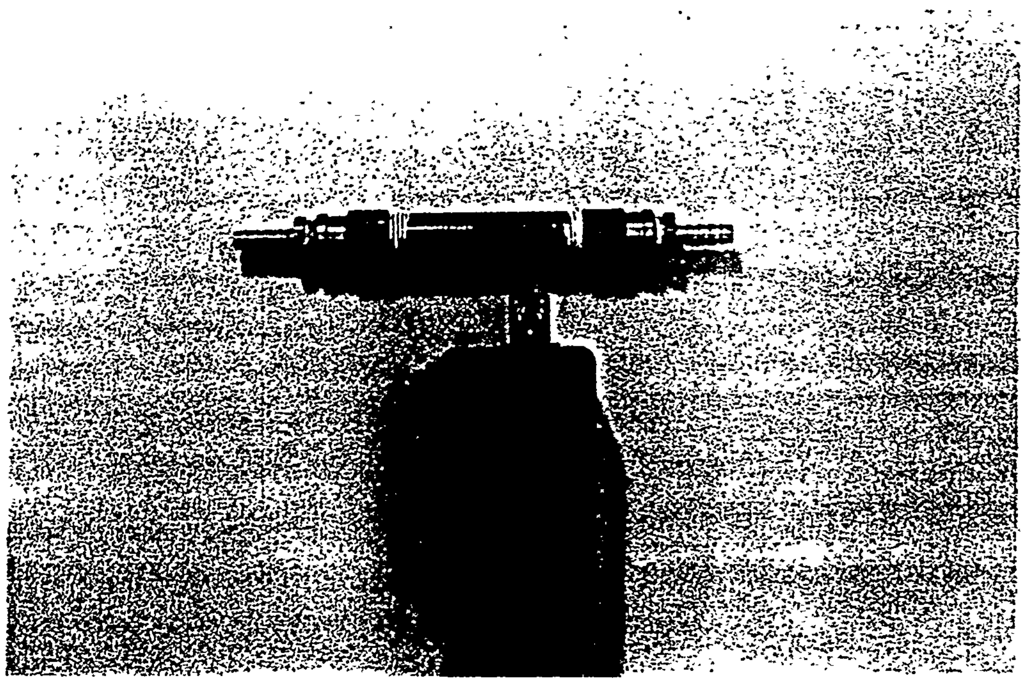
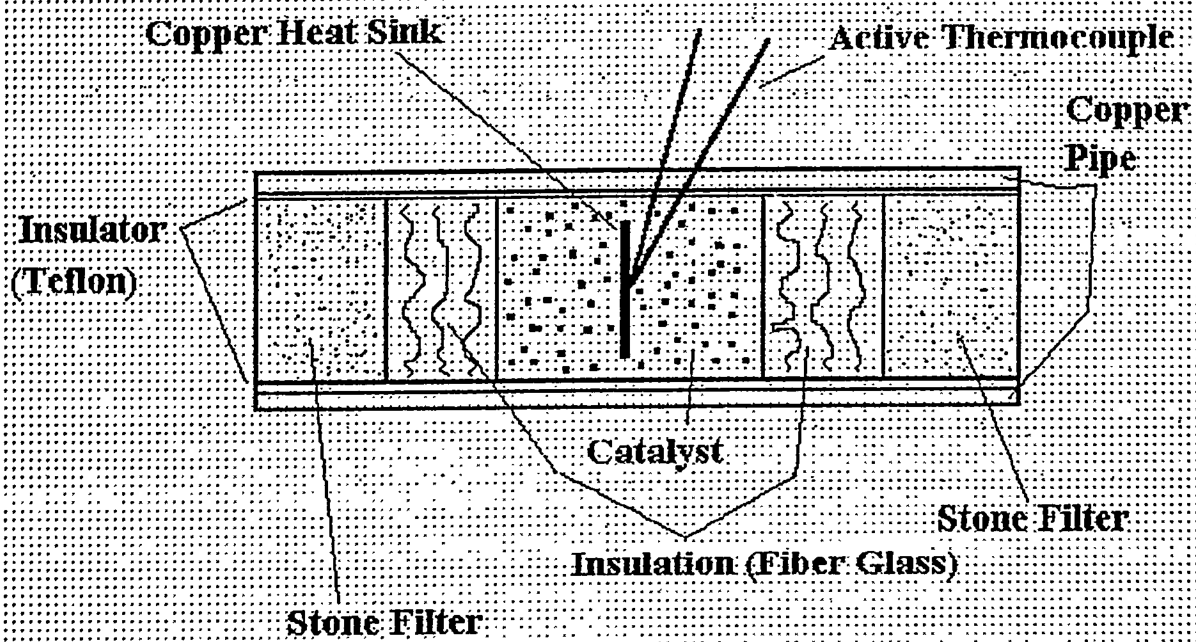


Photo D
Ozone Pipe Monitor Model 11-14-93

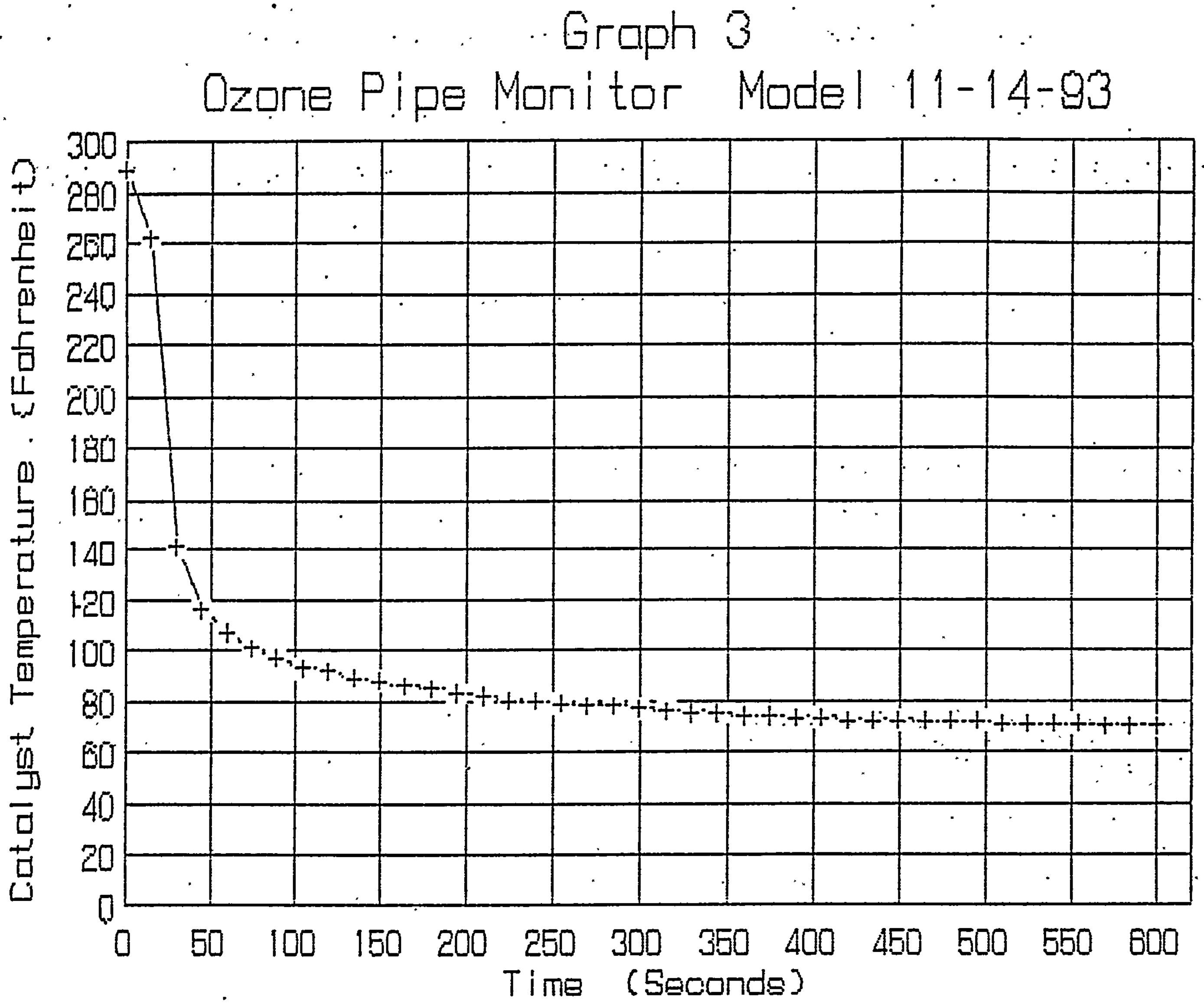
Figure 1



Composition
of the
Model 11-14-93 Ozone Pipe Monitor

The thin piece of Teflon was used in order to give the ozone monitor a fast recovery and response time. The heat from the reaction of the ozone with the catalyst is transferred to the thermocouple heat sink and through the thin Teflon sheet. The heat that passes through the Teflon and to the external pipe is pulled off by a cooling fan. The Graph 3 (Catalyst Temperature vs. Time) shows the time required for the ozone pipe monitor to cool down to a steady state temperature. After approximately 50 seconds the ozone pipe monitor Model 11-14-93 had cooled down by 80%. The oxygen flow and pressure were held constant at 4 scfh (standard cubic feet per hour) and 1 psi (pounds per square inch). The ozone pipe monitor was calibrated against a chemical titration using the KI method (Potassium Iodide). The ozone was measure at different voltage levels by bubbling the

Catalyst Temperature vs. Time

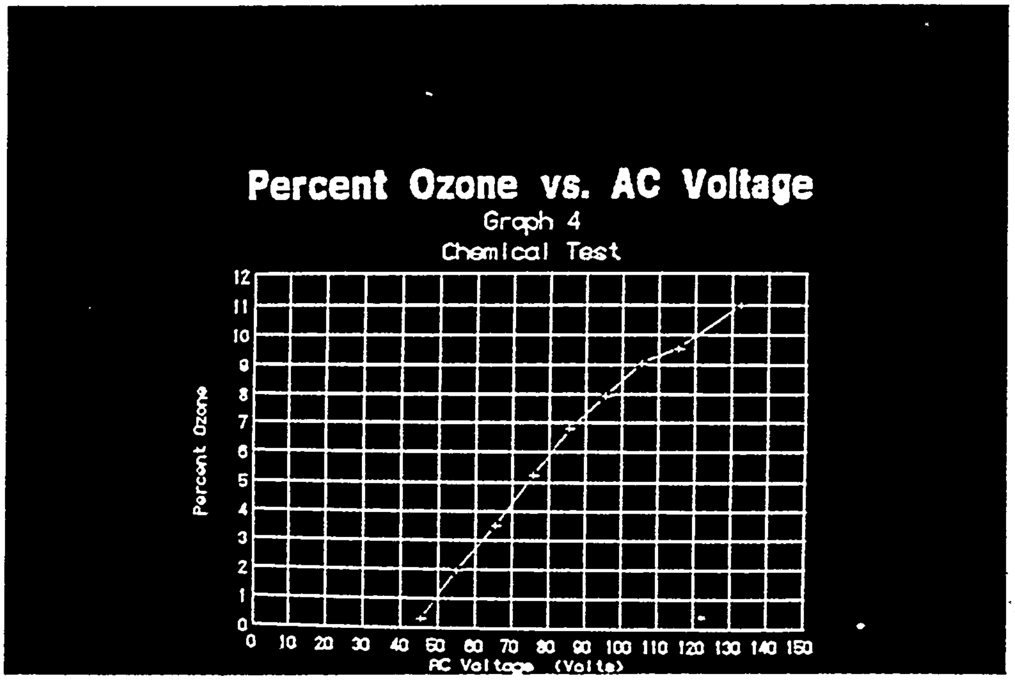


Ozone Generator Pressure		1 psi
Oxygen Flow		4 scfh
Water Flow		50 GPH
Transformer	T182850	
Chopper Card	3013	
Average High Voltage		0 KV
Average Input AC Voltage		0 V

Cooling Down Time with Cooling Fan on Ozone Monitor

ozone through a standard solution of KI. The sample was then titrated and the percentage of ozone was calculated. The Graph 4 (Percent Ozone vs. AC Voltage) shows the different percentages of ozone at the different levels of the input AC voltage. The ozone generator pressure was held at 1 psi while the oxygen flow was held at 4 scfh. Graph 5 (Percent Ozone vs. AC Voltage) shows the percent ozone at a different oxygen flow level. The ozone pipe monitor was tested at an ozone generator pressure of 1 psi and an oxygen flow of 4 scfh. In the Graph 6 (Catalyst Temperature vs. AC Voltage) the catalyst temperature was measured after each increase in input AC voltage. The temperature was measured after a period of about 5 minutes from the time the AC input voltage was increased. The temperature was recorded after 5 minutes in order to give the monitor time to reach the steady state temperature. Graph 7 (Catalyst Temperature vs. AC Voltage) shows the response time of the ozone pipe model 11-14-93 at a different oxygen flow level. Graph 8 (Catalyst Temperature vs. Time) shows the response time or time constant of the ozone pipe monitor. The ozone pipe monitor will reach the steady state temperature within a few minutes. The temperature of the ozone pipe monitor increases with an increase in ozone concentration. For a given ozone concentration, the ozone pipe monitor will reach a given temperature. The temperature will vary a few degrees from test to test depending on the ambient temperature. The ambient temperature will be measured by having a thermocouple connected to a heat sink in line before the ozone pipe monitor. This thermocouple is used to zero out the ambient temperature of the system. The zeroing of the system gives the true value of the heat of reaction from the ozone reacting with the catalyst.

The ozone pipe monitor Model 11-14-93 has a diameter of 3/4 of an inch and a length of 6 inches. From the data and results of the ozone pipe Model 11-14-93 we designed and built an ozone monitor that was smaller. We built a mold to compress the catalyst into a filter. The catalyst was coated with wax and then put into the mold. The mold compressed the catalyst into a filter that was 1/4 in diameter and 1 inch long. Once the catalyst had been compressed, the wax was then driven out of the catalyst filter by heat. After the wax was evaporated off, we had theroreticilly a porous catalyst filter. The catalyst filter was then tightly fitted into an aluminum heat sink. Figure 2 shows the composition of the Catalyst Filter Ozone Monitor.

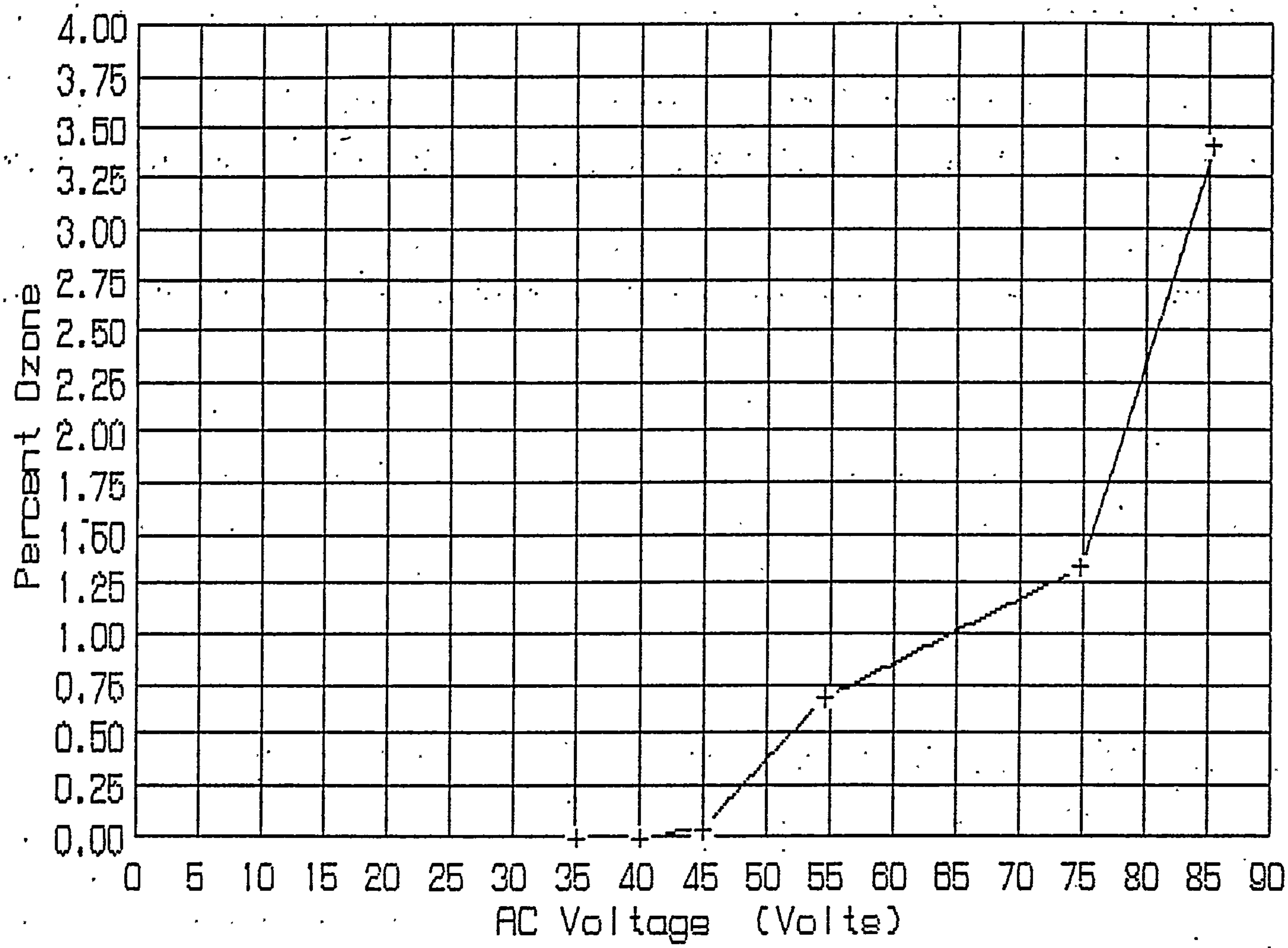


Ozone Generator Pressure		1 psi
Oxygen Flow		4 scfh
Water Flow		50 GPH
Transformer	T182830	
Chopper Card	3013	

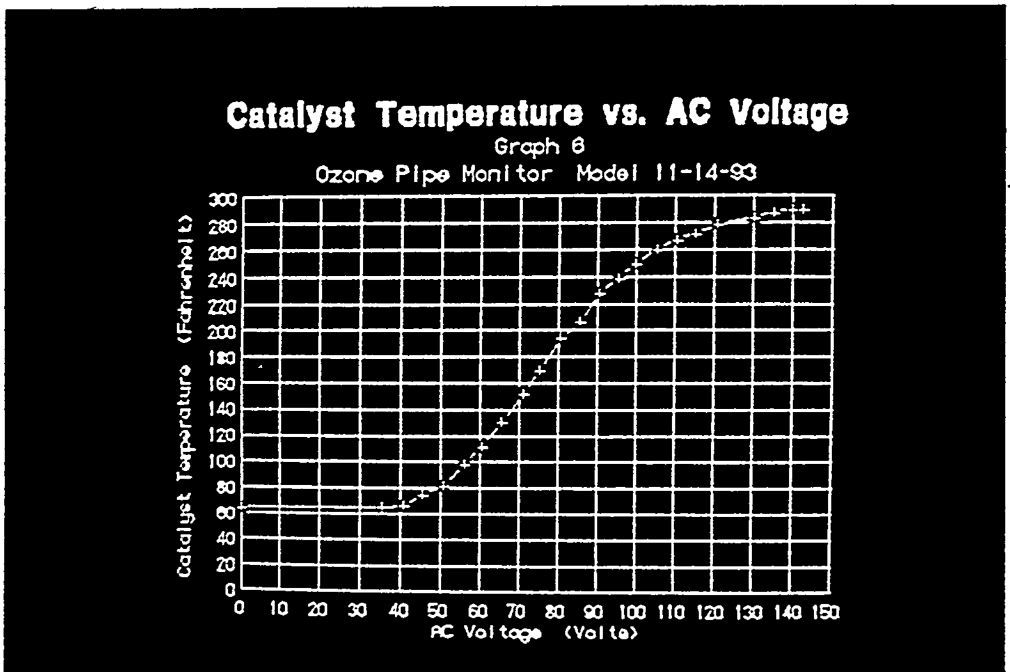
Percent Ozone vs. AC Voltage

Graph 5

Chemical Test



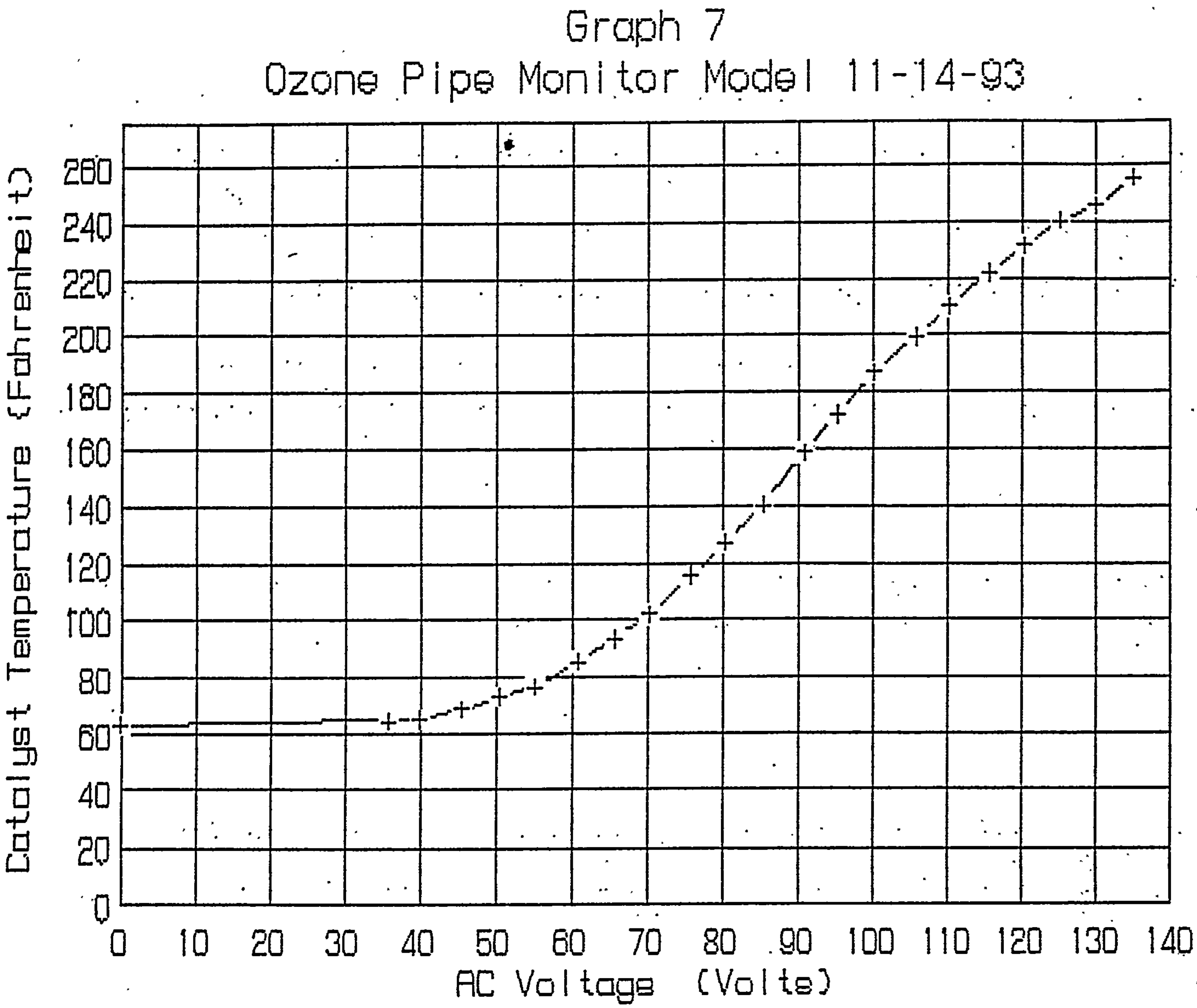
Ozone Generator Pressure		1 psi
Oxygen Flow		10 scfh
Water Flow		50 GPH
Transformer	T182850	
Chopper Card	3013	



Ozone Generator Pressure		1 psi
Oxygen Flow		4 scfh
Water Flow		50 GPH
Transformer	T182850	
Chopper Card	3013	

Cooling Fan on Ozone Monitor

Catalyst Temperature vs. AC Voltage



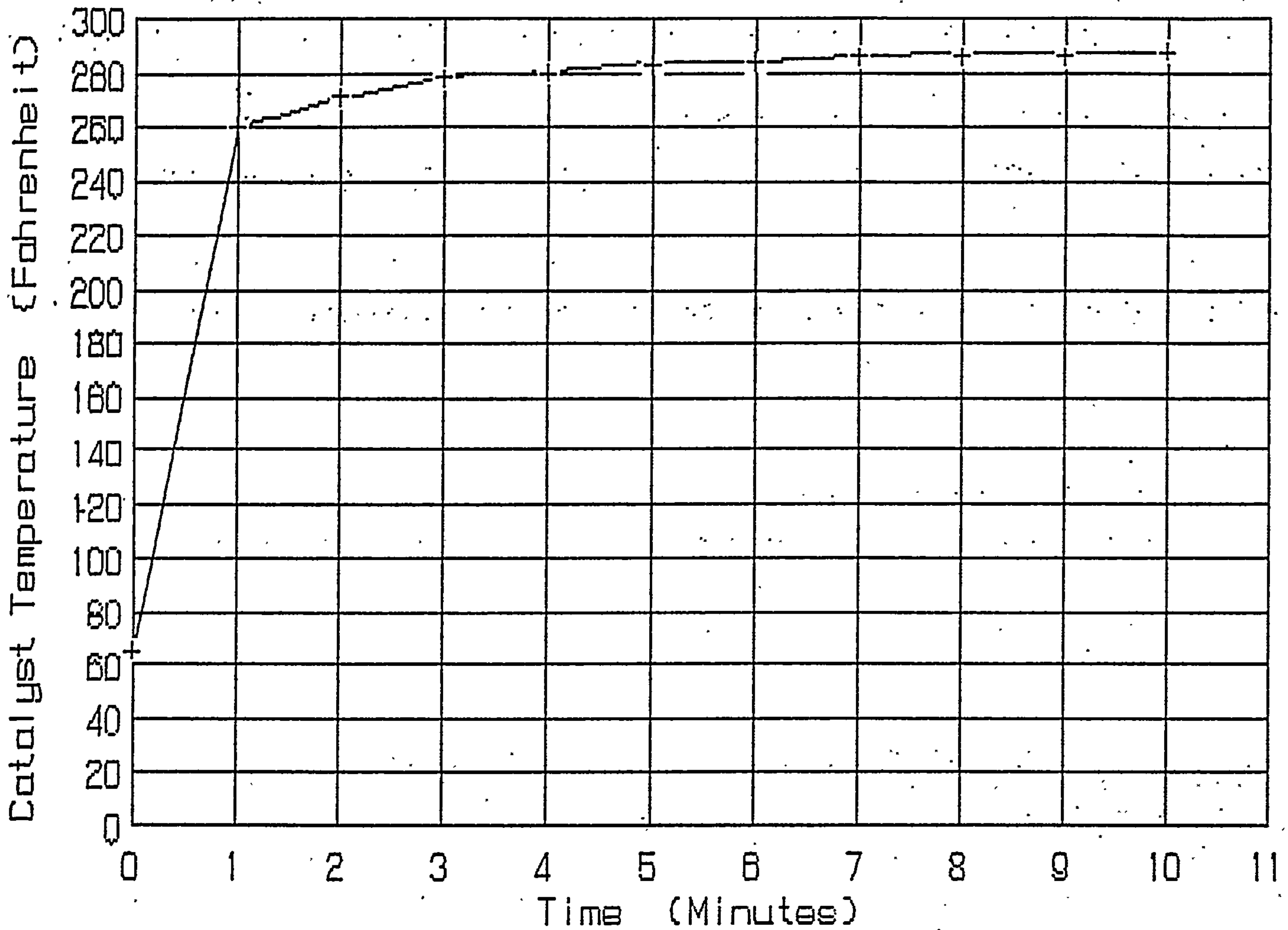
Ozone Generator Pressure		1 psi
Oxygen Flow		10 scfh
Water Flow		50 GPH
Transformer	T182850	
Chopper Card	3013	

Cooling Fan on Ozone Monitor

Catalyst Temperature vs. Time

Graph 8

Ozone Pipe Monitor Model 11-14-93

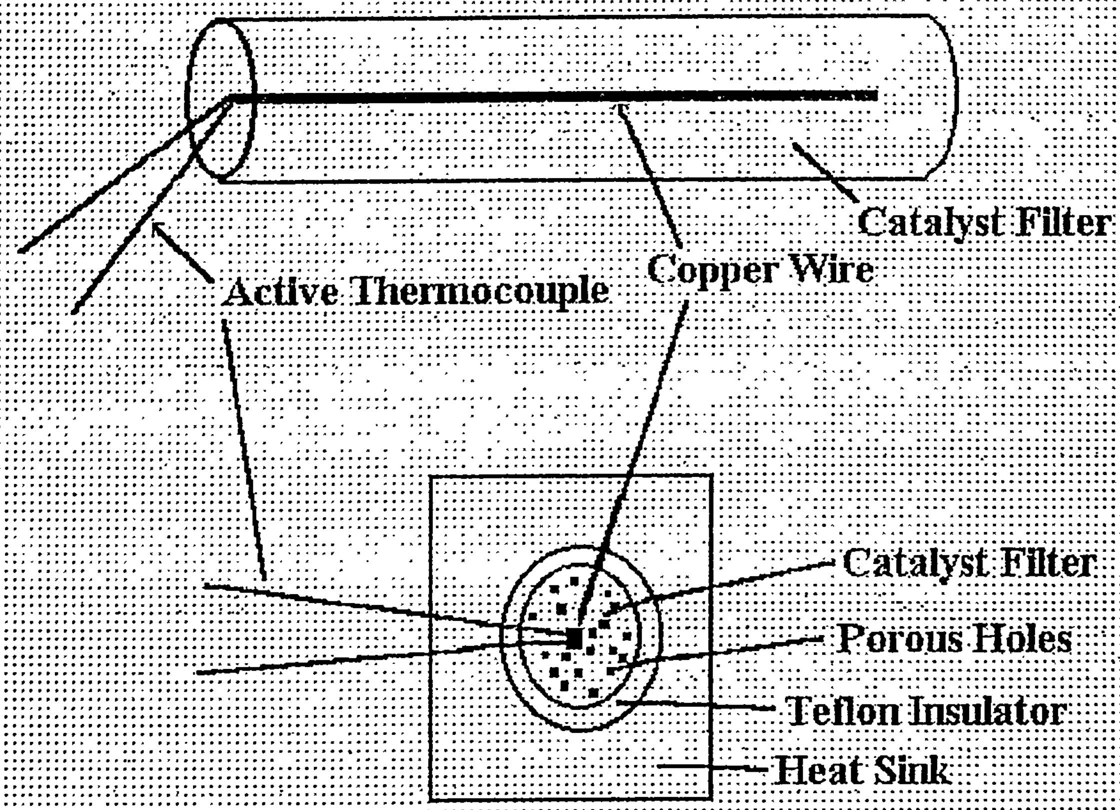


Ozone Generator Pressure		1 psi
Oxygen Flow		4 scfh
Water Flow		50 GPH
Transformer	T182850	
Chopper Card	3013	
Average High Voltage		36 KV
Average Input AC Voltage		131 V

Cooling Fan on Ozone Monitor

Figure 2

Catalyst Filter Ozone Monitor



The filters had a copper wire (thermal conductor) run through the center of the catalyst filter to act as a thermal sensor. The copper wire was then attached to a thermocouple. Next the catalyst filter ozone monitors was wrapped with a sheet of Teflon (0.0005" thick). The catalyst filter was then fitted back into the external aluminum heat sink. Photo E shows the porous catalyst filters and Photo F shows the catalyst filter ozone monitor. The reason for using the very thin Teflon insulator was so the ozone monitor would have a fast time constant. By having a fast heat transfer from the system, the monitor would reach a steady state temperature faster. The main problem with the porous catylyst filter was that it was not porous. When the catalyst coated in the wax was compressed, it was compressed under extreme pressure in order to force the catilyst particles into a solid unit. The

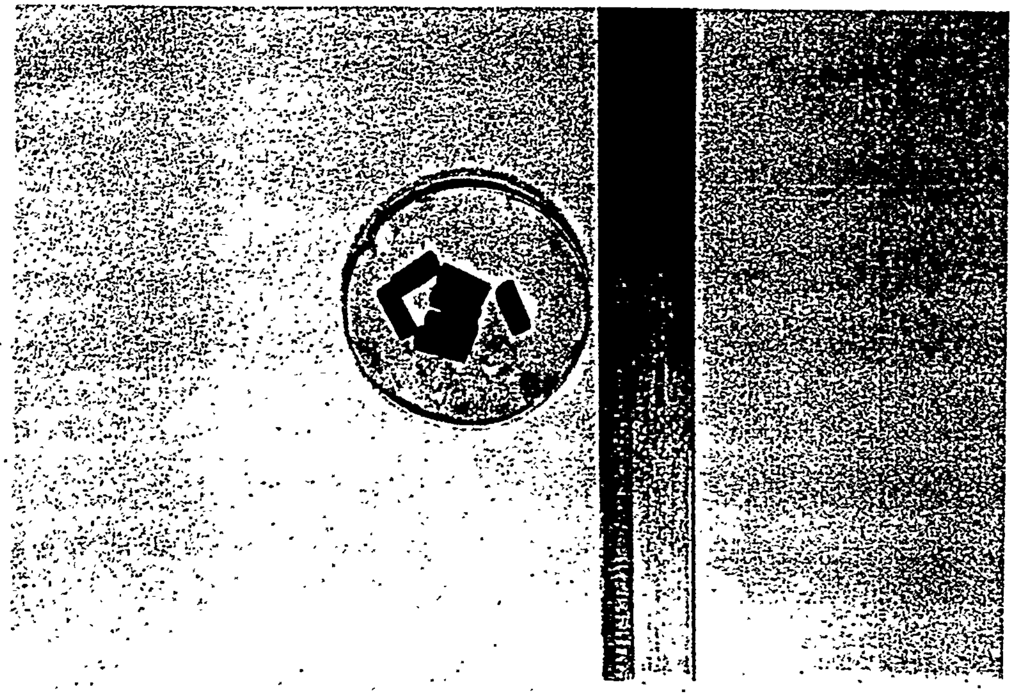


Photo E
Porous Catalyst Filter

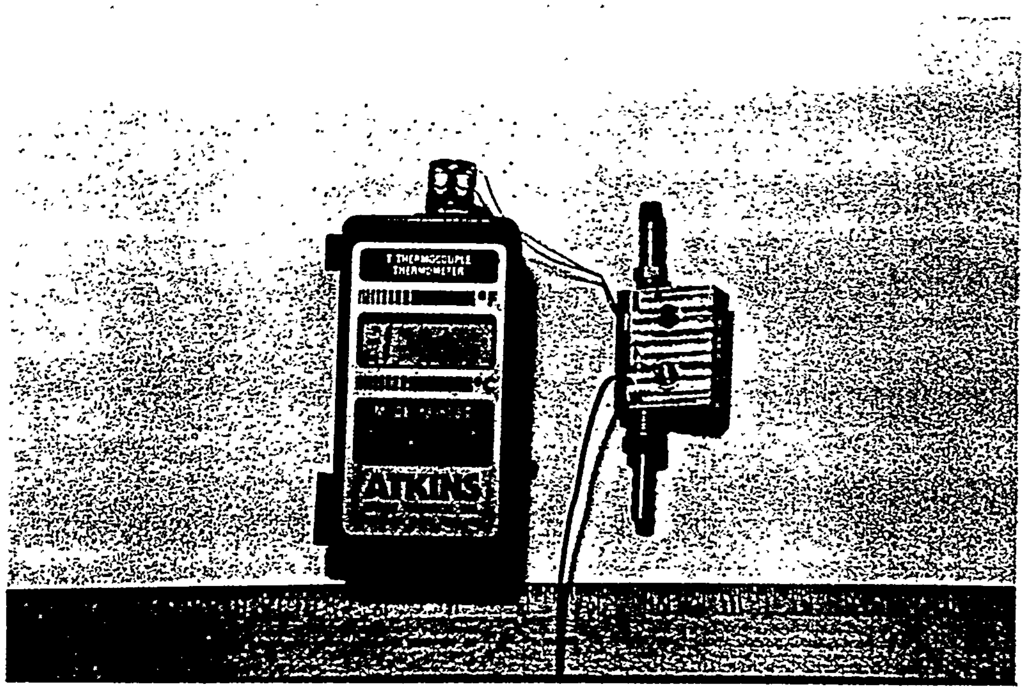


Photo F
Catalyst Filter Ozone Monitor

wax coated catalyst particle under the extreme pressure were broken down into a fine powder. Once the wax was driven out of the solid unit that was removed from the mold, it was brittle and not pourous enough to allow a gass to pass threw. When tested, the catalyst filter ozone monitor did not work. The ozone and oxygen gasses under pressure would not pass threw the monitor.

The final ozone monitor was built using the past data and experimnetal prototype knowledge. This final monitor combined the best features of each of the previous models. It used the medium to large size catalyst particles to allow for the passage of the ozone and oxygen threw the monitor. It uses TEFLON as an insulator for a fast response time. The monitor uses an aluminum heat sink to pull away the generated heat from reaction.

Figure 3 shows the basic overall operation of the complete ozone monitor.

Basic Overall Operation:

1. The oxygen and ozone enter into the ozone monitor and first pass threw a flow control valve. The flow control valve regulates the oxygen and ozone flow threw the catalyst and flow meter.

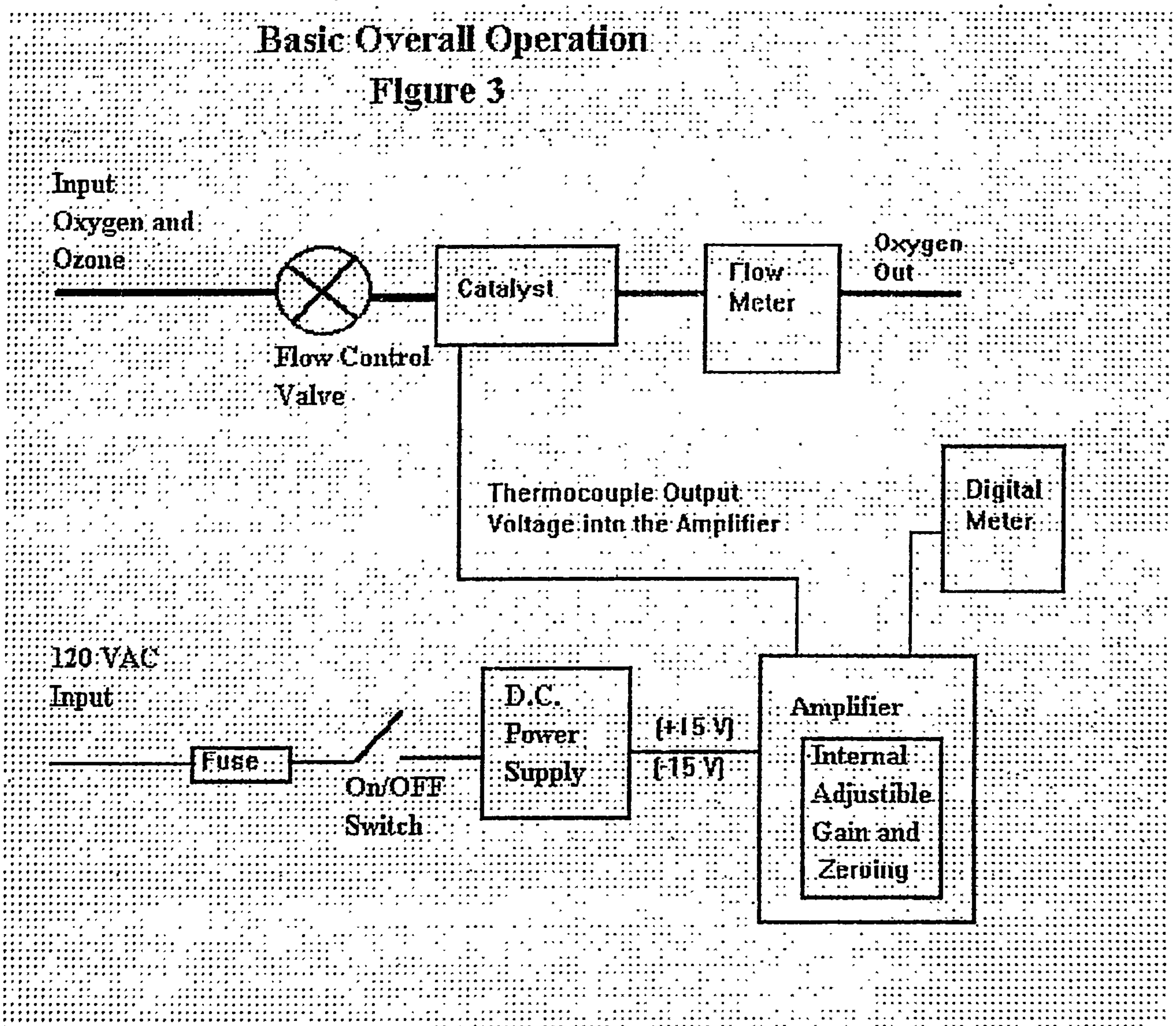
2. As the regulated oxygen and ozone flow passes threw the catalyst, heat is released from the reaction of the ozone with the catalyst to form oxygen. The heat is then transfered to the copper wire (thermal absorber sensor) which is inside the porous catalyst as shown in Figure 2. A fine #60 wire thermocouple that will not extract but a small amount of energy is brased to the end of the copper wire. The heat of reaction is transfered from the catalyst to the copper wire and then is measured by the thermocouple. The heat of reaction creates a voltage at of the thermocouple.

3. As the oxygen leaves the catalyst it passes threw the flow meter and out of the ozone monitor.

4. The ozone monitor operates on 120 VAC. The 120 VAC is fused at 0.5 Amps before the on/off switch. The 120 VAC powers the ± 15D.C. power supply.

5. The thermocouple amplifier with cold-junction compensation is powered by the D.C. power supply at ± 15 VDC. The differential voltage from the thermocouple is amplified to the desired voltage. The gain and zeroing are set by two variable resistors in the thermocouple amplifier circuit.

6. The voltage out of the thermocouple amplifier is inputed into the digital meter and read on the LCD.

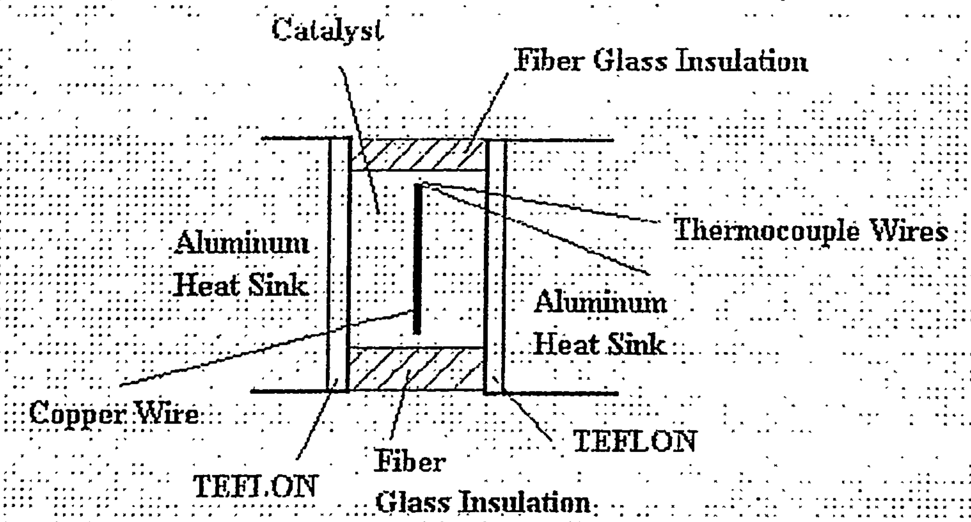


Ozone Monitor Specifics:

1. The aluminum heat sink has a width of 2 inches by a length of 5 inches and a heigth of 3 inches. The inside catalyst camber has length of 3 inches and a diameter of a 1/4 inch. The inside of the chamber is covered with a thin TEFLON sheet. The chamber is then filled with the medium to large size catalyst particles with a size range from 0.015 to 0.030 inches. All of the small catalyst particles were extracted by separation. The catalyst particles are held in the chamber at both ends by fiber glass insulation. The fine thermocouple wires are attached to the end of the copper wire which was inserted into the catalyst before the last piece of fiber glass insulation was put in place. Figure 4 showns the aluminum heat sink with the

catalyst set up. The thermocouple leads are brought out of the chamber by sealed holes in the aluminum heat sink.

Figure 4



Internal Heat Sink/Catalyst Set-UP

2. The flow control valve is a needle valve made by Nuclear Products Company of Cleveland, Ohio. The needle flow control valve is used to control the oxygen and ozone flow threw the ozone monitor. The flow during operation is adjusted to 1 Liter per minute. At this flow level the ozone monitor is calibrated to read the percentage of ozone.

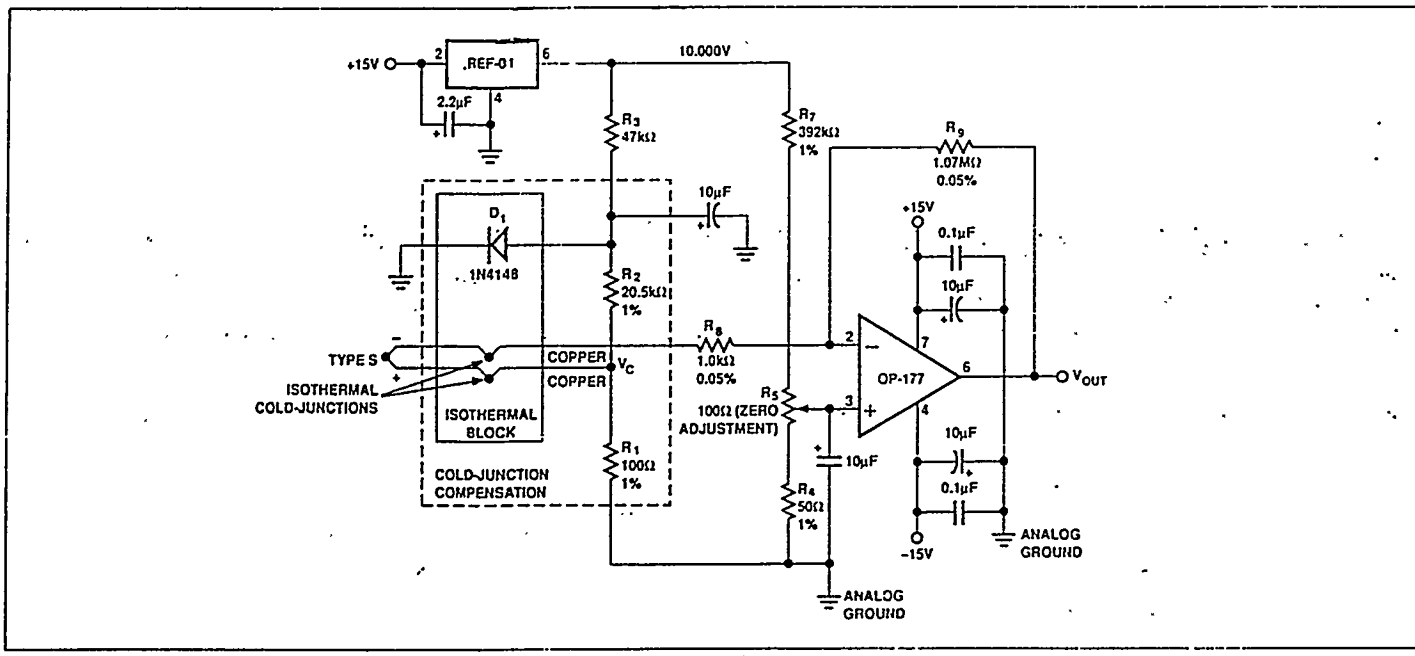
3. The flow meter is supplied by Dwyer Instruments, Inc. of Michigan City, Indiana. The flow meter can be read down to 0.1 Liter per minute and reads full scale at 2.0 Liters per minute.. A flow meter with high accuracy is necessarry so that the gas flow threw the system can be set at the calibration flow of 1 Liter per minute.

4. The D.C. power supply converts the 120 VAC into a regulated ±15 VDC. The D.C. power supply uses a step down transformer to produce the 18 VAC. The 18 VAC passes threw the bridge rectifier that converts the 18 VAC to 21 VDC. A 470 uf capacitor is used to reduce the ripple on the 21 VDC voltage before it enters the regulator. The 21 VDC voltage enters a +15 volt regulator and a -15 volt regulator. The ±15 volt regulators hold the dc voltages to:

+15 Volt Regulator: 15.1 Volts to 14.9 Volts
-15 Volt Regulator: -15.1 Volts to -14.9 Volts

5. The thermocouple amplifier with cold-junction compensation is shown in Figure 5.

Figure 5	OP-177



Thermocouple Amplifier with Cold-Junction Compensation

The thermocouple amplifier uses the operational amplifier (OP-177) made by Analog Devices. This high preformance operational amplifier was desgned for use in instrumentation. In Figure 5, the operational amplifier is used to amplify the voltage from the thermocouple. The outputed voltage from the amplifier is sent to the digital meter were it is read. The REF-01 is a very stable 10.000 voltage regulator. This regulator holds the 10.000 volts constant over the resistor bridge to give the operational amplifier a constant reference point. R5 is used to zero the output of the operational amplifier. R9 is used to increase or decrease the gain on the operational amplifier. The isothermal block is used to keep the temperature of the junction of the thermocouple wire and the copper wire at the same constant temperature. Thermal conductive diode (D1) is used to cancel any added voltages created by the junction of the thermocouple wire and the copper wire. A change in temperature of the isothermal block will create a voltage at the junction of the thermocouple and copper wire. The thermal diode will conduct with a change in temperature of the isothermal block and cancel the created voltage at the thermocouple and copper wire junction.

6. A 120 VAC power Digital Meter was used to display the output voltage from the operational amplifier. The displayed voltage is calibrated to correspond to the percentage of ozone by varing the R9 potentiometer.

7. The fan at the back of the ozone monitor is used to cool and circulate the air inside the ozone monitor. The circulated air will keep the aluminum heat sink and electrical components from over heating.

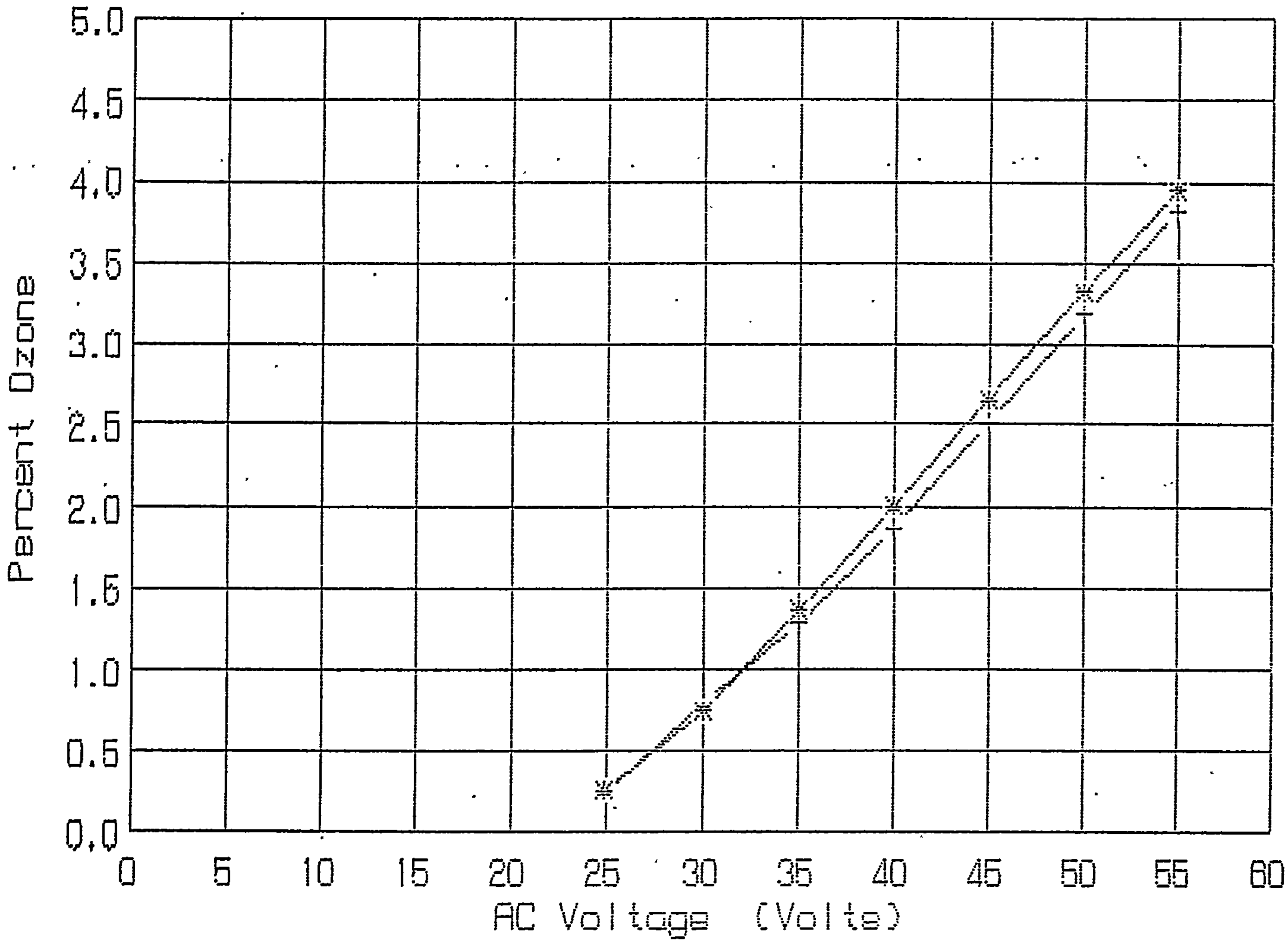
Final Test Data:

Ozone Catalyst Monitor #1 was designed to measure low concentrations of ozone. Ozone Catalyst Monitor #2 was design to measure high concentrations of ozone. Both ozone monitors use the same overall design with basic changes to accommodate for the different ranges of ozone to be measured. Ozone Catalyst Monitor #1 uses a long chamber filled with the catalyst to produce more heat that is released from the reaction of catalyzing the ozone. The TEFLON insulator used in the Ozone Catalyst Monitor #1 is also thicker than the one used in the Ozone Catalyst Monitor #2. The thicker TEFLON insulator and larger catalyst chamber in the Ozone Monitor #1, is more sensitive allowing it to measure ozone at concentrations from 0% to 4%. The Graph 9 (Percent Ozone vs. AC Voltage) shows the test results from the Ozone Catalyst Monitor #1. The Ozone Catalyst was calibrated and tested against the Ultraviolet Ozone Monitor (Model H1) made by IN USA Incorporated, Needham, MA. The Ultraviolet Ozone Monitor is calibrated against a chemical titration using the Potassium Iodide method. Graph 10 (Percent Ozone vs. Cool Down Time) shows that Ozone Catalyst Monitor #1 has a fast response time even with the thicker TEFLON thermal insulator. Photos G and H show the outside and inside of Ozone Catalyst Monitor #1. Ozone Catalyst Monitor #2 uses a shorter catalyst chamber and a thinner TEFLON insulator than Ozone Catalyst Monitor #1. The shorter catalyst chamber and thinner TEFLON insulator allow the monitor to measure the concentration of ozone from 0% to 8%. Graph 11 (Percent Ozone vs. AC Voltage) show the results from the Ozone Catalyst Monitor #2. This monitor was also calibrated and tested against the Ultraviolet Ozone Monitor (Model H1). Photos I and J show the outside and inside of the Ozone Catalyst Monitor #2.

Percent Ozone vs. AC Voltage

Graph 9

Ozone Catalyst Monitor #1



* Ozone Monitor (UV) Model H1

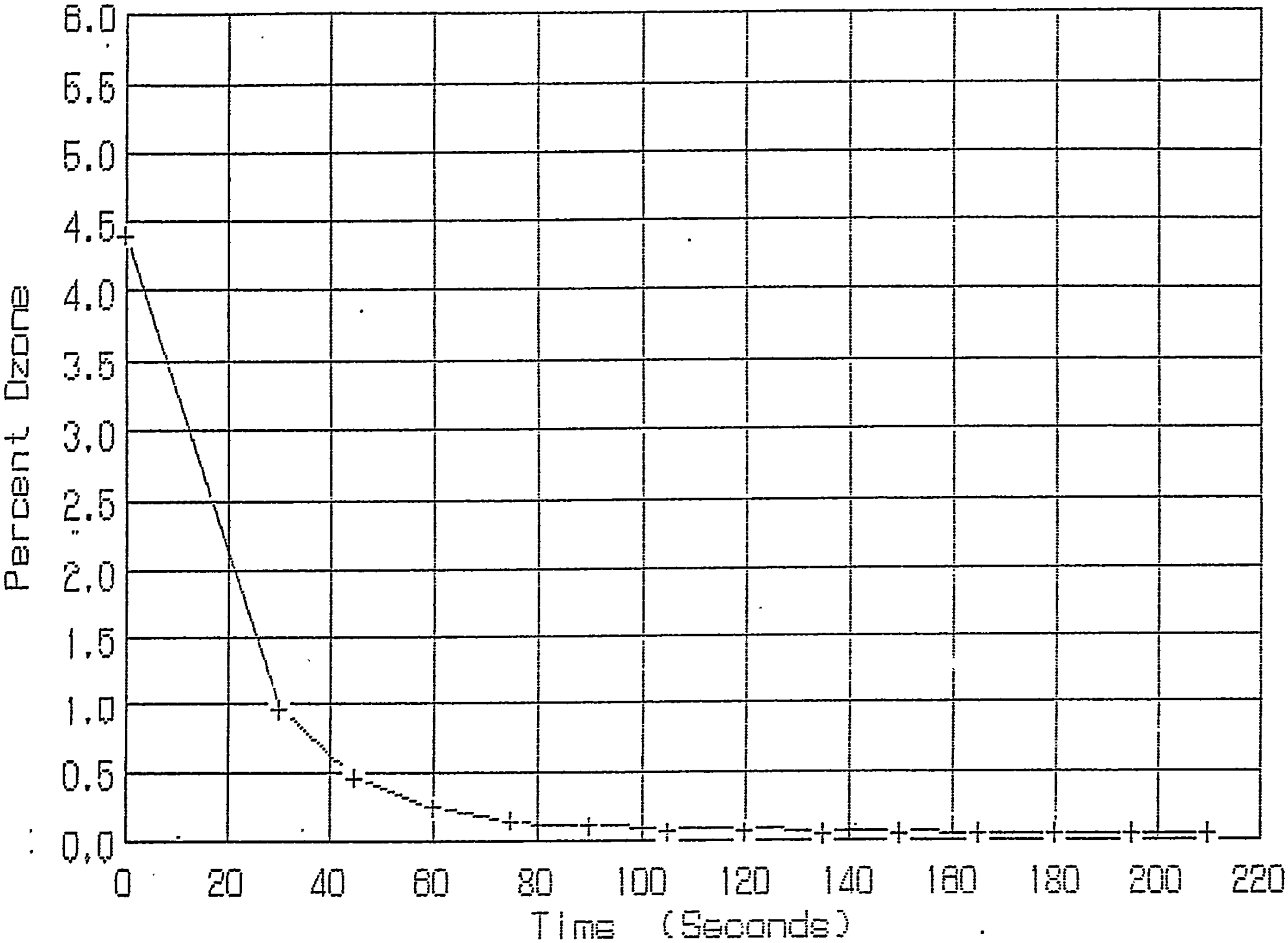
\+ Ozone Catalyst Monitor #1

Oxygen Flow	6.84 SLM
Oxygen Pressure	2.03 psi
Carbon Dioxide Flow	3.63 SLM
Carbon Dioxide Pressure	5.41 psi
Water Flow	100 GPH
Transformer	30059-A-C
Case	005
Chopper Card	3013
Frequency	450 Hz

Percent Ozone vs. Cool Down Time

Graph 10

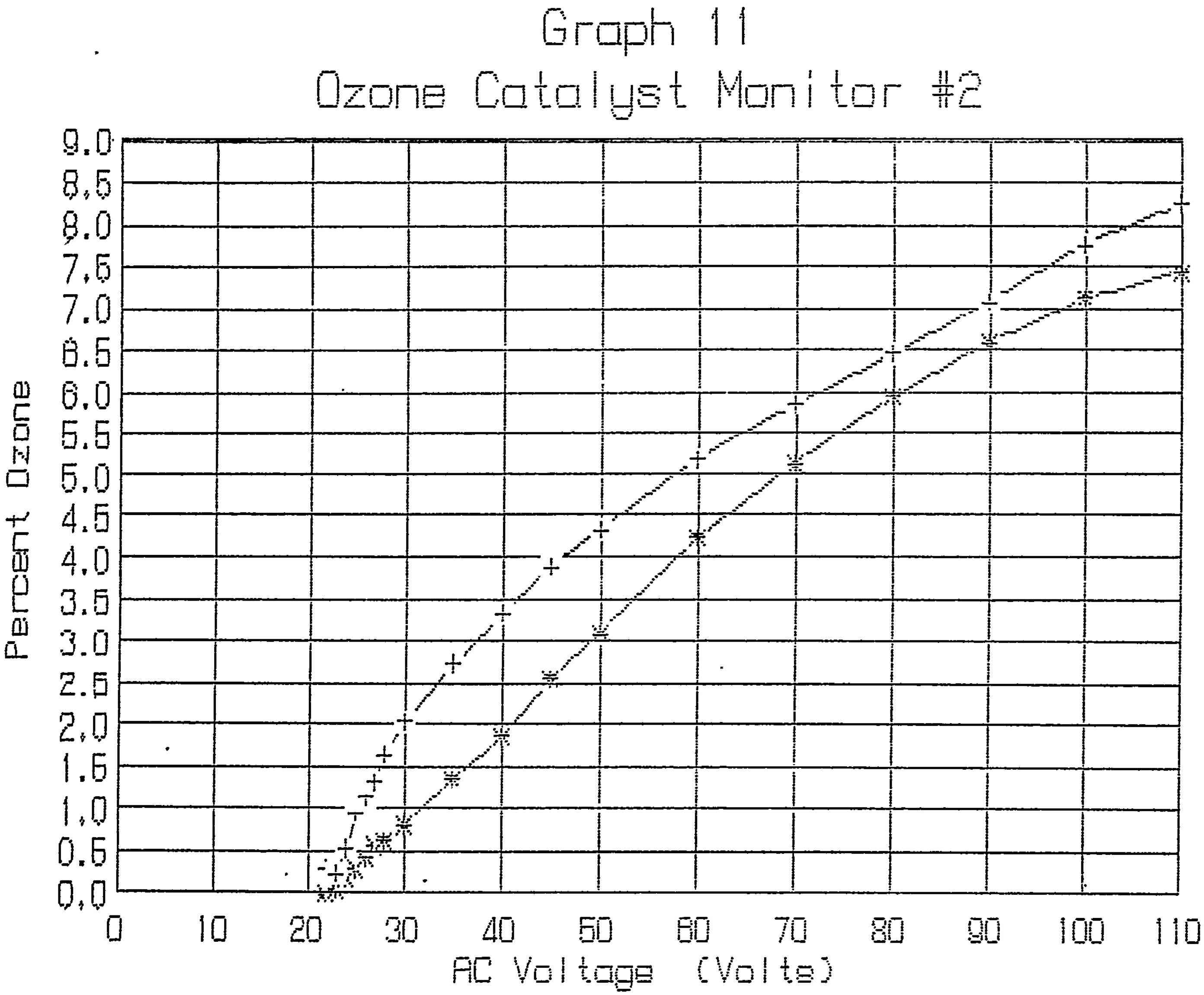
Ozone Catalyst Monitor #1



\+ Ozone Catalyst Monitor #1

Oxygen Flow	6.84 SLM
Oxygen Pressure	2.03 psi
Carbon Dioxide Flow	3.63 SLM
Carbon Dioxide Pressure	5.41 psi
Water Flow	100 GPH
Transformer	30059-A-C
Case	005
Chopper Card	3013
Frequency	450 Hz
AC Voltage	0.0 Volts

Percent Ozone vs. AC Voltage



*	Ozone Monitor (UV) Model H1
+	Ozone Catalyst Monitor #2

Oxygen Flow	6.64 SLM
Oxygen Pressure	2.18 psi
Carbon Dioxide Flow	2.90 SLM
Carbon Dioxide Pressure	3.64 psi
Water Flow	100 GPH
Transformer	30059-A-C
Case	005
Chopper Card	3013
Frequency	450 Hz

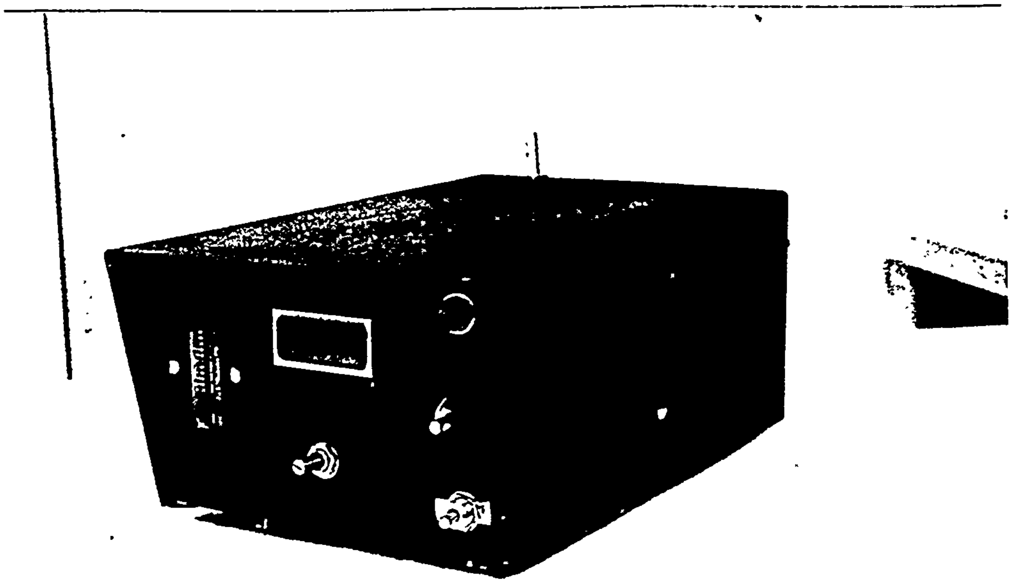


Photo I
Outside of Ozone Catalyst Monitor #2

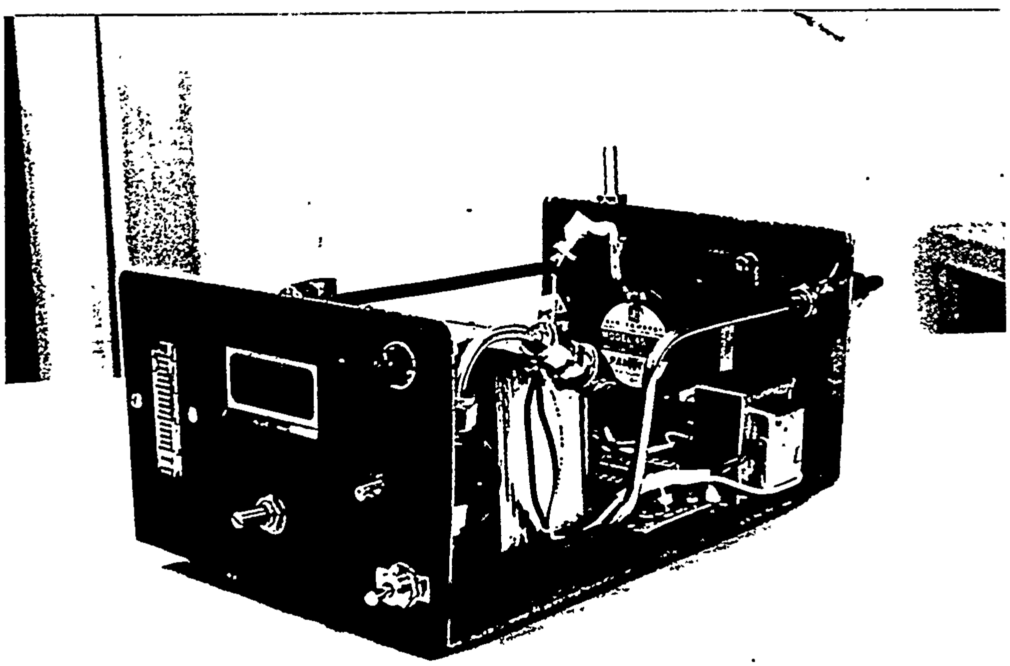


Photo J
Inside of Ozone Catalyst Monitor #2